Environment-friendly Fullerene Separation Methods 1

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8 Abstract: The unique physicochemical properties of fullerenes are to a great extent determined by their purity. 9 Pure fullerenes separated from fullerene soot are currently promising nanomaterials for versatile potential 10 applications. But there are few efficient methods to obtain fullerenes in pure form, most of fullerene properties 11 remain unclear. To gain their optimal properties in potential applications, more efficient methods to separate pure 12 fullerenes are supposed to develop. One of the most active researches in fullerene separation is to find suitable 13 receptors to bind fullerenes and then release them through host-guest interactions based on supramolecular 14 chemistry to obtain pure products. So this review highlights the recent advances in the design of molecular 15 receptors that feature corresponding size, shape or electronic complementary to following as the primary 16 recognizing factor. The method using designed molecular receptors for fullerene separation here is called as 17 selective complexation technology. And some designed polymers that can be used as supports to achieve fullerene selective complexation termology. The some designed portation are also described. Besides, ther two common practical 18 separation methods, improved chromatography and fractional crystallization are presented. All separation 19 20 methods mentioned in this review can achieve selective fullerene separation with recycling process and no special 21 equipment, which conform to the requirement of environment friendly development in 21st century. Each method 22 has its own characteristic depending on the applied fields. Our purpose is to show the readers efficient designed 23 methods exploitable for scalable preparation of high-quality pure fullerenes and stimulate their boarder potential 24 applications.

25 Keywords: Fullerenes; Host-guest interactions; Covalent chemistry; Coordination bonds; Recycle

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46 Abbreviations

47 AC, activated carbon; CVD, chemical vapor deposition; DA, Diels-Alder; DCE, 1,2-dichloroethane; exTTF, 2-[9-48 (1,3-dithiol-2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole; MIL, Matérial Institut Lavoisier; MOFs, metal-<u>4</u>9 organic frameworks; MTN, Mobil Thirty-Nine; ST, super tetrahedron; TFA, trifluoroacetic acid; TMB, 1,2,4-50 51 trimethylbenzene; TTF, tetrathiafulvalene.

1 1. Introduction

2 Fullerenes were discovered in the process of vaporizing graphite via laser irradiation by Kroto in 3 1985 [1]. These spherical carbon cages are built up of carbon atoms with sp² hybridization to form an 4 extended π -system. The building principle of fullerene C_n is based on Euler's theorem, which says that 12 5 pentagonal rings are required for the closure of each ball-shaped network of m hexagons, such that m = 6 $(C_n-20)/2$ [2]. All the dihedral angles deviate from planarity (142 and 138 degrees) and this phenomenon 7 allows fullerenes to change the shape in a sphere [3]. One of the most prominent properties of fullerenes is 8 their excellent ability to play a key role in arrays, conjugates, and hybrids of electron donor-acceptor 9 system [4]. Fullerenes are so chemically reactive that they can associate with most of organics or 10 inorganics to generate new compounds with expected physicochemical properties [2, 5]. Thus, as soon as 11 they were available from fullerene soot, fullerenes were widely studied in various fields [6-8]. The 12 increasing interest in fullerene chemistry leaded to the appearance of numerous researches in multiple 13 disciplines. As shown in Figure 1, the annual number of fullerene-related journal publications (according 14 to Web of ScienceTM) maintains rapid growth during the decades from 1990. Until now, fullerenes have 15 been applied in many different researching fields, such as supercapacitors [9], hydrogen storage [10], 16 nanoelectronics [11], solar cells [12] and biomedical applications [13]. And as a carbon nanomaterial, 17 fullerenes can be applied in controlling environmental problems, such as heavy metal ion pollution [14, 18 15], organic pollution [16-20] and other environmental pollution [21], which are currently treated by many 19 other complicated methods [22, 23]. Among them, the application of fullerenes in biomedicine attracted 20 most attentions [24]. The size of fullerenes (7 - 10 Å in diameter) is similar to many biological active 21 molecules and unique cage configuration coupled with extensive space for derivatization, which endows 22 them with the potential to be biologically active variants (e.g. free radient scavenger, enzyme/protein blocker or antimicrobial action) [25-27]. These potential applications result in that fullerenes are 23 considered as building blocks for today's nanotechnology.

24 25 26 27 28 29 30 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 (Figure 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 runerenes is to vaporize graphite with resistive heating in the arc plasma under low helium pressure [1, 28]. It is not an efficient method, because of the 31 32 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 33 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 34 formation in a plasma [29, 30]. Besides, many other various methods have been proposed to synthesize and purify fullerenes, such as reportation of a carbon source, chemical synthesis and synthesis of reactive 35 36 37 precursors [31-33]. Among all these methods, arc discharge is one of the most widely used method, but it 38 is difficult to control the relation proceeding owing to the intense discharge process and the synthesized 39 products contain many hupurines [29]. Thermal vaporization uses graphite or specific materials with high 40 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 41 42 the environment of inerr gas [34, 35]. Chemical vapor deposition (CVD) is a typical method for fullerene 43 synthesis with simple process, which can be used for macro production. But actually, CVD is generally 44 used for the production of fullerene-related material, carbon nanotubes [36]. As for benzene flame 45 synthesis, the nain manipulation is the combustion of high-purity graphite rod in mixed diluted benzene 46 and oxygen, and it is worth noting that the ratio of fullerenes C_{60} and C_{70} in products can change by 47 controlling the reaction temperature, pressure, the ratio of carbon atoms and oxygen atoms, and residence 48 time of flame [37].

49 Although fullerene synthesis process has been mature with the deeper research in fullerene science. 50 51 52 53 54 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 55 separation methods are sorted to chromatographic technology and non-chromatographic technology [40-56 42]. Traditional chromatography has some basic disadvantages: (i) limit in column loadings, (ii) time-57 consuming process, (iii) irreversible adsorption, (iv) requirement of lots of stationary phases and mobile 58 phases. Non-chromatography also has some limits, like the requirement of prolonged stir and repeated 59 precipitation-filtration manipulations. As a result, the method to achieve efficient fullerene separation

1 with high-purity still remains elusive. Therefore, to obtain fullerenes in high pure form, efficient methods 23456789 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.

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11 12 13 Figure 1. Trends in annual publications of fullerene retrieved from Web of ScienceTM (all databases) by searching publications having "fullerene" in the topic on May th, 2017

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16 2. Selective Complexation for Fullerene Separation through Host-guest Interactions

17 The properties of fullerenes as well as their application in the multiple research fields remain unclear 18 mainly owing to their separation difficulties. The first seminal report of fullerene separation was built on 19 the carbon soot controlled sublimation [43]. Recently, the strategy of designing appropriate molecular 20 receptors for fullerene separation has attracted many researchers attention. Complementarity in size, shape, structure and electronic donor-accent 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 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.

21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 Complementarity used for molecular recognition is associated with point interactions, like metalligand 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 (Figure 2) [3]. The method of host-guest allows gaining selectivity and lead towards fullerene separation by host-guest 40 interactions. This provides a promising methodology to overcome the difficulties of fullerene separation 41 and obtain sustainable advances in fullerene science with a reversible way. Therefore, we specify 42 marcrocycles and cage-like receptors for fullerene separation with a reversible process via 43 complementarity and elaborate on both their benefits and intrinsic drawbacks.



Figure 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].

6 2.1 Designed Receptors for Fullerene Separation through Covalent Chemistry

7 2.1.1 Azacrown Compounds Receptor Decorated with Lipophilic Fragments

8 This section explains the macrocyclic examples of the N-alkylated hexaazacrown compound and the 9 acylated octaazacrown compound. Joehem et al. [51] presented two azacrown compounds, the alkylated 10 hexaazacrown compound and the acylated octaazacrown compound. They are the first synthetic and 11 intentionally designed receptors (14-18 Å in diameter) used to associate with fullerene to form at 1 host-12 guest adduct. All curves of the compounds are reproducible and the connection between azacrown 13 compound and fullerene exhibits a stabilizing effect. Though the diameter of the avalated occazacrown 14 compound is larger than the alkylated hexaazacrown compound, the collapsed area of the acylated 15 octaazacrown compound becomes slightly higher at the air-water interface when the full enes are present, 16 which did not occur on the alkylated hexaazacrown compound. Besides, the alkylated hexaazacrown 17 compound shows similar adsorption to C₆₀ and C₇₀. The host-guest adduct is formed when transferred the mixture of the compound and C_{60} at the surface pressure of 25mNn⁻¹ and decomposed when adduct is transferred at 5mNm⁻¹. And the similar method can be used for the reversible association-dissociation of 18 19 20 21 22 23 24 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. Figure 3 reveals the whole process of N-alkylated hexaazacrown compound and the acylated octaazacrown compound for fullerene separation.



Figure 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].

1 2.1.2 Anion-triggered Binding Covalent Organic Macrocycle

2 3 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 4 5 6 7 8 trifluoroacetic acid (TFA) to treat the monopyrrolo-TTF in a mixed solution of 1.2-dichloroethane and Me₂CO. 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 C₆₀ 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 9 and chloride anion, the 1,3-alternate conformation can be translated to the cone conformation after adding 10 chloride anions. The binding between TTF-calix[4]pyrrole composite and chloride anion in 1,2-11 dichloroethane (DCE) at room temperature is very strong with an association constant up to $2.5 \times 10^{6} M^{-1}$, 12 and the resulting cone conformation was expected to be an excellent receptor for fullerenes [54]. TTF-13 calix[4]pyrrole shows excellent electronic complementarity for fullerenes because it is a well-known 14 electron acceptor while fullerene is an electron donor. That TTF-calix[4]pyrrole associates with fullerene 15 in a 2:1 ratio can form a stable adduct. Notably, there is a perceptible change in the color of the solution in 16 the association process. A solution of TTF-calix[4]pyrrole composite in an acidic mixtur of CH cl₂ and 17 Me₂CO reveals yellow. The translation between the 1,3-alternate conformation and the cone conformation 18 does not change the color of the solution. However, when adding 0.5 equivalents of C₆₀ mixed in CH₂Cl₂, 19 the color turns green. Additionally, it is easy to achieve the release of fullerene from TF-calix[4]pyrrole-20 fullerene adduct by controlling the adding amount of chloride anions. Figure 4 shows the whole process of 21 22 23 24 TTF-calix[4]pyrrole receptor for fullerene separation.



25 26 27 28 29 30 Figure 4. Reported strategies of fulleren capsulation with TTF-calix[4]-pyrrole receptor and release by controlling the amount of chloride among Route 1 is fullerene binding and Route 2 is fullerene release. Reproduced from Ref [52].

31 2.1.3 Porphyrin-based Molecular Receptors

32 33 Both Rowan's cam [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 34 35 36 37 38 39 product in the modynamics. 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. Porphysius 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 40 cage - as the examples synthesized via dynamic chemical chemistry for fullerene binding.

41 Bisporphyrin macrocycle is a covalent organic capsule in rectangular shape, synthesized from 42 porphyrin-based diyne monomer via alkyne metathesis in one step with catalysis of multidentate Mo(vi) 43 alkylidyne [62, 63]. Although it is formed by highly rigid aromatic building blocks, it can associate with 44 C₆₀, C₇₀ and C₈₄ with forming a 1:1 receptor-fullerene adduct. The characterization by UV-Vis titration 45 reveals the highest affinity to C_{84} with high association constant (K_a=2.2×10⁷M⁻¹), which facilitate the 46 selective separation of C_{84} [63]. And the formed adduct can undergo a reversible association-dissociation 47 manipulation by adding acid-base stimuli, which protonates the porphyrin ring and weaken the interaction 48 between porphyrin and C_{84} (Figure 5 (a)).

49 Triporphyrin macrocycle contains three porphyrin moieties. The synthesis process of triporphyrin 50 macrocycle is similar with bisporphyrin macrocycle, one-step cyclooligomerization via alkyne metathesis 1 [64]. This synthesized triporphyrin macrocycle possesses a large internal cavity and reveals host-guest binding interactions with 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 (Figure 5 (b)).

23456789 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 C₇₀ [65]. This demonstrates 10 that transforming the conformation of the porphyrin-based receptors can tailor their selectivity for 11 fullerene binding. The association constant for the porphyrin-based four-armed cage combining with C₇₀ 12 13 $(K_a=1.5\times10^8 M^{-1})$ is 3 orders of magnitude higher than C_{60} $(K_a=1.4\times10^5 M^{-1})$ [66]. This huge gap facilitates the efficient separation of C_{70} . Additionally, the encapsulated fullerene can be released from porphyrin-14 based four-armed cage via TFA treatment. The interaction is reversible by adjusting the pH of the reaction 15 (Figure 5 (c)), which is because the protonation of the non-metallo-porphyrin by TFA weakens the 16 interaction via reducing porphyrin electron-donating ability.

17 Among these three porphyrin-based molecular receptors, porphyrin-based four-armed cage possesses 18 the highest affinity to fullerene C_{70} (K_a=1.5×10⁸M⁻¹), bisporphyrin macrocycle shows highest affinity to 19 20 21 22 23 24 25 26 27 28 fullerene C_{84} (K_a=2.2×10⁷M⁻¹), and the triporphyrin macrocycle reveals the least affinity to fullerene $(K_a=6\times 10^3 \,\mathrm{M}^{-1})$. This is because the difference in the size, shape, structure and electronic donor-accept complementarity between these porphyrin-based molecular receptors and special fullerenes (C600, C70 or C₈₄). 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-nuller ne adduct can be recycled many times.



29 30 31 32 33 34 Figure 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. 35 Route 1 is fullerene binding and fullerene Route 2 is fullerene release. Reproduced from Ref [66]. 36

1 2.1.4 Concave π-extended TTF Derivatives Receptor

2 3 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 4 connection between 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole (exTTF) and 5 fullerene is strong non-covalent interaction, thus a tweezer-like receptor was designed for fullerene 6 separation. The tweezer-like receptor can be synthesized in excellent yield by the covalent connection of 7 8 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.

9 The formed host-guest adducts perform different structures which depend on the reaction solvent and 10 the ratio of exTTF-isophthalate diester receptor and fullerene in stoichiometry. In the case of 11 chlorobenzene solvent at room temperature, mixing the receptor and fullerene forms adduct with the first 12 structure. While in the other case of CHCl₃-CS₂ mixed solvent, the formed adduct exhibits the second 13 structure or the third related to the amount of fullerenes, and the binding curve is in the shape of sigmoidal, 14 which is considered as the standard for connection. The stability of adduct formed by exTTF-isophthalate 15 diester receptor (concave, electron-rich) and fullerene (convex, electron-poor) depends on shape and 16 electronic complementarity. The change of fullerene adsorption in the exTTF-isophthalate diester receptor 17 can be explained with the Hill equation and the Hill coefficient $(n_{\rm H})$, which reflects the extent of 18 connection. The formation of host-guest adduct can be impeded in the value of $n_{\rm H} \ge 2$, which featuring 19 two binding sites only. Figure 6 shows the whole process of exTTF-isophthalate diester receptor for 20 21 22 23 24 fullerene separation. Soon after, Isla et al. [73] synthesized another efficient exTTP based macrocyclic receptor that associates fullerene with micromolar affinity successfully, which possesses a binding constant > 10^{6} M^{-1} to C₆₀.





25 26 27 28 29 Figure 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]

30 2.2 Designed Receptors for Fullerene Separation through Coordination Bonds

31 32 33 34 35 36 With the increase of designed receptors scale and sophistication, the synthetic strategies through covalenchemistry 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.

37 2.2.1 Coordination Metallosupramolecular Mercury-based Cage Containing π -extended Moieties

38 The coordination metal ions based cage is self-assembled by mixing pyridine curved ligand (two 39 anthracenes bound by m-phenylene) and metal ions in acetonitrile at room temperature [74, 75]. Herein, 40 we elaborate on an example of mercury (II) based cage, which adopt a tortile square planar geometry 41 linked with four bent bispyridine ligands [76]. The π -extended moiety of the ligand provides an aromatic 42 shell with an enclosed cavity (diameter up to 1 nm [77]) for strong interactions between mercury-ligands 43 cage and fullerene. The enclosed cavity of mercury-based cage is large enough to encapsulate fullerene

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remove C₆₀ from the adduct in acetonitrile (Route 2), the color of solution turns pale yellow. Hg(II) a. Acetonitrile Acetonitrile b. 2 x Ligands Fullerene Route 1 Rou hv Route 2 Pale yello Colorless Blue Mercury based cage-Pyridine curved ligand Mercury tubular cage fullerene adduct Figure 7. Reported strategies of fullerene encapsulation with hercury-based cage and release after binding and Route 2 is fullerene release.

via π -stacking interaction. Additionally, mercury-based cage shows higher affinity to C₆₀ than C₇₀, 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, mercurybased 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 C₆₀ can be distinguished by the naked

eye according to the change of color (Figure 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

18 19 20 21 22 23 changing the metal-to-ligand ratio. Route 1 is fullerene Reproduced from Ref [76].

24 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 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 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 molar 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) between Zn¹ 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 share to 13.7 Å. This proves that the tetragonal prismatic coordination cage exhibits the potential to dijust 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 40 tetragonal prismatic coordination cage-fullerene adduct. The solid-liquid encapsulation strategy of 41 fullerene within the cage demonstrates that fullerene presumably get into the cage via one of the four 42 lateral apertures, which are big enough for fullerene to moving back and forth. Fullerene release can be 43 achieved by solid washing strategy with appropriate washing solvent, which exhibits low solubility for 44 tetragonal prismatic coordination cage and high solubility for fullerene. Notably, the pure empty cage in 45 the solid remaining can be recovered by dissolving it in acetonitrile and can be reused to encapsulate 46 fullerenes with high efficiency. The reversible process of fullerene encapsulation within the tetragonal 47 prismatic coordination cage is revealed in Figure 8. 48



Figure 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].

3. Fullerene Separation Based on Reversible Diels-Alder Addition

8 9 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 10 covalent attachment of fullerene to peptide resin. This process requires an intermediate product, 11 cyclopentadiene-functionalized compound, which is synthesized by mixing peptide esin in touene with 12 excessive sodium cyclopentadienylide. To provide a control system for researching fullerene binding, 13 Guhr synthesized an ether-containing compound from the reaction of peptide resin and sodium ethoxide in 14 the same reaction condition. Both peptide resin and ether-containing compound show little or no affinity 15 to C_{60} . In contrast, C_{60} can be combined rapidly to cyclopentadiene-functionalized compound via DA 16 reaction by generating a fullerene substituted material. This fullerene substituted material is thermolabile 17 and consequently the decomposition can be done via heating. Concrete manufulation is to heat the mixed 18 C_{60} conjugate in decalin solvent in the absence of maleic anhydrid (or the basis of C_{60} content). This 19 proves that the connection between cyclopentadiene-functionalized compound and fullerene C60 is a 20 reversible association-dissociation process (Figure 9). 21



Figure 9. Reported strategies for fullerene separation via reversible DA addition with cyclopentadienefunctionalized compound Route Vis fullerene binding and Route 2 is fullerene release. Reproduced from Ref [84].

223 24 25 26 27 28 29 30 31 32 33 34 35 36 37 Soon after, Nie me Rotello [85] raised a similar reversible method that attaching special fullerene to a cyclopentadene-functionalized silica support. Cyclopentadiene-functionalized silica gel, produced by the connection of information interval and the set of the connection of the connect C_{70} via ΔA 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 (Figure 10) can be fully reversible without loss of fullerene capacity.



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Figure 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].

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 further study.

11 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.

17 4.1 A New Filtration Method with AC as the Stationary Phase



18 Komatsu et al. [92] raised a practical method that make the solution of fullerene xtract pass through 19 thin layer of activated carbon (AC) to alumina that is used as the stationary phase. This process is based 20 on the π - π interaction between fused aromatic rings, which immobilize_fullerenes in AC pores. The 21 22 23 24 25 26 27 28 29 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-trimed viber 2ene (TMB) as the solvent and controlling the ratio of AC and fullerene mixture being 47:1 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 vicle process without any additional treatment. Thus this method is inexpensive and efficient enough to achieve large-scale pure fullerene production.

30 4.2 Selective Separation of Fullerenes with Metal-organic Frameworks (MOFs) as the Stationary Phase

MOFs are a type of porous materia's constructed by metal-containing (metal ions or clusters) nodes ected by organic ligands [94, 75]. The possess very high specific surface area, adjustable sizes, 31 32 33 34 35 36 37 connected by organic ligands [94, 75]. 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 full areas on MIL-101(Cr) (MIL, Mat érial 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 38 39 vertices while 1,4 ben encuteration of the six edges (Figure 11 (a)). These STs are microporous and the synthesized framework consists of two kinds of mesoporous cages. The two 40 mesoporous ages are delimited by 20 (internal free diameter of ~29 Å) and 28 ST (~34 Å), which are in a 41 2:1 ratio mixture. The smaller 20 ST cages only reveal pentagonal windows with a ~ 12 Å free opening, 42 but the 🕵 ST tages reveal not only pentagonal but also hexagonal windows with a free aperture of ~ 14 Å 43 by 16 Å (Figure 11 (b)). MIL-101(Cr) provides mesoporous pores, large pore windows, unique high 44 surface area and excellent stability in framework and chemical property.

45 For these reasons, MIL-101(Cr) has be designed as a adsorbent for adsorbing fullerenes in a practical 46 and efficient way [98]. The adsorption of fullerenes on MIL-101(Cr) at room temperature contains two 47 phases, adsorption on surface and intraparticle or pore diffusion. Additionally, MIL-101(Cr) shows much 48 higher affinity to C_{70} and especially higher fullerenes (C_n , $n \ge 76$) in comparison with C_{60} . This manner 49 helps to achieve selective separation of C₇₀ and higher fullerenes. Besides, desorption of fullerenes form 50 MIL 101(Cr) is simple. Adding desorption solvent consisting of o-dichlorobenzene, p-xylene and toluene 51 to MIL 101(Cr) under ultrasonication can get isolated fullerenes. And MIL-101(Cr) can recover after the 52 desorption manipulation and reused for fullerenes selective separation (Figure 11 (c)). As a novel 53 adsorbent, MIL-101(Cr) exhibits fast adsorption, simple desorption, high selectivity and renewability for 54 the separation of C_{70} and higher fullerene.



Figure 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 hexagoral windows of MIL-101(Cr). (c) Adsorption and desorption of fullerene in MIL-101(Cr). Reproduced from Ref [97].

7 Traditional chromatography has some basic shortcoming (i) when loadings are limited in the 8 separation process. (ii) Long lasting process is time-consuming and needs amounts of attention. (iii) 9 Adsorption of most fullerenes on the traditional adsorben is irreversible. (iv) The process requires lots of stationary phases and mobile phases. Compared with traditional chromatography, improved chromatographic method tries to overcome these shortcornings. And current improved chromatography possesses four improved aspects: (i) more rapid production of special fullerenes (e.g. fullerenes C_{60} or C_{70}) 10 11 12 13 in pure form, (ii) simpler operations, (iii) reversible adsorption-desorption of fullerene molecules on the 14 improved adsorbent, (iv) less expensive manufacturing process. In short, improved chromatographic 15 method is cost-effective and efficient enough to achieve large-scale pure fullerene production.

16 17

18 **5. Fractional Crystallization**

A facile and lowelost approach to purify C_{60} and C_{70} mixture in gram quantities by fractional crystallization in CS₂ or explicit 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 temperature but an excellent solvent mixed with 2% ethanol for C_{60} when heating up to 306K. 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 (Figure 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

27 In general, the complete process of fractional crystallization includes three steps (Figure 12): (i) 28 Using solvent to dissolve the crude fullerene soot extract through sonication and adding special solvent to 29 the dissolved solution and then stirring to mix well to dissolve C_{60} to a maximum extent. After dissolution, 30 heating the mixed solution and then filtering through a microporous filter to get solid deposit A with high 31 content of C_{60} and leave the mother liquid A with high content of C_{70} . (ii) Evaporating the mother liquid A 32 to about 1/3 in volume, as a consequence, solid deposit B with high content of C_{60} and the mother liquid B 33 with high content of C_{70} can be produced. (iii) Cooling the mother liquid B to get solid deposit C enriched 34 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.

2 3 4

> 56 78

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9 6. Conclusion and Outlook

10 Since fullerenes were studied for more than 100 years, they have remained the primary focus of many 11 scientists in various fields. Fullerenes not only contributed to the exploration of other carbon 12 nanomaterials like carbon nanotubes [101] and graphene [102], but also facilitated the finding of many 13 potential values such as the construction of novel composites and biomedical applications [103]. Though 14 fullerenes are being a mature science, many properties ranging from fundamental synthetic aspects to 15 chemical reactivity remain unknown for higher fullerenes (C_n, n, 70) because of the scarce efficient 16 methods for fullerene separation with high purity. Large-scale synthesis and separation in a reversible way 17 is still a significant challenge for fullerenes.

18 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 19 20 21 $\overline{22}$ 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 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 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 38 (supra-) molecular receptors goes on to be a focus of future research in fullerene separation.

39 In a word, many of the separation methods are in their early stage, especially selective complexation 40 based on molecular chemistry through covalent bonds or coordination bonds. Inevitably, there exist some 41 drawbacks in these separation methods. However, though the techniques of selective complexation, 42 reversible DA addition, improved chromatography and fractional crystallization have some drawbacks 43 waiting to be overcome, they are still available for the selective separation of fullerenes nowadays. At the 44 same time, the more efficient method in an environment-friendly way is still in an urgent need. And it can 45 be expected that fullerenes in pure form will be exploited in multiple fields. As large quantities of 46 fullerenes reach our daily life, to find an applicable disposal procedure is what we need to do next. We are 47 confident that this review will be a powerful resource to strengthen the efforts towards the finding of 48 reversible produce process for fullerene sustainable advances and broaden the frontier of nanoscience and 49 nanotechnology for many years to come.

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