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Bidirectional charge-transfer behavior in carbon-based hybrid nanomaterials

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In recent years there has been a growing interest in finding materials revealing bidirectional charge-transfer characteristics, that is, materials behaving as an electron donor or an acceptor in the presence of redox and photoactive addends, for optoelectronic applications. In this respect, carbon-based nanostructures, such as graphene and carbon nanotubes, have emerged as promising nanomaterials for the development of hybrid systems for bidirectional charge transfer, whose behaviour can be switched from donor-type to acceptor-type by simply changing the electroactive counterpart to which they are anchored. In this review we provide an overview of the main advances that have been made over the past few years in carbon-based hybrid architectures involving different types of carbon nanostructures and photosensitizers. In particular, carbon nanotube and graphene-based hybrid systems will be highlighted.

1. Introduction

During the last decade, a great deal of research effort has been devoted to the investigation of carbon-based nanoforms (CNFs), such as fullerene C_{60}, carbon nanotubes and gra-

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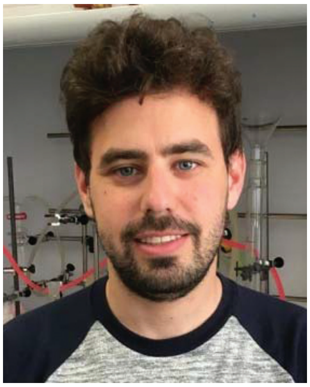

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Luis M. Arellano received his BS degree in chemistry (2013) and his Master's degree in Nanoscience and Nanotechnology (2015) from the University of Castilla-La Mancha (Spain). He holds a fellowship of the Spanish Department of Science, Innovation and Universities and he is currently working on his doctoral thesis in Prof. Langa's group at the institute of Nanoscience, Nanotechnology and Molecular Materials (INAMOL, Toledo, Spain). His main research covers the functionalization and characterization of synthetic carbon allotropes such as fullerenes, nanotubes, graphene and well as doped graphene materials for optoelectronic devices.

phene, due to their superior thermal, mechanical, electrical, optical and chemical properties.[1–4] The combination of these outstanding properties with those arising from different types of electroactive counterparts based on different photosensitizers, with either donor or acceptor behaviour, provides new organic donor–acceptor (D–A) hybrid systems and bring together the best features of the individual constituents in a unique functionalised material with enhanced properties.[5–7]

To date, as-synthesised CNF-hybrid materials have shown promise to break through barriers in future technologies and become imminent building blocks for a wide array of applications, particularly in the production of new light energy harvesting or energy conversion materials, photonic devices, and photocatalysis.[8–17] Thus, considerable efforts have been made to develop donor–acceptor hybrids based on CNFs that undergo efficient photoinduced charge separation processes.[9,18–20]

One of the key factors for the use of carbon-based hybrid nanomaterials in optoelectronic devices is to avoid the disruption of the ideal π-electron system that is responsible for the inherent superior electronic properties and high conductivity of CNFs. To this end, different approaches have been described in the literature to design active D–A architectures based on CNFs with photoactive molecules,[21] namely covalent functionalisation or supramolecular interactions. However, both methods have various advantages and disadvantages and the choice of the appropriate method should be driven by the final application of the material.

Covalent chemistry[13,22,23] involves anchoring of the photoactive molecule through the generation of new bonds between the two entities. This method leads to the saturation of double bonds thus affecting electronic properties of the CNFs. However, despite the disruption of the extended π-conjugated structure, the resulting hybridized materials show higher stability and, in some cases, π-conjugation *via* the new linkage. Furthermore, a slight disruption of the π-conjugated structure can be achieved by simply controlling the degree of functionalisation. On the other hand, the supramolecular or non-covalent approach[22,24] is an alternative strategy to generate CNF-based hybrid materials using only intermolecular forces, thus avoiding the disruption of the π-conjugated structure. However, this type of functionalisation leads to hybrid structures with reduced stability due to the presence of weak binding forces between the entities. Thus, the covalent approach is normally preferred, since hybrid materials obtained through covalent chemistry have a markedly higher solubility in various solvents, which increases their processability, and more efficient electronic communication in the resulting D–A materials.

Finally, it is important to note that bidirectionality can be achieved during the preparation of carbon-based hybrid nanomaterials under certain conditions. In general, CNFs have been employed as electron-acceptor due to the relative positions of their HOMO–LUMO energy levels with respect to a wide variety of photoactive counterparts with electron-donor properties.[25] Additionally, the delocalization of the electrons along the π-conjugated structure facilitates the stabilisation of the radical anion of CNF ($CNF^{\bullet -}$), which favours electron-transfer from the anchored electron-donor moiety to the CNF. Nonetheless, CNFs are able to accept or donate electrons depending on the relative energy levels of the different moieties involved in the formation of the hybrid structure.[11] As an example, CNFs usually act as the electron-acceptor when porphyrins (Pors) or phthalocyanines (Pcs) are involved in the hybrid material, whereas in the presence of fullerenes or perylene diimide they act as the electron-donor (Fig. 1). This is an interesting topic in the fields of materials chemistry and molecular electronics, particularly for the design of new photoactive materials based on CNFs.

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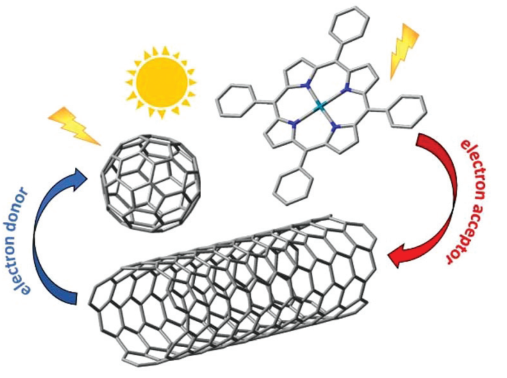

Fig. 1 Bidirectional charge transfer behaviour shown by carbon nanotubes under light excitation when they are interfaced with different types of electroactive counterparts.

In this Minireview, we will cover recent findings made by our research groups, as well as other groups, working in the field of the optoelectronic properties of carbon nanotube and graphene hybrid structures. Particular emphasis will be placed on the bidirectional charge transfer behaviour; typical property of these materials.

2. Bidirectional charge transfer behaviour of carbon nanomaterials covalently functionalised with different photosensitizers

2.1 Hybrid nanomaterials based on carbon nanotubes

Carbon nanotubes (CNTs) constitute a valuable starting material for the preparation of D–A hybrid structures with photo- or electro-active organic units. The remarkable electrical conductivity and good chemical stability of CNTs are promising properties for the formation of novel functional D–A systems where the electron/hole transfer properties are directly related to the π-conjugated structure and the nanotube type, diameter, and chirality.[11,14,26,27] Among the different types of carbon nanotubes, single-walled carbon nanotubes (SWCNTs) have been extensively studied for the development of D–A systems because of their mechanical, electrical and optical properties that are superior to those of multi-walled carbon nanotubes (MWCNTs).[15,28] However, in recent years a new, interesting, and scarcely studied family of CNTs, known as double-walled CNTs (DWCNTs), have attracted significant attention, since these combine the properties of both SWCNTs and MWCNTs, thus exhibiting the high conductivity and flexibility of the SWCNTs and the chemical stability of the MWCNTs.[29–32] However, the most important property of DWCNTs is their capacity to retain conductive behaviour after covalent functionalisation of the outer walls. This unique behaviour is attributed to the presence of an inner shell that will remain intact after the functionalisation of outer tube.[33–40]

In this section, the most relevant results in the development of D–A hybrid structures – including these two classes of CNTs (SWCNTs and DWCNTs) – will be reviewed with an emphasis on the effect of the different electroactive molecules on the bidirectional charge transfer behaviour of the CNTs.

2.1.1 CNTs as electron-accepting unit. Most of the reported studies on covalent attachment on CNTs concern condensation reactions as the method to immobilise different photosensitizers onto the CNT wall, with ester[41–44] or amide[44–46] linkages formed between the components. However, a highly defective CNT framework is generally obtained by this method and the functionalisation takes place mainly on the edges and is not homogeneously distributed on the sidewalls. Thus, different covalent approaches have emerged in recent years to overcome this drawback and extend the π-conjugated system. These approaches include diazonium salt chemistry[47–51] and 1,3-dipolar cycloaddition reactions[52–54] or post-functionalisation by Suzuki cross-coupling,[55] Sonogashira cross-coupling[56–58] and copper-catalysed 'click' chemistry reactions[59–63] (Fig. 2). The methods described here are also applicable to other CNFs, as discussed later for the functionalisation of graphene.

Pors and Pcs have been widely employed as electron donors for the development of D–A hybrid systems with SWCNTs.[22,64] The first example in which Pors and SWCNTs were combined was described by Li *et al.* in 2004.[42] In this work, SWCNTs were covalently tethered with derivatized Pors. Steady-state and time-resolved fluorescence investigations confirmed the occurrence of energy transfer from the Por to the SWCNT and revealed that it was dependent on the length of the tether that linked the porphyrin moiety to the nanotube.

In another example, a Pc derivative was covalently linked by a 1,3-dipolar cycloaddition reaction to the sidewall of SWCNTs followed by esterification of the derivatized CNTs (Fig. 3a).[52]

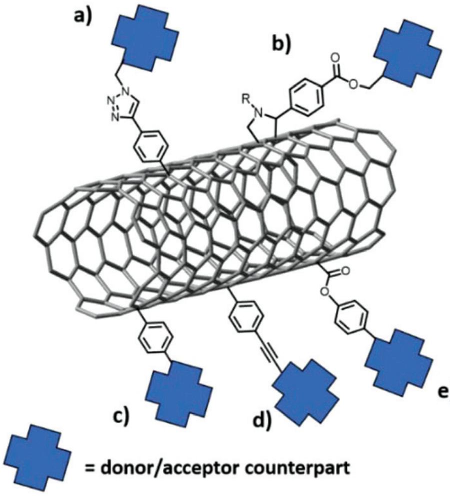

Fig. 2 Covalent Immobilization of different addends onto the CNT sidewall *via* different approaches: (a) 'click' chemistry, (b) 1,3-dipolar cycloaddition, (c) diazonium chemistry, (d) Sonogashira cross-coupling and (e) condensation reaction.

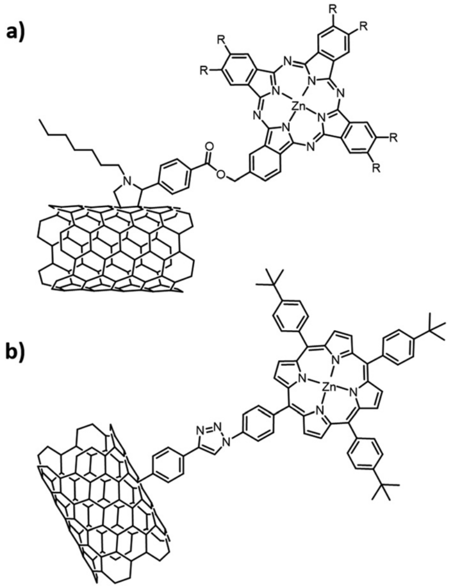

Fig. 3 Representative examples of covalent functionalization of SWCNTs with (a) an electron-donating ZnPc and (b) an electron-donating ZnPor.

Transient absorption experiments demonstrated the existence of photoinduced electron transfer (PET) from the Pc singlet excited state to the conduction band of the SWCNT. A similar approach was followed by D'Souza *et al.* to develop SWCNT–Por hybrid systems.[54] In this study they employed enriched (6,5) and (7,6) SWCNTs. Photoinduced electron transfer was demonstrated by nanosecond transient absorption experiments and the best charge separation efficiency was observed for the (7,6) SWCNT hybrid system.[54]

In a different study, Pcs or Pors were attached to SWCNTs by 'click' chemistry.[63] The resulting materials showed a rapid charge separation process when the electron-donor moieties were selectively photoexcited (Fig. 3b). Interestingly, the combination of the two moieties yielded materials with improved absorption in the visible region and the existence of excited-state interactions in the hybrid material was deduced from the effective quenching of the fluorescence intensity.[63]

Recently, we reported an efficient method to functionalise CNTs using Sonogashira C–C cross-coupling that improved the electronic communication between the units through the extension of the π-conjugation by direct attachment of triple bonds.[56–58] This method provided an excellent tool for the design and functionalisation of D–A hybrid systems. Thus, new covalent hybrids that combined DWCNTs as the electron-acceptor with electron-rich groups, such as MPcs (M = Zn or Si), were synthesised through a two-step synthetic approach.[56] In this study, two different Pcs were used: one fully conjugated peripherally substituted ZnPc, which is frequently used as an electron donor, and a new interesting family of non-conjugated axially substituted SiPcs, which showed a novel axial-bonding with a dipole moment perpendicular to the macrocycle that favours the electronic properties (Fig. 4).

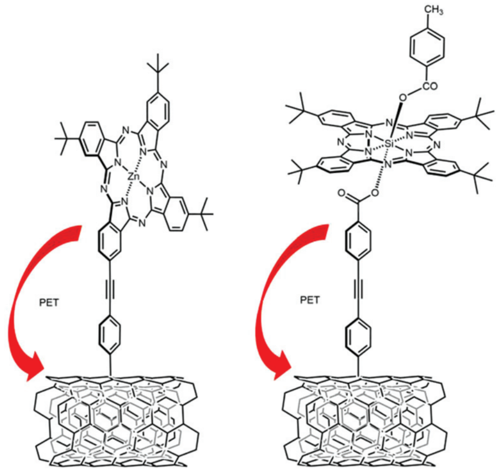

Fig. 4 DWCNT covalent hybrids involving the donors ZnPc and SiPc.

The existence of excited-state interactions in the DWCNT–MPcs hybrid materials was demonstrated by the effective quenching of the corresponding MPc fluorescence signal, which suggests the presence of intraconjugate interactions. Femtosecond transient absorption and photocatalytic electron pooling revealed the occurrence of PET as the main mechanism of deactivation. This process was evidenced by the formation of short-lived ZnPc or SiPc singlet excited states and new transient species in the NIR region attributable to the radical cation ($MPcs^{\bullet+}$), which revealed efficient excited state interactions from the MPc (donor) to the DWCNT (acceptor).[56]

Other electroactive Pors were also explored by our group as counterparts for the covalent functionalisation of SWCNTs and DWCNTs.[57] Here, a comparative study was carried out and both types of CNTs (SWCNTs and DWCNTs) were covalently functionalised with charge-stabilising zinc porphyrins (ZnPor) (Fig. 5).[57] A ZnPor with electron-rich *meso*-triphenylamine (TPA) groups was chosen due to its ability to stabilise the porphyrin radical cation in the charge-separated state, thus favouring the electron-transfer process over energy transfer.[65] Indeed, fluorescence studies suggested that the electron-transfer process was preferred over energy transfer during the deactivation mechanism (Fig. 5). Finally, the existence of electron transfer was confirmed by transient absorption spectroscopy, which revealed the formation of new species ascribed to the radical cation of ZnPor and a red-shift of the van Hove singularities of the nanoconjugates when compared with the *pristine* materials. Further studies based on electron pooling experiments confirmed the existence of photoinduced charge separation through the formation of the radical ion-pair $ZnPor^{\bullet+}$–$SWCNT^{\bullet-}$.[57] Based on these results, it was concluded that this material could be used efficiently as a photocatalyst in light-harvesting schemes.

As mentioned above, the electronic nature of the nanotube and its diameter and chirality play an important role in the final efficiency of the photochemical behaviour in D–A hybrid systems.[11,14,26,27] In general, the nanotubes with larger dia-

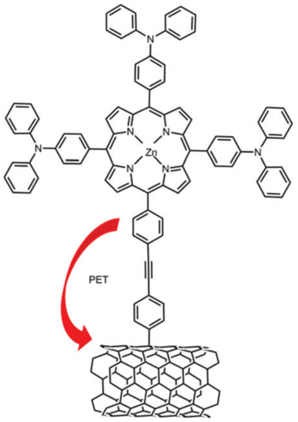

Fig. 5 D–A hybrid system involving an electron donor ZnPor and SWCNT obtained *via* a two-step reaction (diazonium salt chemistry + Sonogashira cross coupling).

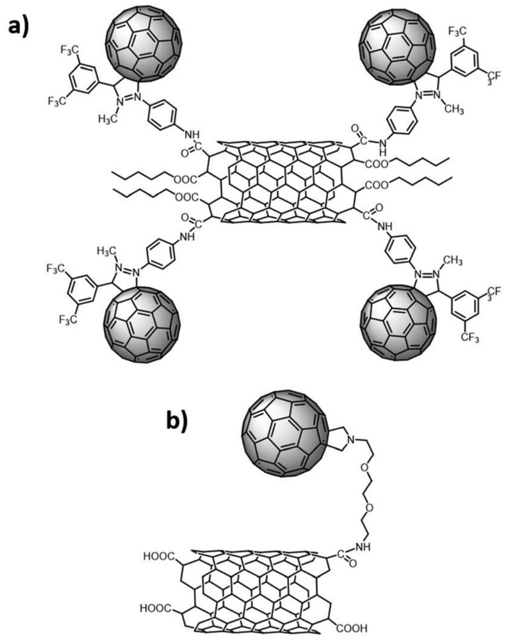

Fig. 6 Hybrid structures involving SWCNTs and different electron-acceptor moieties: (a) pyrazolinofullerene derivatives and (b) pyrrolidino-fullerene derivatives.

meters show stronger interactions, faster charge separation, shorter recombination and better electron pooling efficiency. In this respect, several attempts have been made to optimise the building of D–A hybrid systems involving SWCNTs with different chirality indices.[54,66–69] Our groups reported on CNTs with different chiralities [HipCo, which a complicated mixture (metallic and semiconducting), and enriched semiconducting (6,5 and 7,6) SWCNTs] modified with Zn- and Si-phthalocyanines.[58] The existence of excited-state interactions in these hybrids was probed by fluorescence quenching. The shift and quenching of the fluorescence signal indicated a rapid de-activation of the photoexcited Pcs in the hybrids. Charge separation was further confirmed by femtosecond transient absorption spectroscopy due to the formation of transient species corresponding to $Pc^{\bullet+}$. Finally, electron pooling experiments confirmed the existence of charge separation and provided valid proof for the utility of these materials in catalytic light harvesting applications. The results revealed better catalyst performance for ZnPc derivatives due to its greater electron-donating ability. Additionally, the best electron pooling efficiency was found for SWCNT(6,5) functionalised hybrids.[58]

2.1.2 CNTs as electron-donating unit. Beyond the anchoring of electron-donor such as porphyrins and phthalocyanines, other electroactive molecules have been attached to CNT walls and this has highlighted the bidirectional charge transfer behaviour of carbon-based materials. Thus, a wide range of electron-acceptor molecules has been integrated within the CNT surface.[7,23,70]

Early studies involving CNTs that behaved as electron-donor were based on the anchoring of electron-acceptor fullerene derivatives at the caps of the SWCNTs.[6] In this context, the first hybrid material that combined a C_{60}-fullerene and a SWCNT was developed by our group (Fig. 6a).[71] The new hybrid material was prepared by amide formation between acid-functionalised SWCNTs with an amine-functionalised-C_{60} derivative and its formation was demonstrated by several characterization techniques. However, the existence of electronic communication between the units of this type of system was demonstrated later by Wu *et al.*, who confirmed the existence of ground-state electron transfer from the SWNT to the C_{60} moiety in a grapevine nanohybrid based on CNTs covalently functionalised with C_{60} derivatives (Fig. 6b).[72]

CNTs covalently modified with C_{60} derivatives have also been used to improve optical-limiting devices (Fig. 7).[73,74] In both hybrid structures, better optical-limiting performance was observed in comparison with the individual components. In these systems, the energy transfer was proposed to occur from the ^{1}CNTs* exciton (donor) to form the fullerene singlet excited state (acceptor), followed by a rapid intersystem crossing from the singlet ($^1C^*_{60}$) to the triplet ($^3C^*_{60}$) state of the fullerene unit. It was concluded that the charge transfer between the CNTs and the fullerene moieties may play an important role in the improvement of the process.

More recently, we developed new hybrids based on DWCNTs (as electron-donor) that were combined with electron-acceptor perylenediimides (PDIs).[75] In this work, the covalent decoration of the DWCNT walls was achieved by two different synthetic procedures: amide bond formation using the typical Steglich esterification conditions and 'click' chemistry (Fig. 8).

The existence of ground-state interactions was confirmed by UV-vis spectroscopy. Most importantly, these studies revealed the appearance of a new band that was influenced by the solvent polarity, thus suggesting the existence of a dynamic process that was assigned to charge transfer. This process and the existence of energy or electron transfer processes were also supported by fluorescence deactivation of the new hybrids as

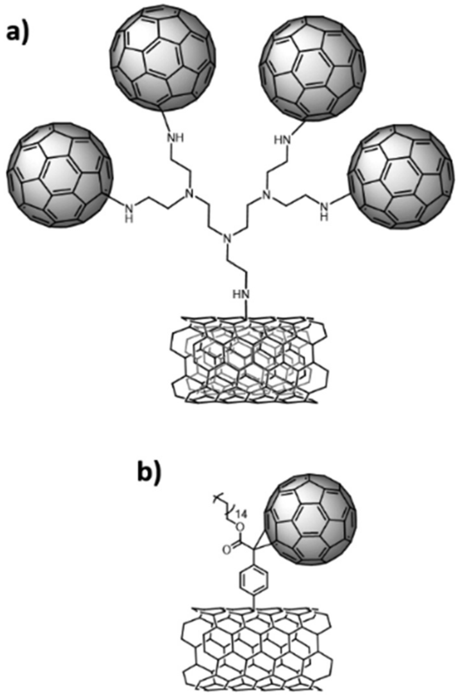

Fig. 7 (a) C_{60}-DWCNT and (b) C_{60}-SWCNT hybrids used in optical-limiting devices.

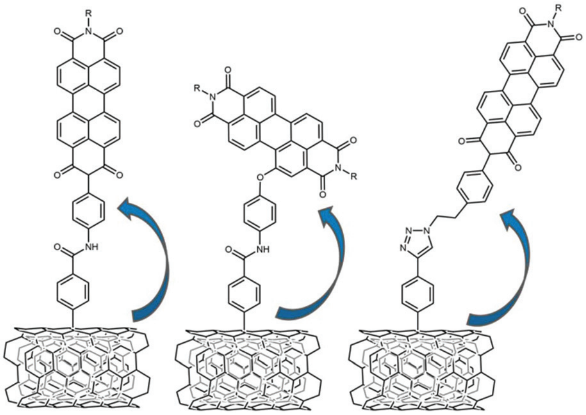

Fig. 8 Covalent grafting of PDIs onto the DWCNT external wall *via* amide bond formation and 'click' chemistry.

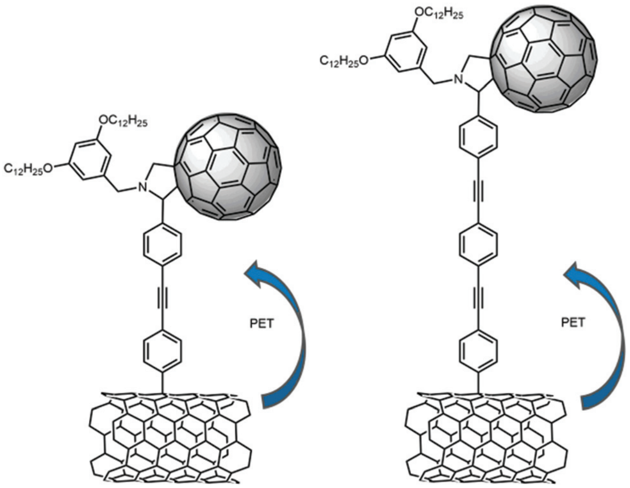

Fig. 9 Different SWCNT-C_{60} nanoconjugates with two different bridge lengths.

compared with the PDIs precursor. Nevertheless, femtosecond absorption studies did not confirm the existence of photoinduced electron transfer because of rapid recombination in the process and the presence of SWCNT impurities, whose exciton peaks masked those arising from the PDI-DWCNTs.[75] Furthermore, due to the poor electron-transfer ability typical of DWCNTs,[43] additional weak evidence of the existence of electron transfer in the hybrid materials was confirmed by electron pooling experiments.

In the same line, we combined SWCNTs with an electron-acceptor C_{60} derivative by a Sonogashira C–C cross-coupling using two different bridges (Fig. 9) in order to study the influence of the distance between the donor (SWCNT) and the acceptor (C_{60}).[76] The existence of electron transfer or energy transfer upon excitation of the SWCNT was established by femtosecond absorption studies. The results supported the existence of photoinduced charge separation in both synthetized hybrids due to the presence of a relatively weak signal at around 1000 nm ascribed to $C_{60}^{\bullet-}$. Similarly, the fast recovery of SWCNT excitonic peaks compared with *pristine* SWCNT due to the competitive electron transfer provided further evidence. Finally, the results of these studies suggested that the increased distance between the donor and the acceptor reduces the existence of charge separation.[76]

2.2 Hybrid nanomaterials based on graphene

Due to its unique structure and remarkable properties, such as good conductivity, high electron mobility, superior chemical stability and large surface-to-volume ratio,[77–80] graphene has generated increasing interest in recent years for device applications.[81–84] Nowadays, *pristine* graphene can be obtained by several methods such as mechanical cleavage,[85] laser ablation and photoexfoliation,[86] epitaxial growth on single-crystal SiC,[87] chemical vapour deposition,[88] sonication/intercalation[89] or ball milling.[90] *Pristine* graphene consists of intact π-lattices of single-layer or few-layer graphene sheets and has the advantageous ability of transferring electrons along its 2D crystal structure without scattering (ballistic transfer).[91] However, this material is fairly insoluble in common solvents and this limits its applicability. This situation has led the scientific community to focus their attention on the fabrication of D–A hybrid structures that are potentially useful for electronic applications and solar energy conversion.[92]

As described for the CNTs, graphene can behave as the electron-donating or electron-accepting unit depending on the electronic nature of the counterpart. Additionally, the formation of such D–A hybrid systems is promising because the interaction between the two units results in a shift in the

Fermi level and the subsequent opening of an electronic band gap. The latter is often desired for the application of graphene in the field of optoelectronics. The development of covalently functionalised hybrids based on graphene and photoactive compounds is a feasible way to achieve this goal.

In this section, we will focus on the most relevant results concerning the association of graphene with electron-donor or electron-acceptor counterparts through covalent interactions as a means to modify its electronic properties and confirm its bidirectional charge transfer behaviour.

2.2.1 Graphene as an electron-accepting unit. Several examples have been described in the literature where the functionalisation of graphene with counterparts that feature electron-donating properties establishes electron D–A systems in which graphene behaves as the electron-acceptor.[25,92] In these systems, spectroscopic and kinetic evidence has been reported not only for ground-state interactions, but also for interactions in the excited state. In this context, the main body of research on the covalent chemical functionalisation of graphene with electron-donating compounds concerns the incorporation of porphyrins and phthalocyanines to afford D–A systems with promising charge separation features.[10,92] Pors and Pcs have been covalently linked by different approaches, such as amide chemistry,[93] 1,3-dipolar cycloaddition reactions,[94] Suzuki cross-coupling,[95,96] and click chemistry.[97] In these systems, photoinduced excitation of the organic electron-donor moiety resulted in promotion to the singlet-excited state and the subsequent charge-separation process, whose efficiency depends on the charge recombination rate.

As in CNTs, the major drawback of graphene is its lack of solubility in aqueous or organic solvents, which hinders its potential applications. To overcome this hurdle, early studies related to the development of graphene D–A systems based on Pors and Pcs were carried out using water-soluble graphene oxide (GO) (Fig. 10).[93,98] In both studies, amine-functionalised porphyrins (Por-NH_2) were covalently bonded to GO *via* amide bonds to yield D–A hybrid structures in which charge transfer occurred from the photoexcited singlet Por to the graphene unit, as confirmed by the existence of fluorescence quenching.[93] Additionally, this GO-Por hybrid showed enhanced nonlinear optical (NLO) properties, behaviour that was ascribed to the PET process from the Por-NH_2 to GO.[98] The photophysical properties of this GO hybrid material were evaluated two years later by steady-state and time-resolved absorption and emission studies together with electrochemistry,[99] which demonstrated the existence of electron transfer from the singlet excited state of the porphyrin to the GO sheet to yield (GO^{-}-Por^{+}).

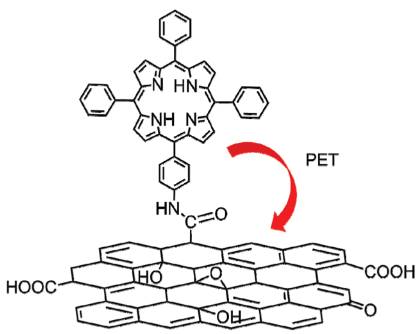

Fig. 10 Representative example of a GO hybrid structure where graphene behaves as the electron-acceptor in a GO-Por hybrid.

In a similar study, an amine-functionalised zinc-phthalocyanine (ZnPc) was covalently attached to GO by amide bond to yield a GO-ZnPc hybrid.[100] The D–A interaction between graphene and ZnPc was again based on charge transfer from the singlet excited state of the ZnPc to the graphene moiety, as confirmed by the existence of fluorescence quenching. In this case, ZnPc hybrids with pure graphene and reduced GO (RGO) were also studied. In all cases the enhanced NLO properties were attributed to the combination of non-linear scattering and light-induced energy or electron transfer from ZnPc to graphene.

In a recent study, a novel GO hybrid covalently functionalised with a zinc porphyrin bearing poly(arylene ether sulfone) through an amide linkage was prepared.[101] The existence of electron or energy transfer from the porphyrin moieties to GO was confirmed by steady and transient fluorescence spectroscopy. Finally, superior NLO performance was established for the polymer-functionalised hybrid material and this was attributed to the effective combination of non-linear scattering, reverse saturable absorption, and the photoinduced electron/energy transfer process from the donor porphyrin moieties to the acceptor graphene unit.[101]

GO has also been combined with other, less common electron-donor counterparts such as ferrocene moieties[102] and terpyridine derivatives.[103] In both cases, the existence of charge transfer processes from the attached electron-donor moiety to the GO sheet resulted in significantly improved electroactive properties that were useful for energy conversion and storage applications. In the D–A systems described above, the main drawback associated with the use of GO for the development of D–A hybrid structures was the limited electrical conductivity typical of this material, which was attributed to the existence of structural defects that disrupted the π-conjugation. In this sense, although chemical reduction of GO to give RGO is a suitable process for the partial recovery of the conjugated structure and the subsequent design of D–A hybrid systems,[96,97,104,105] the method often leads to amorphous carbon[106] and the lattice conductivity is not completely restored. Hence, GO and RGO are not suitable for applications in which the electronic properties are of primary importance. This has led the scientific community to focus on the use of wet exfoliated graphene for the development of D–A systems that have promise for optoelectronic applications.

The first example of exfoliated graphene (EG) covalently functionalised with electron-donating Pors was reported by Feringa *et al.* and this involved cycloaddition chemistry.[107] The quenching of fluorescence (or phosphorescence) and reduced lifetimes suggested the existence of excited state energy/electron transfer between graphene and the covalently attached Pc.

The main advantage of these hybrid materials is that the 1,3-dipolar cycloaddition reaction takes place with a relatively low loading, as deduced from TGA studies. Hence, the π-electronic network of graphene was preserved, thus making the hybrid material suitable for optoelectronic applications.[107]

In a similar approach, the 1,3-dipolar cycloaddition reaction was employed for the synthesis of EG-Pc hybrid structures.[94] Femtosecond transient absorption spectroscopy revealed the existence of ultrafast charge separation from the photoexcited Pc to few-layer graphene followed by a slower charge recombination.[94]

The direct nucleophilic addition of an amine-substituted Pc onto the graphene basal plane also proved to be a suitable approach for the development of D–A hybrid systems.[108] The existence of fluorescence quenching in the hybrid material and femtosecond transient absorption spectroscopy confirmed the electron-transfer process from the photoexcited Pc to graphene.

Recently, the direct covalent coupling of Pors to graphene exfoliated with graphite intercalation was accomplished in a one-pot reductive diazotization approach.[109] The existence of efficient electronic communication between the two units was deduced from fluorescence and Raman studies, thus suggesting the potential application of these systems in optoelectronics.[109]

Beyond the coupling of Pors or Pcs to EG, other photoactive counterparts have also been employed. Thus, a covalently functionalised EG with a bipyridine ruthenium complex resulted in the formation of a novel nanohybrid.[110] Fast photoinduced electron transfer from the ruthenium complex to the graphene sheet was deduced from photocurrent density-time curves, thus demonstrating high potential for applications in photocatalysis. Perylene diimide derivatives have also shown promise for the development of D–A hybrids with graphene.[110]

Electron donor π-extended tetrathiafulvalene (exTTF) units have also been anchored to EG through a combination of arylation and 'click' chemistry.[111] Although reference measurements with SWCNTs confirmed the existence of PET from the exTTF unit to the electron-accepting SWCNTs, in the case of graphene, the low degree of functionalisation did not allow proper photophysical characterization of the hybrid material.[111]

Photoactive poly(fluorene–perylene diimide) derivatives were covalently anchored by a Stille polycondensation reaction with iodobenzyl-functionalised graphene.[112] Steady-state and time-resolved photoluminescence studies revealed energy and/or charge transfer from the PDI core to graphene.[112]

In recent years, a graphene derivative consisting of nitrogen-doped graphene (NG) has emerged as a promising material for optoelectronic applications.[113] Substitutional doping of graphene with N heteroatoms is performed by a facile doping process and this allows the effective modulation of the electronic properties while maintaining high electrical conductivity.[114] Thus, the development of D–A hybrid systems based on NG with different types of counterparts is currently the main focus of our research group.

The first example of a D–A hybrid system based on NG was synthesised by our research groups in 2015.[115] In this work, a porphyrin derivative was anchored by an *N*-alkylation reaction to the pyridinic nitrogen of the graphene lattice. The existence of excited-state interactions in the hybrid material was probed by fluorescence spectroscopy, which revealed fluorescence quenching and suggested the existence of PET from the porphyrin to NG.[115]

Further investigations into the development of D–A hybrid systems based on NG have recently been performed by our group. These will be discussed in detail in the following section.

2.2.2 Graphene as an electron-donating unit. Graphene can also be used as the electron-donor provided that relatively strong electron-acceptor counterparts are employed during the development of D–A hybrid systems.[70] In this context, in early studies on D–A systems in which graphene acted as the electron-donor, our group developed an all-carbon hybrid based on GO combined with the electron acceptor C_{60} by a Cu-catalysed alkyne–azide cycloaddition reaction (Fig. 11).[116] The occurrence of PET from the GO to C_{60} was deduced from laser flash photolysis studies.

In another study, a C_{60} derivative (hydrolysed PCBM) was also employed as the electron acceptor to achieve PET from GO.[117] The charge-transfer interaction between the two units was established by photoluminescence and ultrafast pump–probe transient absorption spectroscopy, which confirmed the existence of PET from GO to the singlet excited state of the fullerene.[117]

The first example of an unmodified few-layer EG covalently functionalised with an electron acceptor Pc was described by Torres *et al.*[118] Physicochemical characterization revealed the existence of ultrafast charge separation from the photoexcited phthalocyanine to few-layer graphene followed by a slower charge recombination. The approach of choice was again the copper catalysed azide–alkyne cycloaddition 'click' chemistry reaction. Electron D–A interactions between the two units were probed through fluorescence studies and pump–probe transi-

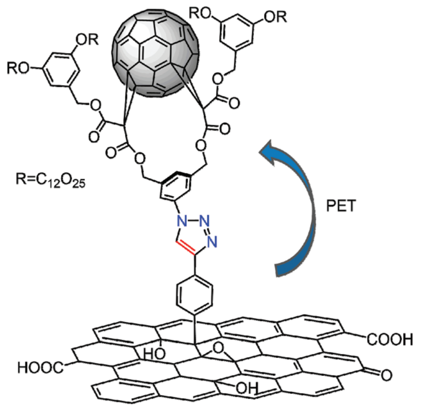

Fig. 11 Schematic representation of the electron-transfer process observed in a GO-C_{60} hybrid where GO behaves as the electron-donor.

ent experiments. The results confirmed the existence of electron transfer from the conduction band of graphene to the PCs.[118]

The most recent study involving an electron-donor graphene unit was reported recently by our groups.[119] In this case, NG was chemically functionalised by *N*-alkylation with an electron-acceptor fulleropyrrolidine (Fig. 12). Femtosecond transient absorption studies followed by photocatalytic electron pooling studies confirmed the existence of charge transfer, where the half-filled HOMO of ${}^1C^*_{60}$ could abstract an electron from the conduction band of N–G.[119]

3. Bidirectional charge transfer behaviour of carbon nanomaterials functionalised with different photosensitizers through supramolecular interactions

Nanocarbons can selectively adsorb or bind molecules based on steric constraints and the type of supramolecular interactions, and such interactions cover a wide range of energy scales depending on the type of interactions between the nanocarbon and adsorbent molecules.[120,121] Such intermolecular interactions alter the intrinsic properties of nanocarbons and this makes these structures effective for optoelectronic, nanoelectronic and sensor applications. A combination of different spectroscopic and microscopic studies is required to understand fully the effect of molecules on nanocarbons and *vice versa*. Surface techniques help in assigning the location of molecules on the nanocarbon surface while FT-IR and Raman techniques provide a wealth of information on both the adsorbent and the nanocarbon surface. Photoluminescence and absorption spectroscopy provide information about nanocarbon electronic transitions and how they are altered by coupling with molecular orbitals, including creating bandgaps in zero-bandgap materials such as graphene. Such studies will provide a deeper understanding of the mechanistic details of interactions and this will be useful for the development of practical applications of these novel materials. As part of this review, recent studies on supramolecularly assembled systems relevant to photonic applications are discussed.[25]

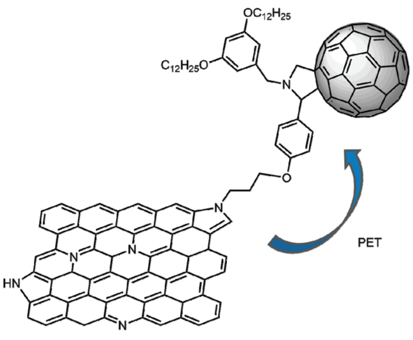

Fig. 12 Schematic representation of the electron-transfer process observed in an NG-C_{60} hybrid where NG behaves as the electron-donor.

Building of supramolecular electron donor-SWCNT (or C_{60}) and electron acceptor-SWCNT *via* self-assembled supramolecular approach has witnessed very good success in recent years.[122] Here, π-stacking ability of pyrene onto the walls of nanotubes was explored. In our earlier work, porphyrin tethered with four entities of pyrene with flexible alkyl chains (Fig. 13, compound **1**) was used to exfoliate and π-stack nanotubes wherein the nanotubes behaved as electron acceptors.[123] This approach was also utilized to decorate nanotubes with C_{60} wherein C_{60} tethered with pyrene (Fig. 13, compound **2**) was used for this purpose.[69] The role of the nanotubes in this donor–acceptor hybrid was that of an electron donor. Subsequently, this approach was modified to introduce the strategy of 'double decker' to envision significance of other intermolecular forces in the construction donor–acceptor hybrids capable of undergoing charge transfer. In these examples the tetrapyrroles acted as electron donor while nanotubes behaved as electron acceptor. This involved metal–ligand axial coordination approach wherein the π-stacking pyrene was functionalized with a nitrogenous base such as phenyl imidazole (Fig. 13, compound **3**)[124] or pyridine and allowed to interact with SWCNTs. Subsequently, the axial ligating nitrogenous base was allowed to interact with metal tetrapyrroles having coordinatively unsaturated metal ion such as zinc. This method was found to be very successfully in terms of decorating nanotubes with a variety of electron donor-sensitizers such as porphyrin, phthalocyanine, naphthalocyanine, *etc*.

Ion-pairing is also found to be a versatile approach to form donor–acceptor hybrids involving SWCNTs.[125] Here, pyrene was functionalized either with carboxylate anion to ion-pair with sensitizers functionalized with cationic peripheral groups (Fig. 13, compound **4**) or pyrene was functionalized with alkyl ammonium cation to ion-pair with sensitizers functionalized with anionic peripheral groups (Fig. 13, compound **5**). Furthermore, the self-assembly approach was extended to included ion-dipole interactions (Fig. 13, compound **6** and **7**). Here, pyrene functionalized with alkyl ammonium cation was allowed to interact with 18-crown-6 functionalized porphyrin donor[126] or fullerene acceptors.[127] Evidence of excited state electron transfer in these donor–acceptor hybrids was secured from photochemical studies involving time-resolved emission and transient absorption studies. Solar cells developed using some of these hybrids revealed light-to-electricity conversion capability of these hybrids.

In another related study, photoinduced electron transfer processes of 'three-layer' supramolecular hybrids, fullerene-porphyrin-SWCNT, which were constructed from semiconducting (7,6)- and (6,5)-enriched SWCNTs and self-assembled *via* π–π interacting long alkyl chain substituted porphyrins (tetrakis(4-dodecylalkoxyphenyl)porphyrins; abbreviated as MP(alkyl)$_4$) (M = Zn and H_2), to which phenylimidazole functionalized fullerene[C_{60}], (C_{60}Im) was coordinated were newly formed (Fig. 14).[128] The intermolecular alkyl–π and π–π inter-

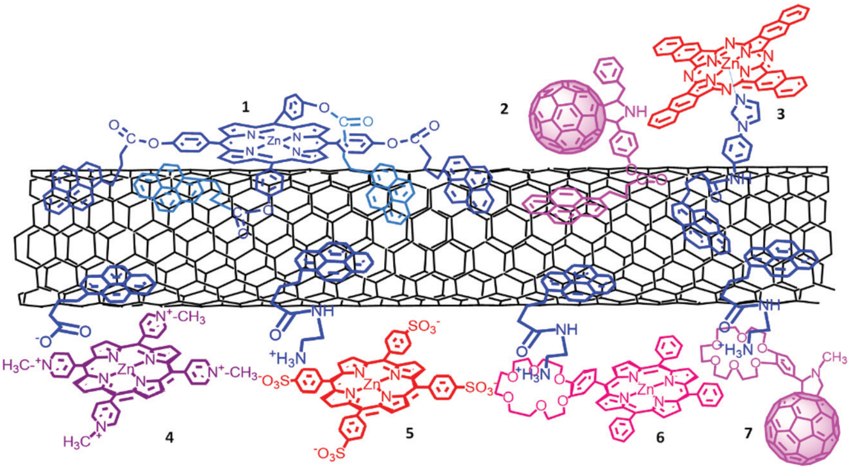

Fig. 13 Self-assembled supramolecular designs developed to form donor-SWCNT (donor = tetrapyrrole, acceptor = SWCNT) and acceptor-SWCNT (acceptor = C_{60} and donor = SWCNT) hybrids using π-stacking (**1** and **2**), and π-stacking with a combination of metal–ligand coordination (**3**), ion-pairing (**4** and **5**) and ion-dipole interactions (**6** and **7**). The photosensitizers are decorated on a single nanotube for simplicity and abbreviated as **1**, **2**, **3**, *etc*. representing different self-assembly protocols.

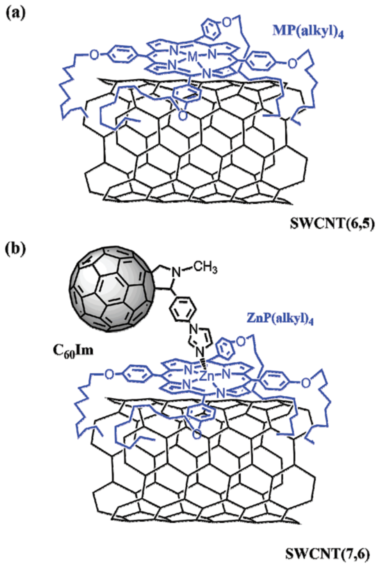

Fig. 14 Schematics of (a) two-layer $MP(alkyl)_4/SWCNT(n,m)$ and (b) three-layer $C_{60}Im$ → $ZnP(alkyl)_4/SWCNT(n,m)$ donor–acceptor nanohybrids.

actions between the $MP(alkyl)_4$ and SWCNT, in addition, coordination between $C_{60}Im$ and Zn ion in the porphyrin cavity are visualized using DFT calculations, predicting donor–acceptor interactions between them in the ground and excited states.

Upon characterization of the donor–acceptor nanohybrids by TEM imaging, steady-state absorption and fluorescence spectra, systematic time-resolved fluorescence studies were performed. The $MP(alkyl)_4$ in two-layered nanohybrids ($MP(alkyl)_4/SWCNT$) revealed efficient quenching of the singlet excited states of $MP(alkyl)_4$ ($^1MP^*(alkyl)_4$) with the rate constants of charge separation (k_{CS}) in the range of $(1–9) \times 10^9$ s^{-1}. Nanosecond transient absorption technique confirmed the electron transfer products, $MP^{\bullet+}(alkyl)_4/SWCNT^{\bullet-}$ and/or $MP^{\bullet-}(alkyl)_4/SWCNT^{\bullet+}$ for the two-layer nanohybrids.

On further coordination of $C_{60}Im$ to ZnP, acceleration of charge separation *via* $^1ZnP^*$ in $C_{60}Im \rightarrow ZnP(alkyl)_4/SWCNT$ was observed to form $C_{60}Im^{\bullet-} \rightarrow ZnP^{\bullet+}(alkyl)_4/SWCNT$ and $C_{60}Im^{\bullet-} \rightarrow ZnP(alkyl)_4/SWCNT^{\bullet+}$ charge separated states as supported by the transient absorption spectra. These characteristic absorptions decay with rate constants due to charge recombination (k_{CR}) in the range of $(6–10) \times 10^6$ s^{-1}, corresponding to the lifetimes of the radical ion-pairs of 100–170 ns. The electron transfer in the nanohybrids has further been utilized for light-to-electricity conversion by the construction of proof-of-concept photoelectrochemical solar cells.

The self-assembly approach was further extended to assemble bio-nano donor–acceptor hybrids to probe excited state electron transfer (Fig. 15).[123] Towards this, porphyrins functionalized with peripheral cations were ion-paired with ssDNA (ss = single stranded) wrapped around SWCNTs. In these 'three-component' hybrids, two kinds of diameter sorted semiconducting SWCNT(*n*,*m*)s of different diameter ((*n*,*m*) = (6,5) and (7,6)), and free-base or zinc porphyrin bearing peripheral positive charges ($(TMPyP^+)M$ (tetrakis(4-*N*-methylpyridyl)porphyrin); M = Zn and H_2) serving as light absorbing photoactive materials were utilized. The donor–acceptor hybrids were held by ion-pairing between the negatively charged phosphate groups of ssDNA on the surface of SWCNT and porphyrin bearing peripheral positive charges. The newly assembled bio-nano donor–acceptor hybrids were characterized by TEM and spectroscopic methods. Photoinduced electron transfer from the singlet excited porphyrin to the SWCNTs directly and/or *via* ssDNA as an electron mediator was established by performing systematic studies involving the steady-state and time-resolved emission as well as the transient absorption studies.

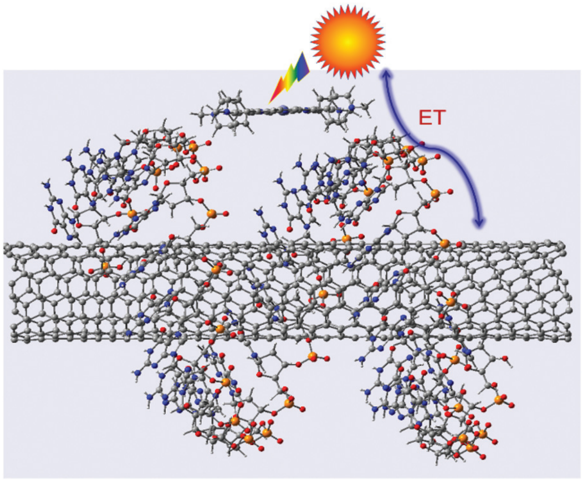

Fig. 15 Geometry optimized structure of $(TMPyP^+)Zn/ssDNA/SWCNT$ (7,6) and predicted excited state electron transfer path.

Higher charge-separation efficiency was demonstrated by the selection of the appropriate semiconductive SWCNTs with right band gap, in addition to the aid of ssDNA as electron mediator.

Having witnessed a very good success in terms of construction and photoinduced electron transfer in self-assembled donor–acceptor hybrids comprising C_{60} and nanotubes with different photosensitizers, such approach was extended to involve mono- and few-layer graphitic materials. Advantageously, the strong π-stacking of aromatic entities were successful in creating a bandgap in graphene, making them suitable for optoelectronic applications.

In a recent study the chlorosulfonic acid exfoliation method[129] was used to obtain a higher yield of exfoliated graphene and this was subsequently functionalised with the custom-synthesised oligothiophene 9T to furnish the corresponding 9T/eG ensemble (Fig. 16).[130] The 9T/eG assembly showed enhanced solubility in common organic solvents and the material was thoroughly characterised by standard spectroscopic and microscopy techniques. Optical studies provided an insight into the electronic interactions between the two components within the 9T/eG ensemble, in both the ground and excited states. The measured fluorescence lifetimes of the oligothiophene were below the time resolution of the instrumentation (50 ps) and this suggests the occurrence of ultrafast photoinduced processes in 9T/eG. The estimated free-energy change for the charge-separated state of 9T/eG *via* the corresponding singlet excited state oligothiophene (^{1}9T*) was exothermic and this reveals the thermodynamic feasibility of such a process in the ensembles. Femtosecond transient spectroscopic studies provided evidence of the occurrence of charge transfer-type interactions in the 9T/eG ensemble from ^{1}9T*. The estimated rate for photoinduced charge separation was found to be 2.2×10^{11} s^{-1} for 9T/eG in THF and this is consistent with ultrafast photoinduced events.[130]

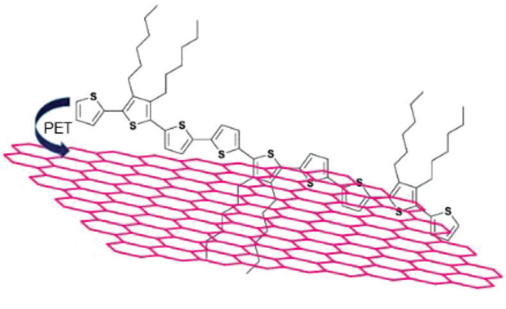

Fig. 16 Non-covalent 9T/eG assembly.

Decoration of graphene with multiple porphyrins was explored. A charged porphyrin salt was stabilised onto exfoliated graphene by taking advantage of π–π interactions, and a second porphyrin light-harvester was anchored through electrostatic interactions with the former unit.[131] The interactions were capable of allowing electronic communication between the second, electrostatically attached, porphyrin and graphene, which effectively quenched its emission. The graphene–porphyrin–porphyrin triad was examined by steady state and time-resolved optical techniques. The porphyrin that was electrostatically stabilised onto the graphene nanoensemble showed faster relaxation of the excited state than its π–π* stacked analogue, thus suggesting a more efficient pathway.

In a study by Parida *et al.*,[132] improved electron transfer efficiency was demonstrated when the photosensitizer, a porphyrin caged in β-cyclodextrin, interacted with graphene carboxylate. This improved efficiency could be useful for designing the next generation of photocatalysts.

In a recent study,[133] a chiral supramolecular light-harvesting nanotube antenna in a hydrogel was established, and the cooperative effect between chirality transfer and energy transfer was successfully demonstrated. The improved efficiency of the energy transfer in the antenna was attributed to enhanced circularly polarized luminescence (CPL), which led to a higher luminescence dissymmetry factor. Excitation of the donor in the assembled triad, namely a cyanostilbene-appended glutamate compound, CG, or intermediate donor, thioflavin ThT, led to a stepwise amplified CPL when compared with that obtained by directly exciting the acceptor, acridine orange, AO. The cooperative effect of chirality and sequential energy transfer, which provided a deep understanding of the natural light-harvesting process in chiral environments, was achieved in this study.

A newly synthesised, regioregular polythiophene with photosensitising ruthenium complexes at the side chains was shown to interact strongly with SWCNTs of 0.9 to 2.0 nm in diameter to form stable dispersions in polar solvents.[134] Ultrafast transient absorption spectroscopy revealed a rapid electron-transfer process from the excited Ru(II) complex to SWCNTs with a time constant of 167 ps. The authors highlighted the fact that the model presented was a simplified description of the photophysics in a complex disordered system that was difficult to analyse in greater detail due to limitations of the instrumentation and the properties of the

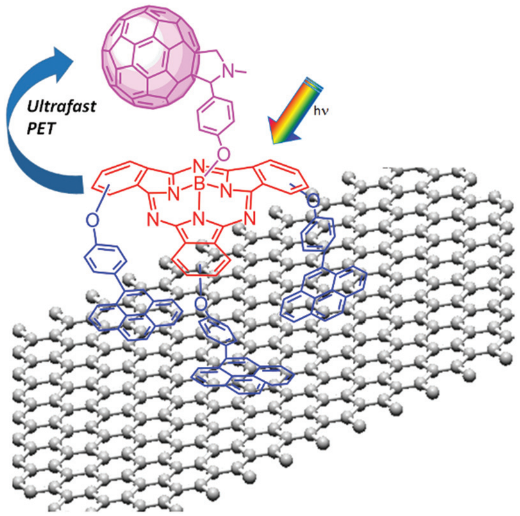

Fig. 17 Structure of the subphthalocyanine-fullerene tethered with three pyrene units, $(Pyr)_3SubPc\text{-}C_{60}$ donor–acceptor conjugate, interacting with graphene.

excited species involved. Nonetheless, the appropriate distance between the donor–acceptor made the photodynamics more manageable in this hybrid.

A new approach to probe the effect of underlying graphene on photochemical charge separation in donor–acceptor conjugates was investigated.[135] In this case, multi-modular donor–acceptor conjugates comprised of three pyrene units, a subphthalocyanine and a fullerene, $((Pyr)_3SubPc\text{-}C_{60})$, were synthesised and characterised. These conjugates were hybridized on few-layer graphene *via* π–π stacking interactions of the three pyrene units (Fig. 17).

These hybrids were characterised by Raman, HR-TEM, spectroscopic and electrochemical techniques. Fine-tuning of the energy levels of the donor–acceptor conjugates upon graphene interaction was observed. Photoinduced charge separation in these conjugates in the absence and presence of graphene was established by femtosecond transient absorption spectroscopy. Accelerated charge separation and recombination was observed in these conjugates upon decorating them on graphene. This observation suggests that the properties of the graphene–donor–acceptor hybrids are mainly attributable to hybrid rigidity upon immobilisation on the graphene surface. These materials could be useful for building fast-responding optoelectronic devices and also for light energy harvesting applications.

4. Conclusions

It is fascinating to consider that nanocarbon materials such as nanotubes and graphene show bidirectional charge transfer behaviour depending on the organic systems used to decorate their surfaces. The examples discussed in this article are mainly from our laboratories and, supported by photochemical studies involving ultrafast pump–probe spectroscopy, confirm the applicability of these materials for energy harvesting and other pertinent optoelectronic applications. Ground-breaking research efforts have shown the captivating electronic properties of these materials both in the ground and excited states and have also laid the path for future efforts, including supramolecular design, charge separation and stabilisation, charge distribution and transfer. Further research is warranted to push forward this field to exploit the full potential of these materials for future electronic device applications. A great deal can be anticipated in the near future from laboratories across the globe, particularly from chemically functionalised, heteroatom doped nanocarbon materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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