Electronic Supplementary Information

Ultrafast Charge Separation in Supramolecular Tetrapyrrole-Graphene Hybrids

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Experimental Section

Chemicals. Graphite flakes and all of the reagents were from Aldrich Chemicals (Milwaukee, WI) while the bulk solvents utilized in the syntheses were from Fischer Chemicals. Synthesis of $\mathbf{2}$ is described elsewhere.¹

Instrumentation. ¹H NMR spectra were obtained from chloroform-d solutions using a Varian 400 MHz NMR spectrometer with tetramethylsilane as an internal standard. The UV-visible spectral measurements were carried out with a Shimadzu Model 1600 UV-visible spectrophotometer. The fluorescence emission was monitored by using a Varian Eclipse spectrometer. All the solutions were purged prior to electrochemical and spectral measurements using argon gas.

Time-resolved Transient Absorption Measurements. Femtosecond laser flash photolysis was conducted using a Clark-MXR 2010 laser system and an optical detection system provided by Ultrafast Systems (Helios). The source for the pump and probe pulses were derived from the fundamental output of Clark laser system (775 nm, 1 mJ/pulse and fwhm = 150 fs) at a repetition rate of 1 kHz. A second harmonic generator introduced in the path of the laser beam provided 410 nm laser pulses for excitation. A 95% of the fundamental output of the laser was used to generate the second harmonic, while 5% of the deflected output was used for white light generation. Prior to generating the probe continuum, the laser pulse was fed to a delay line that provided an experimental time window of 1.6 ns with a maximum step resolution of 7 fs. The pump beam was attenuated at 5 mJ/pulse with a spot size of 2 mm diameter at the sample cell where it was merged with the white probe pulse in a close angle ($<10^{\circ}$). The probe beam after passing through the 2 mm sample cell was focused on a 200 mm fiber optic cable, which was connected to a CCD spectrograph (Ocean Optics, S2000-UV-vis for visible region and Horiba, CP-140 for NIR region) for recording the time-resolved spectra (450-800 and 800-1400 nm). Typically, 5000 excitation pulses were averaged to obtain the transient spectrum at a set delay time. The kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data.

Synthesis of tetrapyrene appended phthalocyanine, 1

Synthesis of 4-pyrenephthalonitrile. Pyrene-1-boronic acid (200 mg, 0.812 mmol), 4-Iodophthalonitrile (160 mg, 0.632 mmol), Potassium carbonate (622 mg, 4.511 mmol) and Pd(PPh₃)₄ (105 mg, 0.090 mmol) were kept in 100 ml RB flask under nitrogen for 20 minutes. Then, THF (20 ml) and toluene (15 ml) were added and whole mixture was heated at 90 0 C for 16 hrs. After cooling at room temperature, the solvent was evaporated and the residue was purified by silica column. The desired compound was eluted by hexanes:choloform (40:60) as a second fraction, light yellow colored compound. Yield = 130mg (63%). ¹HNMR (CDCl₃, 400 MHz). δ 7.90 ppm (d, 1H, Ar-H), 7.95 ppm (d, 1H, Ar-H), 8.01 ppm (m, 2H, Ar-H), 8.05-8.15 ppm (m, 3H, pyrene-H), 8.20 ppm (d, 1H, pyrene-H), 8.21-8.30 ppm (m, 4H, pyrene-H). Mass-ESI [M+H]⁺, calculated-328.37, obtained- 329.60.

Synthesis of 1. 4-(Pyrene-1-yl)phthalonitrile (120 mg, 0.365 mmol) was kept in 100 ml RB flask under nitrogen for 20 minutes. DMAE (3 ml) as a solvent was added and then whole mixture was refluxed for 16 hrs. After cooling at room temperature, the mixture was dissolved in ethanol and THF (1:1) and centrifuged for 2 hrs. After removing the supernatant, the residue was dissolved in minimum of THF and purified by flash column chromatography on silica gel, first with ethanol then with THF as eluent. Yield = 45 mg (9.37%). ¹H NMR (CDCl₃: 400 MHz). δ 7.50 ppm (m, 6H, Ar-H), 7.60 ppm (m, 6H, Ar-H), 7.85 ppm (m, 6H, pyrene-H), 7.90- 8.10 ppm (m, 18H, pyrene-H), 8.15-8.30 ppm (m, 12H, pyrene-H). ¹³C NMR (CDCl₃): ¹³CNMR (CDCl₃). 121.20, 121.40, 123.10, 123.20, 123.25, 123.50, 124.10, 124.60, 125.10, 125.30, 125.40, 125.80, 125.85, 125.95, 126.10, 126.20, 126.80, 127.10, 127.50, 128.10, 128.30, 128.60, 128.70, 128.80, 128.90, 130.20, 131.10, 131.80, 132.10, 133.20, 135.10, 136.10, 136.20, 137.10, 137.25, 138.20. MALDI-mass [M+H]⁺, calculated- 1315.48, obtained- 1316.45. (See Fig. S7, S8 and S9 for MALDI-mass, ¹H and ¹³C NMR spectrum, respectively).

Preparation of few layer graphene by the exfoliation of graphite flakes.² About 130 mg graphite flakes were taken in a beaker to which 60 mL of DCB was added. This was then sonicated using Misonix ultrasonic liquid processor for 4 hours at 20°C. The resulting solution was then centrifuged at 3300 rpm using Fisher Scientific Centrific 228 model for 30 minutes. The supernatant was a very stable solution of few layer graphene.

Preparation of tetrapyrrole:graphene hybrids. A 30 mL of the exfoliated graphene solution in DCB was treated with 30 mg of sensitizers **1** or **2**. The resulting mixture was stirred at room temperature for 72 hours. It was then centrifuged. The unreacted sensitizer present in the supernatant was discarded. Residual hybrid material was subsequently cleaned using methanol, CH_2Cl_2 , DCB and all the unbound porphyrin was washed out. The resulting hybrid was then dried and used for further studies.

For spectroscopic probing of 1 or 2 interacting with 3 (Fig. 1), first, a stock solution of 3 from the previous step in DCB was prepared (about 1 mg in 1 mL). Next, microliters of this sonicated solution (5 μ L aliquots) was added to 1 or 2 and the spectra were recorded. Appropriate controls were also performed to ascertain that the observed changes are not due to dilution (see main text, for details).

References

- E. Maligaspe, A. S. D. Sandanayaka, T. Hasobe, O. Ito and F. D'Souza, *J. Am. Chem. Soc.* 2010, **132**, 8158.
- 2. U. Khan, A. O'Neill, M. Lotya, S. De and J. N. Coleman, Small, 2010, 6, 864.



Fig. S1. (a) absorption and (b) emission spectra of **1** in DCB upon increasing addition of (50 μ L) DCB.



Fig. S2. Raman spectrum ($\lambda_{ex} = 532$ nm) solid samples of exfoliated few-layer graphene (red line) and 1:3 hybrid (black line).



Fig. S3. Absorption spectrum of 1 (red line) and 1:3 (black line) hybrid dissolved in DCB.



Fig. S4. Absorption spectrum of 2 (black line) and 2:3 hybrid (red line) dissolved in DCB.



Fig. S5. Femtosecond transient absorption spectra of **1** in DCB. The bottom panel shows decay of the 580 nm band corresponding to ${}^{1}\text{H}_{2}\text{Pc}^{*}$.



Fig. S6. Femtosecond transient absorption spectra of **2** in DCB. The bottom panel shows decay of the 505 nm band corresponding to 1 ZnP*.



Fig. S7. Matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF) spectrum of **1** with dithranol used as a matrix.



Fig. S8. ¹H NMR spectrum in **1** in CDCl₃.



Fig. S9. ¹³C NMR spectrum in **1** in CDCl₃.