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One-Pot Functionalization of Graphene with Porphyrin through Cycloaddition Reactions

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Abstract: Two types of graphene-based hybrid materials, graphene-TPP (TPP = tetraphenylporphyrin) and graphene-PdTPP (PdTPP = palladium tetraphenylporphyrin), were prepared directly from pristine graphene through one-pot cycloaddition reactions. The hybrid materials were characterized by thermogravimetric analysis (TGA), by TEM, by UV/Vis, FTIR, Raman, and luminescence spectroscopy, and by fluorescence/phosphorescence lifetime measurements. The presence of the covalent linkages between graphene and porphyrin was confirmed by FTIR and Raman spectroscopy and further supported by control experiments. The presence of TPP (or PdTPP) in the hybrid material was demonstrated by UV/Vis spectroscopy, with TGA results indicating that the graphene-TPP and graphene-PdTPP hybrid materials contained approximately 18% TPP and 20% PdTPP. The quenching of fluorescence (or phosphorescence) and reduced lifetimes suggest excited state energy/electron transfer between graphene and the covalently attached TPP (or PdTPP) molecules.

Keywords: cycloaddition • graphene • luminescence • porphyrin • Raman spectroscopy

Introduction

Graphene, a single-atom-thick layer of graphite, has attracted intense scientific interest because of its extraordinary properties,[1] such as the existence of massless Dirac fermions, a room-temperature quantum Hall effect, high charge carrier mobility, and gas-sensing capability at the molecular level. It is widely anticipated that graphene will see applications in supercapacitors,[2] nanoelectronics devices,[3] chemical sensors,[4] and reinforced composite materials[5] in the near future.

For such applications, large-scale preparation of high-purity graphene flakes is essential. Currently, graphene is typically prepared by one of the following methods: mechanical,[6] epitaxial,[7] reduction of graphene oxide,[8] or solvent dispersion of graphite.[9] Further manipulation of graphene itself is made difficult by its tendency to aggregate as a result of the strong π–π interactions between individual flakes. This aggregation makes fabrication of graphene-based materials difficult. For this reason, noncovalent[10] and covalent[11] methods for the functionalization of graphene have been developed. In this context, graphene-based hybrid nanomaterials (combining graphene with other functional components) have attracted widespread attention.[12–14] The hybrid nanomaterials not only combine the unique optical, electrical, magnetic, and chemical properties of each component, but also offer the potential to introduce new properties that can potentially be used in a diverse range of applications. In the majority of reports on graphene-based hybrid nanomaterials, graphene oxide has been used as the starting material.[15] However, the oxygen-containing groups in this material greatly change the intrinsic properties of graphene, therefore potentially affecting the final properties of graphene-based hybrid nanomaterials.[16] Consequently, the development of alternative routes is required.

Recently, preparation of graphene by solvent dispersion methods, developed by a number of groups,[9] including our own,[9f] has attracted particular interest because it gives the advantage of retaining the intrinsic properties of graphene and at the same time it maintains the dispersibility of graphene in certain solvents. The functionalization of graphene through cycloaddition on pristine graphene is a promising choice.[17] In relation to noncovalent methods, covalent functionalization of pristine graphene with other molecules provides stable and well-defined systems. Furthermore, rational design of the process can allow for control of the degree of

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functionalization with the retention of the unique properties of graphene.

Porphyrin, itself a well-known and -studied aromatic molecule, possesses exceptional optical and electronic properties and has been used in various fields as diverse as solar cells, sensors, catalysis, and biology.[18] C_{60}-porphyrin and carbon-nanotube–porphyrin hybrid materials have been prepared for a number of applications.[19] Because of the similarity of graphene, C_{60}, and carbon nanotubes, hybrid materials combining graphene with porphyrin can be envisaged as being useful for applications such as solar cells, sensors, and catalysis. A distinct difference between C_{60}/carbon nanotubes and graphene, however, lies in the accessibility of the edge as well as both faces of the carbon sheet to chemical reaction.

Here we show that graphene-TPP (TPP = tetraphenylporphyrin) and graphene-PdTPP (PdTPP = palladium tetraphenylporphyrin) hybrid materials can be readily prepared through one-pot cycloaddition reactions. The hybrid materials prepared are stable in solution and have been characterized by a number of spectroscopic and microscopy techniques.

Results and Discussion

The method used for the preparation of graphene-TPP and graphene-PdTPP is shown in Scheme 1. Graphene in ODCB was prepared by the procedure reported by Hamilton et al.[9a] TPP-CHO and PdTPP-CHO were synthesized by literature procedures (see the Experimental Section). In brief, graphene in ODCB, sarcosine, and TPP-CHO (or PdTPP-CHO) were treated at 160 °C for one week, and the hybrid materials were purified by multiple filtration/redispersion cycles.

The presence of TPP (or PdTPP) in the graphene-TPP (or graphene-PdTPP) hybrid material was confirmed by UV/Vis spectroscopy. As shown in Figure 1a, TPP-CHO in DMF shows a strong Soret band at 419 nm, together with relatively weaker Q bands.[22] The absorption spectrum of graphene-TPP in DMF also shows a broadened peak at about 421 nm and weaker Q bands, attributed to the absorption of TPP unit in the graphene-TPP hybrid material. The absorption spectra for PdTPP and for graphene-PdTPP are shown in Figure 1b. PdTPP-CHO shows a strong Soret absorption band at 416 nm and also a weaker Q band at 523 nm.[23] For the graphene-PdTPP hybrid material, two broadened bands are observed at 419 and 525 nm and are assigned to the absorption of the covalently tethered PdTPP. In control reactions for both TPP and PdTPP, in which the reactions were performed in the absence of sarcosine (see the Experimental Section), the UV/Vis spectra of the recovered graphene materials did not exhibit the typical porphyrin absorption bands. This supports

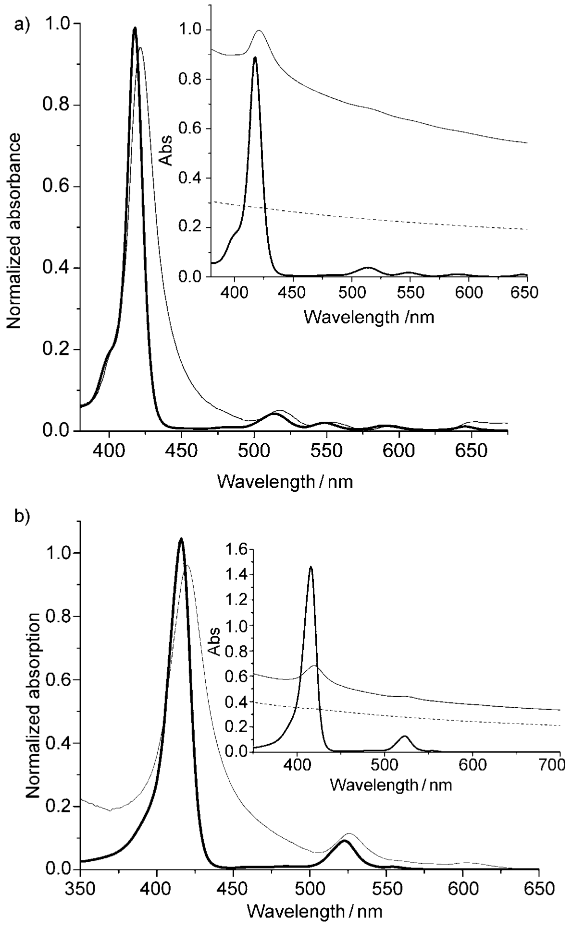
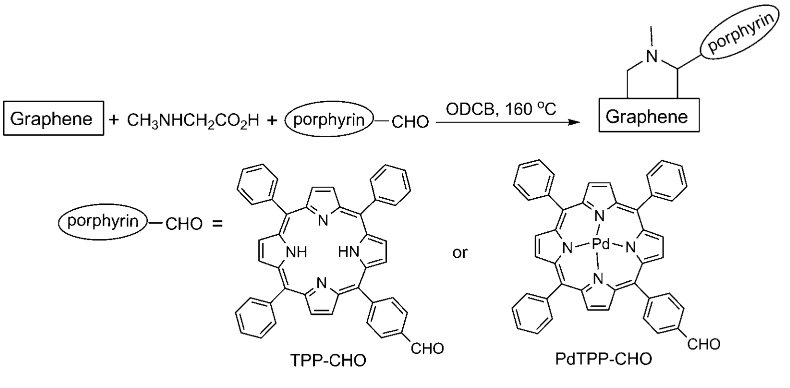


Figure 1. a) UV/Vis absorption spectra of TPP-CHO (thick solid line) and graphene-TPP (thin solid line, baseline corrected) in DMF (Inset: TPP-CHO (thick solid line), graphene-TPP (thin solid line), and the control sample (dashed line)). b) UV/Vis absorption spectra of PdTPP-CHO (thick solid line) and graphene-PdTPP (thin solid line, baseline corrected) in DMF (Inset: PdTPP-CHO (thick solid line), graphene-PdTPP (thin solid line), and the control sample (dashed line)).



Scheme 1. Synthesis of graphene-TPP and graphene-PdTPP hybrid materials.

the conclusion that the porphyrin molecules in the graphene-TPP and graphene-PdTPP hybrid materials are not physisorbed but attached covalently. In addition, the Soret band of each porphyrin shows a small redshift when covalently attached to graphene, which suggests there might be interactions between graphene and porphyrin molecules in the hybrid materials. Additional confirmation of the successful hybridization of PdTPP with graphene was provided by the X-ray photoelectron spectrum collected on a dropcast film of the hybrid material on a polycrystalline copper substrate. Figure 2 shows the Pd 3d core level region, which testifies to the presence of Pd. The Pd $3d_{5/2}$ binding energy of 338.5 eV is in agreement with Pd bonded to N found for similar compounds.[24]

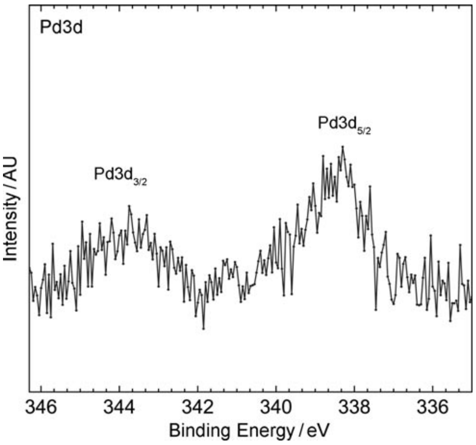


Figure 2. X-ray photoelectron spectrum of the Pd 3d core level region measured on a dropcast graphene-PdTPP film on Cu.

The loading of TPP or PdTPP in the graphene-TPP and graphene-PdTPP hybrid materials was determined by TGA. Figure 3 shows the TGA curves of graphene, graphene-TPP, and graphene-PdTPP. The weight loss observed for graphene is attributed to the defects caused by sonication, which are also apparent from the D/G band ratio in the Raman spectra, and release of trapped solvent. Graphene-TPP and graphene-PdTPP show approximately 18 and 20 % weight loss, respectively, relative to graphene, between 250 and 500 °C. This weight loss corresponds to the loss of TPP or PdTPP molecules covalently attached to graphene. Accordingly, the degree of functionalization was estimated to be one TPP group per 235 carbon atoms in graphene-TPP (0.42 %) and one PdTPP group per 240 carbon atoms in graphene-PdTPP (0.41 %).[25]

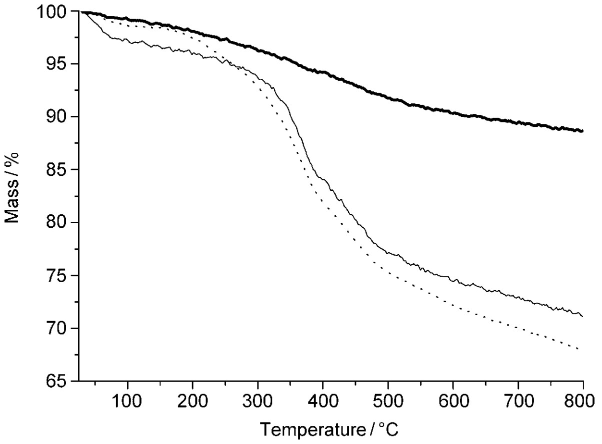


Figure 3. TGA curves of graphene (thick solid line), graphene-TPP (thin solid line), and graphene-PdTPP (dotted line).

Figure 4 shows the FTIR spectra of graphene, graphene-TPP, and graphene-PdTPP. The spectrum of graphene is almost featureless, indicative of a low defect content, whereas for the graphene-TPP and graphene-PdTPP some features of TPP and PdTPP molecules were observed in the 1000–1500 cm^{-1} region. The absence of a carbonyl stretch at about 1700 cm^{-1} for the graphene-TPP and graphene-PdTPP in relation to the spectra of free TPP-CHO and PdTPP-CHO (Figure S1 in the Supporting Information) indicates reaction of the aldehyde moieties.

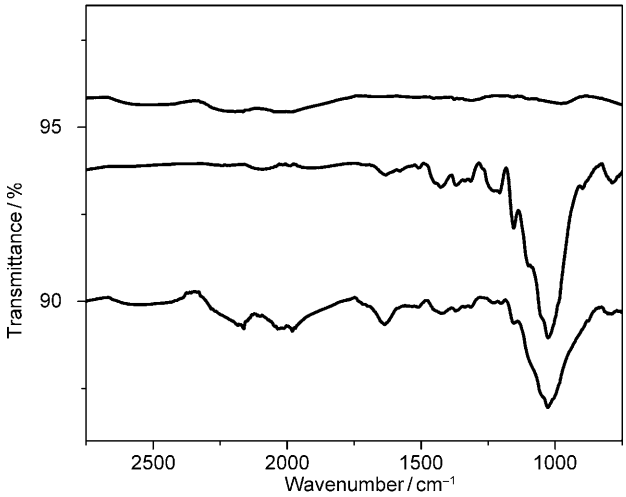


Figure 4. FTIR spectra of graphene (top), graphene-PdTPP (middle), and graphene-TPP (bottom).

Additional evidence for the functionalization was provided by Raman spectroscopy. The Raman spectra of graphite, graphene, graphene-TPP, and graphene-PdTPP are shown in Figure 5. For the graphitic materials, the typical Raman bands are: a defect-induced D band at 1350 cm^{-1}, an in-plane vibration of sp^2 carbon at 1580 cm^{-1} (G band), and a two-phonon double-resonance process at ca. 2700 cm^{-1} (2D band). The D band of graphite is almost invisible, and the 2D band consists of two components with the main peak at about 2718 cm^{-1}.[26] Graphene shows a small D band and a strong G band at 1580 cm^{-1}, with a D/G ratio of 0.22. Both graphene-TPP and graphene-PdTPP show increased D/G ratios (0.40 and 0.42 respectively) relative to graphene. The increased D/G ratio is consistent with the functionalization of graphene through covalent bonding.[17] It is worth mentioning that for graphene and functionalized graphene the

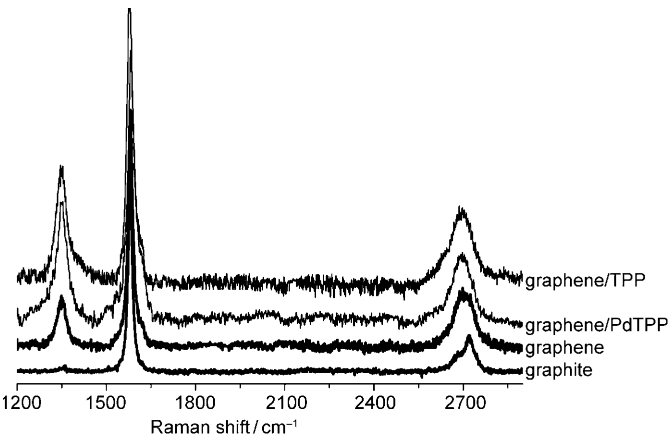


Figure 5. Raman spectra of (bottom to top) graphite, graphene, graphene-PdTPP, and graphene-TPP ($\lambda_{exc} = 532$ nm).

2D bands are shifted to 2700 cm^{-1} relative to graphite. Because of the small size of the graphene flakes and the aggregation of graphene when deposited on the substrate, it is difficult to distinguish single-layer graphene by Raman spectroscopy in the present case. However, by comparing the positions and shapes of the spectra of graphene and functionalized graphene with that of graphite, we assigned the graphene flakes as a mixture of single- and few-layer graphene.[26,17a]

The morphologies of graphene, graphene-TPP, and graphene-PdTPP were investigated by TEM analysis. Figure 6a shows a single-layer graphene flake, as indicated by the electron diffraction pattern (Figure 6a, inset: the inner intensity is stronger than the outer intensity).[9b,f] There are also a large number of few-layer graphene flakes (Figure 6b). As expected,[9a] the graphene starting material consists of single- and few-layer graphene flakes. After the cycloaddition reactions, little change in the morphologies of graphene-TPP and graphene-PdTPP hybrid materials is observed (Figure 6c–f, Figures S2 and S3 in the Supporting Information).

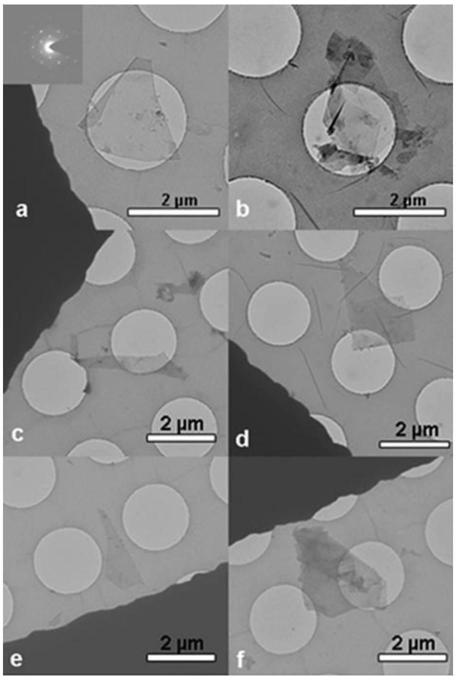


Figure 6. TEM images of a), b) graphene, c), d) graphene-TPP, and e), f) graphene-PdTPP. The samples were prepared by drop casting onto holey carbon grids.

The interaction between graphene and porphyrin in the hybrid materials was studied by fluorescence (or phosphorescence, in the case of PdTPP-CHO) spectroscopy. The Soret band absorption intensities in the graphene-porphyrin hybrids (if allowance is made for the scattering by graphene) were equivalent to those of the free porphyrins for luminescence measurements. When excited at 410 nm, free TPP-CHO shows strong fluorescence at 650 and 710 nm (Figure 7a, solid line). In contrast, for the graphene-TPP hybrid, the fluorescence is quenched significantly (Figure 6a, dotted line). The fluorescence quantum yields are reduced from 4% for TPP-CHO to 0.3% for graphene-TPP. Similar quenching behavior is observed for the graphene-PdTPP hybrid material (Figure 7b). The strong phosphorescence emission at 710 nm for PdTPP-CHO is also quenched in the hybrid material. The phosphorescence quantum yield is reduced from 0.62% for PdTPP-CHO to below 0.01% for graphene-PdTPP.

The luminescence lifetimes of TPP-CHO (or PdTPP-CHO) and of graphene-TPP (or PdTPP) show (Figure 8) that there are strong interactions between the graphene and TPP (or PdTPP). For graphene-TPP the fluorescence decay is biexponential, with a short component of <500 ps and a longer component of 6.2 ns. The short component accounts for the major part of the decay and confirms that rapid quenching of the porphyrin singlet excited state occurs. The biexponential nature of the decay might reflect the location of the porphyrin on the graphene (that is, on the basal plane or near the edge). The relatively minor contribution of the longer-lifetime component is consistent with such an assignment. Comparison of the fluorescence spectra of the covalently modified graphene-TPP both with free TPP-CHO and with a matched mixture of TPP-CHO and graphene show that collisional (dynamic) quenching is not significant (Figure S8 in the Supporting Information).

The phosphorescence decay lifetime of PdTPP-CHO is 44 µs, whereas for the graphene-PdTPP hybrid material the phosphorescence quantum yield and lifetime are diminished considerably and are non-exponential (Figure 9). Fitting of the decay of graphene-PdTPP with a biexponential function gives the values of 80 and 660 ns, the latter component being the lesser of the two (Figure S7 in the Supporting Information). The phosphorescence decay lifetime of the palladium porphyrin is in the microsecond time range and so, unlike fluorescence, phosphorescence can be quenched both dynamically and statically. Dynamic quenching is not as efficient as static quenching, however, as shown by matched solutions of PdTPP-CHO mixed with graphene and of gra-

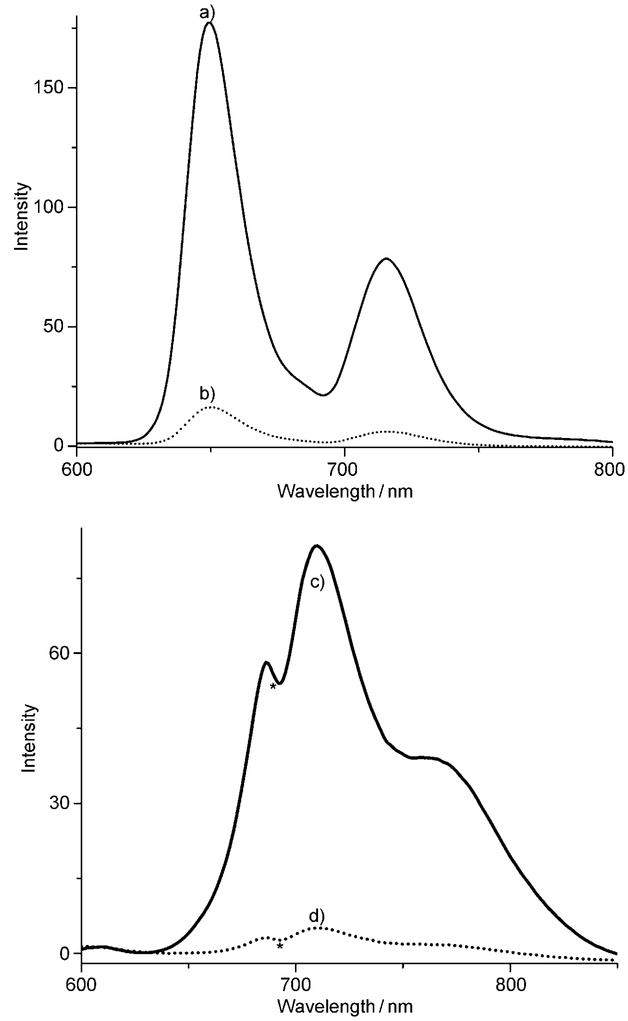


Figure 7. Top: fluorescence emission spectra of a) TPP-CHO (solid line) and b) graphene-TPP (dotted line) at $\lambda_{exc}=410$ nm in DMF. The concentration of porphyrin in both samples (i.e., TPP-CHO and graphene-TPP) was equivalent (0.7 μM) as determined by the intensity of the Soret band with the background due to the porphyrin being taken into account (see Figure S4 in the Supporting Information for the absorption spectra employed). Bottom: phosphorescence emission spectra of c) PdTPP-CHO (solid line) and d) graphene-PdTPP (dotted line) at $\lambda_{exc}=410$ nm. The concentrations of porphyrin in TPP-CHO and in graphene-TPP were kept the same (0.6 μM) according to the Soret band absorption intensity (Figure S5 in the Supporting Information). The absorption spectra were corrected both for graphene-TPP and for graphene-PdTPP by subtraction of the scattering of the graphene. * The dips in the spectra are instrumental artifacts.

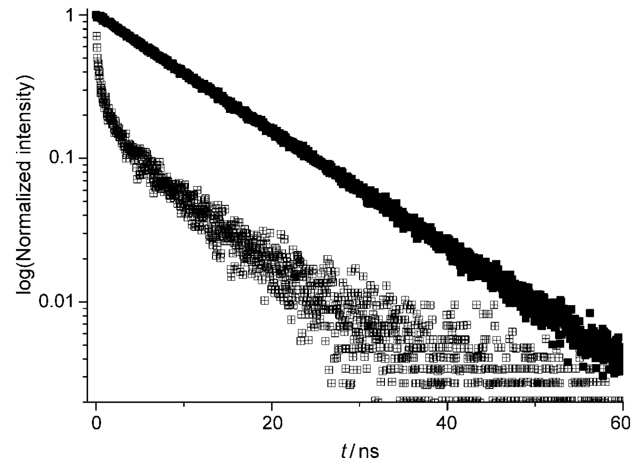


Figure 8. Fluorescence decay traces for TPP-CHO (solid squares) and graphene-TPP hybrid material (open squares) in DMF. For fits see Figure S6 in the Supporting Information.

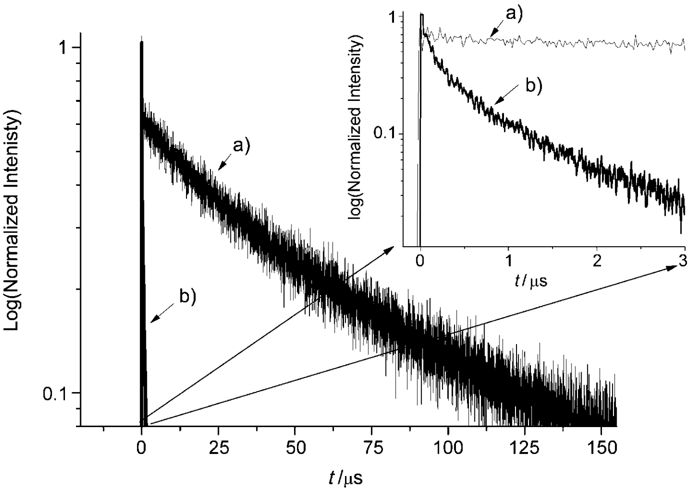


Figure 9. Phosphorescence lifetime measurement for a) PdTPP-CHO (thin line) and b) graphene-PdTPP hybrid material (thick line). The inset shows an expansion of the figure between 1–3 μs.

phene-PdTPP, in which the emission intensity of the covalently attached porphyrin is substantially less than that of the free PdTPP-CHO/graphene mixture (Figure S9 in the Supporting Information).

The absence of absorption bands of the porphyrins in UV/Vis absorption spectra of control samples prepared by the same procedures as for graphene-TPP and graphene-PdTPP, the disappearance of aldehyde peaks in the FTIR spectra of graphene-TPP and graphene-PdTPP, the presence of Pd revealed by XPS, and the increased D/G ratio in the Raman spectra for both of the hybrid materials all indicate the successful functionalization of graphene. From the TGA data the degrees of functionalization of these two hybrid materials are relatively low, which allows for extended patches of undisturbed graphene. The reduced emission lifetimes for both of the hybrid materials are consistent with the fluorescence (or phosphorescence) quenching and the reduction in emission quantum yield data, indicating that either energy- or electron-transfer processes between graphene and the attached porphyrin molecules occur.[27]

Conclusion

Graphene-TPP and graphene-PdTPP hybrid materials have been successfully prepared through one-pot cycloaddition reactions. The presence of TPP or PdTPP in the hybrid materials was confirmed by UV/Vis spectroscopy and XPS. Fluorescence and phosphorescence quenching is observed with concomitant decreases in excited state lifetimes. These observations confirm that energy- and/or electron-transfer quenching between graphene and the covalently bound porphyrin molecules occur. The amounts of TPP or PdTPP present in the hybrid materials were determined by TGA and the covalent linkages were confirmed by Raman and FTIR spectroscopy and further supported by control experiments. TEM images show that the morphologies of the hybrid materials are not affected by the cycloaddition functionalization processes. The relatively low degrees of functionalization of these two hybrid materials might allow for retention of the inherent properties of graphene, especially in comparison with materials prepared, for example, via graphene oxides. In view of the remarkable properties of both graphene and porphyrin, these two hybrid materials might have potential applications in a number of areas, such as solar cells, sensors, and catalysis.[19] With these porphyrin-modified graphenes, further studies with regard to applications to exploit the unique properties of the hybrid materials are underway in our group.

Experimental Section

Chemicals: Graphite flakes (Sigma–Aldrich) and *ortho*-dichlorobenzene (ODCB, 98%, AR, Merck) were used as received without further purification. 5-(4-Methylcarboxyphenyl)-10,15,20-triphenylporphyrin (TPP-COOMe) was obtained by literature procedures.[20] 5-(4-Formylphenyl)-10,15,20-triphenylporphyrin (TPP-CHO) was synthesized from TPP-COOMe by a reduction/oxidation method (see the Supporting Information). Palladation of TPP-CHO was performed by the general method published by Lindsey and co-workers.[21]

Instruments: Sonication was conducted with a low-power sonication bath (Bransonic, PC 620). Centrifugation was performed with a Hermle Z323K centrifuge. Filtration was carried out with a Sintered Micro Filter holder through a 0.45 μm nylon membrane. UV/Vis spectra were obtained with a JASCO V-630 UV/Vis spectrometer. Fluorescence and phosphorescence spectra were measured with a JASCO FP-6200 spectrofluorimeter. Quantum yield measurements were determined with $[Ru(bpy)_3](PF_6)_2$ in water as a reference. Fluorescence lifetime measurements were performed with a time-correlated single-photon-counting system with detection by use of a microchannel plate PMT coupled with a 630 nm long-pass filter. The light source was a Ti:Sapphire laser (400 nm, 1.9 MHz). Phosphorescence lifetime measurements were obtained with a home-built system consisting of a Zolix Omni-λ 300 monochromator coupled with a Zolix PMTH-S1-CR131 PMT detector. Transients were digitized with the aid of a Tektronix DPO 4032 Digital Phosphor Oscilloscope. The light source was an Innolas 400 Nd:YAG laser (excitation at 532 nm, 10 Hz, 40 mW) with a Si-diode trigger sensor. Solutions for phosphorescence measurements were degassed by at least three freeze-pump-thaw cycles. X-ray photoelectron spectroscopy (XPS) data were collected with a dropcast sample of graphene-PdTPP on polycrystalline Cu with a Surface Science SSX-100 ESCA instrument and a monochromatic $Al_{K\alpha}$ X-ray source ($h\nu = 1486.6$ eV). The takeoff angle between the spectrometer detector and the normal to the surface was 37°. Binding energies (±0.1 eV) were referenced to the $Cu2p_{3/2}$ photoemission line at a binding energy of 932.7 eV.[28] Thermal gravimetric analysis (TGA) was performed under N_2 with a Mettler Toledo TGA/SDTA851e system. Transmission electron microscopy (TEM) characterization was carried out with a PHILIPS CM10 instrument operating at 100 KV. Raman spectra were measured with a JOBIN-YVON model T 64000 triple-grating spectrometer (excitation at 532 nm). Raman samples were prepared by drop casting a few drops of the graphene and functionalized graphene on clean gold substrates and were then dried under vacuum. Fourier Transform Infrared Spectroscopy (FTIR) was performed with a Perkin–Elmer Spectrum 400 instrument and a UATR attachment.

Preparation of graphene: Graphite (100 mg) was sonicated for 2 h in ODCB (100 mL), and then centrifuged at 3000 rpm for 30 min. The supernatant was decanted to afford graphene in ODCB. The concentration of graphene in ODCB was 0.01 $mg\,mL^{-1}$.

Preparation of graphene-TPP and graphene-PdTPP hybrid materials: The procedure for the preparation of graphene-TPP and graphene-PdTPP hybrid materials is shown in Scheme 1. The obtained graphene in ODCB (50 mL), sarcosine (25 mg), and TPP-CHO (or PdTPP-CHO, 20 mg) were placed in a 100 mL round-bottomed flask and stirred at 160 °C under N_2 for 1 week. After the reaction was complete, the reaction mixture was filtered through a 0.45 μm nylon membrane. The obtained filter cake was subsequently washed several times with ODCB, DMF, and $CHCl_3$ with use of repeated redispersion, sonication, and filtration steps. The final suspension in $CHCl_3$ was centrifuged at 5000 rpm for 30 min. The precipitate was dried under vacuum to afford the desired graphene-TPP or graphene-PdTPP hybrid material.

Control samples: To confirm the covalent linkages between TPP (or PdTPP) and graphene, control samples were prepared. The obtained graphene in ODCB (50 mL), and TPP-CHO (or PdTPP-CHO, 20 mg) were placed in a 100 mL round-bottomed flask, and stirred at 160 °C under N_2 for 1 week (in the absence of sarcosine). The handling procedures were as above for the hybrid materials.

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