

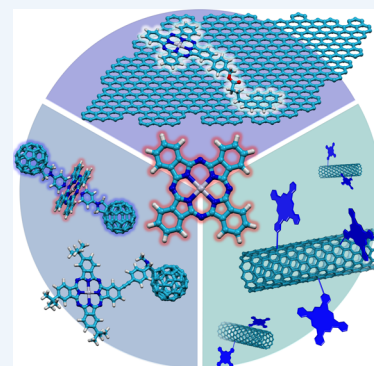
Phthalocyanine–Nanocarbon Ensembles: From Discrete Molecular and Supramolecular Systems to Hybrid Nanomaterials

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CONSPECTUS: Phthalocyanines (Pcs) are macrocyclic and aromatic compounds that present unique electronic features such as high molar absorption coefficients, rich redox chemistry, and photoinduced energy/electron transfer abilities that can be modulated as a function of the electronic character of their counterparts in donor–acceptor (D–A) ensembles. In this context, carbon nanostructures such as fullerenes, carbon nanotubes (CNTs), and, more recently, graphene are among the most suitable Pc “companions”. Pc–C₆₀ ensembles have been for a long time the main actors in this field, due to the commercial availability of C₆₀ and the well-established synthetic methods for its functionalization. As a result, many Pc–C₆₀ architectures have been prepared, featuring different connectivities (covalent or supramolecular), intermolecular interactions (self-organized or molecularly dispersed species), and Pc HOMO/LUMO levels. All these elements provide a versatile toolbox for tuning the photophysical properties in terms of the type of process (photoinduced energy/electron transfer), the nature of the interactions between the electroactive units (through bond or space), and the kinetics of the formation/decay of the photogenerated species. Some recent trends in this field include the preparation of stimuli-responsive multicomponent systems with tunable photophysical properties and highly ordered nanoarchitectures and surface-supported systems showing high charge mobilities. A breakthrough in the Pc–nanocarbon field was the appearance of CNTs and graphene, which opened a new avenue for the preparation of intriguing photoresponsive hybrid ensembles showing light-stimulated charge separation. The scarce solubility of these 1-D and 2-D nanocarbons, together with their lower reactivity with respect to C₆₀ stemming from their less strained sp² carbon networks, has not meant an unsurmountable limitation for the preparation of variety of Pc-based hybrids. These systems, which show improved solubility and dispersibility features, bring together the unique electronic transport properties of CNTs and graphene with the excellent light-harvesting and tunable redox properties of Pcs. A singular and distinctive feature of these Pc–CNT/graphene (single- or few-layers) hybrid materials is the control of the direction of the photoinduced charge transfer as a result of the band-like electronic structure of these carbon nanoforms and the adjustable electronic levels of Pcs. Moreover, these conjugates present intensified light-harvesting capabilities resulting from the grafting of several chromophores on the same nanocarbon platform.



In this Account, recent progress in the construction of covalent and supramolecular Pc–nanocarbon ensembles is summarized, with a particular emphasis on their photoinduced behavior. We believe that the high degree of control achieved in the preparation of Pc–carbon nanostructures, together with the increasing knowledge of the factors governing their photophysics, will allow for the design of next-generation light-fueled electroactive systems. Possible implementation of these Pc–nanocarbons in high performance devices is envisioned, finally turning into reality much of the expectations generated by these materials.

INTRODUCTION

During the last 20 years, considerable effort has been made toward the preparation of donor–acceptor (D–A) systems exhibiting photoinduced charge separation, a fundamental step in natural photosynthesis and solar energy conversion.¹

Among the toolbox of molecular building blocks available for the construction of such D–A ensembles, porphyrinoids hold a privileged position since they possess remarkable light-harvesting features and adjustable redox properties.² In particular, phthalocyanines (Pcs),³ synthetic porphyrin (Por) analogs, have been largely used in a variety of D–A covalent and supramolecular dyads, triads, and more complex arrays.^{4,5} Although both Pcs and Pors have remarkable absorption in the visible region, the latter chromophores lack significant

absorption at wavelengths higher than 550 nm. In contrast, Pcs show excellent light harvesting capabilities over a wide range of the solar light spectrum with a maximum at around 700 nm, where the maximum of the solar photon flux occurs. In addition, Pcs present higher thermal and photochemical stability than Pors, which make them optimal candidates for the preparation of robust, photoactive D–A ensembles. Other remarkable properties of Pcs are their rich redox chemistry and tunable HOMO–LUMO gap, which can be tailored by the adequate choice of peripheral substituents and metal centers in the Pc inner cavity. These features constitute an appealing tool

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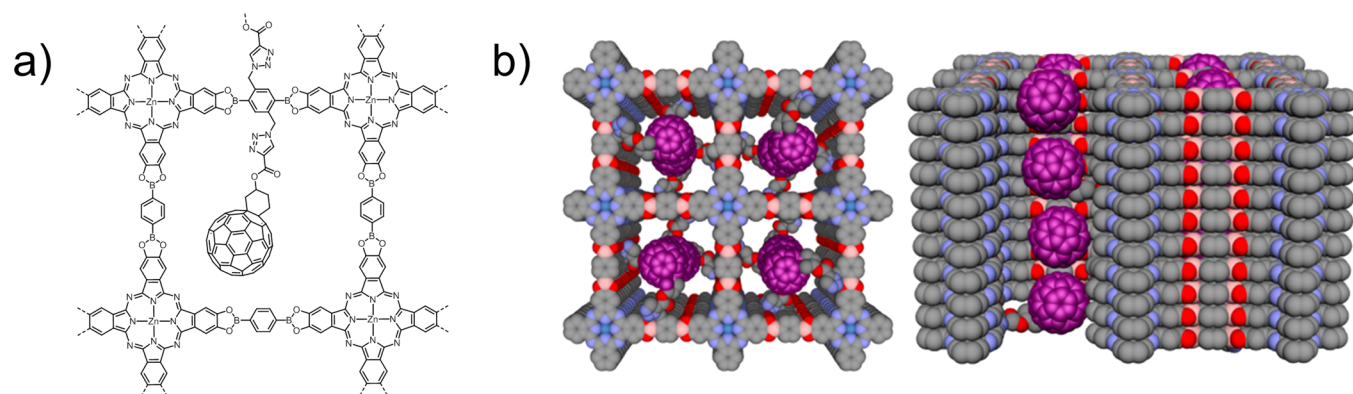


Figure 1. (a) Molecular structure and (b) top (left) and side (right) view of a fragment of D–A Pc-based COF with C₆₀ units (purple) covalently linked to the nanochannels walls. Panel b reproduced with permission from ref 10. Copyright 2014 American Chemical Society.

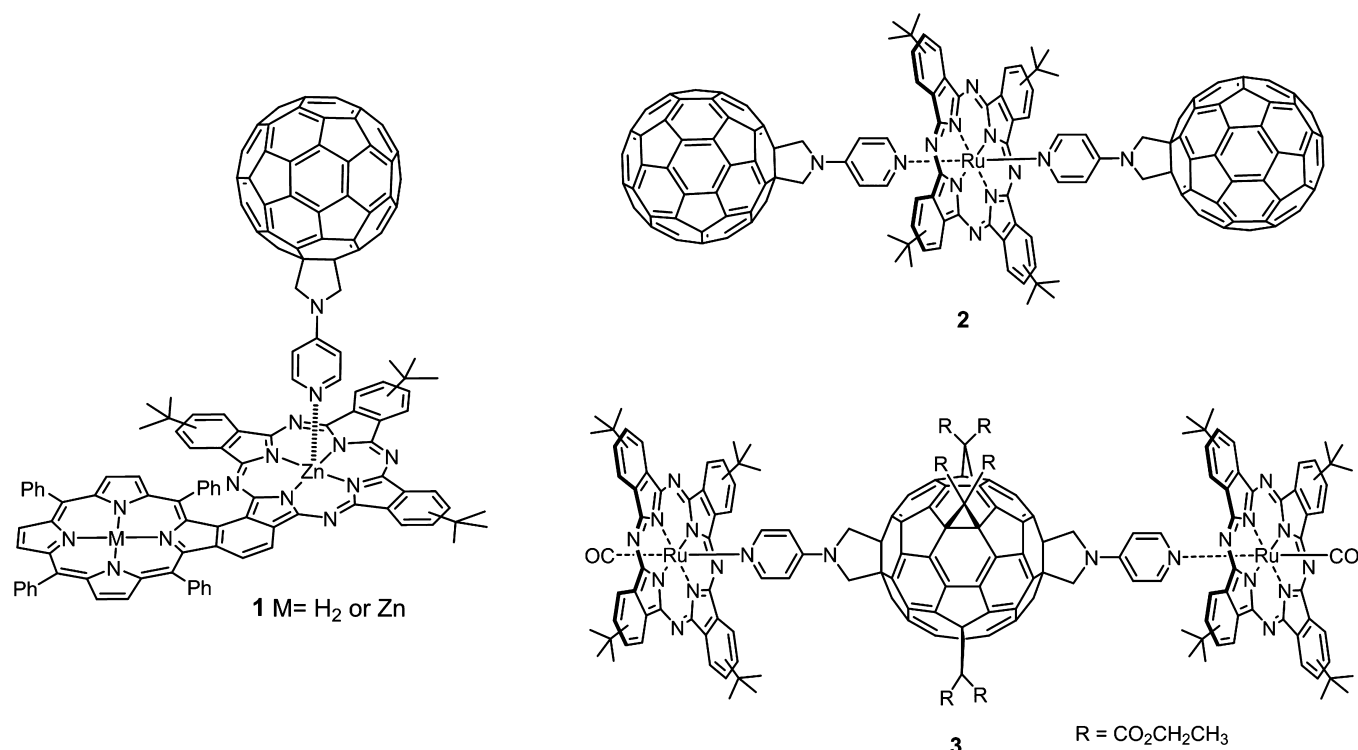


Figure 2. Molecular structures of noncovalent ensembles Zn(II)Pc–Por–C₆₀ (**1**)¹¹ and Ru(II)Pc–C₆₀, **2** and **3**.¹²

for tuning the photophysical properties of Pc-based D–A ensembles. Among the Pc counterparts employed for the preparation of D–A systems, carbon nanostructures such as fullerenes, carbon nanotubes (CNTs), and graphene deserve a special mention due to their outstanding electronic features.

Since their discovery, fullerenes have gained a prominent position in the field of molecular materials. As a result of their excellent electron accepting properties and size confinement, these 0-D cages have raised the interest of a large part of the scientific community, prompting their incorporation into a plethora of molecular multicomponent systems, and as the acceptor component “par excellence” in organic photovoltaic devices.⁶ Although sharing with fullerenes an sp² carbon network, CNTs⁷ and graphene⁸ are nondiscrete structures with extraordinary electrical properties, namely, the ballistic transport of electrons along the main axis of CNTs, and the extraordinarily high mobility of charges in atomically flat graphene. Key for the implementation of these highly insoluble

1-D and 2-D low dimensional nanocarbons into technological applications is to facilitate their processing, which can be achieved through chemical functionalization of their sp² network. Such chemical modification may also allow one to prepare hybrid systems combining the properties of these carbon nanostructures with those of electro- and photoactive molecular building blocks such as Pcs.

This Account underscores the importance of Pc–nanocarbon conjugates as light-powered, electronically active systems for energy conversion schemes, offering an overview on the current state of the art of this field through the examination of selected examples from our group and others.

■ PHTHALOCYANINE–FULLERENE ENSEMBLES

In 1997, the first Pc–C₆₀ conjugate was reported in which the macrocycle and the spherical carbon nanostructure were covalently linked through a Diels–Alder reaction between a Ni(II)Pc bearing a butadiene fragment and C₆₀ fullerene.⁹ Since

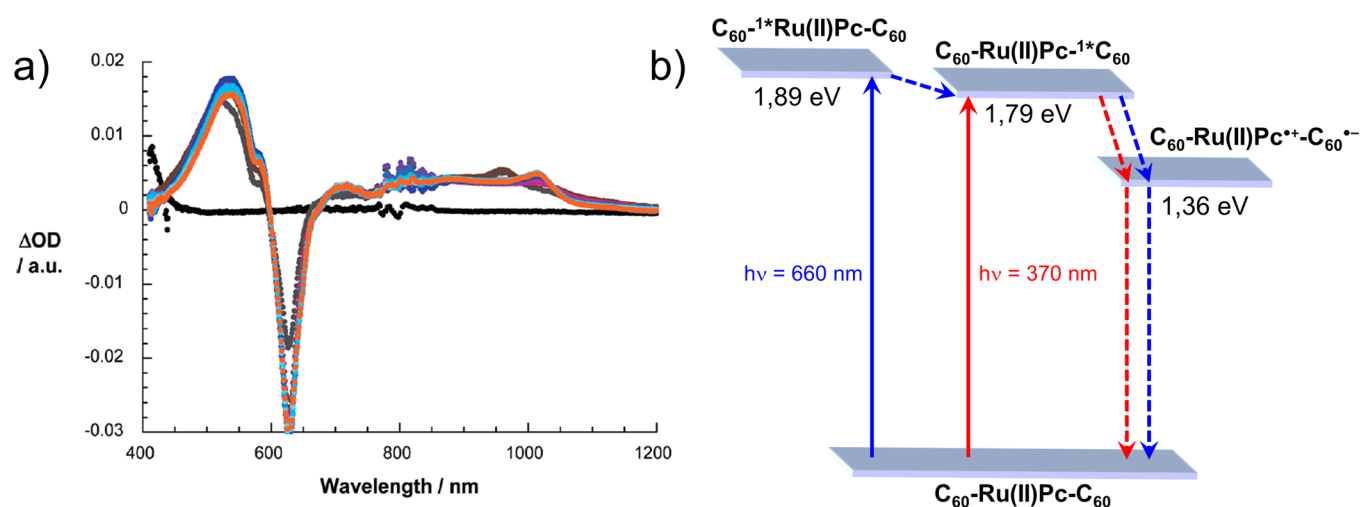


Figure 3. (a) Differential absorption spectra obtained upon femtosecond flash photolysis (387 nm) of A–D–A C_{60} –Ru(II)Pc– C_{60} triad **2** in toluene with several time delays between 0 and 500 ps at room temperature.¹² (b) Energy diagram for the photoinduced energy transfer processes of triad **2** in toluene. Panel a reproduced with permission from ref 12. Copyright 2009 American Chemical Society.

then, many covalent and supramolecular Pc– C_{60} systems have been prepared and studied. In these ensembles, parameters such as (i) the electronic features of the macrocycle, (ii) the nature of the spacer connecting the Pc and C_{60} moieties in covalently linked systems (short/long, rigid/flexible, conjugated/nonconjugated), and (iii) the supramolecular interaction motif(s) used to assemble the two moieties in noncovalent Pc– C_{60} systems have been varied, with the aim of rationalizing how these changes affect the formation and recombination of the photogenerated charged species.⁴

Recently, a general and versatile synthetic strategy for the preparation of chemically stable, segregated Pc– C_{60} alignments has been presented, which relies on the solvothermal synthesis of Pc-based covalent organic frameworks (COFs) and their postfunctionalization by a C_{60} derivative.¹⁰ Pc-based COFs present a porous architecture formed by periodically ordered Pc columnar arrays, which generate aligned 1-D nanochannels. Jiang et al. demonstrated that the interior walls of these open channels, adequately functionalized with azide moieties, could be covalently “grafted” with an ethynyl-functionalized C_{60} derivative via a “click” reaction (Figure 1). By this strategy, the former electron-donating, Pc-based COF architecture is transformed into a photoresponsive COF structure constituted by segregated D–A alignments of stacked Pcs and electron-accepting buckyballs spatially confined into the nanochannels. Interestingly, laser stimulation of this D–A heterojunction triggers photoinduced electron transfer processes, giving rise to photogenerated charge separated species with lifetimes that are strongly affected by the delocalization of radical cation and anion species on the Zn(II)Pc and C_{60} moieties, respectively.

Supramolecular interactions have also been successfully employed for the construction of noncovalent Pc– C_{60} ensembles using Pc and C_{60} derivatives carrying out complementary recognition motifs. In this context, metal–ligand coordination, hydrogen-bonding, or cation–crown ether noncovalent interactions have been widely used, independently or in combination, for the preparation of Pc– C_{60} supramolecular systems.

Metal-directed self-assembly, extensively used in chemistry to prepare supramolecular structures with different shapes and sizes and tunable stability through the careful choice of the

metal and the ligand recognition elements, has proven very efficient for obtaining Pc– C_{60} supramolecular structures. A representative example of these metal–ligand ensembles is constituted by supramolecular D–A system **1**, which results from the complexation of a pyridyl-substituted C_{60} full-eropyrrolidine with a fused, Zn(II)Pc–Por conjugate able to harvest light over a wide range of the solar spectrum due to the complementary absorption of the Por and Pc components (Figure 2).¹¹ Photoexcitation of the Por unit leads to intramolecular energy transfer from the tetrapyrrolic macrocycle (free-base or metalated) to the energetically lower-lying Zn(II)Pc, and a subsequent intramolecular charge transfer from the excited Pc to C_{60} .

Kinetically stable, Pc– C_{60} supramolecular architectures based on metal–ligand interactions can be synthesized using Ru(II) instead of Zn(II) as the metal in the Pc cavity. Moreover, and differently from Zn(II)Pcs, Ru(II)Pcs coordinating two different ligands at their axial positions can also be prepared and isolated. These features have been exploited for the construction of orthogonal A–D–A and D–A–D Pc– C_{60} hybrids (**2** and **3**, respectively) (Figure 2), which exhibited excited-state electronic communication between the two electroactive units.¹²

In particular, 387 nm photoexcitation of ensemble **2** shows the immediate formation of the singlet C_{60} species characterized by an absorption at 950 nm, which decay is simultaneously accompanied by the growth of new features in the visible and near-infrared regions (Figure 3a). Maxima at 535, 715, and 885 nm and 1015 nm match the features of the one-electron-oxidized Ru(II)Pc radical cation and one electron-reduced C_{60} radical anion species, respectively. These observations are rationalized on the basis of free energy changes related to an intramolecular charge transfer between the photoexcited C_{60} (the electron acceptor) and the Ru(II)Pc ground state (the electron donor) to afford the $C_{60}^{\bullet-}/$ Ru(II)Pc^{•+} radical ion pair state.

Additionally, irradiation at 660 nm, which exclusively photoexcites the Ru(II)Pc, leads to the instantaneous formation of the Ru(II)Pc singlet excited state which decays rapidly via singlet–singlet energy transfer to afford the C_{60} singlet excited state (Figure 3b). The latter process is followed by the

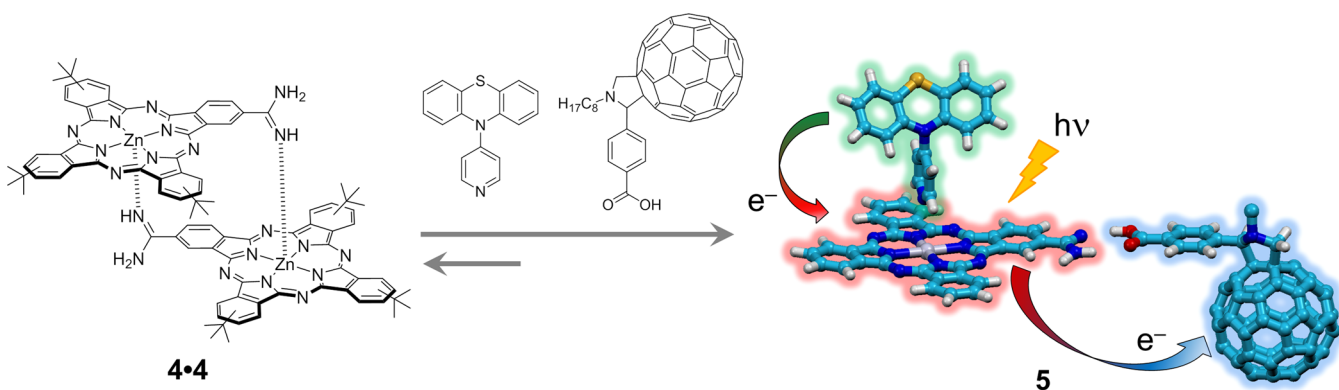


Figure 4. Self-assembly of photoresponsive, D–A supramolecular triad **5** triggered by the disassembly of supramolecular dimer **4•4** in the presence of pyridine and benzoic acid derivatives functionalized with a PTZ donor and a C_{60} acceptor moiety, respectively.¹³

development of both the $Ru(II)Pc^{•+}$ and $C_{60}^{•-}$ radical ion fingerprints, in agreement with the former 387 nm excitation experiment.

This example epitomizes the formation of photoinduced charge separated states in Pc–carbon nanostructure ensembles (*vide infra*). Nevertheless, such states can be reached through energy/electron transfer pathways different from the ones described above.

Pc– C_{60} ensembles held together by the combination of two, or more, “types” of noncovalent interactions have also been prepared with the aim of driving the assembly/disassembly of these supramolecular systems through the use of cooperative or orthogonal stimuli.

For example, the synergistic effect of hydrogen bonding and metal–ligand interactions occurring at two different sites of an amidine-functionalized $Zn(II)Pc$ (**4**) has been used to trigger the dissociation of the spontaneously formed Pc dimer **4•4** and the concomitant formation of three-component phenothiazine (PTZ)–Pc– C_{60} system **5** (Figure 4).¹³ The aforementioned head-to-tail Pc dimer, **4•4**, which results from the self-assembly of Pc **4** via $Zn(II)$ –amidine coordination, shows a high association constant ($K_D \approx 10^{11} M^{-1}$ in toluene) that prevents its dissociation in the presence of either (i) C_{60} -based carboxylic acid or (ii) PTZ-substituted pyridine ligands, which could give rise to competitive carboxylic acid/amidine hydrogen bonding or $Zn(II)$ /pyridyl metal/ligand binding interactions. In contrast, cooperative binding was observed upon the combined addition of both carboxylic acid- and pyridyl-substituted ligands to dimer **4•4** resulting in the quantitative formation of ensemble **5**. Interestingly, laser stimulation of **5** triggers an electron transfer process from the photoexcited Pc to the electron-accepting C_{60} moiety, followed by a charge shift from the electroactive PTZ moiety to the oxidized Pc leading to a $PTZ^{•+}$ –Pc– $C_{60}^{•-}$ supramolecular species, which presented a charge separated lifetime of 7.5 μs in deoxygenated toluene.

Similarly, a combination of metal–ligand and cation–crown ether noncovalent interactions has been used by D’Souza et al. to prepare a multicomponent Pc/ C_{60} supramolecular system (**6**) (Figure 5).¹⁴ The assembly strategy used is based on the K^+ -induced cofacial stacking of two crown ether-containing $Zn(II)Pc$ s and the cooperative “two-point” binding of two fullerene carrying a pyridyl and a terminal ammonium moiety to the two macrocycles through pyridyl– $Zn(II)$, metal–ligand coordination and ammonium/crown ether complexation. Photophysical studies on self-assembled complex **6** revealed

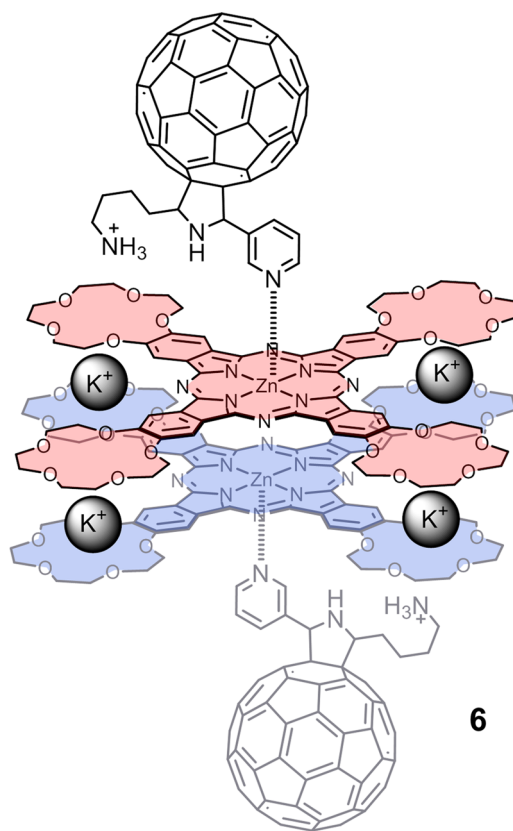


Figure 5. Molecular structure of supramolecular Pc_2 –(C_{60})₂ ensemble **6**.¹⁴

the formation of a photoinduced charge separated species, with a lifetime considerably longer than that of an analogous system in which the Pc is replaced by a Por macrocycle (6.7 μs vs 50 ns). Such increase in the charge separation lifetime was attributed to (i) the cofacial stacking arrangement of the two Pcs in **6** and (ii) the smaller reorganization energy of the electron transfer process for the π -expanded Pc macrocycle relative to the smaller π -conjugated Por system.

Whereas the vast majority of the studies on Pc– C_{60} conjugates reported to date has been carried out in solution, potential applications of these D–A systems in real-life devices rest on the possibility to organize these conjugates in some condensed phases over several length scales. In this respect, the preparation of appropriately functionalized Pc– C_{60} compounds presenting liquid crystalline properties represents an appealing

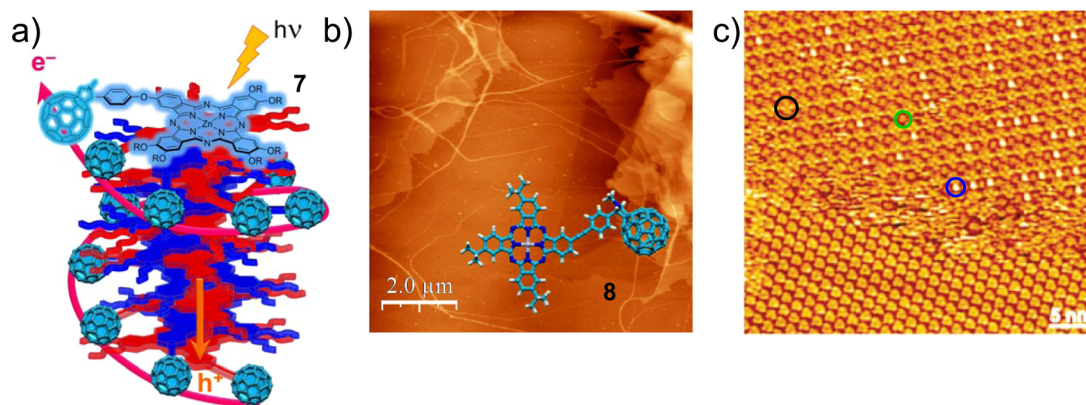


Figure 6. (a) Schematic representation of the columnar arrangement of liquid crystalline Pc–C₆₀ dyad 7.¹⁸ For the sake of clarity, the Pcs have been alternatively colored in red and blue. (b) AFM topographic image of Pc–C₆₀ conjugate 8 (inset) drop-casted on HOPG.¹⁹ (c) STM image of C₆₀ molecules (inside blue circle) deposited on a bimolecular “chessboard” consisting of unsubstituted Zn(II)Pcs (inside dark circle) and octaethyl-substituted Zn(II)Pors (inside green circle) organized on Au(111).²⁵ Panel b reproduced with permission from ref 19. Copyright 2008 Wiley-VCH. Panel c reproduced with permission from ref 25. Copyright 2008 American Chemical Society.

strategy to achieve long-range order with these D–A compounds through their hierarchical self-assembly.

Covalently linked Pc–C₆₀ ensembles able to form liquid crystalline phases have been reported by us¹⁵ and others.^{16–18} These systems, which share as a common structural feature the presence of long alkyl or alkoxy chains surrounding the π -conjugated Pc surface, self-assemble forming discotic liquid crystalline materials through a combination of π – π stacking and aliphatic–aliphatic interactions. Long and flexible aliphatic spacers connecting the Pc and C₆₀ are usually employed with the aim of distancing the two moieties, thus reducing possible deleterious effect of the bulky spherical C₆₀ molecule on the Pc liquid crystalline properties.^{15–17} However, a short and semiflexible bridge has also been used in dyad 7, which forms a liquid crystalline material that exhibits efficient photocurrent generation and good short-range and long-range ambipolar charge transport properties (Figure 6a).¹⁸ Interestingly, pre-heated samples of 7 showed a 5-fold increase in the charge mobility with respect to the unheated material, a phenomenon attributed to a better alignment of the Zn(II)Pc–C₆₀ columns upon thermal treatment, which, in turn, may facilitate the charge transport.

Supramolecular interactions between Pc–C₆₀ conjugate (8) have also been exploited for the “bottom-up” fabrication of electrically conductive thin films. Dyad 8 was deposited by drop-casting on highly ordered pyrolytic graphite (HOPG) and graphite oxide, and the resulting films were investigated by atomic force microscopy (AFM) and conductive-AFM (c-AFM).¹⁹ AFM studies indicated that this D–A conjugate forms micrometer-long fibers and thin films on HOPG (Figure 6b). Interestingly, complementary c-AFM studies carried out on both surface-supported films and fibers showed extremely high electrical conductivity values, which were strongly dependent on the supramolecular order of the dyad within these nanostructures.

The possibility of functionalizing surfaces by co-deposition or sequential deposition of Pc and molecules such as C₆₀^{20–22} or C₆₀-based fragments like corannulene^{23,24} has also been demonstrated. Scanning tunneling microscopy (STM) studies on these surface-supported systems revealed that the porous, 2-D packing motif formed by the Pcs can act as a template for the organization of a guest molecule, leading to the formation of highly ordered, bicomponent supramolecular arrays. More

recently, a three-component system adsorbed on Au(111) has also been prepared (Figure 6c). In this system, a metastable, two-component network formed by unsubstituted Zn(II)Pcs and octaethyl-substituted Pors acts as a supramolecular “chessboard”, promoting the assembly of a third C₆₀ component, which is selectively trapped in the open spaces of the Pc/Por 2-D network.²⁵

Recently, Pcs covalently linked to Y₃N@C₈₀ endohedral metallofullerenes (EMFs) have also been reported.²⁶ EMFs, isolated for the first time in 1999,²⁷ present several advantages with respect to empty fullerenes such as higher absorption coefficients in the visible region of the electromagnetic spectrum and a redox chemistry that can be varied as a function of the encapsulated species. Covalent Y₃N@C₈₀-based Pc dyads have been prepared in low yields via Prato–Maggini and Bingel–Hirsch reactions. However, the poor chemical stability of the systems obtained precluded an accurate electrochemical and photophysical characterization of these ensembles.

■ PHTHALOCYANINE–CARBON NANOTUBE ENSEMBLES

Following the discovery of CNTs, many chemists worldwide started to actively search for efficient chemical protocols aimed at CNT functionalization,²⁸ in some cases “adapting” some of the functionalization methods successfully employed in fullerene chemistry. This research effort has resulted in the preparation of numerous CNT-based materials, in which the tubular species are covalently linked to electron-donating molecules such as ferrocene and tetrathiafulvalene.²⁹ Even more interesting, “grafting” electron-donating organic addenda with good light-harvesting capabilities to electron-accepting CNTs result in D–A hybrid materials, which could be of interest for solar energy conversion schemes.³⁰ Within this framework, our group and others have pursued linking Pcs to single-walled CNTs (SWCNTs) in the search for hybrid nanomaterials for photovoltaic applications.⁴

Pioneering the functionalization of nonoxidized SWCNTs with Pcs, our group has described a two-step procedure based on (i) the 1,3-dipolar cycloaddition of azomethine ylides, formed *in situ* by reaction of *N*-octylglycine and 4-formylbenzoic acid, to pristine SWCNTs and (ii) subsequent esterification reaction of the carboxylic acid-derivatized nano-

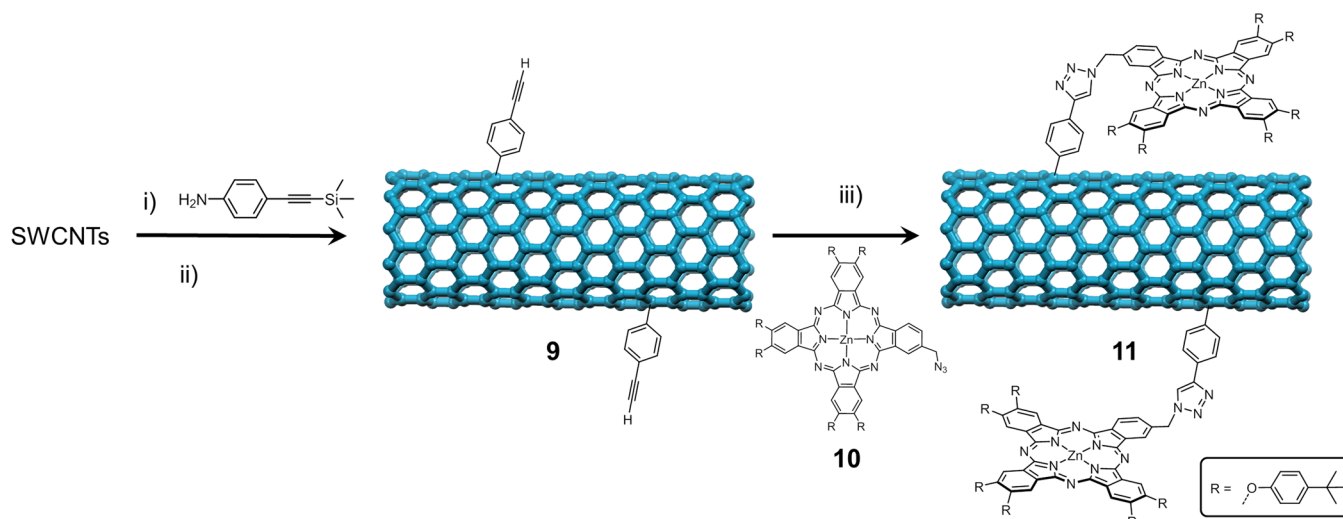


Figure 7. Synthetic route toward Pc-SWCNT nanoconjugate **11**.³² Conditions: (i) isoamyl nitrite, *N*-methylpyrrolidone (NMP), 60 °C, 48 h; (ii) NBu_4F , THF/NMP, rt, 1 h; (iii) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, sodium ascorbate, NMP, 70 °C, 48 h.

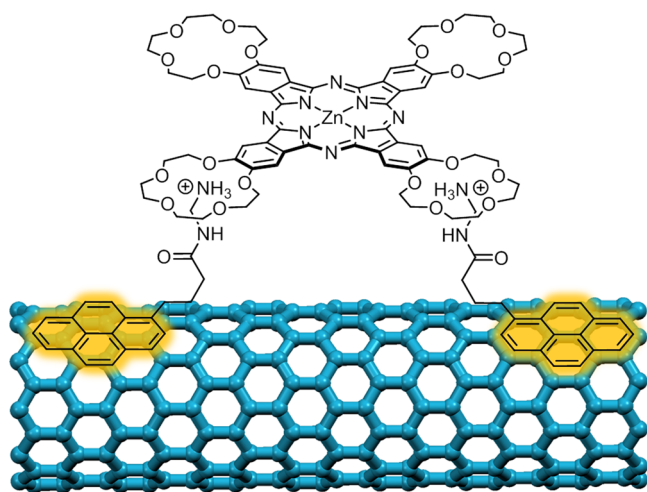
tube material with a hydroxymethyl-substituted Zn(II)Pc .³¹ In a second stage, aiming at preparing Zn(II)Pc-SWCNT materials through a more efficient synthetic strategy, we envisioned the use of high yielding “click chemistry” protocols such as the Huisgen cycloaddition for the introduction of Zn(II)Pcs to adequately functionalized nanotubes.³² For this purpose, preparation of ethynyl-containing SWCNTs **9** was undertaken by Tour reaction of the nanotubes with 4-(trimethylsilyl)ethynylaniline followed by deprotection of the terminal silyl group. Finally, the Cu(I) -catalyzed reaction of the ethynyl-terminated CNTs **9** with azido-functionalized Zn(II)Pc **10** led to the efficient formation of Pc-SWCNT **11** (Figure 7) as demonstrated by thermogravimetric (TGA) analyses. Approximately, an average functionalization of one Zn(II)Pc per 150 carbon atoms was achieved, which is sufficient to provide measurable charge transfer from the Pc to the SWCNT but also low enough to preserve the electronic features of SWCNTs.³³ In this connection, an elegant approach reported by Campidelli and co-workers, aimed at increasing the cross section absorption of the hybrid material while preserving as much as possible the electronic properties of the nanotubes, relies on attaching Zn(II)Pc dendrons rather than single Pc chromophores.³⁴

The use of noncovalent interactions as a tool to functionalize SWCNTs offers, undeniably, significant advantages with respect to the covalent functionalization approach, mainly the preservation of the CNTs’ electronic features. Aromatic molecules such as pyrene, tetrathiafulvalene, and Por have been shown to adhere strongly to the nanotube surface through π - π interactions. In contrast, although they possess an extended aromatic surface, Pcs do not present favorable π -stacking interactions with SWCNTs in solution, and therefore, they do not form stable Pc-SWCNT dispersions. Interestingly, the Pc ring has also shown low affinity toward the sidewalls of SWCNTs grown by catalyst-assisted chemical vapor deposition (CVD) on silicon oxide surfaces.³⁵ Drop-casting a solution of covalently linked Zn(II)Pc-C_{60} conjugate **8** (which molecular structure appears as inset in Figure 6b) on the SWCNT-functionalized SiO_2 surface leads to the supramolecular organization of the conjugate around the nanotube by C_{60} /SWCNT interactions, as suggested by AFM studies.

En route to promote immobilization of Zn(II)Pcs on SWCNTs, some strategies have been envisioned. First to mention, attachment of oligo(ethylene glycol)-type dendritic wedges to the hydrophobic Pc core allows the preparation of stable Pc-SWCNT dispersions, both in polar solvents and in aqueous media.³⁶ Also, linking pyrene to the periphery of a Pc macrocycle provides a way to form stable suspensions of MPc ($M = \text{Zn(II)}, \text{H}_2$) and SWCNTs.³⁷ More recently, an azulenocyanine, a near-infrared absorbing Pc derivative, has been also immobilized on SWCNTs following the same approach.³⁸ A “two-point” binding strategy has been envisioned by Ito, D’Souza, and co-workers to prepare supramolecular Zn(II)Pc-SWCNT ensembles. This approach consists in immobilizing on the nanotube surface pyrene units functionalized with either imidazole³⁹ or alkylammonium⁴⁰ groups, followed by the assembly of the Zn(II)Pc molecules through metal-ligand interactions between the imidazole and the Zn(II) center or dipole-ion interactions between crown-ether-functionalized Zn(II)Pcs and alkyl-ammonium cations (**12**, Figure 8).

Not only pyrene but also other conjugated structures can act as anchoring units leading to supramolecular Pc-SWCNT ensembles. The ability of conjugated poly(*p*-phenylene vinylene) oligomers **13** and **14** (Figure 9) bearing pendant Zn(II)Pcs arms to wrap around SWCNTs was recently established.^{41,42} Importantly, parameters such as size, *n*- (**13**) or *p*-type (**14**) character of the oligomer, and distance between the Zn(II)Pc moiety and the conjugated backbone play a decisive role in the stability of the ensembles.

The ultimate feature that we and others anticipate from these hybrid Pc-SWCNT nanomaterials is the occurrence of excited state electronic interactions between the two components, in particular, photoinduced electron transfer processes able to generate long-lived charge separated states. Important is to mention that the strong donor character of the Zn(II)Pc units, comprising all the above-mentioned nanohybrids, determines the direction of the photoinduced charge separation process, giving rise to metastable species formed by oxidized Zn(II)Pc radical cations and reduced SWCNT species. Some effort has been devoted to determine the structural factors governing the charge separation events taking place in these systems. As a general trend, comparative photophysical studies over dis-



12

Figure 8. Molecular structure of supramolecular Pc–SWCNT assembly **12**.⁴⁰

persions of Zn(II)Pc–SWCNT nano hybrids reveal that noncovalent ensembles formed by π – π interactions between pyrene and SWCNTs show the longest charged separated state lifetimes. In particular, nano hybrids prepared by the “two-point” binding strategy (such as **12**, Figure 8), which present a longer SWCNT-to-Zn(II)Pc distance, exhibit charge separation lifetimes between 60 and 110 ns.^{39,40} Oppositely, *o*-PPV–Pc/SWCNT^{41,42} and oligo(ethylene glycol)-type dendritic Pc/SWCNT³⁶ derivatives show photoinduced charge separation lifetimes 3 orders of magnitude shorter.

Indeed, the photovoltaic properties of the Pc–SWCNT nano hybrids can be eventually proven by their incorporation in photoelectrochemical cells. For this purpose, SnO₂ or indium tin oxide (ITO) electrodes have been modified with Pc–SWCNT conjugates and immersed in a solution of a redox mediator, together with a Pt counter-electrode.³⁷ Maximum incident-photon-to-current (IPCE) efficiencies were found for pyrene–H₂Pc/SWCNT nano hybrid, which shows IPCE values

as large as 23%, this value ranking among the highest reported for D–A SWCNT-based hybrids.⁴³

■ PHTHALOCYANINE–GRAPHENE ENSEMBLES

Graphene, the “rising star” in the carbon nanoform family, not only possesses unique optoelectronic features but also has a large surface area, which is suitable for the preparation of tailored hybrid materials by interaction with other optoelectronically active organic components. Regarding graphene’s covalent functionalization, the absence of strained carbon atoms renders this 2-D material significantly less reactive than fullerenes or CNTs. Initial attempts toward its derivatization consisted in the exfoliation of graphite flakes through oxidation reactions [i.e., graphene oxide formation] followed by chemical functionalization and reduction of the material to recover as much as possible the graphene structure. The main drawback of this route is that, in most of the cases, the intrinsic electronic properties of graphene are not fully recovered. Later on, the liquid-phase exfoliation of graphite⁴⁴ evolved as a method to obtain stable dispersions of few defect, single-to-few-layer graphene which could be further modified by means of protocols previously applied for the functionalization of SWCNTs, such as cycloaddition or insertion reactions.

Taking advantage of this breakthrough, we undertook the covalent linkage of Pcs to nonmodified graphene obtained by sonication-induced, liquid-phase exfoliation of graphite powder in *N*-methylpyrrolidone (NMP).⁴⁵ The few-layer graphene suspension obtained was subjected to a former 1,3-dipolar cycloaddition with a large excess of *N*-methylglycine and 4-formylbenzoic acid with the aim of maximizing the functionalization of the poorly reactive graphene layers. The resulting carboxylic acid-modified graphene **15** was subjected to an esterification reaction with hydroxymethyl-containing H₂Pc **16** resulting in nanoconjugate **17**, which was unequivocally characterized from a combination of different techniques (Figure 10). Thus, AFM, transmission electron microscopy (TEM), and Raman spectroscopy confirmed the single-to-few layer character of the Pc–graphene nano hybrid material, whereas support for the covalent functionalization of the graphene surface was obtained from FTIR. TGA experiments indicated a functionalization ratio of one Pc per 1600 graphene

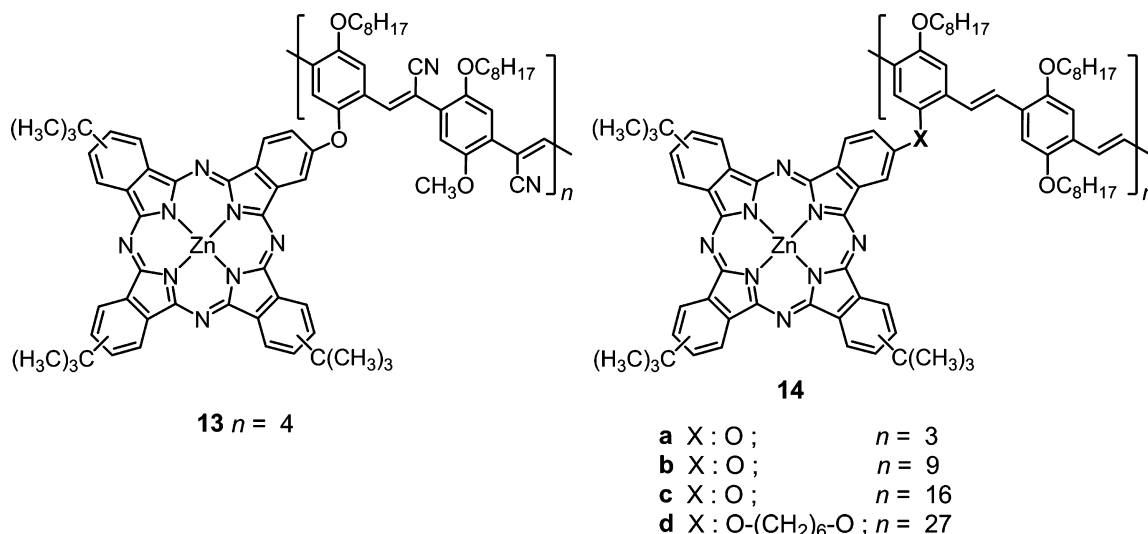


Figure 9. Molecular structures of n-type (**13**)^{41,46} and p-type (**14**)^{41,42,47} Pc-based PPV oligomers.

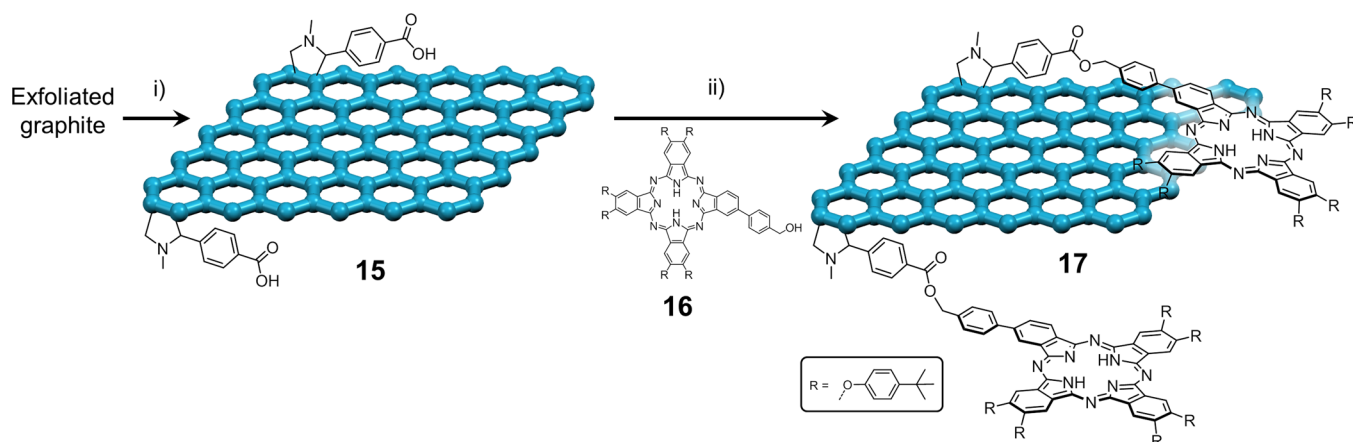


Figure 10. Synthetic route toward Pc–graphene nanoconjugate **17**.⁴⁵ Conditions: (i) 4-formylbenzoic acid, *N*-methylglycine, *N*-methylpyrrolidone, 170 °C, 6 days; (ii) 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide, 1-hydroxybenzotriazole, DMF/THF, rt, 4 days.

carbon atoms, although considering that a high content of few-layer graphene is present in the material, the real Pc-to-graphene carbon ratio at the surface should be higher since the “inner” layers remain unfunctionalized. Yet, a relatively low functionalization degree of the graphene surface was achieved, something beneficial to preserve the graphene electronic properties. Steady-state and time-resolved spectroscopic techniques were used to assess electronic interactions between the Pc molecules and the graphene layers in **17**, demonstrating the electron-accepting ability of graphene. Electron transfer from H₂Pc to graphene was assessed by the formation of the typical features of the one-electron oxidized H₂Pc together with the concomitant bleaching of the graphene-related transitions.

Aromatic building blocks such as pyrene derivatives and conjugated polymers feature strong adhesion capabilities toward graphene through π – π stacking interactions and have been used for the exfoliation of graphite and the stabilization of the resulting exfoliated material.⁴⁶ In this context, Pc-based, single-to-few-layer D–A graphene nanohybrids can be, then, obtained by attaching any of these “anchoring” units to electron-donating Pcs. In particular, *n*-type and *p*-type poly(*p*-phenylene vinylene) oligomers containing lateral Zn(II)Pcs, **13** and **14a–c** respectively (Figure 9), were able to assist the exfoliation of graphite in THF to form stable nanohybrids, which featured charge separation evolving from photoexcited Zn(II)Pc to graphene.^{47,48} To explore its potential in solar energy conversion applications, prototype solar cells were prepared, although low IPCE values (ca. 1%) were achieved.

As in the case of SWCNTs, pyrene is a useful auxiliary unit that can be used to enforce the interaction of pyrene-based Pcs with the graphene surface. Fukuzumi, D’Souza, and co-workers have directly linked four pyrene entities to a H₂Pc macrocycle. Few-layer graphene dispersions obtained by sonicating graphite flakes in different solvents were mixed with solutions of a pyrene-functionalized H₂Pc derivative.⁴⁹ Femtosecond transient absorption spectroscopy carried out on this D–A hybrid provided clear evidence for ultrafast charge separation due to close proximity of the donor and acceptor entities.

More recently, the first reports of covalent⁵⁰ and supramolecular⁵¹ Pc–graphene ensembles showing an “inverted” graphene-to-Pc photoinduced charge transfer dynamics have been reported, based on electron-accepting, alkylsulfonyl-substituted Pcs. In these systems, peripheral functionalization of Pcs with strong electron-withdrawing substituents leads to a

significant reduction of the HOMO and LUMO energies, thus making feasible an electron transfer process from the graphene sheets to the photoexcited Pc in Pc–graphene hybrids. In this context, a covalently linked Pc–graphene ensemble has been prepared by a “click” reaction between an azido-containing electron-accepting Zn(II)Pc and phenylethynyl-derivatized graphene.⁵⁰ On the other hand, linking pyrene to a alkylsulfonyl-functionalized Pc facilitates exfoliation of graphite leading to stable Pc–graphene supramolecular materials **18** (Figure 11).⁵¹ Both ensembles unequivocally show ultrafast

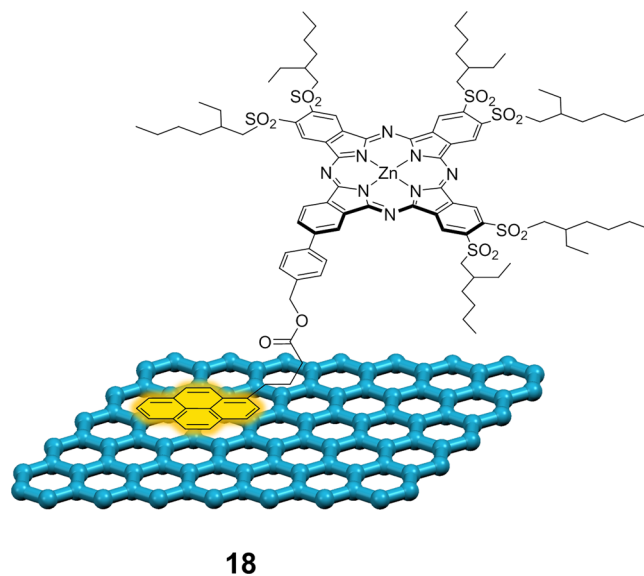


Figure 11. Molecular structure of supramolecular Pc–graphene ensemble **18**.⁵¹

photoinduced charge separation, that is, the generation of the one-electron reduced radical anion species of the Zn(II)Pc and formation of oxidized graphene.

CONCLUSIONS AND OUTLOOK

During the past few decades, significant effort has been made by several researchers and ourselves toward the preparation of D–A, Pc–nanocarbon ensembles able to undergo light-stimulated charge separation, a phenomenon of primary importance in energy solar conversion schemes. In particular,

in a photovoltaic context, Pcs and carbon nanostructures are ideal partners to achieve long-lived charge separated states and high charge mobilities, together with long-term stability of the devices. Although a fine-tuning of the electronic features and relative arrangement of both donor and acceptor moieties is nowadays possible, an accurate prediction of the kinetics of the charge transfer events, both in solution and in bulk, still remains a major issue.

In this Account, we have highlighted some recent advances in the construction of covalent and supramolecular Pc–nano-carbon conjugates and analyzed their photoinduced charge separation features. Along this journey, from the first discrete Pc–C₆₀ conjugates to the latest works involving the functionalization and exfoliation of graphene with Pcs, a great expertise on the chemical protocols toward the preparation of Pc–carbon nanostructure systems and a profound understanding of the factors governing their photophysics have been achieved. Nevertheless, much room for improvement can be still envisaged in this research area. In this regard, some possible future developments may include the following aspects: (1) Achieving fine control of the organization of Pc–carbon nanostructure ensembles in different condensed phases. The preparation of D–A architectures that present a high degree of order, spanning from the nanoscopic to the macroscopic level across multiple length scales, is highly desirable and could lead to a tremendous step forward in the utilization of these D–A systems within the fast-growing fields of nanoscience and nanotechnology. (2) Exploiting further the use of electron-accepting Pcs in carbon nanostructure-based ensembles as a new paradigm of “inverted” D–A systems for photoinduced charge separation. (3) Developing a new family of covalent and supramolecular Pc-based D–A systems containing endohedral fullerenes. These fullerenes, scarcely employed in materials science due to their low availability and reduced chemical reactivity, present a redox chemistry that can be finely tuned as a function of the encapsulated species converting them into either electron donor or acceptor moieties for Pcs. In this context, connecting two redox versatile units such as Pcs and endohedral fullerenes may lead to a plethora of D–A structures that could be screened as components in technologically relevant materials.

To end with, a bright future can be foreseen for these “bright” materials, especially in applications related to solar energy conversion schemes and organic electronics.

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Notes

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