

Supporting Information

Electron-Accepting Phthalocyanine-Pyrene Conjugates: Towards Liquid Phase Exfoliation of Graphite and Photoactive Nanohybrid Formation with Graphene

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1. Supporting Figures

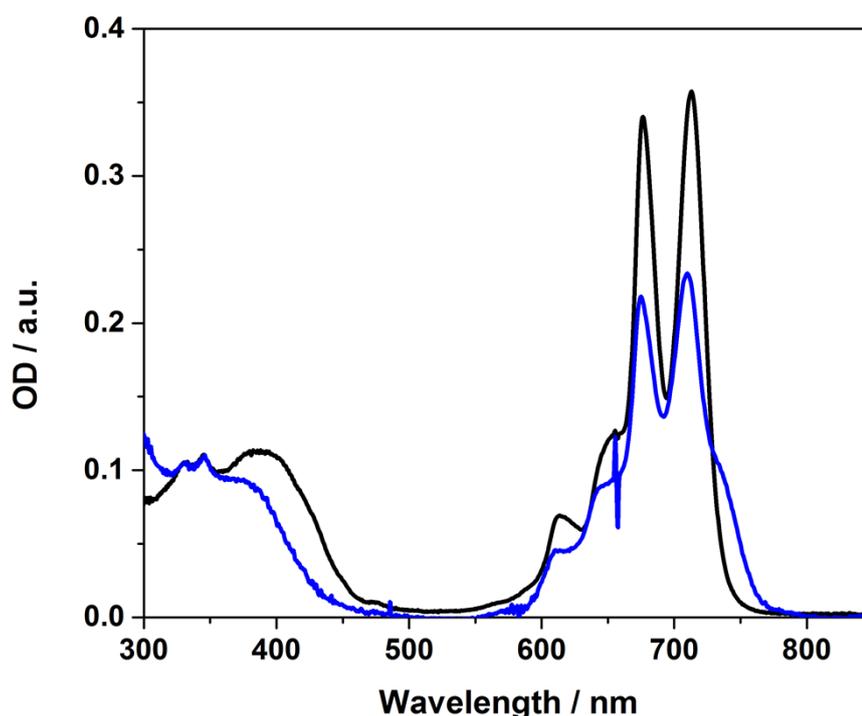


Figure S1. Absorption spectra (visible) of neutral **2** (black) and the corresponding reduced species of **1** (blue) obtained upon electrochemical reduction in acetonitrile:toluene 1:4 (v/v) with 0.1 M TBAPF₆ with an applied potential of -0.7 V vs. Ag-wire.

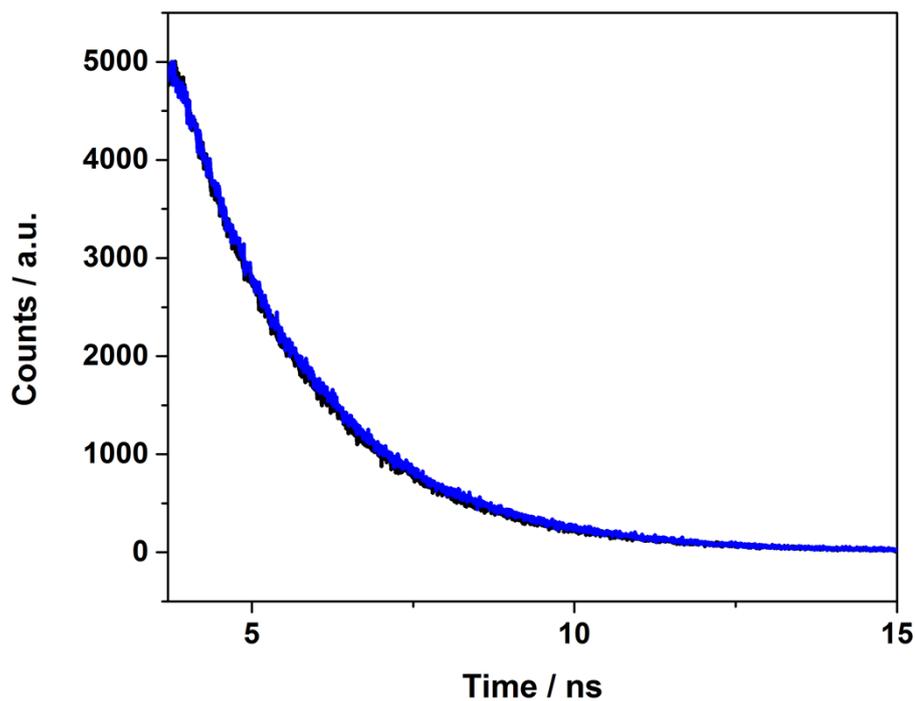


Figure S2. Emission time profiles of **2** (black) and **1** (blue) in DMF following 647 nm excitation wavelength and the corresponding emission maxima as emission wavelengths.

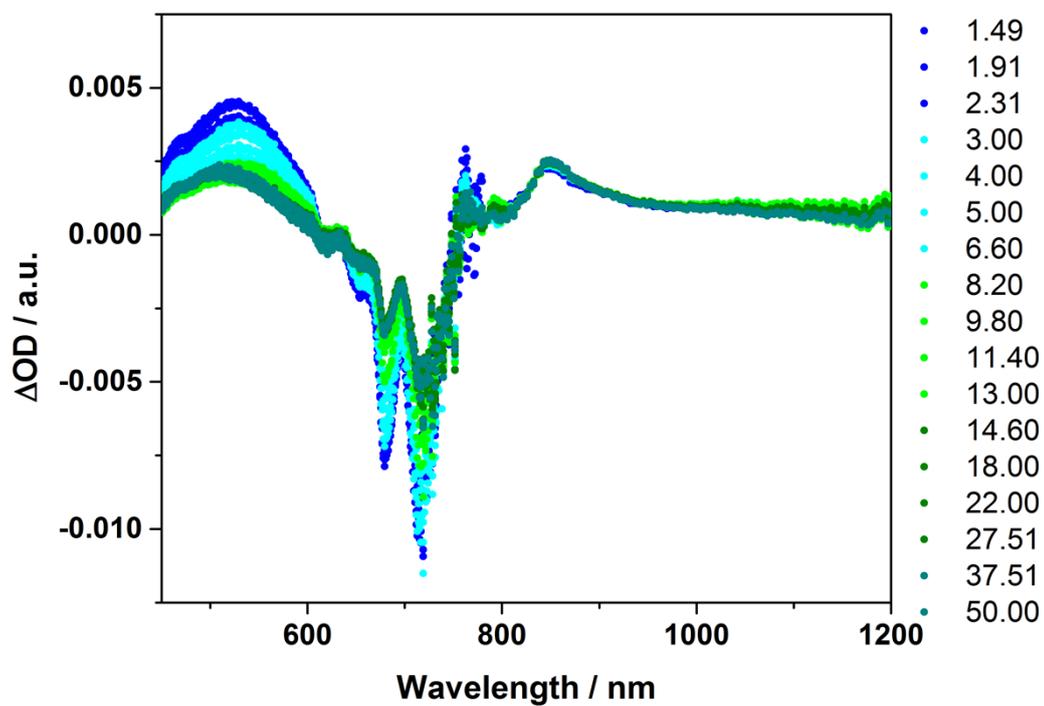


Figure S3. Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (387 nm) of **1** in DMF with time delays between 1.59 and 50 ps at room temperature – for time delays see figure legend.

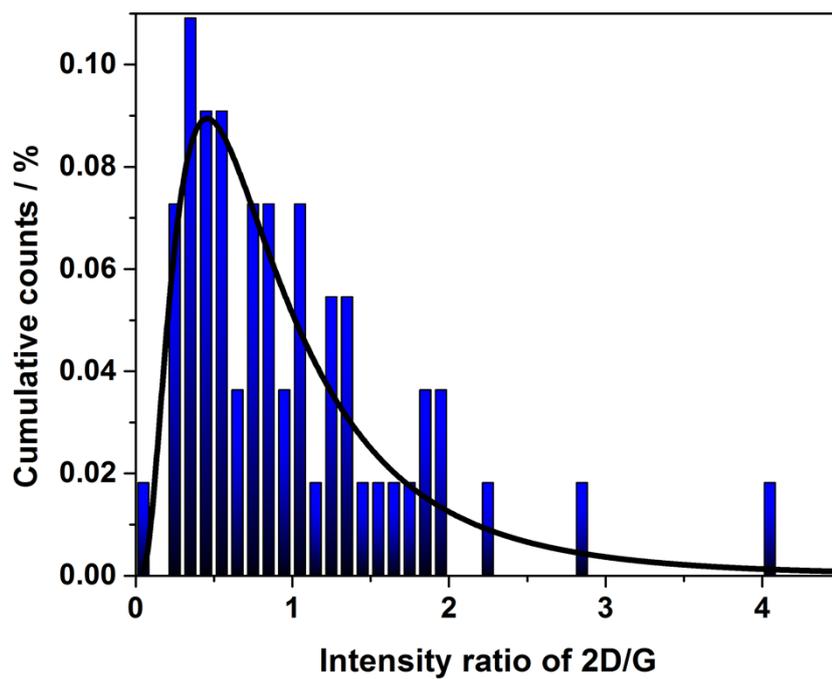
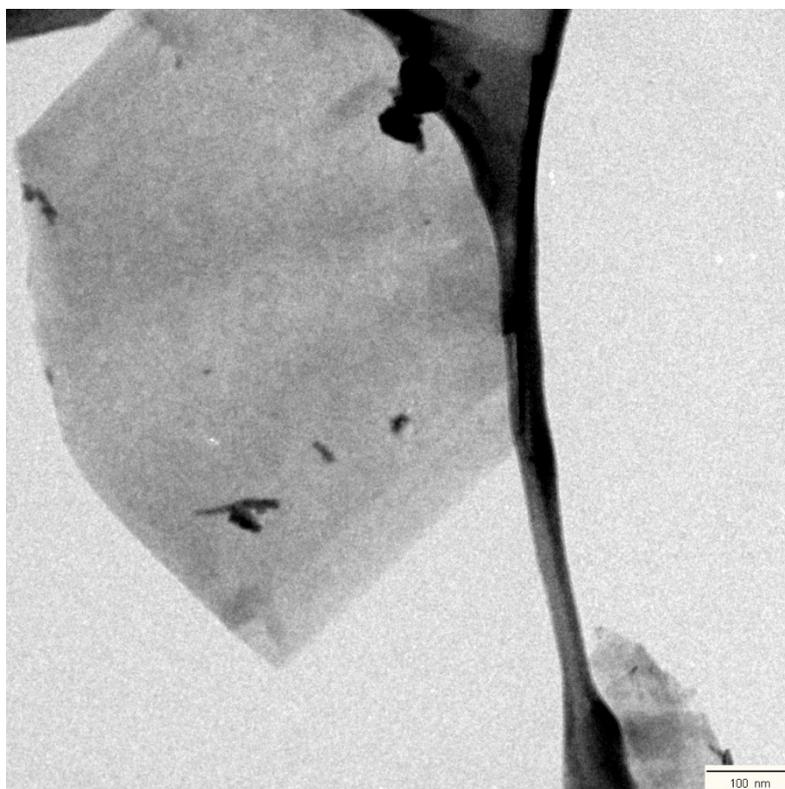


Figure S4. Histogram resulting from the Raman mapping of **1** / nanographene showing relative counts vs. $I(2D) / I(G)$ ratio and the corresponding log-normal distribution. The sample was drop casted from a DMF dispersion onto silicon oxide wafer and was excited at 532 nm.

Figure S5. TEM image of **1** / nanographene on a lacey carbon grid.



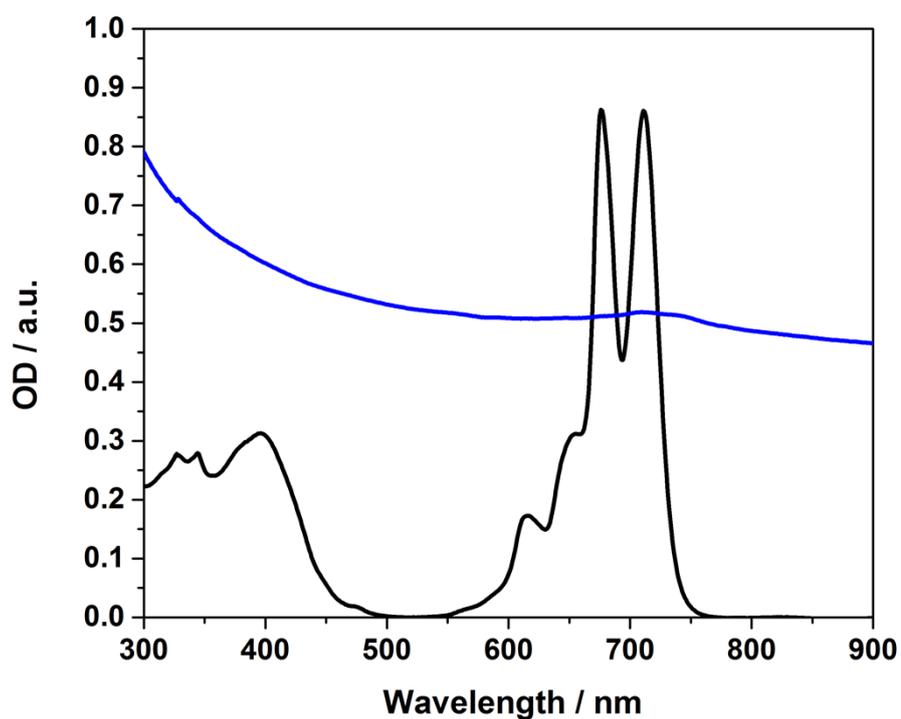


Figure S6. Absorption spectra of the pure compound **1** in DMF (black) and of **1** / nanographene after the 6th exfoliation/enrichment cycle (blue).

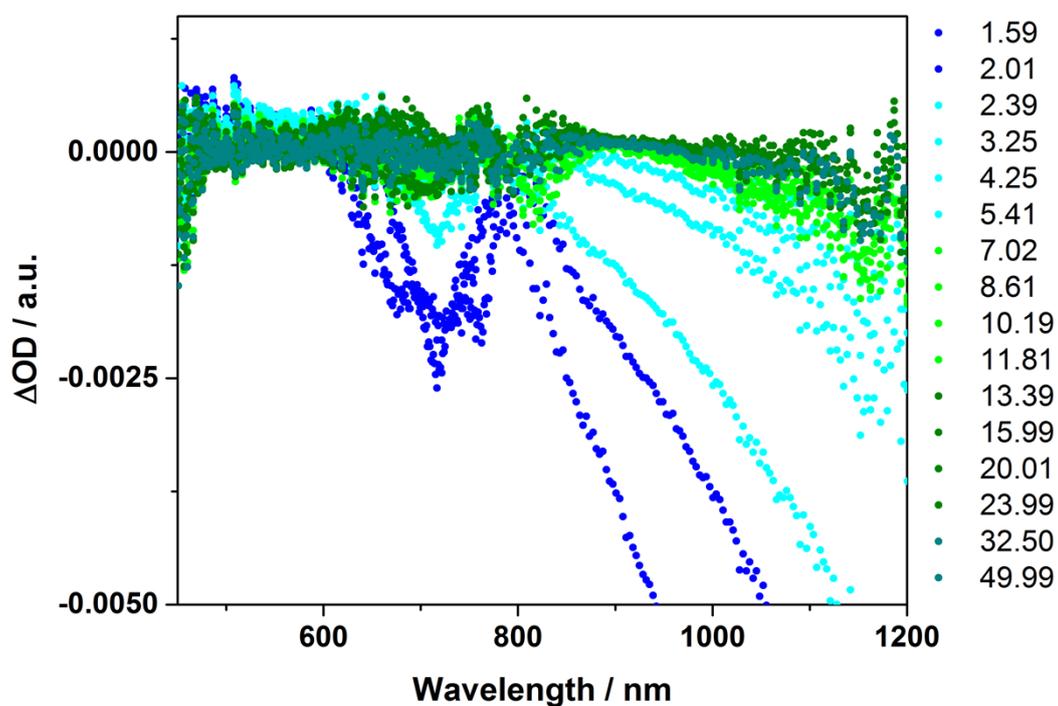


Figure S7. Differential absorption spectra (visible & near-infrared) obtained upon femtosecond pump probe experiments (387 nm) of **1** / nanographene in DMF with time delays between 1.59 and 50 ps at room temperature – for time delays see figure legend.

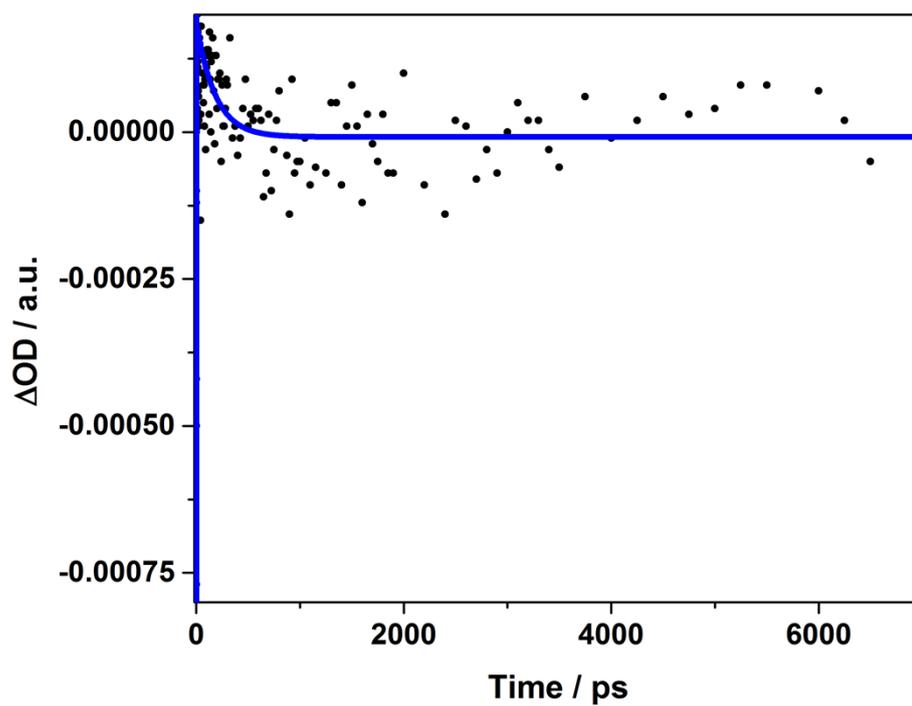


Figure S8. Time absorption profiles of the spectra shown in Figure S7 fit at 760 nm monitoring the charge transfer.

2. Experimental Details

NMR spectroscopy: ^1H spectra were recorded at 300 MHz at 25 °C with a BRUKER AC-300 instrument. NMR data: chemical shifts are given in parts per million, coupling constants are given in hertz.

Mass spectrometry: HRMS spectra were determined on a VG AutoSpec instrument.

Chromatography: Column chromatography was carried out on silica gel Merck-60 (230–400 mesh, 60 Å), and TLC on aluminum sheets pre-coated with silica gel 60 F254 (E. Merck).

Optical characterization

Steady-state absorption spectra were recorded with a Perkin-Elmer Lambda 35. Steady-state emission spectra were recorded with a Fluoromax-3-spectrometer from HORIBA Jobin Yvon. All samples were measured in a fused quartz glass cuvette with a diameter of 10 mm.

Femtosecond transient absorption spectroscopy

Femtosecond transient absorption spectra were obtained with a Ti:sapphire laser system CPA-2101 (Clark-MXR), Inc.) in combination with a Helios TAPPS detection unit from Ultrafast Inc. The initial laser excitation wavelength is 775 nm with a pulse width of 150 fs. The used excitation wavelength was 387 nm, which was generated with a SHG crystal. For the generation of the white light a sapphire crystal of adequate thickness was used. The chirp-effect between 420 and 770 nm is approximately 350 fs. The detection was carried out with two CCD cameras, each for a specific measuring range. The spectral window is therefore 415 to 770 nm and 770 to 1600 nm. The delay line allows spectral acquisition up to time delays of 8000 ps. All samples were measured in a fused quartz glass cuvette with a thickness of 2 mm. Data was acquired with the software HELIOS Visible/nIR (Newport / Ultrafast Systems).

Raman spectroscopy

Raman measurements were carried out with a Renishaw inVia Reflex Confocal Raman Microscope using laser excitations of 532 nm. The sample was prepared by drop casting a dispersion of the materials on a Si substrate with a 200 nm oxide layer.

Atomic force microscopy

AFM images were obtained with a Nanoscope IIIa Multimode, Veeco in tapping mode. The sample was prepared by dip coating a silicon wafer into the corresponding dispersion letting it dry under an airstream.

Transmission electron microscopy

Sample preparation was performed by drop casting and drying the hybrids on lacey carbon coated copper grids. Bright-field TEM images were recorded with an 80 kV EM 900 from Carl Zeiss AG.

Materials

Natural graphite was purchased from Graphit Kropfmühl AG. All other reagents were purchased from commercial suppliers and used without further purification.

Synthesis of 2

To a solution of 1-pyrenebutyric acid (2 mg, 7 μmol) in CH_2Cl_2 (1 mL) at 0 ° C are added EDC (1.5 mg, 10 μmol) and DMAP (0.8 mg, 7 μmol). Stirring at this temperature continues for 20 minutes, after which hydroxy-Pc **1** (13 mg, 7 μmol) is added. After 1 h the mixture is brought to room temperature and is left stirring for an additional 48 hours. Solvents are evaporated and the crude is purified by column chromatography (Hexane/THF, 2:1). Washing with MeOH affords the desired compound as a green solid (10 mg, 65%). UV-Vis (THF): λ_{max} (nm) = 265.5 (4.3), 276.5 (4.4), 327 (4.3), 343.5 (4.4), 370.5 (4.3), 606.5 (3.9), 642 (4.1), 670 (4.5), 703.5 (4.5). HRMS (MALDI-TOF, dithranol): Calcd for $\text{C}_{107}\text{H}_{132}\text{N}_8\text{O}_{14}\text{S}_6\text{Zn}$: 2008.7468. Found: 2008.7473