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Review

Environment-friendly fullerene separation methods

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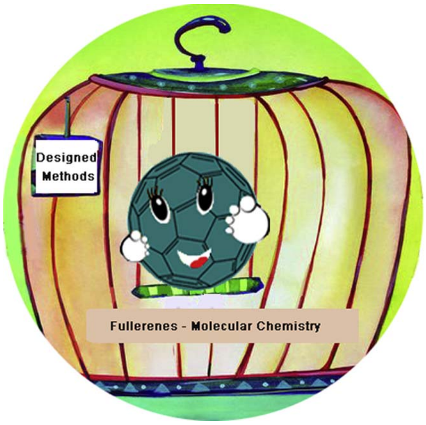
GRAPHICAL ABSTRACT



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ABSTRACT

The unique physicochemical properties of fullerenes are to a great extent determined by their purity. Pure fullerenes separated from fullerene soot are currently promising nanomaterials for versatile potential applications. But there are few efficient methods to obtain fullerenes in pure form, most of fullerene properties remain unclear. To gain their optimal properties in potential applications, more efficient methods to separate pure fullerenes are supposed to develop. One of the most active researches in fullerene separation is to find suitable receptors to bind fullerenes and then release them through host–guest interactions based on supramolecular chemistry to obtain pure products. So this review highlights the recent advances in the design of molecular receptors that feature corresponding size, shape or electronic complementary to fullerenes as the primary recognizing factor. The method using designed molecular receptors for fullerene separation here is called as selective complexation technology. And some designed polymers that can be used as supports to achieve fullerene selective separation via reversible Diels-Alder addition are also described. Besides, other two common practical separation methods, improved chromatography and fractional crystallization, are presented. All separation methods mentioned in this review can achieve selective fullerene separation with recycling process and no special equipment, which conform to the requirement of environment friendly development in 21st century. Each method has its own characteristic depending on the applied fields. Our purpose is to show the readers

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Abbreviations: AC, activated carbon; CVD, chemical vapor deposition; DA, Diels-Alder; DCE, 1,2-dichloroethane; exTTF, 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole; MIL, Matérial Institut Lavoisier; MOFs, metalorganic frameworks; MTN, Mobil Thirty-Nine; ST, super tetrahedron; TFA, trifluoroacetic acid; TMB, 1,2,4-trimethylbenzene; TTF, tetrathiafulvalene

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efficient designed methods exploitable for scalable preparation of high-quality pure fullerenes and stimulate their boarder potential applications.

1. Introduction

Fullerenes were discovered in the process of vaporizing graphite via laser irradiation by Kroto in 1985 [1]. These spherical carbon cages are built up of carbon atoms with sp^2 hybridization to form an extended π-system. The building principle of fullerene C_n is based on Euler's theorem, which says that 12 pentagonal rings are required for the closure of each ball-shaped network of m hexagons, such that $m = (C_n - 20)/2$ [2]. All the dihedral angles deviate from planarity (142 and 138 degrees) and this phenomenon allows fullerenes to change the shape in a sphere [3]. One of the most prominent properties of fullerenes is their excellent ability to play a key role in arrays, conjugates, and hybrids of electron donor–acceptor system [4]. Fullerenes are so chemically reactive that they can associate with most of organics or inorganics to generate new compounds with expected physicochemical properties [2,5]. Thus, as soon as they were available from fullerene soot, fullerenes were widely studied in various fields [6–8]. The increasing interest in fullerene chemistry leaded to the appearance of numerous researches in multiple disciplines. As shown in Fig. 1, the annual number of fullerene-related journal publications (according to Web of Science™) maintains rapid growth during the decades from 1990. Until now, fullerenes have been applied in many different researching fields, such as supercapacitors [9], hydrogen storage [10], nanoelectronics [11], solar cells [12] and biomedical applications [13]. And as a carbon nanomaterial, fullerenes can be applied in controlling environmental problems, such as heavy metal ion pollution [14,15], organic pollution [16–20] and other environmental pollution [21], which are currently treated by many other complicated methods [22,23]. Among them, the application of fullerenes in biomedicine attracted most attentions [24]. The size of fullerenes (7–10 Å in diameter) is similar to many biological active molecules and unique cage configuration coupled with extensive space for derivatization, which endows them with the potential to be biologically active variants (e.g. free radical scavenger, enzyme/protein blocker or antimicrobial action) [25–27]. These potential applications result in that fullerenes are considered as building blocks for today's nanotechnology.

However, most of fullerene researches and applications are limited by the complicated and costly technologies for large-scale production of fullerenes with high purity extent. That may be the reason why the number of fullerene-related journal publications goes down in nearly three years (Fig. 1). Large-scale synthetic route of fullerenes tends to promise their extremely high chemical and practical value. The foremost preparative method used to synthesize and isolate fullerenes is to vaporize graphite with resistive heating in the arc plasma under low helium pressure [6,28]. It is not an efficient method, because of the low yield of fullerenes with high purity and the requirement of harsh reaction conditions, like high temperature (~1600 K). To reach much larger fullerene synthesis, Churilov and co-workers presented another method to control the yielding process in the high-frequency arc plasma via changing the helium pressure and elaborated on the influence of arc temperature and electron concentration on fullerene formation in a plasma [29,30]. Besides, many other various methods have been proposed to synthesize and purify fullerenes, such as vaporization of a carbon source, chemical synthesis and synthesis of reactive precursors [31–33]. Among all these methods, arc discharge is one of the most widely used method, but it is difficult to control the reaction proceeding owing to the intense discharge process and the synthesized products contain many impurities [29]. Thermal vaporization uses graphite or specific materials with high content of carbon, like coal, as raw materials to synthesize fullerenes with carbon atoms vaporizing from raw materials at a very high temperature and then reacting to be carbon clusters to generate fullerenes in the environment of inert gas [34,35]. Chemical vapor deposition (CVD) is a typical method for fullerene synthesis with simple process, which can be used for macro production. But actually, CVD is generally used for the production of fullerene-related material, carbon nanotubes [36]. As for benzene flame synthesis, the main manipulation is the combustion of high-purity graphite rod in mixed diluted benzene and oxygen, and it is worth noting that the ratio of fullerenes C_{60} and C_{70} in products can change by controlling the reaction temperature, pressure, the ratio of carbon atoms and oxygen atoms, and residence time of flame [37].

Although fullerene synthesis process has been mature with the deeper research in fullerene science. But in fullerene separation, it is difficult to achieve selective separation owing to the tiny difference in their nanoscale size and similar physicochemical properties [38]. There are several categories of fullerenes according to the number of carbon atoms. Fullerenes C_{60} are the smallest stable and almost abundant fullerene molecules, followed by C_{70} and other higher fullerenes (C_n, $n > 70$) [39]. The raw fullerene products consist of fullerene fractions and some by-products that are hardly separated. The primary separation methods are sorted to chromatographic technology and non-chromatographic technology [40–42]. Traditional chromatography has some basic disadvantages: (i) limit in column loadings, (ii) time-consuming process, (iii) irreversible adsorption, (iv) requirement of lots of stationary phases and mobile phases. Non-chromatography also has some limits, like the requirement of prolonged stir and repeated precipitation–filtration manipulations. As a result, the method to achieve efficient fullerene separation with high-purity still remains elusive. Therefore, to obtain fullerenes in high pure form, efficient methods for large-scale fullerene selective separation are in demand with reversible manipulation as a key element to achieve sustainability of fullerene separation process. This review elaborates on the selective complexation (including using tailored macrocycles or supramolecular cage-like receptors), reversible Diels-Alder addition (with special polymer supports), improved chromatography and fractional crystallization. Common used methods to assess the sustainability offered by the recent improved methods were firstly discussed. Then the breakthroughs in industrial production or academic technology for further sustainable advances were critically reviewed.

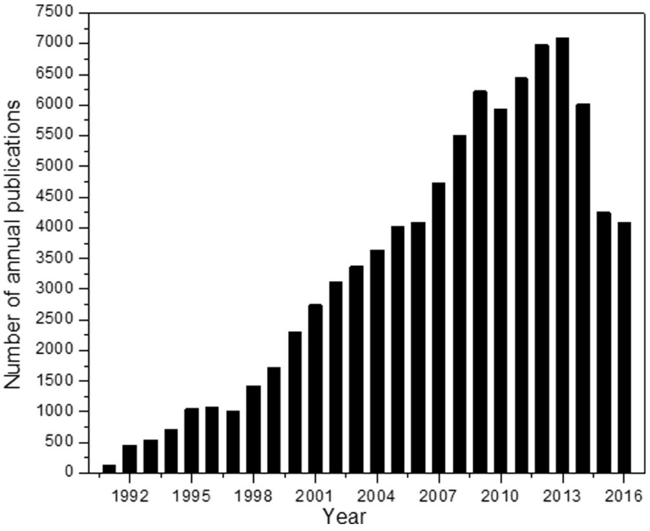

Fig. 1. Trends in annual publications of fullerene retrieved from Web of Science™ (all databases) by searching publications having "fullerene" in the topic on May 9th, 2017.

2. Selective complexation for fullerene separation through host–guest interactions

The properties of fullerenes as well as their application in the multiple research fields remain unclear mainly owing to their separation difficulties. The first seminal report of fullerene separation was built on the carbon soot controlled sublimation [43]. Recently, the strategy of designing appropriate molecular receptors for fullerene separation has attracted many researchers attention. Complementarity in size, shape, structure and electronic donor-accept relying on the interaction between molecular receptors and fullerenes is very important for fullerene recognition [44–47]. The interaction between receptors and fullerenes consists of covalent interaction and non-covalent interaction. And three energetic factors need to be considered when the non-covalent interaction is analyzed [48–50]:

(i) Van der Waals forces. They are based on the available surface area essentially, and relate to repulsion forces and dispersion and play a crucial role in the interaction between receptors and fullerenes. In addition, large extent of interactions are supposed to maximize van der Waals forces to form the stability and selectivity of adduct.
(ii) Electrostatic interactions. They are generated from the static charge distributions of the involved molecules. The curvature of fullerenes leads to an inside-outside polarization and the margin relatively electron is insufficient when faced with the inner.
(iii) Charge-transfer bands. They are found from a spectroscopic analysis about the supramolecular interactions and they are insignificant in terms of the stability of the receptor-fullerene adduct.

Complementarity used for molecular recognition is associated with point interactions, like metal–ligand coordination and hydrogen bonding. When dispersion forces play an outstanding role in the stabilization of adduct formed by designed receptor and fullerene, complementarity is a basic influencing factor. Perez and Martin presented the influence of bidimensional shape that square, octagon and circle showed approximately equal affinity while the hexagon became the weakest binder (Fig. 2) [3]. The method of host–guest allows gaining selectivity and lead towards fullerene separation by host–guest interactions. This provides a promising methodology to overcome the difficulties of fullerene separation and obtain sustainable advances in fullerene science with a reversible way. Therefore, we specify marcrocycles and cage-like receptors for fullerene separation with a reversible process via complementarity and elaborate on both their benefits and intrinsic drawbacks.

2.1. Designed receptors for fullerene separation through covalent chemistry

2.1.1. Azacrown compounds receptor decorated with Lipophilic fragments

This section explains the macrocyclic examples of the N-alkylated hexaazacrown compound and the acylated octaazacrown compound. Joehem et al. [51] presented two azacrown compounds, the alkylated hexaazacrown compound and the acylated octaazacrown compound. They are the first synthetic and intentionally designed receptors (14–18 Å in diameter) used to associate with fullerene to form a 1:1 host–guest adduct. All curves of the compounds are reproducible and the connection between azacrown compound and fullerene exhibits a stabilizing effect. Though the diameter of the acylated octaazacrown compound is larger than the alkylated hexaazacrown compound, the collapsed area of the acylated octaazacrown compound becomes slightly higher at the air–water interface when the fullerenes are present, which did not occur on the alkylated hexaazacrown compound. Besides, the alkylated hexaazacrown compound shows similar adsorption to C_{60} and C_{70}. The host–guest adduct is formed when transferred the mixture of the compound and C_{60} at the surface pressure of 25 mNm^{-1} and decomposed when adduct is transferred at 5 mNm^{-1}. And the similar method can be used for the reversible association-dissociation of C_{70}. This demonstrates the release of fullerene as well as facilitates the separation of C_{60} or C_{70} from higher fullerenes. However, there exists an apparent drawback that this example is unable to separate C_{60} and C_{70} in an efficient way. Fig. 3 reveals the whole process of N-alkylated hexaazacrown compound and the acylated octaazacrown compound for fullerene separation.

2.1.2. Anion-triggered binding covalent organic Macrocycle

The examples of pyrrole-based macrocyclic receptors are scarce. Herein we elaborate on the tetrathiafulvalene (TTF)-calix[4]pyrrole composite [52]. It is synthesized via using excessive trifluoroacetic acid (TFA) to treat the monopyrrolo-TTF in a mixed solution of 1.2-dichloroethane and Me_2CO. When lacking anions, TTF electron donors adopt electron-deficient guests is likely to be in a sandwich through the process of charge transfer [53], whereas there exists a problem that the interaction between the receptor in 1,3-alternate conformation and C_{60} is very weak. Adding an excess of anions to TTF-calix[4]pyrrole can solve the problem. Owing to the mutual attraction between TTF-calix[4]pyrrole and chloride anion, the 1,3-alternate conformation can be translated to the cone conformation after adding chloride anions. The binding between TTF-calix[4]pyrrole composite and chloride anion in 1,2-dichloroethane (DCE) at room temperature is very strong with an association constant up to $2.5 \times 10^6\ M^{-1}$, and the resulting cone conformation was expected to be an excellent receptor for fullerenes [54]. TTF-calix[4]pyrrole shows excellent electronic complementarity for fullerenes because it is a well-known electron acceptor while fullerene is an electron donor. That TTF-calix[4]pyrrole associates with fullerene in a 2:1 ratio can form a stable adduct. Notably, there is a perceptible change in the color of the solution in the association process. A solution of TTF-calix[4]pyrrole composite in an acidic mixture of CH_2Cl_2 and Me_2CO reveals yellow. The translation between the 1,3-alternate conformation and the cone conformation does not change the color of the solution. However, when adding 0.5 equivalents of C_{60} mixed in CH_2Cl_2, the color turns green. Additionally, it is easy to achieve the release of fullerene from TTF-calix[4]pyrrole-fullerene adduct by controlling the adding amount of chloride anions. Fig. 4 shows the whole process of TTF-calix[4]pyrrole receptor for fullerene separation.

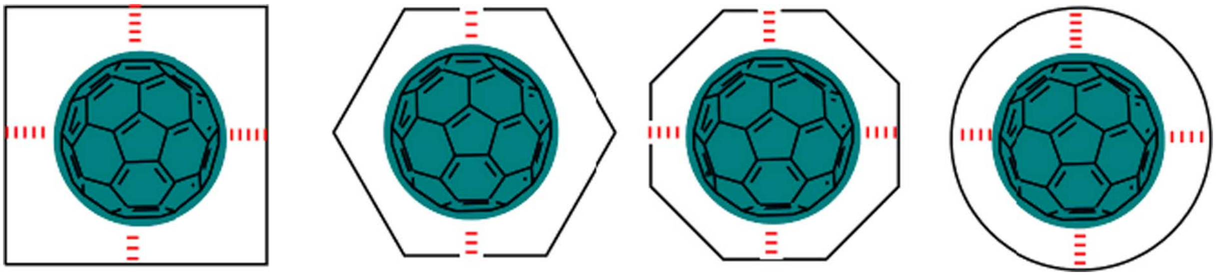

Fig. 2. The influence of bidimensional shape. Square, octagon and circle showed approximately equal affinity while the hexagon became the weakest binder. Reproduced from Ref. [3].

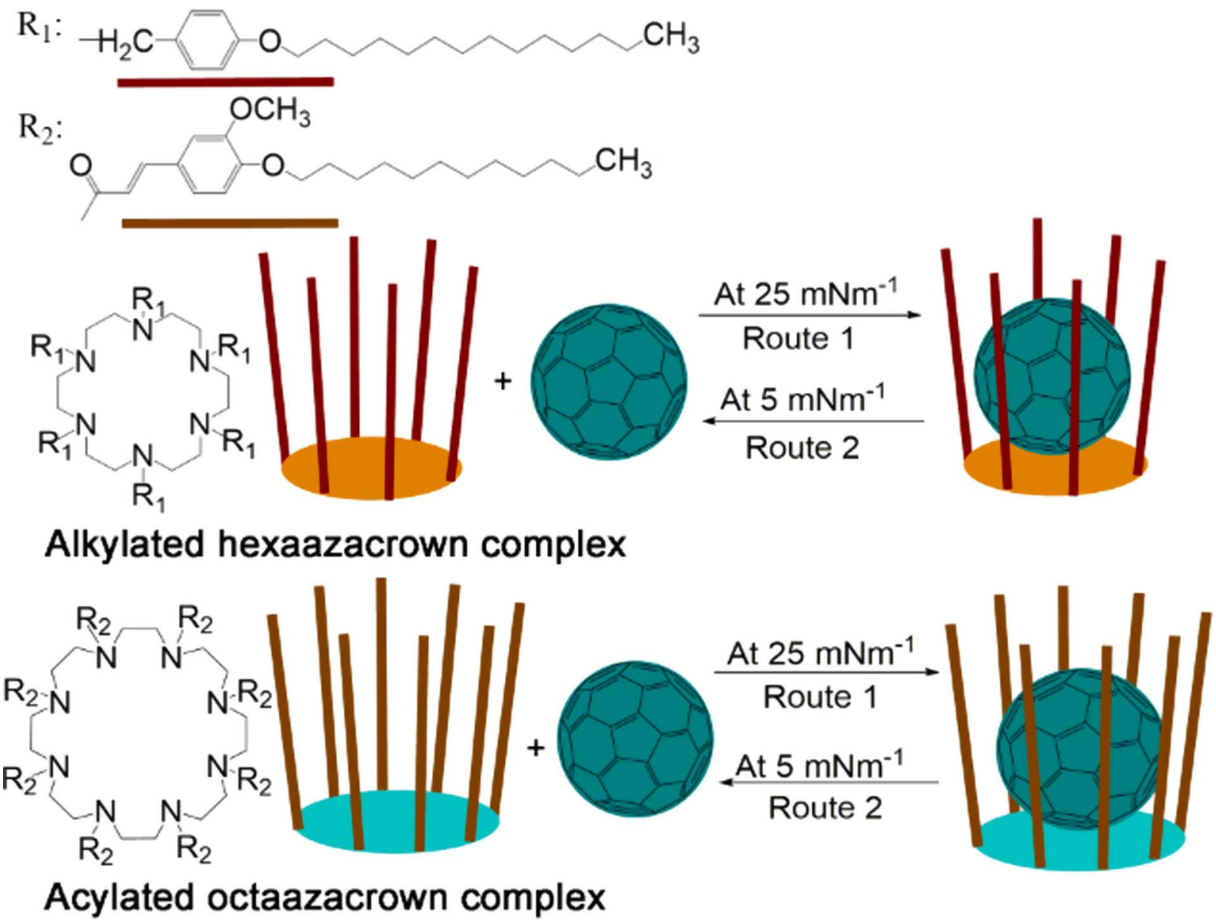

Fig. 3. Reported strategies of fullerene encapsulation with two types of azacrown complexes and release from the azacrown complex-fullerene adduct. Route 1 is fullerene binding and Route 2 is fullerene release. Reproduced from Ref. [51].

2.1.3. Porphyrin-based molecular receptors

Both Rowan's team [55] and Zhang's team [56] elaborated on dynamic covalent chemistry, which can transform those unexpected oligomeric and macrocyclic kinetic intermediates into the most stable product in thermodynamics. Dynamic covalent chemistry like alkyne metathesis [57,58] or condensation can be used to synthesize an organic composite, which have been widely applied as a selective complexation agent to purify fullerenes because of their capability of interacting with fullerenes. Porphyrins have a favored donor–acceptor interaction with fullerenes, and there are many receptors containing porphyrin for encapsulating fullerene [59–61]. Herein we elaborate on three porphyrin-based molecular receptors – bisporphyrin macrocycle, triporphyrin macrocycle and porphyrin-based four-armed cage – as the examples synthesized via dynamic chemical chemistry for fullerene binding.

Bisporphyrin macrocycle is a covalent organic capsule in rectangular shape, synthesized from porphyrin-based diyne monomer via alkyne metathesis in one step with catalysis of multidentate Mo(vi) alkylidyne [62,63]. Although it is formed by highly rigid aromatic building blocks, it can associate with C_{60}, C_{70} and C_{84} with forming a 1:1 receptor-fullerene adduct. The characterization by UV–Vis titration reveals the highest affinity to C_{84} with high association constant ($K_a = 2.2 \times 10^7\ M^{-1}$), which facilitate the selective separation of C_{84} [63]. And the formed adduct can undergo a reversible association-dissociation manipulation by adding acid-base stimuli, which protonates the porphyrin ring and weaken the interaction between porphyrin and C_{84} (Fig. 5(a)).

Triporphyrin macrocycle contains three porphyrin moieties. The synthesis process of triporphyrin macrocycle is similar with bisporphyrin macrocycle, one-step cyclooligomerization via alkyne metathesis [64]. This synthesized triporphyrin macrocycle possesses a large internal cavity and reveals host–guest binding interactions with

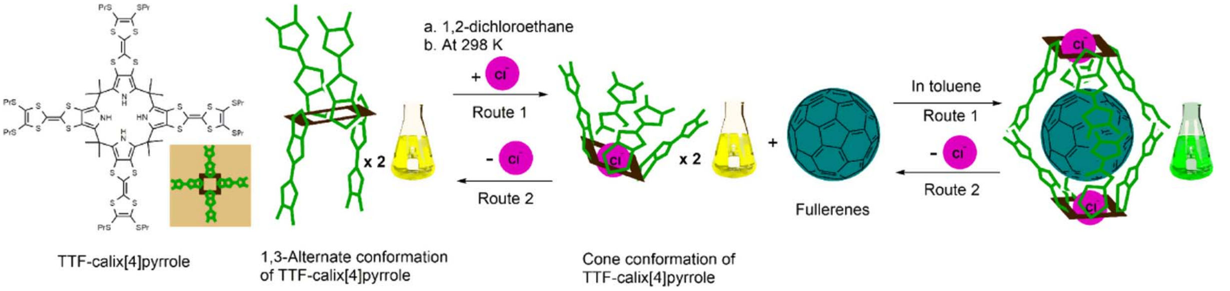

Fig. 4. Reported strategies of fullerene encapsulation with TTF-calix[4]-pyrrole receptor and release by controlling the amount of chloride anions. Route 1 is fullerene binding and Route 2 is fullerene release. Reproduced from Ref. [52].

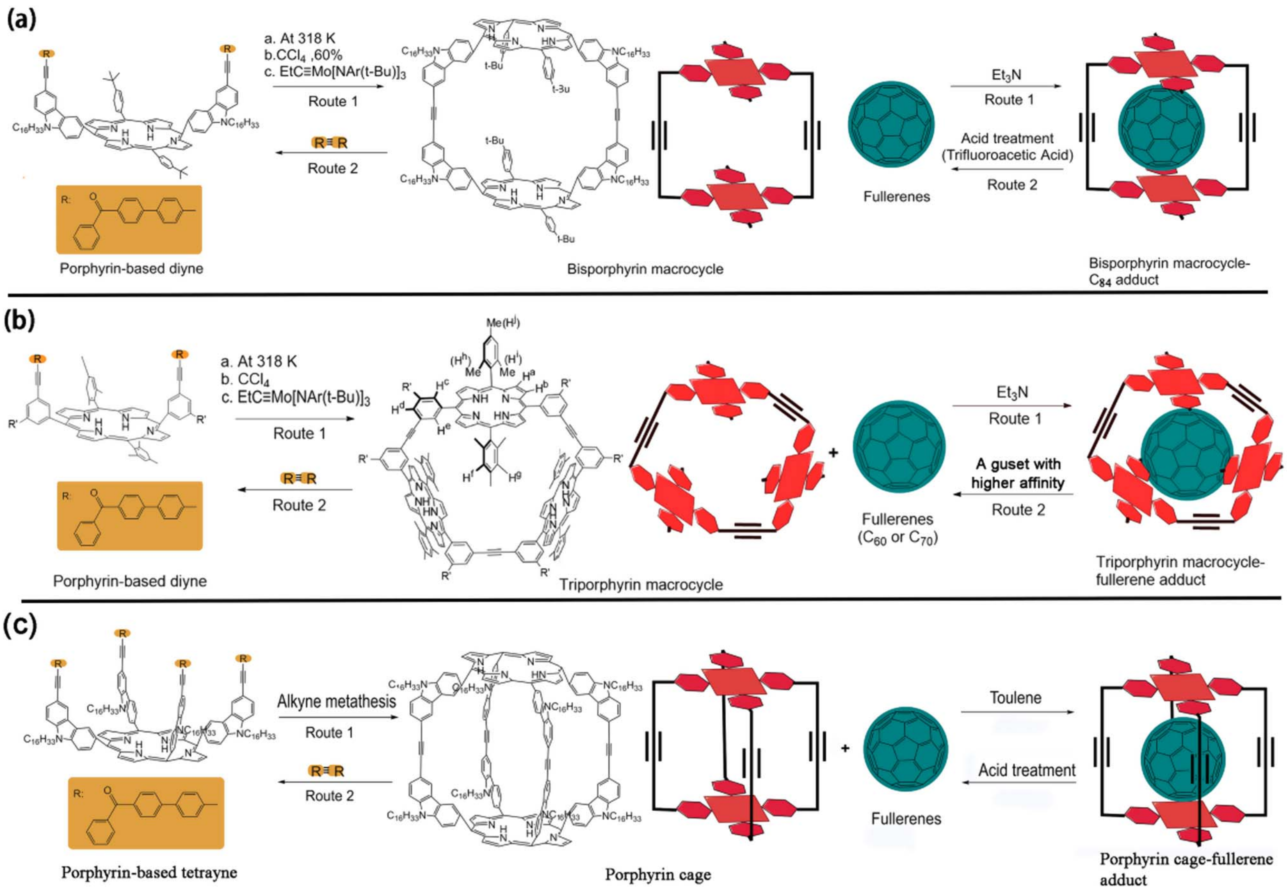

Fig. 5. (a) Reported strategies of fullerene encapsulation with bisporphyrin macrocycle and release by acid treatment. Reproduced from Ref. [63]. (b) Reported strategies of fullerene encapsulation with triporphyrin macrocycle and release by adding a more suitable guest. Reproduced from Ref. [64]. (c) Reported strategies of fullerene encapsulation with porphyrin cage and release by the acid treatment. Route 1 is fullerene binding and fullerene Route 2 is fullerene release. Reproduced from Ref. [66].

fullerene molecules. It shows higher affinity to C_{70} than C_{60}, but no binding with C_{84}. And because the binding affinity between triporphyrin macrocycle and fullerene C_{70} is just $6 \times 10^3\,M^{-1}$, fullerene molecules can be released from this triporphyrin macrocycle easily by finding a guest with a higher affinity (Fig. 5(b)).

Porphyrin-based four-armed cage possesses two porphyrin moieties, associated by double identical rigid spacers with bisporphyrin macrocycle. Compared with bis- and tri-porphyrin macrocycles, porphyrin-based four-armed cage shows higher affinity to C_{70} than other fullerenes. There is an efficient photoinduced electron transfer between porphyrin-based four armed cage and C_{70} [65]. This demonstrates that transforming the conformation of the porphyrin-based receptors can tailor their selectivity for fullerene binding. The association constant for the porphyrin-based four-armed cage combining with C_{70} ($K_a = 1.5 \times 10^8\,M^{-1}$) is 3 orders of magnitude higher than C_{60} ($K_a = 1.4 \times 10^5\,M^{-1}$) [66]. This huge gap facilitates the efficient separation of C_{70}. Additionally, the encapsulated fullerene can be released from porphyrin-based four-armed cage via TFA treatment. The interaction is reversible by adjusting the pH of the reaction (Fig. 5(c)), which is because the protonation of the non-metallo-porphyrin by TFA weakens the interaction via reducing porphyrin electron-donating ability.

Among these three porphyrin-based molecular receptors, porphyrin-based four-armed cage possesses the highest affinity to fullerene C_{70} ($K_a = 1.5 \times 10^8\,M^{-1}$), bisporphyrin macrocycle shows highest affinity to fullerene C_{84} ($K_a = 2.2 \times 10^7\,M^{-1}$), and the triporphyrin macrocycle reveals the least affinity to fullerene ($K_a = 6 \times 10^3\,M^{-1}$). This is because the difference in the size, shape, structure and electronic donor-accept complementarity between these porphyrin-based molecular receptors and special fullerenes (C_{60}, C_{70} or C_{84}). In fullerene release process, it's notable that for both bisporphyrin macrocycle and porphyrin-based four-armed cage, adding plenty of triethylamine to the mixture of protonated porphyrin-based receptors and free fullerenes at the last can neutralize the porphyrin ring and regenerate host–guest adduct, and this acid-base-mediated association-dissociation of porphyrin-based receptor-fullerene adduct can be recycled many times.

2.1.4. *Concave π-extended TTF derivatives receptor*

TTF and its derivatives are excellent electron donors, which provide possibilities for designing new macromolecular and supramolecular receptors [67–70]. Perez and co-workers [71,72] found that the connection between 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9*H*)-ylidene]-1,3-dithiole (exTTF) and fullerene is strong non-covalent interaction, thus a tweezer-like receptor was designed for fullerene separation. The tweezer-like receptor can be synthesized in excellent yield by the covalent connection of two exTTF units serving as recognizing units with an isophthalate diester serving as an adequate spacer. The receptor shows a special solvent-controlled positive homotropic connective binding behavior.

The formed host–guest adducts perform different structures which depend on the reaction solvent and the ratio of exTTF-isophthalate diester receptor and fullerene in stoichiometry. In the case of chlorobenzene solvent at room temperature, mixing the receptor and fullerene forms adduct with the first structure. While in the other case of $CHCl_3$-CS_2 mixed solvent, the formed adduct exhibits the second structure or the third related to the amount of fullerenes, and the binding curve is in the shape of sigmoidal, which is considered as the standard for connection. The stability of adduct formed by exTTF-isophthalate diester receptor (concave, electron-rich) and fullerene (convex, electron-poor) depends on shape and electronic complementarity. The change of fullerene adsorption in the exTTF-isophthalate diester receptor can be explained with the Hill equation and the Hill coefficient (n_H), which reflects the extent of connection. The formation of host–guest adduct can be impeded in the value of $n_H > 2$, which featuring two binding sites only. Fig. 6 shows the whole process of exTTF-isophthalate diester receptor for fullerene separation. Soon after, Isla et al. [73] synthesized another efficient exTTF-based macrocyclic receptor that associates fullerene with micromolar affinity successfully, which possesses a binding constant $> 10^6\ M^{-1}$ to C_{60}.

2.2. Designed receptors for fullerene separation through coordination bonds

With the increase of designed receptors scale and sophistication, the synthetic strategies through covalent chemistry required more synthetic and separation efforts and then generally resulted in low production. Fullerene receptors based on coordination bonds allow the highly complex functional system to be formed in a simple way and with high production of pure fullerenes. Therefore, designed receptors that possess coordination bonds are used widely in fullerene separation and have undergone rapid development in recent years.

2.2.1. Coordination Metallosupramolecular Mercury-based cage containing π-extended moieties

The coordination metal ions based cage is self-assembled by mixing pyridine curved ligand (two anthracenes bound by m-phenylene) and metal ions in acetonitrile at room temperature [74,75]. Herein, we elaborate on an example of mercury (II) based cage, which adopt a tortile square planar geometry linked with four bent bispyridine ligands [76]. The π-extended moiety of the ligand provides an aromatic shell with an enclosed cavity (diameter up to 1 nm [77]) for strong interactions between mercury-ligands cage and fullerene. The enclosed cavity of mercury-based cage is large enough to encapsulate fullerene via π-stacking interaction. Additionally, mercury-based cage shows higher affinity to C_{60} than C_{70}, which facilitates the selective separation of C_{60}. As for the release of fullerene from the cage, it is related to the ratio of metal-to-ligand. Mixing mercury (II) and pyridine curved ligand can produce an intermediate, mercury tubular cage. Tubular cage is synthesized by mixing mercury (II) and pyridine curved ligand in acetonitrile in equivalent, but it does not show affinity to fullerenes. One tubular cage can be decomposed to double ligands and metal ions via utilizing light as the non-invasive stimulus. Otherwise, mercury-based cage is formed via mixing mercury (II) and pyridine curved ligand in a 2:1 ratio. Fast conversion between mercury-based cage and tubular cage can be obtained by controlling the metal-to-ligand ratio. Therefore, we can control the fullerene binding and release with mercury-based receptor in a simple and efficient way. And in particular, the selective separation process of C_{60} can be distinguished by the naked eye according to the change of color (Fig. 7): (i) The initial solution containing mercury-based cage in this step reveals colorless. (ii) The mixed solution after the interaction of the cage and fullerenes reveals blue-violet (Route 1). (iii) After adding 2 equivalents of $Hg(CF_3SO_3)_2$ to the blue-violet solution to remove C_{60} from the adduct in acetonitrile (Route 2), the color of solution turns pale yellow.

2.2.2. Metalloporphyrin-based coordination receptors

Recently, several reports presented a variety of methods to synthesize tetragonal prismatic coordination cages, which can be used for the selective extraction of higher fullerenes [78–81]. Herein we'll describe a coordination cage containing zinc metal ions designed by supramolecular metal-driven self-assembly. It is constructed from two dipalladium(II)-based macrocyclic synthons and four equivs of tetracarboxylate Zn^{II}-porphyrins [82]. Tetragonal prismatic coordination cage provides an enclosed cavity with a large porphyrin-porphyrin interdistance (about 14.1 Å) to encapsulate fullerenes. Fast interaction between the tetragonal prismatic coordination cage and C_{60} or C_{70} occurs after mixing in a 1:1 M ratio. The association constants, $K_a(C_{60}) \sim 3 \times 10^7\ M^{-1}$ and $K_a(C_{70}) \sim 4 \times 10^8\ M^{-1}$, shows that the tetragonal prismatic coordination cage displays high affinity to fullerenes.[82] And there is an adaption in the distance (14.1 Å) between Zn^{II}-porphyrins when the cage encapsulates fullerene. The crystallographic data shows that the encapsulation of C_{60} compresses the distance down to 13.1 Å while encapsulation of C_{70} shrank the distance to 13.7 Å. This proves that the tetragonal prismatic coordination cage exhibits the potential to adjust its structure upon fullerene encapsulation, which reveals the possibility for encapsulating higher fullerene C_{84}. Interestingly, the inclusion complex of fullerenes can be formed via soaking solid capsule in a toluene solution of fullerenes [83]. Stirring the suspended solid capsule to form tetragonal prismatic coordination

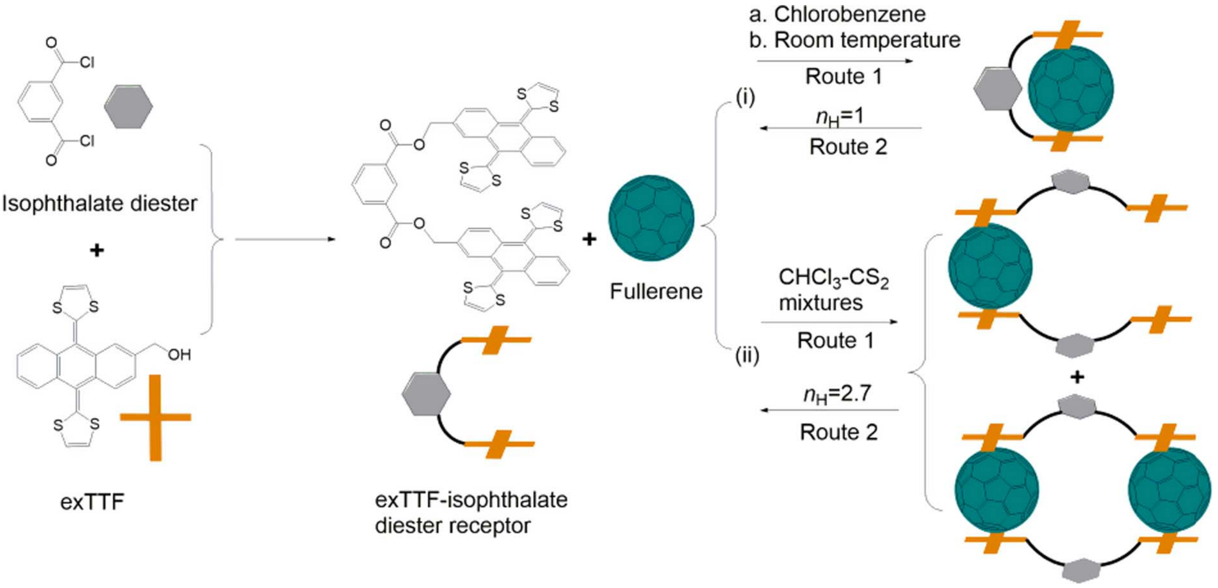

Fig. 6. Reported strategies of fullerene encapsulation with exTTF-isophthalate diester receptor and release from the receptor-fullerene adduct. Route 1 is fullerene binding and Route 2 is fullerene release. Reproduced from Ref. [71].

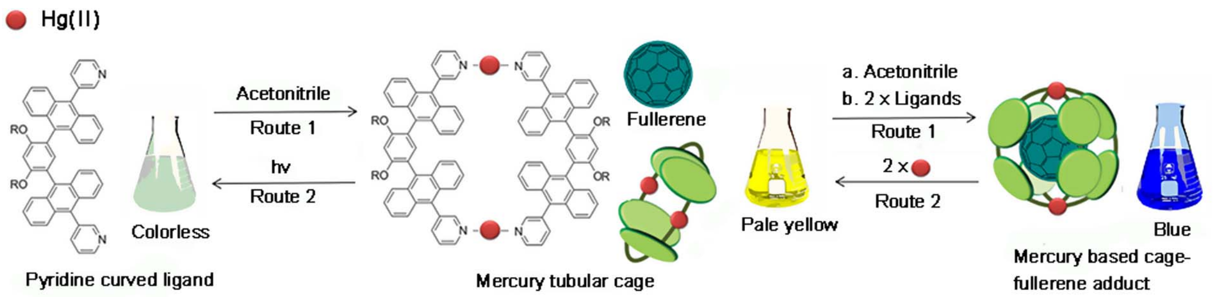

Fig. 7. Reported strategies of fullerene encapsulation with mercury-based cage and release after changing the metal-to-ligand ratio. Route 1 is fullerene binding and Route 2 is fullerene release. Reproduced from Ref. [76].

cage-fullerene adduct. The solid–liquid encapsulation strategy of fullerene within the cage demonstrates that fullerene presumably get into the cage via one of the four lateral apertures, which are big enough for fullerene to moving back and forth. Fullerene release can be achieved by solid washing strategy with appropriate washing solvent, which exhibits low solubility for tetragonal prismatic coordination cage and high solubility for fullerene. Notably, the pure empty cage in the solid remaining can be recovered by dissolving it in acetonitrile and can be reused to encapsulate fullerenes with high efficiency. The reversible process of fullerene encapsulation within the tetragonal prismatic coordination cage is revealed in Fig. 8.

3. Fullerene separation based on reversible Diels-Alder addition

Another alternative to efficient fullerene separation procedures is to attach fullerenes to suitable polymer supports based on reversible Diels-Alder addition. In 1994, Guhr et al. [84] presented a reversible covalent attachment of fullerene to peptide resin. This process requires an intermediate product, cyclopentadiene-functionalized compound, which is synthesized by mixing peptide resin in toluene with excessive sodium cyclopentadienylide. To provide a control system for researching fullerene binding, Guhr synthesized an ether-containing compound from the reaction of peptide resin and sodium ethoxide in the same reaction condition. Both peptide resin and ether-containing compound show little or no affinity to C_{60}. In contrast, C_{60} can be combined rapidly to cyclopentadiene-functionalized compound via DA reaction by generating a fullerene substituted material. This fullerene-substituted material is thermolabile and consequently the decomposition can be done via heating. Concrete manipulation is to heat the mixed C_{60} conjugate in decalin solvent in the absence of maleic anhydride (on the basis of C_{60} content). This proves that the connection between cyclopentadiene-functionalized compound and fullerene C_{60} is a reversible association-dissociation process (Fig. 9).

Soon after, Nie and Rotello [85] raised a similar reversible method that attaching special fullerene to a cyclopentadiene-functionalized silica support. Cyclopentadiene-functionalized silica gel, produced by the connection of chloropropyl-functionalized silica gel and lithium cyclopentadienylide, can bind C_{60} and C_{70} via DA addition to form fullerene-substituted material rapidly. Cyclopentadiene-functionalized silica gel shows higher affinity to C_{60}, which facilitates the selective separation of C_{60} from the mixture with C_{70}. Furthermore, such diene-based materials can be used to separate fullerene C_{60} and C_{70} from other polycyclic aromatics. Decomposition of this fullerene-substituted material can be achieved via heating because of its thermolability. Notably, the complete binding and release process (Fig. 10) can be fully reversible without loss of fullerene capacity.

This section elaborates on a method used for selective fullerene separation through covalent attachment of fullerenes to a polymer support. This covalent attachment based on DA cycloaddition is reversible, and this method allows the recovery of fullerenes upon heating process because of the thermolability of the formed fullerene-substituted maetrials. However, optimization of the method bassed on reversible DA addition and its application to fullerene separation in a large scale need a furhter study.

4. Improved chromatographic method

To isolate pure fullerene, current primary used method is chromatographic technology. The original chromatographic method used for purifying fullerenes C_{60} and C_{70} utilizes neutral alumina and hexane or toluene as the stationary phase and mobile phase, respectively [86,87]. A variety of simple and inexpensive traditional chromatographic methods had been presented to achieve the separation of gram quantities of fullerenes C_{60} and C_{70} [88–91], and herein we focus on two methods.

4.1. A new filtration method with AC as the stationary phase

Komatsu et al. [92] raised a practical method that make the solution of fullerene extract pass through thin layer of activated carbon (AC) to alumina that is used as the stationary phase. This process is based on the π-π interaction between fused aromatic rings, which immobilize

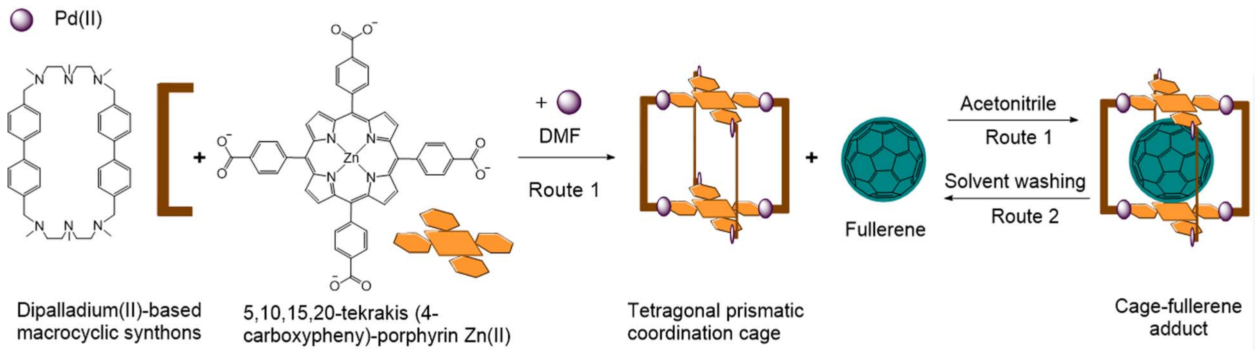

Fig. 8. Reported strategies of fullerene encapsulation with tetragonal prismatic coordination cage and release after solid–liquid solvent washing. Route 1 is fullerene binding and Route 2 is fullerene release. Reproduced from Ref. [82].

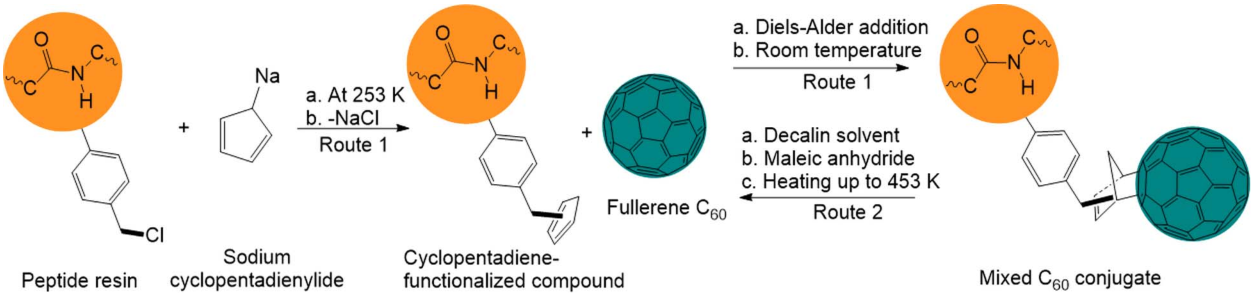

Fig. 9. Reported strategies for fullerene separation via reversible DA addition with cyclopentadiene-functionalized compound. Route 1 is fullerene binding and Route 2 is fullerene release. Reproduced from Ref. [84].

fullerenes in AC pores. The efficiency of separation is related to the diameter of AC pores. Those with diameter (1.0–2.0 nm) a little larger than the size of fullerenes (7.1 Å $< C_n <$ 10 Å) are considered to discriminate fullerene molecules. Besides, different kinds of solvent and the amount of AC can also influence the efficiency of separation. The result of Komatsu's experiment displays that using 1,2,4-trimethylbenzene (TMB) as the solvent and controlling the ratio of AC and fullerene mixture being 4/7:1 in weight could achieve the optimal separation efficiency [93]. This method possesses several characteristics: (i) TMB extract can be directly utilized without any pretreatment and no requirement for post-treatment except concentration. (ii) TMB can recover after concentration and then be reused in cycle process without any additional treatment. Thus this method is inexpensive and efficient enough to achieve large-scale pure fullerene production.

4.2. Selective separation of fullerenes with metal-organic frameworks (MOFs) as the stationary phase

MOFs are a type of porous materials constructed by metal-containing (metal ions or clusters) nodes connected by organic ligands [94,95]. They possess very high specific surface area, adjustable sizes, exceptional pore volumes and acceptable thermal stability [96]. Owing to the semi-organic frameworks and these excellent properties, MOFs are suitable for adsorptive applications. Herein, we focus on the selective adsorption of higher fullerenes on MIL-101(Cr) (MIL, Matérial Institut Lavoisier). MIL-101(Cr) is a super tetrahedron (ST) with Mobil Thirty-Nine (MTN) zeotype structure, formed via the combination of inorganic trimers and organic 1,4-benzene dicarboxylates [97]. Inorganic trimers occupies ST's four vertices while 1,4-benzene dicarboxylates are located at the six edges (Fig. 11(a)). These STs are microporous and the synthesized framework consists of two kinds of mesoporous cages. The two mesoporous cages are delimited by 20 (internal free diameter of ~29 Å) and 28 ST (~34 Å), which are in a 2:1 ratio mixture. The smaller 20 ST cages only reveal pentagonal windows with a ~12 Å free opening, but the 28 ST cages reveal not only pentagonal but also hexagonal windows with a free aperture of ~14 Å by 16 Å (Fig. 11(b)). MIL-101(Cr) provides mesoporous pores, large pore windows, unique high surface area and excellent stability in framework and chemical property.

For these reasons, MIL-101(Cr) has be designed as a adsorbent for adsorbing fullerenes in a practical and efficient way [98]. The adsorption of fullerenes on MIL-101(Cr) at room temperature contains two phases, adsorption on surface and intraparticle or pore diffusion. Additionally, MIL-101(Cr) shows much higher affinity to C_{70} and especially higher fullerenes (C_n, $n \geq 76$) in comparison with C_{60}. This manner helps to achieve selective separation of C_{70} and higher fullerenes. Besides, desorption of fullerenes form MIL 101(Cr) is simple. Adding desorption solvent consisting of o-dichlorobenzene, p-xylene and toluene to MIL 101(Cr) under ultrasonication can get isolated fullerenes. And MIL-101(Cr) can recover after the desorption manipulation and reused for fullerenes selective separation (Fig. 11(c)). As a novel adsorbent, MIL-101(Cr) exhibits fast adsorption, simple desorption, high selectivity and renewability for the separation of C_{70} and higher fullerene.

Traditional chromatography has some basic shortcomings: (i) Column loadings are limited in the separation process. (ii) Long lasting process is time-consuming and needs amounts of attention. (iii) Adsorption of most fullerenes on the traditional adsorbent is irreversible. (iv) The process requires lots of stationary phases and mobile phases. Compared with traditional chromatography, improved chromatographic method tries to overcome these shortcomings. And current improved chromatography possesses four improved aspects: (i) more rapid production of special fullerenes (e.g. fullerenes C_{60} or C_{70}) in pure form, (ii) simpler operations, (iii) reversible adsorption–desorption of fullerene molecules on the improved adsorbent, (iv) less expensive manufacturing process. In short, improved chromatographic method is cost-effective and efficient enough to achieve large-scale pure fullerene production.

5. Fractional crystallization

A facile and low-cost approach to purify C_{60} and C_{70} mixture in gram quantities by fractional crystallization in CS_2 or o-xylene solution, and the experimental result showed that C_{60} was concentrated in the solid deposit while C_{70} was concentrated in the remaining mother liquid was presented [99]. Doome et al. [100] also presented a novel and cost-efficient approach for C_{60} separation through fractional crystallization process in 1,3-diphenylacetone, which is a solid at room

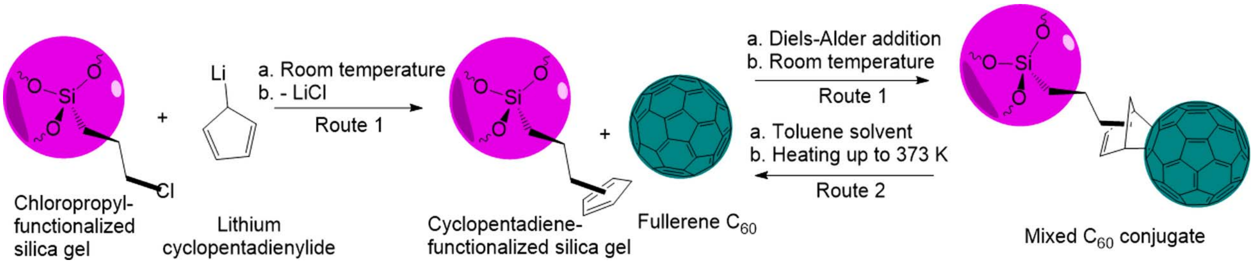

Fig. 10. Reported strategies for fullerene separation via reversible DA addition with silica-supported diene. Route 1 is fullerene binding and Route 2 is fullerene release. Reproduced from Ref. [85].

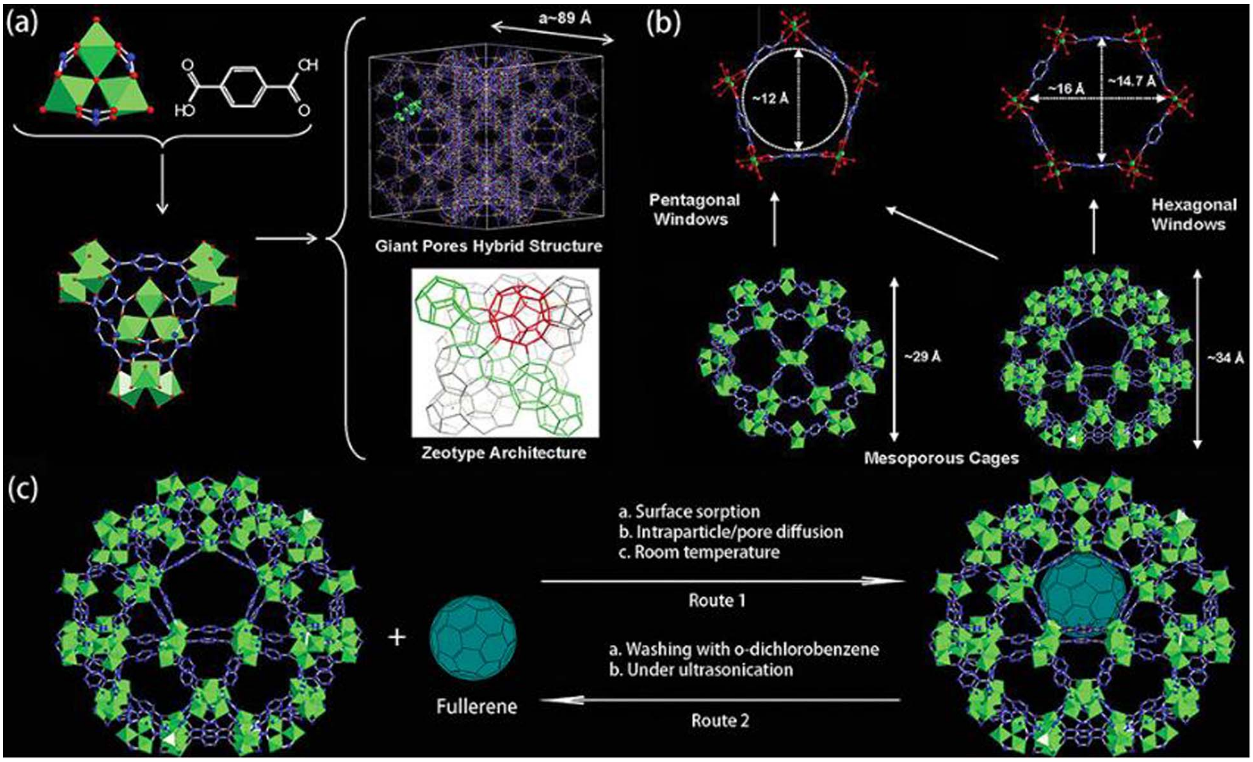

Fig. 11. (a) The synthesized process of MIL-101(Cr), and ball-and–stick representation of one unit cell, and MTN zeotype architecture schematic 3D representation. Carbon atoms, fluorine, oxygen, chromium octahedral are in blue, red, red, and green, respectively. (b) Pentagonal and hexagonal windows of MIL-101(Cr). (c) Adsorption and desorption of fullerene in MIL-101(Cr). Reproduced from Ref. [97]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

temperature but an excellent solvent mixed with 2% ethanol for C_{60} when heating up to 306 K. The key point of fractional crystallization is to extract C_{70} from the crude fullerene mixture into solution by differential dissolution. In this method, using charcoal to adsorb the residual C_{70} can increase the purity of C_{60}.

In general, the complete process of fractional crystallization includes three steps (Fig. 12): (i) Using solvent to dissolve the crude fullerene soot extract through sonication and adding special solvent to the dissolved solution and then stirring to mix well to dissolve C_{60} to a maximum extent. After dissolution, heating the mixed solution and then filtering through a microporous filter to get solid deposit A with high content of C_{60} and leave the mother liquid A with high content of C_{70}. (ii) Evaporating the mother liquid A to about 1/3 in volume, as a consequence, solid deposit B with high content of C_{60} and the mother liquid B with high content of C_{70} can be produced. (iii) Cooling the mother liquid B to get solid deposit C enriched in C_{70}.

The method of fractional crystallization utilizes the slight difference in chemical reactivity of various fullerenes (different in the number of carbon atoms) to achieve the separation. During the separation process, deposits of similar compositions from every procedure of crystallization can achieve a promotion effect. The characteristics of this method contain no losses because the solvent and all the remaining fullerenes can be recovered, no requirement for any special apparatus, easy scaling up, and the potential of being applied in successive production.

6. Conclusion and outlook

Since fullerenes were studied for > 100 years, they have remained the primary focus of many scientists in various fields. Fullerenes not only contributed to the exploration of other carbon nanomaterials like

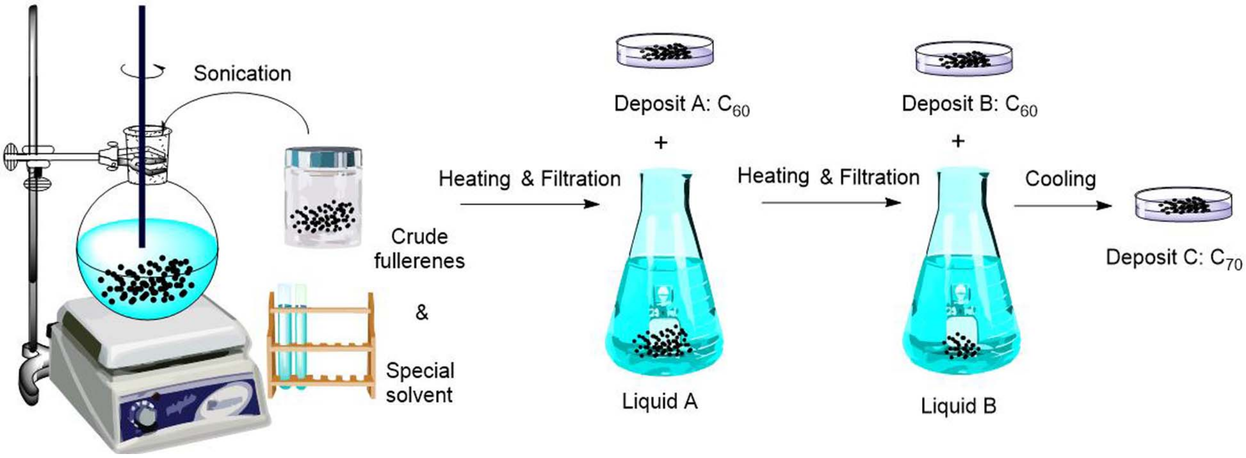

Fig. 12. Process of fractional crystallization.

carbon nanotubes [101] and graphene [102], but also facilitated the finding of many potential values such as the construction of novel composites and biomedical applications [103]. Though fullerenes are being a mature science, many properties ranging from fundamental synthetic aspects to chemical reactivity remain unknown for higher fullerenes (C_n, $n > 70$) because of the scarce efficient methods for fullerene separation with high purity. Large-scale synthesis and separation in a reversible way is still a significant challenge for fullerenes.

In this review, we present four efficient methods – selective complexation, reversible DA addition, improved chromatography and fractional crystallization – for fullerene separation through an environment-friendly way and highlight their sustainable development with recycling process. Selective complexation method with tailored receptors that feature excellent size, shape and electronic complementarity are highlighted. The key elements we need to consider when choosing suitable designed receptors are their tunability and the complementarity with fullerenes. These molecular receptors can bind and release fullerenes via reversible host–guest chemistry to achieve fullerene separation, and different bindings reveal diverse constants. Then we mentioned that using polymer support to bind fullerene via reversible DA addition, and fullerene release can be achieved by controlling the reaction temperature owing to the thermolability of the formed fullerene-substituted materials. But there are still some drawbacks in selective complexation and reversible DA addition method when they are used in industrial manufacturing. It is difficult to analyze the extent of reaction in the process because there is no visible phenomenon. And generally, many designed receptors used for fullerene separation form irreversible binding materials or the micro pores are blocked by secondary materials with higher affinity than fullerenes, which also happens to micro porous materials. So this trouble also exists in chromatographic method. The improved chromatographic techniques above are available for fullerene separation, especially using MIL-101(Cr) as the stationary phase. MIL-101(Cr) is a material with metal–organic framework, which is suitable to be used for fullerene separation. As for fractional crystallization, it is a more mature technology, which is facile and low-cost but time-consuming owing to the multiple crystallizations. Compared with reversible DA addition, improved chromatography and fractional crystallization, presumably the search for fullerene (supra-) molecular receptors goes on to be a focus of future research in fullerene separation.

In a word, many of the separation methods are in their early stage, especially selective complexation based on molecular chemistry through covalent bonds or coordination bonds. Inevitably, there exist some drawbacks in these separation methods. However, though the techniques of selective complexation, reversible DA addition, improved chromatography and fractional crystallization have some drawbacks waiting to be overcome, they are still available for the selective separation of fullerenes nowadays. At the same time, the more efficient method in an environment-friendly way is still in an urgent need. And it can be expected that fullerenes in pure form will be exploited in multiple fields. As large quantities of fullerenes reach our daily life, to find an applicable disposal procedure is what we need to do next. We are confident that this review will be a powerful resource to strengthen the efforts towards the finding of reversible produce process for fullerene sustainable advances and broaden the frontier of nanoscience and nanotechnology for many years to come.

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