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Supramolecular Complexation of Carbon Nanostructures by Crown Ethers

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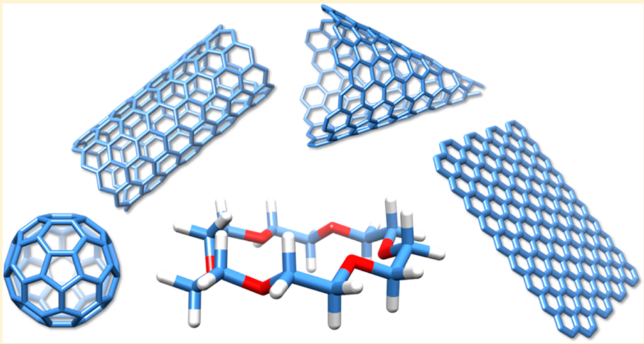
ABSTRACT: Since their discovery, crown ethers as well as the most recent carbon nanostructures, namely fullerenes, carbon nanotubes, and graphene, have received a lot of attention from the chemical community. Merging these singular chemical structures by noncovalent forces has provided a large number of unprecedented supramolecular assemblies with new geometric and electronic properties whose more representative examples are presented in this Synopsis organized according to the different nature of the carbon nanostructures.



INTRODUCTION

The history of modern supramolecular chemistry and its application in synthetic systems can be traced back to the discovery of crown ethers by Pedersen in 1967.[1] Soon afterward, the extraordinary ability of these cyclic compounds to complex different molecules led to other macrocyclic receptors, namely cryptands (Lehn)[2] and spherands (Cram).[3] These seminal discoveries led their designers to win the Nobel Prize in Chemistry "for the development and use of molecules with structure-specific interactions of high selectivity" in 1987, thus starting the so-called "host−guest" chemistry. The relatively easy synthesis and the possibility of modulating their affinity by tuning their substituents, number and type of donor atoms, cavity size, and degree of preorganization have made them one of the most versatile assets in the supramolecular chemist's toolbox.[4]

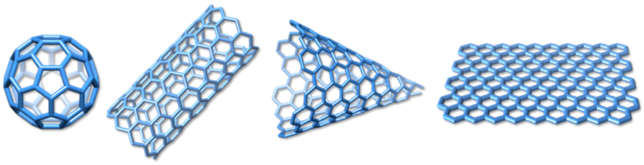


Figure 1. Main carbon nanostructures considered for supramolecular complexation [from left to right: [60]fullerene, single-wall carbon nanotube (SWCNT), single-wall carbon nanohorn (SWCNH) and graphene].

On the other hand, carbon nanostructures represent a less explored field starting with the discovery of fullerenes by Kroto, Smalley, and Curl in 1985,[5] who received the Nobel Prize in Chemistry in 1996. Soon afterward, the finding of multiwall single nanotubes (MWCNTs) by Iijima in 1991[6] and the single wall carbon nanotubes (SWCNTs) independently by Iijima and Bethune in 1993[7,8] became important milestones. More recently, the aforementioned findings have been complemented with the discovery of graphene by Geim and Novoselov in 2004,[9] which was awarded with the Nobel Prize in Physics in 2010.

Although many different forms of carbon are known,[10] we will mainly focus our attention on fullerene and its endohedral derivatives, carbon nanotubes, carbon nanohorns, and graphene (Figure 1).

Given the extraordinary properties of the aforementioned nanostructures, it is not surprising that chemists have combined them together in the search for unprecedented systems. In this Synopsis, we will pinpoint the most relevant examples of their supramolecular complexation by crown ethers.

FULLERENES

Fullerenes are one of the most widely used electron-acceptor molecules given their outstanding electronic properties, namely small reorganization energy,[11] low reduction potential,[12]

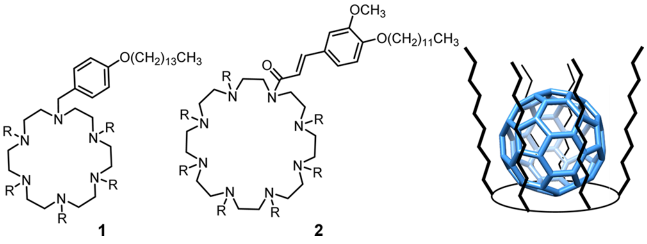


Figure 2. Azacrown ethers used to bind fullerenes and scheme of the supramolecular "basket" envisioned for the 1:1 complex.

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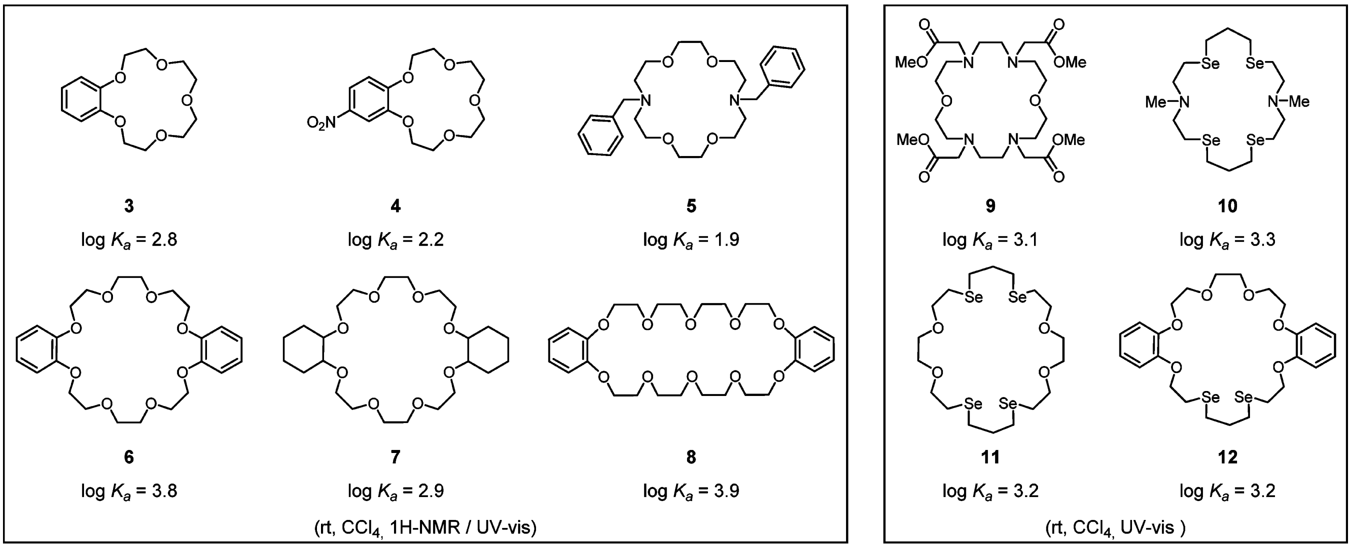
Table 1. Stability Constants for a Series of 1:1 [60]Fullerene·Crown Ether Complexes[a]



[a] Left: crown ethers developed by Mukherjee and co-workers.[17−20] Right: selenacrown ether developed by Liu et al.[21]

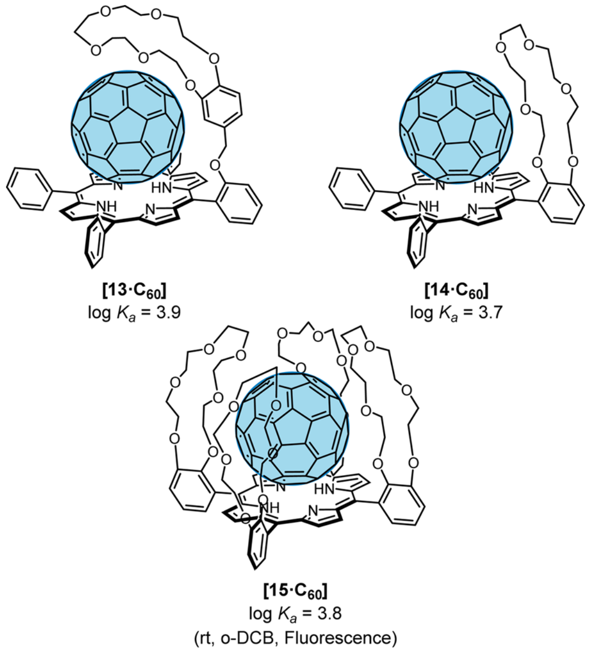
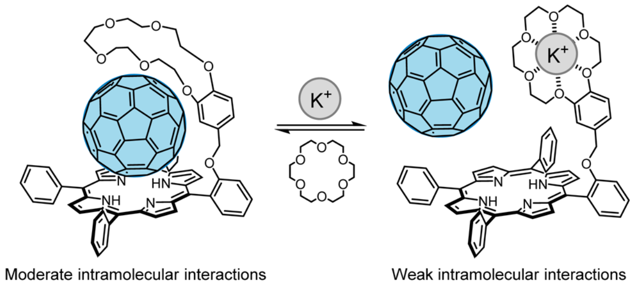


Figure 3. Crown ether appended free-base porphyrin−fullerene donor−acceptor complexes.

Scheme 1. K^+-Induced Switching of Intra- to Intermolecular Association (Forward Reaction) and [18]Crown-6-Induced Reversible Switching (Backward Reaction)



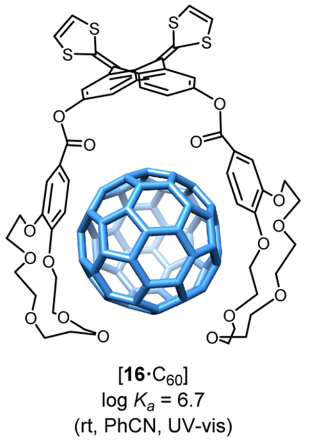


Figure 4. Combination of crown ethers and exTTF as recognition motifs led to robust complexation of C_{60}.

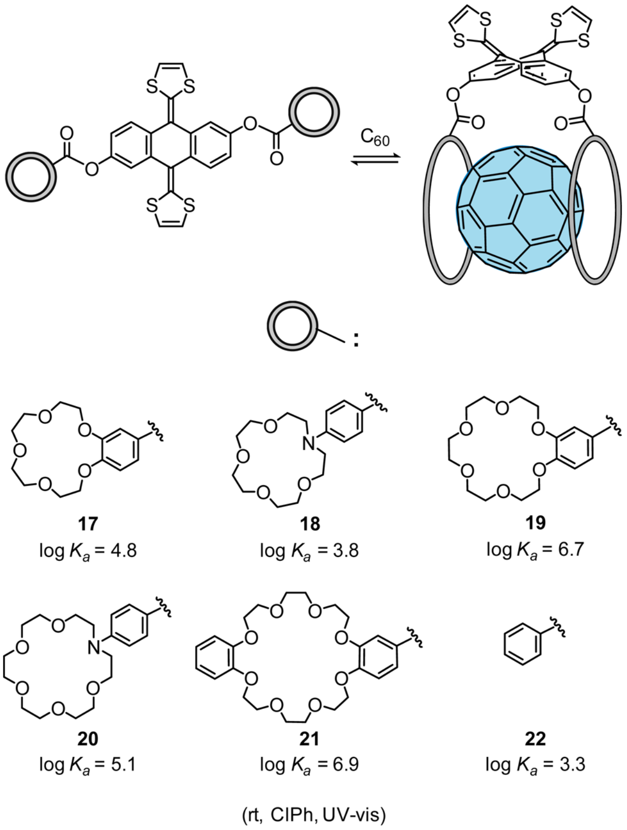
appreciable absorption cross section throughout the solar spectrum,[13] and efficient generation of long-lived charge-separated states.[14,15] Furthermore, their spherical geometry and remarkable hydrophobicity make them appealing systems for 3D supramolecular interactions.

Pristine fullerenes were complexed for the first time with azacrown ethers **1** and **2** bearing long lipophilic chains on the nitrogens (Figure 2). The ability of these systems to act as supramolecular "baskets" was suggested by Effing et al. in view of the additional stability of the crown ether's Langmuir−Blodgett films upon addition of fullerenes.[16]

Following this pioneering work, Mukherjee and co-workers synthesized a series of crown ethers **3−8** to evaluate their affinity toward fullerenes, finding that larger cavities and preorganized systems led to larger binding constants (K_a) and that complexation occurred with the involvement of an electron-transfer process (Table 1, left).[17−20] Liu et al. also observed this size-dependence relationship in a series of selenacrown ethers **9−12** and a better stabilization upon introduction of the heteroatoms (Table 1, right).[21]

D'Souza et al. further exploited this affinity with molecular receptors **13−15** (Figure 3). Addition of porphyrins as a

Scheme 2. Series of exTTF-(crown ether)$_2$ Molecular Tweezers Designed To Host C_{60}



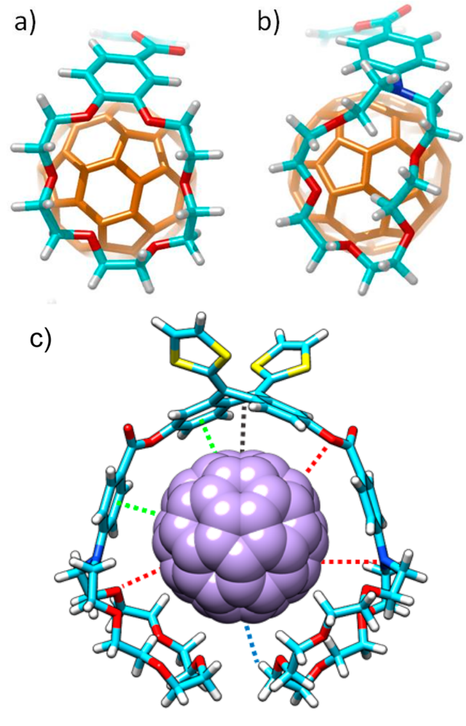
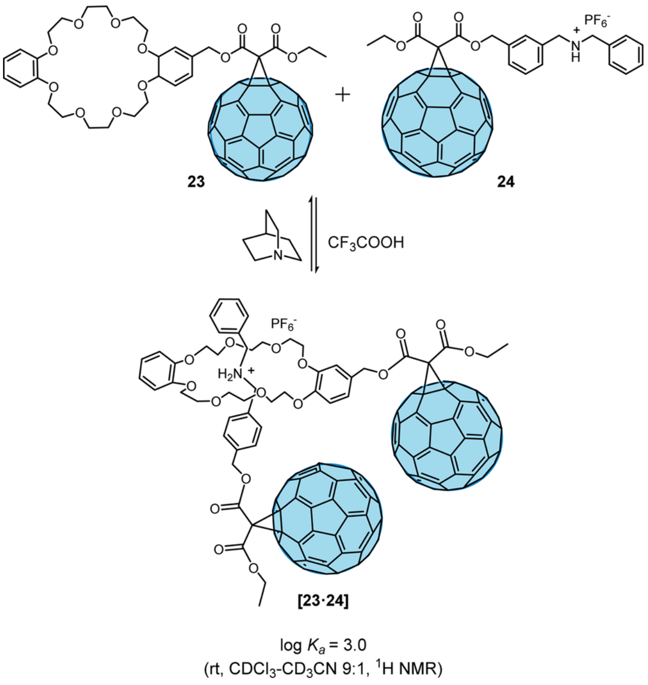


Figure 5. Side view of the optimized geometries calculated for complexes [**19·C$_{60}$**] (a) and [**20·C$_{60}$**] (b). The affinity of our receptors arises as an interplay of donor−acceptor (black), π−π (green), n−π (red), and CH···π (blue) interactions (c).

Scheme 3. pH-Dependent Reversible Threading of the First Supramolecular Fullerene Dyad



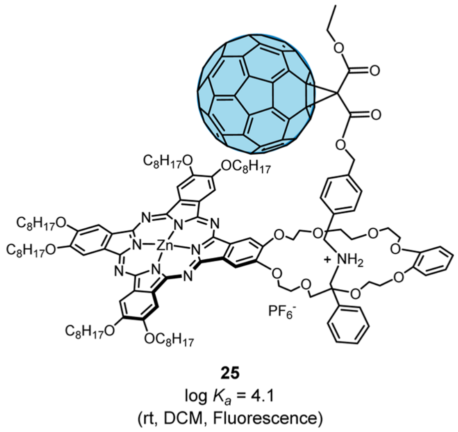


Figure 6. Molecular structures of the first [2]pseudorotaxane Pc/C$_{60}$ dyad.

supplementary recognition motif provided new π−π and charge-transfer interactions, leading to higher affinities. Proximity effects of the crown ethers at different positions of the host molecule and the possibility of having cooperative effects between them explained the trend **14** < **15** < **13**.

Notably, stability of [**13**·C$_{60}$] could be tuned upon addition of a potassium salt. An excess of it led to a decrease of the nucleophility and to an increase on the rigidity of the crown ether moiety, thus weakening the complex. Subsequent addition of [18]crown-6 captured the cation, reversing the equilibrium and recovering the original complex (Scheme 1).[22]

More recently, our group designed molecular tweezer **16**, appended with two benzo[18]crown-6 ethers in an electron donor 9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (exTTF) scaffold offering both geometric (concave-convex) and electronic (donor−acceptor) complementarity (Figure 4). The unique combination of these recognition elements led to

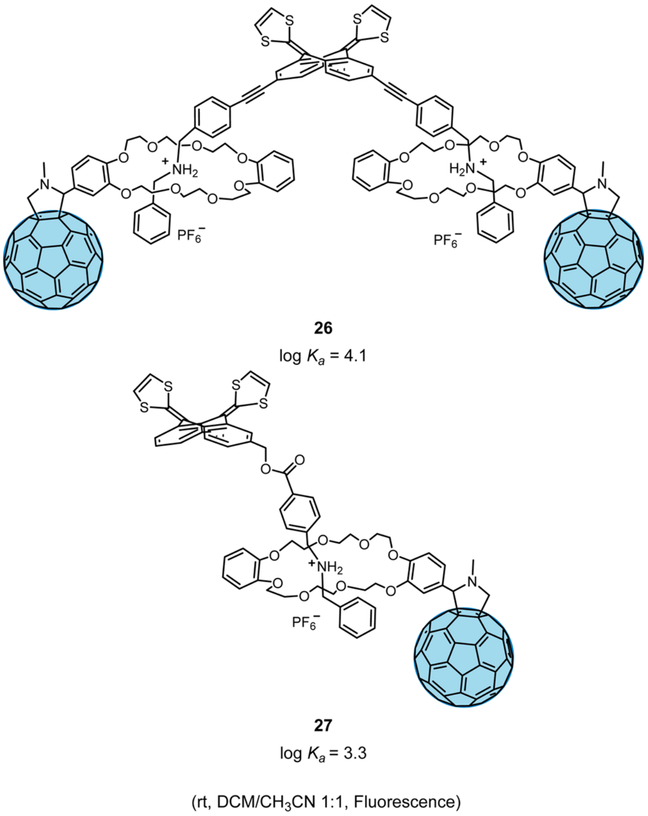
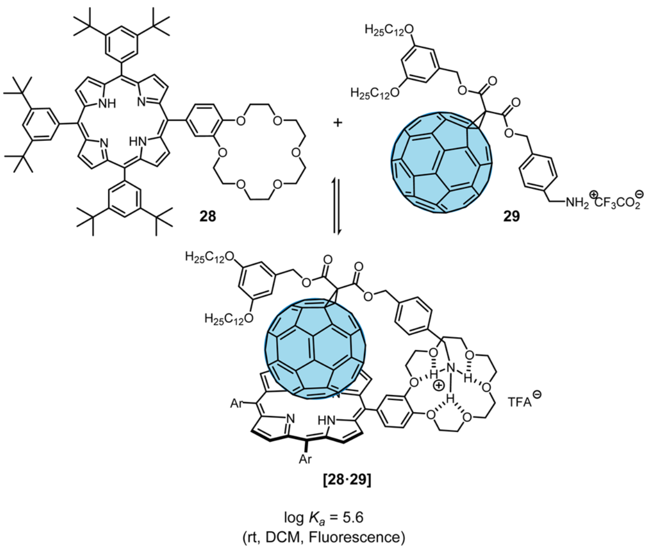


Figure 7. Stability constants of different DB[24]C8 fullerocrown ethers with exTTF-derived ammonium salts.

Scheme 4. Cooperativity between π-Stacking and Ammonium-Crown Ether Interactions Increased K_a by 2 Orders of Magnitude



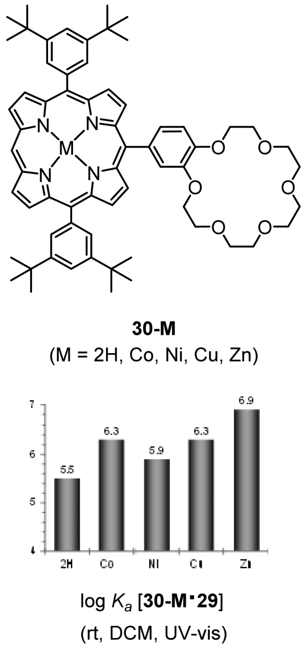


Figure 8. Host molecule **30-M** and its binding constants upon complexation with **29**.

an extraordinarily high affinity toward fullerenes in spite of the low degree of preorganization of the system.[23]

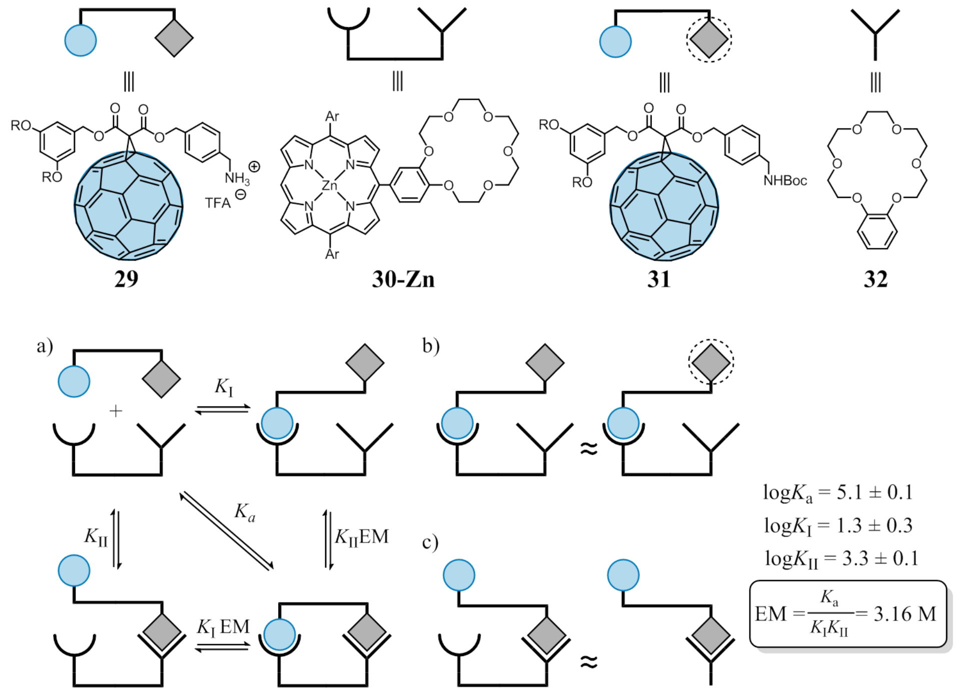
This result spurred our interest in unveiling the nature of supramolecular crown ether–C$_{60}$ affinity. As a result, we performed a detailed evaluation of the supramolecular interactions in receptors **17**–**22** (Scheme 2). The stability of the resulting complexes varied more than 3 orders of magnitude between **21**, the receptor with the larger crown ethers, and **22**, lacking them. Noteworthy, aza-crown ether derivatives **18** and **20** exhibited significantly smaller affinities than their oxygen-bearing analogues **17** and **19** due to the less complementary structure conferred by the additional flexibility of nitrogen atoms (Figure 5, a–b). Additional electrochemical measurements, transient absorption spectroscopy, and theoretical calculations were carried out, underpinning the experimental findings and prompting to a synergetic interplay of donor–acceptor, π–π, n–π, and CH···π interactions as the basis for the affinity of our receptors toward C$_{60}$ (Figure 5, c).[24]

Fullerene Derivatives. Whereas complexation of pristine fullerenes allows us to maintain their electronic conjugation and, thus, all of their singular properties, it has often been chemically modified in order to increase the number of possible recognition motifs as well as the complementarity and preorganization of the host molecule and, therefore, the stability of the supramolecular complexes obtained.[25,26] This becomes critical when working with crown ethers, which are typically highly flexible and need to reorganize themselves at the expense of an entropic cost. To overcome this, chemists have introduced additional recognition motifs to the fullerenes, typically ammonium ions, given their high degree of directionality, selectivity, and large binding constants with crown ethers.[27]

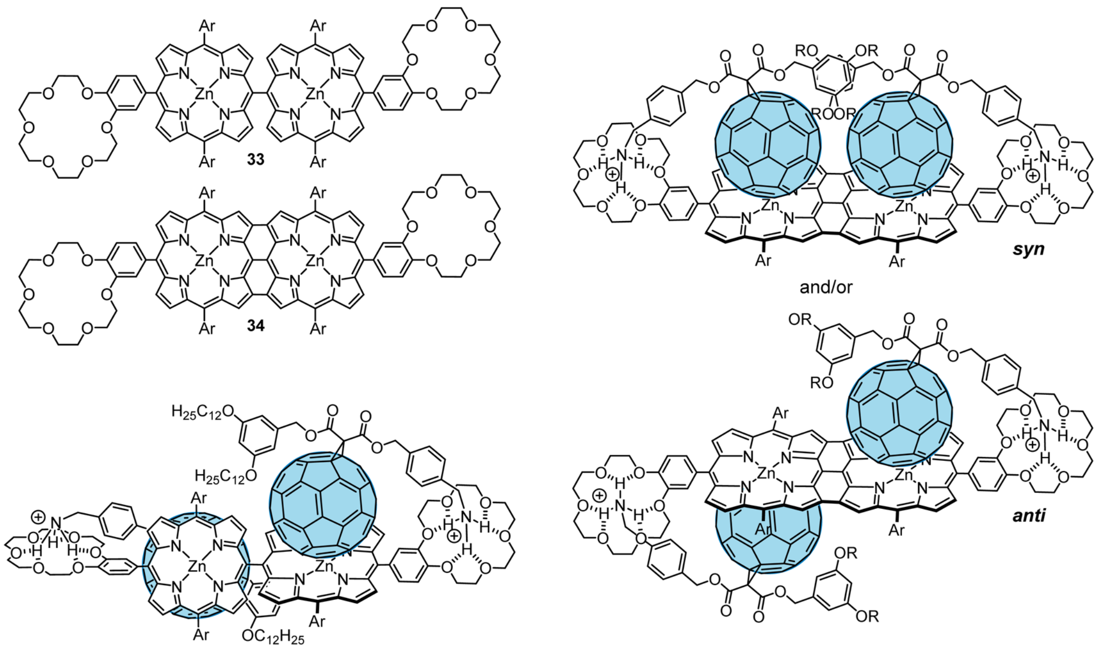
This approach was first used in 1999 by Diederich et al. to combine fullerene derivatives **23**, embedded with a dibenzo-24-crown-8, and fullerene malonate **24**, bearing a dibenzylammonium salt (Scheme 3). Threading of the resulting pseudorotaxane was pH dependent and reversible as supported by fluorescence measurements.[28]

Soon, this strategy expanded into a series of molecularly interlocked donor–acceptor complexes with well-defined structures. The first one, developed in 2002 by Torres and co-workers, consisted on phthalocyanine–fullerene dyad **25**, which exhibited a moderated binding constant in solution (Figure 6). However, the distance between the donor and the acceptor moieties was too large to observe any electronic

Scheme 5. (a) EM (Effective Molarity) of the System Obtained by Evaluating Each Supramolecular Interaction Separately Based on This Scheme. (b) Porphyrin−Fullerene Interaction Assessed by ^{1}H NMR Titration of 30-Zn with the Amino-Protected Methanofullerene 31 in $CDCl_3$ at rt Yielding K_I. (c) Stability of the Ammonium−crown-Ether Association, K_{II}, Evaluated by ^{1}H NMR Titration of 29 with Reference Crown Ether 32[a]



[a] The overall binding constant, K_a, was obtained by UV−vis titration of **30-Zn** with **29** in $CHCl_3$ at rt.



[33•29$_2$]

log K_1 = 8.7
log K_2 = 5.4
α = 0.0005

[34•29$_2$]

log K_1 = 6.8
log K_2 = 5.4
α = 0.04

(rt, DCM, UV-vis)

Figure 9. Supramolecular complexes obtained from host molecules **33** and **34** with guest fullerene **29**.

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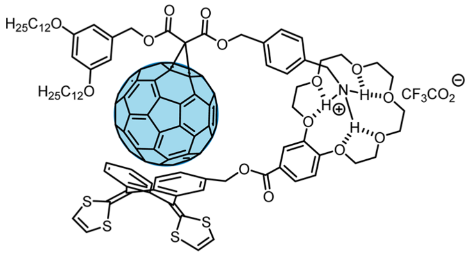
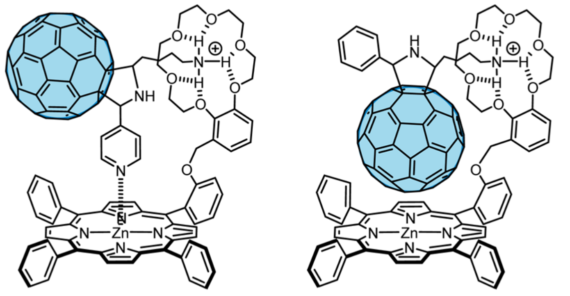


[35·29]
log K_a = 6.3
(rt, $CHCl_3$, UV-vis)

Figure 10. exTTF also offered $\pi-\pi$ interactions as an additional recognition motif while providing better geometrical complementarity.



36
log K_a = 4.6

37
log K_a = 4.2

(rt, PhCN, Fluorescences)

Figure 11. Structure of complex **36**, relying on axial coordination and of complex **37**, relying on π-stacking.

interaction on the ground state.[29] Nevertheless, photochemical investigation showed an effective intracomplex electron-transfer mechanism on the excited state.[30]

Similar structures were obtained by combining fullerene derivatives with other electroactive moieties such as triphenylamine,[31] porphyrin,[32,33] perylene,[34] or terpyridine.[35] In our laboratory, we have also developed some analogous interlocked systems by combining a dibenzo[24]crown-8-fullerene with a series of exTTF-based secondary ammonium salts to obtain complex **26** or the more flexible **27** (Figure 7). UV−vis and CV measurements also revealed negligible electronic communications in the ground state, suggesting that both moieties are not close enough. However, fluorescence analysis suggested an electron transfer from the donor to the acceptor moiety in the excited state.[36]

Given the limitations for obtaining electronic interactions in the ground state with the pseudorotaxane approach, chemists soon explored new designs with primary ammonium salts offering stronger interactions. Following this approach, Nierengarten and co-workers developed a *cup-and-ball* complex conjugating *meso*-crown porphyrin **28** and fullerene malonate **29**. Even though both porphyrin−fullerene and ammonium−crown ether interactions are weak by themselves,[37] their cooperative interplay in [**28·29**] led to a dramatic increase of the overall stability (Scheme 4).[38]

In light of this extraordinary result, the cooperative interplay between the different noncovalent interactions was comprehensively analyzed. For this, **29** was complexed with a series of new metalloporphyrin−crown ether receptors, **30-M**, generating very stable complexes (Figure 8). Using a methanofullerene was crucial in order to circumvent the low solubility of pristine fullerenes and, therefore, the strong entropic influence of desolvation in the overall complexation stability. Spectroscopic, electrochemical, and computational analyses demonstrated the presence of electronic interactions in the ground state, which suggested that the origin of $\pi-\pi$ interactions stems from dispersion forces in free base porphyrins and from a combination of electrostatic and dispersion interactions in metalloporphyrins. The larger than expected stability of **30-Co** was explained on the basis of the strong interaction between fullerenes and group 9 metals. Finally, the high value obtained for the effective molarity (EM) of the system, a parameter accounting for the easier formation of an intramolecular reaction over its intermolecular analogous, proved the nice complementarity of the receptor motifs in the [**30-Zn·29**] (Scheme 5).[39]

The stability of these complexes led us to fuse **30-Zn** into porphyrin dimer **33**, exhibiting two almost orthogonal porphyrin moieties, and into porphyrin tape **34**, where they are fully conjugated (Figure 9). The tendency toward ring closing of **30-Zn** enabled us to simplify the myriad of internal micro equilibria leading to semicomplexed species into a two-step process characterized by K_1 and K_2. Analysis of factor α evidenced a negative cooperativity in the complexation process; i.e., binding of the first molecule of **29** led to a complex where it was more difficult to bind a second equivalent. This fact was justified by the decrease of the donating ability of the second porphyrin moiety once the first fullerene unit has been added, a phenomenon also observed in other porphyrin dyads.[40] Remarkably, the α value of [$\mathbf{34{\cdot}29_2}$] was much higher than for [$\mathbf{33{\cdot}29_2}$], suggesting that this negative effect was partially compensated by the stabilizing $C_{60}-C_{60}$ interactions taking place in the more stable *syn*-disposition of [$\mathbf{34{\cdot}29_2}$].[39]

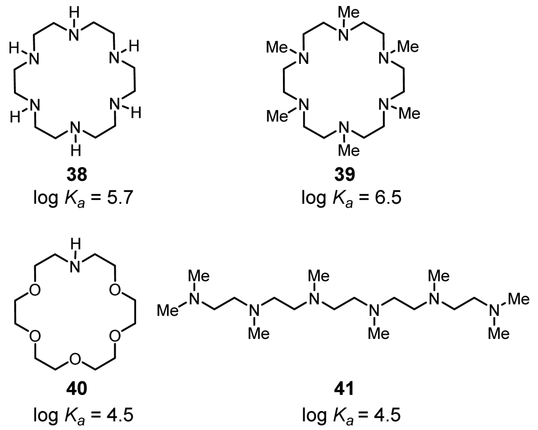
This cup-and-ball strategy has also been reproduced in other supramolecular complexes.[41,42] Among them, we developed system **35** where the planar porphyrin moiety was replaced by the concave surface of an exTTF molecule (Figure 10). The resulting binding constant was even larger than the one found with free base porphyrin **28**, thus highlighting the role of the concave-convex complementarity.[43]

Alternatively, D'Souza and co-workers developed the so-called "two-point" binding strategy, where axial coordination to the metal atom with a pyridine moiety substituted the $\pi-\pi$ stacking between the porphyrin and the fullerene derivatives. This approach enabled obtaining better control over the distances and orientations of the building blocks.[44] In addition, the stronger axial coordination interaction contributed more toward the overall stability of the resulting complexes as seen when comparing **36** to **37**. This approach, however, hinders the direct contact between the porphyrin and the [60]fullerene (Figure 11).[45] Interestingly, it was possible to switch between intra- to intermolecular electron transfer in **37** by addition or extraction of K^+ in a similar way than that observed for [$\mathbf{13{\cdot}C_{60}}$] (Scheme 1).[46]

More complex supramolecular ensembles constituted by various fullerene derivatives or cofacial organization of porphyrins or phtalocyanines have also been prepared.[47−49]

■ ENDOHEDRAL METALLOFULLERENES

In spite of their structural resemblance, endohedral metallofullerenes are intrinsically different from their empty analogues, presenting unique properties such as metal-to-cage electron transfer, larger absorptive coefficients in the visible region of the electromagnetic spectrum, and a low HOMO−



38 log K_a = 5.7

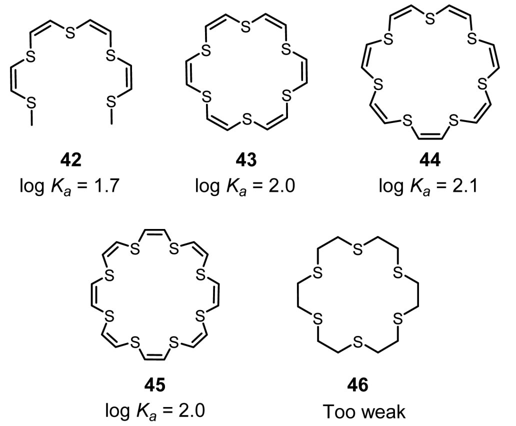
39 log K_a = 6.5

40 log K_a = 4.5

41 log K_a = 4.5

(rt, $PhNO_2$, vis-NIR)

Figure 12. Receptors designed for the complexation of $La@C_{82}$.



42 log K_a = 1.7

43 log K_a = 2.0

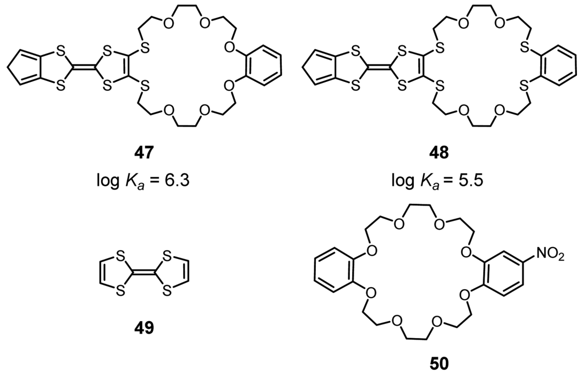
44 log K_a = 2.1

45 log K_a = 2.0

46 Too weak

(rt, $PhNO_2$, vis-NIR)

Figure 13. Receptors designed for the formation of 1:1 complexes with $La@C_{82}$.



47 log K_a = 6.3

48 log K_a = 5.5

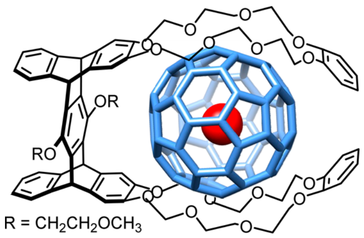
49

50

Figure 14. MPTTF derivatives designed as receptors for $Li^+@C_{60}$ and reference compounds TTF and 4′-nitrobenzene[24]crown-8 ether.

LUMO energy gap.[10,50] Unfortunately, their scarce availability has largely hindered their use up to date.

In this context, the affinity of $La@C_{82}$ toward nitrogen-containing solvents, enabling its preferential extraction from raw soot, led to the study of its 1:1 supramolecular complexes with azacrown ethers **38**−**40** and polyamine **41** (Figure 12). As in previous cases, the affinity increased with the number of heteroatoms, whereas the lower affinity of acyclic polyamine **41** in comparison to **39** pointed to the presence of a macrocycle effect. Further electrochemical studies revealed that crown ethers were acting as donor moieties in electron-transfer processes.[51−55]



R = $CH_2CH_2OCH_3$

[**51**·Li+@C_{60}]
log K_a = 4.1
(rt, PhCN, UV-vis)

Figure 15. Molecular representation of the complex formed between the PCBE host and the $Li^+@C_{60}$ guest.

In order to gain further information on the structure, Akasaka and co-workers developed a new series of sulfur derivatives **42**−**46** including unsaturated crowns **43**−**45**, known to exhibit a rigid structure with the sulfur atoms forced toward the inside of the ring (Figure 13). Vis−NIR spectroscopy and electrochemical studies supported that $La@C_{82}$ formed weak complexes with **43**−**46** via an electron-transfer process where the metallofullerene was reduced to its anion form. Whereas thia-crown ether **44** exhibited the largest binding constant, due to its best complementarity, **46** did not exhibit effective complexation, thus highlighting the importance of the olefinic moiety.[56]

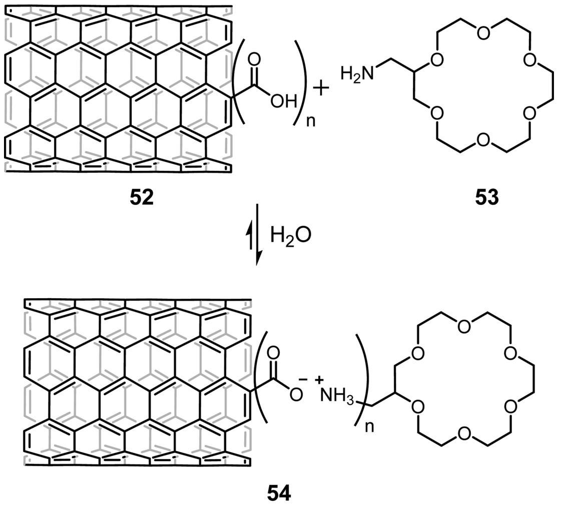
Following these examples, Jeppesen, Fukuzumi, and co-workers obtained strong complexation between $Li^+@C_{60}$ and crown ether functionalized monopyrrolotetrathiafulavelene (MPTTF) derivatives **47** and **48** (Figure 14). Binding constants obtained were much higher than those of their crown size related complexes **11·C$_{60}$** and **12·C$_{60}$**, pinpointing the importance of electrostatic interactions with the endohedral metal. In order to obtain better insights, $Li^+@C_{60}$ was treated separately with TTF and 4′-nitrobenzene[24]crown-8 ether, observing interaction only with the crown ether. In addition, as no charge-transfer band was observed for **47**·$Li^+@C_{60}$, complexation was proposed to occur through the interactions with the crown ethers, something supported by DFT calculations. Theoretical calculations on **48** evidenced that the larger size of the sulfur atoms took further away the fullerene from the crown ether than in **47**, therefore explaining its lower stability.[57]

In sight of these results, a new receptor for $Li^+@C_{60}$ consisting in a rigid pentiptycene-based bis(crown ether) host (PBCE), **51**, was developed (Figure 15). The electron donor character of the scaffold led to a photoinduced electron-transfer process through a rigid distance in the complex. Interestingly, the assisting role of the Li^+ ion inside the cage in the supramolecular recognition is clear when considering that complexation was not observed with C_{60}.[58]

■ CARBON NANOTUBES

In contrast to the rich supramolecular chemistry of fullerenes, carbon nanotubes (CNT) have been considerably less explored due to the difficulty in obtaining homogeneous and well-defined structures. This is a pressing problem considering that the outstanding electronic and mechanical properties of single

Scheme 6. Synthetic Scheme for the SWCNT/Crown Ether Complex 54



walled CNT (SWCNT) require their effective dispersion, solubilization, and separation after overcoming large van der Waals forces between adjacent tubes.[59] Whereas solubilization has mainly been achieved by covalent modification of the SWCNT,[60−63] this approach implies disturbing their π system and electronic properties. As a result, noncovalent methods have emerged as a useful alternative.

In this regard, Wong and co-workers have solubilized oxidized carbon nanotubes, **52**, by conjugating the carboxylic groups present at their ends or oxidized defect sites with 2-aminomethyl-18-crown-6 ether, **53**, achieving high concentrations of complex **54** in different organic solvents. Given the mild reaction conditions and that the adduct does not appear to form in the presence of standard carbodiimide linker reagents, this interaction arises most likely from an $R{-}COO^{-}\,{}^{+}H_3N{-}R$ ionic interaction between the carboxylate anions and the ammonium group and not through a covalent bond (Scheme 6).[64,65]

An alternative strategy to disperse SWCNT consists in forming their respective polyelectrolytes, where nanotubes become negatively charged by reduction and subsequently repelled by Coulombic interactions upon addition of polar aprotic solvents. Following this approach, Martí and co-workers studied the impact of complexing these SWCNT polyelectrolytes with [18]crown-6, finding that trapping the potassium cation shielded their charge from their counterions, preventing their combination and increasing the repulsions between nanotubes (Scheme 7). The resulting solubility of the SWCNT was largely increased, exceeding all previously reported values.[66,67]

Supramolecular interactions have also been used to direct the self-assembly of gold nanowire over CNTs. For this, Sainsbury et al. combined dibenzo[24]crown-8-modified gold nanoparticles, **55**, with dibenzylammonium cation-modified multiwalled carbon nanotube (MWCNT), **56** (Figure 16). As evidenced by several control experiments, the driving force for the formation of the nanowire was the complexation of the MWCNTs with the crown ether moieties to form a surface-confined pseudorotaxane.[68]

Planar pyrene derivatives have also been used as supramolecular anchors providing a versatile platform for obtaining SWCNT hybrids where the main interaction is π-stacking,[69] which not only aids in the exfoliation of the nanotubes but also enables linking different molecules on its surface. This approach was used by D'Souza and co-workers to build SWCNT donor−acceptor hybrids were electron transfer occurred in the excited state from a *meso*-crown porphyrin subunit to the SWCNT in **57**[70] or from the SWCNT to a more acceptor fullerene derivative in **58** (Scheme 8).[71]

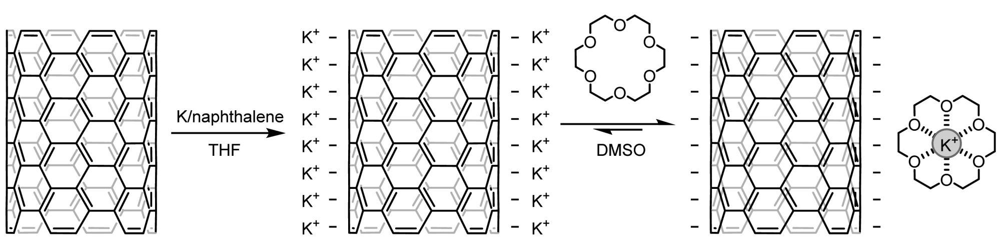
Carbon Nanohorns. Carbon nanohorns (CNHs) are topologically related to carbon nanotubes as they could be considered a capped version of them with a highly constrained end. However, they are easier to obtain pure due to their metal-free synthesis. In spite of this, their supramolecular properties remain largely unexplored. Some remarkable exceptions are the supramolecular dyads developed by Vizuete et al., which demonstrated that CNHs can act as acceptor systems when confronted to strong electron-donating molecules such as porphyrins (**59**)[72] or behave as donor systems when combined with fullerene derivatives (**60**). Transient absorption spectroscopy allowed to determine that, upon excitation, the radical cation of the porphyrin moiety in **59** or the radical anion of the C_{60} moiety in **60** are formed, which implies that the CNHs can both accept an electron from the donor porphyrin or give an electron to the fullerene unit. As in previous cases, the ammonium−crown ether interaction was critical in obtaining stable complexes (Scheme 9).[73]

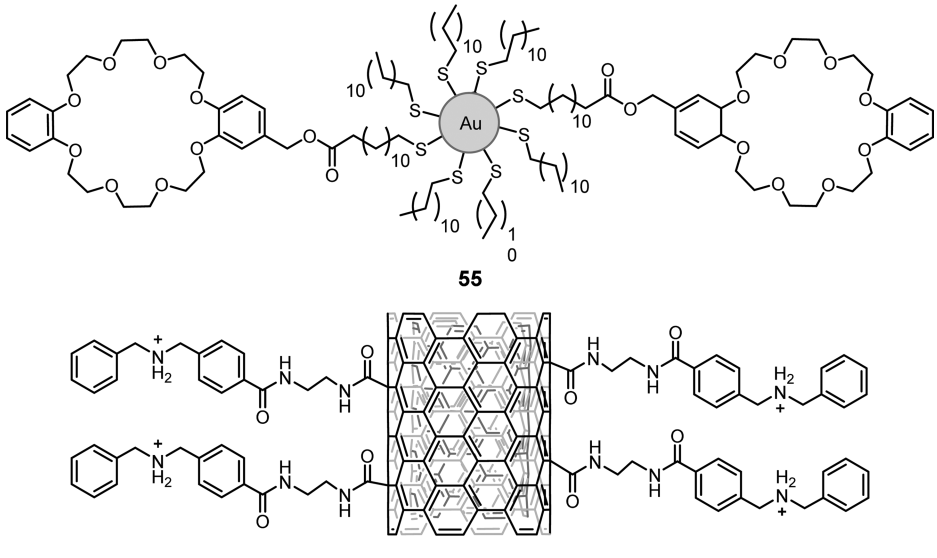
■ GRAPHENE

Surprisingly, whereas all the previous nanostructures can be seen as derivatives from graphene, the supramolecular combination between graphene and crown ethers has not been properly addressed so far. This is striking when considering that many of the previous examples could be taken as benchmarks, that there is already a number of covalent conjugates[74,75] and that crown ethers have even been embedded within the graphene structure.[76]

A notable exception was developed by Wei et al. when [18]crown-6 adsorbed on the surface of graphene was used as a molecular anchor for carbon dots (CDs). Interestingly, fluorescence of the CDs was effectively quenched by addition of a solution containing the crown ether-graphene conjugate

Scheme 7. Scheme of the Crown-Ether-Assisted Dissolution of SWCNT Polyelectrolytes



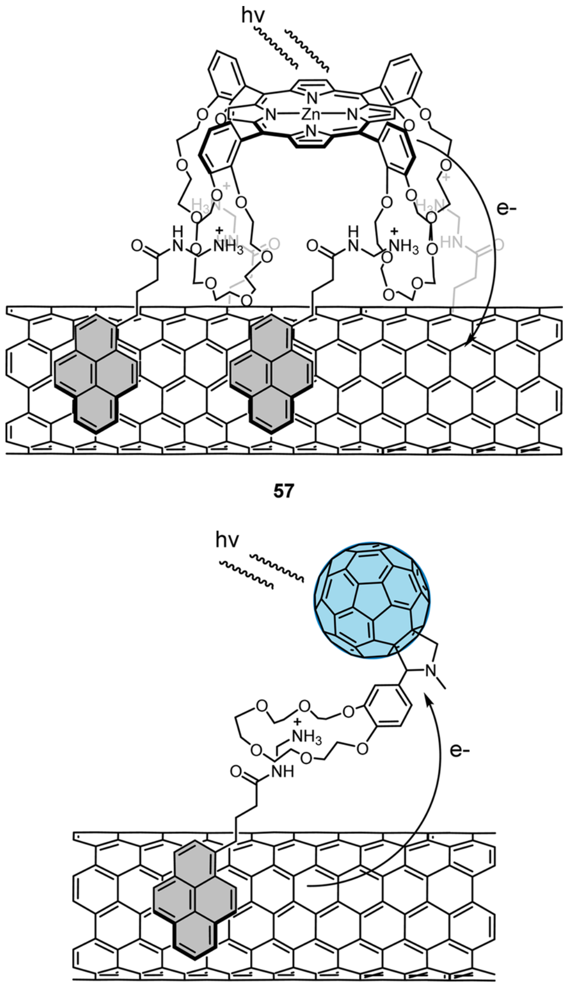


55

56

Figure 16. Building blocks used for the self-assembly of a golden nanowire over CNTs.

Scheme 8. Chemical Structure of SWCNT-Pyr-NH_3^+−Crown−Porphyrin Nanohybrid 57 and of SWCNT-Pyr-NH_3^+−Crown−C_{60} Conjugate 58



57

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through a FRET process. Subsequent addition of a potassium salt would decomplex that supramolecular system due to the stronger affinity of [18]crown-6 toward the potassium salt, thus recovering the fluorescence of the CD. In this manner, this system could be used as an effective all-carbon sensor for potassium determination (Scheme 10).[77]

■ SUMMARY AND OUTLOOK

Along this synopsis, it has been evidenced the extraordinary ability of crown ethers to form supramolecular complexes with different carbon nanostructures and the impact of changing their size and composition in modulating the π−π, n−π, CH−π, dispersion forces, and/or charge-transfer interactions governing this recognition. Furthermore, adding different substituents can significantly modify the efficiency of the complexation process by adding additional recognition motifs which broaden the scope of complexation.

Fullerenes have been, by far, the most widely studied systems for their supramolecular interaction with crown ethers provided their well-defined geometry and electronic properties either in their pristine form or in the wide variety of derivatives prepared along the last three decades.[78−80] Interestingly, these studies have been used as a benchmark for further carbon nanostructures such as CNT and graphene.

Crown ethers have also been used for complexing supramolecularly CNT, and to a lesser extent CNH and graphene, in the search for better solubility and exfoliation properties as well as for their electronic modification by means of photo- and/or electroactive molecules, which represents an easy methodology for n- and p-doping of these materials. As with fullerenes, crown ethers have provided a useful and versatile alternative for the noncovalent chemical modification of these carbon nanostructures, taking advantage of the rich diversity of weak forces stemming from these complementary molecular systems.

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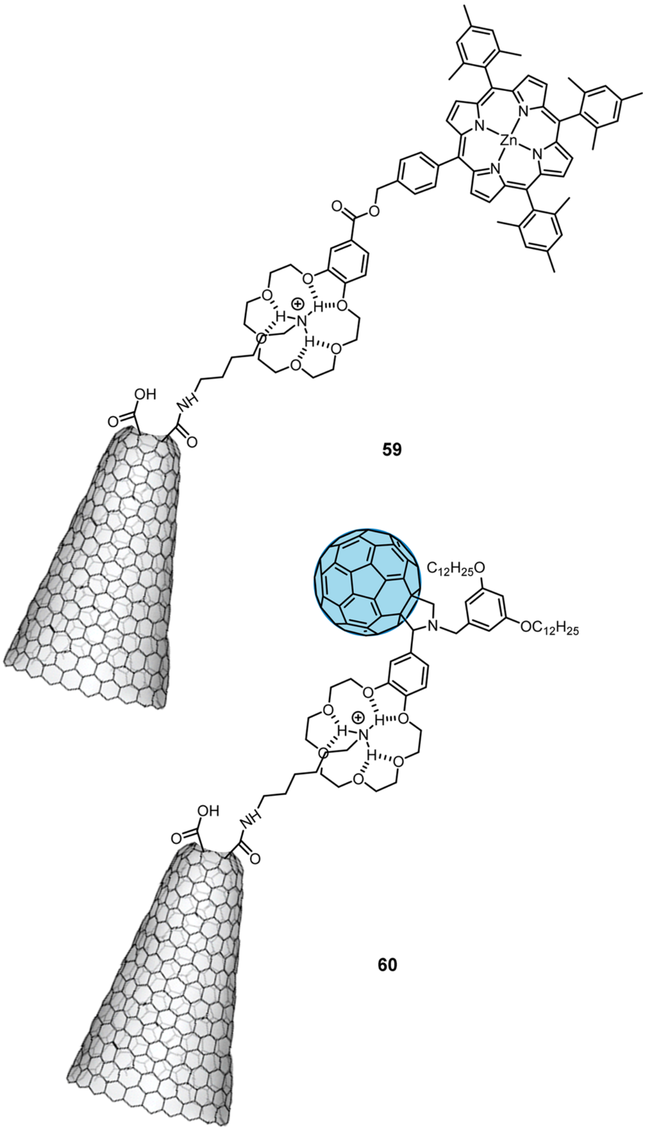
Scheme 9. Electronic Transfer in a Series of Donor−Acceptor Conjugates Where the CNH Can Act as a Donor or as an Acceptor



59

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ORCID

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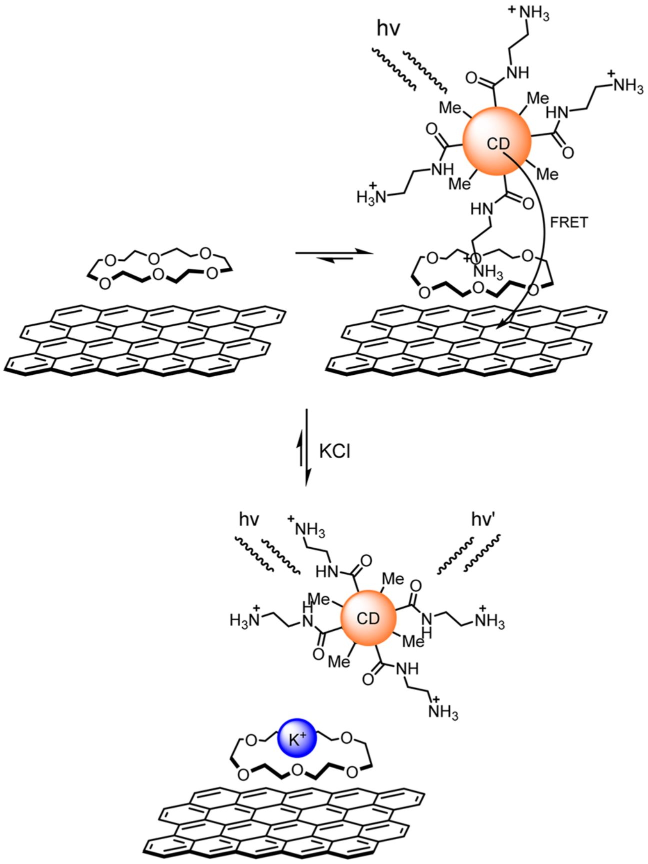
Notes

The authors declare no competing financial interest.

Biographies

Scheme 10. Proposed Mechanism for the Graphene-Based Metal Sensor



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■ REFERENCES

(1) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.
(2) Dietrich, B.; Lehn, J. M.; Sauvage, J. P. *Tetrahedron Lett.* **1969**, *10*, 2885.
(3) Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Lein, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 6752.
(4) Cragg, P. J.; Vahora, R. In *Supramolecular Chemistry*; John Wiley & Sons, Ltd., 2012.
(5) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
(6) Iijima, S. *Nature* **1991**, *354*, 56.
(7) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603.
(8) Bethune, D. S.; Klang, C. H.; de Vries, M. S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. *Nature* **1993**, *363*, 605.
(9) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306*, 666.
(10) Delgado, J. L.; Herranz, M. A.; Martín, N. *J. Mater. Chem.* **2008**, *18*, 1417.
(11) Hiroshi, I.; Kiyoshi, H.; Tsuyoshi, A.; Masanori, A.; Seiji, T.; Tadashi, O.; Masahiro, S.; Yoshiteru, S. *Chem. Phys. Lett.* **1996**, *263*, 545.
(12) Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978.
(13) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Kraetschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630.
(14) Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695.
(15) Castellanos, S.; Vieira, A. A.; Illescas, B. M.; Sacchetti, V.; Schubert, C.; Moreno, J.; Guldi, D. M.; Hecht, S.; Martín, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 13985.
(16) Effing, J.; Jonas, U.; Jullien, L.; Plesnivy, T.; Ringsdorf, H.; Diederich, F.; Thilgen, C.; Weinstein, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1599.
(17) Bhattacharya, S.; Sharma, A.; Nayak, S. K.; Chattopadhyay, S.; Mukherjee, A. K. *J. Phys. Chem. B* **2003**, *107*, 4213.
(18) Saha, A.; Nayak, S. K.; Chottopadhyay, S.; Mukherjee, A. K. *J. Phys. Chem. B* **2003**, *107*, 11889.
(19) Datta, K.; Banerjee, M.; Mukherjee, A. K. *J. Phys. Chem. B* **2004**, *108*, 16100.
(20) Bhattacharya, S.; Sharma, A.; Nayak, S. K.; Mukherjee, A. K. *Spectrochim. Acta, Part A* **2002**, *58*, 2841.
(21) Liu, Y.; Han, J.-R.; Zhao, Y.-L.; Zhang, H.-Y.; Duan, Z.-Y. *J. Inclusion Phenom. Mol. Recognit. Chem.* **2005**, *51*, 191.
(22) D'Souza, F.; Chitta, R.; Gadde, S.; Zandler, M. E.; McCarty, A. L.; Sandanayaka, A. S. D.; Araki, Y.; Ito, O. *J. Phys. Chem. A* **2006**, *110*, 4338.
(23) Grimm, B.; Santos, J.; Illescas, B. M.; Muñoz, A.; Guldi, D. M.; Martín, N. *J. Am. Chem. Soc.* **2010**, *132*, 17387.
(24) Moreira, L.; Calbo, J.; Krick Calderon, R. M.; Santos, J.; Illescas, B. M.; Arago, J.; Nierengarten, J.-F.; Guldi, D. M.; Ortí, E.; Martín, N. *Chem. Sci.* **2015**, *6*, 4426.
(25) Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests*; Royal Society of Chemistry, 1994.
(26) Wittenberg, J. B.; Isaacs, L. In *Supramolecular Chemistry*; John Wiley & Sons, Ltd., 2012.
(27) Rüdiger, V.; Schneider, H.-J.; Solov'ev, V. P.; Kazachenko, V. P.; Raevsky, O. A. *Eur. J. Org. Chem.* **1999**, *1999*, 1847.
(28) Diederich, F.; Echegoyen, L.; Gómez-López, M.; Kessinger, R.; Stoddart, J. F. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1577.
(29) Martínez-Díaz, M. V.; Fender, N. S.; Rodríguez-Morgade, M. S.; Gómez-López, M.; Diederich, F.; Echegoyen, L.; Stoddart, J. F.; Torres, T. *J. Mater. Chem.* **2002**, *12*, 2095.
(30) Guldi, D. M.; Ramey, J.; Martínez-Díaz, M. V.; Escosura, A. d. l.; Torres, T.; Da Ros, T.; Prato, M. *Chem. Commun.* **2002**, 2774.
(31) Sandanayaka, A. S. D.; Sasabe, H.; Araki, Y.; Furusho, Y.; Ito, O.; Takata, T. *J. Phys. Chem. A* **2004**, *108*, 5145.
(32) Maes, M.; Sasabe, H.; Kihara, N.; Araki, Y.; Furusho, Y.; Mizuno, K.; Takata, T.; Ito, O. *J. Porphyrins Phthalocyanines* **2005**, *09*, 724.
(33) Dordevic, L.; Marangoni, T.; De Leo, F.; Papagiannouli, I.; Aloukos, P.; Couris, S.; Pavoni, E.; Monti, F.; Armaroli, N.; Prato, M.; Bonifazi, D. *Phys. Chem. Chem. Phys.* **2016**, *18*, 11858.
(34) Yao, H.; Zhang, H.; Han, M.; Ding, Z.; Zhang, Z.; Liu, Y. *Sci. China: Chem.* **2010**, *53*, 1982.
(35) Ding, Z.-J.; Zhang, Y.-M.; Teng, X.; Liu, Y. *J. Org. Chem.* **2011**, *76*, 1910.
(36) Illescas, B. M.; Santos, J.; Díaz, M. C.; Martín, N.; Atienza, C. M.; Guldi, D. M. *Eur. J. Org. Chem.* **2007**, *2007*, 5027.
(37) Solladié, N.; Walther, M. E.; Herschbach, H.; Leize, E.; Dorsselaer, A. V.; Duarte, T. M. F.; Nierengarten, J.-F. *Tetrahedron* **2006**, *62*, 1979.
(38) Solladié, N.; Walther, M. E.; Gross, M.; Duarte, T. M. F.; Bourgogne, C.; Nierengarten, J.-F. *Chem. Commun.* **2003**, 2412.
(39) Moreira, L.; Calbo, J.; Illescas, B. M.; Aragó, J.; Nierengarten, I.; Delavaux-Nicot, B.; Ortí, E.; Martín, N.; Nierengarten, J.-F. *Angew. Chem., Int. Ed.* **2015**, *54*, 1255.
(40) Sato, H.; Tashiro, K.; Shinmori, H.; Osuka, A.; Murata, Y.; Komatsu, K.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 13086.
(41) Elhabiri, M.; Trabolsi, A.; Cardinali, F.; Hahn, U.; Albrecht-Gary, A.-M.; Nierengarten, J.-F. *Chem. - Eur. J.* **2005**, *11*, 4793.
(42) Nierengarten, J.-F.; Hahn, U.; Trabolsi, A.; Herschbach, H.; Cardinali, F.; Elhabiri, M.; Leize, E.; Van Dorsselaer, A.; Albrecht-Gary, A.-M. *Chem. - Eur. J.* **2006**, *12*, 3365.

DOI: 10.1021/acs.joc.6b03030

(43) Santos, J.; Grimm, B.; Illescas, B. M.; Guldi, D. M.; Martín, N. *Chem. Commun.* **2008**, 5993.

(44) D'Souza, F.; Chitta, R.; Gadde, S.; Zandler, M. E.; Sandanayaka, A. S. D.; Araki, Y.; Ito, O. *Chem. Commun.* **2005**, 1279.

(45) D'Souza, F.; Chitta, R.; Gadde, S.; Zandler, M. E.; McCarty, A. L.; Sandanayaka, A. S. D.; Araki, Y.; Ito, O. *Chem. - Eur. J.* **2005**, *11*, 4416.

(46) Sandanayaka, A. S. D.; Araki, Y.; Ito, O.; Chitta, R.; Gadde, S.; D'Souza, F. *Chem. Commun.* **2006**, 4327.

(47) D'Souza, F.; Maligaspe, E.; Sandanayaka, A. S. D.; Subbaiyan, N. K.; Karr, P. A.; Hasobe, T.; Ito, O. *J. Phys. Chem. A* **2010**, *114*, 10951.

(48) Maligaspe, E.; D'Souza, F. *Org. Lett.* **2010**, *12*, 624.

(49) D'Souza, F.; Maligaspe, E.; Ohkubo, K.; Zandler, M. E.; Subbaiyan, N. K.; Fukuzumi, S. *J. Am. Chem. Soc.* **2009**, *131*, 8787.

(50) Lu, X.; Feng, L.; Akasaka, T.; Nagase, S. *Chem. Soc. Rev.* **2012**, *41*, 7723.

(51) Tsuchiya, T.; Sato, K.; Kurihara, H.; Wakahara, T.; Nakahodo, T.; Maeda, Y.; Akasaka, T.; Ohkubo, K.; Fukuzumi, S.; Kato, T.; Mizorogi, N.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **2006**, *128*, 6699.

(52) Yamada, M.; Akasaka, T. *Bull. Chem. Soc. Jpn.* **2014**, *87*, 1289.

(53) Lu, X.; Akasaka, T.; Nagase, S. *Acc. Chem. Res.* **2013**, *46*, 1627.

(54) Akasaka, T.; Lu, X. *Chem. Rec.* **2012**, *12*, 256.

(55) Yamada, M.; Akasaka, T.; Nagase, S. *Acc. Chem. Res.* **2010**, *43*, 92.

(56) Tsuchiya, T.; Kurihara, H.; Sato, K.; Wakahara, T.; Akasaka, T.; Shimizu, T.; Kamigata, N.; Mizorogi, N.; Nagase, S. *Chem. Commun.* **2006**, 3585.

(57) Supur, M.; Kawashima, Y.; Larsen, K. R.; Ohkubo, K.; Jeppesen, J. O.; Fukuzumi, S. *Chem. - Eur. J.* **2014**, *20*, 13976.

(58) Supur, M.; Kawashima, Y.; Ma, Y.-X.; Ohkubo, K.; Chen, C.-F.; Fukuzumi, S. *Chem. Commun.* **2014**, *50*, 15796.

(59) Girifalco, L. A.; Hodak, M.; Lee, R. S. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *62*, 13104.

(60) Ramesh, S.; Ericson, L. M.; Davis, V. A.; Saini, R. K.; Kittrell, C.; Pasquali, M.; Billups, W. E.; Adams, W. W.; Hauge, R. H.; Smalley, R. E. *J. Phys. Chem. B* **2004**, *108*, 8794.

(61) Holzinger, M.; Vostrowsky, O.; Hirsch, A.; Hennrich, F.; Kappes, M.; Weiss, R.; Jellen, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 4002.

(62) Dyke, C. A.; Tour, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 1156.

(63) Zhang, X.; Sreekumar, T. V.; Liu, T.; Kumar, S. *J. Phys. Chem. B* **2004**, *108*, 16435.

(64) Kahn, M. G. C.; Banerjee, S.; Wong, S. S. *Nano Lett.* **2002**, *2*, 1215.

(65) Banerjee, S.; Kahn, M. G. C.; Wong, S. S. *Chem. - Eur. J.* **2003**, *9*, 1898.

(66) Jiang, C.; Saha, A.; Xiang, C.; Young, C. C.; Tour, J. M.; Pasquali, M.; Martí, A. A. *ACS Nano* **2013**, *7*, 4503.

(67) Anderson, R. E.; Barron, A. R. *J. Nanosci. Nanotechnol.* **2007**, *7*, 3436.

(68) Sainsbury, T.; Fitzmaurice, D. *Chem. Mater.* **2004**, *16*, 2174.

(69) Perez, E. M.; Martin, N. *Chem. Soc. Rev.* **2015**, *44*, 6425.

(70) D'Souza, F.; Chitta, R.; Sandanayaka, A. S. D.; Subbaiyan, N. K.; D'Souza, L.; Araki, Y.; Ito, O. *Chem. - Eur. J.* **2007**, *13*, 8277.

(71) D'Souza, F.; Chitta, R.; Sandanayaka, A. S. D.; Subbaiyan, N. K.; D'Souza, L.; Araki, Y.; Ito, O. *J. Am. Chem. Soc.* **2007**, *129*, 15865.

(72) Vizuete, M.; Gómez-Escalonilla, M. J.; Fierro, J. L. G.; Sandanayaka, A. S. D.; Hasobe, T.; Yudasaka, M.; Iijima, S.; Ito, O.; Langa, F. *Chem. - Eur. J.* **2010**, *16*, 10752.

(73) Vizuete, M.; Gomez-Escalonilla, M. J.; Fierro, J. L. G.; Ohkubo, K.; Fukuzumi, S.; Yudasaka, M.; Iijima, S.; Nierengarten, J.-F.; Langa, F. *Chem. Sci.* **2014**, *5*, 2072.

(74) Ballesteros-Garrido, R.; de Miguel, M.; Domenech-Carbo, A.; Alvaro, M.; Garcia, H. *Chem. Commun.* **2013**, *49*, 3236.

(75) Olsen, G.; Ulstrup, J.; Chi, Q. *ACS Appl. Mater. Interfaces* **2016**, *8*, 37.

(76) Guo, J.; Lee, J.; Contescu, C. I.; Gallego, N. C.; Pantelides, S. T.; Pennycook, S. J.; Moyer, B. A.; Chisholm, M. F. *Nat. Commun.* **2014**, *5*, 5389.

(77) Wei, W.; Xu, C.; Ren, J.; Xu, B.; Qu, X. *Chem. Commun.* **2012**, *48*, 1284.

(78) Kellner, I. D.; von Gernler, M. S.; Tzirakis, M. D.; Orfanopoulos, M.; Drewello, T. *J. Phys. Chem. C* **2014**, *118*, 30253.

(79) Kellner, I. D.; von Gernler, M. S.; Tzirakis, M. D.; Orfanopoulos, M.; Drewello, T. *J. Phys. Chem. C* **2016**, *120*, 786.

(80) Bourgeois, J.-P.; Echegoyen, L.; Fibbioli, M.; Pretsch, E.; Diederich, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2118.