

Hydrogen-Bonding Motifs in Fullerene Chemistry

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In memory of Juan C. del Amo

The combination of fullerenes and hydrogen-bonding motifs is a new interdisciplinary field in which weak intermolecular forces allow modulation of one-, two-, and three-dimensional fullerene-based architectures and control of their function. This Minireview aims to extend the scope of fullerene chemistry to a truly supramolecular level from which unprecedented architectures may evolve. It is shown that electronic communication in C_{60} -based hydrogen-bonded donor–acceptor ensembles is at least as strong as that found in covalently connected systems and that hydrogen-bonding fullerene chemistry is a versatile concept for the construction of functional ensembles.

1. Introduction

In Nature, both covalently and noncovalently bound motifs are widely spread organization principles that regulate the size, shape, and function of all living species on a molecular (nano-) scale. One of the most fascinating and cited examples is double-stranded DNA. In this biopolymeric dimer, cooperativity between noncovalent interactions—involving multiple hydrogen bonds—and hydrophobic interactions generates exceptionally stable architectures. Nature thus provides inspiration for the design of organized structures that perform specific functions.

To engineer multimolecular arrays of nanometer dimensions, a wealth of noncovalent interactions are at our disposal. These comprise ion–ion, ion–dipole, hydrogen-bond, dipole–dipole, and π – π -stacking interactions. Typically, their binding energies range from a few kJ mol^{-1} up to several hundred

kJ mol^{-1} .^[1] Among these interactions, hydrogen bonding has emerged as the most useful, with binding energies between 4 and 120 kJ mol^{-1} . The specificity of hydrogen bonding and its high degree of directionality attracts a lot of attention, as it is responsible for governing many three-dimensional structures in chemical and biological systems.^[2]

One approach to overcome the poor stability of single hydrogen bonds relies on arrays of multiple hydrogen bonds. Alternatively, high values of binding constants have been obtained by combining hydrogen bonds with additional supramolecular interactions such as hydrophobic or electrostatic forces. In this Minireview, we survey some of the most relevant hydrogen-bonding arrays that are known, as well as those few examples in which hydrogen bonds are combined with other noncovalent interactions, such as complementary guanidinium– or amidinium–carboxylate bridges (Figure 1 a and b, respectively).^[3] Association constants (K_a) of around 10 M^{-1} are observed in CHCl_3 for the simplest donor–acceptor (DA) arrays that are built upon one donor (D) and one acceptor (A) site. Triple hydrogen-bonding motifs (e.g. DAD, see Figure 1 c), as pioneered and tested by Whitesides et al.,^[4] Zimmerman and Corbin,^[5] and Meijer and co-workers,^[6] reveal K_a values as large as 10^2 – 10^3 M^{-1} (CHCl_3). Even higher association constants of $K_a \approx 10^5 \text{ M}^{-1}$ (CHCl_3) are observed in self-complementary quadruple hydrogen-bonding motifs (e.g. DADA) as shown in Figure 1 d.^[7] If, however, association constants greater than 10^7 M^{-1} (CHCl_3) are to be realized, self-complementary DDAA motifs become necessary. Meijer and co-workers^[8a] demonstrated the unusual binding strength of a DDAA motif with 2-ureido-4-pyrimidinones (Figure 1 e).

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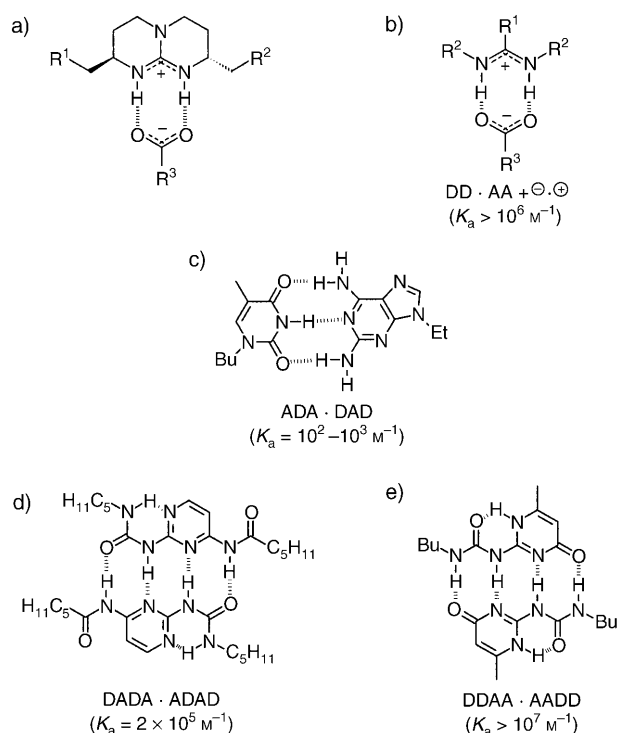
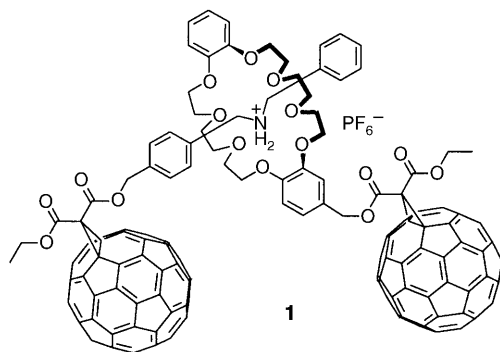


Figure 1. Hydrogen-bonding motifs that display high association constants. K_a values measured in 99:1 toluene/dimethyl sulfoxide (a,b) and in $CHCl_3$ (c–e). D = donor; A = acceptor.

Despite the importance of hydrogen-bonding motifs for the design of supramolecular architectures, their application to fullerenes has only recently been reported. This Minireview has three principle aims: 1) to extend the scope of fullerene chemistry to a truly supramolecular level from which unprecedented architectures evolve, 2) to show that electronic communication in C₆₀-based donor–acceptor ensembles that are connected through hydrogen bonds is at least as strong as that found in covalently connected systems, and 3) to highlight fullerene hydrogen-bonding chemistry as a versatile concept to construct functional ensembles such as molecular machines and optoelectronic devices.

2. Hydrogen-Bonded Fullerene Ensembles

In 1999, Diederich et al. reported the dimer **1** ($K_a = 970 \text{ M}^{-1}$ in $CHCl_3$).^[9] In this ensemble, $N^+ \cdots H \cdots O$ and $C \cdots H \cdots O$ hydrogen bonds together with contributions from ion-



Luis Sánchez received his PhD in organic chemistry in 1997 from the Universidad Complutense de Madrid (UCM; Spain). In 1998 he joined the faculty at the Department of Organic Chemistry at UCM and was promoted to Associate Professor in 2002. During 1999–2000 he was a postdoctoral researcher with Prof. Jan C. Hummelen (University of Groningen, The Netherlands) and worked on the synthesis of C₆₀ derivatives and their application in the preparation of organic solar cells. His current research interests are focused on new supramolecular C₆₀-based ensembles in the study of electron-transfer processes and photovoltaic applications.



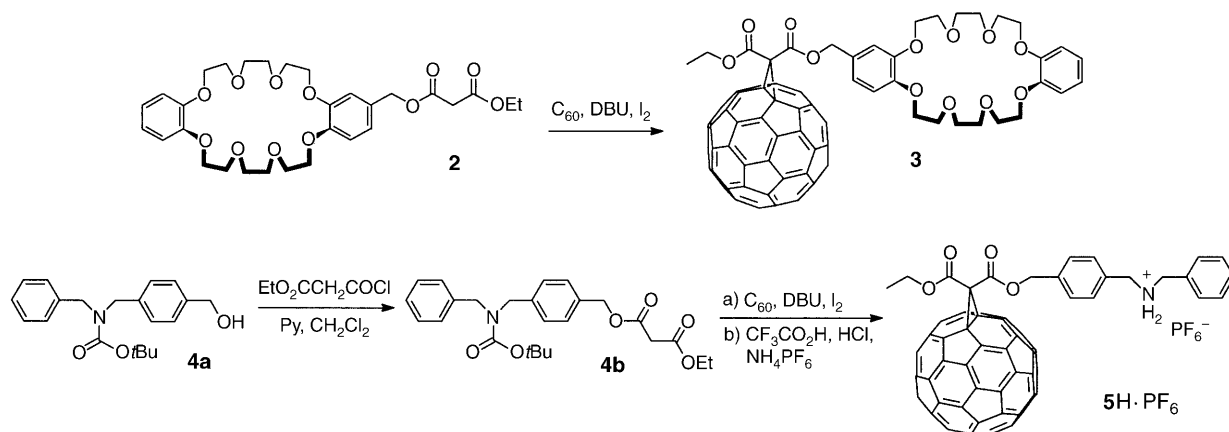
Nazario Martín received his PhD from the Department of Organic Chemistry at the Universidad Complutense de Madrid (Spain) in 1984. After a year in industry, he worked as a postdoctoral fellow (1987–1988) with Prof. M. Hanack at the Institut für Organische Chemie der Universität Tübingen (Germany) on electrically conducting organic materials. Since 1989 he has been Professor of Organic Chemistry at UCM. His research interests focus on electroactive molecules, with emphasis on the covalent and supramolecular chemistry of fullerenes, electron-donor tetrathiafulvalenes, and *p*-conjugated systems in the context of electron-transfer processes and photovoltaic applications.



Dirk M. Guldi studied chemistry at the University of Cologne (Germany) and received his PhD in 1990. He then carried out postdoctoral research at the National Institute of Standards and Technology (Gaithersburg, USA) and at the Hahn-Meitner-Institute, Berlin, and he joined the faculty at the Notre Dame Radiation Laboratory in 1995. He completed his Habilitation at the University of Leipzig in 1999, and since 2004 he is Professor of Physical Chemistry at the Friedrich-Alexander University in Erlangen. His primary research interests include new multifunctional carbon-based nanostructures within the context of light-induced charge separation and solar-energy conversion.

pairing and dispersive interactions are the driving forces for noncovalent, pseudorotaxane-like geometries. On the way to supramolecular dimer **1**, Bingel reactions were carried out between C₆₀ and malonate-appended crown **2** and dibenzyl-amido malonate **4b**, respectively, to afford the methanofullerene **3** and the precursor to **5H**·PF₆ (see Scheme 1). Consecutive deprotection (CF₃CO₂H/CH₂Cl₂), protonation (HCl), and ion exchange (NH₄PF₆/H₂O/acetone) led finally to **5H**·PF₆.

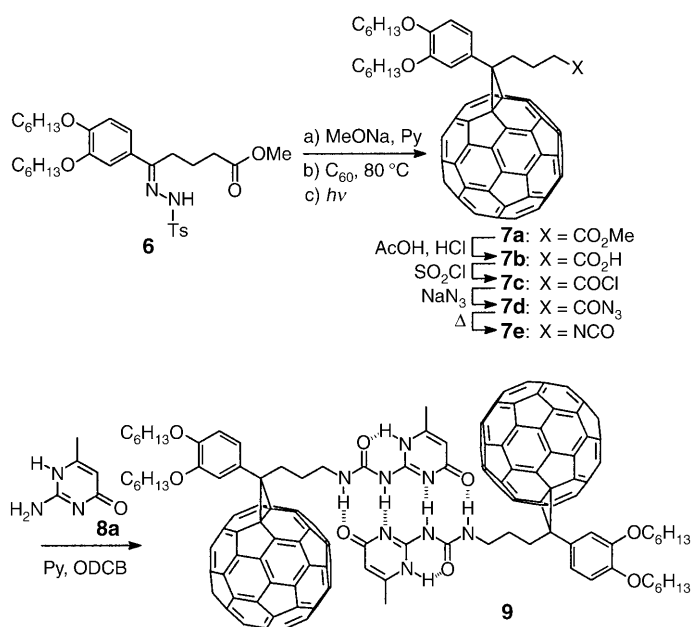
Highly stable hydrogen-bonded fullerene dimers **9** and **12** were prepared through self-complementary 2-ureido-4-pyrimidinone (UP) moieties (Scheme 2). The first step in the preparation of **9** was the 1,3-dipolar cycloaddition of the anion of *p*-tosylhydrazide **6** to C₆₀. Photoisomerization of the formed fulleroid quantitatively yielded methanofullerene **7a**, which was transformed into the acyl azide **7d** through routine chemistry. The final step involved heating of **7d** in the



Scheme 1. Synthesis of precursors for noncovalently linked C_{60} dimer **1**. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; Py = pyridine.

presence of 6-methylisocytosine (**8a**) to afford the monomeric unit of **9** in 71 % yield (Scheme 2).^[10]

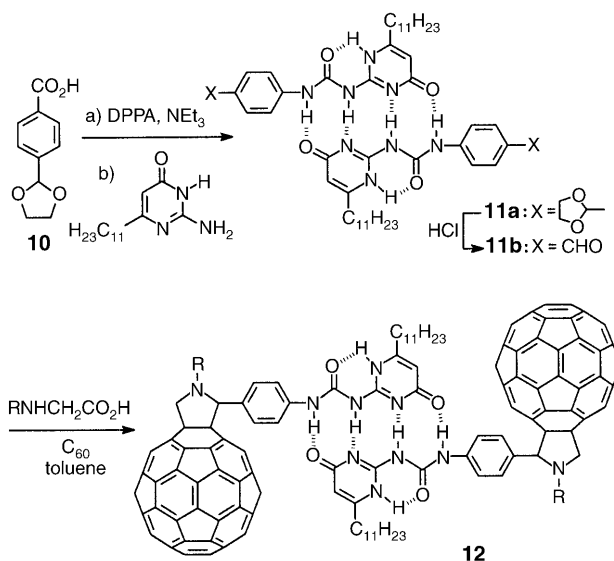
The key step in the synthesis of **12** was the reaction between C_{60} and a bisazomethine ylide generated in situ from dialdehyde **11b** (Scheme 3).^[11] Electrochemical studies of **9** and **12** in the ground states confirmed the absence of



Scheme 2. Synthesis of supramolecular C_{60} dimer **9**. Ts = *p*-toluenesulfonyl; ODCB = *o*-dichlorobenzene.

interactions between the C_{60} units. However, differences were seen when the reactivity of the monomers and dimers in their excited states were studied.^[11] Specifically, the photo-physical findings pointed to strong electronic coupling between the C_{60} termini, mediated through the hydrogen-bonding edges.

Sánchez, Rispens, and Hummelen reported soon afterwards the synthesis of the supramolecular C_{60} polymer **15**^[12] from the C_{60} -diester derivative **13** (Scheme 4). The dynamic behavior of **15** was investigated by 1H NMR spectroscopy. At

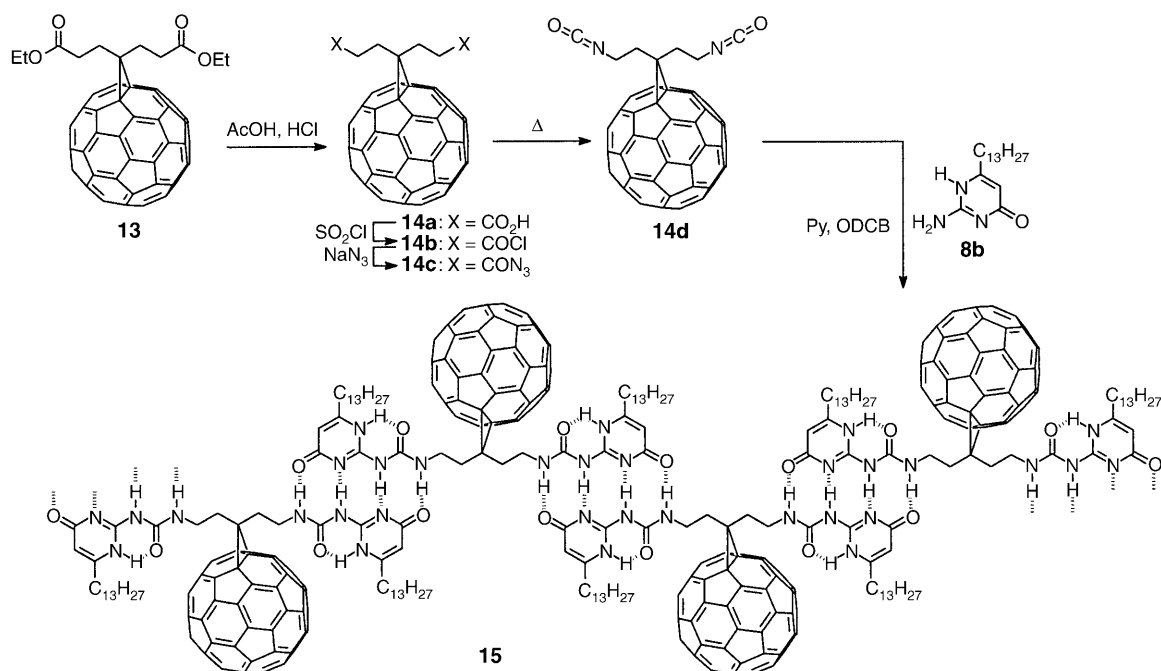


Scheme 3. Synthesis of supramolecular C_{60} dimer **12**. DPPA = diphenylphosphoryl azide; R = $CH_3(OCH_2CH_2)_3$.

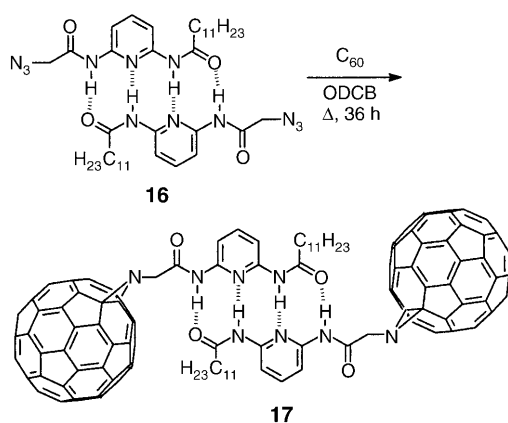
low concentrations (10 mM) different sets of multiple signals were observed. A likely rationale infers the presence of polymeric and low-molecular-weight cyclic aggregates, as has been proposed for related systems.^[13] A fairly high association constant, $K_a = 6 \times 10^7 M^{-1}$, was determined for polymer **15** in chloroform.^[14] The electrochemical behavior of polymer **15** was virtually identical to that of the analogous dimer **9**, and neither **9** nor **15** exhibit notable interactions between the fullerenes.

In line with the DADA concept, 2,6-bis(acylamino)pyridines were probed to integrate two aziridinofullerenes into the supramolecular C_{60} dimer **17**.^[15] This dimer was prepared through 1,3-dipolar cycloaddition of the corresponding hydrogen-bonded azide **16** to C_{60} (Scheme 5). Interestingly, when dilute solutions of **17** were analyzed by scanning electron microscopy (SEM), spherical nanoparticles with diameters of typically around 15 nm were observed which resulted from aggregation.

Bassani and co-workers characterized a variety of supramolecular ensembles resulting from the reaction of fullerene-



Scheme 4. Synthesis of supramolecular C₆₀-based polymer 15.



Scheme 5. Synthesis of DADA hydrogen-bonded C₆₀-based dimer 17.

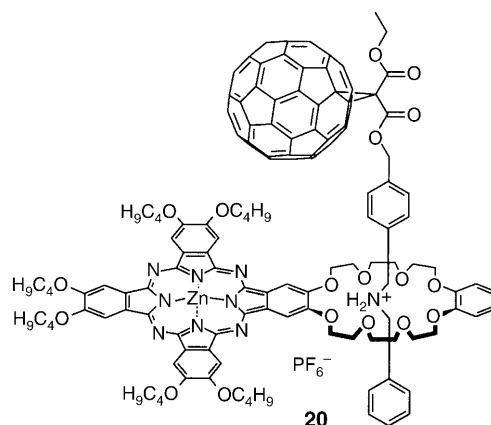
barbituric acid **18** and the melamine derivative triaminotriazine **19**.^[16] Scheme 6, part a, shows several of the resulting architectures obtained. An interesting feature of [60]fullerenes is their susceptibility to undergo topologically controlled [2+2] photocycloaddition reactions. The resulting structures are similar to that obtained through the intermolecular photodimerization of the 1:2 complex formed from melamine template **19** and two molecules of **18** (Scheme 6, part b). Bassani's supramolecular approach represents the first instance of intermolecular photodimerization of a fullerene derivative in solution and an interesting example of supramolecular catalysis.

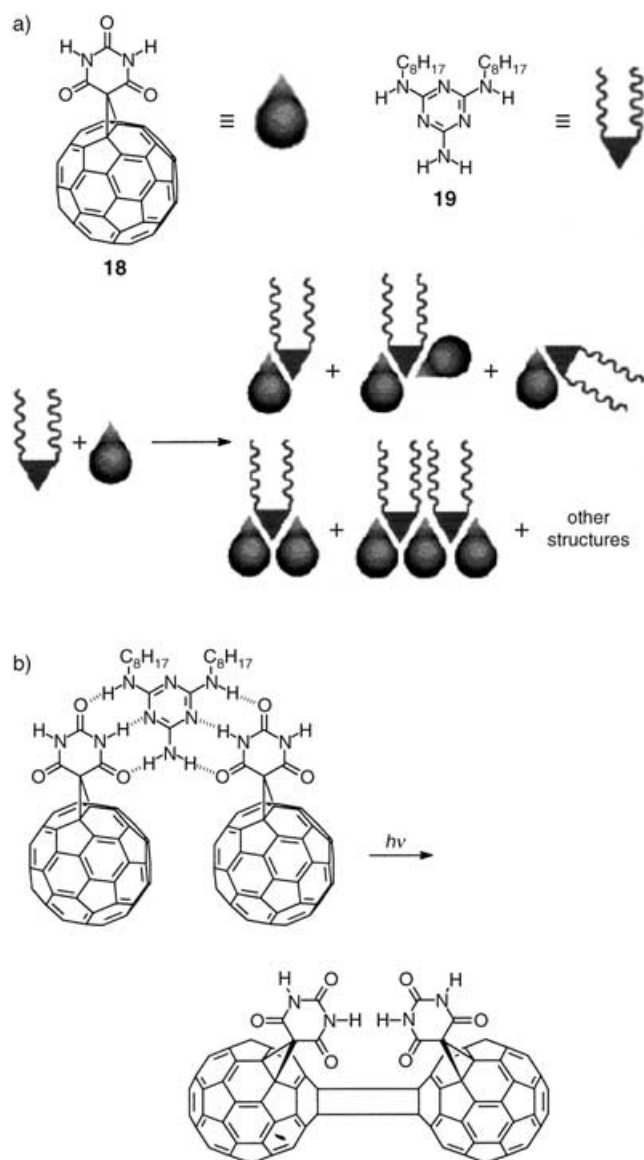
The above cases outline the structural sophistication obtained by combining noncovalent interactions with the covalent chemistry of fullerenes. The integration of hydrogen bonds has led to new supramolecular fullerene architectures that range from dimers to polymers.

3. Hydrogen-Bonding C₆₀-Donor Ensembles

Given the importance of natural photosynthetic processes, the quest for simple models with focus on primary photosynthesis events is one of the most intriguing tasks in chemistry. In this regard, C₆₀ is an excellent candidate for the preparation of photo- and redox-active model systems.

In electron-donor/electron-acceptor ensembles, light excitation typically forces a thermodynamically driven charge-separation (CS) process.^[17] In the case of C₆₀, the lifetimes of such charge-separated radical-ion pairs lie between picoseconds and seconds. In the past, most of these donor-acceptor ensembles were covalently linked^[18] and much less attention was given to hydrogen-bonded model systems.^[19] Only recently did the first examples appear in which C₆₀ is linked to an electron-donor unit through a hydrogen-bonding network. Pseudorotaxane-like molecular recognition motifs that lead to fullerene-(zinc phthalocyanine) (C₆₀-ZnPc) ensembles **20** were reported by Guldi, Torres, Prato, and co-

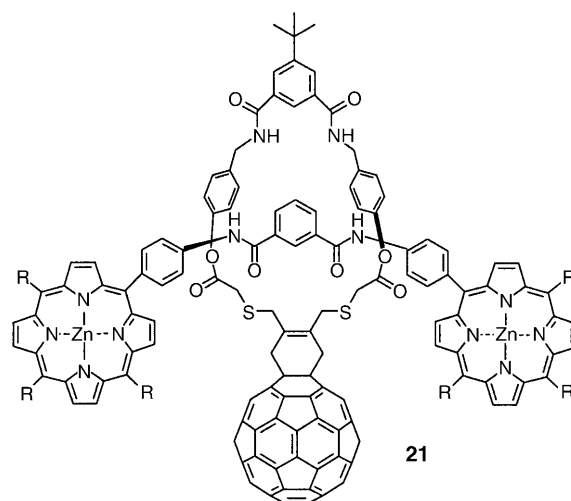




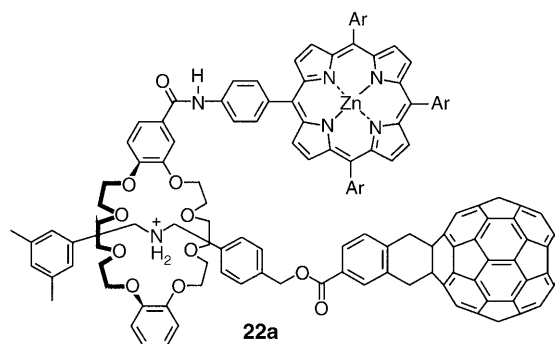
Scheme 6. a) Various supramolecular species formed by hydrogen bonding between C₆₀-barbituric acid **18** and melamine **19**. b) Intermolecular photodimerization process of (18)₂·19, in which a noncovalently bonded species is transformed into one that is covalently bonded. Reprinted with permission from ref. [16]. Copyright (2003) American Chemical Society.

workers.^[20] Charge-separated states (i.e. C₆₀^{•-}·ZnPc^{•+}) with lifetimes of microseconds evolved from an efficient intracomplex electron-transfer process that started from the excited state of the ZnPc fragment. For the sake of comparison, a similar but covalently linked C₆₀-ZnPc dyad that exhibits lifetimes for the radical-ion pair of only 3 ns has been reported.^[21]

Although numerous examples of porphyrin (P)-linked donor-acceptor systems are known,^[22] including several that comprise C₆₀ as an acceptor, no hydrogen-bonded fullerene-porphyrin (C₆₀-P) model systems were reported until recently. One such example was the rotaxane C₆₀-ZnPc dyad **21** prepared by Takata, Ito, and co-workers.^[23] Whereas **21** displays a lifetime of 180 ns for its radical-ion pair, covalently

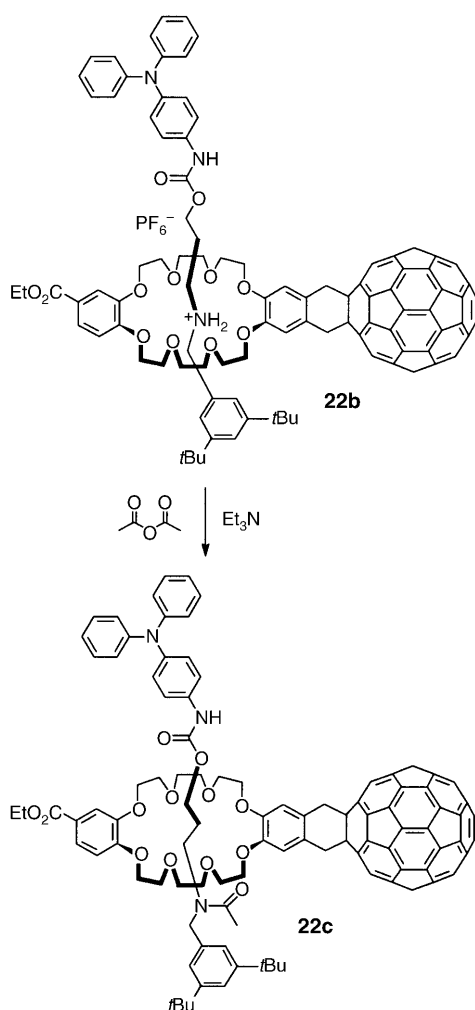


linked C₆₀-P dyads exhibit a longer lifetime of 770 ns.^[24] Takata and co-workers have also synthesized new rotaxanes **22**, in which the [60]fullerene moiety makes up either the axle (**22a**)^[25a] or the wheel (**22b,c**, Scheme 7)^[25b] of the supra-



molecular structure. An attractive interaction between the two chromophores in **22a**, that is, C₆₀ and ZnP, has been established. The consequence of this favorable interaction is noted through the acceleration of the end-capping process, which thus enhances its overall efficiency. Ensembles **22b,c**, which bear triphenylamine (TPA) electron-donor units, showed that noncovalent interactions can be modulated through the positive charge that is placed at the nitrogen atom in the middle of the axle (**22b**, Scheme 7). Acylation of the positively charged amine in **22b** to furnish the neutral amide group in **22c** evoked a shift of the axle with respect to the C₆₀ wheel. In **22b,c** a through-space, intrarotaxane, photoinduced electron-transfer process gives rise to a long-lived CS state, C₆₀^{•-}·TPA^{•+}, whose lifetimes range between 170 and 300 ns. Interestingly, the lifetimes of C₆₀^{•-}·TPA^{•+} in the rotaxanes appear to be longer than those measured for the corresponding covalently bound C₆₀-TPA dyad.^[25b]

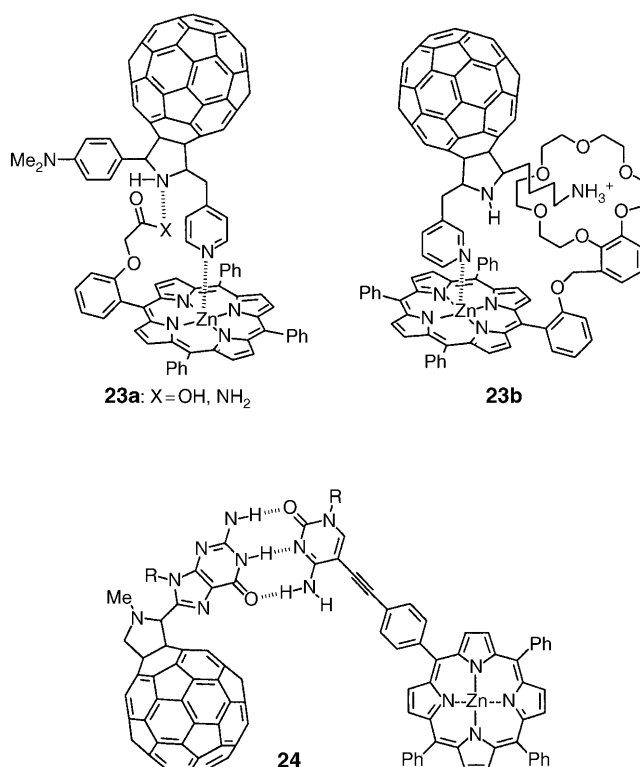
Highly stable supramolecular C₆₀···ZnP complexes **23**, held together through a two-point binding strategy, are well-defined with regards to distance and orientation.^[26] Time-resolved emission and absorption studies have revealed efficient charge-separation processes, with rate constants of



Scheme 7. C₆₀-TPA ensembles tethered by rotaxane structures.

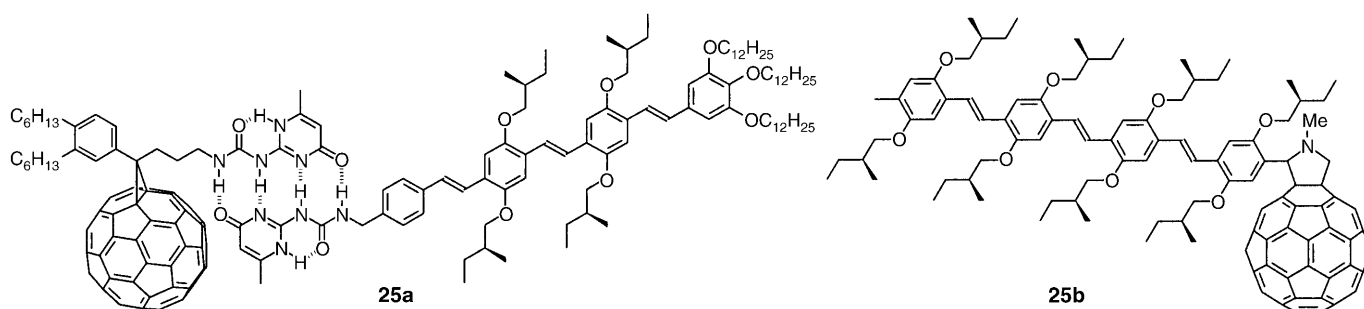
6.3×10^7 and $3.1 \times 10^9 \text{ s}^{-1}$ observed for the formation of the CS states in **23a** and **23b**, respectively.

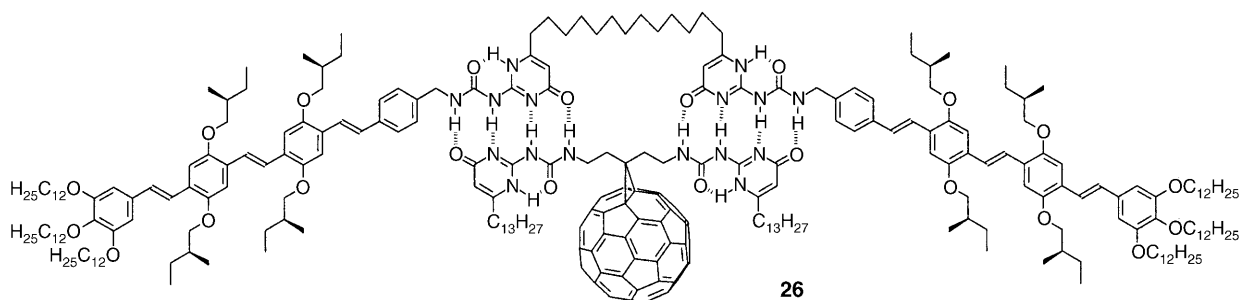
Another remarkable impact on the lifetime of the photo-generated radical-ion pair is seen when C₆₀ is paired with a porphyrin moiety in the form of **24**. The lifetime of the radical-ion pair in **24**, in which C₆₀ and ZnP are tethered by means of a guanosine–cytidine scaffold^[27] is 2.02 μs . This value is higher than those reported for related covalently linked C₆₀-ZnP dyads^[22–24] as a result of the beneficial effect of the hydrogen bonds.



To control the organization in active layers of photo-voltaic cells, **25a** is prepared by mixing **9** (Scheme 2) with an oligophenylene vinylene (OPV) system that bears complementary UP moieties.^[28] In both **25a** and the “covalent” analogue **25b**,^[29] a strong quenching of the OPV fluorescence is observed. Energy transfer from the singlet excited state of OPV to the fullerene is responsible for the quenching. In the covalently bound **25b**^[29] an ultrafast electron-transfer process is followed by an intramolecular energy-transfer process, whereas this sequence does not occur in hydrogen-bonded **25a** as a consequence of the low electronic coupling between the electroactive units in **25a**.^[30]

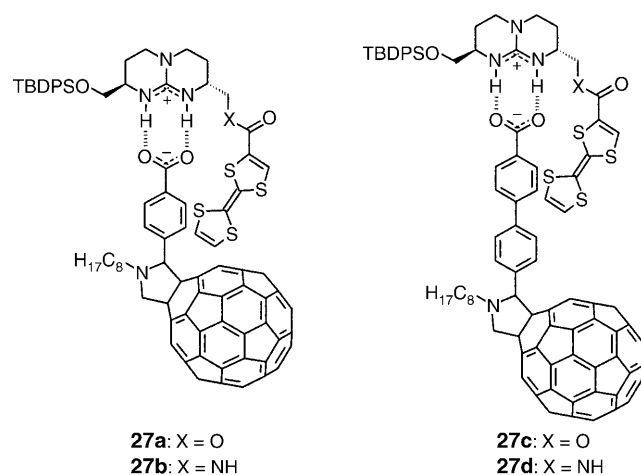
The combination of polymer **15** (Scheme 4) with OPVs functionalized with UP groups allowed the formation of heterodimers linked through quadruple hydrogen bonds. This strategy resulted in new supramolecular donor–acceptor dyads.^[31] Remarkably, in contrast to previous examples in which the self-complementary nature of such hydrogen-bonding motifs led to a statistical mixture of homo- and heterodimers, dyad **26** represents the first example of





preferential formation of functional supramolecular heterodimers linked by UP moieties.

Recently, in collaboration with Mendoza's group we reported a series of hydrogen-bonded C_{60} -TTF ensembles, **27a–d** (TTF = tetrathiafulvalene, TBDPS = *tert*-butyldiphenylsilyl),^[32] in which the tetrathiafulvalenes act as electron



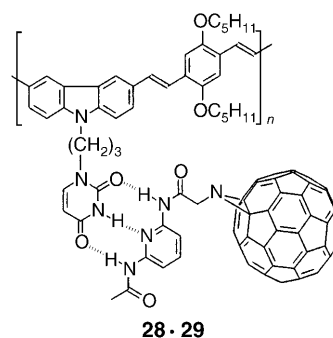
donors.^[33] In these cases, the photoactive units are held together not only through complementary hydrogen bonds but also by strong electrostatic interactions through guanidinium and carboxylate ion pairs. To tune the molecular architecture, two chemical spacers of different lengths (phenyl versus biphenyl) as well as two functional groups (ester and amide) were used. The solvent-dependent nature of the fluorescence quenching in C_{60} -TTF dyads as well as the formation of the $C_{60}^{\cdot-}$ -TTF⁺ radical-ion pairs, together with the flexible nature of the spacer, reflect through-space electron-transfer processes. The lifetimes measured for the radical-ion pair states are in the range of hundred of nanoseconds, thus several orders of magnitude higher than those reported for covalently linked C_{60} -TTF dyads.^[34]

4. Applications of Hydrogen-Bonded Supramolecular Fullerene Complexes

π -Conjugated oligomers/polymers as well as C_{60} are widely used as building blocks for optoelectronic devices such as light-emitting diodes (LEDs)^[35] and organic solar

cells.^[36] In 2001, Meijer and co-workers reported hydrogen-bonded polymers that comprised oligo(*p*-phenylenevinylene) (PPV) moieties connected through multiple self-complementary fourfold hydrogen-bonding motifs.^[37] A photovoltaic device was prepared by mixing this supramolecular polymer with a methanofullerene derivative, and the ensemble was successfully used in the preparation of bulk heterojunction organic solar cells.^[36]

Li, Zhu, and co-workers presented a three-point hydrogen-bonding assembly between C_{60} and a π -conjugated PPV polymer (**28·29**).^[38] In this particular case the noncovalent



linkage was established between the uracil moiety, bound to polymer **28**, and 2,6-diacylamidopyridine **29**, linked to C_{60} . Fluorescence experiments revealed a strong interaction between PPV and C_{60} .

Perylene bisimides (PERYs) are another important class of materials for solar cells. The main features of PERYs include good electron-acceptor capabilities and good light absorption in the visible region. Both features are essential to guarantee good conversion efficiencies.^[39] Diaminopyridine- C_{60} **29** has been used together with the tetraalkoxy-PERY system **30** (Figure 2a).^[40] Irradiation of (**29**)₂-**30** films on indium tin oxide (ITO) electrodes with white light (63.2 mW cm⁻²) generates a steady, rapid, and highly stable anodic photocurrent response. Importantly, the response to on/off cycling is prompt and reproducible (Figure 2b).

5. Summary and Outlook

In summary, the synthesis and applications of multiply hydrogen-bonded C_{60} derivatives have been reviewed here.

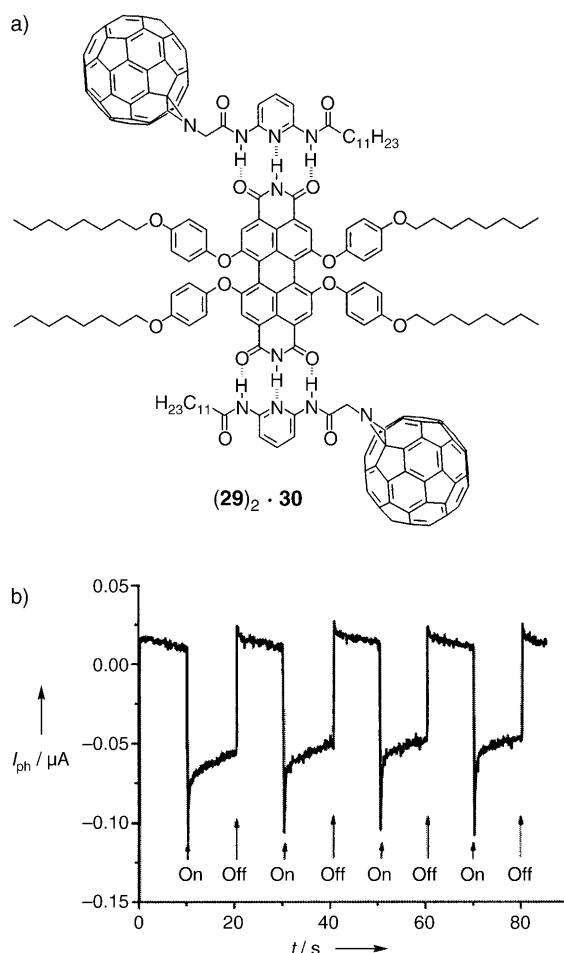


Figure 2. a) Structure of the three-point hydrogen-bonded C₆₀-PERY assembly **(29)₂·30**, and b) time-dependence of the photocurrent (I_{ph}) response of the self-assembled film. Reprinted with permission from ref. [40]. Copyright (2004) American Chemical Society.

Implementing the chemistry of fullerene into supramolecular chemistry has led to original examples of molecular organization that might find application in promising fields such as molecular materials or supramolecular catalysis. Supramolecular chemistry of fullerenes is a thriving field that should furnish future avenues for the integration of C₆₀ as an outstanding photo- and electroactive building block in nanoscience and nanotechnology.

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