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Molecular tweezers for fullerenes*

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Abstract: The search for molecular receptors capable of forming stable associates with fullerenes is a very active field of research in fullerene chemistry, with the purification from fullerite and the self-assembly of nanoscale electronic devices as driving forces. The construction of bivalent, tweezer-like receptors featuring two recognizing units connected through a spacer is one of the most successful design strategies employed in this field. Here, we present an overview of the most significant examples of these "molecular tweezers" for fullerenes.

Keywords: fullerenes; molecular recognition; porphyrins; supramolecular chemistry; tetrathiafulvalenes.

INTRODUCTION

Four years before the discovery of buckminsterfullerene was recognized with the Nobel prize in chemistry [1], the first successful example of a molecular receptor for [60]fullerene had already been reported by Ringsdorf, Diederich, and co-workers. They utilized aza-crown ethers as a scaffold, on which they attached lipophilic alkyl chains [2]. Since then, other classic macrocyclic motifs in supramolecular chemistry, like cyclodextrins [3], cyclotriveratrylenes [4–6], and calixarenes [7–9] have all been utilized in the molecular recognition of fullerenes. The basic design principle behind these receptors is the inclusion of the fullerene guest in the lipophilic cavity of the macrocycles, which is often extended with other organic, typically hydrophobic, addends to adapt it to the size of the guest. This strategy takes advantage of the intrinsic insolubility of the fullerenes, and the recognition event is based fundamentally on van der Waals interactions.

A different strategy involves the identification of organic molecules capable of establishing positive noncovalent interactions with the fullerenes, habitually large aromatic molecules which can interact with the fullerenes through π–π stacking. Once the recognizing motif is pinpointed, if a single unit does not suffice to build an efficient receptor, a suitable spacer is designed so as to hold two or more units at the right distance to recognize the fullerene in question. Within this strategy, perhaps the most popular design has been the connection of two units of the recognizing fragment to form what is often termed a "tweezer" for fullerene [10,11]. Herein, we will focus on this molecular tweezer strategy to recognize fullerenes and give an overview of the examples of such receptors reported in the literature to date.

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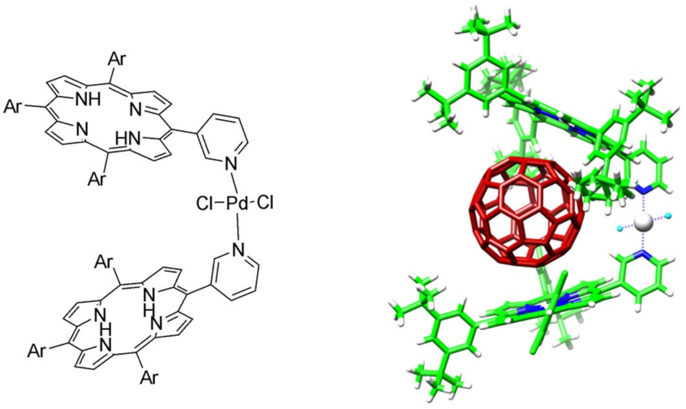
PORPHYRIN-BASED MOLECULAR TWEEZERS FOR FULLERENES

Porphyrins are well known to interact favorably with fullerenes both in solution and in the solid state, which has been exploited in the design of a wide variety of receptors for fullerenes [12,13]. For example, Aida reported the formation of very stable inclusion complexes between fullerenes and a dimeric construct in which two metalloporphyrins are linked by flexible alkyl spacers, forming a macrocycle [14]. Structural variations on this design have led to what is probably the richest collection of receptors for fullerenes [15], including the world-record holder in complex stability, with $K_a = 1.3 \times 10^8$ M^{-1} in 1,2-dichlorobenzene at room temperature [16], and the first chiral sensor for the inherently chiral higher fullerenes [17]. The work of Aida is, nevertheless, based on macrocyclic structures, and we shall not describe it in detail.

Several tweezers featuring porphyrins as binding motifs have also been reported, spearheaded by the work by Boyd and Reed on their "jaws" receptors. The first example of this series was reported in 2000, the structure of the receptor and its complex with C_{60} are depicted in Fig. 1 [18].



1 **1**·C_{60}

Fig. 1 Chemical structure of the "jaws" receptor reported by Boyd and Reed [18], and X-ray crystal structure of its complex with C_{60}.

In receptor **1** the porphyrin units are linked through coordination on a Pd metal center. The use of Pd results in partial metalation of the porphyrin units. Binding of C_{60} and C_{70} to receptor **1** was unambiguously demonstrated by a variety of techniques, including fast atom bombardment (FAB) and matrix-assisted laser desorption/ionization (MALDI) mass spectrometry, ^{1}H and ^{13}C NMR. Remarkably, they succeeded in obtaining single crystals of the **1**·C_{60} complex. In the crystal, the closest Pd to fullerene carbon distance is 2.856 Å, indicating very tight binding of the guest. The binding constant of this receptor toward C_{60} was estimated to be 5.3×10^3 M^{-1} in toluene-d_8 at room temperature. Following their preliminary communication, Boyd and Reed reported very similar receptors, in which the coordination link was substituted with covalent spacers, namely, amides of both the isophthalic and terephthalic acids. These receptors were proven to be worse binders for fullerenes than the receptors connected through a Pd center [19].

A particularly interesting example of molecular tweezer for fullerene was reported by Shinkai and co-workers in 2002 [20]. Their receptor (**2** in Fig. 2) can be switched between a state in which it cannot bind fullerene ("off") and one in which it can ("on") through the coordination of two pyridine addends to either the porphyrins or an external Pd center. When C_{60} is added to a solution of **2** in its "off" state, the authors observed no changes in its UV–vis spectrum. On the contrary, when the same experiment is carried out with **2** in its "on" state, the absorption corresponding to the Soret band of the por-

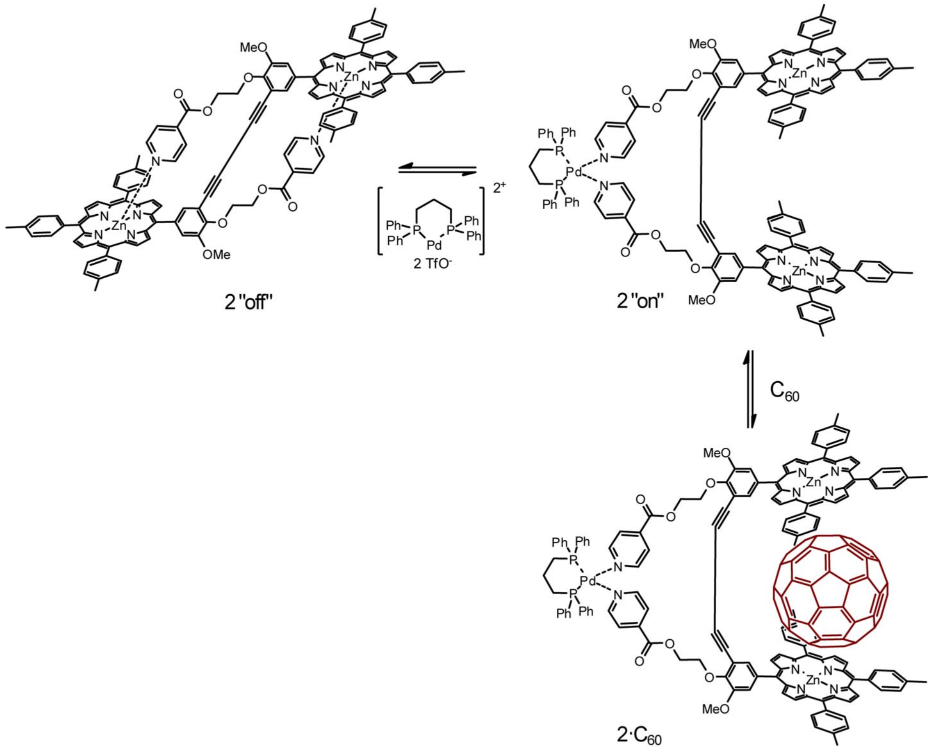
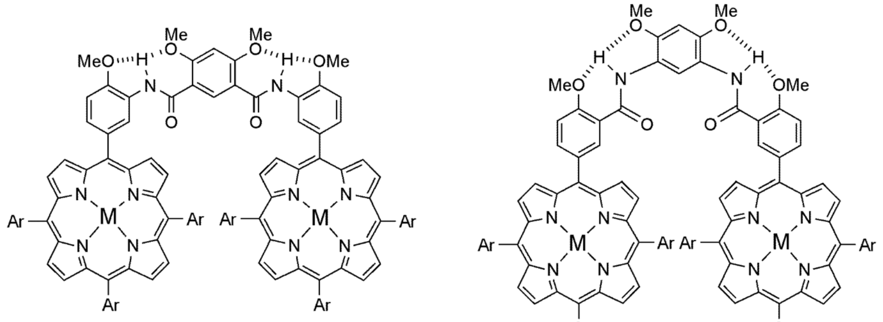


Fig. 2 Structure of the switchable receptor synthesized by Shinkai and co-workers [20] and scheme showing its switching between the "off" and "on" states and its binding to C_{60}.

phyrins decreases in intensity and is bathochromically shifted, an indication of the association of C_{60}. Indeed, through UV–vis titrations, it was estimated that **2** "on" binds [60]fullerene with a respectable stability constant of $K_a = 5.1 \times 10^3$ M^{-1} in toluene:CH_2Cl_2 (50:1).

More recently, the group of Li made use of secondary H-bonding interactions within the spacer to introduce a higher degree of preorganization into the tweezer-like design (Fig. 3) [21]. The result of this is that both porphyrin units are held in a *syn* conformation, enhancing their ability to associate fullerenes. The authors estimated the binding constants of these receptors toward C_{60} and C_{70} through UV–vis titrations. The structure of the receptors is shown in Fig. 3. A significant increase of over one order of magnitude in the binding constants was observed for both **3** and **4** when compared to receptor **1**. For example, **3** binds C_{60} with a binding constant of 1.0×10^5 M^{-1} in toluene at room temperature, whereas **1** shows a binding constant of 5.3×10^3 M^{-1} under the same experimental conditions.

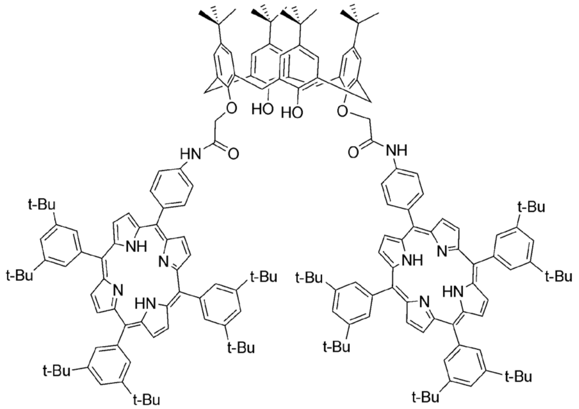
Comparing receptors **3** and **4**, it is immediately apparent that **3** is a stronger binder, associating both C_{60} approximately four times better than **4**. Although the authors of the original manuscript do not comment on this, it beautifully illustrates how even extremely small structural changes, like the change in connectivity of the amide group between **3** and **4**, can result in relatively high changes in the binding constants.



3 **4**

Fig. 3 Chemical structure of receptors **3** and **4** reported by Li [21].

The collaboration between the groups of Armaroli, Boyd, and Reed, has produced a family of porphyrin tweezers for fullerene in which the covalent linkers are calix[4]arenes [22]. The structure of the most efficient binder for C_{60} and C_{70} among the six receptors synthesized is shown in Fig. 4. Receptor **5** showed binding constants of (2.6 ± 0.4) × 10^5 M^{-1} and (2.3 ± 0.2) × 10^6 M^{-1} in toluene at room temperature toward C_{60} and C_{70}, respectively.



5

Fig. 4 Structure of receptor **5** that showed the highest affinity for C_{60} and C_{70} among those described by Armaroli, Boyd, and Reed [22].

In 2008, the group of Morin described a picturesque example of bisporphyrin tweezers for fullerenes. In this case, the two porphyrin units are not covalently but mechanically linked, making use of a [3]rotaxane structure [23], in which the porphyrins decorate the macrocycles (Fig. 5) [24]. The increase in conformational freedom provided by the mechanical bond as compared to the examples where rigid spacers are utilized results in a significant decrease in the binding constants. For example, **6** binds C_{60} in toluene at room temperature with K_a = (4.6 ± 0.3) × 10^3 M^{-1}, close to two orders of magnitude smaller than **5**. Nevertheless, this example illustrates the possibility of utilizing different kinds of spacers, including unconventional ones.

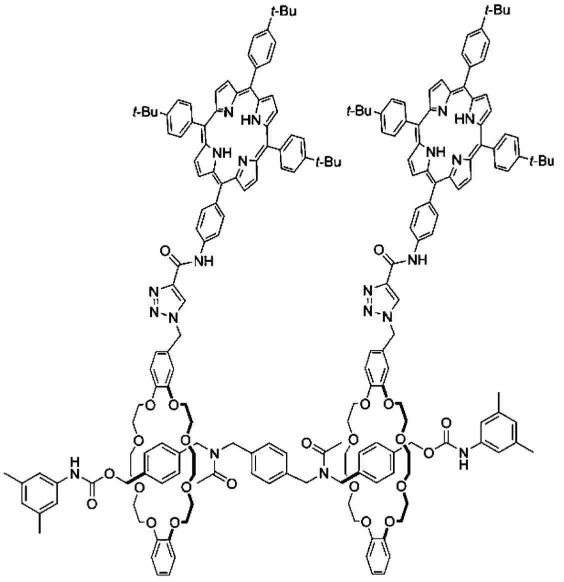


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Fig. 5 Structure of the [3]rotaxane **6** shown in the co-conformation in which it can bind C_{60} [24].

We will conclude this section dedicated to porphyrin tweezers for fullerenes with the work on tripodal porphyrin receptors reported by the groups of Pascu and Sanders [25]. At first sight, their receptors do not strictly fit in the category of molecular tweezers, since they feature three recognizing motifs each, but as we shall see their binding mode is that of a tweezer. The structures of the tripodal hosts **7** and **8** are shown in Fig. 6.

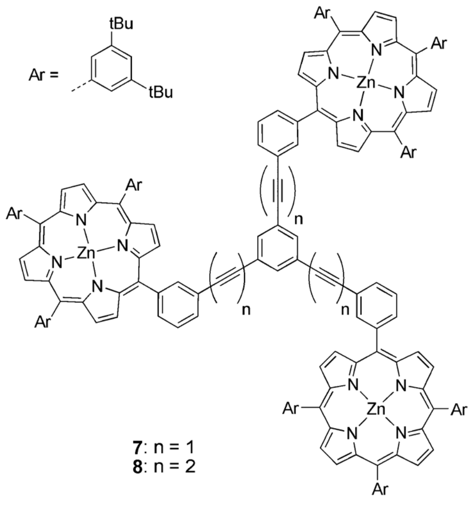


Fig. 6 Chemical structure of the tripodal receptors studied by Pascu and Sanders [25].

Given their chemical structure, in principle several binding modes toward C_{60} can be expected for **7** and **8**, including one in which all three porphyrin units are wrapped around a single C_{60} molecule. In d_8-toluene solution, the authors studied the binding event through by ^1H NMR titrations and Job's plots. For host **8**, a 1:1 binding stoichiometry and a $K_a = (2.5 \pm 0.3) \times 10^3\ M^{-1}$ were determined. The case of receptor **7** is a more complicated one. During the titration of **7** against C_{60} dissimilar binding isotherms and stoichiometries were suggested depending on the ^1H NMR signal under scrutiny. The signals that were shifted upfield suggested a 1:1 binding event, with a K_a between 300 and 1000 M^{-1}, whereas the analysis of the downfield shifted protons indicated a 2:1 C_{60}:**7** stoichiometry. To explain these data, the authors carried out careful qualitative analysis of the NMR data, to conclude that, in solution, **8** binds C_{60} by wrapping it with all three porphyrin units simultaneously, adopting a bowl-like conformation. The smaller receptor, **7**, cannot adopt such conformation, and thus binds C_{60} in a tweezers-like fashion leaving one porphyrin unbound, and explaining the difference in binding constants.

This picture changes when moving from solution to the solid phase. When **8**·C_{60} co-crystals were studied under X-ray diffraction, a dimeric structure was found in which two units of **8**, each binding one fullerene in a pincer-like fashion are linked association of two more units of C_{60}, bound to the external face of the tweezer binding site of one of the molecules of **8** and to the third porphyrin moiety of the other (see Fig. 7).

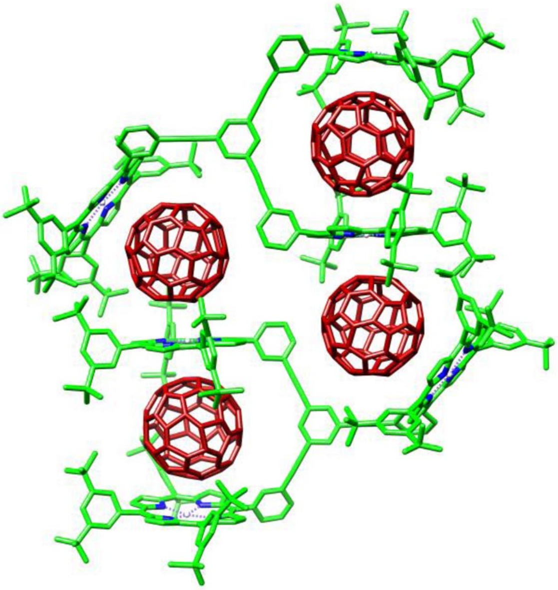


Fig. 7 Solid-state structure of the **8**·C_{60} co-crystal.

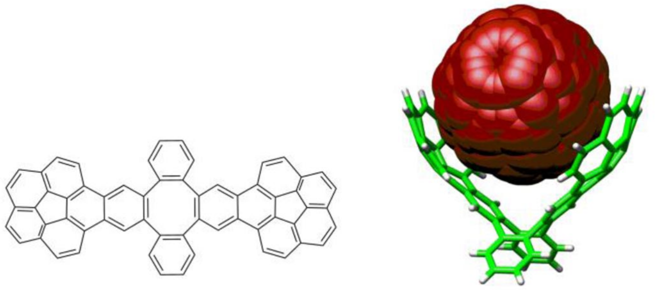
This change in binding mode is explained by the authors on account of the decrease in the entropic cost of an intermolecular binding event such as that shown in Fig. 7 when moving from solution to the solid state. In the case of host **7**, a similar tweezer-like disposition with the third porphyrin unit linking two units of the receptor was found, but in this case the guest of the tweezer cavity was not C_{60}, but toluene, the solvent of crystallization.

MOLECULAR TWEEZERS BASED ON OTHER RECOGNITION MOTIFS

The work carried out with porphyrins has by and large dominated the design of molecular receptors for fullerenes [15]. Nevertheless, our group [26,27] and others [28] have recently been investigating other recognition motifs. In this second part, we will discuss the application of the molecular tweezers design to those novel recognition fragments.

Corannulene, a large conjugated compound consisting of five benzene rings fused into a central five-member ring was first synthesized by flash vacuum pyrolisis in 1966 [29]. Following this, several related examples of bowl-shaped conjugated molecules, which in many cases can be seen as fullerene fragments, have been synthesized. Various attempts at constructing molecular receptors for fullerenes which incorporate one of these bowl-shaped molecules as recognizing elements have been reported [28], but, as could be expected considering their size—nearly identical to that of fullerene and thus too small to associate it—chemical derivatization is necessary to observe binding.

The most successful example of receptor for fullerene based on corannulene is precisely a molecular tweezer, the "buckycatcher" [30]. In the buckycatcher **9**, two units of corannulene are linked through a rigid polycyclic structure (Fig. 8). Host **9** forms stable complexes with C_{60} ($K_a = 8.6 \times 10^3$ M^{-1}, toluene-d_8, room temperature), and X-ray diffraction studies of mixtures of **9** and C_{60} allowed the determination of the solid state structure of the complex (Fig. 8.).


9

9·C_{60}

Fig. 8 Chemical structure of corannulene-based molecular tweezer **9**, and solid state structure of the **9**·C_{60} complex [30]. Please note that the fullerene unit is disordered in the crystal.

Recently, we realized that the shape complementarity between the concave aromatic face of 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9*H*)-ylidene]-1,3-dithiole (exTTF, Fig. 9a) and the exterior of fullerenes should lead to large and positive noncovalent interactions. In fact, density functional theory (DFT) calculations predict positive binding energies of up to 7.00 kcal mol^{-1} between a single unit of exTTF and C_{60} in the gas phase. However, we have not observed conclusive experimental evidence of association in either UV–vis or NMR titrations.

In light of these results, and the precedents described above, we designed receptor **10** (Figs. 9b, c) in which two exTTF units serve as recognizing units, and an isopththalate diester acts as a spacer [31]. Receptor **10** was designed as a proof-of-principle of the validity of exTTF as a building block for fullerene receptors, so easy synthetic access was a priority. Host **10** was obtained in excellent yields from readily available exTTF methyl alcohol and commercially available isophthaloyl dichloride. Upon addition of fullerene to a solution of **10**, we observed changes indicative of association in the UV–vis spectrum of the receptor. Namely, the absorption band characteristic of exTTF, centered at $\lambda = 434$ nm decreases in intensity with increasing concentration of C_{60}. Besides this, after subtraction of the absorption of fullerene, we observe the concomitant appearance of a charge-transfer band at $\lambda = 482$ nm. Nonlinear regression of these spectral changes allowed us to estimate a binding constant of $(3.0 \pm 0.2) \times 10^3$ M^{-1} in chlorobenzene at room temperature. Binding was also observed in the gas phase through MALDI-TOF mass spectrometry (Fig. 9d) and in ^{1}H NMR titrations in toluene-d_8. Considering the modest degree of preorganization of receptor **10**, the considerable stability of the **10**·C_{60} complex demonstrates that exTTF is indeed a very valid fragment as a recognizing motif for fullerene. This is

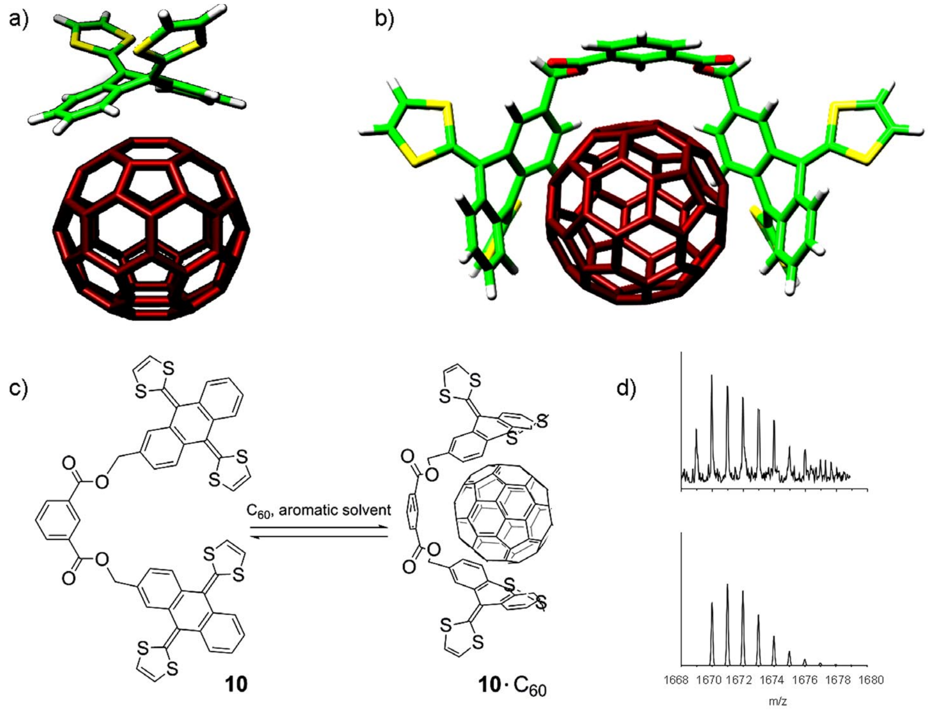


Fig. 9 (a) Molecular model showing the shape complementarity between exTTF and C_{60}. (b) Energy-minimized structure of the **10**·C_{60} complex, as predicted by calculations at the BH&H/6-31G** level. (c) Chemical structure of tweezers **10** and its complex with C_{60}. (d) Experimental (MALDI-TOF, top) and calculated (bottom) mass spectra for the **10**·C_{60} associate.

most probably due to the unique combination of shape and electronic complementarity between exTTF (concave, electron-rich) and fullerene (convex, electron-poor). Indeed, in later work, we have also demonstrated that this is also the case for other π-extended TTF derivatives [32].

The binding behavior of **10** toward C_{60} was proven to be solvent-dependent. Whereas in aromatic solvents the formation of the expected pincer-like complex was observed, in $CHCl_3/CS_2$ mixtures the spectral changes were analogous to those found in chlorobenzene, but the binding isotherm turned out to be sigmoidal in shape. This is generally regarded as indicative of cooperative binding events. Indeed, the binding isotherm fitted very well to the Hill equation, to yield a Hill coefficient of 2.7 ± 0.3 and an apparent binding constant of 3.6×10^3 M^{-1}. A value of $n_H > 2$ rules out the formation of the tweezers-like **10**·C_{60} complex since it features two binding sites only. As 1:1 stoichiometry was experimentally found by continuous variation plots, we interpreted these results, suggesting the formation of a supramolecular tetramer in which two units of C_{60} are sandwiched between two molecules of receptor **10**.

Since exTTF is known to undergo photoinduced electron transfer (PET) when covalently connected to fullerene [33], we decided to investigate whether intermolecular PET processes were also possible in the **10**·C_{60} complex. To do so, we synthesized an analog of **10** featuring a terephthalic ester spacer, and carried out photophysical studies in solution in collaboration with the group of Dirk M. Guldi [34]. We were glad to observe that intracomplex PET does occur from the exTTF units of either receptor and the bound C_{60}. The charge-separated states presented short lifetimes in the range of 3.5–12.7 ps, since the formation of the complexes implies partial orbital overlap between the electroactive units, which facilitates both charge separation and charge recombination processes.

The fairly high binding constant of receptor **10** toward C_{60} got us interested in the role that the concave shape of the recognizing unit (exTTF) played in the overall stabilization of the complex. Shortly before our investigations, the group of Kawase had termed the increase in noncovalent interactions between curved aromatic hosts and guests "concave–convex interactions", and suggested these might play a distinct contribution to the stabilization of the complexes. In order to shed light on whether these concave–convex interactions contributed to stabilize our complexes, and to what extent, we designed and synthesized a collection of structurally related receptors **11–13** (Fig. 10) in which 11,11,12,12-tetracyanoanthraquinodimethane (TCAQ), anthraquinone, and tetrathiafulvalene (TTF) were utilized as recognizing units. These hosts, together with **10**, provided a full collection of receptors in which the size, shape and the electronic character of the recognizing motifs were selectively modified. The binding constants of receptors **10–13** toward C_{60} were investigated through ^{1}H NMR titrations in $CDCl_3$ [35].

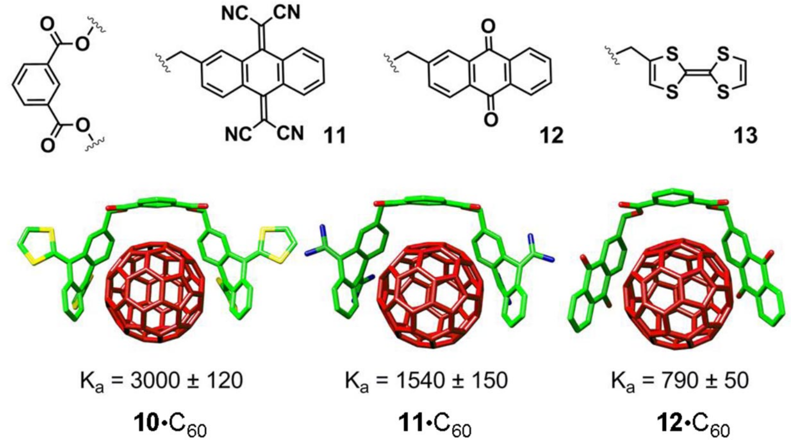


Fig. 10 Chemical structures of receptors **11–13** (top) and structure of the **10**•C_{60}, **11**•C_{60}, and **12**•C_{60} complexes, calculated at the BH&H/6-31G** level with their corresponding binding constants determined by ^{1}H NMR titrations in $CDCl_3$ [35].

Receptor **10** incorporates five aromatic rings—two per recognizing unit plus the isophthalic spacer, a large and concave surface—and is electron-rich. As a consequence, **10** is the strongest binder for C_{60}, with a $K_a = (3.00 \pm 0.12) \times 10^3\ M^{-1}$. In tweezer **11**, TCAQ is the recognizing element. Thus, it portrays identical number of aromatic rings and surface available for recognition as **10** with close to identical curvature, but is electron-poor. The variation in electronic nature has the outcome of a drop-off in K_a to $(1.54 \pm 0.15) \times 10^3\ M^{-1}$. A similar decrease in the association constant is observed when moving from **11** to **12**. In this case, the surface available for van der Waals interactions is similar to that of **10** and **11**, but **12** lacks both the concave–convex and the electronic complementarity. Host **12** shows binding constant of $(0.79 \pm 0.05) \times 10^3\ M^{-1}$. Lastly, no sign of association with C_{60} was observed in the case of tweezers **13**, in which the electron-rich, small, and non-aromatic TTF unit served as recognizing unit.

Comparison of the binding constants of **10** and **11** toward C_{60} suggests a noticeable contribution of coulombic interactions. However, the fact that **13** does not show any sign of complexation toward C_{60} implies that it is not quantitatively comparable to those of π–π and van der Waals forces, since all tweezers featuring large recognizing motifs are capable of associating C_{60} under our experimental conditions. The contribution of concave–convex interactions is illustrated by the cases of receptors **11** and

12. In spite of the more electron-poor character of **11** when compared to **12**, its binding constant toward C_{60} is larger, which can only be justified by the concave shape of the TCAQ recognizing units.

CONCLUSIONS AND OUTLOOK

Here we have presented an overview of the receptors for fullerene, which share a tweezers-like design. The fact that the binding constants found for these receptors are often comparable to those of the synthetically more elaborate macrocyclic-type receptors indicates that the molecular tweezers design is a very valid one, particularly in the search for new recognition motifs, where synthetic availability is a prerequisite.

The porphyrin-based molecular tweezers have been thoroughly studied by several groups, and receptors with binding constants in the order of 10^5–10^6 M^{-1} have been reported. Other binding motifs, like corannulene and π-extended TTF derivatives have also been successfully employed. In the case of our exTTF-based molecular tweezers, their extreme structural simplicity has allowed us to incorporate them as building blocks in linear [36] and branched supramolecular polymers [37], as well as in covalent dendrimers capable of associating multiple units of fullerene [38]. We are currently investigating the possibility of incorporating a higher degree of preorganization in our receptors, either by substituting the isophthalic spacers or by moving to macrocyclic structures [39].

ACKNOWLEDGMENTS

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REFERENCES AND NOTES

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley. *Nature* **318**, 162 (1985).
2. F. Diederich, J. Effing, U. Jonas, L. Jullien, T. Plesnivy, H. Ringsdorf, C. Thilgen, D. Weinstein. *Angew. Chem., Int. Ed. Engl.* **31**, 1599 (1992).
3. T. Andersson, K. Nilsson, M. Sundahl, G. Westman, O. Wennerstroem. *Chem. Commun.* 604 (1992).
4. A. Collet. *Comprehensive Supramol. Chem.* **6**, 281 (1996).
5. J. W. Steed, P. C. Junk, J. L. Atwood, M. J. Barnes, C. L. Raston, R. S. Burkhalter. *J. Am. Chem. Soc.* **116**, 10346 (1994).
6. E. Huerta, G. A. Metselaar, A. Fragoso, E. Santos, C. Bo, J. de Mendoza. *Angew. Chem., Int. Ed.* **46**, 202 (2007).
7. J. L. Atwood, G. A. Koutsantonis, C. L. Raston. *Nature* **368**, 229 (1994).
8. T. Suzuki, K. Nakashima, S. Shinkai. *Chem. Lett.* 699 (1994).
9. T. Haino, M. Yanase, Y. Fukazawa. *Angew. Chem., Int. Ed.* **36**, 259 (1997).
10. The term "molecular tweezer" was coined by Whitlock to describe a molecular receptor featuring two recognizing units separated by a relatively rigid spacer. C. W. Chen, H. W. Whitlock Jr. *J. Am. Chem. Soc.* **100**, 4921 (1978).
11. M. Harmata. *Acc. Chem. Res.* **37**, 862 (2004).
12. M. M. Olmstead, D. A. Costa, K. Maitra, B. C. Noll, S. L. Phillips, P. M. Van Calcar, A. L. Balch. *J. Am. Chem. Soc.* **121**, 7090 (1999).
13. P. D. W. Boyd, C. A. Reed. *Acc. Chem. Res.* **38**, 235 (2005).

14. K. Tashiro, T. Aida, J.-Y. Zheng, K. Kinbara, K. Saigo, S. Sakamoto, K. Yamaguchi. *J. Am. Chem. Soc.* **121**, 9477 (1999).
15. K. Tashiro, T. Aida. *Chem. Soc. Rev.* **36**, 189 (2007).
16. M. Yanagisawa, K. Tashiro, M. Yamasaki, T. Aida. *J. Am. Chem. Soc.* **129**, 11912 (2007).
17. Y. Shoji, K. Tashiro, T. Aida. *J. Am. Chem. Soc.* **128**, 10690 (2006).
18. D. Sun, F. S. Tham, C. A. Reed, L. Chaker, M. Burgess, P. D. W. Boyd. *J. Am. Chem. Soc.* **122**, 10704 (2000).
19. D. Sun, F. S. Tham, C. A. Reed, L. Chaker, P. D. W. Boyd. *J. Am. Chem. Soc.* **124**, 6604 (2002).
20. M. Ayabe, A. Ikeda, S. Shinkai, S. Sakamoto, K. Yamaguchi. *Chem. Commun.* 1032 (2002).
21. Z.-Q. Wu, X.-B. Shao, C. Li, J.-L. Hou, K. Wang, X.-K. Jiang, Z.-T. Li. *J. Am. Chem. Soc.* **127**, 17460 (2005).
22. A. Hosseini, S. Taylor, G. Accorsi, N. Armaroli, C. A. Reed, P. D. W. Boyd. *J. Am. Chem. Soc.* **128**, 15903 (2006).
23. For a leading general review in the field of synthetic molecular machines and interlocked architectures, see: E. R. Kay, D. A. Leigh, F. Zerbetto. *Angew. Chem., Int. Ed.* **46**, 72 (2007).
24. J.-S. Marois, K. Cantin, A. Desmarais, J.-F. Morin. *Org. Lett.* **10**, 33 (2008).
25. L. H. Tong, J.-L. Wietor, W. Clegg, P. R. Raithby, S. I. Pascu, J. K. M. Sanders. *Chem.—Eur. J.* **14**, 3035 (2008).
26. E. M. Pérez, N. Martín. *Chem. Soc. Rev*. **37**, 1512 (2008).
27. E. M. Pérez, B. M. Illescas, M. A. Herranz, N. Martín. *New J. Chem*. **33**, 228 (2009).
28. T. Kawase, H. Kurata. *Chem. Rev*. **106**, 5250 (2006).
29. W. E. Barth, R. G. Lawton. *J. Am. Chem. Soc*. **88**, 380 (1966).
30. A. Sygula, F. R. Fronczek, R. Sygula, P. W. Rabideau, M. M. Olmstead. *J. Am. Chem. Soc.* **129**, 3842 (2007).
31. E. M. Pérez, L. Sánchez, G. Fernández, N. Martín. *J. Am. Chem. Soc.* **128**, 7172 (2006).
32. E. M. Pérez, M. Sierra, L. Sánchez, M. R. Torres, R. Viruela, P. M. Viruela, E. Ortí, N. Martín. *Angew. Chem., Int. Ed.* **46**, 1847 (2007).
33. N. Martín, L. Sánchez, M. A. Herranz, B. Illescas, D. M. Guldi. *Acc. Chem. Res.* **40**, 1015 (2007).
34. S. S. Gayathri, M. Wielopolski, E. M. Pérez, G. Fernández, L. Sánchez, R. Viruela, E. Ortí, D. M. Guldi, N. Martín. *Angew. Chem., Int. Ed.* **48**, 815 (2009).
35. E. M. Pérez, A. L. Capodilupo, G. Fernández, L. Sánchez, P. M. Viruela, R. Viruela, E. Ortí, M. Bietti, N. Martín. *Chem. Commun*. 4567 (2008).
36. G. Fernández, E. M. Pérez, L. Sánchez, N. Martín. *Angew. Chem., Int. Ed*. **47**, 1094 (2008).
37. G. Fernández, E. M. Pérez, L. Sánchez, N. Martín. *J. Am. Chem. Soc*. **130**, 2410 (2008).
38. G. Fernández, L. Sánchez, E. M. Pérez, N. Martín. *J. Am. Chem. Soc*. **130**, 10674 (2008).
39. After this article was sent for publication, we have succeeded in synthesizing very efficient exTTF-based macrocyclic receptors, see: H. Isla, M. Gallego, E. M. Pérez, R. Viruela, E. Ortí, N. Martín. *J. Am. Chem. Soc*. In press. DOI: 10.1021/ja910107m.