Supporting Information

Direct exfoliation of graphite with a porphyrin – creating functionalizable nanographene hybrids

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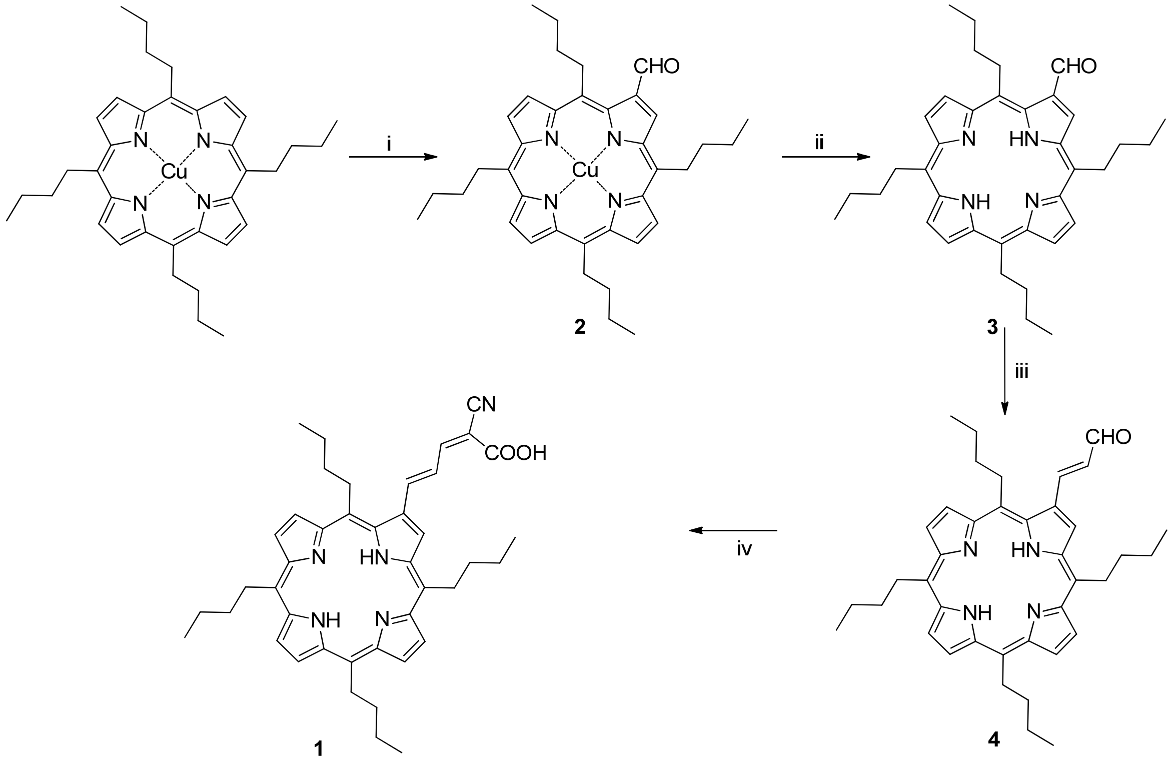


Scheme S1. Synthesis of porphyrin acids. i) *N*-methylformanilide, $POCl_3$, chloroform, 60 ^{o}C; ii) $POCl_3$, water, 0 ^{o}C, iii) (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide, K_2CO_3, 18-crown-6, benzene, reflux; iv) cyanoacetic acid, NH_4OAc, AcOH, THF, 65 ^{o}C.

Experimental Details

Synthesis: The 5,10,15,20-tetrabutylporphyrin and its copper complex (**CuTBP**) were synthesized according to literature procedures.[1] The other reagents were obtained commercially.

2-Formyl-5,10,15,20-tetrabutylporphyrinato copper (II) (2)

Phosphorous oxychloride (4.0 mL, 43 mmol) was added dropwise into *N*-methylformanilide (6.9 mL, 56 mmol) and the resulting orange solution was stirred at room temperature for 10 minutes until it solidified. The solution of **CuTBP** (0.344 g, 0.58 mmol) in chloroform (50 mL) was added and the resulting red mixture was stirred at 60°C for 1.5 h. The mixture was poured into cold water (200 mL), the organic layer separated, washed by diluted ammonia, dried over magnesium sulphate and evaporated to dryness under reduced pressure at 50 °C. The remaining crude product was dissolved in a minimal amount of chloroform and filtered through a pad of silica.

The solvent was removed under reduced pressure at 50 °C and the product treated by methanol to give **2** (0.24 g, 67 %) as a green powder.

FAB-LRMS: *m/z* (%, assignment) cluster at 621 – 627, 623 (100, M^+). HRMS: Calcd for M^+ ($C_{37}H_{44}CuN_4O$): 623.2811, found: 623.2819.

UV-vis ($CHCl_2$): λ_{max} [nm] (ε x 10^{-3}) = 309 (3.13), 434 (5.25), 561 (3.96), 608 (3.89).

2-Formyl-5,10,15,20-tetrabutylporphyrin (3)

Compound **2** (0.24 g, 0.39 mmol) was dissolved in phosphorus oxychloride (15.0 mL), cooled to 0 °C and then water (1.5 mL) was added at once with vigorous stirring in a high, narrow vessel. The resulting green solution was stirred at 0 °C for 30 minutes then poured onto crushed ice (100 g). The resulting green slurry was neutralized by concentrated ammonia solution and a dark powder filtered off. The solid was dissolved in the minimal amount of dichloromethane, filtered through a pad of silica and evaporated to dryness under reduced pressure at 50 °C. The remaining solid was recrystallized from dichloromethane-methanol to give **3** (0.18 g, 82 %) as a dark purple powder.

^1H NMR (500 MHz, $CDCl_3$, TMS): 11.38 (s, 1H, CHO), 9.93 (s, 1H, $H_{\beta\text{-pyrrolic}}$), 9.34 (d, 1H, ^3J = 5.0 Hz, $H_{\beta\text{-pyrrolic}}$), 9.40 (d, 1H, ^3J = 5.0 Hz, $H_{\beta\text{-pyrrolic}}$), 9.36 (d, 1H, ^3J = 5.0 Hz, $H_{\beta\text{–pyrrolic}}$), 9.33 (d, 1H, ^3J = 5.0 Hz, $H_{\beta\text{–pyrrolic}}$), 9.31 (s, 2H, $H_{\beta\text{–pyrrolic}}$), 4.94 – 4.97 (m, 2H, Porph-CH_2), 4.80 – 4.88 (m, 6H, Porph-CH_2), 2.38 – 2.49 (m, 8H, Alk-C2), 1.71 – 1.84 (m, 8H, Alk-C3), 1.08 – 1.15 (m, 12H, Alk-CH_3), -2.315 (br s, 2H, NH).

FAB-LRMS: *m/z* (%, assignment) cluster at 560 – 565, 563 (100, MH^+). HRMS: Calcd for MH^+ ($C_{37}H_{47}N_4O$): 563.3749, found: 563.3747.

UV-vis ($CHCl_2$): λ_{max} [nm] (ε x 10^{-3}) = 435 (5.16), 531 (3.95), 581 (3.60), 620 (3.47), 683 (3.80).

5,10,15,20-Tetrabutyl-2-(2-formylethenyl)porphyrin (4)

Porphyrin aldehyde **3** (0.73 g, 1.3 mmol), 18-crown-6 (52 mg, 0.2 mmol) were dissolved in benzene (80 mL), brought to reflux then (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide (0.56 g, 1.30 mmol) with anhydrous, finely-powdered potassium carbonate (0.18 g, 1.3 mmol) was added every 2 h for 6 h (three times). Afterward the reaction mixture was cooled down and filtered through a pad of silica using chloroform as an eluent. The solvents were removed under reduced pressure at 50 °C and the remaining solid was dissolved in a mixture of tetrahydrofuran (50 mL) and chloroform (13 mL). The concentrated hydrochloric acid (6.5 mL) was added and the resulting green mixture was vigorously stirred for 45 minutes. The acid was neutralized with concentrated ammonia and the organic phase after dilution with dichloromethane (100 mL) was separated, dried over magnesium sulphate and evaporated to dryness under reduced pressure at 50 °C. The crude product was dissolved in minimal amount of dichloromethane, filtered through pad of silica and evaporated to dryness under reduced pressure at 50 °C. The product was recrystallized from dichloromethane-methanol to give **4** (0.61 g, 80 %) as a dark purple powder.

^1H NMR (500 MHz, $CDCl_3$, TMS): δ 10.7 (d, 1H, J = 7.6 Hz, CHO), 9.44 – 9.38 (m, 7H, $H_{\beta\text{-pyrrolic}}$), 8.85 (d, 1H, ^3J = 15.6 Hz, vinyl-H), 7.24 (dd, 1H, ^3J = 7.6 and 15.6 Hz, vinyl-H), 4.89 – 4.83 (m, 6H, Porph-CH_2), 4.77 –

4.74 (m, 2H, Porph-CH_2), 2.51 – 2.42 (m, 8H, Alk-C2), 1.85 – 1.77 (m, 8H, Alk-C3), 1.18 – 1.11 (m, 12H, Alk-CH_3), -2.43 (br s, 2H, NH).

FAB-LRMS: *m/z* (%, assignment) cluster at 756-591, 588 (83 M^+). HRMS: Calcd for M^+ ($C_{39}H_{48}N_4O_1$): 588.3828, found: 588.3844.

UV-vis (CH_2Cl_2): λ_{max} [nm] (ε x 10^{-3}) = 359 (4.38), 410 sh (4.87), 427 (5.20), 530 (4.14), 573 (3.76), 615 (3.62), 674 (3.71).

5,10,15,20-Tetrabutyl-2-(4-carboxy-4-cyanobuta-1,3-dienyl)porphyrin (1)

Porphyrin **4** (0.06 g, 0.1 mmol), cyanoacetic acid (0.09 g, 1.0 mmol), and ammonium acetate (0.08 g, 1.0 mmol) were dissolved in a mixture of tetrahydrofuran (3 mL) and glacial acetic acid (3 mL). The resulting mixture was stirred at 65 °C for 1.5 h then quenched by cold water (20 mL). The dark powder was filtered off, washed several times with water then dried under vacuum at 60 °C to the give product **1** (0.06 g, 92 %) as a brown powder.

^1H NMR (500 MHz, d_6-DMSO): The strong aggregation of this free base porphyrin considerably broadens the ^1H NMR proton resonances so as to make the spectrum uninterpretable. FAB-LRMS: m/z (%, assignment) cluster at 654-659, 655 (92, M^+). HRMS: Calcd for M^+ ($C_{42}H_{49}N_5O_2$): 655.3886, found: 655.3878.

Photophysical measurements: Natural graphite was obtained from Kropfmühl AG. It was ultrasonicated in THF (Sigma Aldrich) in the presence of the porphyrin **1** for 60 min an “Elmasonic P” (Elma) ultrasonication bath at 37 Hz and 100% power setting, followed by centrifugation (10.000 G) for 30 minutes or sedimentation over one week. The supernatant was decanted and, upon sedimentation over night, used for further measurements. Steady state absorption spectroscopy was carried out with quartz cuvettes (10 x 10 mm) with a Cary5000 (Varian) two beam spectrometer. Emission spectroscopy was performed with a FluoroMax-3 (HORIBA Jobin Yvon) with excitation wavelength of 515 nm, slit widths of emission and excitation of 5 nm each. Time correlated single photon counting (TCSPC) spectra were recorded with a Fluorolog system (HORIBA Jobin Yvon) with excitation at 403 nm signal detection with an MCP photomultiplier (Hamamatsu type R3809U-50). The time profiles were recorded at 686 and 750 nm. Transmission electron microscopy (TEM) images and selected area electron diffractograms (SAED) were recorded with a Zeiss EM 900 from a carbon coated copper grid with acceleration voltage of 80 kV. Raman spectra were measured with an Aramis (HORIBA Jobin Yvon) confocal microscope at 532 nm (2.33 eV) and 633 nm excitation wavelengths from spin coated 300 nm silicon-oxide wafer. Femtosecond transient absorption spectra were taken at 387 nm laser pulse (1 kHz, 150 fs pulse width, 200 nJ) by an amplified Ti:sapphire laser system (Clark-MXR). A collimated light beam from a 1000 W xenon lamp equipped with a 350 nm cutoff filter was used for the white illumination.

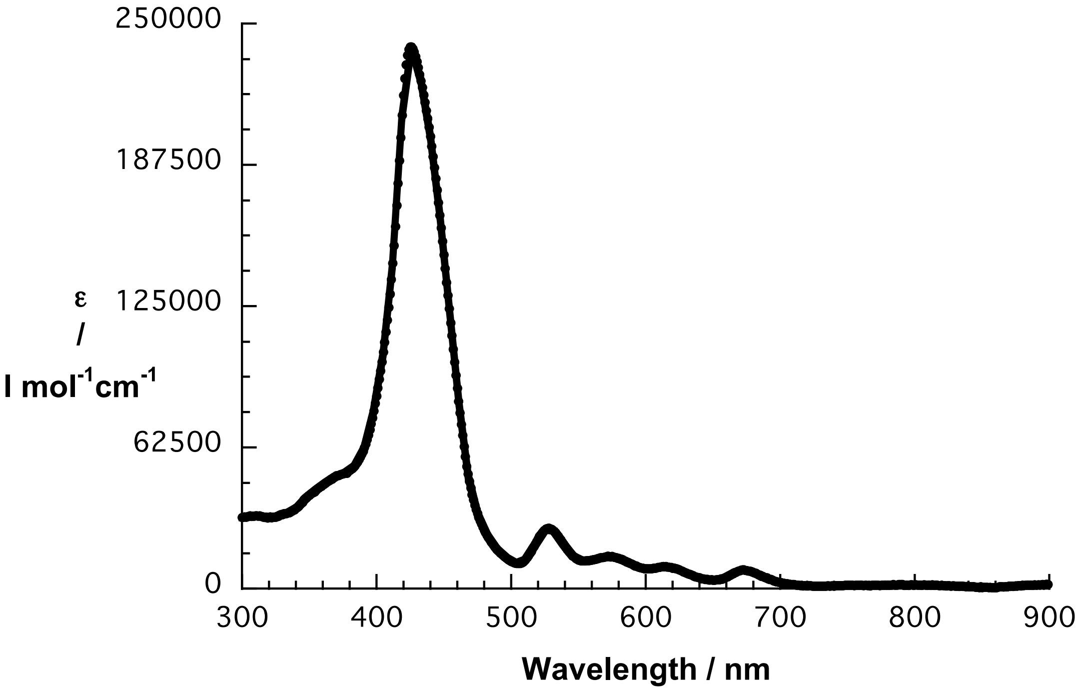
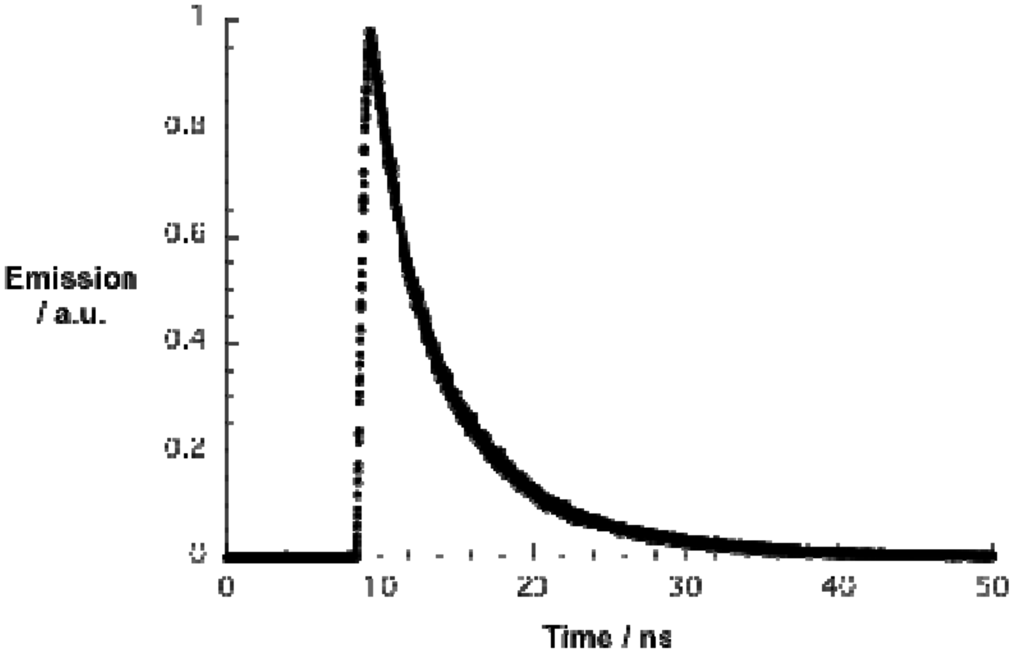


Figure S1. Room temperature absorption spectrum of **1** in THF.



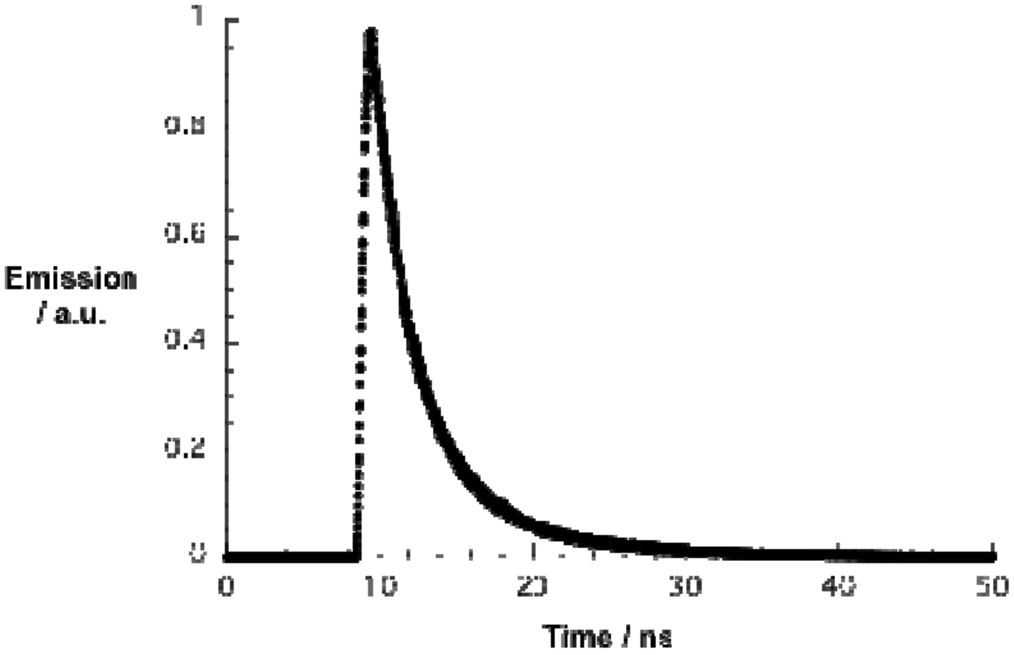
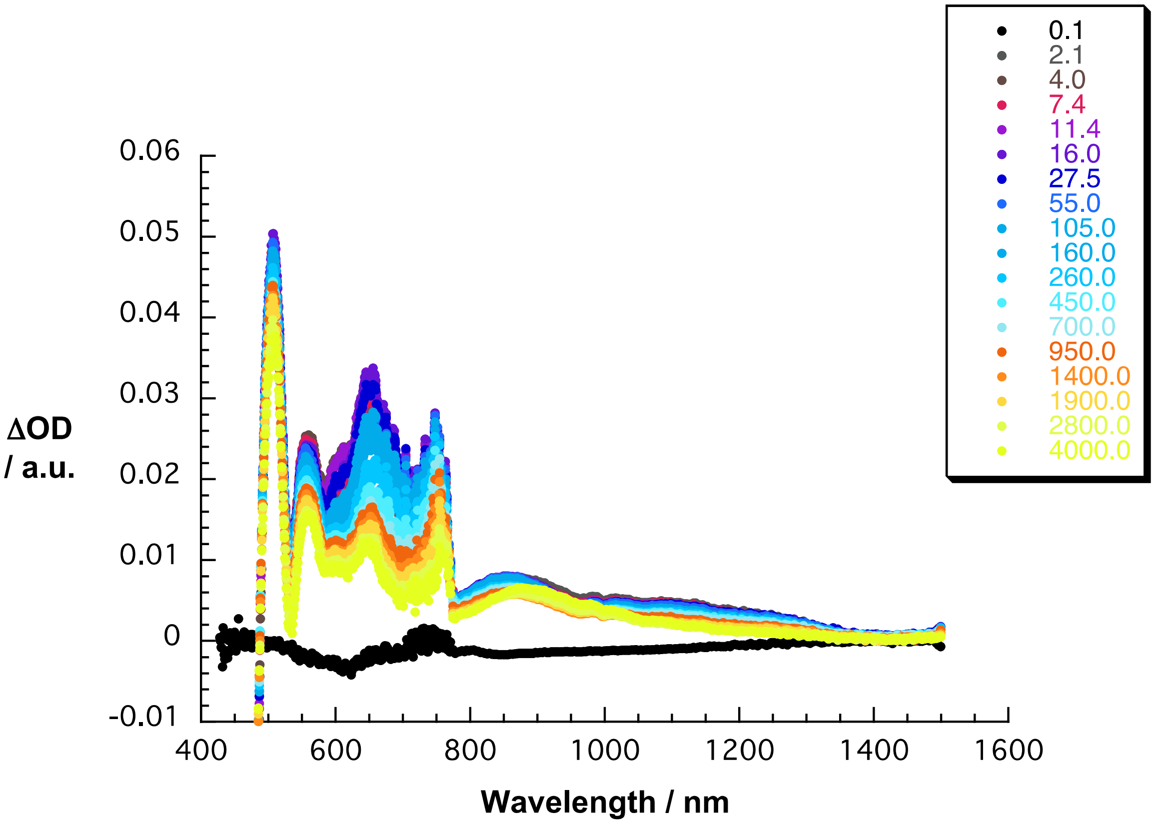


Figure S2. Upper part – bi-exponential fit of the room temperature fluorescence decay of **1** in THF with 403 nm excitation wavelength and 680 nm detection wavelength. Lower part – bi-exponential fit of the room temperature fluorescence decay of **5** in THF with 403 nm excitation wavelength and 750 nm detection wavelength.



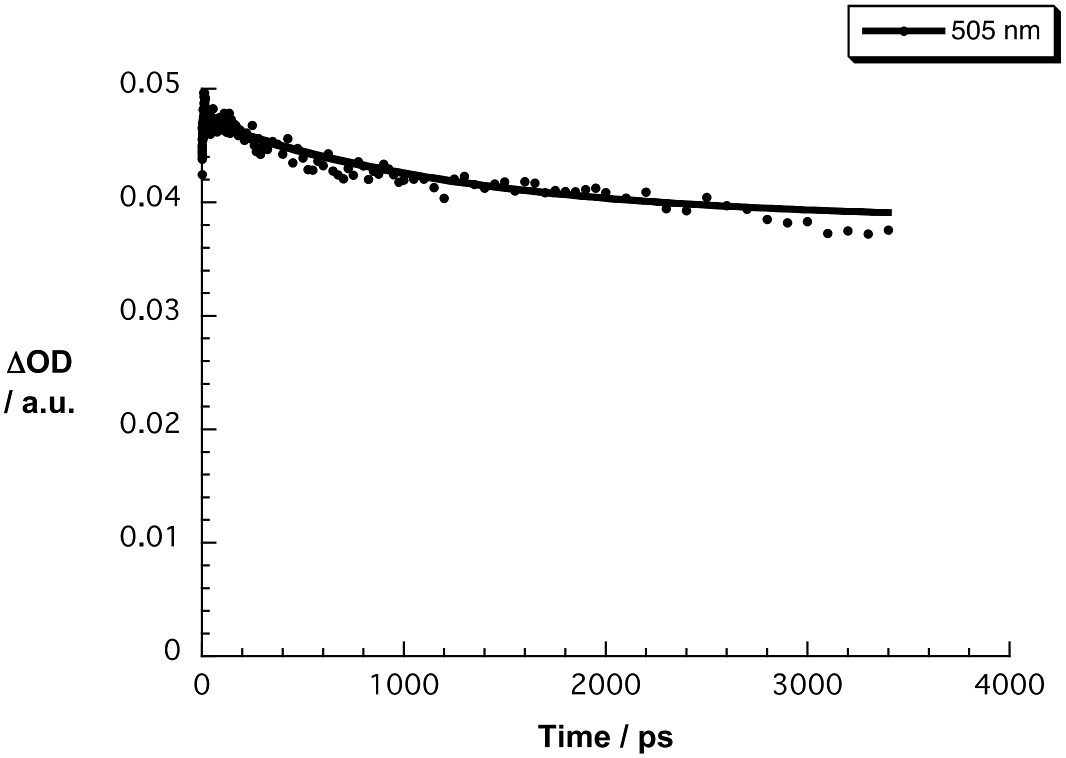
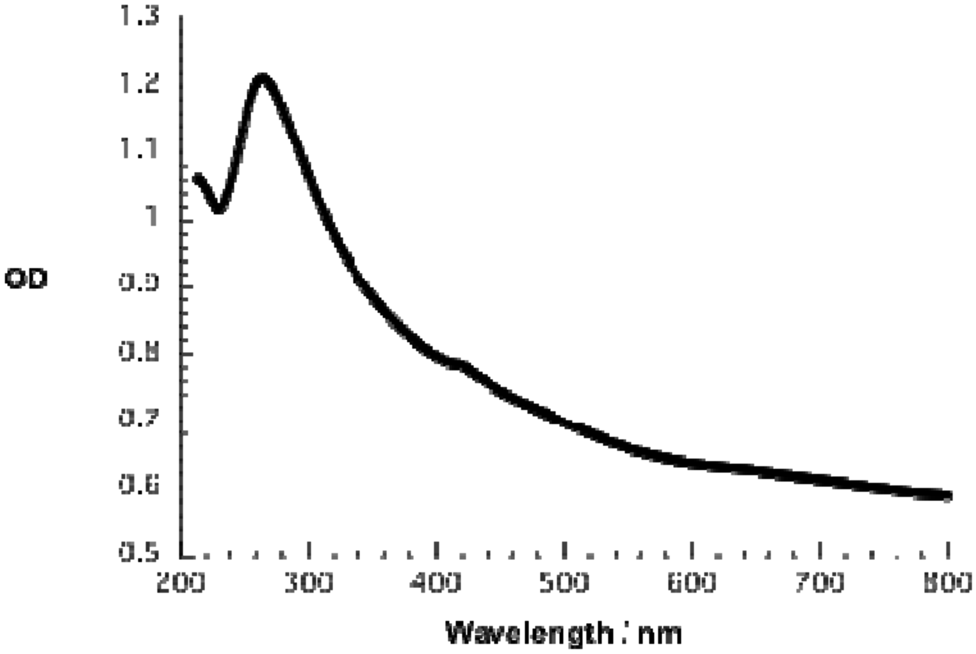


Figure S3. Upper part – differential absorption spectra (visible) obtained upon femtosecond pump probe experiments (387 nm) of **1** in THF with several time delays between 0.1 and 4000.0 ps at room temperature – see Figure legend for details. Lower part – time absorption profiles of the spectra at 505 monitoring the excited state dynamics.



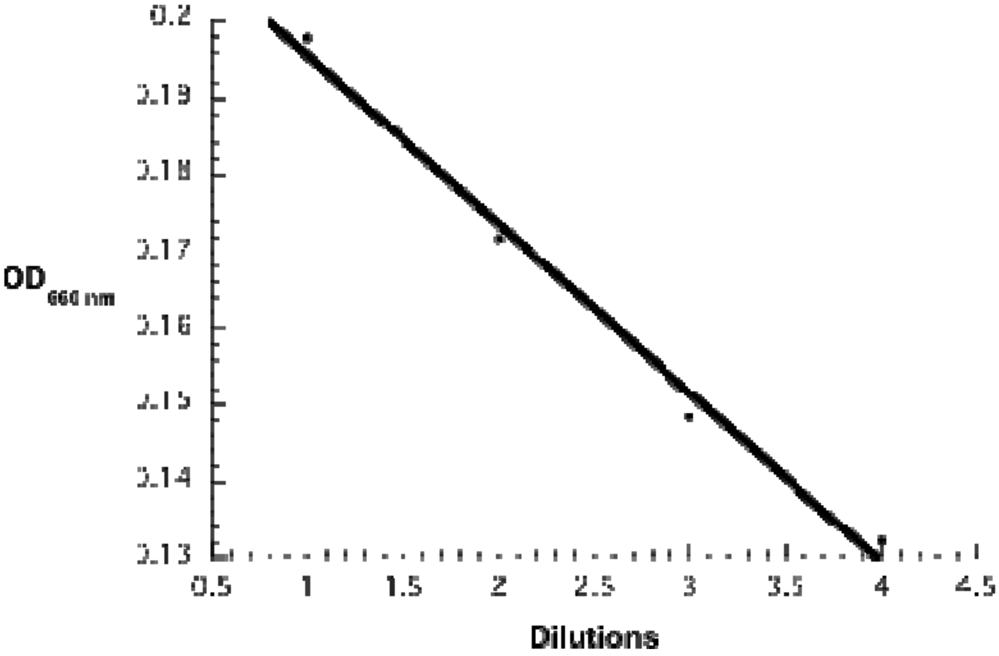


Figure S4. Upper part – absorption spectrum of nanographene / **1** dispersion in THF. Lower part – dilution steps versus optical density of nanographene / **1** dispersion in THF.

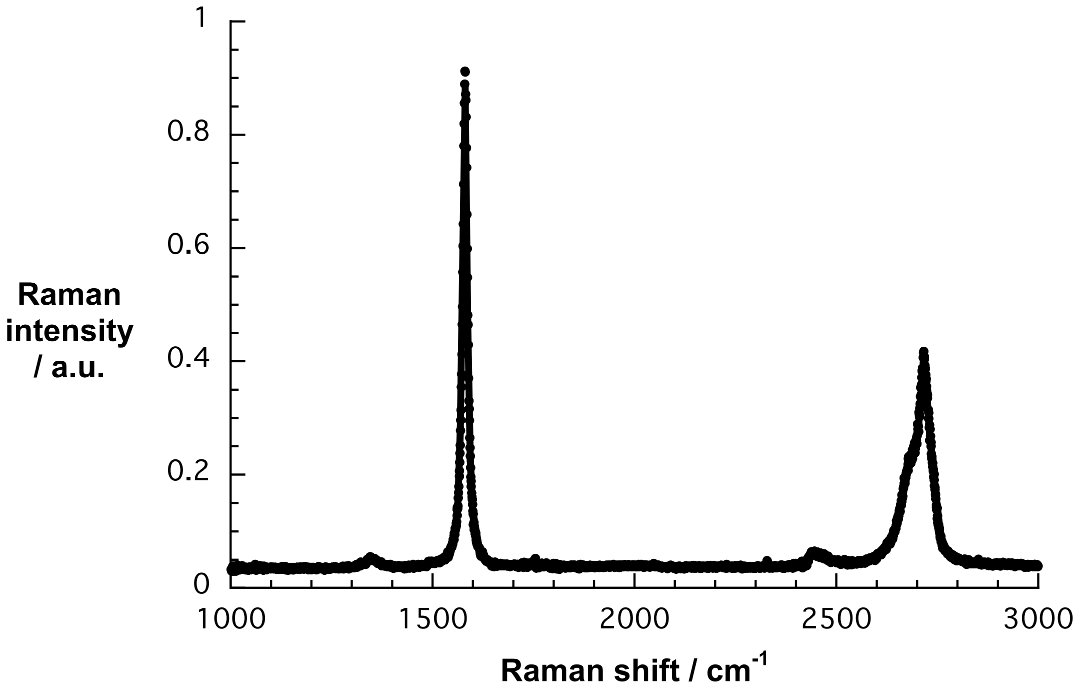


Figure S5. Raman spectrum of graphite dispersion in THF drop-casted onto a silicon oxide wafer and excited at 532 nm.

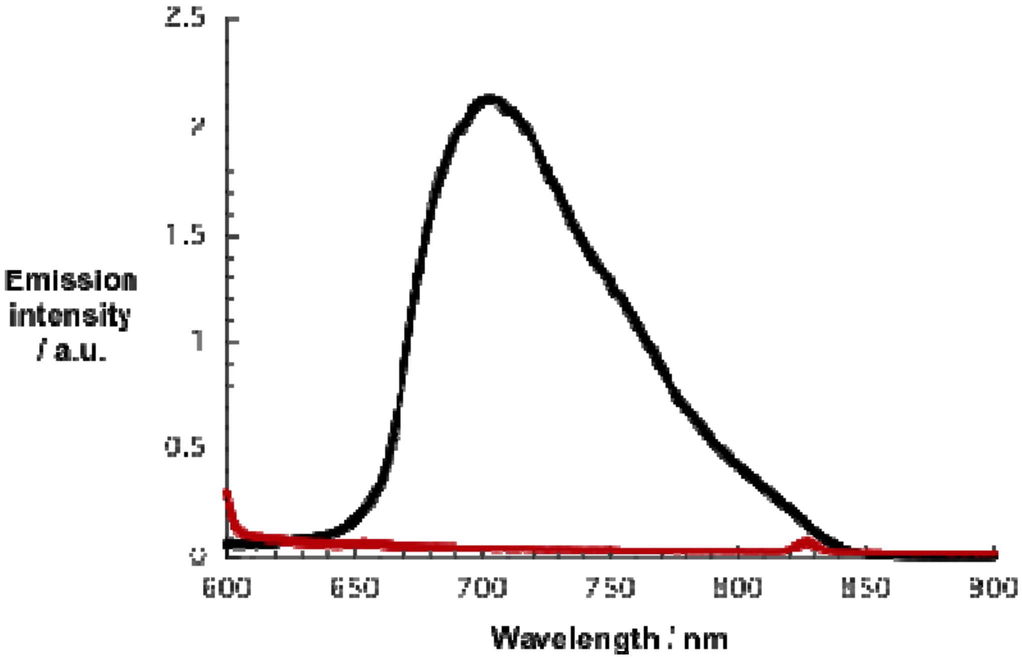


Figure S6. Fluorescence spectra of **1** (black spectrum) and nanographene / **1** (red spectrum) in THF exhibiting the same optical density of 0.05 at the excitation wavelength of 550 nm.

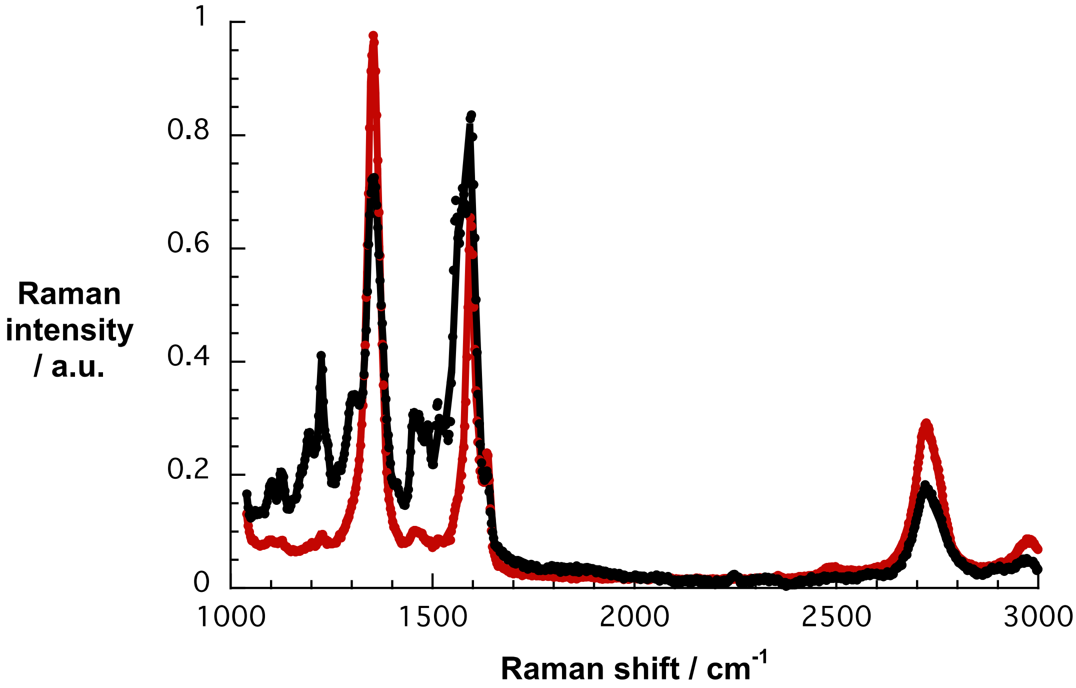


Figure S7. Raman spectra of nanographene / **1** dispersion in THF drop-casted onto silicon oxide wafer and excited at 633 nm prior (black spectrum) and after irradiation (red spectrum) at 3.2 mW for 10 minutes.

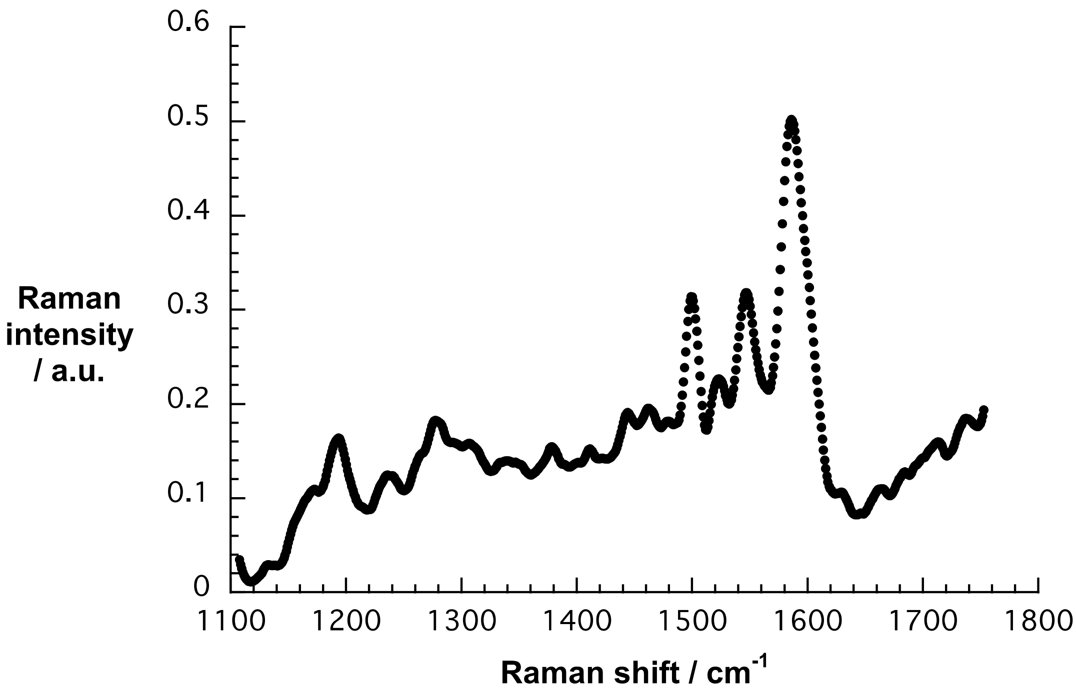
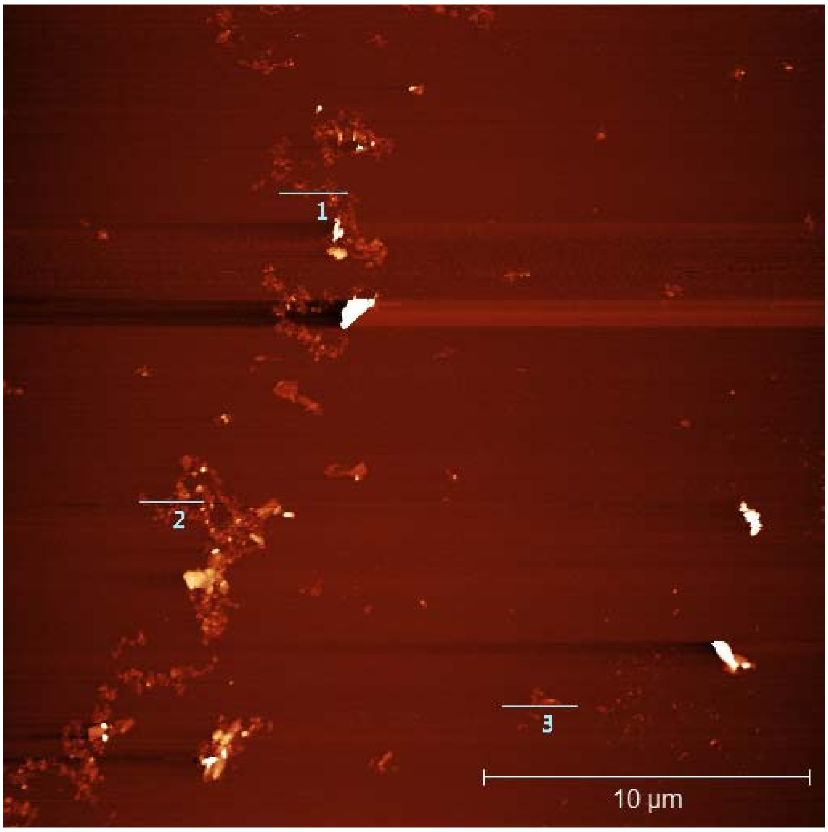
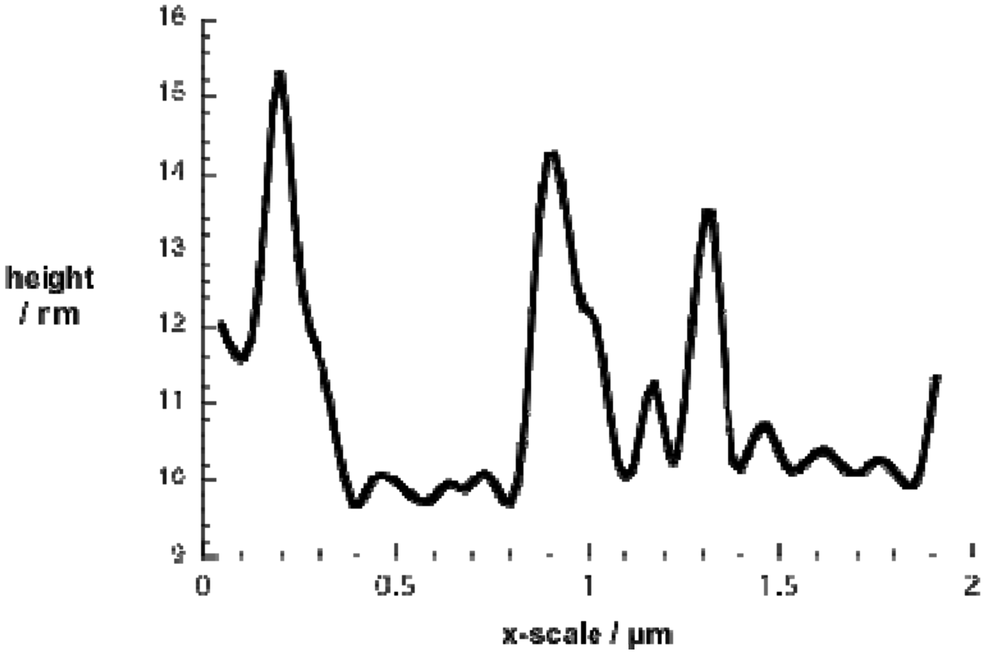
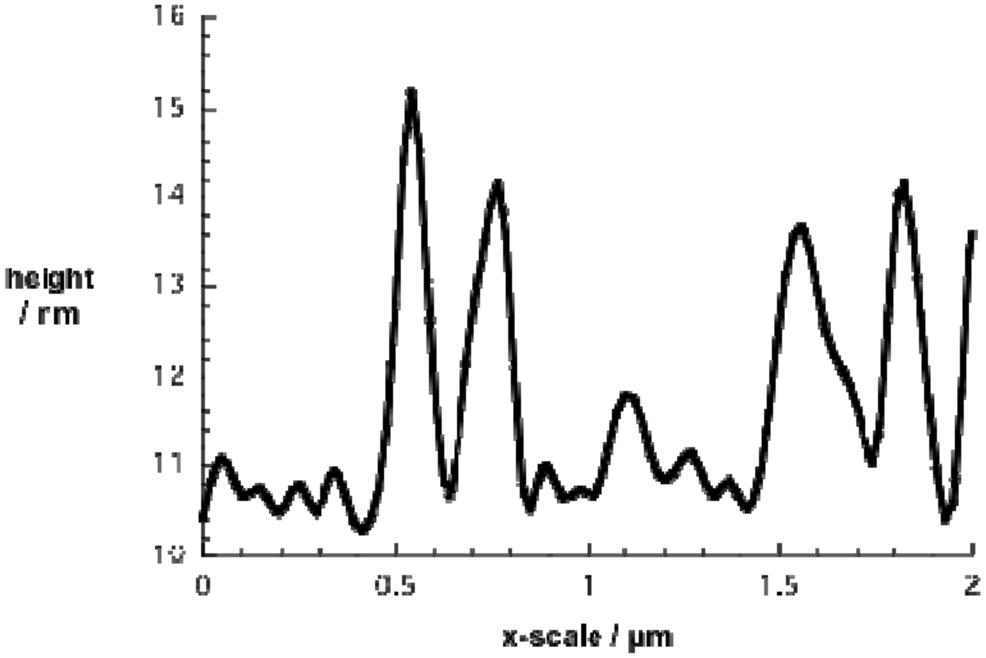


Figure S8. Raman spectrum of solid **1** excited at 1064 nm.


1
2
3
10 µm


16
15
14
13
12
11
10
9
height / nm
0
0.5
1
1.5
2
x-scale / µm



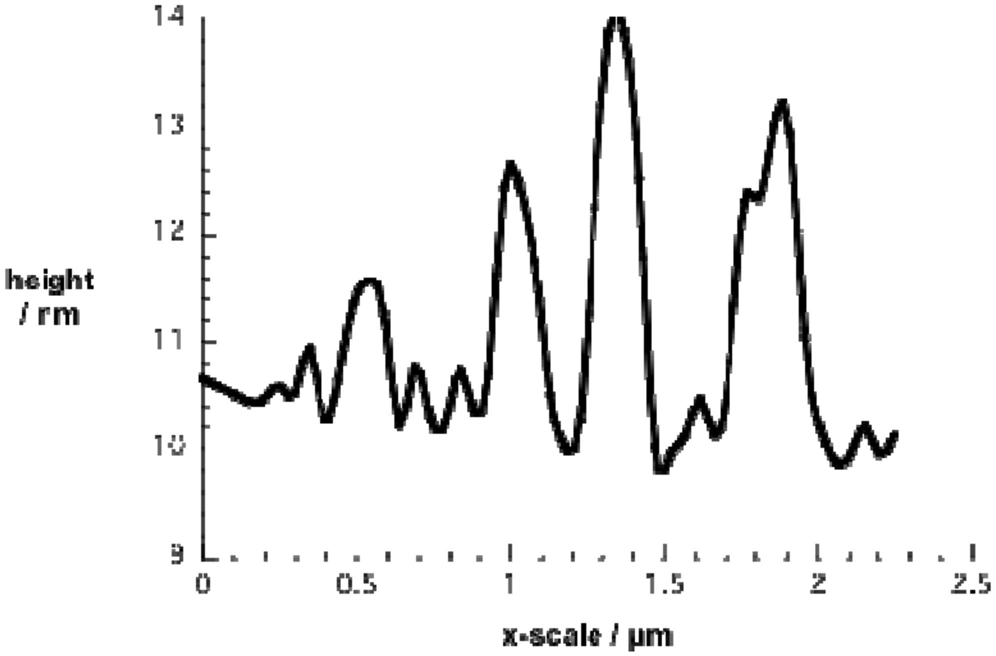


***Figure S9**.* Upper part – AFM image of of nanographene / **1** dispersion in THF drop-casted onto silicon oxide wafer. Upper central part – corresponding height profile at 1. Lower central part – corresponding height profile at 2. Lower part – corresponding height profile at 3.

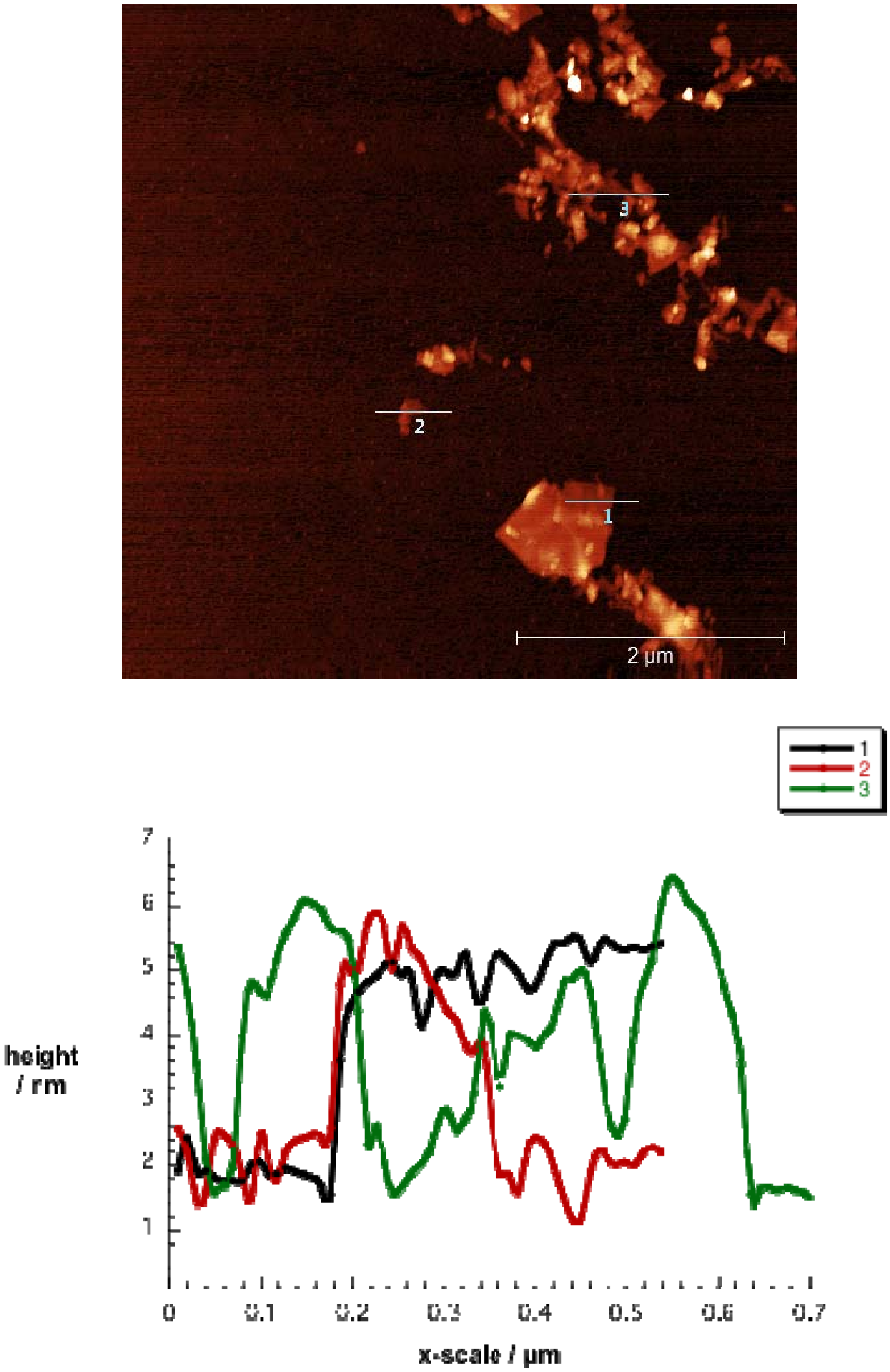


Figure S10. Upper part – AFM image of of nanographene / **1** dispersion in THF drop-casted onto silicon oxide wafer. Lower part – corresponding height profiles at 1, 2, and 3.

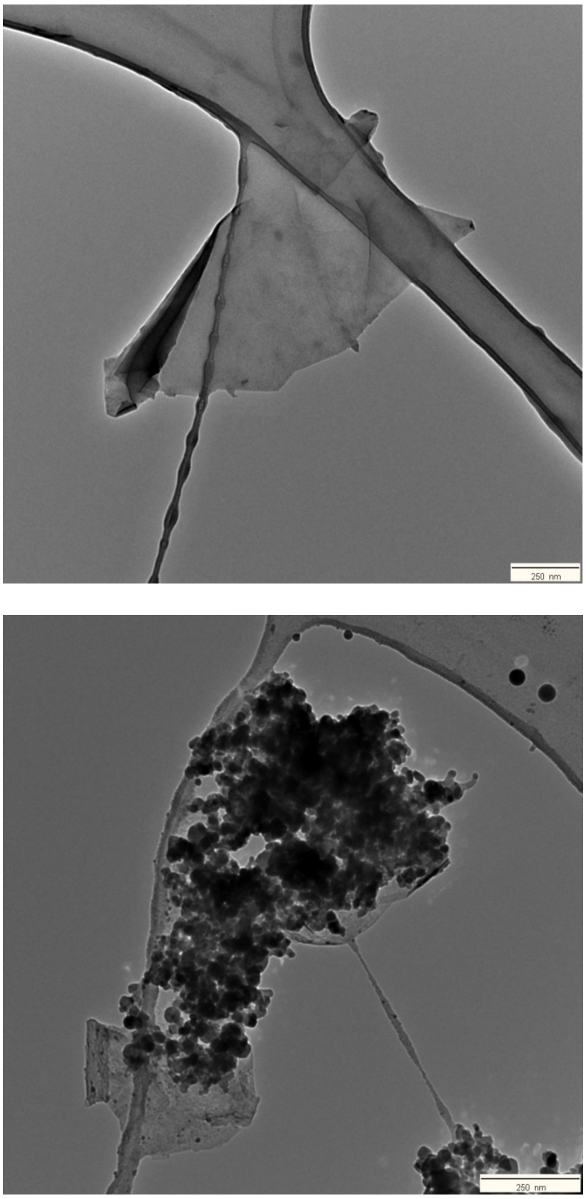


Figure S11. Upper part – TEM image of nanographene / **1** dispersion in THF drop-casted onto lacey carbon grids and without TiO_2. Lower part – TEM image of nanographene / **1** dispersion in THF drop-casted onto lacey carbon grids and with TiO_2.

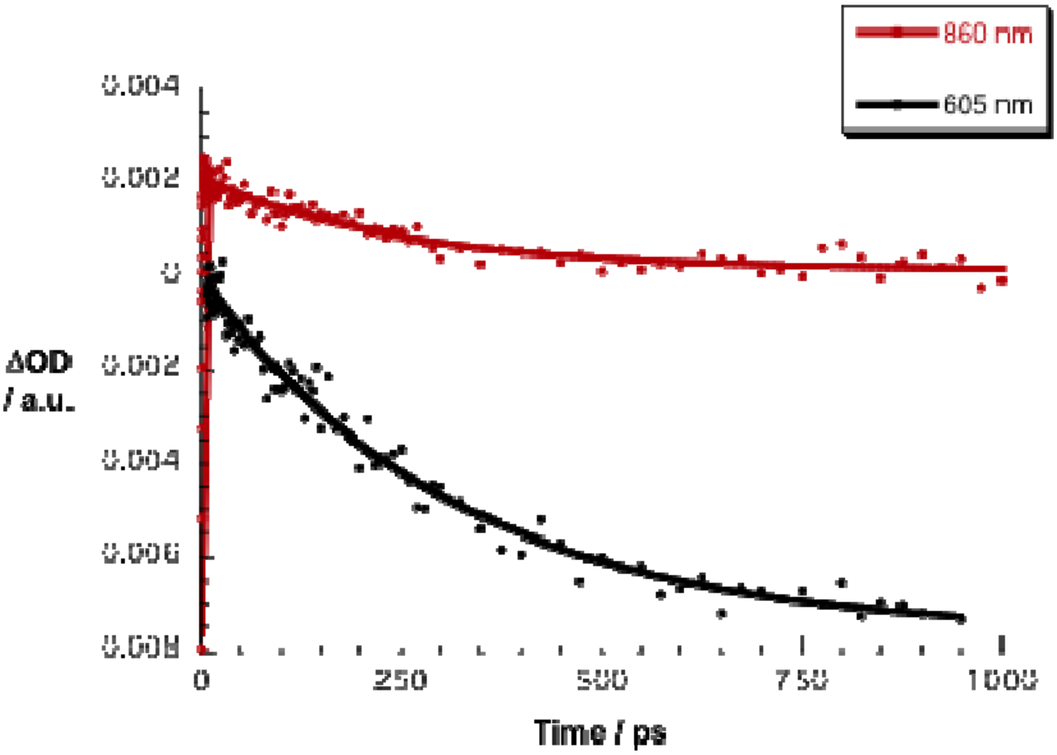


***Figure S12**.* Time absorption profiles of the spectra shown in Figure 4 at 605 (black) and 860 nm (red) monitoring the charge separation and charge recombination dynamics.

References

1. M. O. Senge, I. Bischoff, N. Y. Nelson, K. M. Smith, *J. Porphyrins Phthalocyanines*, **1999**, *3*, 99.