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COMMUNICATION

Supramolecular assembly of graphene with functionalized poly(fluorene-*alt*-phenylene): the role of the anthraquinone pendant groups†

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Hybrid materials composed of graphene and conjugated poly(fluorene-*alt*-phenylene) endowed with redox-active anthraquinone moieties are prepared. Remarkable changes in the electronic properties of the polymer are observed. Effective interactions among the pendant anthraquinone and graphene, likely due to π–π stacking, are confirmed.

In organic photovoltaic devices fast charge separation at the donor–acceptor interface and efficient transport of charges to the electrodes are key parameters since the interpenetrating donor–acceptor phase plays a crucial role in reaching the required device efficiency.[1] Usually the active layer of polymeric devices is a donor–acceptor bulk heterojunction composed of a conjugated donor polymer mixed with acceptor molecules or macromolecules.[2,3] Although [60]fullerene derivatives[4] and carbon nanotubes (CNT)[5] have been explored as efficient electron acceptors for solar energy conversion,[6] graphene has been less investigated in spite of its unique properties.[7] Graphene has high electron mobility and large specific area making it a competitive alternative as electron-accepting material in photovoltaic device applications. In fact, graphene has already been tested as acceptor material by mixing it with P3OT and P3HT donor materials[8,9] and better performances were obtained at moderate contents of graphene, for which better dispersion and interconnection is achieved.

Considering the possibility of using graphene as an acceptor in blends with semiconducting polymers we wondered whether it would be possible to improve its dispersion by tailoring the polymer chemistry. In this regard, functionalization of conducting polymers offers the attractive possibility of developing novel materials, which in addition to the particular optoelectronic properties of the conjugated backbone incorporate specific properties of the modifying groups. With this aim, in this communication we describe the preparation of hybrids of graphene with poly(9,9-dioctylfluorene-*alt*-1,4-yleneethylene-2,5-dihexyloxybenzene) endowed with anthraquinone (ANT) pendant groups, **PFEP–ANT** (Fig. 1) (see ESI† for synthetic details). The **PFEP–ANT**/graphene dispersions have been prepared by ultrasonic mixing of **PFEP–ANT** and expanded graphite[10] and confirmed by Raman (Fig. S2, ESI†).

The UV-vis spectrum of **PFEP–ANT** in Cl_2CH_2 displays an absorption band with a maximum at 425 nm, arising from π–π* transitions in the conjugated polymeric backbone as well as the characteristic bands of the ANT side groups, centered at 275, 303 and 349 nm. Thus, the absorption spectrum consists of the approximate superposition of the absorption features of its constitutive units without significant interaction in the ground state. The **PFEP–ANT/Grf** mixture solution shows the same absorption bands as the **PFEP–ANT** (Fig. 2). However, the less energetic band of the ANT slightly shifts from 349 nm in **PFEP–ANT** to 331 nm in the **PFEP–ANT/Grf** which might be due to aggregation of the ANT moieties induced by the presence of graphene. The UV-vis spectra collected in more polar solvents, *e.g.* NMP and DMF, show almost identical spectra for **PFEP–ANT** and **PFEP–ANT/Grf**

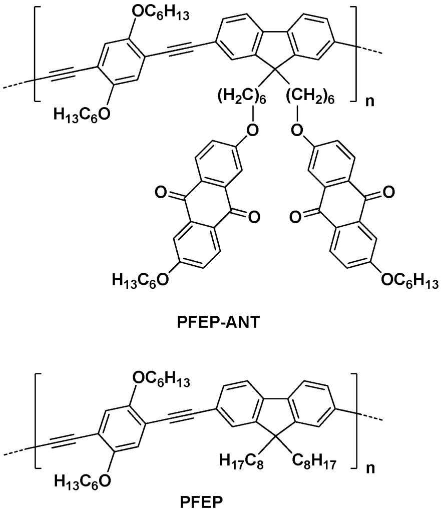

Fig. 1 Chemical structure of **PFEP–ANT**, used to disperse graphene and the reference polymer **PFEP**.

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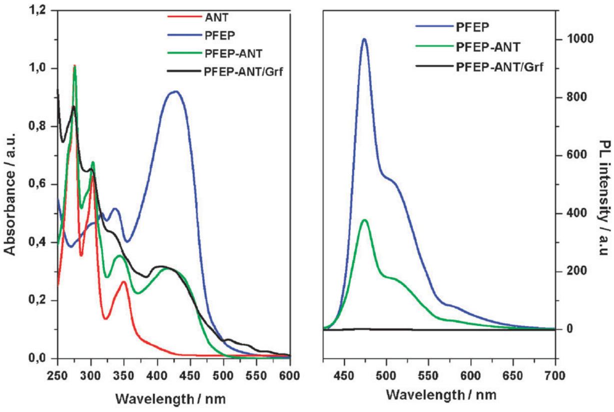

Fig. 2 Left: absorption spectra of **ANT**, **PFEP**, **PFEP–ANT** and **PFEP–ANT/Grf** in Cl_2CH_2 solutions. The concentrations of **ANT**, **PFEP** and **PFEP–ANT** are 0.005, 0.0025 and 0.01 mg mL^{-1} respectively, while it is unknown for **PFEP–ANT/Grf**. Right: fluorescence spectra of **PFEP**, **PFEP–ANT** and **PPF-ANT/Grf** in Cl_2CH_2 solutions. λ_{exc} = 426 nm.

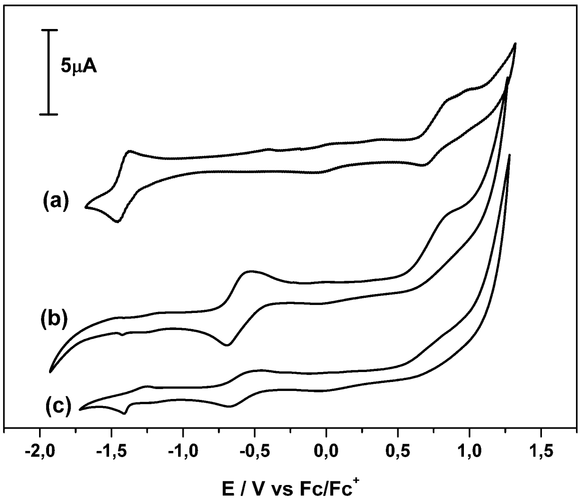

Fig. 3 Cyclic voltammograms of (a) **PFEP–ANT**, (b) **PFEP–ANT/Grf** and (c) **PFEP–ANT/G** in Cl_2CH_2/0.1 M TBAHFP solutions. Scan rate: 100 mV s^{-1}. Values *vs.* Fc/Fc^+.

(Fig. S3, ESI†), indicating the scarce influence of the solvent on the absorption results.

Regarding the emission spectra, the original photoluminescence (PL) of the **PFEP** in Cl_2CH_2 is affected by the presence of the ANT moieties, decreasing the intensity *ca.* 40% in **PFEP–ANT** due to a photoinduced electron transfer from the polymer backbone to the accepting ANT side groups.[11] In addition, for the **PFEP–ANT/Grf** mixture, a total fluorescence quenching (99.4%) is observed. The role of graphene in quenching the PL is confirmed by spectra collected in NMP, a good solvent for dispersing graphene, and in DMF, a poor solvent for graphene, where the PL of **PFEP–ANT** diminished only 38% and 95%, respectively (Fig. S4, ESI†). Although the presence of graphene is crucial to prevent the PL of the **PFEP** backbone, the photophysical reasons why that may occur are not straightforward. This behaviour can be attributed to (i) the fact that the excited fluorophore in the conjugated polymer backbone is quenched by the electronic interactions at the conjugated polymer/graphene interfaces due to the good acceptor ability of graphene[9] or (ii) a more efficient photoinduced electron transfer as a consequence of an increase of the electron acceptor character of the anthraquinone groups because of an interaction between graphene and ANT. The former case implies direct **PFEP/Grf** interactions in which the ANT plays no role, whilst the second possibility involves also significant interactions between graphene and ANT groups. The PL emission of the reference **PFEP** (Fig. 2) decreased *ca.* 85% in the presence of graphene suggesting that mainly **PFEP/Grf** interactions occur. The planar structure of **PFEP** leads us to think in π–π interactions. However, it is known that long alkyl chains have also tendency to interact with graphite laminates, while planar ANT side groups can form π–π interactions with graphene as well. Thus, graphene/polymer (i) and graphene/side groups (alkyl chains and ANT) (ii) interactions could be seen as two additive processes, the former being more significant.

In order to analyze the role of ANT we have studied the electrochemical behavior of **PFEP–ANT/Grf** and compared it with that of **PFEP–ANT**. For **PFEP–ANT**, the diagnostic quasi-reversible reduction wave characteristic of the ANT groups with $E_{1/2}$ at −1.42 V is observed. At positive values, an irreversible oxidation wave with an onset at around 0.7 V corresponding to the conjugated polymer backbone is noticed.

When **PFEP–ANT/Grf** redispersed in Cl_2CH_2 is investigated a new quasi-reversible reduction process with $E_{1/2}$ at −0.61 V appears at the expenses of that at −1.42 V, suggesting an efficient interaction between the ANT moiety and graphene that shifts 0.81 V anodically the reduction potential of the former (Fig. 3). Displacement of this magnitude has been observed for ANT bonded to carbon nanotubes.[12,13] In order to rationalize this behavior the tendency of graphene[14] and 9,10-anthraquinone[15] toward π–π stacking should be considered.

It has been observed for different electroactive compounds (*i.e.* perylenebisimide,[16] chlorophyll)[17] that π-stacked species exhibit different redox potentials in comparison with the corresponding nonaggregated systems. This is due to the fact that π–π stacking may render an effective intermolecular orbital overlap.[18] This orbital overlap between the LUMO level of the ANT and the graphene work function accounts for a splitting of the empty level[19] translating into a larger LUMO bandwidth which is in agreement with the anodic shift of the reduction potential of the anthraquinone moiety. This anodic shift accounts for the more efficient photoinduced electron transfer upon addition of graphene. Given that the orbital overlap depends on the intermolecular distance and orientation,[20] a more densely packed structure may be responsible for a more efficient orbital overlap and therefore a pronounced effect observed for the sample with graphene. Thus, an effective assembly of polymers onto graphitic sheets producing layered structures, confirmed by SEM (Fig. S5, ESI†), seems to play an important role in explaining the electrochemical behavior of **PFEP–ANT/Grf**.

However, other factors influencing the electrochemistry of ANT, *e.g.* electrolyte/solvent,[12,13] should be considered. Experiments conducted in acetonitrile (ACN) and *N*,*N*-dimethylformamide (DMF) displayed a shift of the ANT peak of **PFEP–ANT/Grf** in the same direction as in Cl_2CH_2 confirming the effective

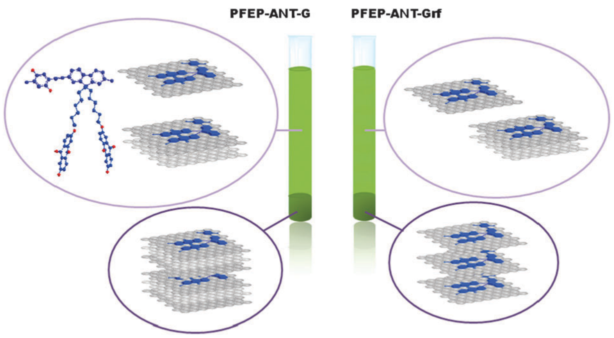

Fig. 4 Proposed assembling of graphene and **PFEP–ANT** when EG and graphite are used as sources of graphene.

graphene/ANT interaction beyond the effects of the surrounding media (Fig. S6, ESI†). We have also checked the influence of the electrolyte in terms of ion pairing effects,[12] by adding different amounts of $LiClO_4$ to the ACN/TBAHFP electrolyte. In the presence of $LiClO_4$ the ANT in **PFEP–ANT/Grf** is reduced at slightly more anodic potential (Fig. S7, ESI†), being these shifts quite small in comparison with the effect produced by the graphene and should be considered additional to the main displacement caused by graphene.

The concentration of few layers of graphene by sonication of the electrochemically expanded graphite (EG)[10] used in this experiment can reach 0.6 mg mL^{-1}. The ultrasonic treatment effectively separates the graphene laminates; therefore the **PFEP–ANT** penetrates into galleries and absorbs onto graphene sheets leading to high graphene/polymer interactions (Fig. 4). After centrifugation, the densely stacked heavy materials precipitate along with the EG that has not been exfoliated while the supernatant contains only traces of lighter species, *e.g.* thinner graphitic and/or free polymer. Therefore the stacking favors graphene/ANT interaction and, consequently a more efficient intermolecular orbital overlapping. In order to check it we repeated the experiments using graphite powder as a source of graphene laminates, since the yield in exfoliated graphene sheets is much lower than that in the other case,[21,22] being ~0.01 mg mL^{-1} (ESI†). The CV curve for this product, named **PFEP–ANT/G** (Fig. 3c), shows two redox couples at cathodic potentials, with $E_{1/2}$ around −1.33 and −0.60 V. While the former is close to the $E_{1/2}$ for the ANT moieties in **PFEP**, the second is similar to that for **PFEP–ANT/Grf**, which suggests that ANT groups could be in two different environments, *i.e.* free and stacked with graphene (see ESI† for further details).

This proves that not only the graphene concentration but also the graphene/polymer assembly influences the electrochemical behavior. The results are logical since the small spacing in graphite allows only the intercalation of small amounts of polymer and, after centrifugation, the solid is composed mostly of pure graphite and pure polymer with small amounts of polymer intercalated graphite (Fig. 4).

In summary, we have prepared hybrid materials of alternating polyfluorene copolymers with graphene with interesting electronic properties and electrochemical behaviour. An effective orbital overlap between the LUMO level of the ANT and the graphene work function is in agreement with the anodic shift of the reduction potential of the ANT and the more efficient PL quenching. Finally, an effective stacking between **PFEP–ANT** and graphene giving ordered structures has been proposed.

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