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

Torsional disorder and planarisation dynamics: 9,10-bis(phenylethynyl)anthracene as a case study

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S1 Quantum-chemical calculations

Table S1: S_1(v=0)←S_0(v=0) transition energy of **BPEA** in the gas phase obtained from TD-DFT calculations with different functionals and the 6-31G(d,p) basis set.

Functional	Transition Energy / eV
B3LYP	2.26
CAM-B3LYP	2.59
CAM-B3LYP-D3BJ	2.58
PW6B95-B3	2.29
M06	2.35
M06-2x	2.60
Experimental in CHX	2.63

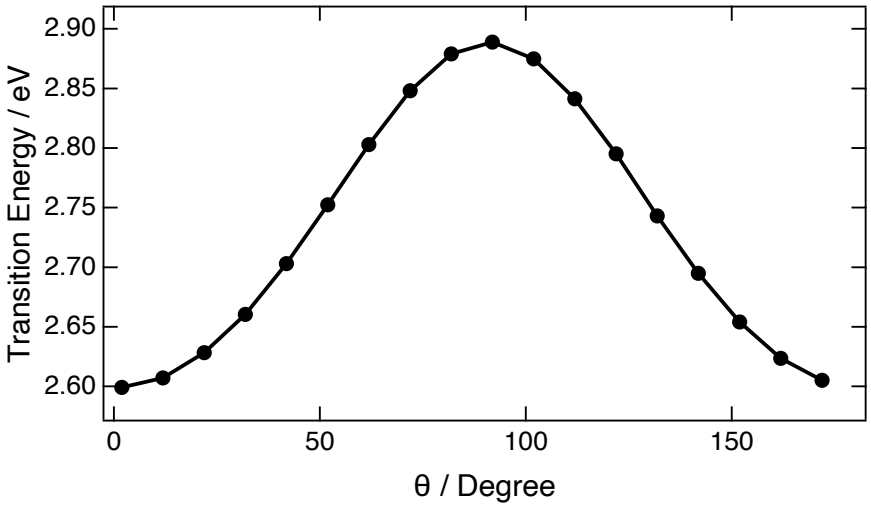

Figure S1: Calculated (M06-2x/6-31G(d,p)) S_1←S_0 transition energy of **BPEA** as a function of the torsion angle θ.

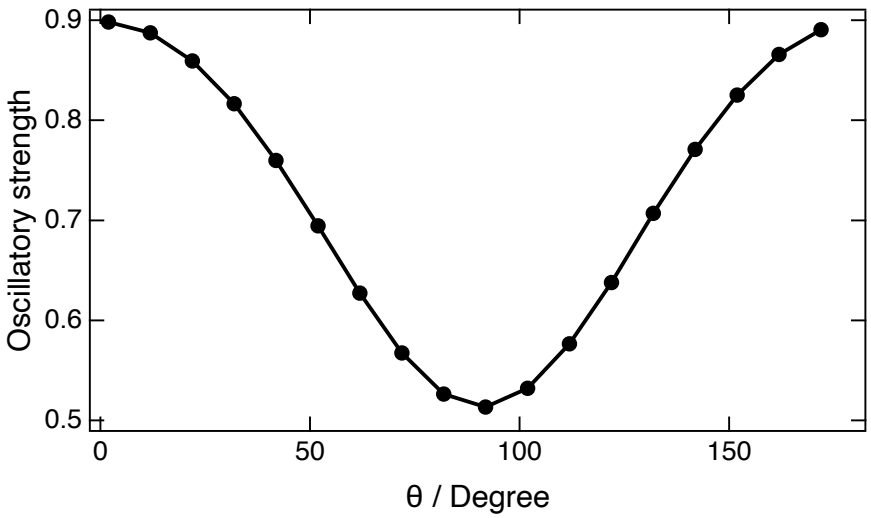

Figure S2: Calculated (M06-2x/6-31G(d,p)) oscillator strength of the $S_1 \leftarrow S_0$ transition of **BPEA** as a function of the torsion angle θ.

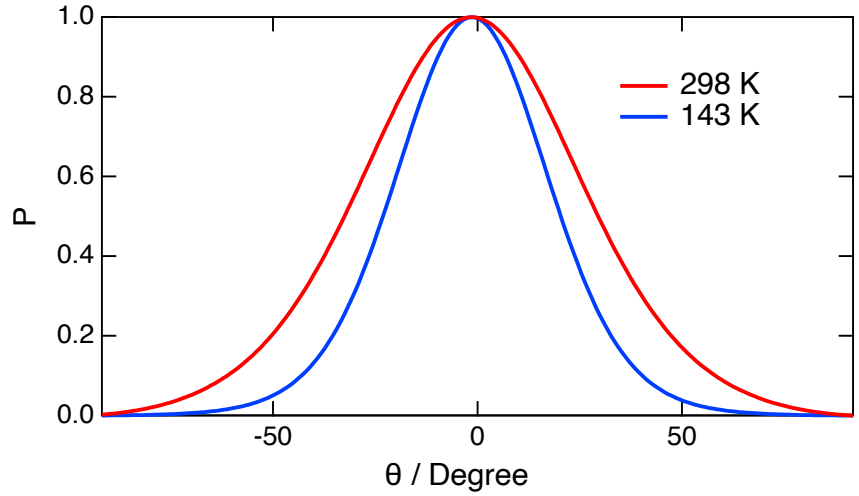

Figure S3: Boltzmann distribution of torsion angle, θ, of **BPEA** in the ground state at two temperatures.

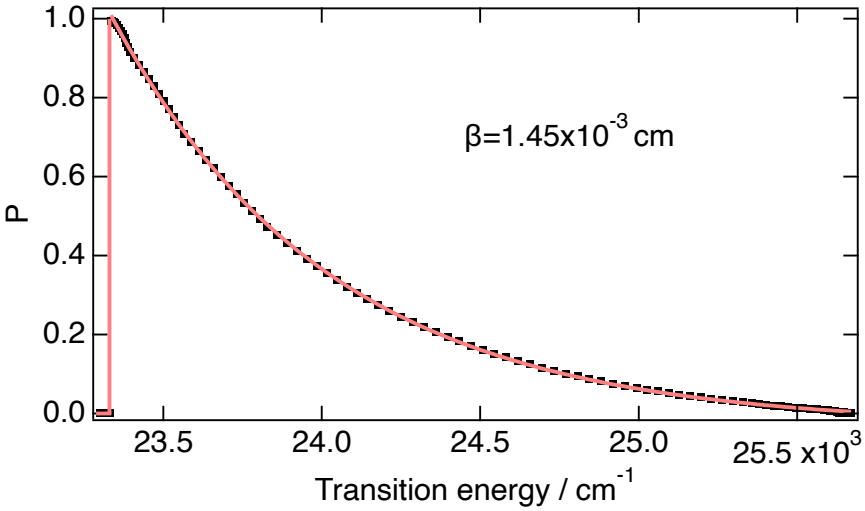

Figure S4: Thermal distribution of the $S_1 \leftarrow S_0$ transition energy of **BPEA** at room temperature and best fit of eq.(1).

S2 Stationary spectroscopy

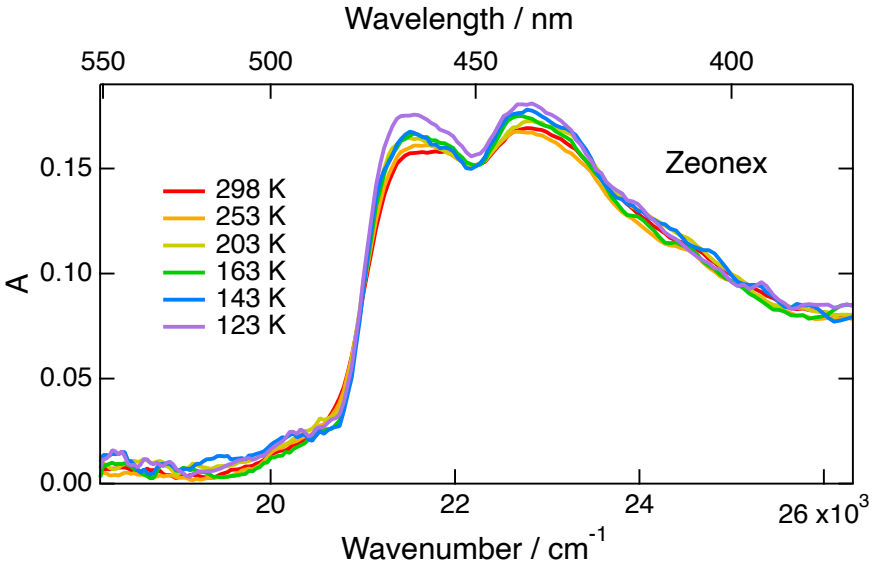

Figure S5: Temperature dependence of the stationary absorption spectrum of **BPEA** in Zeonex.

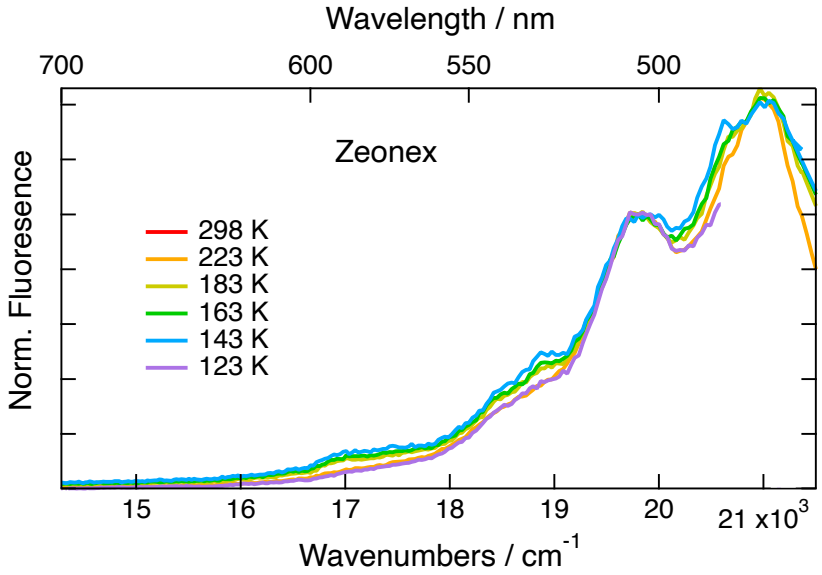

Figure S6: Temperature dependence of the fluorescence spectrum of **BPEA** in Zeonex upon 430 nm excitation. The 123 K spectrum was cut above 20'500 cm^{-1} because of the presence of scattered light.

S3 Femtosecond broadband fluorescence up-conversion spectroscopy (FLUPS)

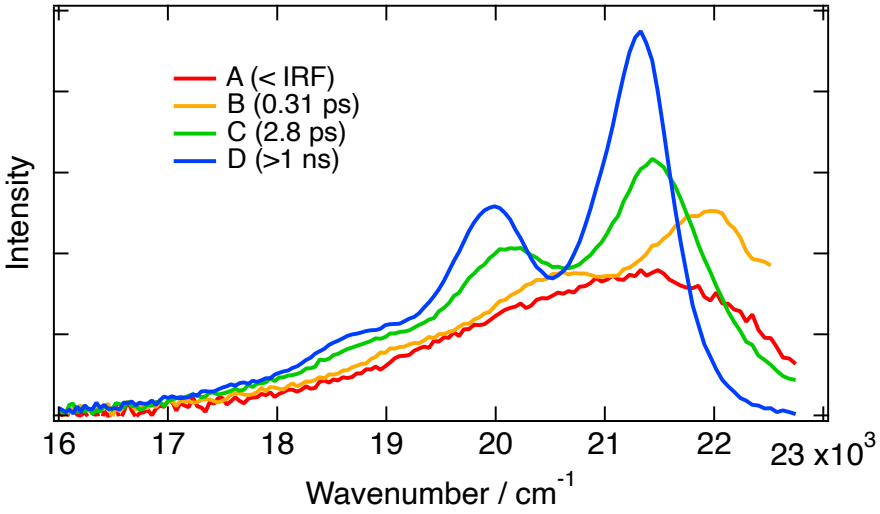

Figure S7: Evolution-associated spectra obtained from a global analysis of the FLUPS data measured with **BPEA** in cyclohexane upon 425 nm excitation assuming a A→B→C→D→ scheme.

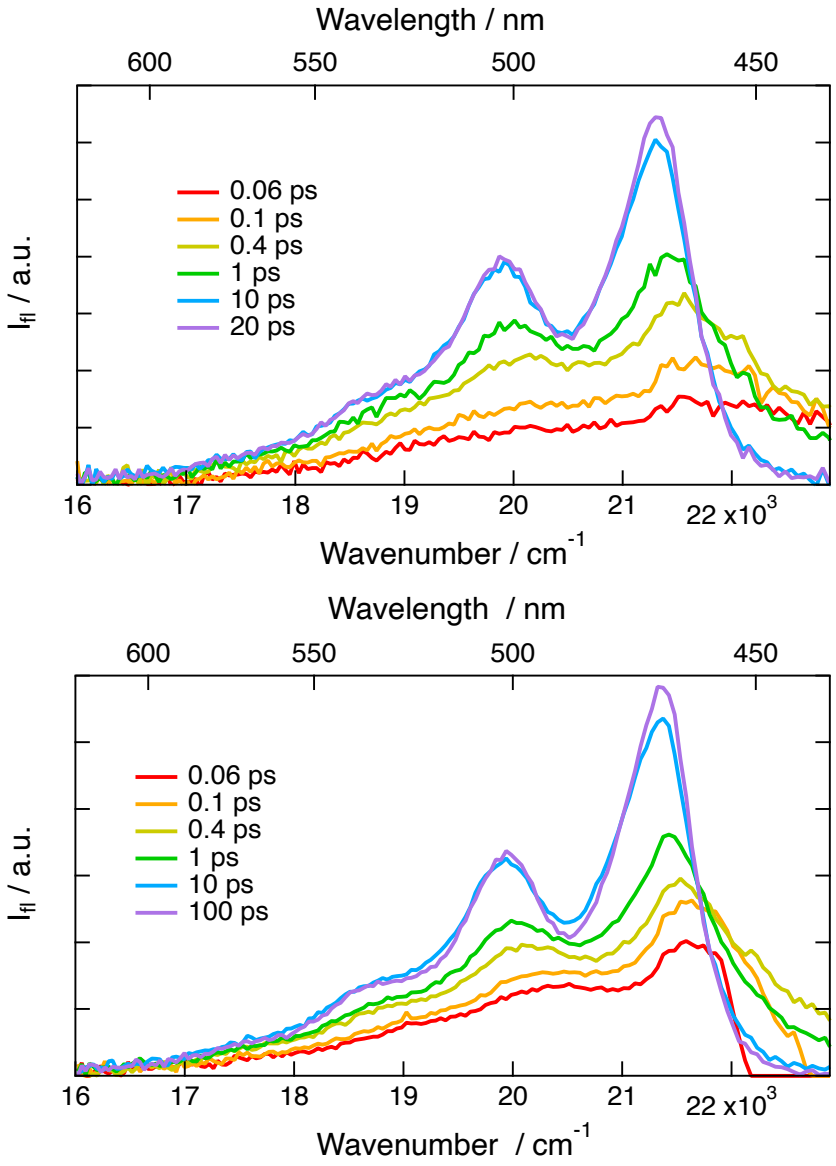

Figure S8: Transient fluorescence spectra recorded at various time delays after 375 (top) and 400 nm (bottom) excitation of BPEA in cyclohexane. The blue side of early spectra upon 400 nm excitation are cut due to the presence of Raman scattering.

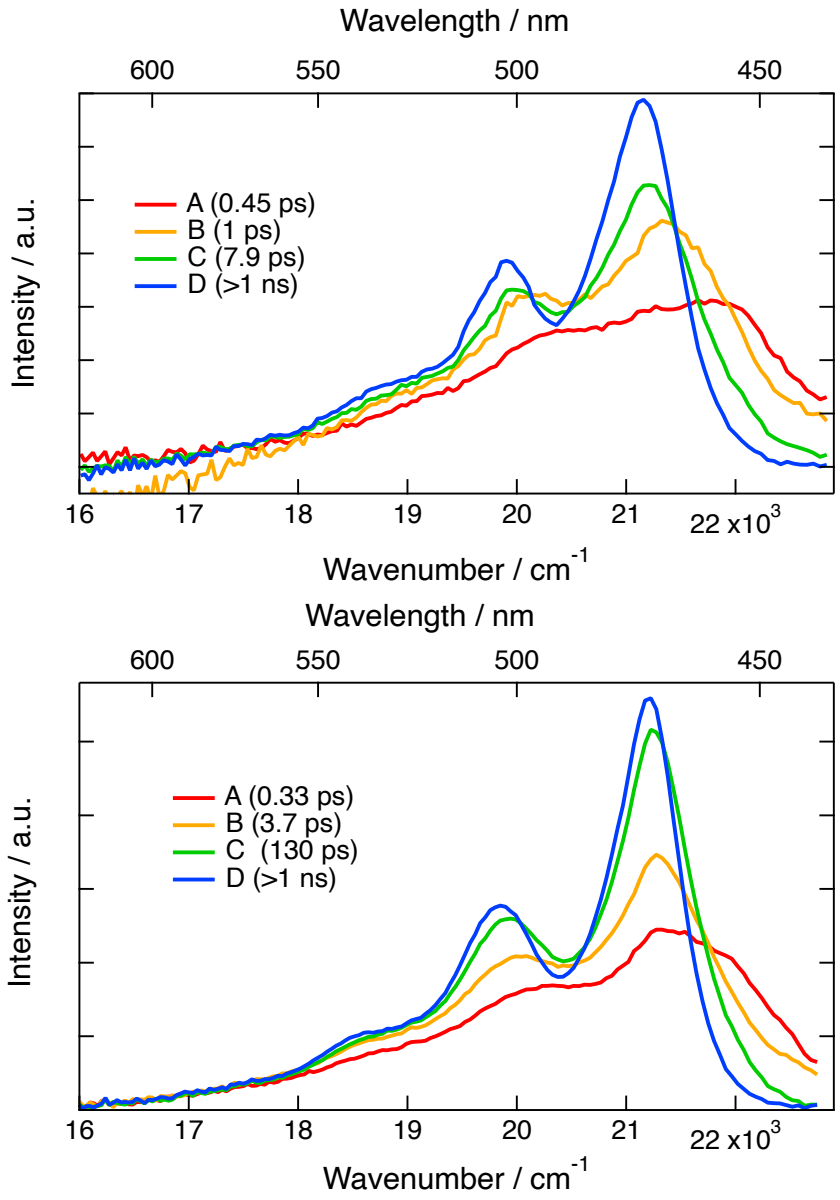

Figure S9: Evolution-associated spectra obtained from a global analysis of the FLUPS data measured with **BPEA** in decaline (top) and paraffin oil (bottom) upon 425 nm excitation assuming a A→B→C→D→ scheme.

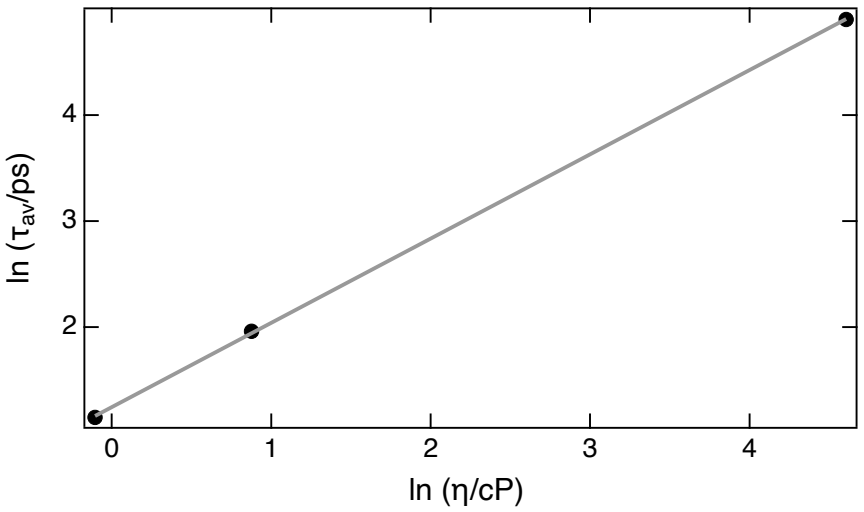

Figure S10: Amplitude-averaged time constant obtained from a (multi)-exponential analysis of the time evolution of β (Figure 6B) vs. viscosity and best fit of eq.(2).

Table S2: Time constants, τ_i, and relative amplitudes, A_i, obtained from a multiexponential analysis of the rise of the fluorescence band area (Figure 5, main text). Error on τ_i: $\pm$10%.

Solvent	τ_1 / ps	A_1	τ_2 / ps	A_2	τ_3 / ps	A_3
cyclohexane	0.12	-0.68	0.67	-0.22	11.9[a]	-0.1
decaline	0.10	-0.65	0.31	-0.15	3.3	-0.20
paraffin oil	0.12	-0.66	0.65	-0.17	120	-0.17

a) this component is assigned to vibrational cooling and not to planarisation.

S4 Electronic transient absorption spectroscopy (TA)

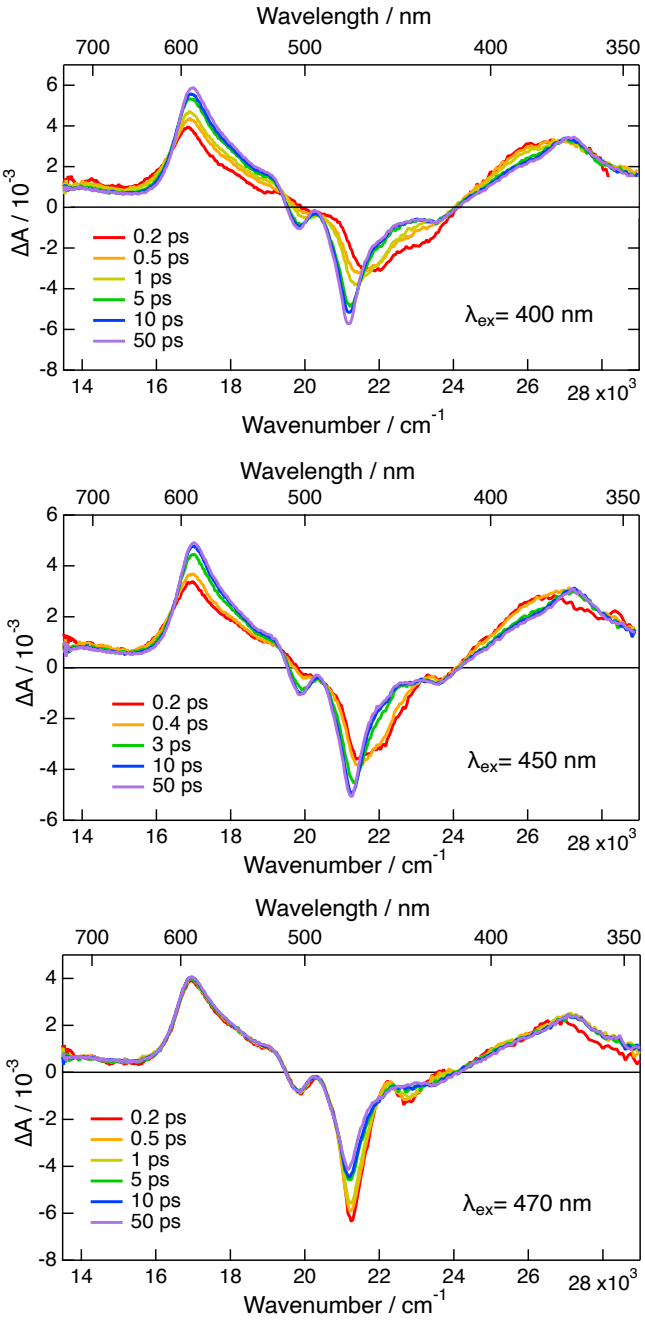

Figure S11: Transient electronic absorption spectra recorded at various time delays after 400, 450, and 470 nm excitation of **BPEA** in decaline.

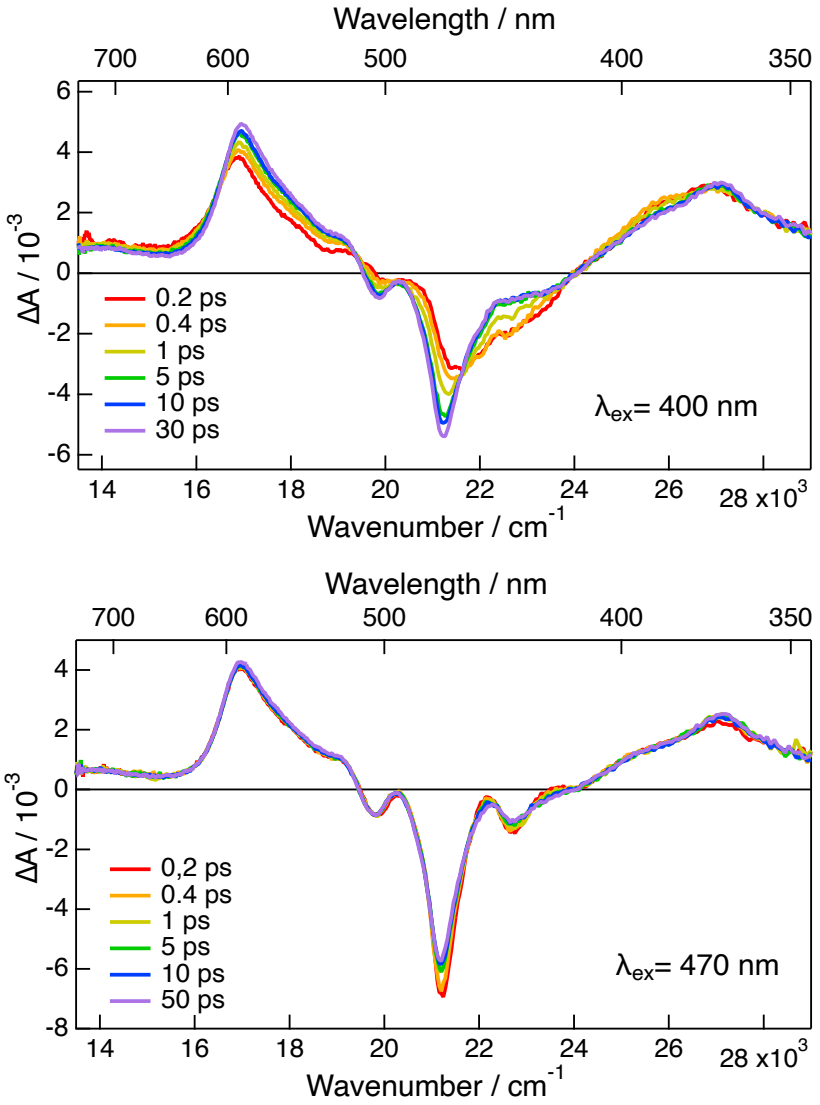

Figure S12: Transient electronic absorption spectra recorded at various time delays after 400 nm (top), and 470 nm (bottom) excitation of **BPEA** in paraffin oil.

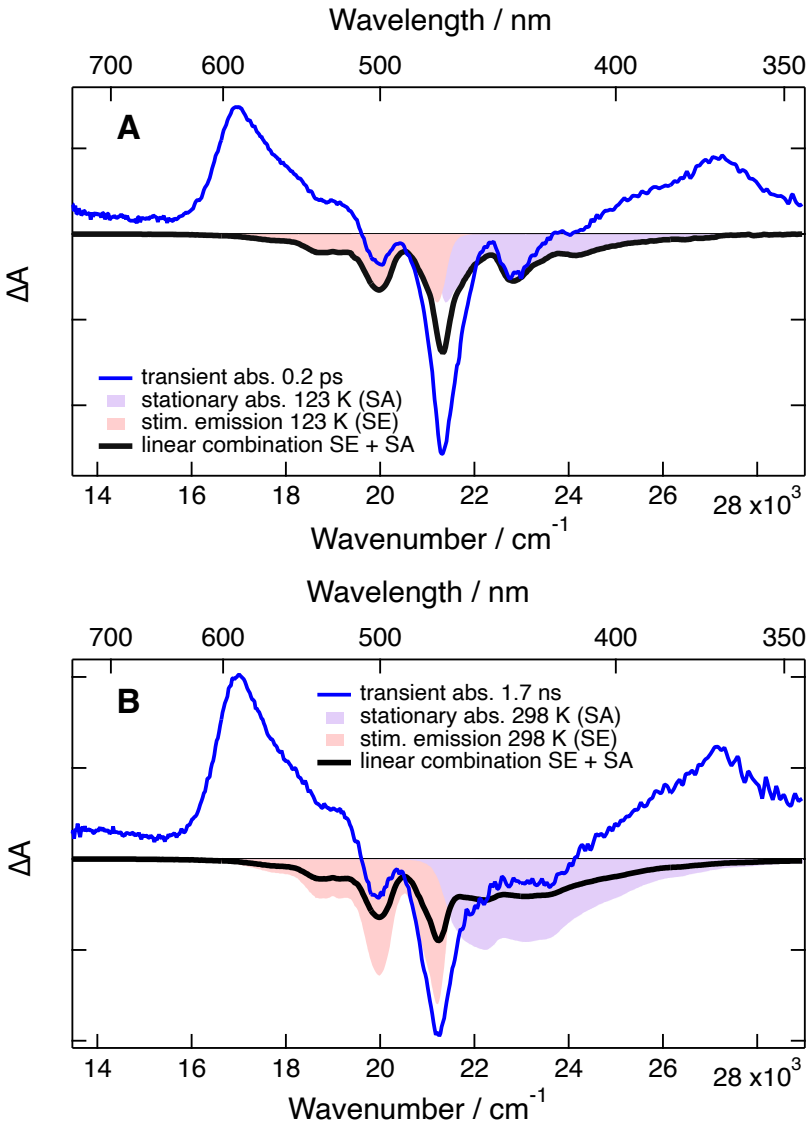

Figure S13: Transient electronic absorption spectra recorded at early (A) and late time (B) after 470 nm excitation of **BPEA** in cyclohexane, negative stationary absorption and stimulated emission spectra of **BPEA** in MTHF at 123 K (A) and cyclohexane at 298 K (B) and linear combinations of the absorption and stimulated emission spectra. The stimulated emission spectra were calculated by multiplying the spontaneous emission spectra by λ^4, where λ is the wavelength.[1]

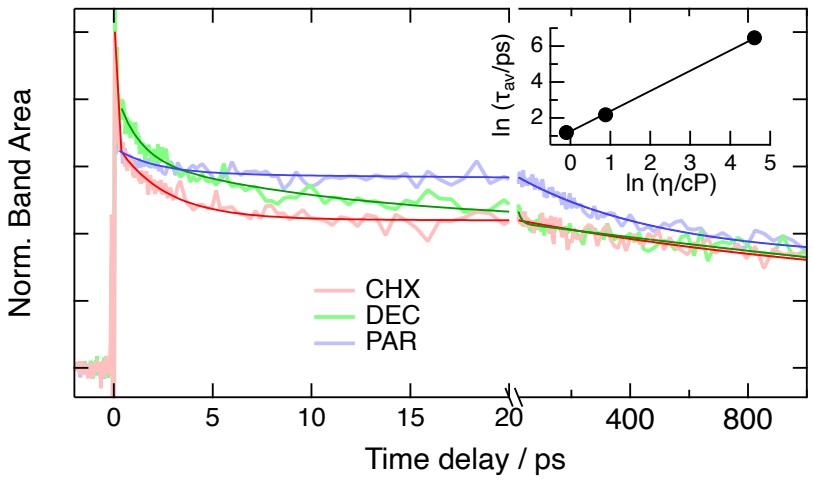

Figure S14: Time profiles of the 440 nm transient band area measured upon 470 nm excitation of **BPEA** and best biexponential fits. The initial spike is associated with vibrational coherence and was not included in the fit. Inset: amplitude-averaged time constant vs. viscosity and best fit of eq.2. (CHX: cyclohexane; DEC: decaline; PAR: paraffin oil).

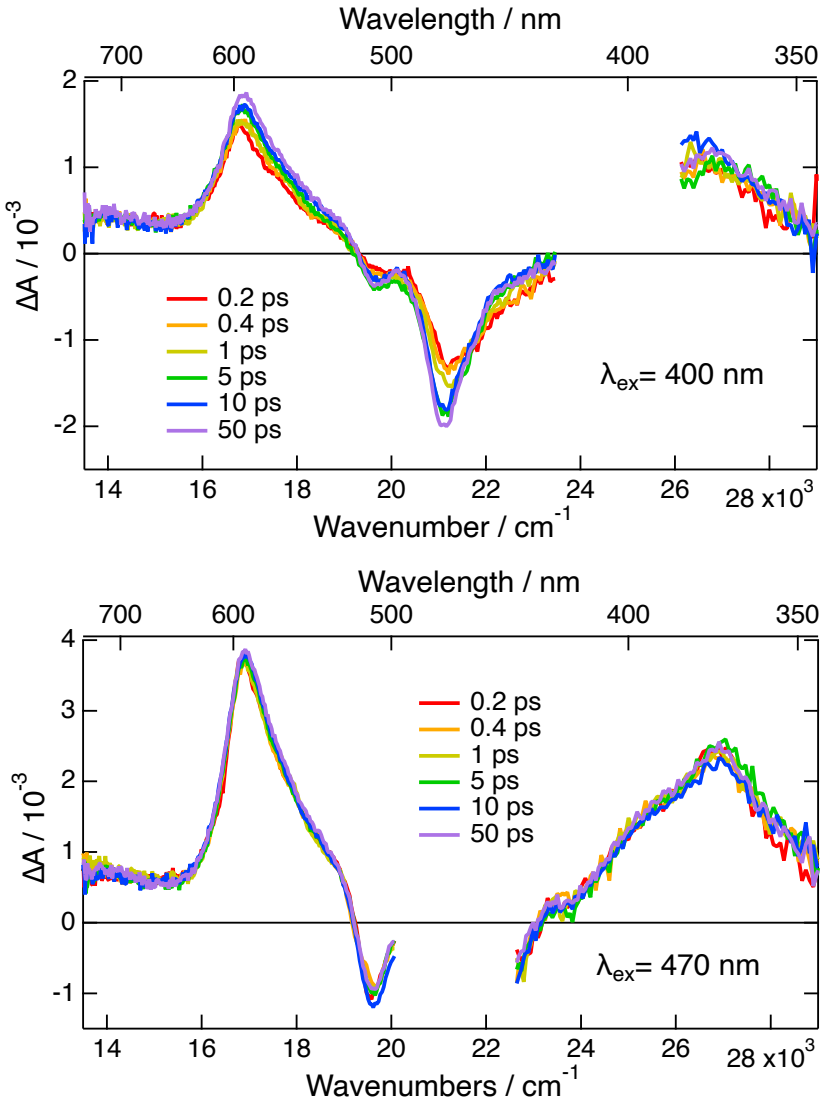

Figure S15: Transient electronic absorption spectra recorded upon 400 nm (top) and 470 nm (bottom) excitation of **BPEA** in Zeonex.

References

[1] A. V. Deshpande, A. Beidoun, A. Penzkofer and G. Wagenblast, *Chem. Phys.*, 1990, **142**, 123–131.