SUPPORTING INFORMATION

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

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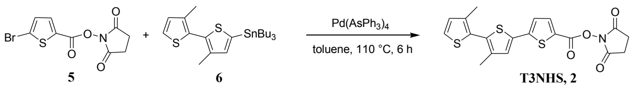
General.

All ^{1}H NMR and ^{13}C 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 $CDCl_3$ resonance referenced to TMS. Mass spectra were collected on a 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 LS50 spectrofluorometer. Fluorescence measurements were made at an excitation wavelength corresponding to the maximum absorption lamda. IR data were acquired on 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 N_2 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 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]. 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.

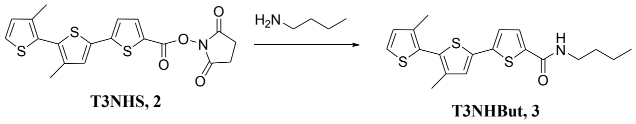
Detailed experimental procedures and complete characterization of compounds **5** [2] and **6** [3] have been published previously.



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 x 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). ^{1}H NMR ($CDCl_3$, TMS/ppm) δ 7.91 (d,

^3J=4.4 Hz, 1H), 7.31 (d, ^3J= 5.2 Hz, 1H), 7.19 (d, ^3J= 4.4 Hz, 1H), 7.18 (s, 1H), 6.94 (d, ^3J= 5.2 Hz, 1H), 2.90 (s, 4H), 2.23 (s, 3H), 2.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 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, 14.83. Anal. calcd for $C_{19}H_{15}NO_4S_3$ (417.52): C, 54.66; H, 3.62. Found: C, 54.75; H, 3.72.



Scheme SI_2. Synthesis of T3NHBut, (3).

N-butyl-3'',4'-dimethyl-[2,2':5',2''-terthiophene]-5-carboxamide, T3NHBut, **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 chromatography by using silica gel and pentane:AcOEt:CH_2Cl_2=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). ^{1}H NMR ($CDCl_3$, TMS/ppm) δ 7.38 (d, ^3J=4.0 Hz, 1H), 7.28 (d, ^3J= 4.8Hz, 1H), 7.07 (s+d, ^3J= 4.0 Hz, 2H), 6.93 (d, ^3J= 5.2 Hz 1H), 6.94 (d, ^3J= 5.2 Hz, 1H), 6.30 (b s, 1H), 3.43 (q, 2H), 2.21 (s, 3H), 2.16 (s, 3H), 1.60 (m, 2H), 1.41 (m, 2H), 0.96 (t, 3H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 161.6, 141.5, 137.5, 137.0, 136.9, 135.4, 130.2, 130.0, 128.6, 128.5, 127.7, 125.4, 123.5, 39.8, 31.8, 29.7, 20.1, 14.8, 13.8. Anal. calcd for $C_{19}H_{21}NOS_3$ (375.57): C, 60.76; H, 5.64. Found C:60.68; H, 5.53.

Synthesis of GOC_6NH_2, (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- hexanediamine [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-hexanediamine (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 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 GOC_6NH_2, 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 GOC6NH$_2$ 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 GOC_6T3, (4).

After mechanical shaking, the above DMF dispersion (10 mL corresponding to 40 mg of GO-NH_2) 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 DCM followed by centrifugation (four washes, 20 mL each). After the final washings the GOC_6T3 samples were carefully dispersed in fresh DCM. To determine the concentration of GOC_6T3, a 1-mL aliquot of this suspension was evaporated to dryness *in vacuo*. After dilution with dichloromethane, GOC_6T3 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 absorbance is 0.09 at 350 nm, while GOC_6T3 absorbs less than 0.25 with the dye contributing less than 0.1. The spectra show a quenching ≤16% of the fluorescence intensity of GOC_6T3 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.

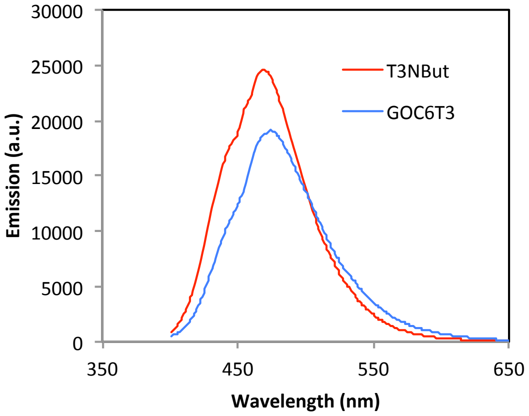


Fig. S1 –Fluorescence spectrum of T3NBut at low conc., compared with the fluorescence spectrum of GOC$_6$T3 obtained for exc. at 350 nm. A(350 nm) = 0.09 for T3NBut on 1 cm. Contribution of dye to absorbance at 350 nm is less than 0.1 for GOC$_6$T3.

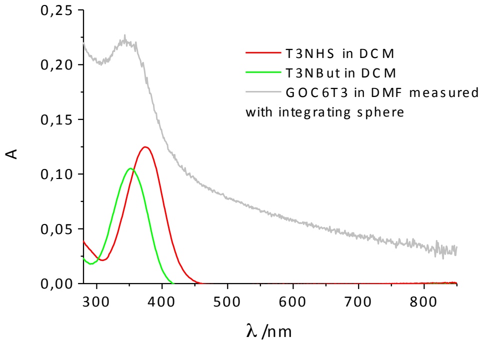


Fig. S2 – Absorption spectra of T3NHS, T3NBut and GOC$_6$T3.

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 λem = 498 nm, slightly red-shifted compared to the experimental value (λem = 454 nm), while for the two protonated forms the emission maximum is almost coincident with the experimental value (λem = 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).

References

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