

# Energy, supramolecular chemistry, fullerenes, and the sky\*

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*Abstract:* The search for cleaner and more abundant sources of energy is one of the major scientific challenges of the 21<sup>st</sup> century. Owing to its privileged position as the central science, chemistry is bound to play a leading role in this quest. Within the search for new materials for organic photovoltaics, some of the work we have carried out concerning the supramolecular chemistry of electron donor and acceptor molecules is presented.

*Keywords:* fullerenes; organic solar cells; self-assembly; solar energy; supramolecular chemistry.

## INTRODUCTION

### The energy problem and the answer in the sky

Robert Malthus published “An Essay on the Principle of Population” between the end of the 18<sup>th</sup> and the beginning of the 19<sup>th</sup> centuries. At that time, the pace at which the human population was increasing seemed unsustainable—Europe’s population doubled during the 18<sup>th</sup> century to reach almost 200 million, and doubled again during the 19<sup>th</sup> century—and it was commonly thought that if nothing was done, Nature would restrict it itself by means of famines and plagues. Malthus distrusted the capacity of humankind to increase food supplies and proposed a planned restriction of population growth, mainly by postponement of marriage and celibacy. Thanks to the scientific and technological developments experienced during the following two centuries, however, we have not only been able to continue to grow as a species, but our standards of living have been raised to undreamed of limits, and life expectancy has rocketed to a world-average of nearly 70 years [1].

At the beginning of the 21<sup>st</sup> century, humankind is facing a challenge of similar if not bigger dimensions, the problem of energy. The 2010 International Energy Outlook from the U.S. government expects a global energy consumption of nearly 790 billion gigajoules ( $7.9 \times 10^{20}$  J) in 2035, a worryingly high figure when compared to the 490 billion gigajoules consumed in 2005 [2]. Moreover, the (ab)use of fossil fuels has triggered an increase in the atmospheric concentration of greenhouse gasses, and brought about the somewhat controversial issue of global warming. In analogy with Malthusian theories, a very common line of thought supports restrictions in the consumption of energy as a solution. Although it is both conceivable and desirable to limit energy consumption in the developed world, it seems unfair to impose it on developing countries

As an alternative, the scientific community has embarked on the search for new, renewable, and more abundant energy sources. In fact, if we wish to maintain our standards of living, even those not particularly sensitive toward environmental issues will agree that the deadline to resort to alternative

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energy supplies is rapidly approaching. There are two definitions under “deadline” in the Merriam-Webster Dictionary, the *first* of which is “a line drawn within or around a prison that a prisoner passes at the risk of being shot”, with the second being the more usual and certainly less disquieting “a date or time before which something must be done”. Unfortunately, Nature seems to be keen on the first definition, and has traditionally been rather unforgiving when it comes to deadlines—evolution is basically a series of unmet deadlines for adaptation. We *need* to face the energy problem, and we’d better do it fast. As chemists, we are particularly well equipped to address this issue [3].

Solar energy is perhaps the cleanest of the energy sources available to humankind, and it surely is the most plentiful. The Earth receives approximately 385 billion exajoules ( $3.85 \times 10^{29}$  J) from the sun yearly. That is close to nine orders of magnitude more than we need, and approximately enough energy per hour to satisfy the world’s consumption in one year. The numbers speak for themselves: For a solution to our problems with energy, we should be looking at the sky.

### Organic photovoltaics: A blue sky science approach

Presently, silicon-based solar cells monopolize the photovoltaic market. Their main drawback is that they have very high production costs, achieving cost parity with fossil fuel energy only after a period of 5–7 years [4]. For some applications, for example, portable devices that need to work under weak illumination conditions, organic solar cells (OSCs) [5–8] should represent a valid and cheaper alternative to inorganic cells, since they are based on organic chromophores with high molar extinction coefficients. In addition, printing polymer technologies can be applied to their fabrication [9] and they are flexible and lightweight. On the downside, they typically show efficiencies lower than 5 %. For comparison, crystalline silicon devices are approaching the theoretical limiting efficiency of 29 %. One of the factors that is limiting the efficiency of OSCs is charge recombination, a process in which the negatively and positively charged species recombine in the active layer before the charges proceed to the electrodes. The nanometric organization of p- and n-type materials is expected to facilitate charge mobility in OSCs, preventing recombination. Thus, to continue to progress, it is crucial that we depart from the view that the properties of bulk materials are determined solely by those of their molecular components, and study their supramolecular organization in depth, as recently advocated by Würthner and Meerholz [10].

At IMDEA Nanoscience, under the direction of Prof. Nazario Martín, we are involved in the synthesis of supramolecular systems between  $\pi$ -extended tetrathiafulvalene derivatives and fullerenes with the aim of gaining a deeper understanding of the noncovalent chemistry of both electron donor and electron acceptor molecules. In the following sections, I will briefly summarize our contributions to the field in the last few years, and as the reader will soon see, few, if any, examples of final OSCs will be mentioned [11]. Although it is our long-term goal to contribute to the construction of more efficient OSCs, it is our belief—together with a significant part of the scientific community—that most truly significant technological innovations have come from basic research. It is hard to think that Sir Humphry Davy was trying to develop a domestic, commercially viable lighting system when he first observed the incandescence of a platinum wire by passing through it the current generated by the most powerful electrical battery in the world at the time. In most cases, curiosity and knowledge come first, applications follow. The supramolecular chemistry of the fullerenes is what we are curious about, and it is what the next few pages will be about.

### HISTORICAL NOTES ON THE NONCOVALENT CHEMISTRY OF FULLERENES

In order to design fullerene receptors able to form complexes of high stability and selectivity, we need to keep in mind that fullerenes are a peculiar kind of guest. As organic molecules, fullerenes are unique in that they are composed of carbon atoms only, lacking any other type of functionality; this, together with their geometry, make them neutral and hardly polarized species. These evident observations have

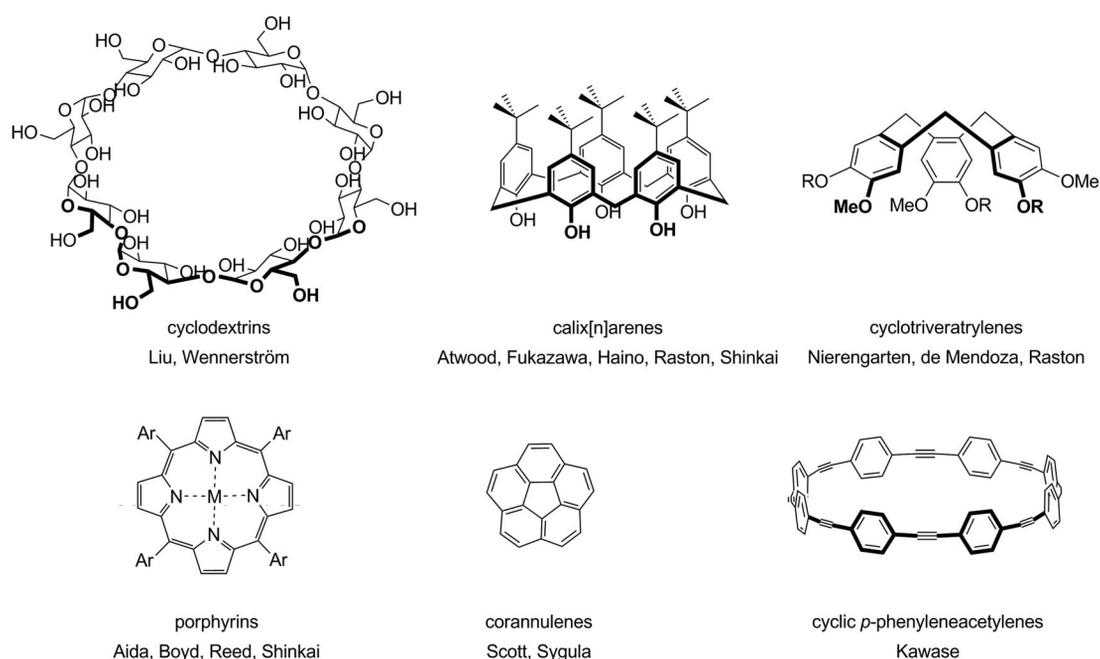
important implications when it comes to the possible noncovalent interactions that we can utilize to associate fullerenes in solution. The impossibility of utilizing strong directional forces, like metal–ligand coordination or hydrogen bonding, to recognize fullerenes, leaves us with  $\pi$ – $\pi$ , van der Waals, and solvophobic interactions as key factors to consider. Fortunately, optimizing all of them requires the same strategy: increasing the surface of the receptor in short contact with the fullerene guest. Thus, the nuts and bolts of the design of hosts for fullerenes is the construction of a nonpolar cavity—preferentially but not necessarily featuring aromatic recognizing units—of the appropriate size to fit the fullerene guest.

The search for molecules capable of associating fullerenes in solution was initiated just seven years after the discovery of  $C_{60}$  and immediately after it became available in sufficient quantities by contact-arc vaporization of graphite [12]. In 1992, the first designed host for fullerenes was reported by Diederich, Ringsdorf, and co-workers [13]. The receptor was based on a macrocyclic azacrown ether in which the nitrogen groups were alkylated or acylated with aromatic groups, further substituted with long alkane chains, forming a lipophilic “cup”. Through a combination of surface pressure-area diagrams, UV–vis spectroscopy, and atomic force microscopy (AFM), the authors showed that the fullerenes preferentially dwelled inside the lipophilic cavities.

In the same year, Wennerström’s group described the encapsulation of  $C_{60}$  by two units of  $\gamma$ -cyclodextrin to obtain water-soluble complexes [14], extending the same concept to  $C_{70}$  two years later [15]. The positive cyclodextrin–fullerene interaction, particularly in water, has been exploited to build organized fullerene nanostructures [16–20]. At approximately the same time, the groups of Raston and Shinkai, working independently, reported the selective purification of  $C_{60}$  from fullerene soot by its selective association with *p*-*tert*-butylcalix[8]arene [21,22]. Drawing from these seminal investigations, several receptors based on calixarenes—mainly calix[5]arenes—have been described [23–34].

Cyclotrimeratrylenes (CTVs) have also been extensively investigated for the molecular recognition of fullerenes. CTV was first found to interact with  $C_{60}$  forming 1:1 complexes in the solid state [35]. Later, mainly by extension of the cavity of CTV or by the construction of dimeric capsules, a rich collection of hosts that work in solution and on surfaces have been conceived and synthesized [36–44].

Porphyrins are well known to interact favorably with fullerenes both in solution and in the solid state, which has been thoroughly exploited in the design of receptors for fullerenes [45,46]. In the paradigmatic 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 [47]. Structural variations on this design have led to what is probably the richest collection of receptors for fullerenes [48], including the world-record holder in complex stability, with  $\log K_a = 8.1$  in 1,2-dichlorobenzene at room temperature [49], and the first chiral sensors for the inherently chiral higher fullerenes [50,51]. Besides Aida’s work on macrocyclic structures, several molecular tweezers featuring porphyrins as binding motifs have also been reported [52,53], spearheaded by the work by Boyd and Reed on their “jaws” receptors [54–56]. More recently, concave recognition motifs [57,58], complementary to the convex surface of the fullerenes, like corannulene [59–61], or cyclophenyleneacetylenes, have been explored [62–65].



**Fig. 1** Chemical structures of some of the most prominent molecular fragments utilized in the recognition of fullerenes, and some of the key authors that have contributed to their development.

## $\pi$ -EXTENDED TTFs AND FULLERENES AS SUPRAMOLECULAR PARTNERS: THE STORY SO FAR

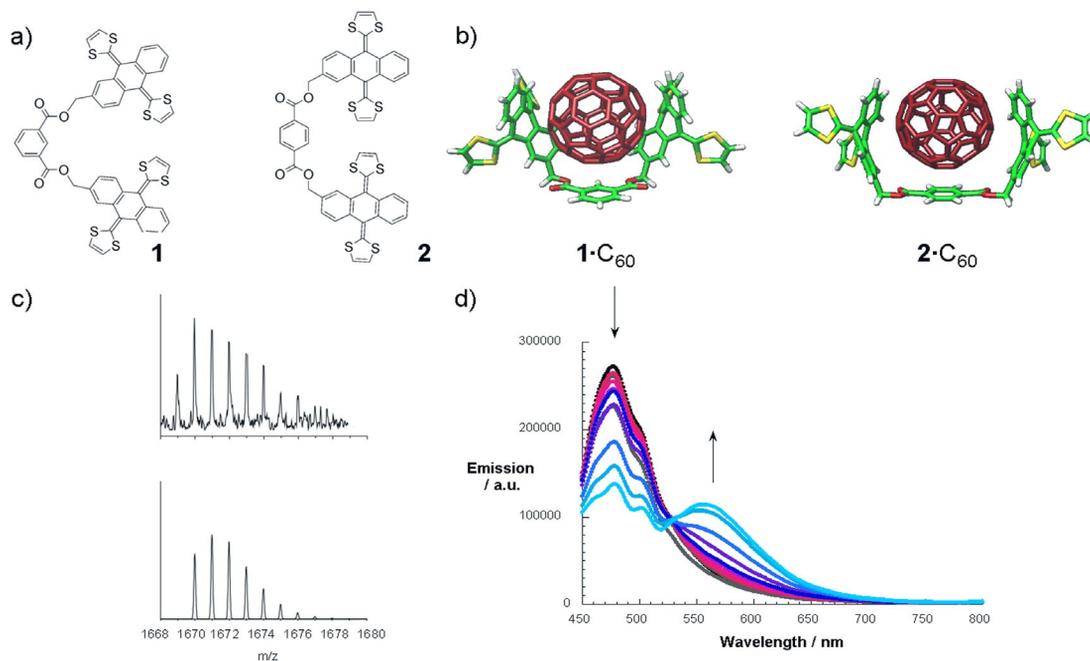
Besides plain scientific curiosity, research into the noncovalent binding of fullerenes is fuelled mainly by the interest in finding new, simpler methods for the purification of a specific fullerene from fullerene soot, or a mixture of fullerenes, and in the control of the nanometric organization of electroactive materials. When addressing the latter, it would be particularly advantageous to combine molecular fragments with electron donor character with the electron-accepting fullerenes.

### Receptors for fullerene based on $\pi$ -extended TTFs

The group of Prof. Nazario Martín has long been involved in the covalent connection of  $C_{60}$  to  $\pi$ -extended tetrathiafulvalenes, which has enabled the fabrication of photo- and electroactive conjugates that act as artificial photosynthetic systems and active molecular materials in organic photovoltaics [66]. However, it was not long ago that we realized that the shape complementarity between the concave aromatic face of 9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (exTTF) and the convex surface of the fullerenes should promote positive noncovalent interactions [58,67].

To test this hypothesis, receptors **1** and **2** were designed. In these hosts, two exTTF units are connected through an isophthalate or a terephthalate diester spacer, respectively, in a simple tweezers-like design [68–70]. Preliminary evidence of binding in the gas phase was observed through matrix-assisted laser desorption/ionization with time-of-flight mass spectrometry (MALDI-TOF-MS), where peaks corresponding to the associated species were detected. The association in solution was studied by UV–vis and fluorescence titrations. During the titration of both **1** and **2** against  $C_{60}$ , we observed changes in the electronic absorption spectrum of the receptor, which pointed to association. In particular, 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 observed the concomitant appearance of a charge-transfer band at  $\lambda = 482$  nm. Fluorescence emission spectra recorded in the course of the titration resulted in mirror images of the absorption spectra. The intensity of the weak emission of exTTF ( $\lambda_{\max} = 470$  nm;  $\Phi = 10^{-3}$ ) is reduced on addition of  $C_{60}$ , while a new emission centered at 557 nm increases at its expense. Nonlinear regression of these spectral changes allowed us to estimate binding constants in the range of  $\log K_a = 3\text{--}4$ .



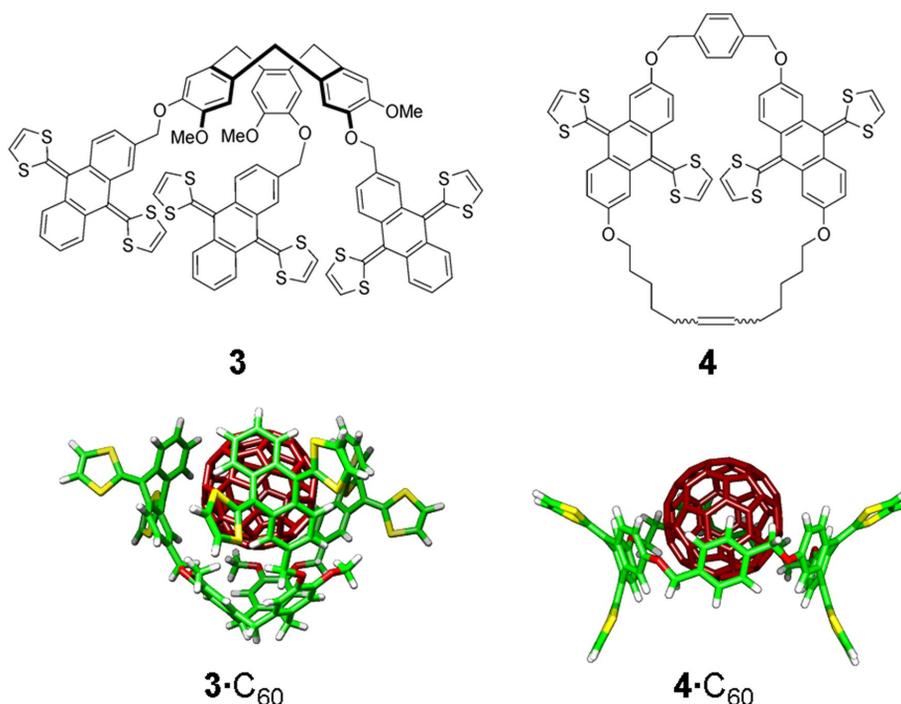
**Fig. 2** (a) Structures of the tweezers-like receptors **1** and **2**. (b) Energy-minimized (BH&H) geometries of their complexes with  $C_{60}$ . (c) Experimental (top, MALDI-TOF) and theoretical (bottom), mass spectrum of  $2 \cdot C_{60}$ . (d) Fluorescence spectra (PhCN, 298 K) of **1** with increasing concentration of  $C_{60}$ ; the arrows indicate the progression of the titration.

Distinctively, exTTF and  $C_{60}$  are complementary not only in a supramolecular sense, but also electronically. Both fragments were known to undergo photoinduced electron transfer (PET) from exTTF to  $C_{60}$  in covalently connected conjugates [66]. A prerequisite for the newly developed exTTF- $C_{60}$  supramolecular systems to find application in OSCs is that PET takes place in solution. Such possibility was investigated in collaboration with the group of Prof. Dirk M. Guldi. We were glad to observe that intracomplex PET does occur from the exTTF units of the receptor and the bound  $C_{60}$ . The charge-separated states are relatively short-lived, with lifetimes in the range of picoseconds, which can be readily understood considering that binding of  $C_{60}$  by either **1** or **2** implies some degree of orbital overlap between the electroactive units, which facilitates both charge separation and charge recombination processes [70].

With these results in hand, we anticipated that increasing the preorganization in our receptors and/or increasing the number of exTTF units should lead to improved binding constants. In this sense, our first attempt was to synthesize the analogue of **1** featuring three exTTF units, utilizing trimesic acid as a spacer. Despite the additional recognizing fragment, we found a very modest increase in stability of the associates compared to the tweezers **1** and **2**, with binding constants in the order of  $\log K_a = 4$ ,

which indicates that, most probably, only two of the three exTTF units are accommodated around  $C_{60}$  in the complex [71].

As a next step, in collaboration with the group of Prof. Javier de Mendoza, we built host **3** (Fig. 3), in which three exTTFs are grafted on a CTV scaffold, expecting that the bowl-shaped CTV would preorganize all three exTTF units to wrap around the fullerene guest [72]. Host **3** was readily obtained via a Mitsunobu protocol from exTTF methylene alcohol and CTV. Its ability to associate  $C_{60}$  and  $C_{70}$  was investigated through UV-vis titrations in chlorobenzene at room temperature. Upon addition of either fullerene, a decrease in intensity of the exTTF band at  $\lambda = 434$  nm was observed accompanied by the emergence of an intense charge-transfer band centered at  $\lambda = 478$  nm for  $C_{60}$  and at  $\lambda = 472$  nm for  $C_{70}$ . During the early steps of the titration (after addition of 1–1.2 equiv of guest), well-defined isosbestic points at 452 nm ( $C_{60}$ ) and 445 nm ( $C_{70}$ ) were formed. Such changes are fully consistent with those found for receptors **1** and **2** and constitute the typical signature of the exTTF-fullerene interaction. Analysis of the titration data yielded binding constants of  $\log K_a = 5.3 \pm 0.2$  and  $6.3 \pm 0.6$  for  $C_{60}$  and  $C_{70}$ , respectively. As expected, DFT calculations (BH&H/TZ2P) supported a structure in which the fullerenes dwell deep into the cavity of the exTTF-CTV host, with the CTV serving as both a bowl-shaped recognition element and as a preorganizing scaffold for the exTTF subunits, all three of which surround the surface of the fullerenes. Unambiguous evidence supporting the binding event was also found through MALDI-TOF and  $^{13}\text{C}$  NMR. Moreover, light-induced electron spin resonance measurements at 298 K confirmed that, upon irradiation with light, intracomplex PET takes place in **3**  $C_{60}$ .



**Fig. 3** Structures of receptors **3** and **4** and energy-minimized (BH&H) models of their associates with  $C_{60}$ .

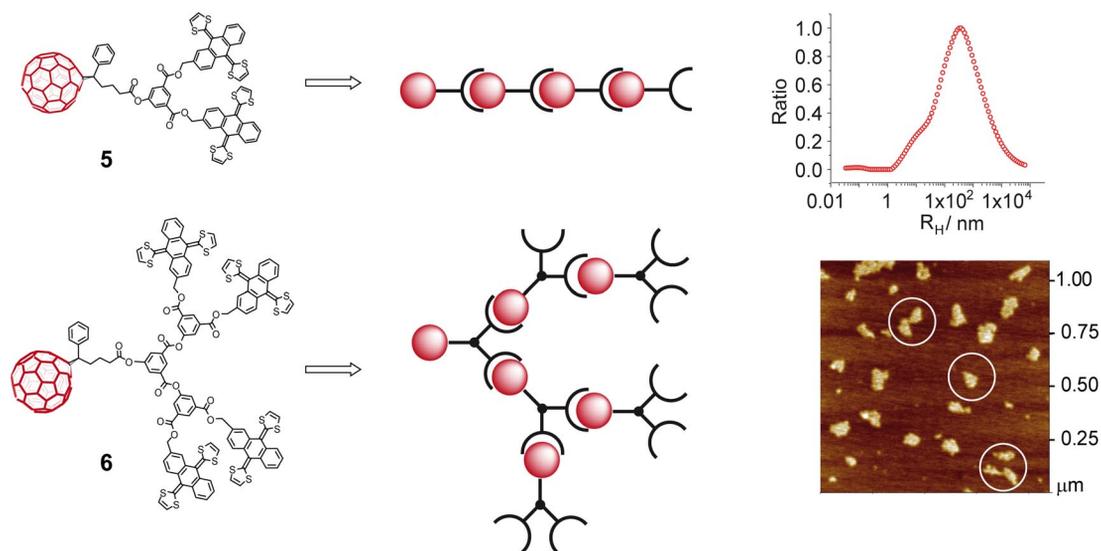
As an alternative approach, we designed and synthesized host **4** (Fig. 3), in which the main structural traits of the tweezers were conserved and a significant improvement in preorganization was expected with the change to a macrocyclic structure. The synthesis of **4** is remarkably simple, consisting of only four steps from commercially or readily available starting materials, and concluding with a

nearly quantitative ring-closing metathesis macrocyclization. As opposed to the tweezers **1** and **2**, in the case of **4** both exTTF units are preorganized for the binding of the fullerene host. Besides restricting conformational freedom, the alkyl linker should provide additional van der Waals interactions with  $C_{60}$ , increasing the stability of the complex. Indeed, we found a binding constant of **4** towards  $C_{60}$  of  $\log K_a = 6.5 \pm 0.5$  in chlorobenzene at room temperature. This represents an improvement of over two orders of magnitude with regards to the tweezers-like receptors, and one of the highest binding constants reported in the literature to date for an all-organic receptor, even superior to most of Aida's porphyrin macrocycles with the exception of the Rh(III) and Ir(III) congeners [49].

We have also explored the use of larger derivatives of exTTF, namely, truxTTFs, in which three dithiole units are covalently connected to a truxene core. Such structures are capable of binding  $C_{60}$  with a binding constant of  $\log K_a = 3.1 \pm 0.3$  [73]. We are currently developing synthetic routes to access more elaborate derivatives of truxTTFs, such as tweezers and cages.

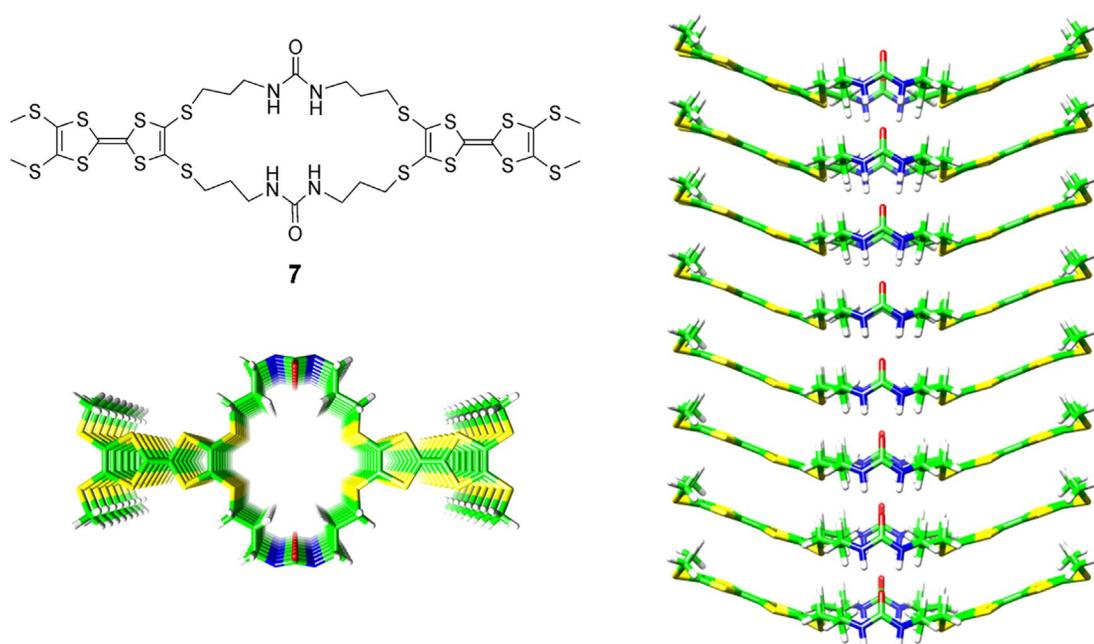
### Organized electroactive nanostructures

The experimental evidence supporting that fully charge-separated states were obtained upon irradiation with light in our exTTF- $C_{60}$  host-guest systems indicated that these might realistically be good candidates to be utilized in the nanometric organization of electroactive materials. With this in mind, we designed **5** and **6** (Fig. 4) as monomers for the construction of supramolecular polymers. Monomer **5** was designed to self-associate in a head-to-tail fashion to form linear oligomers. Thus, a derivative of  $C_{60}$  was covalently linked to one unit of our tweezers-like receptor [74]. On the other hand, **6** was expected to form arborescent oligomers, due to the 2:1 ratio of hosts to guests [75]. In fact, a systematic collection of experiments, including variable concentration and variable temperature NMR, pulse field gradient (PFG) NMR, MALDI-TOF-MS, dynamic light scattering (DLS), and AFM demonstrated that **5** forms linear multimeric supramolecular aggregates, while **6** forms hyperbranched supramolecular aggregates.



**Fig. 4** Structures of monomers **5** and **6**, cartoons showing their idealized self-association. Also shown are: the normalized distribution of hydrodynamic radii ( $R_H$ ) of aggregates of **5** ( $\text{CHCl}_3$ ,  $5.0 \times 10^{-4}$  M, 298 K) and a typical AFM image (tapping mode, air, 298 K) of a drop-cast of a chloroform solution of **6** on mica, with some of the predominant triangular associates formed highlighted.

As an alternative to exploiting the fullerene-exTTF interactions—based on  $\pi$ - $\pi$  and van der Waals interactions—we reasoned that utilizing hydrogen bonds should give us a higher degree of control over the self-assembly process [76]. A series of bis-urea macrocycles that self-assemble to form columnar nanotubes via a combination of strong urea-urea bifurcated hydrogen bonds and aromatic stacking interactions had been reported by Shimizu's group [77–79]. Building on this, we reasoned that such systems could be exploited to organize electroactive materials, and designed macrocycle **7** (Fig. 5), in which two units of di(methylthio)tetrathiafulvalene (DMTTF) are connected to two urea groups through flexible alkyl spacers [80]. Macrocycle **7** is sufficiently soluble in common organic solvents to study its self-association in solution. Through a combination of  $^1\text{H}$  NMR, UV-vis, and cyclic voltammetry experiments, and high-level DFT calculations, we proved that **7** forms nanotubular oligomers. Importantly, we were able to control the assembly process through changes in the polarity of the solvent or by electrochemical stimulation.



**Fig. 5** Structure of macrocycle **7**, and minimum-energy (MPWB1K/6-31G\*\*) structures of its oligomers, showing eight repeating units.

Besides these self-assembling nanostructures, we have synthesized and studied the supramolecular chemistry of covalent dendrimers decorated with up to 12 units of the exTTF tweezers [81]. As expected, such dendrimers are able to bind several units of  $\text{C}_{60}$  in solution. At present, we plan to investigate the synthesis of higher-molecular-weight polymers to (at last!) implement them in OSCs.

## CONCLUSIONS AND OUTLOOK

An initiative like the International Year of Chemistry 2011 is a superb opportunity to reflect upon the significance and relevance of the central science. Chemistry has made enormous contributions to our everyday life: from medicines that have cured millions to polymers that have shaped the world we live in. At the beginning of the 21<sup>st</sup> century, chemistry is bound to play a leading role in what is perhaps the

most pressing, and at the same time one of the most exciting, problems that humanity is facing: the search for alternative sources of energy.

Framed within that search, in the present manuscript I have reviewed some of the work we have carried out at the Universidad Complutense de Madrid and IMDEA Nanoscience concerning the supramolecular chemistry of electron donor and acceptor molecules. Our approach is unlikely to yield immediate practical results, but we are hopeful our studies, together with many others', will help us put together the toolbox we will need to bring OSCs to their full potential.

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