Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information on

Symmetry-Breaking Charge Transfer in the Excited-State in Directly Linked Push-Pull Porphyrin Arrays

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1. Experimental sections

Sample preparation.

Triads **AAA**, **ADA**, and dyad **AD** linear porphyrin arrays are synthesized and the details in synthesis, and basic characterizations are provided.[1]

Steady-state measurements.

Steady-state absorption spectra were measured on a UV/Vis/NIR spectrometer (Varian, Cary5000) and fluorescence spectra were measured on a fluorescence spectrophotometer (Hitachi, F-2500). Fluorescence spectra are spectrally corrected by using correction factor of the fluorescence spectrophotometer. HPLC-grade solvents were purchased from Sigma-Aldrich and used without further purification. All steady-state measurements were carried out by using a quartz cuvette with a pathlength of 1 cm at ambient temperatures.

Picosecond time-resolved fluorescence measurements.

A time-correlated single-photon-counting (TCSPC) system was used for measurements of spontaneous fluorescence decay. As an excitation light source, we used a mode-locked Ti:sapphire laser (Spectra Physics, MaiTai BB) which provides ultrashort pulse (center wavelength of 800 nm with 80 fs at FWHM) with high repetition rate (80 MHz). This high repetition rate was reduced to 800 kHz by using homemade pulse-picker. The pulse-picked output was frequency doubled by a 1-mm-thick BBO crystal (type-I, $\theta = 29.2°$, EKSMA). The fluorescence was collected by a microchannel plate photomultiplier (MCP-PMT, Hamamatsu, R3809U-51) with a thermoelectric cooler (Hamamatsu, C4878) connected to a TCSPC board (Becker & Hickel SPC-130). The overall instrumental response function was about 25 ps (FWHM). A vertically polarized pump pulse by a Glan-laser polarizer was irradiated to samples, and a sheet polarizer set at an angle complementary to the magic angle (54.7°), was placed in the fluorescence collection path to obtain polarization-independent fluorescence decays.

Femtosecond transient absorption measurements.

A femtosecond time-resolved transient absorption (TA) spectrometer used for this study consisted of a femtosecond optical parametric amplifier (OPA, Quantronix, Palitra-FS) pumped by a Ti:sapphire regenerative amplifier system (Quantronix, Integra-C) operating at 1 kHz repetition rate and an accompanying optical detection system. The generated OPA pulses had a pulse width of ~100 fs and an average power of 1 mW in the range 550 to 690 nm, which were used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (2 mm thick) by focusing of small portion of the fundamental 800 nm pulses, which were picked off by a quartz plate before entering into the OPA. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). Intensities of the spectrally dispersed WLC probe pulses were monitored by high speed spectrometer (Ultrafast Systems). To obtain the time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 500 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 6000 pulses were used to excite samples and to obtain the TA spectra at a particular delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7°) using a Glan-laser polarizer with a half-wave retarder to prevent polarization-dependent signals. The cross-correlation FWHM in the pump-probe experiments was less than 200 fs, and chirp of WLC probe pulses was measured to be 800 fs in the 450-850 nm regions. To minimize chirp, all reflection optics were used in the probe beam path, and a quartz cell of 2 mm path length was employed. After completing each set of fluorescence and TA experiments, the absorption spectra of all compounds were carefully checked to rule out the presence of artifacts or spurious signals arising from, for example, degradation or photo-oxidation of the samples in question.

Time-resolved infrared measurements

A time-resolved infrared spectrometer is based on two OPAs pumped by 110-fs laser pulses at 800 nm with a repetition rate of 2 kHz, produced by a commercial Ti:sapphire amplifier (Spitfire Ace, Spectra Physics). Photoexcitation (pump) pulses at 570 nm were generated by frequency doubling of the signal pulse of one OPA in a type I, 1-mm thick BBO crystal. Tunable mid-IR probe pulses (110 fs, 160 cm^{-1}, 1 μJ) were obtained by difference-frequency mixing of the signal and idler pulses of the other OPA in a 1-mm thick, type I $AgGaS_2$ crystal. A motorized linear stage was used to control the optical delay between the pump and the probe pulses. The polarization angle between the pump and the probe pulses was set at the magic angle (54.7°) to recover the isotropic absorption spectrum. The sample was photoexcited by 2 μJ of energy at 570 nm and probed by a small portion of mid-IR pulses (ca. 10 nJ) centered at 1530 cm^{-1}. The broadband mid-IR pulses passed through the sample, were dispersed in a 320 mm monochromator with a 120-lines/mm grating, and were detected by a single MCT array with 1×64 pixels. As a result, a spectral resolution of ca. 1.0 cm^{-1}/pixel at 1530 cm^{-1} was obtained. The instrument response function, determined by transient absorption of the Si wafer, was typically <180 fs.

2. Quantum mechanical calculations

Quantum mechanical calculations were carried out with Gaussian 09 program suite.[2] Geometry optimization in ground state (S_0) was performed by density functional theory (DFT), and simulation of infrared (IR) spectra were also performed using method with B3LYP,[3,4] employing a basis set consisting of 6-31G(d) for all atoms.[5]

3. Supporting figures

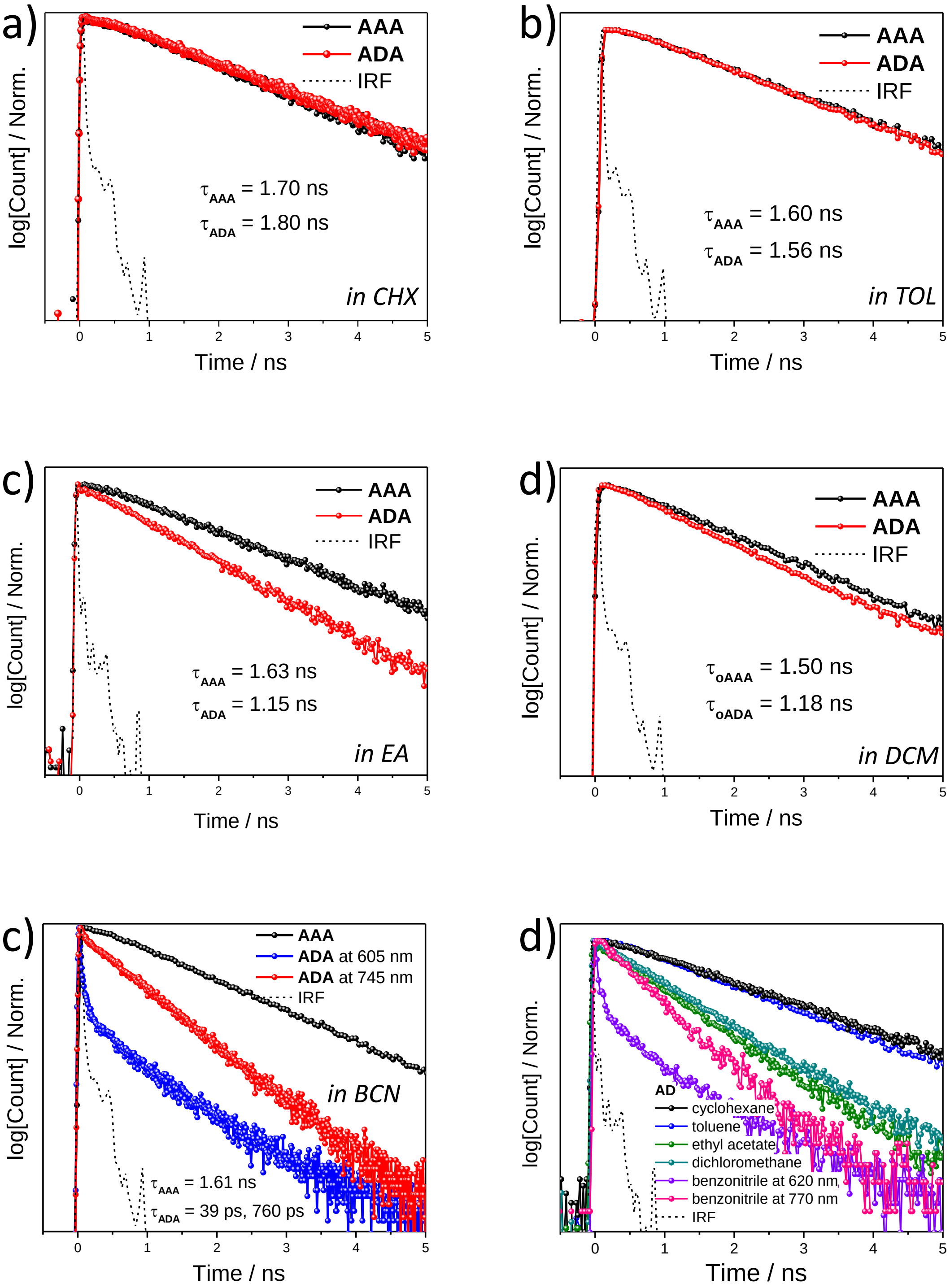

Fig. S1 Fluorescence decay profiles of **AAA**, **ADA**, and **AD** in five solvents. The decay profiles of **AAA** and **ADA** are plotted together in a) CHX: cyclohexane, b) TOL: toluene, c) EA: ethyl acetate, d) DCM: dichloromethane, and e) BCN: benzonitrile measured by time-correlated single photon counting (TCSPC) technique. The decay profiles of **AD** are plotted together in the five solvents. Their lifetimes are listed in Table 1.

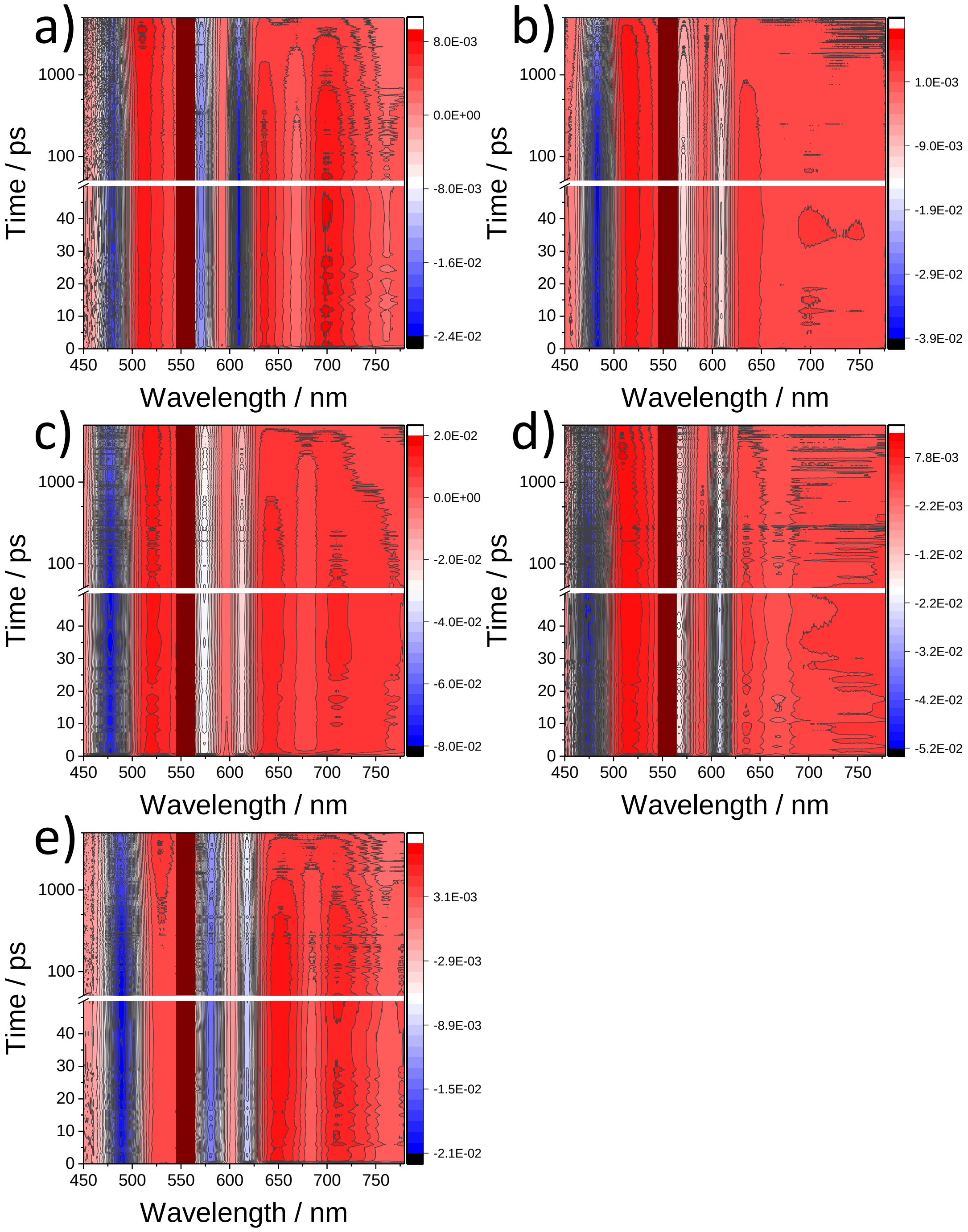

Fig. S2 Femtosecond transient absorption (fs-TA) 2D contour maps of **AAA** in a) CHX, b) TOL, c) EA, d) DCM, and e) BCN.

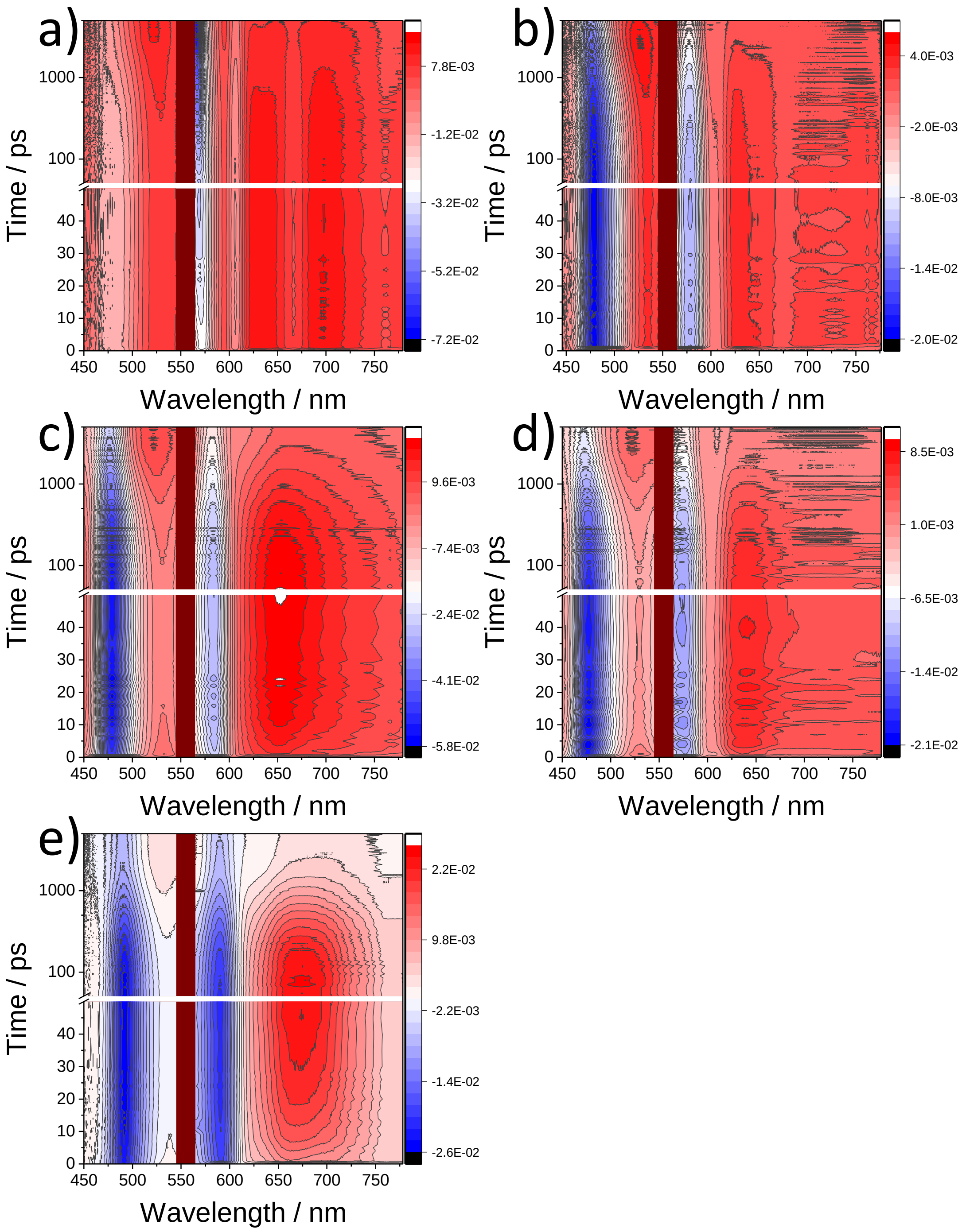

Fig. S3 Femtosecond transient absorption (fs-TA) 2D contour maps of **ADA** in a) CHX, b) TOL, c) EA, d) DCM, and e) BCN.

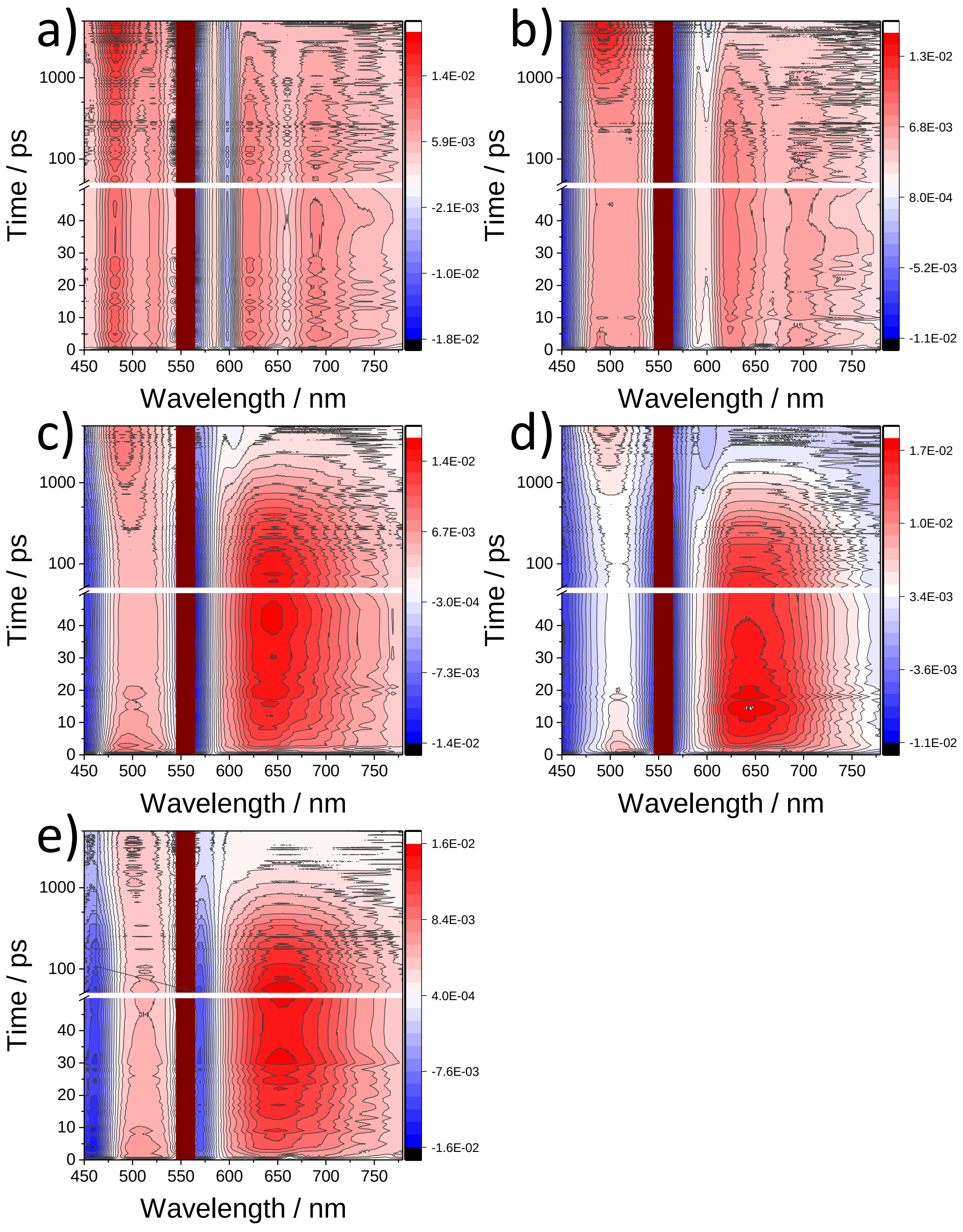

Fig. S4 Femtosecond transient absorption (fs-TA) 2D contour maps of **AD** in a) CHX, b) TOL, c) EA, d) DCM, and e) BCN

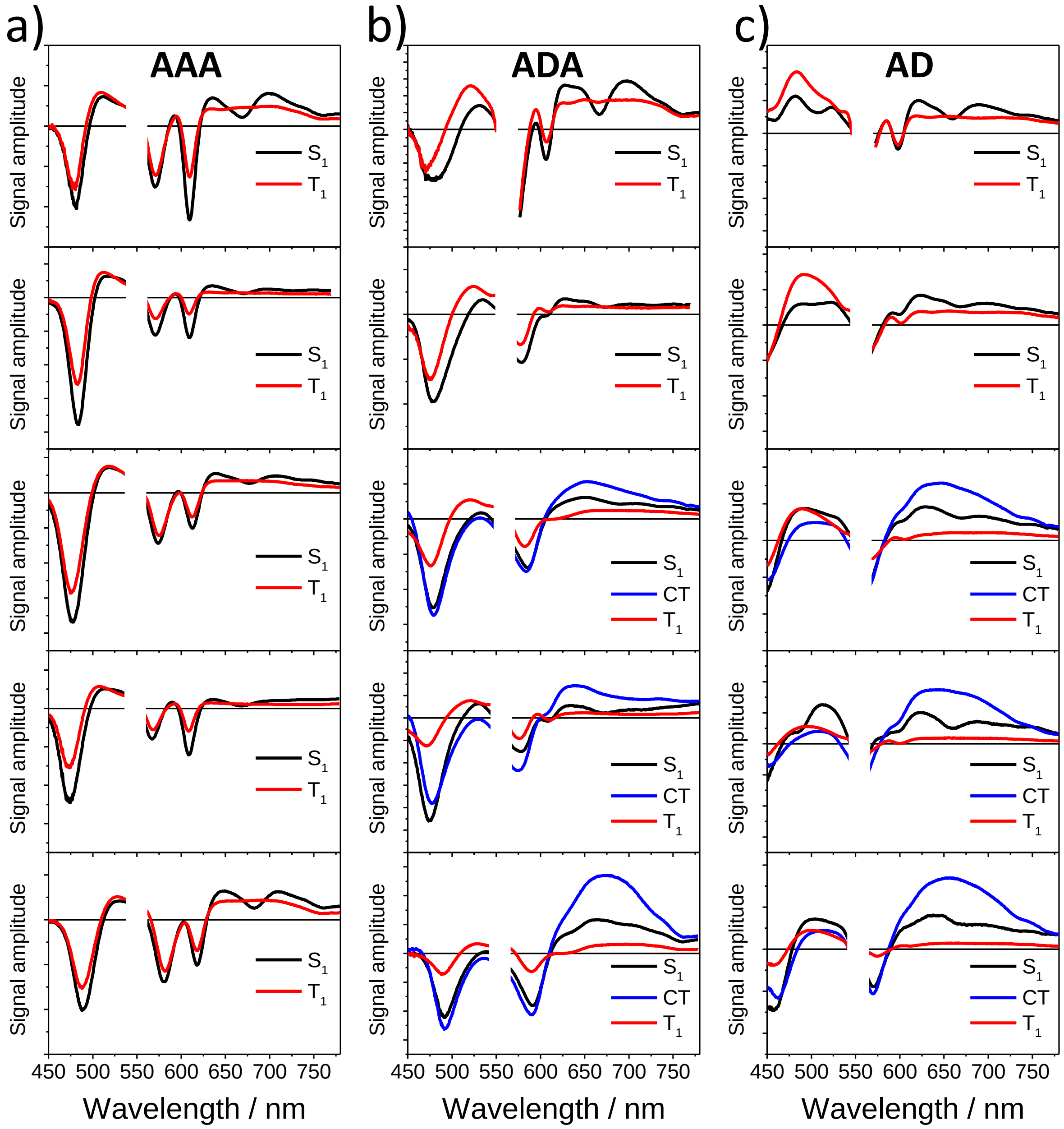

Fig. S5 Evolution-associated spectra (EAS) extracted from transient absorption spectra of a) **AAA**, b) **ADA**, and c) **AD** in five solvents (CHX, TOL, EA, DCM, and BCN from top to bottom). Evolution time constants are listed in Table S1.

Table S1. Time components corresponding to Figure S5. τ_{CT} represents S_1 —> CT state and τ_T represents S_1 state or CT state —> triplet state as their excited state dynamics almost follows sequential model (radiative rate << nonradiative rate).

molecule	solvent	τ_{CT} (ps)	τ_T (ps)
AAA	CHX	-	1700
	TOL	-	1600
	EA	-	1710
	DCM	-	1500
	BCN	-	1610
ADA	CHX	-	1810
	TOL	-	1560
	EA	8	1320
	DCM	3	1180
	BCN	26	673
AD	CHX	-	1900
	TOL	-	1600
	EA	6	910
	DCM	2	690
	BCN	16	500

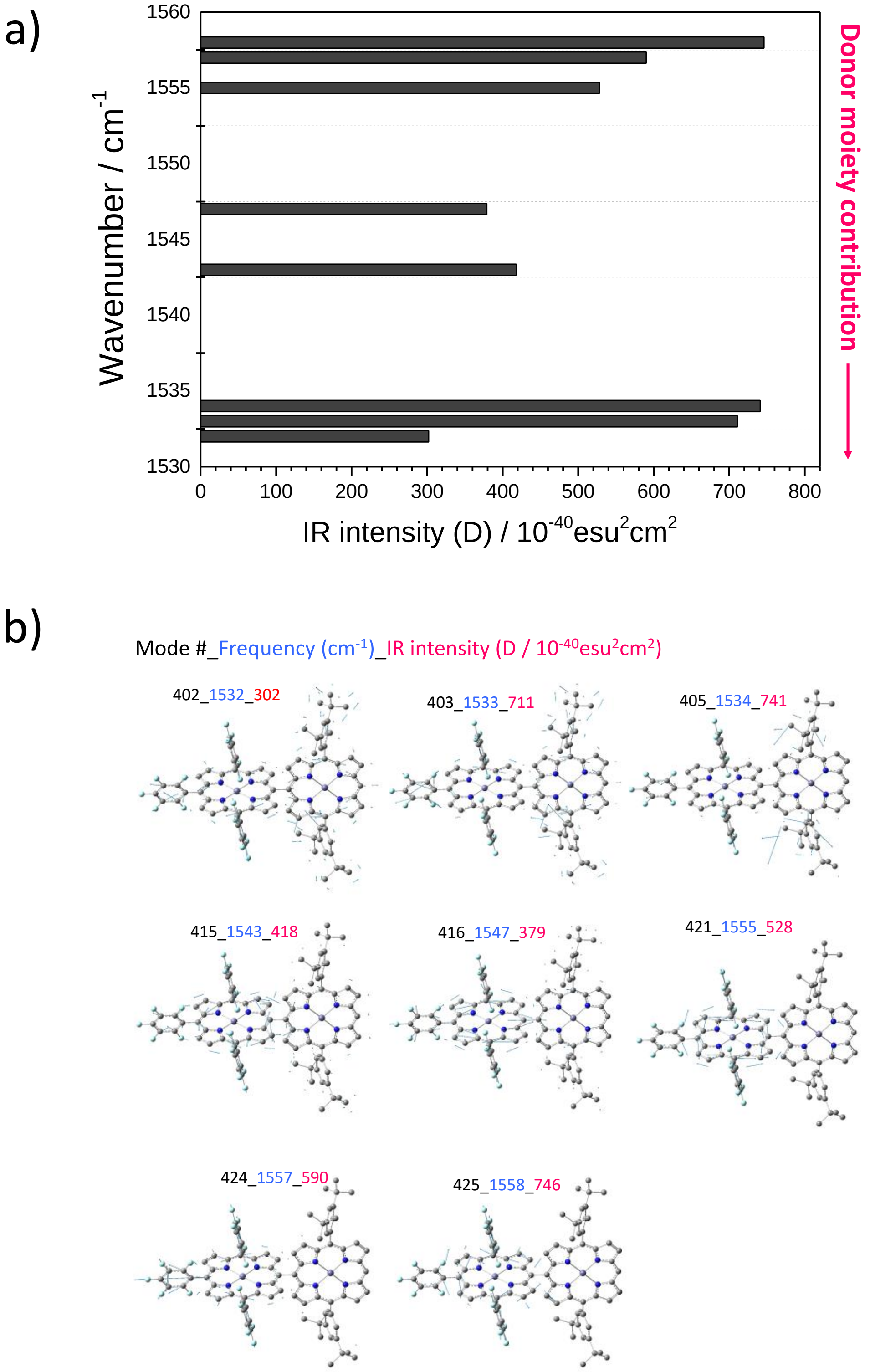

Fig. S6 a) Infrared (IR) intensity and relative contribution of donor moiety on selected vibrational modes for **AD** in the similar range of TRIR measurement which corresponds to conjugated ring vibrational modes, b) each mode is represented with displacement vectors including its mode number, vibrational frequency, and IR intensity.

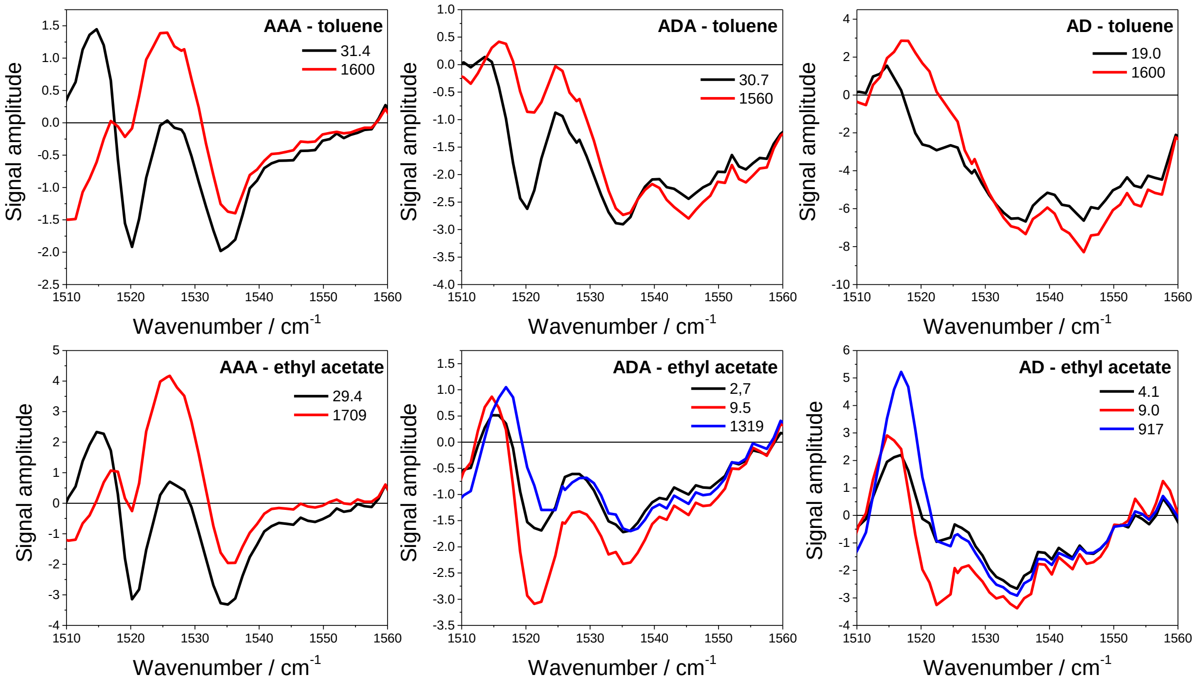

Fig. S7 Evolution-associated spectra (EAS) extracted from TRIR spectra of **AAA**, **ADA** and **AD** until 100 ps in TOL and EA.

Reference

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