

Electronic Supplementary Information

A Corrole-Azafullerene Dyad: Synthesis, Characterization and Electronic Interactions and Photoinduced Charge Separation

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Experimental section

General Information

All chemicals were purchased from commercial sources and used without further purification. For thin layer chromatography (TLC), Riedel–de Haën silica gel F254 plates were used. For flash column chromatography, silica gel 60 (230–400 mesh, 0.04–0.063 nm) was used. NMR spectra were taken on a Bruker AC 300 FT-NMR spectrometer; the chemical shifts are given in parts per million relative to tetramethylsilane.

Photophysics

Steady state absorption and emission spectroscopy: Absorption spectra were measured with a Lambda 2 (Perkin Elmer) UV-vis spectrometer. The spectra were recorded between 300 and 800 nm at 480 nm per min with a 1.0 nm spectral bandwidth. The sample was contained in a 10 mm quartz cuvette. Fully corrected emission spectra were recorded on a FluoroMax-3 spectrometer (Horiba JobinYvon). To avoid aggregation and inner-filter effects, the absorption was adjusted to 0.05 at the excitation wavelength. Time resolved fluorescence spectroscopy: Emission lifetimes were determined by the Time Correlated Single Photon Counting technique using a FlouoroLog3 emission spectrometer (Horiba JobinYvon) equipped with a R3809U-58 MCP (Hamamatsu) and a N-405L laser diode (Horiba JobinYvon) exciting at 403 nm \pm 200 ps FWHM). The fluorescence lifetimes were obtained from exponential fits deconvoluting with the instruments response function (IRF).

Transient absorption: Femtosecond transient absorption measurements were carried out with an amplified Ti/sapphire laser system CPA-2101 femtosecond laser (Clark MXR – output: 775 nm, 1 kHz and 150 fs pulse width) using a transient absorption pump / probe detection system (TAPPS Helios - Ultrafast Systems). The 420 nm excitation wavelength was generated with a NOPA (Clark MXR). Pulse widths of <150 fs and energies of 200 nJ/pulse were selected.

Nanosecond transient absorption laser photolysis measurements were performed with the output from an OPO (Rainbow VIR – Opotek / Quantel, output: 420 nm, 10 mJ / pulse) pumped by the third harmonic (355 nm) of a Nd/YAG laser (Brilliant, Quantel). The optical detection is based on a pulsed (pulser MSP 05 – OptikElektronik Müller) Xenon lamp (XBO 450, Osram), a monochromator (Spectra Pro 2300i, Acton Research), a R928 photomultiplier tube (Hamamatsu Photonics), or a fast InGaAs photodiode (Nano 5, Coherent) with 300-MHz amplification, and a 1-GHz digital oscilloscope (WavePro7100, LeCroy).

Electrochemistry

Measurements were performed with an EG&G Princeton Applied Research potentiostat/galvanostat Model 2273A connected to a personal computer running PowerSuite software.

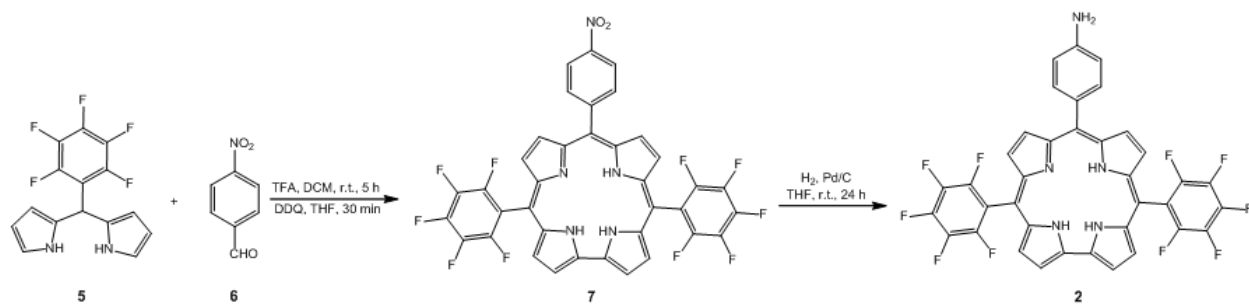
All measurements were performed at room temperature.

Synthesis of 5,15-bis(pentafluorophenyl)-10-(4-aminophenyl)corrole **2**.

A solution of nitro-corrole (70 mg, 0.09 mmol) and 10% Pd/C (15 mg) in THF (5 mL) and triethylamine (65 μ L) was stirred under H₂ at room temperature for 24 h. Then the mixture was filtered on a pad of celite and the solid washed with THF. The solvent was removed from the filtrate and the resulting solid was purified by column chromatography in silica using DCM/Hexane (4:1) as eluent. After removal of the solvents amino-corrole **2** was obtained as a green solid (51 mg, 78%). ¹H-NMR (CDCl₃, 500 MHz) δ (ppm): 9.10 (bs, 2H), 8.78 (d, 2H, *J* = 4.5 Hz), 8.71 (s, 2H), 8.56 (bs, 2H), 7.96 (bs, 2H), 7.05 (d, 2H, *J* = 6.5 Hz), 4.17 (bs, 2H), -2.59 (bs, 2H). MALDI-MS calcd. for C₃₇H₁₇N₅F₁₀ (M⁺): 721.132, found *m/z*: 721.132.

Synthesis of corrole-C₅₉N dyad **3**.

In a suspension of azafullerene-acid **1** (20 mg, 0.026 mmol), amino-corrole **2** (19 mg, 0.026 mmol) and HOBt (7 mg, 0.052 mmol) in dry dichloromethane (20 mL) at 0 °C under N₂, EDCI (20 mg, 0.104 mmol) was added and the mixture was left stirring at r.t. for 5 days. Then, the solvent was evaporated, the residue was re-dissolved in *o*-dichlorobenzene (25 mL) and passed through silica column chromatography using toluene as eluent. The first green fraction was collected and further purified in preparative HPLC (buckyprep, toluene, 10 ml/min. R.t. = 18.6 min) yielding **3** as green dust (3 mg, 8%). ¹H-NMR (CDCl₃, 300 MHz) δ(ppm): 9.12 (d, 2H, *J* = 4.3 Hz), 8.76 (AB, 4H, *J* = 4.8 Hz), 8.58 (d, 2H, *J* = 4.3 Hz), 8.38 (bs, 1H), 8.24 (AB, 4H, *J* = 8.3 Hz), 4.90 (s, 2H), -2.30 (bs, 3H). MALDI-MS calcd. for C₉₈H₁₈N₆OF₁₀ (M⁺): 1484.220, found *m/z*: 1484.138.



Scheme S1. Synthesis of amino-corrole **2**.

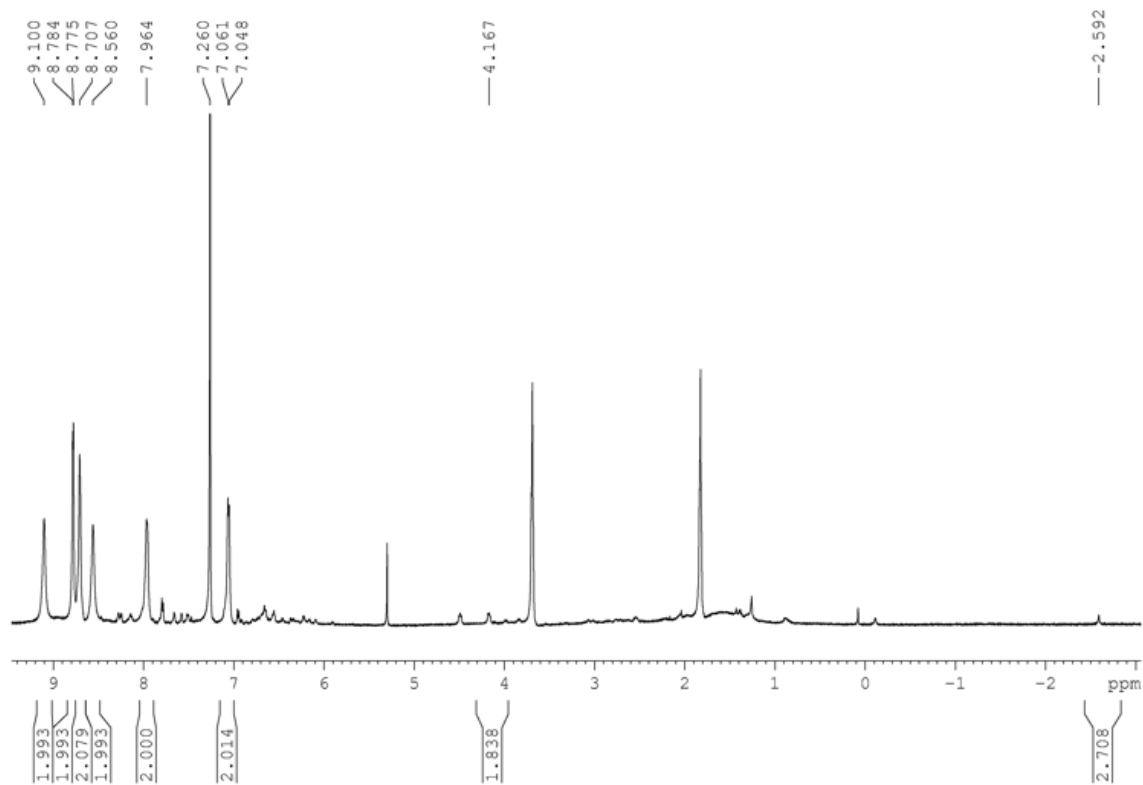


Figure S1. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) spectrum of amino-corrole **2**.

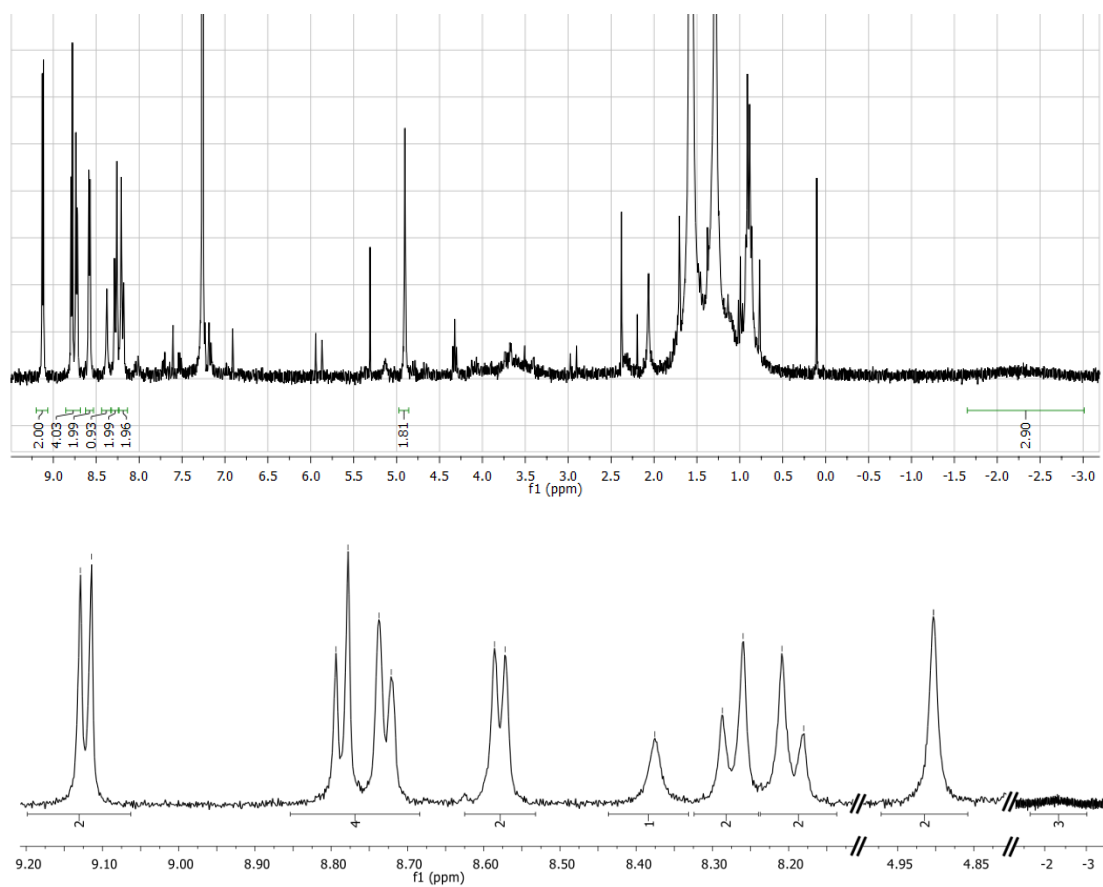


Figure S2. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) spectrum of dyad **3** (expanded region is shown in the bottom panel).

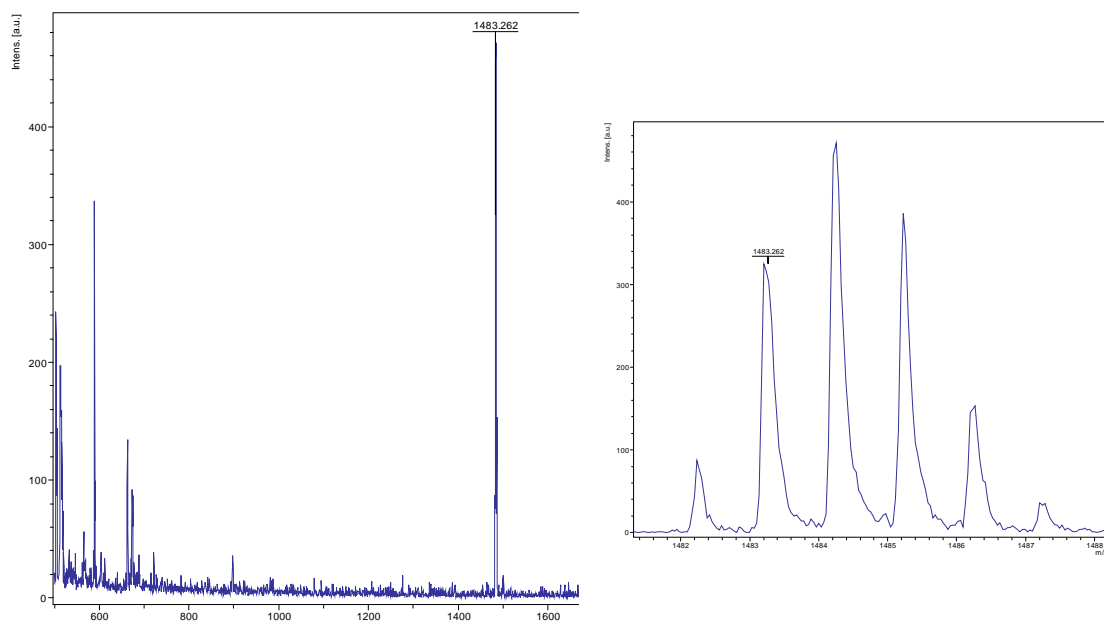


Figure S3. MALDI-MS of dyad **3** (left panel) and isotopic distribution of the molecular ion (right panel).

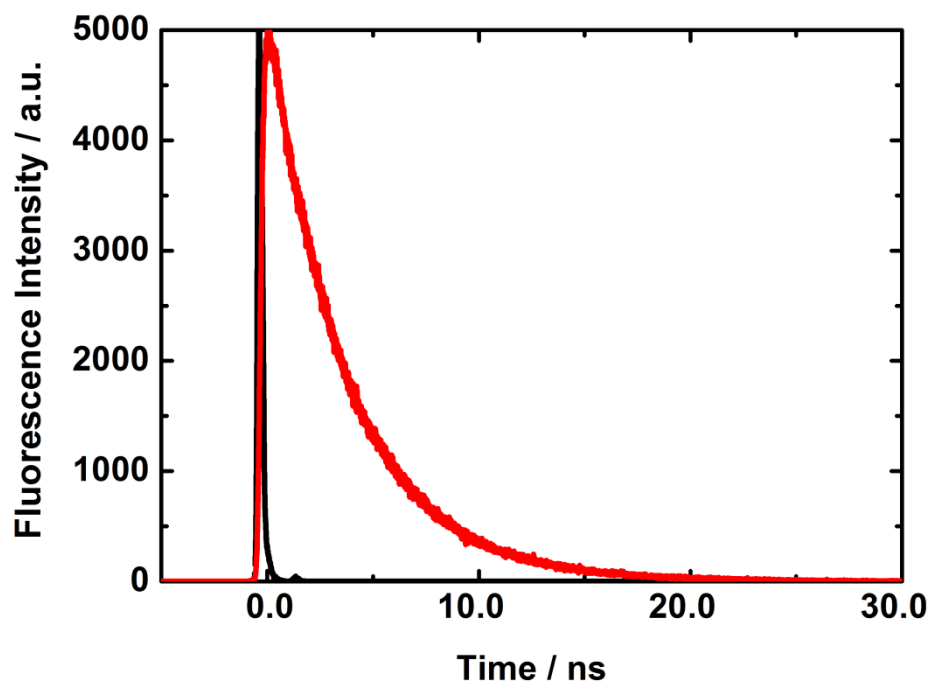


Figure S4. Fluorescence time profile for **2**, obtained in toluene at 660 nm, upon 403 nm photoexcitation. The IRF is shown in black.

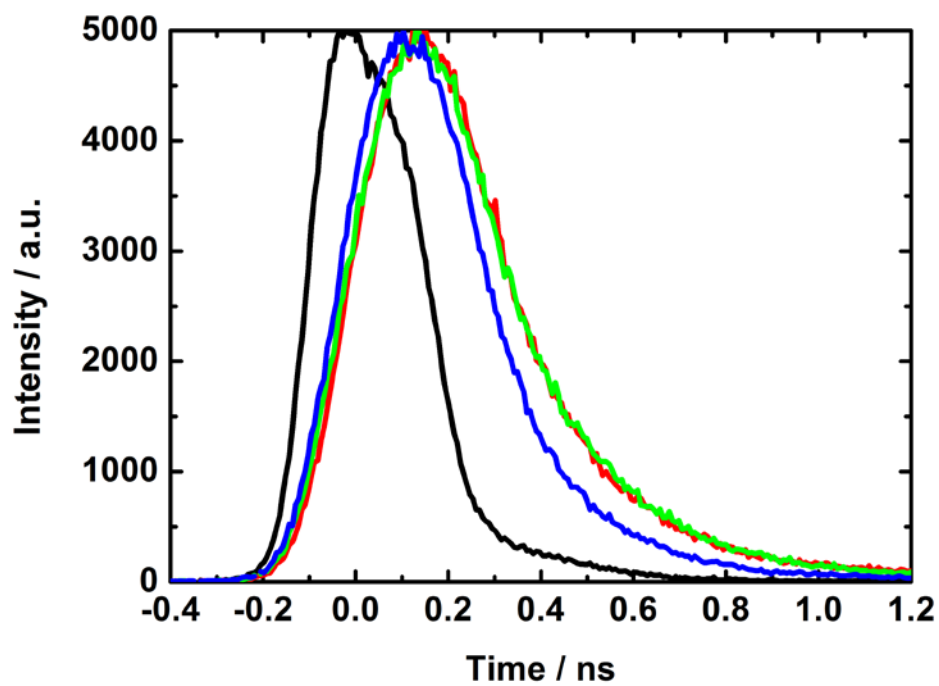


Figure S5. Fluorescence time profiles for **3**, obtained in *o*-xylene (red), toluene (green) and anisole (blue), at 660 nm upon 403 nm photoexcitation. The IRF is shown in black.

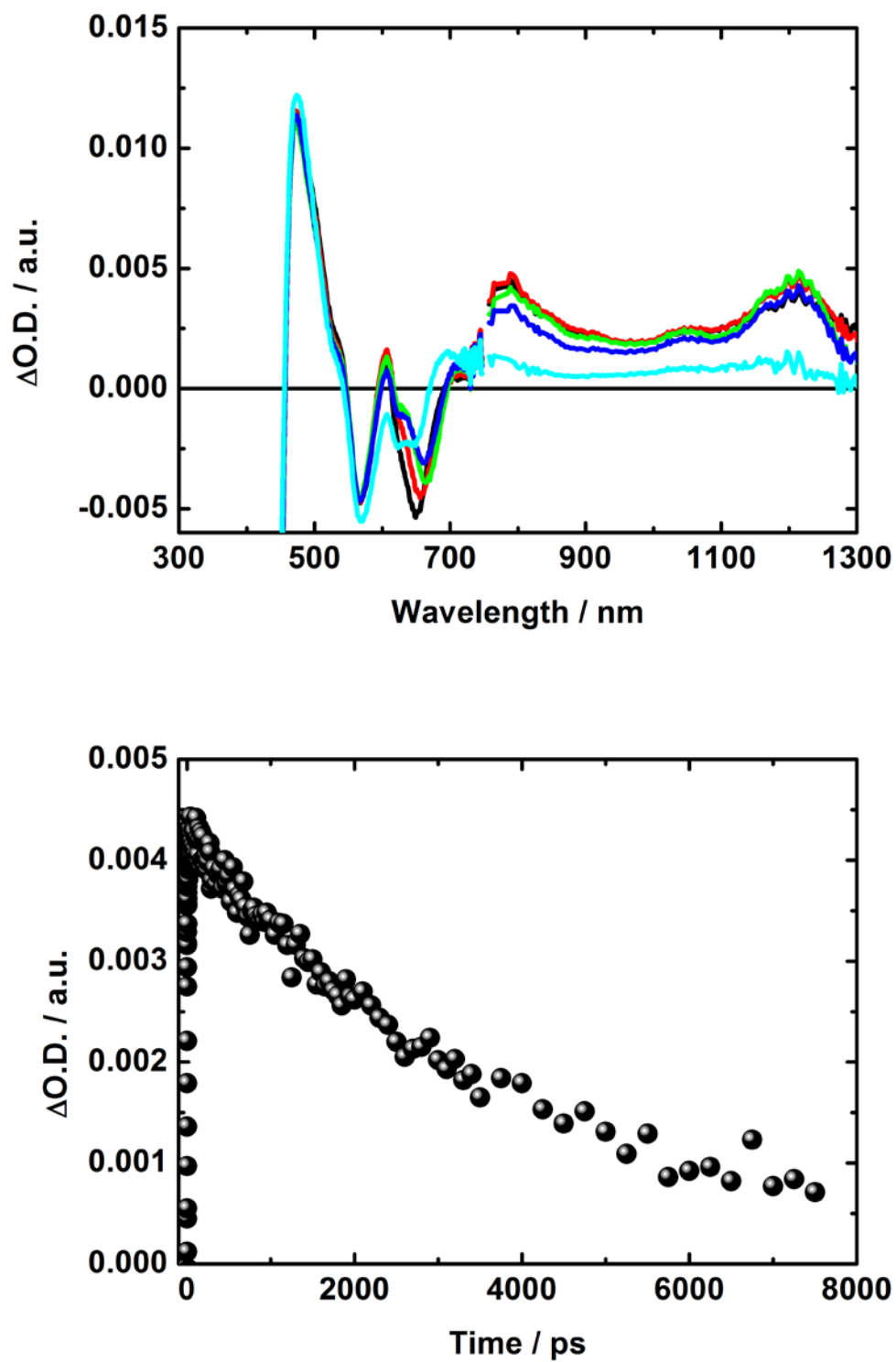


Figure S6. Femtosecond transient absorption spectra of **2**, obtained in argon saturated toluene; 1 ps (black), 10 ps (red), 100 ps (green), 1000 ps (blue) and 7500 ps (cyan) after excitation at 420 nm (upper part). The lower part shows the corresponding time-absorption profile at 1240 nm.

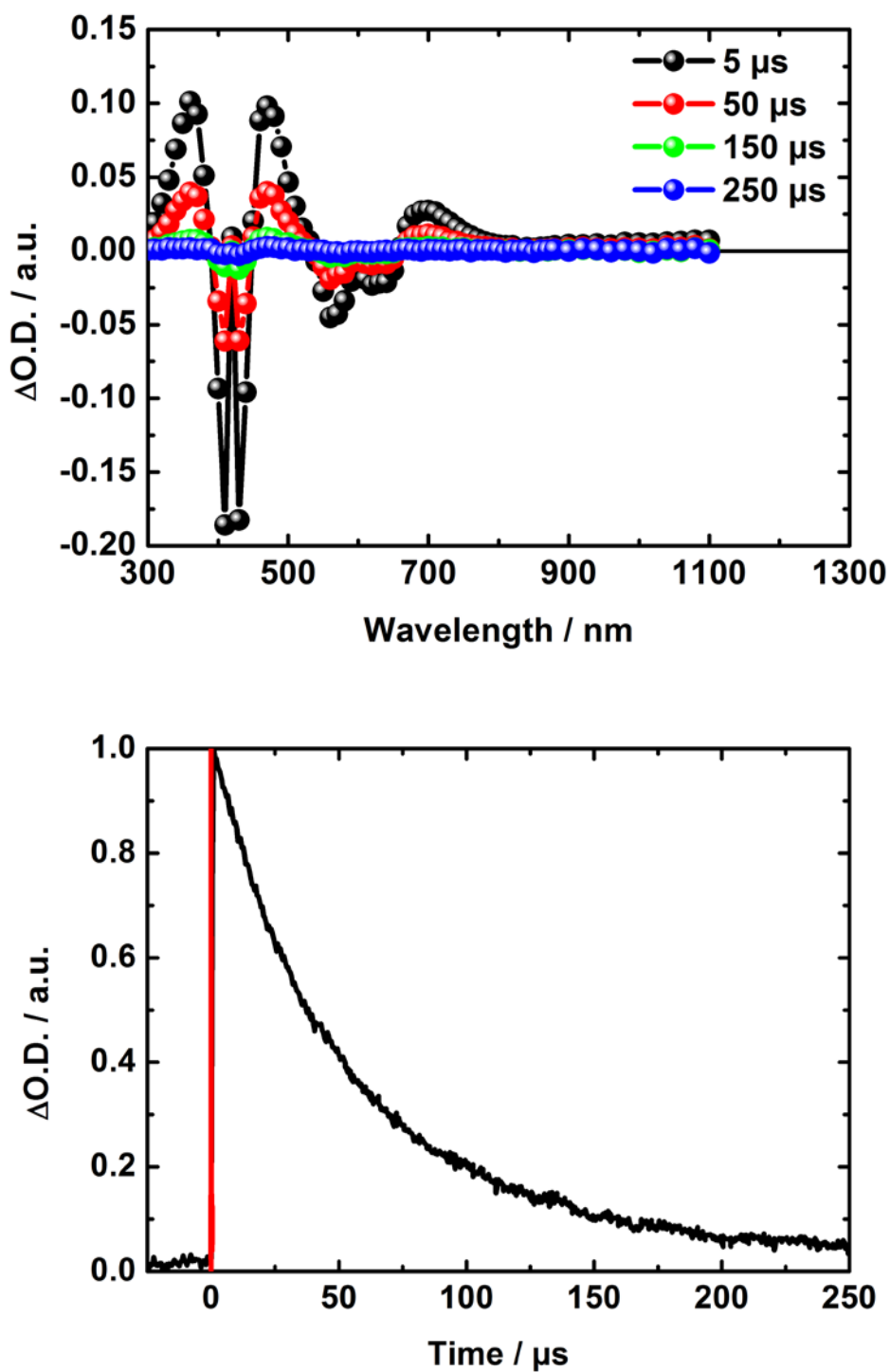


Figure S7. Nanosecond transient absorption spectra of **2**, obtained in argon saturated toluene at different time delays (upper part) and the corresponding time-absorption profiles at 470 nm (lower part), after excitation with ns-laser pulses at 420 nm. The black time-absorption profile was measured under argon saturation, while the red time-absorption profile was measured under oxygen saturation.

Table ST1. Photophysical properties of **2** and dyad **3**.

Material	Fluorescence quantum yield	Fluorescence lifetime	First excited singlet state lifetime^a	Charge separated state lifetime^b
2 in toluene	0.14	3790 ps	3785 ps	---
3 in o-xylene	7.0×10^{-3}	155 ps	166 ps	1021 ps
3 in toluene	4.0×10^{-3}	150 ps	151 ps	983 ps
3 in anisole	3.9×10^{-3}	125 ps	131 ps	682 ps
3 in 2-methyl-THF	1.6×10^{-3}	---	37 ps	247 ps
3 in benzonitrile	1.2×10^{-3}	---	16 ps	65 ps

^aFrom transient absorption time profiles at 1240 nm. ^bFrom transient absorption time profiles at 1040 nm.