Electronic Supplementary Information for

Photochromic and fluorescence switching properties of oxidized triangle terarylenes in solution and in amorphous solid states†

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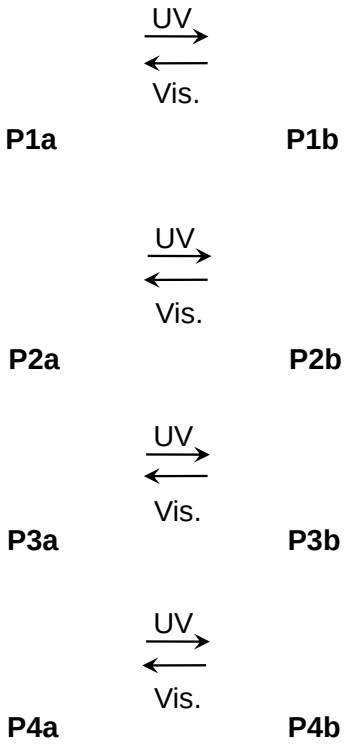
1. *Schemes of photochemical reactions and photochemical properties of precursors **P1-P4***



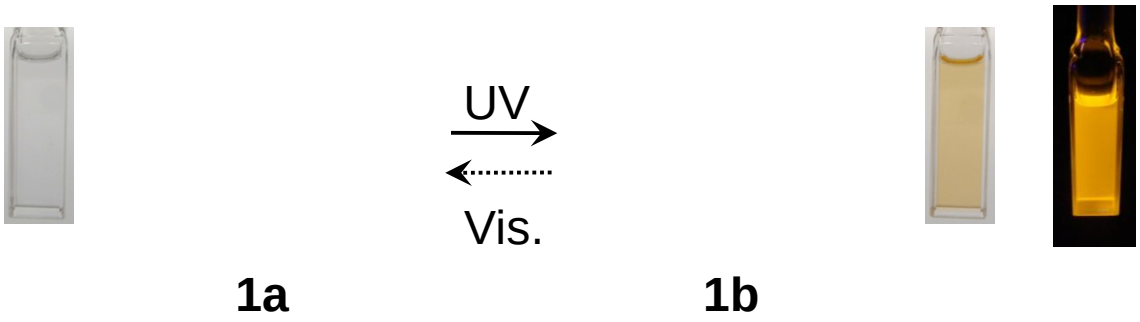
Scheme S1 Molecular structures of photochromic molecules **P1-P4**.

Table S1 Absorption properties and photochromic properties of precursor **P1-P4** in hexane

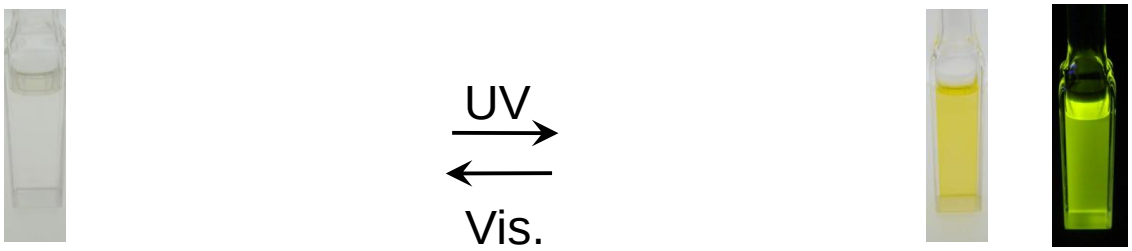
	λ [nm] (ε [10^4 $M^{-1}cm^{-1}$])	a_{pss} (at 313 nm)	Φ_{oc} (at 313 nm)	Φ_{co}
P1a [a]	269 (3.5)	0.90	0.6	—
P1b [a]	610 (0.94)	—	—	0.07 [e]
P2a [b]	273 (2.2) 329 (1.3)	0.44	0.58	—
P2b [b]	539 (1.2) 556 (1.2)	—	—	0.45 [f]
P3a [c]	262 (2.8)	0.79	0.46	—
P3b [c]	562 (1.1)	—	—	0.015 [e]
P4a [d]	258 (1.4)	0.50	0.35	—
P4b [d]	517 (0.91)	—	—	0.35 [f]

[a] T. Nakashima, K. Atsumi, S. Kawai, T. Nakagawa, Y. Hasegawa and T. Kawai, *Eur. J. Org. Chem.*, 2007, 3212-3218. [b] S. Kawai, T. Nakashima, Y. Kutsunugi, H. Nakagawa, H. Nakano and T. Kawai, *J. Mater. Chem.*, 2009, **19**, 3606-3611. [c] M. Irie, K. Sakemura, M. Okinaka and K. Uchida, *J. Org. Chem.*, 1995, **60**, 8305-8309. [d] K. Uchida, E. Tsuchida, Y. Aoi, S. Nakamura and M. Irie, *Chem. Lett.*, 1999, 63-64. [e] irrad at 546 nm [f] irrad at 517 nm

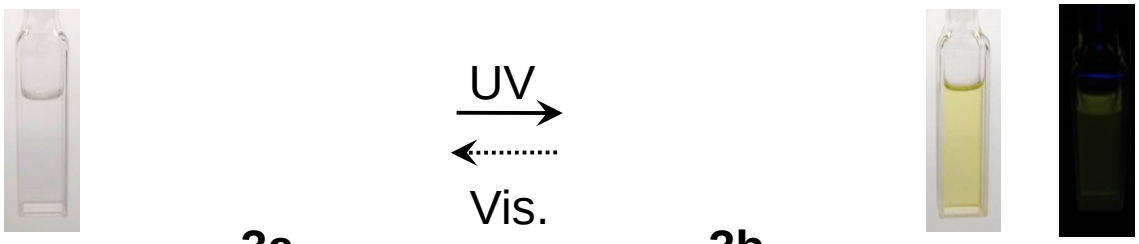
*2. Photographs of compounds **1**, **2**, **3** and **4** in 2-MeTHF in quartz cells*



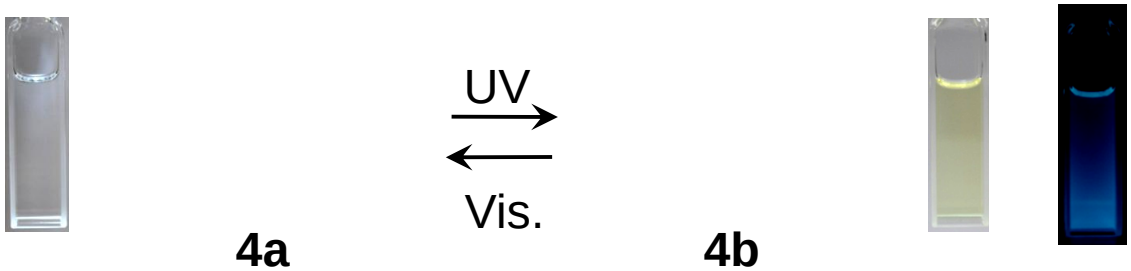
1a **1b**



2a **2b**



3a **3b**



4a **4b**

3. *Crystallographic data for compounds **1b** and **3b***

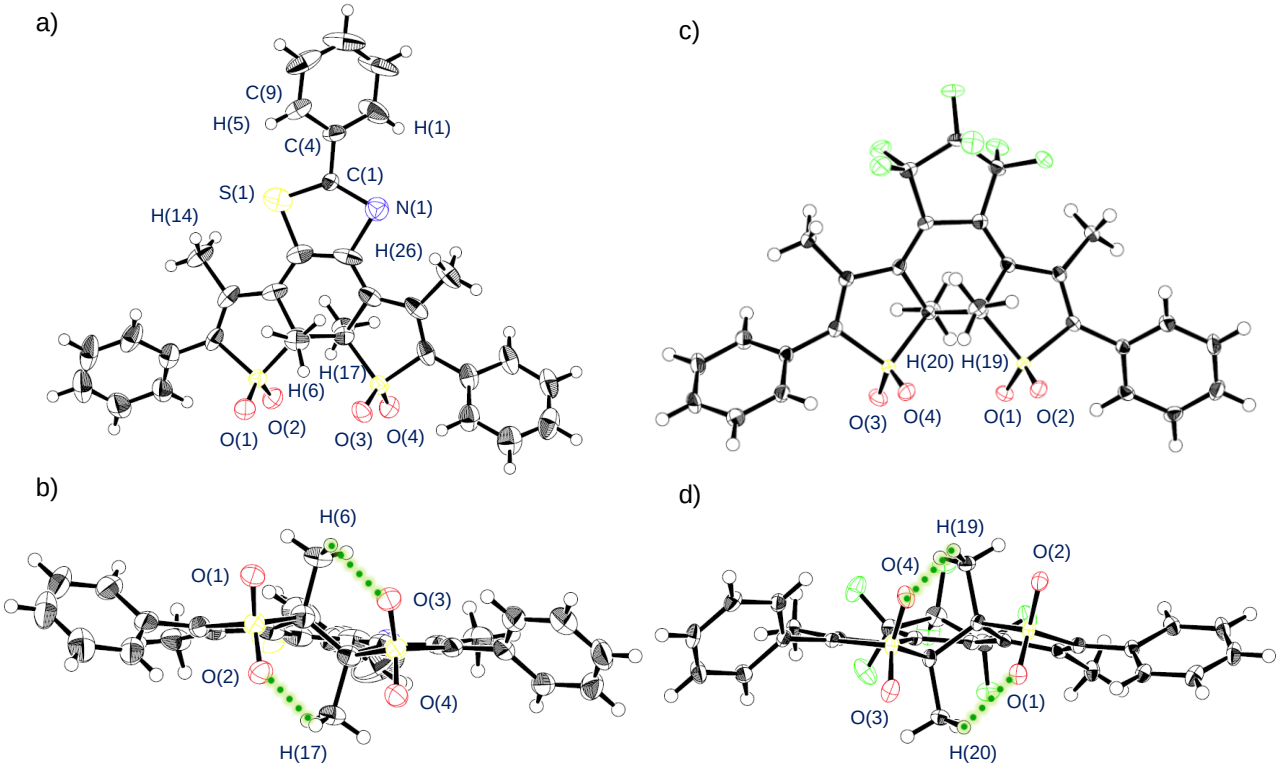


Fig. S1 ORTEP drawings of **1b** and **3b** in crystal, showing 50 % probability displacement ellipsoids; (a) the front view of **1b**, (b) the edge view of **1b**, (c) the front view of **3b** and (d) the edge view of **3b**.

Table S2 Distance between hydrogen atoms of methyl groups and oxygen atoms of SO_2 units evaluated by the X-ray crystallographic structures.

	CH / OS distance [nm]	
1b	0.231 (H17/O2)	0.239 (H6/O3)
3b	0.231 (H19/O4)	0.234 (H20/O1)

*4. Quantum chemical calculations for compounds **1-3** by Gaussian 03 at B3LYP/6-31G(d) level*

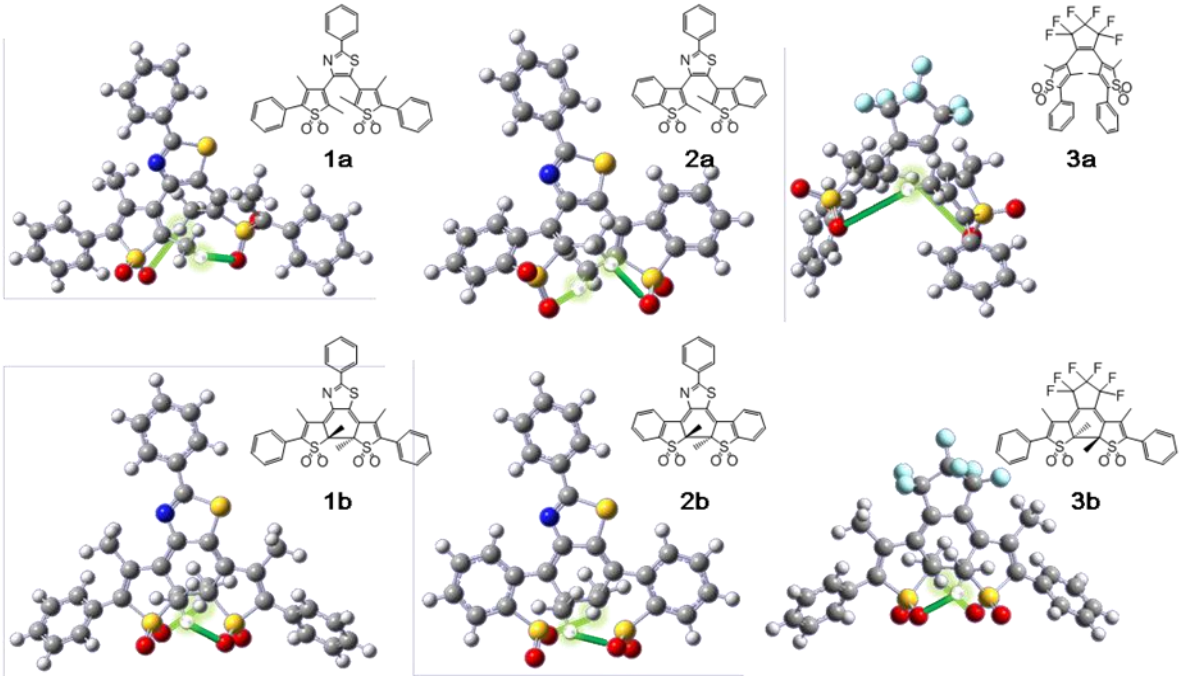


Fig. S2 Optimized molecular structures of **1a**, **1b**, **2a**, **2b**, **3a** and **3b** evaluated with DFT calculations in B3LYP/6-31G(d) level

Table S3 Distance between hydrogen atoms of methyl groups and oxygen atoms of SO_2 units evaluated with the DFT calculations in Fig. S2

compound	CH / OS distance [nm]	
1a	0.306	0.311
1b	0.224	0.224
2a	0.315	0.310
2b	0.222	0.222
3a	0.390	0.382
3b	0.226	0.225

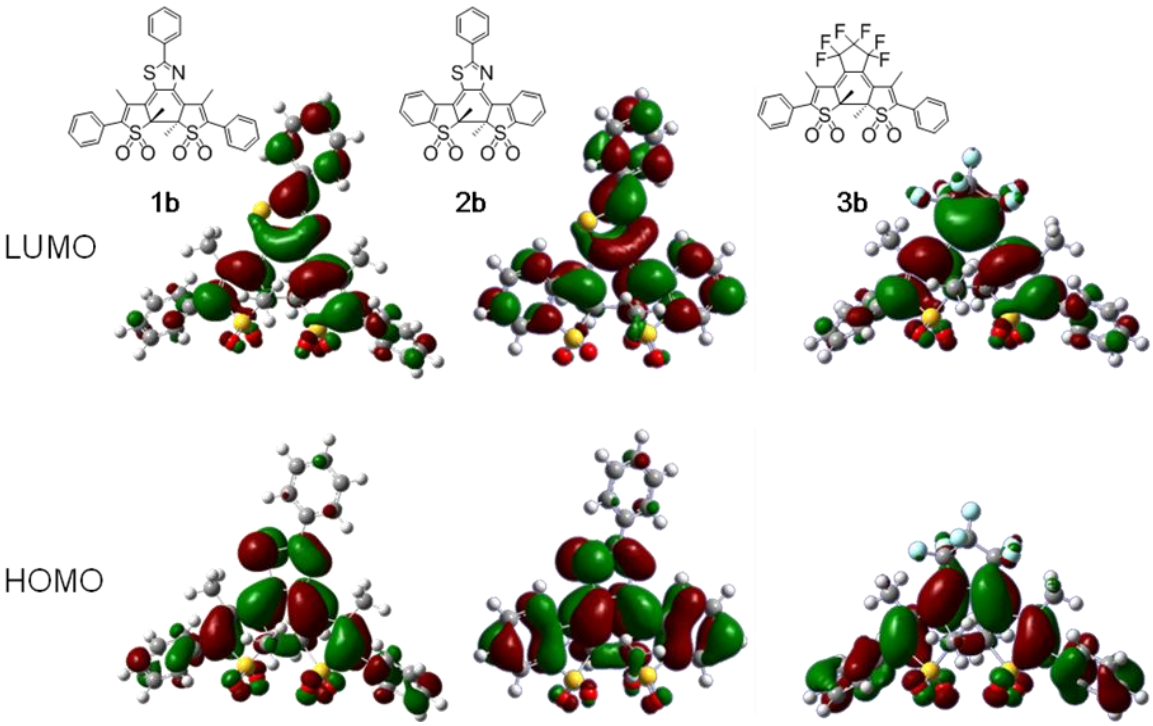


Fig. S3 HOMO and LUMO of ring-closed isomers **1b**, **2b** and **3b** calculated by TD-DFT (B3LYP/6-31G(d))

Table S4 HOMO and LUMO levels and first transition bands of compounds

compound	HOMO [eV]	LUMO [eV]	first transition band [nm] (oscillator strength)
P1b	-4.3767	-2.1658	649.34 (f = 0.2582)
1b	-5.4886	-2.8760	522.35 (f = 0.4117)
P2b	-4.8341	-2.3576	585.42 (f = 0.1998)
2b	-5.6826	-2.8842	487.14 (f = 0.3363)
P3b	-5.0162	-2.4556	573.22 (f = 0.2840)
3b	-6.2897	-3.2991	464.45 (f = 0.5180)

Table S5 Emission quantum yields of **1b**, **2b**, **3b** and **4b** in various solvents

	λ_{ex}	Φ_{em} [a]				
	[nm]	2-MeTHF	1,4-dioxane	toluene	CH_2Cl_2	CH_3CN
1b	400	0.35	0.36	0.33	0.32	0.10
2b	400	0.37	0.33	0.45 [c]	0.29	0.10

[a] after N_2 bubbling

*5. Emission decay profiles of compounds **1b**, **2b**, **3b** and **4b** in 2-MeTHF at r.t.*

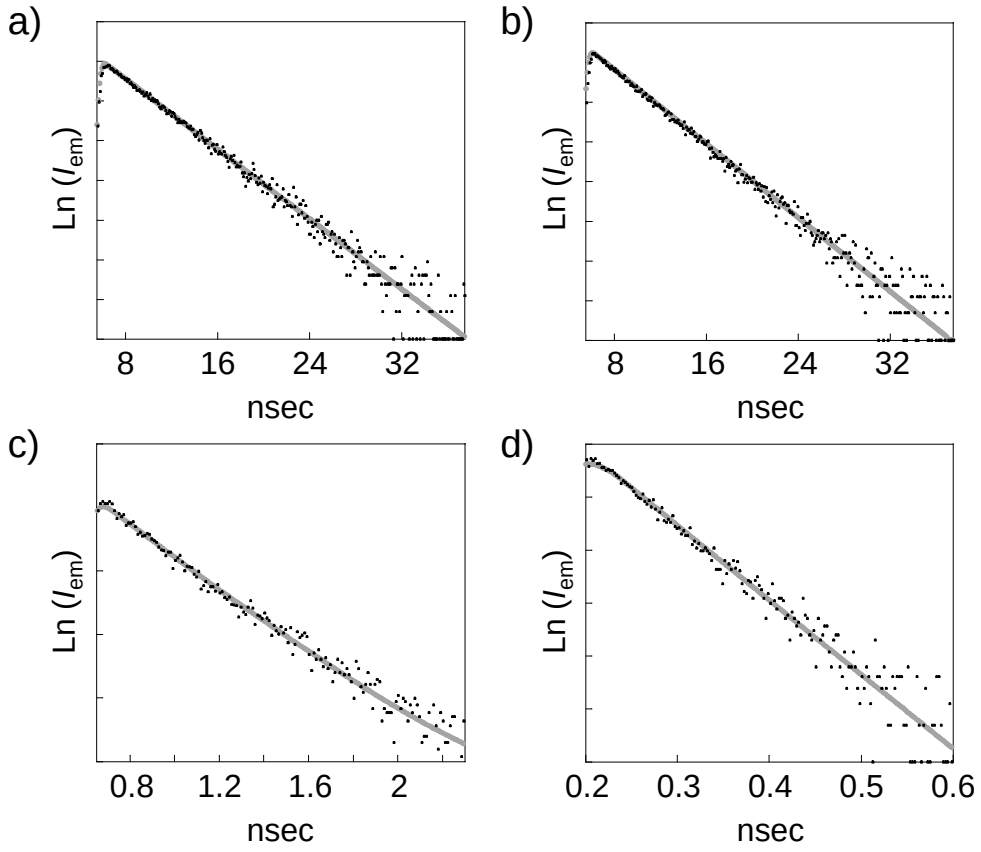


Fig. S4 Emission decay profiles obtained with the time-resolved fluorescence measurements in 2-MeTHF at *r.t.* (a) **1b** (3.0×10^{-5} M), (b) **2b** (4.5×10^{-5} M), (c) **3b** (7.8×10^{-5} M) and (d) **4b** (4.2×10^{-5} M). Excitation was performed with a cavity-dumped Ti:Sapphire pulsed laser (Mira 900F & Pulse Switch, Coherent) through a SHG unit (model 5-050, Inrad) of 400 nm in wavelength (pulse width = ca. 90 fsec) with a repetition frequency of 1 Hz. Gray curves denote fitting profiles based on the single exponential decay with time constants presented in **Table 2**.

*6. Glass transition temperature of **1b***

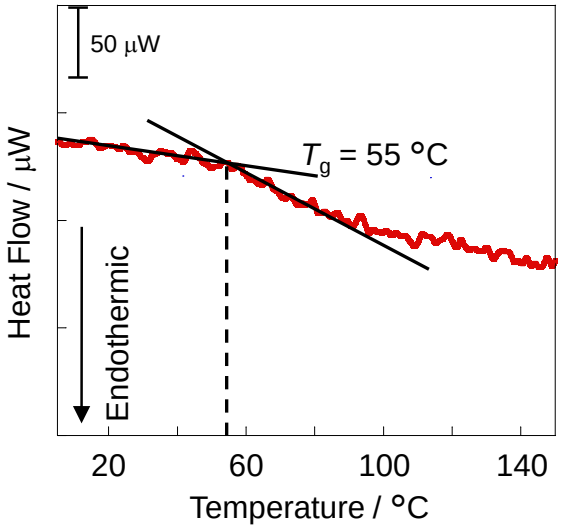


Fig. S5 DSC curve of compound **1b**