Electronic Supplementary Material (ESI) for Journal of Materials Chemistry
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SUPPORTING INFORMATION

Graphene-organic hybrids as processable, tunable platforms for pH-dependent photoemission, obtained by a new modular approach

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General.
All 1H NMR and 13C NMR spectra were recorded at room temperature on a Varian Mercury-400 spectrometer equipped with a 5-mm probe. Chemical shifts were calibrated using the internal CDCl3 resonance referenced to TMS. Mass spectra were collected on an ion trap Finningan Mat GCQ spectrometer operating in electron impact (EI) ionization mode. Each sample was introduced to the ion source region of GCQ via a direct exposure probe (DEP). UV-Vis spectra were recorded using a Perkin-Elmer Lambda 20 spectrometer. Photoluminescence spectra were obtained with a Perkin-Elmer Spectrum BX FT-IR system. Thermal gravimetric analysis measurements were performed on an EXSTAR Thermo Gravimetric Analyzer (TG/DTA) Seiko 6200 under N2 atmosphere (50 mL/min) coupled with a ThermoStar™ GSD 301 T (TGA-MS) for MS gas analysis of volatiles. The Scanning Electron Microscopy (SEM) images were obtained with a ZEISS 1530 instrument. Transmission Electron Microscopy (TEM) observations were carried out with a Fei Tecnai F20 TEM equipped with a Schottky emitter and operating at 80 keV. Laser Confocal Microscopy Fluorescence imaging was performed on an inverted Nikon A1 laser scanning confocal microscope equipped with a set of lasers, Argon ion laser, 637 nm red diode laser and a 405 nm pulsed diode laser (Picoquant, Germany). IR spectra were recorded using Elmer Spectrum BX FT-IR system. Fluorescence imaging was performed on an inverted Nikon A1 confocal laser scanning microscope equipped with a 405 nm pulsed diode laser (Picoquant, Germany). Imaging was carried out on the samples at 20 °C. 1024×1024 and 2048×2048 pixel images were collected using a Nikon PLAN APO VC 60× NA 1.40 oil immersion objective. Scan speed of 1/8 and 1/16 frame/second was used. A dichroic mirror (DM) passing 405/488 nm was selected for spectral detection with a 32 diode array grating resolution was set to 10 nm and DM of 405/488/547/640 was used. Laser Confocal Microscopy Fluorescence imaging was performed on an inverted Nikon A1 laser scanning confocal microscope equipped with a set of lasers, Argon ion laser, 637 nm red diode laser and a 405 nm pulsed diode laser (Picoquant, Germany). IR spectra were recorded using Elmer Spectrum BX FT-IR system. Fluorescence imaging was performed on an inverted Nikon A1 confocal laser scanning microscope equipped with a 405 nm pulsed diode laser (Picoquant, Germany). Imaging was carried out on the samples at 20 °C. 1024×1024 and 2048×2048 pixel images were collected using a Nikon PLAN APO VC 60× NA 1.40 oil immersion objective. Scan speed of 1/8 and 1/16 frame/second was used. A dichroic mirror (DM) passing 405/488 nm was selected in the scan head for all intensity imaging measurements. Using the PMT detector the 500-550 nm emission channel was selected. For spectral detection with a 32 diode array grating resolution was set to 10 nm and DM of 405/488/547/640 was used. Thermal gravimetric analysis measurements were performed on an EXSTAR Thermo Gravimetric Analyzer (TG/DTA - Resolution: ± 0.2 µg) Seiko 6200 under N2 atmosphere (50 mL/min) coupled with a ThermoStar™ GSD 301 T (TGA-MS) for MS gas analysis of volatiles.

Materials and Synthesis.
The water-soluble heavily oxygenated graphene oxide (GO) sheets were generated via a modified Hummers method as described elsewhere. 1,6-Hexanediamine, triethylamine (TEA) were purchased from Sigma-Aldrich, N-Hydroxysuccinimide (NHS) and N-(3-dimethylamino)propyl)-N’-ethylcarbodiimide hydrochloride (EDC·HCl) were purchased from Acros Organics and used as received. Detailed experimental procedures and complete characterization of compounds 5 and 6 have been published previously.

Scheme SI_1. Synthesis of T3NHS, (2).

4’,3’”-Dimethyl-2,2’,5’,2’”terthiophene-5-carboxylic acid 2,5-dioxo-pyrrolidin-1-yl ester, T3NHS, (2). To a 15 mL toluene solution containing 0.08 mmol of tetrakis(triphenylarsine)palladium(0) prepared in situ the bithienyl bromide 5 (0.42 g, 1.38 mmol) was added. The mixture was then heated to reflux and the thienyl stannane 6 (0.80 g, 1.65 mmol) dissolved in 5 mL of toluene added dropwise. The resulting mixture was stirred at reflux for 6 h and then cooled to room temperature. Removal of the solvent in vacuo gave a crude solid that was washed in pentane (3 × 5 mL) then purified by flash chromatography on silica gel (elution with ethyl acetate). Yield: 0.51 g (89%). Amorphous red-orange solid; mp 138-140 °C; EI-MS m/z 417 (M+); absorption maximum, 374 nm; emission maximum, 493 nm in DCM. IR (neat) ν (cm−1) 1738 (CO, carbamate). 1H NMR (CDCl3, TMS/ppm) δ 7.91 (d,
GOC0.25 with the dye contributing less than 0.1. The spectra show a quenching effect at the excitation wavelength. In the case of the free dye, the absorbance is 0.09 at 350 nm, while GOC0.25 absorbs less than 0.25 with the dye contributing less than 0.1. The spectra show a quenching ≤16% of the fluorescence intensity of GOC0.25 compared to T3NBut. Even if, due to absorbance and/or scattering by GO at the excitation wavelength as well as reabsorption of emitted light, some uncertainty affects the measurement of this value, the fluorescence emission of the GO-tethered dye is comparable to that of the free dye.

Fluorescence and absorption spectra of GO-tethered and free dye.

In order to estimate the fluorescence quantum yields of the dye alone and grafted to GO, one needs to obtain the fluorescence spectra for systems absorbing equally at the excitation wavelength and preferentially less than 0.1. This condition is very hard to obtain with modified graphene contributing to absorbance and scattering at the excitation wavelength. In the case of the free dye, the absorbance is 0.09 at 350 nm, while GOC0.25 absorbs less than 0.25 with the dye contributing less than 0.1. The spectra show a quenching ≤16% of the fluorescence intensity of GOC0.25 compared to T3NBut. Even if, due to absorbance and/or scattering by GO at the excitation wavelength as well as reabsorption of emitted light, some uncertainty affects the measurement of this value, the fluorescence emission of the GO-tethered dye is comparable to that of the free dye.

N-butyl-3";4"-dimethyl-[2,2";5";2"-terthiophene]-5-carboxamide, T3NBut. 3. Trimer 2 (0.084 mmol, 35 mg) was dissolved in 5 ml of DCM and buthylamine (0.168 mmol, 12 mg) was then added and the mixture was stirred overnight at room temperature. After this time, the solvent was removed under vacuum and the crude purified by column chromatography using silica gel and pentane:AcOEt:CH2Cl2:70:15:15. T3NBut was isolated as yellow oil in 99% yield (31 mg). EI-MS m/z 375 (M+); absorption maximum, 352 nm; emission maximum, 457 nm in DCM. IR (neat) ν (cm⁻¹) 3300 (NH), 2955 to 2860 (aliphatic CH), 1620 (CO, amide). ¹H NMR (CDCl3, TMS/ppm) δ 169.1, 157.1, 147.7, 137.8, 137.6, 137.1, 134.4, 131.8, 130.3, 129.1, 129.0, 128.2, 125.7, 124.0, 25.6, 14.85. 13C NMR (CDCl3, TMS/ppm) δ 161.6, 141.5, 137.5, 137.0, 136.9, 135.4, 130.2, 130.0, 128.6, 128.5, 127.5, 125.4, 123.5, 39.8, 31.8, 29.7, 14.8, 13.8. Anal. calcd for C20H17NO3S3: C, 54.75; H, 3.72. Found: C, 54.66; H, 3.62. NOS

Synthesis of GOC0.25NH2. (1).

The carboxylic acid groups sited on the edge of GO sheets can be converted to amine groups by reactions with NHS and 1,6-hexanedi amine. 4. GO sheets (50 mg) were added to 10 mL of dry DMF. After 24 h of sonication, NHS (172 mg, 1.5 mmol) and EDC-HCl (288 mg, 1.5 mmol) were added to the solution at 0 °C. After stirring for 2 h, 1,6-hexanedi amine (261 mg, 2.25 mmol) in 4 mL of DMF was added dropwise, and the solution stirred overnight at room temperature. The brown dispersion of GO sheets modified with amine groups obtained was then subjected to 20 min of centrifugation at 18000g, in a Beckman Coulter Allegra™ 64R centrifuge. The surfactants were removed by aspiration with Pasteur pipette, and the aggregates were washed by resuspension in water (20 mL) under mechanical shaking (Heidolph Vortex Shaker) for 30 seconds followed by centrifugation. The latter washing and centrifugation procedure with water was then repeated. The same procedure using ethanol (20 mL) was also carried out twice. To determine the concentration of GOC0.25NH2, a 1-mL aliquot of this suspension was evaporated to dryness in vacuo. Estimated graphene-based material yield: 160 mg. After the final washings the GOC0.25NH2 samples were carefully dispersed in fresh DMF by a 5-min sonication step and diluted to a final concentration of 4 mg/mL for storage.

Synthesis of GOC0.25T3. (4).

After mechanical shaking, the above DMF dispersion (10 mL corresponding to 40 mg of GO-NH2) was mixed with 2 mL of TEA, and compound 2 (21 mg, 0.05 mmol) in DMF (3 mL) was added to the mixture. After stirring overnight at room temperature, the solids were collected by centrifugation (18000g, 20 min) and the supernatant was discarded. The brown solids were washed by resuspension in DMF followed by centrifugation (four washes, 20 mL each). After the final washings the GOC0.25T3 samples were carefully dispersed in fresh DMF. To determine the concentration of GOC0.25T3, a 1-mL aliquot of this suspension was evaporated to dryness in vacuo. After dilution with dichloromethane, GOC0.25T3 was stored at a final concentration of 1 mg/mL. Estimated graphene-based material yield: 22 mg.

Fluorescence and absorption spectra of GO-tethered and free dye.

In order to estimate the fluorescence quantum yields of the dye alone and grafted to GO, one needs to obtain the fluorescence spectra for systems absorbing equally at the excitation wavelength and preferentially less than 0.1. This condition is very hard to obtain with modified graphene contributing to absorbance and scattering at the excitation wavelength. In the case of the free dye, the absorbance is 0.09 at 350 nm, while GOC0.25T3 absorbs less than 0.25 with the dye contributing less than 0.1. The spectra show a quenching ≤16% of the fluorescence intensity of GOC0.25T3 compared to T3NBut. Even if, due to absorbance and/or scattering by GO at the excitation wavelength as well as reabsorption of emitted light, some uncertainty affects the measurement of this value, the fluorescence emission of the GO-tethered dye is comparable to that of the free dye.
Fig. S1 – Fluorescence spectrum of T3NBut at low conc., compared with the fluorescence spectrum of GOC6T3 obtained for exc. at 350 nm. A(350 nm) = 0.09 for T3NBut on 1 cm. Contribution of dye to absorbance at 350 nm is less than 0.1 for GOC6T3.

Fig. S2 – Absorption spectra of T3NHS, T3NBut and GOC6T3.

**Details of DFT calculations**

Excited state geometry optimizations were performed for the three species, using the CAM-B3LYP exchange-correlation functional and a 6-31G* basis set. Calculations were performed in ethanol solution, as in the experimental conditions, by means of the CPCM solvation model.

For the non protonated T3NBut species we calculate an emission maximum of $\lambda_{em} = 498$ nm, slightly red-shifted compared to the experimental value ($\lambda_{em} = 454$ nm), while for the two protonated forms the emission maximum is almost coincident with the experimental value ($\lambda_{em} = 551$ and 544 nm vs. 534 nm).

DFT results indicate T3NBut excited state O-protonation to be slightly favored over N-protonation by 2.8 kcal/mol, thus, although the two tautomers produce essentially the same optical response, we guess the O-protonated species to be present in the experimental conditions.

All calculations were performed by the Gaussian09 program package. (Ref: [http://www.gaussian.com/g_tech/g_ur/m_citation.htm](http://www.gaussian.com/g_tech/g_ur/m_citation.htm)).

**References**