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Supporting Information

Tuning intramolecular electron and energy transfer processes in novel conjugates of $La_2@C_{80}$and electron accepting subphthalocyanines

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Contents

1. General

Spectroscopy: NMR spectra of **1a**were recorded on a Bruker AV 500 spectrometer with a CryoProbe system, locked on deuterated solvents and referenced to the TMS or solvent peaks. The ^{1}HNMR and ^{1}H-^{1}H COSY NMR were performed according to the standard experimental procedures of the Bruker library. Absorption spectra of **1a**, **1a'** were recorded in toluene on a Shimadzu UV-3150 spectrophotometer, and those of **1b** – on Jasco V-660 spectrophotometer, using a 1 cm quartz cell in both cases. Matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectra of **1a**, **1a'** were recorded with a Bruker BIFLEX-III mass spectrometer using 1,1,4,4-tetraphenyl-1,3-butadiene (TPB) as the matrix and those of **1b** – on Bruker Reflex III spectrometer using trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix. The measurements were performed in both positive and negative ion modes.

Steady-state emission: The spectra were recorded on a FluoroMax 3 fluorometer (vis detection) and on a Fluorolog spectrometer (NIR detection). Both spectrometers were built by HORIBA JobinYvon. The measurements were carried out at room temperature.

Time Resolved Absorption: Femtosecond transient absorption studies were performed with 387, 530 and 568 nm laser pulses (1 kHz, 150 fs pulse width) from amplified Ti:Sapphire laser systems (CPA-2101 and CPA-2110 from Clark- MXR, Inc.), the laser energy was 200 nJ. Nanosecond laser flash photolysis experiments were performed with 355 and 532 nm laser pulses from a Quanta-Ray CDR Nd:YAG system (6 ns pulse width) in a front face excitation geometry.

Time resolved emission: Fluorescence lifetimes were measured by using a Fluorolog (Horiba JobinYvon).

Electrochemistry: Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) were carried out in o-DCB using a BAS CW-50 instrument, a conventional three-electrode cell consisting of a platinum working electrode, a platinum counter-electrode, and a saturated calomel reference electrode. 0.05 M $TBAPF_6$ was used as the supporting electrolyte. All potentials were recorded against a SCE reference electrode and corrected against Fc/Fc^+ redox couple. DPV and CV were measured at a scan rate of 20 and 100 mVs^{-1}, respectively.

Materials: All chemicals were of reagent grade, purchased from Wako or Sigma Aldrich and further used without additional purification. $La_2@I_h$-C_{80}(>99%) was prepared and purified according to the previously reported procedure. HPLC were performed on semi preparative and analytic scales using ø10×250 mm Buckyprep column (Cosmosil), ø10×250 mm Buckyprep M column (Cosmosil) and ø4.6×250 mm 5PYE column (Cosmosil), respectively. A mixture of toluene-acetonitrile = 10:1, vol, at 3.5 mL/min flow ratewas used for the isolation of **1a** and **1a’**, whereas for the separation of **1b** a mixture of toluene-dichloromethane-acetonitrile = 84:15:1, vol %, at 5mL/min flow rate was employed.

- Compounds **2a**,[1] **2b**,[2] **3a**[3] and **3b**[2,4]were prepared according to synthetic procedures reported elsewhere.

References

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(3) (a) Ince, M.; Medina, A.; Yum, J.-H.; Yella, A.; Claessens, C. G.; Martinez-Diaz, M. V.; Graetzel, M.; Nazeeruddin, M. K.; Torres, T. *Chem. Eur. J.***2014**, 20, 2016. (b) Claessens, C. G.; Gonzalez-Rodriguez, D.; del Rey, B.; Torres, T.; Mark, G.; Schuchmann, H.-P.; von Sonntag, C.; MacDonald, J. G.; Nohr, R. S. *Eur. J. Org. Chem.* **2003**, 2547.

(4) SubPc-aldehyde **3b** was prepared according to previously reported procedures for the axial substitution of sulfonylated subphthalocyanines.Gonzalez-Rodriguez, D.; Torres, T.; Olmstead,M. M.; Rivera, J.; Herranz, M. A.; Echegoyen, L.; Castellanos, C. A.; Guldi, D. M. *J. Am. Chem. Soc.*, **2006**, *128*, 10680.

2. Synthesis

- **Synthesis of** F_{12}SubPc-$La_2@C_{80}$**1a**:

A mixture of $La_2@C_{80}$ (2 mg, 1.6 µmol), F_{12}SubPc-aldehyde **3a** (2.8 mg, 3.8 µmol) and N-methylglycine (5 mg, 56 µmol) in 30 ml toluene was refluxed for 85 min under argon atmosphere. Then, the mixture was separated by a two-step HPLC procedure, yielding 35% of **1a** (based on consumed $La_2@C_{80}$).

^{1}H NMR (500 MHz, *o*-DCB-d_4): **1a**(major conformer)δ= 6.17 (s (br), 1H; H-2), 6.08 (d (br),^2J= 7.6 Hz,1H; H-6), 4.41 (d, ^2J =9.4Hz, 1H, H-8), 3.65 (s (br), 1H; H-7), 3.14 (d (br),^2J= 8.9 Hz,1H; H-8), 2.82 (s (br), 1H; H-9); the phenyl protons H-4, H-5 are not identifiable in the^{1}H NMR spectrum because of the overlap with the proton signals of *o*-DCB. However, the chemical shift of H-5 was determined as δ=7.05 ppm according to the COSY spectrum; **1a'** (minor conformer)δ= 5.98 (s (br), 1H; H-2'), 5.81 (d (br),^2J= 8.0 Hz,1H; H-6'), 4.10 (d, ^2J =9.2Hz, 1H; H-8'), 3.50 (s (br), 1H; H-7'), 2.90 (d (br), ^2J= 8.9 Hz,1H; H-8'), 2.39 (s (br), 1H; H-9'); the phenyl protons H-4', H-5' are not identifiable in the^{1}H NMR spectrum because of the overlap with the proton signals of *o*-DCB. However, the chemical shift of H-5' was determined as δ=7.30 ppm according to the COSY spectrum.

MALDI-TOF MS (negative mode, TPB): found: 1997 *m/z,* calcd for $La_2C_{113}F_{12}H_{10}N_7OB$, $[M]^-$: 1996.9; UV-vis (toluene): λ_{max} (log ε) =300 (4.7), 574 (4.7).

- **Synthesis of** $(SO_2C_5H_{11})_6$SubPc-$La_2@C_{80}$**1b**:

A mixture of $La_2@C_{80}$ (2 mg, 1.6 µmol), $(SO_2C_5H_{11})_6$SubPc-aldehyde**3b** (30.0 mg, 30.8 µmol) and N-methylglycine (5 mg, 56 µmol) in 15 ml of *o*-DCB was stirred at 115°C for 15 min under argon atmosphere. Then, **1b** was isolated by one-step HPLC in a yield of 0.2% (based on consumed $La_2@C_{80}$).

MALDI-TOF MS (negative mode, TPB): found: 2585.1 *m/z,* calcd for $La_2C_{143}S_6H_{82}BN_7O_{13}$, $[M]^-$: 2585.3; UV-vis (toluene): λ_{max}=300, 530, 580 nm (study of the extinction coefficient of **1b** was hampered by negligible amounts of isolated compound and its poor stability).

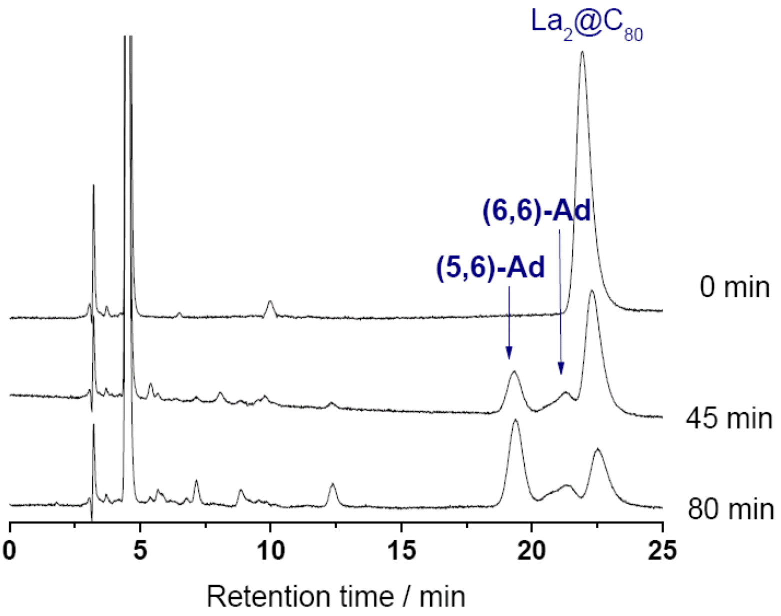

Figure S1. HPLC profiles of the reaction mixture of La$_2$@C$_{80}$, N-methyl glycine and F$_{12}$SubPc-aldehyde **3a** (ø4.6×250 mm 5PYE column, Cosmosil, toluene-acetonitrile = 10:1, vol, 1 mL/min flow rate), showing the formation of conjugate **1a** as a mixture of [5,6]-adduct and isomeric [6,6]-adduct).

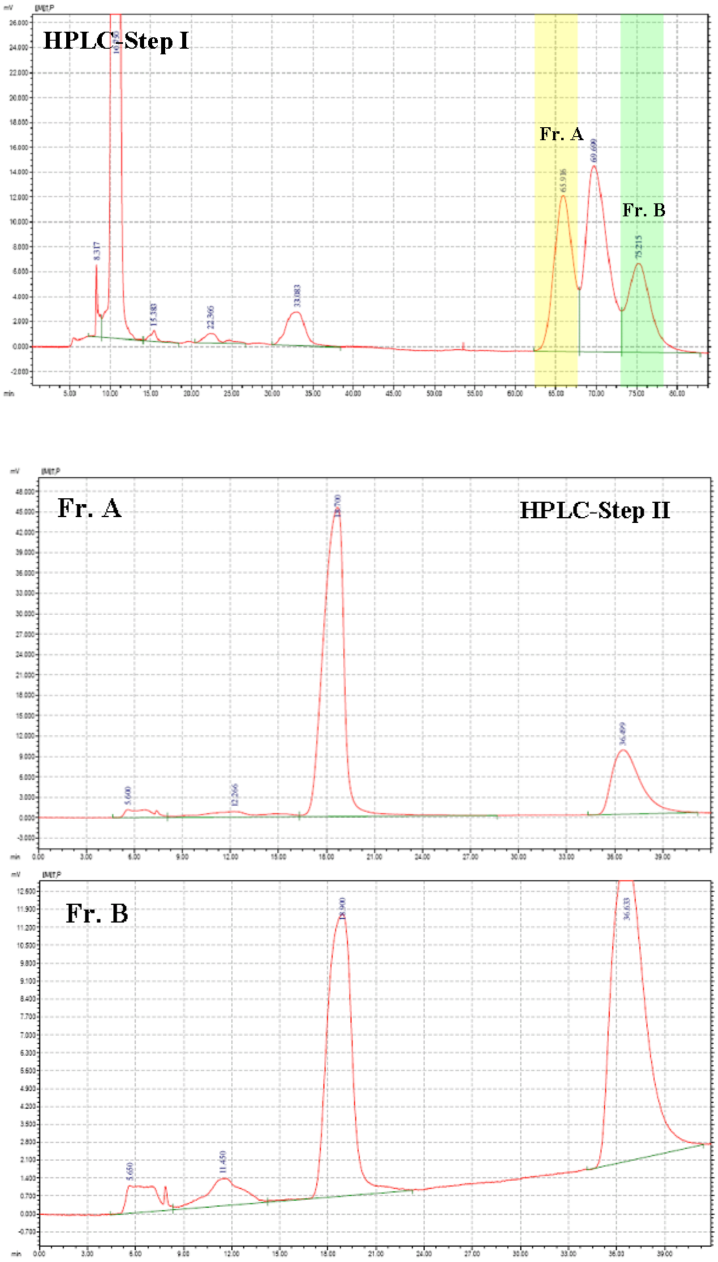

Figure S2. Preparative HPLC profiles of the second stage of separation of the reaction mixture of **1a**. Stage I (top): fractions A and B were roughly separated from unreacted $La_2@C_{80}$ and byproducts (ø10×250 mmBuckyprep column, Cosmosil, toluene-acetonitrile = 10:1, vol, 3.5 mL/min flow rate). Stage II (bottom): fractions A and B were further separated using Buckyprep M column (ø10×250 mm, Cosmosil, toluene-acetonitrile = 10:1, vol, 3.5 mL/min flow rate) to get pure **1a** [5,6]-adduct and its isomeric **1a’** [6,6]-adduct, respectively.

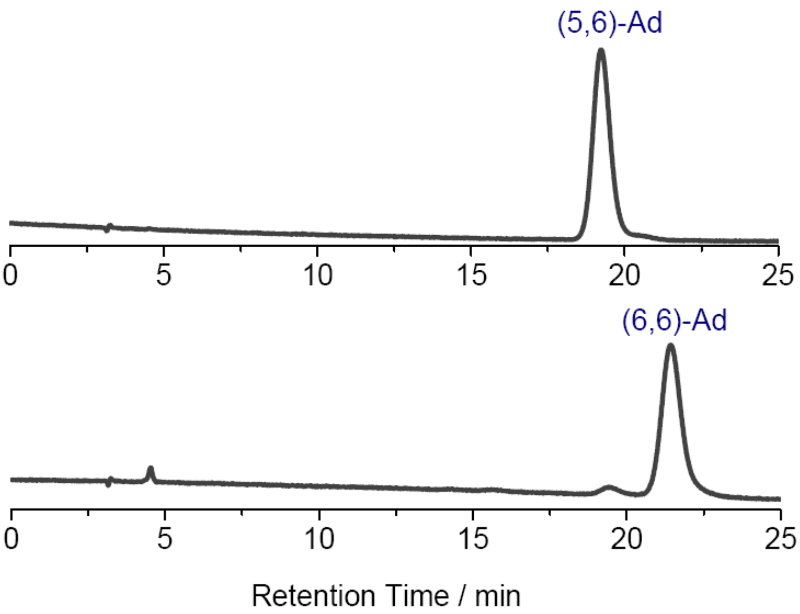

Figure S3. HPLC profiles of the isolated **1a** [5,6]-adduct and isomeric **1a’** [6,6]-adduct on 5PYE column (ø4.6×250 mm, Cosmosil, toluene-acetonitrile = 10:1, vol, 1 mL/min flow rate).

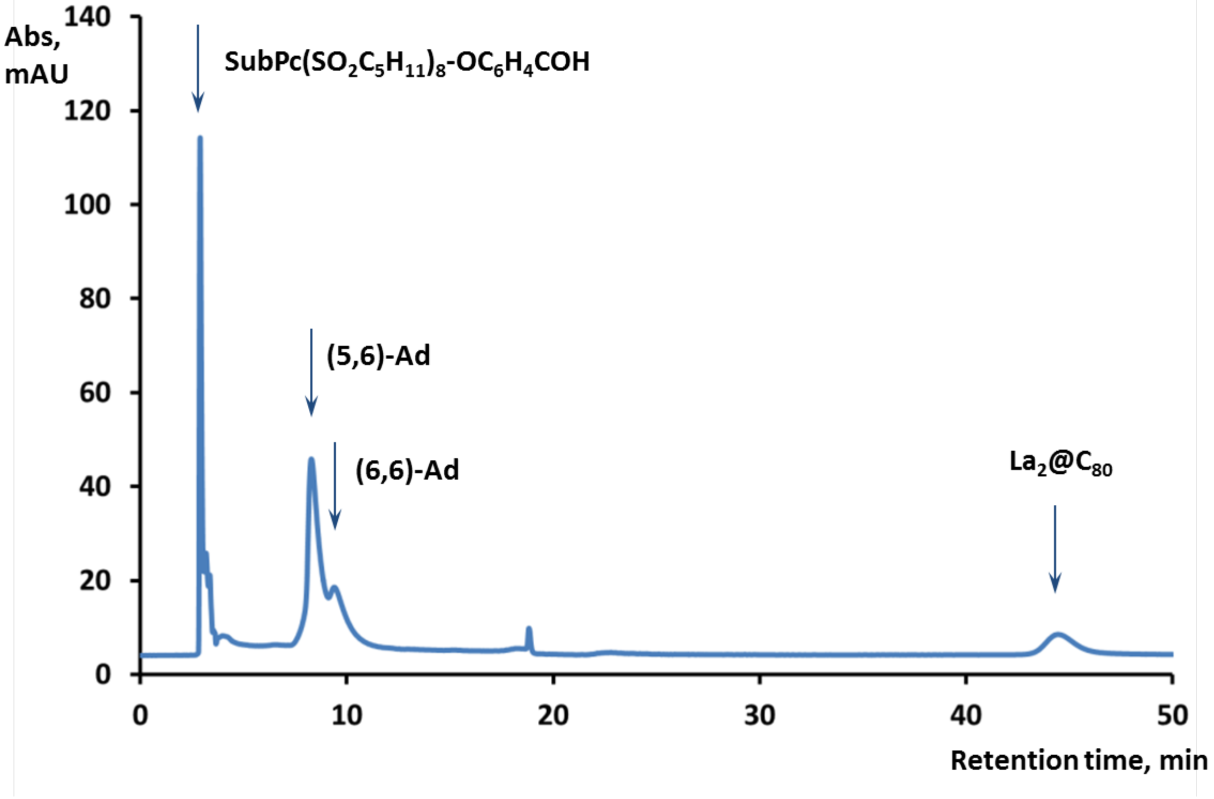

Figure S4. HPLC profiles of the reaction mixture of La$_2$@C$_{80}$, N-methyl glycine and (SO$_2$C$_5$H$_{11}$)$_6$SubPc-aldehyde **3b** (ø4.6×250 mmBuckyprep column, Cosmosil, toluene-dichloromethane-acetonitrile = 84:15:1, vol %, 1 mL/min), showing the formation of conjugate **1b**as a mixture of [5,6]-adduct and isomeric [6,6]-adduct).

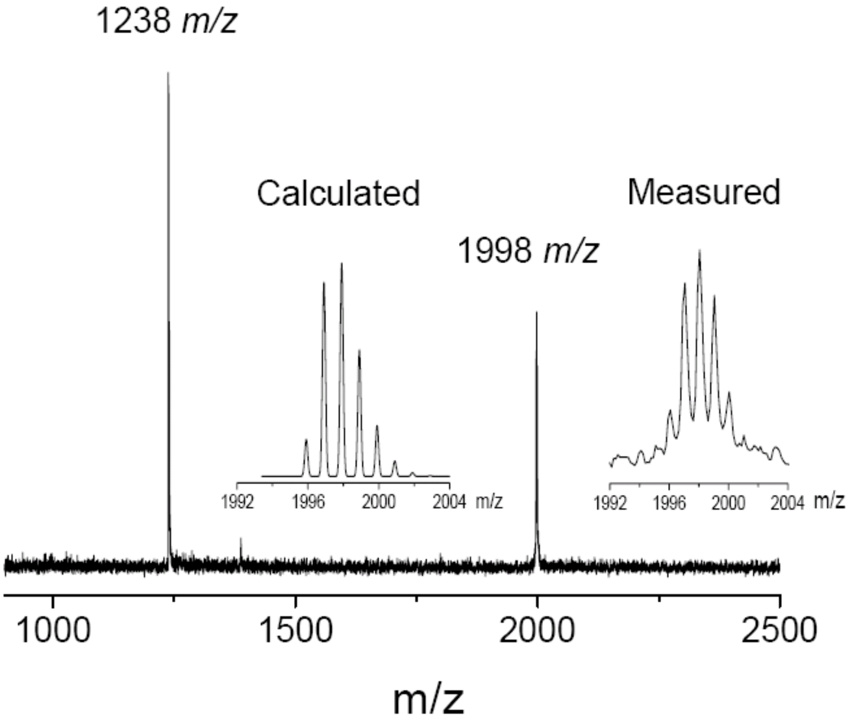

Figure S5. MALDI-TOF mass spectrum of **1a** (negative mode, TPB).

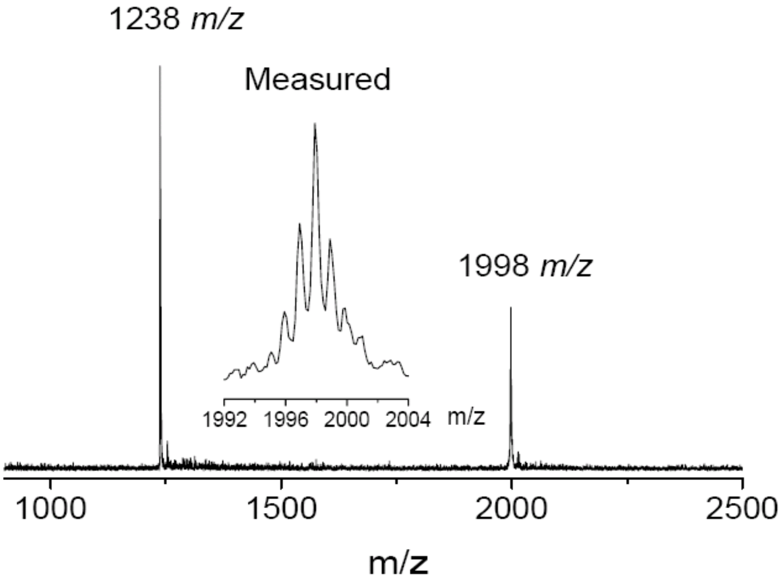

Figure S6. MALDI-TOF mass spectrum of **1a’** (negative mode, TPB).

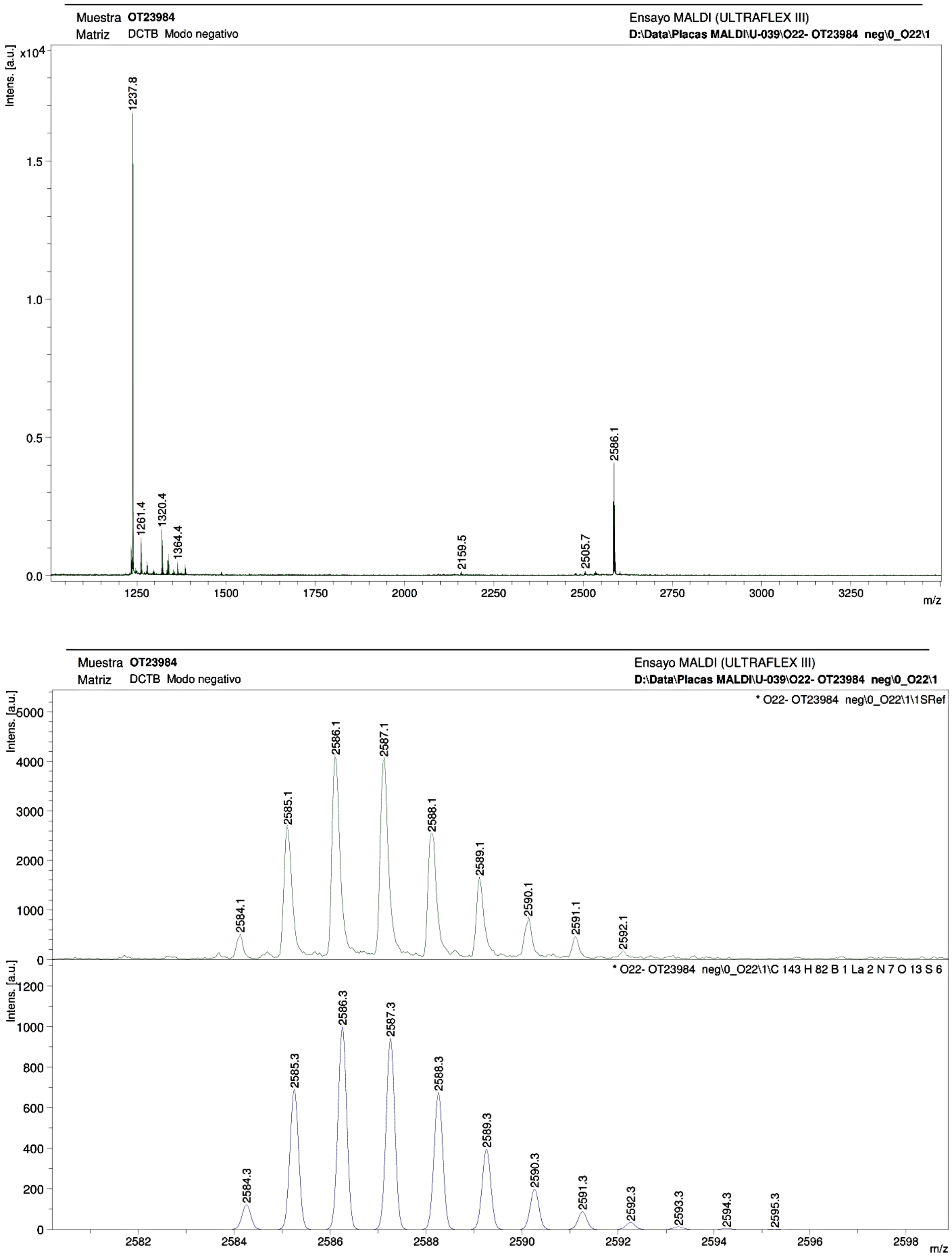

Figure S7. MALDI-TOF mass spectrum of **1b** (negative mode, DCTB).

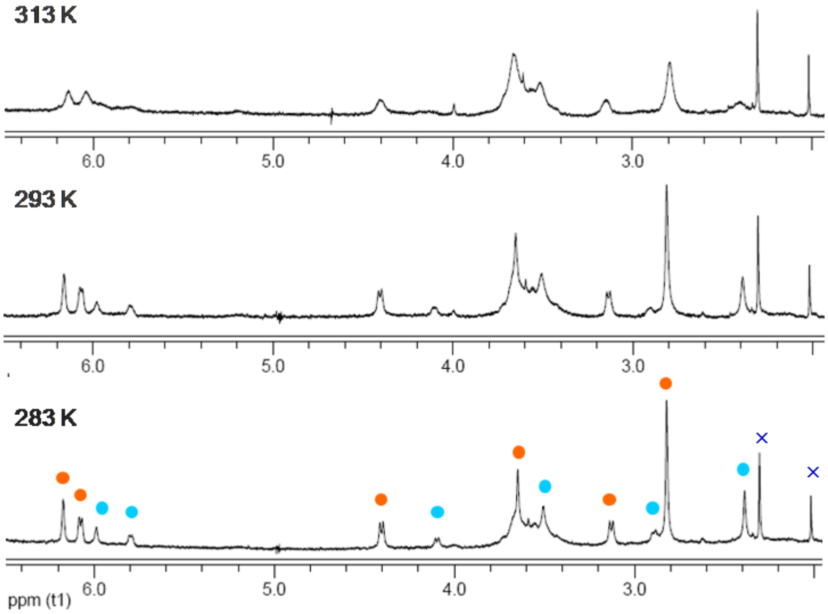

Figure S8. ^{1}H NMR (500 MHz, *o*-DCB-d_4) spectra of **1a** in the range from 6.5 to 2 ppm. Signals marked by orange circles and blue circles are attributed to the protons of major [5,6]- and minor [6,6]-conformer, respectively.

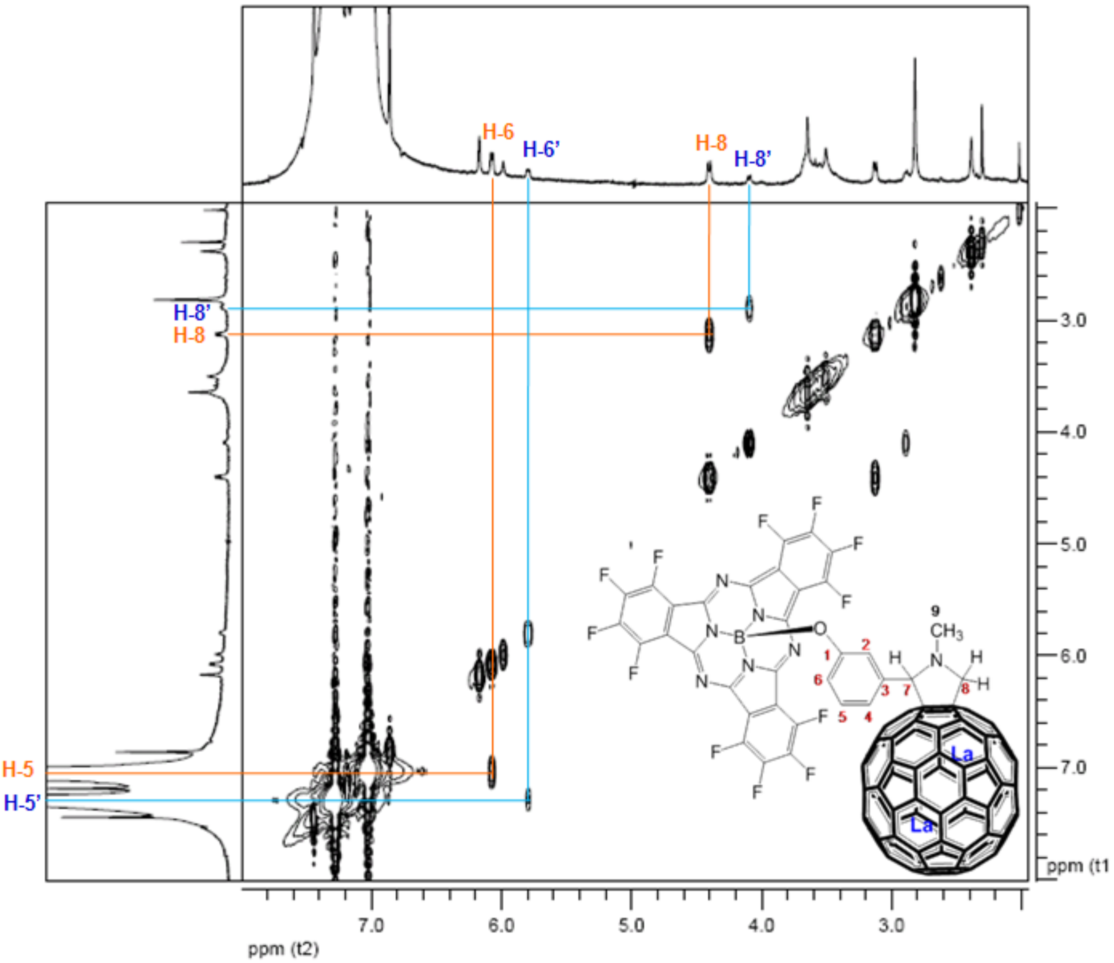

Figure S9. ^{1}H-^{1}H COSY spectrum (500 MHz, *o*-DCB-*d₄*) of **1a**.

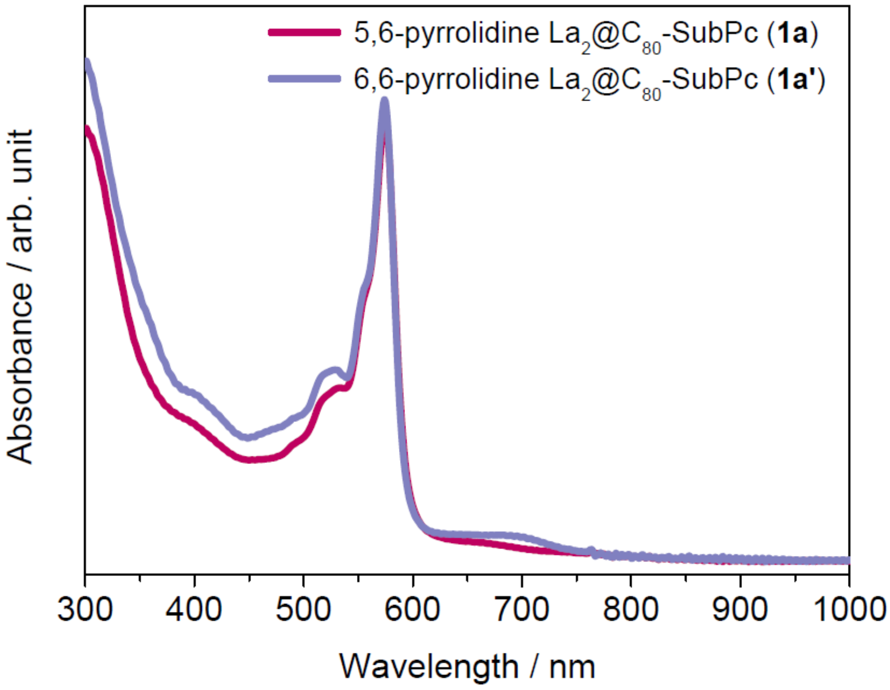

Figure S10. UV-vis-NIR spectra of F$_{12}$SubPc-La$_2$@C$_{80}$ **1a** and **1a’** in toluene, feature absorptions of **1a**: λ_{max} (log ε) =300 (4.7), 574 (4.7)

Note: **1a’** shows a broad absorption at 695 nm, which is absent for **1a** but consistent with that of previously reported [6,6]-pyrrolidine adducts of La$_2$@C$_{80}$.[5]

Reference

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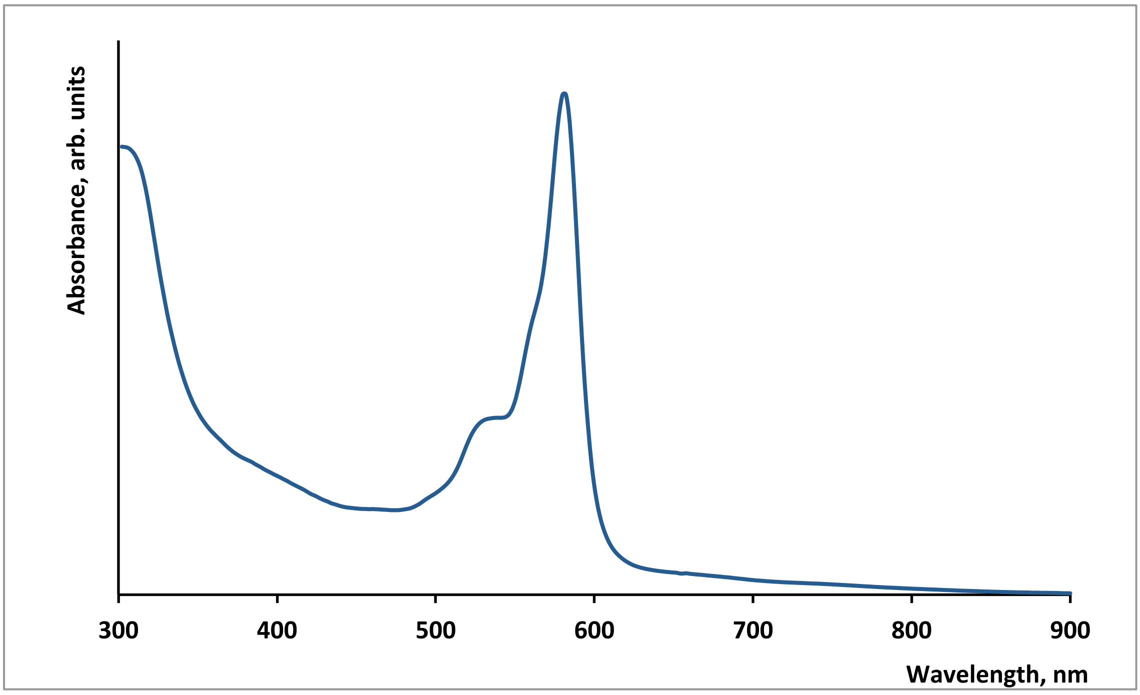


Figure S11. UV-vis-NIR spectrum of $(SO_2C_5H_{11})_6$SubPc-$La_2@C_{80}$ **1b** in toluene (study of the extinction coefficient of **1b** was hampered by negligible amounts of isolated compound and its poor stability).

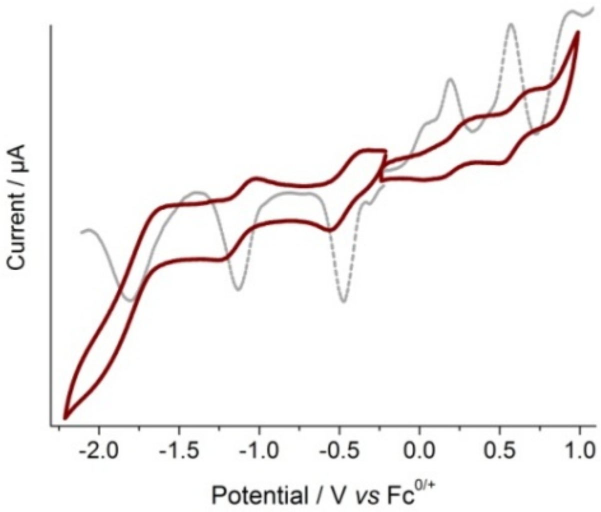


Figure S12.CV (red) and DPV(grey) recorded on a Pt electrode (1 mm)of *o*-dichlorobenzene containing 0.05mol L^{-1} TBAPF$_6$ as supporting electrolyte and**1a**(～10^{-5} mol L^{-1}), at 100 and 20 mVs^{-1}scan rates, respectively.

3. Computational methods

The calculations were carried out using the hybrid density functional theory (DFT) at the M06-2X level as implemented in the Gaussian 09 software package. The SDD basis set with the relativistic effective core potential was employed for La, 3-21G or 6-31G* basis set for B, C, H, O, N, (M06-2X/3-21G~SDD or M06-2X/6-31G*~SDD).

4. Optimized geometries

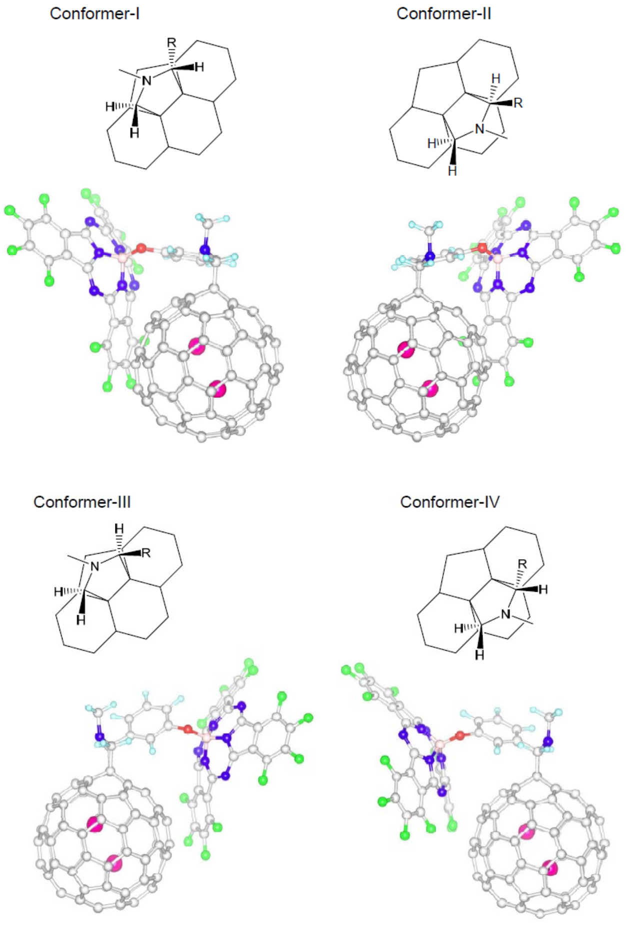


Figure S13. Schematic representation of the addition patterns and DFT-optimized conformers of **1a**.

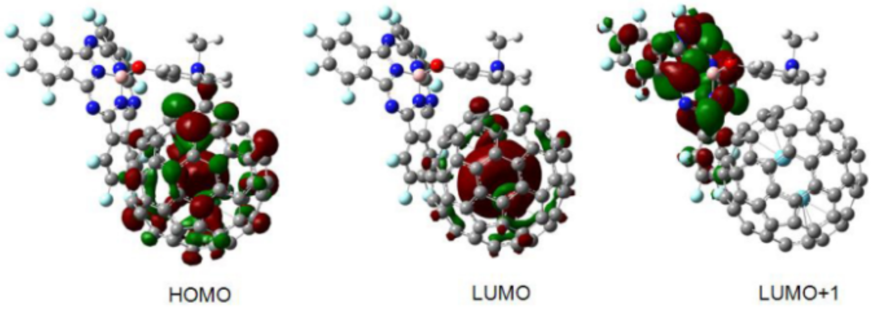


Figure S14.DFT-calculated distribution of molecular orbitals in **1a.**

Table S1. Relative energies (△E in kcal/mol) of the four different conformers of **1a**.

	Conformer **I**	Conformer**II**	Conformer**III**	Conformer**IV**
△E[a]	0.0	3.355	6.400	9.725
△E[b]	0.0	2.288	5.358	8.382

[a] calculated at the level of M06-2X/3-21G~sdd;

[b] calculated at the level of M06-2X/6-31G*~sdd.

5. Time resolved absorption

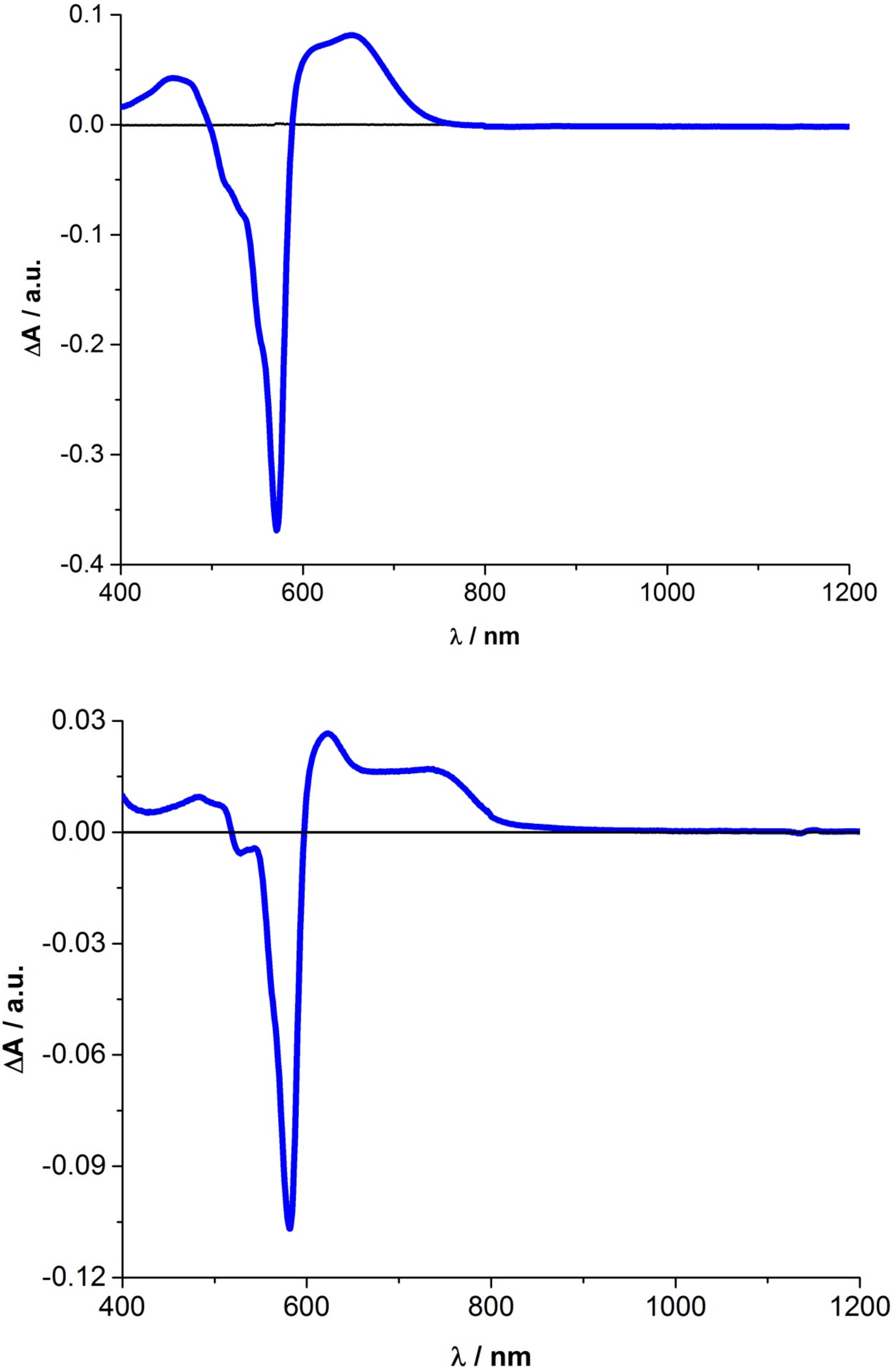
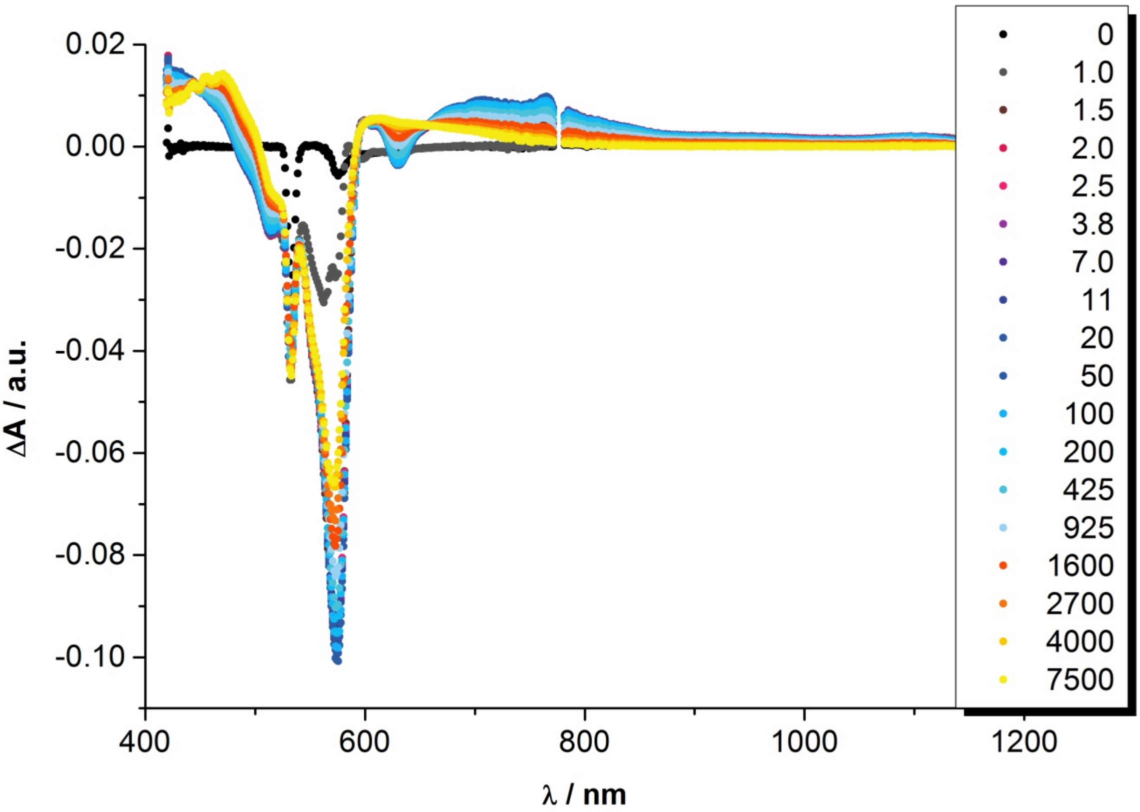


Figure S15. Differential absorption spectra (visible and near infrared) obtained upon electrochemical reduction of **3a** (top) and **3b** (bottom) at an applied bias of −0.5 and −0.3 V in argon-saturated toluene/acetonitrile mixtures (4/1 v/v) at room temperature.



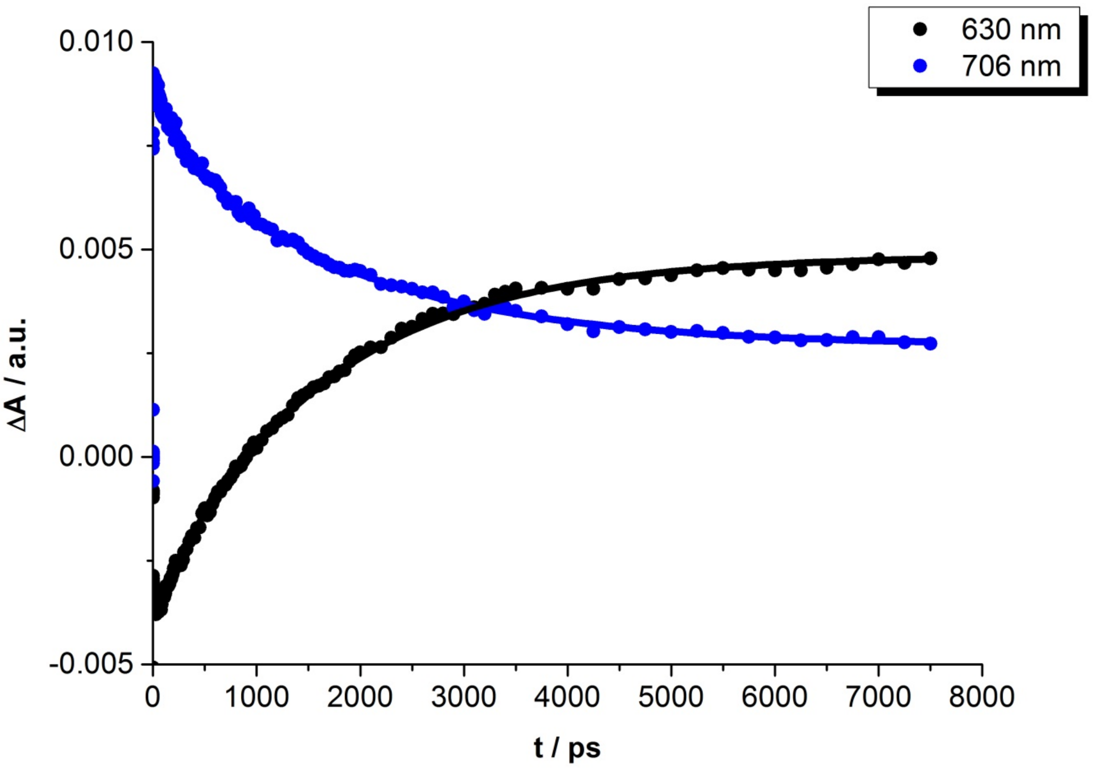


Figure S16.(top) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm) of **3a** (10^{-5} M) in argon-saturated THF with several time delays between 0 and 7500 ps at room temperature. (bottom) Time-absorption profiles of the spectra shown at the top at 630 and 706 nm monitoring the intersystem crossing.

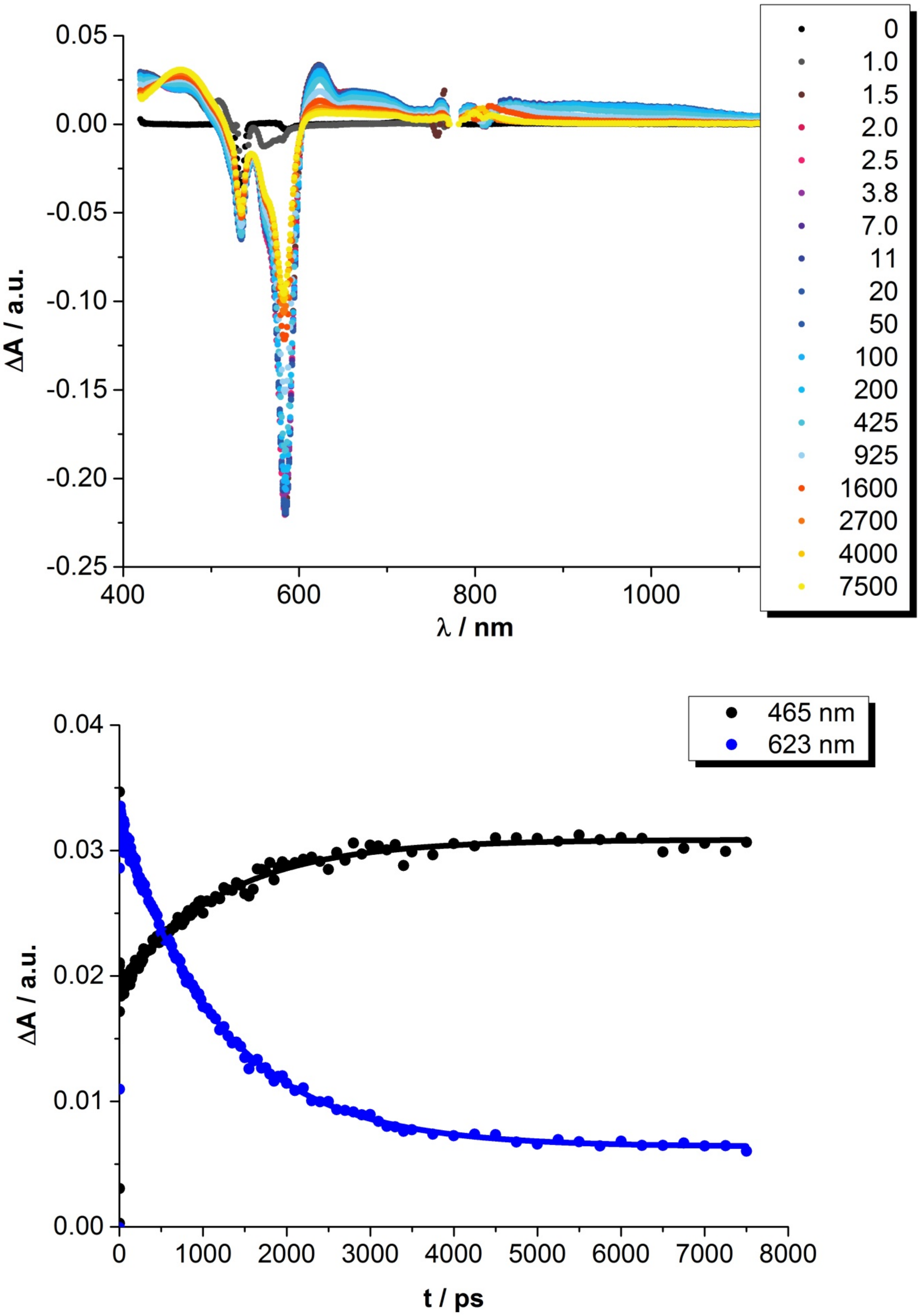
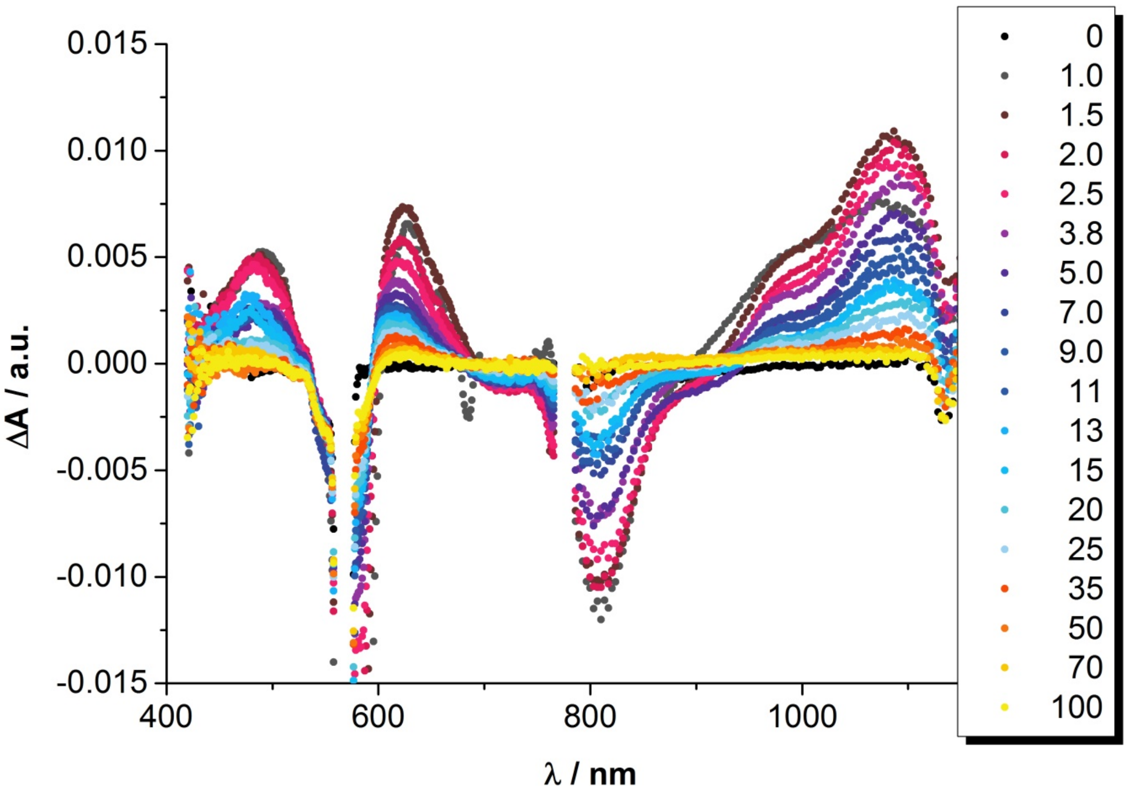


Figure S17.(top) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm) of **3b** (10^{-5} M) in argon-saturated toluene with several time delays between 0 and 7500 ps at room temperature. (bottom) Time-absorption profiles of the spectra shown at the top at 585 and 625 nm monitoring the intersystem crossing.



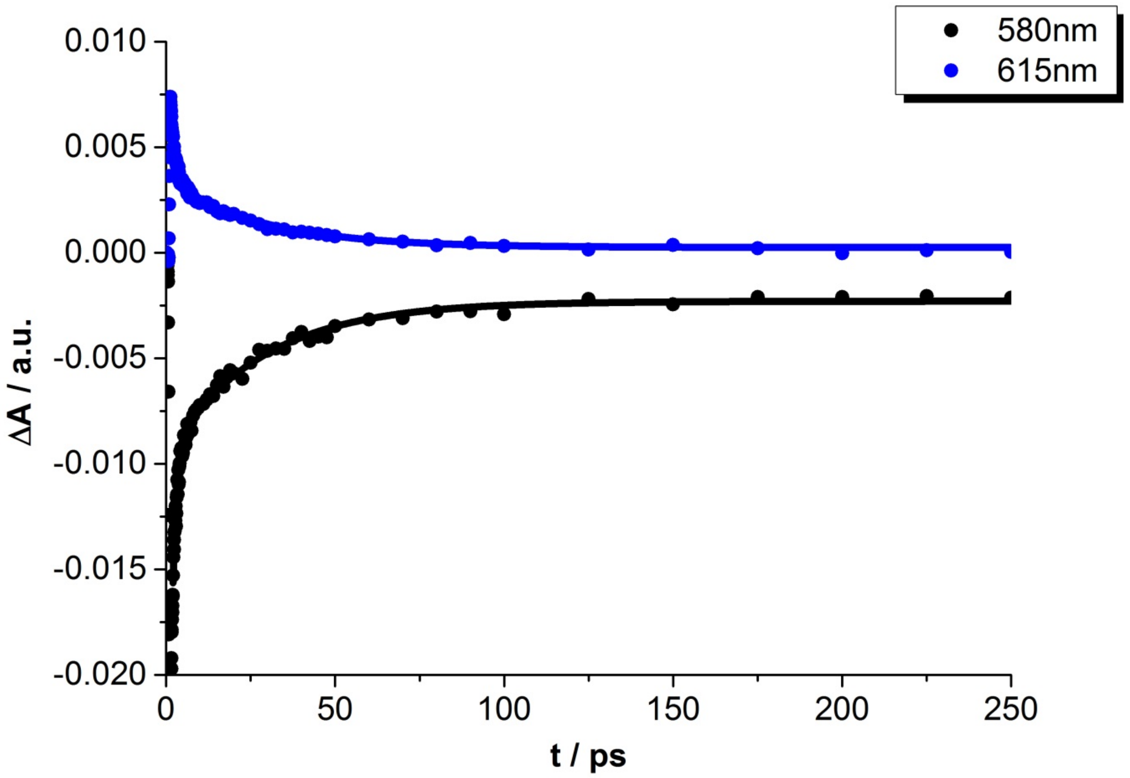


Figure S18.(top) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (568 nm) of **1b** (10^{-5} M) in argon-saturated benzonitrile with several time delays between 0 and 100 ps at room temperature. (bottom) Time-absorption profiles of the spectra shown at the top at 580 and 615 nm monitoring the charge separation and the charge recombination.

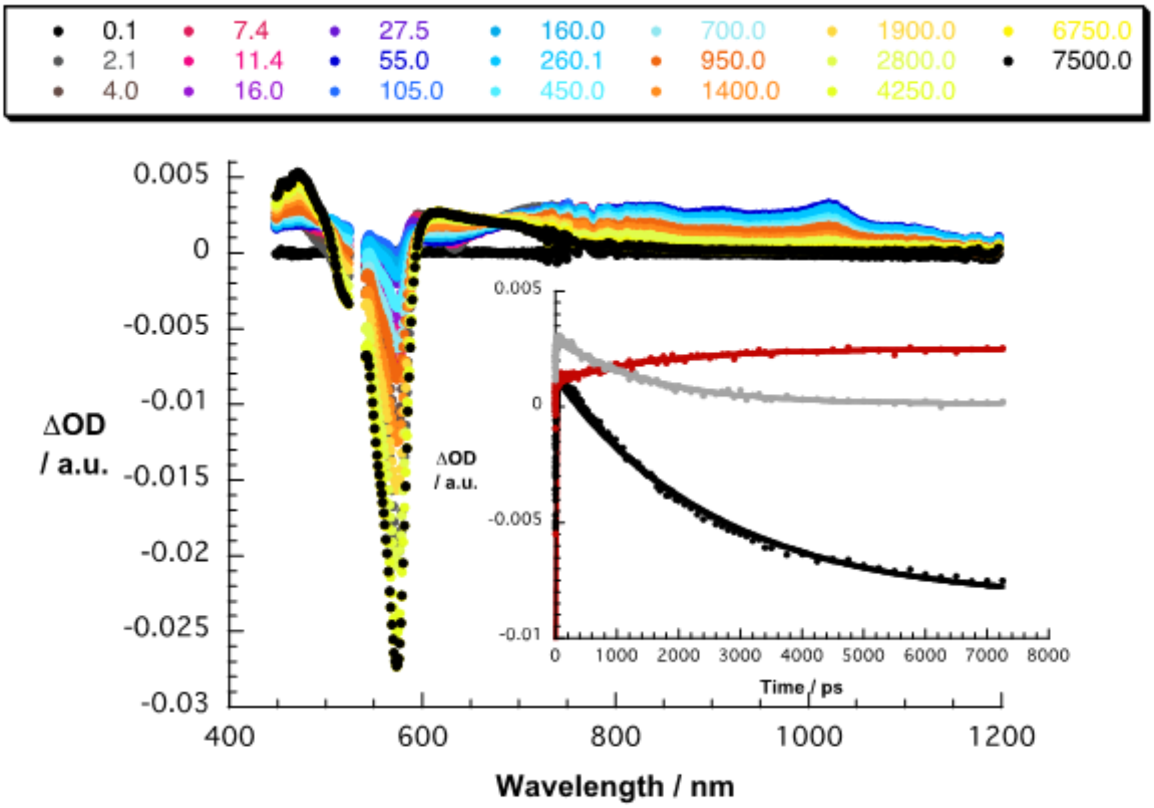


Figure S19. Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm) of **2a** (10^{-5} M) in argon-saturated THF with several time delays between 0.1 and 7500 ps at room temperature. Insert – time-absorption profiles of the spectra shown at the top at 545, 635, and 1025 nm monitoring the energy transfer.

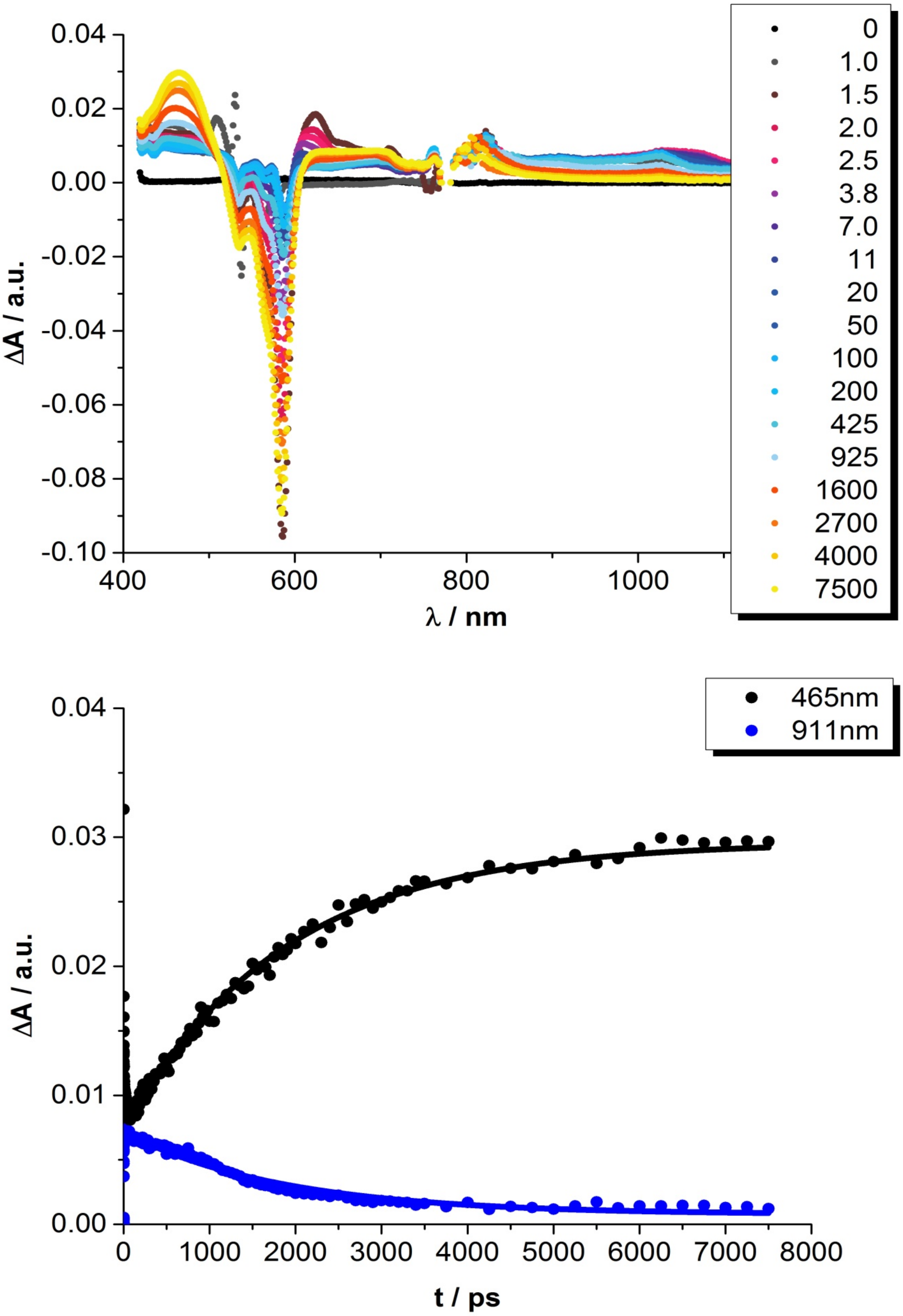


Figure S20.(top) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm) of **2b** (10^{-5} M) in argon-saturated toluene with several time delays between 0 and 7500 ps at room temperature. (bottom) Time-absorption profiles of the spectra shown at the top at 465 and 911 nm monitoring the energy transfer.

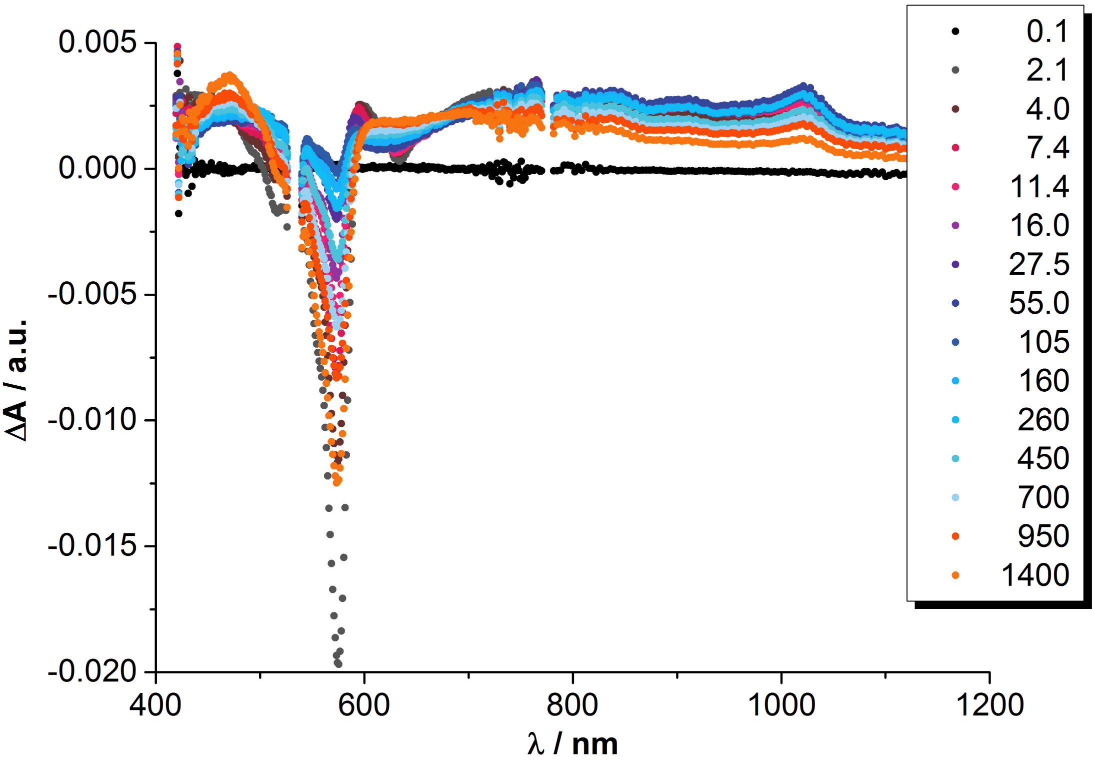


Figure S21. Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm) of **2a** (10^{-5} M) in argon-saturated THF with several time delays between 0 and 1400 ps at room temperature.