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Ultrafast charge separation in supramolecular tetrapyrrole–graphene hybrids†

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Supramolecular donor–acceptor hybrids composed of few-layer graphene as an electron acceptor and phthalocyanine or porphyrin bearing four pyrene entities as photosensitizer donors have been synthesized, and occurrence of ultrafast charge separation in the order of 10^{11} – 10^{12} s^{−1} due to close proximity of the donor and acceptor entities is demonstrated.

Graphene, single layer graphite, due to its remarkable optical and electrical properties has stimulated strong research interests in the areas of materials science, chemistry and physics.¹ In addition, the optically transparent and flexible graphene has high chemical resistance making it an ideal candidate for transparent conducting electrodes, a key component in photovoltaic devices, displays and touchscreens.² Importantly, graphene can be made into an active component for novel solar energy harvesting applications *via* donor–acceptor hybrid formation using visible-light harvesting photosensitizers. In this regard, there have been few articles describing formation of graphene–porphyrin nanohybrids.³ However, utilization of phthalocyanine, a well-known compound for its outstanding electronic properties and strong absorption beyond 700 nm, has been scarce.⁴ Additionally, compared to porphyrins, phthalocyanines are great optical probes to investigate light induced electron transfer due to their characteristic cation radical band in the 800 nm range, sufficiently far from their triplet–triplet absorption band.⁵

Often, two methods are commonly employed to build the donor–acceptor hybrids, *viz.*, covalent linkage⁶ and noncovalent bonding involving well-defined intermolecular interactions.⁷ Noncovalent bonding is preferred over covalent linkage since the latter is known to destroy the π -electronic structure of graphene by partially converting the sp^2 carbons to sp^3 carbons.⁵

In the present study, for the first time, we have constructed graphene–phthalocyanine hybrids by a non-covalent methodology involving π – π interactions. For accomplishing this task, the phthalocyanine macrocycle has been functionalized by directly linking four π -stacking pyrene entities, **1**, to facilitate the π – π interactions and exfoliation of graphene sheets. For comparison, a porphyrin functionalized with four π -stacking pyrene entities, **2**, is also employed. Here, the pyrene entities are covalently linked to the zinc tetraphenylporphyrin macrocycle by flexible linkers (Chart 1).

Scheme 1 shows the synthesis of the photosensitizer donor **1** while the experimental details are given in the ESI.† Briefly, the synthesis involved first preparation of 4-(pyrene-1-yl)phthalonitrile from a reaction between pyrene-1-boronic acid and iodophthalonitrile *via* a Suzuki coupling reaction in the presence of $\text{Pd}(\text{PPh}_3)_4$ and K_2CO_3 . Next, 4-(pyrene-1-yl)phthalonitrile was reacted in dimethylaminoethanol (DMAE) for 16 h to get the phthalocyanine derivative that was further purified by column chromatography.

Few-layered graphene dispersion was obtained by sonicating graphite flakes in *o*-dichlorobenzene (DCB) or *N*-methylpyrrolidine (NMP).⁸ In agreement with a previous report,⁴ both Raman and TEM imaging revealed 2–5 layers of graphene. Fig. 1a shows absorption spectral changes during addition of graphene to a solution of **1** in DCB. Absorption bands of **1**

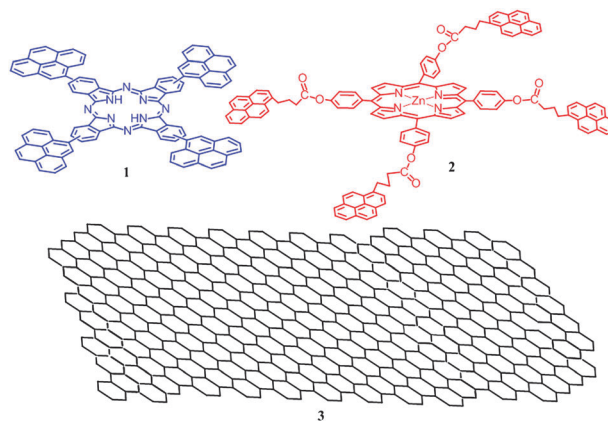


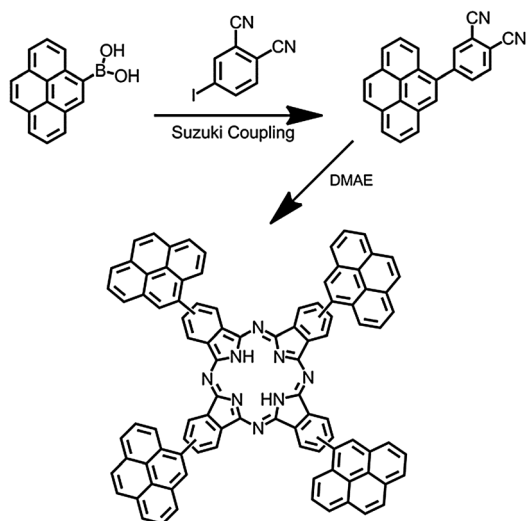
Chart 1 Structures of phthalocyanine directly linked to four pyrene entities **1**, porphyrin linked to four entities of pyrene by flexible covalent bonds, **2**, and graphene sheet (monolayer is shown for simplicity), **3**, employed in the present study.

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Scheme 1 Synthetic procedure used for preparation of **1**.

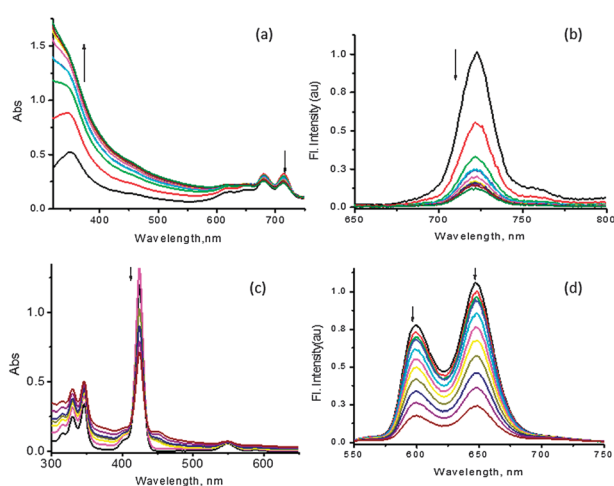


Fig. 1 Optical absorption (a and c) and fluorescence emission (b and d) spectral changes of **1** (a and b) and **2** (c and d) upon increasing addition of graphene, **3**, in DCB. Compound **1** was excited at 680 nm while **2** was excited at 424 nm.

located at 680 and 714 nm revealed diminished intensity while the band at 348 nm revealed an increase in intensity due to overlap of graphene absorption in this spectral range (Fig. 1a). Similarly, upon addition of graphene to a solution of **2** in DCB, the Soret band of **2** located at 424 nm revealed a decrease in intensity while the pyrene peaks located at 328 and 345 nm revealed an increase in intensity due to graphene absorbance in this spectral range (Fig. 1c). These results indicate π -stacking interactions between graphene and pyrene appended phthalocyanine and porphyrin macrocycles.⁵

The fluorescence spectrum of **1** revealed an emission band at 722 nm which revealed quenching over 80% of its original intensity upon addition of graphene in DCB (Fig. 1b). A similar trend was also observed for **2** in which the emission bands located at 600 and 648 nm revealed quenching over 70% of the original intensity (Fig. 1d) indicating occurrence of excited state events in the case of both **1** : **3** and **2** : **3** hybrids.

In order to ascertain that these changes are not due to dilution, in a control experiment, to a solution of **1**, equal amount of DCB (without **3**) was added. As shown in Fig. S1 in ESI,[†] both absorption and emission changes revealed no significant changes indicating that the graphene in solution is responsible for both absorption and emission changes shown in Fig. 1. To isolate the hybrids, an excess amount of **1** or **2** was treated with **3** and the solution was gently sonicated for 2–3 h for hybrid formation in addition to exfoliation of the graphene sheets. At the end, the excess sensitizers were removed by centrifugation of the hybrids (2–4 repetitions), and the donor–acceptor hybrids thus obtained were used for photochemical studies. Both TEM (Fig. 2) and Raman data (Fig. S2, ESI[†]) suggested the presence of few layer graphene while the absorption spectra revealed the presence of sensitizers in the re-dissolved hybrids (Fig. S3 and S4, ESI[†]) as evidenced from their characteristic absorption bands, more so for hybrids involving **1** due to better π -stacking geometry (flat). However, very weak emission of the sensitizers (<10%) in both **1** : **3** and **2** : **3** hybrids was observed.

A femtosecond transient absorption technique was used to monitor excited state events in the newly formed donor–acceptor hybrids. Compound **1**, immediately after excitation, revealed bands at 580 and 820 nm corresponding to instantaneous formation of $^1\text{H}_2\text{Pc}^*$ with some ground state bleaching at 710 nm (Fig. S5, ESI[†]). With time, a 600 nm band appeared corresponding to $^3\text{H}_2\text{Pc}^*$ with an intersystem crossing rate of 300 ps (Fig. S5, ESI[†]). As shown in Fig. 3a, in the case of the **1** : **3** hybrid, the transient features were different from those observed for pristine **1**. That is, the $^1\text{H}_2\text{Pc}^*$ formation was accompanied by a new band at 790 nm characteristic of $\text{H}_2\text{Pc}^{\bullet+}$ formation.⁵ A broad peak appeared in the near-IR region covering 1000–1200 nm, which has been tentatively assigned for $3^{\bullet-}$, that is, for the delocalized radical anion of graphene. The rise and decay of the 790 nm peak were analyzed to evaluate the rates of charge separation, k_{CS} , and charge recombination, k_{CR} . The evaluated k_{CS} and k_{CR} were found to be $1.4 \times 10^{11} \text{ s}^{-1}$ and $5.2 \times 10^9 \text{ s}^{-1}$, respectively (Fig. 3b).

The transient spectral features of **2** were also indicative of fast intersystem crossing of the $^1\text{ZnP}^*$ to $^3\text{ZnP}^*$ with a rate constant of $1.4 \times 10^{10} \text{ s}^{-1}$ (Fig. S6, ESI[†]). However, in the case of the **2** : **3** hybrid, upon excitation, the $^1\text{ZnP}^*$ features were observed at the 500–800 nm region accompanied by ground state bleaching of graphene in the 1000–1400 nm region (Fig. 3c). With time, although not strong due to low concentration of ZnP , transient features corresponding to the formation of $\text{ZnP}^{\bullet+}$ at

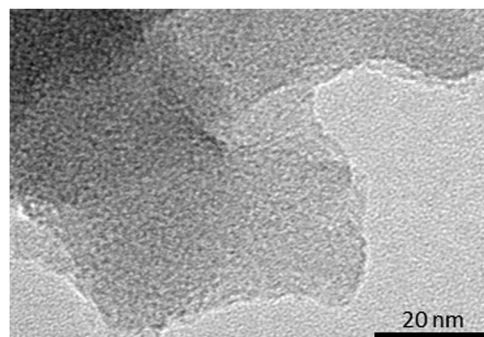


Fig. 2 TEM image of the **2** : **3** hybrid.

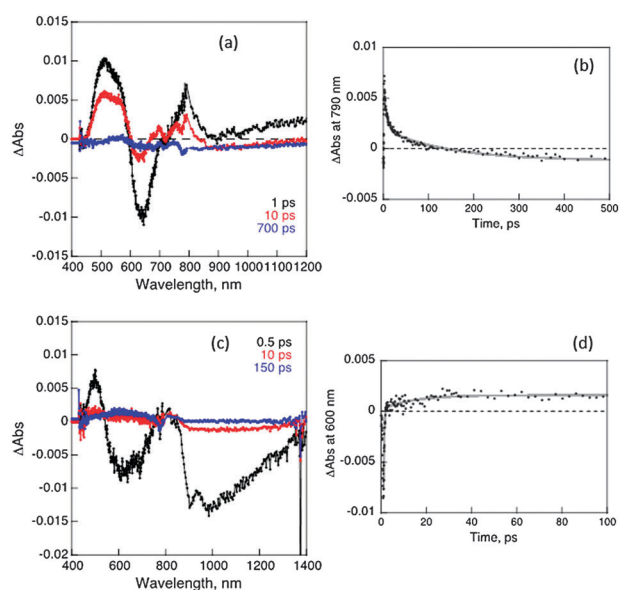


Fig. 3 Femtosecond transient absorption spectra of (a) **1** : **3** and (c) **2** : **3** hybrids in DCB, excited at 400 nm. Figures b and d show the time profile of the radical cation at 790 nm for **1** and 630 nm for **2**, respectively.

around 630 nm were observed revealing charge separation in the hybrid (Fig. 3c). The k_{CS} and k_{CR} evaluated from monitoring the rise and decay of the 630 nm transient band were found to be $3.5 \times 10^{12} \text{ s}^{-1}$ and $7.4 \times 10^9 \text{ s}^{-1}$, respectively (Fig. 3d). These results indicate ultrafast charge separation and relatively slow charge recombination in the self-assembled donor–acceptor hybrids featuring few-layer graphene as one of the active components.

In summary, new supramolecular donor–acceptor hybrids featuring few-layer graphene as an electron acceptor and custom designed phthalocyanine or porphyrin bearing four appropriately positioned pyrene entities for effective π -stacking interactions, as photosensitizer donors, have been elegantly designed, synthesized and characterized by spectral and imaging techniques. The four pyrene entities on the macrocycle facilitated π -stacking interactions between the graphene sheet and the photosensitizer molecules resulting in soluble hybrids. Femtosecond transient absorption spectroscopy provided clear evidence for charge separation in these donor–acceptor hybrids and the measured kinetics of charge separation were in the order of 10^{11} – 10^{12} s^{-1} revealing ultrafast charge separation likely due to close proximity of the donor and acceptor entities. These results point out that the supramolecular donor–acceptor hybrids with graphene as an active component developed here could be used for building light energy harvesting devices. Further studies along this line are in progress in our laboratories.

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