

Electronic Supplementary Information for

Photo-patternable electroluminescence based on one-way photoisomerization reaction of tetraoxidized triangle terarylenes†

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1. General information of the experiment

¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded on a JEOL JNM-AL-300 spectrometer. Mass spectra were measured with mass spectrometers (for: JEOL JMS-700, JEOL AccuTOF JMS-T100LC and PE biosystems Voyager DE-STR, for FAB, ESI and MALDI-TOF MS, respectively). Elemental analyses were performed with an elemental analyzer (Perkin Elmer, 2400II CHNS/O). ATR-IR spectra were recorded on a JASCO FT/IR-4200 spectrometer with ATR PRO410-S. Separative HPLC was performed on a HPLC system (HITACHI, LaChrom ELITE, L-2400 for detector, L-2130 for pump, D-2500 for chromat-integrator) with a packed column (Nacalai Tesque, COSMOSIL 55L-II, 20 × 250 mm). Absorption spectra were studied with a spectrophotometer (JASCO V-670). Photoluminescence spectra were studied with a spectrofluorometer (JASCO FP-6500). PL quantum yields were evaluated by using an absolute PL quantum yield measurement system with an integration sphere (HAMAMATSU Co., C9920-02, PMA-12) for solutions and films. Crystal structures were determined by using an X-ray crystal structural analyzer (Rigaku VariMAX-RAPID). DSC measurements were carried out using a differential scanning calorimeter (Seiko, EXSTAR6000 DSC6200) with a liquid nitrogen cooling system. The heating rate was 5 °C min⁻¹. Thickness measurements of films were determined by using an atomic force microscope (SII nanotechnology, SPA400, SPI3800N). Optical microscope (Olympus, BX51) was used for visible observation and photo-coloration of the amorphous films. Photo-irradiation was carried out with an ultra high-pressure Hg lamp (Ushio, BA-H501, 1 kW) and a Xe short-arc lamp (Ushio, BA-X500, 500 W) as the exciting light sources. Light with appropriate wavelength was obtained through optical filters and/or a monochromator (Shimadzu, SPG-120S, 120 mm, *f* = 3.5). Quantum yields of ring-cyclization reactions in solution were determined by using 1,2-bis(2-methylbenzo[b]thiophene-3-yl)perhexafluorocyclopentene (in hexane) as a reference whose value is 0.35 under UV light irradiation (λ = 313 nm) in hexane. Quantum yields of ring-cycloreversion reactions were determined by using 1,2-bis(3-methylthiophen-2-yl)perhexafluorocyclopentene (in 3-methylpentane) and 1,2-bis(2,4-dimethyl-5-phenylthiophen-3-yl)perhexafluorocyclopentene (in hexane) as reference compounds, whose values are 0.37 at 432 nm in 3-methylpentane and 0.15 at 546 nm, respectively. The current density-voltage-luminance (J-V-L) characteristics were measured using a sorce meter (KEITHLEY 2400) with a photonic multi-channel analyzer (HAMAMATSU Co., PMA-12). OLED patterning was carried out using a halogen lighting system (MORITEX, MHAB-150W) through a color filter Y-42.

2. Quantum chemical calculations for compounds 1, 2 by Gaussian 09 at B3LYP/6-31G(d) level

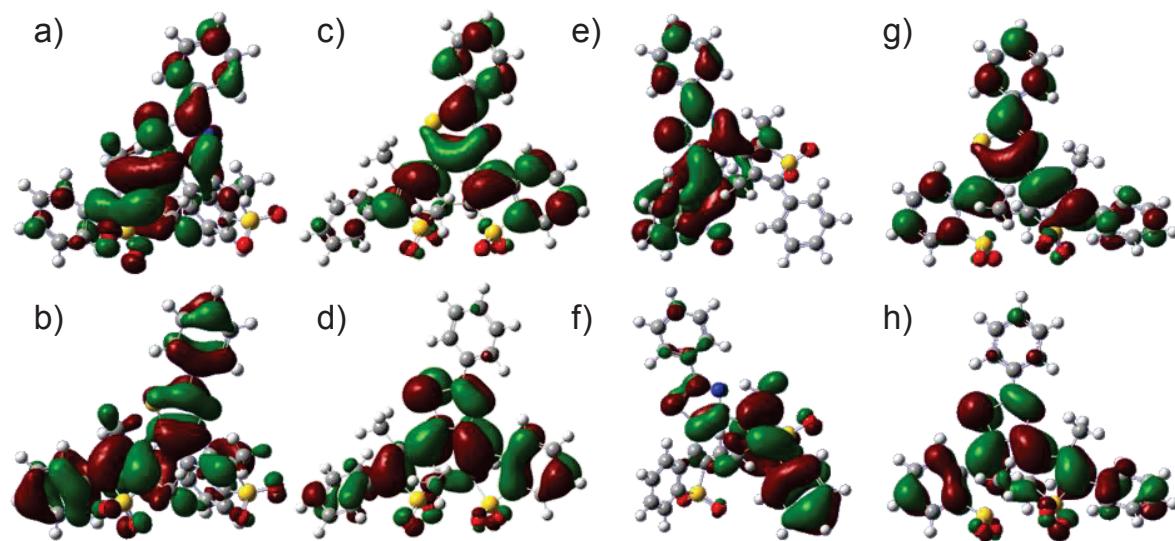
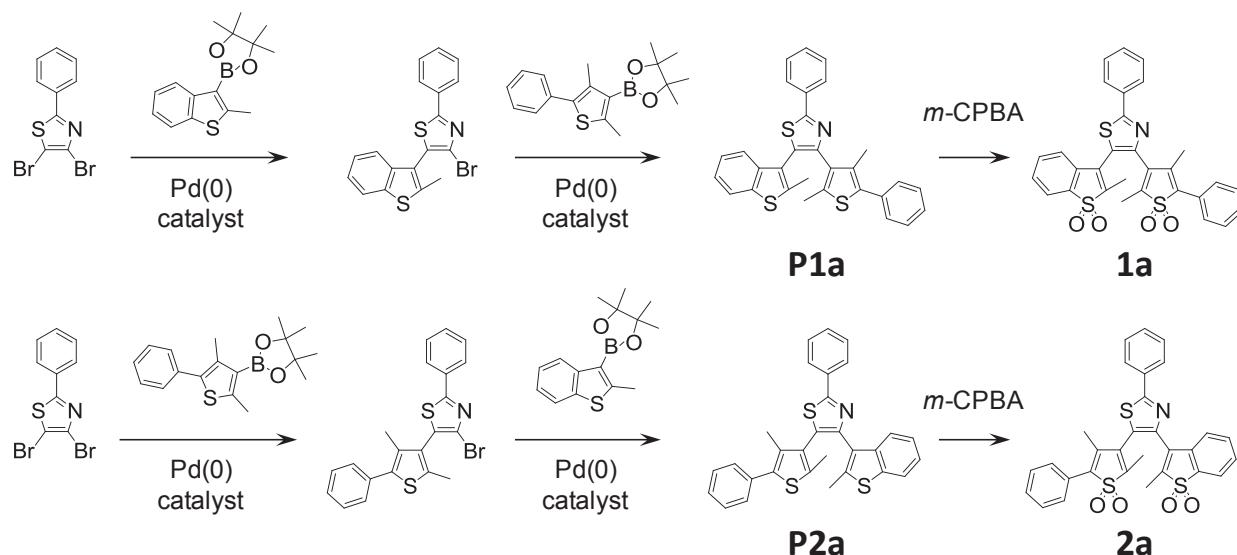


Fig. S1 Electron density distributions of (bottom) HOMOs and (top) LUMOs for compounds (a, b) **1a**, (c, d) **1b**, (e, f) **2a** and (g, h) **2b** which were calculated by TD-DFT (B3LYP/6-31G(d))

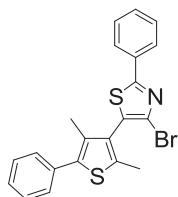
Table S1 HOMO and LUMO levels and first transition bands of compounds **1** and **2**

compound	HOMO [eV]	LUMO [eV]	first transition band [nm] (oscillator strength)
1a	-6.231	-2.442	374.35 ($f=0.0594$)
1b	-5.573	-2.870	506.55 ($f=0.3388$)
2b	-6.095	-2.465	399.23 ($f=0.0398$)
2b	-5.563	-2.917	508.58 ($f=0.4869$)

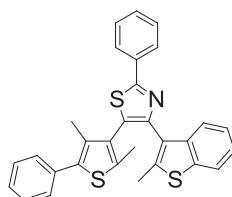
3. Syntheses of oxidized compounds **1a and **2a**, and their precursor compounds **P1a** and **P2a****



Scheme S1 Synthetic scheme for oxidized compounds **1a**, **2a** and their precursors **P1a** and **P2a**

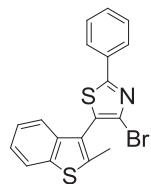


4-bromo-5-(2,4-dimethyl-5-phenylthiophen-3-yl)-2-phenylthiazole. To a mixture containing (2,4-dimethyl-5-phenylthiophen-3-yl)boronic acid pinacol ester (1.13 g, 3.59 mmol), 4,5-dibromo-2-phenylthiazole (0.521 g, 1.63 mmol), PPh₃ (0.054 g, 0.21 mmol) and 2.0 M K₃PO₄ aq. (10 ml, 20 mmol) in 1,4-dioxane (70 ml) after N₂ bubbling for 30 min, was added Pd(PPh₃)₄ (0.11 g, 0.099 mmol). The mixture was refluxed for 36 h under N₂ atmosphere. The resulting solution was quenched with water and neutralized with HCl aq. The organic layer was extracted with ethyl acetate and dried with MgSO₄. The crude solution was evaporated under vacuo and purified by a silicagel column chromatography to afford 0.400 g (0.938 mmol) of solid. ¹H NMR (300 MHz, CDCl₃/TMS): δ (ppm) = 7.95-7.98 (2H, m), 7.40-7.49 (7H, m), 7.33 (1H, t), 2.39 (3H, s), 2.15 (3H, s). MALDI-TOF MS (*m/z*) [M]⁺ Calcd. for C₂₁H₁₆BrNS₂⁺: 425; Found: 425.

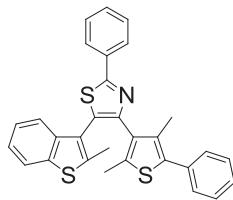


5-(2,4-dimethyl-5-phenylthiophen-3-yl)-4-(2-methylbenzo[b]thiophen-3-yl)-2-phenylthiazole (P2a). To a mixture containing 4-bromo-5-(2,4-dimethyl-5-phenylthiophen-3-yl)-2-phenylthiazole (0.400 g, 0.938 mmol), (2-methylbenzo[b]thiophen-3-yl)boronic acid pinacol ester (0.283 g, 1.03 mmol), PPh₃ (0.062 g, 0.236 mmol) and 2.0 M K₃PO₄ aq. (20 ml, 40 mmol) in 1,4-dioxane (20 ml) after N₂ bubbling for 60 min, was added Pd(PPh₃)₄ (0.064 g, 0.055 mmol). The mixture was refluxed for 48 h under N₂ atmosphere. The resulting solution was quenched with water and neutralized with HCl aq.. The organic layer was extracted with diethylether and dried with

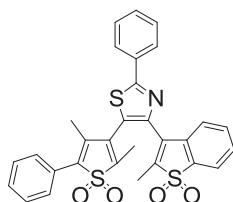
MgSO₄, then was concentrated under vacuo. The crude was purified by a silicagel column chromatography and an HPLC to afford 0.238 g (0.483 mmol) of colorless amorphous solid. ¹H NMR (300 MHz, CDCl₃/TMS): d (ppm) = 8.06-8.09 (2H, m), 7.73-7.76 (2H, m), 7.22-7.49 (10H, m), 2.16 (3H, s), 2.07 (3H, s), 2.00 (3H, s). ESI HRMS (*m/z*) [M+H]⁺ Calcd. for C₃₀H₂₄NS₃⁺: 494.10; Found: 494.11. Element Anal. Calcd. for C₃₀H₂₃NS₃: C, 72.98; H, 4.70; N, 2.84; Found: C, 73.04; H, 4.44; N, 2.83.



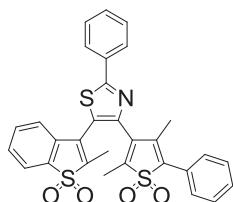
4-bromo-5-(2-methylbenzo[b]thiophen-3-yl)-2-phenylthiazole. To a mixture containing (2-methylbenzo[b]thiophen-3-yl)boronic acid pinacol ester (0.774 g, 2.82 mmol), 4,5-dibromo-2-phenylthiazole (1.17 g, 3.67 mmol), PPh₃ (0.185 g, 0.705 mmol) and 2.0 M K₃PO₄ aq. (20 ml, 40 mmol) in 1,4-dioxane (20 ml) after N₂ bubbling for 60 min, was added Pd(PPh₃)₄ (0.163 g, 0.141 mmol). The mixture was refluxed for 36 h under N₂ atmosphere. The resulting solution was quenched with water and neutralized with HCl aq.. The organic layer was extracted with ethyl acetate and dried with MgSO₄, then was evaporated under vacuo. The crude was purified by a silicagel column chromatography and a GPC to afford 0.353 g (0.914 mmol) of solid. ¹H NMR (300 MHz, CDCl₃/TMS): d (ppm) = 7.97-8.00 (2H, d), 7.80-7.82 (7H, m), 7.46-7.52 (1H, t), 7.31-7.39 (3H, s), 2.56 (3H, s). MALDI-TOF MS (*m/z*) [M]⁺ Calcd. for C₁₈H₁₂BrNS₂⁺: 385; Found: 385.



4-(2,4-dimethyl-5-phenylthiophen-3-yl)-5-(2-methylbenzo[b]thiophen-3-yl)-2-phenylthiazole (P2a). To a mixture containing 4-bromo-5-(2-methylbenzo[b]thiophen-3-yl)-2-phenylthiazole (0.353 g, 0.914 mmol), (2,4-dimethyl-5-phenylthiophen-3-yl)boronic acid pinacol ester (0.302 g, 0.961 mmol), PPh₃ (0.060 g, 0.228 mmol) and 2.0 M K₃PO₄ aq. (10 ml, 20 mmol) in 1,4-dioxane (10 ml) after N₂ bubbling for 60 min, was added Pd(PPh₃)₄ (0.064 g, 0.055 mmol). The mixture was refluxed for 24 h under N₂ atmosphere. The resulting solution was quenched with water and neutralized with HCl aq.. The organic layer was extracted with diethylether and dried with MgSO₄, then was concentrated under vacuo. The crude was purified by a silicagel column chromatography and an HPLC to afford 0.242 g (0.491 mmol) of colorless amorphous solid. ¹H NMR (300 MHz, CDCl₃/TMS, 50 °C): d (ppm) = 8.05-8.08 (2H, m), 7.69-7.76 (2H, m), 7.44-7.47 (3H, m), 7.25-7.36 (7H, m), 2.20 (3H, s), 2.09 (3H, s), 2.00 (3H, s). ESI HRMS (*m/z*) [M+H]⁺ Calcd. for C₃₀H₂₄NS₃⁺: 494.10; Found: 494.11. Element Anal. Calcd. for C₃₀H₂₃NS₃: C, 72.98; H, 4.70; N, 2.84; Found: C, 72.46; H, 4.57; N, 2.76. *Crystallographic Data : CCDC 933134.*



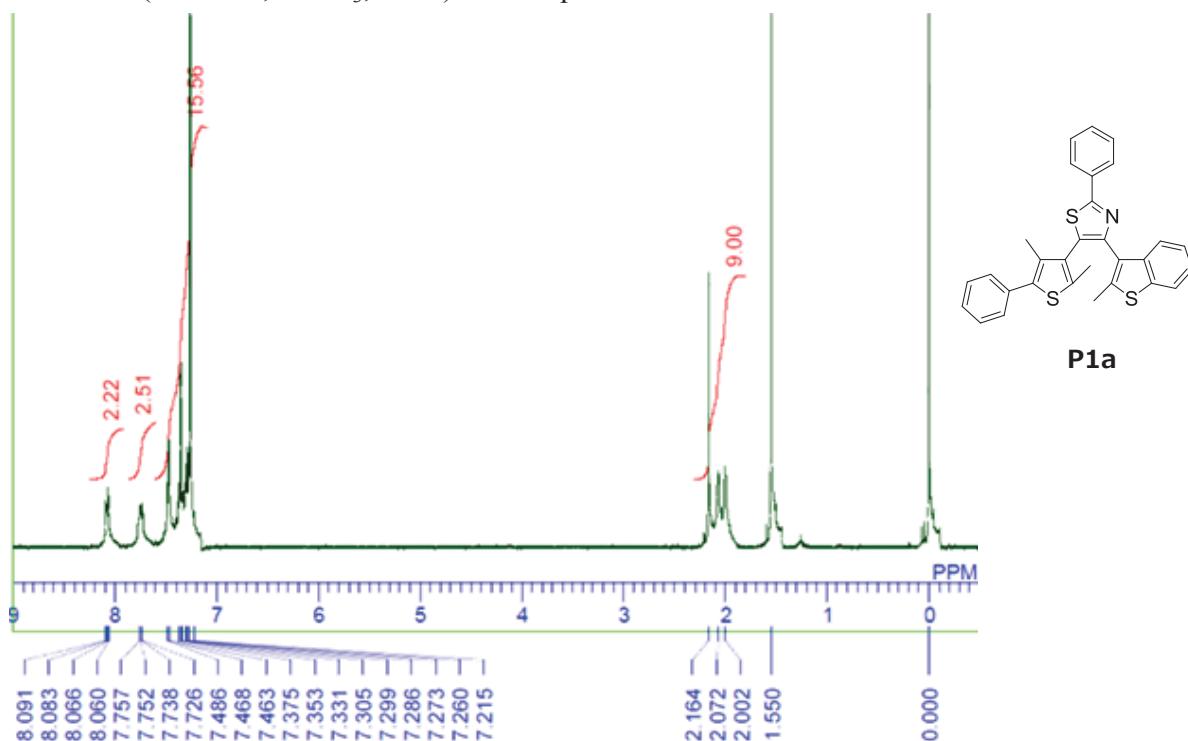
5-(2,4-dimethyl-5-phenylthiophen-3-yl)-4-(2-methylbenzo[b]thiophen-3-yl)-2-phenylthiazole (1a). To a solution of 5-(2,4-dimethyl-5-phenylthiophen-3-yl)-4-(2-methylbenzo[b]thiophen-3-yl)-2-phenylthiazole (30 mg, 0.061 mmol) in CH₂Cl₂ (20 ml) was added 70wt% 3-chloroperbenzoic acid (*m*-CPBA) (0.170 g, 0.687 mmol). The solution was stirred at r.t. in the dark for 48 h. The resulting solution was quenched with Na₂S₂O₃ aq.. The organic layer was extracted with CH₂Cl₂ and dried with MgSO₄, then was concentrated under vacuo. The residue was purified by an HPLC (hexane/ethyl acetate 3 : 1) to afford 20 mg (0.036 mmol) of white solid. ¹H NMR (300 MHz, CDCl₃/TMS): δ (ppm) = 8.02-8.05 (2H, m), 7.84-7.86 (1H, m), 7.52-7.62 (7H, m), 7.43-7.46 (4H, m), 2.16 (3H, s), 2.09 (3H, s), 1.86 (3H, s). ¹³C NMR (75MHz; CDCl₃): δ (ppm) = 170.47, 145.86, 138.94, 136.82, 135.85, 133.87, 133.72, 132.12, 131.87, 131.59, 130.48, 129.93, 129.75, 129.38, 129.16, 129.06, 126.76, 124.27, 121.70, 14.10, 9.11, 8.46. ESI HRMS (*m/z*) [M+Na]⁺ Calcd. for C₃₀H₂₃NO₄S₃Na⁺: 580.07; Found: 580.07. Element Anal. Calcd. for C₃₀H₂₃NO₄S₃: C, 64.61; H, 4.16; N, 2.51; Found: C, 64.79; H, 4.07; N, 2.33.



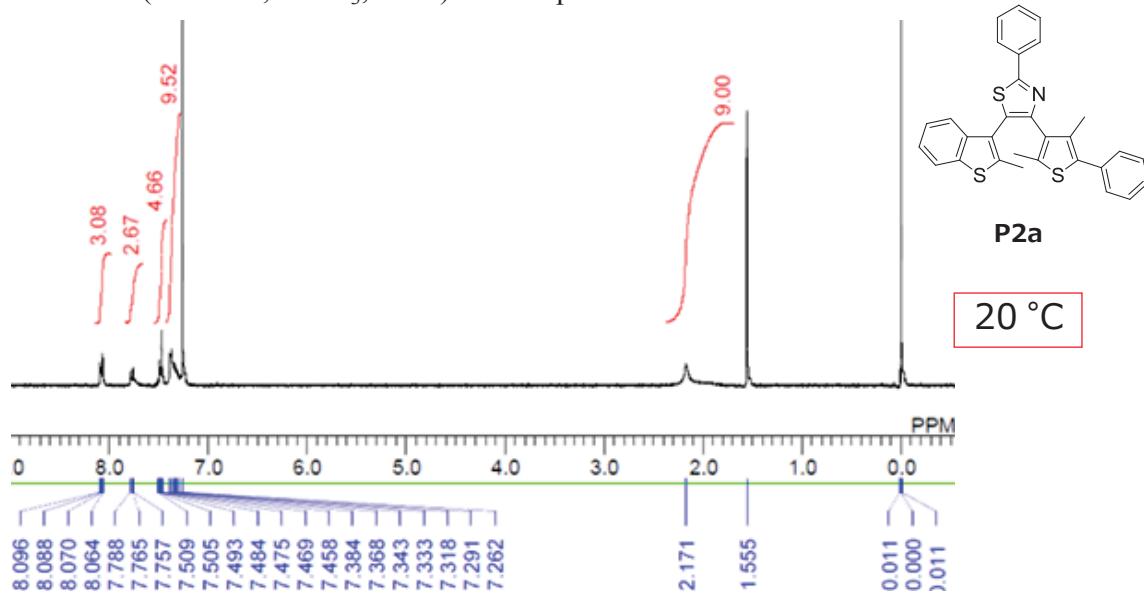
4-(2,4-dimethyl-5-phenylthiophen-3-yl)-5-(2-methylbenzo[b]thiophen-3-yl)-2-phenylthiazole (2a). To a solution of 4-(2,4-dimethyl-5-phenylthiophen-3-yl)-5-(2-methylbenzo[b]thiophen-3-yl)-2-phenylthiazole (0.100 g, 0.203 mmol) in CH₂Cl₂ (200 ml) was added 70wt% 3-chloroperbenzoic acid (*m*-CPBA) (0.480 g, 1.97 mmol). The solution was stirred at r.t. in the dark for 48 h. The resulting solution was quenched with Na₂S₂O₃ aq.. The organic layer was extracted with CH₂Cl₂ and dried with MgSO₄, then was concentrated under vacuo. The residue was purified by an HPLC (hexane/ethyl acetate 3 : 1) to afford 0.080 g (0.143 mmol) of white solid. ¹H NMR (300 MHz, CDCl₃/TMS): δ (ppm) = 8.02-8.05 (2H, m), 7.85-7.88 (1H, m), 7.53-7.62 (7H, m), 7.45-7.47 (4H, d), 2.16 (6H, s), 1.92 (3H, s). ¹³C NMR (75MHz; CDCl₃): δ (ppm) = 170.32, 146.94, 136.32, 135.84, 134.78, 133.74, 132.19, 131.63, 130.30, 129.69, 129.40, 129.21, 129.01, 127.88, 127.17, 126.77, 126.71, 122.71, 122.21, 14.58, 8.80, 8.55. ESI HRMS (*m/z*) [M+Na]⁺ Calcd. for C₃₀H₂₃NO₄S₃Na⁺: 580.07; Found: 580.07. Element Anal. Calcd. for C₃₀H₂₃NO₄S₃: C, 64.61; H, 4.16; N, 2.51; Found: C, 64.84; H, 4.38; N, 2.34.

4. NMR spectra for compounds **1a** and **2a**, and their precursors **P1a** and **P2a**

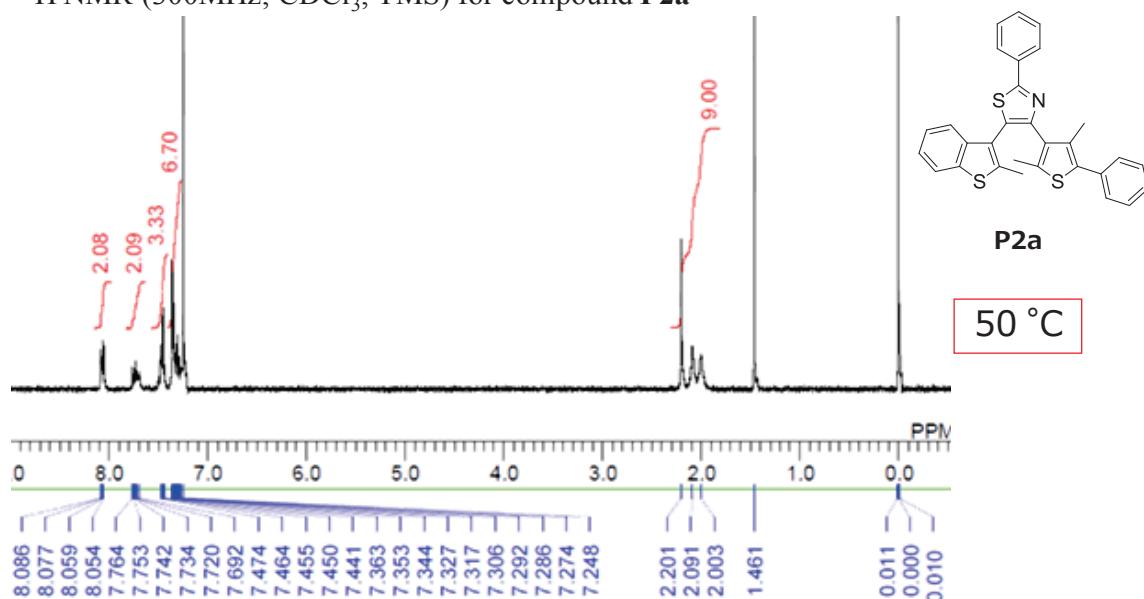
¹H NMR (300MHz; CDCl₃, TMS) for compound **P1a**



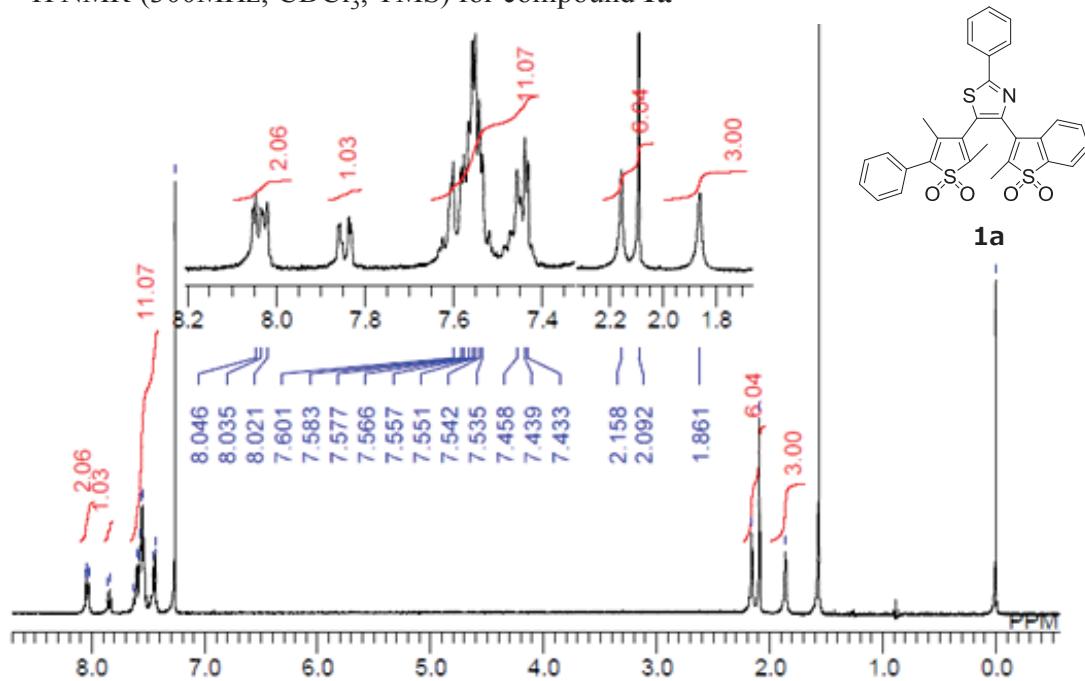
¹H NMR (300MHz; CDCl₃, TMS) for compound **P2a**



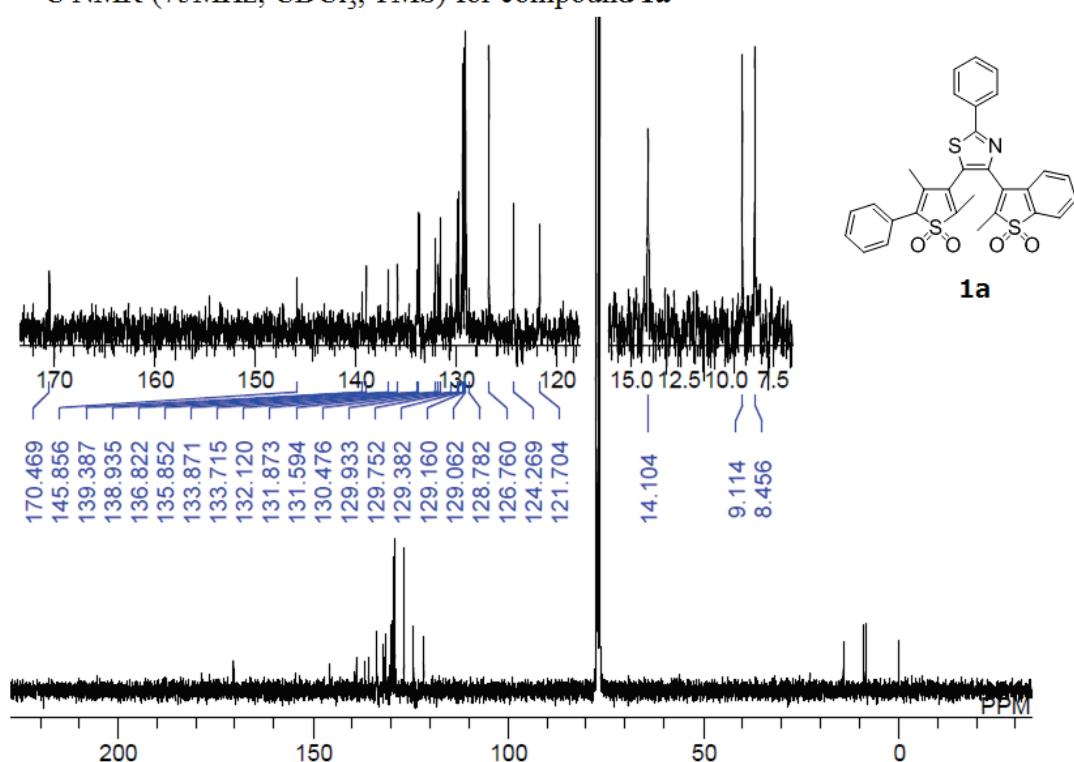
¹H NMR (300MHz; CDCl₃, TMS) for compound P2a



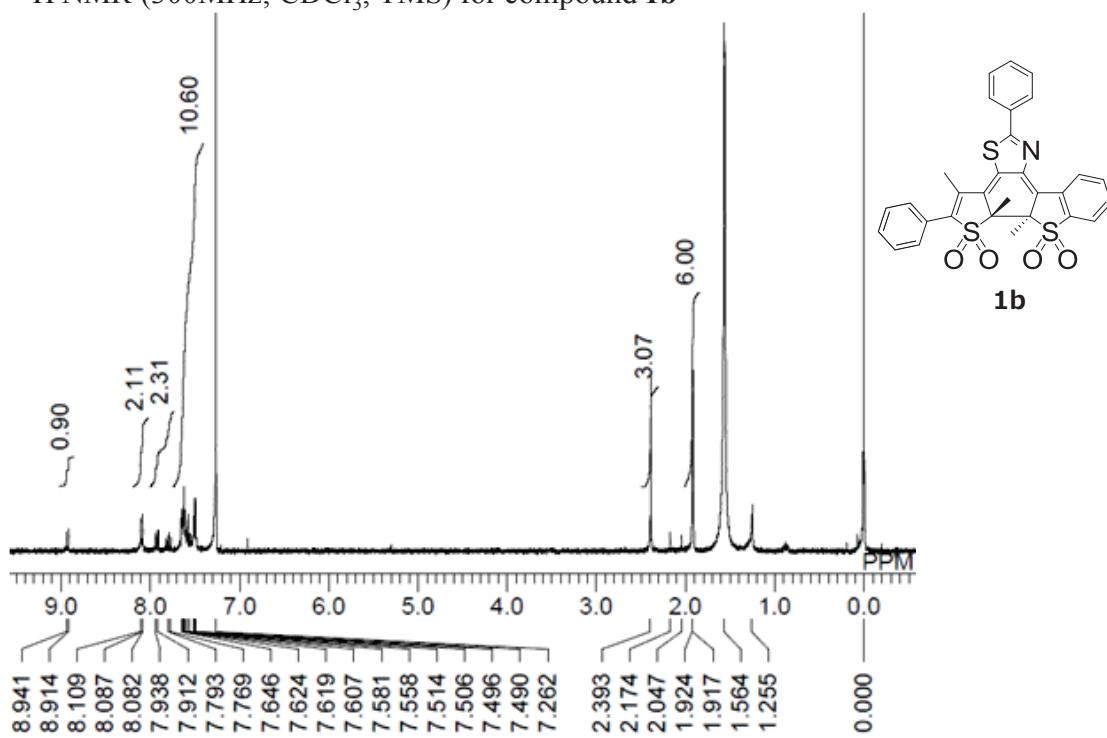
¹H NMR (300MHz; CDCl₃, TMS) for compound 1a



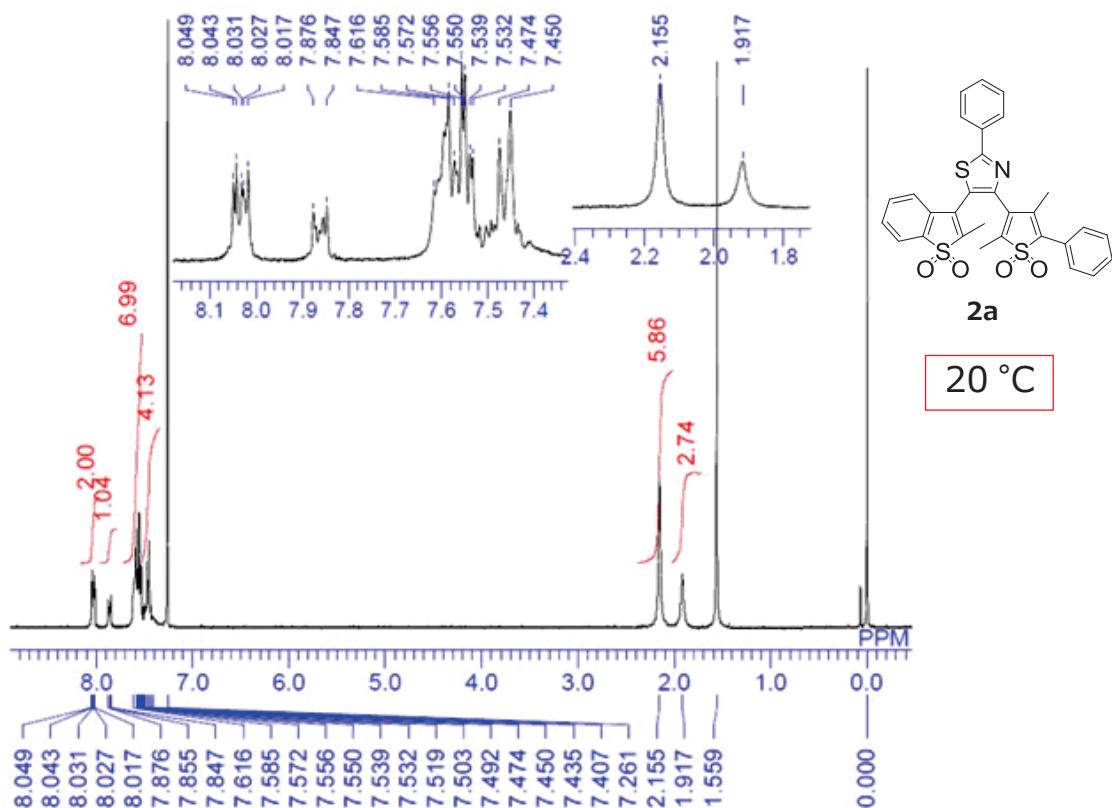
^{13}C NMR (75MHz; CDCl_3 , TMS) for compound **1a**



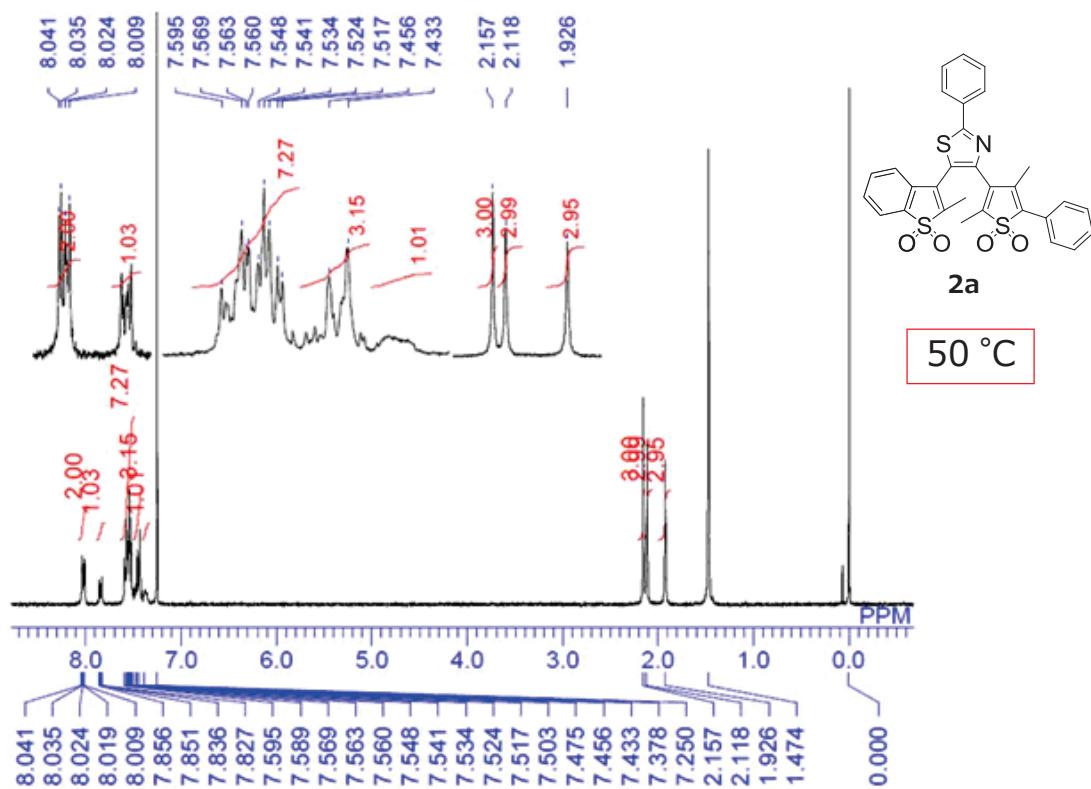
^1H NMR (300MHz; CDCl_3 , TMS) for compound **1b**



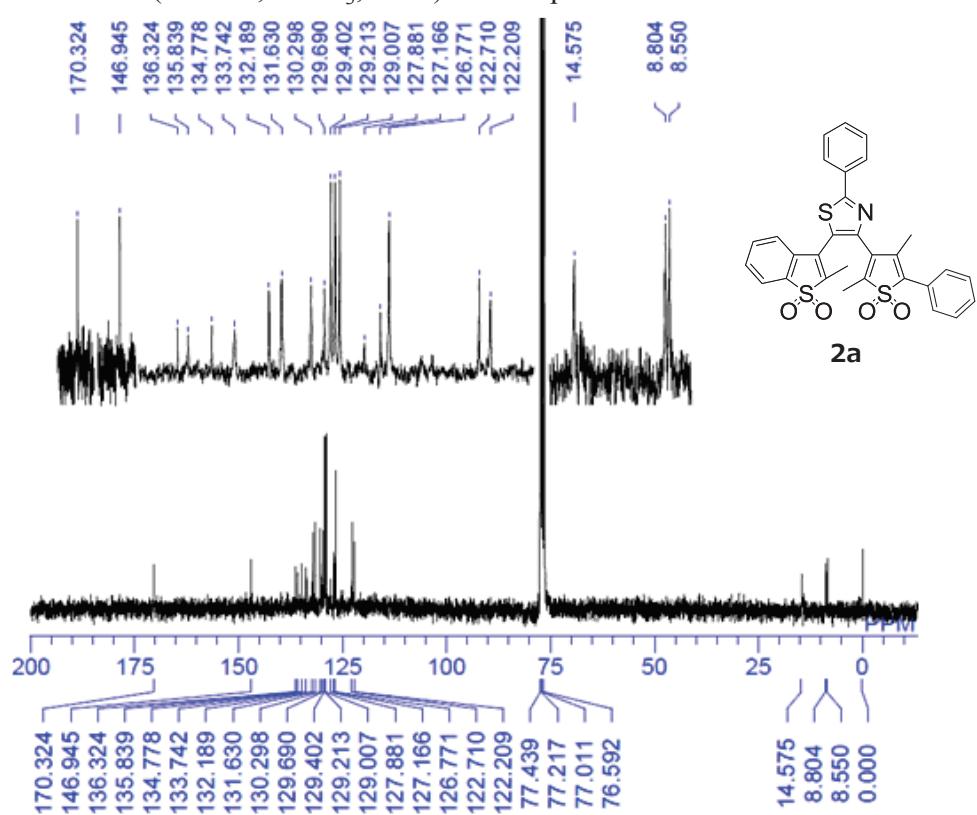
¹H NMR (300MHz; CDCl₃, TMS) for compound 2a



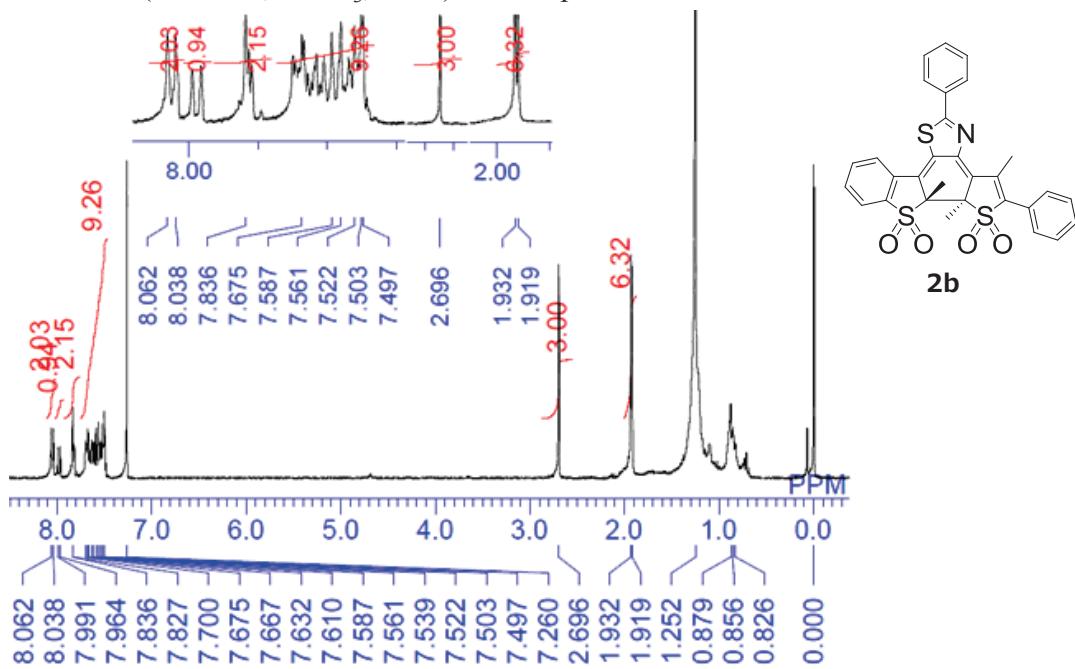
¹H NMR (300MHz; CDCl₃, TMS) for compound 2a



^{13}C NMR (75MHz; CDCl_3 , TMS) for compound **2a**



^1H NMR (300MHz; CDCl_3 , TMS) for compound **2b**



5. Crystallographic data for compound P2a

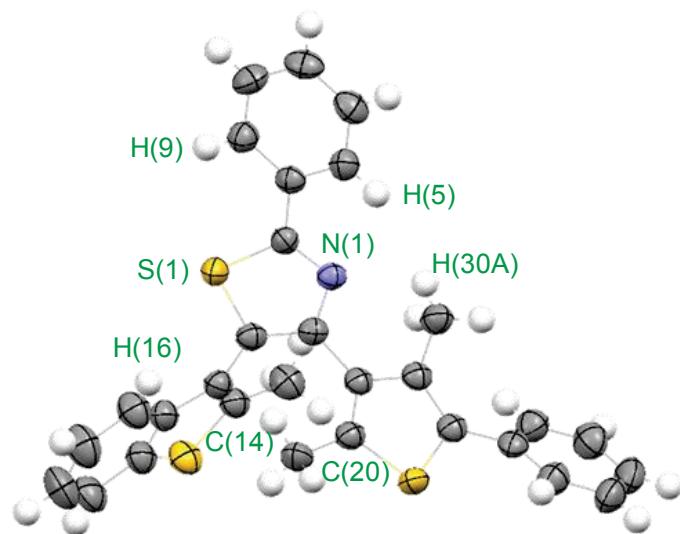


Fig. S2 ORTEP drawings of **P2a** in crystal (crystallographic data number: CCDC 933134), showing 50 % probability displacement ellipsoids.

Table S2 List of characteristic atomic distances in compound P2a evaluated by the X-ray crystallographic structure.

atoms	distance [nm]	
C(14)	C(20)	3.835
S(1)	H(9)	2.779
S(1)	H(16)	3.034
N(1)	H(5)	2.595
N(1)	H(30A)	2.530

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	C ₃₀ H ₂₃ NS ₃
Formula Weight	493.70
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.190 X 0.110 X 0.070 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 14.4429(2) Å b = 19.7021(3) Å c = 8.7116(1) Å β = 96.2127 ° V = 2464.38(6) Å ³
Space Group	P2 ₁ /c (#14)
Z value	4
D _{calc}	1.331 g/cm ³
F ₀₀₀	1032.00
μ (MoKα)	3.204 cm ⁻¹

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoK α ($\lambda = 0.71075 \text{ \AA}$)
Voltage, Current	50kV, 24mA
Temperature	-150.00°C
Detector Aperture	280 x 256 mm
Data Images	111 exposures
ω oscillation Range ($\chi=45.0, \phi=0.0$)	130.0 - 190.0°
Exposure Rate	30.0 sec./°
ω oscillation Range ($\chi=45.0, \phi=180.0$)	0.0 - 162.0°
Exposure Rate	30.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{\max}$	55.0°
No. of Reflections Measured	Total: 24279 Unique: 5636 ($R_{\text{int}} = 0.0245$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.854 - 0.978)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.0521 \cdot P)^2 + 0.7430 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\max}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5636
No. Variables	310
Reflection/Parameter Ratio	18.18
Residuals: R1 ($I > 2.00\sigma(I)$)	0.0355
Residuals: R (All reflections)	0.0379
Residuals: wR2 (All reflections)	0.0928
Goodness of Fit Indicator	1.135
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map	0.64 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.29 e ⁻ /Å ³

6. Glass transition temperatures of **1a** and **1b**

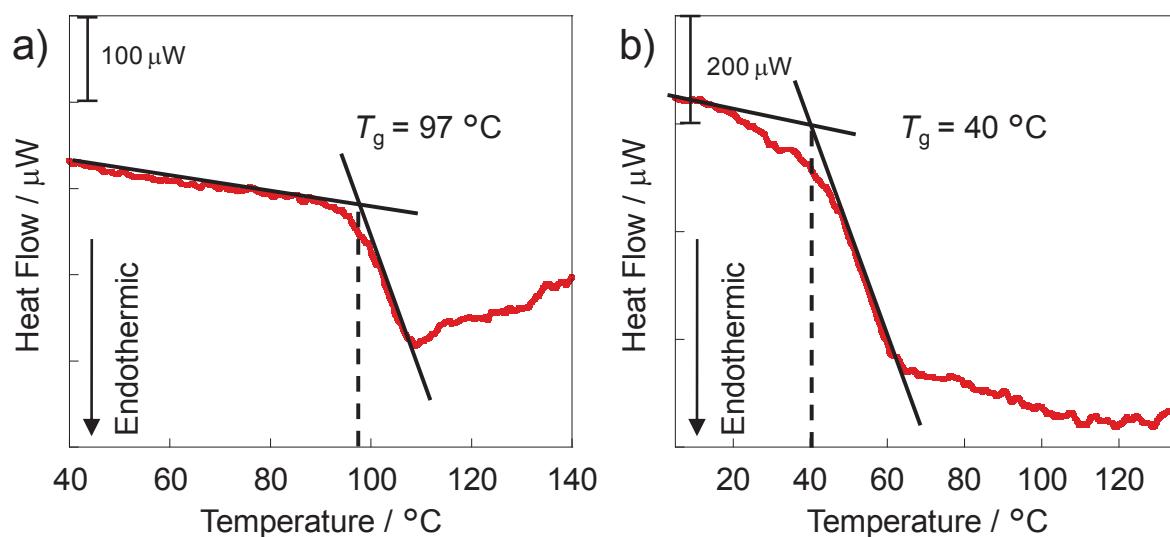


Fig. S3 DSC curves for compounds **1a** and **1b**.

7. The thickness of the film of compound **1** estimated by an atomic force microscope

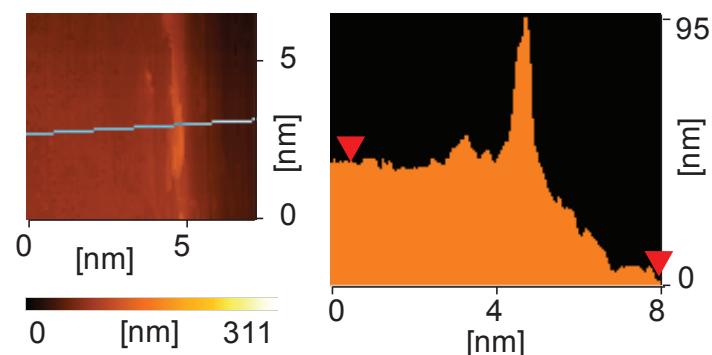


Fig. S4 AFM image of an amorphous film of compound **1**

The thickness of the film was estimated to be ca. 40 nm from difference in height at the scratched mark.

8. Absorption spectral changes for precursor compounds **P1** and **P2** in hexane solutions

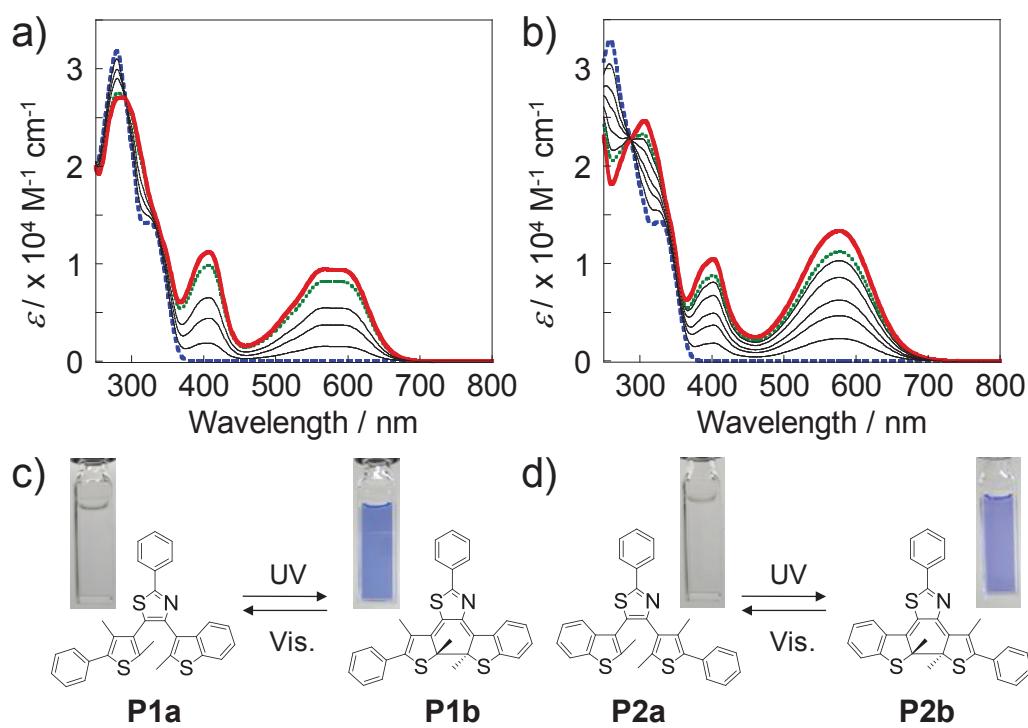


Fig. S5 Absorption spectral changes for precursor compounds, (a) **P1** and (b) **P2** in hexane; open-forms (blue dashed lines), closed-forms (red bold solid lines) and P.S.S. (photostationary state) under irradiation with 313 nm (green dotted lines). Photoisomerization reaction schemes for (c) **P1** and (d) **P2**.

9. Absorption and PL spectra for oxidized compounds **1** and **2** in dichloromethane solutions

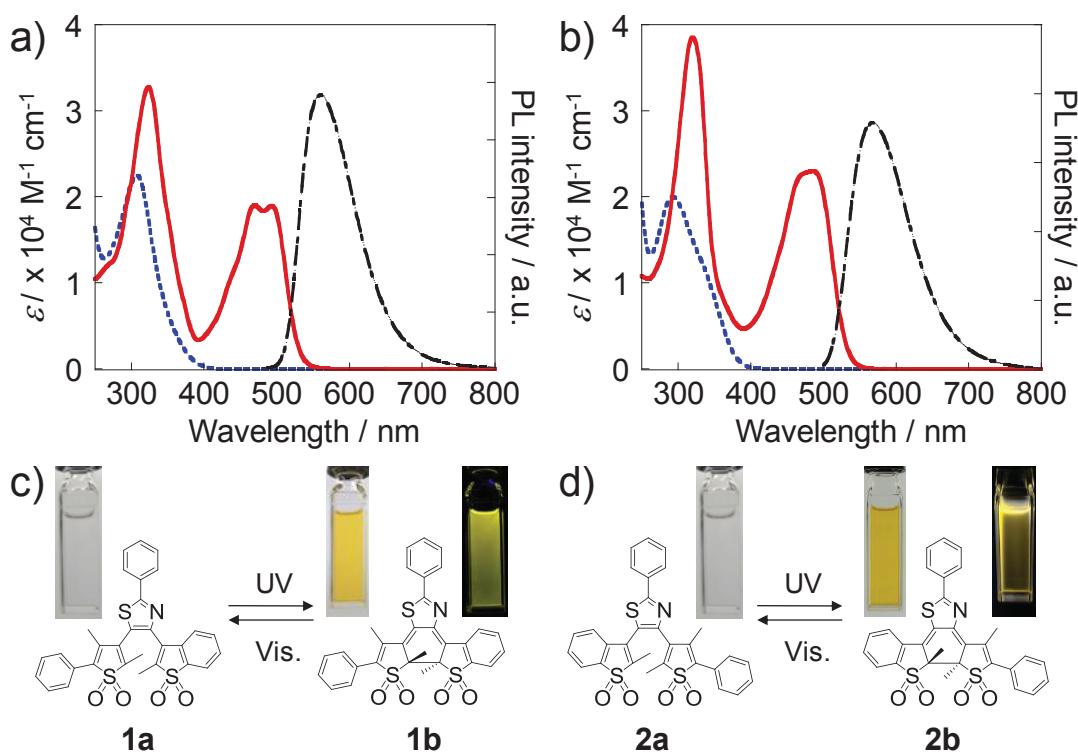


Fig. S6 Absorption and PL spectra for oxidized compounds, (a) **1** and (b) **2** in dichloromethane; open-forms (blue dashed lines), closed-forms (red bold solid lines) and PL spectra of closed-forms (black dot-dashed lines). Photoisomerization reaction schemes for (c) **1** and (d) **2**.

10. Photochemical properties for oxidized compounds 1, 2 and precursor compounds P1, P2

Table S3 Absorption and emission and photochromic properties of terarylenes in solutions

sample	solvent	λ/nm ($\varepsilon/10^4 \text{ M}^{-1} \text{cm}^{-1}$)	α_{pss}^a	Φ_{ab}^b	Φ_{ba}^c	$\lambda_{\text{em}}/\text{nm}$ ($\lambda_{\text{ex}}/\text{nm}$)	Φ_{em}	$\tau_{\text{em}}/\text{ns}$	$k_{\text{f}}/10^7 \text{ s}^{-1}$	$k_{\text{nr}}/10^8 \text{ s}^{-1}$
1a	CH_2Cl_2	306(2.25)	>0.99	0.18 (± 0.01)	-	n.d. ^f				
1b	CH_2Cl_2	324(3.28) 470(1.90) 493(1.90)	-	-	$1.8 \times 10^{-4}^d$	560(470)	0.28	3.3	8.4	2.2
2a	CH_2Cl_2	292(2.00)	>0.99	0.24 (± 0.02)	-	n.d. ^f				
2b	CH_2Cl_2	320(3.86) 486(2.30)	-	-	$< 1 \times 10^{-5}^d$	567(470)	0.31	3.3	9.3	2.1
P1a	hexane	279(3.19) 325(1.43)	0.84	0.58 (± 0.01)	-	n.d. ^f				
P1b	hexane	289(2.71) 407(1.12) 569(0.943)	-	-	0.12 ^e	n.d. ^f				
P2a	hexane	259(3.30) 328(1.45)	0.83	0.66 (± 0.01)	-	n.d. ^f				
P2b	hexane	306(2.46) 402(1.05) 577(1.33)	-	-	0.069 ^e	n.d. ^f				

^a α_{pss} : the coloration conversion ratio at P.S.S. with the irradiation at 313 nm light. ^b Φ_{ab} : ring-closing reaction quantum yield from a-form to b-form at 313 nm. ^c Φ_{ba} : ring-opening reaction quantum yield from b-form to a-form. ^d At 432 nm. ^e At 546 nm. ^f Fluorescence was unobserved at room temperature.

11. Changes of absorbance for compounds **1 and **2** in amorphous films as a time-function of UV light irradiation ($\lambda_{\text{irr}} = 313 \text{ nm}$, 0.16 mW cm^{-2})**

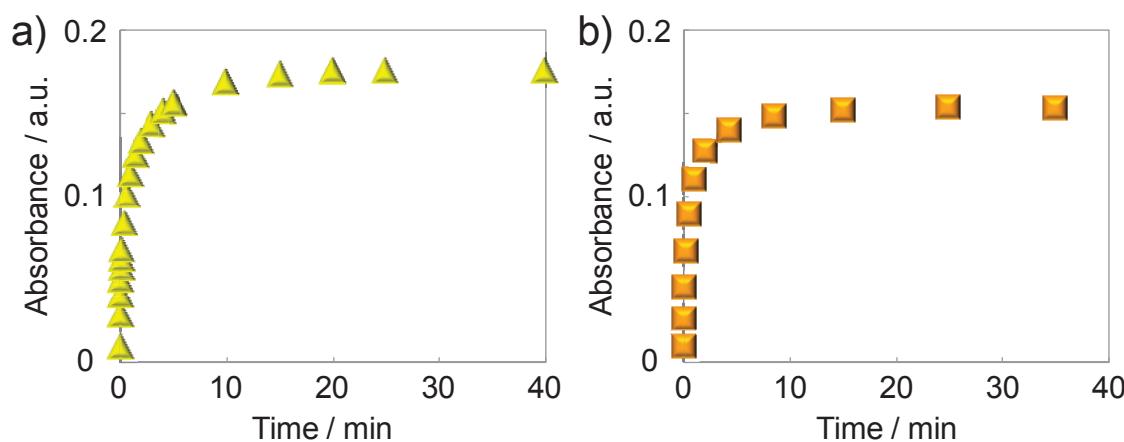


Fig. S7 Absorbance changes (a) at 501 nm for compound **1** and (b) at 500 nm for compound **2** in amorphous films (thickness = $4 \times 10^1 \text{ nm}$) as a time-function of UV light irradiation ($\lambda_{\text{irr}} = 313 \text{ nm}$, 0.16 mW cm^{-2}).

12. Relative PL intensities for compounds **1b, **2b**, and reference compound Alq_3 in amorphous films as time-function of continuous excitation in the air ($\lambda_{\text{ex}} = 425 \text{ nm}$, 0.37 mW cm^{-2}).**

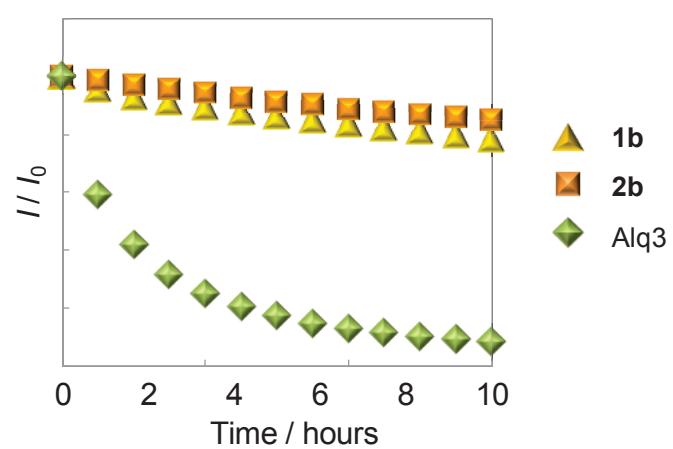


Fig. S8 Relative PL intensities at 583 nm for compound **1** (yellow trigona), at 596 nm for compound **2** (orange squares) and at 530 nm for Alq_3 (green rhombi) in amorphous films as a time-function of irradiation time ($\lambda_{\text{ex}} = 425 \text{ nm}$, 0.37 mW cm^{-2}).

13. The PL pattern from the amorphous films for compound 1 and 2

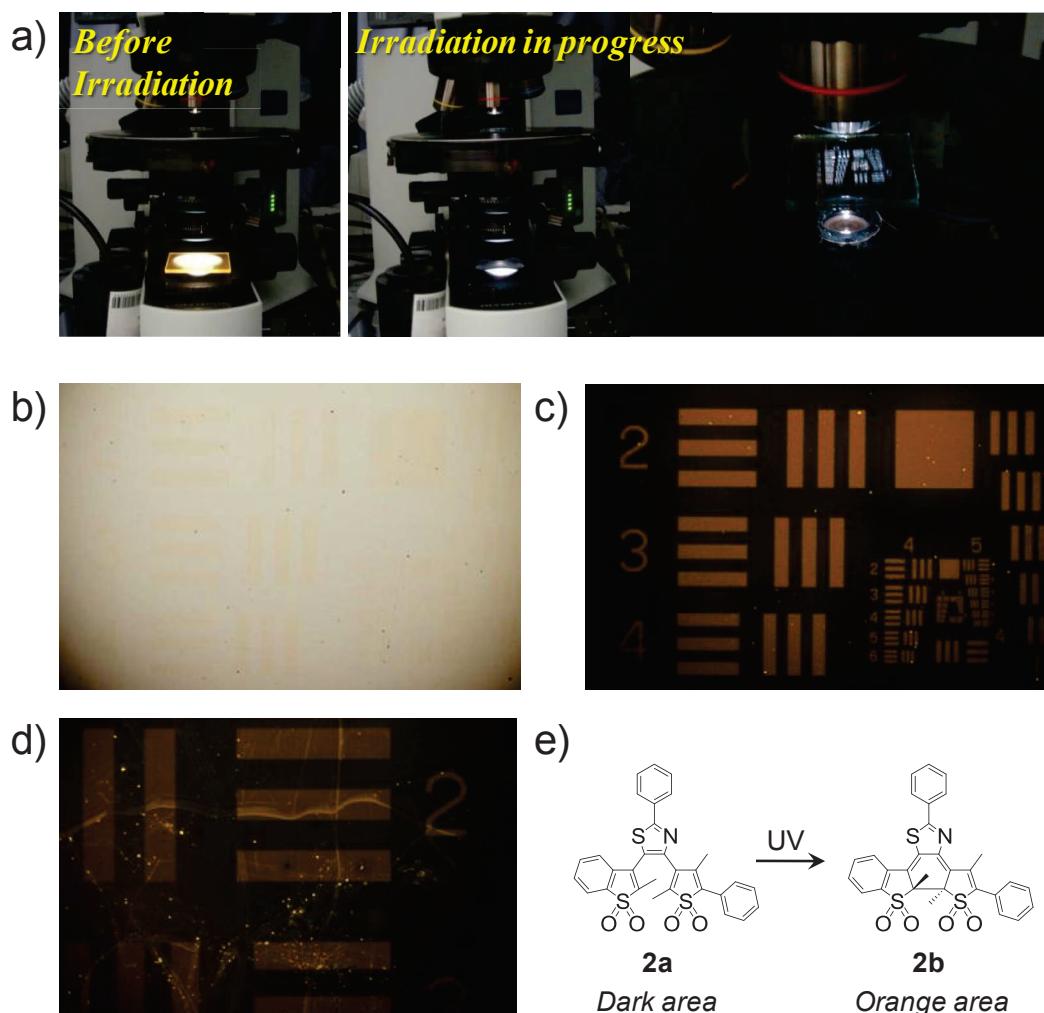


Fig. S9 (a) The photo-coloration process by irradiating with UV-vis light (380-700 nm) through an optical mask (nega-type) using a tungsten lamp composing an optical microscope (Olympus, BX-51). Weak UV component from the tungsten lamp induced the coloration. Because of extremely slow bleaching reactivity, visible light component showed no marked influence on the coloration behaviour. (b) Normal and (c) PL pattern photographs of a transparent amorphous film of compound **1** (thickness = 4×10^1 nm) and (d) PL pattern photograph of a transparent amorphous film of compound **2** (thickness = 4×10^1 nm) on the glass substrate (20×20 mm², thickness = 1 mm). (e) A scheme of photoisomerization reaction from **2a** to **2b**.

14. EQE (external quantum efficiency)-voltage characteristic of the device for compound 1b

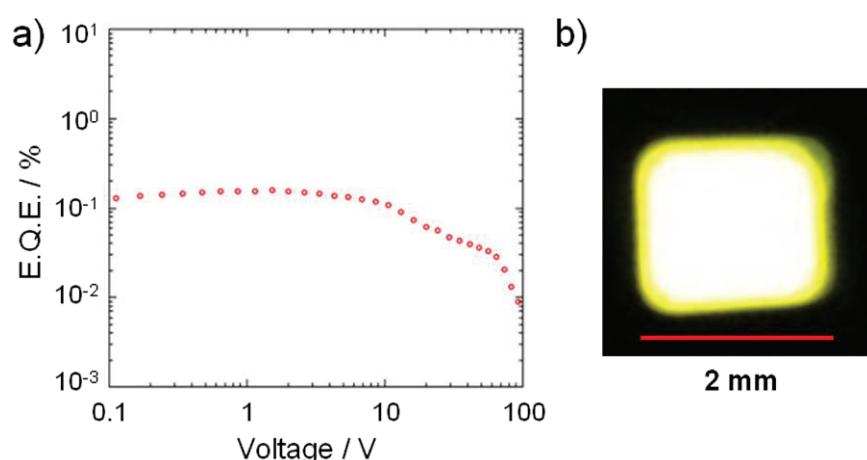


Fig. S10 (a) EQE (external quantum efficiency)-voltage characteristic of a device as glass/ITO/PEDOT:PSS (8 nm)/6wt% of compound **1**: mCP (18 nm)/BCP (40 nm)/LiF (0.8 nm)/Al (64 nm); maximum EQE was estimated to be 0.20%. (b) Photograph of clear yellow EL from the device (a pixel size is $2 \times 2 \text{ mm}^2$).

15. The EL pattern from the device using compound 1

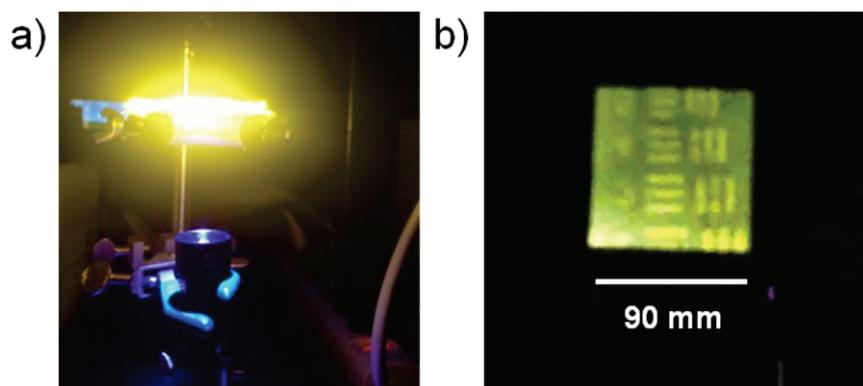


Fig. S11 (a) The photo-bleaching process by irradiating with green light (53 mW cm^{-2}) through a colour filter glass Y-42 and an optical mask (posi-type) by using a halogen lighting system, MORITEX. (b) EL pattern photograph of the device as glass/ITO/PEDOT:PSS (8 nm)/6wt% of compound **1**: mCP (18 nm)/BCP (40 nm)/LiF (0.8 nm)/Al (64 nm).