Curves ahead: molecular receptors for fullerenes based on concave–convex complementarity

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The unique chemical and physical properties of fullerenes are to a great extent determined by their unusual curved shape. One of the most active fields in fullerene chemistry is the search for molecular receptors able to form stable associates with them in solution, with the purification from fullerite and the self-assembly of nanoscale electronic devices as main driving forces. In this *tutorial review* we present a brief overview of the recent advances in the construction of molecular receptors that feature curved concave surfaces complementary to the convex surface of fullerenes as a key recognizing element.

Introduction

From the development of the Roman arch—more as an engineering solution than as an ornament—to Frank Gehry's spectacular twisted metallic structures; from the Phillips curve, which relates the rates of inflation and unemployment, to the suggestive bends of a violin, curved lines and surfaces are as aesthetically pleasing as they are technologically useful, and thus have been and continue to be a commonplace in the arts, mathematics, physics and engineering.

Chemists have also been intrigued by and have made use of a variety of curves, perhaps particularly so in physical chemistry. Take, for instance, the electronic orbits in Rutherford and Bohr's atom model, or the ubiquitous ΔG profiles. Curved organic molecules are less common and, since bonding between two atoms is necessarily depicted as a straight line, one might say that even the very concept of curvature in a molecule would admit of some argument.[1] A less strict criterion, which considers a molecule curved when it presents a distorted three-dimensional shape, away from its preferred bonding angles, is generally accepted and is the one we will adopt in this short review. As a paradigmatic case of a curved molecule, fullerene C_{60}[2,3] is ultimately composed of planar hexagonal and pentagonal rings (20 and 12, respectively), but all of the dihedral angles between them deviate from planarity

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(142° and 138°) which allows it to adopt a spherical shape. We will not consider as curved those systems in which the bend stems from flexible linkers, and thus will regard them as beyond the scope of this review.

Considerations on the design principles for the construction of receptors for fullerenes

There are two main driving forces behind the search for new molecular receptors for fullerenes: their purification from fullerite and the construction of organized electroactive nanostructures by self-assembly. While the former is a classic problem in molecular recognition, the latter seems a rather complex endeavour, lying at the interface between supramolecular chemistry, optoelectronics, nanofabrication, *etc*. In any case, they both share one basic requirement: the formation of stable associates with fullerenes. We will consequently address this problem first.

In order to design receptors able to form complexes of high stability and selectivity, we need to keep in mind that fullerenes are a peculiar kind of guest. Let us see: fullerenes are the third known allotrope of carbon, that is, they are solely made up of carbon atoms and thus devoid of functionality; likewise, they are neutral and hardly—and symmetrically—polarized species. These obvious statements have important implications when it comes to the possible non-covalent interactions that we can or cannot utilize to associate fullerenes in solution. There are several energetic factors to be considered when analyzing the nature of intermolecular interactions: (i) van der Waals forces, (ii) electrostatic interactions, (iii) induction energy, (iv) charge-transfer and (v) desolvation.[4] We will try to weight them separately with respect to the molecular recognition of pristine fullerenes.

(i) **Van der Waals forces:** these account for dispersion and repulsion forces, which are in essence dependent on the available surface area. Fullerenes are spherical—or close to—in shape, and thus present large surface area to volume ratios. Since a large area of interaction should maximize van der Waals interactions, these are going to play a most prominent role in the association of fullerenes, in terms of both the stability and the selectivity of the complexes formed.

(ii) **Electrostatic interactions:** established between the static molecular charge distributions of the molecules involved. To a first approximation, and given the neutral and globally not polarized nature of fullerenes,[5] one would be tempted to consider them largely unimportant. However, the very curvature of fullerenes results in an inside–outside polarization, leaving the periphery relatively electron deficient when compared to the interior.

(iii) **Induction energy:** defined as the interaction between the static charge distribution of one molecule and the induced charge distribution of the other. Although due to their large surface area fullerenes are polarizable species, the relevant parameter in terms of supramolecular interactions is the interaction energy per unit of surface area.[6] Induction should then only play a minor role in the overall stability of the complexes.

(iv) **Charge-transfer:** even though charge-transfer bands are experimentally often found upon complexation of fullerenes with aromatic hosts, it is generally accepted that these are more a spectroscopic result of the different supramolecular interactions than an interaction in themselves. With regard to the stability of the complexes in the ground state, we can safely deem charge-transfer interactions insignificant.

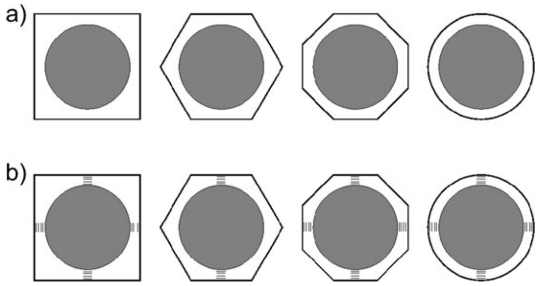


Fig. 1 The influence of shape complementarity on molecular recognition. (a) For a recognition event dependent on dispersion forces: affinity for the grey circumference increases with increasing surface in short contact, from square to circle. (b) For a recognition event based on point interactions (dashed lines): in this case the square, octagon and circle would bind the grey circumference with approximately equal affinity, with the hexagonal receptor being the weakest binder.

(v) **Desolvation:** the intrinsic low solubility of fullerenes in most common solvents directly translates into positive and quantitatively relevant solvophobic interactions.

When it comes to the design of fullerene receptors the optimization of the van der Waals and solvophobic interactions should then be the key issues, and, luckily enough, they both require the same strategy: increasing the surface of the receptor in short contact with the fullerene guest. Indeed, most receptors for fullerenes feature large planar aromatic surfaces and/or non-polar cavities, in which fullerenes find refuge from the solvent, as key recognizing elements.

Shape matters: maximizing short-contacts

The importance of shape complementarity between host and guest in molecular recognition is so well established that little can be said here without descending into unnecessary repetition. Concepts like the lock-and-key principle, preorganization and induced-fit all refer to it, and form part of the supramolecular chemist's everyday jargon. The relative importance that size and shape complementarity acquires depending on the nature of the non-covalent interactions on which the complex formation is based is perhaps not so immediate. The following reflections attempt to qualitatively address this issue. The reader should be warned that we will only consider enthalpic factors and ignore solvation and desolvation processes.

In the case of molecular recognition events based on point interactions (*i.e.* hydrogen bonding, metal–ligand coordination), complementarity is only relevant to the point that it facilitates—or at least permits—the approximation of the functional groups involved. The influence of complementarity, however, becomes fundamental when dispersion forces are predominant in the stabilization of the associates. Fig. 1 provides an intuitive bidimensional illustration of this point. As we increase the number of sides of the "receptor" from four to six to eight to infinity, the surface of the grey circumference

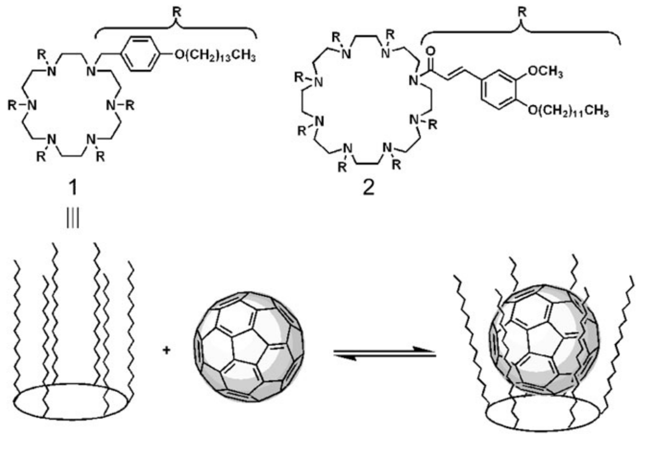


Fig. 2 Chemical structures of the receptors for fullerenes reported by Diederich, Ringsdorf and co-workers and scheme showing their binding mode.

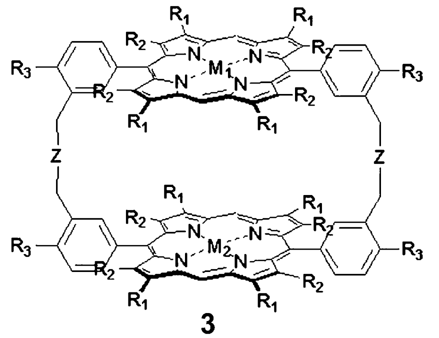
in short contact with the receptor, and thus the magnitude of the positive interactions with it, increases accordingly. On the other hand, if we imagine the recognition event to depend on four hydrogen-bonding groups evenly spaced on the grey circumference, we can easily see how that correlation no longer stands: the square, octagonal and circular receptors would bind with approximately equal affinity, while the hexagon would be the weakest binder, since it allows for only two hydrogen bonds to form.

We have already discussed how the stabilization of fullerene complexes depends essentially on dispersion forces. From that, together with the above considerations, it directly follows that the ideal binder for a given fullerene would be a higher fullerene of adequate size and shape. Indeed, this is true to the point that it promotes the formation of a whole class of all-carbon molecules: the now well known carbon “onions”. Notwithstanding the significance of van der Waals interactions in the formation of these multiwalled fullerenes, they are molecular species—since covalent bonds need to be broken to take them apart—and thus outside the scope of this review.

We will now move on to briefly describe some classic examples of receptors for fullerene, paying attention to both their advantages and their intrinsic limitations, to then continue with the few examples of curved receptors reported to date.

Classic macrocyclic scaffolds as hosts for fullerenes

In 1992, a mere seven years after the discovery of buckminsterfullerene by Smalley, Curl and Kroto,[7] Ringsdorf, Diederich, and co-workers utilized azacrown ethers as macrocyclic scaffolds, which they decorated with lipophilic fragments through *N*-alkylation or acylation, to build the first synthetic, purposely designed receptors for fullerenes (Fig. 2).[8] Mono- and multilayers of these receptors were demonstrated by UV–visible spectroscopy, small angle X-ray scattering, and surface pressure–area isotherm measurements to associate with C_{60} and C_{70} at the air–water interface. Shortly before that, Wennerström had observed that γ-cyclodextrins (CD) formed water-soluble complexes of 2 : 1 stoichiometry with C_{60}.[9]



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	Z	R_1	R_2	R_3	M_1	M_2
3a	$(CH_2)_6$	Hex	Hex	H	Zn(II)	Zn(II)
3b	$(CH_2)_6$	Me	Hex	H	Ir(II)	Ir(II)
3c	$(CH_2)_6$	H	H	*t*Bu	Me, H	Rh(III)

Fig. 3 General structure of the bisporphyrin receptors reported by Aida and table showing the substituents corresponding to selected examples mentioned in the text.

The ability of other classic macrocyclic moieties like calixarenes[10] and cyclotriveratrylenes[11] to associate with fullerenes has also been thoroughly studied.[12] Perhaps the best known example is the selective co-precipitation of *p*-*tert*-butylcalix[8]arene and C_{60} from fullerite, discovered simultaneously and independently by research groups led by Atwood[13] and Shinkai.[14] Receptors based on calix[5]arenes have been extensively investigated by Fukazawa.[15] Cyclotriveratrylene was first shown to form 1 : 1 complexes with [60]fullerene both in solution and the solid state in 1994.[16] Cucurbiturils, calix[*n*]-resorcinarenes, oxacalixarenes and octaphenylcyclotetrasiloxane have also been utilized in the molecular recognition of C_{60}.

Receptors with a flat–convex mismatch. Porphyrins as recognizing motifs for fullerene

Porphyrins are well known to interact favourably 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.[17] As already highlighted by Boyd and Reed in 1999,[18] the host–guest shape mismatch in these supramolecular systems is made up for by a combination of π–π and van der Waals interactions in which the alkyl substituents on the porphyrins play a far from innocent role.

Also in 1999, Aida reported for the first time the formation of very stable inclusion complexes between fullerenes and a dimeric construct in which two metalloporphyrins are linked by flexible alkyl spacers (**3a–c**, Fig. 3).[19] Structural variations on this design have lead to what is surely the richest collection of receptors for fullerenes,[20] including the world-record holder in complex stability, **3b**, with $K_a = 1.3 \times 10^8\ M^{-1}$ in 1,2-dichlorobenzene at room temperature,[21] and the first chiral sensor for the inherently chiral higher fullerenes, **3c**.[22]

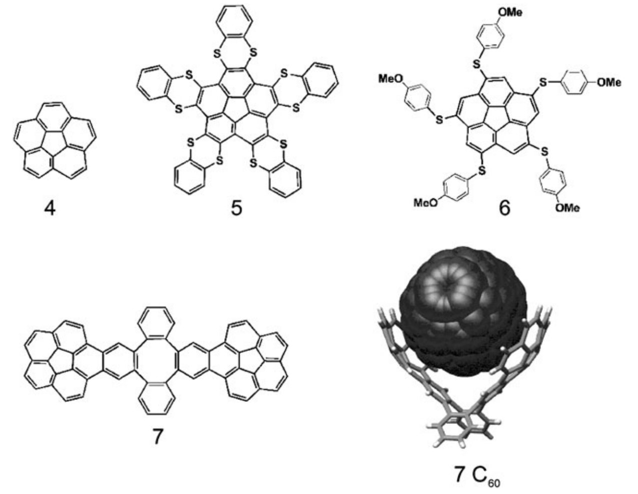

Fig. 4 Chemical structures of corannulene, **4**, and corannulene-based receptors **5**, **6** and **7**. The solid state structure of the **7**·C_{60} complex is also shown.

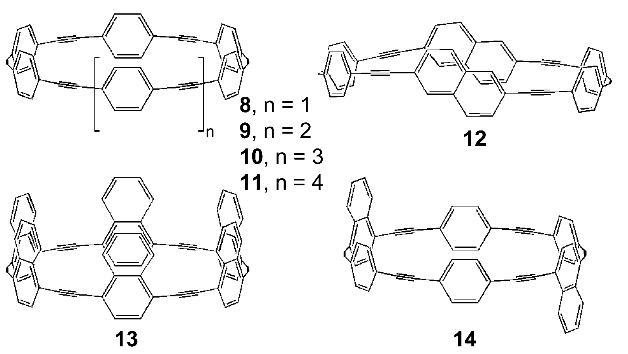

Fig. 5 Chemical structures of some of the rigid carbon nanorings reported by Kawase and co-workers.

Remarkably, the extensive synthetic effort carried out by Aida's group has allowed detailed structure–activity relationships to be established. For instance, it was noticed right at the outset that receptors in which the flexible alkyl spacers were replaced with more rigid unsaturated hydrocarbon chains of approximately equivalent length[23] did not show any sign of association with fullerene. In other words, the preorganization *vs.* conformational flexibility tug-of-war—enthalpy–entropy compensation—lies heavily on the flexibility side in this case. The significance of this effect has been interpreted by the authors as "most likely for adjusting the porphyrin–porphyrin distance".[20] Moreover, the solid state structure of the inclusion complexes shows the alkyl spacers folded in order to maximize van der Waals contacts with [60]fullerene, once more highlighting the important contribution of the alkyl chains to the stabilization of the complexes.

The nature of the metal ion also affects the binding constants to a marked extent. In the case of C_{60}, otherwise structurally identical bisporphyrin receptors show binding constants (benzene, room temperature) increasing from 7.9×10^5 M^{-1} for the free base to 1.9×10^6 M^{-1} for the Co(II) derivative to 2.5×10^7 M^{-1} for the Rh(III) derivative, where a methyl group completes the coordination sphere of the trivalent ion.

But perhaps the most noteworthy feature is the structure of the porphyrin moieties. As is apparent from the X-ray diffraction studies, in the inclusion complexes they adopt a non-planar concave conformation to maximize the positive interactions with the C_{60} guest,[24] even at the expense of some degree of conjugation. This brings us back to the main point of this review, which we will discuss below.

Concave receptors for fullerenes

As illustrated by the distortion from planarity of porphyrins upon binding of fullerenes, experimentally observed in Aida's bisporphyrin receptors for fullerenes, and suggested by the theoretical considerations outlined above, host–guest shape complementarity is particularly important in the molecular recognition of fullerenes. On the other hand, curved molecules are tensioned structures, with bond angles deviating from the preferred ones and consequently are not always an easy synthetic target, which explains why, to date, the examples of concave fullerene receptors are relatively scarce.

Corannulene-based receptors for fullerene

Corannulene, a large conjugated compound consisting of five benzene rings fused into a central five-membered ring (**4**, Fig. 4), was first synthesized by flash vacuum pyrolysis in 1966.[25] Following this, several related examples of bowl-shaped conjugated molecules, which in many cases can be seen as [60]fullerene fragments, have been synthesized (see Fig. 4). Various attempts at constructing molecular receptors for fullerenes which incorporate one of these bowl-shaped molecules as key recognizing elements have been reported.[26] As could be expected considering their size—nearly identical to that of fullerene and thus too small to associate with it—chemical derivatization is necessary to observe binding.

In the design of receptors **5**[27] and **6**[28] the addition of five aromatic rings is intended to increase the cavity size, while maintaining the original bowl shape of corannulene, whereas in **7**[29] two units of corannulene are linked through a rigid aromatic spacer to form a tweezer-like receptor. With regard to the receptors bearing a single corannulene unit, their binding constants increase from 3.0×10^2 M^{-1} for **5**·C_{60} to 1.4×10^3 M^{-1} for **6**·C_{60} in d_8-toluene at room temperature, which has been attributed to the increase in electronic density due to the methoxy substituted rings. Significantly, both of these form one to one complexes with C_{60}. The "buckycatcher" **7** forms more stable complexes (K_a = 8.6×10^3 M^{-1},

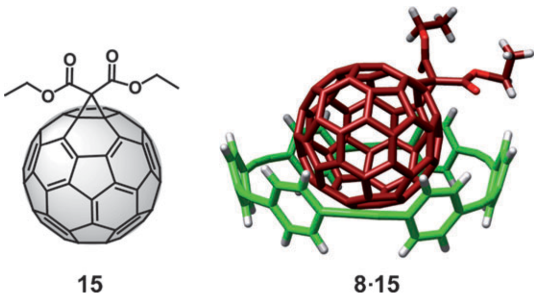

Fig. 6 Chemical representation of guest **15** and solid state structure of its complex with carbon nanoring **8**.

d_8-toluene, room temperature), and X-ray diffraction studies of mixtures of **7** and C_{60} allowed the determination of the solid state structure of the complex (Fig. 4).

Carbon nanorings as molecular receptors for fullerene

A variety of rigid cyclic conjugated organic compounds have been synthesized,[30–33] mainly with the aim of utilizing their non-collapsible cavities for the formation of inclusion complexes. Fullerenes are perhaps the most obvious guests for them and their complexation has often been studied.[26,30]

The contributions by the group of Kawase, in Osaka, are arguably the most abundant and surely the most significant in this field. They first reported the synthesis of cyclic [*n*]*para*-phenyl acetylenes (**8–11** in Fig. 5) in 1996.[32] Their synthetic strategy was based on a key bromination–elimination sequence to obtain the triple bonds of the final product from the less strained, easier to access parent compounds featuring carbon–carbon double bonds.

The diameter of the cavity of **8** is 1.33 nm as found in its solid state structure, a close to perfect fit for C_{60}. Consequently, the group of Kawase went on to investigate the ability of **8** to associate with [60]fullerene. As revealed by UV–Vis titrations, **8** binds fullerene with a binding constant of $K_a = 1.6 \times 10^4$ M^{-1} in benzene at room temperature. The thermodynamic stabilization of the $\mathbf{8}{\cdot}C_{60}$ was estimated to be $\Delta G_{\text{binding}} = 9.9 \pm 0.3$ kcal mol^{-1} through variable temperature (VT) ^{1}H NMR.[32]

The complexation of **8** and a more soluble Bingel-type derivative of fullerene, **15**, was also explored. Although the changes in the absorption spectra of **8** upon addition of **15** were found to be too small to allow determination of a binding constant, VT-NMR experiments provided an insight into the complex stability and a $\Delta G_{\text{binding}} = 9.4 \pm 0.2$ kcal mol^{-1} was found, revealing that the **8**·**15** complex is slightly less stable than the $\mathbf{8}{\cdot}C_{60}$. The structure of the **8**·**15** associate was determined by X-ray diffraction and is shown in Fig. 6. The fullerene fragment does not reside in the centre of the cavity of **8** but slightly above it, forcing the aromatic rings of **8** to tilt and adopt a bowl shape.

With these data in hand, in order to maximize short contacts between host and fullerene, compounds **12**, **13** and **14** (see Fig. 5) were synthesized.[31,34] In these carbon nanorings at least two of the *p*-phenylene moieties are substituted by naphthalene units, in an attempt to increase the depth of the cavity while maintaining its diameter—in the case of **13** and **14**—or moderately increasing it—in the case of **12**. This strategy of structural modification proved to be very successful, as all of the newly synthesized hosts form complexes of remarkable stability with both C_{60} and C_{70}. In fact, the binding constants in benzene could not be measured reliably (that is, they were greater than 5×10^4 M^{-1}) and had to be estimated through fluorescence quenching experiments.[35]

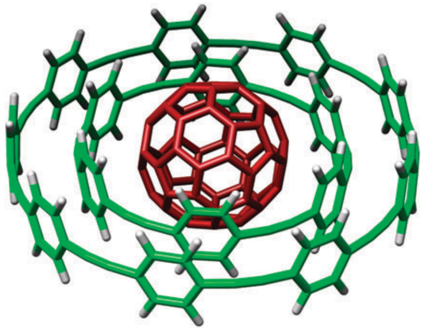

Fig. 7 Cartoon representation of the onion-type $\mathbf{11}{\cdot}\mathbf{8}{\cdot}C_{60}$ complex.

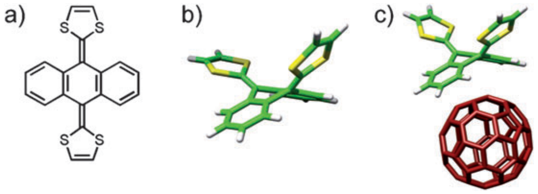

Fig. 8 (a) Chemical structure of exTTF; (b) molecular model showing its characteristic bi-curved shape; (c) cartoon of a theoretical exTTF·C_{60} 1 : 1 complex, showing the good match between the concave aromatic surface of exTTF and the exterior of [60]fullerene.

Nanoring **12** is perhaps the most interesting molecule of this series, since, although it associates with both C_{60} and C_{70}, it shows a high degree of selectivity towards the latter, to the extent that under competitive solid–liquid extraction experiments, **12** was capable of extracting C_{70} almost exclusively from a 1 : 1 mixture of C_{60} and C_{70}.

Futhermore, Kawase's nanorings show an unprecedented mode of association, what the authors term onion-type complexation.[36] Due to their synthetic strategy, **8** and **11** are obtained as mixtures that can be separated by gel permeation chromatography. During purification, nanorings **8** and **11** were found to co-precipitate as a 1 : 1 mixture. Theoretical calculations showed that **11** has a cavity of 1.93 nm in diameter, a perfect fit for **8**, which is 1.33 nm across, if we consider that the van der Waals distance of sp^2 hybridized carbons is 0.34 nm. Indeed, VT-NMR experiments unambiguously proved the formation of **8**·**11** ring-in-ring inclusion complexes. Given the rigidity of the carbon nanorings, it was anticipated that the cavity of **8** in these **8**·**11** associates should still be available for binding fullerene, and that **11** should be capable of binding $\mathbf{8}{\cdot}C_{60}$ complexes. This is in fact the case, as is apparent from NMR titrations at low temperature. All these data provided conclusive evidence for the formation of onion-type complexes like the one shown schematically in Fig. 7.

Concave π-extended tetrathiafulvalene derivatives as receptors for fullerene

Tetrathiafulvalene (TTF) is well known for its electron donor ability, which has been exploited to construct a wide range of molecular devices,[37] including photo- and electroactive

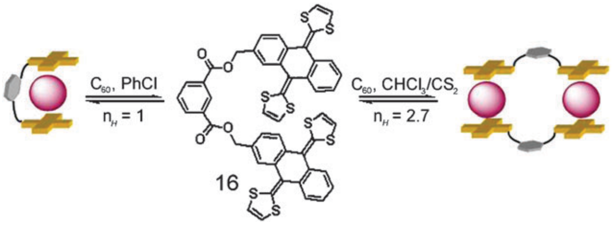

Fig. 9 Chemical structure of receptor **16** and scheme showing its different binding modes with C_{60}.

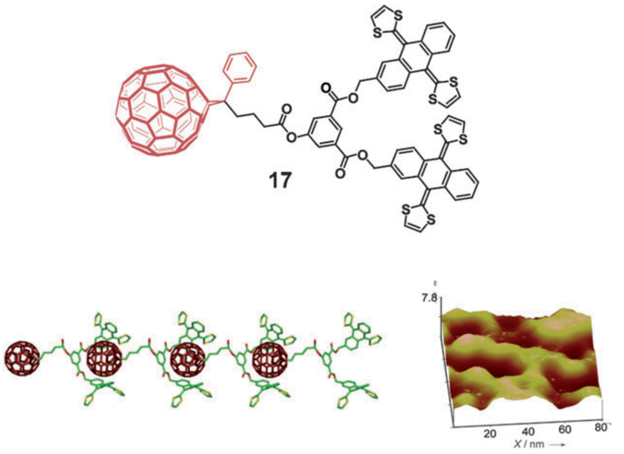

Fig. 10 Chemical structure of monomer **17**, cartoon of $(\mathbf{17})_4$ and AFM images (tapping mode, air, 298 K) of a dropcast of a dichloromethane solution of **17**.

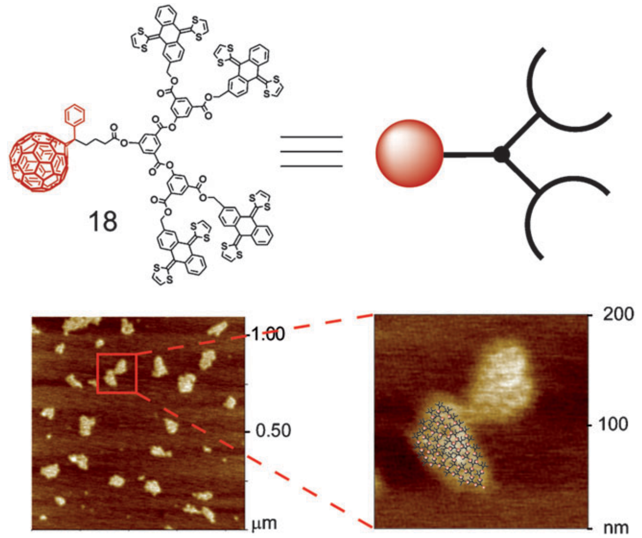

Fig. 11 Chemical structure of monomer **18**, and its schematic representation. AFM images (tapping mode, air, 298 K) confirmed the formation of the supramolecular dendrimers.

donor–acceptor dyads and triads,[38] organic field-effect transistors,[39] cation sensors and bistable molecular shuttles and catenanes.[40–43] Analogously, its π-extended analogues—in which the 1,3-dithiole rings are covalently connected to a π-conjugated core—have mainly been exploited as electron donor fragments.[38] In contrast, the possibility of utilizing their distorted curved shape in the construction of molecular receptors for fullerene had by and large been overlooked.

Recently, we noticed 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. 8) and the convex exterior of fullerenes should lead to large and positive non-covalent interactions. In fact, theoretical calculations (DFT) predicted binding energies up to 7.00 kcal $\mathrm{mol^{-1}}$ between a single unit of exTTF and C_{60}.[44] However, no experimental evidence of association was found in either UV–Vis or NMR titrations.

We thus turned our attention to a tweezer-like design, in which two exTTF units would serve as recognizing units, and an isophthalate diester would act as a spacer. Receptor **16** (Fig. 9) was synthesized in excellent yield from easily available exTTF methyl alcohol and commercially available isophthaloyl dichloride.[45] We were pleased to observe that the electronic absorption spectra of receptor **16** showed significant changes upon addition of fullerene. A decrease in the absorption band characteristic of exTTF ($\lambda_{\max} = 434$ nm) is accompanied by the appearance of what seems to be a charge-transfer band ($\lambda_{\max} = 482$ nm). Fitting of these spectral changes to a 1 : 1 binding isotherm afforded a binding constant of $3.0 \times 10^3\ \mathrm{M^{-1}}$ in chlorobenzene at room temperature. The considerable stability of the $\mathbf{16}{\cdot}C_{60}$ complex—given the lack of preorganization of **16**—demonstrates the validity of exTTF as a building block for fullerene receptors. We were surprised to find that the complexation behaviour of receptor **16** towards C_{60} in $CHCl_3$–CS_2 mixtures was rather different. Although the spectral changes are analogous to those found in chlorobenzene, 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 $3.6 \times 10^3\ \mathrm{M^{-1}}$. Although it is often considered a direct indication of the number of available binding sites on the receptor, the Hill coefficient is best thought of as an interaction coefficient reflecting the extent of cooperativity, with a maximum value equal to the number of binding sites.[46] Thus, a value of $n_{\mathrm{H}} > 2$ rules out the formation of the expected pincerlike $\mathbf{16}{\cdot}C_{60}$ complex since it features two binding sites only. As 1 : 1 stoichiometry was experimentally found by continuous variation plots, this strongly suggests the formation of a supramolecular tetramer in which two units of C_{60} are sandwiched between two molecules of receptor **16**.[47]

The combination of supramolecular and electronic reciprocity between exTTF and C_{60} suggested that this novel host–guest system would be a good candidate to be utilized in the self-organization of electroactive materials. With this in mind, we designed **17** (Fig. 10) as a monomer for the construction of redox-amphoteric supramolecular polymers[48] through π–π and van der Waals interactions.

Indeed, a comprehensive collection of experiments, including variable concentration and VT-NMR, PFG-NMR, MALDI-TOF-MS, dynamic light scattering, and AFM demonstrated that **17** forms linear and/or cyclic multimeric supramolecular aggregates, in solution, gas and solid phase.

The electronic characterization of $(\mathbf{17})_n$ was carried out by means of cyclic voltammetry (CV) and UV–Vis, and showed that there is electronic communication between electroactive fragments in the ground state. We are currently investigating whether this or structurally related systems could be applied to the construction of more efficient optoelectronic devices.

The relationship between dendrimers[49,50] and supramolecular chemistry has been a particularly fruitful one,[51,52] and examples of syntheses of monodisperse dendrimeric architectures through non-covalent interactions abound in the literature.[53,54] Based on our research on electroactive supramolecular polymers, we set out to investigate the possibility of constructing what we called *dynamically polydisperse* supramolecular dendrimers, with the aim of exploring a

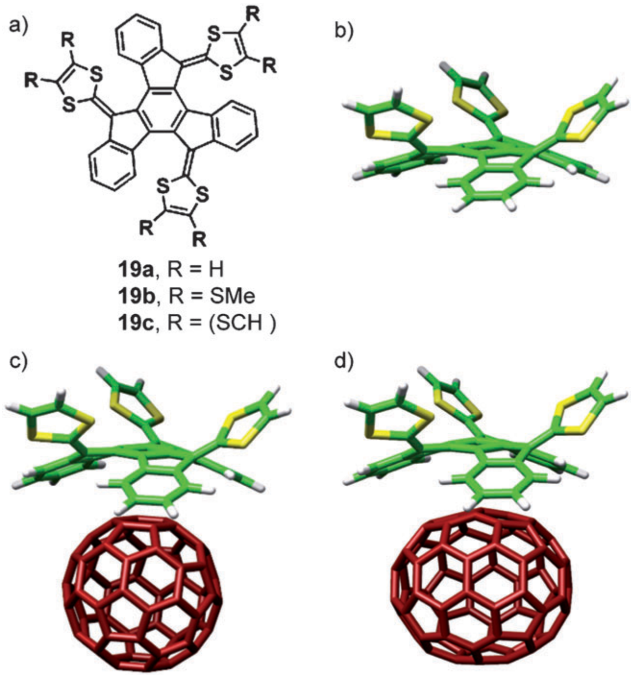

Fig. 12 (a) Chemical structure of truxene-TTFs **19a–c**; (b) solid state structure of (*P*,*P*,*P*)-**19a**; (c) energy minimized (MPWB1K/6-31G** level) structure of the **19a**·C_{60} complex; (d) energy minimized (MPWB1K/6-31G** level) structure of the **19a**·C_{70} complex.

conceptually new type of nanometric organization of electroactive materials that would lie at the interface between dendrimers and supramolecular polymers.

We anticipated that a bifurcated molecule decorated with two units of our receptor for fullerene, and a C_{60} derivative as recognizing units would self-assemble to form arborescent and dynamically polydisperse supramolecular aggregates. Following this, we synthesized **18** (Fig. 11).[55]

All data in solution pointed to the formation of multimeric associates of **18**, and, in particular, low temperature ^{1}H NMR suggested that binding preferentially occurred inside the cavity of the receptor, as anticipated. The size and morphology of the associates were investigated by AFM. As shown in Fig. 11, most of the associates of **18** show a triangular form in which two of the vertices are rounded off, reminiscent of a bunch of grapes. Significantly, all of them are very uniform in height (0.9–1.1 nm). The area, height and shape of the nanometric structures found are in good accordance with what could be expected for branched, flattened oligomers of **18**, since it is well known that dendrimers tend to adopt planar structures when deposited on surfaces.

Based on the same principle of concave–convex complementarity, and with the aim of constructing an electron-donor fragment that would: (1) show good electron-donor properties, (2) absorb light efficiently, preferably in the visible region, and (3) self-assemble with fullerenes in a controlled fashion, we designed and synthesized a new family of TTF derivatives, truxene-TTFs, **19a–c** (Fig. 12).[56]

We noticed that a truxene core would be particularly well suited as a scaffold, since its extended π-delocalized system should result in a significant shift of the electronic absorption spectrum towards the visible region, and at the same time provide a large aromatic surface with which fullerenes might establish favourable non-covalent interactions. As shown in Fig. 12, truxene-TTFs feature three dithiole units connected to a truxene core. To accommodate the dithioles, the truxene moiety breaks down its planar structure and adopts an all-*cis* sphere-like geometry with the three dithiole rings protruding outside. This arrangement results in the generation of a molecule with threefold helical chirality of which only the *P*,*P*,*P*/*M*,*M*,*M* enantiomeric pair can be found in the crystal structure.[56]

The aromatic concave bowl-shape configuration adopted by the truxene core perfectly mirrors the convex surface of fullerenes, suggesting that van der Waals and concave–convex π–π interactions between them should be maximized. Indeed, the association of trux-TTF and fullerenes in solution was investigated by ^{1}H NMR titrations with C_{60} and C_{70} as guests affording binding constants of $(1.2 \pm 0.3) \times 10^3$ M^{-1} and $(8.0 \pm 1.5) \times 10^3$ M^{-1} for C_{60} and C_{70}, respectively.

As is apparent from DFT (MPWB1K/6-31G** level) calculations, this difference in binding constant arises from the increase in surface from C_{60} to C_{70}. In fact, it seems that **19a** is a loose fit even for C_{70}, which together with its inherent chiral character might make it a good candidate for the enantioselective molecular recognition of the higher chiral fullerenes.

Summary and outlook

The search for molecular receptors for fullerenes continues to be a very active area of research. Recently, a variety of these in which the recognizing motif is a concave aromatic surface have been reported. We have overviewed most of the curved receptors for fullerenes reported to date, and the supramolecular systems derived from them.

In our view, a quantitative and fair comparison of the stability of the complexes formed between fullerenes and receptors based on flat or concave recognition motifs would require new experimental evidence, since only the binding constants of receptors with enough structural similarity—that is, dissimilar only with regard to the recognizing units—and studied under experimentally identical conditions can be meaningfully put side by side.[57] Until such data are available, it is obvious that both approaches are complementary, have already produced very successful results and will continue to do so in the years to come.

With regard to the systems developed by our research group, the unique combination of supramolecular and electronic reciprocity between the receptors based on TTF-type curved aromatic systems—exTTF and truxene-TTF—and fullerenes augurs well for their use in the construction of self-assembled nanometric optoelectronic devices. These findings pave the way for the construction of supramolecular architectures able to mimic the photosynthetic process, and therefore of interest in the search for new materials for photovoltaic applications.

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57. We are very grateful for the comments of one of the referees of the original version of this manuscript, who suggested we should produce a comparative study between flat and curved receptors and made us realize the impossibility of carrying it out with the data available in the literature to date. Indeed, a collection of receptors that should shed light on this matter has already been designed, and their synthesis is currently being carried out in our lab.