Supporting Information

The position of nitro group decides about emission properties of π-expanded diketopyrrolopyrroles

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SUMMARY

1. General methods

- *Synthesis*

All chemicals were used as received unless otherwise noted. All reported ^{1}H NMR and ^{13}C NMR spectra were recorded on 500 or 600 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. Mass spectra were obtained via EI MS. For HRMS measurements both quadruple and TOF mass analyzer types were used. Chromatography was performed on silica (Kieselgel 60, 200–400 mesh). DPP **1** and aryl fluorides were prepared according to the literature procedures.[1,2]

- *UV-Vis Absorption and fluorescence*

UV-Vis absorption spectra were recorded with a PerkinElmer Lambda650 spectrophotometer, while fluorescence and steady-state anisotropy measurements were performed with a FLS1000 Edinburgh Fluorometer. Fluorescence spectra are corrected for the excitation intensity and the detector sensitivity. For fluorescence quantum yield measurements, fluorescein in NaOH 0.1 M was used as a reference (quantum yield 0.9).

- *Transient Absorption*

Pump-probe measurements have been performed on the setup described in a former paper.[1] Briefly, the output of a Coherent Legend Elite USP regen amplifier (1 KHz, 800 nm, 40 fs, 3.5 mJ) is redistributed with the help of a series of broadband beam-splitters. 850 μJ of the 800 nm fundamental beam, after passing through a fused-silica wedge plate, is used to pump an Optical Parametric Amplifier (TOPAS, LightConversion) to generate signal (1200-1600 nm) and idler (1600-2300 nm) pulses. Signal second harmonic (generated by one SHG processes in 1mm BBO crystals) is used to produce the pump pulses (0.5-2 μJ) tunable in the 600-760 nm spectral range. The reflection coming from the wedge plate is sent to a computer controllable delay line and then focused on a 2mm CaF2 Window to generate supercontinuum (spectral range 356 - 750 nm). Supercontinuum is further splitted in two pulses, by a 50% beam-splitter, to generate probe and reference pulses. Probe and reference are then focused and spatially overlapped with the pump pulse on the sample, thanks to a 100 EFL spherical mirror. Delay time between pump and probe is continuously adjusted, using the optical delay line mentioned before (bidirectional position reproducibility better than 25 fs, while the maximum available delay time is 1.5 ns). The optical path of the reference is constructed in such a way that it is always the first pulse interacting with the sample, always before pump and probe. Probe and reference are then focused on the entrance of a spectrograph (Jobin-Yvon CP140) and dispersed on two separate arrays (256 pxs, Hamamatsu). Pump pulses are alternatively blocked/unblocked before the sample by an optical chopper (Thorlabs, frequency repetition rate ~70 Hz). Transient absorption spectrum is finally obtained as:

$$\Delta Abs(\lambda,t) = -\log\left(\left(I_{probe}^{on}/I_{ref}^{on}\right) * \left(I_{ref}^{off}/I_{probe}^{off}\right)\right).$$

- *Broadband Ultrashort Pump-probe (US-pp)*

A small fraction of the main output (450 μJ of the 800 nm source) are used for the (US-pp) setup. For Ultrashort pump-probe (US-pp) measurements, a modified version of the setup for two-dimensional visible spectroscopy [J. Mater. Chem. C, 2022, 10, 7216–7226] , have been used.

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[1] Grzybowski, M.; Hugues, V.; Blanchard-Desce, M.; Gryko, D. T.; *Chem. Eur. J.* **2014**, *20*, 12493-12501.

[2] a) FRONTHERA PHARMACEUTICALS - WO2018/151830, **2018**, A1; (Methyl 3-bromo-2-fluoro-5-nitrobenzoate); b) DANA FARBER CANCER INSTITUTE - WO2016/161145, **2016**, A1; (Methyl 3-bromo-4-fluoro-5-nitrobenzoate).

Briefly, ultrafast pulses coming from the Coherent Legend Elite USP are sent to two Non-Collinear Optical Parametric Amplifiers (NOPAs) that generate chirped pulses (max output 2μJ energy per pulse) tunable between 500 and 780 nm with an asymmetric shape and possessing 60 nm (NOPA-a) FWHM. For NIR measurements, NOPA-b has been used to generate NIR pulses with a spectrum covering the 810-915 nm spectral range following the scheme already described in literature.[3] The pulses from NOPA-a are then compressed by means of a couple of chirped mirrors (DCM10 Venteon): after a total of 9 bounces the dispersion introduced by the optics is very well compensated at the sample region, in such a way that the duration retrieved by PG-FROG analysis is around 12 fs. The output of NOPA-b is partially compressed by using the DCM10 Chirped mirrors: unfortunately, it was not possible to compensate the temporal chirp of the 860-915 nm spectral range because it was out of range from the DCM10 spectral response. Such partial compensation introduces an elongation of our instrumental function that has been characterized in 150-160 fs. The output of NOPA-b is then furtherly split in two pulses, by a 50% beam-splitter, to generate probe and reference pulses. The output of NOPA-a was used as the pump pulse, while the Output of NOPA-b was used as a probe. After dispersion compensation, pump pulses follow the scheme [J. Mater. Chem. C, 2022, 10, 7216–7226]to generate two collinear pump pulses for 2D spectroscopy. Blocking one of the two pulses it is possible to acquire pump-probe spectra. Pump pulse is sent to an optical delay line (Physik-Instrumente, having a bidirectional reproducibility better that 5 fs and maxi- mum delay close to 250 ps) to control the delay in respect with the probe pulses. Pump, Probe and Reference beams are focused on the sample by a spherical mirror with 250 mm EFL, but only pump and probe are spatially overlapped on the sample. After the sample, pump is blocked by a beam-stopper while probe and reference are focused on the entrance of a spectrograph (Jobin-Yvon CP140) and dispersed on two separate arrays (256 pxs, Hamamatsu). Intensity of probe and reference is acquired and the transient absorption spectra are finally calculated following the scheme and formula described before.

- Transient-Infrared

The TRIR experiments were performed on $CHCl_3$ and THF solutions of EDPP **7** and EDPP **8**. Transient infrared spectra were collected using a pump probe set-up previously described.Fare clic o toccare qui per immettere il testo. *[J. Phys. Chem. B, 118, 32, 9613 – 9630, J. Chem. Phys, 142, 217, 2015, 212409]* Briefly, part of the output of a Ti:sapphire oscillator system (300 mW, 80 MHz repetition rate, 810 nm central wavelength: Micra Coherent Inc.) is amplified by a regenerative amplifier (Legend-F Inc.), producing femtosecond pulses (~40 fs in length) with an average energy ~3 mJ, 1 KHz repetition rate at 810 nm. 1.2 mJ of the output light is diverted trough an optical parametric amplifier (TOPAS-800 LightConversion) generating several μJ of Signal pulses at 1300-1400 nm. After two passages in two distinct BBO with suitable phase matching angle we obtained the fourth Harmonic at 330-360 nm acting as the pump pulses. The remaining 810 nm light pumps a home-built OPA (Optical Parametric Amplifier). At 6 mm, spectrally broad mid-infrared pulses (width ~250 cm-1) have an energy of 1 mJ per pulse and a pulse duration of ~150 fs. The pump beam passes through a half-wave plate controlling its polarization and through a variable delay line. The probe and reference beams are obtained by reflection from two faces of a wedged CaF2 plate. Pump, probe and reference beams are focused into the sample by a parabolic mirror, and the probe and reference beams are then imaged into a flat-field monochromator equipped with a double 32-channel array infrared detector.

- *Data Analysis*

Data Analysis for transient Absorption and Transient Infrared have been performed using a Global-Target Analysis approach developed within the program package GLOTARAN.[4]

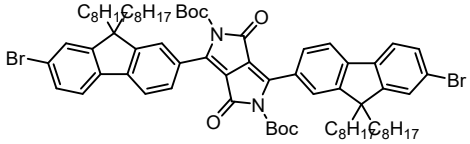
[3] Manzoni, C; Polli, D.; Cerullo, G.; *Rev. Sci. Instrum.* **2006**, *77*, 023103.
[4] Snellenburg, J. J.; Laptenok, S.; Seger, R.; Mullen, K. M.; van Stokkum, I. H. M. Glotaran: A Java-Based Graphical User Interface for the R Package TIMP. Journal of Statistical Software **2012**, *49*, 1–22.

- *Time resolved Fluorescence*

Time resolved fluorescence decay profile has been acquired in the time-correlated single-photon counting (TCSPC) experimental scheme. Time traces have been simulated by convolution of the instrumental function with a single exponential decay as a response function in a custom developed program-package.

2. Experimental Part

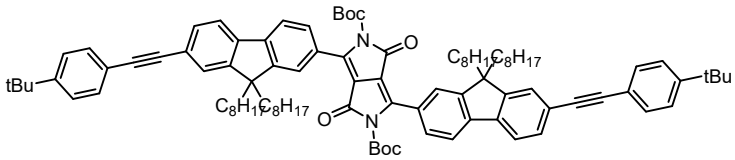
DPP 2



A suspension of **DPP 1** (1.80 g, 1.68 mmol) and a catalytic amount of DMAP (0.02 g, 0.17 mmol) in dry THF (200 mL) was stirred at room temperature under argon atmosphere. After 20 min., Boc_2O (1.10 g, 5.04 mmol) was added. The solution was stirred at 45 °C overnight, and then the solvent and excess of Boc_2O were removed under reduced pressure. The resulting mixture was dissolved in 10 mL of dichloromethane and treated with 100 mL of methanol. The obtained precipitate was filtered off and washed with methanol.

Yield: 1.55 g (71%). Orange solid; m.p. 158-159 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 6H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 6.4 Hz, 4H), 2.06 – 1.91 (m, 8H), 1.48 (s, 18H), 1.24 – 1.17 (m, 8H), 1.17 – 1.00 (m, 32H), 0.82 (t, *J* = 7.2 Hz, 12H), 0.71 – 0.52 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 153.9, 150.2, 148.5, 146.1, 143.5, 139.1, 130.3, 128.1, 127.1, 126.3, 123.2, 122.4, 121.8, 119.5, 112.6, 85.0, 55.7, 40.2, 31.8, 29.9, 29.3, 29.2, 27.7, 23.8, 22.6, 14.1; HRMS (APCI): calcd for $C_{74}H_{99}Br_2N_2O_6$ $[M+H]^+$ 1269.5870, found 1269.5873.

DPP 3

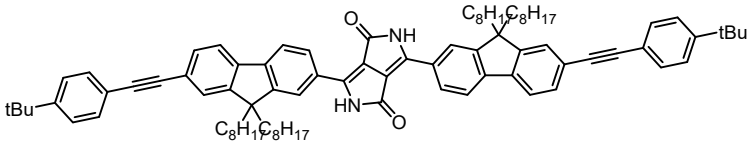


In a Schlenck flask containing a magnetic stirring bar were placed: **DPP 2** (1.50 g, 1.18 mmol), CuI (45 mg, 0.24 mmol), $PdCl_2(PPh_3)_2$ (166 mg, 0.24 mmol), and 4-tert-butylphenylacetylene (747 mg, 4.72 mmol). The vessel was evacuated and backfilled with argon (3 times) and anhydrous, degassed toluene was added (50 mL) followed by dry triethylamine (10 mL). The content of the flask was stirred for 36 h at 80 °C. The mixture was transfer to the separatory funnel and the organic layer was washed with degassed water (3 × 40 mL) and brine. Organic layer was dried over MgSO4 and the solvent was evaporated with Celite. The target product was purified by silica gel chromatography using hexanes / ethyl acetate (20/1) solution as eluent and recrystallized by slow addition of methanol to a solution of the dye in small amount of toluene.

Yield: 1.38 g (82%). Red solid; m.p. 164-165 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 6H), 7.72 (dd, *J* = 7.8, 0.7 Hz, 2H), 7.54 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.53 – 7.50 (m, 6H), 7.41 – 7.38 (m, 4H), 2.08 – 1.97 (m, 8H), 1.50 (s, 18H), 1.35 (s, 18H), 1.23 – 1.17 (m, 8H), 1.16 – 1.01 (m, 32H), 0.81 (t, *J* = 7.2 Hz, 12H), 0.70 – 0.56 (m, 8H);^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 151.7, 151.6,

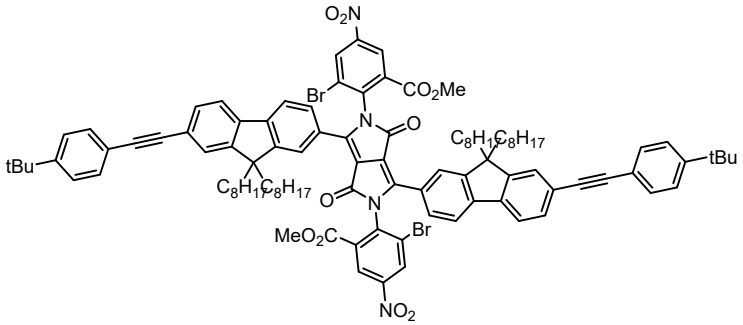
150.9, 148.6, 146.1, 144.0, 140.1, 131.3, 130.8, 128.1, 127.0, 126.0, 125.4, 123.1, 123.0, 120.4, 120.2, 119.7, 112.6, 90.4, 89.7, 85.0, 55.5, 40.3, 34.8, 31.8, 31.2, 30.0, 29.3, 27.7, 23.8, 22.6, 14.1; HRMS (APCI): calcd for $C_{98}H_{125}N_2O_6$ $[M+H]^+$ 1425.9538, found 1425.9542.

DPP 4



To a solution of **DPP 3** (0.4 g, 0.31 mmol) in dichloromethane (50 mL), trifluoroacetic acid (10 mL) was added and stirred for 2 h at rt. Then, the excess reagent and solvent were evaporated under reduced pressure. The resulting mixture was sonicated in 10 mL of CH_2Cl_2 and treated with 60 mL of methanol. The obtained precipitate was filtered off and washed with methanol.
Yield: 324 mg (94%). Dark purple solid; m.p. 329-330 ºC; ^{1}H NMR (500 MHz, $CDCl_3$ + drop TFA-*d*) δ 10.92 (s, 2H), 8.33 (s, 2H), 8.19 (d, *J* = 8.1 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.56 (m, 4H), 7.53 (d, *J* = 8.4 Hz, 4H), 7.41 (d, *J* = 8.4 Hz, 4H), 2.16 – 2.00 (m, 8H), 1.35 (s, 18H), 1.23 – 1.17 (m, 8H), 1.16 – 1.02 (m, 32H), 0.80 (t, *J* = 7.1 Hz, 12H), 0.76 – 0.61 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$ + drop TFA-*d*) δ 164.8, 152.6 (2 signals), 151.9, 146.7, 146.4, 139.5, 131.4, 131.1, 127.9, 126.2, 125.5, 125.1, 124.1, 123.1, 121.1, 121.0, 120.1, 109.9, 91.1, 89.6, 55.6, 40.0, 34.9, 31.8, 31.1, 29.9, 29.2 (2 signals), 23.9, 22.6, 14.0; HRMS (APCI): calcd for $C_{88}H_{109}N_2O_2$ $[M+H]^+$ 1225.8489, found 1225.8492.

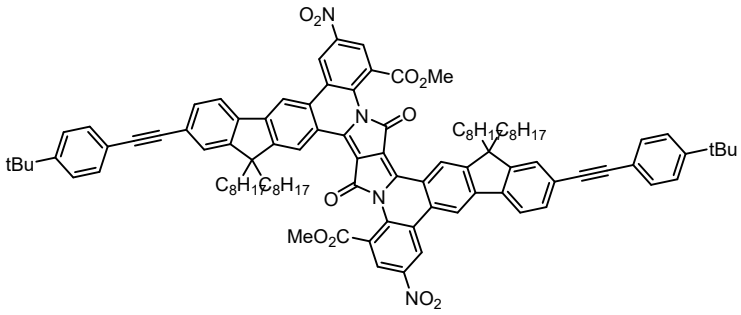
DPP 5



A mixture of **DPP 4** (150 mg, 0.12 mmol), methyl 3-bromo-2-fluoro-5-nitrobenzoate (136 mg, 0.49 mmol), K_2CO_3 (68 mg, 0.49 mmol) in 5 mL of NMP was stirred at 65 °C for 4 days. The solvent was evaporated under vacuum. The solid residue was dissolved in CH_2Cl_2 (100 mL) and the solution was washed with water and brine. Organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The target product was purified by silica gel chromatography using hexanes / ethyl acetate (20/1) solution as eluent and recrystallized by slow addition of methanol to a solution of the dye in small amount of toluene. The product was isolated as a mixture of atropoisomers.
Yield: 179 mg (84%). Red solid; m.p. 311-312 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, *J* = 2.6 Hz, 1H), 8.80 (d, *J* = 2.6 Hz, 1H), 8.75 (t, *J* = 2.6 Hz, 2H), 7.91 – 7.86 (m, 2H), 7.69 – 7.62 (m, 4H), 7.52 – 7.47 (m, 5H), 7.45 (d, *J* = 1.6 Hz, 2H), 7.40 – 7.36 (m, 4H), 7.30 (d, *J* = 1.8 Hz, 1H), 3.87 (s, 3H),

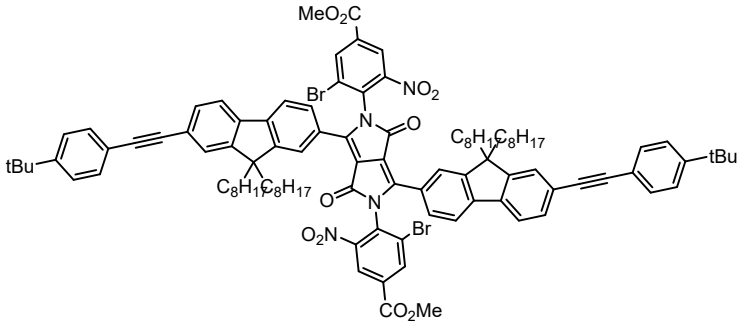
3.86 (s, 3H), 1.89 – 1.78 (m, 4H), 1.76 – 1.59 (m, 4H), 1.34 (s, 18H), 1.26 – 1.18 (m, 8H), 1.18 – 1.06 (m, 16H), 1.05 – 0.92 (m, 12H), 0.86 – 0.79 (m, 12H), 0.61 – 0.28 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 162.8, 160.6, 160.5, 151.7 (2 signals), 151.2 (2 signals), 147.4, 147.3, 147.2 (2 signals), 144.4 (2 signals), 141.5, 141.3, 139.6, 139.5, 133.1, 132.9, 131.5 (2 signals), 131.3, 130.9, 128.8, 128.7, 127.8, 127.3, 125.9, 125.7, 125.4 (2 signals), 125.3, 125.1, 123.5 (2 signals), 122.7, 122.6, 120.6, 120.5, 120.1, 110.8, 110.7, 90.7, 89.5, 55.2, 55.1, 53.5, 53.4, 40.3, 40.1 (2 signals), 34.8, 31.8 (2 signals), 31.2, 30.1, 30.0, 29.4, 29.3 (2 signals), 29.2 (3 signals), 23.8, 23.7, 22.6, 14.1 (2 signals); HRMS (APCI): calcd for $C_{104}H_{117}Br_2N_4O_{10}$ $[M+H]^+$ 1739.7136, found 1739.7140.

DPP 7



A mixture of **DPP 5** (83 mg, 0.048mmol), $Pd(PPh_3)_4$ (11 mg, 0.0095 mmol), CsOPiv (45 mg, 0.19 mmol) in dry toluene (6 ml) was stirred at 115 °C for 16h in Schlenk tube. The mixture was diluted by CH_2Cl_2 (100 ml) and then evaporated with Celite. The target product was purified by silica gel chromatography using hexanes / toluene (1/1) solution as eluent. Crystallization from toluene / methanol afforded analytically pure compound.
Yield: 67 mg (89%). Dark blue solid; m.p. > 400 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.41 (s, 2H), 9.33 (d, *J* = 2.5 Hz, 2H), 8.77 (d, *J* = 2.4 Hz, 2H), 8.57 (s, 2H), 8.00 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.61 (s, 2H), 7.56 – 7.52 (m, 4H), 7.44 – 7.40 (m, 4H), 4.06 (s, 6H), 2.27 – 2.18 (m, 4H), 2.18 – 2.09 (m, 4H), 1.36 (s, 18H), 1.16 – 1.11 (m, 8H), 1.11 – 0.95 (m, 32H), 0.74 (t, *J* = 7.2 Hz, 12H), 0.73 – 0.58 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 159.7, 154.5, 152.3, 152.0, 146.8, 143.8, 141.8, 138.8, 133.5, 131.4 (2 signals), 129.1, 126.3, 125.7, 125.5 (2 signals), 125.4, 125.2, 124.9, 123.8, 123.2, 121.3, 120.6, 119.9, 113.9, 105.7, 91.6, 89.3, 55.8, 52.6, 40.5, 34.9, 31.7, 31.2, 30.00, 29.2 (2 signals), 24.0, 22.5, 14.00; HRMS (APCI): calcd for $C_{104}H_{115}N_4O_{10}$ $[M+H]^+$ 1579.8613, found 1579.8616.

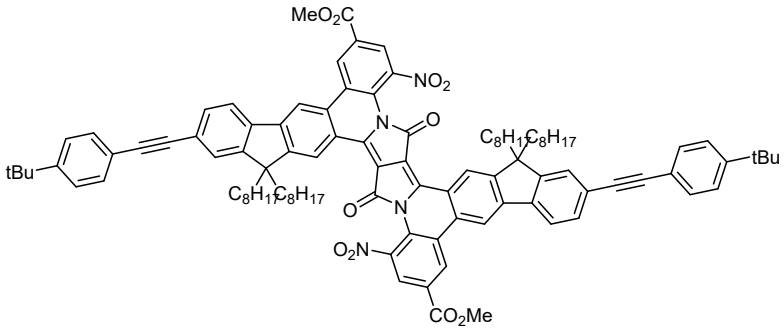
DPP 6



A mixture of **DPP 4** (205 mg, 0.17 mmol), methyl 3-bromo-4-fluoro-5-nitrobenzoate (279 mg, 1.00 mmol), K_2CO_3 (139 mg, 1.00 mmol) in 6 mL of NMP was stirred at 65 °C for 4 days. The solvent

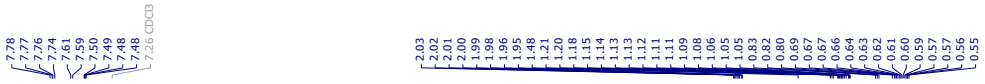
was evaporated under vacuum. The solid residue was dissolved in CH_2Cl_2 (100 mL) and the solution was washed with water and brine. Organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The target product was purified by silica gel chromatography using hexanes / ethyl acetate (20/1) solution as eluent and recrystallized by slow addition of methanol to a solution of the dye in small amount of toluene. The product was isolated as a mixture of atropoisomers.
Yield: 180 mg (62%). Red solid; m.p. 319-320 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 1.9 Hz, 1H), 8.63 (d, *J* = 1.9 Hz, 1H), 8.59 (d, *J* = 1.9 Hz, 1H), 8.54 (d, *J* = 1.9 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.69 – 7.63 (m, 4H), 7.52 – 7.47 (m, 6H), 7.45 – 7.43 (m, 2H), 7.40 – 7.37 (m, 4H), 4.01 (s, 6H), 1.89 – 1.78 (m, 4H), 1.76 – 1.62 (m, 4H), 1.33 (s, 18H), 1.25 – 1.17 (m, 8H), 1.16 – 1.05 (m, 16H), 1.05 – 0.89 (m, 16H), 0.86 – 0.77 (m, 12H), 0.54 – 0.39 (m, 8H); ^{13}C NMR (125 MHz, $CDCll_3$) δ 163.1, 160.0, 151.8, 151.7, 151.2, 148.7, 148.5, 147.1, 146.9, 144.5, 139.7, 138.5, 138.4, 133.8, 133.5, 132.3 (2 signals), 131.3, 130.9, 128.7 (2 signals), 127.3, 126.6, 125.9, 125.7, 125.5, 125.4, 125.3, 125.2, 123.4, 122.6, 122.5, 120.6, 120.5, 120.1, 110.7, 110.6, 90.6, 89.5, 55.2, 53.3, 40.2, 34.8, 31.8 (2 signals), 31.2, 30.0, 29.9, 29.3 (2 signals), 29.2, 23.7, 22.6, 14.1; HRMS (APCI): calcd for $C_{104}H_{117}Br_2N_4O_{10}$ $[M+H]^+$ 1739.7136, found 1739.7139.

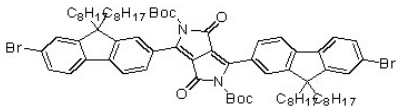
DPP 8

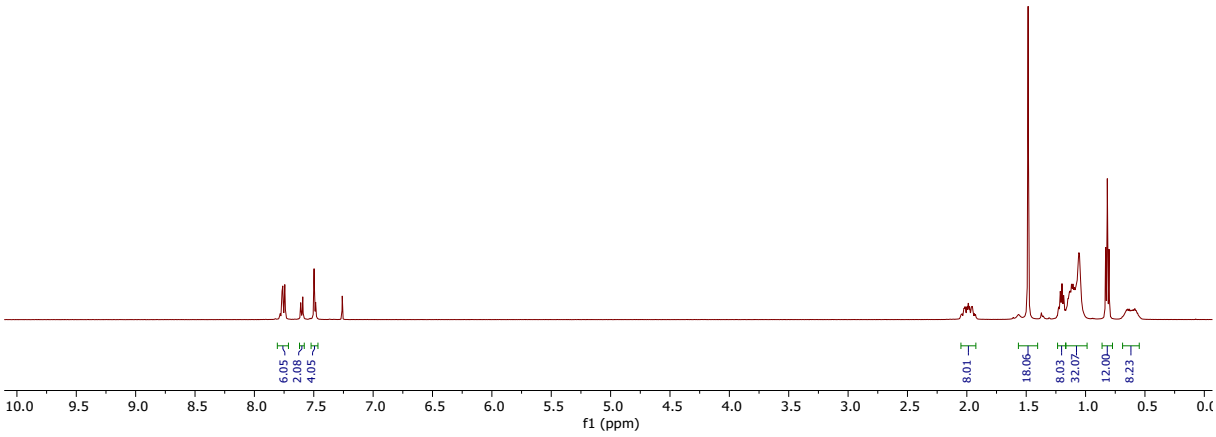


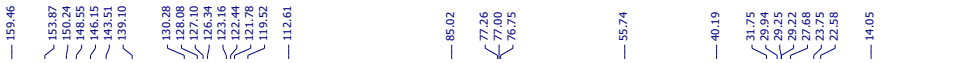
A mixture of **DPP 6** (50 mg, 0.029mmol), $Pd(PPh_3)_4$ (7 mg, 0.0060 mmol), CsOPiv (27 mg, 0.11 mmol) in dry toluene (6 ml) was stirred at 115 °C for 16h in Schlenk tube. The mixture was diluted by CH_2Cl_2 (100 ml) and then evaporated with Celite. The target product was purified by silica gel chromatography using hexanes / toluene (3/2) solution as eluent. Crystallization from toluene / methanol afforded analytically pure compound.
Yield: 35 mg (77%). Dark blue solid; m.p. > 400 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.32 (s, 2H), 9.21 (d, *J* = 1.8 Hz, 2H), 8.70 (d, *J* = 1.7 Hz, 2H), 8.57 (s, 2H), 7.97 (d, *J* = 7.8 Hz, 2H), 7.64 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.61 (d, *J* = 1.4 Hz, 2H), 7.55 – 7.51 (m, 4H), 7.43 – 7.39 (m, 4H), 4.09 (s, 6H), 2.31 – 2.21 (m, 4H), 2.13 – 2.04 (m, 4H), 1.35 (s, 18H), 1.31 – 0.99 (m, 40H), 0.74 (t, *J* = 7.2 Hz, 12H), 0.96 – 0.49 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.8, 159.0, 154.5, 152.7, 151.9, 146.6, 142.4, 141.5, 138.9, 131.4, 131.1, 128.9, 127.8, 127.0, 126.5, 126.4 (2 signals), 126.3, 125.5, 124.7, 124.1, 123.1, 121.1, 120.0, 113.8, 106.0, 91.3, 89.4, 55.9, 53.0, 40.1, 34.9, 31.7, 31.2, 29.9, 29.2 (2 signals), 24.0, 22.5, 14.0; HRMS (APCI): calcd for $C_{104}H_{115}N_4O_{10}$ $[M+H]^+$ 1579.8613, found 1579.8617.

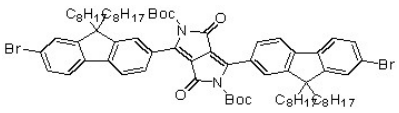
3. Spectral Data

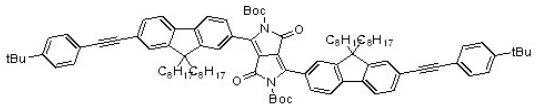








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tBu
$C_8H_{17}C_8H_{17}$
tBu
$C_8H_{17}C_8H_{17}$
Boc

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2.00
2.10
5.91
4.04
8.02
18.13
18.10
8.22
32.27
12.05
8.05
f1 (ppm)


159.51
151.75
151.61
150.90
146.59
146.15
143.97
140.11
131.33
130.83
128.07
127.02
125.99
123.39
123.13
121.03
120.40
120.20
119.68
112.62
90.36
89.66
84.98
77.00 CDCl3
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29.28
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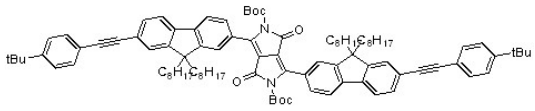
23.79
22.58
14.05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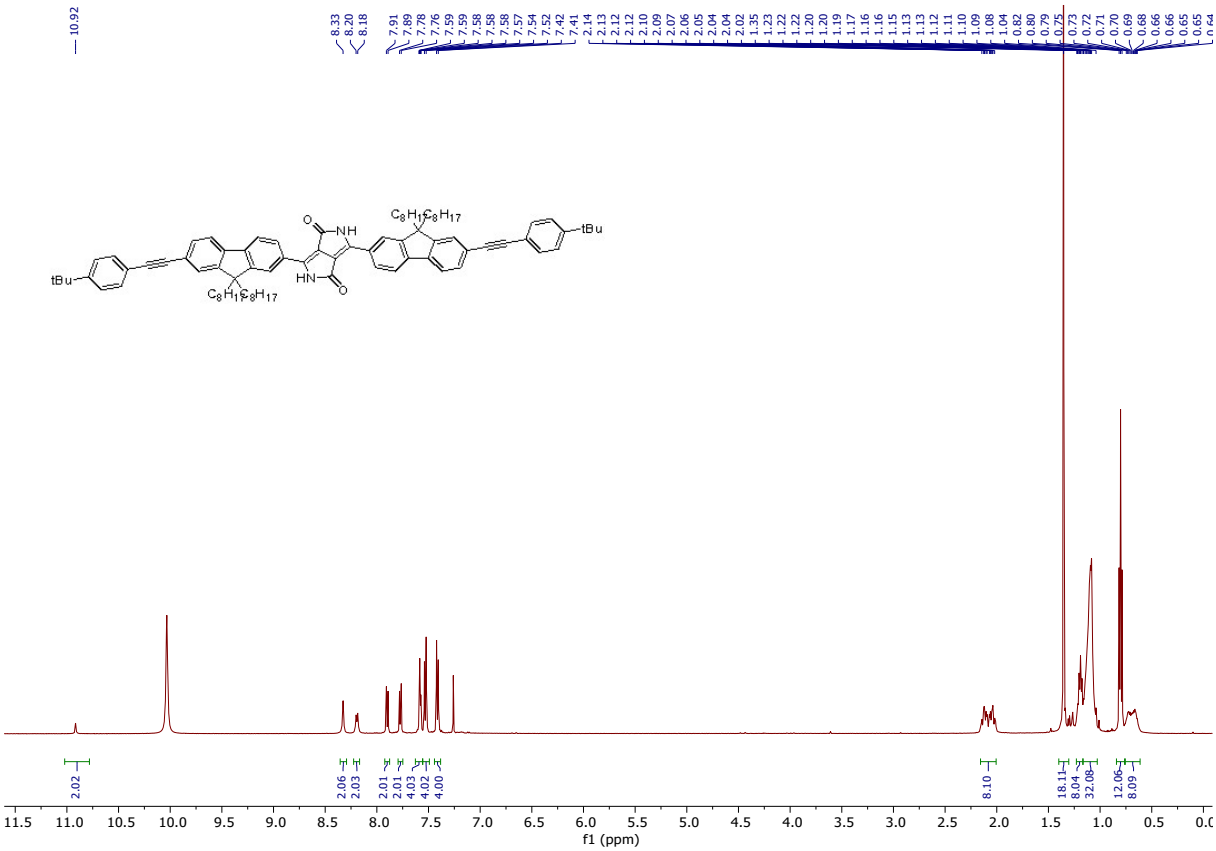
tBu
$C_8H_{17}C_8H_{17}$
tBu
$C_8H_{17}C_8H_{17}$
Boc

f1 (ppm)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7.89
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7.59
7.58
7.58
7.58
7.57
7.54
7.52
7.42
7.41
2.14
2.13
2.12
2.12
2.10
2.09
2.07
2.06
2.05
2.04
2.04
2.02
1.35
1.23
1.22
1.22
1.20
1.20
1.19
1.17
1.16
1.16
1.15
1.13
1.13
1.12
1.11
1.10
1.09
1.08
1.04
0.82
0.80
0.79
0.75
0.73
0.72
0.71
0.70
0.69
0.68
0.66
0.66
0.65
0.65
0.64
NH
HN
O
O
tBu
tBu
C8H17C8H17
C8H17C8H17
2.02
2.06
2.03
2.01
2.01
4.03
4.02
4.00
8.10
18.11
8.04
32.08
12.06
8.09
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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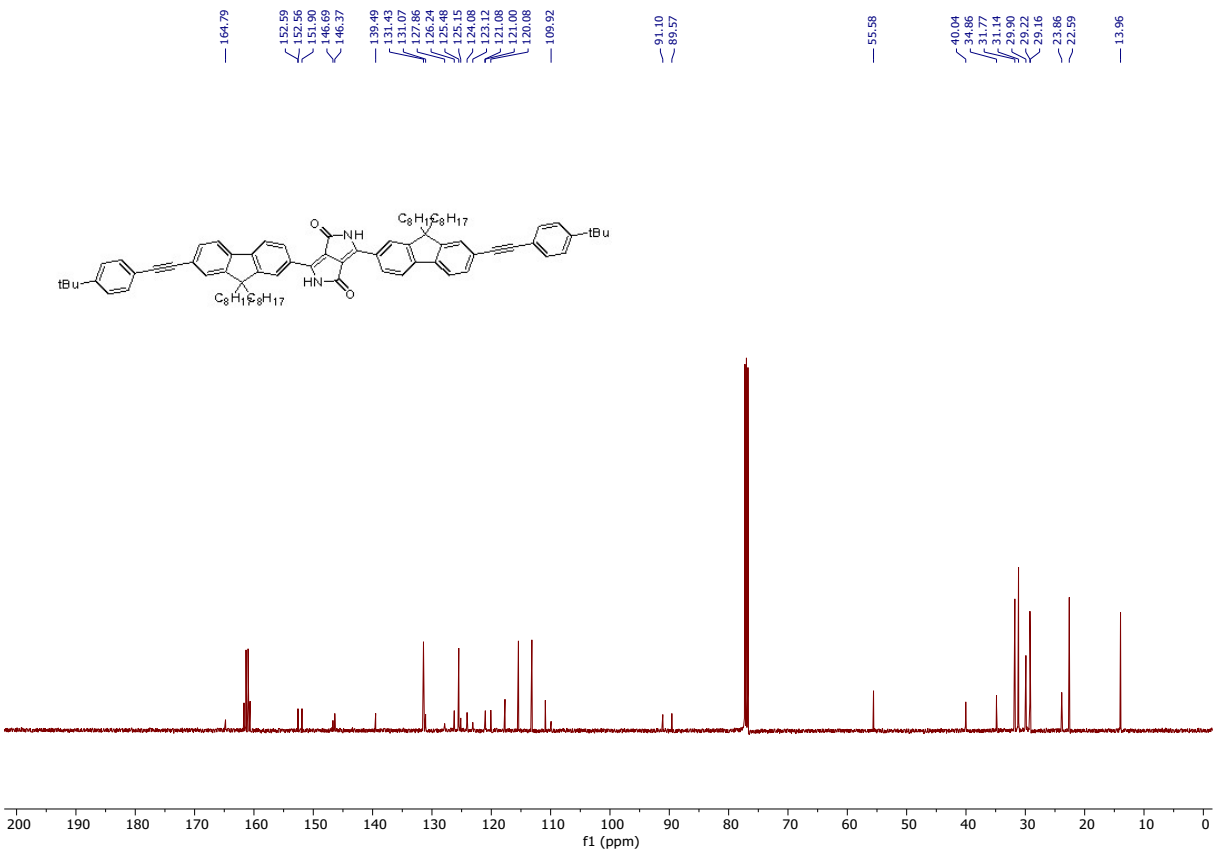
f1 (ppm)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124.08
123.12
121.08
121.00
120.08
109.92
91.10
89.57
55.58
40.04
34.86
31.77
31.14
29.90
29.22
29.16
23.86
22.59
13.96
NH
HN
O
O
tBu
tBu
C8H17C8H17
C8H17C8H17
200
190
180
170
160
150
140
130
120
110
100
90
80
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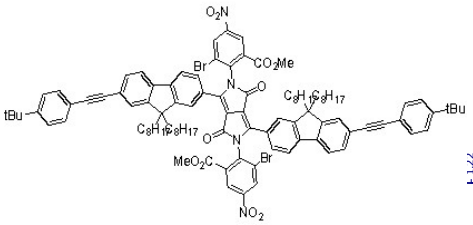
50
40
30
20
10
0
f1 (ppm)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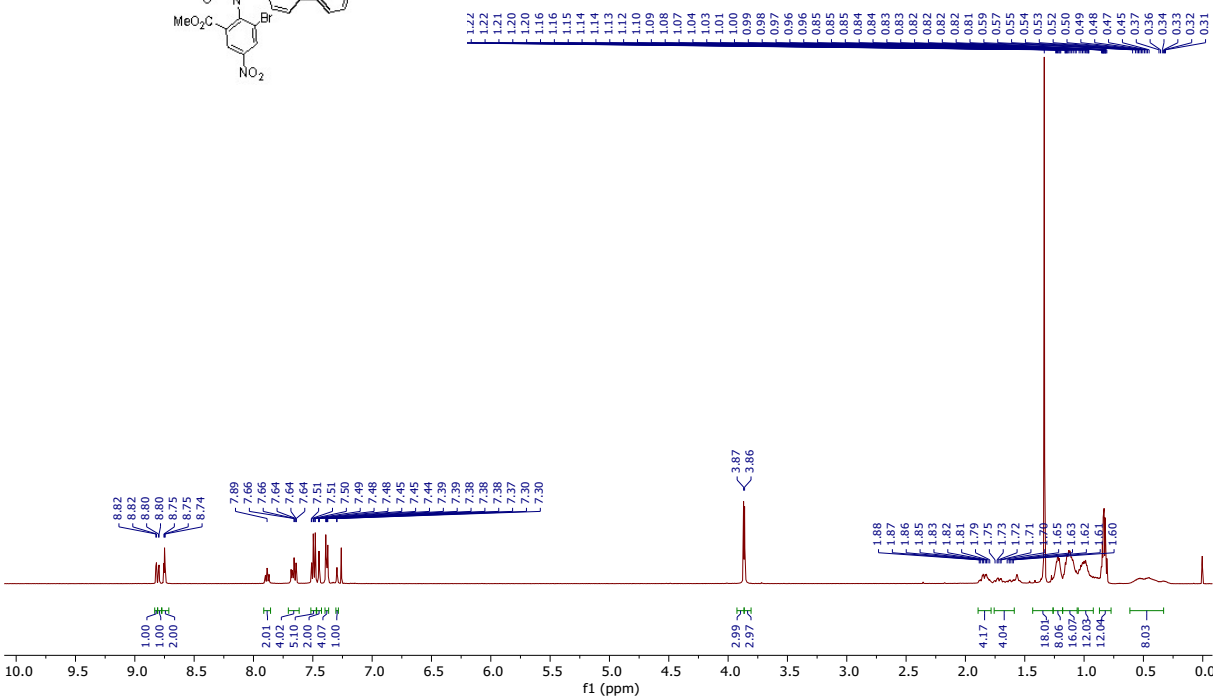
Br
CO2Me
tBu
C8H17C8H17
MeO2C
Br
NO2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7.66
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7.64
7.64
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1.86
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1.83
1.82
1.81
1.79
1.75
1.73
1.72
1.71
1.69
1.65
1.63
1.62
1.61
1.60
1.00
1.00
2.00
2.01
4.02
5.10
2.00
4.07
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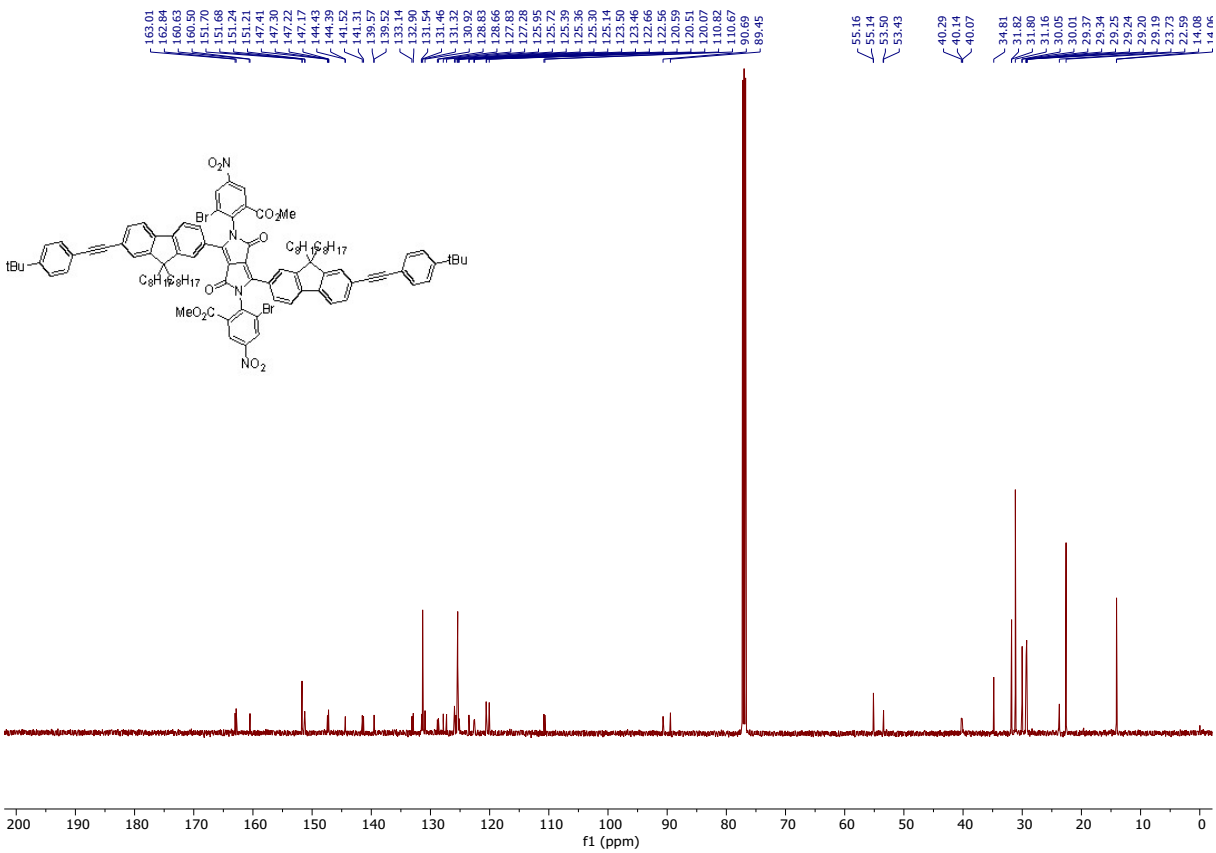
16.07
12.03
12.04
8.03
f1 (ppm)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144.39
141.52
141.31
139.57
139.52
133.14
132.90
131.54
131.46
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130.92
128.83
128.66
127.83
127.28
125.95
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125.39
125.36
125.30
125.14
123.50
123.46
122.66
122.56
120.59
120.51
120.07
110.82
110.67
90.69
89.45
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55.14
53.50
53.43
40.29
40.14
40.07
34.81
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29.24
29.20
29.19
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22.59
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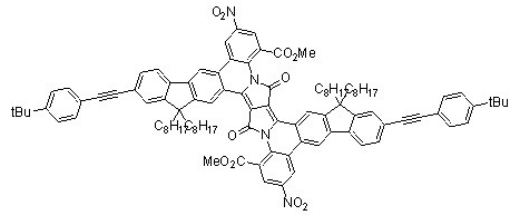
Br
CO2Me
tBu
C8H17C8H17
MeO2C
Br
NO2
f1 (ppm)


O2N
CO2Me
tBu
C8H17C8H17
MeO2C
NO2

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9.33
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8.57
8.01
7.99
7.67
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7.54
7.54
7.53
7.53
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7.43
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7.41
4.06
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2.24
2.23
2.22
2.21
2.20
2.16
2.16
2.14
2.14
2.14
2.12
2.11
1.36
1.13
1.09
1.08
1.07
1.07
1.06
1.06
1.04
1.04
0.75
0.74
0.73
0.66
0.65
0.64
0.63
2.07
2.00
2.03
2.03
2.03
2.04
2.03
4.02
4.00
5.96
4.01
4.03
18.01
8.03
32.00
12.07
8.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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3.0
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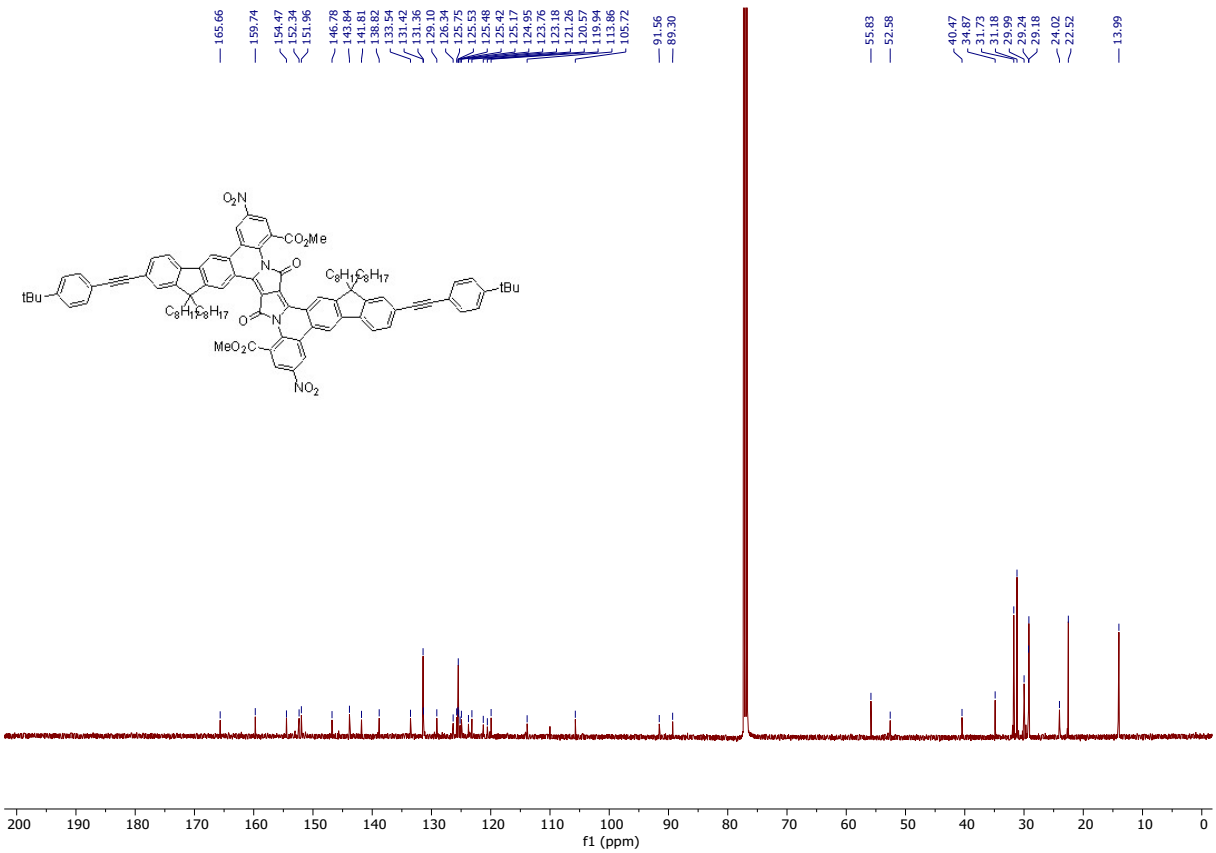
0.5
f1 (ppm)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123.18
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52.58
40.47
34.87
31.73
31.18
29.99
29.24
29.18
24.02
22.52
13.99
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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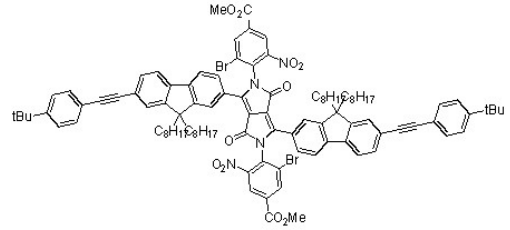
CO2Me
tBu
C8H17C8H17
MeO2C
NO2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Br
NO2
tBu
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O
N
O2N
CO2Me

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1.21
1.20
1.19
1.15
1.15
1.14
1.14
1.13
1.13
1.12
1.11
1.10
1.09
1.08
1.07
1.03
1.02
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0.94
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0.83
0.82
0.81
0.81
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7.51
7.50
7.49
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7.48
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1.83
1.81
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1.00
1.01
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2.02
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4.06
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8.10
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16.03
12.04
8.07
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6.0
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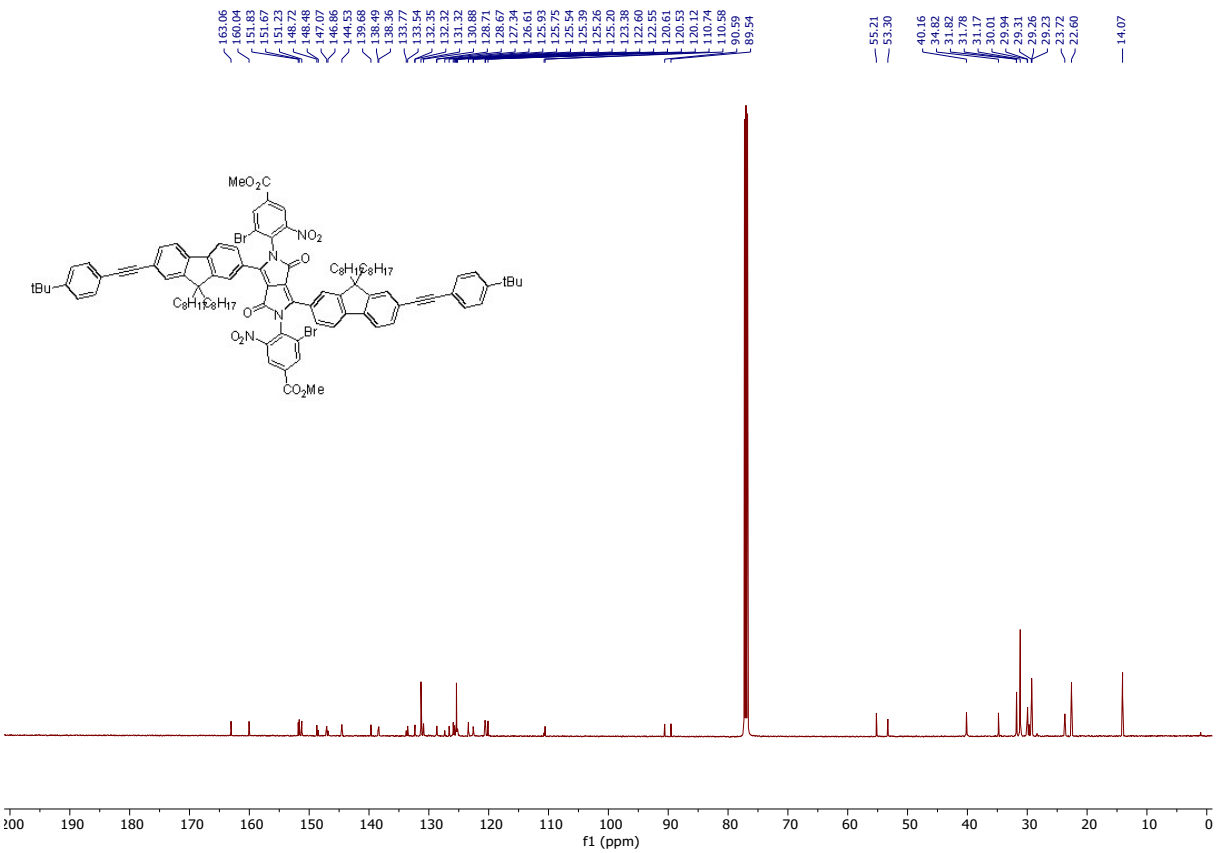
0.0
f1 (ppm)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40.16
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31.82
31.78
31.17
30.01
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29.31
29.26
29.23
23.72
22.60
14.07
MeO2C
Br
NO2
tBu
C8H17C8H17
O
N
O2N
CO2Me
200
190
180
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50
40
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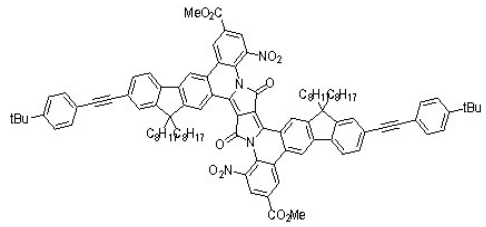
f1 (ppm)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tBu
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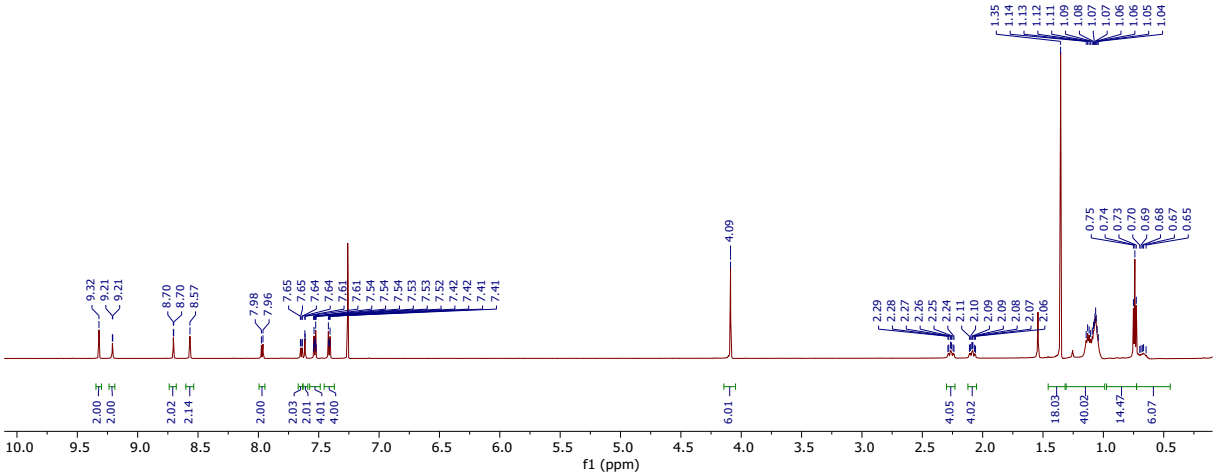
C8H17C8H17
tBu
O2N
CO2Me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1.09
1.08
1.07
1.07
1.06
1.06
1.05
1.04
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0.74
0.73
0.70
0.69
0.68
0.67
0.65
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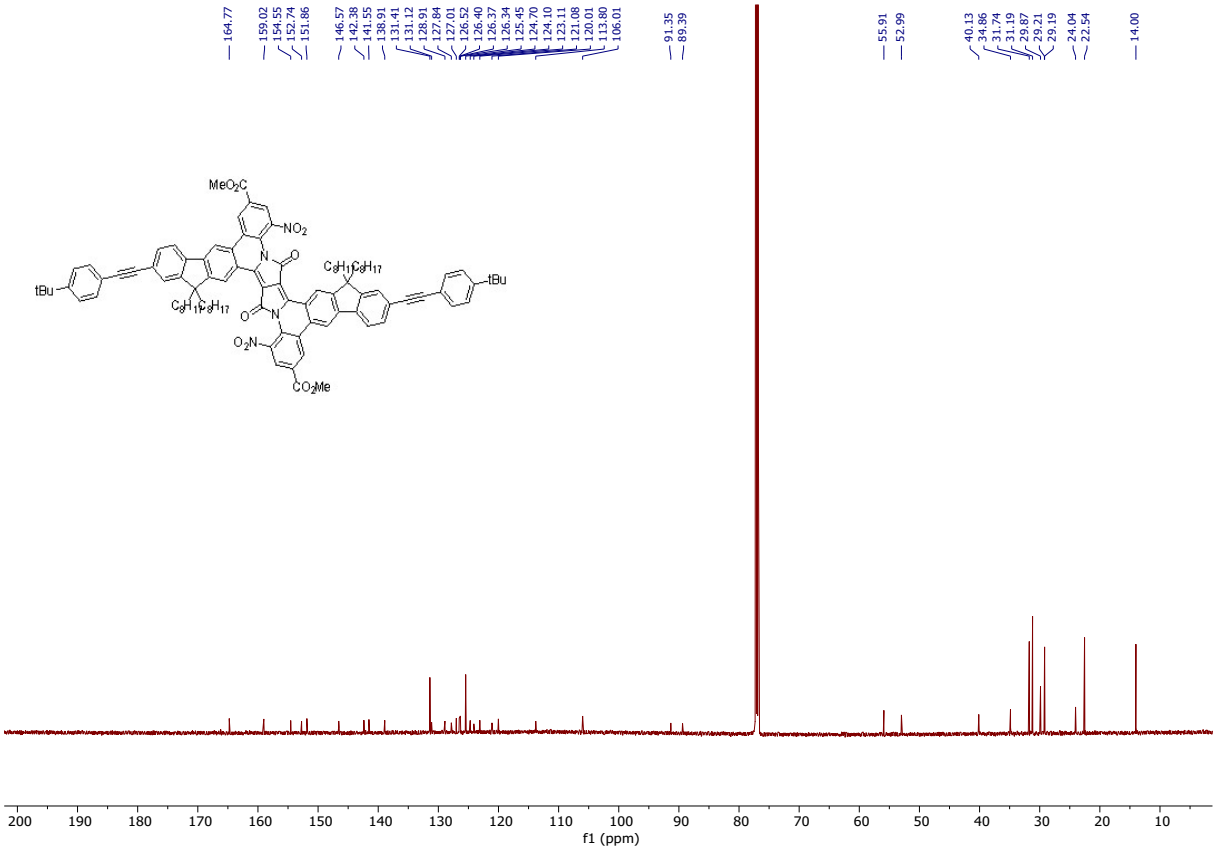
6.07
f1 (ppm)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127.84
127.01
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126.40
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124.70
124.10
123.11
121.08
120.01
113.80
106.01
91.35
89.39
55.91
52.99
40.13
34.86
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29.21
29.19
24.04
22.54
14.00
MeO2C
NO2
tBu
C8H17C8H17
C8H17C8H17
tBu
O2N
CO2Me
f1 (ppm)

4. Photophysical Data

4.1 Absorption Emission and Excitation Spectra

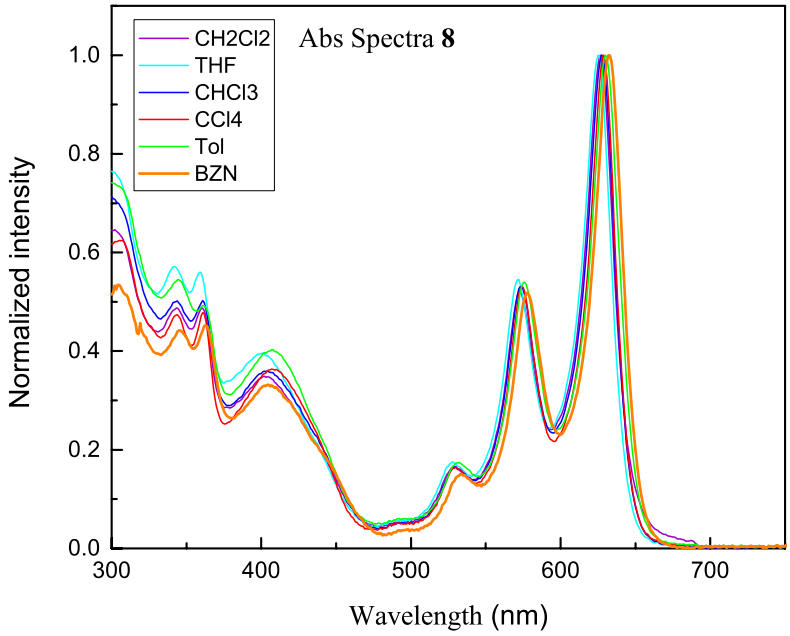


Figure S1. Absorption Spectra in various solvents for EDPP **8**.

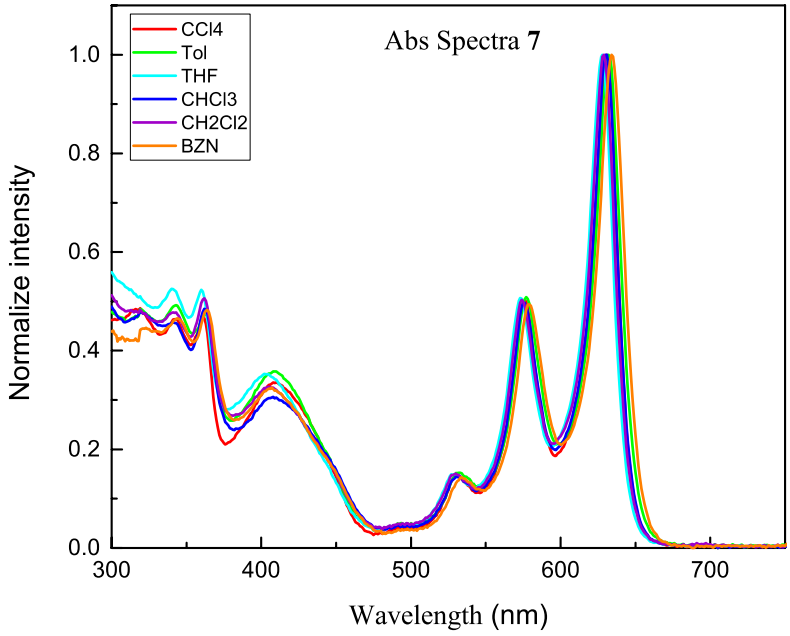


Figure S2. Absorption Spectra in various solvents for EDPP **7**.

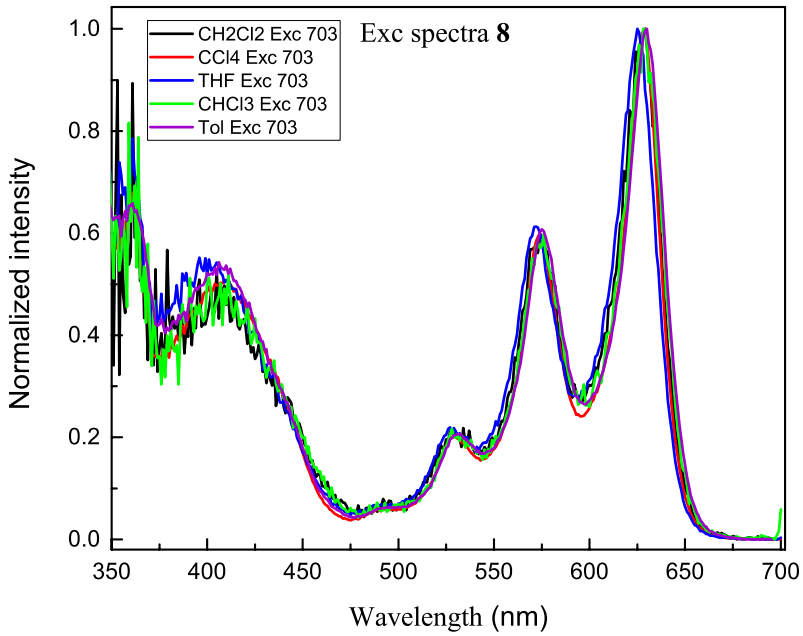


Figure S3. Excitation Spectra in various solvents for EDPP **8**. Fluroescence is detected around 700 nm.

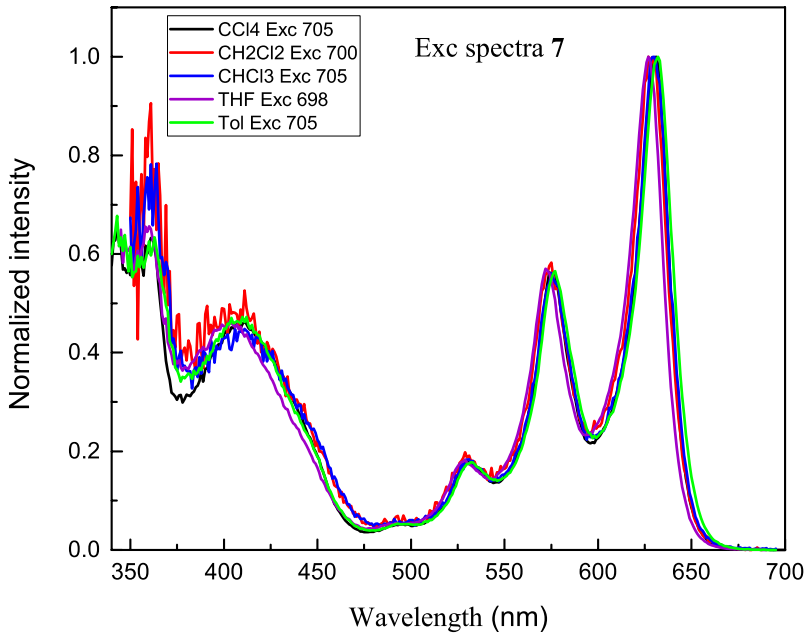


Figure S4. Excitation Spectra in various solvents for EDPP **7**. Fluroescence is detected in the around 700-705 nm spectral range.

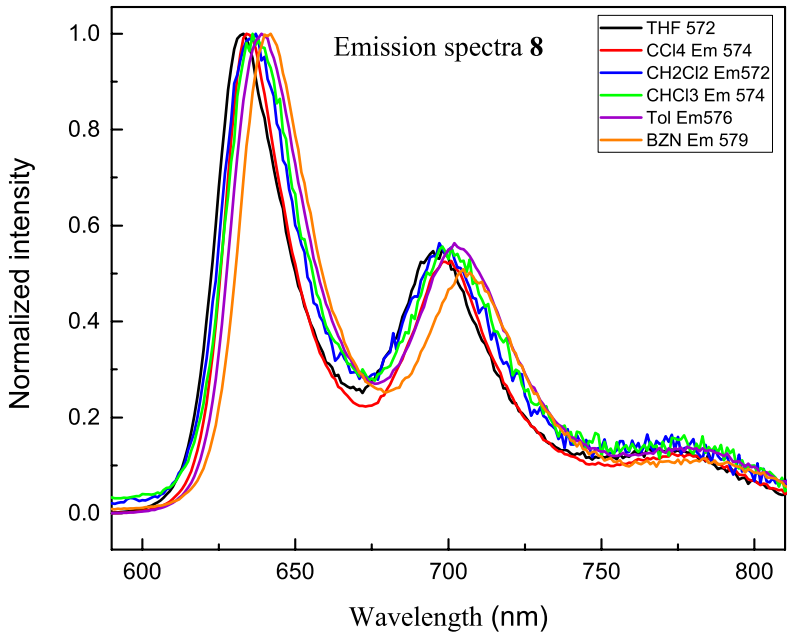


Figure S5. Emission Spectra in various solvents for EDPP **8**. Excitation wavelength is in the the 572-579 nm spectral range.

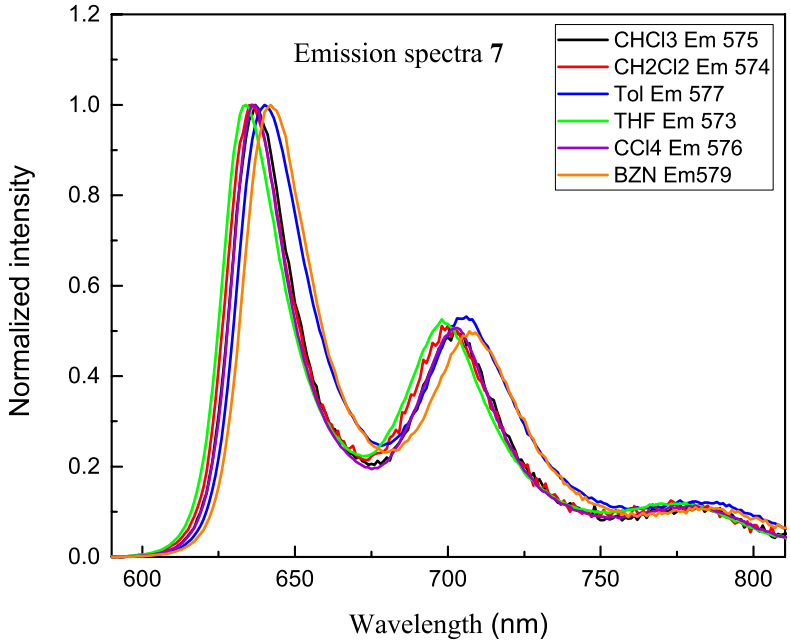


Figure S6. Emission Spectra in various solvents for EDPP **7**. Excitation wavelength is in the the 573-579 nm spectral range.

4.2 Ultrafast Transient Absorption

Here we reported the global analysis of transient absorption measurement performed with a unidirectional sequential model with increasing lifetimes. All the data have been fitted adopting the minimum number of spectro-temporal components to reproduce the data.

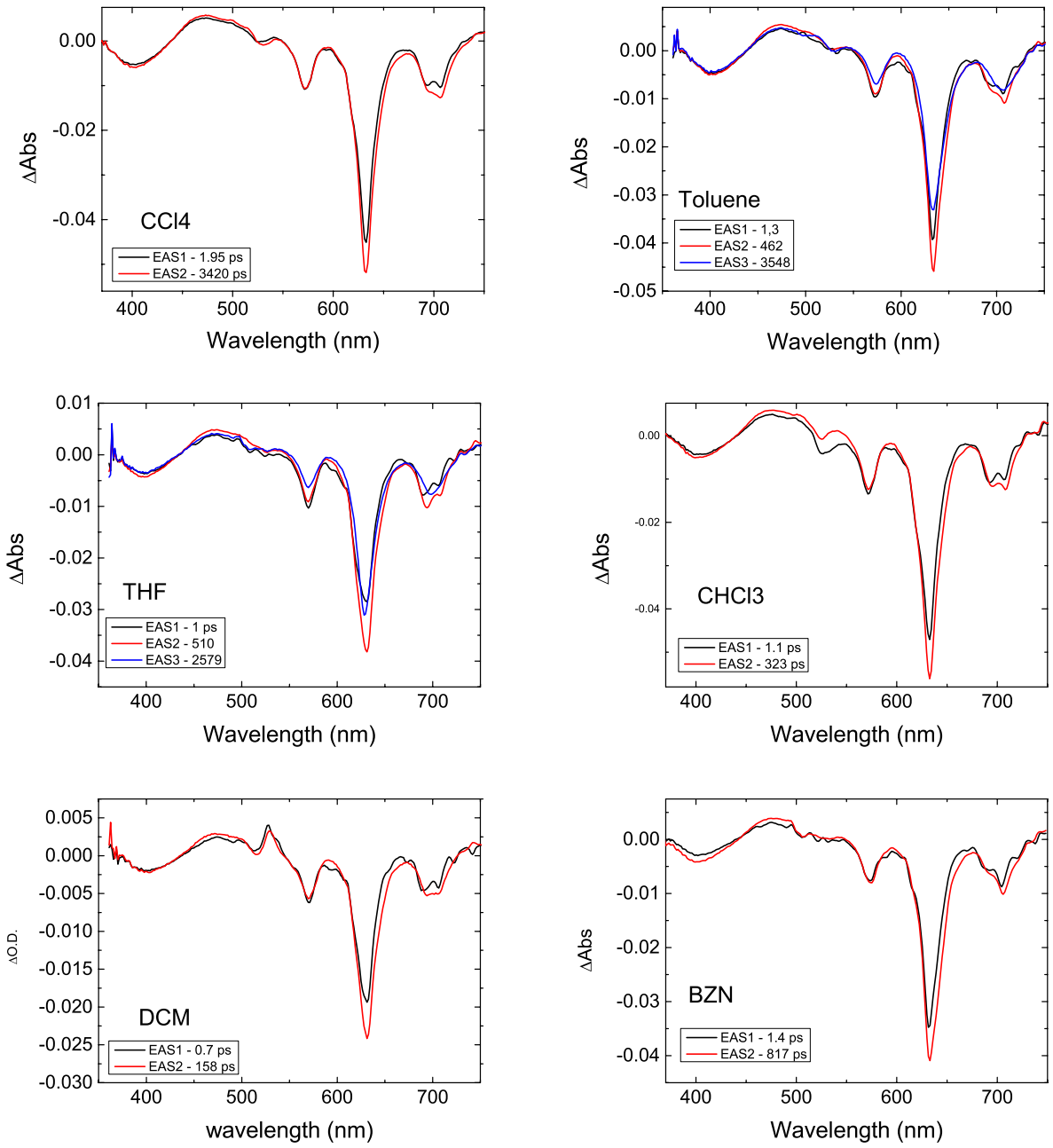
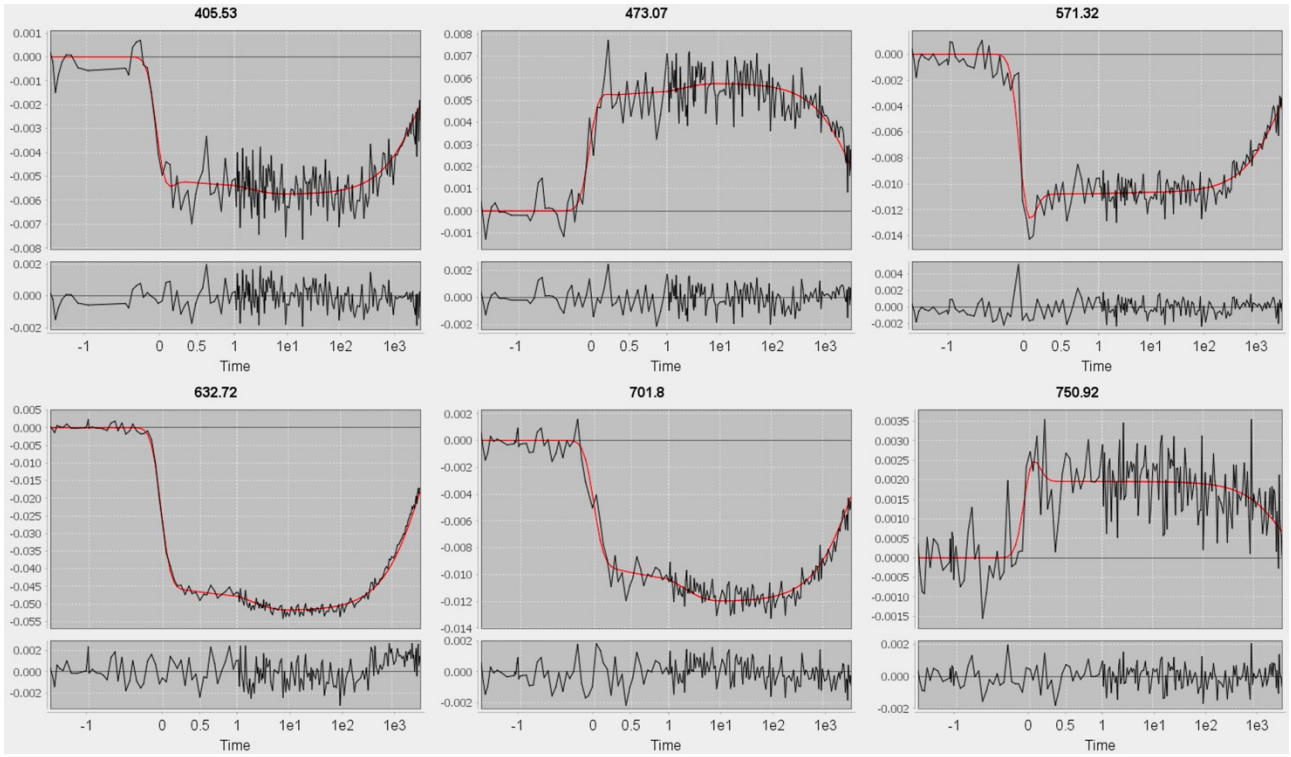
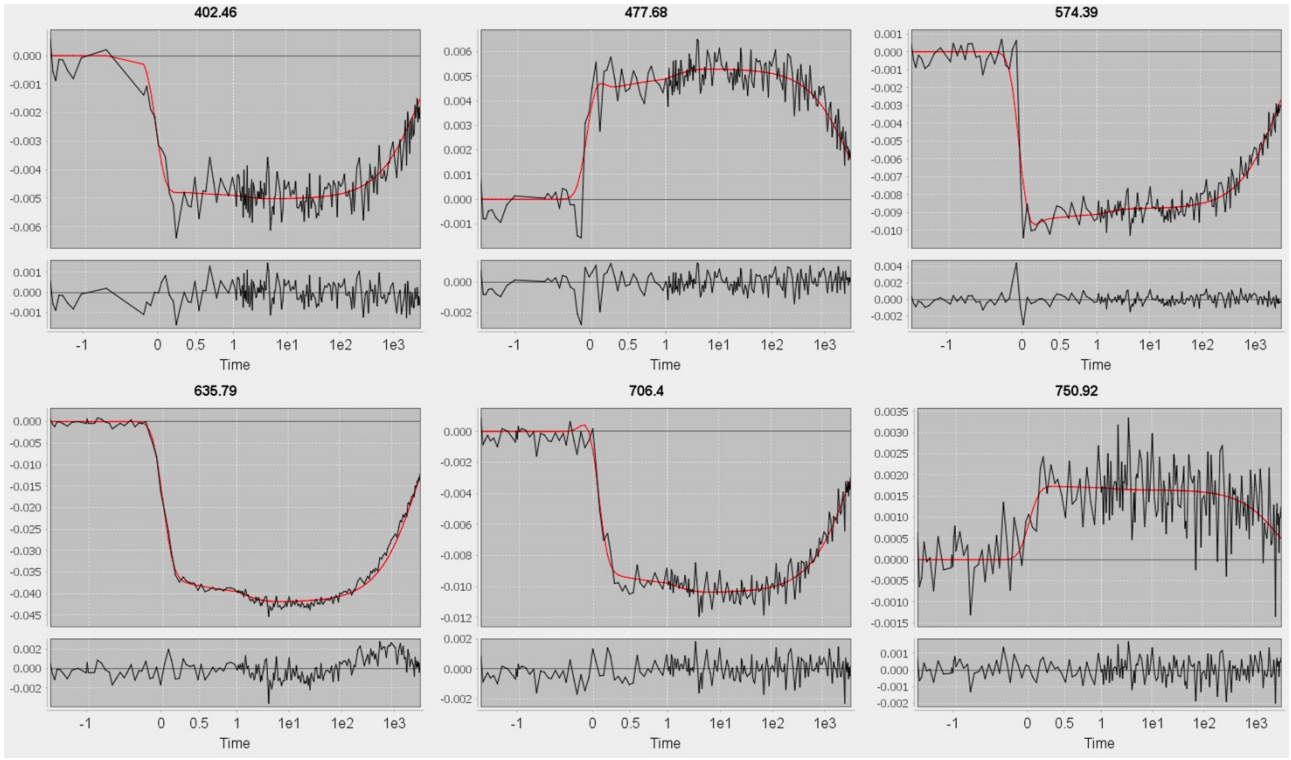


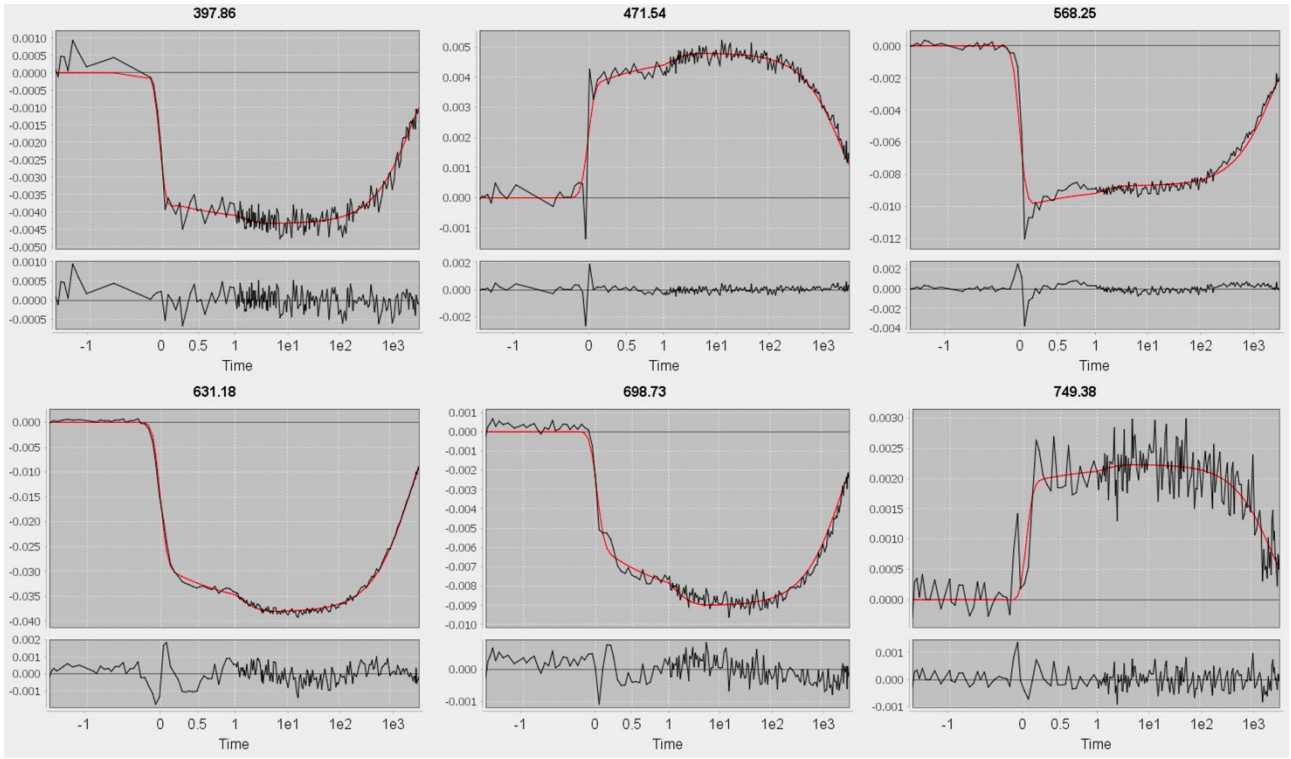
Figure S7a. Evolution Associated Difference Spectra (EADS) of transient absorption measurements EDPP **7** in various solvents.


405.53
473.07
571.32
632.72
701.8
750.92
Time

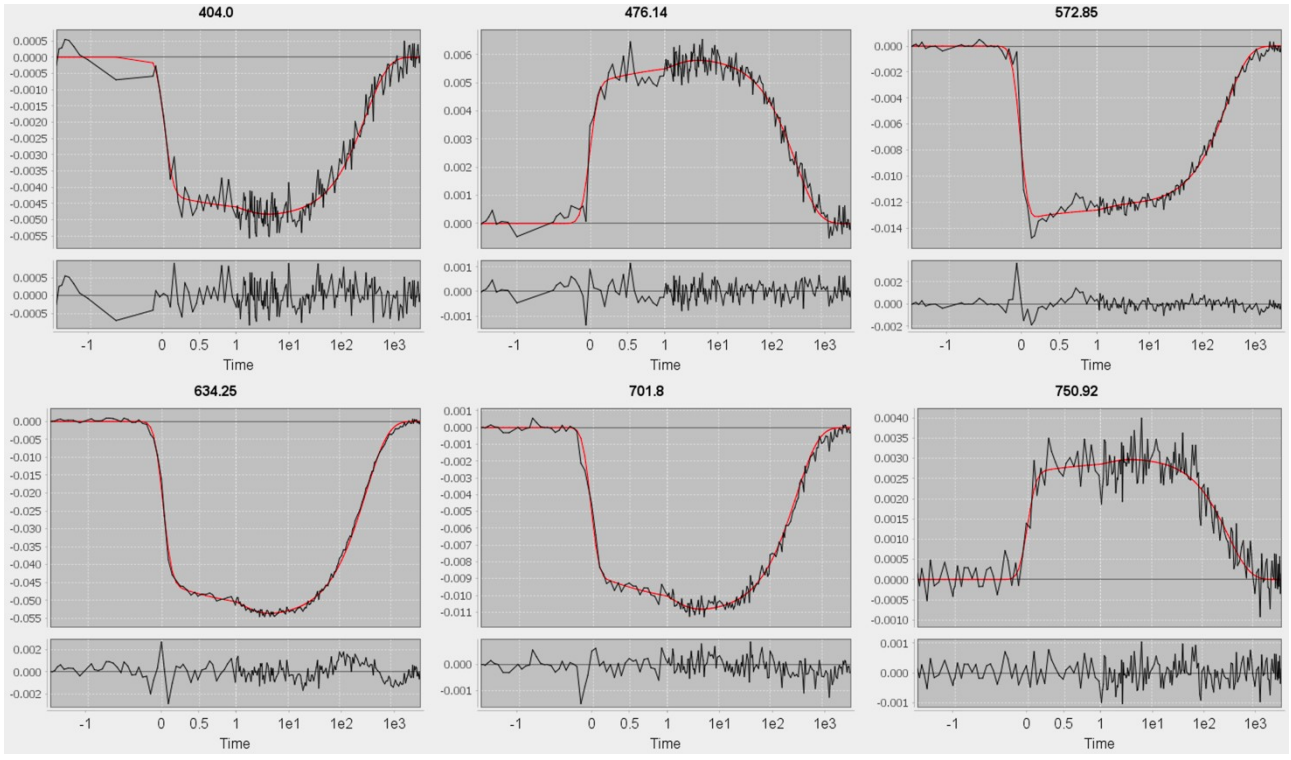
CCl_4


402.46
477.68
574.39
635.79
706.4
750.92
Time

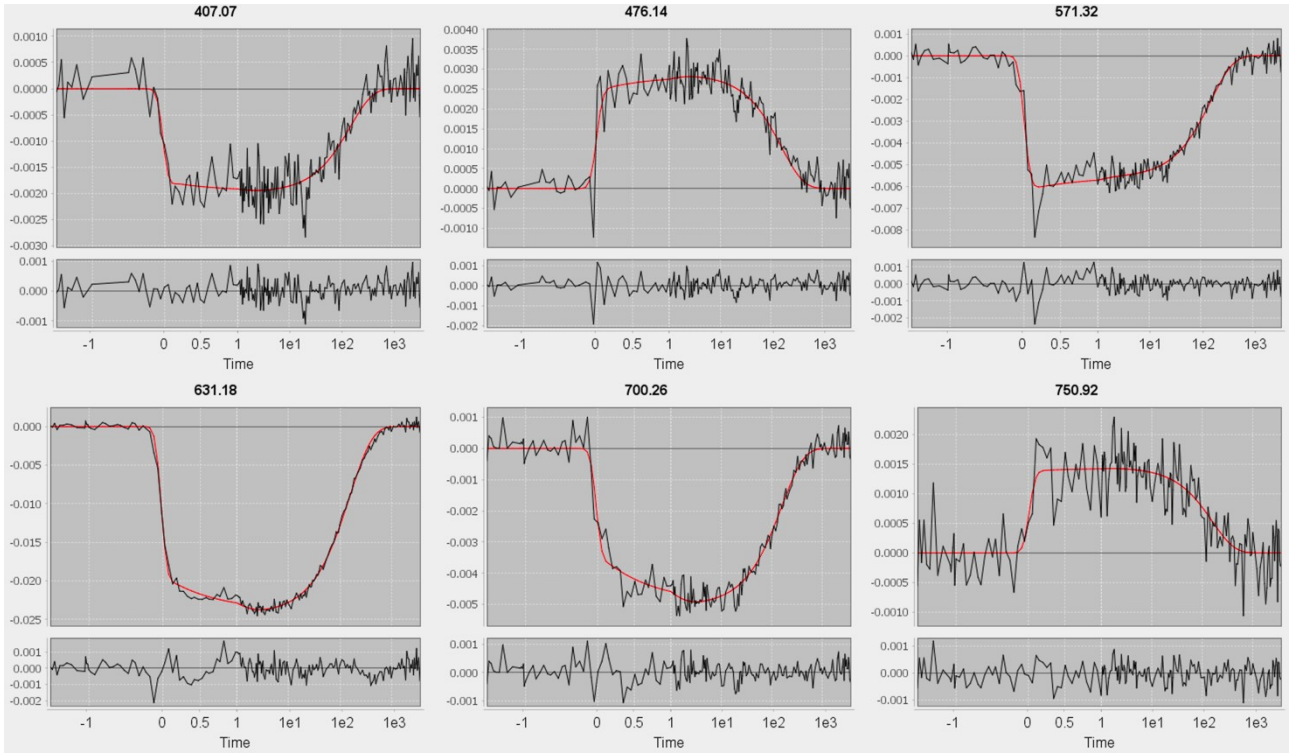
TOL


397.86
471.54
568.25
631.18
698.73
749.38
Time

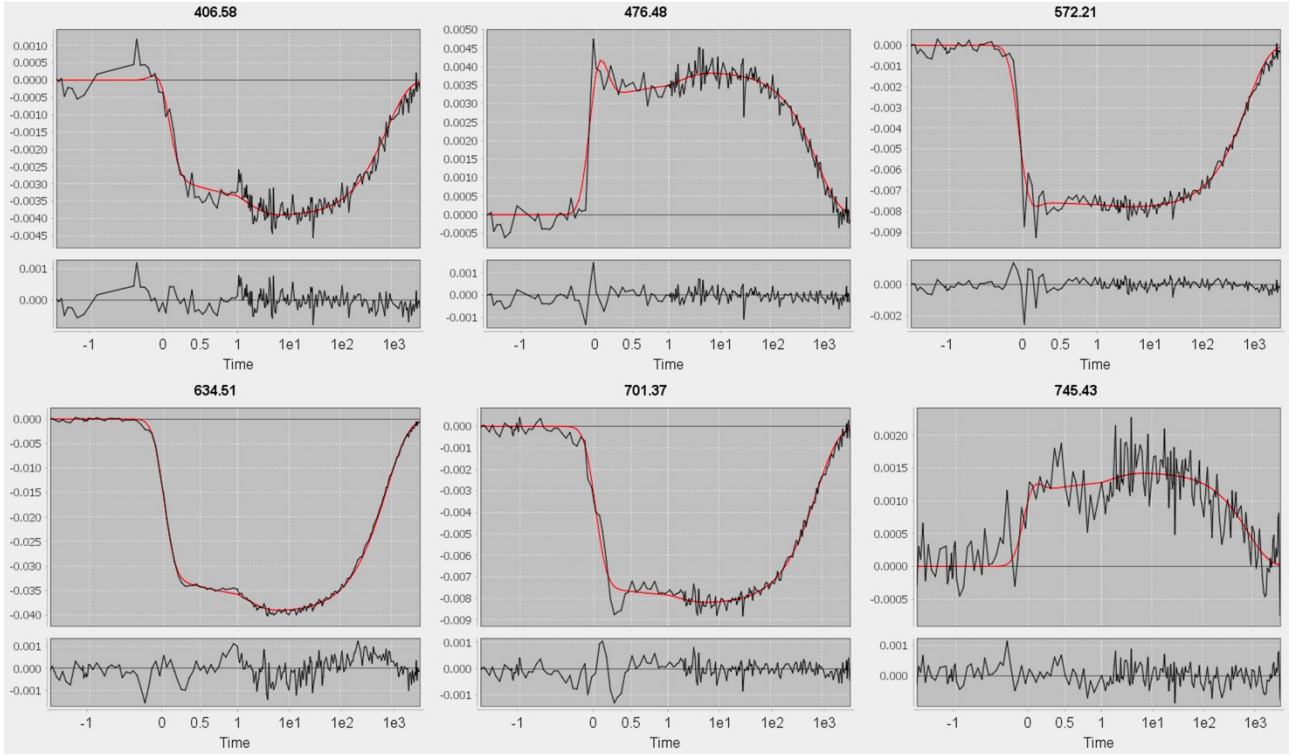
THF


404.0
476.14
572.85
634.25
701.8
750.92
Time

$CHCl_3$



DCM



BZN

Figure S7b. Selected Kinetic traces for EDPP **7** at various wavelength (black line) and the respectives fitting curve (red line) with the sequential model described in the main text.

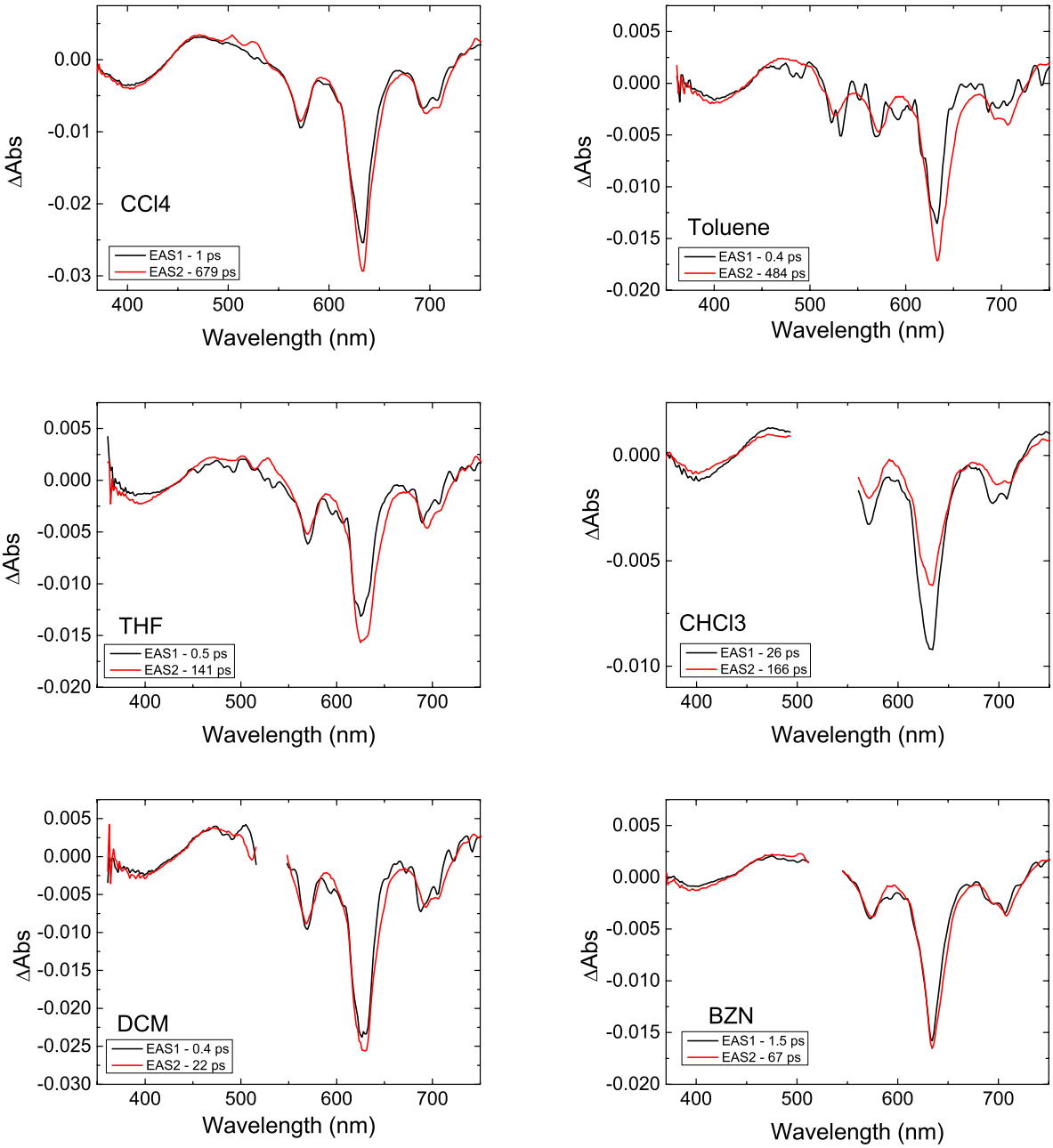
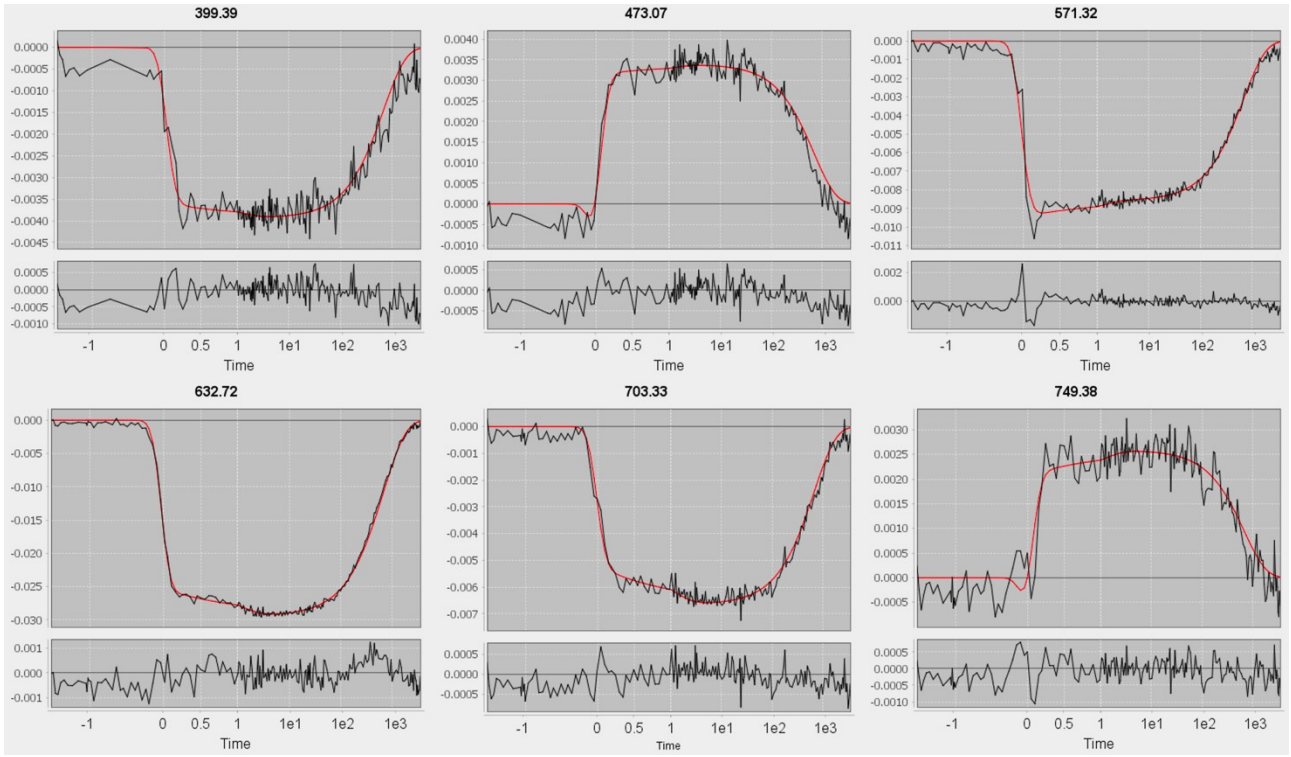
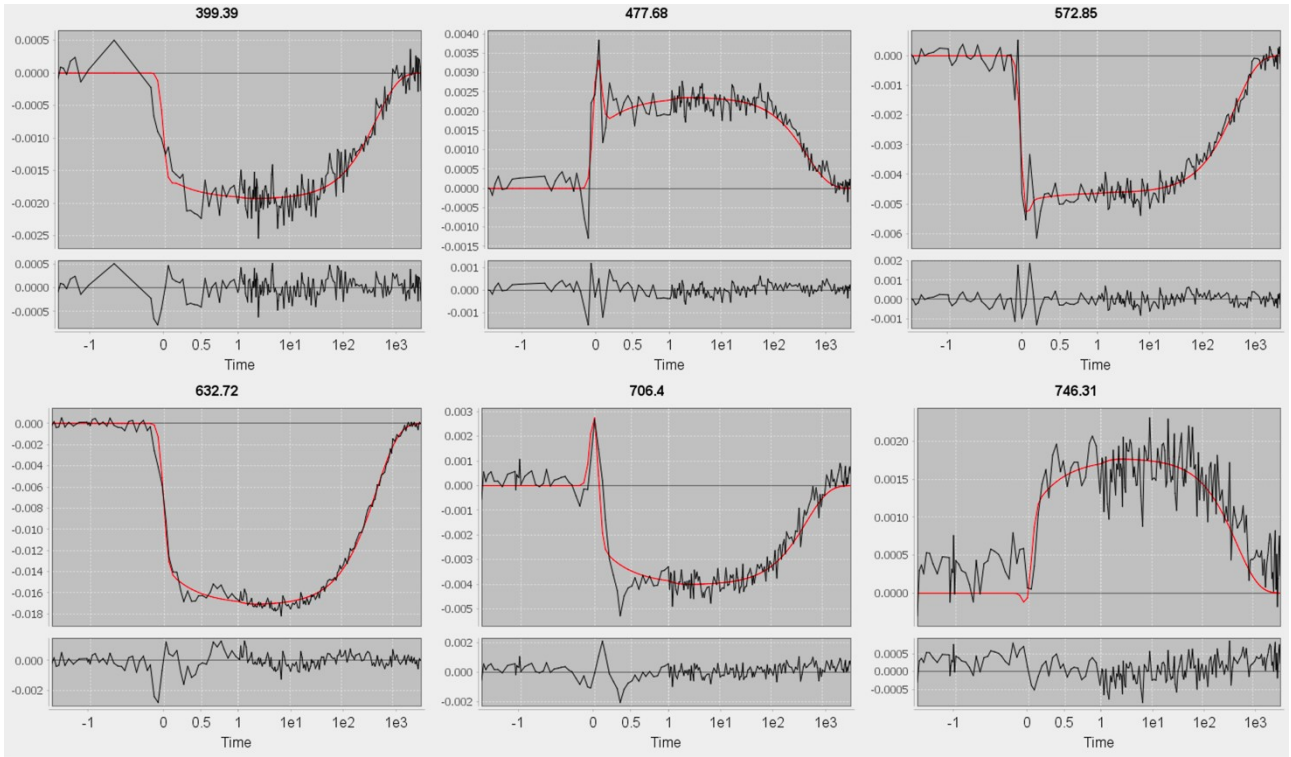


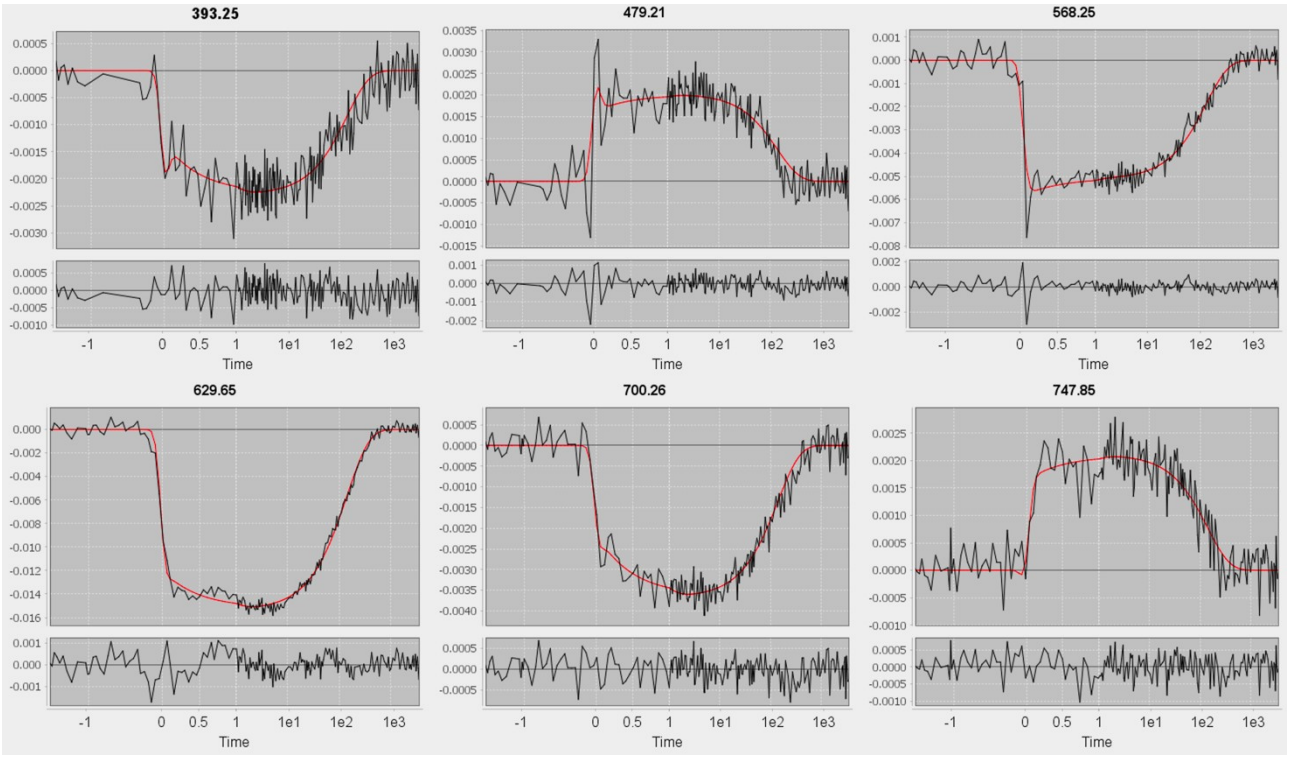
Figure S8. Evolution Associated Difference Spectra of transient absorption measurements EDPP **8** in various solvents.


399.39
473.07
571.32
632.72
703.33
749.38
Time

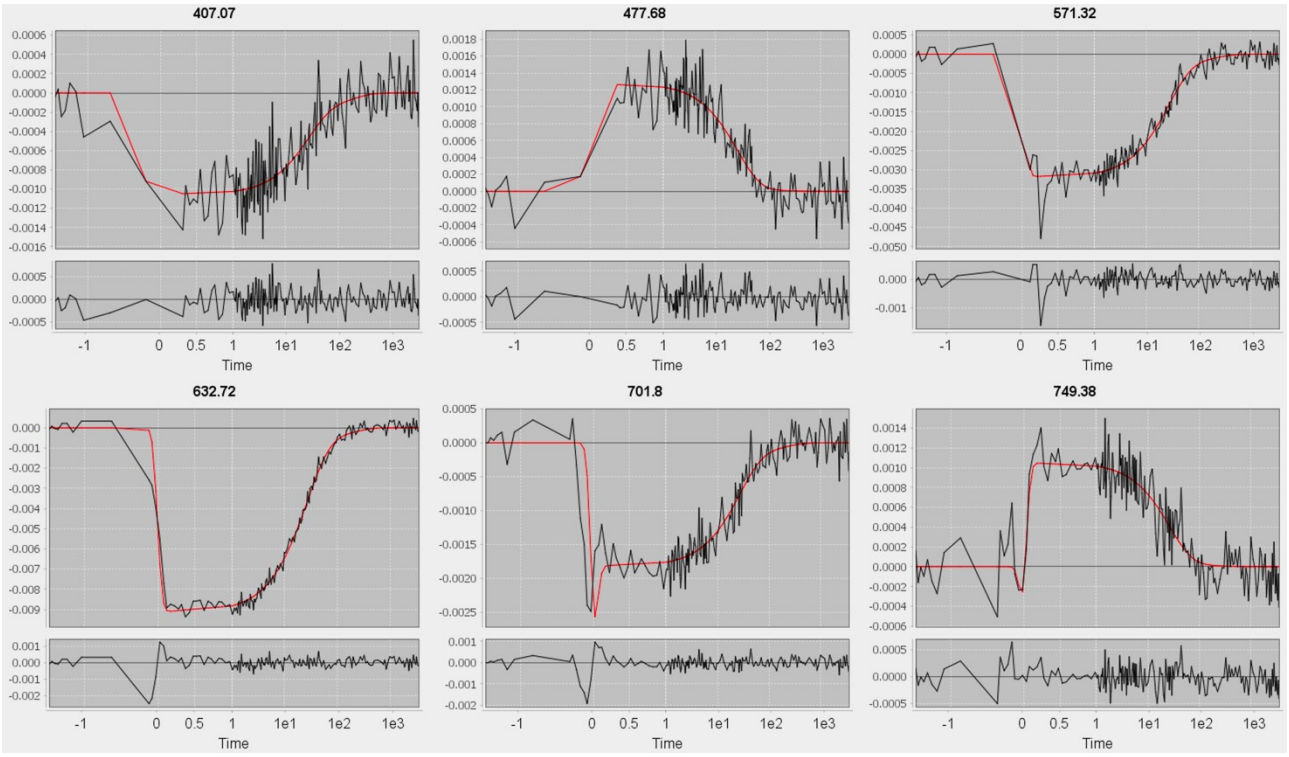
CCl_4


399.39
477.68
572.85
632.72
706.4
746.31
Time

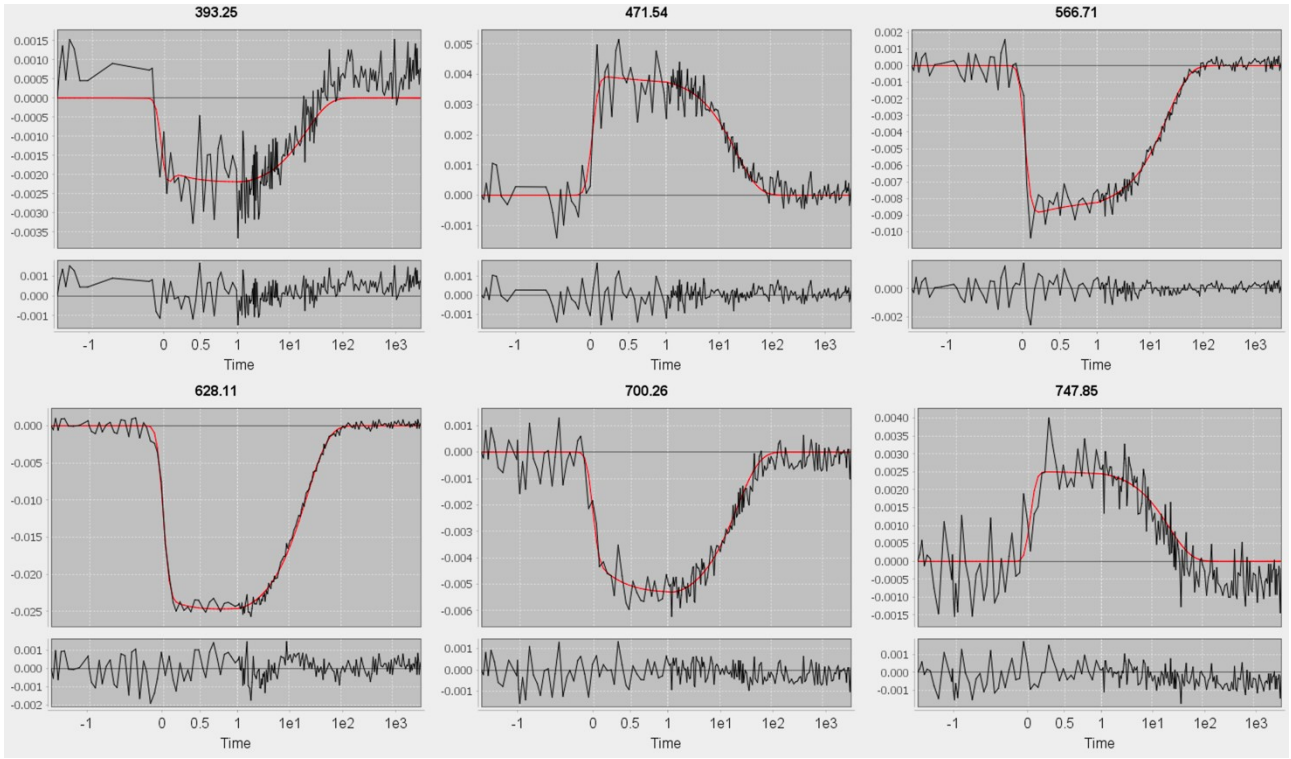
TOL


393.25
479.21
568.25
629.65
700.26
747.85
Time

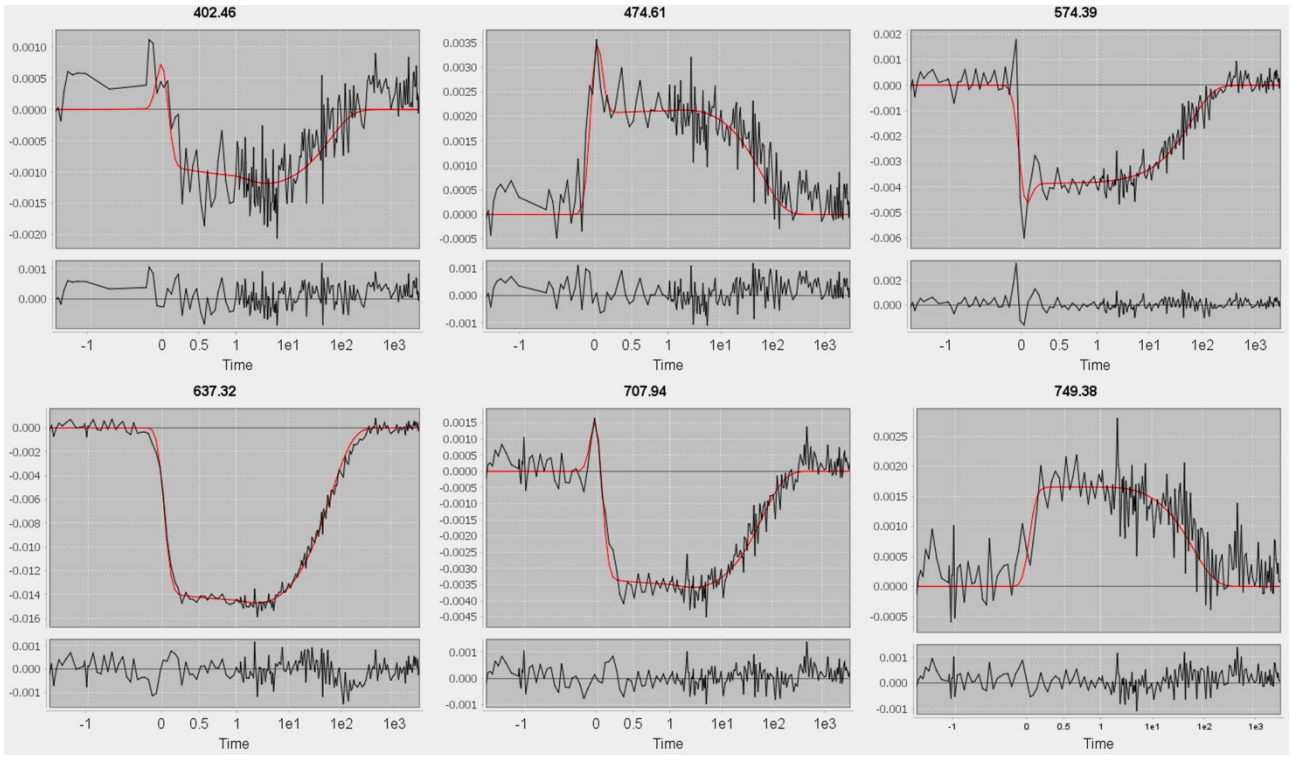
THF


407.07
477.68
571.32
632.72
701.8
749.38
Time

$CHCl_3$



DCM



BZN

Figure S8b. Selected Kinetic traces for EDPP **8** at various wavelength (black line) and the respectives fitting curve (red line) with the sequential model described in the main text.

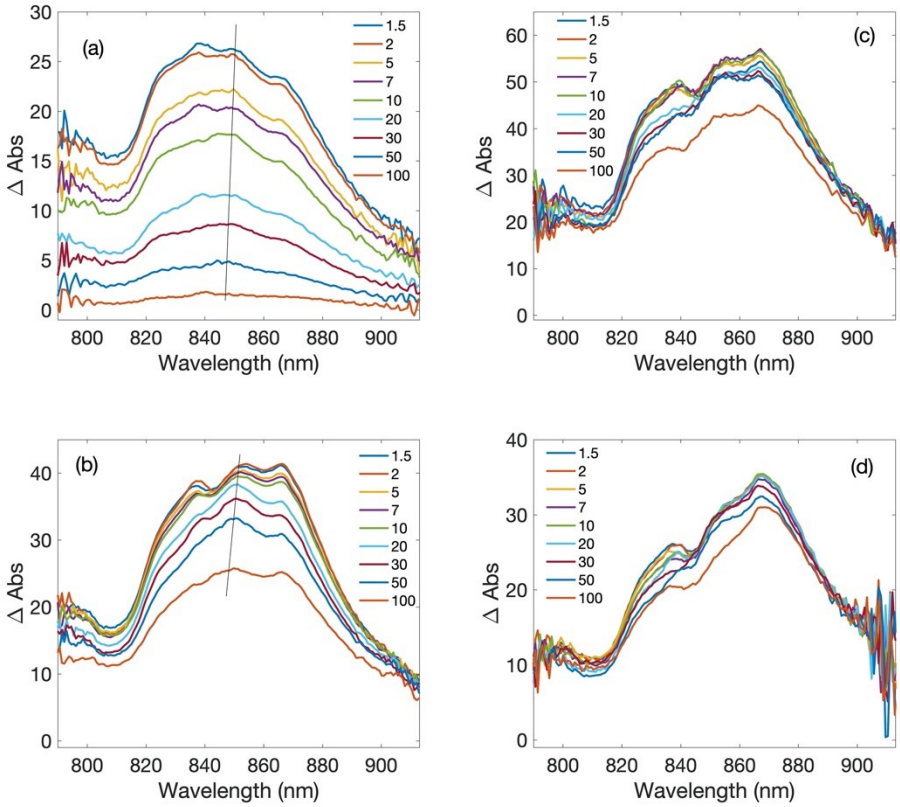


Figure S9. Transient absorption spectra from Broadband transient absorption measurements in the NIR spectral range for EDDP **8**: $CHCl_3$ (a), Tol (c) and for EDDP**7:** $CHCl_3$ (b), Tol (d).

4.3 Temperature dependent Fluorescence Lifetime

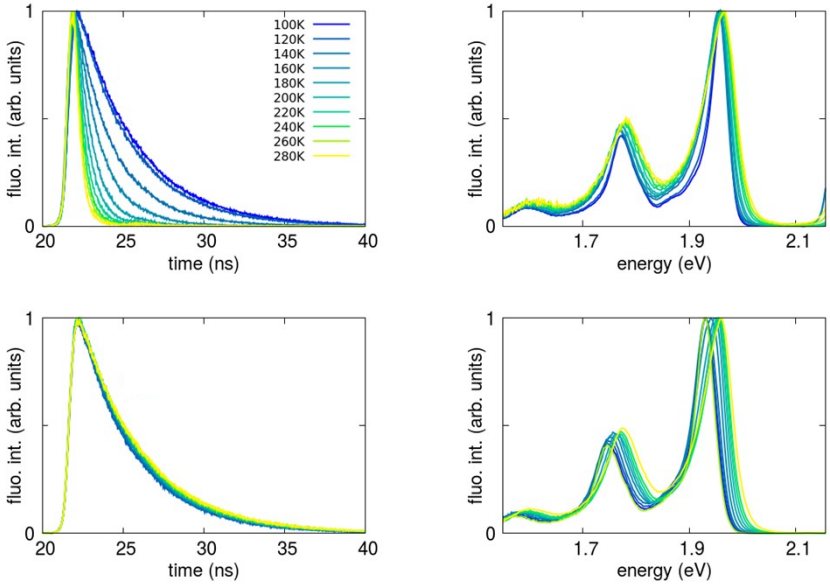


Figure S10. The effect of temperature on the emission lifetimes. Flurescence lifetimes measured in 2-MeTHF EDPP **8** (upper panels) and **7** (lower panels) EDPPs.

T (K)	t (ns)
77	3.62
100	3.6
120	3.35
140	2.49
160	1.65
180	1.15
200	0.77
220	0.63
240	0.54
298	0.178

Table TS1. Temperature dependence of the emission lifetimes measured in 2-MeTHF for EDPP **8**.

4.4 Temperature dependent Ultrafast Broad-band Pump-probe

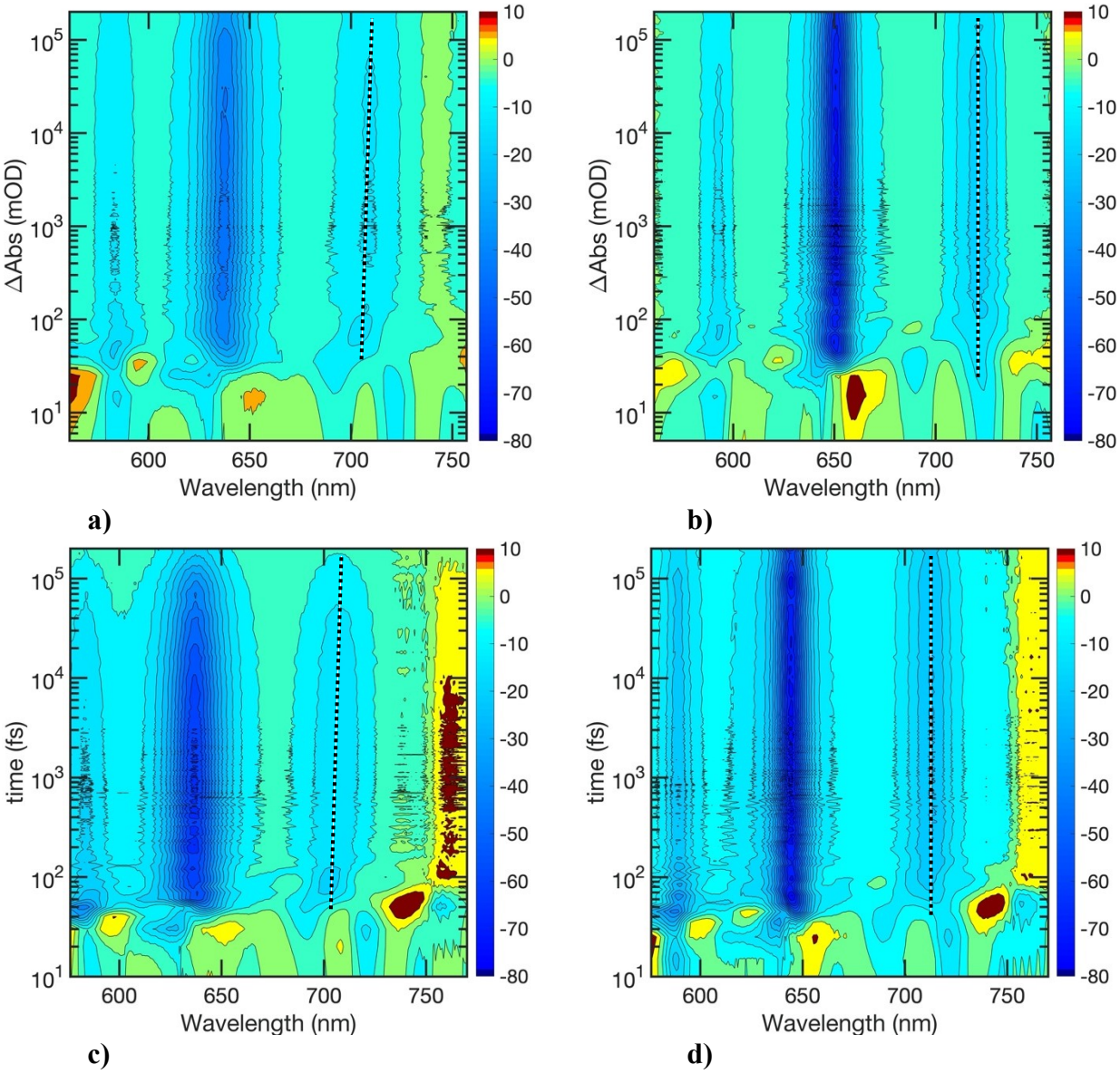


Figure S11. The effect of temperature on pump probe spectra Broadband Pump-probe spectra in 2-MeTHF. EDPP **7** at room temperature **a)** and 77K **b)**. EDPP **8** at room temperature **c)** and 77K **d).**

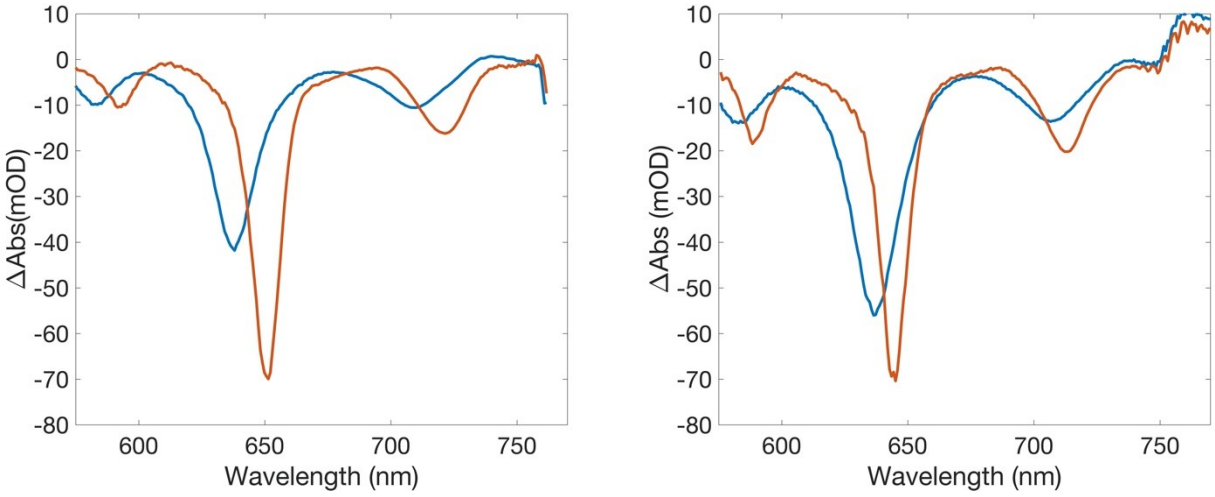


Figure S12. Broadband pump probe spectra in 2-MeTHF measured at 10 ps delay time. EDPP **7** is reported in left panel with room temperature (blue) and 77K (red) spectrum. EDPP **8** is reported in right panel with room temperature (blue) and 77K (red) spectrum.

4.5 Ultrafast transient Infrared spectra

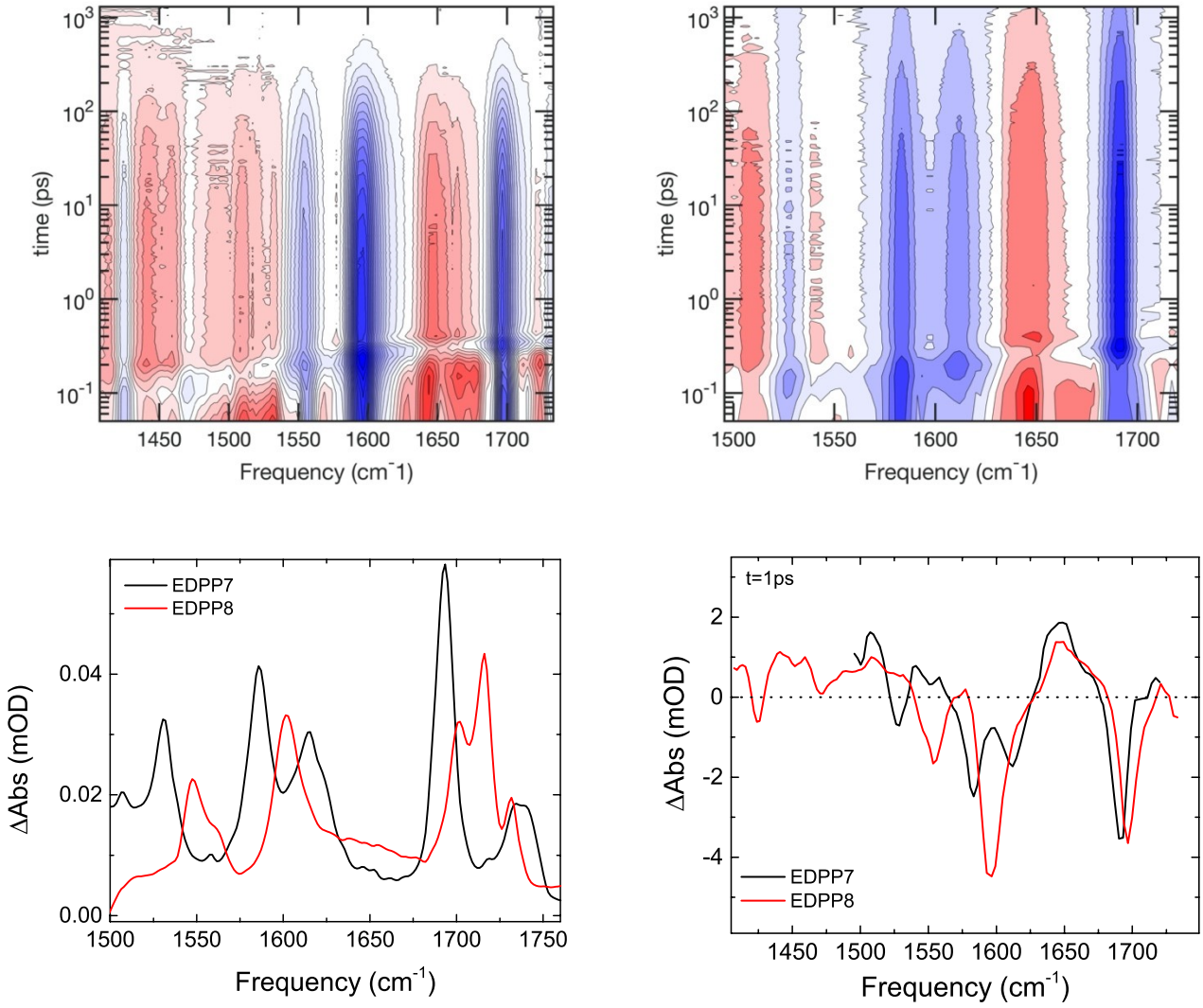


Figure S13. Transient Infrared spectra in THF for EDPP **8** (Upper left panel) and EDPP **7** (Upper right panel). FTIR spectra in THF (lower left panel) and TRIR spectra at 1ps delay time (lower right panel)

5. Additional calculations

In Figure S14, we report the electrostatic potential maps for dye **7** (panel a) and dye **8** (panel b) obtained for the ground state at the DFT level (B3LYP/6-31+G(d,p)) in gas phase. S_1 optimized geometries for molecules **7** (panel c) and **8** (panel d) are also shown.

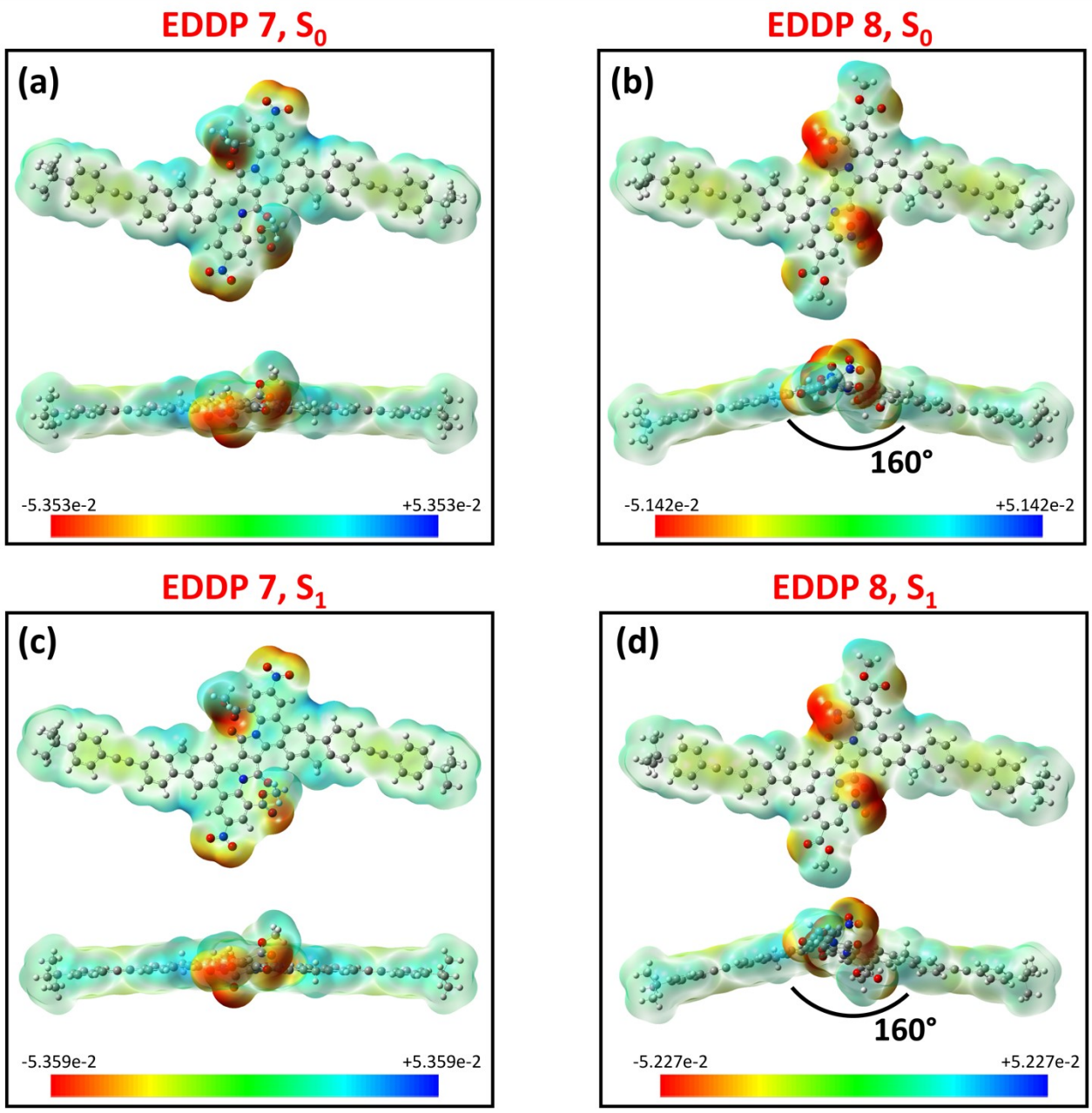


Figure S14. Ground state electrostatic potential (ESP) maps superimposed to optimized geometries for dyes 7 (panel a) and 8 (panel b). ESP values are in atomic units. S1 optimized geometries for molecules 7 (panel c) and 8 (panel d) are also shown. In each panel, the molecule is shown from two different points of view. Carbon atoms in gray, hydrogens in white, oxygens in red, nitrogen atoms in blue. Calculations performed at DFT level (B3LYP/6-31+G(d,p)) in gas phase.

Cartesian coordinates in Å together with the relevant atom symbol for the S0 optimized geometry of EDPP **7** obtained at DFT level (B3LYP/6-31+G(d,p)):

C	9.78823	0.84105	-0.13792
C	9.38248	2.18268	-0.34182
C	8.03983	2.54106	-0.29473
C	7.07970	1.55358	-0.04034
C	7.47296	0.21151	0.16481
C	8.81117	-0.14858	0.11785
C	5.62372	1.63370	0.06222
C	5.11796	0.33577	0.33538
C	6.25724	-0.65778	0.41690
C	4.76367	2.72169	-0.06076
C	3.37747	2.54277	0.08200
C	2.88099	1.23247	0.34468
C	3.76300	0.13024	0.47368
C	0.77381	-1.54591	0.42489
C	0.68227	-0.11895	0.32562
C	-0.67945	0.24690	0.11332
C	-1.45529	-0.90293	0.02719
N	-0.58412	-1.99914	0.13910
C	1.46411	1.03115	0.37154
N	0.59457	2.12778	0.28902
C	-0.77643	1.67817	0.02586
O	-1.69326	2.43813	-0.25271
O	1.67988	-2.30617	0.75068
C	-9.79754	-0.79242	-0.15392
C	-9.39692	-2.13383	0.06095
C	-8.05151	-2.47907	0.12696
C	-7.08322	-1.47820	-0.02227
C	-7.47141	-0.13611	-0.23657
C	-8.81224	0.21088	-0.30293
C	-5.62281	-1.54324	-0.00069
C	-5.10909	-0.23509	-0.19916
C	-6.24771	0.74868	-0.36676
C	-4.76432	-2.62740	0.16021
C	-3.37248	-2.43495	0.13104
C	-2.86938	-1.11350	-0.04490
C	-3.74905	-0.01510	-0.21682
C	-11.17953	-0.45926	-0.22032
C	-1.02199	-3.32203	0.09483
C	1.04465	3.44778	0.27168
C	-0.12843	-4.41263	-0.09348
C	-0.61133	-5.71333	0.01576
C	-1.96550	-5.93065	0.26175
C	-2.86761	-4.88230	0.31941
C	-2.42213	-3.55761	0.20992
C	0.18237	4.55477	0.49607
C	0.63797	5.84147	0.22106

C	1.95979	6.03187	-0.17230
C	2.85988	4.97911	-0.22200
C	2.42966	3.66774	0.01997
C	11.16749	0.49453	-0.19173
C	12.34900	0.19956	-0.23921
C	-12.36245	-0.17219	-0.27958
C	13.73057	-0.14372	-0.29645
C	-13.74615	0.15982	-0.35014
C	14.71007	0.83185	-0.55728
C	16.06090	0.48929	-0.61348
C	16.49719	-0.83010	-0.41409
C	15.50789	-1.79798	-0.15336
C	14.15776	-1.47273	-0.09428
C	-14.73848	-0.83153	-0.20111
C	-16.08614	-0.49895	-0.27328
C	-16.51690	0.82342	-0.49532
C	-15.52097	1.80198	-0.64153
C	-14.16463	1.48457	-0.57167
H	-6.22396	1.53661	0.39686
H	-6.20600	1.25487	-1.33975
H	6.29891	-1.15093	1.39663
H	6.15514	-1.45335	-0.33229
C	1.23833	-4.27126	-0.72641
O	1.35773	-3.71057	-1.79316
O	2.27449	-4.95422	-0.19895
C	2.30651	-5.30753	1.19761
N	-2.45766	-7.30670	0.40229
O	-3.66922	-7.47151	0.56318
O	-1.62876	-8.21799	0.35744
C	-1.15199	4.50644	1.18472
O	-2.06033	5.27699	0.96130
O	-1.14627	3.61884	2.20249
C	-2.37160	3.53394	2.95623
C	-18.02119	1.14071	-0.56857
C	-18.29413	2.63700	-0.81754
C	-18.69695	0.74294	0.76702
C	-18.66134	0.33471	-1.72583
N	2.43589	7.38979	-0.47030
O	3.62452	7.52792	-0.77164
O	1.62064	8.30997	-0.40364
C	17.97964	-1.24027	-0.46960
C	18.18003	-2.29852	-1.58251
C	18.39734	-1.84574	0.89333
C	18.90798	-0.04710	-0.76953
H	10.14059	2.93348	-0.53797
H	7.75079	3.57576	-0.45525
H	9.12377	-1.17683	0.27228
H	5.17678	3.70358	-0.25859
H	3.35623	-0.85812	0.66516
H	-10.16126	-2.89543	0.17356
H	-7.76687	-3.51436	0.29167

H	-9.12076	1.23867	-0.46824
H	-5.18352	-3.61753	0.29322
H	-3.33714	0.97985	-0.35803
H	0.04159	-6.56237	-0.14186
H	-3.91464	-5.11830	0.44252
H	-0.02888	6.68452	0.35074
H	3.89100	5.20134	-0.45644
H	14.40569	1.86155	-0.71646
H	16.77745	1.27612	-0.81796
H	15.79375	-2.83297	0.00793
H	13.42037	-2.24314	0.10818
H	-14.43994	-1.86091	-0.02935
H	-16.81749	-1.29250	-0.15359
H	-15.79345	2.83652	-0.81431
H	-13.41940	2.26498	-0.68956
H	3.36018	-5.47219	1.42534
H	1.91939	-4.49067	1.80829
H	1.74886	-6.22908	1.38456
H	-2.18581	2.78593	3.72644
H	-3.19070	3.22506	2.30280
H	-2.60932	4.50092	3.40511
H	-17.86831	2.97806	-1.76733
H	-17.89334	3.26518	-0.01470
H	-19.37464	2.80911	-0.86117
H	-18.58208	-0.32405	0.98078
H	-18.26672	1.30107	1.60551
H	-19.77036	0.96122	0.72738
H	-18.54548	-0.74421	-1.58489
H	-18.20531	0.59819	-2.68617
H	-19.73442	0.54935	-1.78784
H	17.89586	-1.89694	-2.56109
H	17.58285	-3.19773	-1.40333
H	19.23228	-2.60157	-1.63103
H	18.27043	-1.11722	1.70131
H	17.80580	-2.73127	1.14484
H	19.45136	-2.14537	0.86701
H	18.84003	0.72815	0.00129
H	18.68539	0.41060	-1.73944
H	19.94720	-0.39090	-0.79903

Cartesian coordinates in Å together with the relevant atom symbol for EDPP **8** obtained at DFT level (B3LYP/6-31+G(d,p)):

C	-9.64221	0.69049	0.63176
C	-9.22586	2.03856	0.75256
C	-7.90739	2.40693	0.50701
C	-6.98294	1.42295	0.13500
C	-7.38693	0.07393	0.01274
C	-8.70097	-0.29580	0.25667
C	-5.55797	1.51333	-0.18167
C	-5.08308	0.21467	-0.49880

C	-6.21108	-0.78971	-0.39768
C	-4.70251	2.61144	-0.21308
C	-3.35179	2.44185	-0.56129
C	-2.88245	1.12865	-0.86081
C	-3.75992	0.01663	-0.82911
C	-0.77189	-1.62667	-1.09450
C	-0.68791	-0.19477	-1.20427
C	0.68791	0.19478	-1.20427
C	1.48458	-0.93960	-1.11295
N	0.62944	-2.05026	-1.17991
C	-1.48459	0.93961	-1.11295
N	-0.62944	2.05027	-1.17991
C	0.77189	1.62668	-1.09449
O	1.69319	2.40632	-0.90764
O	-1.69319	-2.40632	-0.90765
C	9.64221	-0.69049	0.63176
C	9.22585	-2.03856	0.75256
C	7.90739	-2.40692	0.50701
C	6.98294	-1.42294	0.13500
C	7.38693	-0.07392	0.01274
C	8.70097	0.29581	0.25667
C	5.55797	-1.51332	-0.18167
C	5.08308	-0.21466	-0.49880
C	6.21108	0.78971	-0.39767
C	4.70251	-2.61143	-0.21309
C	3.35179	-2.44184	-0.56129
C	2.88244	-1.12864	-0.86080
C	3.75992	-0.01662	-0.82911
C	10.99669	-0.33309	0.88480
C	1.09537	-3.35816	-1.13670
C	-1.09537	3.35816	-1.13669
C	0.31626	-4.48162	-1.50695
C	0.73222	-5.77603	-1.23168
C	1.99054	-5.98947	-0.65951
C	2.83423	-4.90144	-0.44473
C	2.42790	-3.58259	-0.68988
C	-0.31626	4.48163	-1.50694
C	-0.73222	5.77604	-1.23168
C	-1.99055	5.98948	-0.65950
C	-2.83424	4.90144	-0.44473
C	-2.42791	3.58259	-0.68988
C	-10.99670	0.33309	0.88480
C	-12.15610	0.02455	1.09868
C	12.15610	-0.02455	1.09867
C	-13.51257	-0.33364	1.34744
C	13.51257	0.33364	1.34744
C	-14.45922	0.63577	1.73955
C	-15.78094	0.27752	1.97828
C	-16.22992	-1.05027	1.84151
C	-15.27949	-2.00701	1.45156
C	-13.94961	-1.66363	1.20857

C	14.45922	-0.63579	1.73953
C	15.78094	-0.27754	1.97827
C	16.22993	1.05025	1.84151
C	15.27950	2.00699	1.45158
C	13.94961	1.66362	1.20859
N	-0.86627	-4.37947	-2.38475
O	-1.77084	-5.19332	-2.22510
O	-0.81383	-3.54474	-3.28768
C	2.50121	-7.35107	-0.33104
O	3.60564	-7.57113	0.13255
O	1.60115	-8.31740	-0.60184
C	2.01650	-9.66695	-0.31063
N	0.86627	4.37948	-2.38474
O	1.77084	5.19333	-2.22508
O	0.81383	3.54475	-3.28768
C	17.70432	1.39644	2.11618
C	18.00366	2.89435	1.91091
C	18.61090	0.58787	1.15548
C	18.05529	1.03082	3.57965
C	-2.50121	7.35107	-0.33104
O	-3.60564	7.57113	0.13255
O	-1.60115	8.31741	-0.60183
C	-2.01650	9.66696	-0.31062
C	-17.70431	-1.39647	2.11618
C	-18.00365	-2.89438	1.91090
C	-18.61090	-0.58790	1.15549
C	-18.05528	-1.03086	3.57966
H	6.38717	1.30063	-1.35297
H	5.99431	1.57227	0.34072
H	-5.99431	-1.57227	0.34072
H	-6.38718	-1.30062	-1.35297
H	-9.95634	2.78701	1.04115
H	-7.60953	3.44698	0.60484
H	-9.02156	-1.32908	0.16464
H	-5.09294	3.59475	0.02025
H	-3.37365	-0.97462	-1.04500
H	9.95633	-2.78701	1.04114
H	7.60953	-3.44698	0.60484
H	9.02156	1.32909	0.16465
H	5.09294	-3.59475	0.02024
H	3.37365	0.97463	-1.04499
H	0.09034	-6.60383	-1.50288
H	3.82757	-5.11430	-0.07171
H	-0.09035	6.60383	-1.50287
H	-3.82758	5.11430	-0.07171
H	-14.14584	1.66875	1.85363
H	-16.47694	1.05508	2.27820
H	-15.56750	-3.04471	1.33041
H	-13.23965	-2.42771	0.90785
H	14.14584	-1.66877	1.85361
H	16.47694	-1.05511	2.27818

H	15.56751	3.04469	1.33044
H	13.23965	2.42772	0.90787
H	2.24475	-9.77124	0.75247
H	1.17031	-10.29404	-0.58841
H	2.90085	-9.92565	-0.89736
H	17.41624	3.52532	2.58663
H	17.80578	3.21371	0.88202
H	19.06157	3.08743	2.11742
H	18.48311	-0.49114	1.28491
H	18.38790	0.82876	0.11053
H	19.66506	0.82335	1.34208
H	17.91114	-0.03529	3.77972
H	17.43132	1.59134	4.28403
H	19.10439	1.27033	3.78829
H	-2.24475	9.77125	0.75248
H	-1.17031	10.29405	-0.58841
H	-2.90086	9.92565	-0.89735
H	-17.41623	-3.52535	2.58661
H	-17.80577	-3.21373	0.88200
H	-19.06156	-3.08746	2.11741
H	-18.48311	0.49111	1.28493
H	-18.38790	-0.82878	0.11054
H	-19.66505	-0.82338	1.34208
H	-17.91114	0.03524	3.77973
H	-17.43130	-1.59139	4.28403
H	-19.10438	-1.27038	3.78829

Cartesian coordinates in Å together with the relevant atom symbol for the S1 optimized geometry of EDPP **7** obtained at DFT level (B3LYP/6-31+G(d,p)):

C	-9.7796611	-0.8443504	-0.1481943
C	-9.3739870	-2.1933463	-0.3255318
C	-8.0357444	-2.5534678	-0.2604360
C	-7.0704266	-1.5621838	-0.0139642
C	-7.4661429	-0.2107343	0.1650181
C	-8.7993415	0.1499817	0.1001291
C	-5.6260400	-1.6457624	0.1009274
C	-5.1120428	-0.3392978	0.3565602
C	-6.2496819	0.6591525	0.4120854
C	-4.7655063	-2.7403593	0.0010083
C	-3.3836213	-2.5674996	0.1452297
C	-2.8736167	-1.2437778	0.3931914
C	-3.7639054	-0.1331126	0.5022203
C	-0.7529698	1.5404816	0.5082906
C	-0.6700750	0.1090814	0.3793990
C	0.6614606	-0.2541603	0.1181832
C	1.4623622	0.9107218	0.0335416
N	0.5831834	1.9993113	0.1859769
C	-1.4778519	-1.0545170	0.4341707
N	-0.5979590	-2.1435670	0.3184165
C	0.7519811	-1.6906104	0.0154065

O	1.6704776	-2.4420673	-0.2952601
O	-1.6579038	2.2874272	0.8775122
C	9.7866066	0.7985797	-0.1924467
C	9.3838180	2.1438698	0.0157715
C	8.0413646	2.4870187	0.0890764
C	7.0685986	1.4817430	-0.0455581
C	7.4614798	0.1336973	-0.2532064
C	8.7987811	-0.2100761	-0.3267863
C	5.6188702	1.5467088	-0.0138310
C	5.0982547	0.2311668	-0.1990730
C	6.2374928	-0.7531848	-0.3674285
C	4.7579951	2.6339228	0.1456215
C	3.3704176	2.4454809	0.1310586
C	2.8550102	1.1119519	-0.0354242
C	3.7446167	0.0084406	-0.2086050
C	11.1627036	0.4692035	-0.2664883
C	1.0158095	3.3225046	0.1422775
C	-1.0446811	-3.4631921	0.3158247
C	0.1130672	4.4113239	-0.0113549
C	0.5930150	5.7138099	0.0918068
C	1.9531981	5.9359885	0.2991817
C	2.8612955	4.8910154	0.3284919
C	2.4204990	3.5620575	0.2237634
C	-0.1733482	-4.5660490	0.5270937
C	-0.6297024	-5.8571676	0.2739278
C	-1.9606674	-6.0557874	-0.0844829
C	-2.8655907	-5.0066859	-0.1262629
C	-2.4368414	-3.6883600	0.0924706
C	-11.1512770	-0.4974473	-0.2207989
C	-12.3338739	-0.1983474	-0.2849147
C	12.3480862	0.1823323	-0.3327208
C	-13.7084740	0.1485494	-0.3610934
C	13.7269084	-0.1478626	-0.4112407
C	-14.6916535	-0.8291646	-0.6123433
C	-16.0388282	-0.4814790	-0.6872771
C	-16.4705209	0.8447153	-0.5172204
C	-15.4787353	1.8143153	-0.2660408
C	-14.1318691	1.4852065	-0.1883263
C	14.7210910	0.8467958	-0.2778442
C	16.0670080	0.5142510	-0.3579551
C	16.4967993	-0.8108044	-0.5729575
C	15.5001322	-1.7923246	-0.7036004
C	14.1452684	-1.4761559	-0.6257216
H	6.2213634	-1.5348236	0.4027639
H	6.1902418	-1.2671075	-1.3359998
H	-6.2987335	1.1689754	1.3827936
H	-6.1400131	1.4415243	-0.3497089
C	-1.2739243	4.2687592	-0.5971038
O	-1.4317387	3.7180319	-1.6641995
O	-2.2936585	4.9434287	-0.0261797
C	-2.2779588	5.2777064	1.3752102

N	2.4406345	7.3121781	0.4331157
O	3.6567916	7.4834327	0.5582121
O	1.6062893	8.2214804	0.4192660
C	1.1797095	-4.5054505	1.1761561
O	2.0852138	-5.2740742	0.9334943
O	1.2010644	-3.6088098	2.1859881
C	2.4498747	-3.5071996	2.8966877
C	17.9998821	-1.1274982	-0.6553702
C	18.2725108	-2.6253566	-0.8949060
C	18.6849617	-0.7181413	0.6722862
C	18.6298594	-0.3291056	-1.8238383
N	-2.4370714	-7.4176074	-0.3567890
O	-3.6332051	-7.5647246	-0.6258777
O	-1.6165752	-8.3352234	-0.3027810
C	-17.9496500	1.2600876	-0.5939868
C	-18.1340886	2.2980264	-1.7290036
C	-18.3756021	1.8941439	0.7536612
C	-18.8812299	0.0658692	-0.8791431
H	-10.1330126	-2.9449384	-0.5154825
H	-7.7470960	-3.5910610	-0.4003138
H	-9.1118810	1.1812161	0.2336372
H	-5.1815283	-3.7234530	-0.1862711
H	-3.3552650	0.8560565	0.6866446
H	10.1484847	2.9068925	0.1167679
H	7.7555395	3.5226943	0.2479322
H	9.1089064	-1.2382985	-0.4866290
H	5.1790331	3.6247871	0.2697435
H	3.3307238	-0.9864303	-0.3473014
H	-0.0680921	6.5608539	-0.0403321
H	3.9097827	5.1315818	0.4273283
H	0.0436257	-6.6964879	0.3931766
H	-3.9001690	-5.2355107	-0.3375407
H	-14.3899243	-1.8628182	-0.7486783
H	-16.7579637	-1.2680395	-0.8829683
H	-15.7622221	2.8531055	-0.1275876
H	-13.3923099	2.2555325	0.0058401
H	14.4225542	1.8770514	-0.1120262
H	16.7993355	1.3084540	-0.2504625
H	15.7730377	-2.8276676	-0.8701631
H	13.3992609	-2.2574535	-0.7313147
H	-3.3219596	5.4534035	1.6371855
H	-1.8838715	4.4464135	1.9615597
H	-1.7018112	6.1885697	1.5584832
H	2.2850770	-2.7514401	3.6642147
H	3.2442632	-3.2001190	2.2124883
H	2.7098202	-4.4672414	3.3484129
H	17.8401208	-2.9743038	-1.8388271
H	17.8791503	-3.2479033	-0.0840878
H	19.3528062	-2.7962656	-0.9455717
H	18.5711250	0.3504038	0.8784816
H	18.2620877	-1.2702132	1.5184329

H	19.7580766	-0.9359520	0.6255490
H	18.5147003	0.7507512	-1.6900685
H	18.1670161	-0.6002720	-2.7787143
H	19.7024474	-0.5437942	-1.8920390
H	-17.8434209	1.8765200	-2.6971824
H	-17.5347398	3.1979978	-1.5615620
H	-19.1844465	2.6044560	-1.7923948
H	-18.2597178	1.1809787	1.5767845
H	-17.7824873	2.7819110	0.9930552
H	-19.4278387	2.1977997	0.7115559
H	-18.8244223	-0.6946672	-0.0929588
H	-18.6529638	-0.4113513	-1.8382366
H	-19.9181922	0.4144198	-0.9243326

Cartesian coordinates in Å together with the relevant atom symbol for the S1 optimized geometry of EDPP **8** obtained at DFT level (B3LYP/6-31+G(d,p)):

C	-9.6446070	0.6953630	0.6427530
C	-9.2320030	2.0505710	0.7309250
C	-7.9178490	2.4181390	0.4789360
C	-6.9833760	1.4277120	0.1310600
C	-7.3860280	0.0695420	0.0416580
C	-8.6955270	-0.2979850	0.2921940
C	-5.5696840	1.5181720	-0.1821980
C	-5.0804710	0.2078280	-0.4696380
C	-6.2054680	-0.7988220	-0.3456730
C	-4.7169010	2.6218730	-0.2389980
C	-3.3683740	2.4564090	-0.5772080
C	-2.8796170	1.1270950	-0.8508720
C	-3.7641180	0.0064960	-0.7947540
C	-0.7498170	-1.6352810	-1.0785680
C	-0.6741490	-0.1963870	-1.1784650
C	0.6740360	0.1964620	-1.1785220
C	1.5056740	-0.9517030	-1.1013160
N	0.6417350	-2.0565480	-1.1756550
C	-1.5057890	0.9517750	-1.1012400
N	-0.6418480	2.0566130	-1.1755870
C	0.7497150	1.6353580	-1.0786990
O	1.6780600	2.4106450	-0.8942400
O	-1.6781350	-2.4105290	-0.8938340
C	9.6444780	-0.6952390	0.6427190
C	9.2318730	-2.0504440	0.7309220
C	7.9177220	-2.4180200	0.4789300
C	6.9832520	-1.4276030	0.1310170
C	7.3859040	-0.0694350	0.0415840
C	8.6954000	0.2980990	0.2921240
C	5.5695630	-1.5180710	-0.1822540
C	5.0803530	-0.2077360	-0.4697370
C	6.2053490	0.7989190	-0.3457830
C	4.7167810	-2.6217730	-0.2390330
C	3.3682580	-2.4563180	-0.5772660

C	2.8795050	-1.1270150	-0.8509750
C	3.7640040	-0.0064130	-0.7948730
C	10.9925220	-0.3405880	0.9017010
C	1.1097280	-3.3637040	-1.1569960
C	-1.1098150	3.3637690	-1.1568450
C	0.3297230	-4.4836450	-1.5379190
C	0.7466420	-5.7819590	-1.2764780
C	2.0079520	-6.0000640	-0.7118040
C	2.8533580	-4.9159930	-0.4880920
C	2.4483760	-3.5909280	-0.7193120
C	-0.3297190	4.4836790	-1.5376370
C	-0.7466390	5.7820070	-1.2762800
C	-2.0080210	6.0001450	-0.7117710
C	-2.8534640	4.9160920	-0.4880980
C	-2.4484850	3.5910140	-0.7192490
C	-10.9926540	0.3407190	0.9017320
C	-12.1528320	0.0305010	1.1218940
C	12.1526980	-0.0303590	1.1218630
C	-13.5028840	-0.3329050	1.3757880
C	13.5027420	0.3330770	1.3757540
C	-14.4625200	0.6390890	1.7345840
C	-15.7804070	0.2742450	1.9788150
C	-16.2149410	-1.0626470	1.8812090
C	-15.2527150	-2.0216670	1.5245240
C	-13.9263050	-1.6726940	1.2762940
C	14.4623930	-0.6388910	1.7345820
C	15.7802730	-0.2740180	1.9788100
C	16.2147840	1.0628790	1.8811680
C	15.2525440	2.0218730	1.5244520
C	13.9261410	1.6728700	1.2762260
N	-0.8558850	-4.3720950	-2.4072720
O	-1.7532030	-5.1980880	-2.2619060
O	-0.8174600	-3.5183630	-3.2938380
C	2.5180470	-7.3655230	-0.3985780
O	3.6237290	-7.5927160	0.0588590
O	1.6157800	-8.3287850	-0.6754700
C	2.0311760	-9.6809260	-0.3990030
N	0.8561160	4.3720120	-2.4066710
O	1.7548650	5.1960920	-2.2592950
O	0.8194510	3.5159510	-3.2910650
C	17.6860550	1.4157510	2.1603780
C	17.9690320	2.9224030	2.0012410
C	18.5962900	0.6467050	1.1707590
C	18.0469210	1.0073190	3.6103110
C	-2.5181240	7.3656180	-0.3986240
O	-3.6238480	7.5928390	0.0586990
O	-1.6158070	8.3288580	-0.6754310
C	-2.0312040	9.6810110	-0.3990260
C	-17.6862190	-1.4154860	2.1604210
C	-17.9692210	-2.9221380	2.0013230
C	-18.5964350	-0.6464510	1.1707780

C	-18.0470840	-1.0070090	3.6103420
H	6.3783630	1.3336130	-1.2884670
H	5.9875020	1.5621710	0.4121860
H	-5.9876320	-1.5620560	0.4123160
H	-6.3784710	-1.3335390	-1.2883460
H	-9.9668340	2.8020920	1.0002020
H	-7.6241370	3.4612940	0.5515400
H	-9.0127450	-1.3343040	0.2253750
H	-5.1146390	3.6079880	-0.0296200
H	-3.3727180	-0.9868870	-0.9919400
H	9.9667020	-2.8019580	1.0002270
H	7.6240090	-3.4611730	0.5515580
H	9.0126200	1.3344160	0.2252810
H	5.1145160	-3.6078830	-0.0296280
H	3.3726030	0.9869650	-0.9920800
H	0.1034180	-6.6067160	-1.5528870
H	3.8467950	-5.1329450	-0.1178850
H	-0.1033450	6.6067440	-1.5525840
H	-3.8469260	5.1330710	-0.1179770
H	-14.1599680	1.6781710	1.8178330
H	-16.4862400	1.0527470	2.2519020
H	-15.5301770	-3.0653460	1.4345470
H	-13.2068680	-2.4378020	1.0020360
H	14.1598590	-1.6779750	1.8178580
H	16.4861180	-1.0525000	2.2519210
H	15.5299880	3.0655540	1.4344480
H	13.2066930	2.4379580	1.0019430
H	2.2634010	-9.7960660	0.6621850
H	1.1836100	-10.3049530	-0.6797160
H	2.9132670	-9.9348220	-0.9913270
H	17.3783350	3.5257020	2.6989890
H	17.7636740	3.2720220	0.9837240
H	19.0257620	3.1196860	2.2094910
H	18.4802170	-0.4370870	1.2668280
H	18.3665090	0.9181000	0.1348360
H	19.6486450	0.8872320	1.3606700
H	17.9147260	-0.0660030	3.7771390
H	17.4207610	1.5389750	4.3347960
H	19.0944790	1.2509680	3.8216280
H	-2.2635360	9.7961700	0.6621360
H	-1.1835950	10.3050160	-0.6796600
H	-2.9132280	9.9349180	-0.9914450
H	-17.3785380	-3.5254280	2.6990900
H	-17.7638640	-3.2717880	0.9838160
H	-19.0259550	-3.1193960	2.2095740
H	-18.4803440	0.4373420	1.2668180
H	-18.3666550	-0.9178780	0.1348630
H	-19.6487960	-0.8869550	1.3606890
H	-17.9148720	0.0663160	3.7771420
H	-17.4209370	-1.5386570	4.3348440
H	-19.0946480	-1.2506350	3.8216600