Supramolecular chemistry of π-extended analogues of TTF and carbon nanostructures†

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Received (in Montpellier, France) 18th September 2008, Accepted 14th November 2008
First published as an Advance Article on the web 16th December 2008
DOI: 10.1039/b816272g

The shrewd combination of complementary electroactive molecular fragments through weak, non-covalent forces can be exploited to construct stimuli-responsive assemblies or to achieve self-ordered arrays of electron donor and/or acceptor moieties to be utilized in optoelectronic devices. Among the electron donors, tetrathiafulvalene (TTF) has been particularly fashionable in this field. Comparatively, the supramolecular chemistry of its π-extended analogues was severely underdeveloped. Herein we present a summary of some recent results in the exploration of the non-covalent chemistry of π-extended analogues of tetrathiafulvalene.

Introduction

Tetrathiafulvalene (TTF) is well known for its electron donor ability, which has been exploited to construct a breadth of molecular devices,[1] including photo and electroactive donor–acceptor dyads and triads,[2] organic field-effect transistors,[3] cation sensors and bistable molecular shuttles and catenanes.[4–7] 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 in covalently linked donor–acceptor conjugates.[2] In contrast, while the supramolecular chemistry of TTF is nowadays a well-trodden path,[8,9] that of its π-extended analogues had remained virtually unexplored. In this perspective, we will summarize the main results obtained by our group in our first steps along that road.

In particular, the construction of versatile nanosized supramolecular electron donor–acceptor systems is one of our major research objectives and to this aim, we have explored the combination of TTFs and π-extended TTFs with different carbon nanostructures,[10] such as fullerenes[10b,c] and carbon nanotubes.[10d–g] Our research plan was clearly divided into two different subjects: (1) the supramolecular chemistry that might arise from the very nature of the π-extended analogues, typically large aromatic surfaces distorted from planarity by the introduction of the sterically demanding 1,3-dithiole rings, and thus fundamentally based on π–π van der Waals interactions; and (2) the application of well established supramolecular motifs—in our case, complementary hydrogen bonding groups—to the construction of non-covalent donor–acceptor conjugates where π-extended analogues act as electron donors. We shall subdivide this review correspondingly, although we will see how, as it is usual in any scientific

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† Dedicated to Professor Jean-Pierre Sauvage on the occasion of his 65th birthday.

endeavour, two initially well separated paths wind, intertwine, and finally merge into one sole body of knowledge.

π-Extended tetrathiafulvalene derivatives as recognizing motifs for fullerenes

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) and the curved exterior of fullerenes and carbon nanotubes should lead to large and positive non-covalent interactions. Indeed, DFT calculations predict positive binding energies of up to 7.00 kcal mol^{-1} between a single unit of exTTF and C_{60}.[11] However, we have not observed conclusive experimental evidence of association in either UV-vis or NMR titrations.

In the light of these results, we decided to follow two different strategies to improve the complexing ability of our exTTF-based receptors: (i) increase the number of exTTF units and (ii) increase the number of dithiole (*i.e.* the electron rich character) and the number of benzene rings (*i.e.* the surface available for van der Waals interactions) in the same molecule.

Following the first strategy, we designed receptor **1** (Fig. 2), in which two exTTF units serve as recognizing units, and an isophthalate diester acts as a spacer. Receptor **1** (Fig. 1) was synthesized in excellent yield from easily available exTTF methyl alcohol and commercially available isophthaloyl dichloride.[12] Upon addition of fullerene to a solution of **1**, we observed significant changes, indicative of association in the UV-vis spectrum of the receptor. Namely, the lowest-energy absorption band (λ_{max} = 434 nm) decreases in intensity with increasing concentration of C_{60}. Besides this, after subtraction of the spectrum of fullerene, we observe the concomitant appearance of a charge-transfer band (λ_{max} = 482 nm). Mathematical treatment of these spectral changes[13] afforded a binding constant of 3.0×10^3 M^{-1} in chlorobenzene at room temperature. The considerable stability of the **1**·C_{60} complex—given the lack of preorganization of **1**—demonstrates the validity of exTTF as a building block for fullerene receptors.

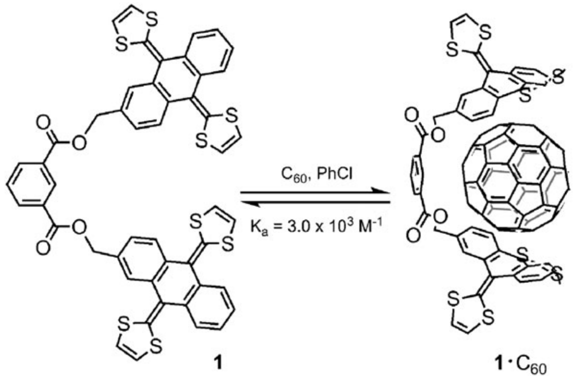

Fig. 1 Chemical structure of receptor **1** and scheme showing its tweezer-like complexation with C_{60} in PhCl.

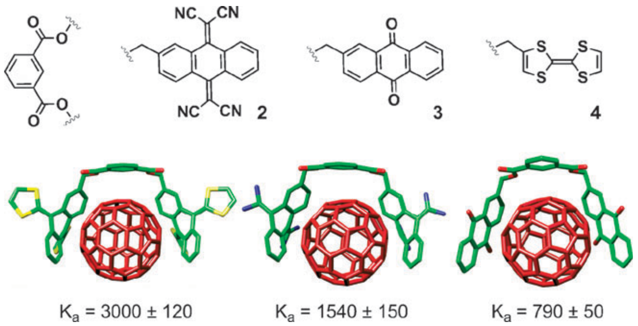

Fig. 2 Chemical structures of receptors **2–4** (top) and structure of the **1**·C_{60}, **2**·C_{60} and **3**·C_{60} complexes, calculated at the BH&H/6-31G** level with their corresponding binding constants, determined by ^{1}H NMR titrations in $CDCl_3$.

The relatively high association constant of receptor **1** towards C_{60} despite its inherent lack of preorganization, got us interested in the specific contribution to the overall stabilization of the complex that arose from the concave shape of the recognizing unit (exTTF). In this regard, the group of Kawase had coined the term "concave–convex interactions" to refer to the increase in non-covalent interactions between curved aromatic hosts and guests, and suggested these might play a distinct role in the stabilization of the complexes.[14–17] In order to get an insight into whether these concave–convex interactions did really contribute to stabilize our complexes, and if so, to what extent, we designed and synthesized a collection of structurally related receptors **2–4** (Fig. 2).[18] These, together with **1**, 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 **1–4** towards C_{60} were investigated through ^{1}H NMR titrations in $CDCl_3$.

Receptor **1** incorporates five aromatic rings—two per recognizing unit plus the isophthalic spacer—a large and concave surface and is electron-rich. Unsurprisingly, **1** is the strongest binder for C_{60}, with a $K_a = (3.00 \pm 0.12) \times 10^3$ M^{-1}. Receptor **2** utilizes 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ) as the recognizing element. Thus, as compared to **1**, it presents an equal number of aromatic rings and surface available for recognition, with close to identical curvature, but electron-poor character. The change in electronic nature results in a decrease of K_a to $(1.54 \pm 0.15) \times 10^3$ M^{-1}. A similar drop-off in the association constant is observed when moving from **2** to **3**. In this case, the surface available for van der Waals interactions is similar to that of **1** and **2**, but **3** lacks both the concave–convex and the electronic complementarity. This results in a binding constant of $(0.79 \pm 0.05) \times 10^3$ M^{-1}. Finally, no sign of association with C_{60} was observed in either the ^{1}H NMR or the electronic absorption spectra of receptor **4**, which is decorated with the electron rich, small and non-aromatic tetrathiafulvalene (TTF) unit.

Comparison of the binding constants of **1** and **2** towards C_{60} suggests a noticeable contribution of coulombic interactions, which is in accordance with previous observations.[1–5] However, the fact that **4** does not show any sign of complexation towards C_{60} implies that this contribution is not quantitatively comparable to those of π–π and van der Waals forces. Remarkably, we observed for the first time that concave–convex complementarity does make its own contribution, even

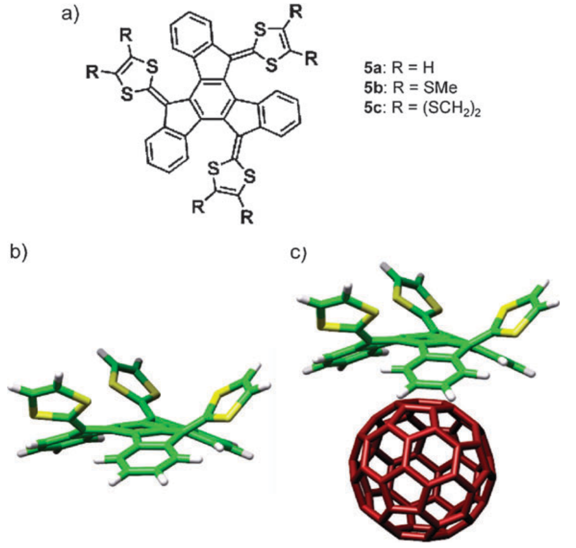

Fig. 3 (a) Chemical structure of truxene-TTFs **5a–5c**; (b) solid-state structure of (*P*,*P*,*P*)-**5a**; (c) energy minimized (MPWB1K/6-31G** level) structure of the **5a**·C_{60} complex.

if quantitatively small, as illustrated by the cases of receptors **2** and **3**. In spite of the more electron-poor character of **2** when compared to **3**, its binding constant towards C_{60} is larger. This can only be justified by the concave shape of the TCAQ recognizing units.

As discussed above, an alternative strategy to the molecular tweezer is the design of a donor molecule bearing more than two dithioles and two benzene rings. With this in mind, we designed and synthesized a new family of TTF derivatives, truxene-TTFs, **5a–5c** (Fig. 3).[19] As shown in Fig. 3, truxene-TTFs feature three 1,3-dithiole rings connected to a truxene core. To accommodate the dithioles, the truxene moiety loses its planar structure and adopts an all-*cis* sphere-like geometry with the three dithiole rings protruding outside (Fig. 3(b)). The concave shape adopted by the truxene core perfectly mirrors the convex surface of fullerenes, indicating 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} in $CDCl_3/CS_2$, respectively. DFT (MPWB1K/6-31G** level) calculations provided a satisfactory explanation for this difference in binding constant, which arises from the increase in surface from C_{60} to C_{70}.

Supramolecular assembly of carbon nanotubes and TTF derivatives

Carbon nanotubes (CNTs) are unique among high-surface-area materials, owing to extended polyaromatic structures favouring supramolecular chemistry with a wide range of important molecules in chemistry, biology and medicine.[10d–g] However, CNTs—in particular single-wall carbon nanotubes (SWNTs)—are strongly and mutually interacting with themselves through non-covalent π–π interactions that are hard to characterize because of the structural heterogeneity of most of the production methods. In addition, they are mixtures that exhibit different chiralities, diameters and length, in which non-NT carbon and metal catalysts are also present in the final material.

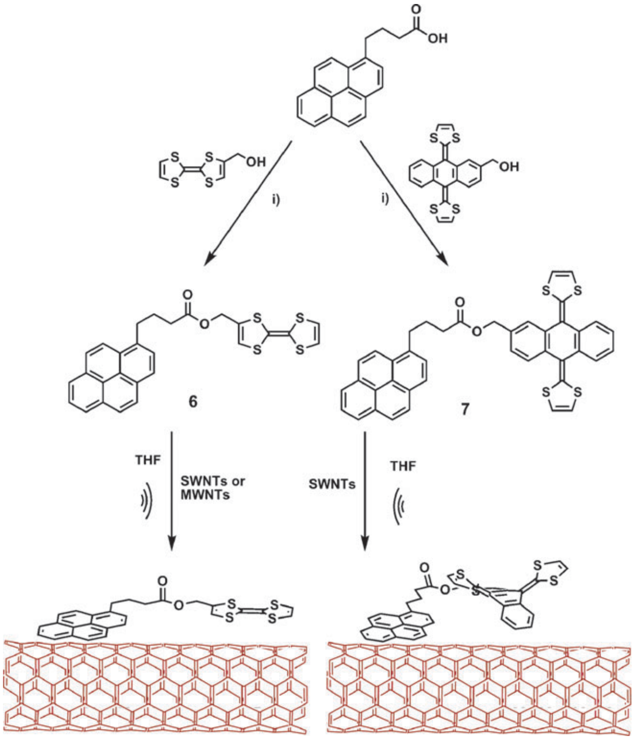

Fig. 4 Synthesis of the pyrene-TTF (**6**) and pyrene-exTTF (**7**) derivatives and their supramolecular hybrids with CNTs. *Reagents and conditions*: (i) 1,3-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)-pyridine (DMAP) and CH_2Cl_2.

Chemical modification of carbon nanotubes by supramolecular means has envisaged as an alternative to overcome this drawback and to achieve a better processability of the samples, while still preserving the electronic properties of the π-conjugated system of CNTs. A considerable effort has being directed towards combining carbon nanotubes with polymers of different nature,[20] porphyrin derivatives,[21] β-cyclodextrins,[22] DNA molecules[23] or amphiphilic α-helical peptides.[24] In this context, pyrene derivatives have played a leading role to immobilize porphyrins, chlorines, fullerenes or proteins onto the surface of SWNTs.[25]

Considering this background, our strategy for the supramolecular modification of carbon nanotubes with electroactive TTF-type derivatives, involved the preparation of bifunctional systems—pyrene-TTF[26] (**6**) or pyrene-exTTF[27] (**7**) (Fig. 4)—where the use of pyrene is particularly crucial to achieve surface immobilization onto CNTs through directed π–π interactions. The synthesis of these new molecules was based on the covalent linkage of both units through a flexible and medium-length chain which favours a facile interaction with the SWNT surface and, where the pyrene fragment functions *exclusively* as a template that guarantees the immobilization of the electron donor onto the CNT surface.

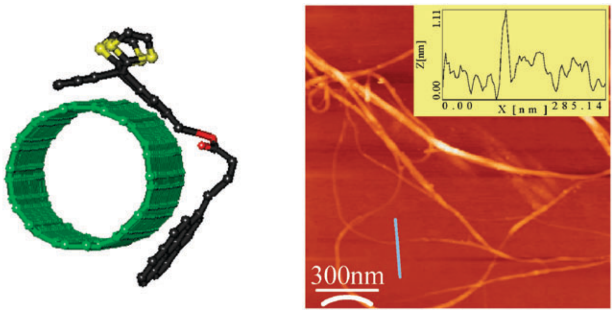

Fig. 5 Cartoon representing a possible molecular structure of the CNT·pyrene-exTTF nanohybrids and AFM image showing thin bundles as well as isolated tubes with diameters of about 1 nm.

Stable dispersions of CNT·pyrene-TTF or CNT·pyrene-exTTF were obtained by using a mixture of 2 mg of the corresponding CNT‡ and 1 mg of **6** or **7**. After a process that involves stirring, sonication and centrifugation, the aggregates were obtained as solids that were redissolved in THF for characterization considering different analytical, spectroscopic and microscopic techniques.

The presence of CNTs in all the studied samples, and also a marked degree of de-bundling when compared with pristine samples, was corroborated by means of transmission electron microscopy (TEM) and atomic force microscopy (AFM). From TEM, SWNT derivatives appear as thin bundles with mean lengths on the order of several micrometers. Typical AFM images reveal the presence of individual SWNTs and thin bundles with diameters of about 1 nm and 3 to 10 nm, respectively (Fig. 5).

Further support for the successful immobilization of **6** and **7** onto the surface of SWNTs was obtained from thermogravimetric analysis (TGA), where a loss weight of about a 6–7% was obtained for SWNT·pyrene-TTF **6** and SWNT·pyrene-exTTF **7** samples, which corresponds to a ratio of a single pyrene-TTF or pyrene-exTTF molecule per 750 carbon atoms of SWNTs. Electrochemical investigations resulted to be particularly relevant for the case of SWNT·pyrene-exTTF nanohybrids: the oxidation processes corresponding to the free pyrene-exTTF **7** molecules (E_{ox}^{1} = +170 mV, E_{ox}^{2} = +1035 mV) were observed together with the presence of pyrene-exTTF **7** molecules non-covalently bonded to the SWNTs structure (E_{ox}^{1} = +170 mV, E_{ox}^{2} = +960 mV). The stabilization of the pyrene radical cation—when interacting with SWNTs—evidence the strong π–π interactions with this planar and aromatic structure.[25a,c]

In complementary work, the photophysical properties of these supramolecular assemblies were investigated by steady-state and time-resolved fluorescence as well as femtosecond transient absorption spectroscopy. Because of the close proximity of the TTF or exTTF to the electron acceptor, a very rapid intrahybrid electron transfer affords a photogenerated radical ion pair, whose lifetime is only a few nanoseconds for the case of SWNTs. Important differences are observed when the CNT·pyrene-TTF series are considered: charge injection into the conduction band of CNTs afforded stable radical ion pair states only for MWNTs, while the lifetimes observed for SWNTs are much shorter, as the rate constant decay for the radical ion pair state indicates ($>3 \times 10^{11}$ s^{-1}).[26] The presence of a large number of concentric tubes, providing different acceptor levels in MWNTs, could be a rational explanation for this additional stabilization of the transient radical ion pairs.

Self-assembled nanostructures based on the exTTF-C_{60} recognition motif

The combination of supramolecular and electronic reciprocity between receptor **1** 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 **8** and **9** (Fig. 6) as monomers for the construction of redox-amphoteric supramolecular polymers[28] and dendrimers[29] through π–π and van der Waals interactions.

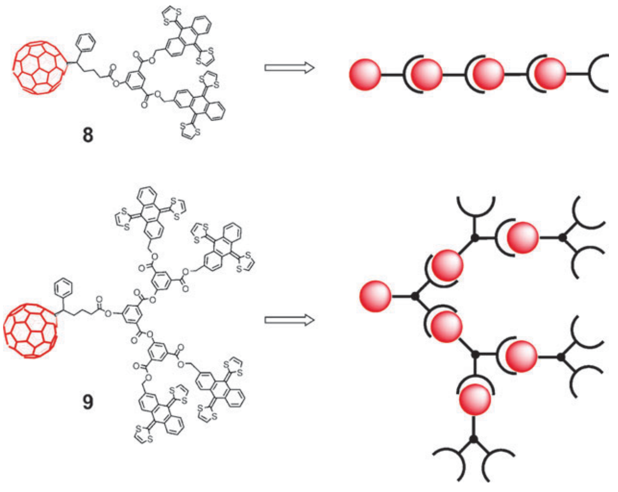

Fig. 6 Chemical structure of monomers **6** and **7**, and schematic representation of their self-assembly.

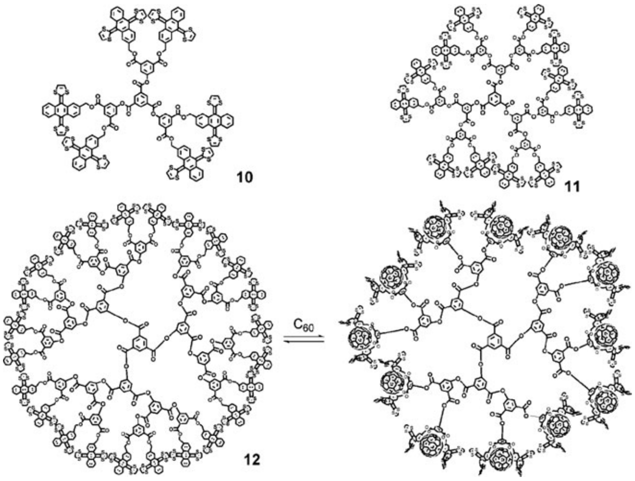

Fig. 7 Schematic representation of the chemical structure of dendrimers **10–12** and of the idealized structure of **12** associating C_{60}.

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‡ Samples of HIPCO SWNTs, double-wall CNTs (DWNTs, OD/ID: <5/1.3–5 nm), very thin multi-wall carbon nanotubes (VTMWNTs, OD/ID: 3–20/1–3 nm), thin multi-wall carbon nanotubes (TMWNTs, OD/ID: 8–15/3–5 nm) or multi-wall carbon nanotubes (MWNTs, OD/ID: 20–40/5–10 nm) were used for the investigations with pyrene-TTF.

Indeed, a thorough collection of experiments, including variable concentration and VT-NMR, PFG-NMR, MALDI-TOF-MS, dynamic light scattering, and AFM demonstrated that **8** forms linear multimeric supramolecular aggregates, while **9** forms arborescent and dynamically polydisperse supramolecular aggregates, both in solution, and in the gas and solid phase.

Besides this non-covalent assemblies, we decided to investigate the possibility of synthesising large covalently linked dendrimers decorated on their periphery with multiple units of receptor **1**. We were able to synthesize dendrimers from 2nd up to 4th generation, (**10–12**, Fig. 7). We were glad to observe that several units of C_{60} were associated by the exTTF rich exterior. Furthermore, UV-vis titration experiments demonstrated the complexation of C_{60} to occur in a positive cooperative manner.[30]

We are currently investigating the possible application of these supramolecular constructs, and in particular, their utilization in the fabrication of optoelectronic devices.

Preorganized supramolecular interactions between π-extended tetrathiafulvalene derivatives and fullerenes

Following the above mentioned second strategy to study exTTF-fullerene supramolecular interactions, we decided to introduce a pre-organizing factor—in particular, ammonium-crown ether recognition motifs. It is well established that this interaction is relatively weak, with a maximun strength of $\sim 10^3$ M^{-1}.[31] However, when additional recognition elements are present, the stability of the complexes dramatically increases. Thus, for example, a high value of the association constant of 3.75×10^5 M^{-1} is obtained for a supramolecular porphyrin–fullerene conjugate based on ammonium-crown ether interactions.[32] This additional stabilization can be attributed to the intramolecular π-stacking of the two chromophores. In this sense, the concave aromatic surface of exTTF introduces an additional recognizing motif which should favor the self assembly of complementary ammonium salt–crown ether interaction.

The first approach to this subject was to synthesize an exTTF based crown ether derivative including two exTTF moieties (**13**, Fig. 8).[33] The complexation between this macrocycle and a fullerene derivative endowed with a secondary ammonium salt (**14**) was investigated by ^{1}H NMR binding titration in $CDCl_3/CD_3CN$, and a $K_a \sim 50$ M^{-1} was obtained. In complementary work, the fullerene–macrocycle complexation was tested in fluorescence experiments. The basis for this approach are electron donor–acceptor interactions between C_{60} and exTTF that affect the singlet excited estate deactivation of the photoexcited fullerene. As expected, the fullerene fluorescence decreases in intensity gradually as the macrocycle was added, allowing to determine a K_a value of (55 ± 5 M^{-1}), in excellent agreement with the data based on NMR experiments.

The weak interaction observed in this case is probably due to the big and hindered cavity of the crown ether **13**. Therefore, in a next step we decided to synthesize a series of exTTF-based secondary ammonium salts and study their self assembly with fullerene C_{60} endowed with a DB24C8 crown ether appendage.[34]

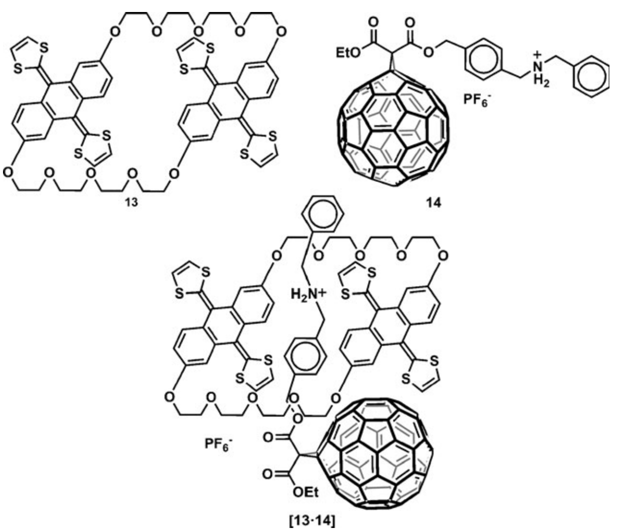

Fig. 8 Chemical structure of macrocycle **13**, ammonium salt **14** and its supramolecular complex.

For the design of these salts we considered different aspects: (i) a rigid or a flexible spacer between the exTTF and the ammonium group; (ii) one or two recognition sites and (iii) different donor ability of the exTTF moiety. Bearing these considerations in mind, compounds **15–18** were prepared, and complexation experiments with DB24C8-fullerene derivative **19** were carried out by ^{1}H NMR titration and fluorescence studies (Fig. 9).

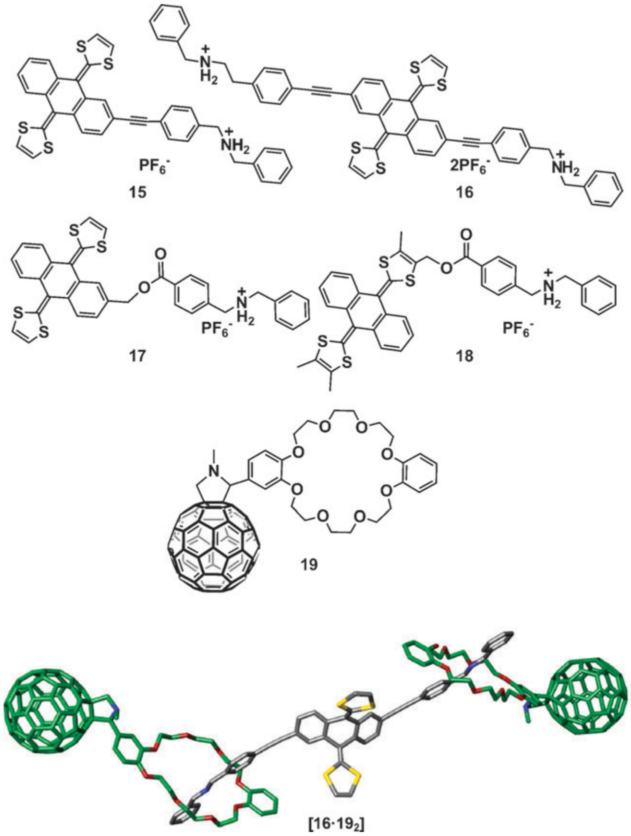

Fig. 9 Chemical structure of **15–19** and complex **16**·**19**$_2$.

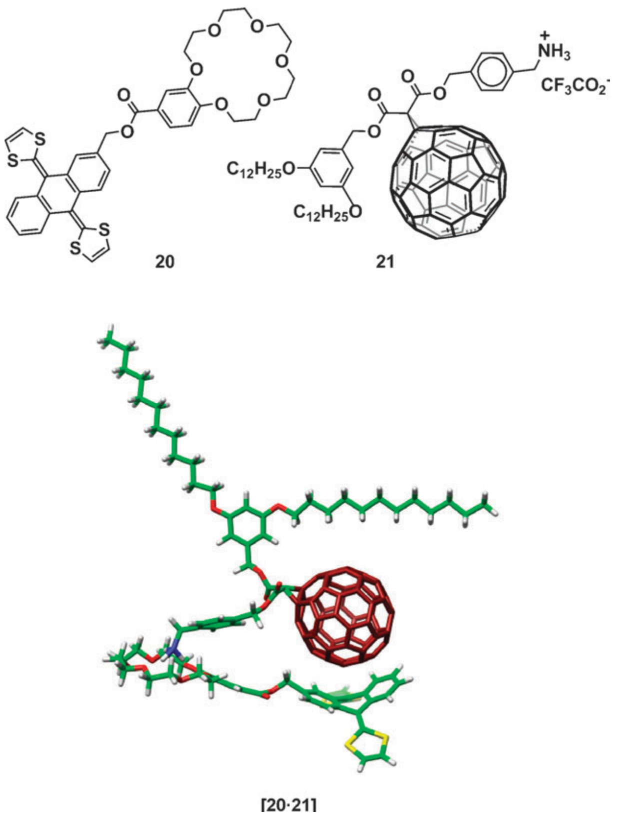

Fig. 10 Chemical structure of crown ether **20**, ammonium salt **21** and molecular model showing its supramolecular complex.

Interestingly, a K_a of 2.2 × 10^3 M^{-1} was calculated for the [**17·19**] complex in $CDCl_3$–CD_3CN, which indicates the relatively high stability of these complexes. The binding constants for the double complex [**16·19$_2$**] and [**18·19**] resulted to be 1.4 × 10^4 M^{-1} and 8.6 × 10^2 M^{-1}, respectively. The enhancement of the constant in [**16·19$_2$**] can be considered mainly associated to the presence of two binding sites, while lower stability of [**18·19**], despite the higher electron donor ability of the exTTF derivative, implies that coulombic interactions must play a secondary role in the overall interactions of these complexes. In accordance with these results, cyclic voltammetry experiments revealed that complexation does not strongly influence the redox properties of the components, thus suggesting that the electroactive units are not spatially close enough to allow measurable electronic interactions between them.

We expected that the linker between the ammonium group and the fullerene should have the perfect length to allow the intramolecular interaction between the fullerene sphere and the π concave surface of exTTF. Therefore, we prepared a new exTTF–crown ether derivative, **20**, and studied the supramolecular interactions with the highly soluble fullerene ammonium salt **21** (Fig. 10).[35] Evidence for complexation of **20** and **21** to form the complex [**20·21**] was obtained from absorption assays in different solvents. Thus, upon addition of **21** to **20**, a decrease of the exTTF absorption band around 440 nm is observed. Concomitant with this decrease, the formation of a new broad absorption band that ranges from 470 to 600 nm, probably a charge-transfer band, is also observed. The variation in absorption at 431 nm fitted to a 1 : 1 binding isotherm, affording a binding constant of (1.58 ± 0.82) × 10^6 M^{-1} in chlorobenzene (a rather similar value of K_a = (2.01 ± 0.79) × 10^6 M^{-1} was calculated in chloroform).

Cyclic voltammetric studies show that oxidation potentials for exTTF are anodically shifted by nearly 100 mV upon complexation, accounting for the high association constant value obtained.

Complementary fluorescence experiments confirmed both the value of K_a (8.23 × 10^5 M^{-1}) and the charge transfer features of the emissions, as these are susceptible to solvent assisted stabilizations and destabilizations in more and less polar solvents, respectively. Indeed, time-resolved transient absorption spectroscopy experiments revealed the photoinduced generation of a charge separated state with a short lifetime (9.3 ps in chlorobenzene).

When looking at the binding constant obtained for [**20·21**] this K_a value is increased by three orders of magnitude relative to the values found for the complexation of the ammonium salt with other crown ether derivatives lacking the exTTF unit. This is also reflected in the tied charge transfer interactions, which leads to a rapid charge recombination, once the radical ion pair state is formed.

Threading the benzylammonium salt **21** through the crown ether **20** facilitates the close proximity of the exTTF unit to the fullerene core by π,π-interaction between the benzene concave rings of the exTTF unit and the fullerene convex sphere, similarly to that previously observed in the related tweezers or truxene-TTFs analogues. The presence of the preorganizing motif gives rise to the cooperativity between π–π and H-bonding interactions, generating a highly stable supramolecular electron donor acceptor hybrid.[36]

Summary and outlook

The first independent reports on the synthesis of π-extended derivatives of TTF, by the groups of Yamashita[37] and Bryce,[38] date back to 1989–1990. In the following years, an extraordinary research effort was dedicated to explore their electrochemical and photophysical properties. In this overview, we have presented some of the first insights into the supramolecular chemistry of several π-extended analogues of TTF, with emphasis on exTTF. The promising results obtained by us, together with those of other groups,[39] augur well for the years to come.

Besides the thorough investigation of the properties of the supramolecular systems already reported, and their application in the constructions of optoelectronic devices, new avenues of research open up before our eyes. For instance, the synthesis of macrocyclic, preorganized receptors for fullerenes based on exTTF—where both the stability and the selectivity of the complexes should be enhanced—and the usage of these novel recognition motifs to synthesize mechanically interlocked architectures, are examples we shall explore in the near future.

Acknowledgements

This work has been supported by the European Science Foundation (05-SONS-FP-021 SOHYD), the MEC of Spain

(CTQ2005-02609/BTQ and Consolider-Ingenio 2010 CSD2007-0010, Nanociencia Molecular) and Comunidad de Madrid (P-PPQ-000225-0505). The contributions of the co-authors of the original research publications to the work presented here are gratefully acknowledged. The MICINN of Spain is thanked by E. M. P. for a Ramón y Cajal contract, co-financed by the European Social Fund.

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