Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Carbon-sulfur bond elongation is the promoting reaction coordinate in the efficient sub-nanosecond intersystem crossing in thianaphthene derivatives

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Supplementary Information

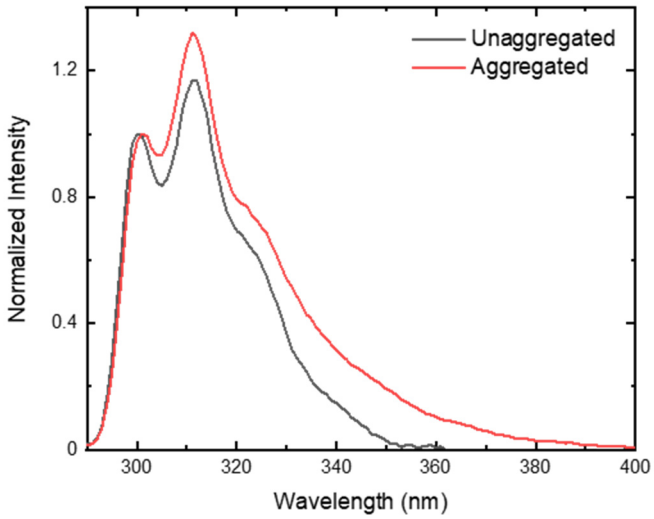

Figure S1. Normalized fluorescence spectra of thianaphene in acetonitrile at concentrations where monomer emission is only observed (< 7×10^{-5} M) and where aggregates or excimer emission is observed (> 7×10^{-5} M).

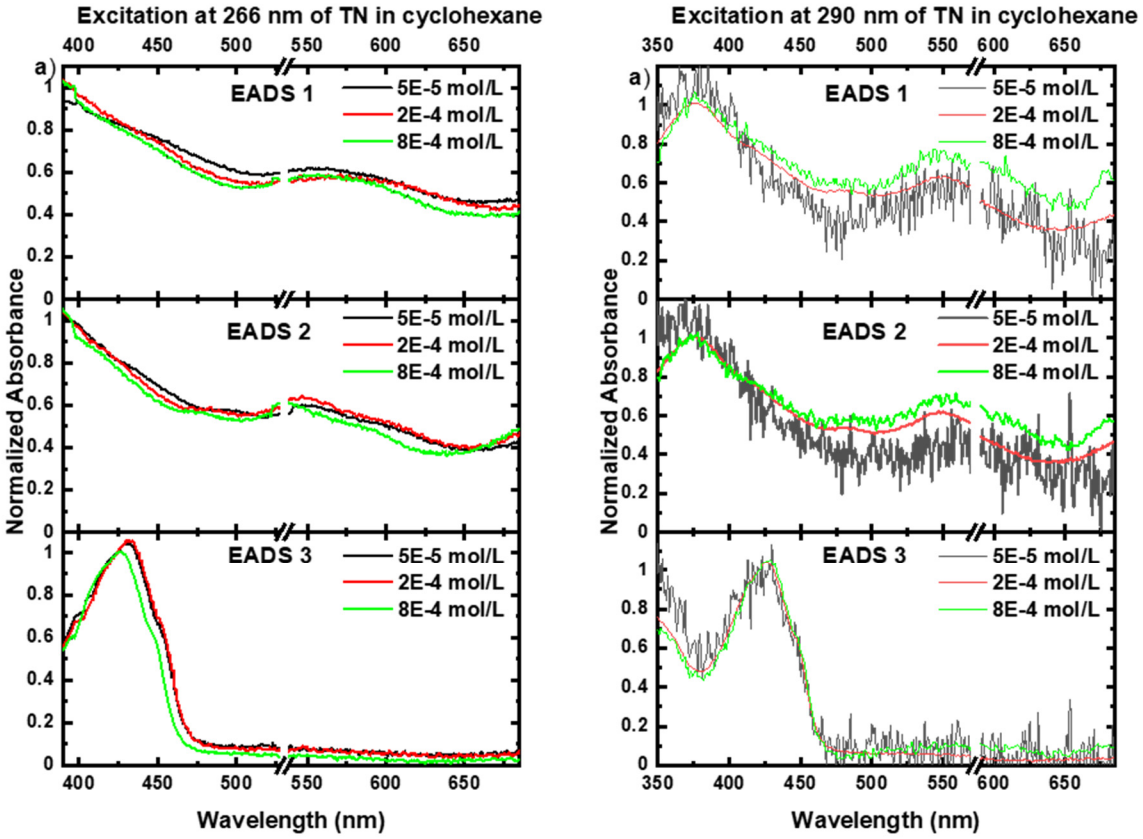

Figure S2. Evolution associated difference spectra of thianaphthene in cyclohexane at excitation of a) 266 nm and b) 290 nm were obtained from global and target analysis. The break is included to remove the overtone signal that comes from the excitation source.

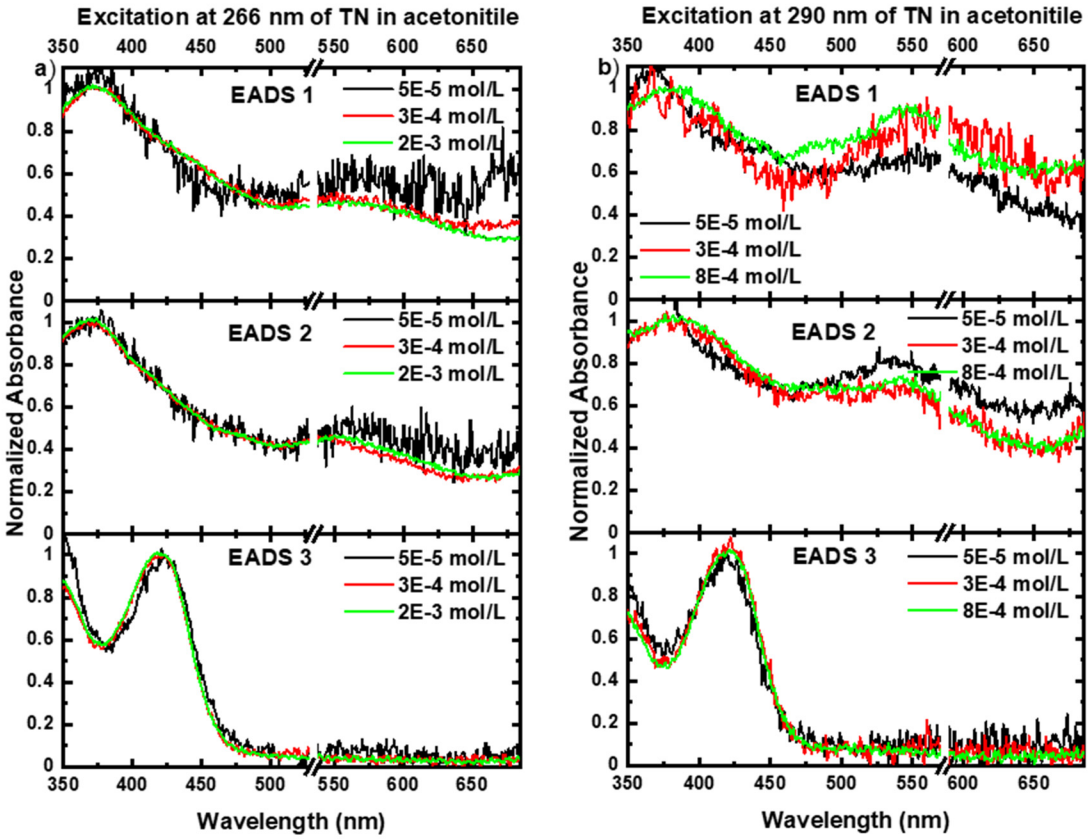

Figure S3. Evolution associated difference spectra of thianaphthene in acetonitrile at excitation of a) 266 nm and b) 290 nm were obtained from global and target analysis. The break is included to remove the overtone signal that comes from the excitation source.

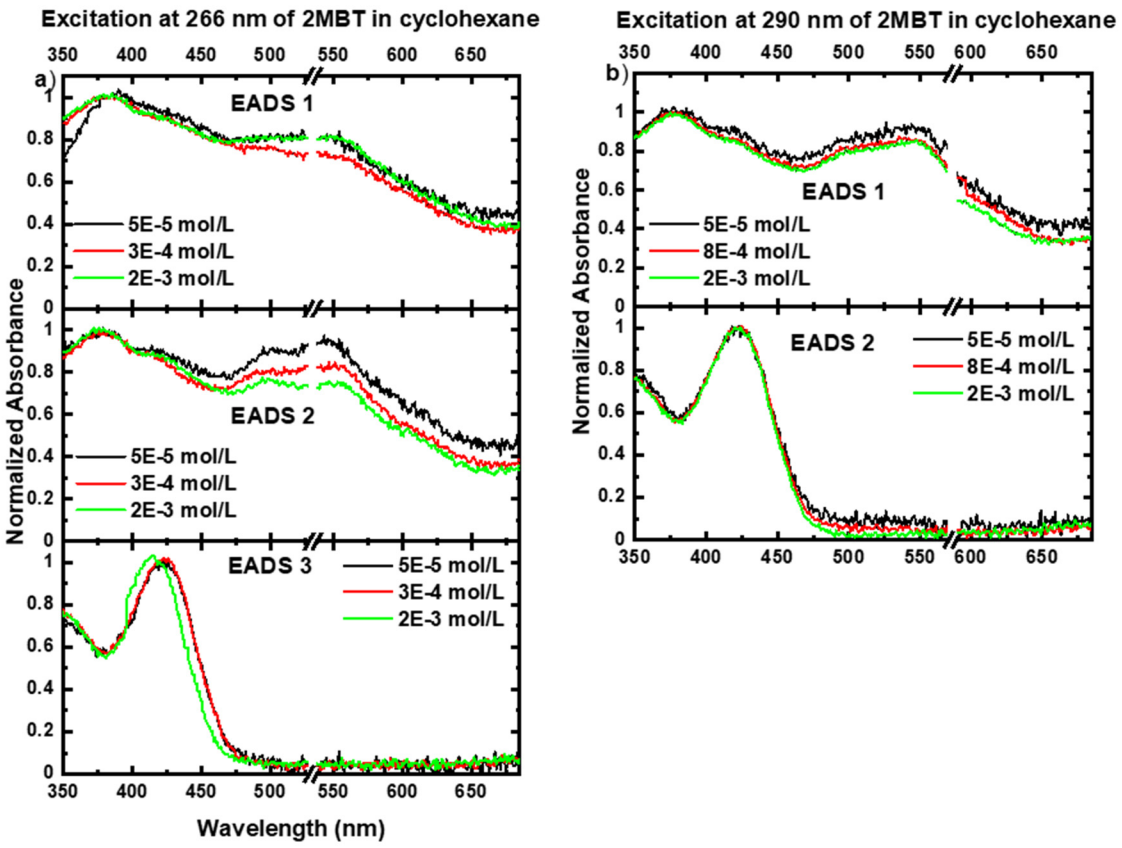

Figure S4. Evolution associated difference spectra of 2-methylbenzothiophene in cyclohexane at excitation of a) 266 nm and b) 290 nm were obtained from global and target analysis. The break is included to remove the overtone signal that comes from the excitation source.

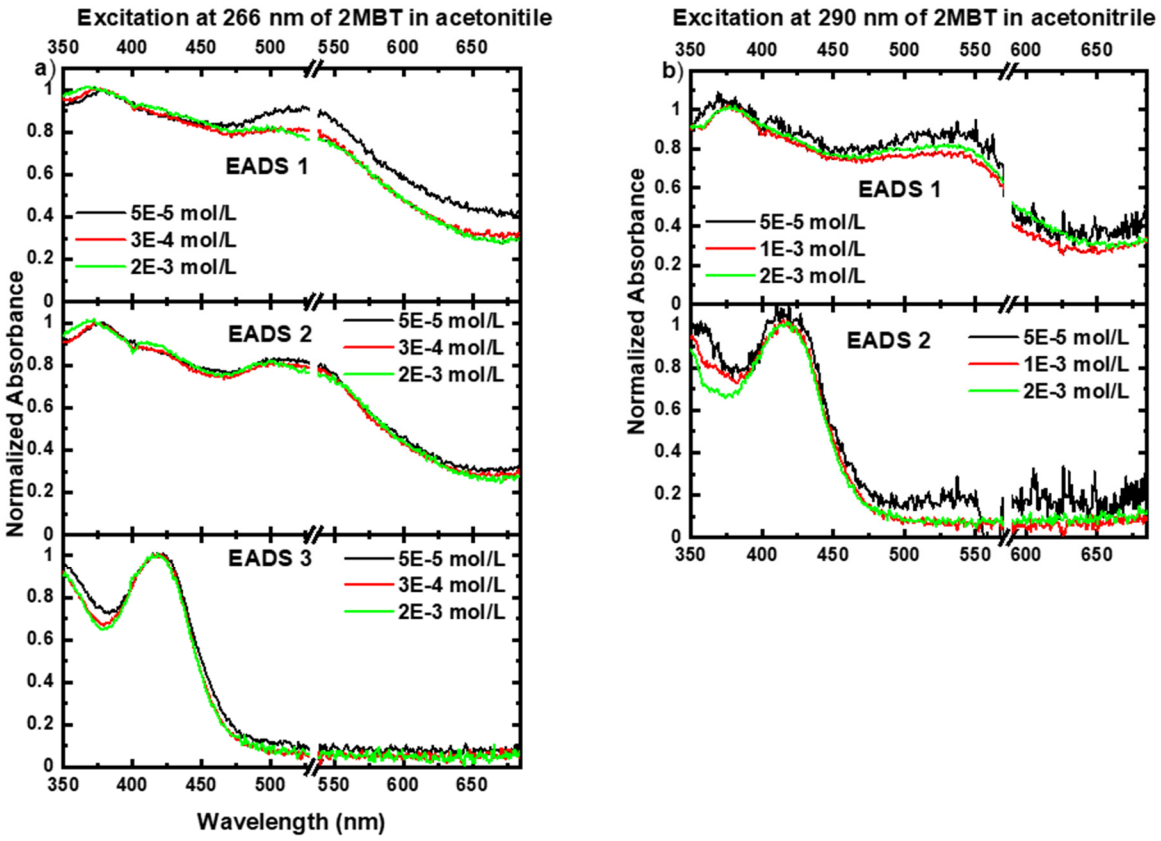

Figure S5. Evolution associated difference spectra of 2-methylbenzothiophene in acetonitrile at excitation of a) 266 nm and b) 290 nm were obtained from global and target analysis. The break is included to remove the overtone signal that comes from the excitation source.

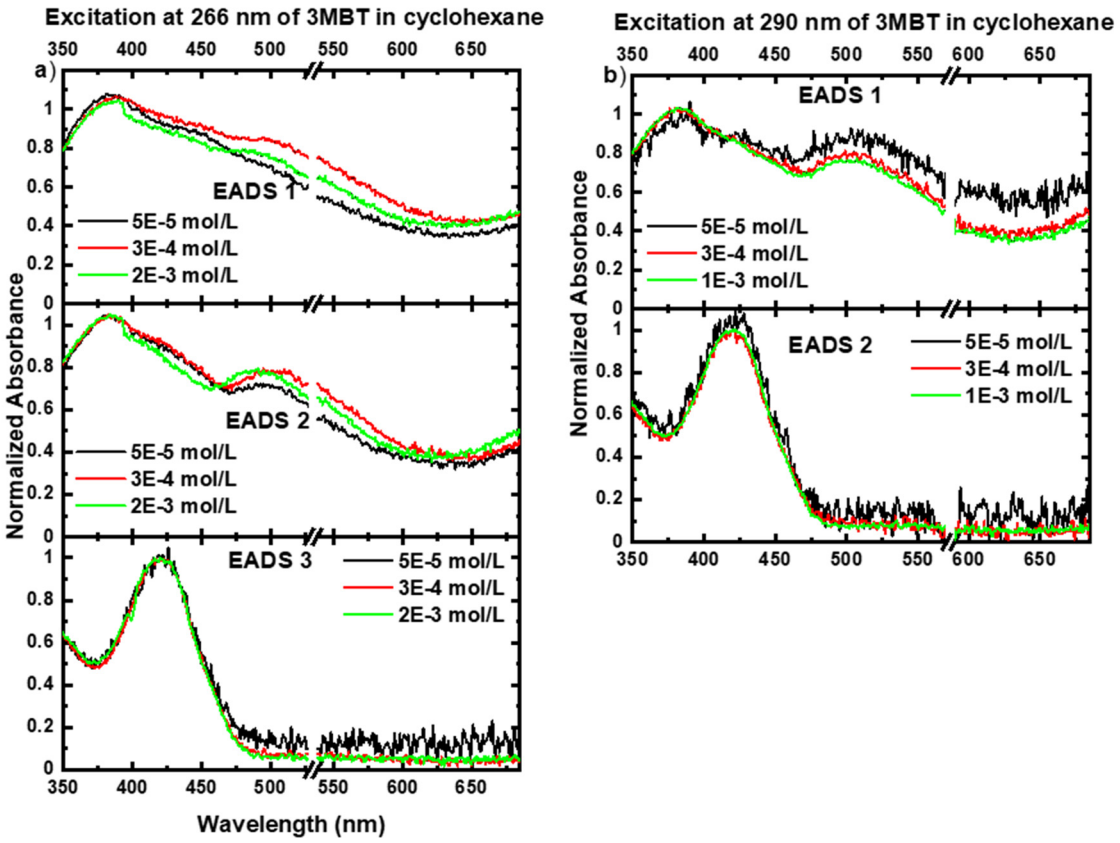

Figure S6. Evolution associated difference spectra of 3-methylbenzothiophene in cyclohexane at excitation of a) 266 nm and b) 290 nm were obtained from global and target analysis. The break is included to remove the overtone signal that comes from the excitation source.

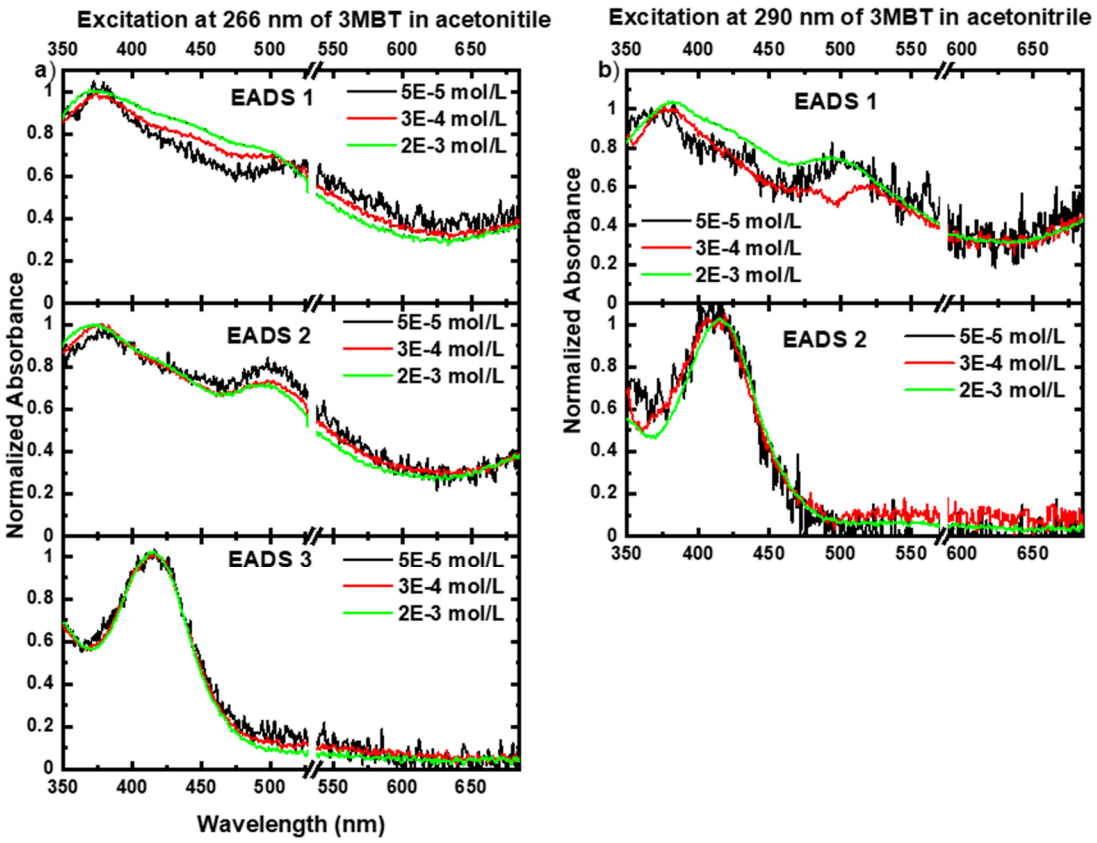

Figure S7. Evolution associated difference spectra of 3-methylbenzothiophene in acetonitrile at excitation of a) 266 nm and b) 290 nm were obtained from global and target analysis. The break is included to remove the overtone signal that comes from the excitation source.

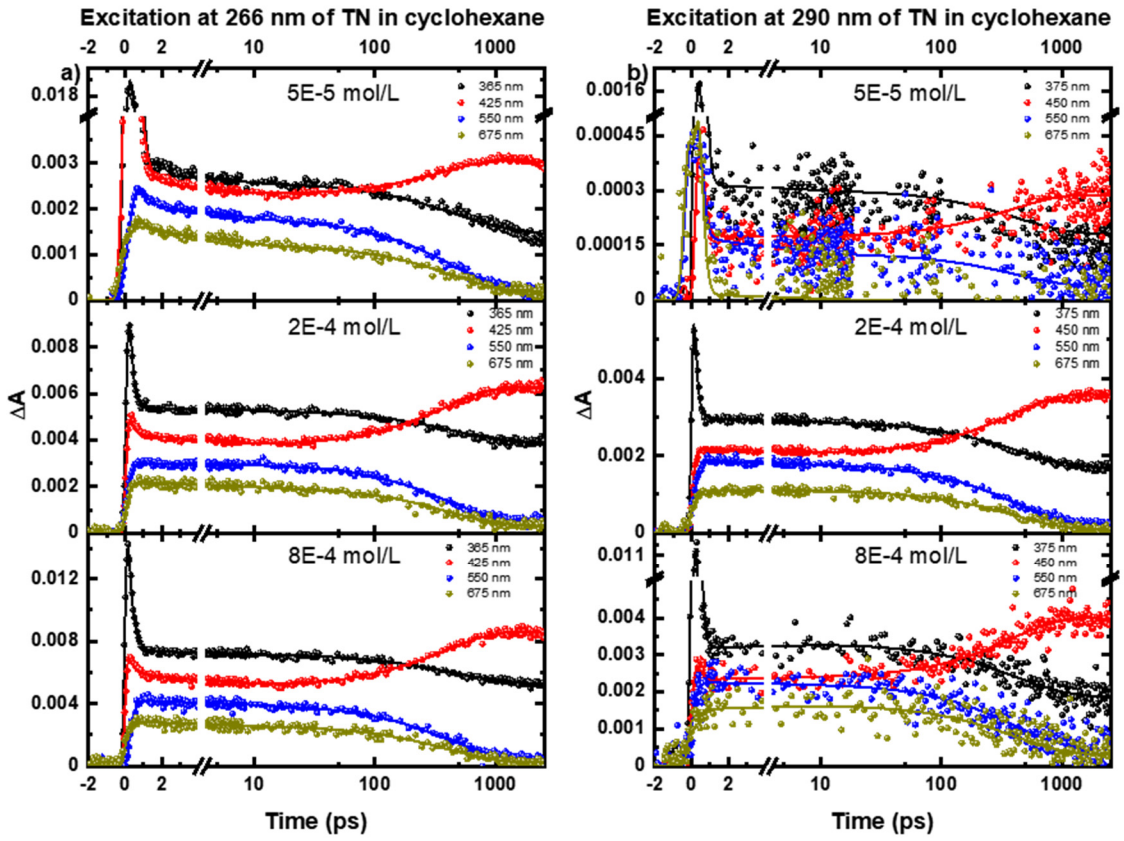

Figure S8. Representative kinetic traces of varying concentrations of thianaphthene in cyclohexane at excitation of a) 266 nm and b) 290 nm performed with Glotaran using a 4-component model.

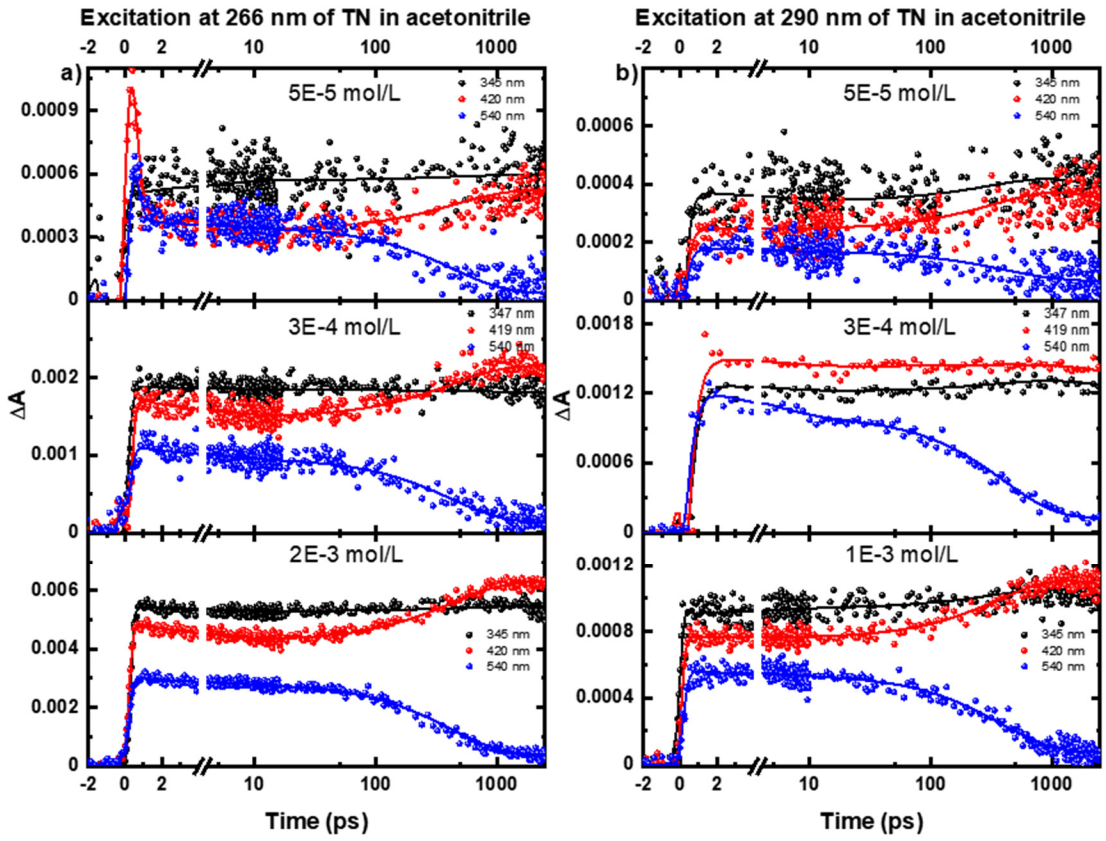

Figure S9. Representative kinetic traces of varying concentrations of thianaphthene in acetonitrile at excitation of a) 266 nm and b) 290 nm performed with Glotaran using a 3-component model.

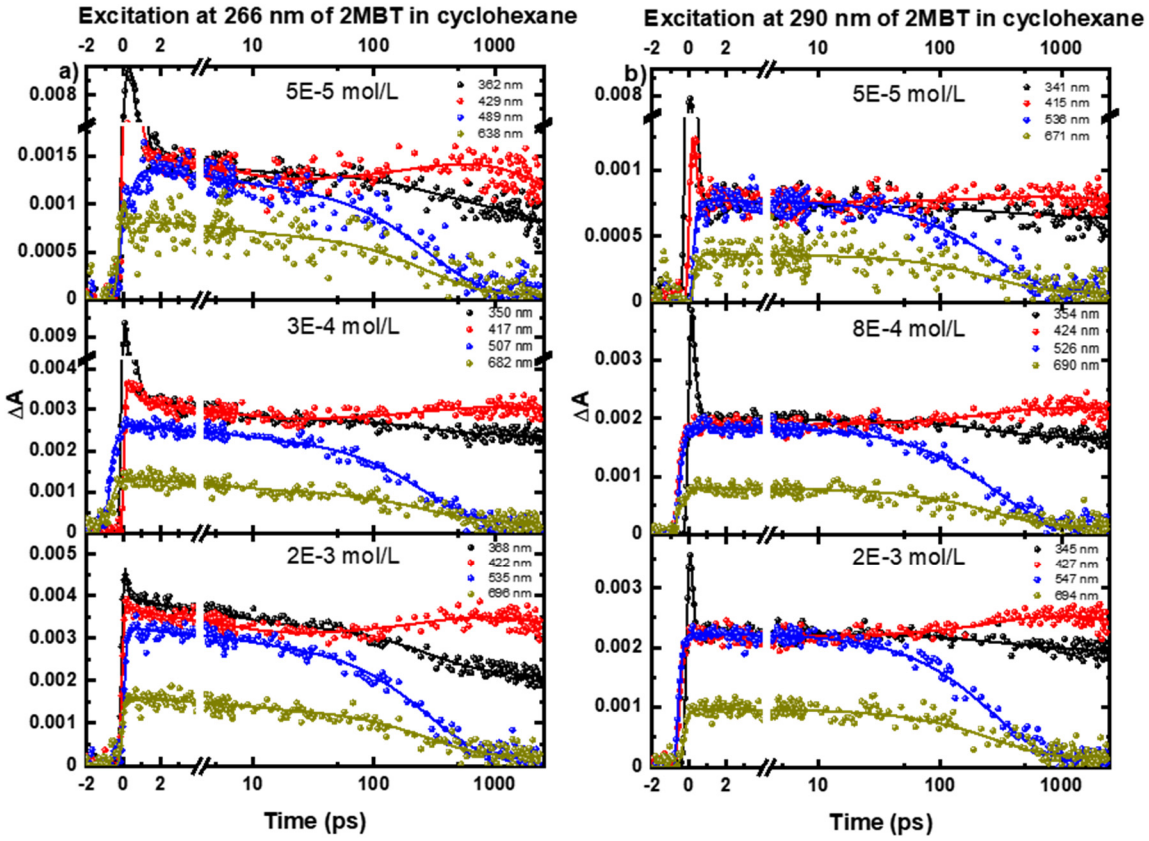

Figure S10. Representative kinetic traces of varying concentrations of 2-methylbenzothiophene in cyclohexane at excitation of a) 266 nm and b) 290 nm performed with Glotaran using a 4-component model for 266 nm and a 3-component model for 290 nm.

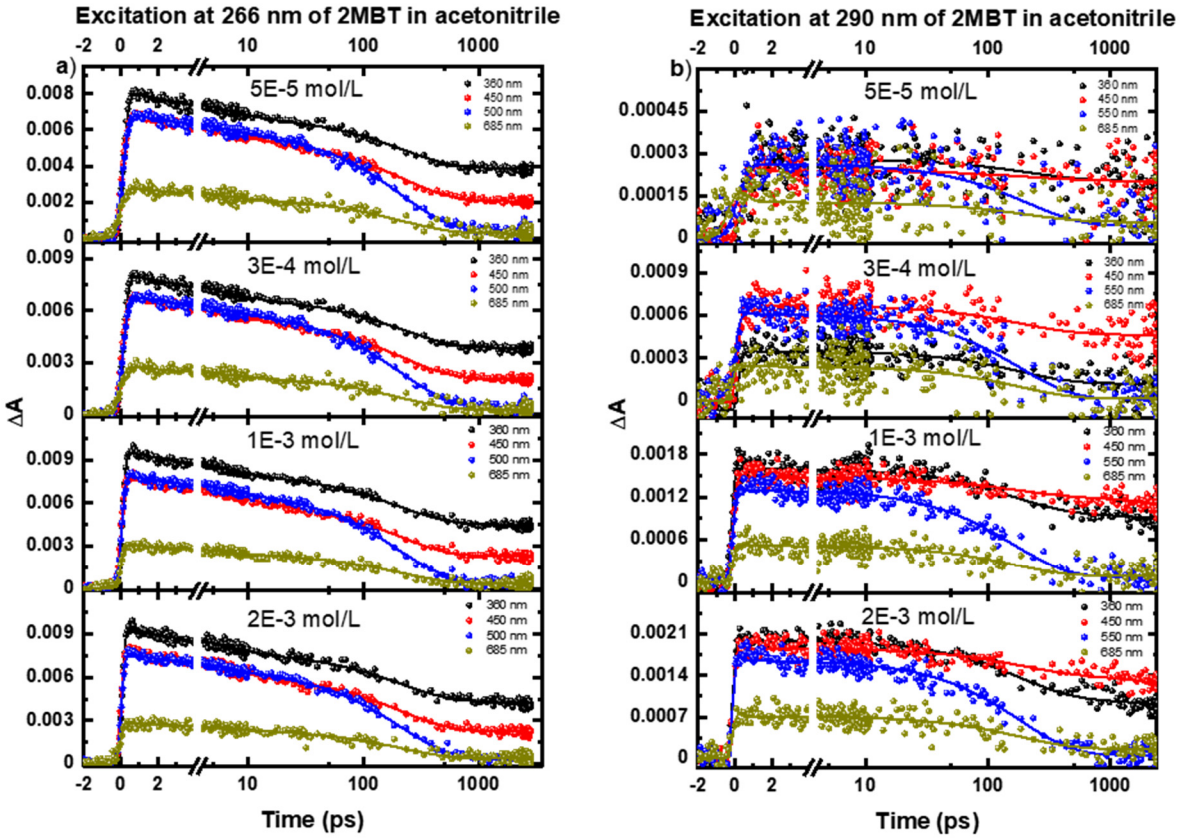

Figure S11. Representative kinetic traces of varying concentrations of 2-methylbenzothiophene in acetonitrile at excitation of a) 266 nm and b) 290 nm performed with Glotaran using a 3-component model for 266 nm and a 2-component model for 290 nm.

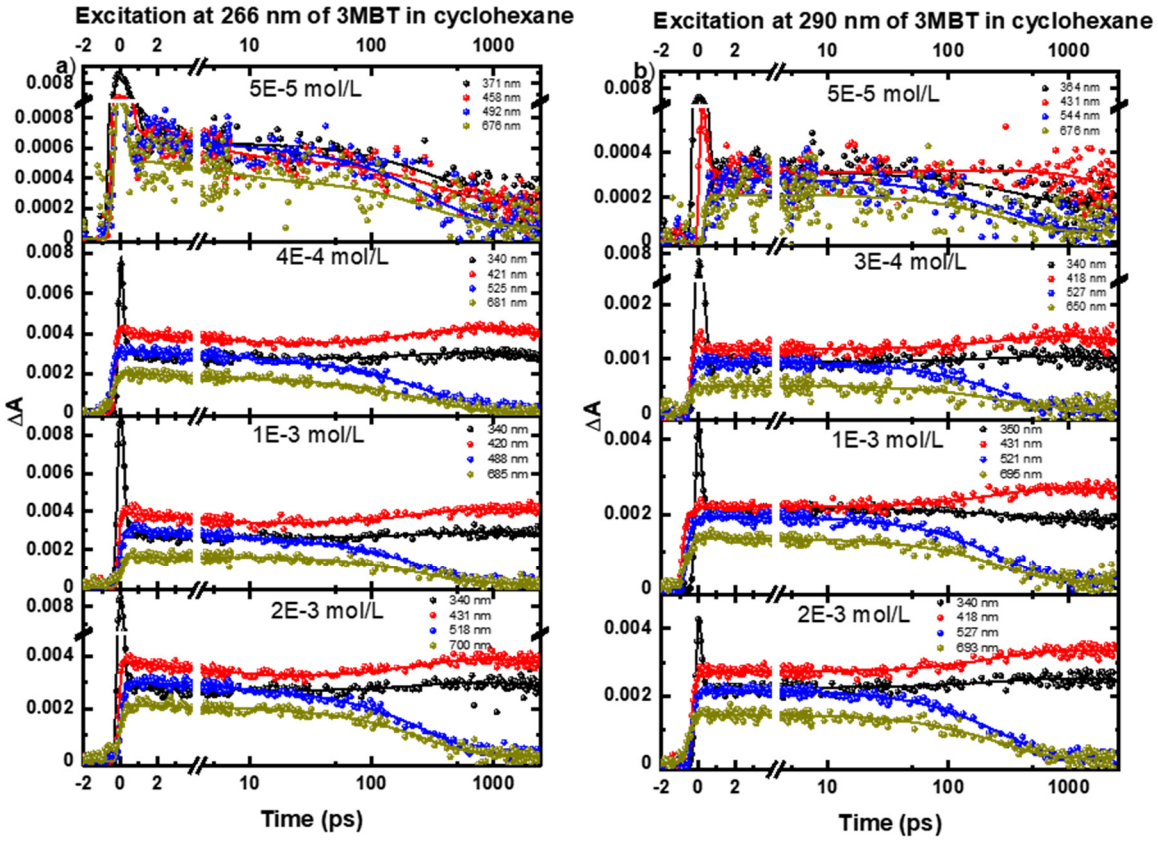

Figure S12. Representative kinetic traces of varying concentrations of 3-methylbenzothiophene in cyclohexane at excitation of a) 266 nm and b) 290 nm performed with Glotaran using a 4-component model for 266 nm and a 3-component model for 290 nm.

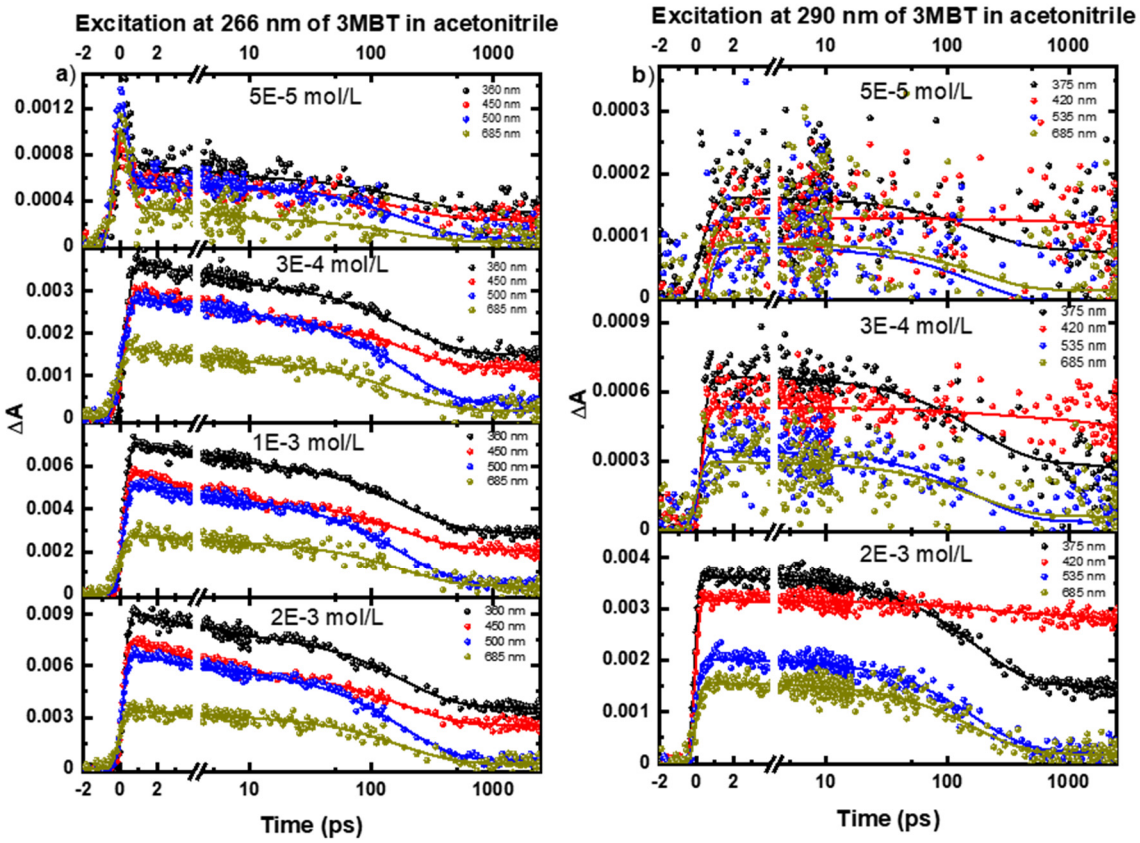

Figure S13. Representative kinetic traces of varying concentrations of 3-methylbenzothiophene in acetonitrile at excitation of a) 266 nm and b) 290 nm performed with Glotaran using a 3-component model for 266 nm and a 2-component model for 290 nm.

Table S1. Vertical excitation energies, electronic structure, and oscillator strengths of TN in acetonitrile at ground state minimum geometry obtained at TDA-PBE0/CPCM/def2-TZVPD level of theory. Components of electronic structure with a contribution less than 0.10 are omitted.

State	Electronic Structure												VEE/eV	f(r)
$S_1(\pi\pi^*)$	H	→	L	0.49;	H-1	→	L	0.21;	H	→	L+1	0.16;	4.76	0.0835
$S_2(\pi\pi^*)$	H	→	L+1	0.47;	H	→	L	0.33;	H-1	→	L+1	0.14;	4.98	0.0417
$S_3(\pi\sigma^*)$	H-1	→	L+2	0.92;									5.35	0.0000
$S_4(\pi\pi^*)$	H-1	→	L	0.50;	H	→	L+1	0.27;					5.68	0.4748
$T_1(\pi\pi^*)$	H	→	L	0.83;									3.42	
$T_2(\pi\pi^*)$	H	→	L+1	0.71;									4.12	
$T_3(\pi\pi^*)$	H-1	→	L	0.77;	H	→	L	0.11;					4.20	
$T_4(\pi\pi^*)$	H-1	→	L+1	0.75;	H	→	L+1	0.13;					4.56	
$T_5(\pi\pi^*)$	H	→	L+5	0.47;	H-2	→	L	0.29;					4.96	
$T_6(\pi\sigma^*)$	H-1	→	L+2	0.81;									5.08	

Table S2. Vertical excitation energies, electronic structure, and oscillator strengths of TN in cyclohexane at ground state minimum geometry obtained at TDA-PBE0/CPCM/def2-TZVPD level of theory. Components of electronic structure with a contribution less than 0.10 are omitted.

State	Electronic Structure												VEE/eV	f(r)
$S_1(\pi\pi^*)$	H	→	L	0.53;	H-1	→	L	0.20;	H	→	L+1	0.14;	4.74	0.0912
$S_2(\pi\pi^*)$	H	→	L+1	0.48;	H	→	L	0.30;	H-1	→	L+1	0.16;	4.97	0.0415
$S_3(\pi\sigma^*)$	H-1	→	L+2	0.92;									5.29	0.0000
$S_4(\pi\pi^*)$	H-1	→	L	0.50;	H	→	L+1	0.29;					5.65	0.5325
$T_1(\pi\pi^*)$	H	→	L	0.82;									3.41	
$T_2(\pi\pi^*)$	H	→	L+1	0.70;									4.11	
$T_3(\pi\pi^*)$	H-1	→	L	0.76;	H	→	L	0.10;					4.18	
$T_4(\pi\pi^*)$	H-1	→	L+1	0.75;	H	→	L+1	0.13;					4.56	
$T_5(\pi\pi^*)$	H	→	L+5	0.47;	H-2	→	L	0.29;					4.95	
$T_6(\pi\sigma^*)$	H-1	→	L+2	0.82;									5.03	

Table S3. Vertical excitation energies, electronic structure, and oscillator strengths of 2MBT in vacuum at ground state minimum geometry obtained at TDA-PBE0/def2-TZVPD level of theory. Components of electronic structure with a contribution less than 0.10 are omitted.

State	Electronic Structure													VEE/eV	f(r)
$S_1(\pi\pi^*)$	H-1	→	L	0.31;	H	→	L	0.31;	H	→	L+1	0.25;		4.74	0.0378
$S_2(\pi\pi^*)$	H	→	L	0.45;	H	→	L+1	0.36;						4.98	0.0637
$S_3(\pi\sigma^*)$	H	→	L+2	0.88;										5.15	0.0004
$S_4(\pi\sigma^*)$	H-1	→	L+2	0.76;										5.60	0.0332
$T_1(\pi\pi^*)$	H	→	L	0.82;										3.41	
$T_2(\pi\pi^*)$	H	→	L+1	0.58;	H-1	→	L	0.19;						4.10	
$T_3(\pi\pi^*)$	H-1	→	L	0.63;	H-1	→	L+1	0.16;	H	→	L	0.12;		4.16	
$T_4(\pi\pi^*)$	H-1	→	L+1	0.63;	H	→	L+1	0.24;						4.44	
$T_5(\pi\sigma^*)$	H	→	L+2	0.75;										4.89	
$T_6(\pi\pi^*)$	H-1	→	L+5	0.49;	H-2	→	L	0.26;						4.93	

Table S4. Vertical excitation energies, electronic structure, and oscillator strengths of 2MBT in acetonitrile at ground state minimum geometry obtained at TDA-PBE0/CPCM/def2-TZVPD level of theory. Components of electronic structure with a contribution less than 0.10 are omitted.

State	Electronic Structure												VEE/eV	f(r)
$S_1(\pi\pi^*)$	H-1	→	L	0.30;	H	→	L	0.30;	H	→	L+1	0.30;	4.73	0.0662
$S_2(\pi\pi^*)$	H	→	L	0.49;	H	→	L+1	0.34;					4.95	0.1079
$S_3(\pi\sigma^*)$	H	→	L+2	0.90;									5.26	0.0003
$S_4(\pi\pi^*)$	H-1	→	L	0.52;	H	→	L+1	0.28;					5.53	0.4220
$T_1(\pi\pi^*)$	H	→	L	0.83;									3.42	
$T_2(\pi\pi^*)$	H	→	L+1	0.63;	H-1	→	L+1	0.12;	H-1	→	L	0.11	4.11	
$T_3(\pi\pi^*)$	H-1	→	L	0.69;	H-1	→	L+1	0.16;					4.20	
$T_4(\pi\pi^*)$	H-1	→	L+1	0.60;	H	→	L+1	0.25;	H-1	→	L	0.12	4.44	
$T_5(\pi\pi^*)$	H	→	L+4	0.47;	H-2	→	L	0.26;					4.95	
$T_6(\pi\sigma^*)$	H-1	→	L+2	0.77;									5.00	

Table S5. Vertical excitation energies, electronic structure, and oscillator strengths of 2MBT in cyclohexane at ground state minimum geometry obtained at TDA-PBE0/CPCM/def2-TZVPD level of theory. Components of electronic structure with a contribution less than 0.10 are omitted.

State	Electronic Structure												VEE/eV	f(r)
$S_1(\pi\pi^*)$	H	→	L	0.35;	H-1	→	L	0.29;	H	→	L+1	0.26;	4.72	0.0763
$S_2(\pi\pi^*)$	H	→	L	0.46;	H	→	L+1	0.36;					4.95	0.1086
$S_3(\pi\sigma^*)$	H	→	L+2	0.89;									5.20	0.0004
$S_4(\pi\pi^*)$	H-1	→	L	0.51;	H	→	L+1	0.30;					5.52	0.4700
$T_1(\pi\pi^*)$	H	→	L	0.83;									3.42	
$T_2(\pi\pi^*)$	H	→	L+1	0.60;	H-1	→	L	0.15;	H-1	→	L+1	0.11;	4.10	
$T_3(\pi\pi^*)$	H-1	→	L	0.67;	H-1	→	L+1	0.16;	H	→	L	0.11;	4.18	
$T_4(\pi\pi^*)$	H-1	→	L+1	0.62;	H	→	L+1	0.25;	H-1	→	L	0.10	4.44	
$T_5(\pi\pi^*)$	H	→	L+5	0.48;	H-2	→	L	0.25;					4.94	
$T_6(\pi\sigma^*)$	H	→	L+2	0.76;									4.95	

Table S6. Vertical excitation energies, electronic structure, and oscillator strengths of 3MBT in the vacuum at ground state minimum geometry obtained at TDA-PBE0/def2-TZVPD level of theory. Components of electronic structure with a contribution less than 0.10 are omitted.

State	Electronic Structure												VEE/eV	f(r)
$S_1(\pi\pi^*)$	H	→	L	0.64;	H-1	→	L	0.15;	H-1	→	L+1	0.10;	4.71	0.0634
$S_2(\pi\pi^*)$	H	→	L+1	0.60;	H-1	→	L	0.19;	H	→	L	0.16;	4.85	0.0058
$S_3(\pi\sigma^*)$	H	→	L+2	0.89;									5.16	0.0004
$S_4(\pi\sigma^*)$	H	→	L+3	0.94;									5.59	0.0028
$T_1(\pi\pi^*)$	H	→	L	0.84;									3.36	
$T_2(\pi\pi^*)$	H	→	L+1	0.69;									4.07	
$T_3(\pi\pi^*)$	H-1	→	L	0.80;									4.17	
$T_4(\pi\pi^*)$	H-1	→	L+1	0.73;	H	→	L+1	0.15;					4.52	
$T_5(\pi\sigma^*)$	H	→	L+5	0.41;	H-2	→	L	0.37	H	→	L+1	0.10	4.86	
$T_6(\pi\pi^*)$	H	→	L+2	0.80;									4.88	

Table S7. Vertical excitation energies, electronic structure, and oscillator strengths of 3MBT in acetonitrile at ground state minimum geometry obtained at TDA-PBE0/CPCM/def2-TZVPD level of theory. Components of electronic structure with a contribution less than 0.10 are omitted.

State	Electronic Structure	VEE/eV	f(r)
$S_1(\pi\pi^*)$	H → L 0.66; H-1 → L 0.14;	4.70	0.1099
$S_2(\pi\pi^*)$	H → L+1 0.62; H → L 0.18; H-1 → L 0.16;	4.83	0.0095
$S_3(\pi\sigma^*)$	H → L+2 0.91;	5.24	0.0000
$S_4(\pi\sigma^*)$	H → L+3 0.96;	5.62	0.0041
$T_1(\pi\pi^*)$	H → L 0.85;	3.38	
$T_2(\pi\pi^*)$	H → L+1 0.71; H-1 → L+1 0.10	4.08	
$T_3(\pi\pi^*)$	H-1 → L 0.80;	4.22	
$T_4(\pi\pi^*)$	H-1 → L+1 0.71; H → L+1 0.15; H-1 → L 0.11	4.53	
$T_5(\pi\pi^*)$	H → L+5 0.39; H-2 → L 0.38	4.88	
$T_6(\pi\sigma^*)$	H → L+2 0.83;	4.96	

Table S8. Vertical excitation energies, electronic structure, and oscillator strengths of 3MBT in cyclohexane at ground state minimum geometry obtained at TDA-PBE0/CPCM/def2-TZVPD level of theory. Components of electronic structure with a contribution less than 0.10 are omitted.

State	Electronic Structure	VEE/eV	f(r)
$S_1(\pi\pi^*)$	H → L 0.70; H-1 → L 0.12;	4.68	0.1171
$S_2(\pi\pi^*)$	H → L+1 0.63; H-1 → L 0.19; H → L 0.14;	4.83	0.0076
$S_3(\pi\sigma^*)$	H → L+2 0.91;	5.20	0.0000
$S_4(\pi\pi^*)$	H-1 → L 0.55; H → L+1 0.25	5.61	0.6461
$T_1(\pi\pi^*)$	H → L 0.84;	3.37	
$T_2(\pi\pi^*)$	H → L+1 0.70;	4.08	
$T_3(\pi\pi^*)$	H-1 → L 0.80;	4.19	
$T_4(\pi\pi^*)$	H-1 → L+1 0.72; H → L+1 0.15;	4.53	
$T_5(\pi\pi^*)$	H → L+5 0.40; H-2 → L 0.38 H → L+1 0.10	4.87	
$T_6(\pi\sigma^*)$	H → L+2 0.82;	4.93	

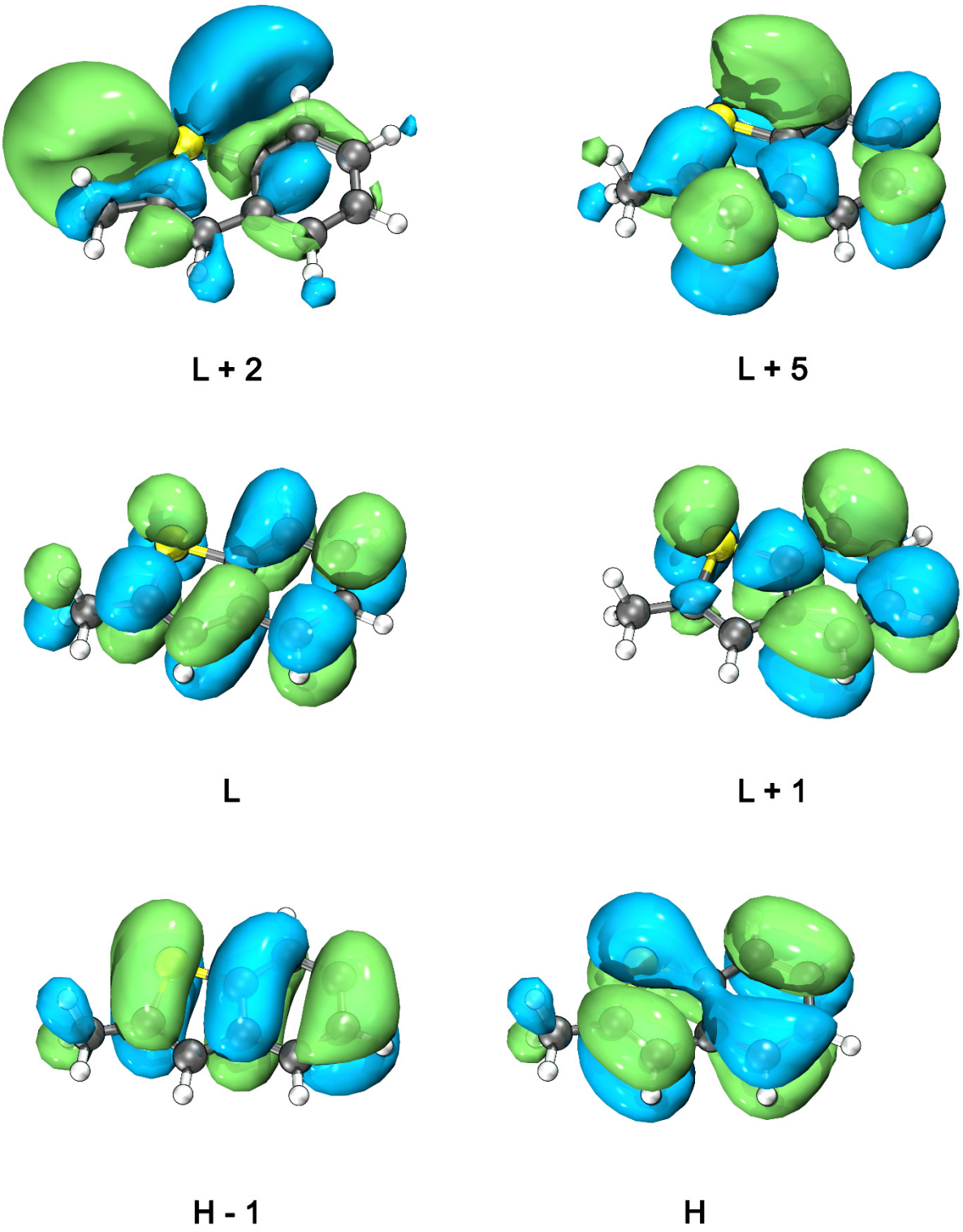

Figure S14. Electron density of 2MBT frontier Kohn-Sham orbitals at the S_0 minimum in vacuum, contour value of the isosurfaces was set to 0.02. Visualized by Multiwfn[2] and VMD[3].

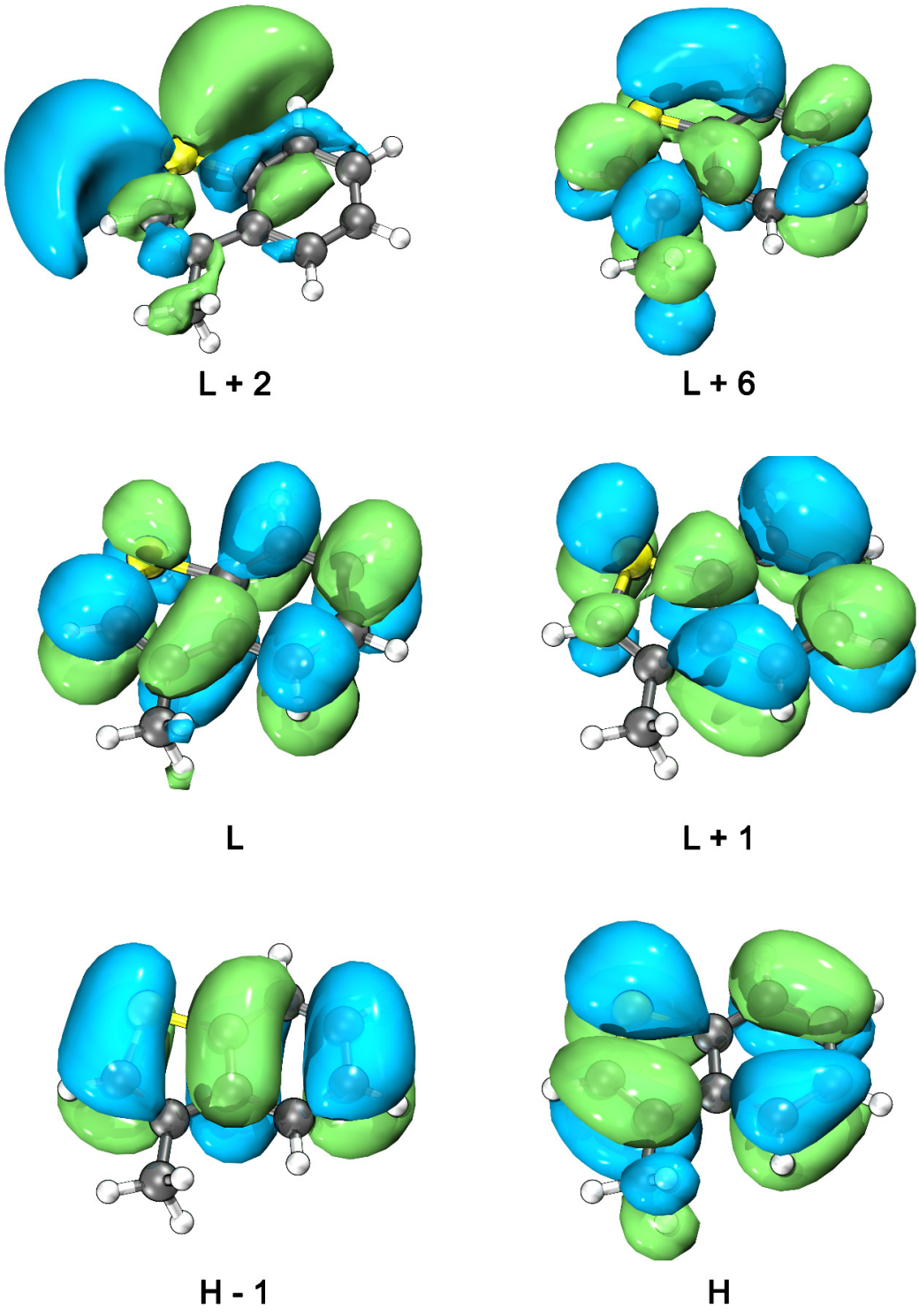

Figure S15. Electron density of 3MBT frontier Kohn-Sham orbitals at the S_0 minimum in vacuum, contour value of the isosurfaces was set to 0.02. Visualized by Multiwfn[2] and VMD[3].

Table S9. Vertical energies in acetonitrile at TN $S_1(\pi\pi^*)$ minimum, S-C2 stretched and S-C7a stretched $S_1(\pi\sigma^*)$ minima, respectively, relative to the ground state minimum energy.

$S_1(\pi\pi^*)$ minimum			S-C2 stretched $S_1(\pi\sigma^*)$ minimum			S-C7a stretched $S_1(\pi\sigma^*)$ minimum		
State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}
$S_1(\pi\pi^*)$	4.66	-	$S_1(\pi\sigma^*)$	4.54	-	$S_1(\pi\sigma^*)$	4.16	-
$T_1(\pi\pi^*)$	3.14	0.0	$T_1(\pi\sigma^*)$	4.14	0.7	$T_1(\pi\sigma^*)$	3.82	0.2
$T_2(\pi\pi^*)$	4.12	0.0	$T_2(\sigma\sigma^*)$	5.00	91.4	$T_2(\sigma\sigma^*)$	4.92	73.0
$T_3(\pi\pi^*)$	4.34	0.0	$T_3(\pi\sigma^*)$	5.14	0.4	$T_3(\pi\pi^*)$	5.46	50.0
$T_4(\pi\pi^*)$	4.88	0.0	$T_4(\pi\pi^*)$	5.92	42.1	$T_4(\pi\sigma^*)$	5.58	0.6
$T_5(\pi\pi^*)$	4.95	0.0						
$T_6(\pi\sigma^*)$	5.32	30.0						

Table S10. Vertical energies in cyclohexane at TN $S_1(\pi\pi^*)$ minimum, S-C2 stretched and S-C7a stretched $S_1(\pi\sigma^*)$ minima, respectively, relative to the ground state minimum energy.

$S_1(\pi\pi^*)$ minimum			S-C2 stretched $S_1(\pi\sigma^*)$ minimum			S-C7a stretched $S_1(\pi\sigma^*)$ minimum		
State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}
$S_1(\pi\pi^*)$	4.64	-	$S_1(\pi\sigma^*)$	4.51	-	$S_1(\pi\sigma^*)$	4.16	-
$T_1(\pi\pi^*)$	3.13	0.0	$T_1(\pi\sigma^*)$	4.10	0.7	$T_1(\pi\sigma^*)$	3.81	0.3
$T_2(\pi\pi^*)$	4.12	0.0	$T_2(\sigma\sigma^*)$	5.00	92.4	$T_2(\sigma\sigma^*)$	4.92	74.3
$T_3(\pi\pi^*)$	4.32	0.0	$T_3(\pi\sigma^*)$	5.18	0.3	$T_3(\pi\pi^*)$	5.46	51.4
$T_4(\pi\pi^*)$	4.88	0.0	$T_4(\pi\pi^*)$	5.93	43.5	$T_4(\pi\sigma^*)$	5.62	0.6
$T_5(\pi\pi^*)$	4.94	0.0						
$T_6(\pi\sigma^*)$	5.27	22.6						

Table S11. Vertical energies in vacuum at 2MBT $S_1(\pi\pi^*)$ minimum, S-C2 stretched and S-C7a stretched $S_1(\pi\sigma^*)$ minima, respectively, relative to the ground state minimum energy.

$S_1(\pi\pi^*)$ minimum			S-C2 stretched $S_1(\pi\sigma^*)$ minimum			S-C7a stretched $S_1(\pi\sigma^*)$ minimum		
State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}
$S_1(\pi\pi^*)$	4.65	-	$S_1(\pi\sigma^*)$	4.28	-	$S_1(\pi\sigma^*)$	4.14	-
$T_1(\pi\pi^*)$	3.27	0.0	$T_1(\pi\sigma^*)$	3.88	0.6	$T_1(\pi\sigma^*)$	3.80	0.3
$T_2(\pi\pi^*)$	4.00	0.0	$T_2(\sigma\sigma^*)$	4.69	93.2	$T_2(\sigma\sigma^*)$	5.01	68.1
$T_3(\pi\pi^*)$	4.10	0.0	$T_3(\pi\sigma^*)$	5.00	1.5	$T_3(\pi\pi^*)$	5.41	49.0
$T_4(\pi\pi^*)$	4.93	0.0	$T_4(\pi\pi^*)$	5.74	39.5	$T_4(\pi\sigma^*)$	5.54	0.6
$T_5(\pi\pi^*)$	5.05	0.1						
$T_6(\pi\sigma^*)$	5.49	25.8						

Table S12. Vertical energies in acetonitrile at 2MBT $S_1(\pi\pi^*)$ minimum, S-C2 stretched and S-C7a stretched $S_1(\pi\sigma^*)$ minima, respectively, relative to the ground state minimum energy.

$S_1(\pi\pi^*)$ minimum			S-C2 stretched $S_1(\pi\sigma^*)$ minimum			S-C7a stretched $S_1(\pi\sigma^*)$ minimum		
State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}
$S_1(\pi\pi^*)$	4.63	-	$S_1(\pi\sigma^*)$	4.34	-	$S_1(\pi\sigma^*)$	4.13	-
$T_1(\pi\pi^*)$	3.28	0.0	$T_1(\pi\sigma^*)$	3.96	0.6	$T_1(\pi\sigma^*)$	3.81	0.3
$T_2(\pi\pi^*)$	4.03	0.0	$T_2(\sigma\sigma^*)$	4.71	90.7	$T_2(\sigma\sigma^*)$	5.01	65.3
$T_3(\pi\pi^*)$	4.12	0.0	$T_3(\pi\sigma^*)$	4.93	1.8	$T_3(\pi\pi^*)$	5.41	46.8
$T_4(\pi\pi^*)$	4.94	0.0	$T_4(\pi\pi^*)$	5.69	36.5	$T_4(\pi\sigma^*)$	5.51	0.6
$T_5(\pi\pi^*)$	5.16	0.1						
$T_6(\pi\sigma^*)$	5.59	26.0						

Table S13. Vertical energies in cyclohexane at 2MBT $S_1(\pi\pi^*)$ minimum, S-C2 stretched and S-C7a stretched $S_1(\pi\sigma^*)$ minima, respectively, relative to the ground state minimum energy.

$S_1(\pi\pi^*)$ minimum			S-C2 stretched $S_1(\pi\sigma^*)$ minimum			S-C7a stretched $S_1(\pi\sigma^*)$ minimum		
State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}
$S_1(\pi\pi^*)$	4.62	-	$S_1(\pi\sigma^*)$	4.31	-	$S_1(\pi\sigma^*)$	4.14	-
$T_1(\pi\pi^*)$	3.28	0.0	$T_1(\pi\sigma^*)$	3.92	0.7	$T_1(\pi\sigma^*)$	3.81	0.3
$T_2(\pi\pi^*)$	4.02	0.0	$T_2(\sigma\sigma^*)$	4.70	92.5	$T_2(\sigma\sigma^*)$	5.01	67.1
$T_3(\pi\pi^*)$	4.11	0.0	$T_3(\pi\sigma^*)$	4.98	1.5	$T_3(\pi\pi^*)$	5.41	48.0
$T_4(\pi\pi^*)$	4.40	0.0	$T_4(\pi\pi^*)$	5.72	38.3	$T_4(\pi\sigma^*)$	5.53	0.6
$T_5(\pi\pi^*)$	4.94	0.1						
$T_6(\pi\sigma^*)$	5.10	26.0						

Table S14. Vertical energies in vacuum at 3MBT $S_1(\pi\pi^*)$ minimum, S-C2 stretched and S-C7a stretched $S_1(\pi\sigma^*)$ minima, respectively, relative to the ground state minimum energy.

$S_1(\pi\pi^*)$ minimum			S-C2 stretched $S_1(\pi\sigma^*)$ minimum			S-C7a stretched $S_1(\pi\sigma^*)$ minimum		
State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}
$S_1(\pi\pi^*)$	4.52	-	$S_1(\pi\sigma^*)$	4.55	-	$S_1(\pi\sigma^*)$	4.11	-
$T_1(\pi\pi^*)$	3.17	0.0	$T_1(\pi\sigma^*)$	4.13	0.8	$T_1(\pi\sigma^*)$	3.75	0.3
$T_2(\pi\pi^*)$	4.07	0.0	$T_2(\sigma\sigma^*)$	5.14	91.5	$T_2(\sigma\sigma^*)$	5.05	67.8
$T_3(\pi\pi^*)$	4.46	0.0	$T_3(\pi\sigma^*)$	5.16	5.9	$T_3(\pi\pi^*)$	5.28	61.8
$T_4(\pi\pi^*)$	4.84	0.0	$T_4(\pi\pi^*)$	5.88	46.4	$T_4(\pi\sigma^*)$	5.65	0.5
$T_5(\pi\pi^*)$	4.92	0.0						
$T_6(\pi\sigma^*)$	5.17	9.7						

Table S15. Vertical energies in acetonitrile at 3MBT $S_1(\pi\pi^*)$ minimum, S-C2 stretched and S-C7a stretched $S_1(\pi\sigma^*)$ minima, respectively, relative to the ground state minimum energy.

$S_1(\pi\pi^*)$ minimum			S-C2 stretched $S_1(\pi\sigma^*)$ minimum			S-C7a stretched $S_1(\pi\sigma^*)$ minimum		
State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}
$S_1(\pi\pi^*)$	4.50	-	$S_1(\pi\sigma^*)$	4.62	-	$S_1(\pi\sigma^*)$	4.09	-
$T_1(\pi\pi^*)$	3.19	0.0	$T_1(\pi\sigma^*)$	4.21	0.8	$T_1(\pi\sigma^*)$	3.76	0.3
$T_2(\pi\pi^*)$	4.07	0.0	$T_2(\pi\sigma^*)$	5.08	1.6	$T_2(\sigma\sigma^*)$	5.05	66.4
$T_3(\pi\pi^*)$	4.50	0.0	$T_3(\sigma\sigma^*)$	5.15	90.2	$T_3(\pi\pi^*)$	5.28	58.6
$T_4(\pi\pi^*)$	4.84	0.0	$T_4(\pi\pi^*)$	5.87	43.9	$T_4(\pi\sigma^*)$	5.60	0.5
$T_5(\pi\pi^*)$	4.93	0.0						
$T_6(\pi\sigma^*)$	5.24	9.8						

Table S16. Vertical energies in cyclohexane at 3MBT $S_1(\pi\pi^*)$ minimum, S-C2 stretched and S-C7a stretched $S_1(\pi\sigma^*)$ minima, respectively, relative to the ground state minimum energy.

$S_1(\pi\pi^*)$ minimum			S-C2 stretched $S_1(\pi\sigma^*)$ minimum			S-C7a stretched $S_1(\pi\sigma^*)$ minimum		
State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}	State	E/eV	$\langle T_n\|\hat{H}_{SO}\|S_1\rangle$/cm^{-1}
$S_1(\pi\pi^*)$	4.48	-	$S_1(\pi\sigma^*)$	4.58	-	$S_1(\pi\sigma^*)$	4.09	-
$T_1(\pi\pi^*)$	3.18	0.0	$T_1(\pi\sigma^*)$	4.17	0.8	$T_1(\pi\sigma^*)$	3.76	0.3
$T_2(\pi\pi^*)$	4.07	0.0	$T_2(\pi\sigma^*)$	5.13	9.5	$T_2(\sigma\sigma^*)$	5.05	67.4
$T_3(\pi\pi^*)$	4.48	0.0	$T_3(\sigma\sigma^*)$	5.14	90.8	$T_3(\pi\pi^*)$	5.28	60.4
$T_4(\pi\pi^*)$	4.84	0.0	$T_4(\pi\pi^*)$	5.87	45.4	$T_4(\pi\sigma^*)$	5.60	0.5
$T_5(\pi\pi^*)$	4.92	0.0						
$T_6(\pi\sigma^*)$	5.20	10.4						

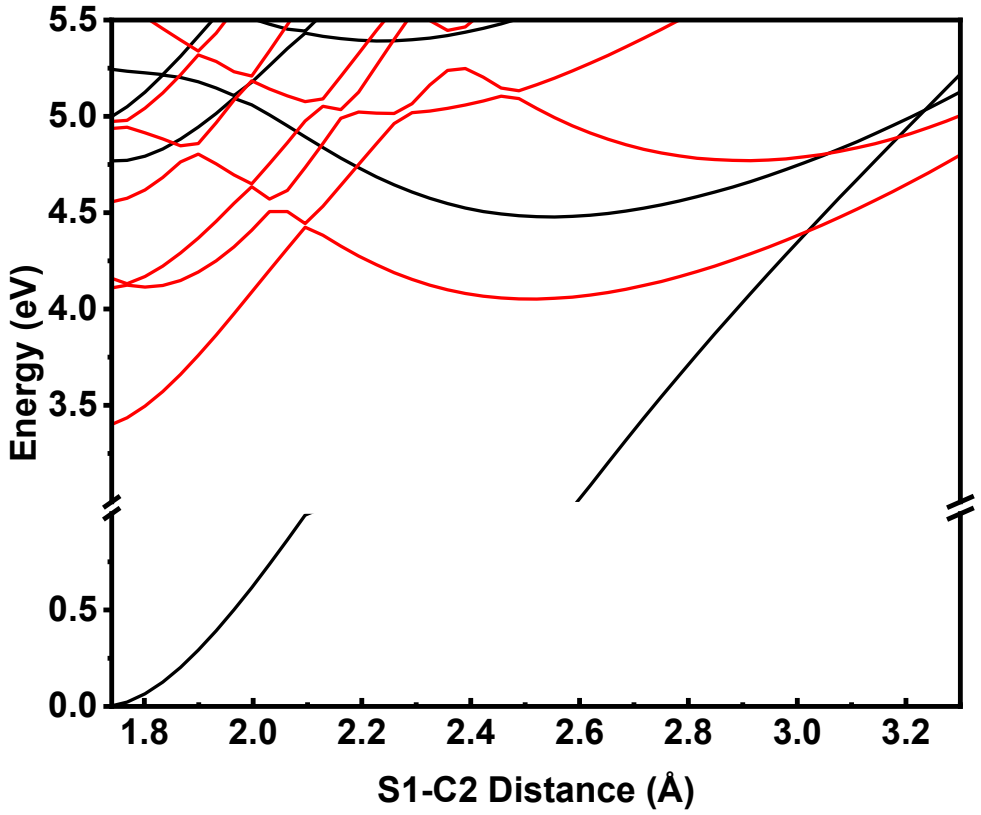

Figure S16. Single point energy of linear interpolated geometries between TN ground state minimum and S-C2 stretched $S_1(\pi\sigma^*)$ minimum in the vacuum. Points of each step are connected with straight lines. Singlet states are black lines and triplet states are red lines. The horizontal break is introduced to better highlight the excited state topography.

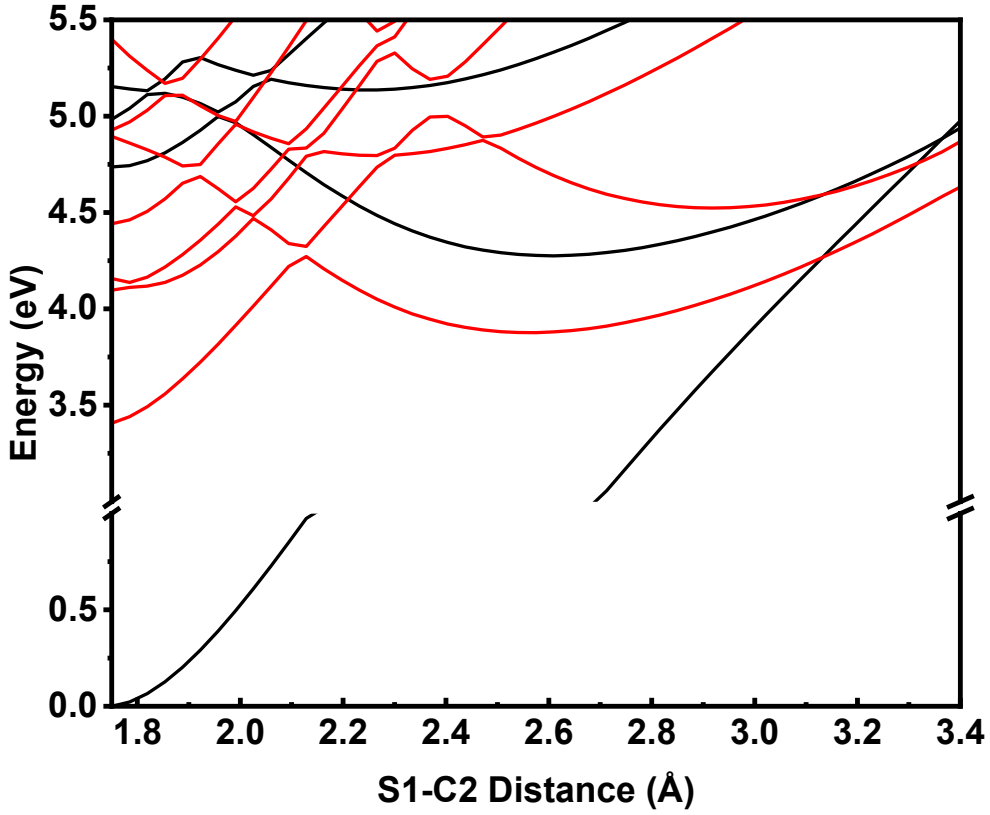

Figure S17. Single point energy of linear interpolated geometries between 2MBT ground state minimum and S-C2 stretched $S_1(\pi\sigma^*)$ minimum in the vacuum. Points of each step are connected with straight lines. Singlet states are black lines and triplet states are red lines. The horizontal break is introduced to better highlight the excited state topography.

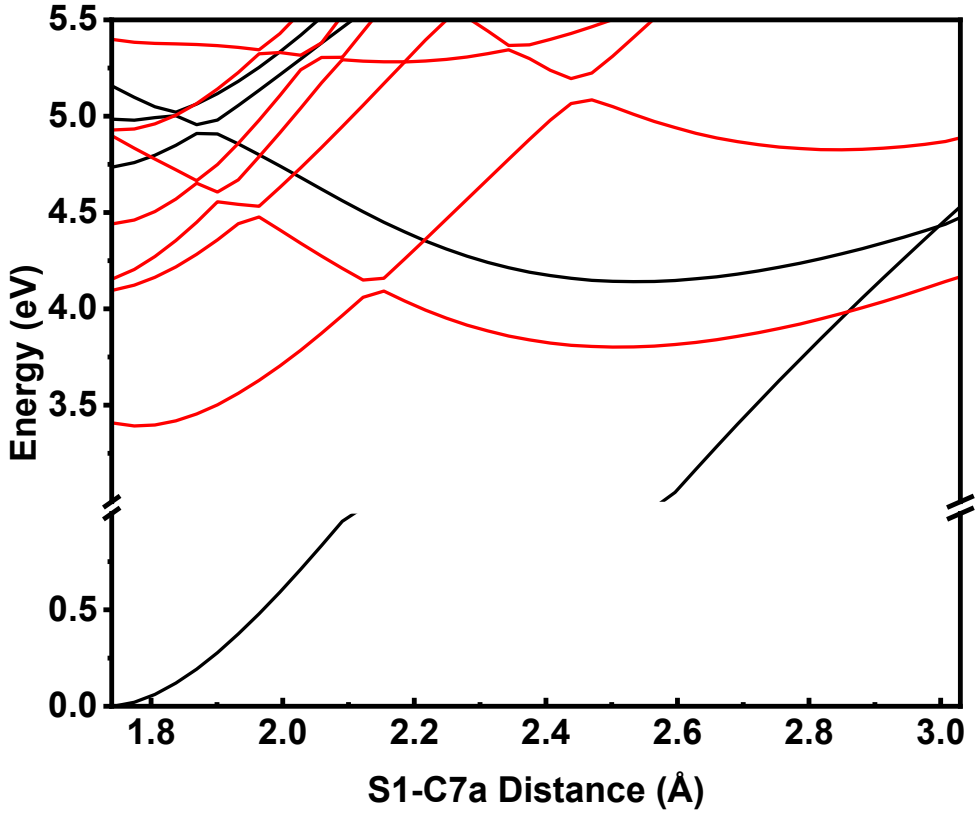

Figure S18. Single point energy of linear interpolated geometries between 2MBT ground state minimum and S-C7a stretched $S_1(\pi\sigma^*)$ minimum in the vacuum. Points of each step are connected with straight lines. Singlet states are black lines and triplet states are red lines. The horizontal break is introduced to better highlight the excited state topography.

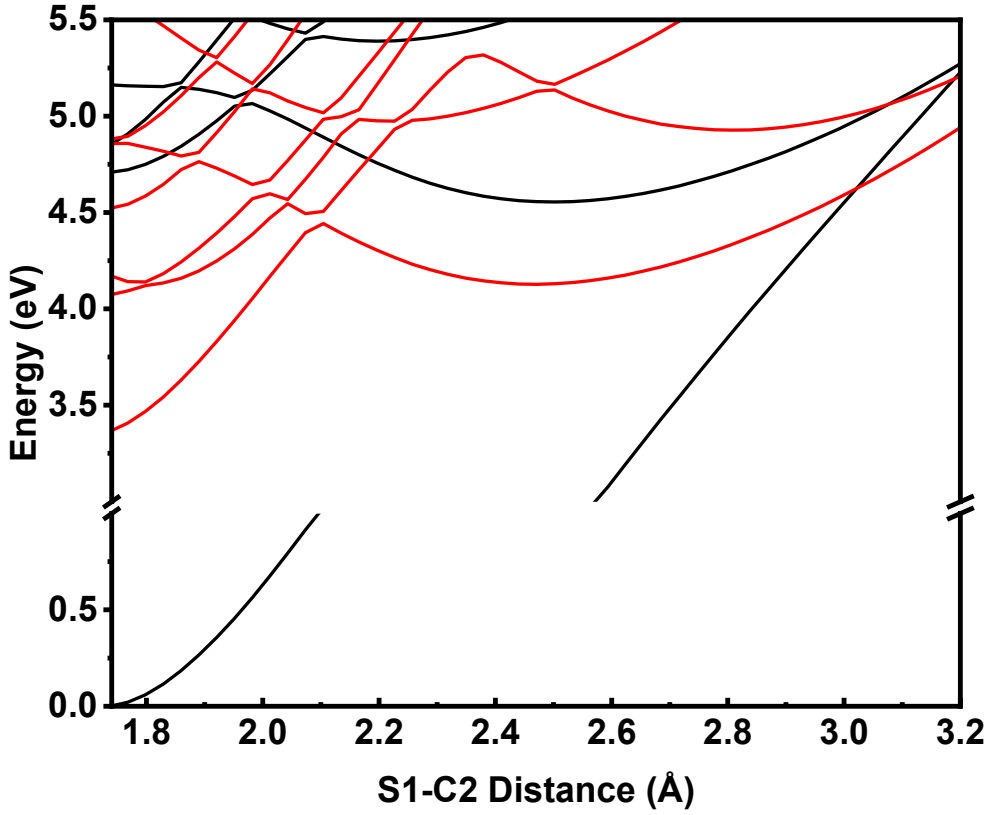

Figure S19. Single point energy of linear interpolated geometries between 3MBT ground state minimum and S-C2 stretched $S_1(\pi\sigma^*)$ minimum in the vacuum. Points of each step are connected with straight lines. Singlet states are black lines and triplet states are red lines. The horizontal break is introduced to better highlight the excited state topography.

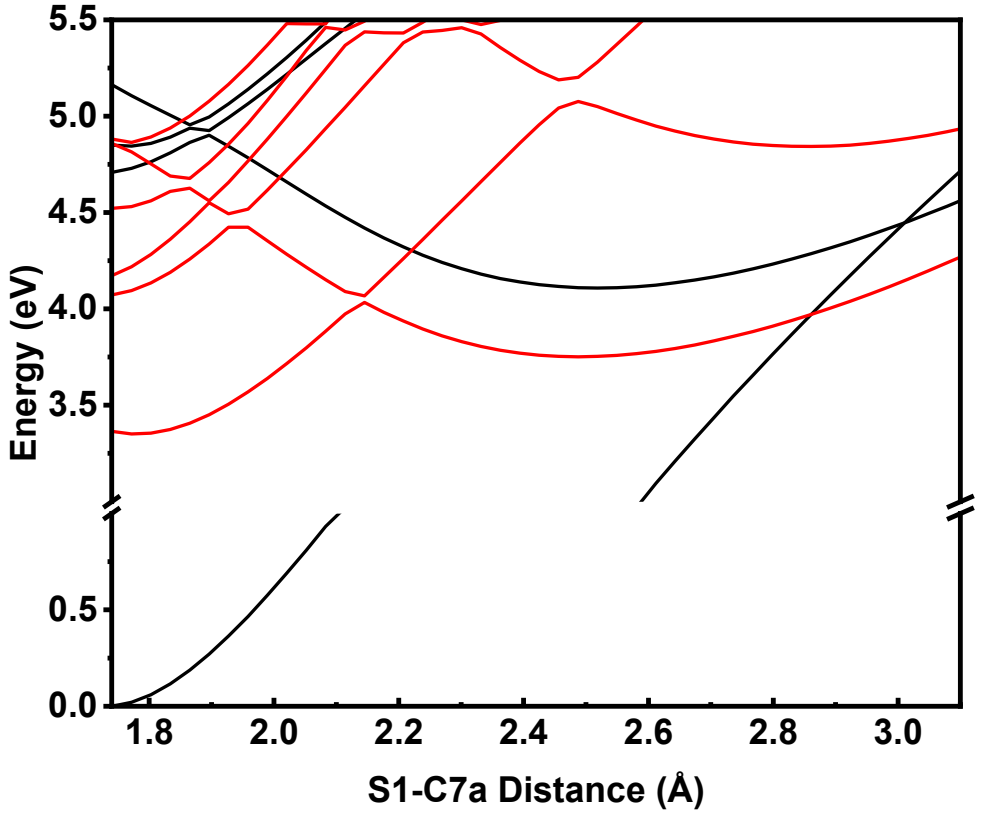

Figure S20. Single point energy of linear interpolated geometries between 3MBT ground state minimum and S-C7a stretched $S_1(\pi\sigma^*)$ minimum in the vacuum. Points of each step are connected with straight lines. Singlet states are black lines and triplet states are red lines. The horizontal break is introduced to better highlight the excited state topography.

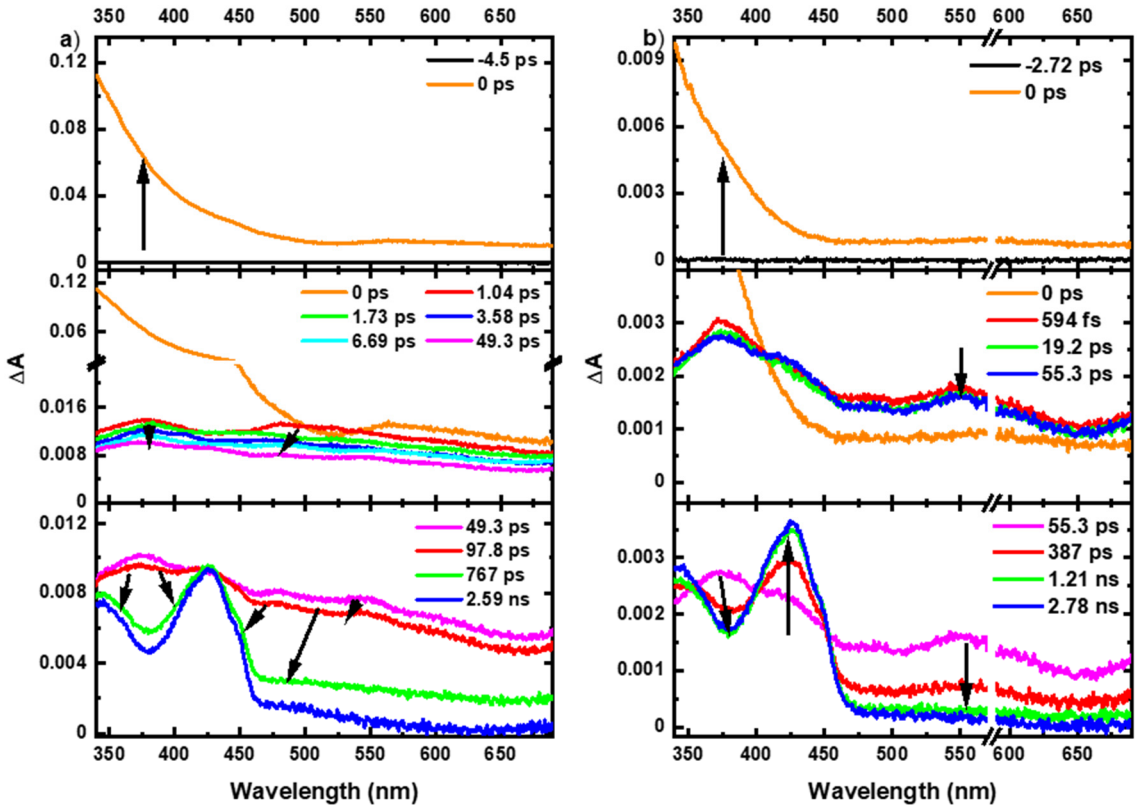

Figure S21. Spectral evolution of the transient absorption spectra of thianaphthene in cyclohexane after excitation of (a) 266 nm and (b) 290 nm. Breaks on the horizontal axis were used to exclude the overtone signal produced from the excitation source. The arrows displayed in these figures are not used to highlight specific wavelengths but to draw attention to trends. The spectra at a time delay of 0 ps is due to the coherent signal of the solvent.

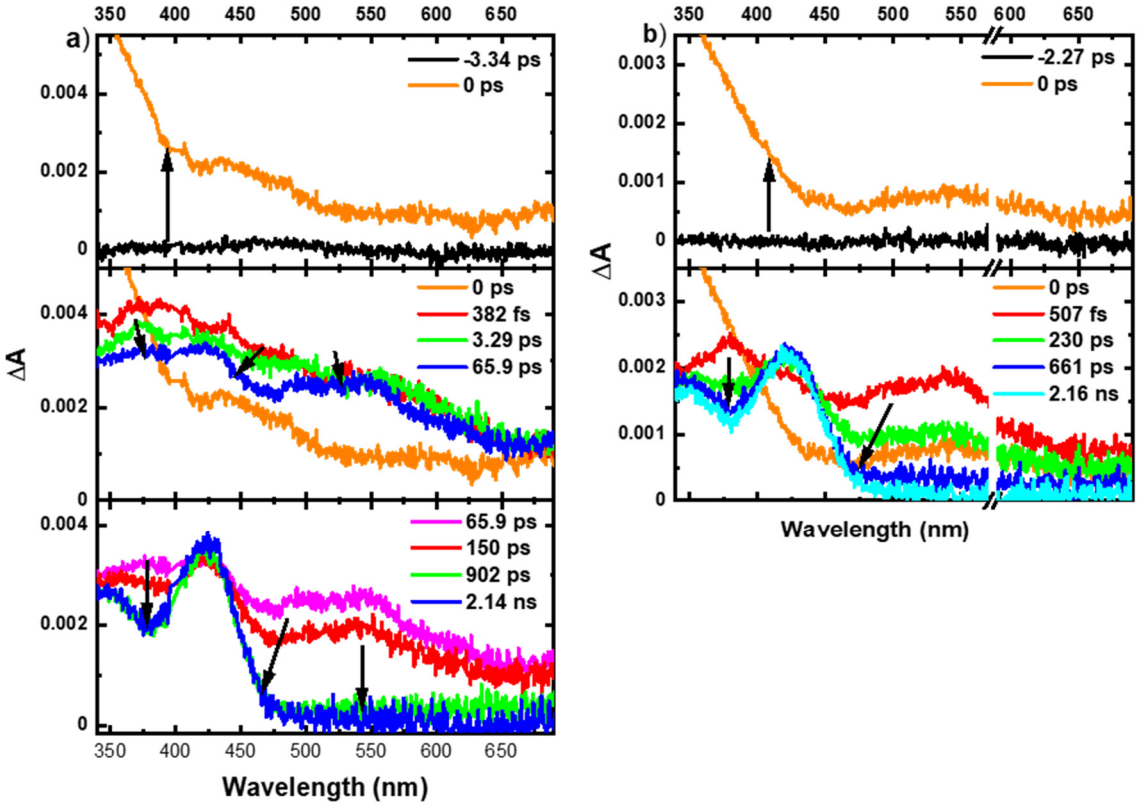

Figure S22. Spectral evolution of the transient absorption spectra of 2-methylbenzothiophene in cyclohexane after excitation of (a) 266 nm and (b) 290 nm. Breaks on the horizontal axis were used to exclude the overtone signal produced from the excitation source. The arrows displayed in these figures are not used to highlight specific wavelengths but to draw attention to trends. The spectra at a time delay of 0 ps is due to the coherent signal of the solvent.

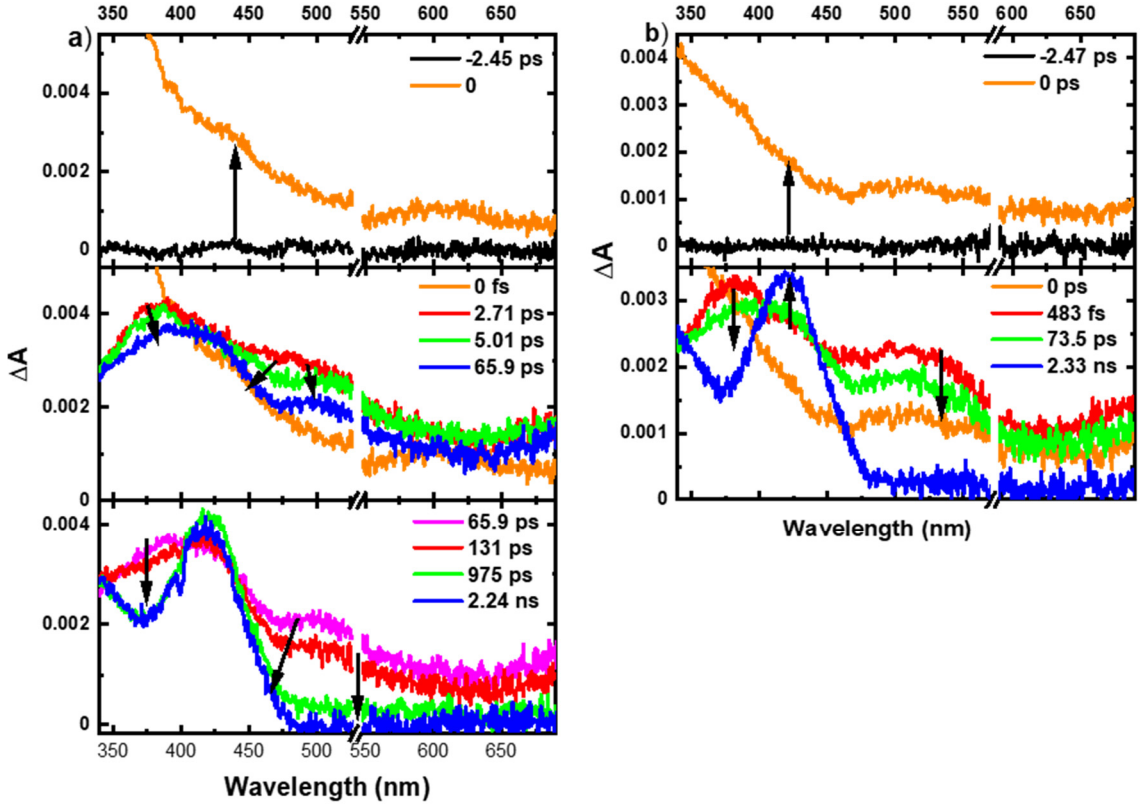

Figure S23. Spectral evolution of the transient absorption spectra of 3-methylbenzothiophene in cyclohexane after excitation of (a) 266 nm and (b) 290 nm. Breaks on the horizontal axis were used to exclude the overtone signal produced from the excitation source. The arrows displayed in these figures are not used to highlight specific wavelengths but to draw attention to trends. The spectra at a time delay of 0 ps is due to the coherent signal of the solvent.

Table S17. Band peaks of EADS of TN, 2MBT, and 3MBT obtained from femtosecond broadband transient absorption measurements in cyclohexane and acetonitrile. Values in parentheses indicate shoulders.

Compound	Solvent	Ex. λ (nm)	EADS1 (λ_{abs}/nm)	EADS2 (λ_{abs}/nm)	EADS3 (λ_{abs}/nm)
TN	Acetonitrile	266	370, (445), 558	353, 548	421
		290	376, (485), 548	382, 541	422
	Cyclohexane	266	378, 557	483, 549	425
		290	373, 485, 550	377, 485, 550	425
2MBT	Acetonitrile	266	372, 523	375, 509	418
		290	-	377, 540	417
	Cyclohexane	266	382, (423), 546	377, (419), 498, 545	423
		290	-	377, (419), 498, 545	423
3MBT	Acetonitrile	266	373, (500)	372, 497	417
		290	-	380, 493	416
	Cyclohexane	266	388, (494)	384, 502	420
		290	-	384, 502	420

Cartesian Coordinates of Optimized Geometries of Thianapthene Derivatives in Angstrom

Thianapthene Ground State Geometry

C	-3.97754971	2.46994205	0.00019918
C	-5.06171040	1.61637047	0.00029748
C	-4.88253403	0.22775757	0.00005642
C	-3.61857468	-0.32120128	-0.00025123
C	-2.50007267	0.51989259	-0.00033923
C	-2.70030388	1.91579645	-0.00013636
H	-4.11696423	3.54448214	0.00020935
H	-6.06436208	2.02732998	0.00047037
H	-5.75050491	-0.42094360	0.00013304
H	-3.48438124	-1.39716359	-0.00033656
C	-1.10934038	0.18524798	-0.00027826
C	-0.31267777	1.27873796	0.00028604
S	-1.19290710	2.75914022	-0.00097548
H	-0.73316622	-0.82936933	-0.00011985
H	0.76689929	1.30647040	0.00078510

Thianapthene $S_1(\pi\pi^*)$ Geometry

C	-3.96453617	2.48325450	0.00008081
C	-5.10315880	1.60046845	0.00005285
C	-4.91117550	0.24083573	0.00002333
C	-3.62126987	-0.33757683	-0.00001043
C	-2.48801045	0.51115688	-0.00006013
C	-2.71137025	1.90843120	0.00004898
H	-4.09629718	3.55737460	0.00012421
H	-6.10142726	2.01773140	0.00005437
H	-5.77272064	-0.41755751	0.00003076
H	-3.50095088	-1.41381772	0.00001104

C	-1.11128482	0.19042645	-0.00013361
C	-0.25584387	1.30079273	0.00002647
S	-1.18268078	2.73325416	0.00020045
H	-0.73773459	-0.82631946	-0.00030062
H	0.82031101	1.33403542	-0.00014848

Thianapthene $S_1(\pi\sigma^*)$, S-C2 Elongation Geometry

C	-4.90097597	2.84020443	0.55036819
C	-5.92662876	1.93516378	0.55417782
C	-5.64011925	0.56254437	0.56408362
C	-4.32918441	0.11338689	0.57006210
C	-3.26550367	1.00242644	0.56643130
C	-3.54349536	2.41291873	0.55625972
H	-5.09394560	3.90564138	0.54275237
H	-6.95520670	2.27432636	0.54959007
H	-6.45251274	-0.15499758	0.56710936
H	-4.12263861	-0.95125098	0.57773138
C	-1.88617999	0.54796826	0.57260232
C	-0.89806059	1.41793286	0.56875952
S	-2.30911306	3.54711382	0.55124877
H	-1.73368405	-0.53702585	0.58042798
H	0.17378871	1.24780707	0.57229547

Thianapthene $S_1(\pi\sigma^*)$, S-C7a Elongation Geometry

C	-4.83536407	2.88059131	0.56958621
C	-5.89759307	1.96573496	0.56336381
C	-5.65749690	0.59368691	0.56242872
C	-4.36167978	0.12084184	0.56765916
C	-3.28630025	1.03453076	0.57393831
C	-3.55464164	2.40486052	0.57474749

H	-5.04661757	3.94618215	0.57019998
H	-6.92089421	2.32864600	0.55921682
H	-6.48990975	-0.09949624	0.55758885
H	-4.16334849	-0.94687693	0.56697958
C	-1.93355239	0.62144603	0.57951068
C	-0.89104838	1.55043496	0.58565522
S	-1.10374307	3.19139892	0.58712907
H	-1.69125723	-0.43696911	0.57904949
H	0.12696681	1.16845792	0.58973661

Thianapthene $T_1(\pi\pi^*)$ Geometry

C	-3.94346015	2.46599006	-0.00061622
C	-5.07526032	1.59413529	0.01395165
C	-4.90114668	0.22021121	0.01738773
C	-3.63310644	-0.34057263	0.00875615
C	-2.48456265	0.50357987	-0.01127747
C	-2.70194970	1.92364196	-0.01846161
H	-4.08883357	3.53967181	-0.00696608
H	-6.07108890	2.01907393	0.01315253
H	-5.76992478	-0.42775077	0.02782033
H	-3.50321513	-1.41631478	0.01602673
C	-1.15592674	0.16648986	-0.05187162
C	-0.25073470	1.34159338	-0.09491800
S	-1.15829058	2.79657891	-0.05822011
H	-0.78094087	-0.84803076	-0.08128899
H	0.78029121	1.34419267	0.22652498

Thianapthene $T_1(\pi\sigma^*)$, S-C2 Elongation Geometry

C	-4.92079997	2.84549503	0.55025764
C	-5.93795649	1.92363442	0.55423981

C	-5.63240364	0.55919462	0.56415339
C	-4.31637413	0.13536770	0.56994941
C	-3.25910594	1.04381353	0.56614766
C	-3.56359028	2.44250406	0.55599623
H	-5.13104076	3.90793115	0.54259400
H	-6.97052050	2.25100844	0.54973067
H	-6.43206772	-0.17254665	0.56732964
H	-4.09095736	-0.92546102	0.57763686
C	-1.89242893	0.56472135	0.57243736
C	-0.83468517	1.35674220	0.56938289
S	-2.35011398	3.61737878	0.55071213
H	-1.77642221	-0.52293596	0.58010505
H	0.22500706	1.13731233	0.57322727

Thianapthene $T_1(\pi\sigma^*)$, S-C7a Elongation Geometry

C	-4.89373731	2.89388713	0.56933645
C	-5.93117863	1.95911339	0.56320505
C	-5.65282083	0.59235700	0.56244987
C	-4.34725627	0.14733465	0.56775971
C	-3.28304804	1.07433610	0.57400373
C	-3.60615044	2.42890505	0.57453732
H	-5.11460836	3.95623027	0.56990164
H	-6.96235721	2.29726167	0.55899147
H	-6.46742871	-0.12205215	0.55766486
H	-4.12890015	-0.91630475	0.56717841
C	-1.92589058	0.64954511	0.57958275
C	-0.84554539	1.52162718	0.58582560
S	-0.97399922	3.17729928	0.58769787
H	-1.72326620	-0.41815239	0.57892432

H	0.14970733	1.08208248	0.58973096

2-Methylbenzothiophene Ground State Geometry

C	-1.58002849	-1.32734454	-0.00002287
C	-2.77969753	-0.64214816	0.00000589
C	-2.80522813	0.75607727	0.00003984
C	-1.63352029	1.48429184	0.00004713
C	-0.40486381	0.81680174	0.00001587
C	-0.39974135	-0.59243819	-0.00002074
H	-1.56032554	-2.41081195	-0.00006222
H	-3.71113830	-1.19604209	-0.00000585
H	-3.75852427	1.27164375	0.00005995
H	-1.65876165	2.56845381	0.00007806
C	0.92267038	1.34979113	0.00003539
C	1.88835531	0.39994954	0.00004674
S	1.21856182	-1.20231578	-0.00009144
H	1.14409171	2.41014262	0.00009030
C	3.36303148	0.59049369	0.00005031
H	3.82589644	0.13760250	0.88093845
H	3.60044896	1.65502912	0.00064727
H	3.82574193	0.13863190	-0.88145154

2-Methylbenzothiophene $S_1(\pi\pi^*)$ Geometry

C	-1.56944938	-1.33527865	-0.08400725
C	-2.82448428	-0.63251945	-0.01715193
C	-2.83729353	0.74131758	0.04872450
C	-1.65115929	1.49818576	0.06771638
C	-0.40205188	0.82529809	0.03989165
C	-0.41742757	-0.58859633	-0.04455636
H	-1.54509938	-2.41508067	-0.15434456

H	-3.74965766	-1.19390395	-0.02325600
H	-3.78721001	1.26255756	0.08885463
H	-1.68794203	2.57998536	0.10857140
C	0.90703468	1.34308617	0.02656449
C	1.93425118	0.37757244	-0.09890792
S	1.22625445	-1.17853958	-0.10189126
H	1.13211584	2.40151006	0.09229229
C	3.39414336	0.58282628	-0.00598229
H	3.75424753	0.60126329	1.03631057
H	3.66960239	1.54062854	-0.45561008
H	3.95109425	-0.20250430	-0.52281771

2-Methylbenzothiophene $S_1(\pi\sigma^*)$, S-C2 Elongation Geometry

C	-4.88241867	2.83079664	0.69157747
C	-5.91378267	1.93955710	0.59735955
C	-5.63892940	0.56775456	0.46990479
C	-4.33577673	0.11111920	0.43894410
C	-3.25967678	0.98816662	0.53231606
C	-3.52667684	2.39798991	0.66338619
H	-5.06774079	3.89301370	0.79050031
H	-6.93972985	2.28629237	0.62052350
H	-6.45767323	-0.13863398	0.39519477
H	-4.13600336	-0.95027145	0.34023021
C	-1.89682825	0.51223974	0.50029929
C	-0.87854676	1.34584354	0.58903948
S	-2.28945401	3.52449679	0.78197958
H	-1.75546490	-0.57257764	0.39896486
C	0.56882896	1.19840108	0.58893531
H	0.99751347	1.60448761	1.51101141

H	0.88948766	0.14790226	0.49339402
H	1.01395250	1.76814343	-0.23336134

2-Methylbenzothiophene $S_1(\pi\sigma^*)$, S-C7a Elongation Geometry

C	-4.83948504	2.86723614	0.76702899
C	-5.89821147	1.96188847	0.60613406
C	-5.65162124	0.60570890	0.40527676
C	-4.35352542	0.14061314	0.36288275
C	-3.28229810	1.04557372	0.52558931
C	-3.55566822	2.40127913	0.72650664
H	-5.05637864	3.92073437	0.92206860
H	-6.92317592	2.31913966	0.63830659
H	-6.48048505	-0.08109431	0.28226952
H	-4.15039658	-0.91470839	0.20534204
C	-1.93132624	0.63697000	0.49042611
C	-0.86865935	1.54388878	0.64750822
S	-1.13572640	3.17014233	0.87754728
H	-1.69435227	-0.41223067	0.33507132
C	0.53023823	1.00958940	0.63304410
H	0.62069575	0.15410701	-0.04064955
H	1.24259994	1.78033504	0.34437848
H	0.79925926	0.66768627	1.63808235

2-Methylbenzothiophene $T_1(\pi\pi^*)$ Geometry

C	-1.52848555	-1.31617894	-0.10178483
C	-2.75535059	-0.63505162	0.09509015
C	-2.78676019	0.75072619	0.19028674
C	-1.62455732	1.49520553	0.10085567
C	-0.37931169	0.84137965	-0.10043582
C	-0.38321705	-0.58942342	-0.20881734

H	-1.51552168	-2.39666645	-0.18246805
H	-3.67429162	-1.20479500	0.15759079
H	-3.73489945	1.25435851	0.33851918
H	-1.65097033	2.57553815	0.18340075
C	0.87549506	1.38535285	-0.24638789
C	1.95978830	0.37389882	-0.43059036
S	1.24767748	-1.21070248	-0.50270135
H	1.08677991	2.44743354	-0.25401824
C	3.31786803	0.56554753	0.12399704
H	3.30052300	0.62033420	1.22614122
H	3.75399265	1.50148504	-0.23675408
H	3.98820973	-0.25063387	-0.15152304

2-Methylbenzothiophene $T_1(\pi\sigma^*)$, S-C2 Elongation Geometry

C	-4.93723925	2.83786083	0.69159947
C	-5.94634231	1.91409828	0.59446602
C	-5.62832998	0.55705483	0.46904072
C	-4.31046587	0.14711053	0.44283983
C	-3.25649276	1.05891038	0.53925795
C	-3.57439776	2.45084072	0.66803222
H	-5.15606242	3.89408341	0.78953722
H	-6.98163333	2.23230661	0.61467323
H	-6.42114656	-0.17817118	0.39183999
H	-4.07563216	-0.90727121	0.34522242
C	-1.89582402	0.57734925	0.50662127
C	-0.82205221	1.34565194	0.58962942
S	-2.38177802	3.64130249	0.79230105
H	-1.78109648	-0.50794319	0.40489770
C	0.61964947	1.13302113	0.58311017

H	1.07182069	1.51215902	1.50486975
H	0.87987685	0.06909742	0.48503949
H	1.08822649	1.67726021	-0.24277838

2-Methylbenzothiophene $T_1(\pi\sigma^*)$, S-C7a Elongation Geometry

C	-4.91421346	2.86920250	0.83649777
C	-5.93990015	1.95011240	0.60437938
C	-5.64433891	0.61376254	0.33503987
C	-4.33402796	0.18489718	0.29498889
C	-3.28192816	1.09758860	0.52674227
C	-3.62041168	2.42293727	0.79211956
H	-5.14935230	3.90786622	1.04562536
H	-6.97462343	2.27620283	0.63336997
H	-6.44910278	-0.08955147	0.15665057
H	-4.10276407	-0.85519787	0.08544208
C	-1.92365825	0.68440393	0.49177829
C	-0.83335407	1.52945591	0.71061311
S	-1.04442290	3.15138593	1.04301728
H	-1.71966840	-0.36237162	0.27989209
C	0.55356061	0.95971364	0.64357089
H	0.54022788	-0.10915046	0.42119650
H	1.13633311	1.47092327	-0.12555215
H	1.07312816	1.11467820	1.59144183

3-Methylbenzothiophene Ground State Geometry

C	-1.64232686	1.25047777	0.00002671
C	-2.68186356	0.34157717	0.00002770
C	-2.43073642	-1.03454103	0.00002543
C	-1.13807671	-1.51557141	0.00002178
C	-0.06584261	-0.61738351	0.00001996

C	-0.33903611	0.76397994	0.00002319
H	-1.83752577	2.31625112	0.00003081
H	-3.70452394	0.69999913	0.00003165
H	-3.26315529	-1.72836531	0.00002693
H	-0.95004273	-2.58345044	0.00002023
C	1.34466219	-0.89636720	0.00001351
C	2.07302601	0.24597142	0.00000791
S	1.12325032	1.68570909	0.00002922
C	1.90994150	-2.27479449	0.00001382
H	3.15068864	0.32643750	-0.00000178
H	2.99997349	-2.25488686	-0.00005456
H	1.58122580	-2.83521041	-0.88025825
H	1.58133542	-2.83516572	0.88035588

3-Methylbenzothiophene $S_1(\pi\pi^*)$ Geometry

C	-1.63062577	1.27239399	0.00003075
C	-2.70677778	0.31837242	0.00003372
C	-2.45817169	-1.02745174	0.00004221
C	-1.13617094	-1.55028237	0.00005087
C	-0.06495095	-0.62835316	0.00003472
C	-0.34660716	0.74202040	0.00002548
H	-1.81693524	2.33689281	0.00002241
H	-3.72805564	0.67943404	0.00002678
H	-3.29283321	-1.71944399	0.00004455
H	-0.95816470	-2.61737053	0.00007998
C	1.34324403	-0.89335181	0.00001156
C	2.12899037	0.27425879	-0.00000654
S	1.14596447	1.64070278	-0.00000672
C	1.91153256	-2.25394466	-0.00000024

H	3.20419002	0.35079004	-0.00000824
H	3.00077600	-2.24775944	0.00004631
H	1.55782451	-2.81109391	-0.87522584
H	1.55774448	-2.81114689	0.87515838

3-Methylbenzothiophene $S_1(\pi\sigma^*)$, S-C2 Elongation Geometry

C	-4.89522280	2.84355860	0.55028525
C	-5.93523757	1.95450397	0.55400161
C	-5.66391540	0.58130298	0.56395918
C	-4.35734978	0.11444748	0.57006928
C	-3.27638043	0.98415053	0.56656534
C	-3.54393730	2.39877128	0.55633836
H	-5.07114902	3.91191194	0.54262175
H	-6.95898624	2.30785294	0.54930171
H	-6.48334107	-0.12831265	0.56695292
H	-4.18011784	-0.95340749	0.57773424
C	-1.89095718	0.51385653	0.57285432
C	-0.93898044	1.43078466	0.56870815
S	-2.31054625	3.53505828	0.55134588
H	0.13776256	1.28194108	0.57211329
C	-1.63180196	-0.97210997	0.58357936
H	-2.06597179	-1.44669353	1.46921664
H	-2.06203930	-1.45876435	-0.29741428
H	-0.56006833	-1.16523776	0.58728746

3-Methylbenzothiophene $S_1(\pi\sigma^*)$, S-C7a Elongation Geometry

C	-4.82064580	2.87614931	0.56963292
C	-5.89699547	1.98216174	0.56337985
C	-5.67385398	0.60839621	0.56238471
C	-4.38404142	0.11411005	0.56756683

C	-3.29419733	1.00664189	0.57387451
C	-3.54759785	2.37603930	0.57473780
H	-5.01004612	3.94608848	0.57033797
H	-6.91508120	2.35962358	0.55926464
H	-6.51480727	-0.07466493	0.55752539
H	-4.21873475	-0.95821712	0.56674284
C	-1.92737798	0.58374420	0.57949067
C	-0.91799556	1.55841351	0.58556246
S	-1.15570149	3.19505625	0.58692134
H	0.10947067	1.19994480	0.58972701
C	-1.55691820	-0.85513458	0.57902702
H	-1.97190007	-1.36634017	1.45385448
H	-1.96393917	-1.36372062	-0.30105087
H	-0.47569871	-0.98975489	0.58373341

3-Methylbenzothiophene $T_1(\pi\pi^*)$ Geometry

C	-1.61409601	1.24414081	0.03385936
C	-2.70302910	0.33720807	-0.08042330
C	-2.46793421	-1.02542611	-0.15655572
C	-1.17741602	-1.53397598	-0.12577560
C	-0.06971876	-0.65360330	-0.00785393
C	-0.35059177	0.74820278	0.07334561
H	-1.79968196	2.30988674	0.09710284
H	-3.71556029	0.72028259	-0.09936871
H	-3.30556088	-1.70795433	-0.24323022
H	-1.01221794	-2.60264413	-0.19234686
C	1.27978021	-0.94620769	0.07153544
C	2.11702264	0.28144222	0.22210529
S	1.14561327	1.69047720	0.22942251

C	1.91538383	-2.27625314	0.06378058
H	3.15430396	0.34520328	-0.07752469
H	2.63347283	-2.36081721	-0.76189512
H	1.18926117	-3.08330567	-0.03049829
H	2.49194236	-2.43198934	0.98468092

3-Methylbenzothiophene $T_1(\pi\sigma^*)$, S-C2 Elongation Geometry

C	-4.90557694	2.84270492	0.55028342
C	-5.94012775	1.94074391	0.55409894
C	-5.65370016	0.57404271	0.56401971
C	-4.34368299	0.12682694	0.56998586
C	-3.26546281	1.01156115	0.56638040
C	-3.55578686	2.41619064	0.55619081
H	-5.09492372	3.90906736	0.54262000
H	-6.96694459	2.28553308	0.54946744
H	-6.46323414	-0.14696240	0.56710789
H	-4.15410468	-0.93864119	0.57764556
C	-1.88976531	0.52567934	0.57275603
C	-0.88658165	1.39557333	0.56902040
S	-2.33994308	3.58834781	0.55093272
H	0.18237381	1.21447877	0.57263277
C	-1.65072668	-0.96308950	0.58349836
H	-2.09111852	-1.43199769	1.46873976
H	-2.08712571	-1.44410843	-0.29721090
H	-0.58180838	-1.17233624	0.58735130

3-Methylbenzothiophene $T_1(\pi\sigma^*)$, S-C7a Elongation Geometry

C	-4.86026051	2.88278937	0.56945821
C	-5.91735382	1.97311101	0.56327539
C	-5.66396827	0.60265034	0.56242050

C	-4.36674706	0.13010898	0.56766409
C	-3.28407983	1.03317932	0.57395250
C	-3.58038699	2.39253241	0.57460294
H	-5.05749229	3.95005909	0.57012436
H	-6.94189175	2.33096715	0.55910741
H	-6.49111760	-0.09724262	0.55760247
H	-4.18721068	-0.93931078	0.56690889
C	-1.91319301	0.60346402	0.57958289
C	-0.88070184	1.54213674	0.58571408
S	-1.06790314	3.19008763	0.58732303
H	0.13447384	1.14936585	0.58977471
C	-1.57476646	-0.84774109	0.57895660
H	-1.99758051	-1.34887741	1.45497885
H	-1.98962719	-1.34626150	-0.30234412
H	-0.49625453	-1.00248150	0.58361023