Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for:

Excited-state dynamics of thiophene substituted betaine pyridinium compounds

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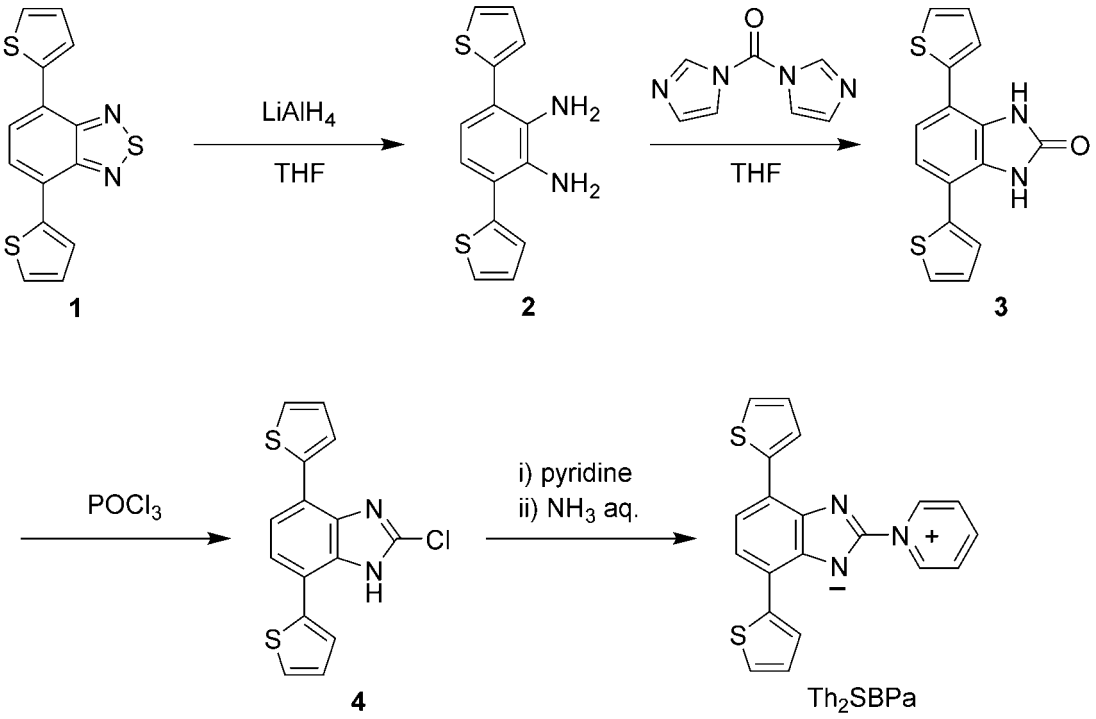
I. Synthesis of Th_2SBPa and Th_4SBPa

All the chemicals were purchased from Tokyo Kasei and Aldrich and used as received, unless otherwise noted. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F–254). ^{1}H–NMR spectra were obtained at 500 MHz with a JMN-ECP500A (JEOL) spectrometer. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane.

1. Synthesis of Th_2SBPa.

Scheme S1. Synthesis of Th_2SBPa.



The compound **1** was prepared according to the literature procedures.[1]

Synthesis of 2 and 3. To a solution of **1** (270 mg, 0.899 mmol) in THF (12 mL) was slowly added $LiAlH_4$ (68 mg, 1.8 mmol) at 0 ^oC under nitrogen. After stirring for 2 h at 0 ^oC, $LiAlH_4$ (68 mg, 1.8 mmol) was additionally added. Stirring for 2 h, after the excess $LiAlH_4$ was quenched, the precipitate was filtered off over Celite. The filtrate was evaporated to dryness to obtain a crude product, which was used without further purification because of its instability. To a solution of the crude product in THF (12 mL) was added 1,1'-carbonyldiimidazole (655 mg, 4.04 mmol) and the solution was heated at 40 ^oC. After stirring for 5 h, 1,1'-carbonyldiimidazole (328 mg, 2.02 mmol) was additionally added and stirred for overnight. The solvent was evaporated to dryness and the residue was washed with acetonitrile to obtain **3** (263 mg, 0.881 mmol) in 98% yield in 2 steps. ^1H NMR (DMSO-d_6, 500 MHz): δ 10.86 (s, 2H), 7.61 (d, J = 5.0 Hz, 2H), 7.50 (d, J = 4.0 Hz, 2H), 7.19 (dd, J = 4.0 Hz, 2H), 7.15(s, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 138.62, 128.27, 126.84, 125.82, 125.65, 120.78, 115.19. FAB-MS: *m/z* 299 $[M+H]^+$. Anal. Calcd. for $C_{15}H_{10}N_2OS_2$: C, 60.38; H, 3.38; N, 9.39. found: C, 60.54; H, 3.49; N, 9.39.

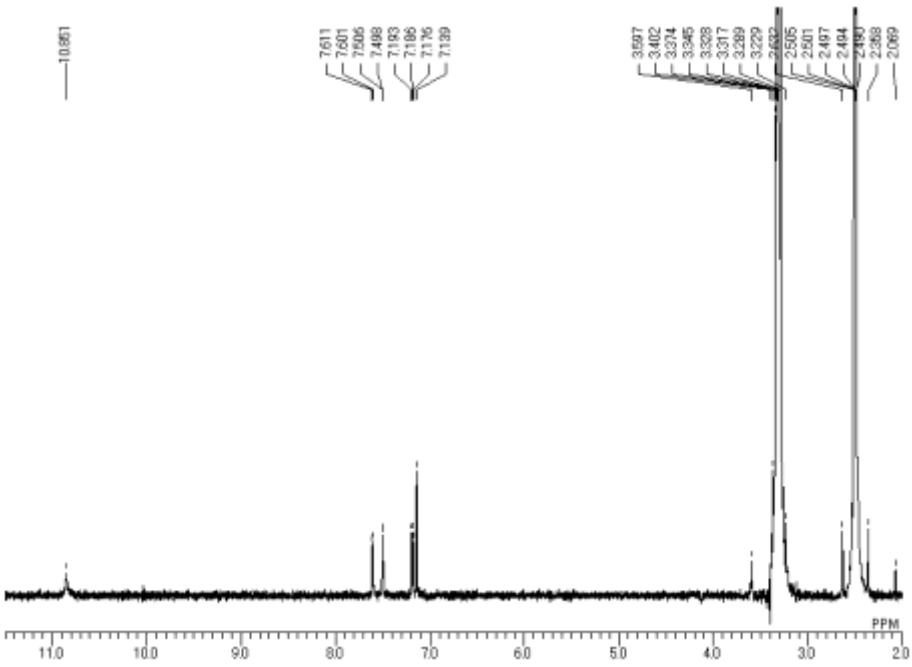


Figure S1. ^{1}H NMR spectrum of **3** in DMSO-d_6.

Synthesis of 4 and Th_2SBPa. Compound **3** (256 mg, 0.859 mmol) was suspended in phosphoryl chloride (3 mL) and the solution was refluxed for 3 h. The solvent was evaporated to dryness and the residue was washed with water to obtain crude **4** (162 mg). This mixture was used without further purification because of its instability. The crude compound (150 mg) was dissolved in pyridine (3 mL) and the solution was refluxed for 5 h. The solvent was evaporated to dryness and the residue was dissolved in dichloromethane and the solution was washed with water. The organic layer was dried over Na_2SO_4. After filtration, the solution was evaporated to dryness. The residue was dissolved in methanol (4 mL) and NH_3 aq. was added to the solution (pH ~9), which

was allowed to react for overnight. The reaction solution was poured into dichloromethane and washed with water. The organic layer was dried over Na_2SO_4. After filtration, the solution was evaporated to dryness. The residue was washed with methanol and recrystallized from methanol-chloroform to yield Th_2SBPa (18.1 mg, 0.050 mmol) in 6.3% yield in 2 steps. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.17 (d, J = 7.0 Hz, 2H), 8.71 (t, J = 7.0 Hz, 1H), 8.33-8.30 (m, 4H), 7.58 (d, J = 6.0 Hz, 2H), 7.47 (s, 2H), 7.25 (dd, J = 3.0 Hz, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 145.44, 143.28, 141.89, 139.09, 139.08, 127.82, 127.44, 124.97, 124.48, 122.28, 117.13. FAB-MS: m/z 360 $[M+H]^+$. Anal. Calcd. for $C_{20}H_{13}N_3S_2/0.5H_2O$: C, 65.19; H, 3.83; N, 11.40. found: C, 65.14; H, 3.82; N, 11.22.

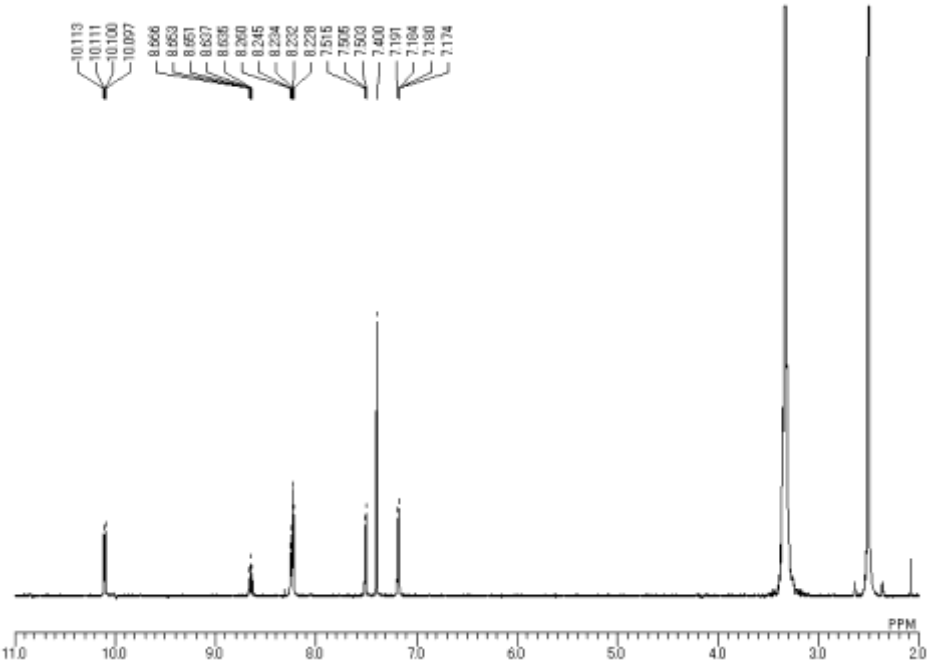
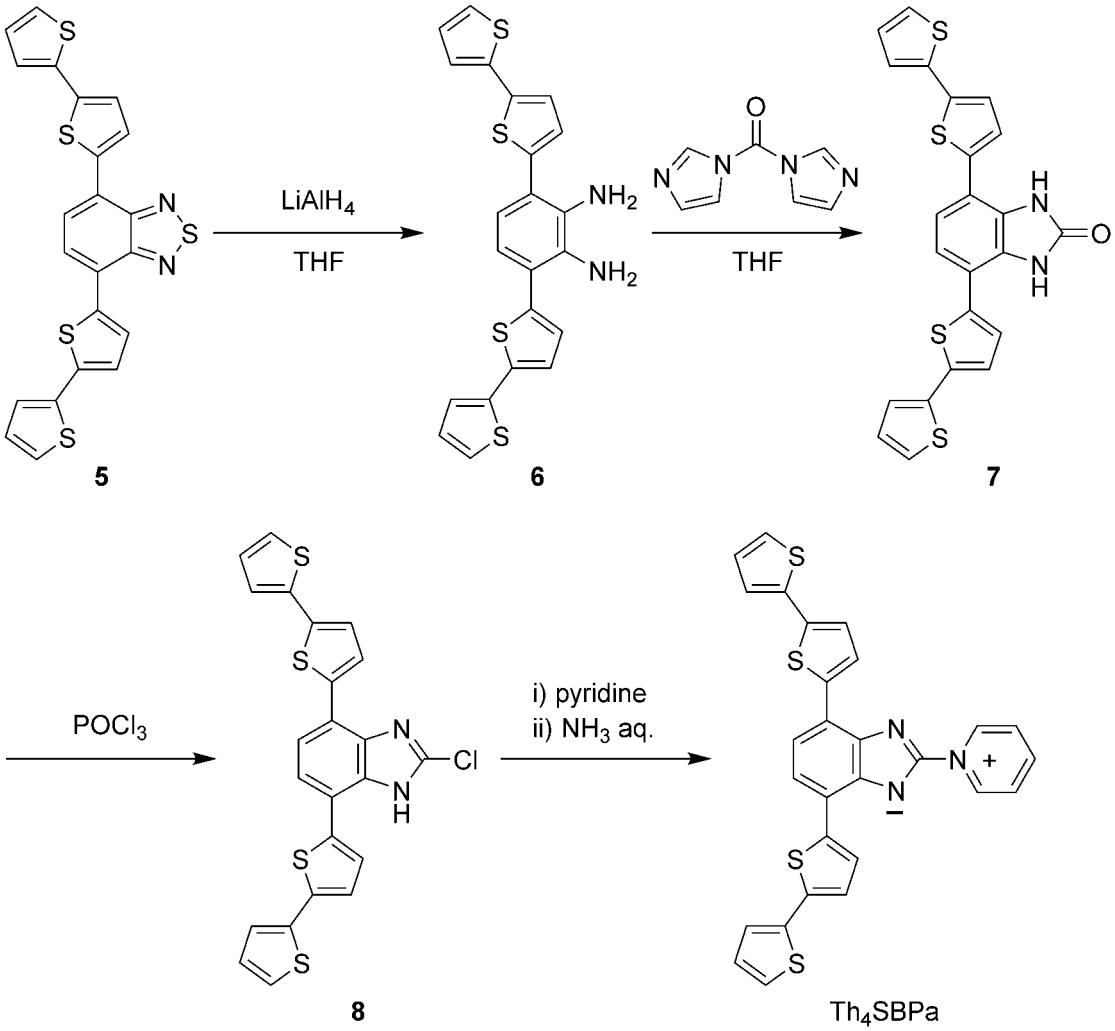


Figure S2 ^{1}H NMR spectrum of Th_2SBPa in DMSO-d_6.

2. Synthesis of Th_4SBPa.

Scheme S2. Synthesis of Th_4SBPa.



The compound **5** was prepared according to the literature procedures.[2]

Synthesis of 6 and 7. To a solution of **5** (241 mg, 0.516 mmol) in THF (120 mL) was slowly added $LiAlH_4$ (69 mg, 1.8 mmol) at 0 °C under nitrogen. After stirring for 2 h at room temperature, the reaction mixture was warmed to 60 °C and stirred for overnight. After the excess $LiAlH_4$ was quenched, the precipitate was filtered off over Celite. The

filtrate was evaporated to dryness to obtain a crude product, which was used without further purification because of its instability. To a solution of the crude product in THF (80 mL) was added 1,1'-carbonyldiimidazole and the solution was heated at 40 °C for one week. During the reaction, 1,1'-carbonyldiimidazole (1.00 g, 6.19 mmol) was successively added to complete the reaction. The solvent was evaporated to dryness and the residue was washed with acetonitrile to obtain **7** (148 mg, 0.320 mmol) in 62% yield in 2 steps. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.99 (2H, s), 7.55 (2H, dd, J = 3.5, 1.5 Hz), 7.48 (2H, d, J = 5.0 Hz), 7.40-7.37 (4H, m), 7.18 (2H, s), 7.13 (2H, t, J = 4.0 Hz). The ^{13}C NMR spectrum could not be measured due to its low solubility.

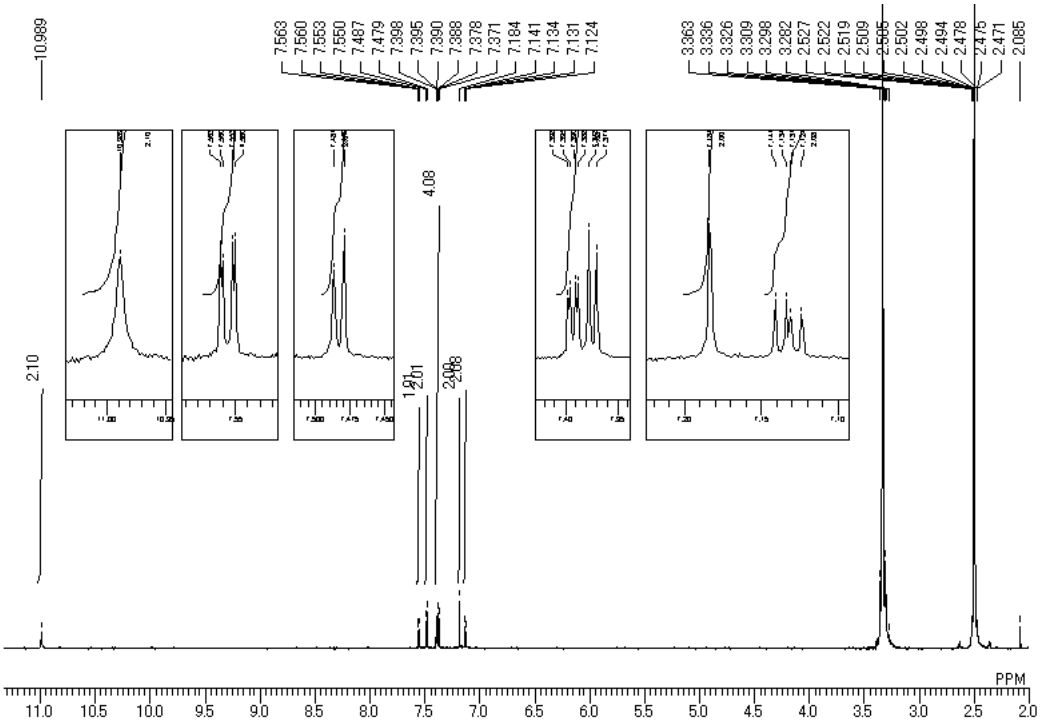


Figure S3. ^{1}H NMR spectrum of **7** in DMSO-d_6.

Synthesis of 8 and Th_4SBPa. Compound **7** (200 mg, 0.432 mmol) was suspended in phosphoryl chloride (3 mL) and the solution was refluxed for 6 h. The solvent was evaporated to dryness and the residue was washed with water to obtain crude **8** (243 mg). This mixture was used without further purification because of its instability. The crude compound (225 mg) was dissolved in pyridine (12.5 mL) and the solution was refluxed for 7 h. The solvent was evaporated to dryness and the residue was dissolved in dichloromethane and the solution was washed with water. The organic layer was dried over Na_2SO_4. After filtration, the solution was evaporated to dryness. The residue was dissolved in methanol and THF and NH_3 aq. was added to the solution (pH ~9), which was allowed to react for overnight. The reaction solution was poured into dichloromethane and washed with water. The organic layer was dried over Na_2SO_4. After filtration, the solution was evaporated to dryness. The residue was washed with methanol and THF to yield Th_4SBPa (26.3 mg, 0.050 mmol) in 12% yield in 2 steps. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.11 (d, J = 5.5 Hz, 2H), 8.66 (t, J = 7.0 Hz, 1H), 8.26 (t, J = 7.0 Hz, 2H), 8.14 (d, J = 3.5 Hz, 2H), 7.51 (dd, J = 3.0, 1.5 Hz, 2H), 7.44 (s, 2H), 7.38 (d, J = 3.5 Hz, 2H), 7.34 (d, J = 3.5 Hz, 2H), 7.12 (dd, J = 3.5, 2.0 Hz, 2H). The ^{13}C NMR spectrum could not be measured due to its low solubility.

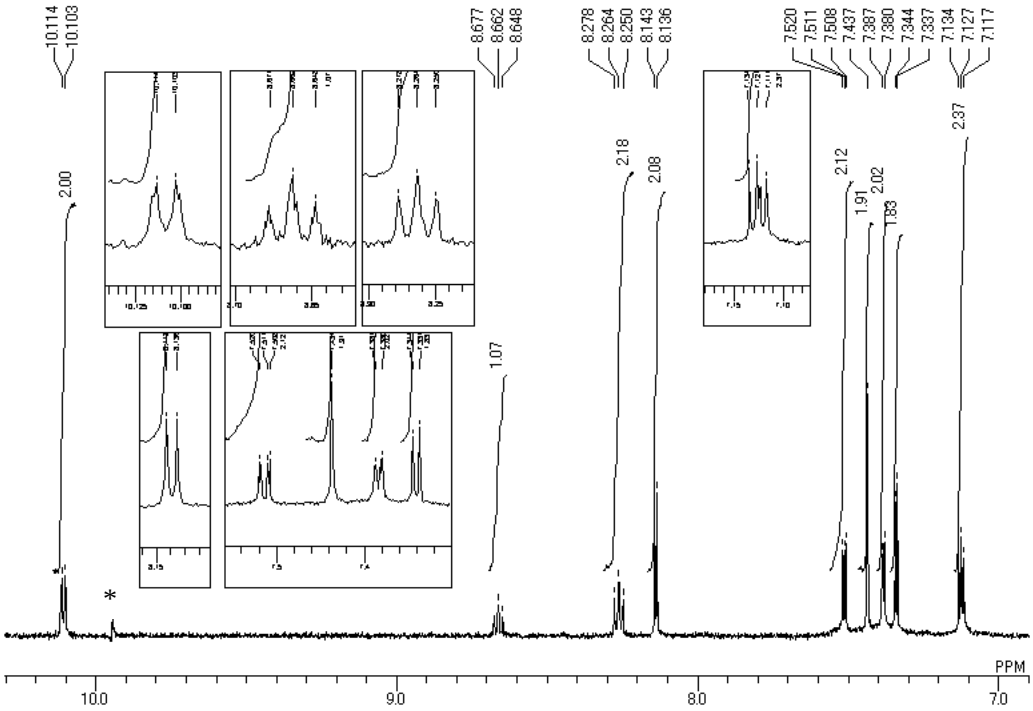


Figure S4 ^{1}H NMR spectrum of Th_4SBPa in DMSO-d_6.

(The asterisk means the experimental artifact)

[1] Karikomi, M.; Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6791.
[2] van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Meijer, E. W. *Chem. Eur. J.* **1998**, *4*, 1235.

II. TDDFT results

Table S1. PCM-TDDFT calculated wavelength (λ), oscillator strength (f), and main MO excitations (only contributions > 10% are given) for the four lowest-energy $S_0 \rightarrow S_n$ transitions of TH_2SBPa and TH_4SBPa in toluene, THF, and MeCN.

		Toluene			THF			MeCN		
		Excit.	λ (nm)	f	Excit.	λ (nm)	f	Excit.	λ (nm)	f
Th_2SBPa	$S_0 \rightarrow S_1$	H→L (0.693)	670	0.053	H→L (0.692)	576	0.075	H→L (0.961)	543	0.088
	$S_0 \rightarrow S_2$	H-1→L (0.659) H→L+1 (-0.118)	458	0.465	H-1→L (0.668)	420	0.448	H-1→L (0.669)	405	0.436
	$S_0 \rightarrow S_3$	H→L+1 (0.694) H-1→L (0.101)	401	0.074	H→L+1 (0.658)	368	0.922	H→L+1 (0.658)	366	0.887
	$S_0 \rightarrow S_4$	H→L+2 (0.660)	371	0.974	H→L+2 (0.695)	360	0.056	H→L+2 (0.699)	344	0.051
Th_4SBPa	$S_0 \rightarrow S_1$	H→L (0.691)	740	0.132	H→L (0.690)	644	0.206	H→L (0.688)	612	0.258
	$S_0 \rightarrow S_2$	H-1→L (0.668) H-2→L (0.143)	484	0.1658	H-1→L (0.201) H→L+1 (0.636)	448	1.393	H→L+1 (0.668)	447	1.458
	$S_0 \rightarrow S_3$	H→L+1 (0.667)	452	1.614	H-1→L (0.634) H-2→L (0.157) H→L+1 (-0.202)	400	0.280	H-1→L (0.667) H-2→L (0.164)	435	0.136
	$S_0 \rightarrow S_4$	H-2→L (0.561) H-1→L (-0.188) H→L+2 (-0.351) H→L+3 (0.103)	432	0.112	H-2→L (0.621) H-1→L (-0.202) H→L+2 (0.130) H→L+3 (0.191)	383	0.152	H-2→L (0.608) H-1→L (-0.195) H→L+3 (0.263)	389	0.136

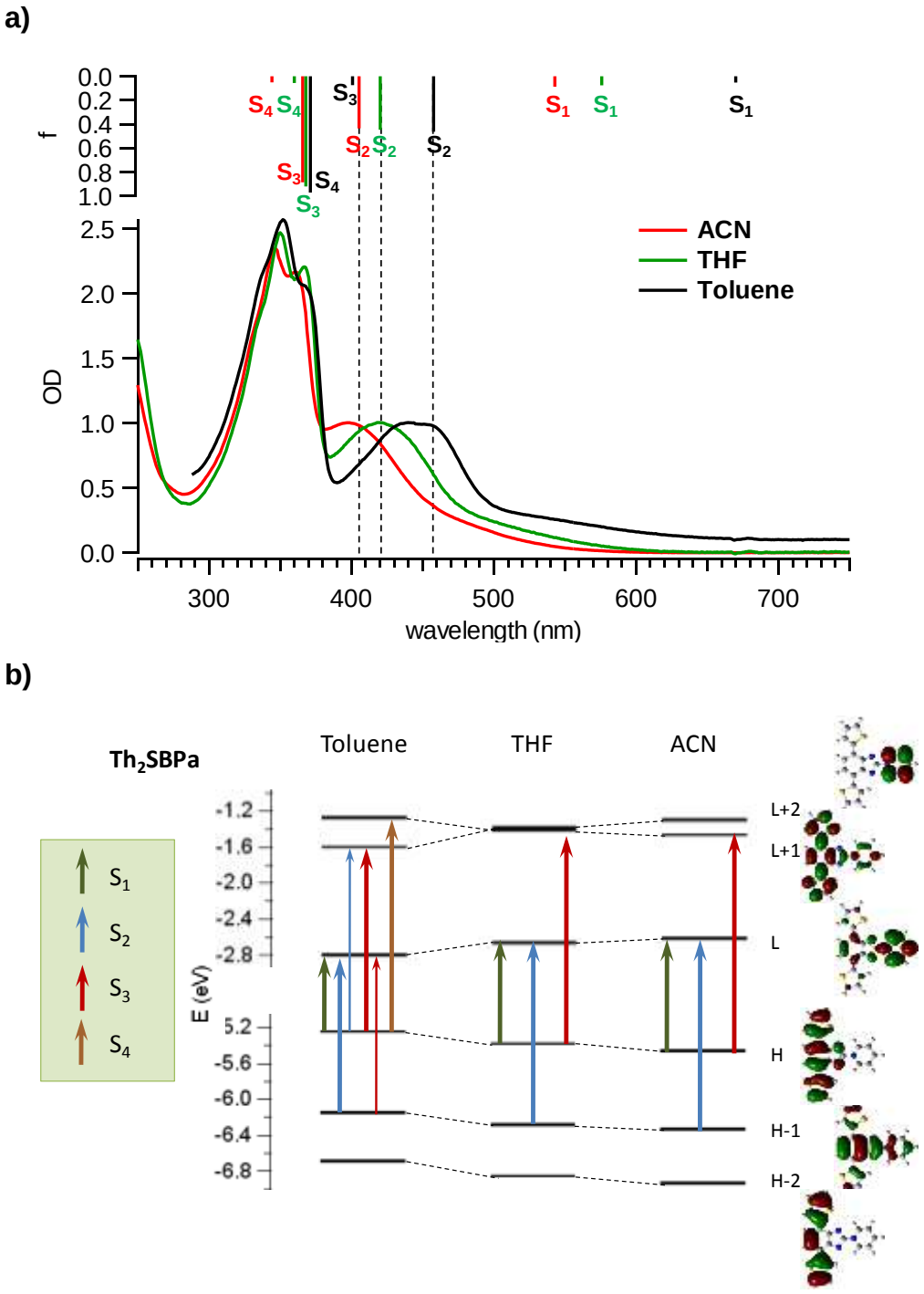


Figure S.5 Absorption characteristics of Th_2SBPa: a) stationary absorption spectra and PCM-TDDFT transitions in three solvents of different polarity; b) PCM-DFT energy diagram and representation of the orbitals involved in the four lowest energy transitions.

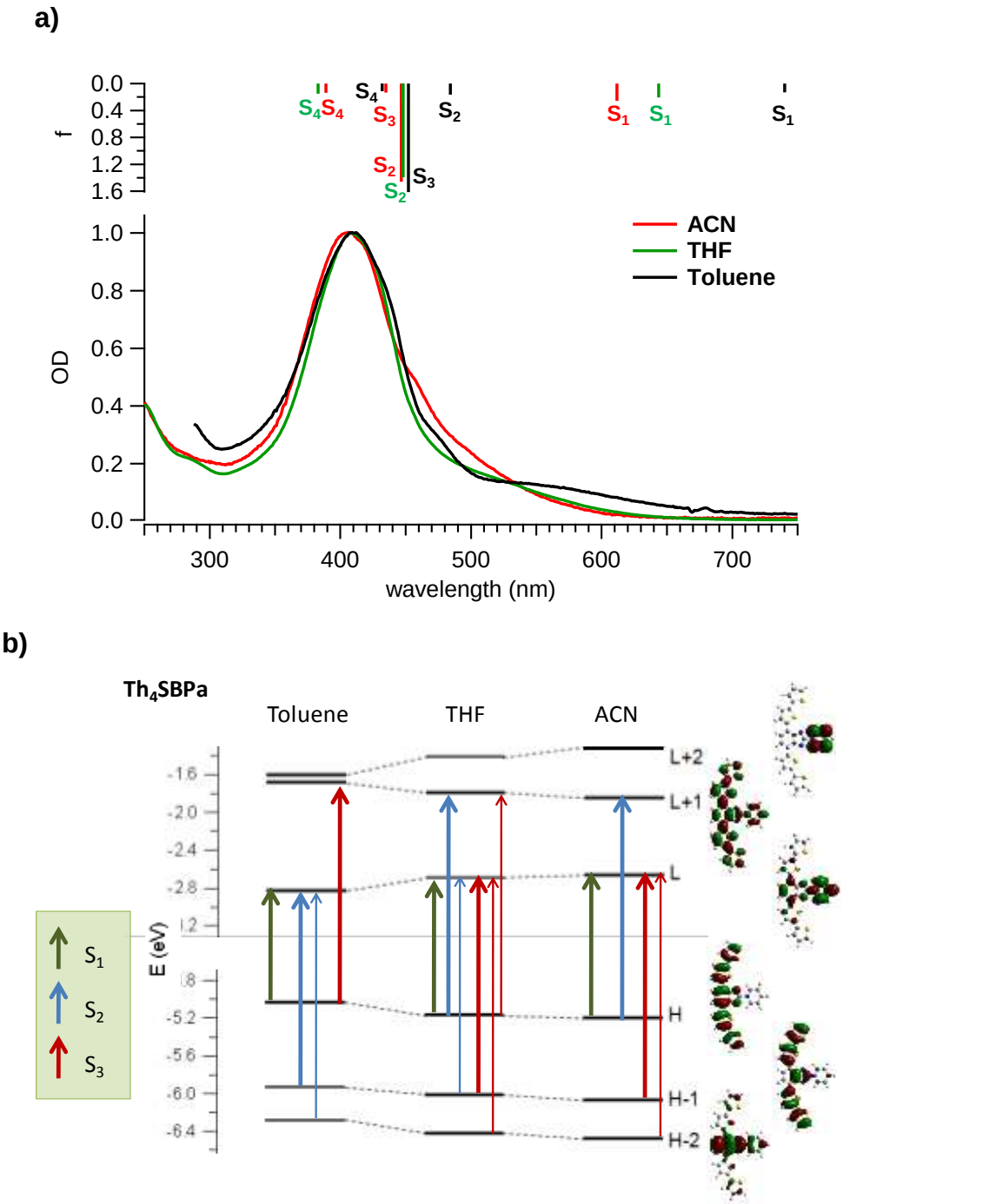


Figure S.6 Absorption characteristics of Th_4SBPa: a) stationary absorption spectra and PCM-TDDFT transitions in three solvents of different polarity; b) PCM-DFT energy diagram and representation of the orbitals involved in the four lowest energy transitions.

III. Time resolved spectroscopic results

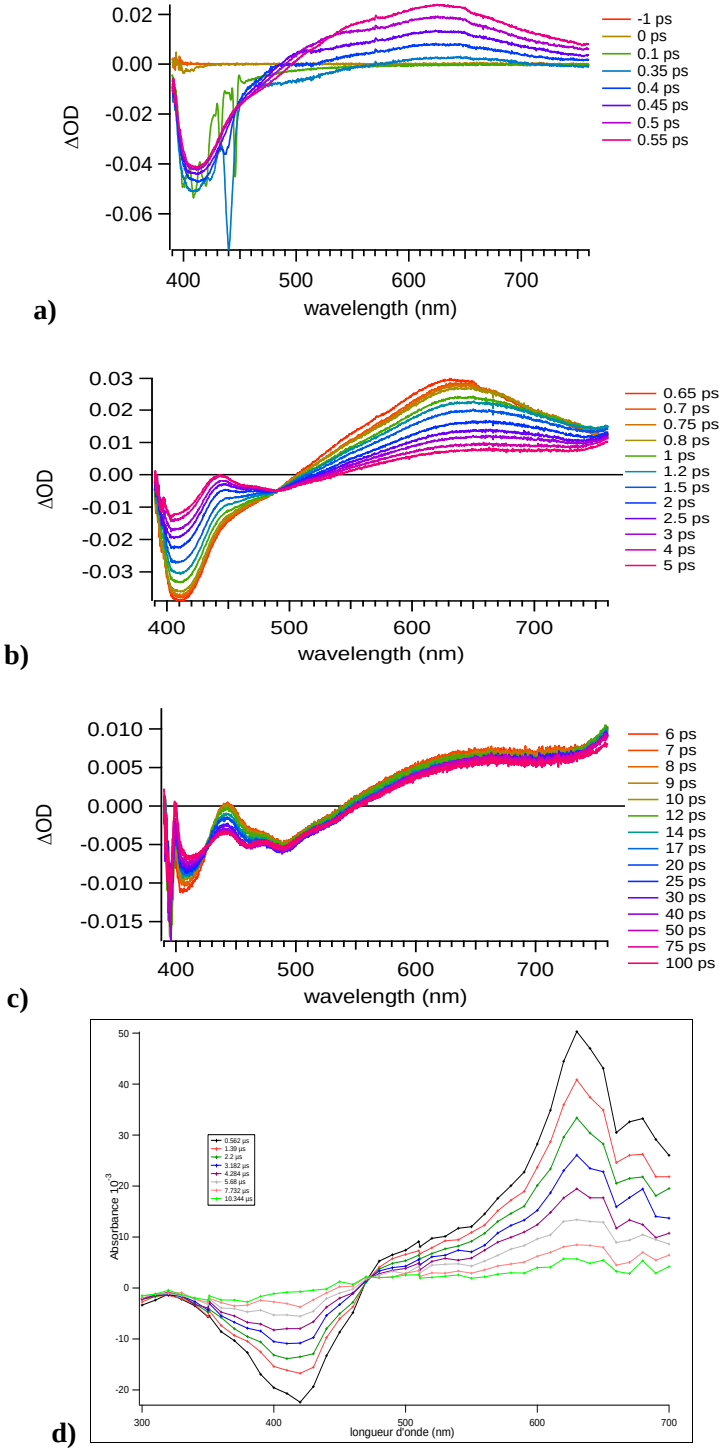


Figure S7. Femtosecond transient absorption spectra of Th_4SBPa in ACN after 390 nm excitation, divided into three temporal windows (a-c); Nanosecond laser flash photolysis of Th_4SBPa in ACN after excitation with 355 nm (d).

Solvent effect for TH_2SBPa transient signal excited at 390 nm.

Similar spectral evolution as in THF shown in fig.2 is found upon 390 nm excitation of Th_2SBPa in all solvents. The corresponding global fitting characteristic times τ_1, τ_2, and τ_3 are listed in Table 1 where the solvent polarity, viscosity, and solvation time are also given. There is no clear correlation between time τ_2 and any one of these solvent characteristics due to specific interactions occuring efficiently for betaine pyridinium. The lack of significant influence of the solvent viscosity indicates that the S_2(ICT) → S_1(ICT) process is probably not accompanied by a large-amplitude molecular distortion such as a twist of the donor and acceptor moieties, as previously concluded for the SBPa molecule. The weak polarity effect can be due to the fact that, both the S_1 and S_2 states having ICT character and differing only by the degree of charge transfer, the S_2 → S_1 relaxation might occur without causing important reorganization of the solvent cage. This difference compared with SBPa, for which S_2 → S_1 process was controlled by the solvation dynamics may be rationalized by the presence of high steric hindrance thiophene disrupting the homogeneity of the solvation cavity. Consider now the solvent influence on the S_1(ICT) state lifetime τ_3. The τ_3 values being much larger than the mean solvation time in all solvents, a control by solvation is unlikely. There is a manifest dependency of τ_3 on the solvent polarity. For instance, in the THF (τ_3 = 7.6 ps), BuCN (τ_3 = 5.9 ps), and MeOH (τ_3 = 4.9 ps) solvents of comparable viscosity but notably different polarity, the τ_3 value decreases clearly with increasing polarity. This influence of the solvent polarity, much less pronounced for the SBPa molecule (see ref 15), can be reasonably interpreted as a manifestation of the energy gap law. In case of fast IC between two potential energy surfaces, the rate of deactivation from the upper surface to the lower one increases as the energy gap between them decreases. In the case of Th_2SBPa, the large solvatochromism of the S_0 → S_1 absorption band, confirmed by the calculation (Fig. S1), reveals that the energy gap between the two surfaces decreases in polar solvents, in agreement with the decreasing τ_3 value. In contrast, in the case of SBPa, no significant

influence of the solvent was predicted on the $S_0 \rightarrow S_1$ transition energy [15], which infers a constant gap in all solvents consistent with the lack of patent effect of the solvent polarity on τ_3. Now, if solvents OcCN and THF are compared, the former being twice as polar as the second, a faster IC kinetics is expected by considering only the polarity effect. In reality, the slower IC kinetics observed in OcCN (τ_3 = 13.8 ps) than in THF (τ_3 = 7.6 ps) indicates that the solvent viscosity also plays a role in this kinetics.