Fullerene Receptors

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Wraparound Hosts for Fullerenes: Tailored Macrocycles and Cages

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cage compounds · fullerenes · host–guest systems · macrocycles · supramolecular chemistry

Dedicated to Professor Tomás Torres on the occasion of his 60th birthday

Custom-made macrocyclic receptors for fullerenes are proving a valuable alternative to achieve the affinity and selectivity required to meet challenges such as the selective extraction of higher fullerenes, their chiral resolution, or the self-assembly of functional molecular materials. In this Minireview, we highlight some of the important breakthroughs that this class of fullerene hosts has already produced.

1. Introduction

Fullerenes have been in the spotlight of chemical research right from their discovery in 1985,[1] earning Kroto, Kurl, and Smalley one of the most immediate Nobel prizes in chemical sciences, in 1996. Fullerenes' ability to work as electron acceptors has arguably centered most of the research efforts in their chemistry.[2] Nowadays, fullerene derivatives are the benchmark n-type materials for the construction of organic photovoltaic devices.[3,4]

The search for molecular receptors for fullerenes was initiated just seven years after the discovery of C_{60} and immediately after it became available in sufficient quantities by contact-arc vaporization of graphite.[5] From the point of view of molecular recognition, fullerenes are very peculiar guest molecules. Their unusual shape (approximately spherical, maximizing the surface-to-volume ratio) and chemical nature (unpolarized polyenes) restrict the types of noncovalent forces that can be utilized for their association to dispersion forces (π–π and van der Waals).[6] Thus, the nuts and bolts of the design of hosts for fullerenes are the construction of a nonpolar cavity—preferentially but not necessarily featuring aromatic recognizing units—of the appropriate size to fit the fullerene guest.

In 1992, the group of Ringsdorf et al. reported the first purposely designed hosts for fullerenes.[7] Their receptors were based on a macrocyclic azacrown ether in which the nitrogen atoms were alkylated or acylated with aromatic groups further substituted with long alkane chains, forming a lipophilic "cup". Simultaneously, Wennerström and co-workers had reported the association of C_{60} by two units of γ-cyclodextrin, thus permitting the solubilization of the fullerene in water.[8] At approximately the same time, the groups of Raston and Shinkai, working independently, reported the selective purification of C_{60} from fullerene soot by its selective association with *p-tert*-butylcalix[8]arene.[9] The latter examples encouraged the utilization of calixarenes, calixnaphthalenes, resorcinarenes, cyclotriveratrylenes (CTVs), and cyclodextrins for the design of fullerene receptors, which exhibited binding constants in the range of $\log K_a = 1$–3 in apolar solvents. The corresponding literature has already been gathered in excellent reviews and will not be extensively discussed herein.[10,11] The construction of macrocyclic hosts is a tried and tested strategy to improve both affinity and selectivity of host systems.[11] Accordingly, the last decade has witnessed important developments thanks to the new generations of macrocyclic receptors for fullerenes. These advances are the focus of the present Minireview.

2. Fully Organic Macrocycles

2.1. Arene-Based Receptors

As mentioned in the Introduction, calixarenes and CTVs were proven to be efficient receptors toward fullerenes early on. The possibility of associating two or more of these units to improve the affinity and selectivity of the receptor for fullerene guests was tested by Matsubara et al. with the CTV unit[12] and Wang and Gutsche with calixarene-based derivatives.[13] In the former case, the authors described the recognition properties of CTV-based hosts **1**–**3** (Figure 1). Surprisingly, the authors did not report important modifications in terms of binding ability. For instance, derivative **2** displays just a slight improvement in affinity toward C_{60}

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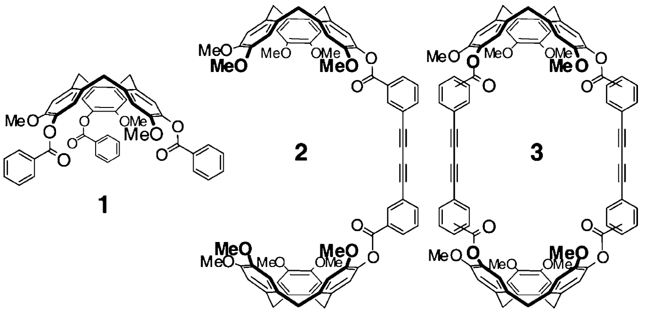

Figure 1. Structures of compounds **1**–**3**.

compared to CTV **1** ($\log K_a = 4.26$ and $\log K_a = 3.95$ in benzene at 298 K, respectively).[12a,b] The insertion of a second linker in *m*-**3** does not lead to a significant increase in the binding constant, either, with $\log K_a = 4.29$ under identical experimental conditions.[12c] This situation presumably results from the long and rigid 1,4-diphenylbuta-1,3-diyne spacer, which prevents efficient synergic binding by both CTV moieties. The fact that cage *p*-**3** binds C_{60} worse than **1** ($\log K_a = 3.79$ in the same conditions) also supports this assumption. In this sense, the reduction of the butadiyne spacers to their alkyl counterparts would have probably been relevant, as reported later with macrocyclic porphyrin dimers.[14] In the case of Wang and Gutsche,[13] results were even worse, since their calix[4]- and -[6]arene-based cages did not show any affinity toward C_{60}, which can again be ascribed to a lack of flexibility of the linkers.

However, one should keep in mind that rigidity does not necessarily constitute a problem. Provided that the size and shape of the receptor match the dimensions of the guest, and that the latter can access the cavity of the host, rigidity can be considered as an advantage. Indeed, an inflexible host displays a high degree of preorganization, which typically results in the formation of more stable complexes.

This concept is nicely illustrated with the cyclo-*p*-phenyleneacetylene (CPPA) family described by Kawase et al.[15] The very rigid cyclo-*p*-hexaphenyleneacetylene proved to be an efficient host for [60]- and [70]fullerenes with binding constants of $\log K_a = 4.2$ and 4.3 in benzene at room temperature, as measured by UV/Vis titrations.[15b,c] Fluorescence measurements were also performed and showed a decrease in the emission intensity when aliquots of C_{60} were added. The corresponding Stern–Volmer constant[16] proved to be as high as $\log K_{sv} = 4.8$. For comparison, the Stern–Volmer constant with C_{70} was higher ($\log K_{sv} = 5.1$), in agreement with the slightly higher affinity of cyclo-*p*-hexaphenyleneacetylene toward C_{70}.

Regarding cyclic *p*-aryleneacetylenes and their binding ability toward fullerenes, a significant improvement could be achieved thanks to rational modifications of the host structure.[15c] Indeed, authors increased the size of the aromatic surface of the host by replacing some of the phenyl units by naphthyl ones. In this manner, the dispersion forces respon-

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sible for the recognition phenomenon are strengthened, which allows receptor **4a** to bind C_{60} with an association constant as high as $\log K_a = 5.0$ in benzene at room temperature. Nicely, the supramolecular association **4a**·**4b** proved to be an efficient receptor towards C_{60}, affording the so-called "onion-type" carbon nanostructure C_{60}·**4a**·**4b** represented in Figure 2.[15e]

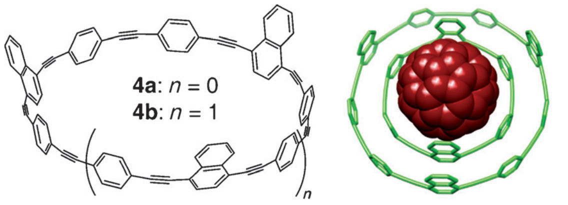


Figure 2. Compounds **4a,b** (left) and a representation of their onion-like supramolecular nanostructure with C_{60} (right). Carbon atoms of the host are depicted in green and C_{60} in dark red.

Very recently, the team of Pasini described several chiral receptors displaying two[17a] or three[17b] axially chiral (*R*)-binaphthyl moieties linked through rigid spacers (Figure 3).[17]

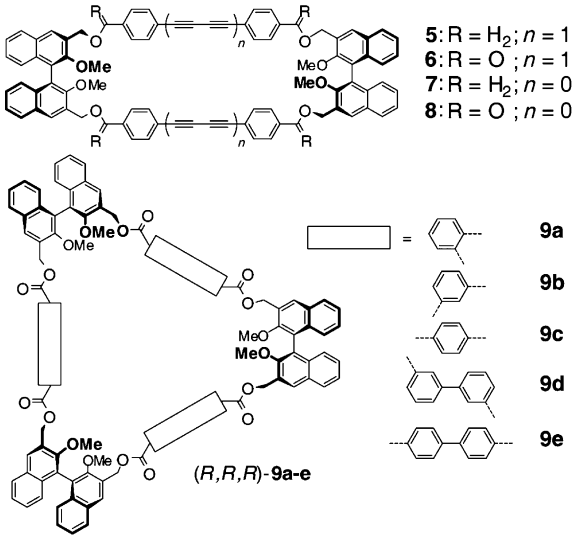


Figure 3. Binaphthalene-based receptors **5–9**.

Their host–guest properties are strongly dependent on their molecular structure. For example, while compound **8** binds [60]fullerene with $\log K_a = 3.50$ in toluene at 298 K, **7** does not have any detectable affinity toward C_{60} under the same conditions. The fact that macrocycles **9b** and **9c**, that is, *meta*- and *para*-substituted analogues, form complexes of different stoichiometry with C_{60} is also a nice illustration of a small structural variation inducing a significant difference on the binding properties. Indeed, **9c** binds [60]fullerene in a 1:1 fashion, while **9b**·C_{60} exists as a mixture of complexes of different stoichiometries. Using the Hill equation, authors deduced an apparent association constant for each binding event of $\log K_{app} = 3.1$ in toluene at 298 K and a Hill coefficient of 2.9, which the authors interpret as meaning that 2.9 molecules of **9b** are interacting with the fullerene guest on average.[18] Beyond the simple recognition properties of these hosts, their most interesting feature certainly lies on their inherent chirality. For instance, the circular dichroism study performed on **5**·C_{60} shows a Cotton effect in absorption bands peculiar to C_{60}. Such a chiral induction offers promising perspectives for the chiral resolution of higher fullerenes but also for developing new methods to functionalize these carbon nanostructures enantioselectively.[19]

2.2. Aromatic Heterocycles for Fullerene Recognition

Apart from porphyrin-based macrocyclic hosts, which will be described in the second part of this Minireview, nitrogen-containing heterocycles, such as pyridine and pyrrole, have recently been used for the preparation of fullerene hosts. The interaction between the host and the C_n guest is generally the result of dispersion forces. As a consequence, the presence of heteroatoms within the aromatic moieties is likely to modify the electronic distribution and the polarizability of the corresponding receptors and thus their binding properties. In this context, Wang et al. reported important contributions with two families of compounds, namely azacalix[*m*]arene[*n*]-pyridines and azacalix[*n*]pyridines.[20] The preparation of derivatives **10a** and **10b** (Figure 4) is remarkably straightforward; they are both obtained in three steps starting from 1,3-diaminobenzene and 2,6-dibromopyridine.[21] Unlike **10b**, the addition of **10a** to a C_{60} solution does not lead to any color change, thus suggesting that no interaction takes place with the smaller macrocycle **10a**, as was confirmed by UV/Vis and fluorescence titrations. These studies demonstrate that **10b** forms 1:1 complexes with both C_{60} and C_{70}, and the authors report binding constants of $\log K_{sv} = 4.8$ and 5.1 in toluene at 298 K for C_{60} and C_{70}, respectively, although they neglect the effect of possible dynamic quenching.[16] Later, the same team reported the synthesis of a new series of macrocycles constructed with pyridine rings only (**11a–g** in Figure 4).[22] The recognition properties of these hosts toward fullerenes were studied by fluorescence spectroscopy, taking only static quenching into account. Surprisingly, this exhaustive work does not show significant differences between receptors **11a–g** in terms of fullerene recognition, even though their diameters (at least in the solid state) are extremely different.

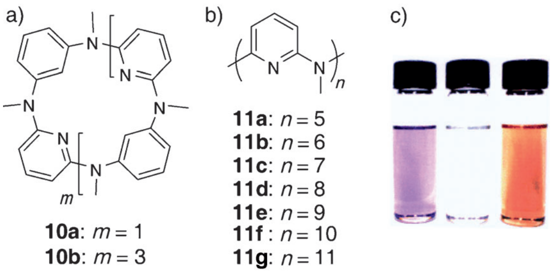


Figure 4. a,b) Macrocycles **10** and **11** involving pyridine rings and c) solutions of C_{60} (left), **10b** (center), and C_{60}·**10b** (right).

The same assessment could be set out for two fullerene receptors, described by the same team, endowed with one and two calix[1]arene[4]pyridine units.[23] In this particular case, the authors measured a lower binding constant for the host made up of two recognition units.

The 1,8-naphthyridine moiety is another example of a nitrogen-containing aromatic unit recently utilized to prepare **12**, a receptor that also displays two triptycene units (Figure 5).[24] The recognition phenomenon was confirmed by means of fluorescence spectroscopy, which showed that **12** binds both fullerenes in a 1:1 stoichiometry, with $\log K_{sv} = 4.9$ in toluene at room temperature.

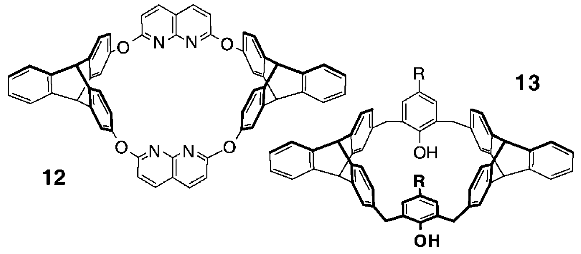


Figure 5. Rigid macrocycles based on triptycene units proposed by Chen and co-workers.

As far as triptycene derivatives are concerned, we wish to underline the role of this fragment in the recognition process through the example of compound **13**.[25] Its structure can be compared with calix[6]arene. However, while calix[6]arene binds fullerenes C_{60} and C_{70} in a 2:1 stoichiometry, **13** forms 1:1 inclusion complexes with both C_{60} and C_{70}. This particular feature is due to the rigidity of the triptycene moieties, which prevents the existence of the double-cone conformation observed in the 2:1 inclusion complexes between calix[6]arene and fullerenes. Thanks to the high degree of preorganization supplied by this unit, which is likely to increase both the affinity and the selectivity of receptors, we believe that triptycene-based receptors are appealing hosts for future developments in the supramolecular chemistry of fullerenes.

To date, pyrrole-based macrocyclic receptors for fullerenes remain scarce. The first example was described by Sessler, Jeppesen, and co-workers with derivative **14**, which results from the fusion of four tetrathiafulvalene units to a calix[4]pyrrole scaffold (Figure 6).[26] Compound **14** mainly exists in the 1,3-alternate conformation in solution and interacts with C_{60} only very weakly. Yet, thanks to the affinity of calix[4]pyrroles for chloride anion, it is possible to switch this molecule to its cone conformation, which affords the deep and electron-rich cavity **14**·Cl^- (Scheme 1).

The authors demonstrated that in dichloromethane C_{60} is surrounded by two units of **14**·Cl^- and that the formation of the 2:1 complex is governed by two sequential equilibria, which lead to C_{60}·(**14**·Cl^-) ($\log K_1 = 3.4$) and C_{60}·(**14**·Cl^-)$_2$ ($\log K_2 = 4.1$). Further achievements were reported later by taking advantage of the features of compound **14**.[27] For example, it was possible to control the encapsulation and the release of the fullerene guest thanks to complexation/precipitation sequences (Scheme 1).[27b] Starting from a mixture of **14** and C_{60}, the addition of tetrabutylammonium chloride provokes inclusion of the guest within C_{60}·(**14**·Cl^-)$_2$, while the subsequent addition of sodium tetraphenylborate precipitates the chloride anions and regenerates the free fullerene and **14** in its 1,3-alternate conformation.

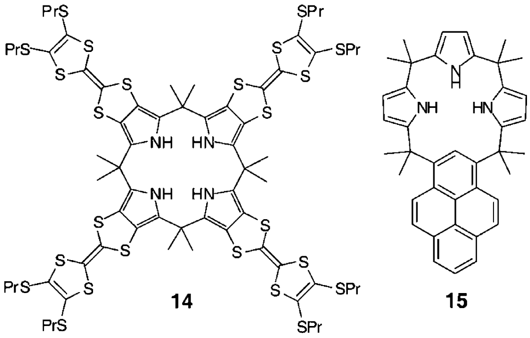
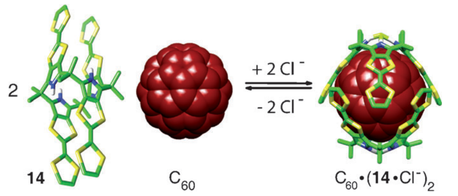


Figure 6. Calix[4]pyrrole **14** and receptor **15**.



Scheme 1. Fullerene encapsulation and release upon complexation and precipitation of chloride anions. C green, S yellow, N blue, H white, Cl light green, C_{60} dark red.

In the latter example, the recognition phenomenon is undoubtedly the result of both the shape of the receptor, which surrounds the convex fullerene guest, and the electron-rich nature of the host, which contains four tetrathiafulvalene units. Indeed, electronic complementarity is also relevant for the design of such receptors, since fullerenes are well-known electron acceptors. Calix[4]pyrrole does not intrinsically interact with C_{60}, whether with or without chloride anion. Consequently, whether the pyrrole rings were participating in the recognition process or not was not clear until recently. Macrocycle **15**, initially designed as a fluoride receptor, is made up of three pyrrole units and one pyrene unit and forms stable C_{60}·(**15**·F^-) and C_{70}·(**15**·F^-) 1:1 complexes in a [D_8]toluene/CD_3CN (95/5) mixture.[28] Considering that neither calix[4]pyrrole nor pyrene alone are able to generate stable complexes with fullerenes, example **15** definitely confirms that pyrrole rings contribute to the recognition of fullerenes.

2.3. π-Extended TTF-Based Hosts

Tetrathiafulvalene (TTF)-containing derivative **14** proved to be an efficient receptor toward [60]fullerene. However, most TTF derivatives suffer from the planarity and small surface of the electroactive unit, which results in relatively small interactions between the TTF-based host and the fullerene guest.[29] In this regard, derivative **16**, a π-extended TTF derivative (exTTF) with a concave aromatic shape complementary to the convex surface of fullerenes, proved to be a remarkably successful building block for fullerene hosts (Figure 7).[30,31]

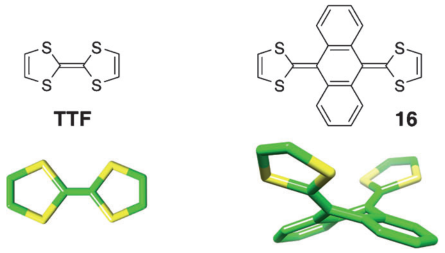


Figure 7. a) Structures of TTF and exTTF building-blocks; b) their optimized geometry (*PM3 method—Hyperchem*). Color code as in Scheme 1.

Unlike cyclotriveratrylene-based receptors **1–3**, derivatives **16–20** (Figure 7 and Figure 8) display extremely different binding abilities. Monomer **16** does not form any stable complex with fullerenes, despite its geometric and electronic complementarity.[31] Nevertheless, compound **17**, an exTTF-based tweezers, benefits from the synergistic effect of both units to bind C_{60} with a binding constant of $\log K_a = 3.5$ in chlorobenzene at room temperature, which is relatively high considering its lack of preorganization.[31] This result encouraged us to design macrocycle **18b**, a preorganized host which should limit the entropic cost associated with bringing both exTTF units together. This strategy proved to be worthwhile, as macrocycle **18b** is one of the best fully organic receptors ever reported, with a binding constant of $\log K_a = 6.5$ in chlorobenzene, a very good solvent for fullerenes, and up to $\log K_a = 7.5$ in benzonitrile, a less competitive solvent.[32]

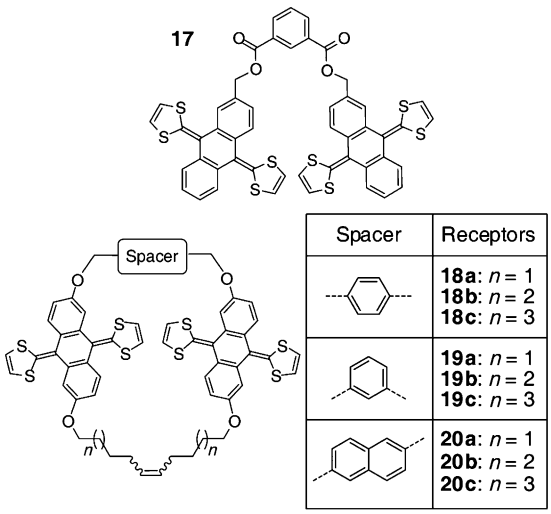


Figure 8. Extended TTF-based receptors **17–20**.

We have thoroughly investigated the recognition properties of a whole family of exTTF-based macrocycles **18–20** by systematically modifying the spacer (*p*-phenylene, *m*-phenylene, and 2,6-naphthylene) and the alkenyl chain length ($n = 1, 2, 3$).[33] This study allowed us to discover some remarkably efficient macrocyclic hosts for fullerenes; for instance, **20c** binds C_{70} with $\log K_a = 6.1$ in chlorobenzene at room temperature. Moreover, we also showed how small structural variations lead to important changes in the binding ability. For example, **18c**, binds C_{60} with $\log K_a = 3.5$, a binding constant three orders of magnitude smaller than its closely related congener **18b**. Beyond measuring very different binding constants along this series of macrocycles, we also found changes in the stoichiometry of the complexes. For example, **18a** and **19a** both bind [60]- and [70]fullerene in a 1:1 and a 2:1 fashion, respectively. Yet, a different situation arises with **20a** which forms 1:1 complexes with both fullerenes, thanks to its slightly larger diameter.

It has been well known that fullerenes interact with crown ether derivatives since the pioneering work reported by Mukherjee and coworkers.[34] Taking advantage of this feature, we described an excellent host for [60]- and [70]fullerenes which involves two crown-ether units around a central exTTF.[35] The synergistic n–π and π–π interactions of crown ethers and exTTF allow this derivative to bind C_{60} and C_{70} with a micromolar affinity in chlorobenzene.

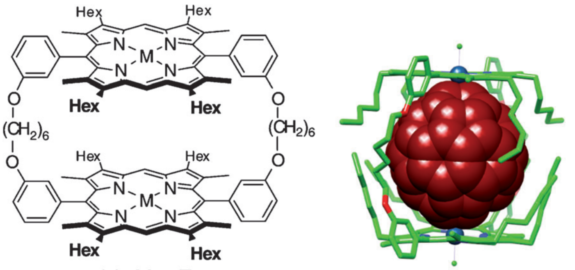
As far as crown-like macrocycles are concerned, we would finally like to stress an important breakthrough reported by Akasaka and co-workers, which deals with endohedral fullerenes.[36] The authors described the selective precipitation of $La@C_{82}$ and $La_2@C_{80}$ in the presence of the azacrown derivative 1,4,7,10,13,16-hexaazacyclooctadecane, which made the separation by HPLC techniques easier. These findings are thus of utmost importance for a more global utilization of endohedral fullerenes.

3. Metal-Containing Macrocycles

3.1. Porphyrin-Based Receptors

A significant portion of the hosts for fullerenes described to date has made use of the porphyrin–fullerene interactions.[37] In 1999, Aida, Saigo, and co-workers synthesized a cyclic dimer of a zinc porphyrin (**21**, Figure 9) and studied its ability to associate C_{60}.[14] Compound **21** was actually the best host for fullerene described at the time, with $\log K_a = 5.8$ in benzene at room temperature. This finding opened an avenue for the development of a whole family of cyclic metalloporphyrin dimers with outstanding properties. A comprehensive account of such systems up to 2007 has been published,[38] so we focus below on the most recent developments.

Tashiro, Aida, and co-workers showed that a single iridium porphyrin was capable of interacting with [60]fullerene to form a 1:1 complex with a binding constant of $\log K_a = 5.3$ in benzene. In accordance with such a high binding constant for a single porphyrin, the corresponding dimeric macrocycle **22** (Figure 9) shows a $\log K_a = 8.1$ toward C_{60} in 1,2-dichlorobenzene (*o*-DCB) at room temperature, which to date constitutes a world record in complex stability.[39] More importantly, structural analysis both in the solid state through

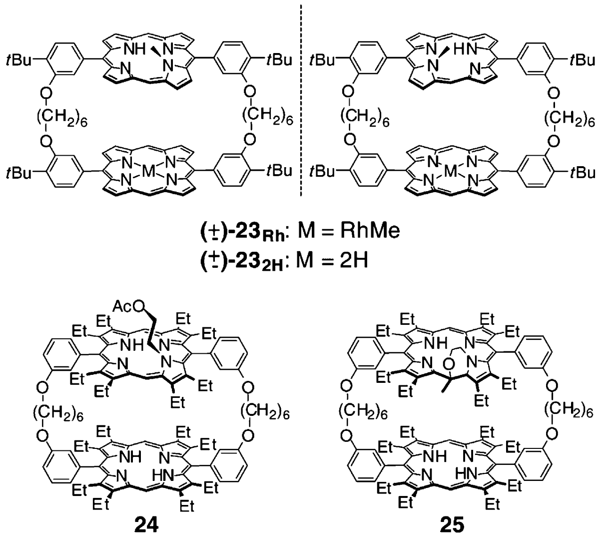


21: M = Zn
22: M = MeIr

Figure 9. Structures of compounds **21** and **22** (left) and the X-ray structure of the C$_{60}$·**22** complex (right). Color code as in Scheme 1; Ir blue balls.

X-ray diffraction and in solution through NMR spectroscopy showed that the corresponding porphyrin dimer **22** forms coordination bonds with fullerenes in a η^2 fashion at very low temperatures, distorting the guest in an ellipsoidal shape. Regarding porphyrin-based receptors, frontiers between supramolecular and covalent chemistry have clearly been reached with iridium(III) porphyrins.

Such a powerful family of receptors is particularly promising for applications like the enantioselective recognition of higher fullerenes. In this context, the insertion of asymmetry is necessary. Regarding cyclic porphyrin hosts, asymmetry was achieved in an elegant manner in compounds **23**–**25** (Figure 10). Instead of inserting chiral centers at the periphery of the hosts, desymmetrization was achieved on a porphyrin ring which directly interacts with the electronic cloud of the fullerene guest. Studying the interactions of these hosts with the smallest chiral fullerene, C$_{76}$, Aida and co-workers were able to show that compound **23**$_{\mathbf{Rh}}$ is suitable for sensing chirality in a racemic mixture but also for quantifying the enantiomeric excess in NMR spectroscopy experiments.[40] Though chiral and strongly interacting with C$_{76}$, host **23**$_{\mathbf{Rh}}$ did not display any enantioselectivity. Luckily, this feature is an asset to quantify the enantiomeric excess in chiral fullerene mixtures, since binding constants for both enantiomers have to be equal for this purpose.



(±)-23$_{\mathbf{Rh}}$: M = RhMe
(±)-23$_{\mathbf{2H}}$: M = 2H

24
25

Figure 10. Structures of chiral derivatives **23**–**25**.

A second generation of chiral hosts, **24** and **25** (Figure 10), was described very recently.[41] These receptors present three major differences with **23**$_{\mathbf{Rh}}$ and **23**$_{\mathbf{2H}}$: 1) pyrrole rings are substituted with ethyl groups in the β and β′ positions, 2) porphyrin units are not metallated, and 3) they are more distorted. Such differences are expected to help chiral discrimination, since metallation increases the affinity of porphyrin rings for fullerenes excessively and thus decreases the selectivity, and a more distorted structure is meant to be more discriminating toward both enantiomers. With this in mind, macrocycle **25**, one of the most distorted phlorin derivatives ever described, was expected to be the most suitable for enantioselective extractions. However, its distortion was also responsible for a decrease in the binding ability toward C$_{76}$, which prevented such an extraction. A first step was finally achieved in 2010 with derivative **24**, which allows the collection of fractions enriched in (+) or (−)-C$_{76}$ with a 7% *ee* after a single extraction.[41]

A new trend in the field of fullerene hosting is to increase the number of interacting porphyrin units within the macrocycles. The first example was recently reported by Anderson and co-workers with compound **26** (Figure 11).[42] As calculated from UV/Vis and fluorescence titrations (Figure 11), the resulting rigid structure presents remarkable advantages in terms of fullerene recognition. In particular, **26** shows extremely high binding constants toward C$_{60}$ ($\log K_a = 6.2$), C$_{70}$ ($\log K_a = 8.2$), and C$_{86}$ ($\log K_a > 9$), all in toluene at room

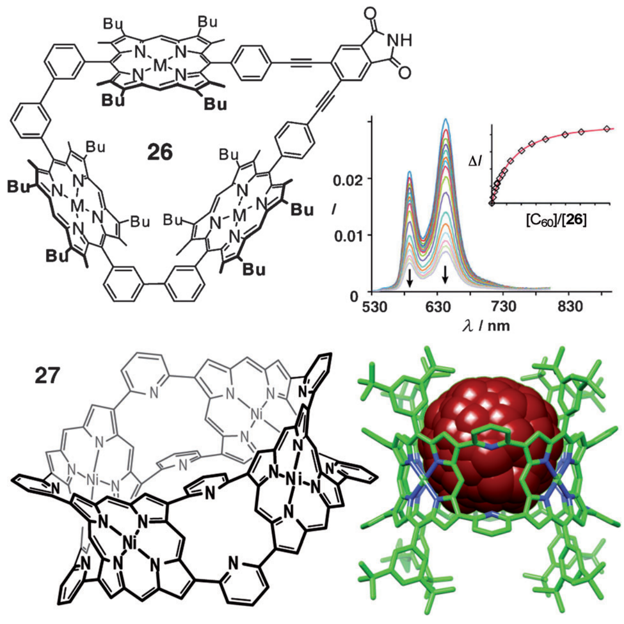
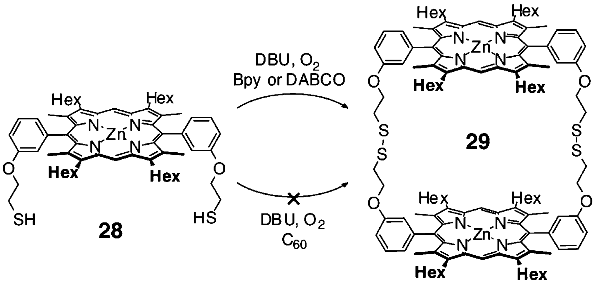


Figure 11. Top: Receptor **26** displaying three porphyrin units (left) and evolution of the fluorescence emission of **26** (9.3×10^{-8} M) upon addition of C$_{60}$ in toluene (right). The inset shows the fit of the fluorescence changes to a 1:1 binding isotherm. Reproduced with permission from reference [42]. Bottom: Nanobarrel **27** (left; 3,5-di-*tert*-butylphenyl substituents are omitted for clarity) and the X-ray crystal structure of its complex with C$_{60}$ (right). Color code as in Scheme 1.

temperature. Moreover, the remarkable difference between the stabilities of the associates of **26** with C_{60} and with the higher fullerenes also endows **26** with a high degree of selectivity, as nicely illustrated with competition experiments monitored by mass spectroscopy.

To date, the receptor displaying the highest number of porphyrin units was described by Osuka and co-workers with the so-called "nanobarrel" **27**, which features four linked porphyrin units (Figure 11).[43] In this work, the authors report the elegant synthesis of this host and the solid-state structures of both **27** and C_{60}·**27**. These reveal that **27** displays concave porphyrin units that are shape-complementary with fullerenes. Despite the expected synergistic effect of the four concave porphyrin units, the calculated binding constant ($\log K_a = 5.7$ in toluene) is not as large as could be anticipated. This situation is presumably due to the use of nickel porphyrins. Indeed, previous studies showed a decrease in the binding ability by one order of magnitude when switching from zinc to nickel in macrocyclic porphyrin dimers.[44] The extreme rigidity of host **27** could also be detrimental, as a certain degree of flexibility may be required to optimize the porphyrin–C_{60} distances.[14]

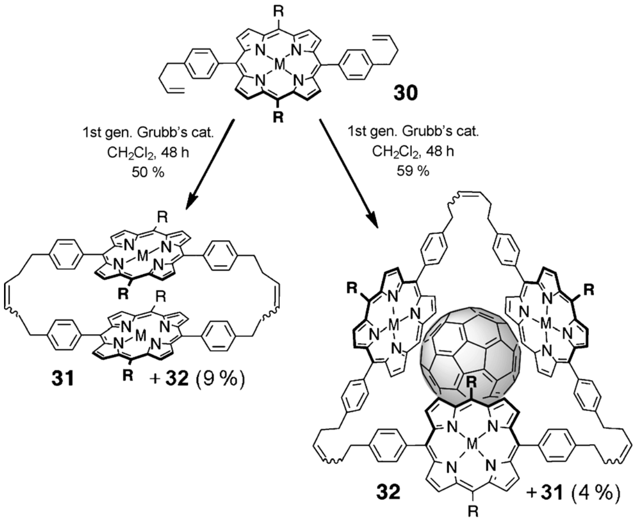
The attractive porphyrin–fullerene interaction has also been explored in dynamic combinatorial chemistry (DCC).[45] First attempts were performed by Sanders and co-workers with the precursor **28** (Scheme 2).[46] This dithiol derivative can be efficiently dimerized in the presence of bipyridine (Bpy) or 1,4-diazabicyclo[2.2.2]octane (DABCO) to afford the cyclic dimer **29**. Given the strong affinity of fullerenes for this host, the influence of C_{60} on the dynamic equilibrium leading to **29** was also investigated. Unfortunately, the radicals RS• generated during the experiment react with the fullerene template, thus ruling out the possibility of using dynamic disulfide chemistry in the presence of a fullerene template.



Scheme 2. Templating effects leading to **29**. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

Later, this templating approach was successfully followed by Langford and co-workers.[47] The strategy relies on the utilization of a template fullerene guest that preorganizes porphyrin subunits before the cyclization reaction. In this manner, the final equilibrium can be displaced toward the best fullerene host (Scheme 3).

For instance, the metathesis reaction of porphyrin derivative **30** in the absence of fullerene template mainly leads to the formation of the macrocyclic dimer **31** (50% yield) and affords the cyclic trimer **32** as a side product (9% yield). The same reaction carried out in the presence of C_{60} or C_{70} results in the trimer **32** as the major product (59% yield), while dimer **31** becomes the side product (4% yield). Performing the reaction with either fullerene does not significantly modify the final state, which is not surprising, since **32** is sufficiently large and flexible to accommodate both C_{60} and C_{70}. In principle, using higher fullerenes would be of particular interest to extend this concept and prepare molecules capable of extracting them selectively.



Scheme 3. Templated synthesis of macrocycle **32**.

Increasing the binding ability of fullerene receptors is also interesting for the preparation of functional materials, although examples along these directions remain scarce.[48] To our knowledge, the majority of the work concerning this issue has been reported by the Tani group. Their studies focus on the self-assembly of macrocyclic dimers **33** and **34** (Figure 12).[49–51]

Thanks to the pyridyl-substituted porphyrin units and to the rigidity of these molecules, an original network of C–

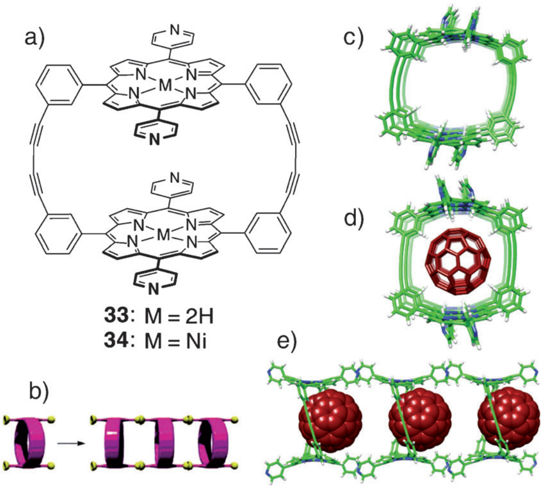


Figure 12. a) Compounds **33**–**34**, b) their self-assembly, and X-ray crystal structures of c) **34** and d,e) C_{60}·**34**. Color code as in Scheme 1.

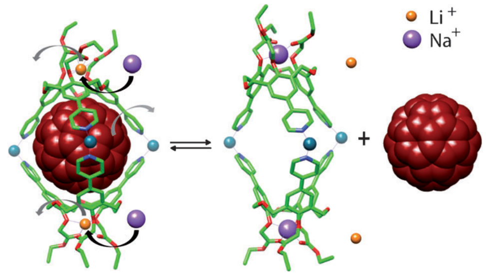
H···N hydrogen bonds between the pyrrole β-hydrogen atoms and the pyridyl nitrogen atoms as well was π–π interactions between adjacent pyridyl rings is formed, thus allowing the growth of supramolecular nanotubes. In the case of **34**, this arrangement is maintained when C_{60} is cocrystallized with the host.[49] The linear organization of the guests in this material encouraged authors to thoroughly study the conductivity of the corresponding materials.[50] These measurements notably demonstrated that such an organization does give rise to an anisotropic and high conductivity ($\sigma = 0.72\ cm^2V^{-1}s^{-1}$) along the fullerene axis. A very different situation arises when C_{60} and **37** are cocrystallized.[51] Indeed, nanotubes are no longer observed in the solid state, and fullerenes are organized in a zig-zag fashion. This structural modification consequently results in a decreased conductivity (0.13–0.16 $cm^2V^{-1}s^{-1}$) and a lower anisotropy. Also noteworthy are the results obtained with C_{60}·**34** concerning organic photovoltaics, as the authors were able to prepare a photoelectrochemical cell capable of converting solar energy with 0.33 % efficiency.

3.2. Cycles and Cages Assembled by Metals

In this section, we underline an interesting strategy for the hosting of fullerenes, which consists of using programmed building blocks that self-assemble into capsules. In particular, the utilization of metal–ligand interactions allows the construction of these receptors in a straightforward and simple manner and offers a lever to tune host features such as geometry and solubility.

In order to prepare fullerene receptors, palladium(II)–pyridine coordination chemistry has been widely used for various reasons: 1) the simple way these bonds are created, 2) the possibility to access miscellaneous host geometries by tuning the angle between pyridyl rings, and 3) the dynamic character of the Pd···N bonds, which allows the convergence of the system toward the most thermodynamically stable state.[52] The first example of such a self-assembled capsule was described by Shinkai and co-workers in 1999 with the homooxacalix[3]arene-based complex **36** (Figure 13).[53] By mixing ligand **35** and 1,3-bis(diphenylphosphino)propane palladium(II) triflate in a 2:3 ratio, the metal-assembled cage was quantitatively obtained. Out of various guests, under study, fullerene C_{60} was the only one associated with $\log K_a = 1.7$ in 1,2-dichloroethane at 25 °C. Its inclusion leads to the appearance of a new set of signals in both the ^1H and the ^{13}C NMR spectra, showing that free and bound C_{60} are in slow exchange on the NMR time scale, even at temperatures as high as 90 °C. In contrast, the signals in the NMR spectrum of ligand **35** were hardly modified in the presence of fullerene, which demonstrates that formation of the dimeric capsule is critical for the recognition event.

The influence of preorganization was made even clearer with a subsequent thorough study.[54] Cage **36** was functionalized with OCH_2CO_2Et chains at the lower rims of homooxacalix[3]arene scaffolds, which allowed the authors to assess the effect of alkali-metal complexation in these sites. As deduced from the ^1H NMR spectrum, the addition of the small lithium cation splays 4-(4-pyridyl)phenyl moieties, resulting in the reinforcement of the multipoint interaction between fullerene and its container ($\log K_a = 3.3$ in 1,2-dichloroethane at 25 °C). Unlike lithium, the bigger sodium cation narrows the cavity and decreases the binding constant by almost three orders of magnitude ($\log K_a = 0.7$ in 1,2-dichloroethane at 25 °C). Besides, authors took advantage of this feature to perform competition experiments involving C_{60}·(**36**·Li)$_2$ and an excess of sodium perchlorate (Scheme 4).



Scheme 4. Exclusion of C_{60} from (**36**·Li)$_2$ upon sodium complexation. Color code as in Scheme 1; O red, Pd light blue, Li orange, Na purple.

This experiment resulted in a decrease of the ^{13}C NMR signal associated with included C_{60} from 40 % to 10 % versus the total guest concentration. Later, a similar capsule (**37**) was prepared by Pirondini et al. starting from a resorcinarene derivative (Figure 14).[55] Single crystals of this metallacage were obtained and their study by X-ray diffraction revealed

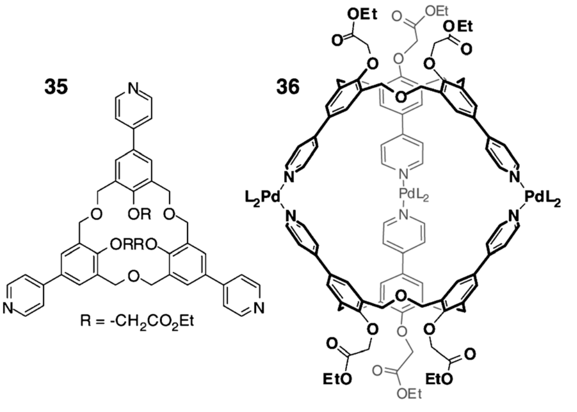


Figure 13. Metallacage **36** and its precursor **35**. L = 1,3-(diphenylphosphino)propane.

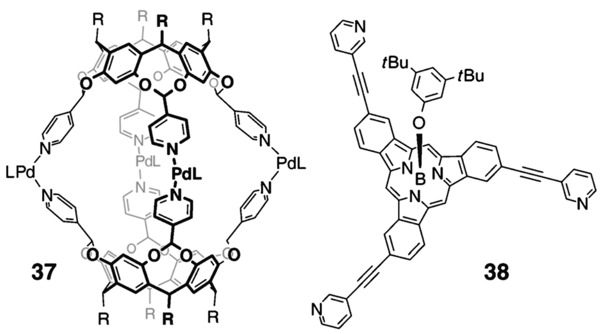
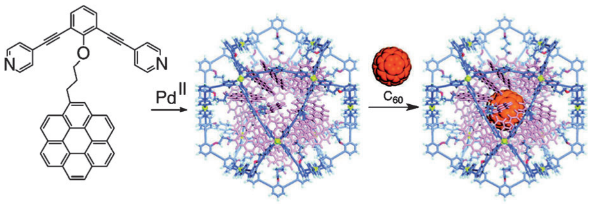


Figure 14. Structures of metallacage **37** and subphthalocyanine **38** (R = -CH_2CH_2Ph, L = 1,3-(diphenylphosphino)propane).

the size of the cavity. Its diameter measures approximately 1.2 nm, which is suitable to host a C_{60} derivative. By using methanofullerene derivatives as guests, this assertion could be confirmed by NMR spectroscopy and mass spectrometry with the appearance of new sets of signals in both the ^{1}H and ^{13}C NMR spectra and the detection of the fullerene inclusion complex, respectively.

A similar strategy was explored by allowing derivative **38** (Figure 14) and (ethylenediamine)palladium(II) nitrate ([(en)Pd(NO_3)$_2$]) to react.[56] With this example, Torres and Claessens proposed a nice evolution in this category of receptors with the incorporation of electroactive and luminescent subphthalocyanine moieties. Noticeably, the affinity of C_{60} for the cavity allows a tremendous increase of the fullerene solubility in acetone (from 1 μg mL^{-1} to ca. 1 mg mL^{-1}), which makes this receptor a powerful phase-transfer catalyst for C_{60}. In this regard, Fujita and co-workers recently reported the self-assembly of coronene derivative **39** to form the $M_{12}L_{24}$ complex **40** (M = Pd^{II}; L = **39**, see Scheme 5).[57] Assuming that π-extended coronene platforms interact with [60]fullerene, the authors prepared nanocapsules that contain 24 coronene units. Within the cavity, a pseudo-solvent phase forms, as demonstrated from the ^{1}H NMR spectrum (no significant broadening or splitting of the signals).



Scheme 5. Ligand **39**, its complex **40** in the presence of palladium(II), and the corresponding C_{60}-containing metallacage C_{60}•**40**. C blue, O red, N dark blue, Pd yellow. The pseudo-solvent phase is purple.

Just like the **38**$_2$[Pd^{II}(en)]$_3$ metallacage, **40** acts as a phase-transfer catalyst that helps C_{60} solubilization in dimethylsulfoxide, a very poor solvent for fullerenes. Furthermore, the role of coronene units was clearly evidenced by performing similar extraction experiments with analogues of **40** in which it was replaced with either methoxy or 4-chloronaphthyl-1-oxy groups, which proved unable to solvate C_{60}.

Very recently, the same team reported an outstanding study dealing with crystalline sponges for fullerenes.[58] By cocrystallizing 2,4,6-tris(4-pyridyl)-1,3,5-triazine and Co^{II} thiocyanate, a new metal–organic framework (MOF) **41** (Figure 15) was obtained, which proved to be an extremely efficient host for different organic guests, including fullerenes, in the solid state. Their experiments consisted in immersing crystals of **41** in a saturated solution of guest and studying the corresponding solids. With tetrathiafulvalene and diphenylamine, the inclusion phenomenon could be easily monitored in a single-crystal to single-crystal manner.[59] Indeed, mixing single crystals of **41** with these species suspended in water does not break the crystalline state of the solid. On the contrary, guests diffuse within the porous material and occupy specific sites within the coordination network, namely the tetrahedra made up of four ligands and six cobalt(II) corners (Figure 15 a), as shown unequivocally by X-ray crystallography.

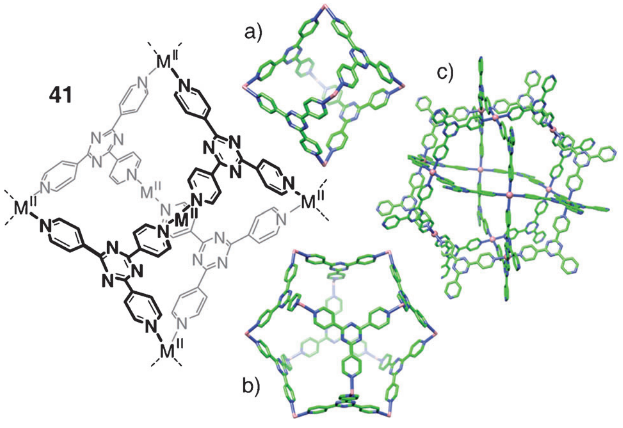
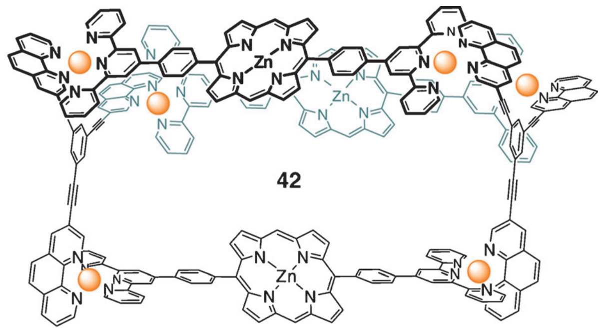


Figure 15. Cages formed from 2,4,6-tris(pyridyl)-1,3,5-triazine and Co^{II}. Color code as in Scheme 1; Co pink.

The crystalline structure of **41** also reveals the presence of other cavities within the MOF. These cubohedrons, defined by twelve metal centers and eight or twenty-four ligands, are represented in Figure 15 b,c. Their higher dimensions and the observation of large channels (diameter 1.19 nm) in the X-ray structure encouraged authors to investigate the inclusion properties of **41** toward fullerenes. Remarkably, they have been able to demonstrate that fullerenes C_{60} and C_{70} incorporate into the network up to 35 % in weight. The resulting materials exhibited excellent retention abilities with half-lives of 15 and 25 days, respectively, when immersed in toluene. This difference underlines the fact that the hosting solid has different affinities for these guests. This feature was illustrated by competition experiments with C_{60}/C_{70} (1:1) mixture, which resulted in enrichment in C_{70} of up to 93 % after two successive extractions. Starting from fullerene soot, the proportions of higher fullerenes C_{76}, C_{78}, and C_{84} could be increased by 2.6–2.7 fold, which makes such porous solids very promising materials for the extraction of higher fullerenes. In the future, we believe significant improvements will result from a careful optimization of the shape and the size of the cavities by utilizing new metals and ligands in these MOFs and also by adapting the electronic properties of the self-assembled ligands.

Apart from zinc–,[60] palladium–, or cobalt–pyridyl coordination chemistry, we also underline the recent results described by Schmittel et al. with a new C_{60} receptor taking advantage of both the utilization of metalloporphyrin units and self-assembling copper(I) ions.[61] Thanks to the singular coordination chemistry of this metal ion, the authors proposed the synthesis of **42** (Figure 16), a prismatic metallacage. The different starting materials, that is, copper(I) hexafluorophosphate tetraacetonitrile complex and both the phenanthroline- and the terpyridine-based ligands, are not likely to form **42** without template. However, the authors were able to



42

Figure 16. C_3-symmetric metallacage **42**. Cu orange.

show that the same reaction could be quantitatively performed when carried out in the presence of 1,3,5-tris(4-pyridyl)benzene or [60]fullerene. As expected, the latter molecules facilitate the formation of **42** by acting as a glue toward porphyrin units stabilizing the 11-membered supramolecular assembly. This example, together with that described by Langford and others,[47] demonstrates how fullerenes are not only possible guests but also possible templates for the construction of sophisticated supramolecular architectures.

4. Summary and Outlook

In this Minireview, we underline how the new generation of macrocyclic hosts for fullerenes holds promise to fulfill many of the goals the scientific community is facing within this field. The key feature of these species is their high degree of preorganization that lowers the entropic cost for binding the fullerene guests. This characteristic also allows association of fullerenes with increased selectivities, particularly in the case of rigid hosts that cannot adapt their shape to the guest. However, we should keep in mind that this increase in selectivity requires in return a much more careful fine tuning of the structure of the host. Through this Minireview, we have seen how very small changes lead to significant differences in the binding ability, resulting in both successes[33,41] and failures.[13,33] However, the new custom-made macrocycles have started to address issues like the enantioselective extraction of higher fullerenes[40,41] and have opened avenues to push back the limits reached with non-macrocyclic receptors.

Moreover, we shed light on the new strategies that will help the community in the near future, by providing tools to prepare receptors in a straightforward manner. Utilizing fullerenes as templates for the construction of receptors endowed with several recognition motifs seems a promising approach to displace the equilibrium toward the isolation of the best host. By preparing the fully covalent macrocycle **32**, the team of Langford reported the corresponding proof-of-principle.[47] Recently, de Mendoza and co-workers have also successfully utilized an appealing strategy to selectively bind C_{70} and C_{84} in a CTV-based capsule obtained by self-association through hydrogen bonding.[62]

In a reciprocal manner, fullerene molecules can also be used to tune the properties of molecular materials, for example carbon nanotubes.[63] In this context, spectacular results have been reported by Sanders and co-workers with the morphological tuning of amino acid based self-assemblies.[64] The helical structures developed by this team,[65a,b] as well as by the groups of Toniolo[65c] and Kawauchi and Yashima,[66] are extremely promising materials both for the purification of higher fullerenes and for their chiral resolution. These results pave the way for developing efficient and structurally simple materials which will allow the purification of higher fullerenes on larger scales. It is our feeling that the incorporation of the latter in organic electronics and photovoltaics may be achieved in the next few years.

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