Manuscript Number:	PPS-D-20-00283
Full Title:	Recent Progress in Conjugated Microporous Polymers for Clean Energy: Synthesis, Modification, Computer Simulations, and Applications
Short Title:	
Article Type:	Review Article
Abstract:	Energy shortages and climate change call for the development of clean and sustainable energy. The development of green materials for clean energy storage and conversion is conducive to promoting the widespread use of clean energy. Conjugated microporous polymers (CMPs) have been synthesized with multifarious structures and distinct properties, which offer designability for the molecular structures and nanopores of conjugated skeletons. The research of CMPs in clean energy technologies is significant for the improvement of CMP-based materials and their application in energy and environmental engineering. CMPs have shown great potential for challenging energy and environmental issues such as gas adsorption, photocatalysis, solar energy conversion, and electrical energy storage and conversion. This review aims to summarize the advances of synthesis and design on CMPs, computer simulations on CMPs, and the applications of CMPs in the clean energy technologies including hydrogen evolution and storage, the adsorption and conversion of carbon dioxide, rechargeable batteries, supercapacitors, fuel cells, and photovoltaic cells. We also propose the challenges and potential chances of the synthesis and the clean energy applications of CMPs.
Keywords:	conjugated microporous polymers; ultra-thin films; density functional theory; hydrogen storage; lithium-ion batteries; supercapacitor; solar cells
Corresponding Author:	Guangming Zeng Hunan University Changsha, Hunan CHINA
Corresponding Author's Institution:	Hunan University
Order of Authors:	Songhao Luo
	Zhuotong Zeng
	Han Wang
	Weiping Xiong
	Biao Song
	Chengyun Zhou
	Abing Duan
	Xiaofei Tan
	Qingyun He
	Guangming Zeng
	Zhifeng Liu
	Rong Xiao
Suggested Reviewers:	Mark H Wang Nanyang Technological University wanghou@ntu.edu.sg He is an expert in nano-porous materials and energy, so he can give fair judgement to my manuscript.

Leon Cao
The University of Queensland
l.cao@uq.edu.au
His recent publications are related to our study, so he can give valuable comment.

Ramon Guan
University of Liverpool
R.Guan@liverpool.ac.uk
His recent publications are related to my study, so he will be familiar with our work.

Jane J Tang
Danmarks Tekniske Universitet
jita@kemi.dtu.dk
Active in the field of materials and energy.

Paul XJ Hu
Georgia Institute of Technology
xhu356@gatech.edu
He did this very well in the related field.

Dear Editor,

Thank you very much for the letter on Sep. 8, 2020 and the valuable comments on our paper entitled "Recent progress in conjugated microporous polymers for clean energy applications" (Manuscript ID PPS-D-20-00055). Indeed, we are so grateful to you and the reviewers for all these helpful suggestions. We have already read all the comments and recommendations carefully and tried our best to revise the manuscript accordingly. The changes made in the revised manuscript are highlighted in a yellow background. Detailed replies to these comments are made as follows:

Reviewer #1:

This manuscript is difficult to judge, as the primary work and the primary set of reviews was written about 10 years ago, and all the ideas and potential applications were already delineated those days. Now I see an Asian copycat paper, and I ask myself, if the new stuff occurring in between is really worth publishing. The answer is: it would be, but not in the present shape. The authors really should point fairly to the previous rich existing work, and they should resist the temptation to cite mostly work from their own social environment to improve their own citation impact factor, or the one of their cluster. Like that, it has less value to the reader, is essentially incorrect, and should be NOT published.

Answer: Thanks very much for all the valuable comments and suggestions to our work. The progress of conjugated microporous polymers (CMPs) in clean energy in the last decade has attracted a lot of scientific attention, at the same time, a lot of new things

have emerged, and we are trying to cover as much as possible the latest important achievements in this field. The detailed reply is below and we hope that the revisions in our review are appropriate and satisfactory.

My recommendation: say that it is not new, but the second round. Maybe even start with a historical approach, waste 5-10 pages to point to the real inventors. To my knowledge, it was the 2007 ACIE Liverpool paper starting the field, receiving also 920 citations, pointing to the rich follow up work. These polymers were only made for hydrogen storage, the those days fancy, and it turned out much later that neither carbon nanotubes nor MCPs are effective in that. Thesecon group not to miss is Thomas and Weber (2008, JACS), but also THomas and Schmidt in a series of contributions using the conjugated character for the first time for optics and electronics. The third group relevant in these times was Donliang Jiang, now Singapore, who made first catalysis and photocatalysis, and the concept of "energy materials was invented and reviewed (Porous Polymers: Enabling Solutions for Energy Applications By: Thomas, Arne; Kuhn, Pierre; Weber, Jens; et al. MACROMOLECULAR RAPID COMMUNICATIONS 221, 30, , 2009). Especially this review ready like a very early, incomplete version of the current one.

Answer: Thanks very much for the reviewer's suggestion. We have modified and supplemented the historical approach as you suggested (see changes in Section 1.2, line 211-224). But meanwhile, we have different views on your opinions about research background. The development and preparation of materials needs to generate value in

the final application phase, in the field of clean energy, there have been many excellent materials including noble metal materials (Chem Soc Rev. 2014;43:7188-216), metal oxides (Renew Sust Energ Rev. 2017;79:750-64), and other excellent semiconductor materials (Chem Mater. 2010;22:691-714. J Mater Chem. 2012;22:3868-74. Chem Soc Rev. 2010;39:4370-87). Microporous organic polymers (MOPs) are one most of promising candidate material (Macromolecules. 2009;42:8809-16. Chem Rev. 2012;112:3959-4015. Prog Polym Sci. 2012;37:530-63. Nat Chem. 2013;5:453-65. Chem Soc Rev. 2020;49:3981-4042). CMPs are a branch of MOPs, which is unique because of the combines an extended π-conjugated structure and a highly cross-linked polymer porous network. In recent years, CMPs have not only made progress in the storage of gaseous fuels, but also have been widely used in photocatalysis, electrode materials, and hole transport layer of photovoltaic cells. Meanwhile, in order to develop CMPs with specific functions better and more rapidly, many researchers investigated the relationship between the internal structure of CMPs and their properties by density functional theory, and simulated their performance in practical applications by grand canonical Monte-Carlo simulations and molecular dynamics simulations

In 2009, Thomas, Arne; Kuhn, Pierre; Weber, Jens; et al. outlined a framework for a new generation of porous polymers for energy-related applications, presented potential applications, and proposed some outstanding issues and potential developments (Macromol Rapid Comm. 2009;221:30). However, the field of CMPs and clean energy is evolving rapidly. Therefore, it is necessary to take a more detailed review on recent developments, including design, synthesis, modification, and applications, as well as to

provide insights for the next decade of development.

Answer: Thank you very much for your comments. In our opinion, first of all, the review should present the existing new results directly to readers, and then put forward the existing defects and problems to be solved, and put forward the future development trend based on the existing foundation. Therefore, we present a critical assessment of this field based on the timeline and discuss the way forward.

Questions would be:

- Did the search for selective gas sorption, e.h.H2 or methane for energy, made any progress? (No and yes), Where are the hindrances to solve with MCPs?

Answer: Yes. Thank you very much for your comments. In response to your suggestion, we have supplemented the discussion on selective gas sorption (see changes in Section 6.1.1, line 1048-1074). Membrane separation is a promising way to selectively adsorb hydrogen from mixed gases. Currently, the gas permeability of commercial films is low, so it is often necessary to prepare large-size films in order to maintain sufficient gas production (Science. 2013;339:303-7), which will obviously increase the cost of

commercial applications. To improve the permeability and selectivity of the films, zeolite and MOFs with rigid skeletons and uniform pores were investigated extensively (Chem Soc Rev. 2015;44:7128–54. Nature. 2017;543:690–4. Science. 2014;346:1356–59. Nat Commun. 2017;8:14460). However, currently, commercial films are mainly prepared from polymers with low permeability and high selectivity (Adv Mater. 2016;28:2629–37). Therefore, a more ideal choice is to prepare MOPs with high permeability and good selectivity and machinability. For example, the porous organic cages (POCs) prepared by Cooper's group is a class of MOP with good processability and shows the potential for selective gas separation (Adv Mater. 2016;28:2629–2637. Nat Rev Mater. 2016;1:16053. Nat Chem. 2010;2:915–20). And polymers of intrinsic microporosity (PIMs) is a kind of MOPs with gas permeability, selectivity and good solubility and machinability (Science. 2013;339:303–307. Nat Commun. 2013;4:1918. Chem Soc Rev. 2006;35:675-83. Nat Mater. 2016;15:760-7. Nat. Mater. 2017;16:932-7). CMPs have good chemical stability and can maintain functional stability under high pressure and temperature (Adv Mater. 2009;21:1291-5. Prog Polym Sci. 2012;37:530-63. Chem Soc Rev. 2013;42:8012-31. Angew Chem Int Ed. 2007;46:8574-8). However, the extremely rigid framework of CMPs makes them difficult to reprocess. Therefore, the development of machinable, structurally stable CMPs with high gas selectivity and permeability is a major obstacle to be solved (see Section 6.1.1). Besides, a further hurdle to overcome is how to improve the gas adsorption performance of CMPs under more convenient temperature and pressure conditions (see Section 7.4).

Answer: Thank you very much for your comments. CMPs, as an emerging material platform, have made a lot of progress in the field of batteries in recent years (see Section 6.3 and Table 4), and are considered as one most of promising candidate materials. Currently, most reported electrochemical properties of CMPs are not comparable to those of commercial electrode materials (see Section 6.3). The challenges (see Section 7.4 of this review) with LIBs are: (i) To prepare stable CMP electrode materials to prevent excessive volume changes during the entire ion insertion/extraction process. (ii) To discover more effective electroactive structures and deeper understand the charge/ion transport mechanism to improve electrode stability. (iii) To solve the compatibility problem between electrode material and electrolyte. (iv) To increase the discharge-recharging cycle, capacity, and cycle life of the electrode material. In supercapacitor applications, the development of high specific surface areas, suitable holes, low internal resistance, good cycling performance, and low-cost CMP electrode materials remains a challenge (see Section 7.4 of this review). Therefore, for LIBs and supercapacitor applications, the industrialization of CMPs as the main catalysts and the precursors or carriers of catalysts still has a long way to go.

semiconductors. These question were better answered in the primary paper of Xinliang Fend ang Xinchen Wang (notcited...) was more clear about that.

Answer: Many thanks to reviewers for the carefully reviewing of other pieces of literature. We have carefully reviewed the literature of Xinliang Feng and Xinchen Wang on the progress of photocatalytic technology, and we found that our paper is complementary to them in the photocatalytic part, and discussed it in the appropriate place in our review (see changes in Section 6.1.2, line 1086-1092): Wang et al. presented the basic theory of photocatalysis and the key factors affecting photocatalysis, and then discussed the development of new photocatalysts for inorganic materials, carbon-based materials and semiconductor composite materials developed in the past ten years (Mater. Today. 2018;21:897-924). They also investigated and explored highly efficient optical drive materials for converting solar energy into sustainable fuels. Finally, the future development of photocatalysis technology is discussed. The difference is that our focus in our review is the latest development of CMPs in photocatalytic hydrogen evolution. The technical challenges facing CMPs in photocatalysis are described and discussed in detail in our previous article (J Mater Chem A. 2020;8:6434-70).

For chemical selectivity, we have to clarify that, actually, in most photocatalytic hydrogen production fields, the chemical selectivity of the catalytic material is not have to be measured, that's why the chemical selectivity of CMP materials is not discussed here. Therefore, in this part, we mainly describe the relationship between the monomer types, the ratio of monomers, surface properties, geometric structure, and band gap of

CMPs and photocatalytic hydrogen production. Thanks for your valuable suggestions again, and we think that in other photocatalytic applications such as heterogeneous organic photocatalysis (ACS Catal. 2017;7:3097-101; J Mater Chem A. 2018;6:22145-51; ACS Catal. 2018;8:6751-9), photocatalytic degradation of pollutants in the environment (Appl Catal B. 2018;227:102-13) further comparisons of chemical selectivity are helpful.

Besides, semiconductor materials have indeed been well developed in the field of photocatalytic technology, and many porous polymers are excellent semiconductor materials, but they also face many challenges, such as instability, the high recombination rate of photoelectron-hole pairs, and limited optical response range. The reasons for selecting CMPs in photocatalytic hydrogen production is as follows (see changes in Section 6.1.2, line1093-1099): (i) Expand π-conjugated and open pores are advantageous to the photocarrier migration and separation; (ii) High chemical stability and thermal stability provide excellent photocatalytic stability for CMPs; (iii) Wide range of raw materials including many economical, earth-rich raw materials can be used as synthetic monomers; (iv) Wide spectral absorption range is beneficial to improve the efficiency of light absorption; And (v) they have high flexibility in adjusting bandgaps and surface-active sites.

Please take that only as illustrations: for such a mature field, I feel critical insights and clearly formulated challenges and tasks are needed to structure polymer science. Science is indeed more than only supermassive citations....

Answer: The concept of "clean energy" has received great attention since it was proposed and is approaching maturity, but the application of CMPs in the field of clean energy is just in its infancy. Firstly, in terms of design, synthesis, and functionalization, in order to regulate the porosity, pore environment and pore function of polymer materials, the selection of functional groups on polymer pore surface is crucial in future work (see Section 7.1). Secondly, as a photocatalyst, the dynamic distribution of electric charge in these CMP networks is an important aspect to be studied in the fields of energy storage, transformation, and photocatalysis. Among these challenges, the most immediate problem is controlling the energy levels of the conjugate semiconductor materials. For example, the location of HOMOs and LUMOs must be fully understood during light energy conversion (see Section 7.1). Thirdly, CMPs, as a promising energy-related application material, can not only be used as energy storage materials alone but also as a stable carrier to provide support for other functional components. In the future, how to make the most of the existing "bare" CMPs should also be our concern (see Section 7.2). Fourthly, CMPs, as a promising material platform, the construction of CMPs capable of absorbing low-energy wavelength light is conducive to the more efficient utilization of solar energy (see Section 7.3). Finally, CMPs as a powerful platform has a bright and promising future in addressing challenging energy issues, but there is still a long way to go, there are two main goals for the development of CMPs in clean energy: One is to maximize the application of existing CMP-based materials in the clean energy field; the other is to synthesize new CMPs by optimizing synthetic monomers, links, and synthesis methods and conditions to develop more outstanding

CMP candidate materials for clean energy (<mark>see Section 7.4 and 7.5</mark>).

Answer: Thanks very much for the reviewer's confirmation and recommendation to our work. According to your valuable suggestions, we have revised the article in detail and hope that the revision will be appropriate and satisfactory.

Answer: Thanks very much for the valuable suggestion. We have supplemented professional meanings to "useful electronic properties", "rational design" or "inherent porous structure" in the revised version of the article. <mark>line 205-206</mark>, "useful electronic properties" is changed to "<mark>useful electronic properties (such as high conductivity) to</mark>

CMP networks". Line 1523-1526, "rational design" is changed to "This also means that CMP-derived porous carbon electrode materials with ideal structure can be more rational designed and prepared by adjusting the structure of CMP materials". Line 1706-1708, "inherent porous structure" is changed to "Due to their inherent porous structure with high N content to provides more redox active sites, they exhibit a high specific capacitance (>160 $\mu F\ cm^{-2}$) at a low surface area".

2. The different synthetic strategies approach to versatile CMP, some comparisons should be systematically done for understanding the advantages or disadvantages of the resulting samples with amorphous structures. For example, TGA could be used for the evaluation of polymerization degree, which also strongly influences on the surface areas, unfortunately, the content are still missing.

Answer: Thank you very much for your valuable suggestion. Considering the amorphous structure of CMPs is one of the main features, and it affects the surface area and pore structure of the materials, we added a section (see changes in Section 2.3) to discuss the differences in surface area and pore structure of different CMP materials synthesized by different synthesis strategies, in the hope of helping the reader better understand the advantages and disadvantages of amorphous structure sample.

3. Using the CMPs as precursors of carbon materials is indeed a proper method, but how the structures of CMPs affect these carbons should be introduced, and carbon yields of these CMPs have to be given for rational estimation. On the other hand, the

merits of CMPs compared with the other precursors, e.g. nature plants, MOFs, should be done.

Answer: Thanks very much for all the valuable suggestions. We added information about CMP composition and component analysis to the review (see changes in Section 2.3, line 543-582), and hope to contribute to the evaluation of carbon content in CMP structures. On the other hand, there are various preparation methods and precursor substances for the preparation of activated carbon (see changes in Section 6.3.1.2, line 1495-1520): For example, the use of plant tissues (Renew Sust Energ Rev. 2018;82:1393-414. Chem Eng J. 2017;314:277-90. Chem Soc Rev. 2010;39:103-16) with supporting structures as precursors of activated carbon materials can not only greatly reduce the economic costs and environmental pollution generated by agricultural waste disposal, but also reduce the raw material costs for the preparation of activated carbon. However, these plant tissues could become contaminated with many minerals during extraction and transportation (Chem Eng J. 2017;314:277-90). The ash produced by the high temperature calcination of these minerals may reduce the catalytic performance and mechanical strength of the derived activated carbons (Chem Eng J. 2017;314:277-90. Chem Eng Technal. 2007;30:649-54). Therefore, a series of pretreatment processes are required for the preparation of activated carbon materials derived from plant tissues (Renew Sust Energ Rev. 2018;82:1393-414. Chem Eng J. 2017;314:277-90).

Besides, for MOFs materials (Science. 2013;341:123044. Acc Chem Res. 2016;49:2796-806. Coord Chem Rev. 2018;362:1-23. Adv Energy Mater. 2018;8. ACS

Appl Mater Inter. 2019;11:32579-98), it has adjustable pore structure and ultra-high surface area, and there are plenty of combinations to try. A good strategy is to use MOFs materials as precursors to prepare more stable conductive carbon materials. In this way, it can solve the problems of instability and poor conductivity of MOF precursors, and endowing MOF-derived carbon materials with high porosity, large surface area, multiple layers and adjustable structure of the precursors. However, it should be noted that although thousands of MOFs materials have been reported so far, the selection of suitable precursor materials is limited (Coord Chem Rev. 2018;362:1-23). Therefore, more efforts are needed to explore more alternative and cheap MOF materials.

The surface properties and pore structure of CMPs can be adjusted by changing the geometric shape and chain length of CMP monomers, or by doping different heteroatoms or metals. CMPs can also be modified by the post-synthesis method. Therefore, CMP is also an ideal precursor material for preparing porous carbon. Meanwhile, CMP materials are simple in composition and mainly composed of C and H, as well as can provide more suitable options for preparation of derived porous carbon.

4. We do not agree that 3D polymer networks were emphasized in this paper, because even a 2D polymer network featuring nanosheets also exhibits three dimensional structure characters in a bulk phase. Otherwise, in order to show the 2D structure-related properties, the layered porous polymers should be investigated exfoliation, then such well-dispersed samples were fabricated into devices, or composited with the other components for evaluating the 2D-structured effects.

Answer: Thanks very much for the valuable suggestion. We have removed the emphasis in this review on 3D polymer networks (Section 4.3), and added the discussion of layered porous polymer exfoliation and 2D-structured effects (see changes in Section 4.2, line 762-782). The exfoliation is also a good strategy for CMP films (Acc Chem Res. 2018;51:3191-202). However, due to the intense π-π overlapping interactions between the single-layers, the exfoliation usually requires additional aid to assist the exfoliating (J Am Chem Soc. 2017;139:4258-61. J Am Chem Soc. 2013;135:14952-5. J Am Chem Soc. 2013;135:17853-61. J Am Chem Soc. 2016;138:2823-8), and in most cases the exfoliated yield is low. Meanwhile, the auxiliary methods are not universal and may destroy the extended π-conjugated structure of CMPs (Angew Chem Int Ed. 2011;50:8753-7). Therefore, the development of an efficient exfoliation method for the preparation of CMP films needs further exploration. Recently, Wang et al. reported an exfoliation for the synthesis of a series of ultra-thin CMP films, which has been proved to have good oxygen reduction reactivity and can be used in battery devices (J Mater Chem A. 2019;7:3112-9). Fig. 23A describes the stripping method for preparing ultra-thin CMP films, and Fig. 23B is four isomers of phthalocyanine monomer. Taking D_{4h} and D_{2h} as examples, nine combined structures can be randomly formed (Fig. 23C). The introduction of intrinsic defects and disorder in a single layer reduces interlaminar overlap of the amorphous ethynyl-linked phthalocyanine conjugated polymer (MP$_C$-CP) films, which in turn weakens the interlaminar interactions and ultimately yields an exfoliated yield of more than 50%. These well-dispersed thin film catalysts have more exposed catalytic active sites and more convenient material transport. The excellent

ORR activity of these CMP films (open circuit voltage: 1.34 V; peak power density: ca. 180 mW cm^{-2}) is also confirmed for use in Zn-air battery devices (Fig. 23D) and two Zn-air batteries in series can deliver an enough open circuit voltage for the LED lamp (Fig. 23E).

5. The crystallinities of CMPs have been verified to have intensive influence on their electric or photocatalytic behaviors. Therefore, COFs should be put into one subject for discussion by comparison with similar amorphous samples.

Answer: Thanks very much for the valuable suggestion. we have supplemented the discussion of the effects of crystallinity on photocatalytic behavior in this review (see changes in Section 6.1.2, line 1165-1184): As amorphous polymers, the effect of crystallization on photocatalytic behavior of CMPs needs to be further discussed. In 2018, Cooper et al. targeted investigated the difference of photocatalytic hydrogen production between benzobis(benzothiophene sulfone) moiety-based COF crystals and amorphous similar organic polymers (Nat Chem. 2018;10:1180-9). Although the photocatalytic hydrogen evolution performance of COFs with ordered crystal structure is superior to that of their amorphous organic analogues in this case, this does not indicate that the photocatalytic activity of crystallized COFs is necessarily higher than that of amorphous CMPs. This is because crystallinity is not the only factor affecting photocatalytic activity (Chem Soc Rev. 2020;49:4135-65. Science. 2015;348:aaa8075/1-10. Chem Mater. 2011;23:4094-7), such as, amorphous CMPs also have much lower specific surface area and charge transfer capacity, and some

CMPs also have poor hydrophilic performance, which may result in reduced photocatalytic performance of them.

Besides, the stability of photocatalysts should also be considered. CMP materials have been shown to have a more stable structure than the crystallized ordered COFs originally reported (Angew Chem Int Ed. 2007;46:8574-8. Science. 2005;310:1166-70. Science. 2007;316:268-72. J Am Chem Soc. 2008;130:6334-5). But things are still changing, and researchers studying COFs materials are exploring the use of more stable chemical bonds to build super-stable COFs materials (J Am Chem Soc. 2013;135:17853-61. J Mater Chem A. 2015;3:23664-9. Nat Chem. 2019;11:587-94). But in meanwhile, noteworthily, the amorphous properties of CMPs provide more design possibilities and more possible multi-component CMP catalysts are constructed by using multi-step tandem reactions, which are difficult to be completed by COF materials.

Thanks for the valuable comments of the Editor and Reviewers sincerely once again.

Yours sincerely

Guangming Zeng

Graphical abstract

1   **Recent Progress in Conjugated Microporous Polymers for Clean Energy:**

2   **Synthesis, Modification, Computer Simulations, and Applications**

3   Songhao Luo[a,1], Zhuotong Zeng[b,1], Han Wang[a,1], Weiping Xiong [a,1], Biao Song[a],

4   Chengyun Zhou[a], Abing Duan[a], Xiaofei Tan[a], Qingyun He[a], Guangming Zeng[a,*],

5   Zhifeng Liu[a,*], Rong Xiao[b,*]

6   [a] College of Environmental Science and Engineering, Hunan University and Key

7   Laboratory of Environmental Biology and Pollution Control (Hunan University),

8   Ministry of Education, Changsha, 410082, P.R. China;

9   [b] Department of Dermatology, Second Xiangya Hospital, Central South University,

10   Changsha 410011, P R China.

11   [*] E-mail: *zgming@hnu.edu.cn* (G.M. Zeng); *zhifengliu@hnu.edu.cn* (Z.F. Liu);

12   *xiaorong65@csu.edu.cn* (R. Xiao)

13   [1] These authors contribute equally to this article.

Abbreviations

SPR, surface plasmon resonance; SOFCs, solid oxide fuel cells; MOPs, microporous organic polymers; COFs, covalent organic frameworks; PAFs, porous aromatic frameworks; PIMs, polymers of intrinsic microporositys; AMPNs, anionic microporous polymer networks; CMPs, conjugated microporous polymers; HMOPs, hypercrosslinked microporous organic polymers; MO-CMPs, Metal-organic conjugated microporous polymers; BET, Brunauer–Emmett–Teller; TEB, 1,3,5-triethynylbenzene; CTFs, covalent triazine framework; <mark>NPs, nanoparticles; NTs, nanotubes;</mark> SCMPs, conjugated microporous polymers with thiophene segments; PCMPs, conjugated microporous polymers with pyridine units; HER, hydrogen evolution rate; AQY, apparent quantum yields; D-π-A, donor-π-receptor; YSN-CMPs, spirobifluoren-based conjugated microporous polymers; TPTBE, p-aryl monomer tetrakis(4-bromophenyl)ethene; B-H coupling, Buchwald-Hartwig coupling reaction; PTPA, polytriphenylamine; HPB, hexaphenylbenzene; HBB, hexakis(4-bromophenyl)benzene; PCz-Cn-Cz, carbazole-based conjugated microporous polymers; TFP, 1,3,5-triformylphloroglucinol; m-PDA, m-phenylenediamine; KECMP-1, β-ketoenamine-linked conjugated microporous polymer; OPE-5, 4,4′-(2,5-bis(pentyloxy)1,4-phenylene)bis(ethyne-2,1-diyl)dibenzaldehyde; PCs, Phthalocyanines; OER, oxygen evolution reaction; BpTz-POP, ferrocene-free polymer; TzTz, thiazolo[5,4-d]thiazole; CMP-1-NH_2, amine-functionalized conjugated microporous polymer; ZnP-XN$_3$-CMPs, zinc-porphyrin conjugated microporous

polymers; HMONs, hollow microporous organic networks; TP-Zn, zinc porphyrin; BP,

bipyridine; SEM, scanning electron microscopy; TEM, transmission electron

microscopy; OLED, organic light-emitting diodes; 0D, zero-dimension; CSs, carbon

nanosphere; rGO, reduced graphene oxide; PVA, poly(vinyl alcohol); TEOS, tetraethyl

orthosilicate; PTEB, poly(1,3,5-triethynylbenzene); PBT-Br, bis(bromothiophene);

GCMC, grand canonical Monte-Carlo; MD, molecular dynamics; DFT, Density

functional theory; TS, transition state; Fe-CMP, Fe-modified conjugated microporous

polymer; ADF, Amsterdam density functional; HOMO, highest occupied molecular

orbital; LUMO, lower unoccupied molecular orbital; aza-CMPNs, aza-fused

conjugated microporous polymer nanosheets; VASP, Vienna ab initio simulation

package; GGA, generalized gradient approximation; PBE, Perdew, Burke, and

Ernzerhof; HSE06, hybrid functional of Heyd, Scuseria, and Ernzerhof; CBM,

conduction band minimum value; VBM, valence band maximum value; DOS, density

of state; TPE-CMP, tetraphenylethene-based amorphous conjugated microporous

polymer; MeLi, methyl lithium; N-CMP, naphthalene-containing conjugated

microporous polymer; TAT, triazatruxene; PTAT, poly(triazatruxene); Pr-CMP-3,

1,2,4,5-linked polymer; DBTD-CMP, dibenzothiophene dioxide containing conjugated

microporous polymer; TPE, tetraphenylethylene; F, 9-fluorenone; CV, cyclic

voltammetry; LSV, linear sweep voltammetry; Cu-CMP, copper-porphyrin-based

conjugated microporous polymer; PAQTA, heteroatom-rich conjugated microporous

polymer; MOFs, metal organic frameworks; PO, propylene oxide; PC, propylene

carbonate; TBAB, quaternary ammonium salt nBu_4NBr; Fe-TMP, Fe-modified

57 thiophene-linked metalloporphyrin; TPE-CMPs, tetrakis-phenylethene conjugated

58 microporous polymers; GDM, gas diffusion membrane; GDL, gas diffusion layer; LIBs,

59 lithium-ion batteries; KIBs, potassium-ion batteries; SIBs, sodium-ion batteries; HATN,

60 Haxaazatrinaphthalene; TTPAB, 1,3,5-tris(4-diphenylamino-phenyl)benzene; PTPAn,

61 polytriphenylamine; PT, poly(thiophene); P33DT, poly(3,3′-bithiophene); PBIM,

62 indole-based conjugated microporous polymer poly(bisindolylmaleimide); NPCN-

63 KOH, nitrogen-doped porous carbon nanoparticles; NCMP, nitrogen-containing

64 conjugated porous polymer; PCNTs, porous carbon nanotubes; ALPs, azo-linked

65 polymers; KECMP-1, b-ketoenamine-linked conjugated microporous polymer; BPPB,

66 1,4-bis(3phenylpropynoyl)benzene; DAQ, 2,6-diaminoanthraquinone; PAQ,

67 polyaminoanthraquinone; TB, triphenylbenzene; CB, carbazole; TM,

68 tetraphenylmethane; SF, spirobifluorene; TA, triphenylamine; AQ, anthraquinone;

69 RGO-I, 4-iodophenylsubstituted graphene; HRTEM, high-resolution transmission

70 electron microscopy; AFM, atomic force microscopy; GCD, galvanostatic charge-

71 discharge; ORR, oxygen reduction reaction; Pcs, Phthalocyanines; Pors, porphyrins;

72 TPA, tris-(4-aminophenyl)amine; PDI, perylenediimide; CNT, carbon nanotube;

73 ferrocene (Fc); OPV, organic photovoltaic; PSCs, perovskite solar cells; PCE, power

74 conversion efficiency; HTL, hole-transporting layer; ESL, electronic selective layer;

75 ITO, indium tin oxide; PEDOT:PSS, poly(3,4-

76 ethylenedioxythiophene):polystyrenesulfonate; EP, electropolymerization; EC,

77 electrochemical; IPCE, incident-photon-to-current conversion efficiency; EQE,

78 external quantum efficiency.

Abstract:

Energy shortages and climate change call for the development of clean and sustainable energy. The development of green materials for clean energy storage and conversion is conducive to promoting the widespread use of clean energy. Conjugated microporous polymers (CMPs) have been synthesized with multifarious structures and distinct properties, which offer designability for the molecular structures and nanopores of conjugated skeletons. The research of CMPs in clean energy technologies is significant for the improvement of CMP-based materials and their application in energy and environmental engineering. CMPs have shown great potential for challenging energy and environmental issues such as gas adsorption, photocatalysis, solar energy conversion, and electrical energy storage and conversion. This review aims to summarize the advances of synthesis and design on CMPs, computer simulations on CMPs, and the applications of CMPs in the clean energy technologies including hydrogen evolution and storage, the adsorption and conversion of carbon dioxide, rechargeable batteries, supercapacitors, fuel cells, and photovoltaic cells. We also propose the challenges and potential chances of the synthesis and the clean energy applications of CMPs.

Keywords: conjugated microporous polymers; ultra-thin films; density functional theory; hydrogen storage; lithium-ion batteries; supercapacitor; solar cells

Content

1. Introduction

1.1 Research Background

Energy shortages and environmental pollution are global challenges. Traditional fossil energy reserves are limited. The use of large amounts of fossil energy can cause environmental pollution and global warming [1-3]. To meet this challenge, finding new energy systems that can replace fossil energy is needed urgently. Clean energy has a lower environmental impact than traditional energy [4-8], which is the most promising candidate for the energy future. However, the supply of these energy sources is volatile, so to develop strategies for storing and transforming clean energy is required. Today, many effective devices and techniques have been developed to store and transform clean energy including photocatalytic hydrogen production and hydrogen storage [9-11], rechargeable batteries [12-14], oxygen reduction devices [15-17], photovoltaic devices [18-20], and supercapacitors [21-23]. To improve the energy storage and conversion efficiency of these devices, many materials have been developed and used as catalysts or electrode materials [24-26].

The common choices are inorganic active materials such as transition metal oxides and graphite [27-29]. In 2014, the recent advances, the mechanism in detail, and new challenges and prospects in plasma-based nanogold catalysts in organic and clean energy conversion systems are discussed [30]. Due to the surface plasmon resonance (SPR) effect in plasma-based catalysts, the near-field of local plasma and scattering

171 effect are improved, and e−–h+ pairs are stimulated, thus greatly increasing the catalytic

172 activity and efficiency of solar-energy conversion. Hossain et al. highlighted the

173 application of $BaCeO_3$ and $BaZrO_3$ electrolyte materials in proton-conducting solid

174 oxide fuel cells (SOFCs) [31].

175 Furthermore, the novel microporous organic polymers (MOPs) are becoming to be

176 new candidate materials for clean energy due to their large surface area, structural

177 modularity, and excellent physicochemical properties [32-36], such as, covalent organic

178 frameworks (COFs) [37-41], porous aromatic frameworks (PAFs) [42], polymers of

179 intrinsic microporosity (PIMs) [43,44], anionic microporous polymer networks

180 (AMPNs) [45,46], conjugated microporous polymers (CMPs) [47-51], and

181 hypercrosslinked microporous organic polymers (HMOPs) [52]. The historical

182 development of these MOPs is shown in Fig. 1 [42,47,53-57]. Javier's group critically

183 reviewed the application and development of mesoporous materials in the field of clean

184 energy [58], and gave many examples of the development of mesoporous structures,

185 including the preparation of different scale pore systems with layered structures, which

186 brings hope for better and cleaner energy production. Xia et al. discussed the application

187 of COFs in the field of clean energy, and proposed the design principles laid the

188 foundation for the rational design of COFs and the applications in clean energy [59].

189 CMPs are a class of amorphous structures that have recently received increasing

190 attention due to their adjustability, expanded π-conjugation, and permanent building

191 links [60].

192 **Please insert Fig. 1**

193   Emerged as a powerful platform for solving deteriorating environmental and energy

194   problems, CMPs have been widely used as adsorbents [61,62], heterogeneous catalysts

195   [57,63-66], light-harvesting materials [67,68], luminescent materials [49,69],

196   photovoltaic materials [70,71], and photocatalysis [72], because they have many

197   advantages, such as: (i) The π-conjugated structure extending along the polymer

198   backbone provides excellent physicochemical stability, rich porous structure, and high

199   surface area. (ii) The highly crosslinked polymeric structure and high surface area

200   provide greater pore space to accommodate carriers and large contact surface areas to

201   shorten ion diffusion distance, ensuring high electrochemical activity and fast kinetics

202   [73-75]. (iii) The highly crosslinked polymer structure can effectively inhibit the

203   dissolution of the active material in the organic electrolyte and improve cycle stability

204   [73,76].

205   **1.2 Representative Advances**

206   CMPs refers to the macromolecular compounds that hold microporous networks and

207   π-conjugation resulting from alternating single and multiple bonds [48,77,78]. These

208   bonds result from the overlap of two p-orbitals (or d-orbitals) crosswise with an

209   intermediary σ-bond, which provides useful electronic properties (such as high

210   conductivity) to CMP networks. The large variety of molecular building blocks that can

211   be coupled in this way allows the control of functionality and structure in CMPs, and

212   this structural diversity has led to the rapid growth of these materials since their

213   discovery (Fig. 2) [47,57,67,76,79-94]. Almost all covalent bonds in CMPs are formed

214   by irreversible kinetic routes, so all CMPs (excluding covalent triazine frameworks) are

215   amorphous. In 2007, the unique porous materials, conjugated microporous

216   poly(aryleneethynylene) networks with Brunauer–Emmett–Teller (BET) surface areas

217   up to 834 $m^2\,g^{-1}$ were reported for the first [47]. In 2008, the CMPs with BET surface

218   areas up to 1000 $m^2\,g^{-1}$ were produced [95]. As well as, Thomas et al. constructed CMPs

219   based on spirobifluorene blocks and proposed for the first time to use these

220   photoluminescent CMPs for photoelectric applications [80]. In the same year, CMPs

221   prepared by homocoupling routes of 1,3,5-triethynylbenzene (TEB) were also reported

222   [79] and confirmed to display visible-light catalytic activity for overall water splitting

223   in 2017 [92]. In 2009, Thomas et al. also outlined a framework for a new generation of

224   porous polymers for energy-related applications, presented potential applications, and

225   proposed some outstanding issues and developments [96]. Metal-supported high

226   surface area metal-organic CMPs (MO-CMPs) were synthesized in 2011 [57], etc. In

227   recent years, these CMPs are becoming important functional materials [48,57,97] and

228   are further explored for use in the field of clean energy.

229   **Please insert Fig. 2**

230   In the development process of CMPs in the field of clean energy, Jiang's group

231   comprehensively reviewed the design principles, structural research, and functional

232   exploration, as well as potential application prospects of CMP materials [77]. Wang et

233   al. briefly summarized the latest developments and trends in the field of photocatalytic

234   water splitting using CMPs [98]. As well as, we reviewed the energy transfer

235   phenomena of CMPs and the basic principles of photocatalysis, and proposed the

236 strategy of improving the photocatalytic performance of CMPs [72]. To the best of our

237 knowledge, there is no specific and detailed review for the CMPs in the field of clean

238 energy. In recent years, CMPs have made rapid progress in the field of clean energy,

239 and it is time to make a comprehensive and detailed summary and analysis of the topic

240 of CMPs as a platform for clean energy. In this review, we aim to present the latest

241 research advances in CMPs for clean energy including hydrogen storage materials,

242 carbon dioxide capture and conversion, metal-ion rechargeable batteries,

243 supercapacitors, fuel cells, and photovoltaic cells (Fig. 3). We first present an overview

244 discussion and a summary of the synthesis strategies for CMP nanoparticles (NPs),

245 nanotubes (NTs), and films. Then, a computer simulation that predicts and guides the

246 synthesis and application of CMP materials is recommended. Furthermore, the use of

247 CMPs with excellent properties in the field of clean energy is described. Finally, we

248 discuss in detail the future trends and major challenges in the development of CMPs in

249 the clean energy field. We sincerely hope that this will stimulate readers' interest in the

250 exploration of clean energy, who is advised to further read the cited articles.

251 **Please insert Fig. 3**

252 **2. Synthesis Strategies of CMPs**

253 The diversity of monomers and the variety of reactive groups make CMPs with

254 diverse network structures and molecular functions. The reaction monomer of CMPs

255 include π units such as arenes, fused aromatic rings, heterocyclic units

256 phenylethynylene derivatives, macrocyclic systems, and so on, and the reactive groups

257 such as iodoarenes, aromatic boronic acids, bromoarenes, cyano-substituted arenes,

258 ethynyl-substituted arenes, and amino-substituted arenes, aromatic aldehydes [77].

259 CMP networks are usually formed by the reaction between two or more different

260 monomers or, some by the homocoupling of a single monomer. The main challenge is

261 to design a simple and productive synthesis route that can control the structural and

262 photoelectric properties of CMPs to improve the performance of these networks in

263 energy storage. This includes improved control at the molecular level, the establishment

264 of topologies, the construction of porous structures, the regulation of band gaps, and

265 changes in structural dimensions. So far, a variety of synthetic methods have been

266 developed for the preparation of CMPs, including the noble metal catalysis and non-

267 noble metal catalysis methods. Quintessential examples of these synthetic methods are

268 summarized in Table 1 [47,49,55,91,99-104].

269 **Please insert Table 1**

270 **2.1 Noble Metal-Catalyzed Synthesis**

271 Noble metal-catalyzed cross-coupling reactions are the first to be developed and are

272 also the most versatile strategy for the synthesis of CMP materials. The structure of

273 CMPs can be regulated by adjusting the comonomer molar ratio, and the reaction

274 conditions. The advantages of these reactions are (i) mild reaction conditions, easy

275 availability of substrates, good selectivity, easy post-synthesis functionalization, and

276 good tolerance to functional groups, (ii) single synthesis precursor, simple reaction

14

277   route, and high synthetic yield, (iii) high specific surface area. To date, various new

278   CMP materials with adjustable structure and multifunction have been synthesized by

279   noble metal-catalyzed cross-coupling reactions [83,105,106], which have great

280   application prospects in clean energy systems. In this section, the up-to-date progress

281   of this synthetic strategy is present in detail, including the Sonogashira-Hagihara

282   reaction, the Suzuki cross-coupling reaction, the Yamamoto reaction, and the

283   Buchwald-Hartwig coupling reaction.

284   **2.1.1 Sonogashira-Hagihara Reaction**

285   The construction of the porous structure of CMPs requires the cross-coupling of

286   building blocks of different geometric shapes. To construct conjugated porous

287   structures, the monomers are first connected by the Pd-catalyzed Sonogashira-Hagihara

288   cross-coupling reaction (Hereinafter referred to as Sonogashira-Hagihara reaction) with

289   π-conjugated bonds [47,95,107]. In 2007, Jiang et al. combined the symmetrical core

290   of C3 with the symmetrical linker of C2 through Sonogashira-Hagihara reaction to

291   synthesize a series of polymer networks, namely CMP-1, CMP-2, CMP-3, and CMP-4

292   [47]. The pore size, surface area, and gas absorption of these materials can be attuned

293   by changing the length of the link. CMP-1 contains two acetylene and one benzene on

294   the arm, and its BET surface area is larger than the other three CMPs, indicating that

295   the length of the polymer arm is inversely proportional to its surface area. In the

296   following year, Jiang et al. then synthesized two other CMPs (CMP-0 and CMP-5) and

297   the CMP-0 (S_{BET}: 1018 m^2 g^{-1}) arm has only one ethylene and one benzene [95]. The

298   BET surface area of CMP-0 exceeds that of CMP-1.

299   The polymer networks TCMP-0, TNCMP-2, TCMP-3, and TCMP-5 based on

300   triazine were synthesized by Sonogashira-Hagihara reaction in 2012 [108]. In structural

301   principle, these networks are isomorphic with the previously reported CMP-3 [47],

302   CMP-0 and CMP-5 [95], and NCMP-2 [109]. As shown in Fig. 4, benzene nodes in

303   these triazine-based network TCMP materials are replaced by 1,3,5-triazine units,

304   which proves that nodes of CMPs can be adjusted and replaced reasonably. Meanwhile,

305   the porosity of these polymers is comparable to that of previously reported 1,3,5-linked

306   benzene CMP systems, but TCMPs showed better CO_2 absorption capacity. The

307   TNCMP-2 displayed the highest surface area (995 m^2 g^{-1}) and higher CO_2 absorption

308   capacity (1.45 mmol g^{-1} at 1 bar at 298 K).

309   **Please insert Fig. 4**

310   At the same porosity, selecting suitable monomers could effectively improve the

311   physicochemical stability and adsorption capacity of the polymer network. Li's group

312   used the Sonogashira-Hagihara reaction to synthesize CMPs with thiophene segments

313   (SCMPs) [110]. Their electron-thiophene building units combine rich porosity and

314   conjugated network structure, resulting in better adsorption capacity. In another

315   example, Li's group used arylethynylenes and 2,6-dibromomethyl pyridine as raw

316   materials, novel functional CMPs with pyridine units (PCMPs) were synthesized by

317   Sonogashira-Hagihara reaction [111]. They find that the choice of vinyl monomer has

318   a noteworthy effect on the BET specific surface area of the resulting CMPs.

319   Furthermore, the molar ratio of the monomer has a significant effect on the surface area,

320 which in turn affects the gas adsorption performance of CMPs [112,113]. Li's group

321 synthesized a class of CMP networks using the Sonogashira-Hagihara reaction by using

322 1,3,5-triethylbenzene and 1,4-diethylbenzene as monomers (Fig. 5A) and used these

323 CMPs as a porous model to reveal the influence of monomer ratio on the porosity of

324 CMPs [112]. The results show that with the increase of the molar ratio of 1,3,5-

325 triacetylene benzene to 1,4-diacetylene benzene, the surface area and total pore volume

326 of these HCMP samples is decreased, but the mesopore and micropore volume is

327 increased, which caused the improvement of the hydrogen adsorption capacity of

328 HCMP samples (Fig. 5B). This can provide useful guidance for the design of new CMP

329 hydrogen storage materials.

Please insert Fig. 5

331   Recently, Xiang's group synthesized L-PDBT, L-PDBT-O, N-PDBT, and N-PDBT-

332 O by Sonogashira-Hagihara reaction (Fig. 6A) [114]. In the field of clean energy, the

333 design and synthesis of better hydrophilic CMP materials are beneficial to the exposure

334 of photocatalytic active sites to the water environment, thus increasing photocatalytic

335 activity. For these reasons, the morphology and surface polarity of these polymers can

336 be adjusted by changing the structure block (Fig. 6A), so that CMPs have high

337 hydrophilicity, which is more conducive to the production of hydrogen by

338 photocatalytic water splitting. The measurement results of the water contact angle (Fig.

339 6B) show that N-PDBT-O has good water compatibility and adsorption performance.

340 Compared with L-PDBT-O, polymer network N-PDBT-O exhibited better

341 photocatalytic H_2 evolution activity [hydrogen evolution rate (HER): 366 μmol h^{-1},

342 AQY): 3.7%, λ > 420 nm] because the synergistic effect of high hydrophilicity and BET

343 surface area leads to more effective absorption of visible light by N-PDBT-O. The

344 hydrophilic control strategy can also be applied to the design of other CMP-based

345 photocatalysts to improve their photocatalytic activity, which provides an effective

346 strategy for the design of higher hydrophilic CMP-based photocatalysts.

347 **Please insert Fig. 6**

348 **2.1.2 Suzuki Cross-Coupling Reaction**

349 Suzuki-Miyaura cross-coupling reaction (hereinafter referred to as Suzuki reaction),

350 a reaction of aryl or alkenyl boric acid or boric acid ester with chlorine, bromine, aryl

351 iodide or olefin catalyzed by noble metal Pd-based compounds, which was first reported

352 by Akira Suzuki in 1979 [115,116]. This synthetic method has the advantages of

353 commercial availability of boric acid, wide compatibility of functional groups, mild

354 reaction conditions, etc. [117,118], so it has the potential of scale. However, the Suzuki

355 reaction is sensitive to oxygen, which causes the homocoupling and the by-product of

356 deboronated. Therefore, the gas should be eliminated strictly in the reaction process.

357 Here, a series of donor-π-receptor (D-π-A) CMPs with different polymer structures and

358 components are synthesized by Suzuki reaction using pyrene, benzothiadiazole,

359 benzene (or biphenyl) as a donor, a receptor, and a crosslinking agent unit, respectively

360 [65]. By adjusting the monomer species and the ratio of pyrene to benzothiazole in the

361 reaction process, the molecular structure of CMPs can be adjusted (Fig. 7), and then

362 improving their photocatalytic performance. This work highlights the molecular

363   structure as one of the key factors in the design of efficient CMP photocatalysts, which

364   provides a promising platform for efficient organic photocatalysts. Given the wide

365   range of electron donor and acceptor units and the universality of the Suzuki reaction,

366   there is an opportunity to produce a wide range of CMPs for use in clean energy.

367   **Please insert Fig. 7**

368 2.1.3 Heck Reaction

369   Heck reaction also is known as the Mizoroki-Heck reaction. Since Heck and

370   Mizoroki independently discovered this reaction in the late 1960s, it has been applied

371   more and more widely through continuous improvement of catalysts and reaction

372   conditions, so that it has become one of the important reactions forming the C—C bond.

373   In recent years, through the Heck reaction of 1,3,5-tri(4-ethenylphenyl) benzene and

374   aromatic halides, a new class of luminescent microporous organic polymer LMOPs has

375   been constructed (Fig. 8), which has a large surface area, narrow pore size distribution,

376   and strong luminescent performance [100,119]. The one-pot synthesis strategy is

377   expected to produce a variety of luminescent porous organic polymers, which could be

378   widely used in the fields of organic photovoltaic and photocatalysis.

379   **Please insert Fig. 8**

380 2.1.4 Yamamoto Reaction

381   Yamamoto coupling reaction, also known as Yamamoto reaction, is a cross-coupling

382   reaction in which halogenated aromatic hydrocarbons form C-C bonds under the

383 catalysis of transition metal Ni [120-124]. The CMPs formed by Yamamoto coupling

384 of tetrakis(4-iodophenyl)methane and tetrakis(4-bromophenyl)-1,3,5,7-adamantane

385 monomers (Fig. 9) with BET surface areas of 3160 and 3180 m^2 g^{-1}, respectively, top

386 all the CMPs in term of BET surface areas [107]. In 2009, Thomas et al. first prepared

387 a series of spirobifluoren-based CMPs (YSN-CMPs) by Yamamoto coupling reaction,

388 in which, when 2,2',7,7'-tetrabromo-9,9'-spirobifluorene was self-polymerized, the

389 specific surface area of the CMP was 1275 m^2 g^{-1} [125]. Results have shown that the

390 bond length and configuration of different structural units can greatly affect the pore

391 structure and BET surface area of CMPs. For example, when 2,2',7,7'-tetrabromo-9,9'-

392 spirobifluorene was copolymerized with p-dibromobenzene, the specific surface area

393 of the polymer networks decreased to 887 m^2 g^{-1}, when it was copolymerized with m-

394 dibromobenzene, the specific surface area decreased to 361 m^2 g^{-1}, when it was

395 copolymerized with o-dibromobenzene, the specific surface area was only 5 m^2 g^{-1}

396 [125].

397 **Please insert Fig. 9**

398 Besides, p-aryl monomers are beneficial to the formation of porous structures [126].

399 Jiang's group used the Yamamoto coupling reaction to synthesize a novel conjugated

400 microporous polymer (TPE-CMP) with a p-aryl monomer tetrakis(4-

401 bromophenyl)ethene (TPTBE) [49]. In this reaction, the tetraphenylethene (TPE) units

402 are directly connected to form a chain network, which limits the rotation of the phenyl

403 group and enables the CMP to has a high luminescent activity, which has great potential

404 in the production of hydrogen by the visible light solution of water. It should be noted

405 that the disadvantage of the synthesis of CMP materials by the Yamamoto reaction is

406 that the Ni catalyst is easy to oxidize and absorb water, resulting in inactivation.

407 Therefore, the condition of no water and no oxygen should be strictly controlled in the

408 reaction process, which increases the preparation cost of CMPs to some extent.

409 **2.1.5 Buchwald-Hartwig Coupling Reaction**

410 Buchwald-Hartwig coupling reaction (B-H coupling) is a coupling reaction of

411 halogenated aromatic hydrocarbons and aromatic amines to form C—N bonds under

412 the action of a small amount of palladium catalyst. In 2008, Germain et al. first prepared

413 the polyaniline network structure by B-H coupling and used it for hydrogen adsorption

414 [127]. In 2014, Liao et al. extended this method to the efficient preparation of CMPs

415 [91,128]. A series of conjugated microporous polytriphenylamine (PTPA) networks

416 (Fig. 10A) and Hexaphenylbenzene (HPB)-based CMPs (HCMPs) (Fig. 10B) through

417 the B-H coupling of tris(4-bromophenyl)amine core [128] and aromatic amine linkers

418 or hexakis(4-bromophenyl)benzene (HBB) core and aryl diamine linkers [91]. The

419 specific surface area and pore structure of PTPAs can be regulated by changing the

420 conjugate length and rigidity of aromatic amine. Longer conjugate length and stronger

421 rigidity of aromatic amine can synthesize CMPs with larger specific surface area up to

422 530 m^2 g^{-1}.

423 **Please insert Fig. 10**

2.2 Non-Noble Metal-Catalyzed Synthesis

Noble metal-catalyzed cross-coupling reactions are an important strategy for the synthesis of CMP materials. However, noble metal catalysts are expensive, sensitive to oxygen, difficult to recycle, and the catalyst solvents are toxic. Therefore, some non-noble metal-catalyzed synthesis reactions for the synthesis of CMP materials have developed. These reactions have advantages such as the use of cheap catalysts, ambient temperature reaction conditions, high yields, and only a single monomer is required, which are the keys to expanding the preparation of CMP materials. This section presents non-noble metal-catalyzed chemical synthesis methods for preparing conjugated microporous polymers in detail. It mainly includes oxidation coupling reaction, Schiff-base reaction, and Friedel-Crafts reaction, heterocycle linkages, phenazine ring fusion reaction, and cyclotrimerization reaction. These methods are providing an effective way for large-scale preparation of high-efficiency CMP materials for the clean energy field.

2.2.1 Oxidative Coupling Reaction

Oxidative polymerization is the process by which a compound containing active hydrogen atoms is dehydrogenated to form a polymer in the presence of an oxidation catalyst. According to the different oxidation forms, it can be divided into chemical oxidation polymerization and electrochemical oxidation polymerization. Chemical oxidation polymerization is the reaction of monomer dehydrogenation polymerization under the action of oxidants such as $FeCl_3$ [129].

Chen et al. used carbazole-based oxidative coupling polymerization to prepare

445   various of microporous conjugated polycarbazoles (CPOP-2–7) with eternal porosity

446   and special functions [130]. 2D and 3D conjugated structures with non-planar rigid

447   conformation have been proved to be excellent candidate materials for the preparation

448   of conjugated core structures. The synthesis routes of monomers are shown in Fig. 11A,

449   carbazolyl groups can be simply introduced into these conjugated core structures, which

450   provide conditions for the preparation of multifunctional polymer networks. As shown

451   in Fig. 11B, taking multipurpose carbazolyl-bearing 2D and 3D conjugated central with

452   non-planar rigid conformation as linking units, a series of CPOPs are synthesized.

453   Because no need boric acid, alkyl, halo groups, and other functional groups for the

454   coupling polymerization reaction, so the properties get from monomer could be fully

455   retained, and because each carbazole group in a monomer has two reaction sites, so

456   makes the oxidation coupling polymerization of carbazolyl easy to form a porous

457   polymer. As well as due to the high degree of crosslinking, the pore structure of the

458   polymer is more stable and durable. The BET specific surface area of these porous

459   polymer materials is between 510 and 1430 m^2 g^{-1}, and the pore sizes are between 0.59

460   and 0.66 nm.

461   **Please insert Fig. 11**

462   A carbazole-based CMP prepared by oxidative coupling polymerization has

463   permanent micropores, high luminescent properties, and plentiful nitrogen activation

464   sites, so it shows a high adsorption capacity of carbon dioxide with good selectivity and

465   is an attractive functional material in clean energy applications [131]. In 2016, Yang's

466   group reported four carbazole-based CMPs (PCz-Cn-Cz) by using $FeCl_3$ catalyzed

467   oxidation coupling method [101]. These polymers have the same rigid backbone

468   (carbazole) and different soft-bonded alkylene chains, but the pore width and pore size

469   distribution of the four polymers not seem to differ significantly. These four polymers

470   all have a high specific surface area ($>750 \ m^2 \ g^{-1}$) and good adsorption capacity of gases

471   (H_2, CO_2, CH_4, CO), which have broad application prospects in the field of clean energy

472   and environmental engineering. Meanwhile, because carbazoles are electron-rich group

473   [132], so $FeCl_3$-catalyzed oxidative coupling reaction of carbazole and the electron-

474   deficient unit can provide a greener and more environmentally friendly alternative to

475   metal-free, visible light-driven solid CMP photocatalysts synthesis. In addition, two

476   novel porphyrin-based CMPs (Porp-TPE-CMP and Porp-Py-CMP) formed by $FeCl_3$

477   catalyzed oxidative coupling reaction between pyrrole and aromatic aldehyde catalyzed

478   also have the ability of gas adsorption [133]. Their BET specific surface areas are 547

479   and 31 $m^2 \ g^{-1}$, respectively, and their CO_2/N_2 and CO_2/CH_4 selectivity are 55.28 and

480   4.11, respectively. These strategies provide a viable strategy for the storage of

481   greenhouse gases and chemical hydrides.

482   **2.2.2 Schiff-Base Reaction**

483   In 2016, Chai et al. used Schiff-base reaction of 1,3,5-triformylphloroglucinol (TFP)

484   and m-phenylenediamine (m-PDA) to synthesize an innovative β-ketoenamine-linked

485   CMP (KECMP-1) [102]. The synthesis route is shown in Fig. 12, this preparation

486   strategy uses only a single reactant and has the advantages of metal-free catalysis and

487   template-free, as well as the BET specific surface area of the synthesized polymer

488   network is up to 691 m^2 g^{-1}. Meanwhile, the introduction of N—H groups into the

489   polymer pore surface using a bottom-up strategy is conducive to the formation of the

490   interaction between N—H···O and CO_2, thus enhancing the CO_2 adsorption capacity

491   of the polymer network. In 2018, CoCMP and ZnCMP were synthesized by a Schiff-

492   base condensation reaction between metal-phthalocyanine tetra-amine and 4,4′-(2,5-

493   bis(pentyloxy)1,4-phenylene)bis(ethyne-2,1-diyl)dibenzaldehyde   (OPE-5)   [134].

494   Among them, CoCMP, where Co^{2+} is steadied by the N$_4$-coordination of

495   Phthalocyanines (PCs), and as a catalytic center. CoCMP showed stable and efficient

496   electrocatalytic activity to oxygen evolution reaction (OER) (overpotential: 340 mV).

497   This demonstrates the importance of Co^{2+} in OER catalysis. Meanwhile, the inactivity

498   of ZnCMP to OER indicates that the introduction of metal ions should be wisely

499   selected in addition to the selection of reaction conditions when designing CMP

500   electrocatalysts.

501   **Please insert Fig. 12**

502   Recently, the polymer network (FcTz-POP) formed by introducing iodine-affinity

503   group ferrocene into the polymer network through Schiff-base reaction is quite stable,

504   with a significantly increased iodine vapor adsorption capacity (396 wt. %, 348k,

505   atmospheric pressure), higher than that of the ferrocene-free polymer (BpTz-POP) (216

506   wt. %, 348K, atmospheric pressure) [135]. This guides the further introduction of other

507   functional groups into the CMP networks through Schiff-base reaction to achieve

508   specific effects for the application of clean energy.

2.2.3 Heterocycle Linkages

A high porosity benzimidazole-chain polymer was synthesized by a simple template-free condensation reaction of 2,3,6,7,10,11-hexaaminotriphenylene with tetrakis(4-formylphenyl)methane, which has a wide application prospect in gas storage and separation [136]. As well as under solvent-heat conditions, catalyst-free condensation of aldehydes with dithiooxamide to form the thiazolothiazole-linked microporous polymer, which reveals high selective absorption of CO_2 at room temperature and pressure [137]. Recently, Feng's group systematically reported the formation of thiazolo[5,4-d]thiazole (TzTz) linkages, and three novel TzTz-linked POPs, namely TzTz-POP-3, TzTz-POP-4, and TzTz-POP-5 were synthesized by triphenylbenzene, tetraphenylpyrene, and tetra(hydroxyphenyl)methane cores, respectively [103], which exhibited excellent thermochemical stability and chemoselectivity.

2.2.4 Phenazine Ring Fusion Reaction

Aza-CMP construction by built-in aza units and micropores, which has fused skeletons, compact aza units, and micropores to facilitate the formation of charge separation layers [138]. Therefore, it has great potential as a high-energy storage device. Compared to Aza-CMP, TIPS-CMP synthesis by the cyclocondensation of 1,2,3,4,5,6-hexaketocyclohexane and 3,6-di(triisopropylsilyl)ethynyl-1,2,4,5-benzenetetraamine after decontamination at reflux in a 1:4 mixture of dioxane and acetic acid (Fig. 13A) [104], has increased dispersion attributed to the highly distorted aromatic structure (Fig. 13B), which is conducive to the exfoliation of individual layers and the reduction of the

interaction between dispersed layers in organic media. Uniform, coherent, optically transparent, and semiconducting films can be obtained with this enhanced dispersant. This shows that twist is a very powerful strategy for improving the dispersibility and processing properties of conjugated microporous polymers.

Please insert Fig. 13

2.2.5 Cyclotrimerization Reaction

Cyanocyclization is a method to prepare porous polymers under ionic heat after mixing $ZnCl_2$ with monomers, in which $ZnCl_2$ acts as a solvent, catalyst, and template pore-making agent. The CMPs obtained by this method is also called covalent triazine polymers (CTFs) [139]. For example, in 2008, Thomas' group for the first time obtained CTFs formed from nitrile molecules 1,4- dicyanobenzene in a $ZnCl_2$ melt at 400 °C (Fig. 14) [55]. CTFs with different pore structures and characteristics can be prepared by regulating temperature [140], monomer types [141], and reaction kinetics parameters [142]. Later, in 2010, Liu's group realized the precise regulation of the pore diameter and specific surface area of CMP by using the cyclotrimerization reaction of alkynyl monomers of different lengths [143].

Please insert Fig. 14

2.3 Comparison of Synthesis and Processing

In general, CMPs with different characteristics can be obtained in different coupling reactions catalyzed by noble metals. For example, the CMP obtained through the

27

Sonogashira-Hagihara coupling reaction contains an alkynyl group, which can be post-processed and functionalized. C-N bonds can be introduced into CMPs by using the Buchwald-Hartwig coupling reaction, which give them a certain degree of redox properties, making them better applicable to the field of clean energy. And Yamamoto Reaction is the first choice for the synthesis of high-surface-area CMPs.

These noble metal catalyzed synthesis reactions are the most commonly used and tend to mature, but the noble metal catalysts used in the synthesis process need to be removed through the cumbersome extraction process (such as Soxhlet extraction). Non-noble metal-catalytic processes are an option to avoid the use of metal catalysts that are difficult to eliminate. Meanwhile, these synthesis strategies have many other advantages, such as, the advantages of oxidative polymerization, such as the use of cheap catalysts, ambient temperature reaction conditions, high yield, and single monomer [144-148], to simplify production and reduce the cost, which required for large-scale preparation of porous materials. And Schiff-base reaction has the advantage of producing nitrogenous CMPs, which exhibit good electrocatalytic activity, and can be used for CO_2 adsorption [149-151].

Since the diversity of synthetic monomers and microporous structure of CMPs are two main characteristics of CMPs and generally affect the properties of materials. Therefore, it is important to investigate the differences in surface area and pore structure of different CMPs in different synthetic reactions. Surface area information of CMPs is usually calculated using physical adsorption isotherms [152-154]. The most common method is to use Brunauer-Emmett-Teller (BET) theory to get BET surface area and

information about pore size distribution from the BET plot. However, before gas uptake measurements, it is necessary to investigate the chemical properties and structural changes of CMPs through thermogravimetric analysis (TGA) experiments [155-157].

In addition, when using CMP as a precursor material for porous carbon materials, the effect of the structure and composition of CMPs on these derived carbons should be considered, and the carbon yield of these CMPs should be reasonably assessed. CHN analysis techniques can provide information about the composition of CMP materials, including carbon, hydrogen, and nitrogen content [152], which are usually of concern when preparing derived porous carbon. Meanwhile, in order to further understand how the composition and structure of CMPs affect the performance and structure of these derived carbons, some auxiliary characterization experiments are usually needed, such as scanning electron microscopy image (SEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) measurements, powder X-ray diffraction (XRD) analysis, ^{13}C solid-state nuclear magnetic resonance (NMR) spectroscopy, inductively coupled plasma emission spectrum (ICP-OES), etc.

3. Post-Synthetic Functionalization of CMPs

In addition to the selection of monomer molecular size, monomer ratio, and reaction conditions to regulate CMPs, post-synthetic modification of the CMPs backbone structure is another effective way to regulate their structure and properties. The functionalization of CMPs can be achieved by introducing different functional groups into the polymer networks. In the past few years, extensive research on the post-

593   functionalization of organic materials have conducted, and often use so-called "click"

594   chemistry [158-162], such as Huisgen reaction (copper-catalyzed 3 + 2 cycloadditions

595   of azides), copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC), thiol-yne click

596   chemistry, and so on. In this section, post-synthetic modification to improve the

597   properties of CMP materials is discussed.

598   Post-synthetic functionalization can modify the morphology and properties of CMPs

599   by modifying their molecular structure [163,164]. As shown in Fig. 15A, radical thiol-

600   yne chemistry of CMPs with aliphatic alcohols can adjust their functionalization degree

601   and morphology, and then adjust their porosity and optical properties by changing the

602   amount of thiol [165]. Similarly, an amine-functionalized CMP (CMP-1-NH$_2$) can

603   modify amines into amides with different chiral alkyl chains to control surface

604   functional groups and microporosity, and then reasonably adjust its BET specific

605   surface area, pore-volume, CO$_2$ adsorption capacity, and isothermal heat capacity (Fig.

606   15B) [166].

607   **Please insert Fig. 15**

608   "Clicking post-synthetic modification", adjusts the fluoride content in the CMP

609   framework by controlling the ratio of azide groups to improve gas capture ability. As

610   shown in Fig. 16, first, a series of zinc-porphyrin CMPs (ZnP-XN$_3$-CMPs, X = 5, 25,

611   and 50%) are synthesized from zinc porphyrin units, and then the azide groups are

612   introduced into the pores of ZnP-XN$_3$-CMPs to form ZnP-XF-CMPs (X = 5, 25, and

613   50%) [167]. The measurement result represented the CO$_2$ capacity of ZnP-XF-CMPs,

614   X = 5, 25, and 50% at 298 K and 1.0 bar was 34, 52, and 90 mg g^{-1}, respectively, which

615   was 1.31, 1.68, and 1.84 times higher than that of the ZnP-XN$_3$-CMPs, X =5, 25, and

616   50%.

---

617   **Please insert Fig. 16**

---

618   Besides, the CMPs have a π-conjugated skeleton that also can be further adjusted by

619   a postoxidation reaction to form a network with an extended π-structure [168]. Firstly,

620   two CMPs with similar structure and high surface area, namely BO-CMP-1 and BO-

621   CMP-2, are prepared using the Suzuki reaction. Afterward, the postoxidation process

622   converts the biolefin benzoquinone blocks in the skeleton into the tetrabenzocoronene

623   segments to form oBO-CMP-1 and oBO-CMP-2 with an extended π-structure. The

624   method uses monomer with extended π-structures to prevent low polymerization

625   problems caused by direct synthesis and can adjust the structure, porosity, and even the

626   gas adsorption behavior of the main polymers, which provides a direct and simple post-

627   modulation process for CMPs.

628   **4. Morphological Control of CMPs**

629   Traditionally synthesized CMPs are amorphous powder materials, which are

630   insoluble and infusible, and restrict further applications. With the in-depth study of

631   CMP materials, other forms of CMP materials are synthesized one after another, such

632   as nanospherical, nanotubular, thin-film, and bulk CMPs according to the actual

633   application conditions under different synthesis methods. For example, CMP networks

634   with nanospherical, nanotubular, and thin-film structures constructed by template

635 synthesis can be used in high-performance energy-related applications. And high-

636 quality CMP films are excellent materials in the field of clean energy, which are

637 outstanding hole conductors with controllable thickness to be utilized directly in device

638 fabrication.

639 **4.1 CMP Nanospheres and Nanotubes**

640 Nanospheres and nanotubes have promising applications in gas storage separation,

641 energy storage, and solar energy conversion [169-171]. However, the control method

642 of CMP nanospheres and nanotubes is still a great challenge owing to the poor

643 dispersibility and solution processing of porous material. Both the structure of the

644 monomer and reaction solvent may affect the morphology of CMPs, and the formation

645 mechanism of the micromorphology of CMPs and the mechanism of the reaction

646 conditions affecting their morphology still need to be further studied. As an example of

647 the shape effect in materials science, hollow spheres exhibit better electrochemical and

648 photocatalytic properties than non-hollow spheres, so many examples of hollow

649 structures have been reported for the synthesis of porous materials [172,173]. After

650 noble metal-catalyzed synthesis, template replication strategy [174-176] and layer-by-

651 layer method [87,177] are effective methods for controllable synthesis of CMP

652 networks with hollow structures. Among them, the hard template method based on

653 silicon dioxide [178-180] has been used to construct a microporous polymer network

654 with a quasi-zero-dimension structure.

655 Silicon dioxide can be easily removed by chemical etching in reaction with HF or

656 NaOH. Therefore, hollow polymer networks are often obtained by chemical etching of

657 silica templates. For instance, Kang et al. used the silicon spheres template method to

658 prepare the shape-controlled hollow microporous organic networks (HMONs) [179].

659 Fig. 17 illustrated the synthetic route for the H-MONs using a silica template. Silica

660 spheres were obtained by the St.ber method [181] and added to the polymerization

661 process. The resulting mixture was then treated with HF solution to remove the silica

662 template to obtain H-MONs. Meanwhile, the thickness of the shell of H-MONs can be

663 well controlled by changing the synthesis conditions.

664 **Please insert Fig. 17**

665 Besides, controlled synthesis of zinc porphyrin (TP-Zn)-based CMP (Zn-CMP)

666 microspheres uniformly dispersed in solution is obtained by Sonogashira reaction of

667 5,10,15,20-tetrakis(4-ethynylphenyl)porphyrin-Zn(II)   and   brominated   monomers

668 directed by bidentate bipyridine (BP)-type ligands [182]. These spheres can be adjusted

669 between 320 and 740 nm in diameter, and the coordination between BP and TP-Zn

670 proved to be the key to forming the spheres. This strategy facilitates the handling and

671 separation of polymer microspheres and is suitable for the most halogenated monomers.

672 Given the universality of the chemical coordination method and the diversity of the

673 monomer structure of CMPs, it is of great significance in the large-scale preparation of

674 functional CMP spheres. However, it is important to note that these schemes

675 significantly reduce the specific surface area while forming the desired morphology of

676 the porous polymer [183,184], which may affect the application performance of CMPs.

677 The layer-by-layer template synthesis method maintains a layered CMPs with

678　managable chemical composition and regulating nanostructure. In 2016, Feng's group

679　used the functionalized carbon nanotubes as templates to layer-by-layer prepare CMPs

680　with controllable nanotube morphology and reasonable layered structure for the first

681　time [177]. As shown in Fig. 18A, first, the preparation of *p*-bromobenzene

682　functionalized carbon nanotubes (SWNT-Br) by SWNTs functionalized using the 4-

683　bromobenzodiazepine tetrafluoroborate. Later, CMP-PT was produced by Sonogashira

684　reaction of SWNT-Br, M2, and M3. Finally, three-layered CMP PTbBbT was

685　synthesized layer-by-layer using SWNT-Br or two-layered CMP-PTbB as template and

686　M1 and M2 or M2 and M3 as monomers at the same conditions. The scanning electron

687　microscopy (SEM) and transmission electron microscopy (TEM) confirm the nanotube

688　morphology of the CMPs (Fig. 18B). The as-prepared CMP nanotubes own high

689　specific surface areas (623 m^2 g^{-1}) and electronic interactions with electron acceptors

690　(n-type) SWNTS, which has a high catalytic activity to ORR. Meanwhile, the prepared

691　CMP nanotubes are also good precursors for the preparation of heteroatom-doped

692　porous carbon nanotubes by pyrolysis (Fig. 18A). This novel synthesis route provides

693　a new idea for the preparation of porous materials with excellent performance for

694　energy storage, energy conversion, optoelectronic devices, and other clean energy fields.

695　Meanwhile, it is worth noting that the drawbacks of these layer-by-layer templating

696　methods are tedious operation processes and large energy consumption [113]. Therefore,

697　there is still a great need to develop convenient, simple, easy to handle, and low energy

698　consumption methods for producing CMP materials with controlled morphology.

699　**Please insert Fig. 18**

34

4.2 CMP Films

CMP films, an excellent hole conductor with controllable thickness, have many remarkable physical properties, covering high porosity, extended π-conjugated, facilitating exciton delocalization, and high electron transfer rate. The high-quality CMP films are excellent materials in the field of clean energy and can be directly used in the fabrication of devices [178,185]. Spreading the π-conjugated structure of CMPs to film structure can not only significantly enhance their charge transport, but also bring other good properties, such as excellent mechanical properties, flexibility, isotropy, and so on [186,187]. Common methods for the synthesis of CMP thin films are shown in Fig. 19: (A) solution spray-coating [84], (B) layer-by-layer self-assembly [188], (C) electrochemical deposition [189], (D) interfacial polymerization [190], and (E) surface-initiated polymerization [191].

Please insert Fig. 19

Interfacial polymerization usually uses two incompatible solvents to dissolve monomers and/or initiators, catalysts, etc. [192] and has been developed for the synthesis of self-supporting and thick-controlled CMP nanometer-thin films, also known as a soft template synthesis method. In 2017, Chen et al. used interfacial polymerization based on the new polymerization strategy of Sonogashira-Hagihara reaction and oil-water interfacial Schiff-base reaction to prepare CMP nanofilms with independent and controllable thickness [190]. The thickness of CMP nanofilms can be controlled in 30–200nm by changing the concentration of monomer, and independent

721 macroscopic nanofilms can be easily transferred to various substrates, both are of great

722 practical value in practical application.

723 Electrochemical deposition, an electrochemical route for the preparation of

724 electroactive polymer films by solution polymerization and in situ deposition in one pot

725 [71,193,194]. Compared with the usual spin coating, it only needs a slight amount of

726 precursor solution to synthesize thin films that meet the thickness requirements [195-

727 199], so it can effectively reduce the material consumption and thus reduce the cost.

728 Electrochemical deposition films have the features of high crosslinking density,

729 controllable structure, and good stability, which are applied in supercapacitors [189],

730 organic light-emitting diodes (OLED) [195,197], induced emission devices [200], and

731 so on [201].

732 In 2015, Jiang's group reported a strategy of preparing thiophene-based CMP films

733 by electropolymerization at the solution electrode interface and revealed the conducting

734 properties of CMP materials for the first time [71]. As shown in Fig. 20, the unique

735 reaction site (Fig. 20A, blue arrows) of each thiophene subunit is electropolymerized

736 via the C—C bond to form a thin film (Fig. 20B). Fig. 20C reveal the optimal single

737 hole structure obtained by calculation, this multi-arm arrangement facilitates the

738 formation of a porous π-skeleton. This strategy could be widely extended to the

739 synthesis of other porous polythiophene films, which are expected to be used in high-

740 performance photovoltaic devices and could stimulate further structural and

741 performance exploration.

742 **Please insert Fig. 20**

743   Besides, the template method can be used to prepare CMP films. Fig. 21A shows the

744   route for the preparation of zero-dimension (0D), 1D, and 2D CMP materials that using

745   carbon nanosphere (CSs), SWNTs, and reduced graphene oxide (rGO) as the templates,

746   respectively [90]. The SEM and TEM of the as-prepared CMPs indicate that most

747   monomers have polymerized on the surface of the template (Fig. 21B). Remarkably,

748   dimensionality has an important impact on CMPs in terms of photoluminescence [90].

749   The inverse decay rate (τ_{eff}) reduction of nanocarbon directed CMPs up to 38-46% be

750   superior to amorphous CMPs. Meanwhile, the porous carbons prepared by pyrolyzed

751   of the corresponding dimension of CMPs showed more effective catalytic performance

752   for the ORR compared to advanced noble-metal catalysts, and the relationship between

753   electrochemical catalytic performance and dimension is 2D > 1D > 0D [90].

754   **Please insert Fig. 21**

755   Lindemann et al. realized the surface modification of CMP thin films and nanofilms

756   based on orthogonal click chemistry [202]. The reaction scheme of surface modification

757   is shown in Fig. 22, first, the Cu(I)-catalyzed alkyne-azide cycloaddition (CuAAC)

758   reaction is used for the preparation of the CMP nanofilms by a layer-by-layer method,

759   then, the thiol yne reaction is used to modify the alkyne moieties of the surface of the

760   last layer of the CMP films to realize the surface modification. This post-synthesis

761   functionalization for the outer surface of CMP nanofilms plays a positive role in

762   increasing the variability of them and facilitates the application of CMP materials in

763   catalysis, sensing, or other optics/electronics devices.

764   **Please insert Fig. 22**

Besides, the exfoliation is also a good strategy for CMP films [203]. However, due to the intense π-π overlapping interactions between the single-layers, the exfoliation usually requires additional aid to assist the exfoliating [204-207], and in most cases the exfoliated yield is low. Meanwhile, the auxiliary methods are not universal and may destroy the extended π-conjugated structure of CMPs [138]. Therefore, the development of an efficient exfoliation method for the preparation of CMP films needs further exploration. Recently, Wang et al. reported a exfoliation for the synthesis of a series of ultra-thin CMP films, which has been proved to have good oxygen reduction reactivity and can be used in battery devices [208]. Fig. 23A describes the stripping method for preparing ultra-thin CMP films, and Fig. 23B is four isomers of phthalocyanine monomer. Taking D_{4h} and D_{2h} as examples, nine combined structures can be randomly formed (Fig. 23C). The introduction of intrinsic defects and disorder in a single layer reduces interlaminar overlap of the amorphous ethynyl-linked phthalocyanine conjugated polymer (MP_C-CP) films, which in turn weakens the interlaminar interactions and ultimately yields an exfoliated yield of more than 50%. These well-dispersed thin film catalysts have more exposed catalytic active sites and more convenient material transport. The excellent ORR activity of these CMP films (open circuit voltage: 1.34 V; peak power density: ca. 180 mW cm^{-2}) is also confirmed for use in Zn-air battery devices (Fig. 23D) and two Zn-air batteries in series can deliver an enough open circuit voltage for the LED lamp (Fig. 23E).

Please insert Fig. 23

5. Computer Simulations of CMPs in Clean Energy Applications

Computer simulations, including quantum calculations (ab initio, density functional theory, etc.), grand canonical Monte-Carlo (GCMC) simulations, and molecular dynamics (MD) simulations, are used to theoretically study the mechanism of CMPs transition, and to explore the structure-activity relationship between molecular structure and the final polymer. This is the basis for the further preparation of CMPs with precisely subdivided structures and is key for the synthesis and application of CMPs. With the further development of computer technology and the maturity of calculation methods, computer simulations and traditional experimental methods complement each other, which will bring a bright future to the development of porous polymer materials [209].

5.1 Quantum Calculations Guide Functional Design in CMPs

Density functional theory (DFT), one of the basic theory of quantum calculations, is a quantum mechanical method to study the electronic structure of multi-electron systems, which is often used to guide the functional design of CMP materials in recent years [210-214]. In 2014, Srinivasu and Ghosh reported the electronic structure and adsorption properties of the 2D CMPs, 1,3,5-triethynyl (CMP-1), and benzene, 1,3,5-tributadiyne (HCMP-1), based on the DFT [215]. Results found that lithium atoms exist on both sides of the C6 ring of the two CMPs. Each lithium-ion site carries almost a unit of positive charge, which can bind to H_2 molecules through ion-induced dipole

806   interactions, thereby increasing the H_2 adsorption performance of CMPs. Furthermore,

807   in 2017, Fan et al. reported the electron structure and adsorption properties of single-

808   walled CMP nanotubes containing substituted benzene and ethylene units by the

809   density-functional tight-binding method augmented with a van der Waals dispersion

810   term [216]. The calculation results show that increasing the junction agent or adding

811   substituents (AOH or ANH$_2$ substituents) in the node could reduce the bandgap of the

812   nanotubes and bring about a larger expanded π-conjugation system, to improve the

813   bonding strength of the adsorbent and adsorbents, which is conducive to improving the

814   adsorption capacity in terms of energy.

815   Metal doping, the types of doped metals, and the doping amount could affect the

816   catalytic performance of CMP catalysts. Therefore, Xu's group were used spin-

817   polarized DFT method to design a novel 2D CMP of porphyrin units and thiophene

818   chain and introduced a series of metal atoms (Fe, Mg, Mn, and Cu) into the center of

819   the porphyrin ring to enhance their ability to reduce CO_2 [217]. Calculations show that

820   the CMPs are stable under environmental conditions, and the transition state (TS)

821   search calculation shows that the Fe-modified CMP (Fe-CMP) has the highest catalytic

822   activity for the reduction of CO_2. Fig. 24A shows the 2D geometric structure of Fe-

823   CMP after optimization. The calculation of energy band structure and frontier orbital

824   distribution further proved its semi-metallic properties and high electron occupancy,

825   both of which are key factors affecting photocatalytic performance. Meanwhile, the

826   possible mechanism of CO_2 photocatalytic reduction is calculated. As shown in Fig.

827   24B, CO_2 is eventually reduced to methane by the COOH* pathway and several

828   thermodynamic steps.

829

---

830   Additionally, the Amsterdam density functional (ADF) program can guide

831   conductive CMP materials. Xu has designed three different open-shell systems that

832   contain thiophene building blocks, with a lower highest occupied molecular orbital

833   (HOMO) and a lower unoccupied molecular orbital gap (LUMO) [218]. He calculated

834   the electronic hopping rate k for the hole/electron transfer from one molecule to

835   another molecule of the monomers and compared their conductivity at different

836   geometry. The k is calculated based on the formula shown in Eqs. (1) [219,220]:

$$k = \frac{2\pi V^2}{h} \times \sqrt{\frac{\pi}{\lambda k_B}} \times exp\left\{-\frac{\lambda}{4k_BT}\right\} \tag{1}$$

837   In the equation, V is the electronic coupling for the hole/electron transfer, which is

838   calculated by ADF, and h is Plank constant, and k_B is Boltzmann constant, T is the

839   temperature in kelvin. If V is high, the electronic hopping rate k is high, and the

840   conductivity of the materials is high. It is finding that for the same monomer, the

841   electron coupling of the eclipsed configuration is higher, that is, the charge-transfer

842   performance of the eclipsed configuration is better than that of the staggered

843   configuration. On this basis, it is conducive to establish the design principles for

844   constructing conductive CMP materials, such as build a similar open-shell system,

845   adjust the properties of the connecting thiophene groups, switch groups with steric

846   hindrance, and extend the π-conjugated structure.

5.2 Quantum Calculations on Solar Energy Conversion in CMPs

In 2013, Zwijnenburg et al. proposed the DFT method of pyrene-based CMP model ring fragment [221]. The calculations and the optical absorption and fluorescence spectroscopy complementary can explain the relationship between the significant redshift in the spectrum and the existence of the network structure of strained rings. The relationship denotes that the addition of strained rings can adjust the absorption and fluorescence spectra of polymers to optimize their potential applications, such as photocatalysis and photoelectricity, which can be used to explain the reason why bandgap engineering controls the photophysical properties of porous organic polymers. Although these model studies provide some significant preliminary insight, additional simulations of bulk systems can enable a more complete understanding of the mechanism of action of these types of CMPs.

Additionally, Wang et al. reported that cellular network-like aza-fused CMP nanosheets (aza-CMPNs) are an energy feasible photocatalytic OER under visible light irradiation [222]. All first-principles calculations are completed with the DFT method applied in the Vienna ab initio simulation package (VASP). The exchange-correlation functional of generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) and hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06) is used for geometric optimization and electronic structure calculations, respectively. As well as van der Waals correction of Grime's D3 scheme is incorporated to describe the weak interlayer interaction in aza-CMP multilayers. The optimized structures of the aza-CMPN and multilayer are illustrated in Fig. 25A and the optimized structure of

869 bulk CMP is showed in Fig. 25B. The calculations reveal the possible active sites in the

870 CMPs photocatalytic OER procedure. Fig. 25C summarizes each basic thermodynamic

871 step involved in OER and Fig. 25D shows the optimized structures of *OH (S_1), *O

872 (S_2), and *OOH (S_3) on active site 4. the carbon atom 4 gather holes under illumination

873 to adsorb H_2O molecules and then release one proton to form *OH (S_1), and the S_1 site

874 continue to release a proton to form *O (S_2). Then, H_2O and *O to form *OOH (S_3),

875 and a proton released from *OOH, later, O_2 molecules are isolated from the surface of

876 aza-CMPNs to begin a new cycle.

877 **Please insert Fig. 25**

878   The first-principle predict the level of CMP nanosheets (CMPNs) theoretical

879 conduction band minimum value (CBM) and valence band maximum value (VBM)

880 (Fig. 26A), and to calculate the density of state (DOS) indicates that CMPNs VBM and

881 CBM is mainly contributed by p orbitals of carbon atoms in benzene rings and 1,3-

882 diyne links, and the delocalization of p-orbitals revealed by the charge of VBM and

883 CBM at Γ k-point distribute over the entire polymer frameworks (Fig. 26B) [92], which

884 demonstrated the energy feasibility of CMPNs photocatalytic OER from water splitting.

885 Both single-site and dual-site procedures of OER in aqueous solution are considered

886 here. The single-site procedure is denoted follow (stage 2 to 5):

$$S_0 + H_2O \rightarrow S_1^s + H^+ + e^- \tag{2}$$

$$S_1^s \rightarrow S_2^s + H^+ + e^- \tag{3}$$

$$S_2^s + H_2O \rightarrow S_3^s + H^+ + e^- \tag{4}$$

$$S_1^s \rightarrow S_0 + O_2 + H^+ + e^- \tag{5}$$
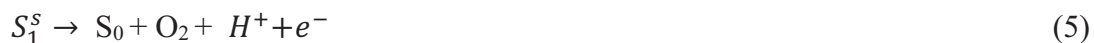
887 In these formulae, S_0 represents the bare surface, S_1^s, S_2^s, and S_3^s represent the

888 intermediate products of *OH, *O, and *OOH at a single active site on the catalyst

889 surface, respectively. In the dual-site procedure, stage (2) and (3) is identical as a single-

890 site procedure ($S_1^s = S_1^d$, $S_2^s = S_2^d$), while the intermediate product of *OOH in the

891 single-site procedure is substituted with an intermediate product of *O*OH at two

892 adjacent active sites, and stage (5) is substituted with step (7) and (8).

$$S_2^d + H_2O \rightarrow S_3^d + H^+ + e^- \tag{6}$$

$$S_3^d \rightarrow S_4^d + H^+ + e^- \tag{7}$$

$$S_4^d \rightarrow S_0 + O_2 \tag{8}$$

893 In these formulae, S_3^d and S_4^d represent the intermediate products of *O*OH and

894 *O*O at adjacent active sites, respectively.

895 **Please insert Fig. 26**

896 **5.3 GCMC and MD Simulations for Prediction of Properties of CMPs**

897 GCMC and MD simulations, two common computer simulation methods, often used

898 for the synthesis, design modification, and predict the application effects of CMP

899 materials, and to gain additional insights into the relationship between structure and

900 properties. They greatly reduce the data and analysis errors caused by humans and help

901 to save experimental costs, assist in improving the accuracy of experimental results,

902 and accelerate research progress. The rational simulation and analysis of newly

903 designed polymer materials include the analysis of reported monomers and links to

ensure that the structural characteristics of the model can be maintained with minimal

energy. The rationalization of porous polymer materials is conducive to the realization

of optimal structural properties of these materials and the stimulation of potential

functions. However, to accurately model their structures is a challenge owing to the

randomness of amorphous porous polymers. To meet this challenge, many research

groups have used MD simulations to study these porous polymer materials. The motion

of atoms in a material system determines the overall structure and properties of the

material. Therefore, a series of steps repeated many times to implement the analysis of

larger systems or small clusters are needed. Fig. 27A [223-226] explains a general

simulation pathway, and the formation of bonds and the number of atoms is the key to

achievement. Fig. 27B [227] shows the cross-linking procedures achieved during

synthesis. Meanwhile, the GCMC simulations with the assistance of prediction of gas

adsorption.

Please insert Fig. 27

Jiang et al. used model clustering to study structural geometry, flexibility, and

porosity, and pointed out that these fragments are unlikely to capture entanglement and

connectivity of the extended networks, resulting in excessive pore volume [47,95].

Therefore, the relaxed state of the polymerized main chain in the calculation to maintain

consistency with the experimental gas absorption at higher pressure is needed to

consider. In 2014, Suresh et al. used MD and GCMC simulations to assist in the design

of a new type of CMPs with large surface area and gas storage capability, and

introduced the structure model of tetraphenylethene-based amorphous CMP (TPE-

926   CMP) and its gas storage performance [228]. This structural model takes all future

927   characteristics into calculations, and MD simulations are carried out on the model

928   oligomer of TPE-CMP in a force field. The binding energy (~30 kJ mol^{-1}) of CO_2 and

929   the polymer is obtained in the calculation based on the force field, and the density of

930   the polymer is calculated to be 0.8 g cm^{-3}. Fig. 28A shows the reasonable structural

931   model for TPE-CMP, the yellow areas shown in Fig. 28B represents the gaps in the

932   polymer and Fig. 28C displays the optimized configuration of CO_2 in TPE-CMP

933   attained through MD simulations. The GCMC simulations shown in Fig. 28D considers

934   the relaxation of the polymer during gas absorption, the blue circle is an estimation

935   from the GCMC simulations that recreates the CO_2 adsorption isotherm of the polymer

936   materials. In contrast, as can be seen from the red box in Fig. 28D, the gas absorption

937   predicted by GCMC simulations is slightly lower than the experimental value under

938   high pressure because the relaxation effect of the polymerized main chain is not

939   considered in the calculation.

940   **Please insert Fig. 28**

941   The addition of the A4 monomer is conducive to increasing the porosity of the

942   polymers [69], while the B2 monomer is used to ameliorate the solubility of the polymer

943   networks [84]. Here, Abbott and Colina used MD simulations to study a series of

944   pyrene-based CMPs with different monomer ratios to provide insight into porosity and

945   ring construction in bulk models [229]. The LAMMPS simulation package [230] was

946   used to simulate all energy minimization and molecular dynamics in the polymerization

947   and equilibrium processes. During the polymerization process, the Lennard-Jones

948 cutoff time was adjusted according to the previous work [231] to simulate the solvation

949 state of the system more accurately. The simulations are finding that the surface area of

950 the system increased with the ratio of four functional monomers to two functional

951 monomers because the cross-linking degree of the polymers is effectively improved.

952 These results support the rationalization of the spectral displacement based on the

953 network ring induced strain, which can limit the rotation of the benzene ring to prepare

954 larger conjugated structures to improve the optical properties of CMPs.

955 **6. CMPs as Platforms for Clean Energy**

956   Clean energy refers to the technology system of clean, efficient, and systematic

957 application of environmentally friendly energy. (i) Clean energy is not just a simple

958 classification of energy; (ii) Clean energy focuses on cost and efficiency while ensuring

959 environmentally friendly; (iii) The environmentally friendly of clean energy means that

960 the environmental impact is under control. In recent years, CMPs and their

961 composites/derivatives have been widely used in the fields of energy generation,

962 conversion, and storage owing to their unique expanded π-system, controllable

963 electronic energy levels, and unique morphological properties. Their applications in

964 clean energy include: (i) Storing energy molecules (such as hydrogen molecules) in

965 pore structures; (ii) Store the energy in a polymer pore structure, such as batteries, in

966 the form of chemical bonds; (iii) The energy is stored in the structural recombination

967 and secondary valences of the pore structure, such as the compressed double-layer

968 structure of the supercapacitor; (iv) The semiconductor structure of CMPs generates

969 photoelectron hole pairs under photoexcitation, which are then converted into electrical

970 energy (photovoltaic cells) or chemical energy (artificial photosynthesis).

6.1 CMPs as Platforms for Hydrogen Energy

972 Hydrogen as an efficient, clean, and sustainable renewable energy source, comes

973 mainly from water splitting, has high calorific value, and carbon-free emissions during

974 combustion [232-234], and has attracted the attention of research institutions and

975 industry over the past decade. On January 17, 2017, a total of 13 leading clean energy-

976 related companies launched a global initiative called the Hydrogen Council at the World

977 Economic Forum in Davos, Switzerland [235]. This initiative expresses the important

978 role of hydrogen energy in promoting energy transformation. Promoting the

979 globalization of hydrogen energy can help achieve the goal of mitigating global

980 warming. Therefore, advanced materials need to be developed for hydrogen production

981 and storage.

982 CMPs with the adjustable high porosity and controlled structural properties are an

983 excellent candidate in the hydrogen energy field. Here, our discussion includes (i)

984 CMPs for hydrogen storage, (ii) CMP materials applied to photocatalytic hydrogen

985 evolution from water splitting, and (iii) they as catalysts supports or precursors for

986 hydrogen evolution.

6.1.1 CMPs for Hydrogen Storage

988 The use of hydrogen requires a safe, compact method of storage, but hydrogen is

989 often stored in cylinders in an energy-intensive manner, posing additional risks.

990 Therefore, it is best to convert the hydrogen into a condensed state, or the most direct

991 method is to use a hydrogen adsorption material. Hydrogen, as an energy storage

992 medium, has attracted the attention of research institutions and industry over the past

993 decade. The weak bonding strength of hydrogen and adsorbent is the key obstacle to

994 fabricate hydrogen storage materials with good hydrogen storage properties under ideal

995 hydrogen storage kinetics. CMP materials are the adsorption materials which has made

996 much progress in recent years [126,236,237], the progress of hydrogen storage capacity

997 of CMPs in recent years is summarized in detail in Table 2 [79,84,143,147,150,238-

998 244]. Most of the reported adsorption values were measured at a temperature of 77K,

999 which is well below the usual temperature range required for practical applications.

1000 Also, some reports give maximum adsorption values, while others report adsorption

1001 values at specific pressures (usually 1 bar). Therefore, it is difficult to synthesize all the

1002 reported values to make a judgment. Here, we discuss quintessential examples of

1003 strategies to improve hydrogen adsorption in recent years.

1004 **Please insert Table 2**

1005 At a specific pressure and temperature (1.13 bar, 77.3 K), micropores rather than

1006 mesopores are the main reason for H_2 adsorption. High surface area HCMP-1 and

1007 HCMP-2 were synthesized using homocoupling of 1,3,5-triethynylbenzene or 1,4-

1008 diethynylbenzene [79]. Although the apparent BET surface area (827 m^2 g^{-1}) of HCMP-

1009 2 is slightly smaller than that of HCMP-1 (842 m^2 g^{-1}), the adsorption capacity of

1010 HCMP-2 (131 cm^3 g^{-1}) on H_2 is higher than that of HCMP-1 (107 cm^3 g^{-1}), which can

1011   be attributed to the higher micropore surface area and ultramicropore volume observed

1012   in HCMP-2. Microwave-assisted rapid synthesis is a new synthesis technology, which

1013   has great industrial application potential in organic synthesis and material preparation

1014   and is conducive to enhancing the hydrogen adsorption capacity of organic microporous

1015   polymers. In 2010, microwave-enhanced ionothermal polymerization is used in the

1016   synthesis of porous polymer materials, can be in a few minutes to obtain high surface

1017   area (2390 m^2 g^{-1}) triazine-based CMPs (CTFs), they have higher adsorption capacity

1018   of hydrogen (1.78 wt. %, 1 bar, and 77 K) [245]. It is worth noting that this method is

1019   a simple and efficient method for the preparation of this kind of triazine-based porous

1020   material, which provides an opportunity for the large-scale preparation of highly

1021   efficient and economical polymer-based hydrogen adsorption materials.

1022   Besides, lithium gives CMPs an extremely high ability to store H_2, which is a big

1023   step forward in their application [238,242,246]. In 2016, with the guidance of computer

1024   simulations, methyl lithium (MeLi) was designated as a new lithium dopant for the

1025   preparation of lithium-doped CMPs [246]. MeLi, as a cluster of positive charges,

1026   creates a more intimate bonding condition for H_2 molecules, and naphthalene-

1027   containing CMP (N-CMP) was designated as the matrix material to inhibit the gathering

1028   effect of lithium. It is more noteworthy that through strong interaction, MeLi can be

1029   selectively fixed to the pre-designed active site, which is conducive to obtaining the

1030   optimal doping amount. This significantly improves the hydrogen storage capacity of

1031   CMPs. MeLi doped N-CMP (MeLi@N-CMP) has enhanced the absorption capacity of

1032 H_2 not only at low temperatures but also at close to ambient temperature. Compared

1033 with undoped N-CMP, the hydrogen adsorption capacity of MeLi@N-CMP at 77 K and

1034 80 bar (6.5 wt. %) and at 273 K and 80 bar (1.0 wt. %) maintained an increase of 150%

1035 and 100%, respectively.

1036 Recently, Yang et al. designed and synthesized triazatruxene (TAT) with three

1037 coplanar indole moieties (Fig. 29A and B), and using FeCl₃ catalytic oxidative coupling

1038 polymerization (Fig. 29C) to further prepare high crosslinking poly(triazatruxene)

1039 (PTAT) [242]. The point-to-face metal-coordination interaction (cation–π) between the

1040 surface of PTAT aromatic structures and the cation is beneficial to capture more lithium

1041 ions, and the captured lithium ions are well dispersed on the PTAT surface to ensure

1042 adequate Li^+ content in the PTAT (Fig. 29D and E). The lithium-doped CMP (Li^+–PTAT)

1043 can spontaneously adsorb hydrogen molecules by electrostatic charge-quadrupole and

1044 charge-induced dipole interactions to obtain excellent hydrogen absorption properties

1045 (Fig. 29F). Fig. 29G shows that Li^+–PTAT has a higher hydrogen absorption value of

1046 7.3 wt. % (1 bar, 77K) than PTAT at 1.9 wt. % (1 bar, 77K) under the same conditions.

1047 The adsorption value is also higher than the previously reported lithium-doped MOF

1048 [247] and lithium-doped CMP [242] (Fig. 29H). Also, the high hydrogen absorption

1049 value of 0.32 wt. % is maintained for Li^+–PTAT at 273 K at 1 bar (Fig. 29I), which

1050 proves its potential application value.

1051 **Please insert Fig. 29**

1052 Furthermore, the development of selective hydrogen adsorption has attracted much

1053 attention. Membrane separation is a promising way to selectively adsorb hydrogen from

1054 mixed gases. Currently, the gas permeability of commercial films is low, and it is often

necessary to prepare large-size films in order to maintain sufficient gas production [44], which obviously increases the cost of commercial applications. To improve the permeability and selectivity of the films, zeolite and MOFs with rigid skeletons and uniform pores were investigated extensively [248-251]. However, presently, commercial films are mainly prepared from polymers with low permeability and high selectivity [252]. Therefore, a more ideal choice is to prepare MOPs with high permeability and good selectivity and machinability. For example, the porous organic cages (POCs) prepared by Cooper's group is a class of MOP with good processability and shows the potential for selective gas separation [252-254]. And polymers of intrinsic microporosity (PIMs) is a kind of MOPs with gas permeability, selectivity and good solubility and machinability [44,255-257]. CMPs have good chemical stability and can maintain functional stability under high pressure and temperature [34,48,77]. However, the extremely rigid framework of CMPs makes it difficult to reprocess. Therefore, the development of machinable, structurally stable CMPs with high gas selectivity and permeability is a major obstacle to be solved.

Recently, Loh et al. succeeded in synthesizing a solution-processable conjugated microporous thermoset (CMT) [258], which has outstanding H_2 permeability and solubility and processability, and maintains stable microporous structure and internal pore connectivity even under high temperature and pressure. Due to the internal pore connectivity of CMT can promote the redistribution of gas molecules, CMT can obtain H_2 permeability higher than the most advanced ultra-pore PIM while possessing similar selective hydrogen adsorption capacity [44,257]. Meanwhile, noteworthily, the

solubility and machinability of CMT plus its centrally distributed pore diameter distribution is conducive to the production of large-area film products.

6.1.2 CMPs for Photocatalytic Hydrogen Evolution

Photocatalytic technology has many important features [259-261], such as: (i) It can be operated under mild temperature and pressure; (ii) The mother and intermediate products can be completely mineralized without secondary pollution; (iii) Low operating cost. Hydrogen produced by photocatalytic water splitting has been regarded as a popular technology to solve the energy crisis and environmental pollution [262-266]. At present, most used inorganic photocatalytic materials have complex preparation strategies, limited reserves, and low photocatalytic activity in visible light, which is not conducive to further development [267,268]. In terms of sustainable development, it is necessary to develop a metal-free, flexible design, synthesis of diverse organic polymer photocatalysts with adjustable structure and properties for photocatalytic hydrogen evolution [269-273]. Wang et al. presented the basic theory of photocatalysis and the key factors affecting photocatalysis, and then discussed the development of new photocatalysts for inorganic materials, carbon-based materials and semiconductor composite materials developed in the past ten years [274]. They also investigate and explore highly efficient optical drive materials for converting solar energy into sustainable fuels. Finally, the future development of photocatalysis technology is discussed. CMP materials as photocatalyst have followed advantages [275-279]: (i) Expand π-conjugated structure and open pores are advantageous to the

photocarrier migration and separation; (ii) High chemical stability and thermal stability provide excellent photocatalytic stability for CMPs; (iii) Wide range of raw materials including many economical, earth-rich raw materials can be used as synthetic monomers; (iv) Wide spectral absorption range is beneficial to improve the efficiency of light absorption; And (v) they have high flexibility in adjusting bandgaps and surface-active sites.

In 2016, Cooper's group reported the relative importance of junction geometry, comonomer length, and planarization degree to the photocatalytic hydrogen evolution rate of CMPs, demonstrating the potential of CMPs as a photocatalyst for hydrogen evolution [280], but the relevant design rules are not well understood. For example, it is still necessary to investigate the catalytic efficiency of CMP materials with different surface areas, geometric shapes, and bandgaps, as well as to investigate the effects of substituent patterns and conjugate lengths on the photocatalytic performance of CMP materials to establish a more detailed structural-performance relationship. Therefore, Jiang's group synthesized three perylene-containing CMPs (Pr-CMPs) through the Suzuki reaction of hydroquinone as raw material for photocatalytic hydrogen evolution [281]. The results show that the pore properties and band gaps of Pr-CMPs are adjusted by changing the kind and the connection positions of the substituents. By adjusting the benzenes connection site, is a good way to adjust the structure and optical properties of polymers, among them, the hydrogen evolution rate of 1,2,4,5-linked polymer (Pr-CMP-3) under ultraviolet irradiation is the highest (12.1 mol h^{-1}) in the three kinds of polymers, this is because Pr-CMP-3 has high surface area, wide light absorption

1120 spectrum, and the extension of the π-conjugate structure. These results indicate that

1121 bond geometry is one of the key factors affecting the photocatalytic activity of CMPs.

1122 Subsequently, the effect of the length of the crosslinking agent on the photocatalytic

1123 properties of hydrogen production is reported. Jiang et al. reported a series of

1124 dibenzothiophene dioxide containing CMP (DBTD-CMP) photocatalysts [66]. Among

1125 them, there is a short benzene cross-linked photocatalyst DBTD-CMP1 exhibit the most

1126 active hydrogen evolution rate of 2460 $\mu mol\,h^{-1}\,g^{-1}$ without Pt cocatalyst in visible light.

1127 This may be because the increase of the length of the crosslinking agent leads to the

1128 increase of the polymer skeleton distortion, which reduces the conjugation degree and

1129 planeness of the main molecular chain, hinders the photoinduced carrier transport and

1130 separation, and thus reduces the photocatalytic activity. Furthermore, it is worth noting

1131 that after the loading of 3 wt. % Pt catalyst, the Pt-loaded DBTD-CMP1 displays a

1132 remarkable high hydrogen evolution rate (9200 $\mu mol\,h^{-1}\,g^{-1}$).

1133 Rigid pyrene unit is a common building unit of CMP materials [65,282,283]. Jiang's

1134 group designed a series of donor-π-acceptor (D-π-A) CMP photocatalysts using pyrene,

1135 benzothiadiazole, and benzene (biphenyl) as the donor, acceptor, and π-crosslinker units,

1136 respectively, and compared the effects of the molecular structure and the ratio of donor

1137 to the receptor on the photocatalytic properties of CMPs [65]. The donor unit, π-

1138 crosslinker unit, and acceptor unit are indispensable in enhancing the photocatalytic

1139 performance. Meanwhile, the ratio of donor to acceptor has a big impact on the

1140 photocatalytic performance of the CMPs, when the ratio of pyrene to benzothiadiazole

1141 is 9:2, the photocatalytic hydrogen evolution rate of the CMP (PyBT-2) is as high as

1142 106 μmol h^{-1} under ultraviolet irradiation. Furthermore, they designed two CMP

1143 photocatalysts (PyDOBT-1 and PyDOBT-2) copolymerization of pyrene and

1144 dibenzothiophene-S,S-dioxide as building blocks, and investigated the effect of a

1145 connection mode of dibenzothiophene-S,S-dioxide on photocatalytic hydrogen

1146 evolution [283]. The results showed that the photocatalytic activity of PyDOBT-1 (Fig.

1147 30A) with 3,7-connection mode was higher than that of PyDOBT-2 with 2,8-connection

1148 mode. The photocatalytic hydrogen production rate of "naked" PyDOBT-1 was 5697

1149 μmol h^{-1} g^{-1} under visible light irradiation, and the photocatalytic hydrogen production

1150 rate of Pt-load PyDOBT-1 reached a maximum of 12986 μmol h^{-1} g^{-1} (Fig. 30B). The

1151 higher photocatalytic activity of PyDOBT-1 may be due to the 3,7-connection mode,

1152 which enhances the conjugated chain length and improves the coplanar property of the

1153 polymerized main chain to facilitate the transfer of charge along the polymer chain.

1154 Their work suggests that rational molecular design is the key to the development of

1155 effective CMP photocatalysts.

1156 **Please insert Fig. 30**

1157 Recently, Maji et al. synthesized a series of CMPs (F$_{0.1}$CMP, F$_{0.5}$CMP, and F$_{2.0}$CMP)

1158 using tetraphenylethylene (TPE) as the donor and 9-fluorenone (F) as the acceptor (Fig.

1159 31A), and adjusted the optical properties of these CMPs by bandgap engineering to

1160 enhanced photocatalytic water splitting for hydrogen production [284]. As shown in

1161 Fig. 31B, by increasing the content of F, the emission color of CMP materials changes

1162 from green to red, and the bandgap of F$_x$CMP can be adjusted from 2.8 eV to 2.1 eV,

1163 thus enhancing its visible light absorption. Among all the CMPs, F$_{0.5}$CMP (2.3 eV)

1164 displayed the highest hydrogen evolution rate under broad-spectrum irradiation (Fig.

1165 31C). Compared with CMP materials without F, the photocatalytic activity of the D-A

1166 CMP containing F is observably enhanced. Interestingly, the CMPs display emissions

1167 in the 540-580 nm with the assistance of energy transfer in the TPE segment.

Please insert Fig. 31

1169 As amorphous polymers, the effect of crystallization on photocatalytic behavior of

1170 CMPs needs to be further discussed. In 2018, Cooper et al. targeted investigated the

1171 difference of photocatalytic hydrogen production between benzobis(benzothiophene

1172 sulfone) moiety-based COF crystals and amorphous similar organic polymers [285].

1173 Although the photocatalytic hydrogen evolution performance of COFs with ordered

1174 crystal structure is superior to that of their amorphous organic analogues in this case,

1175 this does not indicate that the photocatalytic activity of crystallized COFs is necessarily

1176 higher than that of amorphous CMPs. This is because crystallinity is not the only factor

1177 affecting photocatalytic activity [286-288], such as, amorphous CMPs also have much

1178 lower specific surface area and charge transfer capacity, and some CMPs also have poor

1179 hydrophilic performance, which may result in reduced photocatalytic performance of

1180 them.

1181 Besides, the stability of photocatalysts should also be considered. CMP materials

1182 have been shown to have a more stable structure than the crystallized ordered COFs

1183 originally reported [37,47,54,80]. But things are still changing, and researchers

1184 studying COFs materials are exploring the use of more stable chemical bonds to build

1185 super-stable COFs materials [206,289,290]. But in meanwhile, noteworthily, the

amorphous properties of CMPs provide more design possibilities, and more possible multi-component CMP catalysts are constructed by using multi-step tandem reactions, which are difficult to be completed by COF materials.

6.1.3 CMPs as Supports or Precursors of Catalysts for Hydrogen Evolution

In addition to being used as catalysts directly, CMPs can also be used as (electro-) catalysts carriers to assist in the synthesis of composite catalysts with excellent catalytic properties. This type of composite catalysts usually combines the properties of two or more materials with different properties and can have a synergistic effect in an application. As well as, CMPs can also be used as precursors of catalysts for hydrogen production through pyrolysis.

Alkordi's group used pyridine-based porous polymer materials and graphene composites (PyPOP@G) as carriers and then electrodepositing Pt metal uniformly in the pores for forming the composite material (PyPOP-Pt@G) (Fig. 32A) [291]. The main chain of PyPOP in this system is rich in Lewis-base binding sites and microporous matrix, which can provide support for Pt species and binding sites for G. The properties of the material were evaluated by cyclic voltammetry (CV), linear sweep voltammetry (LSV), and controlled potential electrolysis (scan rate of 100 mV/s for the CVs and 10 mV/s for the LSVs). Fig. 32B indicates that the initial performance of the electrode is improved after the reduction of Pt(IV) in the cycling process. As shown in Fig. 32C, the overlaying CV scan no observe the deterioration of the electro-catalytic properties of the composite, indicating its high durability and stability. And as shown in Fig. 32D,

58

1207 the Tafel inset (~37 mV/decade) of the catalyst indicates that there is a rate-limiting

1208 step of Heyrovsky type in PyPOP-Pt@G catalyzed hydrogen evolution reaction, which

1209 provides an in-depth understanding of the mechanism of proton electric reduction. The

1210 core of Heyrovsky-type step is the hypothesis of the active site of a single metal atom

1211 (Eqs. 9−11) [291]:

$$H_3O^+ + e^- + M \leftrightarrow M-H + H_2O \qquad \text{Volmer step} \qquad (9)$$

$$M-H + H_3O^+ + e^- \leftrightarrow H_2 + H_2O + M \qquad \text{Heyrovsky step} \qquad (10)$$

$$2M-H \leftrightarrow H_2 + 2M \qquad \text{Tafel step} \qquad (11)$$

1212 The Heyrovsky step mentioned above may be caused by the delay of the diffusion of

1213 hydrated protons into the electroactive catalytic site in the microporous matrix.

1214 **Please insert Fig. 32**

1215 Meanwhile, CMPs are an effective precursor of functional heteroatomic doping of

1216 porous carbon [292-295]. Cui et al. reported that a nitrogen-rich porous carbon material

1217 derived from a novel copper-porphyrin-based CMP (Cu-CMP) has a high surface area

1218 and a inimitable tubular nanostructure that can be used as a functional catalyst for

1219 encapsulating copper/copper oxide nanoparticles for hydrogen evolution [296]. Among

1220 them, the use of Cu-CMP850 as the catalyst, show the good performance of electrical

1221 catalytic hydrogen evolution, with relatively low potential (0.19 V, 1.0 mA cm^{-2}) and

1222 high current density of 50 mA cm^{-2} at an overpotential of 0.47 V, and Tafel slope of

1223 ~135 mV decade^{-1}, the Faraday efficiency of 90% under the application potential of

1224 0.34 V, as well as high durability.

1225 Doping some single or double hetero atoms such as N, S, Ru, and Co can

1226 significantly improve the performance of carbon materials [292,297-299]. Wang et al.

1227 used carbon fiber cloth to chemically deposit a kind of heteroatom-rich CMP (PAQTA),

1228 then adding Co salt pyrolysis to prepare Co nanocrystalline composite porous carbon

1229 materials doped with heteroatoms for efficient and stable electrocatalytic hydrogen

1230 evolution reaction [300]. PAQTA was impregnated with $Co(acac)_2$ solution and then

1231 pyrolyzed in nitrogen at high temperature, followed using acid etching to prepare the

1232 CoNOC catalysts (Fig. 33A). Among them, the CONOC-900 showing a Tafel slope of

1233 21 mV decade^{-1}, an approximate rectangular CV curve, and negligible polarization

1234 curve attenuation and loss of current density (the green line in Fig. 33B). DFT

1235 calculations show that the excellent electrochemical performance of the catalysts is due

1236 to (i) rapid transfer of electrons from cobalt nanocrystals to graphene layers, and (ii)

1237 the reduction of Fermi level of the neighboring C atom owing to N,O-dual doping. This

1238 results in a decrease in the free energy of hydrogen adsorption, which enhances the

1239 performance of electrocatalytic hydrogen evolution.

1240 **Please insert Fig. 33**

1241 **6.2 CMPs for Adsorption and Conversion of Carbon Dioxide**

1242 The constant emission of carbon dioxide (CO_2) caused by the heavy use of fossil

1243 fuels is a major factor causing global climate change [301,302]. The progress of

1244 efficient methods of CO_2 capture, storage, and conversion of CO_2 into useful fuels is a

1245 significant aspect in the effective reduction of CO_2 emissions, and has important

1246 implications for alleviating the current energy crisis and global warming [303].

1247 Currently, some solid porous materials (such as zeolite, carbon, aluminum oxide, and

1248 metal organic frameworks (MOFs) with gas selection capabilities [304,305] are used to

1249 adsorb and separate CO_2. To meet the requirements of sustainable development,

1250 researchers should give priority to the development of advanced materials that can not

1251 only absorb CO_2 but also catalyze its conversion into liquid fuels [306,307]. The

1252 materials used in this strategy first need to be able to capture and convert CO_2 without

1253 the need for additional energy at environmental conditions to avoid the generation of

1254 new CO_2. CMPs as a platform for CO_2 storage and catalytic conversion to provide a

1255 feasible clean energy technology.

1256 **6.2.1 CMPs for Carbon Dioxide Adsorption**

1257   Due to the high porosity and regulable pore surface function of CMPs [102,308-311],

1258 they are promising in enhancing CO_2 capture and storage. Table 3 summarizes the CO_2

1259 uptake by CMPs reported in recent years [63,131,144,147,241,244,293,312-321].

1260   **Please insert Table 3**

1261   Some polar groups, such as $-NO_2$ [322], arylamines [323], $-OH$ [324], $-COOH$ [313],

1262 $-SO_3H$ [324], and heterocyclic nitrogen atoms [325] can modify the surface of porous

1263 materials, which can significantly increase the binding energy of CO_2, thus increasing

1264 the absorption rate and/or selectivity of CO_2. Therefore, Zhu's group investigated the

1265 influence of $-COOH$, $-NH_2$ and $-OH$ on the CO_2 adsorption capacity of polymer

1266 networks [312]. The groups $-COOH$, $-NH_2$, and $-OH$ are merged into the networks of

1267 the PAFs synthesized Sonogashira–Hagihara reactions of tri(4-ethynylphenyl)amine

1268 with various aryl halides. Noteworthily, compared to "naked" PAFs, the $-NH_2$

1269 functionalized PAF-33–NH_2 displays the highest CO_2 isosteric heat (32.9 kJ mol^{-1}) and

1270 the –COOH functionalized PAF-33–COOH shows the maximum CO_2 uptake per unit

1271 areas (4.37 and 2.71 μmol m^{-2}) at 273 and 298 K. This indicates that the integration of

1272 functional groups is conducive to enhancing the interaction between PAF networks and

1273 CO_2 molecules, thus enhancing their adsorption properties. Furthermore, PAFs can be

1274 modified by post-metallization (such as Li, Na, K, Mg) [314]. Interestingly, the CO_2

1275 isosteric heats of adsorption are depending on the type of light metal ion and follow the

1276 order of PAF-26-COOMg < PAF-26-COOLi < PAF-26-COOK < PAF-26-COONa.

1277 Considering the highly modular nature of CMPs, the introduction of chemical

1278 functions after functionalization can make them more absorbent and selective to CO_2

1279 absorption. Thomas et al. prepared PCZNs by Yamamomo reaction and introduced a

1280 series of secondary building units by post functionalization (Fig. 34A) [126]. The

1281 porosity and N-content of the polymers are both key factors affecting the absorption of

1282 CO_2. Both factors can change with the change of chemical structure and concentration

1283 of the secondary monomer. In this case, these factors are enhanced by introducing

1284 functional groups using post-functionalization, such as PCZN-8 can obtain a higher

1285 CO_2 absorption value and high-efficiency CO_2/N_2 selective separation (the green line

1286 in Fig. 34B; Table 3).

1287 **Please insert Fig. 34**

1288 The pore properties of polymer networks can be well adjusted by adjusting the length

1289 and geometry of the links to enhance CO_2 adsorption property. Xu et al. prepared a

series of A6 + Mx (x = 2, 3, 4, 6) type polyphenylene CMPs (A6CMPs) through modulating the monomer length and geometry by the polymerization reaction of 1,3,5-tris(3,5dibromophenyl)benzene (A6) and a series of benzene polymerization boronic or ethynyl (MX, X represents the number of functional groups) [326]. A6CMP-4 (M3), A6CMP-3 (M2), and A6CMP-6 (M4) showed BET specific surface area of 960, 1042, and 1115 m^2 g^{-1}, respectively, correspond to the CO_2 adsorption capacity of 1045, 963, and 925 mg g^{-1} at 60 bar and 318 K, respectively, and A6CMP-7 (M6) showed BET specific surface area of 571 m^2 g^{-1} corresponds to the CO_2 adsorption capacity of ~875 mg g^{-1}. Interestingly, A6CMP-1 has a low BET specific surface area of 571 m^2 g^{-1}, exhibited the largest CO_2 capture capacity of 740 mg g^{-1} yet it showed the maximum CO_2 adsorption capacity of 1218 mg g^{-1}. In 2017, Thomas et al. further investigated the relationship between carbon dioxide adsorption performance of CMPs and the number of functional groups [327]. They synthesized a series of cyanovinyl-based nitrogen-rich microporous polymers by metals-catalyzed polymerization (Fig. 35A) for the capture of carbon dioxide. A point diagram reveals that the structure-adsorbability relationship is linear, with the adsorption capacity of CO_2 proportional to the number of functional groups. As shown in Fig. 35B, as the number of functional groups from P4 to P1 increases, their CO_2 adsorption capacity gradually increases, which are 32, 99, 103, and 111 mg g^{-1} at 1 bar and 273K, respectively.

Please insert Fig. 35

6.2.2 CMPs for Carbon Dioxide Conversion

Capturing CO_2 and converting it into useful chemicals or high-calorific energy is a promising clean energy technology to effectively combat global warming. Adding metal-organic molecules to CMP networks can produce materials that capture and simultaneously convert CO_2. The salen-Co/Al has previously been reported as a homogeneous catalyst for cyclic carbonates generation from carbon dioxide and epoxides at low temperatures and pressures [328]. The introduction of this component into CMP networks has resulted in a serious of Co/Al-coordinated CMPs [63], which have outstanding CO_2 capture and conversion properties at ambient conditions, and their adsorption capacity is comparable to that of some previously reported inorganic catalysts [329,330]. Meanwhile, these CMPs also can be used as heterogeneous catalysts catalytic CO_2 with propylene oxide (PO) reaction to propylene carbonate (PC) under environmental conditions. In the existence of quaternary ammonium salt nBu_4NBr (TBAB), Co-CMP and Al-CMP showed remarkably high catalytic activities in the conversion of CO_2 at ambient conditions. Single catalyst Co-CMP has good durability, which can be reused for 22 times without significant reduction in catalytic activity. This strategy combines the functions of gas storage and catalysis, and provides a new idea for one-step, low-cost CO_2 emission reduction, which is worthy of further study.

Based on the module features of 2D CMPs and the excellent catalytic activity of metalloporphyrin derivatives to CO_2 conversion, Chen et al. designed a new 2D CMPs constituted by metalloporphyrin serves as the main structural and functional unit and

1332 thiophene as the link for the emission reduction of CO_2 [217]. Furthermore, to improve

1333 the ability of CMP to catalyze the conversion of carbon dioxide, a series of metal atoms

1334 (Fe, Mg, Mn, and Cu) were introduced into CMP networks to modify the electronic

1335 properties of metalloporphyrin units. The calculation results show that these CMPs

1336 have the properties of catalysis, high stability, and adjustable electronic structure, and

1337 Fe-modified thiophene-linked metalloporphyrin (Fe-TMP) has the highest catalytic

1338 activity for the reduction of CO_2.

1339 To our best knowledge, the single homogeneous catalytic process has the

1340 disadvantages of difficult separation of catalysts, difficult purification of products, and

1341 difficult recovery of expensive catalysts, as well as the residual metals in products that

1342 may cause serious problems for environmental applications. To solve the above

1343 problems, it has been reported that loading a homogeneous catalyst on a solid porous

1344 carrier is an effective strategy. CMPs are promising materials that can selectively adsorb

1345 CO_2 and reduce CO_2 back to liquid fuel under mild conditions when loaded with

1346 homogeneous metal nanoparticles as an electrocatalyst.

1347 Ampelli et al. synthesized tetrakis-phenylethene CMPs (TPE-CMPs) by Yamamoto

1348 reaction, and then Pt (or Fe) nanoparticles were deposited on their surface by sol

1349 immobilization method to modify TPE-CMP to create and the active catalytic CO_2

1350 reduction site on the CO_2 adsorption site of the polymers [120]. The gas diffusion

1351 membrane (GDM) based on the metal-doped CMPs is used as part of an

1352 electrochemical device for CO_2 reduction to liquid fuel. The schematic of the

1353 experimental apparatus and the GDM assembly are shown in Fig. 36. The anode

1354 working in the liquid phase is in contact with one side of the Nafion membrane, and the

1355 cathode working in the gas phase is in contact with the free side of gas diffusion layer

1356 (GDL). CO_2 penetrates through GDL and is absorbed on the surface of metal-doped

1357 TPE-CMP, then, it reacts with metal nanoparticles (Pt or Fe) at the catalytic active site

1358 to form liquid fuel. The characterization and testing of electrocatalytic materials by a

1359 small device between the working electrode and the counter electrode indicate that this

1360 electrocatalytic device has advantages over common liquid phase electrochemical

1361 systems in that it does not take into account the solubility of CO_2, does not require the

1362 recovery of liquid-phase products, and has better selectivity for high-chain

1363 hydrocarbons and oxygen-containing compounds. Polymer electrocatalysts loaded with

1364 appropriate metal catalysis sites are one of the keys to the preparation of high-efficiency

1365 electrode materials. The other one, the assembly of multilayer composite electrode

1366 materials to ensure good proton mobility and conductivity is also the key to improve

1367 the overall efficiency of the electrocatalytic device.

1368 **Please insert Fig. 36**

1369 Although electrochemical systems vary greatly in operating conditions and product

1370 distribution, to improve the efficiency of the system, the key points should be

1371 considered. Besides the key issues mentioned above, the rate-determining steps of the

1372 CO_2 reduction process are not yet clear [331,332]. An increase in the number of CO_2

1373 adsorption sites could be an advantageous measure to accelerate reduction, especially

1374 since these sites selectively adsorb and catalyze carbon dioxide, which requires further

1375 investigation.

6.3 CMPs for Batteries

CMPs can be used as electrode materials and as precursors to electrical energy storage materials for lithium-ion batteries (LIBs). (i) The high surface area of CMPs can improve the contact area with the electrolyte, which provides more surface locations for reversible reactions to occur. (ii) CMPs have a short ion migration distance, fast kinetic speed, and high energy storage capacity, which is conducive to the development of high-performance LIBs. (iii) CMPs can crosslink redox-active modules into highly stable porous electrodes, which has been sought after in the exploration of the next generation of green batteries. Furthermore, CMPs can also be used as electrode materials for potassium-ion batteries (KIBs) and sodium-ion batteries (SIBs). Here summarize CMP materials as a platform for metal-ion batteries (Table 4) [74-76,333-346].

Please insert Table 4

6.3.1 CMPs for Lithium-Ion Batteries

LIBs are a clean energy storage device, which has the advantages of recyclability, low-cost application, and high-energy-density, and plays a significant role in the application of mobile electronic products and electric vehicles [24,347-349]. To widely apply LIBs, to develop high-performance electrode material is needed, which is the core component of LIB systems [24]. To date, the electrode materials of LIBs mainly include inorganic active materials [350-354], organosulfur compounds [24], organic radical compounds [355,356], organic carbonyl compounds [357-359], and conducting

polymers [360-362]. Due to the rapid growth of energy demand and serious environmental problems, there is still a great need to develop electrode materials for green batteries. Organic polymer materials have been widely studied as electrode materials due to their ease of synthesis, reproducibility of raw materials, structural diversity, and design flexibility, as well as the redox properties of their synthetic monomers [363-365]. In the past years, important progresses have been achieved for CMPs as electrode materials in LIBs (Table 4).

6.3.1.1 CMPs as Electrode Materials for LIBs

Due to the high surface area and multisurface reaction sites, the robust porous network and insoluble organic solvent properties, as well as monomer diversity and the variety of synthesis methods, a series of CMP electrode materials have been used for LIBs [74,333,336,366,367]. For example, Jiang et al. reported that the hexaazatrinaphthalene CMP (HATN-CMP) cathode material of LIBs has a first cycle capacity of 147 mAh g^{-1} and the capacity retention rate of 61.9% after 50 charge-discharge cycles [76]. Yang et al. used carbazole and benzothiadiazole based CMPs as free anodes, with capacities of 1047 and 215, 161 and 117, 117 mAh g^{-1} at 20, 500, 1000 and 2000 mA g^{-1}, respectively [333].

The construction of CMP networks is helpful to prevent the leakage of electroactive units. A newly designed hexaazatrinaphthalene CMP (HATN-CMP) prepared by haxaazatrinaphthalene (HATN) unit to construct the skeleton with redox activity and the crosslinked porous skeleton with high surface area for LIB energy storage (Fig. 37A and B) [76]. The HATN edge may leak during the recharging and discharging cycle

process, while the HATN unit can be interwoven into the network of HATN-CMP to greatly reduce the leakage of the HATN unit into the electrolyte. In the crosslinked skeleton, the redox-active units and graded nanopores work together to facilitate the electrochemical processes involved in energy storage and release. Therefore, the CMP network structures not only make efficient use of the active cell of the batteries but also enhances their cycling performance. The redox-active unit in the HATN-CMP skeleton serves as the active unit of the energy storage and power supply module, and the high surface area of its inherently open nanopores contact with lithium ions to promote charge dynamics. Compared with the HATN, the HATN-CMP with built-in redox-active skeleton and permanent nanopores has a nearly uniform coulomb efficiency, high capacity, and excellent cycling stability. HATN-CMP shows the capacity of 91mA h g^{-1} (Fig. 37C) after 50 cycles, which is much higher than that of monomer HATN (13mAh g^{-1}), and compared with HATN monomer, which only lost 30% of its original capacity (Fig. 37D, black curve) in 2 cycles and only retained 25% after 50 cycles, HATN-CMP still retained 62% of its original capacity after 50 cycles (Fig. 37D, red curve). This significant reduction in capacity is related to the ease with which the HATN monomer on the cathode surface dissolves into the electrolyte. Meanwhile, the discharge-charge capacity reflects that HATN-CMP maintains a coulomb efficiency of up to 100% over 50 cycles, which proves the high efficiency of charge and ion in the electrochemical reaction.

Please insert Fig. 37

The high surface area of CMPs improves the contact area with the electrolyte, which

1441 provides more surface locations for electrode reversible reactions, and is beneficial to

1442 the reversible redox reaction of Li^+ and shortens the Li^+ diffusion path resulting in

1443 reduced charge transfer resistance, thus improving the performance of the battery

1444 [75,337,368]. PTTPAB was designed and synthesized by chemical oxidation

1445 polymerization of triphenylamine derivative 1,3,5-tris(4-diphenylamino-

1446 phenyl)benzene (TTPAB) (Fig. 38A) [335]. The corresponding PTTPAB powder has

1447 the unique microporous structure (the average micropore diameter of 0.68 nm, the

1448 mesopore diameter of ~2-5nm) and flowering spherical shape (BET specific surface

1449 area, 595 m^2 g^{-1}) (Fig. 38B), which are beneficial to enhance the rate performance of

1450 the battery. Compared with a typical p-doped radical polymers polytriphenylamine

1451 (PTPAn), The PTTPAB shows a more stable cycle-specific capacity (Fig. 38C, 86.7

1452 mAh g^{-1}) over 50th charging/discharging cycle, and higher coulomb efficiency (Fig.

1453 38D, 98%), as well as better rate performance (Fig. 38E, 84, 82, 81, 80, 84 mAh g^{-1}) at

1454 a current rate of 50-500mA g^{-1}.

1455 **Please insert Fig. 38**

1456 In addition to the high surface area of the fine pore structure that can enhance the

1457 electrochemical performance of CMPs, the molecular structure also greatly affects the

1458 electrochemical performance. Polythiophene, an N-doped conjugated polymer with

1459 reversible redox behavior, the content, cross-linked porous structure and surface area

1460 of thiophene play an important role in improving its electrochemical performance.

1461 Through the structural design and synthesis of a series of thiophene-containing CMPs

1462 with different thiophene contents and specific surface areas, namely poly(thiophene)

1463 (PT) and poly(3,3′-bithiophene) (P33DT) (Fig. 39A), the influence of the molecular

1464 structure of CMPs on the electrochemical performance of LIB was compared [75]. The

1465 results show that the content of thiophene, crosslinked pore structure, and specific

1466 surface area play an important role in improving the electrochemical properties of

1467 thiophene. Compared with PT (Fig. 39B, 141 mAh g^{-1} at 3000 mA g^{-1}), P33DT has

1468 better rate performance (Fig. 39B, 387 mAh g^{-1} at 5000 mA g^{-1}). P33DT anode has a

1469 high capacity (Fig. 39B, 1215mAh g^{-1} at 45mA g^{-1}) and longer cycle life (Fig. 39C, 663

1470 mAh g^{-1} at 500 mA g^{-1} after 1000 cycles) due to its unique structure of highly

1471 crosslinked porous characteristics, high thiophene content and large specific surface

1472 area. Fig. 39D shows the charging and discharging mechanism of thiophene conjugated

1473 polymer.

1474 **Please insert Fig. 39**

1475 Cation−π interaction [369-371], effectively aggregates Li^+ around the polymer chain

1476 and further reduces the diffusion distance of lithium ions, allowing Li^+ to react more

1477 quickly with the active groups on the polymer surface. As a representative aromatic

1478 compound, indole has abundant electronic structure [372,373], makes it easier to form

1479 a cation-interaction with Li^+. Meanwhile, introducing heteroatoms such as O and N into

1480 conjugated systems can promote redox reactions at active sites with lone pair electrons

1481 [374-376]. The unique aromatic structure of indoles containing N-heteroatoms also

1482 provides high redox activity and many active sites to receive Li^+ through a reversible

1483 electrochemical Li addition reaction to form a cation−π interaction. As shown in Fig.

1484 40A, indole-based CMP poly(bisindolylmaleimide) (PBIM) obtained by FeCl$_3$ catalytic

1485 oxidative coupling reaction [337]. The cationic-π interaction formed and unconfined at

1486 the discharge-charging process are shown in Fig. 40B. The PBIM prepared as the anode

1487 material of LIB showed high capacity (Fig. 40C, 1172 mAh g^{-1} at 50 mA g^{-1}), high

1488 coulomb efficiency (Fig. 40C, 99.2%), excellent cycle life (Fig. 40C, 1000 cycles), and

1489 ascendant rate performance (Fig. 40D, 0.05, 0.1, 0.3, 0.5, 1, 2, and 2.5C at 807, 701,

1490 589, 525, 427, 323, and 214 mAh g^{-1}, respectively; 1C = 1967 mA g^{-1}), which are

1491 attributed to the reversible cationic interaction and the unique aromatic structure

1492 containing N heteroatoms. To develop new electrode materials for large-scale energy

1493 storage applications, further exploration of CMP materials is still needed, especially the

1494 development of diverse CMP materials in terms of application.

1495 **Please insert Fig. 40**

1496 **6.3.1.2 CMPs as Precursors for Electrode Materials of LIBs**

1497 Porous activated carbon, a special hard carbon, has high surface area and abundant

1498 internal porous structure, and is a promising candidate for high-performance LIB anode

1499 materials. There are various preparation methods and precursor substances for the

1500 preparation of activated carbon. For example, the use of plant tissues with supporting

1501 structures [377-379] as precursors of activated carbon materials can significantly

1502 reduce not only the economic costs and environmental pollution from agricultural waste

1503 disposal, but also the raw material costs for the preparation of activated carbon.

1504 However, these plant tissues can become contaminated with many minerals during

1505 extraction and transportation [378]. The ash produced by the high temperature

1506 calcination of these minerals may reduce the catalytic performance and mechanical

72

strength of the derived activated carbons [378,380]. Therefore, a series of pretreatment processes are required for the preparation of activated carbon materials derived from plant tissues [377,378].

Besides, for MOFs materials [381-385], it has adjustable pore structure and ultra-high surface area, and there are plenty of combinations to try. A good strategy is to use MOF materials as precursors to prepare more stable conductive carbon materials. In this way, it can solve the problems of instability and poor conductivity of MOF precursors, and endowing MOF-derived carbon materials with high porosity, large surface area, multiple layers and adjustable structure of the precursors. However, it should be noted that although thousands of MOFs materials have been reported so far, the selection of suitable precursor materials is limited [383]. Therefore, more efforts are needed to explore more alternative and cheap MOFs materials.

The surface properties and pore structure of CMPs can be adjusted by changing the geometric shape and chain length of CMP monomers, or by doping different heteroatoms or metals. CMPs can also be modified by the post-synthesis method. Therefore, CMP is also an ideal precursor material for preparing porous carbon. Meanwhile, CMP materials are simple in composition and mainly composed of C and H, as well as can provide more suitable options for preparation of derived porous carbon. Based on the easily adjustable porosity of CMPs, the performance of CMP-derived porous carbon can be changed by adjusting the length of the monomer pillar in the CMP precursors [386]. This also means that CMP-derived porous carbon electrode materials with ideal structure can be more rational designed and prepared by adjusting the

structure of CMP materials, which may provide an idea for the rational design and preparation of CMP-derived porous carbon anode materials as high-performance LIBs. Nitrogen-doped porous carbon nanoparticles (NPCN-KOH) with the improved porous structure were obtained by pyrolysis of nitrogen-containing conjugated porous polymer (NCMP) and high-temperature activation of KOH [387]. NPCN-KOH has a more disordered structure and a high specific surface area of 1845 m^2 g^{-1}. These unique functions ensure that NPCN-KOH has a high reversible capacity of 818 mAh g^{-1}, a high rate performance of 818 mAh g^{-1} at 0.1C, and long cycle life (527 mAh g^{-1}, the capacity retention rate of 97.6% after 600 cycles). As well as the reversible capacity of NPCN-KOH is 857 mA h g^{-1} at 0.1C, which is exceeding other porous carbon [388-390].

More stable composites can be obtained by embedding metals or metal oxides into the CMP-derived materials [391-394]. After the synthesis of porous carbon nanotubes (PCNTs) by the simple pyrolysis of CMP nanotubes, the incorporation of MnO nanoparticles into PCNTs (Fig. 41A, MnO-PCNTs) can further improve the performance of PCNTs [392]. As shown in Fig. 41B, the microstructure of MnO-PCNTs is like that of PCNTs, and the MnO nanoparticles are located inside the PCNT. Compared to PCNTs (276.4, 228.0, 199.7, 170.1, 155.7, 138.1, 114.6, 93.3, and 79.7 mAh g^{-1}) and MnO-CNTs (545.9, 466.1, 419.5, 351.1, 301.2, 235.4, 170.1, 127.6, and 101.9 mAh g^{-1}), MnO-PCNTs have better rate performance MnO-PCNTs (539.3, 447.7, 392.2, 345.1, 313.0, 282.2, 227.4, 179.2 and 160.8 mAh g^{-1}) at 0.2 to 0.5, 1, 2, 3, 5, 10, 20 and 30C, respectively. This suggests that the addition of MnO nanoparticles can greatly improve the performance of PCNTs and that MnO-PCNTs have a unique

1551 structure to prevent MnO from being crushed in the process of repeated charging-

1552 discharging cycles. The impedance data of the equivalent circuit (Fig. 41C, inset)

1553 represent, compared with PCNTs (235 U) and MnO-CNTs (258 U), the charge transfer

1554 resistance of MnO-PCNTs is 173 U (Fig. 41C), which is because MnO nanoparticles

1555 are dispersed in PCNTs, which made the composite materials have high electron

1556 conductivity and ion diffusion ability.

1557 **Please insert Fig. 41**

1558 Recently, Fe_3O_4-SPC is successfully prepared by simply pyrolysis SCMP and mixing

1559 it with $Fe(NO_3)_3 \cdot 9H_2O$ and $Fe(CH_3COO)_2 \cdot 4H_2O$ [394]. The protection of SPC avoids

1560 the huge volume change caused by the crushing of Fe_3O_4 during the repeated

1561 discharge/charge cycle. Fe_3O_4-SPC is a graded polymer composed of nanoparticles and

1562 containing Fe_3O_4 crystals with a face-centered cubic structure. Compared to naked

1563 Fe_3O_4, these special structures enable Fe_3O_4-SPC to exhibit good cyclic capacitance of

1564 897.2 mAh g^{-1} at 0.6 A g^{-1} over 300 cycles, which can be attributed to the reversible

1565 growth of the gelatinous polymer layer under the action of transition metal oxides

1566 [395,396]. Furthermore, the reversible capacity of Fe_3O_4-SPC (926 mAh g^{-1} at 100 mA

1567 g^{-1}) is higher than the Fe_3O_4, which are attributed to sulfur-enriched host and an open

1568 porous structure to provide more lithium storage site.

1569 **6.3.2 CMPs for Sodium-Ion Batteries**

1570 Energy storage is critical to the sustainable development of energy, leading to a

1571 growing demand for energy storage devices, especially for integrated energy storage

1572 systems, and the development of advanced energy storage technologies beyond LIBs is

1573 expected. SIBs are expected to complement this field because they are lighter, more

1574 flexible, more environmentally friendly, and have a high global stockpile. CMPs

1575 provide an effective platform for the development of the next generation of advanced

1576 SIBs with multifunctional organic/polymer electrodes [343].

1577 Recently, highly porous azo-linked polymers (ALPs) have been used for the first time

1578 as redox-active electrode materials for a new rechargeable SIBs [344]. ALPs are highly

1579 cross-linked polymers with high surface area and a π-conjugated microporous property,

1580 which eliminates the solubility problem of organic electrodes in common electrolytes,

1581 facilitates the absorption of electrolytes, and assist ion transport and charge transfer.

1582 Among them, the theoretical capacity of ALP-8 polymer with azo-linked was calculated

1583 based on a four-electron redox reaction (Fig. 42A). The tilt of the charge-discharge

1584 curve (Fig. 42B) is due to the complex electronic properties and redox reactions in the

1585 amorphous structure as well as the embedding of Na^+ [397,398]. As can be seen from

1586 Fig. 42B, the contribution of Na^+ embedding to capacitance is small. The ALP-8

1587 electrode showed high cycling performance, and the reversible capacity (2nd) is 194

1588 mAh g^{-1} (70% of the theoretical capacity) at 0.3 C (Fig. 42C), and maintain a specific

1589 discharge capacity of 170 mAh g^{-1} after 150 cycles. In the case of high current density,

1590 the limited mobility of Na^+, and the decrease of electronic conductivity of the cathode

1591 material tend to reduce the capacity. Therefore, the discharge capacity of the battery at

1592 different current densities was measured to verify its rate capacity, as shown in Fig.

1593 42D, ALP-8 shows excellent rate performance of 108, 88, 70, 57, 42 mAh g^{-1} at 1, 4,

1594 10, 20, and 40 C (1 C = 278 mA g^{-1}), respectively.

1596 6.3.3 CMPs for Potassium-Ion Batteries

1597 Additionally, KIBs also are competitive energy storage devices due to the K$^+$/K redox

1598 potential (2.93 V relative to the standard hydrogen electrode) similar to Li$^+$/Li (3.04 V)

1599 [399]. However, the cycle stability of the KIBs is generally poor due to the large volume

1600 changes caused by the insertion/extraction of K$^+$ [400-404]. The extended π-conjugated

1601 structure of CMPs is conducive to improving the cyclic stability and rate performance

1602 of KIBs [346]. However, the relationship between the structural and performance of

1603 CMPs needs further exploration.

1604 Recently, two series of CMPs (Fig. 43A, bromated benzene (Bz)-containing CMPs

1605 and benzothiadiazole (BT)-containing CMPs) with different structural units were used

1606 as the anode for KIBs [345]. A comparative study of the structure-performance

1607 relationship shows that the LUMO distribution, LUMO energy level, and bandgap have

1608 a great influence on the storage capacity of K$^+$. The high delocalization of LUMO orbit

1609 is conducive to the high charge delocalization along with the polymer networks, and

1610 reduces the charge density of the redox-active site, thus achieving high redox activity

1611 and inhibiting side reactions between the polymer and the electrolyte. The electronic

1612 structure of CMPs can be adjusted by synthesis control. For example, the LUMO energy

1613 level and bandgap of Bz-containing CMPs can drop from PhBT to PyBT. Low LUMO

1614 levels and narrow band gaps confer high electron affinity and conductivity on CMPs.

1615 Therefore, the polymer PyBT composed of pyrene and benzothiadiazole units exhibits

1616 excellent KIB electrochemical properties, such as excellent rate performance at

1617 different current densities from 30 to 500 mA g^{-1} (Fig. 43B), a high reversible capacity

1618 of 428 mAh g^{-1} at 30 mA g^{-1} and excellent capacity retention of 272 mAh g^{-1} at 50 mA

1619 g^{-1} over 500 cycles (Fig. 43C). The K storage mechanism of PyBT (Fig. 43D) was

1620 investigated by FTIR spectral analysis under different discharge-charge states (Fig. 43E

1621 and F). The introduction of the BT unit is beneficial to the increase of the redox activity

1622 of CMP electrodes.

1623 **Please insert Fig. 43**

1624 **6.4 CMPs for Supercapacitors**

1625 Supercapacitors, because of their long cycle stability, high energy density, superfast

1626 charging and discharging rate, low maintenance costs, and safety of such outstanding

1627 features and attention [405-407]. Normally, supercapacitors store energy in two

1628 different ways: (i) non-Faradaic processes about electrochemical double-layer (EDL),

1629 and (ii) Faradaic processes generated by a reversible redox process (pseudocapacitance)

1630 at the electrode interface. In EDL-based supercapacitors, the principle of electrical

1631 energy storage is through adsorbing ions to the surface of an electrode in response to

1632 the applied potential, and improve the porous electrode can promote maximum

1633 capacitance. While in pseudocapacitors, a rapid and reversible redox reaction in the

1634 electrode surface produces Faradic pseudocapacitance and can generate the capacitance

1635 associated with the electrode charging potential within the entire electrode. Therefore,

1636 pseudocapacitors capacitance than involves only the capacitance of EDL.

1637   Carbon and carbon allotropes, such as carbon nanotubes and graphene, are one of the

1638 main research materials for electrode materials for commercial supercapacitors owing

1639 to their high conductivity, large surface area, good chemical stability, pore structure

1640 engineering, heteroatoms doping, and the potential of new carbon materials [408-410].

1641 Additionally, CMPs as an emerging material platform for supercapacitors have got

1642 attention from scientific researchers and engineers [343,411-414]. They can be used as

1643 the electrode materials or precursors of carbon electrode material for supercapacitors

1644 owing to their high surface area, inherent micropore volume, and conductive network

1645 skeleton (Table 5) [189,343,412-419].

1646   **Please insert Table 5**

6.4.1 CMP as Electrode Materials for Supercapacitors

1648   In 2011, Jiang et al. first reported the effect of the synthetic aza-fused CMPs (Aza-

1649 CMPs) on supercapacitors' energy storage and power supply [138]. Aza-CMPs have a

1650 conductivity aza-fused skeleton, closely aza-fused element, and the inherent micropore

1651 and high surface area, prompting the concentration of proton, ion of fast-moving, and

1652 the formation of the electrostatic charge separation layer, thus are used as electrode

1653 materials for the preparation of supercapacitors with larger capacity, higher energy

1654 density, and good cycle life. In 2016, A novel b-ketoenamine-linked CMP (KECMP-1)

1655 synthesized by Schiff-base microwave-assisted condensation of 1,3,5-

1656 triformylphloroglucinol with m-phenylenediamine [420]. KECMP-1 displays a high

1657   specific capacitance of 252 F g^{-1} at 1 A g^{-1}, excellent cycling stability and long cycle

1658   life (retaining 130% of the initial capacitance of 160 F g^{-1} at 20 A g^{-1} over 10000 cycles)

1659   for supercapacitors, which is much better than that of similar COF electrodes'

1660   electrochemical performance [421]. The remarkable electrochemical properties of

1661   KECMP-1 are due to its unique N-H groups and abundant pores that facilitate rapid ion

1662   and electron transport through the interface between the electrodes.

1663   The introduction of redox-active structural units into the electrode material [416,422]

1664   can significantly enhance the capacitance of the supercapacitor [406]. 1,4-bis(3-

1665   phenylpropynoyl)benzene (BPPB) with reversible redox behaviors were crosslinked to

1666   form CMP materials, and then form the hollow shell structure H-CMP-BPPB by

1667   template synthesis [418]. The hollow structure of H-CMP-BPPB may be beneficial to

1668   the diffusion of electrolyte into the CMP material, to make full use of the redox

1669   substances in the material [179,423,424]. As shown in Fig. 44A, CMP-BPPB, and a

1670   CMP without BPPB are prepared using monodisperse silica spheres as hard templates

1671   and 1,3,5-triethynylbenzene and 1,4-diiodobenzene as the reactant, and then obtained

1672   H-CMP-BPPB and hollow CMP without BPPB (H-CMP) through etching of silica

1673   templates. The hollow structure of the polymer materials is shown in Fig. 44B. H-CMP-

1674   BPPB coin type pseudocapacitor has high cycling stability, after 10 000 cycles,

1675   maintained capacitances of 90%, and 85% of the first cycle capacitance at 1 and 6A g^{-}

1676 ^{1}, respectively (Fig. 44C). As well as the Nyquist plots of H-CMP-BPPB and TEM

1677   analysis before and after the reaction also indirectly proves the stability of H-CMP-

1678   BPPB (Fig. 44D). Furthermore, the introduction of carbonyl groups has very little effect

1679 on the chemical composition of CMP, which may be beneficial to the material's weight

1680 to the capacitance ratio.

1681 **Please insert Fig. 44**

1682 Strong electron donor 2,6-diaminoanthraquinone (DAQ) combined with receptor

1683 aryl bromides to form a series of novel CMPs, namely, polyaminoanthraquinone (PAQ)

1684 networks such as PAQTA, PAQTB, PAQCB, PAQTM, and PAQSF (Fig. 45A) [412].

1685 The surface area of PAQs can be up to $600m^2\,g^{-1}$, which has good dispersibility in polar

1686 solvents and can be processed into flexible electrodes for supercapacitors. Compared

1687 to other electronic donors including triphenylbenzene (TB), carbazole (CB),

1688 tetraphenylmethane (TM), and spirobifluorene (SF), the triphenylamine (TA) in

1689 PAQTA network is the strongest electron donor, so to the effective combination of

1690 anthraquinone (AQ) all the charge. Considering the relatively high redox properties of

1691 PAQTA and its minimum surface area compared with other PAQs, the larger capacity

1692 of PAQTA may depend on the redox activity mechanism rather than the double layer

1693 mechanism. The redox mechanism of PAQTA is based on the amalgamation of a strong

1694 electron donor unit TA and a receptor unit AQ (Fig. 45B, C, and D), of which AQ's

1695 redox mechanism involves the reduction of two electrons (Fig. 45B). TA, which can be

1696 oxidized to free radical cations, obtain two-electron delocalized bipolarons (Fig. 45C),

1697 providing extra redox-active sites. The total discharge process is shown in Fig. 45D, of

1698 which AQ and bipolaron are reduced, AQ ion and TA are oxidized. These two processes

1699 involve the concurrent exchange of protons and anions with the electrolyte.

1700 **Please insert Fig. 45**

1701 Besides, the inimitable nitrogen-rich properties and porous structure of these

1702 polymers also contribute to their high electrochemical properties. Two redox-active

1703 CMPs (TAT-CMP-1 and TAT-CMP-2) prepared by nitrogen-rich and highly conductive

1704 triazatruxene building blocks were used as outstanding electrode materials for

1705 supercapacitors application [416]. Fig. 46A display the prepare routes of TAT-CMP-1

1706 and TAT-CMP-2, which show the unique porous and nitrogen-rich structure.

1707 Galvanostatic charge-discharge tests (Fig. 46B, C) reveal rapid ion transport and

1708 electron propagation in these CMP electrodes. The discharge slopes suggest the

1709 relationship between the electrochemical properties of these polymers and their

1710 nitrogen content. Due to their inherent porous structure with high N content to provides

1711 more redox active sites, they exhibit a high specific capacitance (>160 $\mu F\ cm^{-2}$) at a

1712 low surface area. Importantly, cyclic experiments (Fig. 46D) of TAT-CMP-1 and TAT-

1713 CMP-2 indicate that they have outstanding cyclic stability, with cycle efficiency of 95%

1714 and 83%, respectively, at 10 A g^{-1} over 10000 cycles. The nitrogen groups are conducive

1715 to trigger pseudocapacitance and affect the capacitance of the polymer materials, which

1716 provides a pathway for the rational design of electrode materials with excellent

1717 properties for supercapacitors.

1718 **Please insert Fig. 46**

1719 As described in the previous section, 2D CMP materials with high electrical

1720 conductivity, good redox activity, and a large porosity rate are prepared. These porous

1721 membranes with large surface area, low energy band, and high ion transport rate can be

1722 used as electrode materials with high capacity and wide potential window for

1723   supercapacitors [413,425]. In 2018, 2D CMP composites (Fc-CMPs/rGO) were

1724   prepared using 2D rGO and Fc-CMPs with built-in redox-active ferrocene elements

1725   [413]. The covalent binding of Fc-CMPs with rGO through the surface initiates

1726   polymerization, and the porous polymer shell completely wraps the outer surface of the

1727   graphene nanosheet to form a sandwich structure. The storage mechanism of Fc-

1728   CMPs/rGO not only depends on the ion adsorption on the electrode surface but also can

1729   store the pseudocapacitance through the redox reaction on the surface, so the total

1730   capacitance is increased. Then, the high porosity of Fc-CMPs is beneficial to electrolyte

1731   transfer and improves the utilization efficiency of ferrocene units. As well as, the

1732   synergy between Fc-CMPs and highly conductive rGO leads to rapid electrochemical

1733   reaction kinetics, providing excellent electrical conductivity during the charging and

1734   discharging process. This reasonable combination of redox-active CMPs and

1735   conductive rGO in a 2D porous skeleton opens a way for the design and manufacture

1736   of a new generation of supercapacitors.

1737   **6.4.2 CMPs as Templates and/or Precursors of Electrode Materials for**
1738   **Supercapacitors**

1739   CMP materials are conjugated in nature and many of them can be used directly for

1740   electrochemical applications. Additionally, some CMP materials are not conductive.

1741   High-temperature carbonization can improve the porosity and conductivity of carbon-

1742   based materials [426-428]. CMPs can be used as precursors and/or templates to prepare

1743   porous carbon materials with excellent electrochemical properties through pyrolysis

1744 [90,429,430]. These CMP-derived carbon materials are excellent electrode materials

1745 for supercapacitors. For example, compared to porous carbon without a template, the

1746 hierarchically porous carbon nanosheets obtained by pyrolysis conversion of carbon-

1747 rich graphene-templated CMP hybrids (G-CMPs) that showed better electrochemical

1748 performance as electrode material [431]. The use of these porous carbon electrode

1749 materials for supercapacitors resulted in a 48% increase in capacitance. Their CV

1750 curves show typical symmetrical and rectangular shapes, indicating ideal capacitance

1751 behavior. As well as, the layered pore structure of the sandwich with a large aspect ratio

1752 is conducive to the rapid ion transport.

1753   Cooper's group directly carbonized poorly conducting CMP electrodes to produce

1754 porous engineered carbon, which generally helps ions flow through the electrode [432].

1755 The effect of carbonization activation on the capacitive behavior of CMPs was

1756 investigated by using voltammetry and static current charging and discharging

1757 techniques. These conductive carbonized CMPs exhibit ideal ultra-capacitive behavior

1758 with a high capacitance of 175 F g^{-1} in an acidic electrolyte and no significant

1759 capacitance attenuation after 10,000 cycles. Moreover, the investigation also reveals

1760 that the specific capacitance they can reach in alkaline solution is as high as 260 F g^{-1},

1761 and their performance does not decline significantly after 10,000 charge-discharge

1762 cycles. Carbonization is an activation method that converts the original CMP materials

1763 with poor electrical conductivity into porous carbon materials with better electrical

1764 conductivity than the original CMPs and common carbon materials. These preliminary

1765 investigations pave the way for further improvements in the performance of

supercapacitors.

To directly pyrolysis CMPs into 2D porous carbon nanosheets, Yuan et al., the first to use 4-iodophenylsubstituted graphene (RGO-I) template as a guide to building rich nitrogen graphene CMP sandwich structures (GMPs), then, GMP sandwiches are directly pyrolysis to prepare the structurally clear plastic-doped porous carbon/graphene nanosheets (Fig. 47A) [433]. The microporous polymer shells spontaneously grow on both sides of the graphene 2D template, ensuring the complete separation of sheets of graphene-based complexes even during the subsequent high-temperature treatment. SEM, high-resolution transmission electron microscopy (HRTEM), and atomic force microscopy (AFM) showed that all GMPs have uniform sheet shapes (Fig. 47B). The obtained 2D GMP hybrids have a large aspect ratio and BET specific surface area up to 852 $m^2\,g^{-1}$. Porous carbon and graphene have good electrical conductivity and two-dimensional electron transport capacity, which can realize rapid charge transfer in the process of charging and discharging. As well as the close contact between the porous carbon and the graphene layer, the optimal interface interaction provides a large electrochemically active surface area for charge transfer and a minimum ionic diffusion length during charging and discharging, thus effectively improving the capacitance performance of the supercapacitor. Interestingly, a series of three separate GMP-based supercapacitors shows enhanced capacitance (Fig. 47C and D). Compared with single-cell supercapacitors, the galvanostatic charge-discharge (GCD) working voltage of three GMP-based supercapacitors connected in series is increased by 3 times at the same current density and almost the same charge and

1788   discharge time (Fig. 47D).

1789   **Please insert Fig. 47**

1790   Doping and good porosity are two important factors in the application of porous

1791   carbon materials. Carbonized doped CMP skeletons is a very advantageous strategy for

1792   the preparation of porous carbon electrode materials. Ren's group carbonized

1793   reasonably designed n-doped CMP precursor to prepare N-doped porous carbon

1794   material (NPCM-1) [434]. Because nitrogen doping improves electrical properties and

1795   optimizes pore structure, NPCM-1 shows good performance in ultra-capacitor energy

1796   storage. Also, Lim et al. synthesized iron-porphyrin CMP by Suzuki reaction and first

1797   time through pyrolysis to obtain Fe-Nx/C electrode material (Fe-P800) [435]. The

1798   formation of the M-N-C bond between the metal and the carbon material establishes a

1799   direct interaction, which in turn significantly improves the conductivity of the material.

1800   Compared with pure nitrogen-doped porous carbon (P800), the specific capacitance of

1801   Fe-P800 is increased by twice, showing robust stability. The metal (iron) center has an

1802   electronic access point, which provides a fusiform effect for charge transfer to the

1803   conductive graphite matrix through its highly reversible redox reaction, thus improving

1804   the performance.

1805   **6.5 CMPs for Fuel Cells**

1806   Fuel cells first appeared in the 19th century, H. Davy used carbon as fuel, oxygen as

1807   oxidant and nitric acid as the electrolyte to prepare carbon and oxygen batteries. In 1839,

1808   W. Grove used platinum as the electrode, sulfuric acid as the electrolyte, and oxygen as

1809 the fuel and oxidant to obtain electricity from gas and oxygen. The name of "fuel cells"

1810 was first proposed by L. Mond and C. Langer in 1889. However, due to the limitation

1811 of technological levels, such as the cost of the noble metal platinum electrode, the

1812 production of oxygen and many other obstacles cannot be overcome, so people

1813 gradually forget about the fuel cells. Today in the 21st century, energy crisis and

1814 environmental pollution have become two major problems in human development.

1815 Meanwhile, more than 200 years have passed since the concept of fuel cells was

1816 proposed, they seem to have become one of the most potential options to solve the

1817 energy crisis and environmental pollution. Currently, the use of CMPs as an oxygen

1818 reduction electrodes for fuel cells [436-440], in particular, the redox activity and

1819 conductive CMPs, is aimed at addressing three essential points that limit the

1820 development of oxygen reduction reaction (ORR): (i) construction of low-cost

1821 electrode materials, (ii) construction of conductive structures, and (iii) production of

1822 sufficient O_2 binding sites in porous networks. Here, recent advances in the use of

1823 CMPs as a platform for fuel cells are described (Table 6) [436-438,440-445], including

1824 CMPs as an electrode catalyst for fuel cells, and CMPs as catalysts carriers or catalysts

1825 precursors for fuel cells.

1826 **Please insert Table 6**

1827 **6.5.1 CMPs as Electrode Catalysts for Fuel Cells**

1828 Currently, pure metal-free original CMPs as oxygen reduction catalysts used in fuel

1829 cells are still rarely reported. Maji et al. prepared electrochemical active CMPs, TPA-

1830 BP-1 and TPATPE-2, by Sonogashira–Hagihara coupling of tris(4bromophenyl)amine

1831 with 1,1,2,2,-4,4´-diethynylbiphenyl and with tetrakis(4-ethynylphenyl)ethane,

1832 respectively (Fig. 48A) [442]. The prepared CMPs system has a dense nitrogen site that

1833 is easy to bind to oxygen molecules. The prepared CMPs system has a dense nitrogen

1834 site that is easy to bind to oxygen molecules, and tris(4-bromophneyl) amine as hole-

1835 transporting bodies, and 1,1,2,2,tetrakis(4-ethynylphenyl)ethane and 4,4´-

1836 diethynylbiphenyl as suitable acceptors, the whole system is easier to transfer electrons

1837 and easier to carry out electrocatalytic reduction and has appropriate ORR onset

1838 potential and good current stability. Cyclic voltammetric curves, linear sweep

1839 voltammetric curves, and the chronoamperometric study indicate the potential

1840 application of these metal-free CMPs in ORR (Fig. 48B). These metal-free porous

1841 organic catalysts open the way for low-cost and effective fuel cells due to the

1842 appropriate donor nodes and acceptor units in their structure.

1843 **Please insert Fig. 48**

1844 Phthalocyanines (Pcs) and porphyrins (Pors), nitrogen-rich conjugated macrocycles,

1845 both have excellent electrocatalytic activity, and CMPs based on Pcs-Pors are still

1846 infrequent. Liu et al. proposed a strategy to alternately connect phthalocyanine

1847 monomers and porphyrin monomers into 2D conjugated porous networks through

1848 aromatic linkage, including FePcZnPor-CMP, ZnPcFePor-CMP, FePcFePor-CMP, and

1849 ZnPcZnPor-CMP [441]. The main advantage of this strategy is that the 2D porous

1850 network structure composed of conjugated macrocycles and aromatic links and the

1851 complete π-conjugated structure is conducive to the complete exposure of the catalytic

1852 active sites and the promotion of electron transfer. The results of CV showed that two

1853 kinds of FePc-CMPs showed excellent ORR catalytic activity in an alkaline

1854 environment, with $E_{1/2}$ up to 0.863-0.866 V. These results are beneficial to the design

1855 and synthesis of new catalysts with enhanced ORR catalytic properties.

1856 **6.5.2 CMPs as Supports of Catalysts for Fuel Cells**

1857 CMPs are excellent carriers of catalytic active components because of their highly

1858 stable porous skeleton [446]. In the previous discussion, Roy et al. demonstrated the

1859 role of TPA as a redox center in electrochemical reduction [442]. Recently, Maji et al.

1860 reported a donor-receptor CMPs (TPA-PDI) based on tris-(4-aminophenyl)amine (TPA)

1861 and perylenediimide (PDI) with stable charge separation and semiconductor behavior

1862 [212]. PDA and its derivatives are excellent electron acceptor parts that bind to TPA to

1863 produce efficient electron transfer within the networks. TPA is the redox catalytic

1864 activity center, which can reduce metal salts into their nanoparticles. TPA-PDI, with

1865 their conductivity and natural oxygen binding site, is an excellent metal-free catalyst

1866 for catalytic ORR, and can also be used as an excellent carrier of metallic (Au and Co)

1867 NPs (Fig. 49A). The Au and Co NPs are uniformly and stably loaded on the TPA-PDI

1868 matrix (Fig. 49B-E), and the two new nanocomposites (Au@TPA-PDI and Co@TPA-

1869 PDI) have significantly improved overall electrocatalytic activity and stability.

1870 **Please insert Fig. 49**

6.5.3 CMPs as Precursors of Catalysts for Fuel Cells

As mentioned above, the graphene excitation strategy is an emerging strategy for the synthesis of CMP films with large aspect ratio and high specific surface area, which can be used for the pyrolysis of heteroatom-doped 2D porous carbon. Feng's group based on monomers of thiophene-, thiazole- and pyridine- polymerized with 1,3,5-triethynylbenzene on the surface of graphene via Sonogashira-Hagihara reaction to obtain a large aspect ratio and high surface area porous polymer nanosheet (GMPs), thiophene-containing GMP-S, thiazole-containing GMP-NS, and pyridine-containing GMP-N, then template-less thermal carbonization of the polymer nanosheets produced 2D heteroatom-doped porous carbon (GMC), GMC-S, GMC-NS, and GMC-N (Fig. 50A) [430]. The TEM images (Fig. 50B) display many independent flakes in a form like graphene. CV (Fig. 50C) shows that the ORR onset potential of GMC-S is 0.15 V and the peak potential is 0.28 V, lower than that of GMC-NS and GMC-N. The galvanostatic charge/discharge curves experiment (Fig. 50D) shows GMCs' excellent ORR performance and excellent supercapacitive behavior (244-304 F g^{-1} at 0.1 A g^{-1}).

Please insert Fig. 50

Furthermore, Feng's group prepared templated 1D CMP by the layer-by-layer templating method and used it as a precursor for direct pyrolysis to product 1D three-layers heteroatom-doped porous carbon nanotube (CNT). The CNT has a high specific surface area of up to 750 m^2 g^{-1}, graded porous structure, and outstanding electrochemical catalytic performance for ORR [177]. The Diffusion-limited current

density of 4.4 mA cm^{-2} and electron transfer number of 3.8 of three-layer CNT are superior to the correlated arbitrary 1D porous carbon, which shows that reasonable design and control of the shape types of CMP and derived heteroatomized porous carbon is an excellent strategy for the preparation of fuel cells with excellent performance.

Similarly, Scherf et al. prepared a MoS$_2$ template Co-containing CMP (MoS$_2$-Co-CMP) sandwich using a structurally oriented, base plane functionalized MoS$_2$ template [447]. MoS$_2$-Co-CMP pyrolysis and acid leaching resulted in a MoS$_2$-cored layered porous carbon hybrid (MoS$_2$-Co-C) with a high specific surface area. Layered porous carbon shells with uniformly distributed N-doped atoms, and catalysis of CoN and/or CoNC motifs are involved, as well as, there may be a synergistic effect between the MoS$_2$ template and the heteroatom-doped porous carbon shell. Therefore, the MoS$_2$-Co-C sample has a high electrochemical energy storage capacity for ORR, its high capacitance value is up to 288 F g^{-1}, and it has significant cycling stability (capacitance retention of 99% at 5 A g^{-1} over 4000 cycles).

Klaus et al. synthesized Fe/Co N-doped carbon without templates using porphyrin-based CMPs as precursors [437]. It has inherent porosity and large surface area, excellent thermal stability, and high density of MN$_4$ (CoN$_4$ and FeN$_4$) units with precise connections. The reasonable localization of the active site of MN$_4$ is conducive to enhancing the performance of non-noble metal-based catalysts for ORR. Among them, the presence of CoN$_4$ contributes to the increase of the ratio of catalytic active substances, and the spatial distance between CoN$_4$- and FeN$_4$- sites can compensate for

1914 the catalytic selectivity of CoN_4, as well as the FeN_4 site has a higher electron density.

1915 Meanwhile, Chen's group prepared N-rich porous organic polymers by Schiff-base

1916 method of ferrocene (Fc) with melamine/melem, as a precursor, the polymers were

1917 carbonized to obtain N-doped porous carbon nanocomposites [444]. Among them, The

1918 N-Fc-800 as a cathode catalyst to assemble a rechargeable zinc-air battery, showed

1919 excellent catalytic activity, with a high onset potential of 0.96 V and a half-wave

1920 potential of 0.82 V, as well as excellent stability and charging and discharging cycles

1921 (200 cycles). These non-noble metal catalysts are conducive to improving the

1922 electrochemical performance of the ORR catalytic material, which contributes to the

1923 development of new, cost-effective, and environmentally friendly materials for fuel

1924 cells.

1925 Wang et al. loaded metal nanoparticles in situ into N-doped carbon matrixes (MNCs)

1926 based on heat-treated metallophthalocyanine-CMPs [445]. Various metal nanoparticles,

1927 including Co, Fe, and Cu, can be uniformly immobilized in the porous N-doped carbon

1928 frameworks and interact with the N active site, which acts as a catalyst for ORR and

1929 show enhanced diffusion kinetics. Due to the effective synthesis strategy and specific

1930 structure, the obtained MNCs showed high catalytic performance on ORR in both

1931 alkaline and acidic media, with a larger half-wave potential and a favorable limiting

1932 current, and almost carried out oxygen reduction reaction for the four-electron transfer

1933 pathway. MNCs, as a cathode catalyst for Zn-air batteries with stability and methanol

1934 acceptance, provides a new strategy for the design and preparation of highly active

1935 ORR composite catalysts for fuel cells.

6.6 CMPs for Solar Cells

Organic photovoltaic (OPV) devices, under irradiation, the active layer is stimulated by light to generate a charge that is transmitted to the electrode to provide a photovoltaic effect, which has always been the star attraction in the field of clean energy [80,448,449]. Among them, perovskite solar cells (PSCs) has the advantages of a high light absorption factor, wide spectral absorption range, rapid carrier migration speed, and long diffusion length, and the solid PSCs can overcome the technical difficulties of encapsulation in practical application, their power conversion efficiency (PCE) has increased from 3.8% to more than 20% in the past few years [450-452]. PSCs generally consist of metal electrode, hole-transporting layer (HTL), perovskite layer, mesoscopic support, and electronic selective layer (ESL). Currently, indium tin oxide (ITO) is usually used as an anode to collect holes, and low-power function metals (such as Al and Ag) are usually used as cathodes to collect electrons. The insertion of the HTL between the ITO electrode and the active layer can facilitate hole extraction and thus enhance PCE [453,454]. Poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) is used as the main material in the HTL owing to its high conductivity, low opacity, and outstanding film formation [455]. However, the moisture absorption and acidity of PEDOT:PSS tends to erode ITO, resulting in poor chemical stability of PEDOT-based devices and a rapid decline inefficiency, which greatly reduces the actual service life of solar cells. To find the candidate materials of PEDOT:PSS and improve the stability of PSCs, many attempts have been made in the search for new HTL materials, such as transition metal oxides [456-460] and other conducting polymers

[461-464]. Although these materials have made progress in some aspects, the search for effective HTL materials remains one of the major challenges for organic photovoltaic cells. CMPs have monomers with non-planar configuration, adjustable morphology and structure, and skeletons conducive to charge transmission [86,465,466], which are popular materials for HTL in recent years.

The porous aromatic matrix (PAF-86) thin film prepared by Zhu et al., using the electropolymerization (EP) method, was used as a stable HTL material for the first time in inverted PSCs (Fig. 51A) [467]. The monomer M1 of PAF-86 film not only has the function of electronic and electrochemical (EC) to provide effective active sites. The prepared PAF-86 film has the advantages of dense and smooth surface, reasonable pore structure, strong electronic blocking ability, and good stability. Meanwhile, the EP process is simple, controllable, and operates under environmental conditions, so it is appropriate for industrial large-scale production. The J-V curve of PSC shows that the PAF-86 film has PCE of 9.84%, J_{sc} of 18.23 mA cm^{-2}, V_{oc} of 0.91 V, fill factor of 0.59 (Fig. 51B), and the corresponding incident-photon-to-current conversion efficiency (IPCE) spectra (Fig. 51C) showed that the comprehensive current density consistent with the result of J-V was 18.23 mA cm^{-2}, the IPCE value can reach about 70% in the range of wavelength 390 ~ 760 nm. At room temperature of 20 ~ 30℃ and relative humidity of 30 ~ 35%, the PAF-86 thin-film PSC has excellent stability and retains about 80% PCE in the air without encapsulation. Under the same condition, the PCE performance of the PSC device based on PEDOT:PSS drops sharply to 4% of the original PSC. Compared with other existing HTL materials, PAF- 86 thin-film has the

1980 following advantages, small dosage of monomer, synthesis of mild conditions, energy

1981 consumption is reduced, and the cost high polymer chemical and mechanical stability,

1982 which is advantageous to the assembly of flexible, lightweight, portable organic

1983 photovoltaic devices and provides more choices for PSCs HTL materials.

1984 **Please insert Fig. 51**

1985 Based on the carbazole group, Zhou et al. were successfully prepared a pH neutral

1986 CMP films by in-situ electrochemical deposition, which were used as HTL materials in

1987 OPVs (Fig. 52A) [468]. This strategy has the following advantages: (i) The non-planar

1988 configuration of the monomer of the CMP films can promote charge transfer. (ii) The

1989 film thickness can be precisely controlled by the scanning cycle and the cost can be

1990 saved. (iii) A pH neutral CMP films helps prevent erosion of OPVs. The morphologies

1991 and energetics of the synthesized CMP films and PEDOT:PSS are shown in Fig. 52B.

1992 Compared with PEDOT:PSS (-4.94 eV), CMP thin films has higher work function (WF,

1993 -5.03 eV), which can promote hole extraction of OPVs, and the surface roughness of

1994 CMP is slightly lower, which is conducive to solution deposition of OPVs active layer.

1995 The J-V curve (Fig. 52C) of the device indicates that the efficiency of CMP device is

1996 slightly higher than that of PEDOT:PSS device, V_{oc} increases from 0.78 to 0.80 V, and

1997 J_{sc} increases from 15.94 to 16.14 mA cm^{-2}, which may be due to the built-in potential,

1998 modulated charge composition, and deeper HOMO level of CMP films. It can be seen

1999 from the external quantum efficiency spectrum (Fig. 52D) that CMP films have higher

2000 external quantum efficiency (EQE) in two spectral ranges (360nm to 470nm and 520nm

2001 to 700nm), which confirms the increase of J-V. Meanwhile, the illumination intensity-

2002 dependent J_{sc} in these two devices (Fig. 52E) indicated that the main bimolecular charge

2003 was approximately retained in the solar cells of CMP-based HTL. In terms of practical

2004 applications, electrochemical polymerization of CMP films shows great potential in

2005 OPVs.

2006 **Please insert Fig. 52**

2007 **7. Conclusions and Perspectives**

2008 The clean energy systems will be the most important system in the energy field of

2009 the future. Compared with other inorganic and organic materials, the unique multi-

2010 function CMPs can provide adjustable and improved functions, which has been

2011 regarded as a breakthrough start in this field. CMPs have organic structures, conductive

2012 skeletons, and adjustable energy levels, and scientists are working on using CMP

2013 materials for energy-related applications. As previously mentioned, as a classic π-

2014 conjugated polymer, they offer a new platform with opportunities in the application of

2015 this type of polymers in gas storage, photocatalysis, and energy storage. However, to

2016 make these polymer network structures more efficient and able to compete with other

2017 excellent materials that have been developed, some significant exploration and

2018 improvements are needed. Here, we give a summary and a discussion of the challenges

2019 and future directions in the field, including design and synthesis, functionality, and

2020 applications.

7.1 Adjustment of Pore and Bandgap Structure

Most CMPs synthesis routes involve metal-catalyzed carbon-carbon cross-coupling reactions. However, simple polymerization techniques without metal catalysts need to be further developed, allowing the use of industrial-scale metal-free polymerization routes while preserving the properties of the polymers. They are amorphous and have no long-period molecular ordering, but the flexibility of molecular design, structural tunability, and variety of synthesis methods give CMP with different structures and function the characteristic of "predictable". Based on carefully selecting the monomer or functional group and the multifunctional connector, CMPs can adjust various properties, including pore properties and electronic structure.

Efforts in design, synthesis, and function over the past few years have led to advances in the field of property regulation of CMPs. As a powerful platform for the design of porous materials, CMPs have made progress in the field of property regulation in design, synthesis, and function over the past few years. They provide an effective strategy for regulating porosity, pore environment, and function. However, the current realization of CMP materials with a high surface area of more than 5000 m^2 g^{-1} remains a formidable challenge. High surface area, definite pore size, and controlled pore size distribution are important for selective adsorption and storage of fuel molecules or chemicals of CMP. The careful selection of functional groups on the surface of CMP pores is expected to lead to a breakthrough based on synthetic reactions in an adjustment of pore structure and characteristics of CMPs.

Furthermore, as a platform for designing π-conjugated materials, CMPs can be used

2043   to develop 3D polymer networks for exciton migration and carrier transport. The

2044   enhancement of charge carrier mobility and conductivity of these polymer materials is

2045   important for photoelectric applications. In this respect, the synthesis of low bandgap

2046   CMPs is particularly important but remains challenging. To systematically study the

2047   electronic structure-property correlation of CMPs are needed, which is not clear in

2048   many CMP photo- and electro-catalysts but is helpful for their further design. Similarly,

2049   the dynamic distribution of charge in these CMP networks is an important aspect to be

2050   explored in areas such as energy storage, conversion, and catalysis. Of these challenges,

2051   the most immediate concern is controlling the energy levels of such conjugated

2052   semiconductor materials. For example, in the process of light energy conversion, one

2053   must fully understand the location of the HOMOs and the LUMOs. In fact, in some

2054   field, such as photocatalytic devices, a mismatch in the energy levels of equipment

2055   components made of polymer materials can lead to inefficiencies in the devices. The

2056   development of a reliable method or technique to predict and/or specify their HOMOs

2057   and LUMOs levels would be a breakthrough for these materials.

2058   **7.2 Development of CMP Composites and Derived Materials**

2059   At present, CMP materials serve as promising energy storage materials [75,469]

2060   although they have many advantages unmatched by other porous materials, there are

2061   still many places to be explored. Doping behavior [360,470] can enhance the catalytic

2062   activity and stability of traditional CMP catalysts. As a platform for designing

2063   collaborative catalytic systems, the resulting CMP composites can be used in energy

2064 conversion systems if different functions, such as photo-capture components, redox-

2065 active components, and catalytic centers, can be doped into the networks. However, the

2066 intrinsic relationship between doping behavior and the specific properties of these

2067 CMPs has not yet been established, by doping accurately obtain excellent features of

2068 CMP catalyst still need further exploration.

2069 Besides, CMPs encapsulate nanoparticles [154,471-473] to produce composites that

2070 can be used for energy applications in more demanding environments. For our best

2071 knowledge, some metal-free CMPs cannot alone provide the energy and environment

2072 required for the conversion of light energy. With the further development of CMPs, the

2073 research on the reaction mechanism of their light energy conversion extends to how to

2074 maximize the utilization of the "naked" CMP materials that have been developed. The

2075 features of existing excellent CMPs have not yet been systematically developed and

2076 need to be fully explained before CMP application research can be extended. CMPs has

2077 design flexibility and diversity of building monomer, in the case that CMPs cannot meet

2078 the requirements of light energy conversion. Individuals can through the metal loading

2079 or post-synthesis modification to introduced various impurity atoms and metal species

2080 into the porous networks effectively to realize the control metal-mixed compound

2081 synthesis and heterostructure and to simplify the metal recovery process. As the study

2082 continued to expand, CMPs, as a whole platform, show urgency not only in light energy

2083 conversion but also in other areas of clean energy, such as electrical energy storage.

2084 Finally, porous carbon is widely used in the field of clean energy [474-478]. CMPs

2085 as their precursors' pyrolysis to prepare CMPs derived porous carbon materials

[177,443] is a promising strategy. For example, the pyrolysis of MPc-CMPs is an effective strategy for the construction of N-doped carbon compounds without the need for additional templates [445]. However, the loss of coordination of metal nitrogen during direct pyrolysis requires attention in the synthesis of other CMP-derived materials using this strategy.

7.3 Extend the Optoelectronic Applications of CMPs

In recent years, it has been found that CMPs can replace the traditional homogeneous catalyst effectively in a variety of optoelectronic applications [72]. In terms of morphology, these polymer materials have broken through simple amorphous powders, such as nanoparticles and nanotubes, thin films, and macroscopic bulks. The further development of CMPs in optoelectronic applications, especially under the condition of a continuous flow of photoreactor, needs to solve the problems of photon flux and continuous reaction. For example, these materials need to be compatible with a variety of solvents in a flow reactor and react very efficiently at low energy wavelengths [117]. Compared with traditional photocatalysts, the construction of CMPs which can absorb low-energy wavelengths of light is conducive to efficient utilization of energy, greater optical stability, and less photodegradation. Most of the reported work has focused on the electron donor (p-type) component, such as carbazole and tetraphenylvinyl, and the corresponding CMPs [49,176,479], as well as the introduction of electron acceptor (n-type) species to build a promising transfer of charge/energy [480,481]. Furthermore, as mentioned in our previous review [72], water wettability and biocompatibility of CMP

2107   materials also need to be addressed when attempting to compete with more

2108   conventional and mature photocatalysts such as enzymes, especially for larger-scale

2109   optoelectronic applications.

2110   **7.4 Application Prospects of CMPs in Clean Energy**

2111   CMPs as a new class of porous materials still have challenges in practical application

2112   [326,482-485]. For example, in the field of hydrogen energy: (i) How to improve the

2113   hydrogen adsorption performance of CMPs at a convenient temperature. (ii) How to

2114   synthesize more heat-stable CMPs and use them in the pyrolysis of chemical hydrides

2115   to produce hydrogen. (iii) How to improve the catalytic activity of CMPs and clarify

2116   the specific catalytic mechanism. (iv) How to develop other hydrogen production

2117   methods. Meanwhile, LIBs are very common in clean energy devices, and CMPs have

2118   shown great potential as an electrode material for LIBs. The integration of the

2119   advantages of CMPs into traditional LIB materials would facilitate the development of

2120   a new generation of batteries. However, currently, most reported electrochemical

2121   properties of CMPs are not comparable to those of commercial electrode materials. The

2122   challenges with LIBs are: (i) To prepare stable CMP electrode materials to prevent

2123   excessive volume changes during the entire ion insertion/extraction process. (ii) To

2124   discover more effective electroactive structures and deeper understand the charge/ion

2125   transport mechanism to improve electrode stability. (iii) To solve the compatibility

2126   problem between electrode material and electrolyte. (iv) To increase the discharge-

2127   recharging cycle, capacity, and cycle life of the electrode material.

For fuel cells, the low cost and adjustable properties of CMPs can act as electrolytes, electrode catalysts, and catalyst precursors for fuel cells. The major challenges that remain are improving efficiency, energy density, and improving reliability and reducing application costs. Meanwhile, as a kind of renewable energy storage device, the supercapacitor has been widely used in various electroluminescent devices. In supercapacitor applications, the development of high specific surface areas, suitable holes, low internal resistance, good cycling performance, and low-cost CMP electrode materials remains a challenge. Therefore, for fuel cells, LIBs, and supercapacitor applications, the industrialization of CMPs as the main catalysts and the precursors or carriers of catalysts still has a long way to go. Additionally, the investigation of the application of CMPs in solar cells has just started, and the corresponding reports are still very few, but the application of CMPs in solar cells is one of the future research priorities.

7.5 Summary

In summary, the past efforts in design, synthesis, and functional exploration have shown that CMPs are a powerful platform for structural and functional design, and many CMP-based materials with high chemical and thermal stability and excellent performance have been reported. We look forward to a bright and promising future for CMPs as a robust platform for addressing challenging environmental and energy issues. Currently, there are two main goals for the development of CMPs in clean energy: One is to maximize the application of existing CMP-based materials in the clean energy

2149 field; the other is to synthesize new CMPs by optimizing synthetic monomers, links,

2150 and synthesis methods and conditions to develop more outstanding CMP candidate

2151 materials for clean energy. Finally, CMP materials and clean energy are a rapidly

2152 growing field that will yield many excellent results even as we write this review.

2153 Therefore, it is difficult to consider all the work in the limited space and time, and we

2154 apologize to our readers for this.

2155 **Conflicts of Interest**

2156 There are no conflicts of interest to declare.

2166 **References**

2167 [1] Davis SJ, Caldeira K, Matthews HD. Future CO2 emissions and climate change

2168 from existing energy infrastructure. Science. 2010;329:1330-3.

2169 [2] Wang W, Tade MO, Shao Z. Research progress of perovskite materials in

2170 photocatalysis- and photovoltaics-related energy conversion and environmental

2171 treatment. Chem Soc Rev. 2015;44:5371-408.

2172 [3] Le Quere C, Korsbakken JI, Wilson C, Tosun J, Andrew R, Andres RJ, Canadell JG,

2173 Jordan A, Peters GP, van Vuuren DP. Drivers of declining CO2 emissions in 18

2174 developed economies. Nat Clim Change. 2019;9:213-7.

2175 [4] Li S-L, Xu Q. Metal-organic frameworks as platforms for clean energy. Energy

2176 Environ Sci. 2013;6:1656-83.

2177 [5] Kittner N, Lill F, Kammen DM. Energy storage deployment and innovation for the

2178 clean energy transition. Nature Energy. 2017;2:17125/1-6.

2179 [6] Gao M, Zhu L, Peh CK, Ho GW. Solar absorber material and system designs for

2180 photothermal water vaporization towards clean water and energy production. Energy

2181 Environ Sci. 2019;12:841-64.

2182 [7] Wang Q, Domen K. Particulate photocatalysts for light-driven water splitting:

2183 Mechanisms, challenges, and design strategies. Chem Rev. 2020;120:919-85.

2184 [8] Wang Z, Li C, Domen K. Recent developments in heterogeneous photocatalysts for

2185 solar-driven overall water splitting. Chem Soc Rev. 2019;48:2109-25.

2186 [9] He T, Pachfule P, Wu H, Xu Q, Chen P. Hydrogen carriers. Nat Rev Mater.

2187 2016;1:16067/1-17.

2188 [10] Li Y, Fu Z-Y, Su B-L. Hierarchically structured porous materials for energy

2189 conversion and storage. Adv Funct Mater. 2012;22:4634-67.

2190 [11] Ji L, Meduri P, Agubra V, Xiao X, Alcoutlabi M. Graphene-based nanocomposites

2191   for energy storage. Adv Energy Mater. 2016;6:1502159/1-73.

2192   [12] Lee S, Kwon G, Ku K, Yoon K, Jung S-K, Lim H-D, Kang K. Recent progress in

2193   organic electrodes for li and na rechargeable batteries. Adv Mater. 2018;30:1704682/1-

2194   45.

2195   [13] Hwang J-Y, Myung S-T, Sun Y-K. Recent progress in rechargeable potassium

2196   batteries. Adv Funct Mater. 2018;28:1802938/1-45.

2197   [14] Hu Z, Zhu Z, Cheng F, Zhang K, Wang J, Chen C, Chen J. Pyrite FeS2 for high-

2198   rate and long-life rechargeable sodium batteries. Energy Environ Sci. 2015;8:1309-16.

2199   [15] Xia BY, Yan Y, Li N, Wu HB, Lou XW, Wang X. A metal-organic framework-

2200   derived bifunctional oxygen electrocatalyst. Nature Energy. 2016;1:15006/1-8.

2201   [16] Nie Y, Li L, Wei Z. Recent advancements in Pt and Pt-free catalysts for oxygen

2202   reduction reaction. Chem Soc Rev. 2015;44:2168-201.

2203   [17] Borghei M, Lehtonen J, Liu L, Rojas OJ. Advanced biomass-derived

2204   electrocatalysts for the oxygen reduction reaction. Adv Mater. 2018;30:1703691/1-27.

2205   [18] Xiao Z, Yuan Y, Shao Y, Wang Q, Dong Q, Bi C, Sharma P, Gruverman A, Huang

2206   J. Giant switchable photovoltaic effect in organometal trihalide perovskite devices. Nat

2207   Mater. 2015;14:193-8.

2208   [19] Cao W, Xue J. Recent progress in organic photovoltaics: device architecture and

2209   optical design. Energy Environ Sci. 2014;7:2123-44.

2210   [20] Song T-B, Chen Q, Zhou H, Jiang C, Wang H-H, Yang Y, Liu Y, You J, Yang Y.

2211   Perovskite solar cells: film formation and properties. J Mater Chem A. 2015;3:9032-50.

2212   [21] Wang F, Wu X, Yuan X, Liu Z, Zhang Y, Fu L, Zhu Y, Zhou Q, Wu Y, Huang W.

2213   Latest advances in supercapacitors: from new electrode materials to novel device

2214   designs. Chem Soc Rev. 2017;46:6816-54.

2215   [22] Shao Y, El-Kady MF, Wang LJ, Zhang Q, Li Y, Wang H, Mousavi MF, Kaner RB.

2216   Graphene-based materials for flexible supercapacitors. Chem Soc Rev. 2015;44:3639-

2217   65.

2218   [23] Yang P, Mai W. Flexible solid-state electrochemical supercapacitors. Nano Energy.

2219   2014;8:274-90.

2220   [24] Liang Y, Tao Z, Chen J. Organic electrode materials for rechargeable lithium

2221   batteries. Adv Energy Mater. 2012;2:742-69.

2222   [25] Liang YL, Zhang P, Chen J. Function-oriented design of conjugated carbonyl

2223   compound electrodes for high energy lithium batteries. Chem Sci. 2013;4:1330-7.

2224   [26] Yokoji T, Kameyama Y, Maruyama N, Matsubara H. High-capacity organic

2225   cathode active materials of 2,2′-bis-p-benzoquinone derivatives for rechargeable

2226   batteries. J Mater Chem A. 2016;4:5457-66.

2227   [27] Ellis BL, Lee KT, Nazar LF. Positive electrode materials for Li-ion and Li-batteries.

2228   Chem Mater. 2010;22:691-714.

2229   [28] Zhang M, Qu BH, Lei DN, Chen YJ, Yu XZ, Chen LB, Li QH, Wang YG, Wang

2230   TH. A green and fast strategy for the scalable synthesis of Fe_2O_3/graphene with

2231   significantly enhanced Li-ion storage properties. J Mater Chem. 2012;22:3868-74.

2232   [29] Malavasi L, Fisher CA, Islam MS. Oxide-ion and proton conducting electrolyte

2233   materials for clean energy applications: structural and mechanistic features. Chem Soc

2234   Rev. 2010;39:4370-87.

2235 [30] Wang C, Astruc D. Nanogold plasmonic photocatalysis for organic synthesis and

2236 clean energy conversion. Chem Soc Rev. 2014;43:7188-216.

2237 [31] Hossain S, Abdalla AM, Jamain SNB, Zaini JH, Azad AK. A review on proton

2238 conducting electrolytes for clean energy and intermediate temperature-solid oxide fuel

2239 cells. Renew Sust Energ Rev. 2017;79:750-64.

2240 [32] Dawson R, Laybourn A, Clowes R, Khimyak YZ, Adams DJ, Cooper AI.

2241 Functionalized conjugated microporous polymers. Macromolecules. 2009;42:8809-16.

2242 [33] Wu D, Xu F, Sun B, Fu R, He H, Matyjaszewski K. Design and preparation of

2243 porous polymers. Chem Rev. 2012;112:3959-4015.

2244 [34] Dawson R, Cooper AI, Adams DJ. Nanoporous organic polymer networks. Prog

2245 Polym Sci. 2012;37:530-63.

2246 [35] Colson JW, Dichtel WR. Rationally synthesized two-dimensional polymers. Nat

2247 Chem. 2013;5:453-65.

2248 [36] Taylor D, Dalgarno SJ, Xu Z, Vilela F. Conjugated porous polymers: incredibly

2249 versatile materials with far-reaching applications. Chem Soc Rev. 2020;49:3981-4042.

2250 [37] Côté AP, Benin AI, Ockwig NW, Keeffe M, Matzger AJ, Yaghi OM. Porous,

2251 crystalline, covalent organic frameworks. Science. 2005;310:1166-70.

2252 [38] Han SS, Furukawa H, Yaghi OM, Goddard WA. Covalent organic frameworks as

2253 exceptional hydrogen storage materials. J Am Chem Soc. 2008;130:11580–1.

2254 [39] Ding SY, Wang W. Covalent organic frameworks (COFs): from design to

2255 applications. Chem Soc Rev. 2013;42:548-68.

2256 [40] Beaudoin D, Maris T, Wuest JD. Constructing monocrystalline covalent organic

2257 networks by polymerization. Nat Chem. 2013;5:830-4.

2258 [41] Wang H, Zeng Z, Xu P, Li L, Zeng G, Xiao R, Tang Z, Huang D, Tang L, Lai C,

2259 Jiang D, Liu Y, Yi H, Qin L, Ye S, Ren X, Tang W. Recent progress in covalent organic

2260 framework thin films: fabrications, applications and perspectives. Chem Soc Rev.

2261 2019;48:488-516.

2262 [42] Ben T, Ren H, Ma S, Cao D, Lan J, Jing X, Wang W, Xu J, Deng F, Simmons JM,

2263 Qiu S, Zhu G. Targeted synthesis of a porous aromatic framework with high stability

2264 and exceptionally high surface area. Angew Chem Int Ed. 2009;48:9457-60.

2265 [43] McKeown NB, Gahnem B, Msayib KJ, Budd PM, Tattershall CE, Mahmood K,

2266 Tan S, Book D, Langmi HW, Walton A. Towards polymer-based hydrogen storage

2267 materials: engineering ultramicroporous cavities within polymers of intrinsic

2268 microporosity. Angew Chem Int Ed. 2006;45:1804-7.

2269 [44] Carta M, Malpass-Evans R, Croad M, Rogan Y, Jansen JC, Bernardo P, Bazzarelli

2270 F, McKeown NB. An efficient polymer molecular sieve for membrane gas separations.

2271 Science. 2013;339:303-7.

2272 [45] Fischer S, Schmidt J, Strauch P, Thomas A. An anionic microporous polymer

2273 network prepared by the polymerization of weakly coordinating anions. Angew Chem

2274 Int Ed. 2013;52:12174-8.

2275 [46] Zhao Q, Dunlop JW, Qiu X, Huang F, Zhang Z, Heyda J, Dzubiella J, Antonietti

2276 M, Yuan J. An instant multi-responsive porous polymer actuator driven by solvent

2277 molecule sorption. Nat Commun. 2014;5:4293/1-8.

2278 [47] Jiang J-X, Su F, Trewin A, Wood CD, Campbell NL, Niu H, Dickinson C, Ganin

2279   AY, Rosseinsky MJ, Khimyak YZ, Cooper AI. Conjugated microporous

2280   poly(aryleneethynylene) networks. Angew Chem Int Ed. 2007;46:8574-8.

2281   [48] Cooper AI. Conjugated microporous polymers. Adv Mater. 2009;21:1291-5.

2282   [49] Xu Y, Chen L, Guo Z, Nagai A, Jiang D. Light-emitting conjugated polymers with

2283   microporous network architecture: interweaving scaffold promotes electronic

2284   conjugation, facilitates exciton migration, and improves luminescence. J Am Chem Soc.

2285   2011;133:17622-5.

2286   [50] Ren S, Bojdys MJ, Dawson R, Laybourn A, Khimyak YZ, Adams DJ, Cooper AI.

2287   Porous, fluorescent, covalent triazine-based frameworks via room-temperature and

2288   microwave-assisted synthesis. Adv Mater. 2012;24:2357-61.

2289   [51] Bunz UH, Seehafer K, Geyer FL, Bender M, Braun I, Smarsly E, Freudenberg J.

2290   Porous polymers based on aryleneethynylene building blocks. Macromol Rapid

2291   Commun. 2014;35:1466-96.

2292   [52] Xu S, Luo Y, Tan B. Recent development of hypercrosslinked microporous organic

2293   polymers. Macromol Rapid Commun. 2013;34:471-84.

2294   [53] Budd PM, Ghanem BS, Makhseed S, McKeown NB, Msayib KJ, Tattershall CE.

2295   Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic

2296   nanoporous materials. Chem Commun. 2004:230-1.

2297   [54] El-Kaderi HM, Hunt JR, Mendoza-Cortes JL, Cote AP, Taylor RE, O'Keeffe M,

2298   Yaghi OM. Designed synthesis of 3D covalent organic frameworks. Science.

2299   2007;316:268-72.

2300   [55] Kuhn P, Antonietti M, Thomas A. Porous, covalent triazine-based frameworks

2301 prepared by ionothermal synthesis. Angew Chem Int Ed. 2008;47:3450-3.

2302 [56] Uribe-Romo FJ, Hunt JR, Furukawa H, Klock C, O'Keeffe M, Yaghi OM. A

2303 crystalline imine-linked 3-D porous covalent organic framework. J Am Chem Soc.

2304 2009;131:4570-1.

2305 [57] Jiang J-X, Wang C, Laybourn A, Hasell T, Clowes R, Khimyak YZ, Xiao J,

2306 Higgins SJ, Adams DJ, Cooper AI. Metal-organic conjugated microporous polymers.

2307 Angew Chem Int Ed. 2011;50:1072-5.

2308 [58] Linares N, Silvestre-Albero AM, Serrano E, Silvestre-Albero J, Garcia-Martinez

2309 J. Mesoporous materials for clean energy technologies. Chem Soc Rev. 2014;43:7681-

2310 717.

2311 [59] Lin CY, Zhang D, Zhao Z, Xia Z. Covalent organic framework electrocatalysts for

2312 clean energy conversion. Adv Mater. 2018;30:1703646/1-16.

2313 [60] Lee J-SM, Cooper AI. Advances in conjugated microporous polymers. Chem Rev.

2314 2020;120:2171-214.

2315 [61] Chen Q, Luo M, Hammershoj P, Zhou D, Han Y, Laursen BW, Yan CG, Han BH.

2316 Microporous polycarbazole with high specific surface area for gas storage and

2317 separation. J Am Chem Soc. 2012;134:6084-7.

2318 [62] Zhang C, Yang X, Zhao Y, Wang XY, Yu M, Jiang JX. Bifunctionalized conjugated

2319 microporous polymers for carbon dioxide capture. Polymer. 2015;61:36-41.

2320 [63] Xie Y, Wang T-T, Liu X-H, Zou K, Deng W-Q. Capture and conversion of CO2 at

2321 ambient conditions by a conjugated microporous polymer. Nat Commun.

2322 2013;4:1960/1-7.

2323 [64] Yang C, Ma BC, Zhang L, Lin S, Ghasimi S, Landfester K, Zhang KA, Wang X.

2324 Molecular engineering of conjugated polybenzothiadiazoles for enhanced hydrogen

2325 production by photosynthesis. Angew Chem Int Ed. 2016;55:9202-6.

2326 [65] Xu Y, Mao N, Zhang C, Wang X, Zeng J, Chen Y, Wang F, Jiang J-X. Rational

2327 design of donor-pi-acceptor conjugated microporous polymers for photocatalytic

2328 hydrogen production. Appl Catal B. 2018;228:1-9.

2329 [66] Wang Z, Yang X, Yang T, Zhao Y, Wang F, Chen Y, Zeng JH, Yan C, Huang F,

2330 Jiang J-X. Dibenzothiophene dioxide based conjugated microporous polymers for

2331 visible-light-driven hydrogen production. ACS Catal. 2018;8:8590-6.

2332 [67] Chen L, Honsho Y, Seki S, Jiang DL. Light-harvesting conjugated microporous

2333 polymers: Rapid and highly efficient flow of light energy with a porous polyphenylene

2334 framework as antenna. J Am Chem Soc. 2010;132:6742-8.

2335 [68] Rao KV, Haldar R, Maji TK, George SJ. Dynamic, conjugated microporous

2336 polymers: visible light harvesting via guest-responsive reversible swelling. PCCP.

2337 2016;18:156-63.

2338 [69] Jiang J-X, Trewin A, Adams DJ, Cooper AI. Band gap engineering in fluorescent

2339 conjugated microporous polymers. Chem Sci. 2011;2:1777-81.

2340 [70] Gu C, Huang N, Chen Y, Zhang H, Zhang S, Li F, Ma Y, Jiang D. Porous organic

2341 polymer films with tunable work functions and selective hole and electron flows for

2342 energy conversions. Angew Chem Int Ed. 2016;55:3049-53.

2343 [71] Gu C, Huang N, Chen Y, Qin L, Xu H, Zhang S, Li F, Ma Y, Jiang D. π-Conjugated

2344 microporous polymer films: Designed synthesis, conducting properties, and

photoenergy conversions. Angew Chem Int Ed. 2015;54:13594-8.

[72] Luo S, Zeng Z, Zeng G, Liu Z, Xiao R, Xu P, Wang H, Huang D, Liu Y, Shao B, Liang Q, Wang D, He Q, Qin L, Fu Y. Recent advances in conjugated microporous polymers for photocatalysis: designs, applications, and prospects. J Mater Chem A. 2020;8:6434-70.

[73] Zhang C, Yang X, Ren WF, Wang YH, Su FB, Jiang JX. Microporous organic polymer-based lithium ion batteries with improved rate performance and energy density. J Power Sources. 2016;317:49-56.

[74] Su C, He H, Xu L, Zhao K, Zheng C, Zhang C. A mesoporous conjugated polymer based on a high free radical density polytriphenylamine derivative: its preparation and electrochemical performance as a cathode material for Li-ion batteries. J Mater Chem A. 2017;5:2701-9.

[75] Zhang C, He Y, Mu P, Wang X, He Q, Chen Y, Zeng J, Wang F, Xu Y, Jiang J-X. Toward high performance thiophene-containing conjugated microporous polymer anodes for lithium-ion batteries through structure design. Adv Funct Mater. 2018;28:1705432/1-9.

[76] Xu F, Chen X, Tang Z, Wu D, Fu R, Jiang D. Redox-active conjugated microporous polymers: a new organic platform for highly efficient energy storage. Chem Commun. 2014;50:4788-90.

[77] Xu Y, Jin S, Xu H, Nagai A, Jiang D. Conjugated microporous polymers: design, synthesis and application. Chem Soc Rev. 2013;42:8012-31.

[78] Vilela F, Zhang K, Antonietti M. Conjugated porous polymers for energy

2367 applications. Energy Environ Sci. 2012;5:7819-32.

2368 [79] Jiang J-X, Su F, Niu H, Wood CD, Campbell NL, Khimyak YZ, Cooper AI.

2369 Conjugated microporous poly(phenylene butadiynylene)s. Chem Commun. 2008:486-

2370 8.

2371 [80] Weber J, Thomas A. Toward stable interfaces in conjugated polymers:

2372 Microporous poly(p-phenylene) and poly(phenyleneethynylene) based on a

2373 spirobifluorene building block. J Am Chem Soc. 2008;130:6334-5.

2374 [81] Schmidt J, Weber J, Epping JD, Antonietti M, Thomas A. Microporous conjugated

2375 poly(thienylene arylene) networks. Adv Mater. 2009;21:702-5.

2376 [82] Chen L, Yang Y, Jiang D. CMPs as scaffolds for constructing porous catalytic

2377 frameworks: A built-in heterogeneous catalyst with high activity and selectivity based

2378 on nanoporous metalloporphyrin polymers. J Am Chem Soc. 2010;132:9138-43.

2379 [83] Li A, Sun H-X, Tan D-Z, Fan W-J, Wen S-H, Qing X-J, Li G-X, Li S-Y, Deng W-

2380 Q. Superhydrophobic conjugated microporous polymers for separation and adsorption.

2381 Energy Environ Sci. 2011;4:2062-5.

2382 [84] Cheng G, Hasell T, Trewin A, Adams DJ, Cooper AI. Soluble conjugated

2383 microporous polymers. Angew Chem Int Ed. 2012;51:12727-31.

2384 [85] Liu X, Xu Y, Jiang D. Conjugated microporous polymers as molecular sensing

2385 devices: Microporous architecture enables rapid response and enhances sensitivity in

2386 fluorescence-on and fluorescence-off sensing. J Am Chem Soc. 2012;134:8738-41.

2387 [86] Gu C, Chen Y, Zhang Z, Xue S, Sun S, Zhang K, Zhong C, Zhang H, Pan Y, Lv Y,

2388 Yang Y, Li F, Zhang S, Huang F, Ma Y. Electrochemical route to fabricate film-like

conjugated microporous polymers and application for organic electronics. Adv Mater.

2013;25:3443-8.

[87] Xu Y, Nagai A, Jiang D. Core–shell conjugated microporous polymers: a new

strategy for exploring color-tunable and -controllable light emissions. Chem Commun.

2013;49:1591-3.

[88] A S, Zhang Y, Li Z, Xia H, Xue M, Liu X, Mu Y. Highly efficient and reversible

iodine capture using a metalloporphyrin-based conjugated microporous polymer. Chem

Commun. 2014;50:8495-8.

[89] Ding X, Han B-H. Metallophthalocyanine-based conjugated microporous

polymers as highly efficient photosensitizers for singlet oxygen generation. Angew

Chem Int Ed. 2015;54:6536-9.

[90] Zhuang X, Gehrig D, Forler N, Liang H, Wagner M, Hansen MR, Laquai F, Zhang

F, Feng X. Conjugated microporous polymers with dimensionality-controlled

heterostructures for green energy devices. Adv Mater. 2015;27:3789-96.

[91] Liao Y, Weber J, Mills BM, Ren Z, Faul CFJ. Highly efficient and reversible iodine

capture in hexaphenylbenzene-based conjugated microporous polymers.

Macromolecules. 2016;49:6322-33.

[92] Wang L, Wan Y, Ding Y, Wu S, Zhang Y, Zhang X, Zhang G, Xiong Y, Wu X,

Yang J, Xu H. Conjugated microporous polymer nanosheets for overall water splitting

using visible light. Adv Mater. 2017;29:1702428/1-8.

[93] Li Y, Duan Q, Wang H, Gao B, Qiu N, Li Y. Construction of two-dimensional

porphyrin-based fully conjugated microporous polymers as highly efficient

photocatalysts. Journal of Photochemistry and Photobiology A-Chemistry. 2018;356:370-8.

[94] Mu P, Zhang Z, Bai W, He J, Sun H, Zhu Z, Liang W, Li A. Superwetting monolithic hollow-carbon-nanotubes aerogels with hierarchically nanoporous structure for efficient solar steam generation. Adv Energy Mater. 2019;9:1802158/1-9.

[95] Jiang J-X, Su F, Trewin A, Wood CD, Niu H, Jones JTA, Khimyak YZ, Cooper AI. Synthetic control of the pore dimension and surface area in conjugated microporous polymer and copolymer networks. J Am Chem Soc. 2008;130:7710-20.

[96] Thomas A, Kuhn P, Weber J, Titirici M-M, Antonietti M. Porous polymers: Enabling solutions for energy applications. Macromol Rapid Commun. 2009;30:221-36.

[97] Wang X, Maeda K, Thomas A, Takanabe K, Xin G, Carlsson JM, Domen K, Antonietti M. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. Nat Mater. 2009;8:76-80.

[98] Wong YL, Tobin JM, Xu Z, Vilela F. Conjugated porous polymers for photocatalytic applications. J Mater Chem A. 2016;4:18677-86.

[99] Wang X, Zhao Y, Wei L, Zhang C, Jiang J-X. Nitrogen-rich conjugated microporous polymers: impact of building blocks on porosity and gas adsorption. J Mater Chem A. 2015;3:21185-93.

[100] Sun L, Liang Z, Yu J, Xu R. Luminescent microporous organic polymers containing the 1,3,5-tri(4-ethenylphenyl)benzene unit constructed by Heck coupling reaction. Polym Chem. 2013;4:1932-8.

2433 [101] Gu C, Bao Y, Huang W, Liu D, Yang R. Four simple structure carbazole-based

2434 conjugated microporous polymers with different soft connected chains. Macromol

2435 Chem Phys. 2016;217:748-56.

2436 [102] Chai S, Liu H, Zhang X, Han Y, Hu N, Wei L, Cong F, Wei H, Wang L. Synthesis

2437 of a novel beta-ketoenamine-linked conjugated microporous polymer with N-H

2438 functionalized pore surface for carbon dioxide capture. Appl Surf Sci. 2016;384:539-

2439 43.

2440 [103] Biswal BP, Becker D, Chandrasekhar N, Seenath JS, Paasch S, Machill S,

2441 Hennersdorf F, Brunner E, Weigand JJ, Berger R, Feng X. Exploration of thiazolo[5,4-

2442 d]thiazole linkages in conjugated porous organic polymers for chemoselective

2443 molecular sieving. Chemistry-A European Journal. 2018;24:10868-75.

2444 [104] Marco AB, Cortizo-Lacalle D, Perez-Miqueo I, Valenti G, Boni A, Plas J,

2445 Strutyński K, De Feyter S, Paolucci F, Montes M, Khlobystov AN, Melle-Franco M,

2446 Mateo-Alonso A. Twisted aromatic frameworks: Readily exfoliable and solution-

2447 processable two-dimensional conjugated microporous polymers. Angew Chem Int Ed.

2448 2017;56:6946-51.

2449 [105] Deng S, Zhao P, Dai Y, Huang B, Hu A. Synthesis of soluble conjugated

2450 polymeric nanoparticles through heterogeneous Suzuki coupling reaction. Polymer.

2451 2015;64:216-20.

2452 [106] Chen Y, Sun H, Yang R, Wang T, Pei C, Xiang Z, Zhu Z, Liang W, Li A, Deng

2453 W. Synthesis of conjugated microporous polymer nanotubes with large surface areas as

2454 absorbents for iodine and CO_2 uptake. J Mater Chem A. 2015;3:87-91.

2455 [107] Holst JR, Stöckel E, Adams DJ, Cooper AI. High surface area networks from

2456 tetrahedral monomers: Metal-catalyzed coupling, thermal polymerization, and "click"

2457 chemistry. Macromolecules. 2010;43:8531-8.

2458 [108] Ren S, Dawson R, Laybourn A, Jiang J-x, Khimyak Y, Adams DJ, Cooper AI.

2459 Functional conjugated microporous polymers: from 1,3,5-benzene to 1,3,5-triazine.

2460 Polym Chem. 2012;3:928-34.

2461 [109] Jiang J-X, Trewin A, Su F, Wood CD, Niu H, Jones JTA, Khimyak YZ, Cooper

2462 AI. Microporous poly(tri(4-ethynylphenyl)amine) networks: Synthesis, properties, and

2463 atomistic simulation. Macromolecules. 2009;42:2658-66.

2464 [110] Qian X, Zhu Z-Q, Sun H-X, Ren F, Mu P, Liang W, Chen L, Li A. Capture and

2465 reversible storage of volatile iodine by novel conjugated microporous polymers

2466 containing thiophene units. ACS Appl Mater Inter. 2016;8:21063-9.

2467 [111] Zang JK, Zhu ZQ, Sun HX, Liang WD, Li A. Synthesis of functional conjugated

2468 microporous polymers containing pyridine units with high BET surface area for

2469 reversible CO2 storage. React Funct Polym. 2016;99:95-9.

2470 [112] Tan D, Fan W, Xiong W, Sun H, Li A, Deng W, Meng C. Study on adsorption

2471 performance of conjugated microporous polymers for hydrogen and organic solvents:

2472 The role of pore volume. Eur Polym J. 2012;48:705-11.

2473 [113] Bao L, Sun H, Zhu Z, Liang W, Mu P, Zang J, Li A. Synthesis and properties of

2474 tubular-shape conjugated microporous polymers with high purity. Mater Lett.

2475 2016;178:5-9.

2476 [114] Wang X, Chen B, Dong W, Zhang X, Li Z, Xiang Y, Chen H. Hydrophilicity-

2477 controlled conjugated microporous polymers for enhanced visible-light-driven

2478 photocatalytic H2 evolution. Macromol Rapid Commun. 2019;40:1800494/1-8.

2479 [115] Miyaura N, Suzuki A. Stereoselective synthesis of arylated (E)-alkenes by the

2480 reaction of alk-1-enylboranes with aryl halides in the presence of palladium catalyst. J

2481 Chem Soc, Chem Commun. 1979:866-7.

2482 [116] Miyaura N, Yamada K, Suzuki A. A new stereospecific cross-coupling by the

2483 palladium-catalyzed reaction of 1-alkenylboranes with 1-alkenyl or 1-alkynyl halides.

2484 Tetrahedron Lett. 1979;20:3437-40.

2485 [117] Tobin JM, Liu J, Hayes H, Demleitner M, Ellis D, Arrighi V, Xu Z, Vilela F.

2486 BODIPY-based conjugated microporous polymers as reusable heterogeneous

2487 photosensitisers in a photochemical flow reactor. Polym Chem. 2016;7:6662-70.

2488 [118] Xu M, Han X, Wang T, Li S, Hua D. Conjugated microporous polymers bearing

2489 phosphonate ligands as an efficient sorbent for potential uranium extraction from high-

2490 level liquid wastes. J Mater Chem A. 2018;6:13894-900.

2491 [119] Sun L, Zou Y, Liang Z, Yu J, Xu R. A one-pot synthetic strategy via tandem

2492 Suzuki–Heck reactions for the construction of luminescent microporous organic

2493 polymers. Polym Chem. 2014;5:471-8.

2494 [120] Ampelli C, Genovese C, Errahali M, Gatti G, Marchese L, Perathoner S, Centi G.

2495 CO2 capture and reduction to liquid fuels in a novel electrochemical setup by using

2496 metal-doped conjugated microporous polymers. J Appl Electrochem. 2015;45:701-13.

2497 [121] Zhang Q, Yu S, Wang Q, Xiao Q, Yue Y, Ren S. Fluorene-based conjugated

2498 microporous polymers: Preparation and chemical sensing application. Macromol Rapid

2499   Commun. 2017;38:1700445/1-6.

2500   [122] Yuan Y, Huang H, Chen L, Chen Y. N,N '-bicarbazole: A versatile building block

2501   toward the construction of conjugated porous polymers for CO2 capture and dyes

2502   adsorption. Macromolecules. 2017;50:4993-5003.

2503   [123] Liu Q, Li G, Tang Z, Chen L, Liao B, Ou B, Zhou Z, Zhou H. Design and

2504   synthesis of conjugated polymers of tunable pore size distribution. Mater Chem Phys.

2505   2017;186:11-8.

2506   [124] Mane S, Li Y-X, Liu X-Q, Yue MB, Sun L-B. Development of adsorbents for

2507   selective carbon capture: Role of homo- and cross-coupling in conjugated microporous

2508   polymers and their carbonized derivatives. ACS Sustain Chem Eng. 2018;6:17419-26.

2509   [125] Schmidt J, Werner M, Thomas A. Conjugated microporous polymer networks via

2510   yamamoto polymerization. Macromolecules. 2009;42:4426-9.

2511   [126] Liao Y, Cheng Z, Trunk M, Thomas A. Targeted control over the porosities and

2512   functionalities of conjugated microporous polycarbazole networks for CO2-selective

2513   capture and H-2 storage. Polym Chem. 2017;8:7240-7.

2514   [127] Germain J, Svec F, Fréchet JMJ. Preparation of size-selective nanoporous

2515   polymer networks of aromatic rings: Potential adsorbents for hydrogen storage. Chem

2516   Mater. 2008;20:7069-76.

2517   [128] Liao Y, Weber J, Faul CFJ. Conjugated microporous polytriphenylamine

2518   networks. Chem Commun. 2014;50:8002-5.

2519   [129] Ueda M, Abe T, Awano H. Synthesis of poly (2, 5-dialkoxyphenylene).

2520   Macromolecules. 1992;25:5125-30.

2521 [130] Chen Q, Liu D-P, Luo M, Feng L-J, Zhao Y-C, Han B-H. Nitrogen-containing

2522 microporous conjugated polymers via carbazole-based oxidative coupling

2523 polymerization: Preparation, porosity, and gas uptake. Small. 2014;10:308-15.

2524 [131] Zhang Y, A S, Zou Y, Luo X, Li Z, Xia H, Liu X, Mu Y. Gas uptake, molecular

2525 sensing and organocatalytic performances of a multifunctional carbazole-based

2526 conjugated microporous polymer. J Mater Chem A. 2014;2:13422-30.

2527 [132] Zhi Y, Ma S, Xia H, Zhang Y, Shi Z, Mu Y, Liu X. Construction of donor-acceptor

2528 type conjugated microporous polymers: A fascinating strategy for the development of

2529 efficient heterogeneous photocatalysts in organic synthesis. Appl Catal B. 2019;244:36-

2530 44.

2531 [133] Xu Y, Cui D, Zhang S, Xu G, Su Z. Facile synthesis of conjugated microporous

2532 polymer-based porphyrin units for adsorption of CO_2 and organic vapors. Polym Chem.

2533 2019;10:819-22.

2534 [134] Singh A, Roy S, Das C, Samanta D, Maji TK. Metallophthalocyanine-based

2535 redox active metal-organic conjugated microporous polymers for OER catalysis. Chem

2536 Commun. 2018;54:4465-8.

2537 [135] Wang Y, Tao J, Xiong S, Lu P, Tang J, He J, Javaid MU, Pan C, Yu G. Ferrocene-

2538 based porous organic polymers for high-affinity iodine capture. Chem Eng J.

2539 2020;380:122420/1-5.

2540 [136] Rabbani MG, El-Kaderi HM. Template-free synthesis of a highly porous

2541 benzimidazole-linked polymer for CO_2 capture and H_2 storage. Chem Mater.

2542 2011;23:1650-3.

2543 [137] Zhu X, Tian C, Jin T, Wang J, Mahurin SM, Mei W, Xiong Y, Hu J, Feng X, Liu

2544 H, Dai S. Thiazolothiazole-linked porous organic polymers. Chem Commun.

2545 2014;50:15055-8.

2546 [138] Kou Y, Xu Y, Guo Z, Jiang D. Supercapacitive energy storage and electric power

2547 supply using an aza-fused π-conjugated microporous framework. Angew Chem Int Ed.

2548 2011;50:8753-7.

2549 [139] Wang H, Jiang D, Huang D, Zeng G, Xu P, Lai C, Chen M, Cheng M, Zhang C,

2550 Wang Z. Covalent triazine frameworks for carbon dioxide capture. J Mater Chem A.

2551 2019;7:22848-70.

2552 [140] Kuhn P, Forget A, Su D, Thomas A, Antonietti M. From microporous regular

2553 frameworks to mesoporous materials with ultrahigh surface area: Dynamic

2554 reorganization of porous polymer networks. J Am Chem Soc. 2008;130:13333-7.

2555 [141] Kuhn P, Forget A, Hartmann J, Thomas A, Antonietti M. Template-free tuning of

2556 nanopores in carbonaceous polymers through ionothermal synthesis. Adv Mater.

2557 2009;21:897-901.

2558 [142] Kuhn P, Thomas A, Antonietti M. Toward tailorable porous organic polymer

2559 networks: A high-temperature dynamic polymerization scheme based on aromatic

2560 nitriles. Macromolecules. 2009;42:319-26.

2561 [143] Yuan S, Dorney B, White D, Kirklin S, Zapol P, Yu L, Liu D-J. Microporous

2562 polyphenylenes with tunable pore size for hydrogen storage. Chem Commun.

2563 2010;46:4547-9.

2564 [144] Qiao S, Du Z, Yang R. Design and synthesis of novel carbazole-spacer-carbazole

2565   type conjugated microporous networks for gas storage and separation. J Mater Chem

2566   A. 2014;2:1877-85.

2567   [145] Qiao S, Du Z, Huang W, Yang R. Influence of aggregated morphology on carbon

2568   dioxide uptake of polythiophene conjugated organic networks. J Solid State Chem.

2569   2014;212:69-72.

2570   [146] Qiao S, Wang T, Huang W, Jiang J-X, Du Z, Shieh F-K, Yang R. Dendrimer-like

2571   conjugated microporous polymers. Polym Chem. 2016;7:1281-9.

2572   [147] Sun C-J, Wang P-F, Wang H, Han B-H. All-thiophene-based conjugated porous

2573   organic polymers. Polym Chem. 2016;7:5031-8.

2574   [148] Geng T, Zhu Z, Wang X, Xia H, Wang Y, Li D. Poly{tris 4-(2-Thienyl)phenyl

2575   amine} fluorescent conjugated microporous polymer for selectively sensing picric acid.

2576   Sens Actuators, B. 2017;244:334-43.

2577   [149] Pandey P, Katsoulidis AP, Eryazici I, Wu Y, Kanatzidis MG, Nguyen ST. Imine-

2578   linked microporous polymer organic frameworks. Chem Mater. 2010;22:4974-9.

2579   [150] Rabbani MG, Sekizkardes AK, El-Kadri OM, Kaafarani BR, El-Kaderi HM.

2580   Pyrene-directed growth of nanoporous benzimidazole-linked nanofibers and their

2581   application to selective CO2 capture and separation. J Mater Chem. 2012;22:25409-17.

2582   [151] Xu C, Hedin N. Synthesis of microporous organic polymers with high CO2-over-

2583   N2 selectivity and CO2 adsorption. J Mater Chem A. 2013;1:3406-14.

2584   [152] Haikal RR, Soliman AB, Amin M, Karakalos SG, Hassan YS, Elmansi AM,

2585   Hafez IH, Berber MR, Hassanien A, Alkordi MH. Synergism of carbon nanotubes and

2586   porous-organic polymers (POPs) in CO2 fixation: One-pot approach for bottom-up

2587   assembly of tunable heterogeneous catalyst. Appl Catal B. 2017;207:347-57.

2588   [153] Shanmugaraju S, Umadevi D, Savyasachi AJ, Byrne K, Ruether M, Schmitt W,

2589   Watson GW, Gunnlaugsson T. Reversible adsorption and storage of secondary

2590   explosives from water using a Troger's base-functionalised polymer. J Mater Chem A.

2591   2017;5:25014-24.

2592   [154] Zhou H, Wu C, Wu Q, Guo B, Liu W, Li G, Su Q, Mu Y. Palladium nanoparticles

2593   supported on a carbazole functionalized mesoporous organic polymer: synthesis and

2594   their application as efficient catalysts for the Suzuki-Miyaura cross coupling reaction.

2595   Polym Chem. 2017;8:1488-94.

2596   [155] Zhi Y, Li K, Xia H, Xue M, Mu Y, Liu X. Robust porous organic polymers as

2597   efficient heterogeneous organo-photocatalysts for aerobic oxidation reactions. J Mater

2598   Chem A. 2017;5:8697-704.

2599   [156] Cai L, Li Y, Li Y, Wang H, Yu Y, Liu Y, Duan Q. Synthesis of zincphthalocyanine-

2600   based conjugated microporous polymers with rigid-linker as novel and green

2601   heterogeneous photocatalysts. J Hazard Mater. 2018;348:47-55.

2602   [157] Ju P, Wu S, Su Q, Li X, Liu Z, Li G, Wu Q. Salen-porphyrin-based conjugated

2603   microporous polymer supported Pd nanoparticles: highly efficient heterogeneous

2604   catalysts for aqueous C-C coupling reactions. J Mater Chem A. 2019;7:2660-6.

2605   [158] Iha RK, Wooley KL, Nyström AM, Burke DJ, Kade MJ, Hawker CJ. Applications

2606   of orthogonal "click" chemistries in the synthesis of functional soft materials. Chem

2607   Rev. 2009;109:5620-86.

2608   [159] Lowe AB, Hoyle CE, Bowman CN. Thiol-yne click chemistry: A powerful and

2609   versatile methodology for materials synthesis. J Mater Chem. 2010;20:4745-50.

2610   [160] Liang L, Astruc D. The copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC)

2611   "click" reaction and its applications. An overview. Coord Chem Rev. 2011;255:2933-

2612   45.

2613   [161] An Q, Hassan Y, Yan X, Krolla-Sidenstein P, Mohammed T, Lang M, Braese S,

2614   Tsotsalas M. Fast and efficient synthesis of microporous polymer nanomembranes via

2615   light-induced click reaction. Beilstein J Org Chem. 2017;13:558-63.

2616   [162] Yao B, Mei J, Li J, Wang J, Wu H, Sun JZ, Qin A, Tang BZ. Catalyst-free thiol–

2617   yne click polymerization: A powerful and facile tool for preparation of functional

2618   poly(vinylene sulfide)s. Macromolecules. 2014;47:1325-33.

2619   [163] Schwab MG, Crespy D, Feng X, Landfester K, Mullen K. Preparation of

2620   microporous melamine-based polymer networks in an anhydrous high-temperature

2621   miniemulsion. Macromol Rapid Commun. 2011;32:1798-803.

2622   [164] Liu Y, Cui Y, Zhang C, Du J, Wang S, Bai Y, Liang Z, Song X. Post-cationic

2623   modification of a pyrimidine-based conjugated microporous polymer for enhancing the

2624   removal performance of anionic dyes in water. Chemistry-A European Journal.

2625   2018;24:7480-8.

2626   [165] Kiskan B, Weber J. Versatile postmodification of conjugated microporous

2627   polymers using thiol-yne chemistry. ACS Macro Lett. 2012;1:37-40.

2628   [166] Ratvijitvech T, Dawson R, Laybourn A, Khimyak YZ, Adams DJ, Cooper AI.

2629   Post-synthetic   modification   of   conjugated   microporous   polymers.   Polymer.

2630   2014;55:321-5.

2631 [167] Cui D, Yao C, Xu Y. Conjugated microporous polymers with azide groups: a new

2632 strategy for postsynthetic fluoride functionalization and effectively enhanced CO2

2633 adsorption properties. Chem Commun. 2017;53:11422-5.

2634 [168] Yang S-J, Ding X, Han B-H. Conjugated microporous polymers with extended

2635 pi-structures for organic vapor adsorption. Macromolecules. 2018;51:947-53.

2636 [169] Liu L, Deng Q-F, Hou X-X, Yuan Z-Y. User-friendly synthesis of nitrogen-

2637 containing polymer and microporous carbon spheres for efficient CO2 capture. J Mater

2638 Chem. 2012;22:15540-8.

2639 [170] Gao PF, Zheng LL, Liang LJ, Yang XX, Li YF, Huang CZ. A new type of pH-

2640 responsive coordination polymer sphere as a vehicle for targeted anticancer drug

2641 delivery and sustained release. J Mater Chem B. 2013;1:3202-8.

2642 [171] Tabata K, Braam D, Kushida S, Tong L, Kuwabara J, Kanbara T, Beckel A, Lorke

2643 A, Yamamoto Y. Self-assembled conjugated polymer spheres as fluorescent

2644 microresonators. Sci Rep. 2014;4:5902/1-5.

2645 [172] Chen JS, Archer LA, Wen Lou X. SnO2 hollow structures and TiO2 nanosheets

2646 for lithium-ion batteries. J Mater Chem. 2011;21:9912-24.

2647 [173] Mahmoud MA, Narayanan R, El-Sayed MA. Enhancing colloidal metallic

2648 nanocatalysis: Sharp edges and corners for solid nanoparticles and cage effect for

2649 hollow ones. Acc Chem Res. 2013;46:1795-805.

2650 [174] Li G, Li Y, Liu H, Guo Y, Li Y, Zhu D. Architecture of graphdiyne nanoscale

2651 films. Chem Commun. 2010;46:3256-8.

2652 [175] Wu K, Guo J, Wang C. Dispersible and discrete metalloporphyrin-based CMP

2653 nanoparticles enabling colorimetric detection and quantitation of gaseous SO2. Chem

2654 Commun. 2014;50:695-7.

2655 [176] Gu C, Huang N, Gao J, Xu F, Xu Y, Jiang D. Controlled synthesis of conjugated

2656 microporous polymer films: Versatile platforms for highly sensitive and label- free

2657 chemo- and biosensing. Angew Chem Int Ed. 2014;53:4850-5.

2658 [177] He Y, Gehrig D, Zhang F, Lu C, Zhang C, Cai M, Wang Y, Laquai F, Zhuang X,

2659 Feng X. Highly efficient electrocatalysts for oxygen reduction reaction based on 1D

2660 ternary doped porous carbons derived from carbon nanotube directed conjugated

2661 microporous polymers. Adv Funct Mater. 2016;26:8255-65.

2662 [178] Senkovskyy V, Senkovska I, Kiriy A. Surface-initiated synthesis of conjugated

2663 microporous polymers: Chain-growth kumada catalyst-transfer polycondensation at

2664 work. ACS Macro Lett. 2012;1:494-8.

2665 [179] Kang N, Park JH, Jin M, Park N, Lee SM, Kim HJ, Kim JM, Son SU.

2666 Microporous organic network hollow spheres: Useful templates for nanoparticulate

2667 Co3O4 hollow oxidation catalysts. J Am Chem Soc. 2013;135:19115-8.

2668 [180] Li B, Yang X, Xia L, Majeed MI, Tan B. Hollow microporous organic capsules.

2669 Sci Rep. 2013;3:2128/1-6.

2670 [181] Stöber W, Fink A, Bohn E. Controlled growth of monodisperse silica spheres in

2671 the micron size range. J Colloid Interface Sci. 1968;26:62-9.

2672 [182] Ji G, Yang Z, Zhao Y, Zhang H, Yu B, Xu J, Xu H, Liu Z. Synthesis of

2673 metalloporphyrin-based conjugated microporous polymer spheres directed by

2674 bipyridine-type ligands. Chem Commun. 2015;51:7352-5.

2675 [183] Schwab MG, Fassbender B, Spiess HW, Thomas A, Feng X, Mullen K. Catalyst-

2676 free preparation of melamine-based microporous polymer networks through Schiff base

2677 chemistry. J Am Chem Soc. 2009;131:7216-7.

2678 [184] Silverstein MS. PolyHIPEs: Recent advances in emulsion-templated porous

2679 polymers. Prog Polym Sci. 2014;39:199-234.

2680 [185] Kim M, Byeon M, Bae J-S, Moon S-Y, Yu G, Shin K, Basarir F, Yoon T-H, Park

2681 J-W. Preparation of ultrathin films of molecular networks through layer-by-layer cross-

2682 linking polymerization of tetrafunctional monomers. Macromolecules. 2011;44:7092-

2683 5.

2684 [186] Palma-Cando A, Scherf U. Electrochemically generated thin films of

2685 microporous polymer networks: Synthesis, properties, and applications. Macromol

2686 Chem Phys. 2016;217:827-41.

2687 [187] Zhang Q, Dong H, Hu W. Electrochemical polymerization for two-dimensional

2688 conjugated polymers. Journal of Materials Chemistry C. 2018;6:10672-86.

2689 [188] Lindemann P, Tsotsalas M, Shishatskiy S, Abetz V, Krolla-Sidenstein P, Azucena

2690 C, Monnereau L, Beyer A, Gölzhäuser A, Mugnaini V, Gliemann H, Bräse S, Wöll C.

2691 Preparation of freestanding conjugated microporous polymer nanomembranes for gas

2692 separation. Chem Mater. 2014;26:7189-93.

2693 [189] Zhang H, Zhang Y, Gu C, Ma Y. Electropolymerized conjugated microporous

2694 poly(zinc-porphyrin) films as potential electrode materials in supercapacitors. Adv

2695 Energy Mater. 2015;5:1402175/1-6.

2696 [190] Chen Z, Chen M, Yu Y, Wu L. Robust synthesis of free-standing and thickness

2697   controllable conjugated microporous polymer nanofilms. Chem Commun.

2698   2017;53:1989-92.

2699   [191] Liang B, Wang H, Shi X, Shen B, He X, Ghazi ZA, Khan NA, Sin H, Khattak

2700   AM, Li L, Tang Z. Microporous membranes comprising conjugated polymers with rigid

2701   backbones enable ultrafast organic-solvent nanofiltration. Nat Chem. 2018;10:961-7.

2702   [192] Raaijmakers MJT, Benes NE. Current trends in interfacial polymerization

2703   chemistry. Prog Polym Sci. 2016;63:86-142.

2704   [193] Gu C, Zhang Z, Sun S, Pan Y, Zhong C, Lv Y, Li M, Ariga K, Huang F, Ma Y. In

2705   situ electrochemical deposition and doping of C60 films applied to high-performance

2706   inverted organic photovoltaics. Adv Mater. 2012;24:5727-31.

2707   [194] Zhao R, Zhan X, Yao L, Chen Q, Xie Z, Ma Y. Electrochemical deposition of

2708   azobenzene-containing network films with high-contrast and stable photoresponse.

2709   Macromol Rapid Commun. 2016;37:610-5.

2710   [195] Gu C, Fei T, Yao L, Lv Y, Lu D, Ma Y. Multilayer polymer stacking by in situ

2711   electrochemical polymerization for color-stable white electroluminescence. Adv Mater.

2712   2011;23:527-30.

2713   [196] Lv Y, Yao L, Gu C, Xu Y, Liu D, Lu D, Ma Y. Electroactive self-assembled

2714   monolayers for enhanced efficiency and stability of electropolymerized luminescent

2715   films and devices. Adv Funct Mater. 2011;21:2896-900.

2716   [197] Gu C, Dong W, Yao L, Lv Y, Zhang Z, Lu D, Ma Y. Cross-linked multifunctional

2717   conjugated polymers prepared by in situ electrochemical deposition for a highly-

2718   efficient blue-emitting and electron-transport layer. Adv Mater. 2012;24:2413-7.

2719 [198] Li M, Ishihara S, Ohkubo K, Liao M, Ji Q, Gu C, Pan Y, Jiang X, Akada M, Hill

2720 JP, Nakanishi T, Ma Y, Yamauchi Y, Fukuzumi S, Ariga K. Electrochemical synthesis

2721 of transparent, amorphous, C60-rich, photoactive, and low-doped film with an

2722 interconnected structure. Small. 2013;9:2064-8.

2723 [199] Mergel O, Kühn PT, Schneider S, Simon U, Plamper FA. Influence of polymer

2724 architecture on the electrochemical deposition of polyelectrolytes. Electrochim Acta.

2725 2017;232:98-105.

2726 [200] Gu C, Huang N, Wu Y, Xu H, Jiang D. Design of highly photofunctional porous

2727 polymer films with controlled thickness and prominent microporosity. Angew Chem

2728 Int Ed. 2015;54:11540-4.

2729 [201] Zhao R, Han J, Huang M, Liu F, Wang L, Ma Y. Photoresponsive conjugated

2730 microporous polymer films fabricated by electrochemical deposition for controlled

2731 release. Macromol Rapid Commun. 2017;38:1700274/1-6.

2732 [202] Lindemann P, Schade A, Monnereau L, Feng W, Batra K, Gliemann H, Levkin P,

2733 Braese S, Woell C, Tsotsalas M. Surface functionalization of conjugated microporous

2734 polymer thin films and nanomembranes using orthogonal chemistries. J Mater Chem A.

2735 2016;4:6815-8.

2736 [203] Zhu J, Yang C, Lu C, Zhang F, Yuan Z, Zhuang X. Two-dimensional porous

2737 polymers: From sandwich-like structure to layered skeleton. Acc Chem Res.

2738 2018;51:3191-202.

2739 [204] Wang S, Wang Q, Shao P, Han Y, Gao X, Ma L, Yuan S, Ma X, Zhou J, Feng X,

2740 Wang B. Exfoliation of covalent organic frameworks into few-layer redox-active

2741   nanosheets as cathode materials for lithium-ion batteries. J Am Chem Soc.

2742   2017;139:4258-61.

2743   [205] Bunck DN, Dichtel WR. Bulk synthesis of exfoliated two-dimensional polymers

2744   using hydrazone-linked covalent organic frameworks. J Am Chem Soc.

2745   2013;135:14952-5.

2746   [206] Chandra S, Kandambeth S, Biswal BP, Lukose B, Kunjir SM, Chaudhary M,

2747   Babarao R, Heine T, Banerjee R. Chemically stable multilayered covalent organic

2748   nanosheets from covalent organic frameworks via mechanical delamination. J Am

2749   Chem Soc. 2013;135:17853-61.

2750   [207] Mitra S, Kandambeth S, Biswal BP, Khayum M A, Choudhury CK, Mehta M,

2751   Kaur G, Banerjee S, Prabhune A, Verma S, Roy S, Kharul UK, Banerjee R. Self-

2752   exfoliated guanidinium-based ionic covalent organic nanosheets (iCONs). J Am Chem

2753   Soc. 2016;138:2823-8.

2754   [208] Liu W, Wang C, Zhang L, Pan H, Liu W, Chen J, Yang D, Xiang Y, Wang K,

2755   Jiang J, Yao X. Exfoliation of amorphous phthalocyanine conjugated polymers into

2756   ultrathin nanosheets for highly efficient oxygen reduction. J Mater Chem A.

2757   2019;7:3112-9.

2758   [209] Tabor DP, Roch LM, Saikin SK, Kreisbeck C, Sheberla D, Montoya JH,

2759   Dwaraknath S, Aykol M, Ortiz C, Tribukait H, Amador-Bedolla C, Brabec CJ,

2760   Maruyama B, Persson KA, Aspuru-Guzik A. Accelerating the discovery of materials

2761   for clean energy in the era of smart automation. Nat Rev Mater. 2018;3:5-20.

2762   [210] Wu T, Wang T, Sun L, Deng K, Deng W, Lu R. A DFT exploration of efficient

catalysts based on metal-salen monomers for the cycloaddition reaction of CO2 to propylene oxide. Chemistryselect. 2017;2:4533-7.

[211] Yang Z-D, Wu W, Zeng XC. Electronic and transport properties of porous graphenes: two-dimensional benzo- and aza-fused pi-conjugated-microporous-polymer sheets and boron-nitrogen co-doped derivatives. Journal of Materials Chemistry C. 2014;2:2902-7.

[212] Bhattacharyya S, Samanta D, Roy S, Radhakantha VPH, Maji TK. In situ stabilization of Au and Co nanoparticles in a redox-active conjugated microporous polymer matrix: Facile heterogeneous catalysis and electrocatalytic oxygen reduction reaction activity. ACS Appl Mater Inter. 2019;11:5455-61.

[213] Li S, Yang Z-D, Zhang G, Zeng XC. Electronic and transport properties of porous graphene sheets and nanoribbons: benzo-CMPs and BN codoped derivatives. Journal of Materials Chemistry C. 2015;3:9637-49.

[214] Fan W-J, Yang G-J, Chi J-W, Yu Y, Tan D-Z. Theoretical study of the physisorption of organic molecules on conjugated microporous polymers: the critical role of skeleton structures on binding strength. RSC Adv. 2016;6:54841-7.

[215] Srinivasu K, Ghosh SK. Hydrogen adsorption in lithium decorated conjugated microporous polymers: a DFT investigation. RSC Adv. 2014;4:4170-6.

[216] Fan W-J, Zhao Y-L, Hu Y-C, Shi H, Tan D-Z, Zhang R-Q. Design of conjugated microporous polymer nanotubes for efficient benzene molecular adsorptions. Int J Quantum Chem. 2018;118:25492/1-10.

[217] Chen C, Tang C, Xu W, Li Y, Xu L. Design of iron atom modified thiophene-

2785   linked metalloporphyrin 2D conjugated microporous polymer as CO2 reduction

2786   photocatalyst. PCCP. 2018;20:9536-42.

2787   [218] Xu L. Design of open-shell pi-conjugated microporous polymer film with super-

2788   high conductivity. Macromol Chem Phys. 2018;219:1700600/1-6.

2789   [219] Marcus RA. Chemical and electrochemical electron-transfer theory. Annu Rev

2790   Phys Chem. 1964;15:155-96.

2791   [220] Marcus RA. Electron transfer reactions in chemistry. Theory and experiment. Rev

2792   Mod Phys. 1993;65:599-610.

2793   [221] Zwijnenburg MA, Cheng G, McDonald TO, Jelfs KE, Jiang J-X, Ren S, Hasell

2794   T, Blanc F, Cooper AI, Adams DJ. Shedding light on structure-property relationships

2795   for conjugated microporous polymers: The importance of rings and strain.

2796   Macromolecules. 2013;46:7696-704.

2797   [222] Wang L, Wan Y, Ding Y, Niu Y, Xiong Y, Wu X, Xu H. Photocatalytic oxygen

2798   evolution from low-bandgap conjugated microporous polymer nanosheets: a combined

2799   first-principles calculation and experimental study. Nanoscale. 2017;9:4090-6.

2800   [223] Das S, Heasman P, Ben T, Qiu S. Porous organic materials: Strategic design and

2801   structure–function correlation. Chem Rev. 2017;117:1515-63.

2802   [224] Jiang S, Jelfs KE, Holden D, Hasell T, Chong SY, Haranczyk M, Trewin A,

2803   Cooper AI. Molecular dynamics simulations of gas selectivity in amorphous porous

2804   molecular solids. J Am Chem Soc. 2013;135:17818-30.

2805   [225] Thomas JMH, Trewin A. Amorphous PAF-1: Guiding the rational design of

2806   ultraporous materials. J Physl Chem C. 2014;118:19712-22.

2807   [226] Fayon P, Trewin A. Formation mechanism of ultra porous framework materials.

2808   PCCP. 2016;18:16840-7.

2809   [227] Abbott LJ, Colina CM. Atomistic structure generation and gas adsorption

2810   simulations of microporous polymer networks. Macromolecules. 2011;44:4511-9.

2811   [228] Suresh VM, Bonakala S, Roy S, Balasubramanian S, Maji TK. Synthesis,

2812   characterization, and modeling of a functional conjugated microporous polymer: CO2

2813   storage and light harvesting. J Physl Chem C. 2014;118:24369-76.

2814   [229] Abbott LJ, Colina CM. Porosity and ring formation in conjugated microporous

2815   polymers. J Chem Eng Data. 2014;59:3177-82.

2816   [230] Plimpton S. Fast parallel algorithms for short-range molecular dynamics. Journal

2817   of Computational Physics. 1995;117:1-19.

2818   [231] Abbott LJ, Colina CM. Formation of microporosity in hyper-cross-linked

2819   polymers. Macromolecules. 2014;47:5409-15.

2820   [232] Asahi R, Morikawa T, Irie H, Ohwaki T. Nitrogen-doped titanium dioxide as

2821   visible-light-sensitive photocatalyst: designs, developments, and prospects. Chem Rev.

2822   2014;114:9824-52.

2823   [233] Zhang J, Chen Y, Wang X. Two-dimensional covalent carbon nitride nanosheets:

2824   synthesis, functionalization, and applications. Energy Environ Sci. 2015;8:3092-108.

2825   [234] Foit SR, Vinke IC, de Haart LGJ, Eichel R-A. Power-to-syngas: An enabling

2826   technology for the transition of the energy system? Angew Chem Int Ed. 2017;56:5402-

2827   11.

2828   [235] None. Hydrogen Council launched in Davos as 13 major companies join to

2829   promote hydrogen. Fuel Cells Bulletin. 2017:1. 10.1016/S464-2859(17)30001-9.

2830   [236] Chen Q, Luo M, Wang T, Wang J-X, Zhou D, Han Y, Zhang C-S, Yan C-G, Han

2831   B-H. Porous organic polymers based on propeller-like hexaphenylbenzene building

2832   units. Macromolecules. 2011;44:5573-7.

2833   [237] Chen Q, Wang J-X, Yang F, Zhou D, Bian N, Zhang X-J, Yan C-G, Han B-H.

2834   Tetraphenylethylene-based fluorescent porous organic polymers: preparation, gas

2835   sorption properties and photoluminescence properties. J Mater Chem. 2011;21:13554-

2836   60.

2837   [238] Li A, Lu R-F, Wang Y, Wang X, Han K-L, Deng W-Q. Lithium-doped conjugated

2838   microporous polymers for reversible hydrogen storage. Angew Chem Int Ed.

2839   2010;49:3330-3.

2840   [239] Reich TE, Jackson KT, Li S, Jena P, El-Kaderi HM. Synthesis and

2841   characterization of highly porous borazine-linked polymers and their performance in

2842   hydrogen storage application. J Mater Chem. 2011;21:10629-32.

2843   [240] Reich TE, Behera S, Jackson KT, Jena P, El-Kaderi HM. Highly selective

2844 CO_2/CH_4 gas uptake by a halogen-decorated borazine-linked polymer. J Mater Chem.

2845   2012;22:13524-8.

2846   [241] Bhunia A, Vasylyeva V, Janiak C. From a supramolecular tetranitrile to a porous

2847   covalent triazine-based framework with high gas uptake capacities. Chem Commun.

2848   2013;49:3961-3.

2849   [242] Yang L, Ma Y, Xu Y, Chang G. Cation-π induced lithium-doped conjugated

2850   microporous polymer with remarkable hydrogen storage performance. Chem Commun.

2851 2019;55:11227-30.

[243] Zeng W, Zhang Y, Zhao X, Qin M, Li X, Jin W, Zhang D. One-pot synthesis of conjugated microporous polymers based on extended molecular graphenes for hydrogen storage. Polymer. 2019;174:96-100.

[244] Rao KV, Mohapatra S, Kulkarni C, Maji TK, George SJ. Extended phenylene based microporous organic polymers with selective carbon dioxide adsorption. J Mater Chem. 2011;21:12958-63.

[245] Zhang W, Li C, Yuan Y-P, Qiu L-G, Xie A-J, Shen Y-H, Zhu J-F. Highly energy- and time-efficient synthesis of porous triazine-based framework: microwave-enhanced ionothermal polymerization and hydrogen uptake. J Mater Chem. 2010;20:6413-5.

[246] Xu D, Sun L, Li G, Shang J, Yang R-X, Deng W-Q. Methyllithium-doped naphthyl-containing conjugated microporous polymer with enhanced hydrogen storage performance. Chemistry-A European Journal. 2016;22:7944-9.

[247] Mulfort KL, Hupp JT. Chemical reduction of metal−organic framework materials as a method to enhance gas uptake and binding. J Am Chem Soc. 2007;129:9604-5.

[248] Rangnekar N, Mittal N, Elyassi B, Caro J, Tsapatsis M. Zeolite membranes – a review and comparison with MOFs. Chem Soc Rev. 2015;44:7128-54.

[249] Jeon MY, Kim D, Kumar P, Lee PS, Rangnekar N, Bai P, Shete M, Elyassi B, Lee HS, Narasimharao K, Basahel SN, Al-Thabaiti S, Xu W, Cho HJ, Fetisov EO, Thyagarajan R, DeJaco RF, Fan W, Mkhoyan KA, Siepmann JI, Tsapatsis M. Ultra-selective high-flux membranes from directly synthesized zeolite nanosheets. Nature. 2017;543:690-4.

2873   [250] Peng Y, Li Y, Ban Y, Jin H, Jiao W, Liu X, Yang W. Metal-organic framework

2874   nanosheets as building blocks for molecular sieving membranes. Science.

2875   2014;346:1356-9.

2876   [251] Wang X, Chi C, Zhang K, Qian Y, Gupta KM, Kang Z, Jiang J, Zhao D. Reversed

2877   thermo-switchable molecular sieving membranes composed of two-dimensional metal-

2878   organic nanosheets for gas separation. Nat Commun. 2017;8:14460/1-10.

2879   [252] Song Q, Jiang S, Hasell T, Liu M, Sun S, Cheetham AK, Sivaniah E, Cooper AI.

2880   Porous organic cage thin films and molecular-sieving membranes. Adv Mater.

2881   2016;28:2629-37.

2882   [253] Hasell T, Cooper AI. Porous organic cages: soluble, modular and molecular pores.

2883   Nat Rev Mater. 2016;1:16053/1-14.

2884   [254] Holst JR, Trewin A, Cooper AI. Porous organic molecules. Nat Chem.

2885   2010;2:915-20.

2886   [255] Song Q, Cao S, Zavala-Rivera P, Ping Lu L, Li W, Ji Y, Al-Muhtaseb SA,

2887   Cheetham AK, Sivaniah E. Photo-oxidative enhancement of polymeric molecular sieve

2888   membranes. Nat Commun. 2013;4:1918/1-9.

2889   [256] Jimenez-Solomon MF, Song Q, Jelfs KE, Munoz-Ibanez M, Livingston AG.

2890   Polymer nanofilms with enhanced microporosity by interfacial polymerization. Nat

2891   Mater. 2016;15:760-7.

2892   [257] Rose I, Bezzu CG, Carta M, Comesaña-Gándara B, Lasseuguette E, Ferrari MC,

2893   Bernardo P, Clarizia G, Fuoco A, Jansen JC, Hart Kyle E, Liyana-Arachchi TP, Colina

2894   CM, McKeown NB. Polymer ultrapermeability from the inefficient packing of 2D

136

2895   chains. Nat Mater. 2017;16:932-7.

2896   [258] Liu W, Jiang S-D, Yan Y, Wang W, Li J, Leng K, Japip S, Liu J, Xu H, Liu Y,

2897   Park I-H, Bao Y, Yu W, Guiver MD, Zhang S, Loh KP. A solution-processable and ultra-

2898   permeable conjugated microporous thermoset for selective hydrogen separation. Nat

2899   Commun. 2020;11:1633/1-7.

2900   [259] Chong MN, Jin B, Chow CWK, Saint C. Recent developments in photocatalytic

2901   water treatment technology: A review. Water Res. 2010;44:2997-3027.

2902   [260] Liu Y, Liu Z, Huang D, Cheng M, Zeng G, Lai C, Zhang C, Zhou C, Wang W,

2903   Jiang D, Wang H, Shao B. Metal or metal-containing nanoparticle@MOF

2904   nanocomposites as a promising type of photocatalyst. Coord Chem Rev. 2019;388:63-

2905   78.

2906   [261] Jiang L, Yuan X, Pan Y, Liang J, Zeng G, Wu Z, Wang H. Doping of graphitic

2907   carbon nitride for photocatalysis: A reveiw. Appl Catal B. 2017;217:388-406.

2908   [262] Liu J, Liu Y, Liu N, Han Y, Zhang X, Huang H, Lifshitz Y, Lee S-T, Zhong J,

2909   Kang Z. Metal-free efficient photocatalyst for stable visible water splitting via a two-

2910   electron pathway. Science. 2015;347:970-4.

2911   [263] Zou W, Zhang L, Liu L, Wang X, Sun J, Wu S, Deng Y, Tang C, Gao F, Dong L.

2912   Engineering the Cu2O–reduced graphene oxide interface to enhance photocatalytic

2913   degradation of organic pollutants under visible light. Appl Catal B. 2016;181:495-503.

2914   [264] Yu H, Shi R, Zhao Y, Waterhouse GIN, Wu L-Z, Tung C-H, Zhang T. Smart

2915   utilization of carbon dots in semiconductor photocatalysis. Adv Mater. 2016;28:9454-

2916   77.

2917 [265] Zhang G, Lan Z-A, Wang X. Surface engineering of graphitic carbon nitride

2918 polymers with cocatalysts for photocatalytic overall water splitting. Chem Sci.

2919 2017;8:5261-74.

2920 [266] Mahmood J, Li F, Jung S-M, Okyay MS, Ahmad I, Kim S-J, Park N, Jeong HY,

2921 Baek J-B. An efficient and pH-universal ruthenium-based catalyst for the hydrogen

2922 evolution reaction. Nat Nanotechnol. 2017;12:441-6.

2923 [267] Chen X, Shen S, Guo L, Mao SS. Semiconductor-based photocatalytic hydrogen

2924 generation. Chem Rev. 2010;110:6503-70.

2925 [268] Li Y, Wang H, Xie L, Liang Y, Hong G, Dai H. MoS2 nanoparticles grown on

2926 graphene: an advanced catalyst for the hydrogen evolution reaction. J Am Chem Soc.

2927 2011;133:7296-9.

2928 [269] Sprick RS, Bonillo B, Clowes R, Guiglion P, Brownbill NJ, Slater BJ, Blanc F,

2929 Zwijnenburg MA, Adams DJ, Cooper AI. Visible-light-driven hydrogen evolution

2930 using planarized conjugated polymer photocatalysts. Angew Chem Int Ed.

2931 2016;55:1792-6.

2932 [270] Yu H, Shi R, Zhao Y, Bian T, Zhao Y, Zhou C, Waterhouse GIN, Wu L-Z, Tung

2933 C-H, Zhang T. Alkali-assisted synthesis of nitrogen deficient graphitic carbon nitride

2934 with tunable band structures for efficient visible-light-driven hydrogen evolution. Adv

2935 Mater. 2017;29:1605148/1-7.

2936 [271] Cheng W, Su H, Tang F, Che W, Huang Y, Zheng X, Yao T, Liu J, Hu F, Jiang Y,

2937 Liu Q, Wei S. Synergetic enhancement of plasmonic hot-electron injection in Au

2938 cluster-nanoparticle/C3N4 for photocatalytic hydrogen evolution. J Mater Chem A.

2939 2017;5:19649-55.

2940 [272] Wang Y, Silveri F, Bayazit MK, Ruan Q, Li Y, Xie J, Catlow CRA, Tang J.

2941 Bandgap engineering of organic semiconductors for highly efficient photocatalytic

2942 water splitting. Adv Energy Mater. 2018;8:1801084/1-10.

2943 [273] Yu Y, Yan W, Wang X, Li P, Gao W, Zou H, Wu S, Ding K. Surface engineering

2944 for extremely enhanced charge separation and photocatalytic hydrogen evolution on g-

2945 C3N4. Adv Mater. 2018;30:1705060/1-8.

2946 [274] Kong D, Zheng Y, Kobielusz M, Wang Y, Bai Z, Macyk W, Wang X, Tang J.

2947 Recent advances in visible light-driven water oxidation and reduction in suspension

2948 systems. Mater Today. 2018;21:897-924.

2949 [275] Vyas VS, Lau VW-h, Lotsch BV. Soft photocatalysis: Organic polymers for solar

2950 fuel production. Chem Mater. 2016;28:5191-204.

2951 [276] Li L, Cai Z, Wu Q, Lo W-Y, Zhang N, Chen LX, Yu L. Rational design of porous

2952 conjugated polymers and roles of residual palladium for photocatalytic hydrogen

2953 production. J Am Chem Soc. 2016;138:7681-6.

2954 [277] Han XL, Xu MY, Yang S, Qian J, Hua DB. Acetylcysteine-functionalized

2955 microporous conjugated polymers for potential separation of uranium from radioactive

2956 effluents. J Mater Chem A. 2017;5:5123-8.

2957 [278] Wang F, Ren F, Mu P, Zhu ZQ, Sun HX, Ma CH, Xiao CH, Liang WD, Chen LH,

2958 Li A. Hierarchical porous spherical-shaped conjugated microporous polymers for the

2959 efficient removal of antibiotics from water. J Mater Chem A. 2017;5:11348-56.

2960 [279] Liras M, Iglesias M, Sanchez F. Conjugated microporous polymers incorporating

bodipy moieties as light-emitting materials and recyclable visible-light photocatalysts. Macromolecules. 2016;49:1666-73.

[280] Sprick RS, Bonillo B, Sachs M, Clowes R, Durrant JR, Adams DJ, Cooper AI. Extended conjugated microporous polymers for photocatalytic hydrogen evolution from water. Chem Commun. 2016;52:10008-11.

[281] Xu Y, Mao N, Feng S, Zhang C, Wang F, Chen Y, Zeng J, Jiang J-X. Perylene-containing conjugated microporous polymers for photocatalytic hydrogen evolution. Macromol Chem Phys. 2017;218:1700049/1-9.

[282] Xu YF, Zhang C, Mu P, Mao N, Wang X, He Q, Wang F, Jiang JX. Tetra-armed conjugated microporous polymers for gas adsorption and photocatalytic hydrogen evolution. Sci China Chem. 2017;60:1075-83.

[283] Zhao Y, Ma W, Xu Y, Zhang C, Wang Q, Yang T, Gao X, Wang F, Yan C, Jiang J-X. Effect of linking pattern of dibenzothiophene-s,s-dioxide-containing conjugated microporous polymers on the photocatalytic performance. Macromolecules. 2018;51:9502-8.

[284] Mothika VS, Sutar P, Verma P, Das S, Pati SK, Maji TK. Regulating charge-transfer in conjugated microporous polymers for photocatalytic hydrogen evolution. Chemistry-A European Journal. 2019;25:3867-74.

[285] Wang X, Chen L, Chong SY, Little MA, Wu Y, Zhu W-H, Clowes R, Yan Y, Zwijnenburg MA, Sprick RS, Cooper AI. Sulfone-containing covalent organic frameworks for photocatalytic hydrogen evolution from water. Nat Chem. 2018;10:1180-9.

2983   [286] Wang H, Wang H, Wang Z, Tang L, Zeng G, Xu P, Chen M, Xiong T, Zhou C, Li

2984   X, Huang D, Zhu Y, Wang Z, Tang J. Covalent organic framework photocatalysts:

2985   structures and applications. Chem Soc Rev. 2020;49:4135-65.

2986   [287] Slater AG, Cooper AI. Function-led design of new porous materials. Science.

2987   2015;348:aaa8075/1-10

2988   [288] Wan S, Gándara F, Asano A, Furukawa H, Saeki A, Dey SK, Liao L, Ambrogio

2989   MW, Botros YY, Duan X, Seki S, Stoddart JF, Yaghi OM. Covalent organic frameworks

2990   with high charge carrier mobility. Chem Mater. 2011;23:4094-7.

2991   [289] Biswal BP, Kandambeth S, Chandra S, Shinde DB, Bera S, Karak S, Garai B,

2992   Kharul UK, Banerjee R. Pore surface engineering in porous, chemically stable covalent

2993   organic frameworks for water adsorption. J Mater Chem A. 2015;3:23664-9.

2994   [290] Guan X, Li H, Ma Y, Xue M, Fang Q, Yan Y, Valtchev V, Qiu S. Chemically

2995   stable polyarylether-based covalent organic frameworks. Nat Chem. 2019;11:587-94.

2996   [291] Soliman AB, Hassan MH, Tran Ngoc H, Abugable AA, Elmehalmey WA,

2997   Karakalos SG, Tsotsalas M, Heinle M, Elbahri M, Fontecave M, Alkordi MH. Pt

2998   Immobilization within a tailored porous-organic polymer graphene composite:

2999   Opportunities in the hydrogen evolving reaction. ACS Catal. 2017;7:7847-54.

3000   [292] Lu C, Tranca D, Zhang J, Rodríguez Hernández Fn, Su Y, Zhuang X, Zhang F,

3001   Seifert G, Feng X. Molybdenum carbide-embedded nitrogen-doped porous carbon

3002   nanosheets as electrocatalysts for water splitting in alkaline media. ACS Nano.

3003   2017;11:3933-42.

3004   [293] Liao Y, Cheng Z, Zuo W, Thomas A, Faul CFJ. Nitrogen-rich conjugated

microporous polymers: Facile synthesis, efficient gas storage, and heterogeneous catalysis. ACS Appl Mater Inter. 2017;9:38390-400.

[294] Xu F, Wu D, Fu R, Wei B. Design and preparation of porous carbons from conjugated polymer precursors. Mater Today. 2017;20:629-56.

[295] Wang H, Cheng Z, Liao Y, Li J, Weber J, Thomas A, Faul CFJ. Conjugated microporous polycarbazole networks as precursors for nitrogen-enriched microporous carbons for CO_2 storage and electrochemical capacitors. Chem Mater. 2017;29:4885-93.

[296] Cui S, Qian M, Liu X, Sun Z, Du P. A copper porphyrin-based conjugated mesoporous polymer-derived bifunctional electrocatalyst for hydrogen and oxygen evolution. ChemSusChem. 2016;9:2365-73.

[297] Su J, Yang Y, Xia G, Chen J, Jiang P, Chen Q. Ruthenium-cobalt nanoalloys encapsulated in nitrogen-doped graphene as active electrocatalysts for producing hydrogen in alkaline media. Nat Commun. 2017;8:14969/1-10.

[298] Zhang L, Xiao J, Wang H, Shao M. Carbon-based electrocatalysts for hydrogen and oxygen evolution reactions. ACS Catal. 2017;7:7855-65.

[299] Qu K, Zheng Y, Jiao Y, Zhang X, Dai S, Qiao S-Z. Polydopamine-inspired, dual heteroatom-doped carbon nanotubes for highly efficient overall water splitting. Adv Energy Mater. 2017;7:1602068/1-8.

[300] Wang H, Hou B, Yang Y, Chen Q, Zhu M, Thomas A, Liao Y. Cobalt nanocrystals encapsulated in heteroatom-rich porous carbons derived from conjugated microporous polymers for efficient electrocatalytic hydrogen evolution. Small. 2018;14:1803232/1-

3027   6.

3028   [301] Arakawa H, Aresta M, Armor JN, Barteau MA, Beckman EJ, Bell AT, Bercaw

3029   JE, Creutz C, Dinjus E, Dixon DA, Domen K, DuBois DL, Eckert J, Fujita E, Gibson

3030   DH, Goddard WA, Goodman DW, Keller J, Kubas GJ, Kung HH, Lyons JE, Manzer

3031   LE, Marks TJ, Morokuma K, Nicholas KM, Periana R, Que L, Rostrup-Nielson J,

3032   Sachtler WMH, Schmidt LD, Sen A, Somorjai GA, Stair PC, Stults BR, Tumas W.

3033   Catalysis research of relevance to carbon management: Progress, challenges, and

3034   opportunities. Chem Rev. 2001;101:953-96.

3035   [302] Pervaiz M, Sain MM. Carbon storage potential in natural fiber composites.

3036   Resour Conserv Recy. 2003;39:325-40.

3037   [303] Gray HB. Powering the planet with solar fuel. Nat Chem. 2009;1:7.

3038   10.1038/nchem.141.

3039   [304] Farha OK, Özgür Yazaydın A, Eryazici I, Malliakas CD, Hauser BG, Kanatzidis

3040   MG, Nguyen ST, Snurr RQ, Hupp JT. De novo synthesis of a metal–organic framework

3041   material featuring ultrahigh surface area and gas storage capacities. Nat Chem.

3042   2010;2:944-8.

3043   [305] Yang D-A, Cho H-Y, Kim J, Yang S-T, Ahn W-S. CO_2 capture and conversion

3044   using Mg-MOF-74 prepared by a sonochemical method. Energy Environ Sci.

3045   2012;5:6465-73.

3046   [306] Ampelli C, Centi G, Passalacqua R, Perathoner S. Synthesis of solar fuels by a

3047   novel photoelectrocatalytic approach. Energy Environ Sci. 2010;3:292-301.

3048   [307] Herron JA, Kim J, Upadhye AA, Huber GW, Maravelias CT. A general

3049 framework for the assessment of solar fuel technologies. Energy Environ Sci.

3050 2015;8:126-57.

3051 [308] Yu M, Wang X, Yang X, Zhao Y, Jiang J-X. Conjugated microporous copolymer

3052 networks with enhanced gas adsorption. Polym Chem. 2015;6:3217-23.

3053 [309] Wang W, Zhouab M, Yuan D. Carbon dioxide capture in amorphous porous

3054 organic polymers. J Mater Chem A. 2017;5:1334-47.

3055 [310] Rabbani MG, Islamoglu T, El-Kaderi HM. Benzothiazole- and benzoxazole-

3056 linked porous polymers for carbon dioxide storage and separation. J Mater Chem A.

3057 2017;5:258-65.

3058 [311] Zhou H, Zhang QY, Lu XB. Synthesis and catalytic application of N-heterocyclic

3059 carbene copper complex functionalized conjugated microporous polymer. RSC Adv.

3060 2016;6:44995-5000.

3061 [312] Yuan R, Ren H, Yan Z, Wang A, Zhu G. Robust tri(4-ethynylphenyl)amine-based

3062 porous aromatic frameworks for carbon dioxide capture. Polym Chem. 2014;5:2266-

3063 72.

3064 [313] Dawson R, Adams DJ, Cooper AI. Chemical tuning of CO_2 sorption in robust

3065 nanoporous organic polymers. Chem Sci. 2011;2:1173-7.

3066 [314] Ma H, Ren H, Zou X, Meng S, Sun F, Zhu G. Post-metalation of porous aromatic

3067 frameworks for highly efficient carbon capture from CO_2 + N-2 and CH4 + N-2

3068 mixtures. Polym Chem. 2014;5:144-52.

3069 [315] Zhang X, Lu J, Zhang J. Porosity enhancement of carbazolic porous organic

3070 frameworks using dendritic building blocks for gas storage and separation. Chem Mater.

3071 2014;26:4023-9.

[316] Jeon HJ, Choi JH, Lee Y, Choi KM, Park JH, Kang JK. Highly selective CO2-capturing polymeric organic network structures. Adv Energy Mater. 2012;2:225-8.

[317] Jiang F, Sun J, Yang R, Qiao S, An Z, Huang J, Mao H, Chen G, Ren Y. A facile approach to prepare a microporous polycarbazole P-tetra(4-(N-carbazolyl)phenyl)silane network with high CO2 storage and separation properties. New J Chem. 2016;40:4969-73.

[318] Qiao S, Wei H, Wang T, Huang W, Gu C, Yang R, Li X. A ribbon-like ultramicroporous conjugated polycarbazole network for gas storage and separation. New J Chem. 2016;40:3172-6.

[319] Qiao S, Huang W, Wei H, Wang T, Yang R. Fine tailoring the steric configuration of initial building blocks to construct ultramicroporous polycarbazole networks with high CO2 uptake and selectivity of CO2 over N-2. Polymer. 2015;70:52-8.

[320] Qiao S, Huang W, Du Z, Chen X, Shieh F-K, Yang R. Phosphine oxide-based conjugated microporous polymers with excellent CO2 capture properties. New J Chem. 2015;39:136-41.

[321] Wang S, Liu Y, Yu Y, Du J, Cui Y, Song X, Liang Z. Conjugated microporous polymers based on biphenylene for CO2 adsorption and luminescence detection of nitroaromatic compounds. New J Chem. 2018;42:9482-7.

[322] Banerjee R, Furukawa H, Britt D, Knobler C, O'Keeffe M, Yaghi OM. Control of pore size and functionality in isoreticular zeolitic imidazolate frameworks and their carbon dioxide selective capture properties. J Am Chem Soc. 2009;131:3875-7.

3093   [323] Vaidhyanathan R, Iremonger SS, Shimizu GKH, Boyd PG, Alavi S, Woo TK.

3094   Direct observation and quantification of CO_2 binding within an amine-functionalized

3095   nanoporous solid. Science. 2010;330:650-3.

3096   [324] Lu W, Yuan D, Sculley J, Zhao D, Krishna R, Zhou H-C. Sulfonate-grafted porous

3097   polymer networks for preferential CO_2 adsorption at low pressure. J Am Chem Soc.

3098   2011;133:18126-9.

3099   [325] Xie L-H, Suh MP. High CO_2-capture ability of a porous organic polymer

3100   bifunctionalized with carboxy and triazole groups. Chemistry-A European Journal.

3101   2013;19:11590-7.

3102   [326] Qin L, Xu G-J, Yao C, Xu Y-H. Conjugated microporous polymer networks with

3103   adjustable microstructures for high CO_2 uptake capacity and selectivity. Chem

3104   Commun. 2016;52:12602-5.

3105   [327] Yassin A, Trunk M, Czerny F, Fayon P, Trewin A, Schmidt J, Thomas A.

3106   Structure-thermodynamic-property relationships in cyanovinyl-based microporous

3107   polymer networks for the future design of advanced carbon capture materials. Adv

3108   Funct Mater. 2017;27:1700233/1-9.

3109   [328] North M, Pasquale R, Young C. Synthesis of cyclic carbonates from epoxides and

3110 CO_2. Green Chem. 2010;12:1514-39.

3111   [329] Xie K, Umezawa N, Zhang N, Reunchan P, Zhang Y, Ye J. Self-doped $SrTiO_{3-\delta}$

3112   photocatalyst with enhanced activity for artificial photosynthesis under visible light.

3113   Energy Environ Sci. 2011;4:4211-9.

3114   [330] Cheng H, Huang B, Liu Y, Wang Z, Qin X, Zhang X, Dai Y. An anion exchange

approach to Bi2WO6 hollow microspheres with efficient visible light photocatalytic reduction of CO2 to methanol. Chem Commun. 2012;48:9729-31.

[331] Broicher C, Foit SR, Rose M, Hausoul PJC, Palkovits R. A bipyridine-based conjugated microporous polymer for the ir-catalyzed dehydrogenation of formic acid. ACS Catal. 2017;7:8413-9.

[332] Qiao J, Liu Y, Hong F, Zhang J. A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. Chem Soc Rev. 2014;43:631-75.

[333] Zhang S, Huang W, Hu P, Huang C, Shang C, Zhang C, Yang R, Cui G. Conjugated microporous polymers with excellent electrochemical performance for lithium and sodium storage. J Mater Chem A. 2015;3:1896-901.

[334] Lin Z-Q, Xie J, Zhang B-W, Li J-W, Weng J, Song R-B, Huang X, Zhang H, Li H, Liu Y, Xu ZJ, Huang W, Zhang Q. Solution-processed nitrogen-rich graphene-like holey conjugated polymer for efficient lithium ion storage. Nano Energy. 2017;41:117-27.

[335] Chen Z, Li W, Dai Y, Xu N, Su C, Liu J, Zhang C. Conjugated microporous polymer based on star-shaped triphenylamine-benzene structure with improved electrochemical performances as the organic cathode material of Li-ion battery. Electrochim Acta. 2018;286:187-94.

[336] Wang J, Chen CS, Zhang Y. Hexaazatrinaphthylene-based porous organic polymers as organic cathode materials for lithium-ion batteries. ACS Sustain Chem Eng. 2018;6:1772-9.

[337] Wei W, Chang G, Xu Y, Yang L. An indole-based conjugated microporous

polymer: a new and stable lithium storage anode with high capacity and long life induced by cation-pi interactions and a N-rich aromatic structure. J Mater Chem A. 2018;6:18794-8.

[338] Wang X, Zhang C, Xu Y, He Q, Mu P, Chen Y, Zeng J, Wang F, Jiang J-X. Conjugated microporous polytetra(2-thienyl)ethylene as high performance anode material for lithium- and sodium-ion batteries. Macromol Chem Phys. 2018;219:1700524/1-8.

[339] Chen Z, Xu N, Li W, Zhao R, Dong Y, Liu J, Su C, Wang J, Zhang C. Effect of trace hydrofluoric acid in a LiPF6 electrolyte on the performance of a Li-organic battery with an N-heterocycle based conjugated microporous polymer as the cathode. J Mater Chem A. 2019;7:16347-55.

[340] Meng L, Ren S, Ma C, Yu Y, Lou Y, Zhang D, Shi Z. Synthesis of a 2D nitrogen-rich pi-conjugated microporous polymer for high performance lithium-ion batteries. Chem Commun. 2019;55:9491-4.

[341] Molina A, Patil N, Ventosa E, Liras M, Palma J, Marcilla R. New anthraquinone-based conjugated microporous polymer cathode with ultrahigh specific surface area for high-performance lithium-ion batteries. Adv Funct Mater. 2020;30:1908074/1-11.

[342] Ren S-B, Ma W, Zhang C, Chen L, Wang K, Li R-R, Shen M, Han D-M, Chen Y, Jiang J-X. Exploiting polythiophenyl-triazine-based conjugated microporous polymer with superior lithium-storage performance. ChemSusChem. 2020;13:1–9.

[343] Chen Y, Li H, Tang M, Zhuo S, Wu Y, Wang E, Wang S, Wang C, Hu W. Capacitive conjugated ladder polymers for fast-charge and -discharge sodium-ion

3159   batteries and hybrid supercapacitors. J Mater Chem A. 2019;7:20891-8.

3160   [344] Weeraratne KS, Alzharani AA, El-Kaderi HM. Redox-active porous organic

3161   polymers as novel electrode materials for green rechargeable sodium-ion batteries. ACS

3162   Appl Mater Inter. 2019;11:23520-6.

3163   [345] Zhang C, Qao Y, Xiong P, Ma W, Bai P, Wang X, Li Q, Zhao J, Xu Y, Chen Y,

3164   Zeng JH, Wang F, Xu Y, Jiang J-X. Conjugated microporous polymers with tunable

3165   electronic structure for high-performance potassium-ion batteries. ACS Nano.

3166   2019;13:745-54.

3167   [346] Tian B, Zheng J, Zhao C, Liu C, Su C, Tang W, Li X, Ning G-H. Carbonyl-based

3168   polyimide and polyquinoneimide for potassium-ion batteries. J Mater Chem A.

3169   2019;7:9997-10003.

3170   [347] Balogun M-S, Qiu W, Wang W, Fang P, Lu X, Tong Y. Recent advances in metal

3171   nitrides as high-performance electrode materials for energy storage devices. J Mater

3172   Chem A. 2015;3:1364-87.

3173   [348] Zhu G-N, Wang Y-G, Xia Y-Y. Ti-based compounds as anode materials for Li-

3174   ion batteries. Energy Environ Sci. 2012;5:6652-67.

3175   [349] Trogadas P, Ramani V, Strasser P, Fuller TF, Coppens M-O. Hierarchically

3176   structured nanomaterials for electrochemical energy conversion. Angew Chem Int Ed.

3177   2016;55:122-48.

3178   [350] Chan CK, Peng H, Liu G, McIlwrath K, Zhang XF, Huggins RA, Cui Y. High-

3179   performance lithium battery anodes using silicon nanowires. Nat Nanotechnol.

3180   2008;3:31-5.

3181 [351] Scrosati B, Garche J. Lithium batteries: Status, prospects and future. J Power

3182 Sources. 2010;195:2419-30.

3183 [352] Mao Y, Duan H, Xu B, Zhang L, Hu Y, Zhao C, Wang Z, Chen L, Yang Y. Lithium

3184 storage in nitrogen-rich mesoporous carbon materials. Energy Environ Sci.

3185 2012;5:7950-5.

3186 [353] Kang N, Park JH, Choi J, Jin J, Chun J, Jung IG, Jeong J, Park J-G, Lee SM, Kim

3187 HJ, Son SU. Nanoparticulate iron oxide tubes from microporous organic nanotubes as

3188 stable anode materials for lithium ion batteries. Angew Chem Int Ed. 2012;51:6626-30.

3189 [354] Jiang J, Zhu J, Ai W, Fan Z, Shen X, Zou C, Liu J, Zhang H, Yu T. Evolution of

3190 disposable bamboo chopsticks into uniform carbon fibers: a smart strategy to fabricate

3191 sustainable anodes for Li-ion batteries. Energy Environ Sci. 2014;7:2670-9.

3192 [355] Janoschka T, Hager MD, Schubert US. Powering up the future: Radical polymers

3193 for battery applications. Adv Mater. 2012;24:6397-409.

3194 [356] Su C, Ye Y, Xu L, Zhang C. Synthesis and charge–discharge properties of a

3195 ferrocene-containing polytriphenylamine derivative as the cathode of a lithium ion

3196 battery. J Mater Chem. 2012;22:22658-62.

3197 [357] Renault S, Oltean VA, Araujo CM, Grigoriev A, Edström K, Brandell D.

3198 Superlithiation of organic electrode materials: The case of dilithium

3199 benzenedipropiolate. Chem Mater. 2016;28:1920-6.

3200 [358] Lee KY, Hwang H, Shin D, Choi W. Enhanced thermopower wave via nanowire

3201 bonding and grain boundary fusion in combustion of fuel/CuO–Cu2O–Cu hybrid

3202 composites. J Mater Chem A. 2015;3:5457-66.

3203 [359] Kim S-M, Kim MH, Choi SY, Lee JG, Jang J, Lee JB, Ryu JH, Hwang SS, Park

3204 J-H, Shin K, Kim YG, Oh SM. Poly(phenanthrenequinone) as a conductive binder for

3205 nano-sized silicon negative electrodes. Energy Environ Sci. 2015;8:1538-43.

3206 [360] Novák P, Müller K, Santhanam KSV, Haas O. Electrochemically active polymers

3207 for rechargeable batteries. Chem Rev. 1997;97:207-82.

3208 [361] Zhu LM, Lei AW, Cao YL, Ai XP, Yang HX. An all-organic rechargeable battery

3209 using bipolar polyparaphenylene as a redox-active cathode and anode. Chem Commun.

3210 2013;49:567-9.

3211 [362] Casado N, Hernández G, Veloso A, Devaraj S, Mecerreyes D, Armand M.

3212 PEDOT radical polymer with synergetic redox and electrical properties. ACS Macro

3213 Lett. 2016;5:59-64.

3214 [363] Armand M, Tarascon JM. Building better batteries. Nature. 2008;451:652-7.

3215 [364] Song Z, Zhou H. Towards sustainable and versatile energy storage devices: an

3216 overview of organic electrode materials. Energy Environ Sci. 2013;6:2280-301.

3217 [365] Shi Y, Peng L, Ding Y, Zhao Y, Yu G. Nanostructured conductive polymers for

3218 advanced energy storage. Chem Soc Rev. 2015;44:6684-96.

3219 [366] Zhu Z, Hong M, Guo D, Shi J, Tao Z, Chen J. All-solid-state lithium organic

3220 battery with composite polymer electrolyte and pillar[5]quinone cathode. J Am Chem

3221 Soc. 2014;136:16461-4.

3222 [367] Patra BC, Khilari S, Satyanarayana L, Pradhan D, Bhaumik A. A new

3223 benzimidazole based covalent organic polymer having high energy storage capacity.

3224 Chem Commun. 2016;52:7592-5.

3225 [368] Dai Y, Li W, Chen Z, Zhu X, Liu J, Zhao R, Wright DS, Noori A, Mousavi MF,

3226 Zhang C. An air-stable electrochromic conjugated microporous polymer as an emerging

3227 electrode material for hybrid energy storage systems. J Mater Chem A. 2019;7:16397-

3228 405.

3229 [369] Mahadevi AS, Sastry GN. Cation−π interaction: Its role and relevance in

3230 chemistry, biology, and material science. Chem Rev. 2013;113:2100-38.

3231 [370] Craven TW, Cho M-K, Traaseth NJ, Bonneau R, Kirshenbaum K. A miniature

3232 protein stabilized by a cation−π interaction network. J Am Chem Soc. 2016;138:1543-

3233 50.

3234 [371] Chang G, Yang L, Yang J, Stoykovich MP, Deng X, Cui J, Wang D. High-

3235 performance pH-switchable supramolecular thermosets via cation–π interactions. Adv

3236 Mater. 2018;30:1704234/1-6.

3237 [372] Alzubi M, Arias S, Louzao I, Quiñóa E, Riguera R, Freire F. Multipodal dynamic

3238 coordination involving cation–π interactions to control the structure of helical polymers.

3239 Chem Commun. 2017;53:8573-6.

3240 [373] Gebbie MA, Wei W, Schrader AM, Cristiani TR, Dobbs HA, Idso M, Chmelka

3241 BF, Waite JH, Israelachvili JN. Tuning underwater adhesion with cation–π interactions.

3242 Nat Chem. 2017;9:473-9.

3243 [374] Han X, Chang C, Yuan L, Sun T, Sun J. Aromatic carbonyl derivative polymers

3244 as high- performance li- ion storage materials. Adv Mater. 2007;19:1616-21.

3245 [375] Sakaushi K, Nickerl G, Wisser FM, Nishio-Hamane D, Hosono E, Zhou H,

3246 Kaskel S, Eckert J. An energy storage principle using bipolar porous polymeric

frameworks. Angew Chem Int Ed. 2012;51:7850-4.

[376] Wu J, Rui X, Wang C, Pei W-B, Lau R, Yan Q, Zhang Q. Nanostructured conjugated ladder polymers for stable and fast lithium storage anodes with high-capacity. Adv Energy Mater. 2015;5:1402189/1-6.

[377] González-García P. Activated carbon from lignocellulosics precursors: A review of the synthesis methods, characterization techniques and applications. Renew Sust Energ Rev. 2018;82:1393-414.

[378] Rashidi NA, Yusup S. A review on recent technological advancement in the activated carbon production from oil palm wastes. Chem Eng J. 2017;314:277-90.

[379] Titirici M-M, Antonietti M. Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization. Chem Soc Rev. 2010;39:103-16.

[380] Soleimani M, Kaghazchi T. Agricultural waste conversion to activated carbon by chemical activation with phosphoric acid. Chem Eng Technal. 2007;30:649-54.

[381] Furukawa H, Cordova KE, O'Keeffe M, Yaghi OM. The chemistry and applications of metal-organic frameworks. Science. 2013;341:123044/1-12.

[382] Salunkhe RR, Kaneti YV, Kim J, Kim JH, Yamauchi Y. Nanoarchitectures for metal-organic framework-derived nanoporous carbons toward supercapacitor applications. Acc Chem Res. 2016;49:2796-806.

[383] Chen Y-Z, Zhang R, Jiao L, Jiang H-L. Metal-organic framework-derived porous materials for catalysis. Coord Chem Rev. 2018;362:1-23.

[384] Li X, Zheng S, Jin L, Li Y, Geng P, Xue H, Pang H, Xu Q. Metal-organic

framework-derived carbons for battery applications. Adv Energy Mater. 2018;8:1800716/1-25.

[385] Luo S, Zeng Z, Zeng G, Liu Z, Xiao R, Chen M, Tang L, Tang W, Lai C, Cheng M, Shao B, Liang Q, Wang H, Jiang D. Metal organic frameworks as robust host of palladium nanoparticles in heterogeneous catalysis: Synthesis, application, and prospect. ACS Appl Mater Inter. 2019;11:32579-98.

[386] Zhang Q, Sun H, Wang X, Zhu Z, Liang W, Li A, Wen S, Deng W. Conjugated microporous polymer-derived porous hard carbon as high-rate long-life anode materials for lithium ion batteries. Energy Technology. 2013;1:721-5.

[387] Zhang Q, Dai Q, Yan C, Su C, Li A. Nitrogen-doped porous carbon nanoparticle derived from nitrogen containing conjugated microporous polymer as high performance lithium battery anode. J Alloys Compd. 2017;714:204-12.

[388] Qin D-D, Wang T, Song Y-M, Tao C-L. Reduced monoclinic BiVO4 for improved photoelectrochemical oxidation of water under visible light. Dalton Transactions. 2014;43:7691-4.

[389] Li X, Zhu X, Zhu Y, Yuan Z, Si L, Qian Y. Porous nitrogen-doped carbon vegetable-sponges with enhanced lithium storage performance. Carbon. 2014;69:515-24.

[390] Han X, Han P, Yao J, Zhang S, Cao X, Xiong J, Zhang J, Cui G. Nitrogen-doped carbonized polyimide microsphere as a novel anode material for high performance lithium ion capacitors. Electrochim Acta. 2016;196:603-10.

[391] Zhang QT, Ge SW, Wang XM, Sun HX, Zhu ZQ, Liang WD, Li A. Novel

MnO/conjugated microporous polymer derived-porous hard carbon nanocomposite for superior lithium storage. RSC Adv. 2014;4:41649-53.

[392] Zhang Q, Dai Q, Li M, Wang X, Li A. Incorporation of MnO nanoparticles inside porous carbon nanotubes originated from conjugated microporous polymers for lithium storage. J Mater Chem A. 2016;4:19132-9.

[393] Li X, Niu S, Nan D, Li B, He Y-B, Kang F. Sp-sp(2) hybrid-conjugated microporous polymer-derived Pd-encapsulated porous carbon materials for lithium-sulfur batteries. Chem Commun. 2019;55:10084-7.

[394] Zhang Q, Meng Y, Li M, Wang X. Thiophene containing conjugated microporous polymers derived sulfur-enriched porous carbon supported Fe3O4 nanoparticles with superior lithium storage properties. Journal of Materials Science-Materials in Electronics. 2019;30:1425-33.

[395] Hu Y-Y, Liu Z, Nam K-W, Borkiewicz OJ, Cheng J, Hua X, Dunstan MT, Yu X, Wiaderek KM, Du L-S, Chapman KW, Chupas PJ, Yang X-Q, Grey CP. Origin of additional capacities in metal oxide lithium-ion battery electrodes. Nat Mater. 2013;12:1130-6.

[396] Pan L, Zhu X-D, Xie X-M, Liu Y-T. Smart hybridization of TiO2 nanorods and Fe3O4 nanoparticles with pristine graphene nanosheets: Hierarchically nanoengineered ternary heterostructures for high-rate lithium storage. Adv Funct Mater. 2015;25:3341-50.

[397] Okubo M, Hosono E, Kim J, Enomoto M, Kojima N, Kudo T, Zhou H, Honma I. Nanosize effect on high-rate li-ion intercalation in LiCoO2 electrode. J Am Chem Soc.

3313   2007;129:7444-52.

3314   [398] Okubo M, Kim J, Kudo T, Zhou H, Honma I. Anisotropic surface effect on

3315   electronic structures and electrochemical properties of LiCoO2. J Physl Chem C.

3316   2009;113:15337-42.

3317   [399] Eftekhari A, Jian Z, Ji X. Potassium secondary batteries. ACS Appl Mater Inter.

3318   2017;9:4404-19.

3319   [400] Chen Y, Luo W, Carter M, Zhou L, Dai J, Fu K, Lacey S, Li T, Wan J, Han X,

3320   Bao Y, Hu L. Organic electrode for non-aqueous potassium-ion batteries. Nano Energy.

3321   2015;18:205-11.

3322   [401] Lei K, Li F, Mu C, Wang J, Zhao Q, Chen C, Chen J. High K-storage performance

3323   based on the synergy of dipotassium terephthalate and ether-based electrolytes. Energy

3324   Environ Sci. 2017;10:552-7.

3325   [402] Jian Z, Luo W, Ji X. Carbon electrodes for K-Ion batteries. J Am Chem Soc.

3326   2015;137:11566-9.

3327   [403] Zhang W, Mao J, Li S, Chen Z, Guo Z. Phosphorus-based alloy materials for

3328   advanced potassium-ion battery anode. J Am Chem Soc. 2017;139:3316-9.

3329   [404] Han C, Han K, Wang X, Wang C, Li Q, Meng J, Xu X, He Q, Luo W, Wu L, Mai

3330   L. Three-dimensional carbon network confined antimony nanoparticle anodes for high-

3331   capacity K-ion batteries. Nanoscale. 2018;10:6820-6.

3332   [405] Béguin F, Presser V, Balducci A, Frackowiak E. Carbons and electrolytes for

3333   advanced supercapacitors. Adv Mater. 2014;26:2219-51.

3334   [406] Wang Q, Yan J, Fan Z. Carbon materials for high volumetric performance

3335   supercapacitors: design, progress, challenges and opportunities. Energy Environ Sci.

3336   2016;9:729-62.

3337   [407] Niu H, Zhou D, Yang X, Li X, Wang Q, Qu F. Towards three-dimensional

3338   hierarchical ZnO nanofiber@Ni(OH)2 nanoflake core–shell heterostructures for high-

3339   performance asymmetric supercapacitors. J Mater Chem A. 2015;3:18413-21.

3340   [408] Yu D, Goh K, Wang H, Wei L, Jiang W, Zhang Q, Dai L, Chen Y. Scalable

3341   synthesis of hierarchically structured carbon nanotube–graphene fibres for capacitive

3342   energy storage. Nat Nanotechnol. 2014;9:555-62.

3343   [409] Xu Y, Tao Y, Zheng X, Ma H, Luo J, Kang F, Yang Q-H. A metal-free

3344   supercapacitor electrode material with a record high volumetric capacitance over 800

3345   F cm−3. Adv Mater. 2015;27:8082-7.

3346   [410] Xu F, Tang Z, Huang S, Chen L, Liang Y, Mai W, Zhong H, Fu R, Wu D. Erratum:

3347   Facile synthesis of ultrahigh-surface-area hollow carbon nanospheres for enhanced

3348   adsorption and energy storage. Nat Commun. 2015;6:7863/1-2

3349   [411] Ringk A, Lignie A, Hou Y, Alshareef HN, Beaujuge PM. Electropolymerized

3350   star-shaped benzotrithiophenes yield pi-conjugated hierarchical networks with high

3351   areal capacitance. ACS Appl Mater Inter. 2016;8:12091-100.

3352   [412] Liao Y, Wang H, Zhu M, Thomas A. Efficient supercapacitor energy storage using

3353   conjugated microporous polymer networks synthesized from Buchwald-Hartwig

3354   coupling. Adv Mater. 2018;30:1705710/1-10.

3355   [413] Khattak AM, Sin H, Ghazi ZA, He X, Liang B, Khan NA, Alanagh HR, Iqbal A,

3356   Li L, Tang Z. Controllable fabrication of redox-active conjugated microporous

3357   polymers on reduced graphene oxide for high performance faradaic energy storage. J

3358   Mater Chem A. 2018;6:18827-32.

3359   [414] Liu W, Ulaganathan M, Abdelwahab I, Luo X, Chen Z, Tan SJR, Wang X, Liu Y,

3360   Geng D, Bao Y, Chen J, Loh KP. Two-dimensional polymer synthesized via solid-state

3361   polymerization for high-performance supercapacitors. ACS Nano. 2018;12:852-60.

3362   [415] Zhang M, Zhao T, Dou J, Xu Z, Zhang W, Chen X, Wang X, Zhou B. Bottom-up

3363   construction of conjugated microporous polyporphyrin-coated graphene hydrogel

3364   composites with hierarchical pores for high-performance capacitors. Chemelectrochem.

3365   2019;6:5946. 10.1002/celc.201901586.

3366   [416] Li X-C, Zhang Y, Wang C-Y, Wan Y, Lai W-Y, Pang H, Huang W. Redox-active

3367   triazatruxene-based conjugated microporous polymers for high-performance

3368   supercapacitors. Chem Sci. 2017;8:2959-65.

3369   [417] Bandyopadhyay S, Singh C, Jash P, Hussain MW, Paul A, Patra A. Redox-active,

3370   pyrene-based pristine porous organic polymers for efficient energy storage with

3371   exceptional cyclic stability. Chem Commun. 2018;54:6796-9.

3372   [418] Choi J, Ko JH, Kang CW, Lee SM, Kim HJ, Ko Y-J, Yang M, Son SU. Enhanced

3373   redox activity of a hollow conjugated microporous polymer through the generation of

3374   carbonyl groups by carbonylative Sonogashira coupling. J Mater Chem A.

3375   2018;6:6233-7.

3376   [419] Li H, Lyu W, Liao Y. Engineering redox activity in conjugated microporous

3377   polytriphenylamine networks using pyridyl building blocks toward efficient

3378   supercapacitors. Macromol Rapid Commun. 2019;40:1900455/1-7.

3379 [420] Chai S, Hu N, Han Y, Zhang X, Yang Z, Wei L, Wang L, Wei H. The microwave-

3380 assisted solvothermal synthesis of a novel beta-ketoenamine-linked conjugated

3381 microporous polymer for supercapacitors. RSC Adv. 2016;6:49425-8.

3382 [421] Wei H, Chai S, Hu N, Yang Z, Wei L, Wang L. The microwave-assisted

3383 solvothermal synthesis of a crystalline two-dimensional covalent organic framework

3384 with high CO2 capacity. Chem Commun. 2015;51:12178-81.

3385 [422] Choi J, Kim ES, Ko JH, Lee SM, Kim HJ, Ko Y-J, Son SU. Hollow and

3386 microporous triphenylamine networks post-modified with TCNE for enhanced

3387 organocathode performance. Chem Commun. 2017;53:8778-81.

3388 [423] Wang X, Feng J, Bai Y, Zhang Q, Yin Y. Synthesis, properties, and applications

3389 of hollow micro-/nanostructures. Chem Rev. 2016;116:10983-1060.

3390 [424] Cho K, Yoo J, Noh H-W, Lee SM, Kim HJ, Ko Y-J, Jang H-Y, Son SU. Hollow

3391 structural effect of microporous organocatalytic polymers with pyrrolidines: dramatic

3392 enhancement of catalytic performance. J Mater Chem A. 2017;5:8922-6.

3393 [425] Sun M, Kuang P, Qin L, Gu C, Xie Z, Ma Y. In situ synthesis of electroactive

3394 conjugated microporous fullerene films capable of supercapacitive energy storage.

3395 Chem Commun. 2017;53:9602-5.

3396 [426] Zhu Y, Murali S, Stoller MD, Ganesh KJ, Cai W, Ferreira PJ, Pirkle A, Wallace

3397 RM, Cychosz KA, Thommes M, Su D, Stach EA, Ruoff RS. Carbon-based

3398 supercapacitors produced by activation of graphene. Science. 2011;332:1537-41.

3399 [427] Li Y, Zhu H, Shen F, Wan J, Han X, Dai J, Dai H, Hu L. Highly conductive

3400 microfiber of graphene oxide templated carbonization of nanofibrillated cellulose. Adv

3401   Funct Mater. 2014;24:7366-72.

3402   [428] Zheng S, Ju H, Lu X. A high-performance supercapacitor based on KOH

3403   activated 1D C70 microstructures. Adv Energy Mater. 2015;5:1500871/1-9.

3404   [429] Ashourirad B, Sekizkardes AK, Altarawneh S, El-Kaderi HM. Exceptional gas

3405   adsorption properties by nitrogen-doped porous carbons derived from benzimidazole-

3406   linked polymers. Chem Mater. 2015;27:1349-58.

3407   [430] Zhuang X, Zhang F, Wu D, Forler N, Liang H, Wagner M, Gehrig D, Hansen MR,

3408   Laquai F, Feng X. Two- dimensional sandwich- type, graphene- based conjugated

3409   microporous polymers. Angew Chem Int Ed. 2013;52:9668-72.

3410   [431] Yuan K, Guo-Wang P, Hu T, Shi L, Zeng R, Forster M, Pichler T, Chen Y, Scherf

3411   U. Nanofibrous and graphene-templated conjugated microporous polymer materials for

3412   flexible chemosensors and supercapacitors. Chem Mater. 2015;27:7403-11.

3413   [432] Lee J-SM, Wu T-H, Alston BM, Briggs ME, Hasell T, Hu C-C, Cooper AI.

3414   Porosity-engineered carbons for supercapacitive energy storage using conjugated

3415   microporous polymer precursors. J Mater Chem A. 2016;4:7665-73.

3416   [433] Yuan K, Hu T, Xu Y, Graf R, Shi L, Forster M, Pichler T, Riedl T, Chen Y, Scherf

3417   U. Nitrogen-doped porous carbon/graphene nanosheets derived from two-dimensional

3418   conjugated microporous polymer sandwiches with promising capacitive performance.

3419   Mater Chem Front. 2017;1:278-85.

3420   [434] Xu Y, Wu S, Ren S, Ji J, Yue Y, Shen J. Nitrogen-doped porous carbon materials

3421   generated via conjugated microporous polymer precursors for CO2 capture and energy

3422   storage. RSC Adv. 2017;7:32496-501.

3423 [435] Lim AC, Jadhav HS, Seo JG. Electron transport shuttle mechanism via an Fe-N-

3424 C bond derived from a conjugated microporous polymer for a supercapacitor. Dalton

3425 Transactions. 2018;47:852-8.

3426 [436] Lu G, Yang H, Zhu Y, Huggins T, Ren ZJ, Liu Z, Zhang W. Synthesis of a

3427 conjugated porous Co(II) porphyrinylene-ethynylene framework through alkyne

3428 metathesis and its catalytic activity study. J Mater Chem A. 2015;3:4954-9.

3429 [437] Brüller S, Liang H-W, Kramm UI, Krumpfer JW, Feng X, Müllen K. Bimetallic

3430 porous porphyrin polymer-derived non-precious metal electrocatalysts for oxygen

3431 reduction reactions. J Mater Chem A. 2015;3:23799-808.

3432 [438] Zhang W, Cui T, Yang L, Zhang C, Cai M, Sun S, Yao Y, Zhuang X, Zhang F.

3433 Hollow-structured conjugated porous polymer derived Iron/Nitrogen-codoped

3434 hierarchical porous carbons as highly efficient electrocatalysts. J Colloid Interface Sci.

3435 2017;497:108-16.

3436 [439] Yang S-J, Ding X, Han B-H. Conjugated microporous polymers with dense

3437 sulfonic acid groups as efficient proton conductors. Langmuir. 2018;34:7640-6.

3438 [440] Hu L, Gu S, Yu W, Zhang W, Xie Q, Pan C, Tang J, Yu G. Facile preparation of

3439 CoO nanoparticles embedded N-doped porous carbon from conjugated microporous

3440 polymer for oxygen reduction reaction. J Colloid Interface Sci. 2019;562:550-7.

3441 [441] Liu W, Wang K, Wang C, Liu W, Pan H, Xiang Y, Qi D, Jiang J. Mixed

3442 phthalocyanine-porphyrin-based conjugated microporous polymers towards unveiling

3443 the activity origin of Fe-N-4 catalysts for the oxygen reduction reaction. J Mater Chem

3444 A. 2018;6:22851-7.

3445 [442] Roy S, Bandyopadhyay A, Das M, Ray PP, Pati SK, Maji TK. Redox-active and

3446 semi-conducting donor-acceptor conjugated microporous polymers as metal-free ORR

3447 catalysts. J Mater Chem A. 2018;6:5587-91.

3448 [443] Su Y, Yao Z, Zhang F, Wang H, Mics Z, Canovas E, Bonn M, Zhuang X, Feng X.

3449 Sulfur-enriched conjugated polymer nanosheet derived sulfur and nitrogen co-doped

3450 porous carbon nanosheets as electrocatalysts for oxygen reduction reaction and zinc-air

3451 battery. Adv Funct Mater. 2016;26:5893-902.

3452 [444] Zhou B, Liu L, Cai P, Zeng G, Li X, Wen Z, Chen L. Ferrocene-based porous

3453 organic polymer derived high-performance electrocatalysts for oxygen reduction. J

3454 Mater Chem A. 2017;5:22163-9.

3455 [445] Li Q, Shao Q, Wu Q, Duan Q, Li Y, Wang H-g. In situ anchoring of metal

3456 nanoparticles in the N-doped carbon framework derived from conjugated microporous

3457 polymers towards an efficient oxygen reduction reaction. Catal Sci Technol.

3458 2018;8:3572-9.

3459 [446] Kim S-J, Mahmood J, Kim C, Han G-F, Kim S-W, Jung S-M, Zhu G, De Yoreo

3460 JJ, Kim G, Baek J-B. Defect-free encapsulation of Fe-0 in 2D fused organic networks

3461 as a durable oxygen reduction electrocatalyst. J Am Chem Soc. 2018;140:1737-42.

3462 [447] Yuan K, Zhuang X, Hu T, Shi L, Sfaelou S, Polnick U, Forster M, Pichler T, Riedl

3463 T, Feng X, Chen Y, Scherf U. 2D heterostructures derived from MoS2-templated,

3464 cobalt-containing conjugated microporous polymer sandwiches for the oxygen

3465 reduction reaction and electrochemical energy storage. ChemElectroChem.

3466 2017;4:709-15.

3467 [448] Bildirir H, Gregoriou VG, Avgeropoulos A, Scherfd U, Chochos CL. Porous

3468 organic polymers as emerging new materials for organic photovoltaic applications:

3469 current status and future challenges. Mate Horiz. 2017;4:546-56.

3470 [449] An Y, Liao X, Chen L, Yin J, Ai Q, Xie Q, Huang B, Liu F, Jen AKY, Chen Y.

3471 Nonhalogen solvent-processed asymmetric wide-bandgap polymers for nonfullerene

3472 organic solar cells with over 10% efficiency. Adv Funct Mater. 2018;28:1706517/1-9.

3473 [450] Saliba M, Matsui T, Seo J-Y, Domanski K, Correa-Baena J-P, Nazeeruddin MK,

3474 Zakeeruddin SM, Tress W, Abate A, Hagfeldt A, Grätzel M. Cesium-containing triple

3475 cation perovskite solar cells: improved stability, reproducibility and high efficiency.

3476 Energy Environ Sci. 2016;9:1989-97.

3477 [451] Chen W, Zhang J, Xu G, Xue R, Li Y, Zhou Y, Hou J, Li Y. A semitransparent

3478 inorganic perovskite film for overcoming ultraviolet light instability of organic solar

3479 cells and achieving 14.03% efficiency. Adv Mater. 2018;30:1800855/1-10.

3480 [452] Wang Y, Wu T, Barbaud J, Kong W, Cui D, Chen H, Yang X, Han L. Stabilizing

3481 heterostructures of soft perovskite semiconductors. Science. 2019;365:687-91.

3482 [453] Tan Za, Li S, Wang F, Qian D, Lin J, Hou J, Li Y. High performance polymer

3483 solar cells with as-prepared zirconium acetylacetonate film as cathode buffer layer. Sci

3484 Rep. 2014;4:4691/1-9.

3485 [454] Egger DA, Edri E, Cahen D, Hodes G. Perovskite solar cells: Do we know what

3486 we do not know? J Phys Chem Lett. 2015;6:279-82.

3487 [455] Jeng J-Y, Chiang Y-F, Lee M-H, Peng S-R, Guo T-F, Chen P, Wen T-C.

3488 CH3NH3PbI3 perovskite/fullerene planar-heterojunction hybrid solar cells. Adv Mater.

3489   2013;25:3727-32.

3490   [456] Li X, Choy WCH, Xie F, Zhang S, Hou J. Room-temperature solution-processed

3491   molybdenum oxide as a hole transport layer with Ag nanoparticles for highly efficient

3492   inverted organic solar cells. J Mater Chem A. 2013;1:6614-21.

3493   [457] Tan Za, Qian D, Zhang W, Li L, Ding Y, Xu Q, Wang F, Li Y. Efficient and stable

3494   polymer solar cells with solution-processed molybdenum oxide interfacial layer. J

3495   Mater Chem A. 2013;1:657-64.

3496   [458] Park JH, Seo J, Park S, Shin SS, Kim YC, Jeon NJ, Shin H-W, Ahn TK, Noh JH,

3497   Yoon SC, Hwang CS, Seok SI. Efficient CH3NH3PbI3 perovskite solar cells employing

3498   nanostructured p-type nio electrode formed by a pulsed laser deposition. Adv Mater.

3499   2015;27:4013-9.

3500   [459] Zuo C, Ding L. Solution-processed Cu2O and CuO as hole transport materials

3501   for efficient perovskite solar cells. Small. 2015;11:5528-32.

3502   [460] Chen W-Y, Deng L-L, Dai S-M, Wang X, Tian C-B, Zhan X-X, Xie S-Y, Huang

3503   R-B, Zheng L-S. Low-cost solution-processed copper iodide as an alternative to

3504   PEDOT:PSS hole transport layer for efficient and stable inverted planar heterojunction

3505   perovskite solar cells. J Mater Chem A. 2015;3:19353-9.

3506   [461] Fang Z, Chellappan V, Webster RD, Ke L, Zhang T, Liu B, Lai Y-H. Bridged-

3507   triarylamine starburst oligomers as hole transporting materials for electroluminescent

3508   devices. J Mater Chem. 2012;22:15397-404.

3509   [462] Henson ZB, Zhang Y, Nguyen T-Q, Seo JH, Bazan GC. Synthesis and properties

3510   of two cationic narrow band gap conjugated polyelectrolytes. J Am Chem Soc.

3511 2013;135:4163-6.

3512 [463] Zhou H, Zhang Y, Mai C-K, Seifter J, Nguyen T-Q, Bazan GC, Heeger AJ.

3513 Solution-processed pH-neutral conjugated polyelectrolyte improves interfacial contact

3514 in organic solar cells. ACS Nano. 2015;9:371-7.

3515 [464] Cui Y, Jia G, Zhu J, Kang Q, Yao H, Lu L, Xu B, Hou J. The critical role of anode

3516 work function in non-fullerene organic solar cells unveiled by counterion-size-

3517 controlled self-doping conjugated polymers. Chem Mater. 2018;30:1078-84.

3518 [465] Ren S, Dawson R, Adams DJ, Cooper A. Low band-gap benzothiadiazole

3519 conjugated microporous polymers. Polym Chem. 2013;4:5585-90.

3520 [466] Vinodh R, Babu CM, Abidov A, Peng MM, Palanichamy M, Cha WS, Jang HT.

3521 Microporous spheres of tiny semiconducting graphene sheets from hypercross-linked

3522 polymers: absorption and CO2 sorption characteristics. Adv Polym Tech. 2018;37:714-

3523 23.

3524 [467] Wang Y, Zhang S, Wu J, Liu K, Li D, Meng Q, Zhu G. Electropolymerization

3525 porous aromatic framework film as a hole-transport layer for inverted perovskite solar

3526 cells with superior stability. ACS Appl Mater Inter. 2017;9:43688-95.

3527 [468] Yang S, Yang C, Zhang X, Zheng Z, Bi S, Zhang Y, Zhou H. A conjugated

3528 microporous polymer film fabricated by in situ electro-chemical deposition as a hole

3529 transporting layer in organic photovoltaics. Journal of Materials Chemistry C.

3530 2018;6:9044-8.

3531 [469] Su Y, Liu Y, Liu P, Wu D, Zhuang X, Zhang F, Feng X. Compact coupled

3532 graphene and porous polyaryltriazine-derived frameworks as high performance

3533   cathodes for lithium-ion batteries. Angew Chem Int Ed. 2015;54:1812-6.

3534   [470] Hu Z, Chen Z, Zhang K, Zheng N, Xie R, Liu X, Yang X, Huang F, Cao Y. Self-

3535   doped N-type water/alcohol soluble-conjugated polymers with tailored backbones and

3536   polar groups for highly efficient polymer solar cells. Solar RRL. 2017;1:1700055/1-12.

3537   [471] Wang ZJ, Ghasimi S, Landfester K, Zhang KAI. Photocatalytic suzuki coupling

3538   reaction using conjugated microporous polymer with immobilized palladium

3539   nanoparticles under visible light. Chem Mater. 2015;27:1921-4.

3540   [472] Wei F, Cai X, Nie J, Wang F, Lu C, Yang G, Chen Z, Ma C, Zhang Y. A 1,2,3-

3541   triazolyl based conjugated microporous polymer for sensitive detection of p-

3542   nitroaniline and Au nanoparticle immobilization. Polym Chem. 2018;9:3832-9.

3543   [473] Ayed C, Huang W, Li R, da Silva LC, Wang D, Suraeva O, Najjar W, Zhang KAI.

3544   Conjugated microporous polymers with immobilized TiO2 nanoparticles for enhanced

3545   visible light photocatalysis. Part Part Syst Char. 2018;35:1700234/1-10.

3546   [474] Yang XW, Zhuang XD, Huang YJ, Jiang JZ, Tian H, Wu DQ, Zhang F, Mai YY,

3547   Feng XL. Nitrogen-enriched hierarchically porous carbon materials fabricated by

3548   graphene aerogel templated Schiff-base chemistry for high performance

3549   electrochemical capacitors. Polym Chem. 2015;6:1088-95.

3550   [475] Zhuang X, Zhang F, Wu D, Feng X. Graphene coupled Schiff-base porous

3551   polymers: towards nitrogen-enriched porous carbon nanosheets with ultrahigh

3552   electrochemical capacity. Adv Mater. 2014;26:3081-6.

3553   [476] Katekomol P, Roeser J, Bojdys M, Weber J, Thomas A. Covalent triazine

3554   frameworks prepared from 1,3,5-tricyanobenzene. Chem Mater. 2013;25:1542-8.

3555 [477] Roberts AD, Li X, Zhang H. Porous carbon spheres and monoliths: morphology

3556 control, pore size tuning and their applications as Li-ion battery anode materials. Chem

3557 Soc Rev. 2014;43:4341-56.

3558 [478] Hao L, Ning J, Luo B, Wang B, Zhang Y, Tang Z, Yang J, Thomas A, Zhi L.

3559 Structural evolution of 2D microporous covalent triazine-based framework toward the

3560 study of high-performance supercapacitors. J Am Chem Soc. 2015;137:219-25.

3561 [479] Liu J, Yee KK, Lo KK, Zhang KY, To WP, Che CM, Xu Z. Selective Ag(I)

3562 binding, H2S sensing, and white-light emission from an easy-to-make porous

3563 conjugated polymer. J Am Chem Soc. 2014;136:2818-24.

3564 [480] Guo J, Xu Y, Jin S, Chen L, Kaji T, Honsho Y, Addicoat MA, Kim J, Saeki A,

3565 Ihee H. Conjugated organic framework with three-dimensionally ordered stable

3566 structure and delocalized π clouds. Nat Commun. 2013;4:2736/1-8.

3567 [481] Chen L, Furukawa K, Gao J, Nagai A, Nakamura T, Dong Y, Jiang D.

3568 Photoelectric covalent organic frameworks: converting open lattices into ordered

3569 donor–acceptor heterojunctions. J Am Chem Soc. 2014;136:9806-9.

3570 [482] Jin S, Supur M, Addicoat M, Furukawa K, Chen L, Nakamura T, Fukuzumi S,

3571 Irle S, Jiang D. Creation of superheterojunction polymers via direct polycondensation:

3572 Segregated and bicontinuous donor–acceptor π-columnar arrays in covalent organic

3573 frameworks for long-lived charge separation. J Am Chem Soc. 2015;137:7817-27.

3574 [483] Wang ZJ, Garth K, Ghasimi S, Landfester K, Zhang KA. Conjugated microporous

3575 poly(benzochalcogenadiazole)s for photocatalytic oxidative coupling of amines under

3576 visible light. ChemSusChem. 2015;8:3459-64.

3577   [484] Huang N, Wang P, Jiang DL. Covalent organic frameworks: a materials platform

3578   for structural and functional designs. Nat Rev Mater. 2016;1:16068/1-19.

3579   [485] Zeng Y, Zou R, Zhao Y. Covalent organic frameworks for CO2 capture. Adv

3580   Mater. 2016;28:2855-73.

Figure Captions

Fig. 1. Historical development of microporous organic polymers (MOPs). Solubility film-forming PIMs. [53], Copyright 2004. Reproduced with permission from the Royal Society of Chemistry. Synthesis of crystalline COFs with exceptionally high surface areas. [54], Copyright2007, Reproduced with permission from the American Association for the Advancement of Science. CMPs which combine porosity with extended π-conjugation. [47], Copyright 2007. Reproduced with permission from the John Wiley & Sons Inc. More robust crystalline COF analogs. [55,56], Copyright 2008 and 2009. Reproduced with permission from the John Wiley & Sons Inc and American Chemical Society. Robust and highly porous aromatic frameworks. [42], Copyright 2009. Reproduced with permission from the John Wiley & Sons Inc. Metal-organic CMPs (MO-CMPs) comprising catalytic metal centers. [57], Copyright 2011. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 2. Quintessential examples of CMP materials development. A milestone in the development of CMP materials. 2007. [47], Copyright 2007. Reproduced with permission from the John Wiley & Sons Inc. 2008. [79,80], Copyright 2008. Reproduced with permission from the Royal Society of Chemistry and the American Chemical Society. 2009. [81], Copyright 2009. Reproduced with permission from the John Wiley & Sons Inc. 2010. [67,82], Copyright 2010. Reproduced with permission from the American Chemical Society. 2011. [57,83], Copyright 2011. Reproduced with permission from the John Wiley & Sons Inc and the Royal Society of Chemistry. 2012. [84,85], Copyright 2012. Reproduced with permission from the John Wiley & Sons Inc and the American Chemical Society. 2013. [86,87], Copyright 2013. Reproduced with permission from the John Wiley & Sons Inc and the Royal Society of Chemistry. 2014. [76,88], Copyright 2014. Reproduced with permission from the Royal Society of Chemistry. 2015. [89,90], Copyright 2015. Reproduced with permission from the John Wiley & Sons Inc. 2016. [91], Copyright 2016. Reproduced with permission from the American Chemical Society. 2017. [92], Copyright 2017. Reproduced with permission from the John Wiley & Sons Inc. 2018. [93], Copyright 2018. Reproduced with permission from Elsevier Science Ltd. 2019. [94], Copyright 2019. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 3. CMPs as a powerful platform for the application in clean energy.

Fig. 4. Synthesis of the triazine monomer and molecular structures of TCMP networks. [108], Copyright 2012. Reproduced with permission from the Royal Society of Chemistry.

Fig. 5. (A) Synthesis route and structure for HCMP1–HCMP5. (B) Volumetric H2 adsorption isotherms for HCMP1–HCMP5 up to 1.0 bar at 77.3 K. [112], Copyright 2012. Adapted with permission from Elsevier Science Ltd.

Fig. 6. (A) Synthetic route and representative structures of the L-PDBT, N-PDBT, L-PDBT-O, N-PDBTO. (B) Water contact angle measurements of L-PDBT, N-PDBT, L-PDBT-O, and N-PDBT-O. [114], Copyright 2018. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 7. Suzuki reaction to the networks and the diversity of the molecular structure of CMPs. [65], Copyright 2018. Reproduced with permission from Elsevier Science Ltd.

Fig. 8. Syntheses of LMOPs by Heck reaction and representative molecular structures of LMOPs. [100], Copyright 2013. Reproduced with permission from the Royal Society of Chemistry.

Fig. 9. The Yamamoto reaction to the synthesis of polymer networks 1 and 3. [107], Copyright 2010. Reproduced with permission from the American Chemical Society.

Fig. 10. (A) PTPAs synthesized by Buchwald-Hartwig coupling reaction. [128], Copyright 2010. Reproduced with permission from the Royal Society of Chemistry. (B) HCMPs synthesized by the Buchwald-Hartwig coupling reaction. [91], Copyright 2016. Reproduced with permission from the American Chemical Society.

Fig. 11. (A) Synthetic routes to monomers Cz-4, Cz-6, and Cz-7. (B) Preparation of microporous conjugated polymers CPOP-2~7. [130], Copyright 2013. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 12. Schiff-base condensation polymerization to the synthesis of KECMP-1. [102], Copyright 2016. Reproduced with permission from Elsevier Science Ltd.

Fig. 13. (A) Solvothermal synthesis and structures of Aza-CMP and TIPS-CMP. (B) Chemical structure (with twist angles) of TIPS-CMP. [104], Copyright 2017. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 14. Cyclotrimerization reaction of cyano monomer to the synthesis of CTFs. [55], Copyright 2008. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 15. (A) Post-modification of the structure of the CMPs by using –SH monomers. [165] , Copyright 2011. Reproduced with permission from the American Chemical Society. (B) Post-modification of the CMPs with amidation reaction. [166] Copyright 2013. Reproduced with permission from Elsevier Science Ltd.

Fig. 16. Schematic representation of (A) ZnP-XN$_3$-CMPs (X = 5, 25, 50, 75 and 100%) and (B) ZnP-XF-CMPs (X = 5, 25 and 50%). [167], Copyright 2017. Reproduced with permission from the Royal Society of Chemistry.

Fig. 17. Synthetic route for H-MONs using a silica template. [179], Copyright 2013.

Reproduced with permission from the American Chemical Society.

Fig. 18. (A) Random and layer-by-layer controlled synthesis of 1D CMPs. (B) Morphology characterization of the as-prepared 1D CMPs. [177], Copyright 2016. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 19. (A) Solution spray-coating. [84] , Copyright 2012. Reproduced with permission from the John Wiley & Sons Inc. (B) Layer-by-layer self-assemble. [188], Copyright 2014. Reproduced with permission from the American Chemical Society. (C) Electrochemical deposition. [189], Copyright 2015. Reproduced with permission from the John Wiley & Sons Inc. (D) Interfacial polymerization. [190], Copyright 2017. Reproduced with permission from the Royal Society of Chemistry. And (E) Surface-initiated polymerization. [191], Copyright 2018, Reproduced with permission from the Springer Nature. for the preparation of the CMP films.

Fig. 20. (A) Structure of thiophene-based monomers BTT and TTB. The blue arrows indicate the carbon positions for the C—C bond formation in the polymerization reaction. (B) Setup of the three-electrode electrochemical cell. (C) The pore structures of the BTT-CMP and TTB-CMP films (inset: photos of the films). [71], Copyright 2015. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 21. (A) Dimensionally controlled synthesis of BODIPY-based CMPs. (B) SEM (left) and TEM (right) images of 0D, 1D, and 2D CMP. [90], Copyright 2015. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 22. Surface modification of CMP-nanomembranes using photoinduced thiol–yne click chemistry. [202], Copyright 2016. Reproduced with permission from the Royal Society of Chemistry.

Fig. 23. (A) Synthesis of the amorphous ethynyl-linked phthalocyanine conjugated polymer (MP_C-CP) films. (B) The four kinds of isomers (with D_{4h}, D_{2h}, C_{2v} and C_s symmetry) for tetra-β-substituted phthalocyanines. (C) Nine quadrilateral structure models fabricated from four phthalocyanine molecules with D_{4h} or D_{2h} symmetry. (D) Schematic of the Zn–air battery. (E) Photographs of a LED light (≈ 2 V) powered by two zinc–air batteries with a mixture of the films and RuO as the cathode in series. [208], Copyright 2019. Reproduced with permission from the Royal Society of Chemistry.

Fig. 24. (A) The optimized structure of the Fe-CMP unit cell; The HOMO and LUMO of the Fe-CMP with an isosurface of 0.03 e $Å^{-3}$. (B) The overall pathway of CO_2 reduction and the activation barrier of each basic step. [217], Copyright 2018. Reproduced with permission from the Owner Societies.

Fig. 25. (A) Top and side views of the optimized structures of aza-CMPN with the different

number of layers. (B) Top and side view of the optimized structure of bulk aza-CMP. (C) Each basic thermodynamic step involved in OER. (D) Proposed photocatalytic pathway of the OER on the active site "4". [222], Copyright 2017. Reproduced with permission from the Royal Society of Chemistry.

Fig. 26. (A) Calculated band structures for PTEPB and PTEB from Γ (0.0, 0.0, 0.0) to M (0.0, 0.5, 0.0) and K (0.333, 0.667, 0.0) k-point in the first Brillouin zone along with the calculated density of states (DOS). (B) The top and side views of charge distribution of VBM and CBM at Γ(0.0, 0.0, 0.0) k-point of PTEPB and PTEB. [92], Copyright 2017. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 27. (A) The theoretical technique for the formation of amorphous porous organic materials. [223], Copyright 2016. Reproduced with permission from the American Chemical Society. The route was adapted from Trewin et al. [224-226]. (B) Cross-linking exercise of dichloroxylene starting from (top) recognition of closest reactive pair of atoms (here a Cl atom and an H atom) followed by (middle) development of a bond linking the cross-linking sites corresponding to the closest pair of reactive atoms whereupon the reactive pair of atoms is removed and eventually ending with (below) equilibration. Carbon, chlorine, and hydrogen atoms are colored gray, green, and white, respectively. [227], Copyright 2011. Reproduced with permission from the American Chemical Society.

Fig. 28. (A) Computed model structure for TPE-CMP at a density of 0.798 g cm^{-3}. (B) Pore architecture in the structural model. (C) Optimized geometry of CO_2 in TPE-CMP. (D) Comparison of the adsorption isotherms at 195 K between the experiment (violet line) and that calculated from GCMC simulations (red squares). [228], Copyright 2014. Reproduced with permission from the American Chemical Society.

Fig. 29. (A-F) Synthetic route of the conjugated microporous polymer PTAT. (G) Hydrogen adsorption and desorption isotherms of the Li$^+$–PTAT and PTAT at 77 K; (H) The hydrogen uptake capacities of reported lithium-doped MOF [251], and CMP [242], PTAT and Li$^+$–PTAT; (I) Hydrogen adsorption and desorption isotherms of the Li$^+$–PTAT and PTAT at 273 K. [242], Copyright 2019. Reproduced with permission from the Royal Society of Chemistry.

Fig. 30. (A) molecular structure of PyDOBT-1; (B) Hydrogen generation of the polymers under visible light. [283], Copyright 2018. Reproduced with permission from the American Chemical Society.

Fig. 31. (A) The preparation route of F$_x$CMPs. (B) F$_x$CMPs with adjustable bandgap photocatalytic water splitting for hydrogen production. (C) Hydrogen evolution rate of F$_x$CMPs. [284], Copyright 2019. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 32. (A) Synthesis route of the PyPOP-Pt@G, C (Orange, Teal in Graphene Sheet), N (blue), Br (Break Red), Cl (Yellow), Pt (Green), H (White). (B) The first few cyclic voltammetry (CV) scans for a fresh electrode of the PyPOP-Pt@G on a glassy carbon electrode (GCE) (left); The CVs for GCE casted with the PyPOP-Pt@G with scan rate 100 mV/s (middle); Linear sweep voltammetry (LSV) for GCE casted with PyPOP-Pt@G with scan rate 10 mV/s with inset (right). [291], Copyright 2017. Reproduced with permission from the American Chemical Society.

Fig. 33. (A) Synthesis route of CoNOCs. (B) Polarization curves and corresponding Tafel plots obtained in 0.5 m H_2SO_4, CV curves of CoNOC-900, capacitive current density as a function of scan rate, Nyquist plots, and durability. [300], Copyright 2018. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 34. (A) The functionalized route to polycarbazole networks (PCZNs); (B) CO2 adsorption isotherms of PCZNs at 273 K, and CO_2 and N_2 adsorption isotherms measured at 298 K. [126], Copyright 2017. Reproduced with permission from the Royal Society of Chemistry.

Fig. 35. (A) Metal-catalyzed reactions for P2, P3, and P4, and molecular structure of P1, P2, P3, and P4. (B) The CO_2 adsorption capacity of P1, P2, P3, and P4 at 273 K. [327], Copyright 2017. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 36. (A) The schematic of the electrochemical device for the gas-phase CO_2 reduction, and (B) Gas diffusion membrane (GDM) assembly. [120], Copyright 2015. Reproduced with permission from Springer Nature.

Fig. 37. (A) Schematic representation of the synthesis of hexaazatrinaphthalene CMP (HATN-CMP) and the elementary pore structure. (B) The photos of HATN-CMP electrodes and lithium batteries thus fabricated. (C) Cycle stability and (D) capacity retention ratio of HATN-CMP (filled circle) and monomer (open circle) cathode electrodes within 50 cycles under 100 mA g^{-1}. [76], Copyright 2014. Reproduced with permission from the Royal Society of Chemistry.

Fig. 38. (A) The synthetic route of PTPAn and PTTPAB samples. (B) SEM images of powder samples of PTPA and PTTPAB. (C) Cycling stability of PTTPAB and PTPAn at a current of 20mAg h^{-1} between 2.5 and 4.2 V. (D) Coulomb Efficiency of PTTPAB and PTPAn. (E) Rate performance of PTTPAB and PTPA polymers. [335], Copyright 2018. Reproduced with permission from Elsevier Science Ltd.

Fig. 39. (A) Synthetic routes to the polymers of PT and P33DT and their notional polymer structures (left) and SEM images (right) for PT and P33DT. (B) The rate performance at different current densities from 45 to 5000 mA g^{-1}. (C) the cyclability at 500 mA g^{-1} of PT and P33DT. (D) The schematic redox reaction mechanisms of PT (top) and P33DT (bottom). [75], Copyright 2017. Reproduced with permission from the John

Fig. 40. (A) The synthetic route of PBIM and (B) reaction mechanisms. (C) Cycle performance at a current density of 1000 mA g^{-1}. (D) The rate performance at different current densities from 0.05C to 2.5C. [337], Copyright 2018. Reproduced with permission from the Royal Society of Chemistry.

Fig. 41. (A) Schematic illustration of the reaction for the CMP nanotubes synthesis (top). Schematic illustration of the fabrication of MnO–PCNTs and MnO–CNTs (below). (B) SEM image of MnO–PCNTs (top), and SEM images of MnO–CNTs (control, below). (C) EIS of the fresh cells loaded with PCNTs, MnO–PCNTs, and MnO–CNTs. [392], Copyright 2016. Reproduced with permission from the Royal Society of Chemistry.

Fig. 42. (A) Synthetic route of ALP-8 and its redox mechanism with sodium ions. (B) Galvanostatic charge/discharge profiles of ALP-8 battery at 0.3 C, (C) cycle stability and Coulombic efficiency up to 150 cycles at 0.3 C, and (D) rate capability at different current densities. [344], Copyright 2019. Reproduced with permission from the American Chemical Society.

Fig. 43. (A) Notional polymer structures of the Bz-containing CMPs (top) and the BT-containing CMPs (below). (B) Rate performance of PyBT at a current density from 30 to 500 mA g^{-1}. (C) Cycling stability and Coulombic efficiency of PyBT at 50 mA g^{-1}. (D) Proposed K storage mechanism. (E) Charge/discharge curves of the first cycle at 30 mA g^{-1} for PyBT. (F) Ex situ FT-IR spectra of a PyBT-based battery recorded at different states. [345], Copyright 2019. Reproduced with permission from the American Chemical Society.

Fig. 44. (A) Synthetic schemes for H-CMP and H-CMP-BPPB. (B) SEM images and TEM images of H-CMP and H-CMP-BPPB. (C) Cycling performance of symmetric coin cell type pseudocapacitors (inset) of H-CMP-BPPB (current densities: 1 and 6 A g^{-1}). (D) Nyquist plots (left) and TEM images (right) of H-CMP-BPPB before and after 10000 cycles. [418], Copyright 2018. Reproduced with permission from the Royal Society of Chemistry.

Fig. 45. (A) Synthetic route of the PAQs. (B-D) Proposed redox reactions, i.e., charge/discharge mechanism for PAQTA. [412], Copyright 2018. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 46. (A) Synthesis route and the three-dimensional view of TAT-CMP-1 and TAT-CMP-2 in an amorphous periodic cell (grey: carbon, white: hydrogen, blue: nitrogen, red: oxygen and n-hexyl groups (R) are omitted for clarity). Galvanostatic charge-discharge curves of (B) TAT-CMP-1 and (C) TAT-CMP-2 at different current densities, and (D) cycling number for TAT-CMP-1 and TAT-CMP-2. [416], Copyright 2017. Reproduced with permission from the Royal Society of Chemistry.

Fig. 47. (A) Preparation of graphene-based conjugated microporous polymer sandwiches and related nitrogen-doped microporous carbon nanosheets. (i) Sodium dodecylbenzenesulfonate, 4-iodophenyl diazonium salt, 0 ℃ (2 h) to room temperature (RT) (4 h); (ii) building blocks: tris(4-ethynylphenyl)amine and 2,5-dibromopyridine, or 2,5-dibromopyrazine, or 2,4,6-trichloro-1,3,5-triazine, argon, Pd(PPh₃)₄, CuI, Et₃N, DMF, 120 ℃, 3 days; (iii) argon, RT to 800 ℃, 10 ℃ min⁻¹, 2h. (B) SEM (left), and AFM (right, inset: thickness analyses along the marked line) of GMP2N. (C) CV and (D) GCD curves of three GMP2NC-based supercapacitor devices connected in series. [433], Copyright 2017. Reproduced with permission from the Royal Society of Chemistry and the Chinese Chemical Society.

Fig. 48. (A) Synthetic scheme towards the fabrication of two redox-active and semi-conducting CMPs. (B) Cyclic voltammetric curves for TPA-BP-1 under O₂ saturated (blue) and N₂ saturated (red), TPA-TPE-2 under O₂ saturated (red) and N₂ saturated (blue) (left); Linear sweep voltammetric curves observed under different rotation speeds of glassy carbon electrode for TPABP-1 and TPA-TPE-2 (middle); Chronoamperometric study for TPA-BP-1 and TPA-TPE-2 (right). [442], Copyright 2018. Reproduced with permission from the Royal Society of Chemistry.

Fig. 49. (A) Schematic Representation Showing in Situ Stabilization of Au and Co NPs in the CMP Matrix. (B) TEM image of Au NPs stabilized in the matrix of TPA−PDI. (C) HRTEM image of Au@TPA−PDI showing lattice fringes. (D) TEM image of Au NPs stabilized in the matrix of TPA−PDI. (E) HRTEM image of Co@TPA−PDI showing lattice fringes. [212], Copyright 2019. Reproduced with permission from the American Chemical Society.

Fig. 50. (A) Preparation of GMPs and related graphene-based microporous carbons (GMCs). Graphene-based 2D porous carbons (GMCs) and their ORR performances: (B) TEM image of GMC-S; (C) CV curves of GMCs in N₂-saturated (dashed line) and O₂-saturated (solid line) 0.1m KOH at a scan rate of 50 mV s⁻¹; (D) galvanostatic charge/discharge curves of MC-S and GMC-S at a current density of 0.1 Ag⁻¹. [430], Copyright 2013. Reproduced with permission from the John Wiley & Sons Inc.

Fig. 51. (A) Schematic representation of the device structure and Structural formula of PAF-86. (B) J−V curve of the PAF film based PSC, and (C) IPCE spectra and integral photocurrent of the PAF film based PSC. [467], Copyright 2017. Reproduced with permission from American Chemical Society.

Fig. 52. (A) Energy alignment of the CMP film and other materials (top), and Device configuration of organic solar cells with the CMP film as a hole transporting layer (below). (B) KPFM images of PEDOT:PSS and various CMP films captured by atomic force microscopy in the Kelvin probe mode: WFs of PEDOT:PSS and CMP films, and roughnesses of PEDOT:PSS and CMP films. (C-E) J–V characteristics of devices under 1 sun irradiation (100 mW cm⁻²) based on CMP films prepared under

different CV deposition conditions: (C) J–V curves and (D) EQE data of PEDOT:PSS-
and CMP-devices, and (E) Irradiation intensity-dependent Jsc of PEDOT:PSS and
CMP containing devices. [468], Copyright 2018. Reproduced with permission from
the Royal Society of Chemistry.

Fig. 1.

Fig. 2.
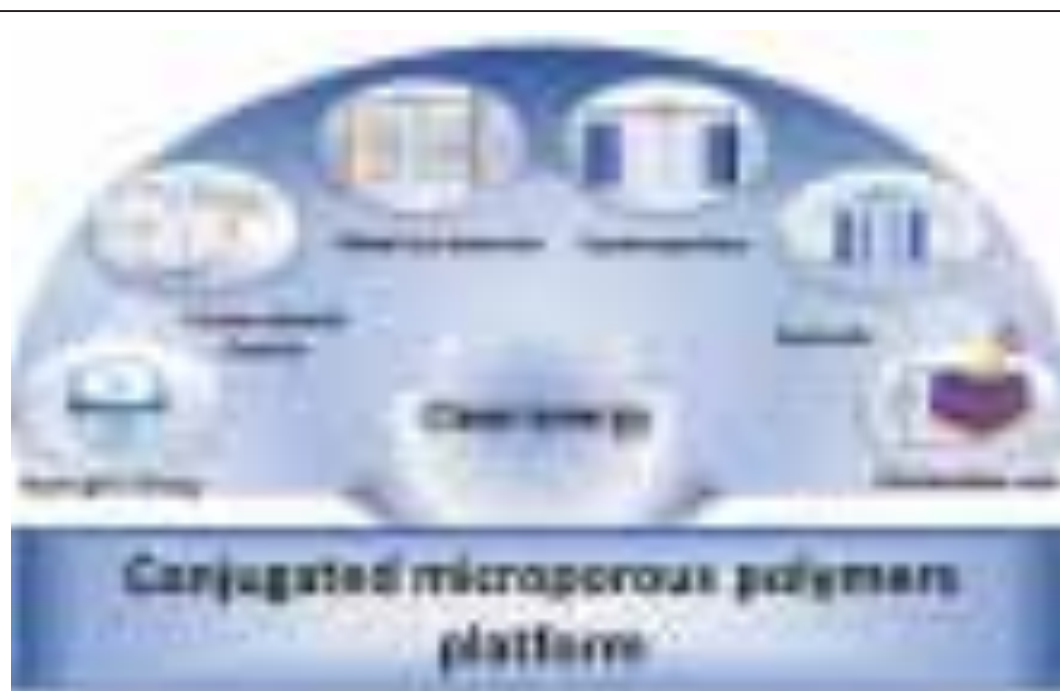
Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.
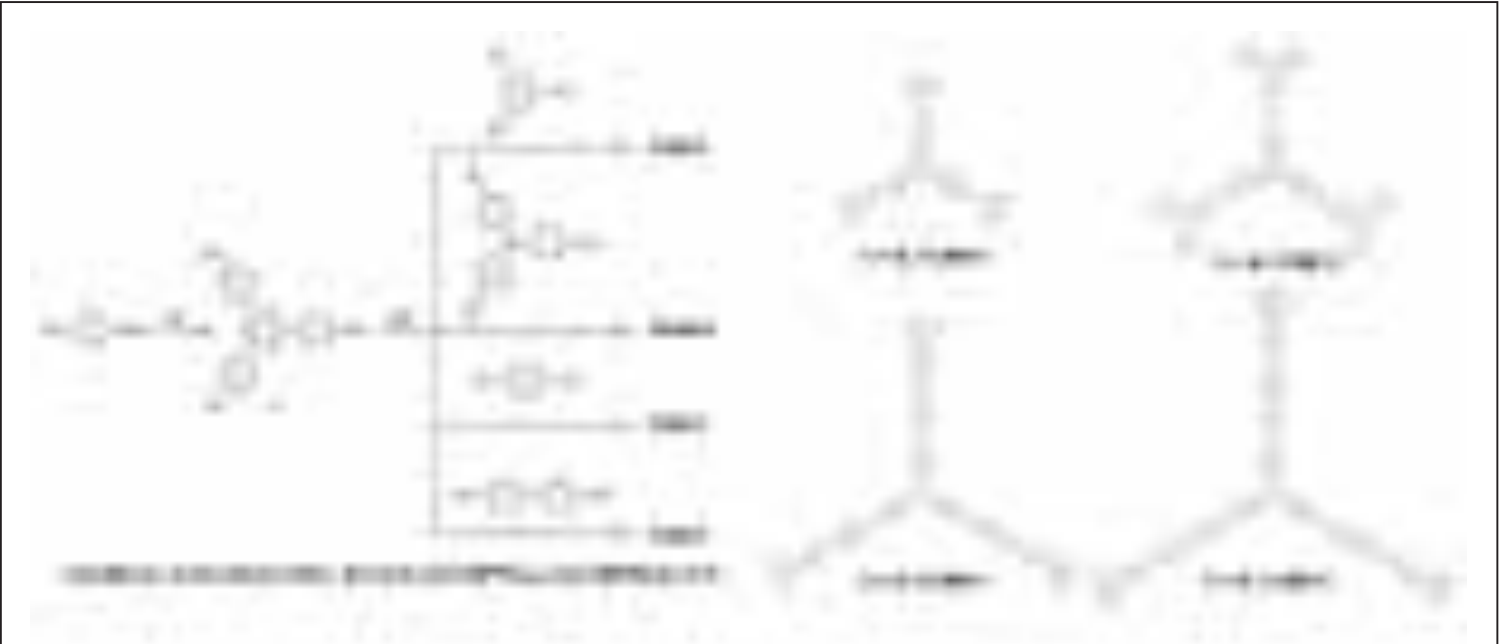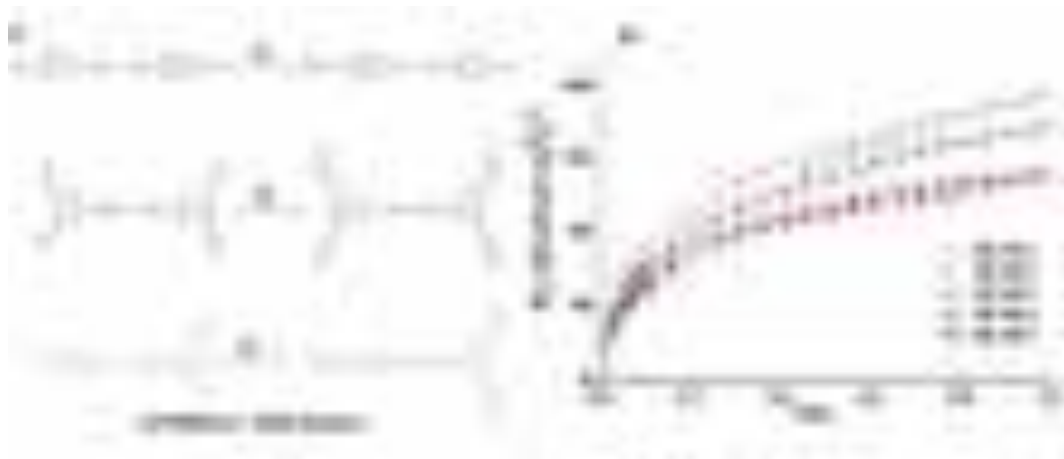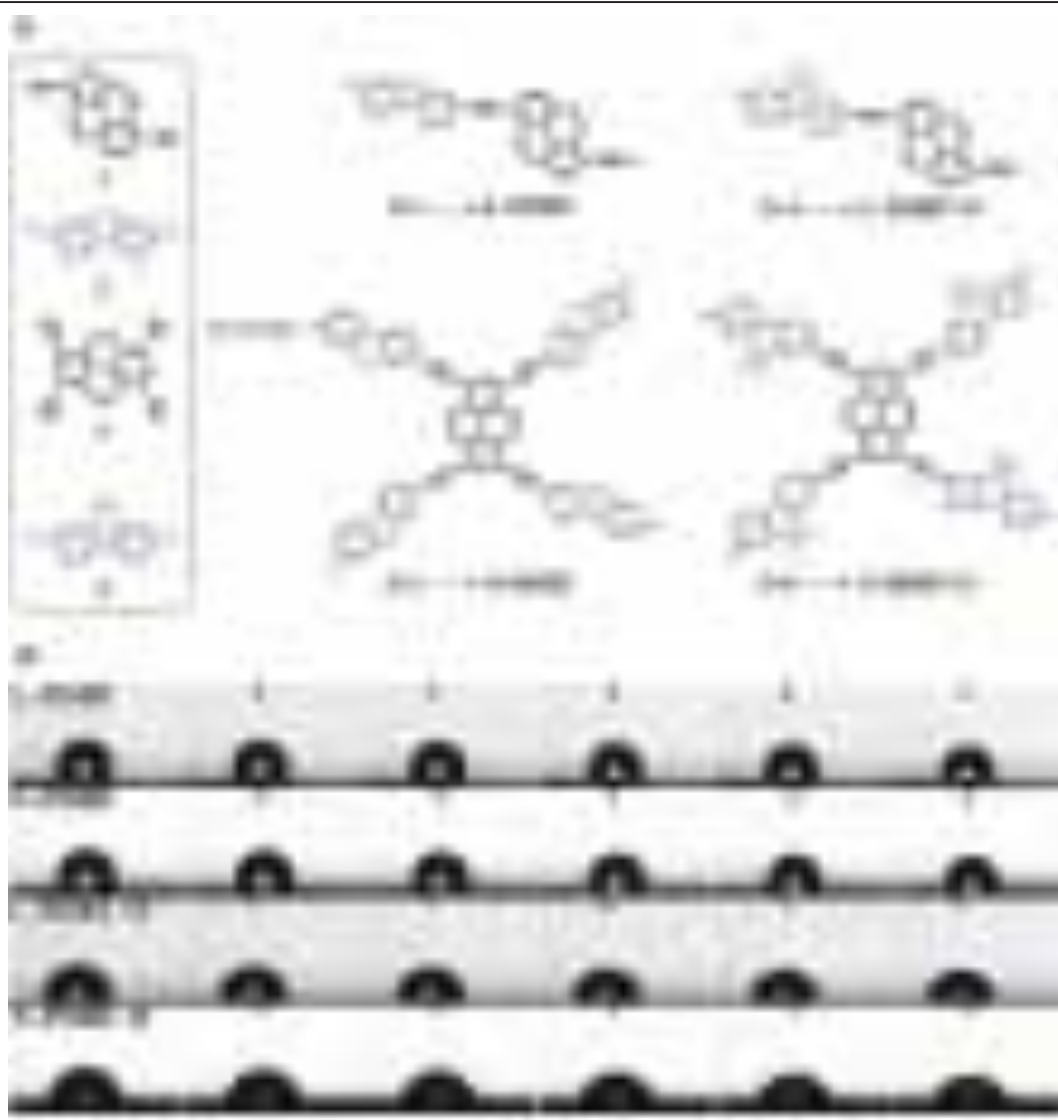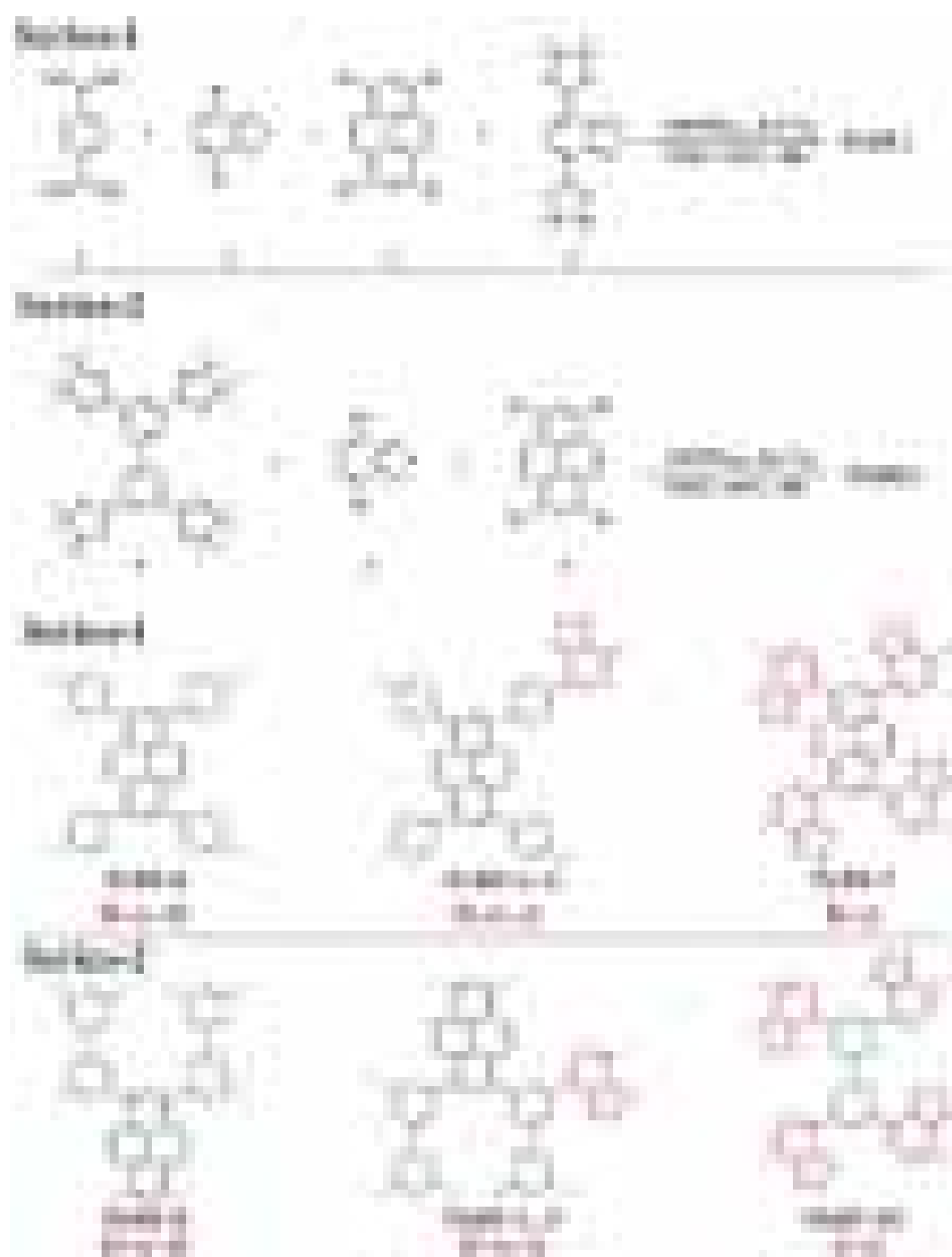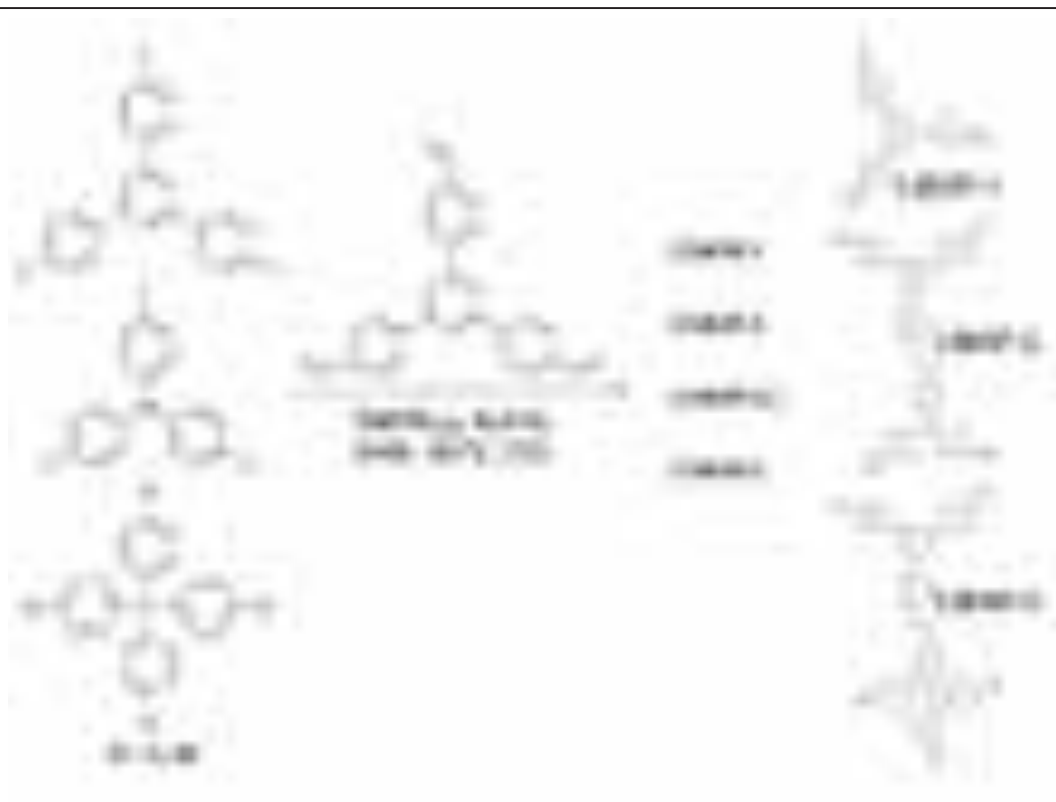
Fig. 8.
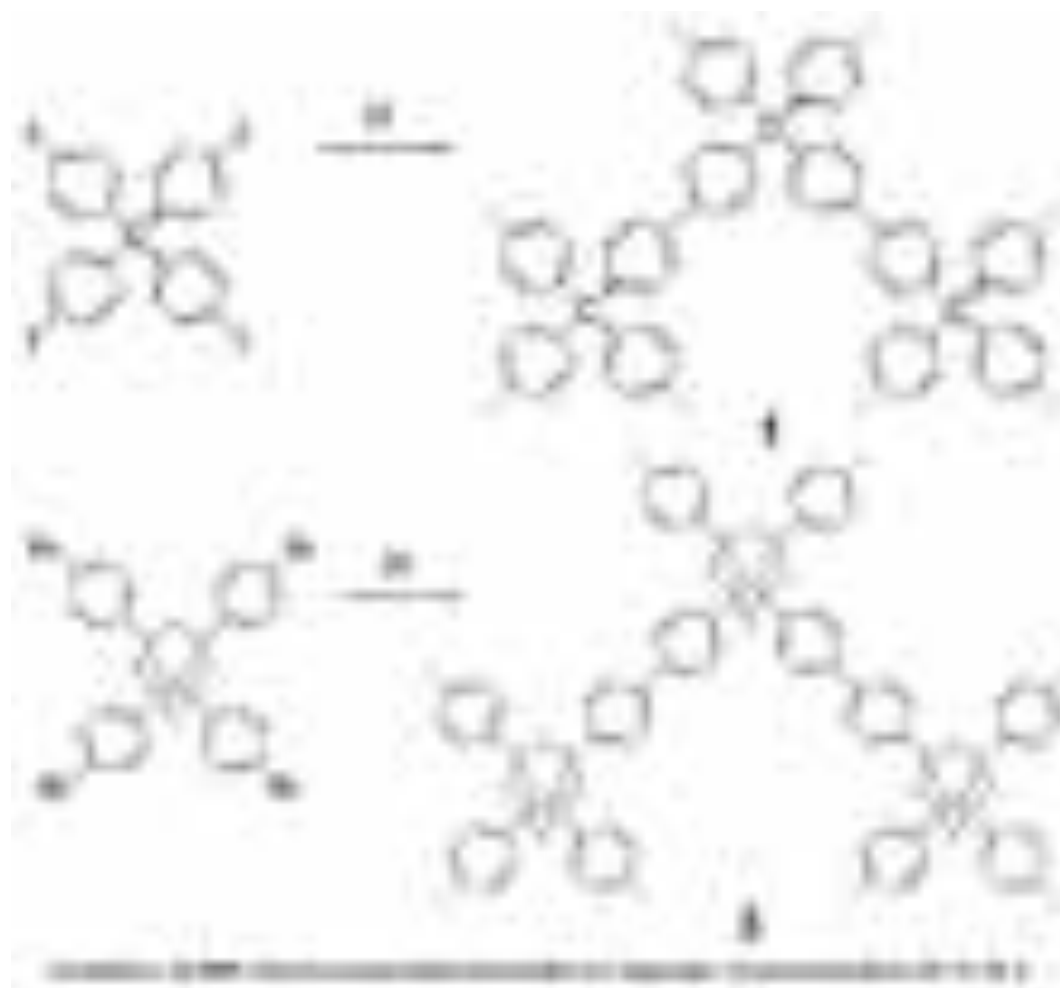
Fig. 9.
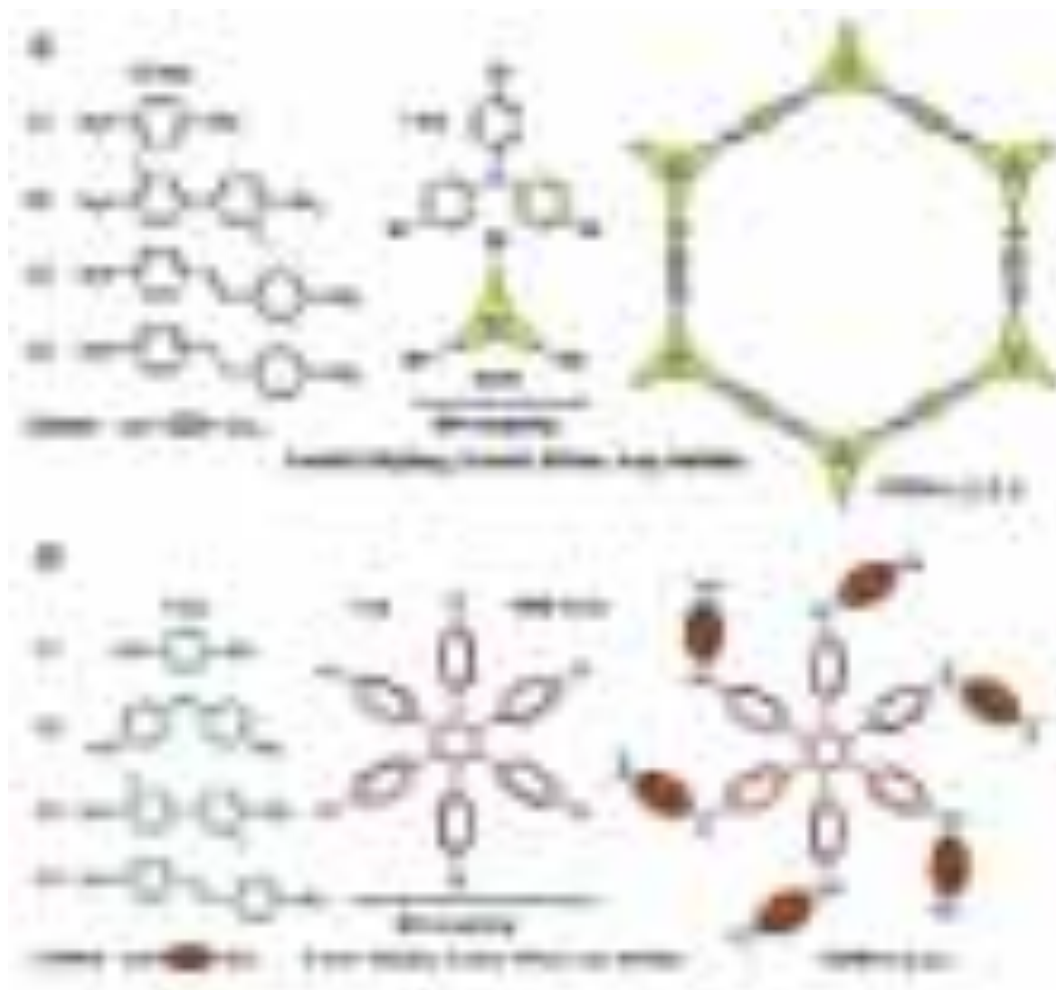
Fig. 10.
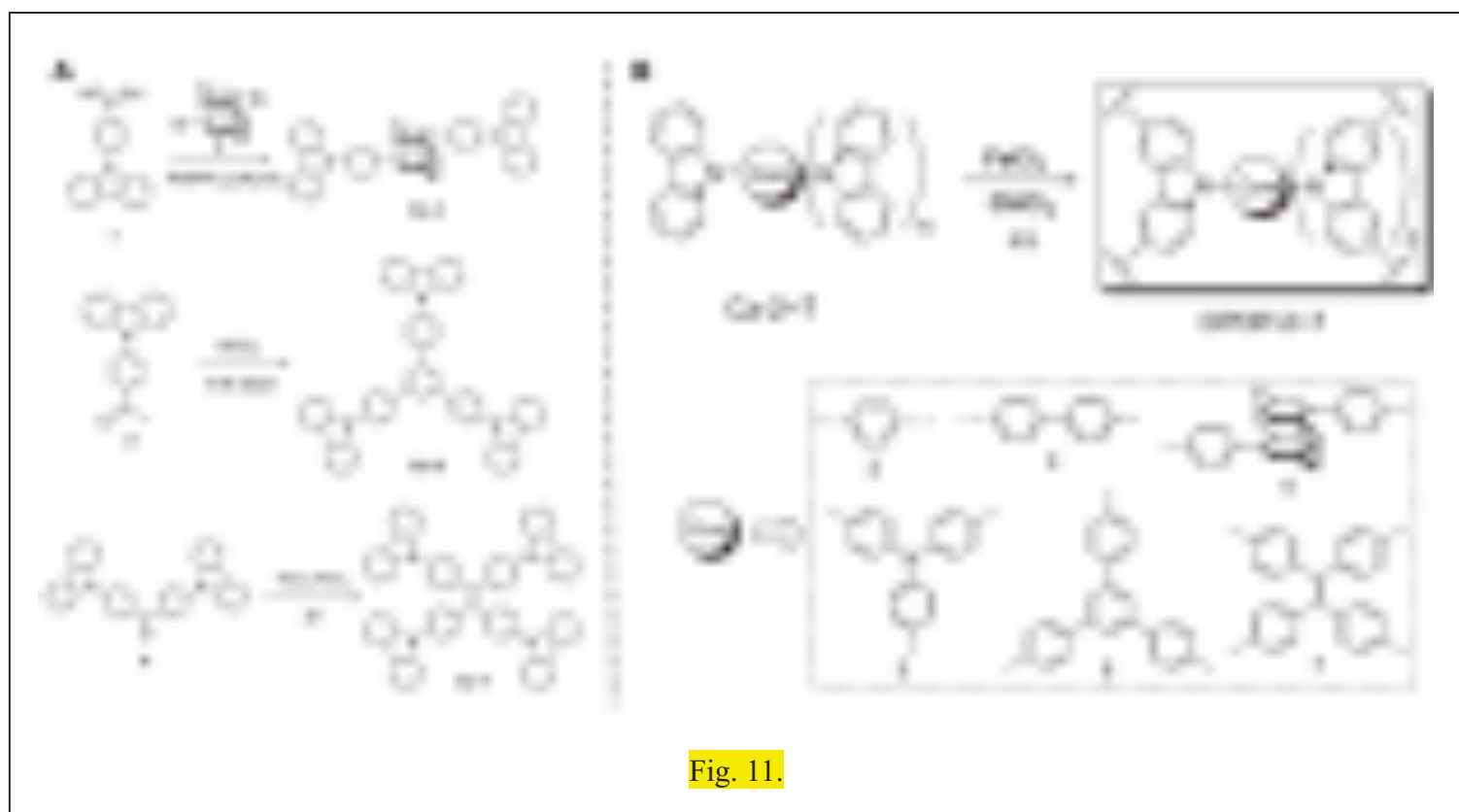
Fig. 11.

Fig. 12.
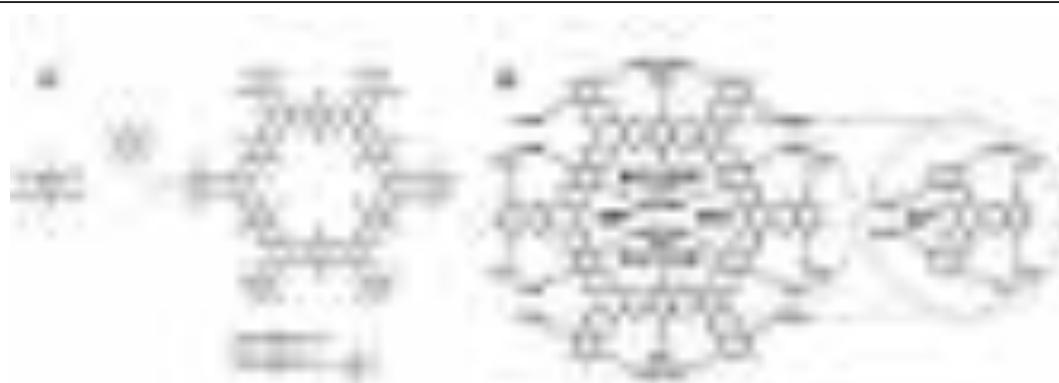
Fig. 13.

Fig. 14.
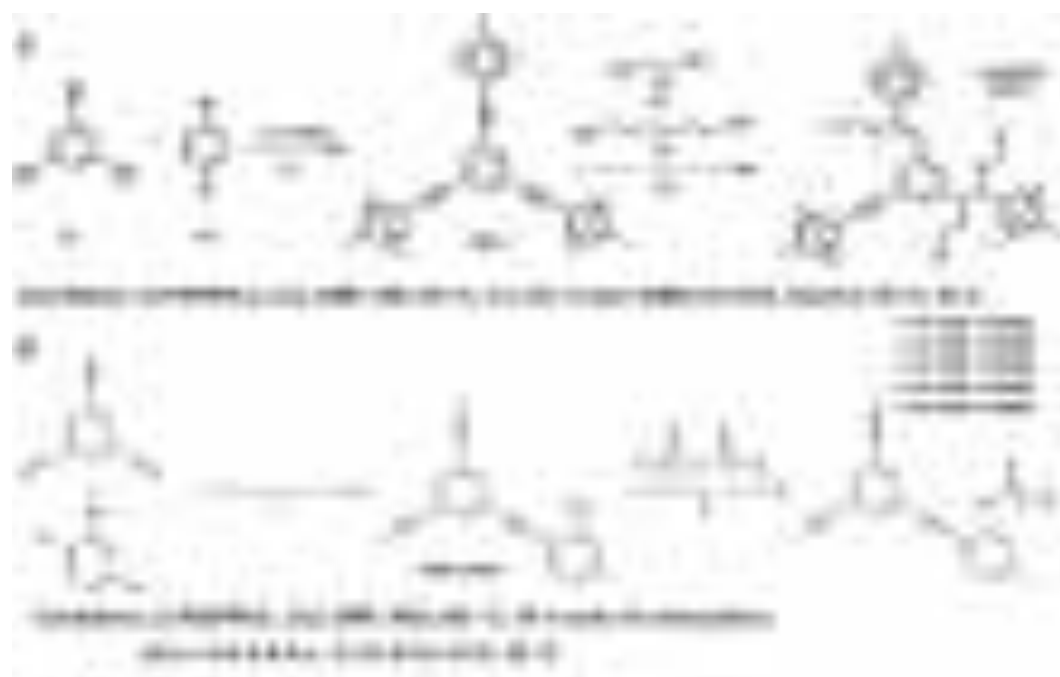
Fig. 15.

Fig. 16.

Fig. 17.
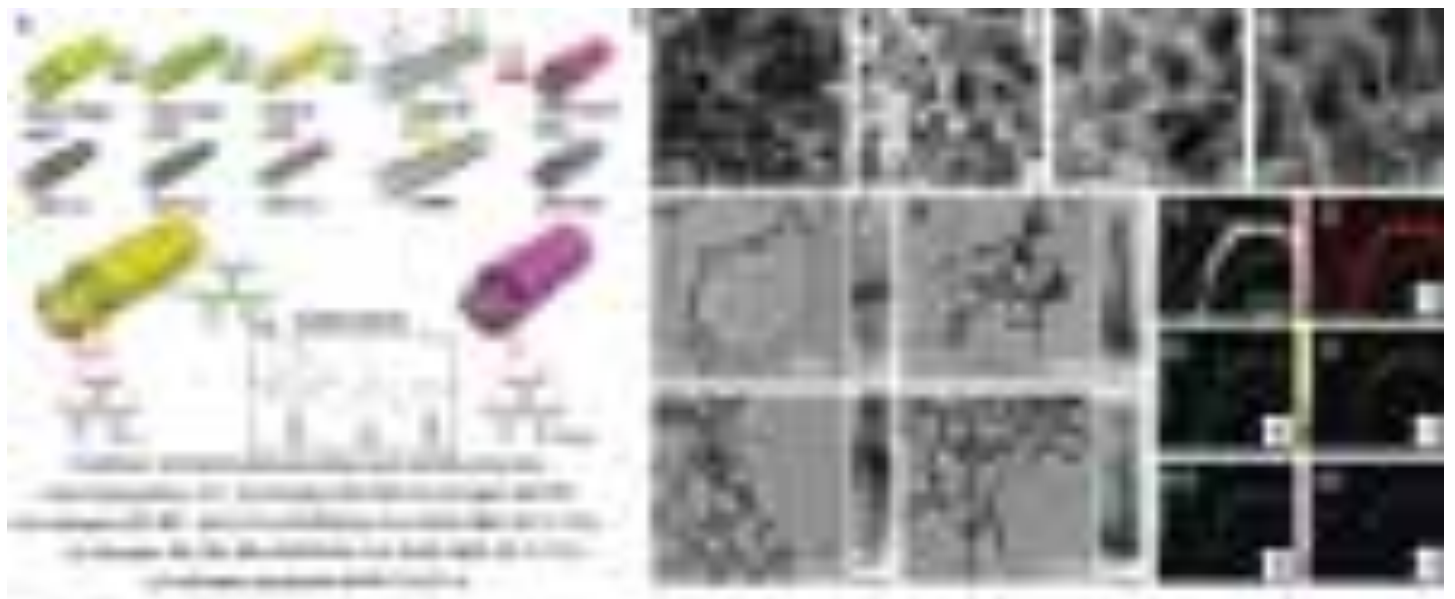
Fig. 18.
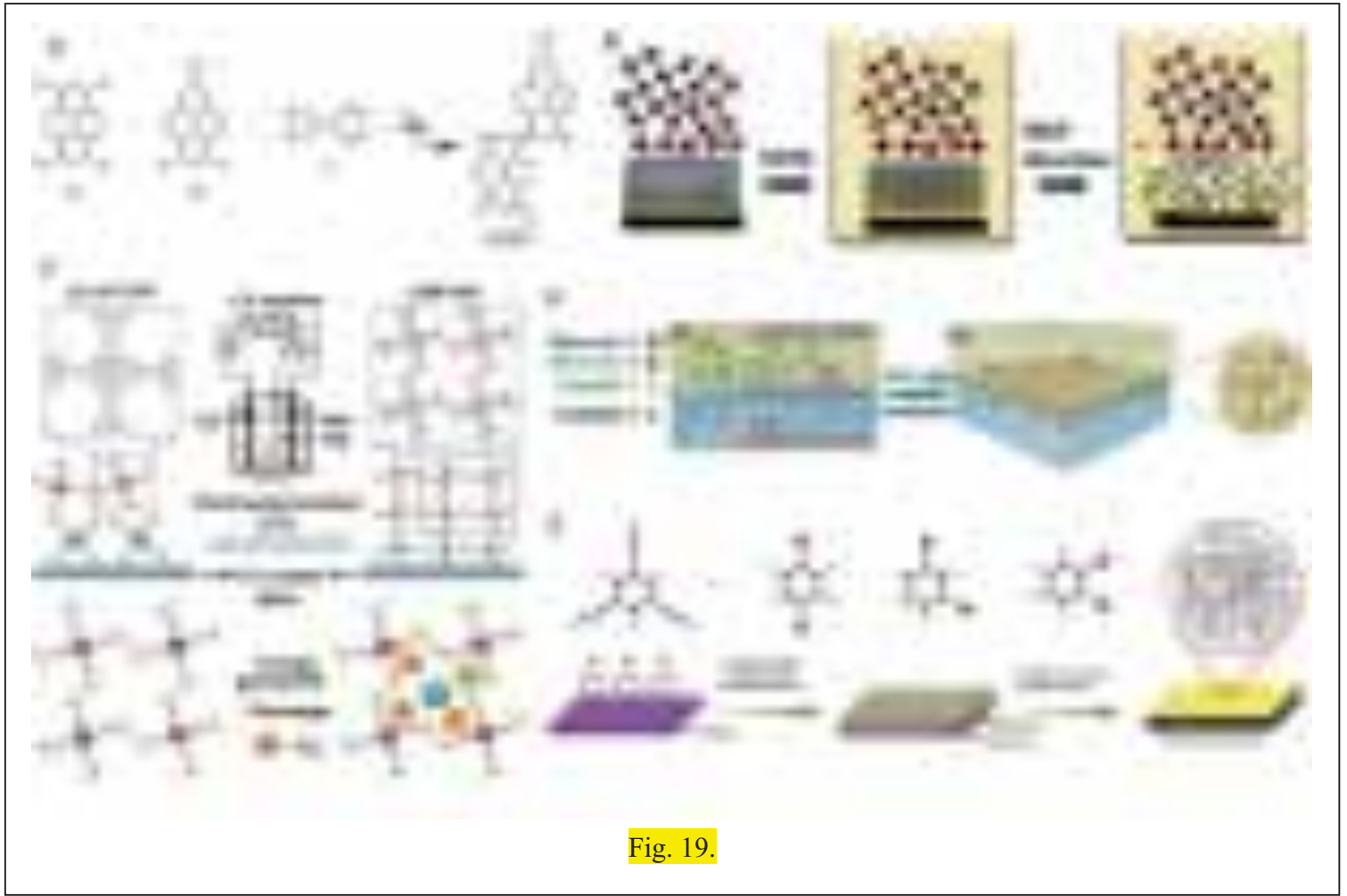
Fig. 19.

Fig. 20.
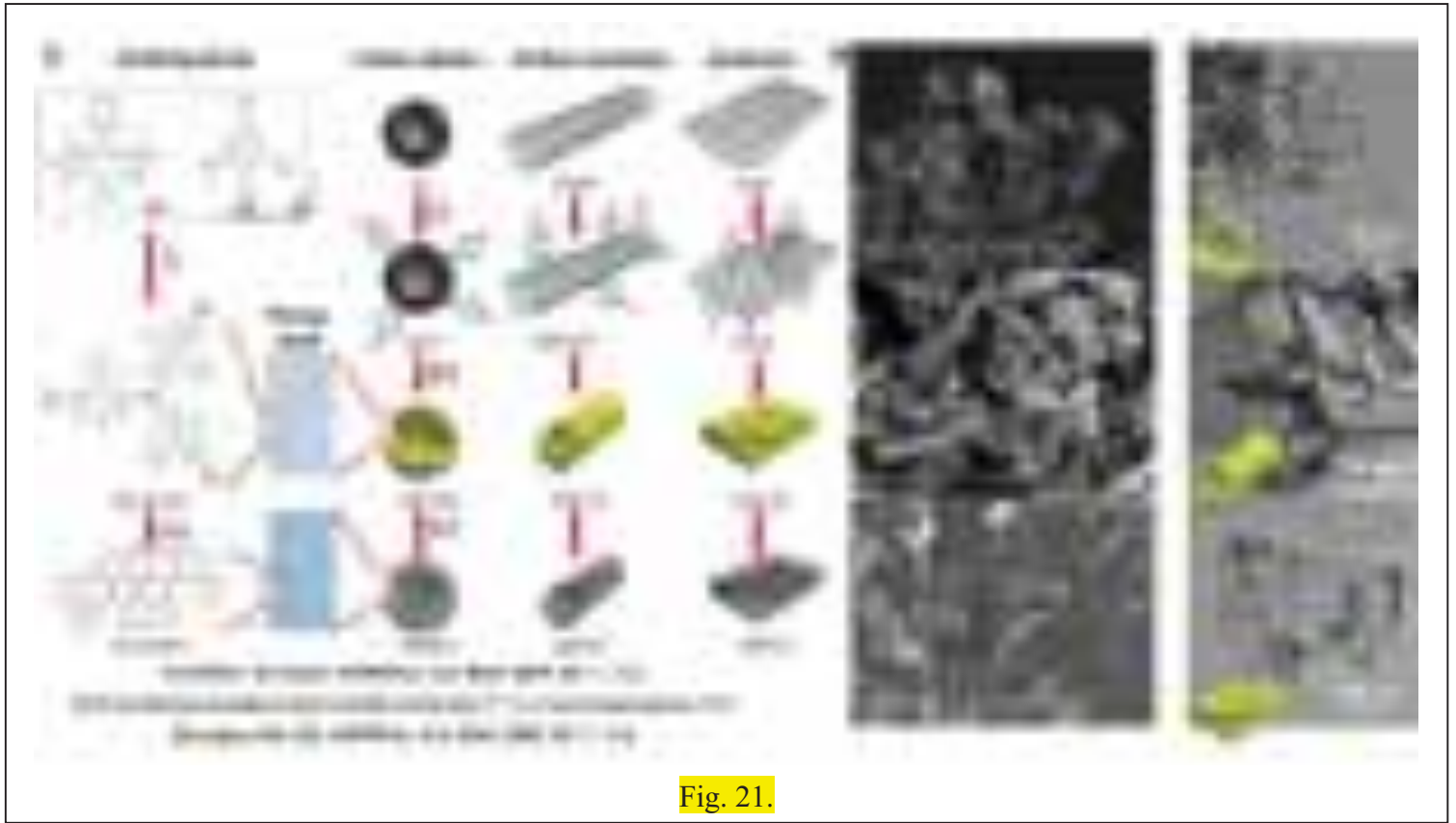
Fig. 21.

Fig. 22.
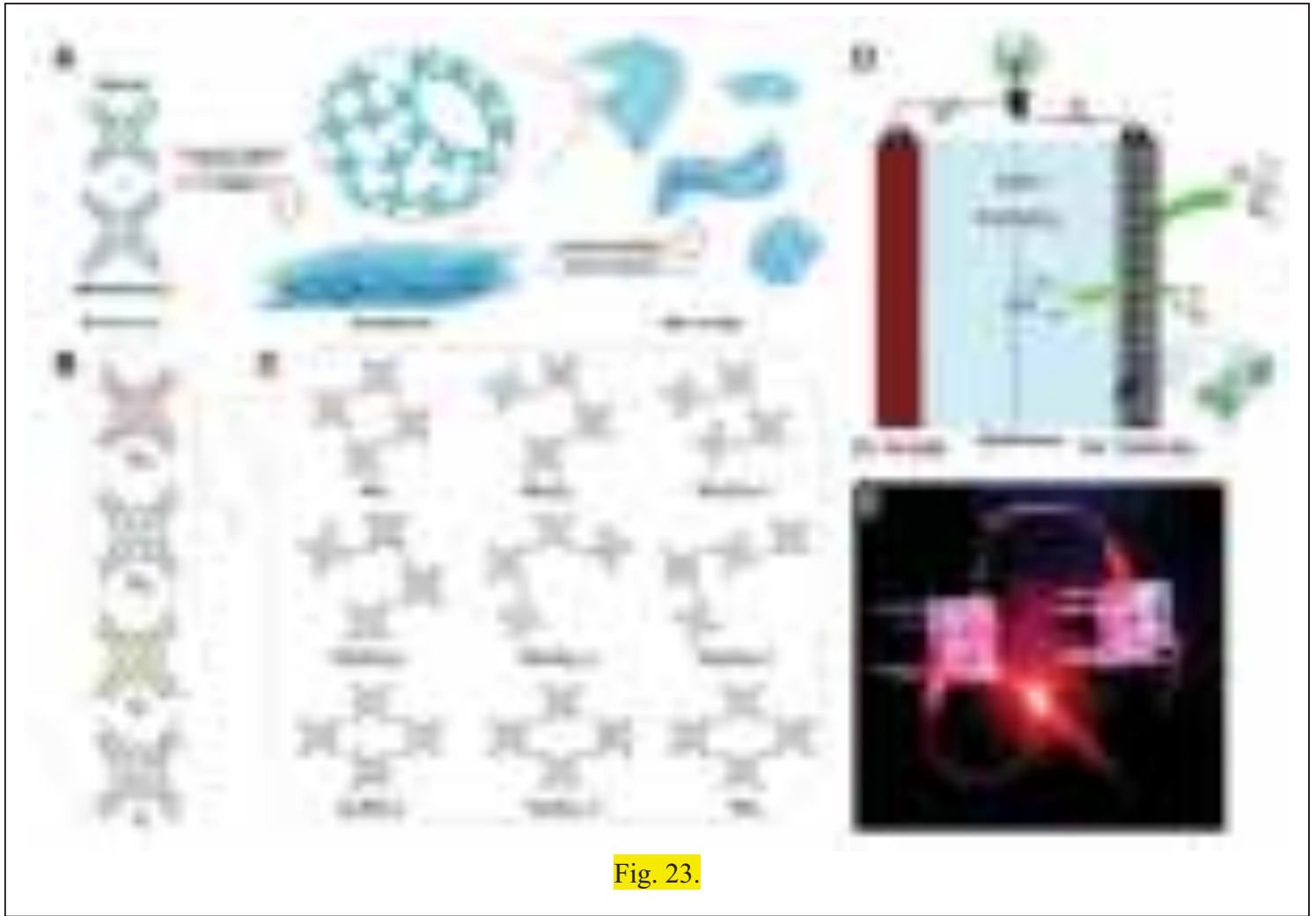
Fig. 23.
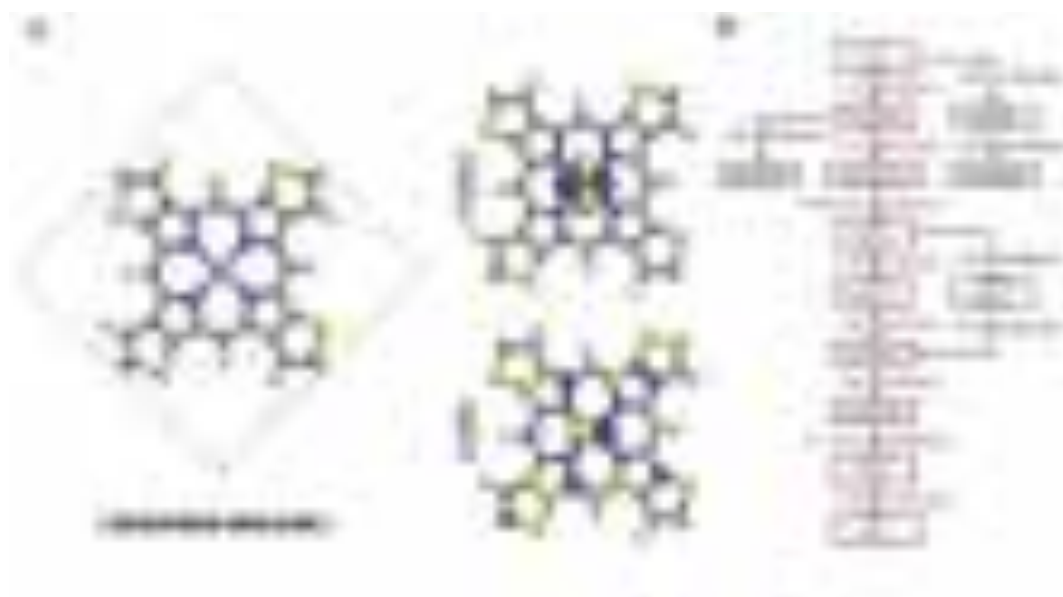
Fig. 24.
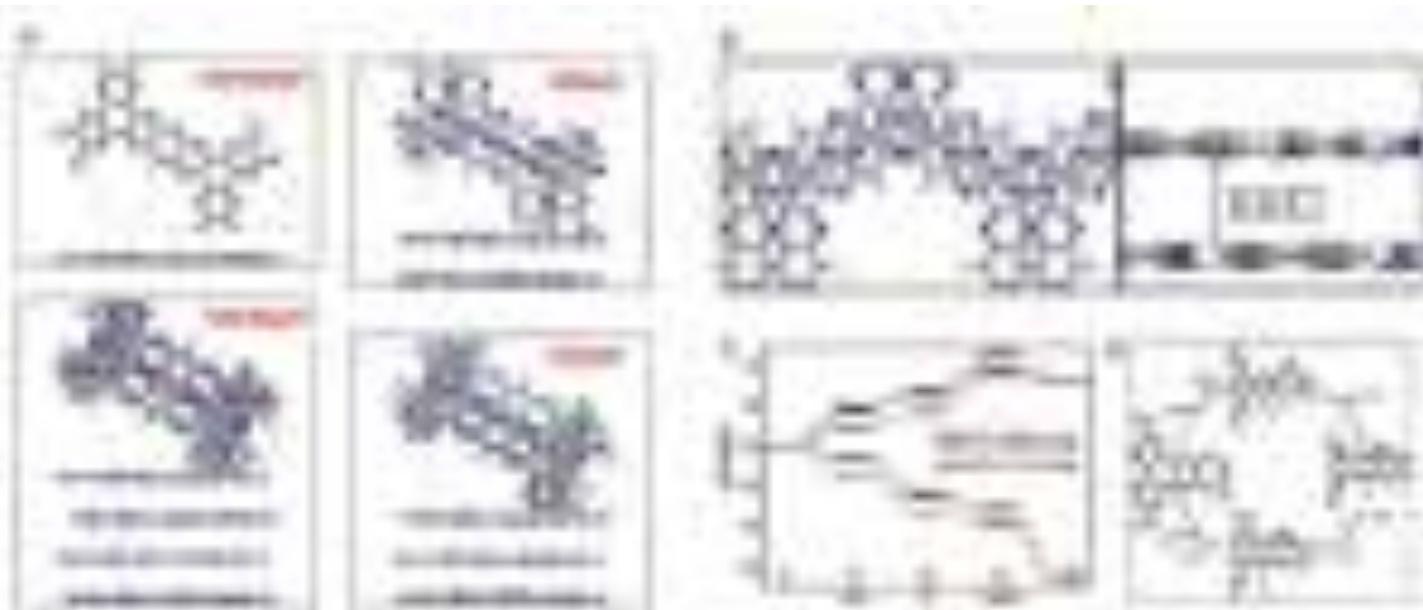
Fig. 25.
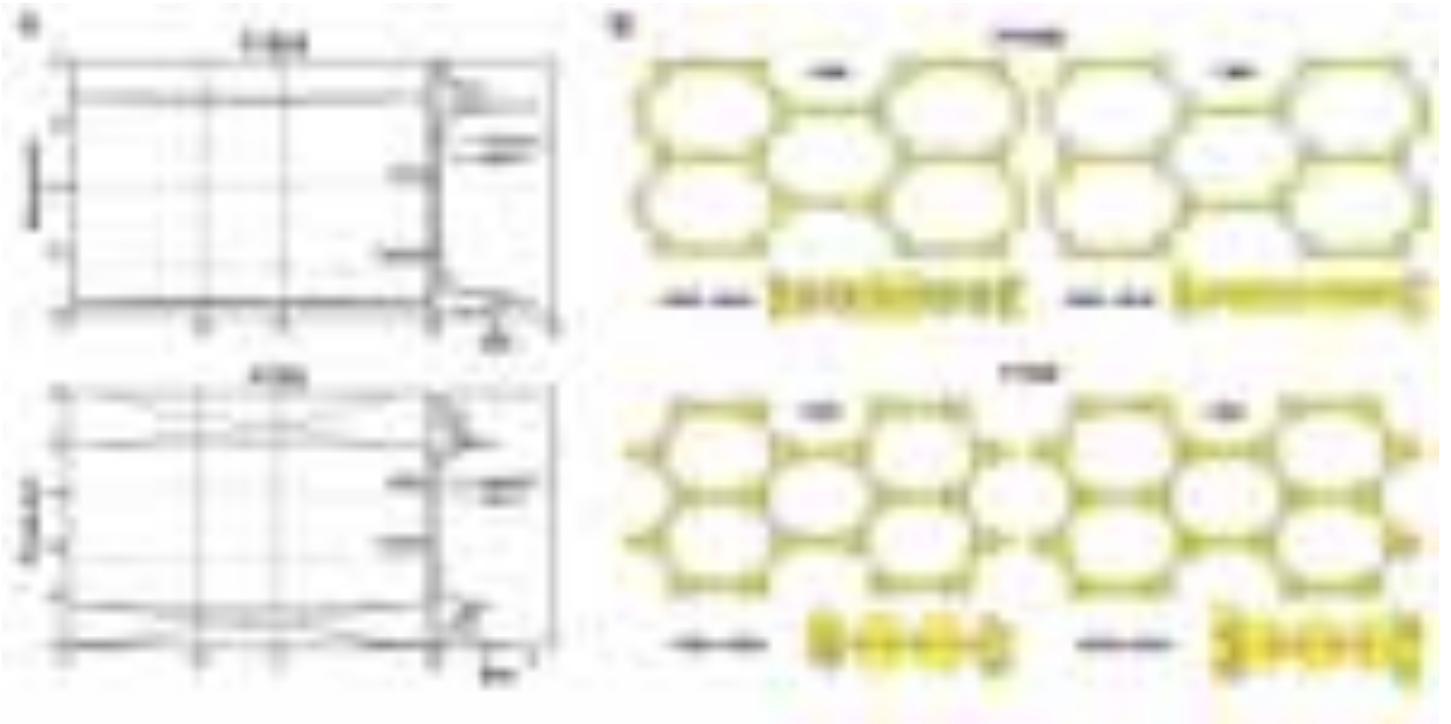
Fig. 26.

Fig. 27.
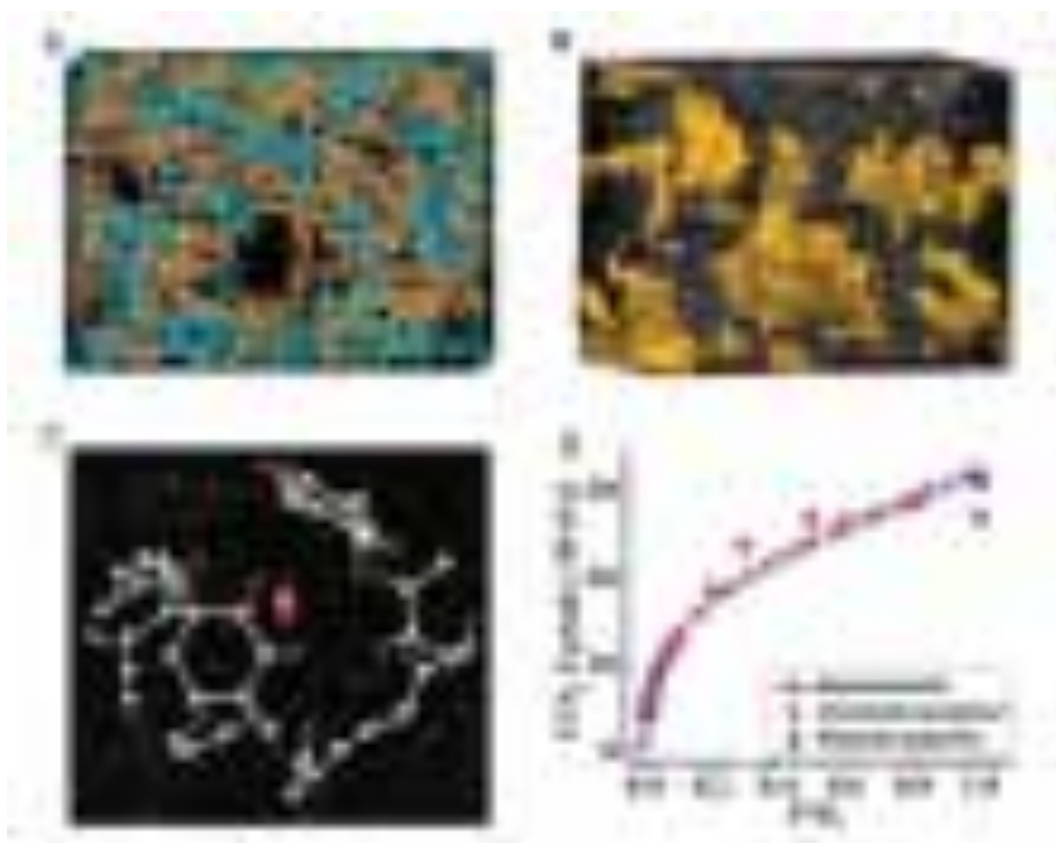
Fig. 28.
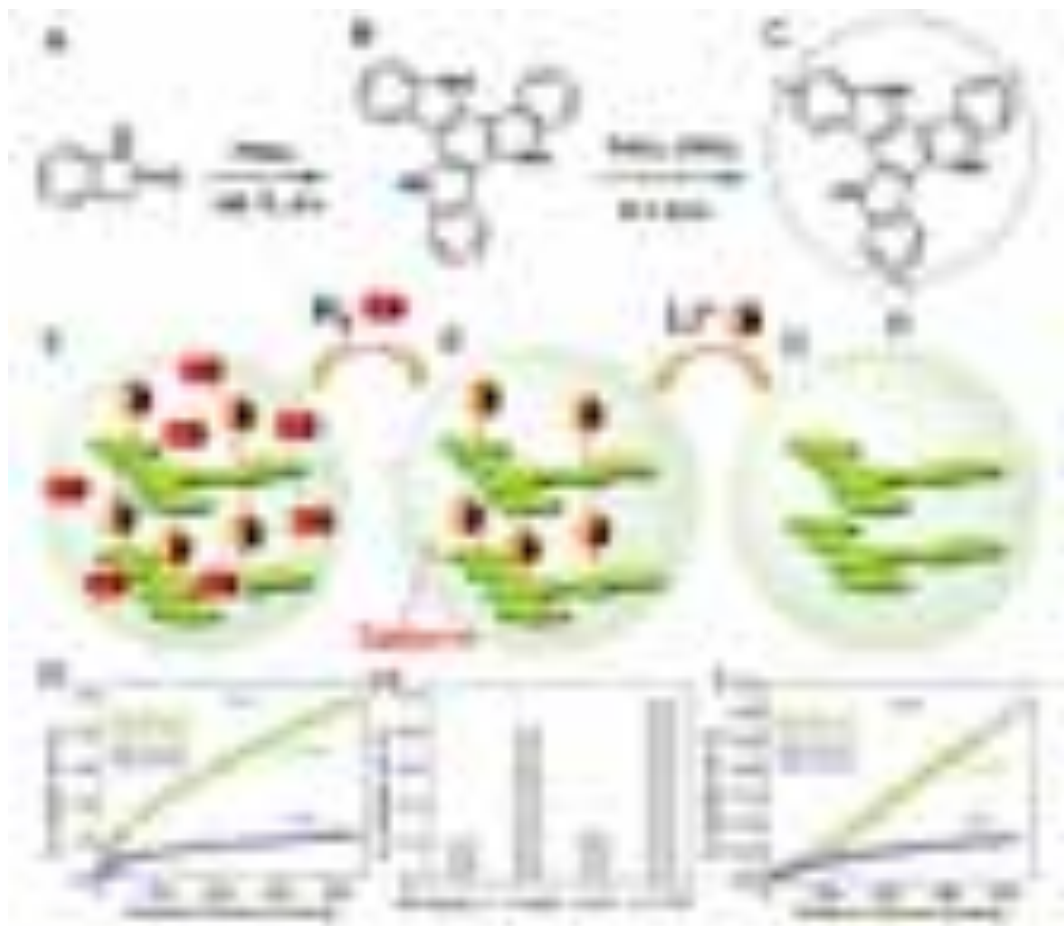
Fig. 29.
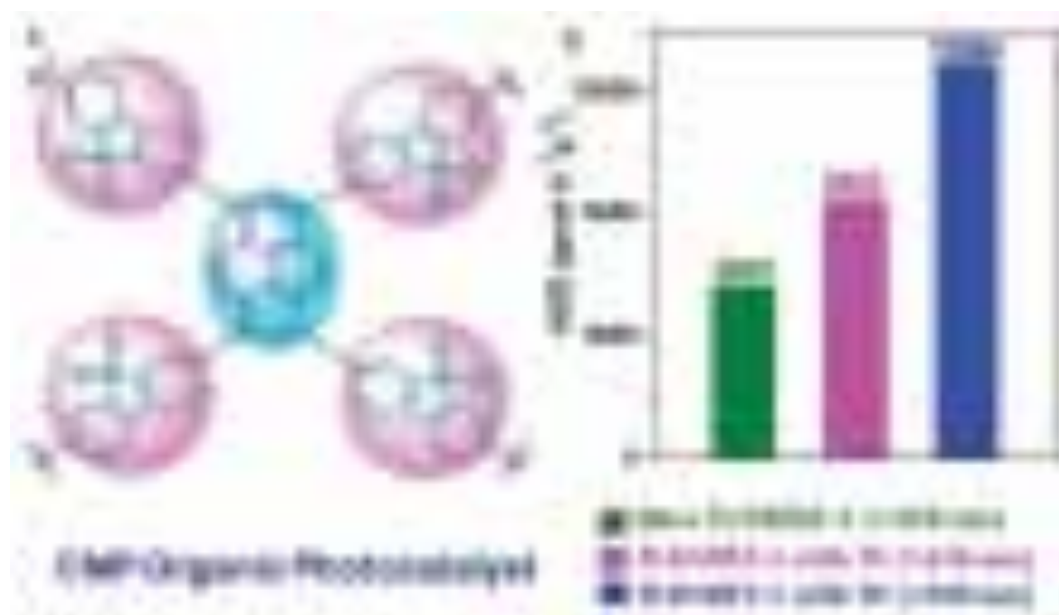
Fig. 30.
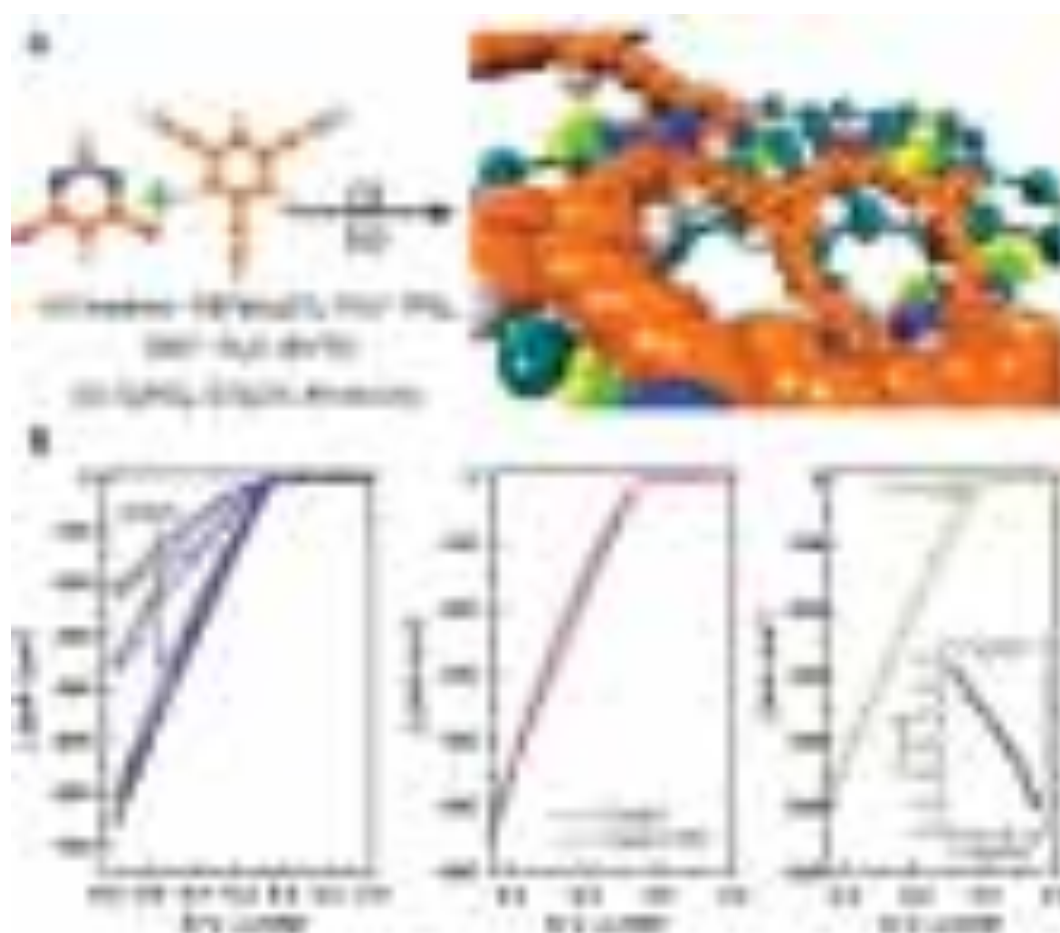
Fig. 31.

Fig. 32.

208

Fig. 33.

Fig. 34.

Fig. 35.

211

Fig. 36.

Fig. 37.

213

Fig. 38.

214

Fig. 39.

Fig. 40.

Fig. 41.

217

Fig. 42.

Fig. 43.

Fig. 44.

220
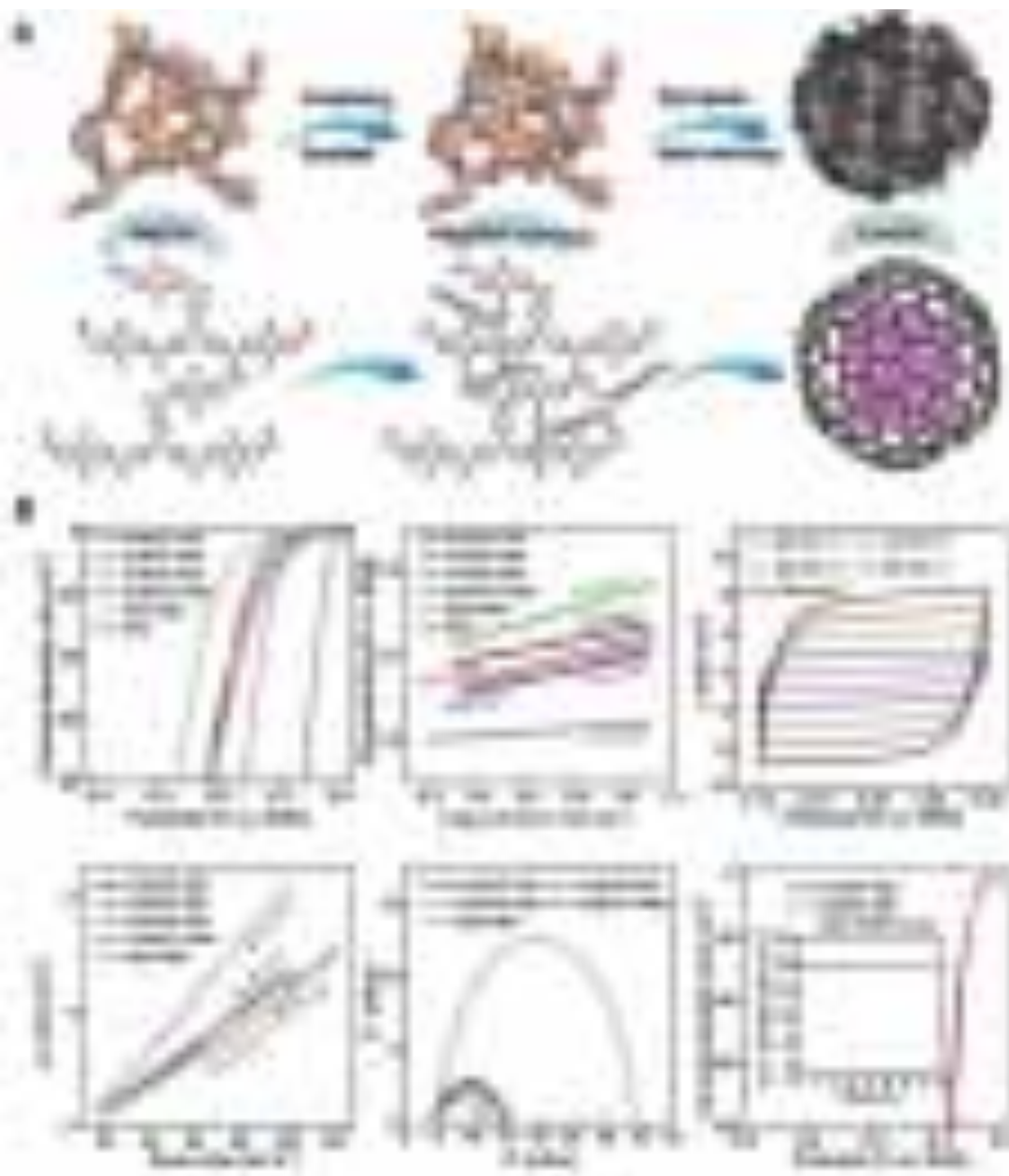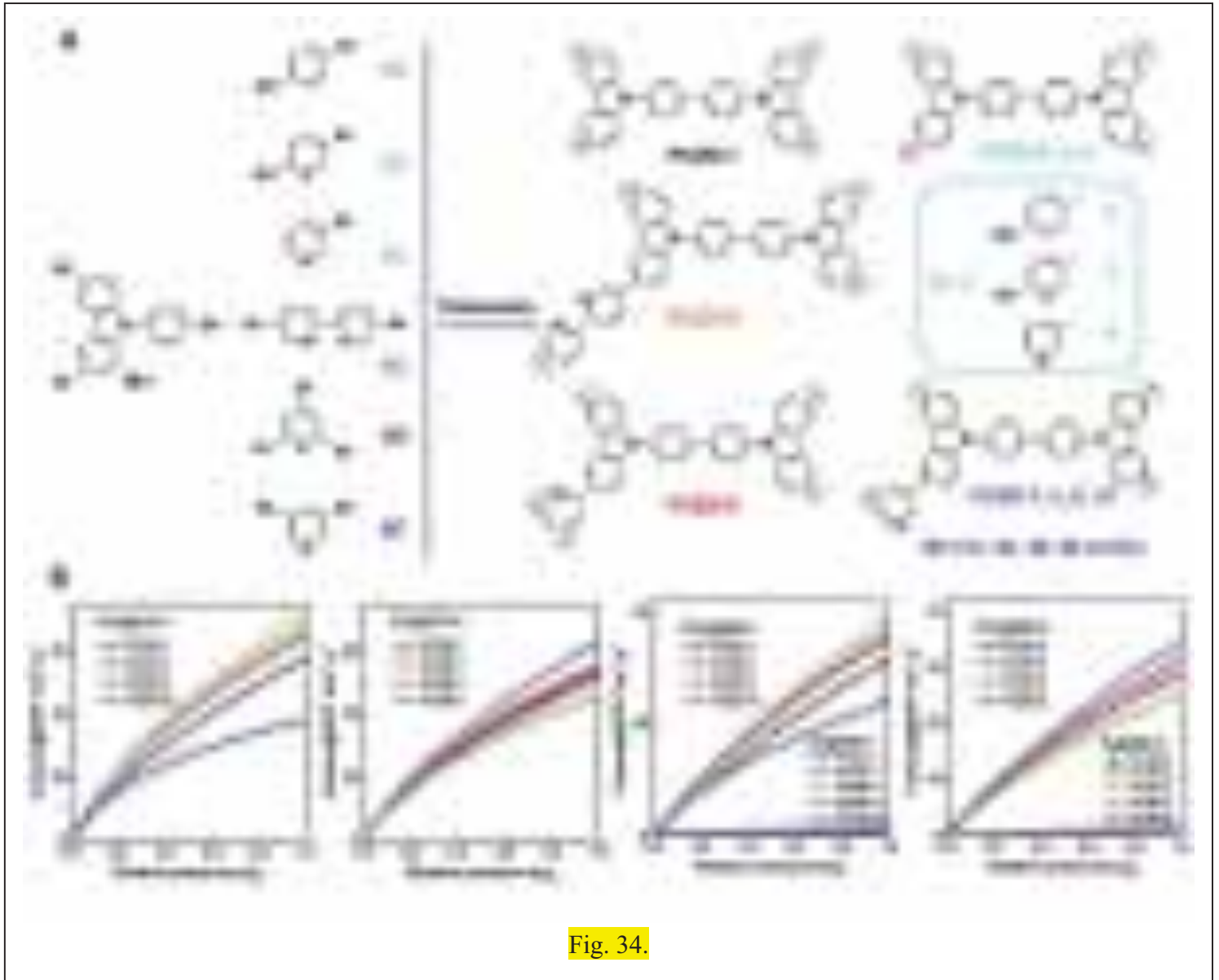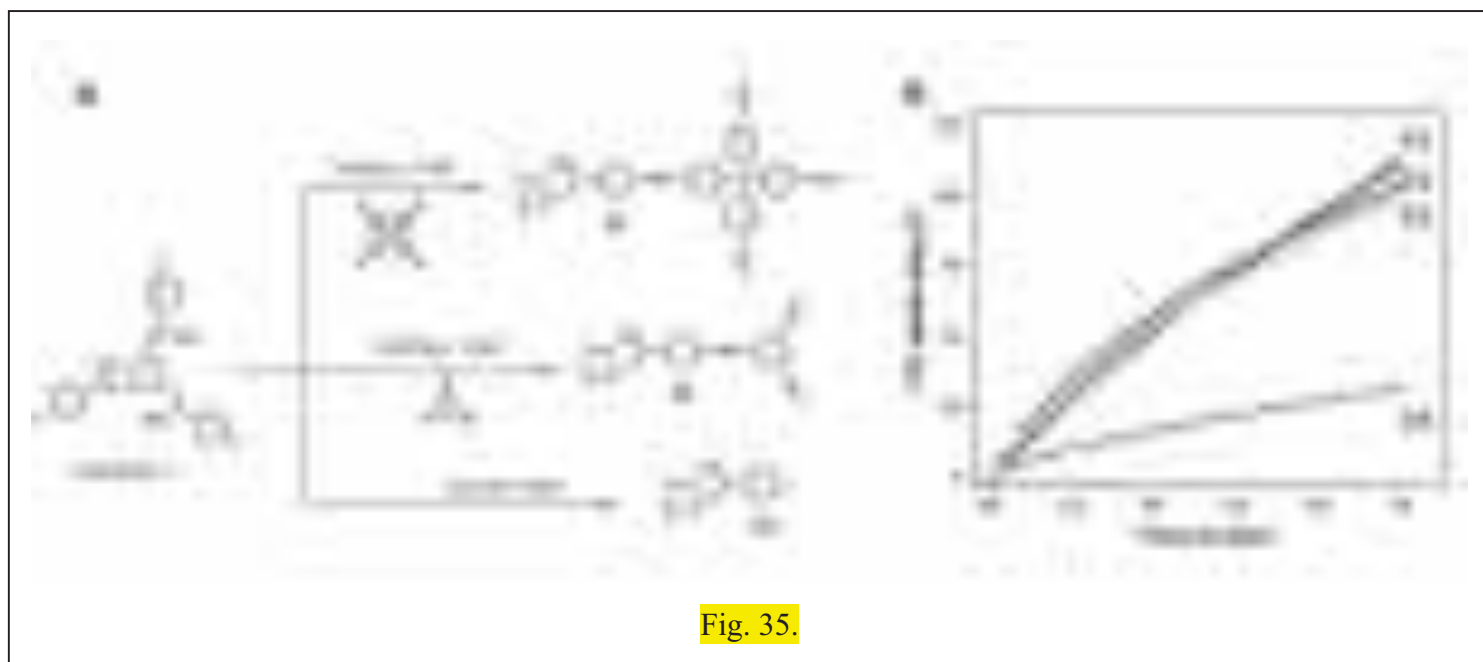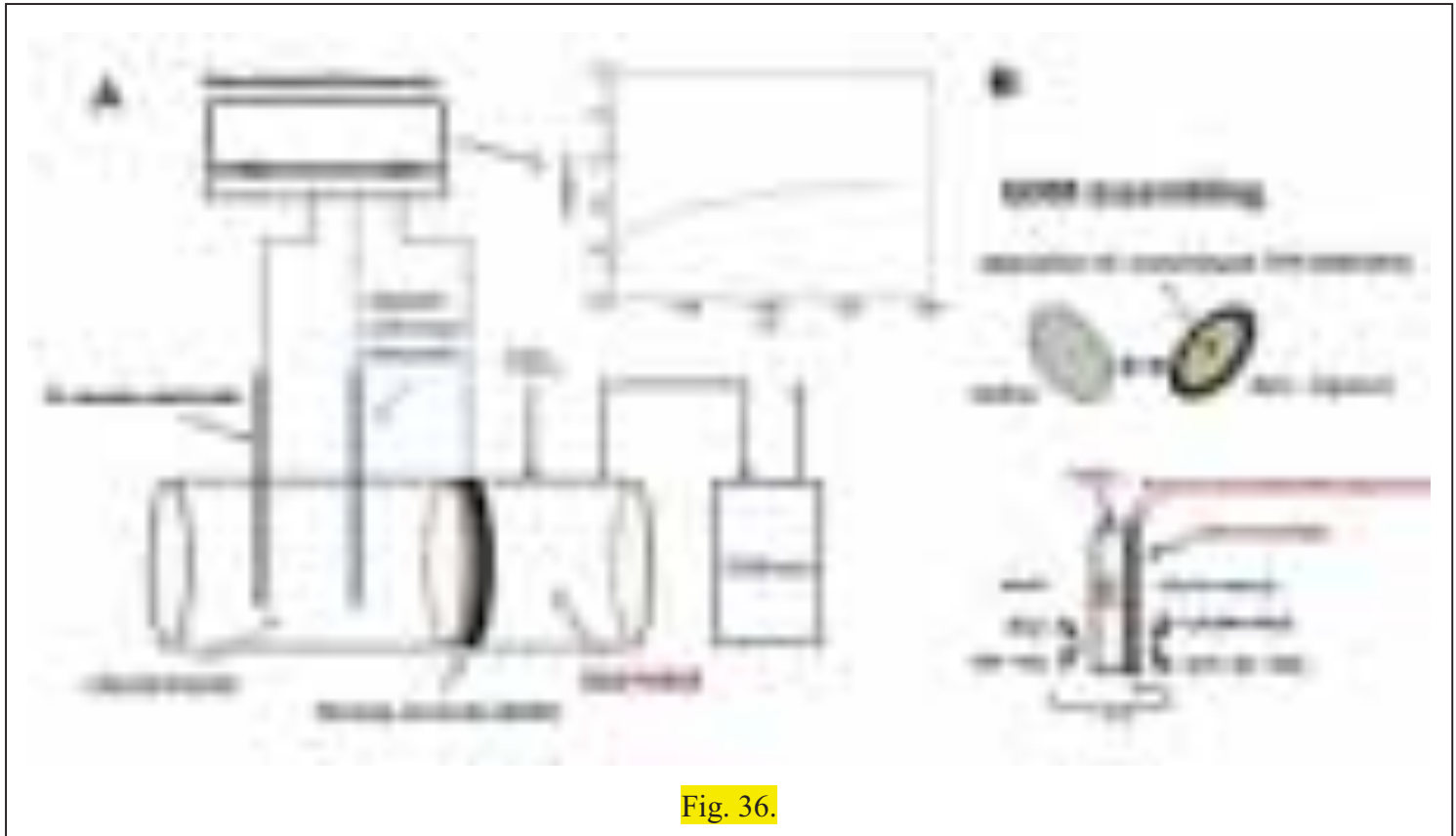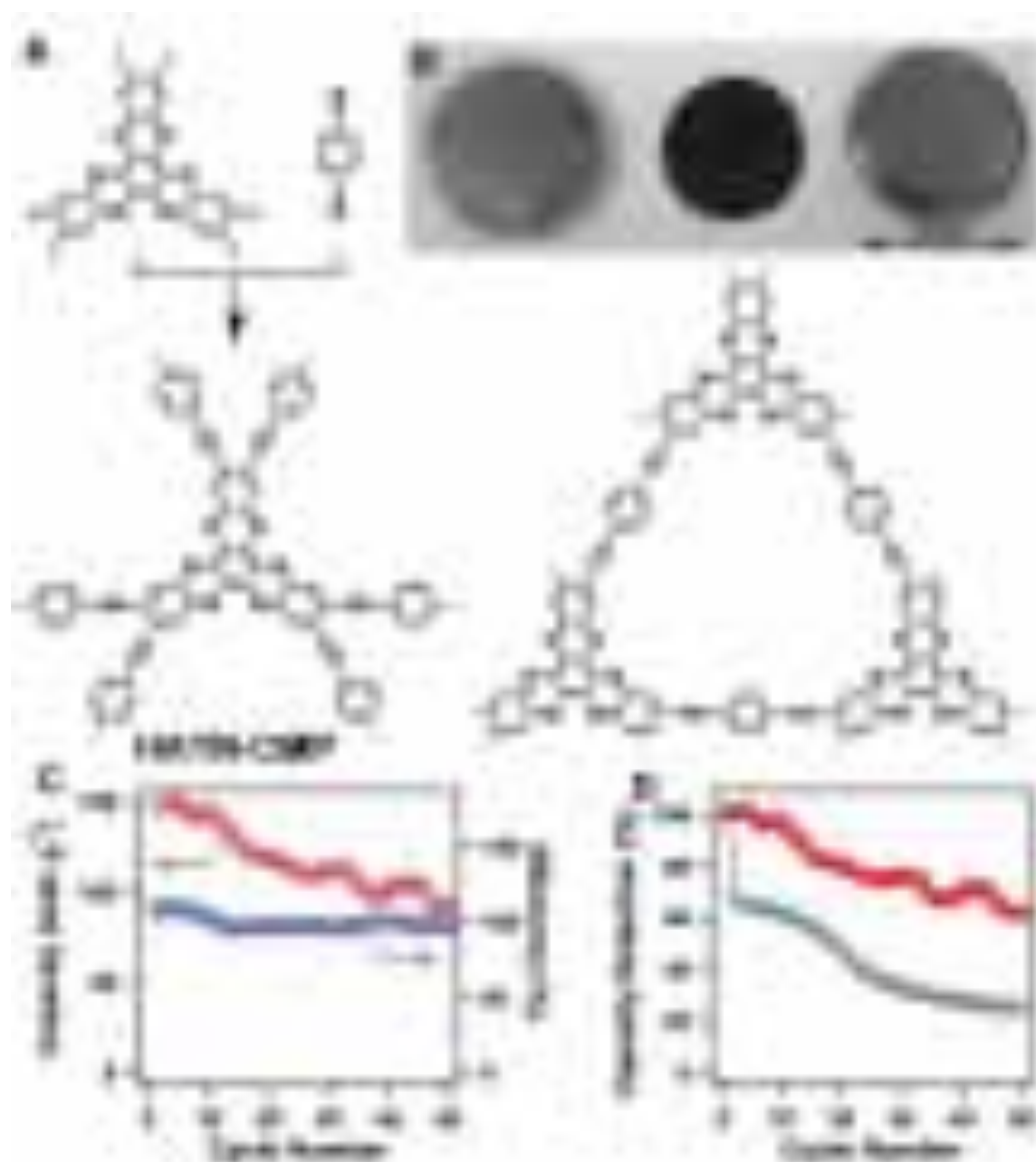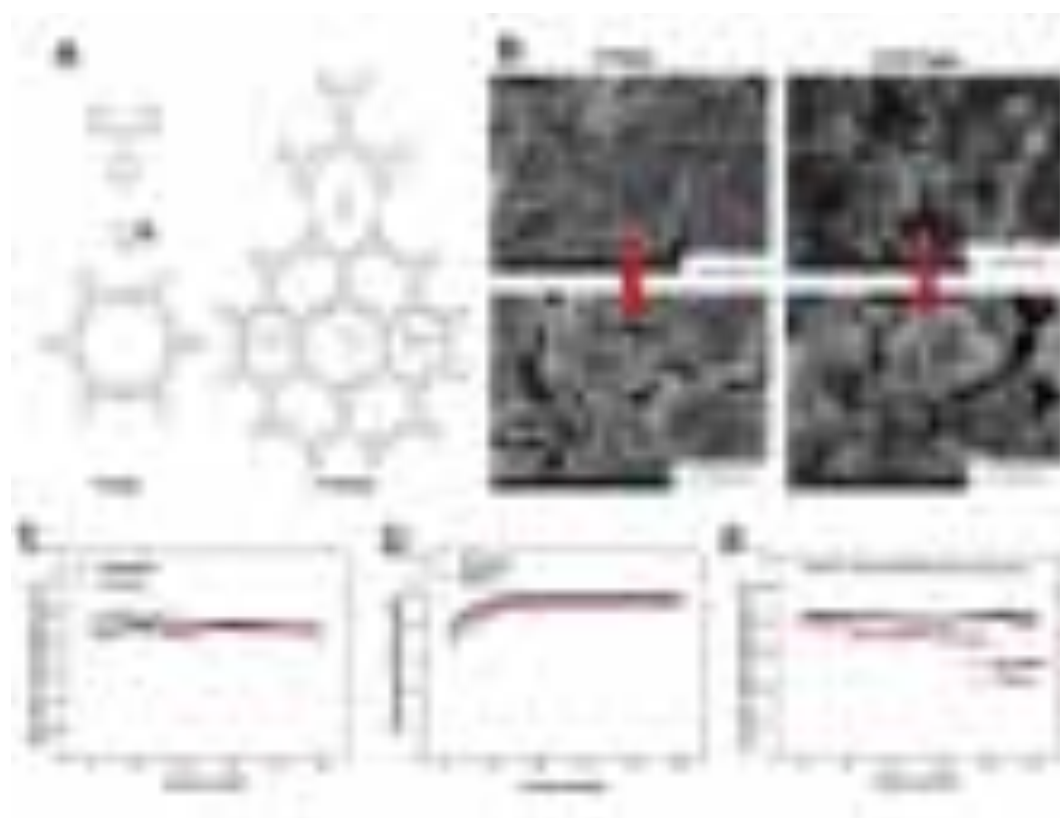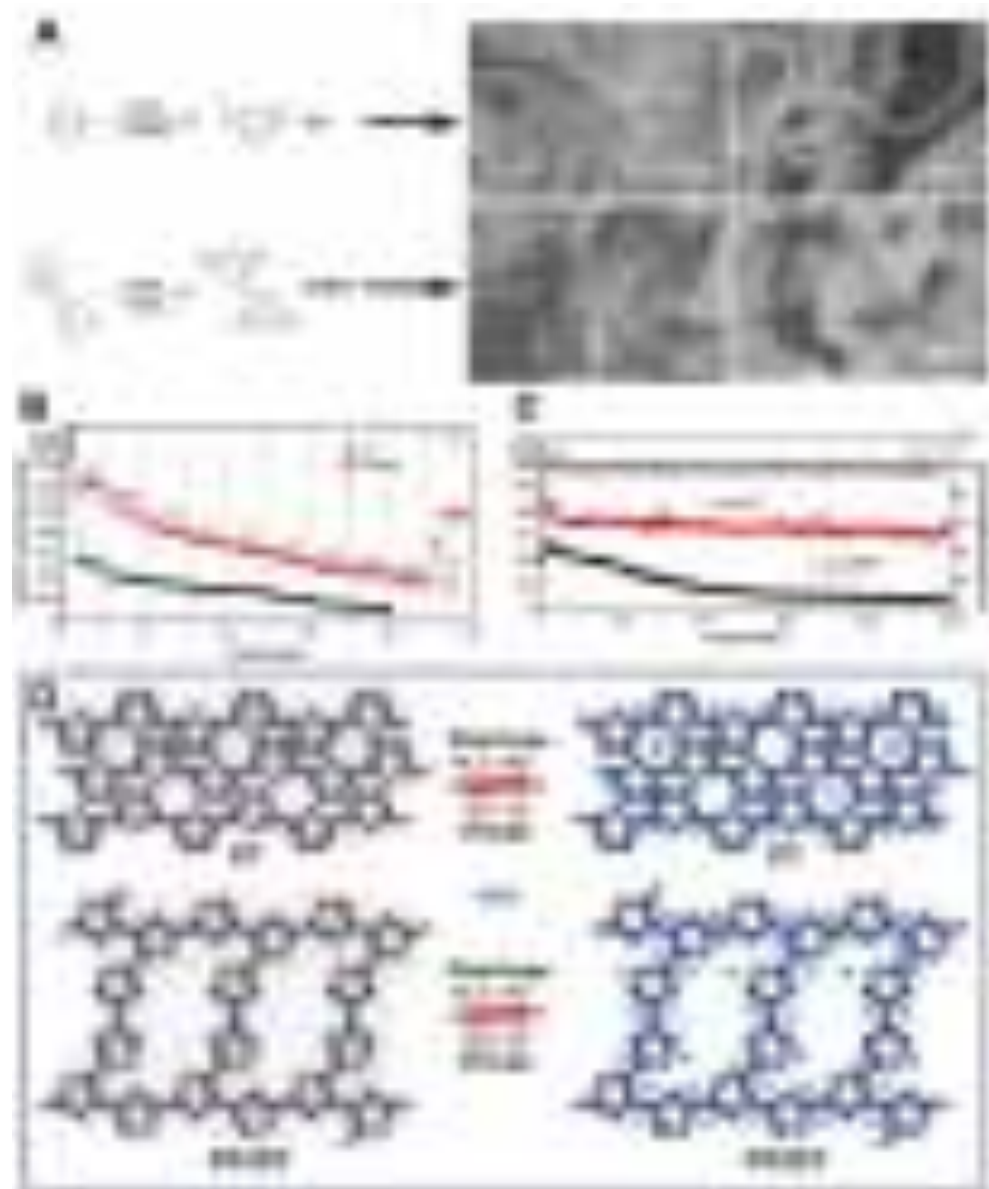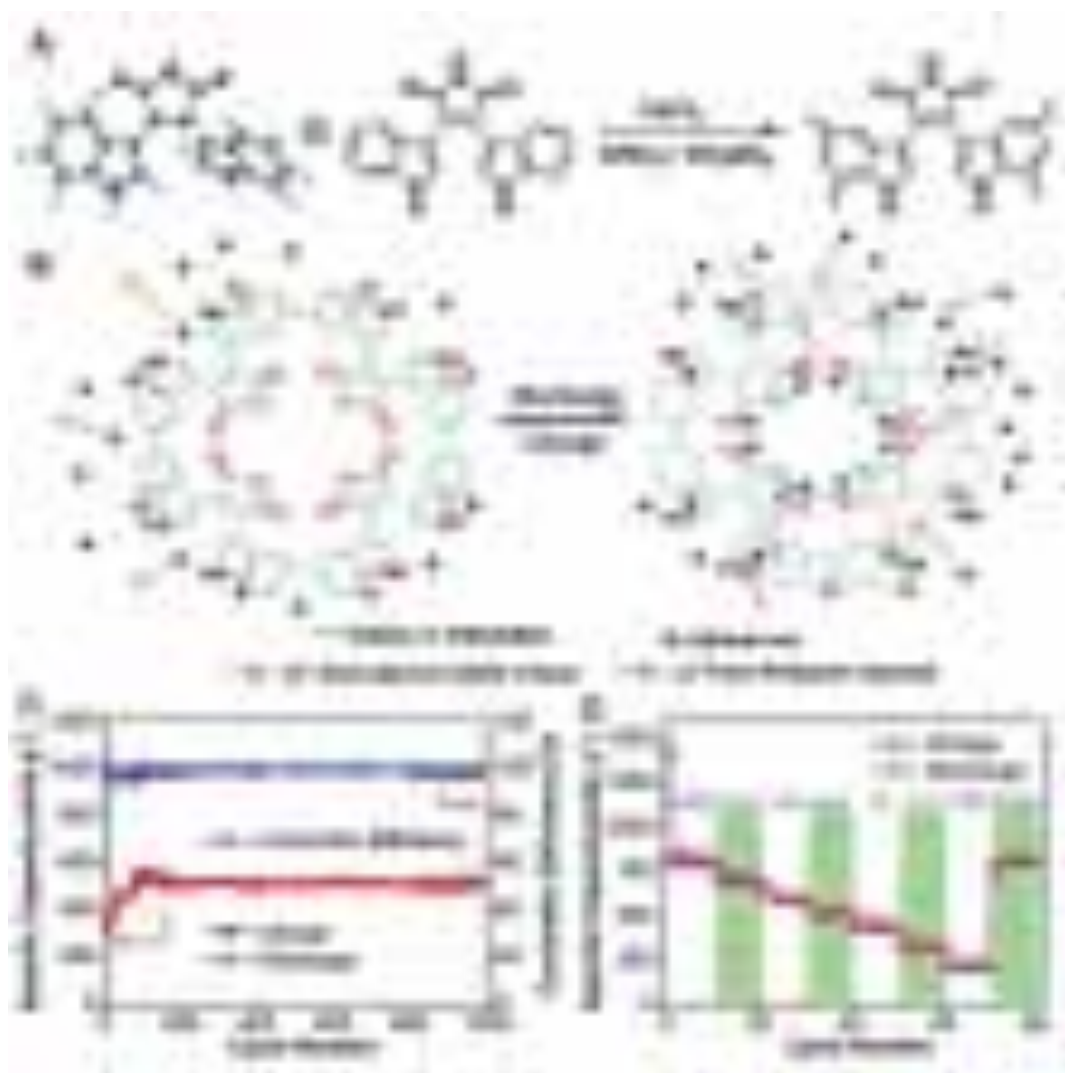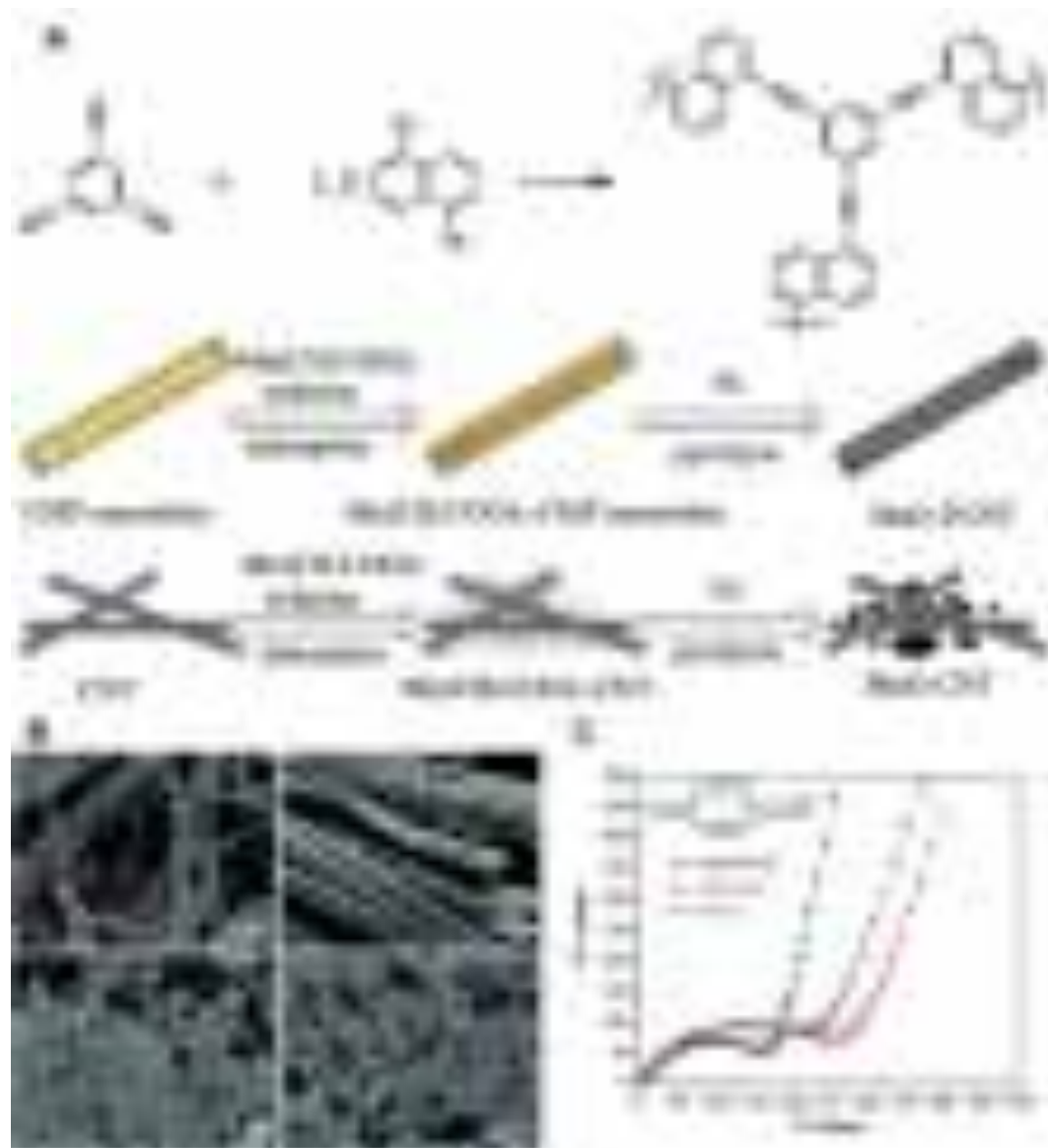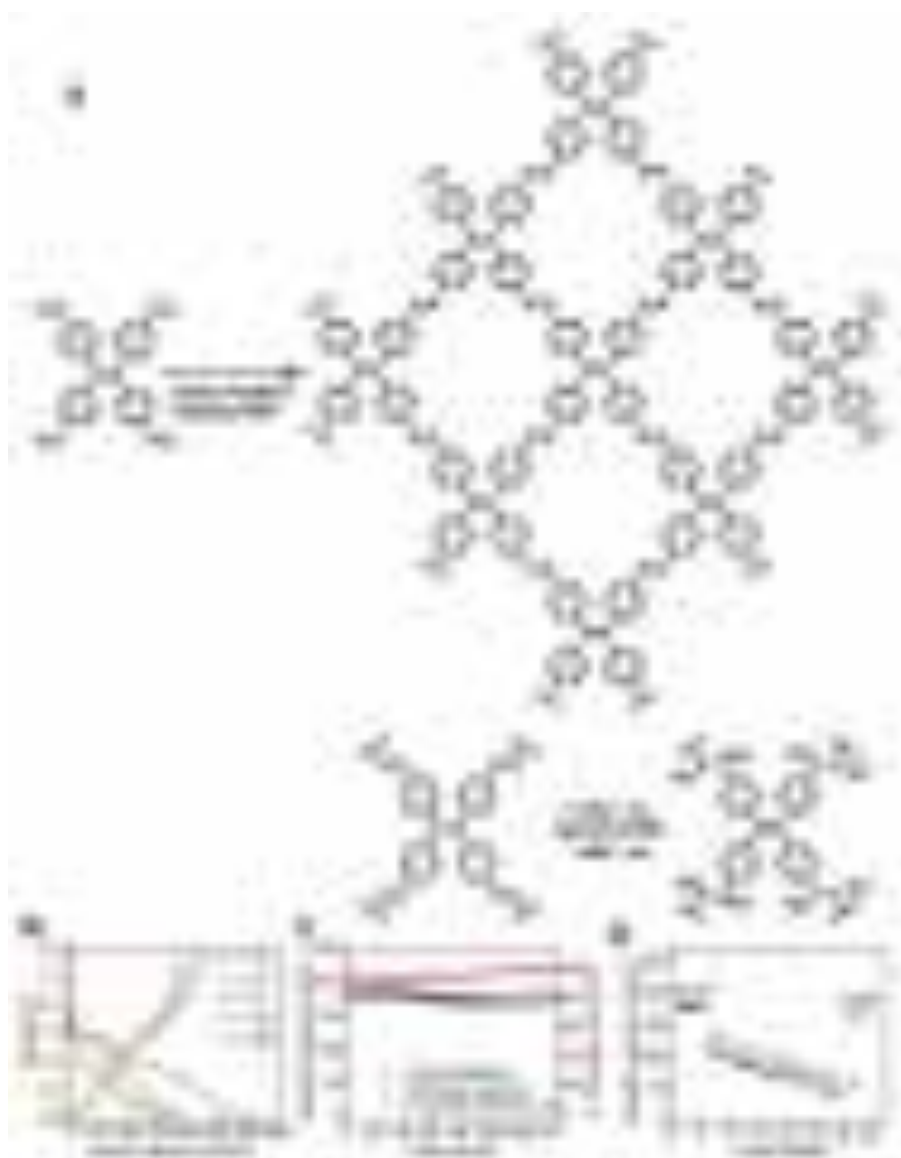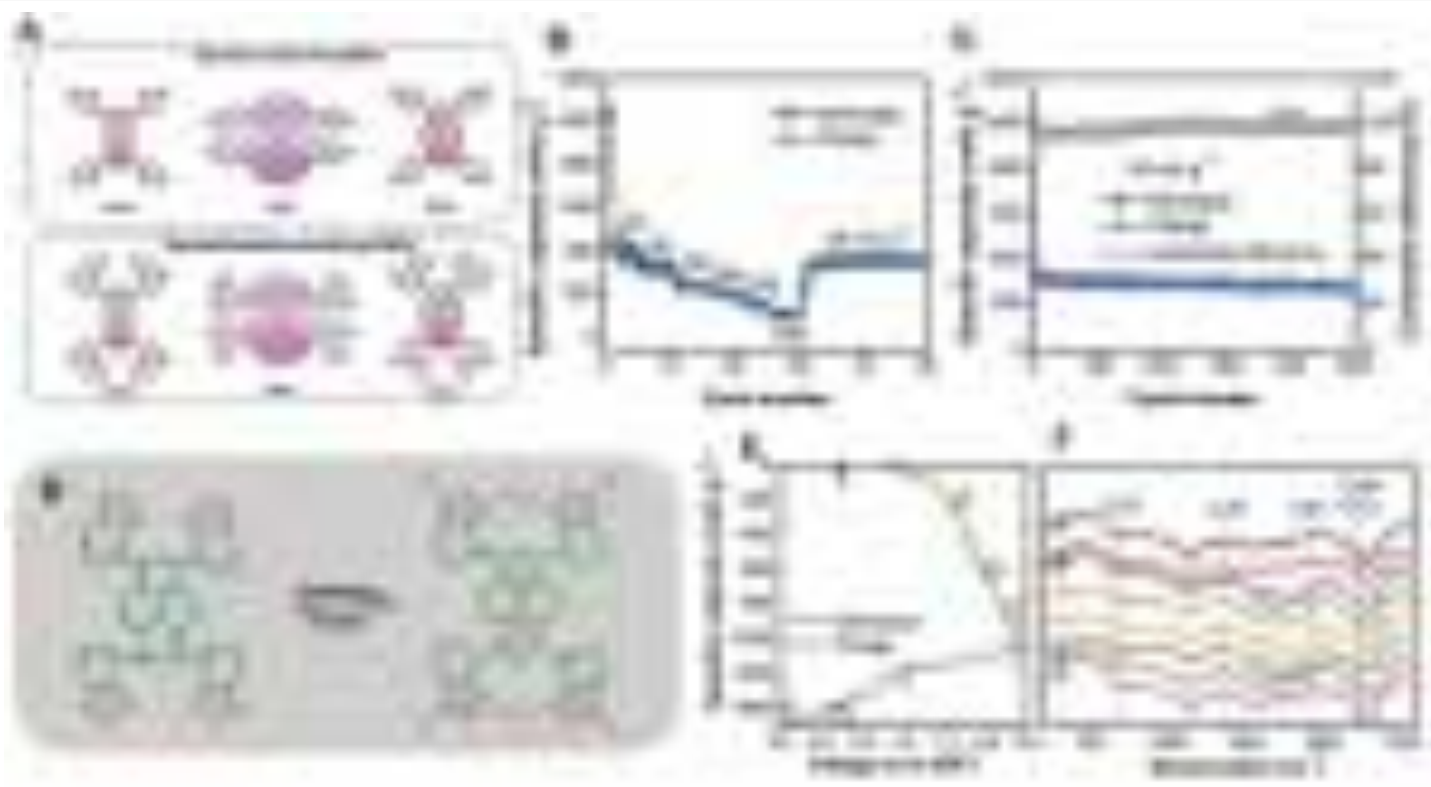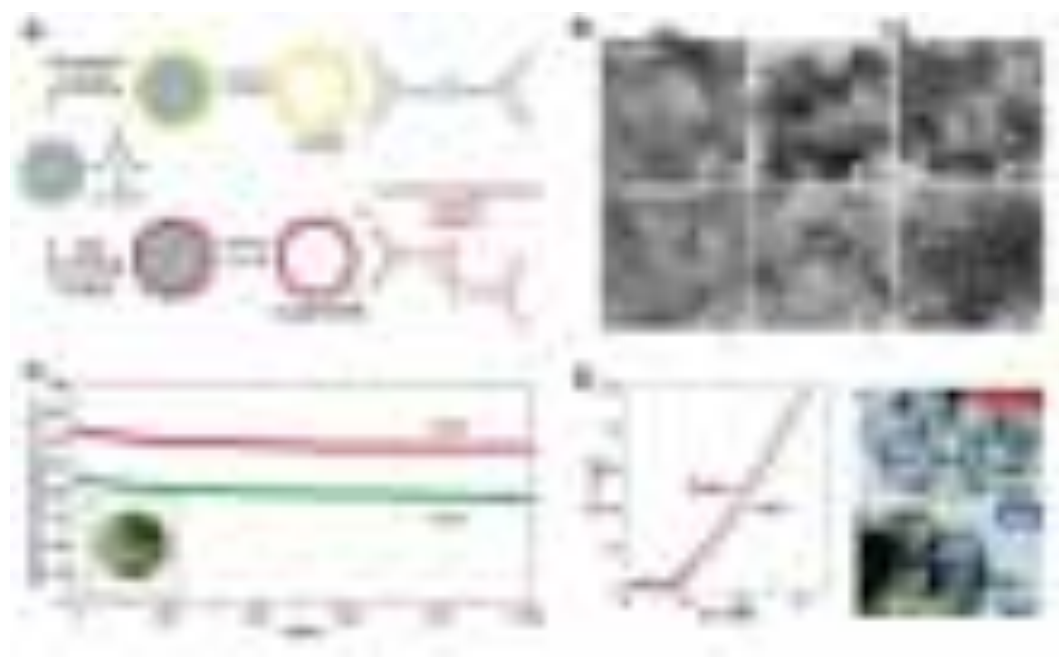
Fig. 45.
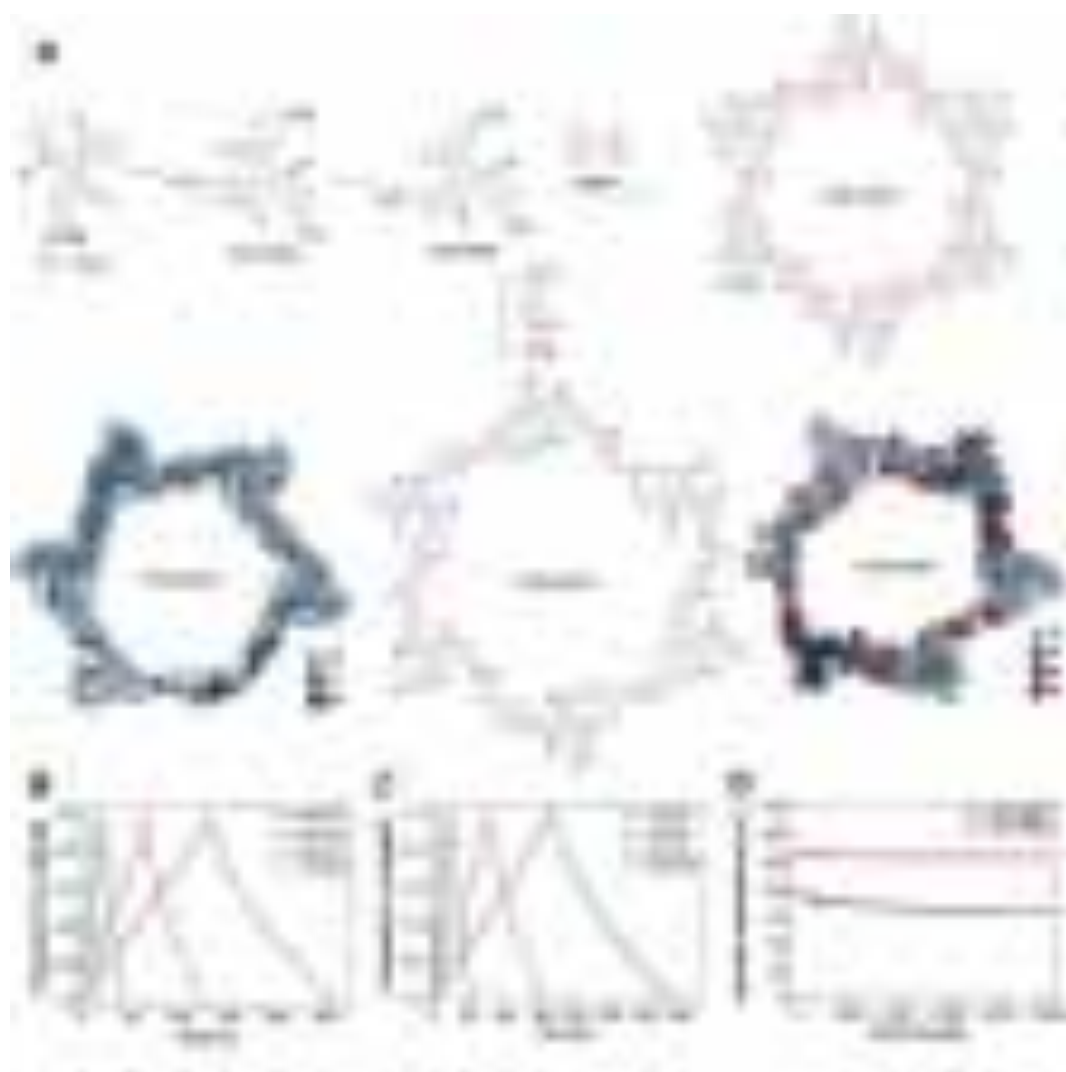
Fig. 46.
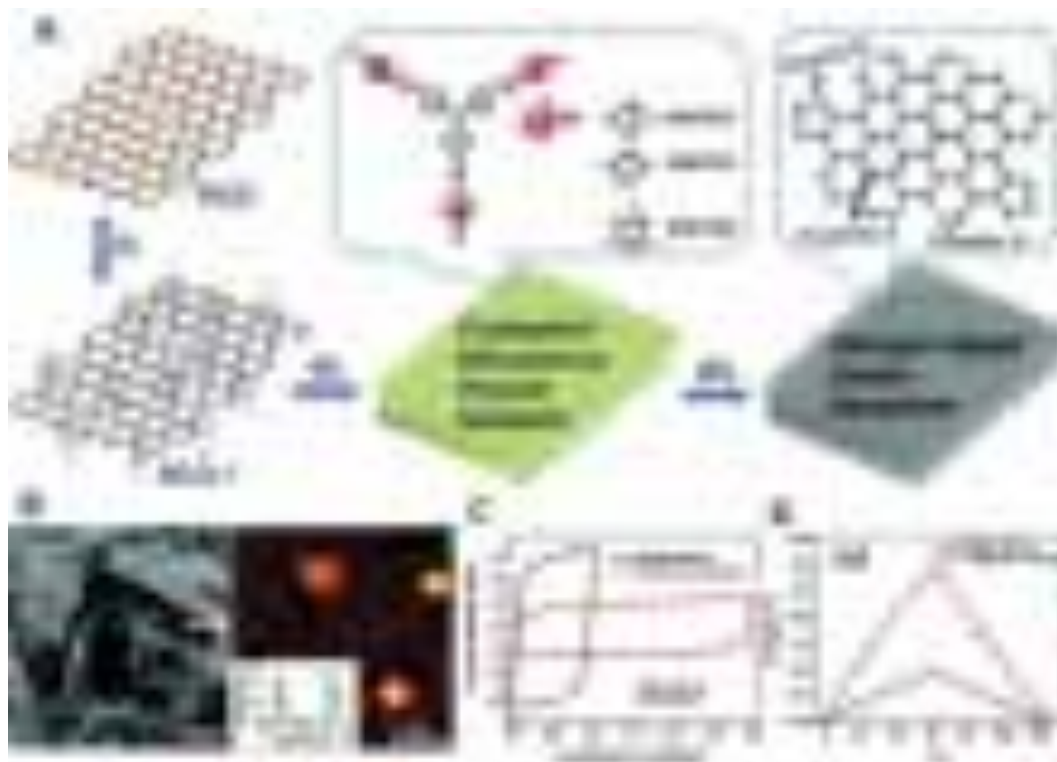
Fig. 47.

Fig. 48.

Fig. 49.

Fig. 50.

227
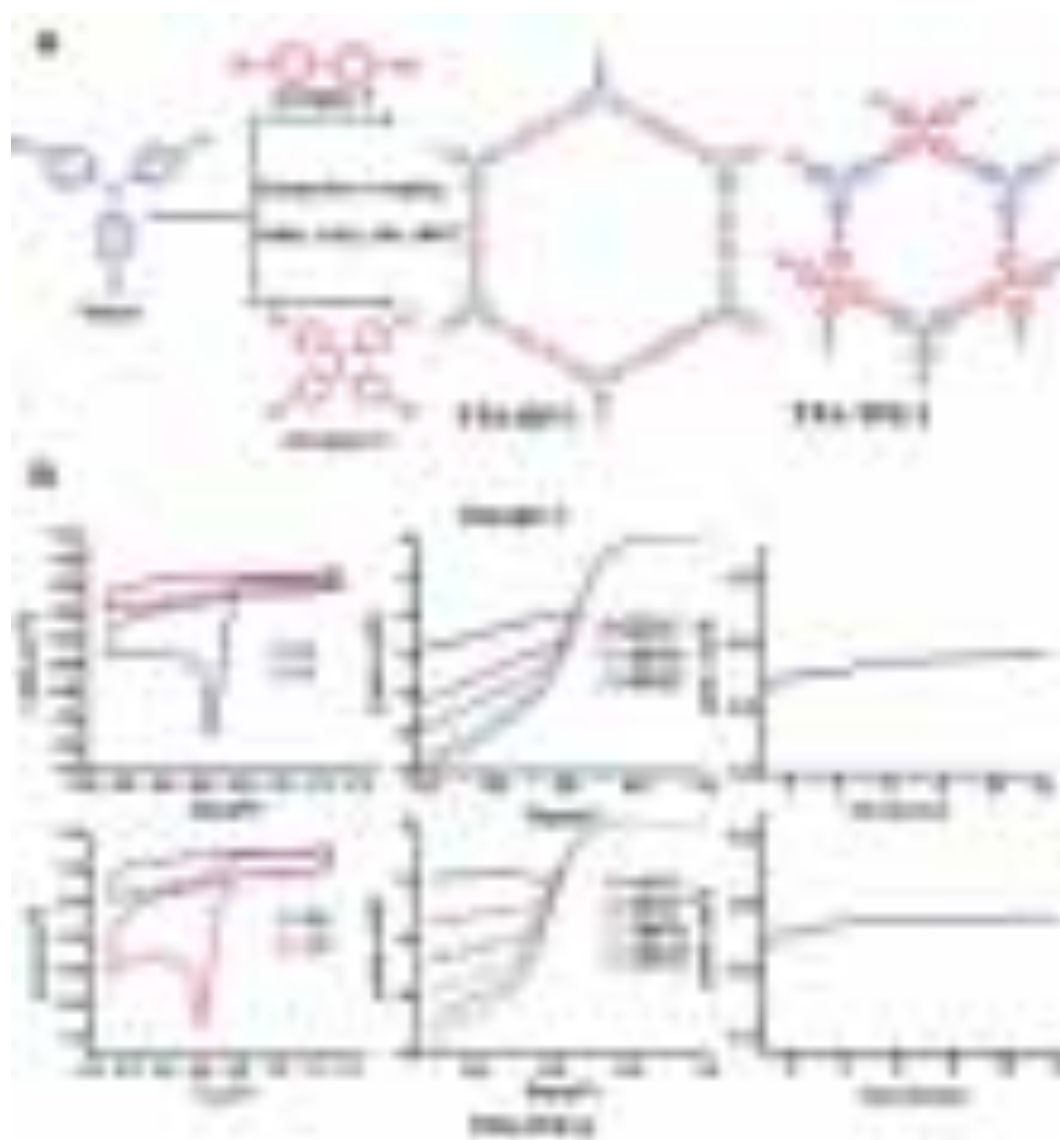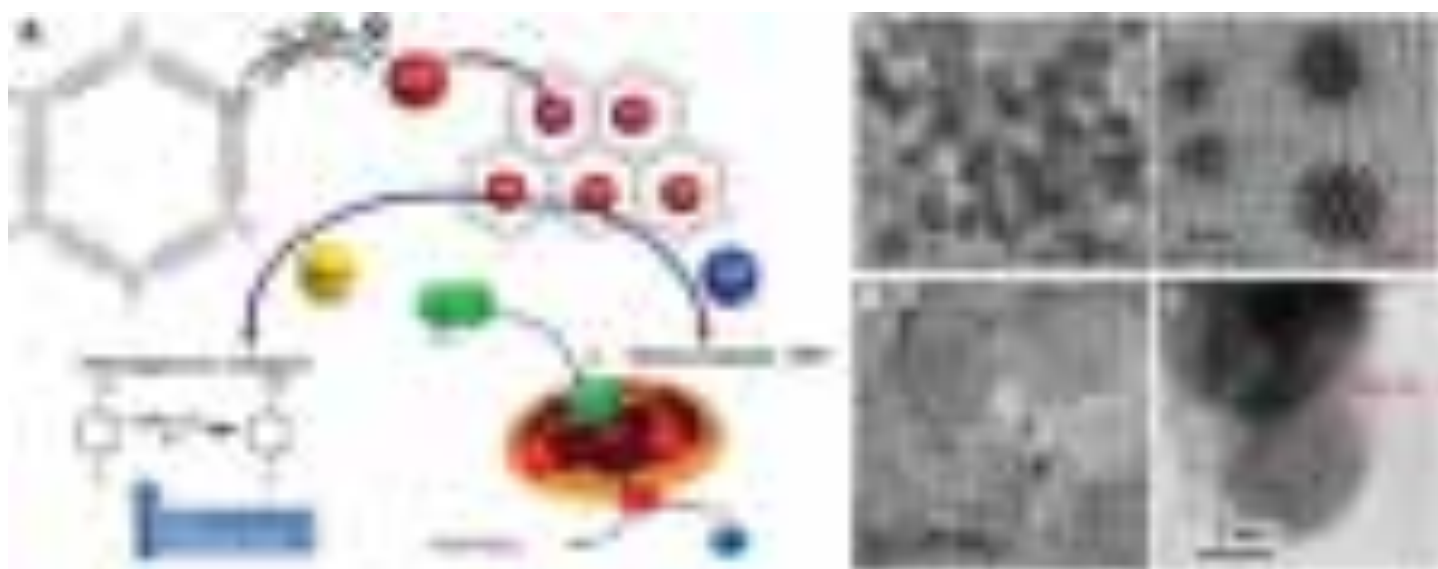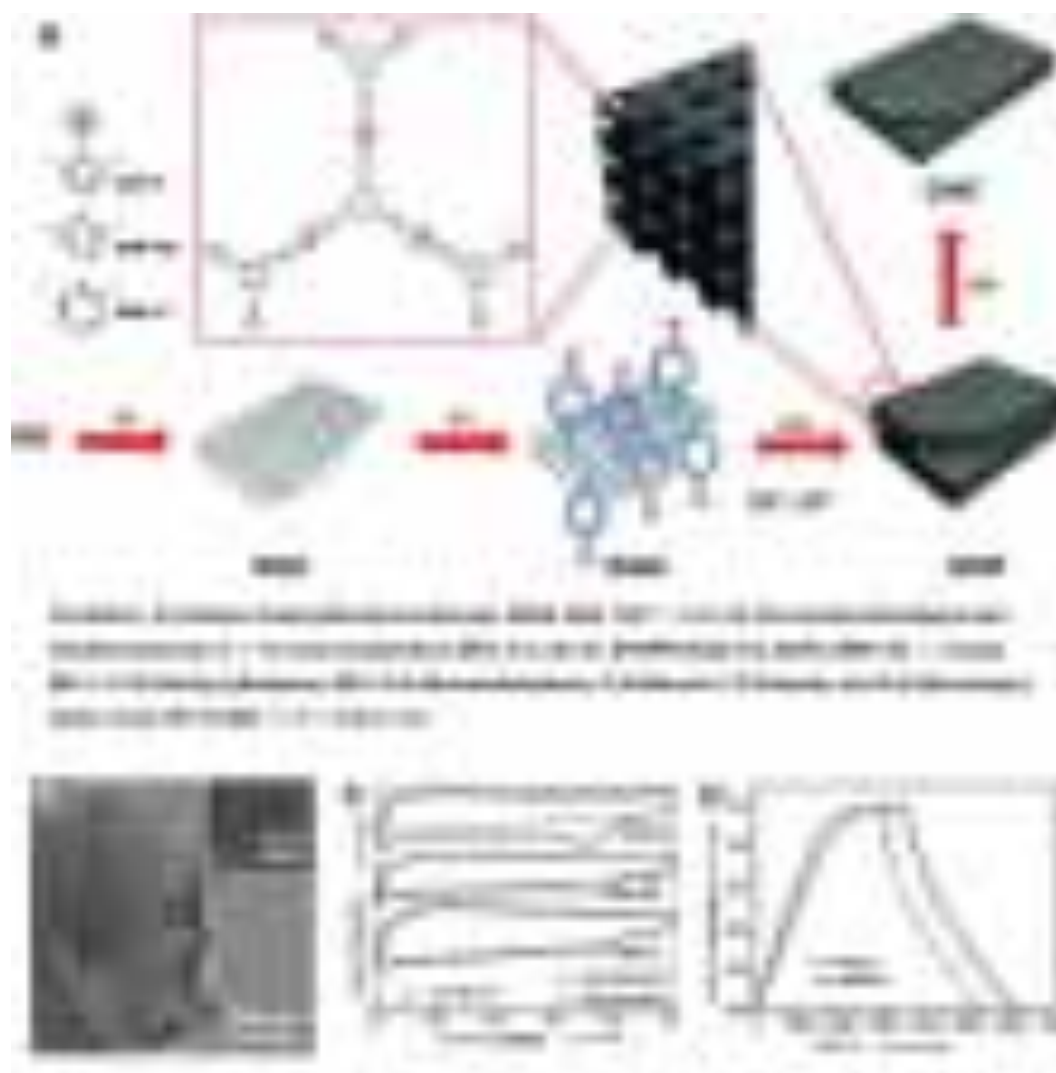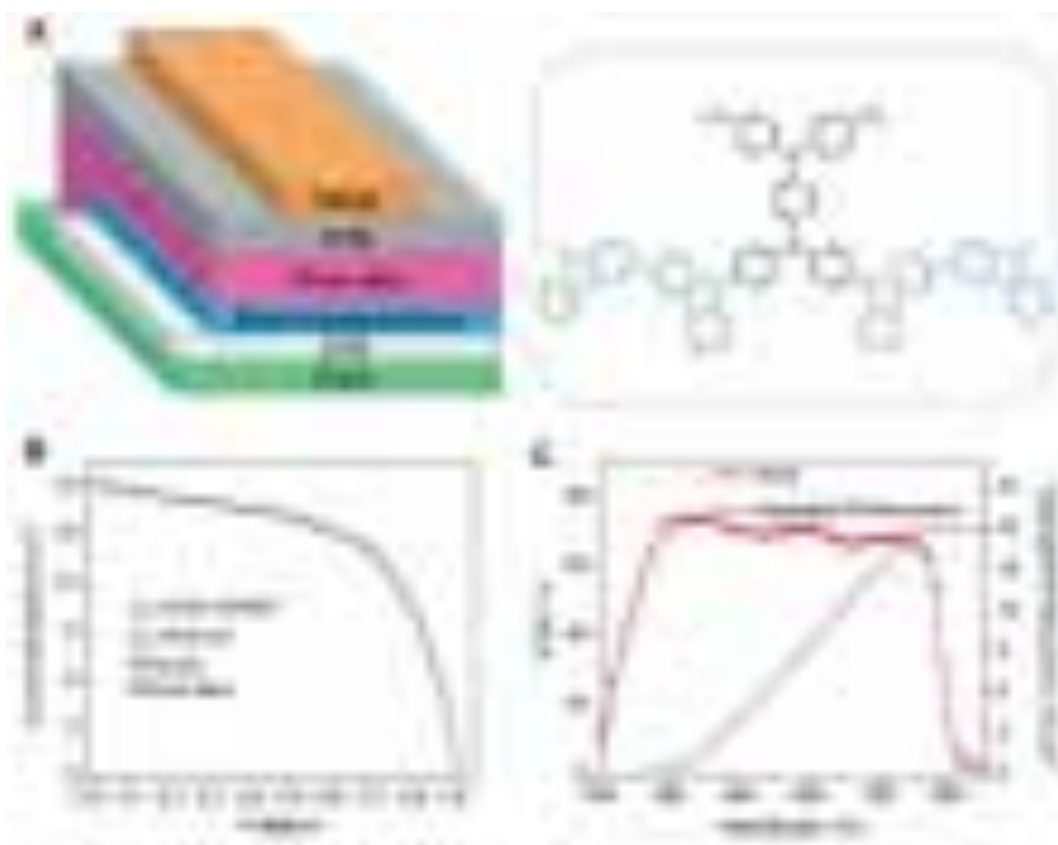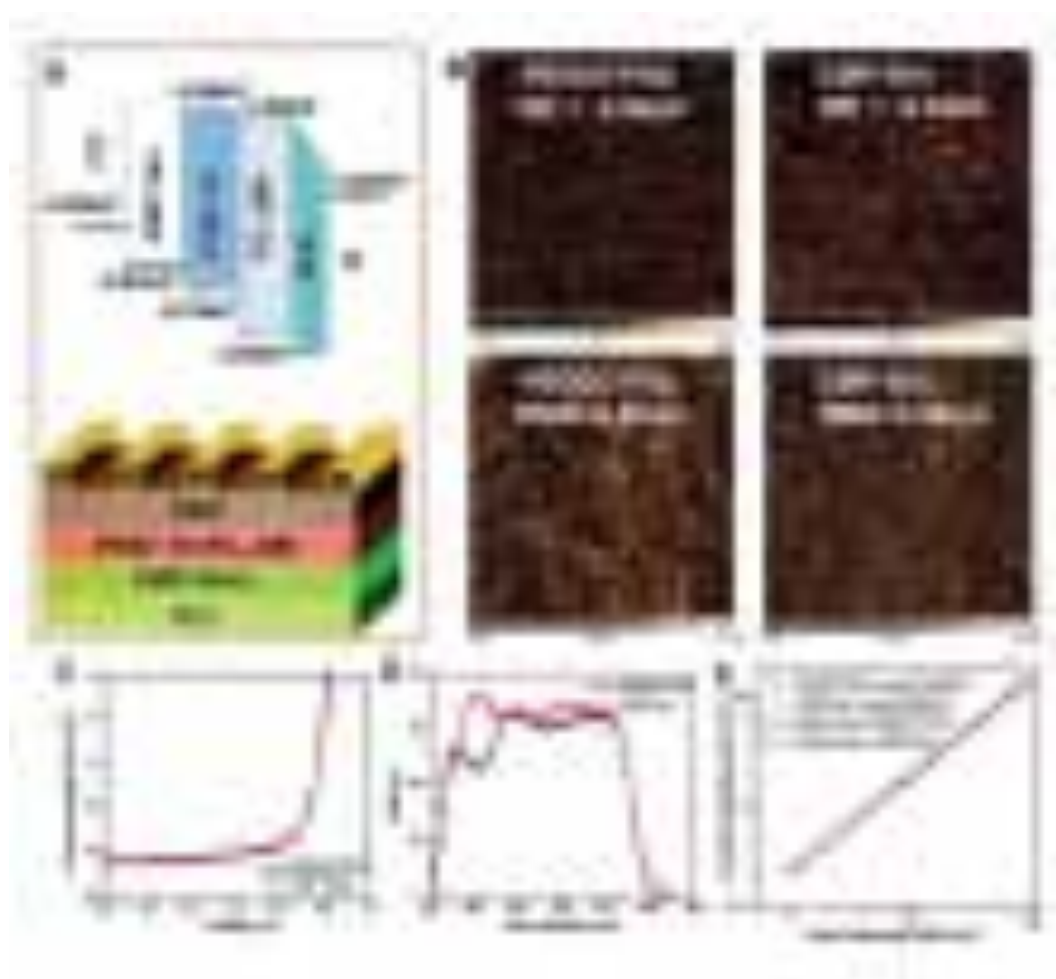
Fig. 52.

Tables

Table 1

Classic reaction routes for the preparation of CMPs

Category	Reaction type	Reaction formula	Representative CMPs	Ref.
Noble-metal catalyzed synthesis	Sonogashira-Hagihara coupling	X = Cl, Br, I, OTf; Pd(0)/Cu(I), Base	CMP-1, CMP-2, CMP-3, CMP-4	[47]
	Suzuki coupling	X = Cl, Br, I, OTf; Y = (OH)$_2$, (OR)$_2$, pinacol; Pd(0), Base, DMF/water	DA-CMP1, DA-CMP2, Azo-CMP1, Azo-CMP2	[99]
	Heck coupling	X = Br, I, OTf; Pd(0), Base	LMOP-1, LMOP-2, LMOP-3	[100]
	Yamamoto coupling	X = Cl, Br, I, OTf; Ni(0), bipy	TBTPE, TPE-CMP, TPE-LP	[49]
	Buchwald-Hartwig coupling	X = Cl, Br, I, OTf; Pd(0), Base	HCMP-1, HCMP-2, HCMP-3, HCMP-4	[91]
Non-noble metal catalyzed synthesis	Oxidative coupling	FeCl$_3$ or AlCl$_3$, CHCl$_3$	PCz–Cn–Cz (n = 3–6)	[101]
	Schiff-based reaction		KECMP-1	[102]
	Heterocycle linkages	1. N$_2$; 2. O$_2$	TzTz-POP-3, TzTz-POP-4, TzTz-POP-5	[103]
	Phenazine ring fusion reaction	AlCl$_3$, heat	TIPS-CMP	[104]

Cyclotrimerization

$X \equiv X$

X = C, N

$\longrightarrow$

CTF-1

[55]

231
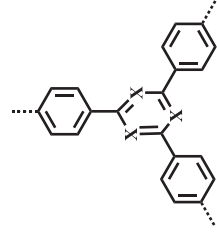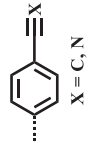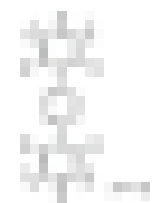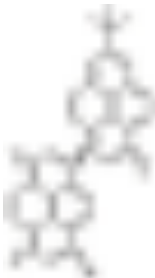
Table 2

Summary of hydrogen storage in CMPs

CMPs	Molecular structure	S_{BET} $(m^2\ g^{-1})$	V_{total} $(cm^3\ g^{-1})$	P (bar)	T (K)	H_2 (wt. %)	Ref.
Li–CMP	–	795	1.61	1	77	6.1	[238]
POP-1		1031	0.641	60	77/87	2.78/2.31	[143]
POP-2		1013	0.712	60	77/87	2.71/2.14	[143]
POP-3		1246	0.729	60	77/87	3.07/2.51	[143]
POP-4		1033	0.730	60	77/87	2.35/1.75	[143]
BLP-1(Cl)		1364	0.746	1	77	1.10	[239]
BLP-1(Br)		503	0.303	1	77	0.68	[239]
BLP-2(Cl)		1174	0.649	1	77	1.30	[239]
BLP-2(Br)		849	0.571	1	77	0.98	[239]

BLP-10(Cl)		924	0.67	1	77/87	1.3/0.9	[240]
PCTF-1		2235	1.56	1	77	1.86	[241]
PCTF-2		784	0.38	1	77	0.9	[241]
ThPOP-1		1050	0.69	1	77	2.23	[147]
ThPOP-2		160	0.27	1	77	1.03	[147]
PTAT		304	–	1	77	1.9	[242]
Li+–PTAT	–	281	–	1	77	7.3	[242]
CMP-G1		997	1.32	1/20	77	1.27/2.69	[243]
CMP-G2		786	0.87	1/20	77	1.01/2.14	[243]
HCMP-1		842	1.16	1.13	77.3	107[a]	[79]

233

HCMP-2		827	1.35	1.13	77.3	131[a]	[79]
p-PPF		269	0.20	45	77	67[b]	[244]
m-PPF		229	0.15	45	77	56[b]	[244]
SCMP-1		505	1	1	77	3.8[c]	[84]
BILP-10		787	–	40	77	27.3[d]	[150]
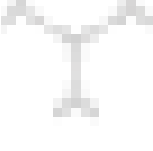
[a] H_2 uptake (cm^3 g^{-1}); [b] H_2 uptake (mL g^{-1}); [c] H_2 uptake (mmol g^{-1}); [d] H_2 uptake (g L^{-1}).

0
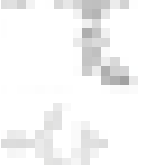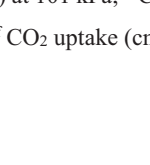
Table 3

Summary of Carbon dioxide capture and storage in CMPs

CMP sample	Molecular structure	S_{BET} (m² g⁻¹)	V_{total} (cm³ g⁻¹)	T (K)	CO_2 (mmol g⁻¹)	Ref.
PAF-33		821	–	273	2.16	[312]
PAF-33–NH₂		370	–	273	1.19	[312]
PAF-33–COOH		445	–	273	1.94	[312]
PAF-34		953	–	273	2.50	[312]
PAF-34–OH		771	–	273	2.21	[312]
PAF-35		567	–	273	1.77	[312]
CMP-1		837	0.45	298/273	1.18/2.05	[313]
CMP-1-(CH₃)₂		899	0.75	298/273	0.94/1.64	[313]
CMP-1-(OH)₂		1043	0.71	298/273	1.07/1.80	[313]
CMP-1-NH₂		710	0.39	298/273	0.95/1.64	[313]
CMP-1-COOH		522	0.30	298/273	0.95/1.60	[313]
CMP		772	1.21	298	71.0	[63]

Co-CMP		965	2.81	298	79.3	[63]
Al-CMP		798	1.41	298	76.5	[63]
MFCMP-1		840	0.52	273	3.69	[131]
PAF-26-COOH		717	0.36	273	286[a]	[314]
PAF-26-COOK		430	0.20	273	572[a]	[314]
p-PPF		269	0.20	195/273	73.0/44.9[b]	[244]
m-PPF		229	0.15	195/273	41.5/24.2[b]	[244]
Cz-POF-1		2065	1.57	273	202[b]	[315]
Cz-POF-2		671	0.42	273	77[b]	[315]
Cz-POF-3		1927	1.35	273	210[b]	[315]
Cz-POF-4		914	0.60	273	121[b]	[315]
PON-1		1447	1.0	195/298	976/109[c]	[316]
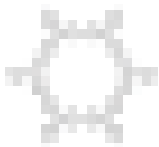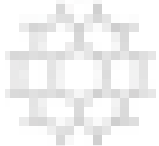
PON-2		189	0.83	195/298	482/34[c]	[316]
PON-3		44	0.09	195/298	525/37[c]	[316]
P-1		611	0.95	273	8.9[d]	[144]
P-2		1222	1.55	273	14.5[d]	[144]
P-TCzPhSi		1856	1.7	273	23.5[d]	[317]
P-TCzTAT		1028	0.76	273/298	18.15/10.69[d]	[318]
P-BCz		640	0.85	298	9.27[d]	[319]
P-TCz		1109	1.31	298	16.02[d]	[319]
P-HCz		790	1.20	298	9.41[d]	[319]
TEPO-1		485	0.82	273/298	6.52/3.65[e]	[320]
TEPO-2		534	0.30	273/298	7.62/3.93[e]	[320]
TEPO-3		592	0.30	273/298	8.40/5.33[e]	[320]

237
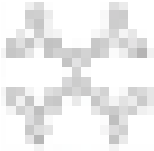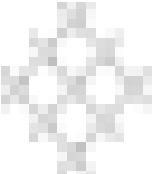
ThPOP-1		1050	0.69	273	15.0[e]	[147]
ThPOP-2		160	0.27	273	4.0[e]	[147]
NCMP1		58	0.15	273/298	6.1/3.5[e]	[293]
NCMP2		280	0.30	273/298	8.2/4.4[e]	[293]
NCMP3		485	0.57	273/298	11.0/6.5[e]	[293]
PCTF-1		2235	1.56	273	44.9[f]	[241]
PCTF-2		784	0.38	273	24.2[f]	[241]
CMP-LS1		493	0.32	273/298	31/17[f]	[321]
CMP-LS2		1576	1.06	273/298	87/47[f]	[321]
CMP-LS3		643	0.37	273/298	42/24[f]	[321]

[a] CO_2 uptake (mg cm^{-3}) at 101 kPa; [b] CO_2 uptake (cm^3 g^{-1}) at 30 bar; [c] CO_2 uptake (mg g^{-1}); [d] CO_2 uptake (wt. %) at 1.1 bar; [e] CO_2 uptake (wt. %); [f] CO_2 uptake (cm^3 g^{-1}).

1

Table 4

Summarizes CMP materials as a platform for metal-ion batteries
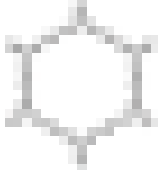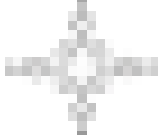
CMPs	molecular structure	S_{BET} $(m^2\ g^{-1})$	V_{total} $(cm^3\ g^{-1})$	CR/CN	RC/rate	CE%	Ref.
Lithium-ion batteries							
PDCzBT		1166	0.7	312/400 (200 mA g^{-1})	215/500	>98 (10th)	[333]
HATN-CMP		616	0.63	61.9%/50	147/100	100 (50th)	[76]
NG-HCP		72.56	0.2548	76.9%/230	1320/20	100	[334]
PTDATA		560.58	–	98.2/100 (20 mA g^{-1})	125.4/50	95 (45th)	[74]
PTPAn		11	–	93%/50	81/50	92	[335]
PTTPAB		595	0.13	96%/150	84/50	98	[335]
HATNPF1		384	0.27	92%/1200	312.5/100	100	[336]
PBIM		711	0.317	807/ (0.05C)	1172/50	99.2 (60th)	[337]
PTTE		312	–	80.8%/100	834/200	46 (initial)	[338]
PT		13	0.07	90/1000 (500 mA g^{-1})	141/3000	–	[75]
P33DT		696	0.53	79.9%/1000	387/5000	43.1 (initial)	[75]

PTPADTz		~657	–	95/20 (20 mA g^{-1})	80/50	–	[339]
NGA-CMP400	–	521.3	0.31	701.2/500 (1 A g^{-1})	874.3/100	46.6 (initial)	[340]
IEP-11-E12		2000	–	90%/5000	47/30C	100	[341]
TzThBT		406	–	326/1500 (5 A g^{-1})	1599/50	100 (500th)	[342]
Sodium-ion batteries							
PDCzBT		1166	0.7	119/200 (50 mA g^{-1})	145/20	>96 (15th)	[333]
PYT-TABQ/ rGO	–	–	–	98%/1400	245/200	>92 (initial)	[343]
ALP-8		550	–	90%/150	180/0.3C	96 (150th)	[344]
PTTE		312	–	88.1%/50	326/50	100 (100th)	[338]
Potassium-ion batteries							
PyBT		493	–	272/500 (50 mA g^{-1})	428/30	99.5 (500th)	[345]
PI-CMP		110	–	60.2%/200	–	–	[346]

CR: capacity retention (mA h g^{-1}); CN: cycle number; RC: reversible capacity (mA h g^{-1})/rate: current density (mA g^{-1}); CE: coulombic efficiency.
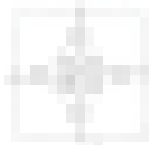
2

Table 5

Conductive CMPs for supercapacitors in recent years
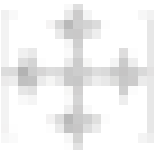
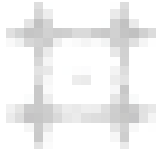| CMPs	Molecular structure	S_{BET} $(m^2\ g^{-1})$	V_{total} $(cm^3\ g^{-1})$	CD	SC	CR/CN	Electrolyte	Ref.
TAT-CMP-1		88	–	1	141	83%/10000	1.0 M Na$_2$SO$_4$	[416]
TAT-CMP-2		106	–	1	183	95%/10000	1.0 M Na$_2$SO$_4$	[416]
Zn-mTCPP		–	–	5	142	–	0.1 M Bu$_4$NPF$_6$	[189]
PYBDA		136	–	0.5	456	100%/2000	2 M H$_2$SO$_4$	[417]
H-CMP-BPPB		622	0.18	1	189	90%/10000	1 M H$_2$SO$_4$	[418]
Fc-CMPs/rGO	–	800.1	–	0.5	470	95%/8000	1 M H$_2$SO$_4$	[413]
PAQTA		331	–	1	576	85%/6000	0.5 M H$_2$SO$_4$	[412]
CAP-1		704	0.34	1	81	–	2 M KCl	[414]
CAP-2		594	0.38	1	240	~80%/10000	2 M KCl	[414]
PYT-TABQ/rGO	–	–	–	1	312.5	94.5%/10000	1 M Na$_2$SO$_4$	[343]
PTPA-25		33	–	0.5	335	65%/5000	1.0 M H$_2$SO$_4$	[419]
GH-CMP		219.2	–	0.2	208	92.6%/10000	1 M H$_2$SO$_4$	[415]

CD: current density (A g^{-1}); SC: specific capacitance (F g^{-1}); CR: capacity retention/CN: cycle number.

3

Table 6

CMPs or CMP derivatives for oxygen reduction reactions of fuel cells

CMPs	Molecular structure	S_{BET} $(m^2\ g^{-1})$	V_{total} $(cm^3\ g^{-1})$	E_{onset}	$E_{1/2}$	Electrolyte	Ref.
CoPEF		311	–	0.42	–	0.5 M H_2SO_4	[436]
ZnPcFePor-CMP		442	0.22	0.902	0.724	0.1 M KOH	[441]
FePcFePor-CMP	–	322	0.17	0.934	0.863	0.1 M KOH	[441]
FePcZnPor-CMP	–	404	0.22	0.936	0.866	0.1 M KOH	[441]
TPA-BP-1		468	–	0.80	–	0.1 M KOH	[442]
TPA-BP-2		117	–	0.82	–	0.1 M KOH	[442]

CMP derivatives	CMP precursor	Molecular structure[a]	S_{BET}[b] $(m^2\ g^{-1})$	V_{total}[c] $(cm^3\ g^{-1})$	E_{onset}	$E_{1/2}$	Electrolyte	Ref.
Fe/Co-CMP-800	Fe/Co-CMP		372	–	0.88	0.78	0.5 M H_2SO_4	[437]
N/S-2DPC-60	2DP-S		953	0.80	0.86	0.75	0.1 M KOH	[443]
HPC-Fe/N-700	HCMP-Fe		518	–	0.92	0.84	0.1 M KOH	[438]
N-Fc-800	Fc-melamine-POP		511	–	0.96	0.82	0.1 M KOH	[444]

| CoNCs800 | CoPc-CMP | | 59.8 | – | 0.905 | 0.807 | 0.1 M KOH | [445] |
| CoO/ZnO@N-PC | ST-CMP | | 1236 | 0.68 | 0.91 | 0.85 | 0.1 M KOH | [440] |

E_{onset} for onset potential (V vs. RHE); $E_{1/2}$: half-wave potential; [a] molecular structure of precursor; [b, c] BET surface area, and pore volume of CMP derivatives.

Supplementary Material

Click here to access/download

Supplementary Material
3. 20-055-R0-refs-edt-revised by ZengGM and LuoSH.docx

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: