

## Supporting Information

# Nanographene Favors Electronic Interactions with the Electron Acceptor Rather Than the Electron Donor in a Planar Fused Push-Pull Conjugate

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## Synthesis of TTF-PDI 1

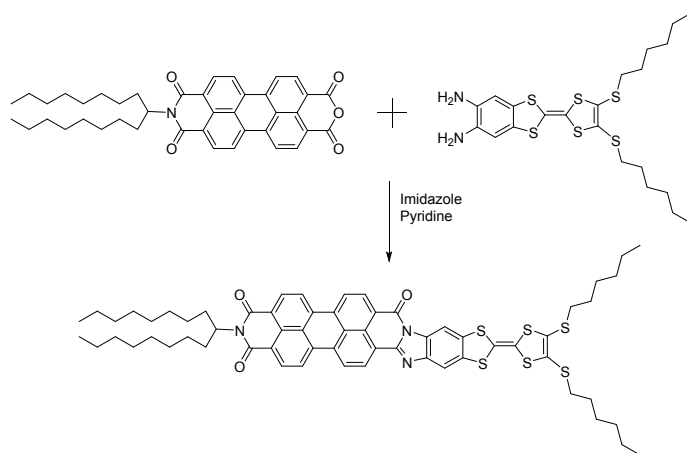
### Materials

The compounds *N*-(1-octylnonyl)perylene-3,4,9,10-tetracarboxylic acid 3,4-anhydride-9,10-imide<sup>1</sup> and 5,6-diamino-2-(4,5-bis(hexylthio)-1,3-dithio-2-ylidene)benzo[*d*]-1,3-dithiole<sup>2</sup> were prepared according to the literature procedures. All other chemicals and solvents were purchased from commercial sources and were used without further purification.

### Physical measurements

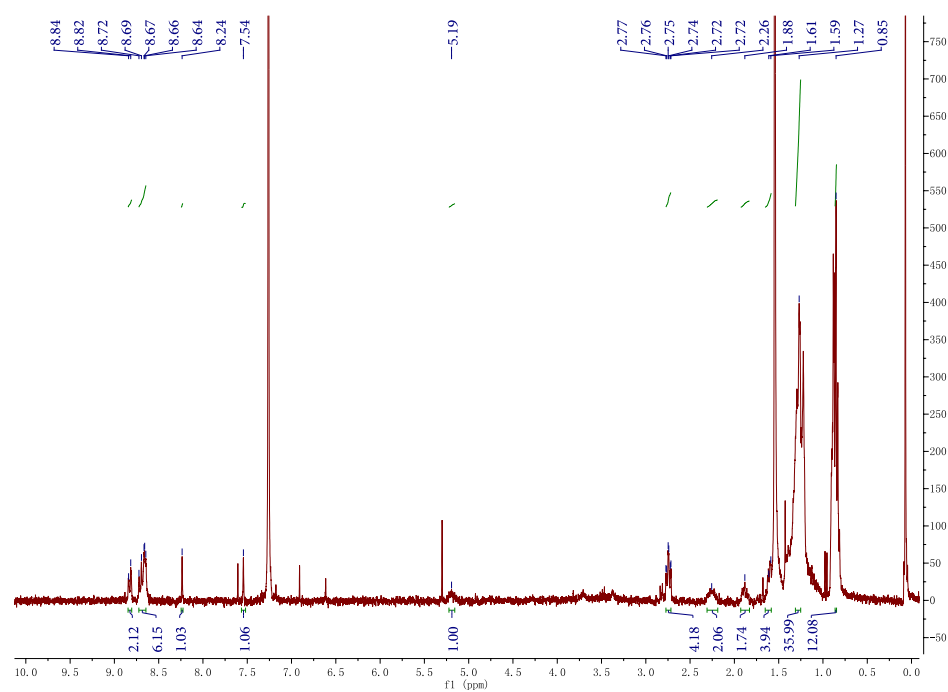
<sup>1</sup>H NMR spectrum was carried out on a Bruker AC 300 spectrometer operating at 300.18 MHz. Chemical shifts are reported in ppm referenced to residual solvent protons ( $\delta$  = 7.26 ppm for CDCl<sub>3</sub>). FT-IR data were collected on a FT/IR-4700 FTIR Spectrometer from JASCO. Mass spectrum was recorded on a FTMS 4.7T BioAPEX II for MALDI ionisation method.

**Scheme 1.** A synthetic route to the target compound PDI-TTF 1.

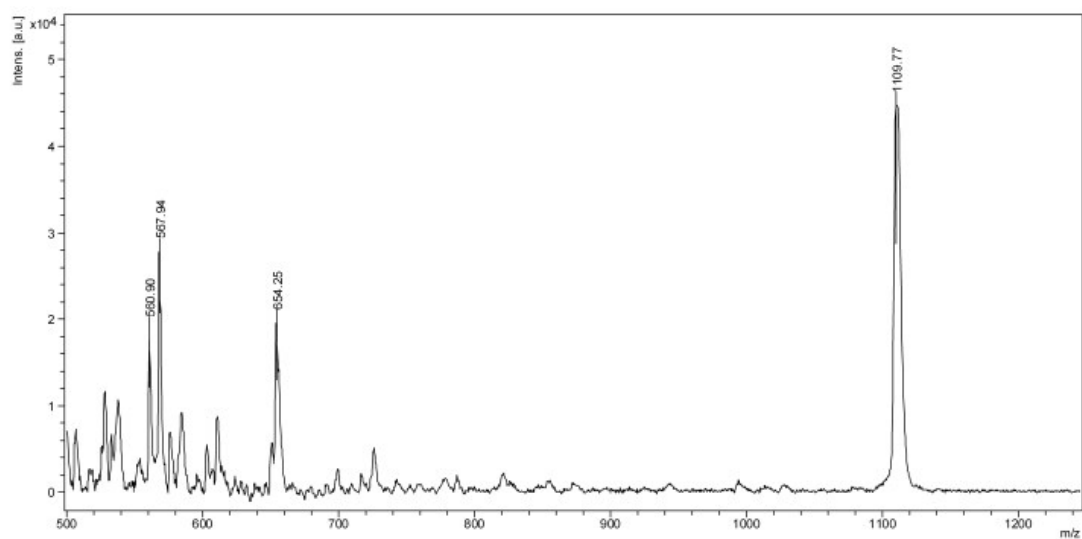


A mixture of *N*-(1-octylnonyl)perylene-3,4,9,10-tetracarboxylic acid 3,4-anhydride-9,10-imide (55 mg, 87  $\mu$ mol), 5,6-diamino-2-(4,5-bis(hexylthio)-1,3-dithio-2-ylidene)benzo[*d*]-1,3-dithiole (27 mg, 52  $\mu$ mol) and imidazole (225 mg, 3.3 mmol) in pyridine (6 mL) was refluxed for 23 h at 130 °C under N<sub>2</sub>. After evaporation of pyridine, the purple residue was subjected to column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub> then CHCl<sub>3</sub>) to yield the deep-purple product. Yield 43 % (26 mg, 23  $\mu$ mol). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.82 (d, *J* = 6 Hz, 2H), 8.66 (m, 6H), 8.24 (s, 1H), 7.50 (s, 1H), 5.19 (br, 1H), 2.75 (t, 4H), 2.26 (br, 2H), 1.88 (br, 2H), 1.59 (m, 4H), 1.27 (m, 36H), 0.85 (m, 12H). Selected IR data (cm<sup>-1</sup>): 3273 (br), 2922 (s), 2852 (m), 1693 (s), 1652 (m), 1592 (m), 1497 (w), 1438 (w), 1341 (s), 802 (s), 716 (s). MS (MALDI-TOF, DCTB as matrix, positive) calcd. for C<sub>63</sub>H<sub>71</sub>N<sub>3</sub>O<sub>3</sub>S<sub>6</sub> 1109.38, found 1109.77.

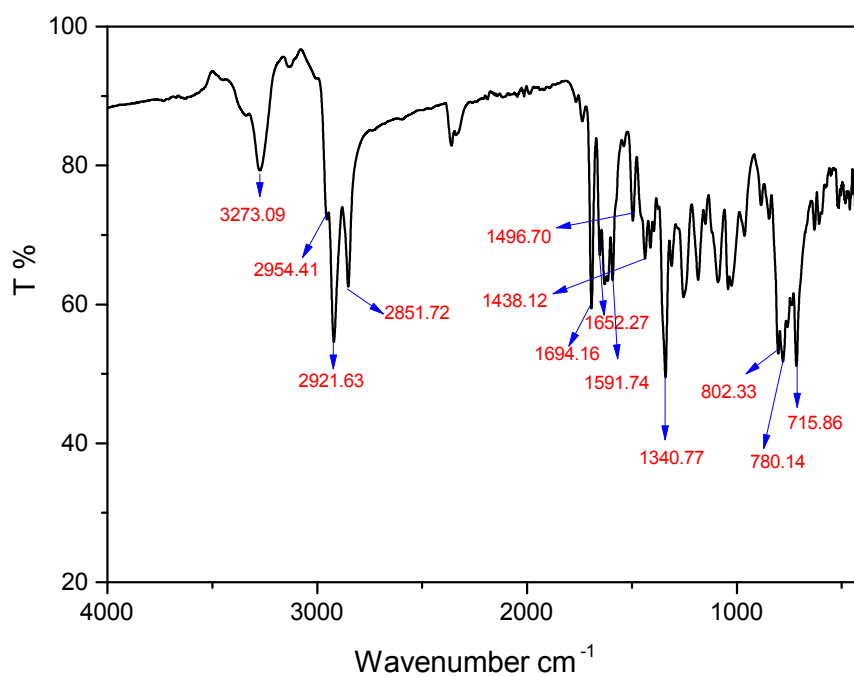
### $^1\text{H}$ NMR spectrum



### MALDI-TOF-MS spectrum



## IR spectrum

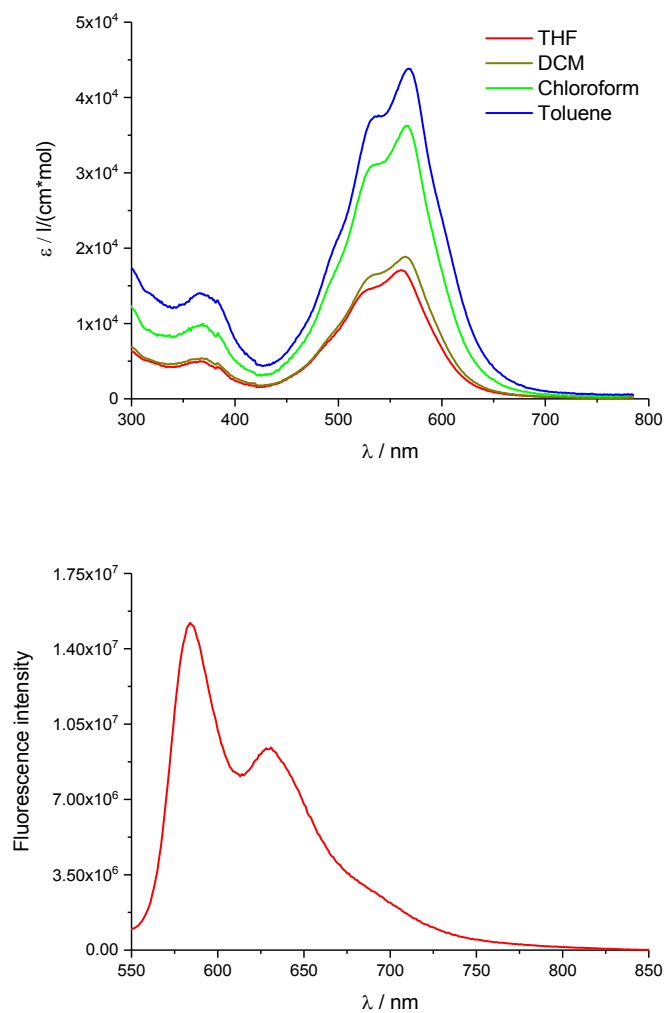


## References

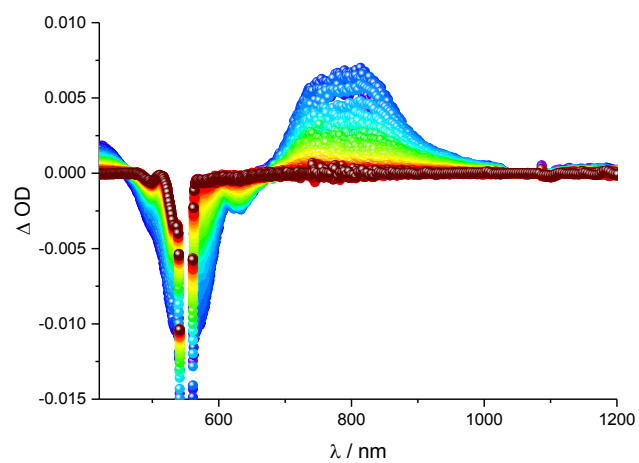
- 1) a) M. Jaggi, C. Blum, N. Dupont, J. Grilj, S.-X. Liu, J. Hauser, A. Hauser, S. Decurtins, *Org. Lett.* **2009**, *11*, 3096; b) L. D. Wescott, D. L. Mattern, *J. Org. Chem.* **2003**, *68*, 10058.
- 2) H-P. Jia, S.-X. Liu, L. Sanguinet, E. Levillain, S. Decurtins, *J. Org. Chem.* **2009**, *74*, 5727.



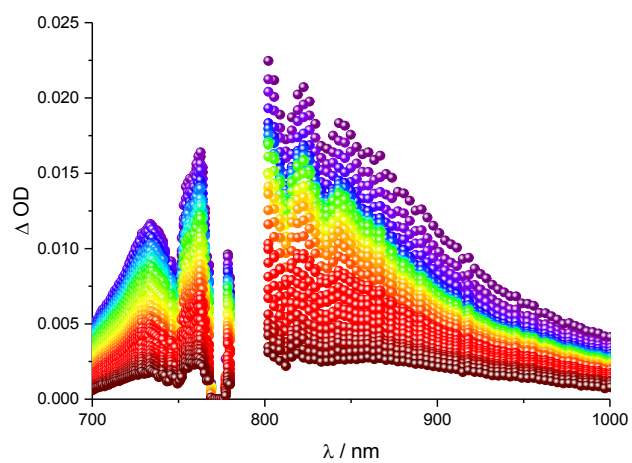
## Figures S1 – S14



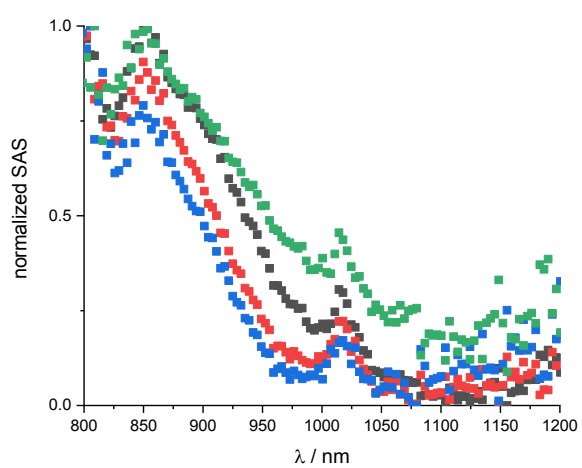
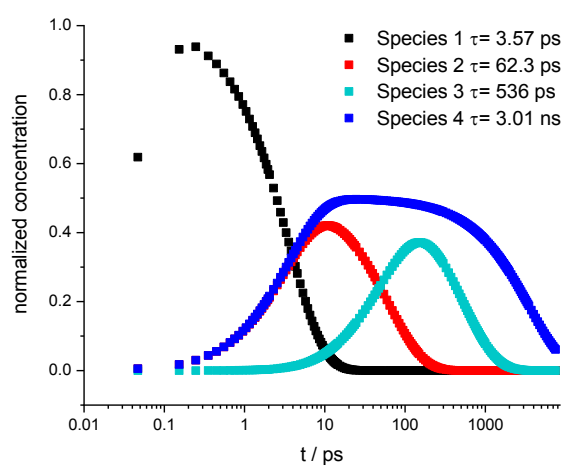
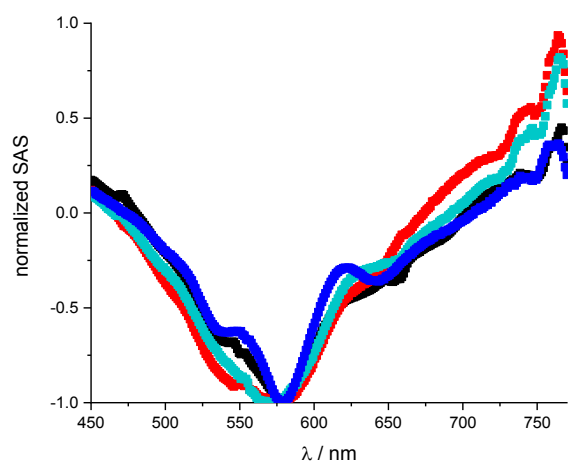
**Figure S1:** Upper part – absorption spectra of **1** in THF (red), Dichloromethane (grey),  $\text{CHCl}_3$  (green) and toluene (blue); Lower part – fluorescence spectrum of **1** upon excitation at 530 nm in THF with an absorption of 0.18 at the excitation wavelength.

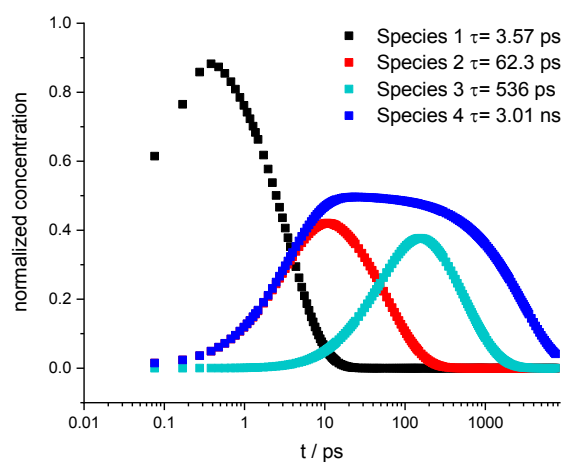


**Figure S2:** Differential absorption spectra (visible and near infrared) obtained upon femtosecond pump probe experiments (550 nm) of **1** in THF with time delays between 0.5 (blue) and 15.11 ns (red).

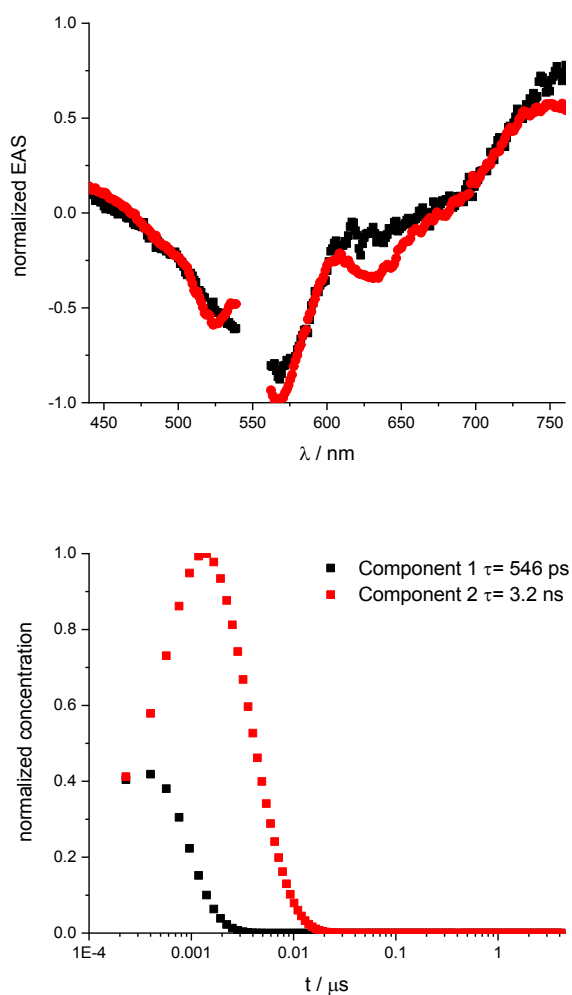


**Figure S3:** Differential absorption spectra (visible and near infrared) obtained upon femtosecond pump probe experiments (530 nm) of **1** in THF with time delays between 2 (blue) and 1050 ps (red).

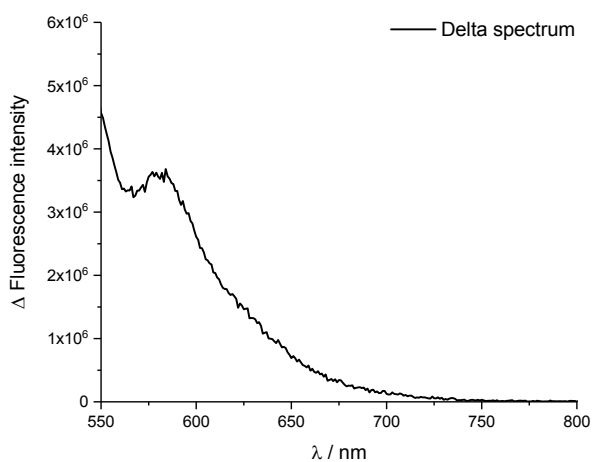
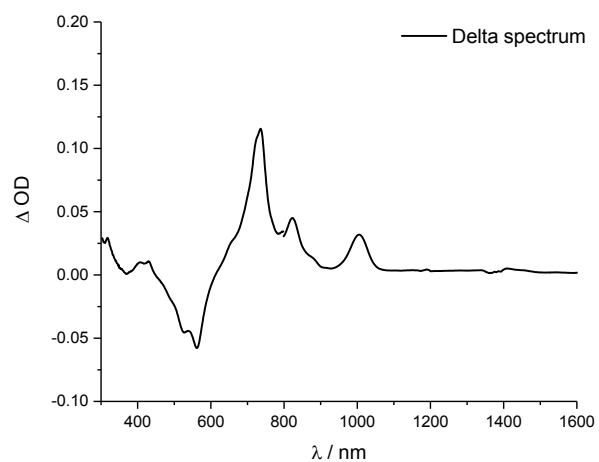




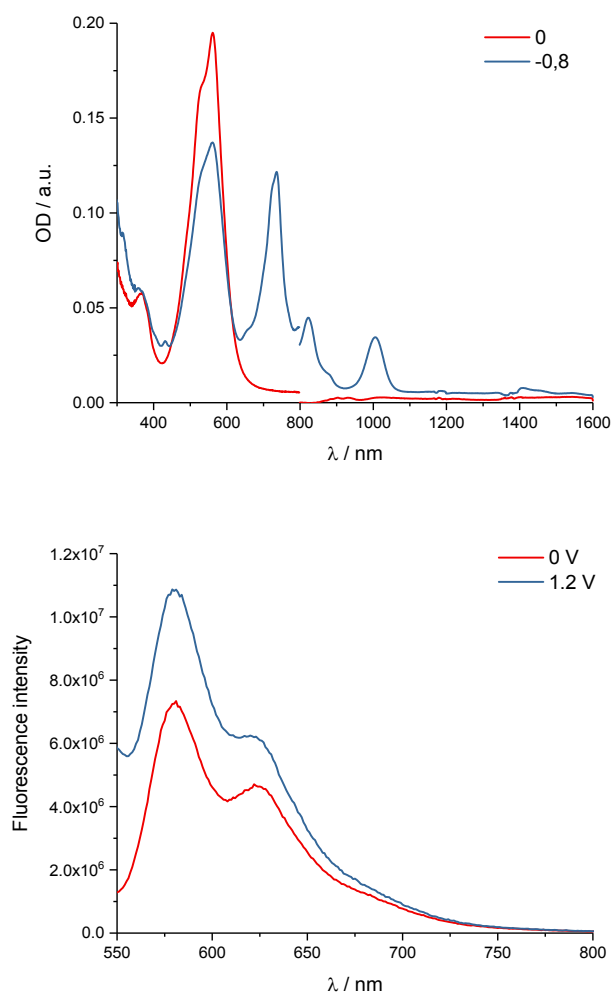
**Figure S4:** Upper part – Species associated spectra of **1** in the visible obtained by global target analysis. Central upper part - corresponding concentration-time profiles. Central lower part – Species associated spectra of **1** in the NIR obtained by global target analysis. Lower part – corresponding concentration time profiles.



**Figure S5:** Upper part – Species associated spectra of **1** in the visible obtained by global analysis. Central upper part - corresponding concentration-time profiles. Central lower part – Species associated spectra of **1** in the NIR obtained by global analysis. Lower part – corresponding concentration time profiles.

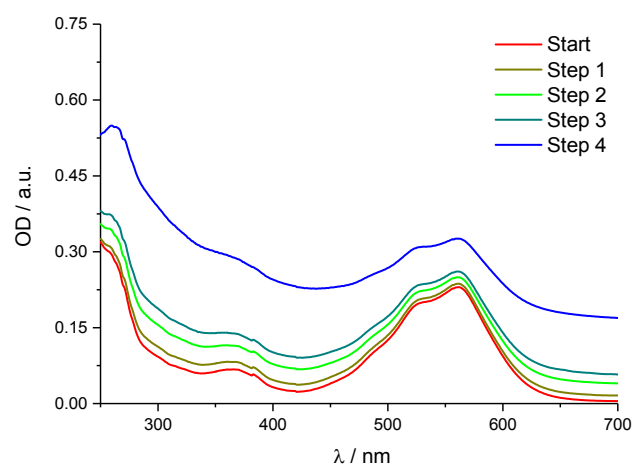
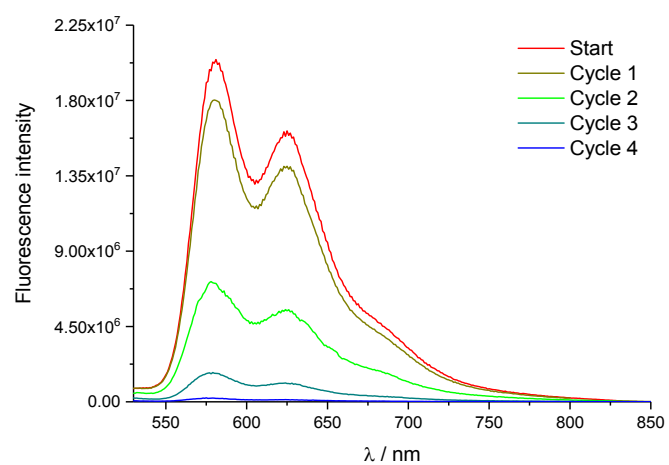
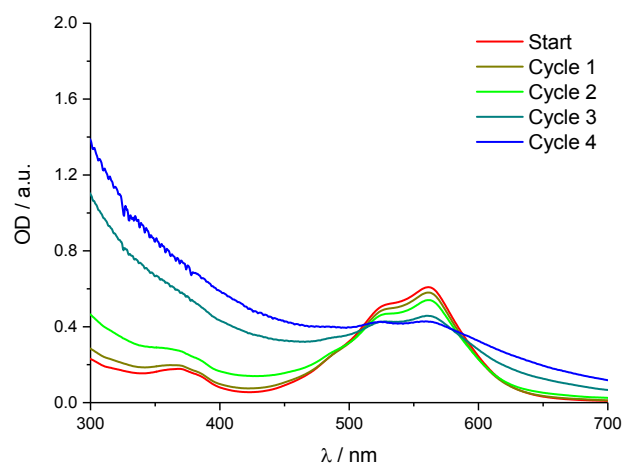


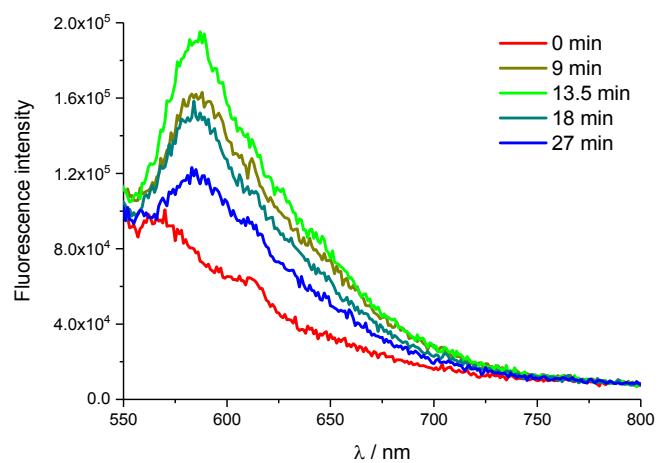
**Figure S6:** Upper part – differential absorption spectra (visible and near infrared) obtained upon spectroelectrochemical reduction of **1** in THF at a voltage of -0.8 V vs Ag wire. Lower part – differential fluorescence spectra obtained upon spectroelectrochemical oxidation of **1** in THF at a voltage of 1.2 V vs Ag wire.



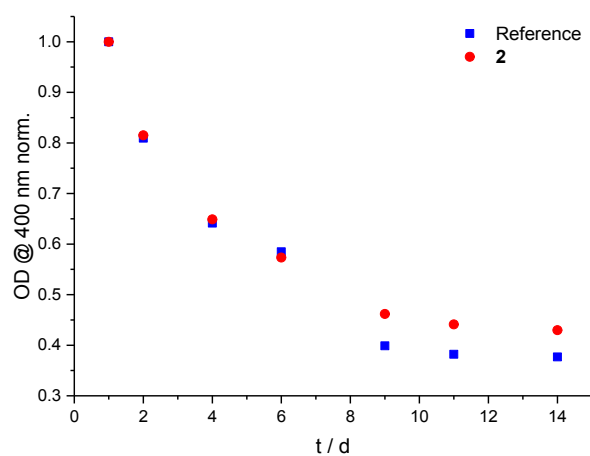
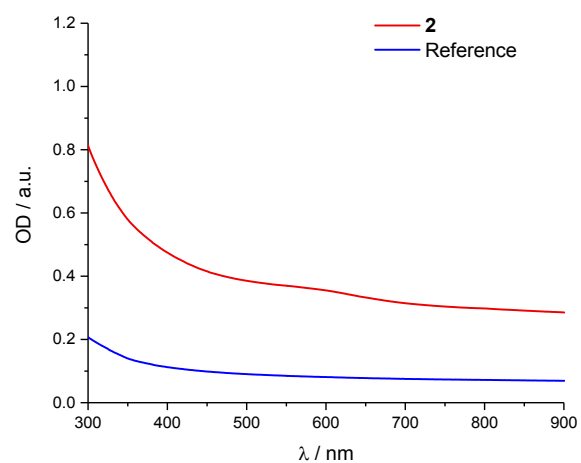
**Figure S7:** Upper part – absorption spectra (visible and near infrared) obtained upon spectroelectrochemical reduction of **1** in THF at a voltage of -0.8 V vs Ag wire. Lower part – fluorescence spectra obtained upon spectroelectrochemical oxidation of **1** in THF at a voltage of 1.2 V vs Ag wire.



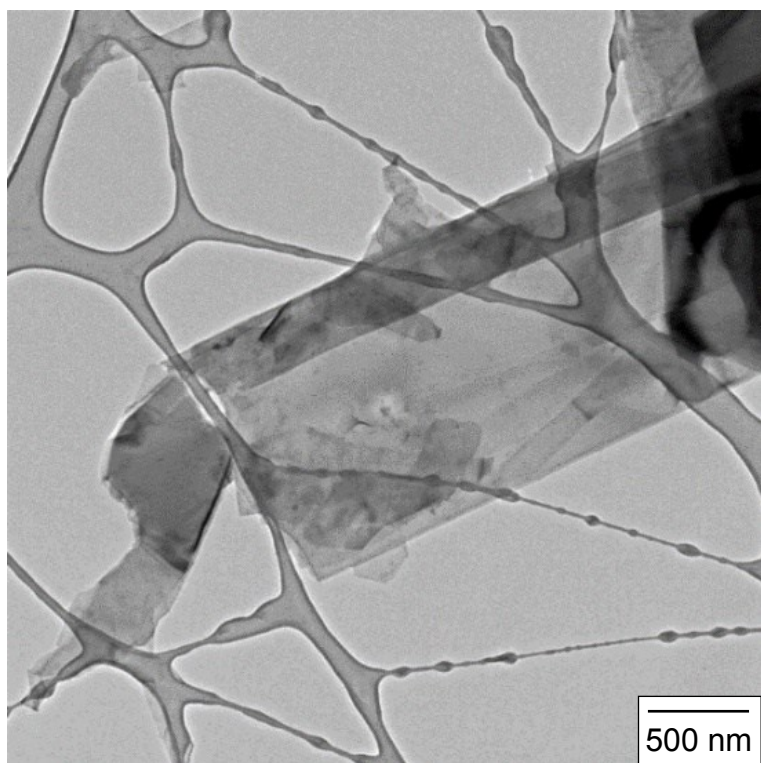
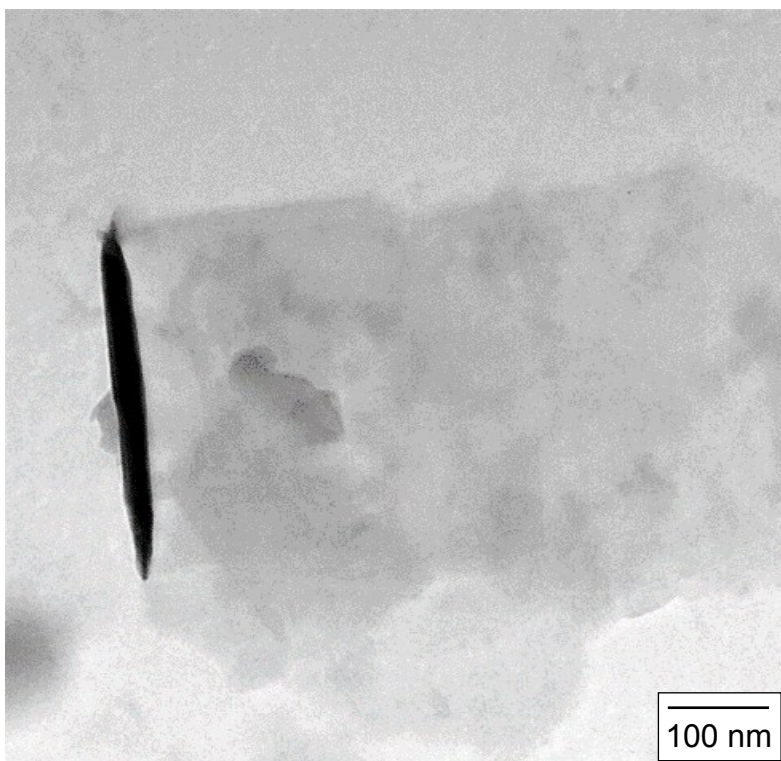




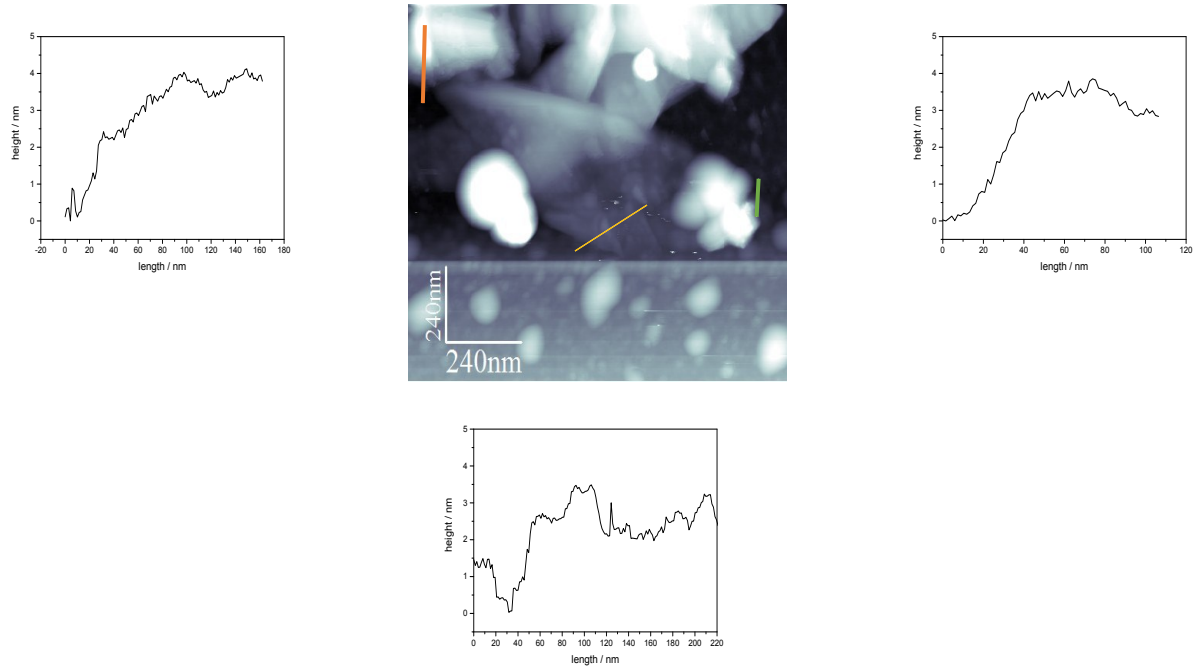
**Figure S8:** Upper part – absorption spectra of **1** upon several enrichment cycles with graphite. Central upper part – corresponding fluorescence spectra of **1** upon several enrichment cycles with graphite. Central lower part – absorption spectra of hybrid formation with titration of  $5 \times 10^{-6}$  M solution of **1** with preexfoliated graphene dispersion. Lower part – fluorescence spectra of hybrid formation upon diffusion of **1** into preexfoliated graphene dispersion.



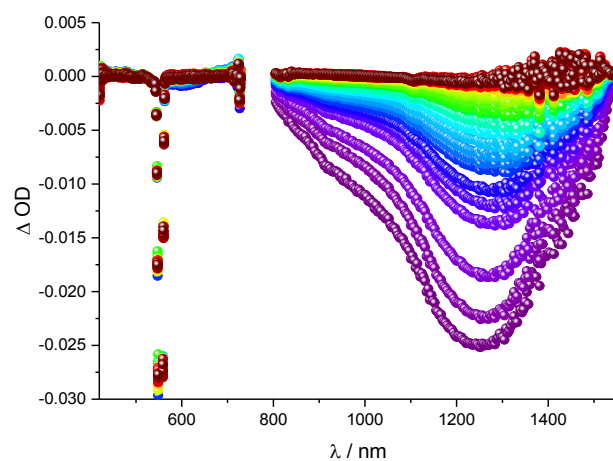
**Figure S9:** Upper part – absorption spectra of **2** and a reference dispersion after centrifuging at 11g for 20 min. Lower part – normalized optical density @ 400 nm monitored over 2 weeks.



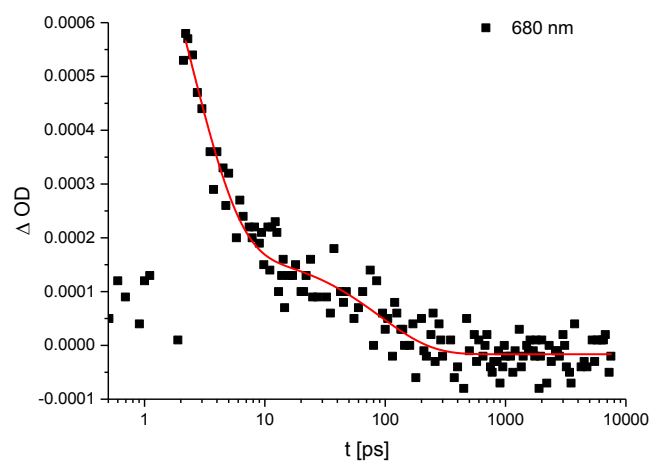
**Figure S10:** Upper part - TEM image of **2** drop casted on a lacey carbon grid. Lower part - TEM image of **2** drop casted on a lacey carbon grid.



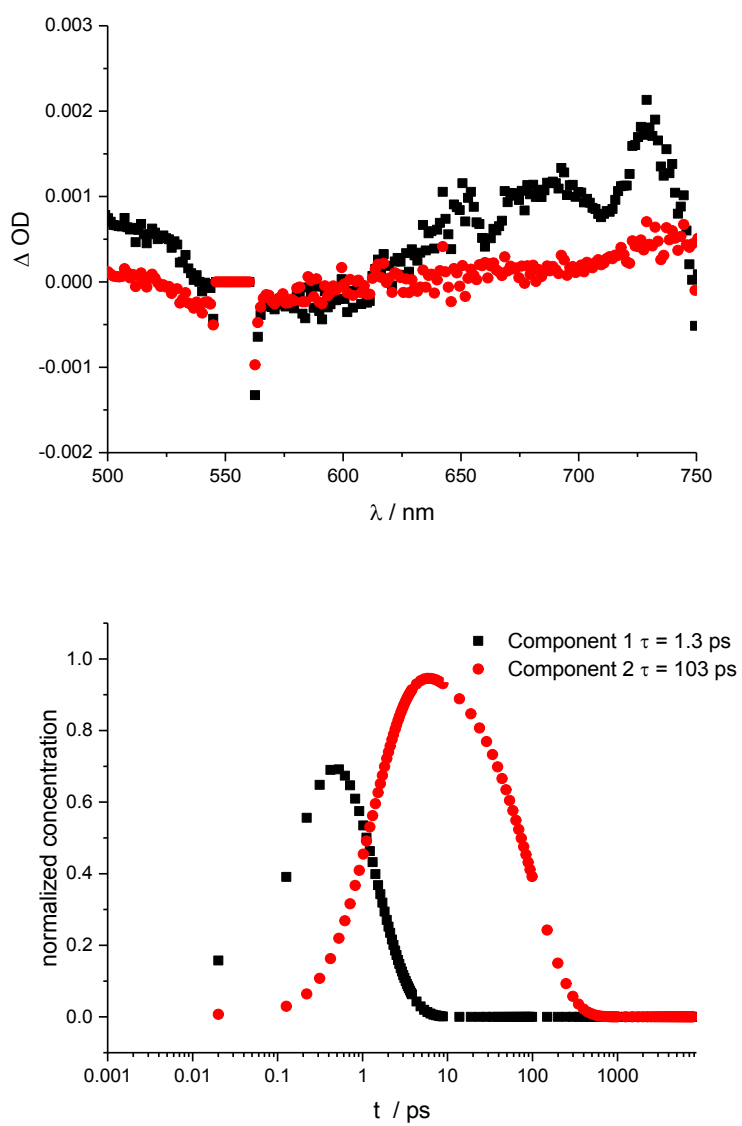
**Figure S11:** Tapping mode AFM image of **2** on a Si/SiO<sub>2</sub> surface – 1 μm × 1 μm. Corresponding height profiles at three different locations.



**Figure S12:** Differential absorption spectra (visible and near infrared) obtained upon femtosecond pump probe experiments (550 nm) of **2** in THF with time delays shown between 1.3 (blue) and 20 ps (red).



**Figure S13:** Time absorption profile of the spectra shown in Figure 3 at 680 nm.



**Figure S14.** Upper part - deconvoluted transient absorption spectra of **2** obtained by global analysis. Lower part - corresponding concentration-time profiles.



## Methods

### Steady state spectroscopy

Steady-state absorption spectra were recorded with a Perkin-Elmer Lambda 2 spectrometer. Steady-state fluorescence spectra were detected with a Fluoromax-3-spectrometer from HORIBA JobinYvon. All samples were measured in a fused quartz glass cuvette with a diameter of 10mm.

### Femtosecond transient absorption spectroscopy

Femtosecond transient absorption spectroscopy 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 wavelengths were 530 and 550 nm. The generation of white light was performed with a sapphire crystal of adequate thickness. The chirp effect in the region of 420 to 770 nm is approximately 350 fs. The detection was carried out with two CCD cameras, each for a specific measuring range. The spectral window covers 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 were acquired with the software HELIOS Visible/nIR (Newport/Ultrafast Systems).

### Spectroelectrochemistry

For spectroelectrochemistry, a Pt net was used as the working electrode, a Pt sheet as the counter electrode, and an Ag wire as the quasi reference electrode. As electrolyte, 0.1 M TBAPF<sub>6</sub> (tetrabutylammonium hexafluorophosphate) was used. The potentials were applied with a METROHM PGSTAT 101 and the absorption spectra were recorded using a UV/nIR Cary500 spectrometer. Fluorescence spectra were obtained with a Fluoromax-3-spectrometer from HORIBA JobinYvon.

### Raman spectroscopy

Raman measurements were carried out with a WITec alpha 300 R using laser excitations of 532 nm. The sample was prepared by drop casting a dispersion on a Si substrate with a 300 nm oxide layer.

### 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 using an 80 kV EM 900 from Carl Zeiss AG.

### Atomic force microscopy

AFM images were obtained by using a NanoscopeIIIa Multimode, Veeco in tapping mode. The sample was prepared by drop casting a dispersion on a Si substrate with a 300 nm oxide layer.