ESI for
Photosynergetic amplification of radiation input: from efficient UV induced cycloreversion to sensitive X-ray detection

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1. Experimental details

1-1. General

^{1}H and ^{13}C NMR (300, 400, and 600 MHz) spectra were recorded on JEOL JNM-AL300, JEOL JNM-ECP400, and JEOL JNMECA600 spectrometers, respectively. Reversed-phase HPLC separation was performed with a LaChrom Elite apparatus (Hitachi). Mass spectrometry and high-resolution mass spectrometry were performed on JEOL JMS-Q1000TD and JMS-700 MStation JMS-S3000 spectrometers, respectively. UV/Vis spectra, quantum yields of photochromic reactions ($\varphi_{c\text{-}o}$ and $\varphi_{o\text{-}c}$) and photo-induced fading reaction were measured using a JASCO V-660, V-760 spectrophotometer and a Shimadzu QYM-01 set-up, respectively. For kinetic thermal analyses, the temperature was controlled by a JASCO ETC 505 T temperature controller. Stopped-flow measurements were conducted with a rapid-scan stopped-flow spectroscopic system (Unisoku).

1-2. Oxidative cycloreversion experiments

Oxidative cycloreversion experiments were performed by mixing the requisite amounts of the oxidising agent tris(4-bromophenyl)ammonium hexachloroantimonate with the closed forms of **1**, **3**, **4** and **5** in acetonitrile and monitoring the evolution of absorbance at λ_{max}, with constant stirring to avoid the effect of diffusion on the electron transfer.

1-3. UV-induced cycloreversion experiments

UV-induced cycloreversion experiments were performed on the closed forms of **1**, **3, 4** and **5** in chloroform solution by monitoring the evolution of absorbance at λ_{max}, with constant stirring to avoid the effect of diffusion on the electron transfer. Chloroform solution of closed from was prepared by diluting the 0.3 mL solutions of the compounds in toluene which was irradiated with LED-UV light at 313 nm until a photostationary state was achieved. Then the solution irradiated with a controlled number of photons in a QYM machine (SHIMADZU QYM-01) and absorption changes ware monitored using the QYM machine.

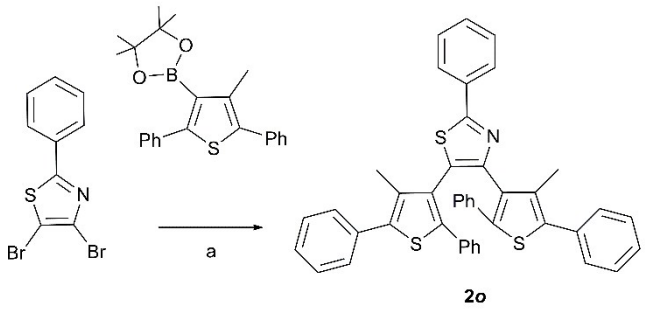
1-4. X-ray induced cycloreversion experiments

X-ray induced cycloreversion experiments were performed the closed forms of **1**, **2, 4** and **5** in chloroform solution which was prepared in the same method as UV induced cycloreversion experiments monitoring the evolution of absorbance at λ_{max} after X-ray irradiation for six seconds, with constant stirring to avoid the effect of diffusion on the electron transfer. The irradiation source of X-ray (XRB80, Spellman) was a conventional X-ray tube equipped with a tungsten anode target and beryllium window. The applied tube

voltage and current were 40 kV and 0.052 -5.2 mA, respectively.

1-5. Synthesis

1o[1] and **5o**[2] were synthesised as previously reported. **2 o**, **3 o** and **4 o** were prepared according to the routes depicted in Schemes S1, S2 and S3 from starting materials prepared in methods similar to those of **1o** and **5o**.



2o

Scheme S1: Synthesis of **2 o**: a) $[Pd(PPh_3)_4]$, PPh_3, 2 M Na_2CO_3 K_3PO_4 Water/1,4-dioxane

2o) 4,5-bis(4-methyl-2,5-diphenylthiophen-3-yl)-2-phenylthiazole: 4,5-dibromo-2-phenylthiazole (322 mg, 0.85 mmol.), 4,4,5,5-tetramethyl-2-(4-methyl-2,5-diphenylthiophen-3-yl)-1,3,2-dioxaborolane (751 mg, 2.35 mmol.), PPh_3 (162 mg, 0.43 mmol.) and 2 M aqueous K_3PO_4 (15 mL) were dissolved in 1,4-dioxane (15 mL). After 15 minutes stirring under N_2 atmosphere, $Pd(PPh_3)_4$ (352 mg, 30 mol%) was added and the mixture refluxed under N_2 atmosphere at 110 °C for 72 h. Thereafter, the organic layer was extracted with chloroform, and the combined extracts were washed with water and dried over anhydrous Na_2SO_4. The sample was then filtered and the filtrate was concentrated in vacuo. Silica gel column chromatography (hexane:ethyl acetate, 40:1) of the residue and Reversed-Phase HPLC (acetonitrile) afforded 4,5-bis(4-methyl-2,5-diphenylthiophen-3-yl)-2-phenylthiazole (0.12 g, 19 % yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.26-8.25 (m, 4H), 8.19-8.17 (m, 2H), 7.70-7.61 (m, 8H), 7.56-7.48 (m, 9H), 7.46-7.42 (m, 2H) 1.57 (s, 6H); ^{13}C NMR (151 MHz, CD_3CN, 25 °C, TMS): δ = 166.0, 150.0 , 129.2, 128.5, 128.4, 128.3, 128.2, 127.3, 126.4, 116.2, 94.4, 83.9, 77.3, 77.1, 76.9, 56.4, 40.3, 38.6, 34.7, 33.3, 28.8, 25.0, 24.5, 15.0, 14.5, 13.0 ppm; HRMS (MALDI SpiralTOF): *m/z* calcd. for $C_{43}H_{31}NS_3$ $[M]^+$: 657.16131; found 657.16125.

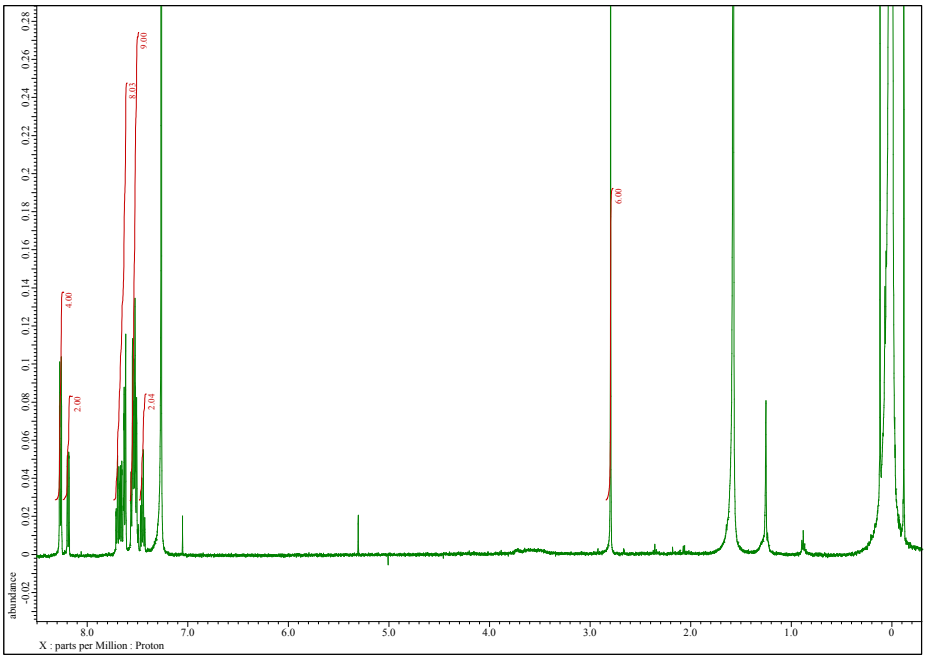


Fig. S1 ^{1}H NMR spectrum of **2o** (500 MHz, $CDCl_3$/TMS, 25 °C).

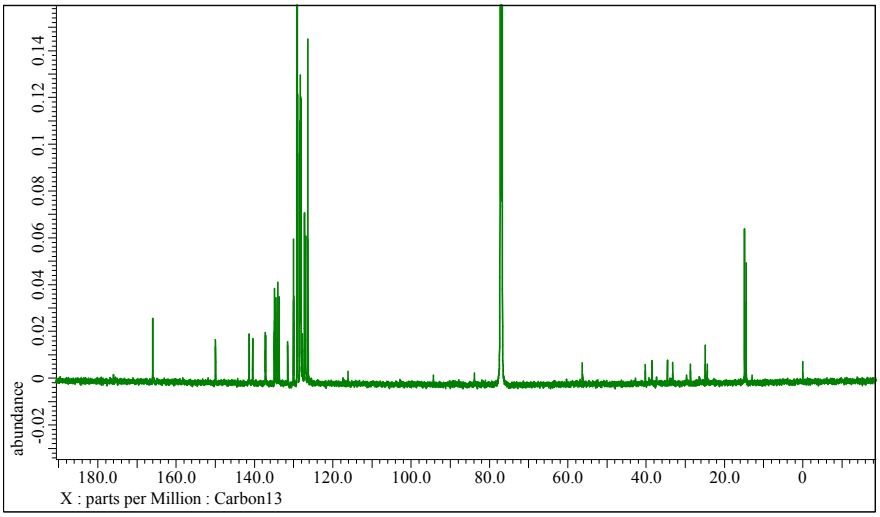


Fig. S2 13C NMR spectrum of **2o** (151 MHz, CD_3CN, 25 °C, TMS).

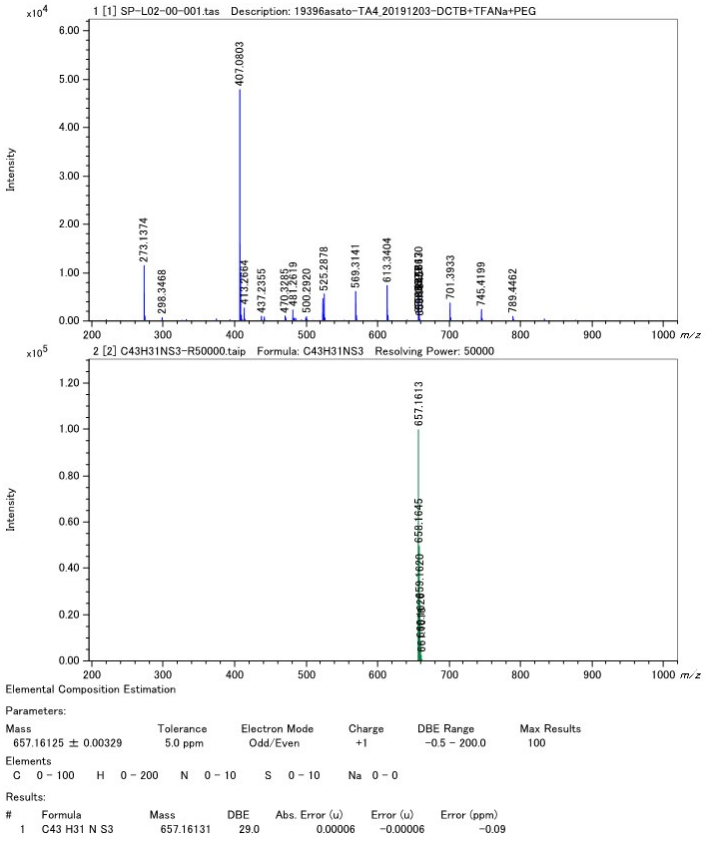
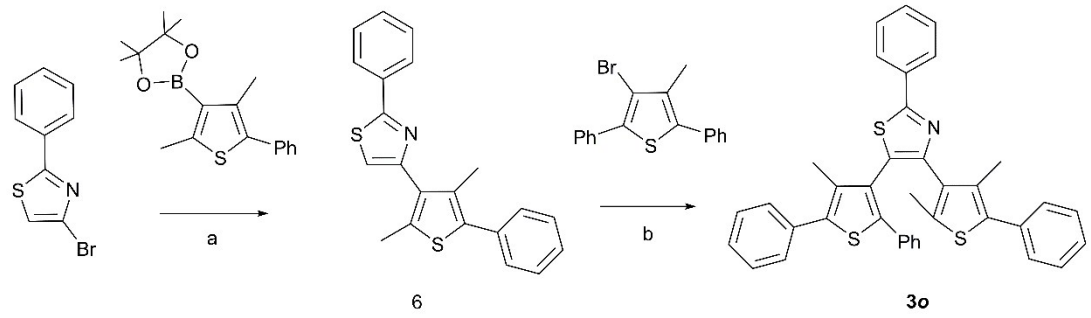


Fig. S3 HRMS data of **2o**. A MALDI Spiral TOF system (JEOL, JMS-S3000) was used with polyethylene glycol.



as an internal standard.

Scheme S2: Synthesis of **3o**: a) $[Pd(PPh_3)_4]$, PPh_3, 2 M K_3PO_4, Water / 1,4 -dioxane, b) $[Pd(OAc)_2]$, pivalic acid, di-*tert*-butylmethylphosphine tetrafluoroborate, mesitylene.

6) 2-(2,4-dimethyl-5-phenylthiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: 4-bromo-2-phenylthiazole (694 mg, 2.9 mmol), 4,4,5,5-tetramethyl-2-(3,5-dimethyl-2-phenylthiophen-3-yl)-1,3,2-dioxaborolane (1.20 g, 3.2 mmol), PPh_3 (379 mg, 1.4 mmol.) and 2 M aqueous K_3PO_4 (10 mL) were dissolved in 1,4-dioxane (10 mL). After 15 minutes stirring under N_2 atmosphere, $Pd(PPh_3)_4$ (369 mg, 0.32 mmol.) was added and stirred under N_2 atmosphere at 110 °C for 72 h. Thereafter, the organic layer was extracted with chloroform, and the combined extracts were washed with water and dried over anhydrous Na_2SO_4. The

sample was then filtered and the solution was concentrated in vacuo. Silica gel column chromatography (hexane:ethyl acetate, 10:1) of the residue afforded **6** (582 mg, 58 % yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.07-7.92 (m, 3H), 7.49-7.27 (m, 7H), 7.19 (s, 1 H), 2.52 (s, 3H), 2.26 (s, 3H).

3o) 4-(2,4-dimethyl-5-phenylthiophen-3-yl)-5-(4-methyl-2,5-diphenylthiophen-3-yl)-2-phenylthiazole: **6** (0.58 g, 1.6 mmol.), 3-bromo-4,5-dimethyl-2-phenylthiophene (593 mg, 1.8 mmol.), di-*tert*-butylmethylphosphine tetrafluoroborate (40 mg, 0.16 mmol.), Cs_2CO_3 (1.08 g, 3.3 mmol.), $Pd(OAc)_2$ (18 mg, 0.08 mmol.), and pivalic acid (51 mg, 0.5 mmol.) were dissolved in mesitylene (6 mL). The mixture was heated under reflux at 150 °C overnight. Thereafter, it was filtered through celite, extracted with ethyl acetate, and the combined extracts were washed with water and dried over anhydrous Na_2SO_4. Silica gel column chromatography (hexane:ethyl acetate, 9:1) and gel permeation chromatography afforded **3*o*** (98 mg, 10 % yield) as a colourless powder. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.04 (dd, J = 2.4 Hz, 8.0 Hz, 2 H), 7.54-7.45 (m, 7H), 7.40-7.28 (m, 6 H), 7.19-7.11 (m, 3H), 7.03-6.98 (m, 2H), 2.36 (s, 3 H), 1.84 (s, 3H), 1.59 (br-s, 1 H), 1.29 (br-s, 1 H) 0.87 (br-s, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C, TMS): δ = 166.5, 150.4, 142.3, 138.5, 135.6, 134.8, 134.5, 134.2, 134.1, 130.4, 129.6, 129.5, 129.4, 129.3, 128.9, 128.8, 128.7, 128.0, 127.9, 127.2, 126.6, 31.0, 30.1, 15.6, 14.4, 14.1 ppm; HRMS (MALDI SpiralTOF): *m*/*z* calcd. for $C_{38}H_{29}NS_3^+$: 595.14566 [M^+]; found: 595.14529.

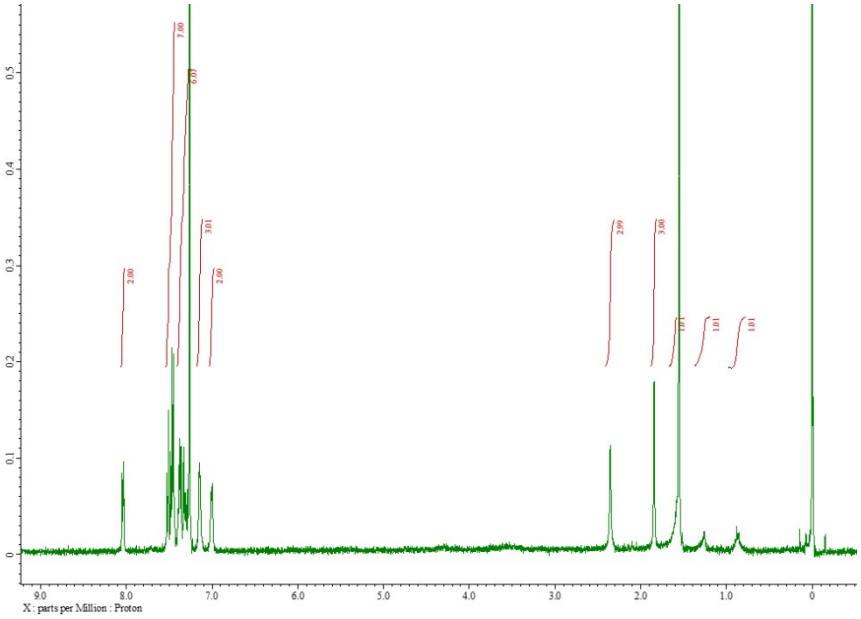


Fig. S4 ^{1}H NMR spectrum of **3o** (600 MHz, $CDCl_3$/TMS, 25 °C).

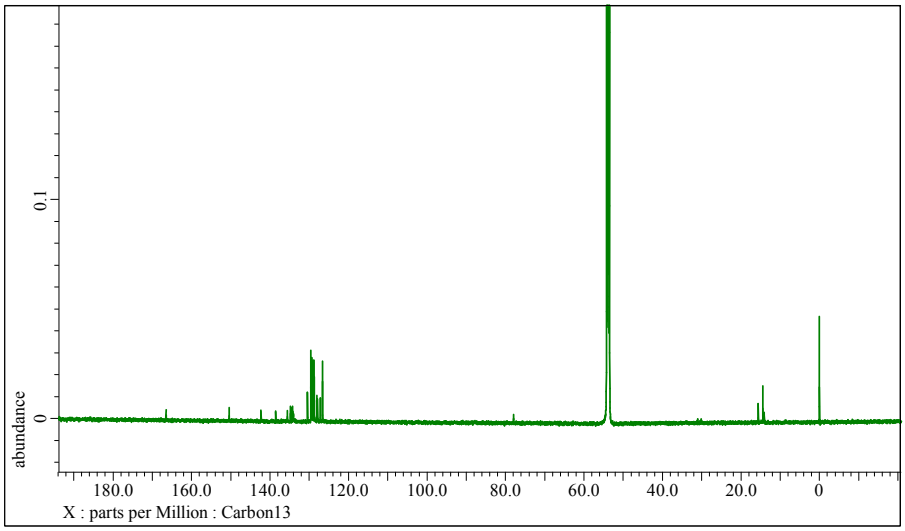


Fig. S5 ^{13}C NMR spectrum of **3o** (151 MHz, $CDCl_3$, 25 °C, TMS).

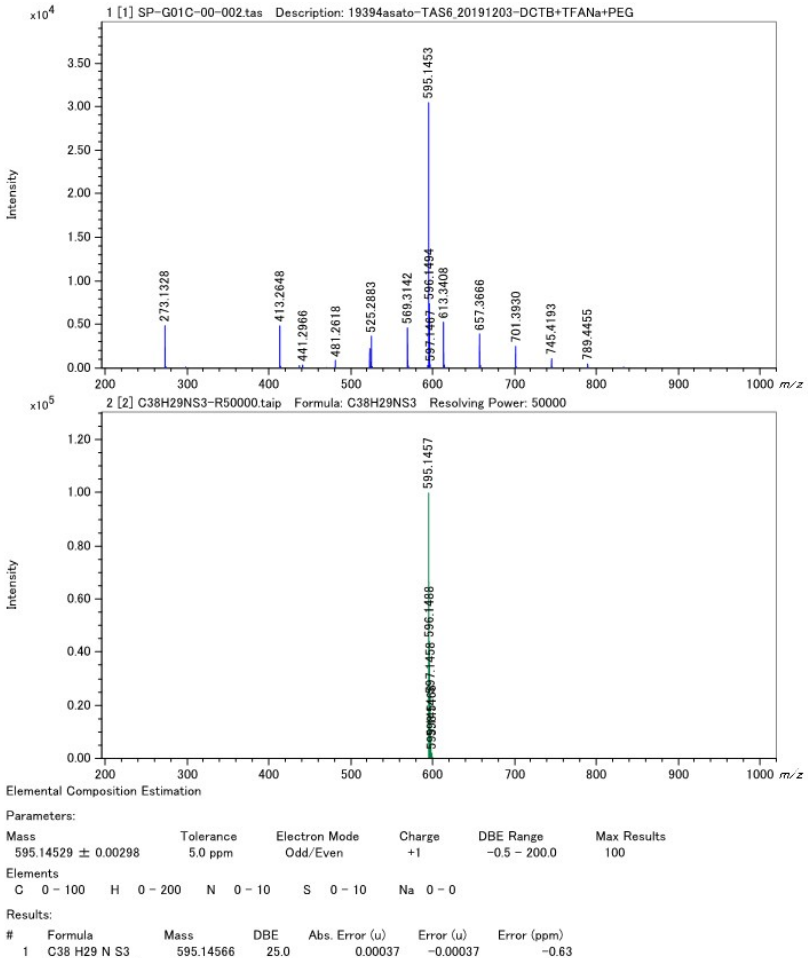
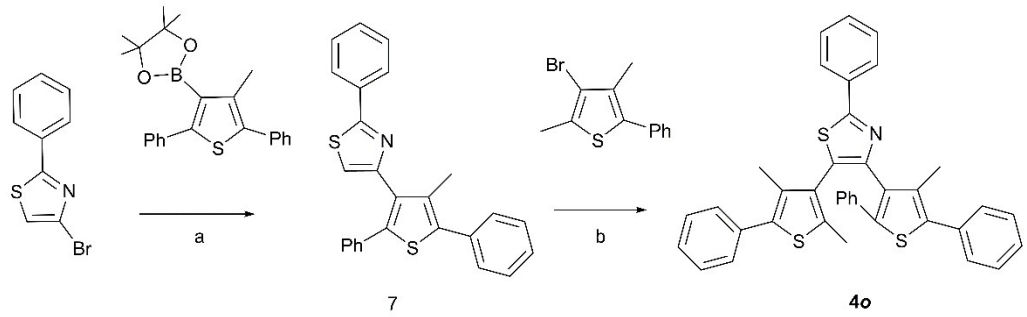


Fig. S6 HRMS data of **3o.** A MALDI Spiral TOF system (JEOL, JMS-S3000) was used with polyethylene glycol as an internal standard.



Scheme S3: Synthesis of **3 o**: a) $[Pd(PPh_3)_4]$, PPh_3, 2 M K_3PO_4, Water / 1,4-dioxane; b) $Pd(OAc)_2$, pivalic acid, di-*tert*-butylmethylphosphine tetrafluoroborate, mesitylene.

7) 4-(4-methyl-2,5-diphenylthiophen-3-yl)-2-phenylthiazole: 4-bromo-2-phenylthiazole (1.07 g, 3.7 mmol), 4,4,5,5-tetramethyl-2-(4-methyl-2,5-diphenylthiophen-3-yl)-1,3,2-dioxaborolane (972 mg, 4.1 mmol), PPh_3 (547 mg, 1.9 mmol.) and 2 M aqueous K_3PO_4 (15 mL) were dissolved in 1,4-dioxane (15 mL). After 15 minutes stirring under N_2 atmosphere, $Pd(PPh_3)_4$ (427 mg, 0.37 mmol.) was added and the solution refluxed under N_2 atmosphere at 110 °C for 36 h. Thereafter, the organic layer was extracted with chloroform, and the combined extracts were washed with water and dried over anhydrous Na_2SO_4. The sample was then filtered and the filtrate concentrated in vacuo. Silica gel column chromatography (hexane:ethyl acetate, 20:1) of the residue afforded **7** (0.18 g, 23 % yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ= 8.07-8.02 (m, 3H), 7.49-7.30 (m, 12H), 7.18 (s, 1 H), 2.52 (s, 3H).

4o) 5-(2,4-dimethyl-5-phenylthiophen-3-yl)-4-(4-methyl-2,5-diphenylthiophen-3-yl)-2-phenylthiazole: 7 (180 mg, 0.44 mmol), 3-bromo-2,4-dimethyl-5-phenylthiophene (141 mg, 0.53 mmol.), di-*tert*-butylmethylphosphine tetrafluoroborate (11 mg, 0.044 mmol.), Cs_2CO_3 (220 mg, 0.88 mmol), pivalic acid (14 mg, 0.13 mmol.) and $Pd(OAc)_2$ (4.9 mg, 0.022 mmol.) were dissolved in mesitylene (6 mL). The mixture was heated under reflux at 150 °C overnight. Thereafter, it was filtered through Celite, extracted with ethyl acetate, and the combined extracts washed with water and dried over anhydrous Na_2SO_4. Silica gel column chromatography (hexane: ethyl acetate, 9:1) and gel permeation chromatography afforded ***4 o*** (89.3 mg, 34 % yield) as a as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.08 (d, J = 8.0 Hz, 2 H), 7.58-7.35 (m, 7 H), 7.21-7.03 (m, 6H) 7.00-6.95 (m, 3H), 6.99-6.26 (m, 2H), 2.39 (s, 3H), 1.87 (s, 1H), 1.66 (s, 1H), 1.54 (s, 3H), 1.44 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C, TMS): δ = 134.9, 133.8, 133.1, 132.7, 130.1, 129.4, 128.7, 128.6, 128.5, 127.4, 127.3, 127.1, 126.5, 29.8, 15.2, 14.9, 14.7, 14.6, 14.1, 14.0 ppm; HRMS (MALDI SpiralTOF): *m/z* calcd. for $C_{38}H_{29}NS_3$: 595.14566 [M^+]; found:595.14511.

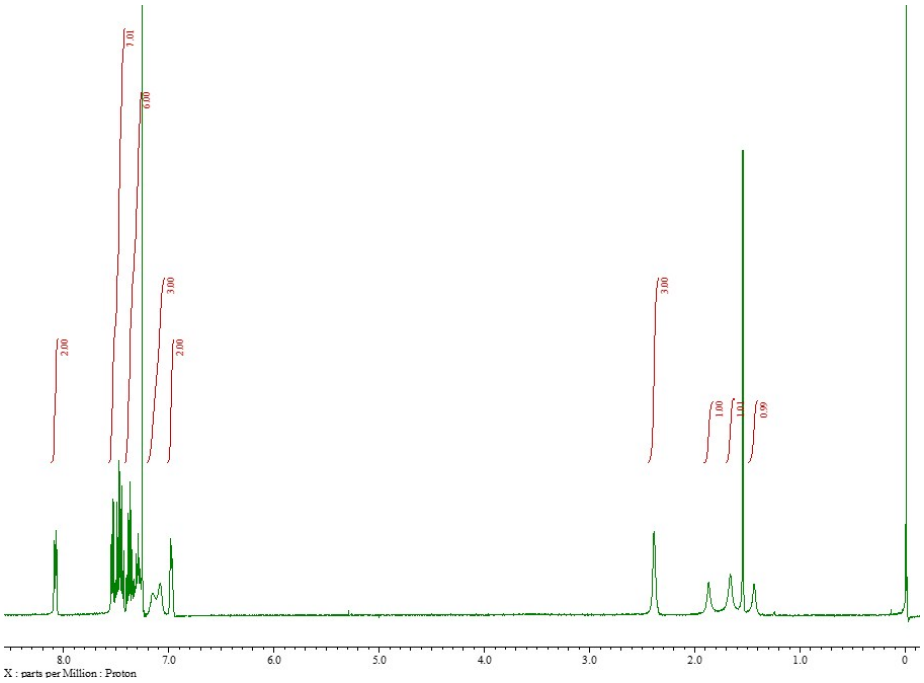


Fig. S7 ^{1}H NMR spectrum of **4o** (400 MHz, $CDCl_3$/TMS, 25 °C).

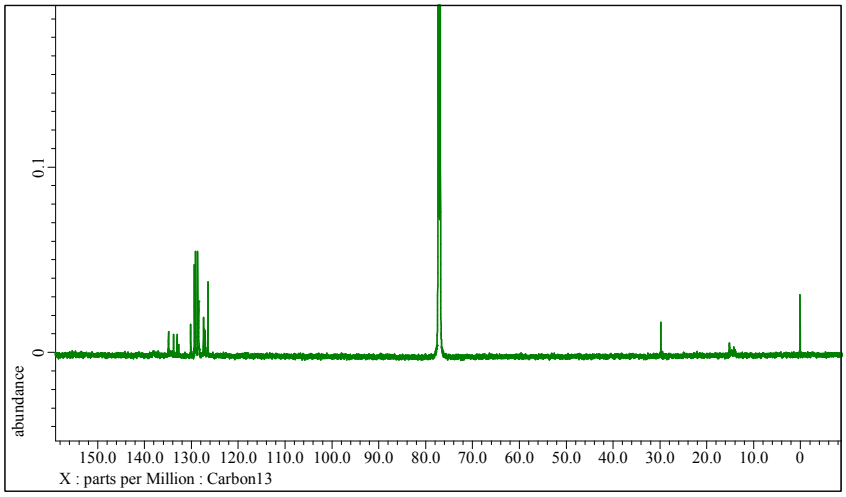


Fig. S8 ^{13}C NMR spectrum of **4o** (151 MHz, $CDCl_3$, 25 °C, TMS).

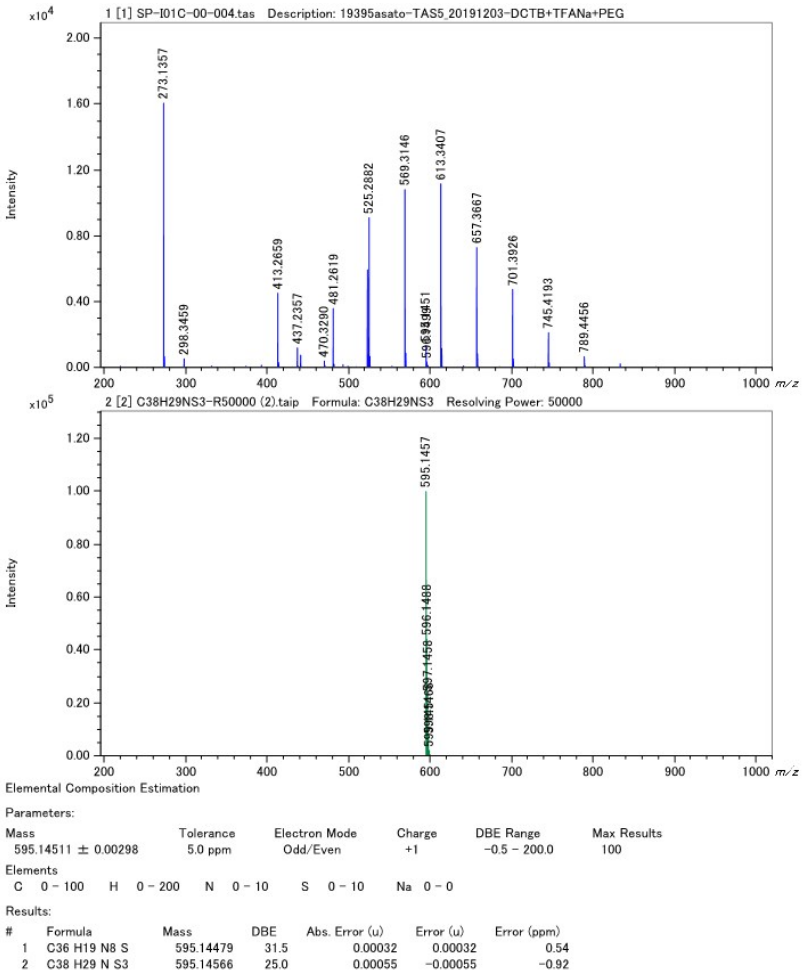


Fig. S9 HRMS data of **4o.** A MALDI Spiral TOF system (JEOL, JMS-S3000) was used with polyethylene glycol as an internal standard.

2. Supplementary Tables and Figures

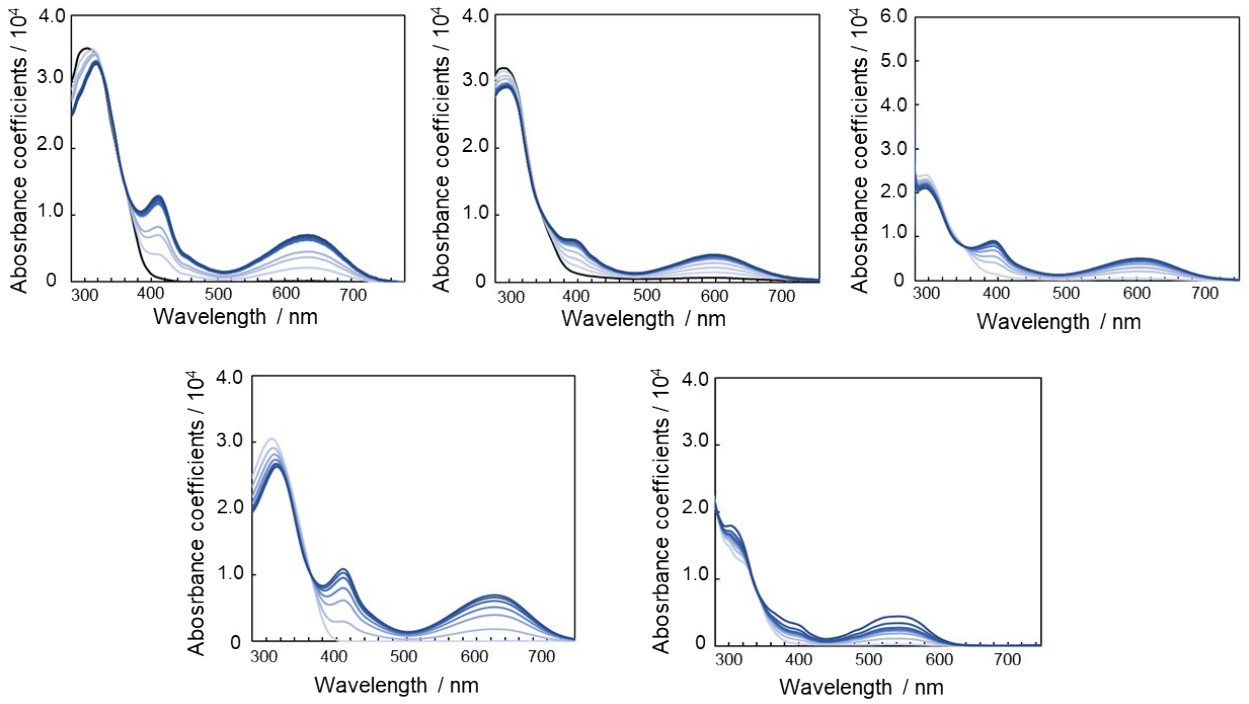


Fig. S10 with abs coefficients based on the open forms. In the visible region, new bands appear for compounds (**1**-**5**) upon irradiation with UV light at 365 nm in acetonitrile. Each spectrum was taken every after irradiation for 30 s. Visible light irradiation turns them back to the **o** form. Concentration of **o** forms = (1) 3.0 x 10^{-5} M (2) 3.7 x 10^{-5} (3) 1.5 x 10^{-5} (4) 5.2 x 10^{-5} (5) 4.0 x 10^{-5}.

Table S1. Optical and photochemical properties of **1**-**5** in acetonitrile.

	λ_O /nm ($\varepsilon \times 10^{-4}$ $M^{-1}cm^{-1}$)	$\lambda_{max,\,C}$ / nm ($\varepsilon \times 10^{-4}$ $M^{-1}cm^{-1}$)	Conversion ratio of **c**-form at PSS
1	313 (2.2)	610 (1.1)	0.59
2	292 (3.1)	610	-
3	299 (2.4)	614 (1.1) *	0.52
4	299 (2.4)	613 (1.2) *	0.54
5	280 (2.2)	539 (1.2)	0.44

***** The molar absorption coefficients of **c**-forms (ε) were determined based on the data of ^{1}H NMR and absorption spectra after the UV irradiation (Figs. S11, 12). The conversion ratios of **c**-forms in the PSS were estimated based on the obtained ε values.

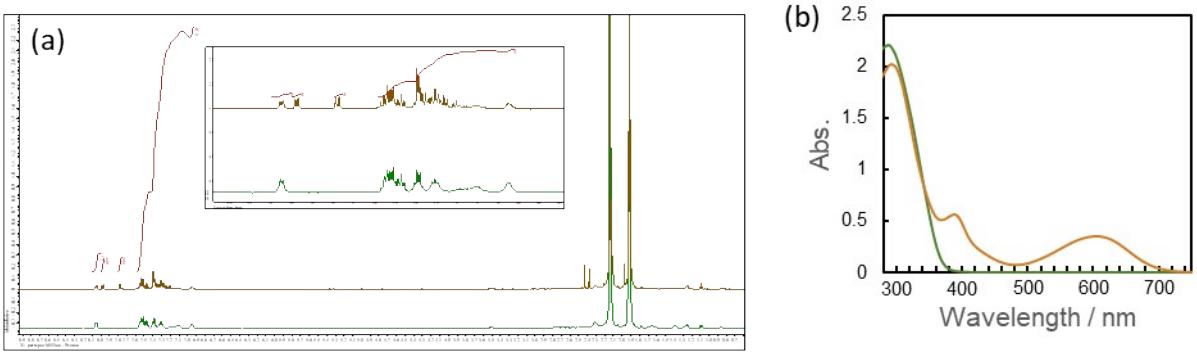


Fig. S11 a) ^{1}H NMR spectra of **3o** before (Green) and after the UV light irradiation for 3 min (Brown) (400 MHz, CD_3CN, 25 °C). The conversion of **c** form after UV light irradiation was 36 %. b) Absorption spectra of **3o**/**3c** solution (Brown) and open form (Green). The ^{1}H NMR sample solution was diluted and the absorbance was measured. After visible light irradiation, the absorbance of open form was measured. Concentration of **c** forms in **o**/**c** solution is 3.0 x 10^{-5} M which is determined from conversion of **c** form in ^{1}H NMR.

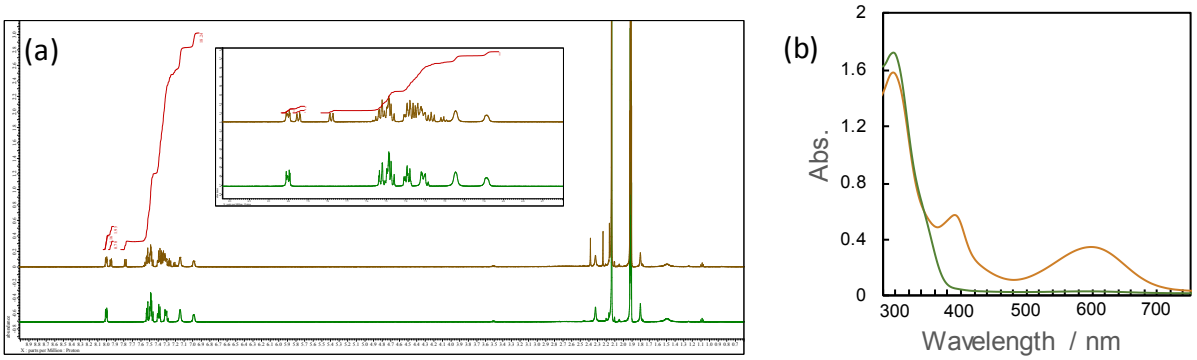


Fig. S12 a) ^{1}H NMR spectra of **4o** before (Green) and after the UV light irradiation for 3 min (Brown) (400 MHz, CD_3CN, 25 °C). The conversion of **c** form after UV light irradiation was 38 %. b) Absorption spectra of **4o**/**4c** solution (Black) and open form (Red). The ^{1}H NMR sample solution was diluted and the absorbance was measured. After visible light irradiation, the absorbance of open form was measured. Concentration of **c** forms in **o**/**c** solution is 2.7 x 10^{-5} M which is determined from conversion of **c** form in ^{1}H NMR.

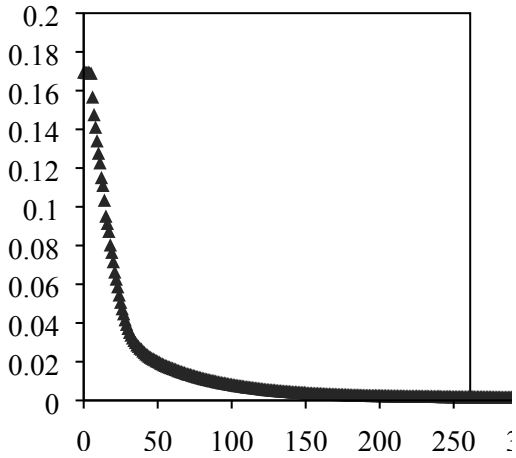


Fig. S13 Decay in absorbance at 613nm after adding 0.02 eq. TBPA in acetonitrile (0.05 mL) into acetonitrile solution of **1*c*** (1.5 x 10^{-5} M, 3 mL).

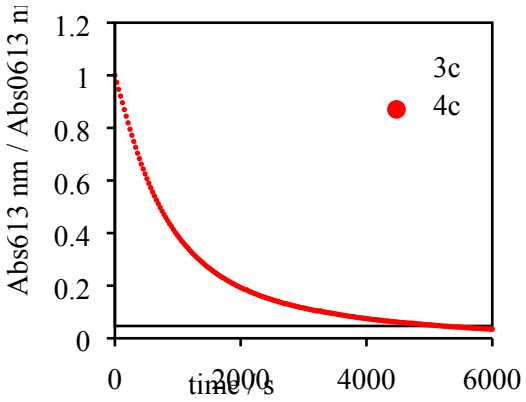


Fig. S14 Decay in absorbance after adding 0.001 eq. TBPA in acetonitrile (0.05 mL) into acetonitrile solution (3 mL) of **3c** and **4c**. Concentration of ***c*** forms = ca. 2.0 x 10^{-5} M.

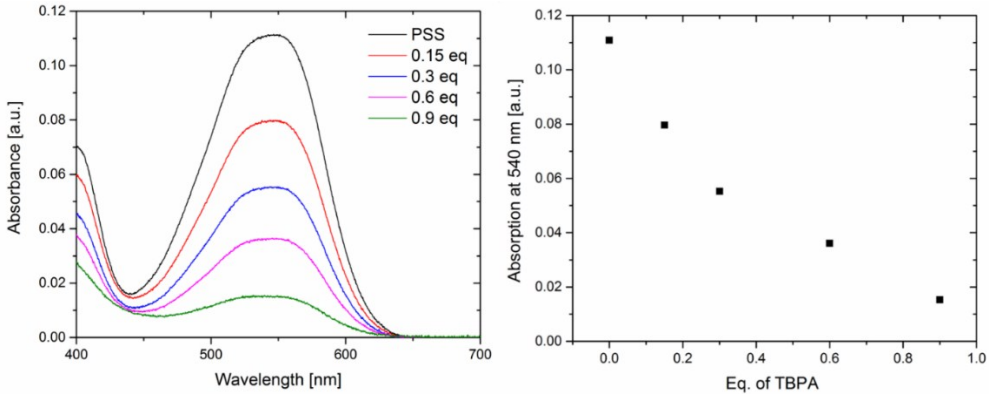


Fig. S15 a) Absorption spectra after adding TBPA in acetonitrile (0.05 mL) into acetonitrile solution of **5c** (3 mL). Concentration of **c** forms = 1.0 x 10^{-5} M; b) Absorbance after addition of TBPA in acetonitrile (0.05 mL) into acetonitrile solutions of **5c** (1.0 x 10^{-5}M, 3mL). As **5c** showed no cascade

reaction, the absorbance reached to a steady state immediately after addition of TBPA.

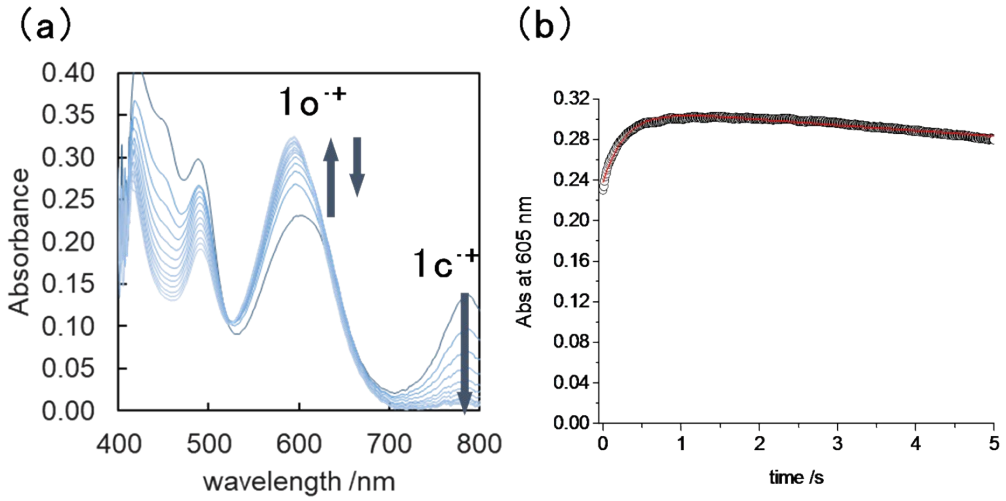


Fig. S16 (a) Stopped-flow absorption spectral changes upon mixing acetonitril solutions of **1c** (2.3 x 10^{-5} M) and TBPA (2.3 × 10^{-5} M). Time intervals are 0.1 s. The recording of spectra started 5 ms after the injection of both solutions and stopped after 10 s; (b) Deacay of absorbance at 539 nm (circles) and curve fitting (red line) for the evolution of kinetic parameters, k_2 and k_3 for **1c**$^{\bullet+}$/**1o**$^{\bullet+}$/**1o** based on the sequential reaction model with the parameters of Table S2.[3]

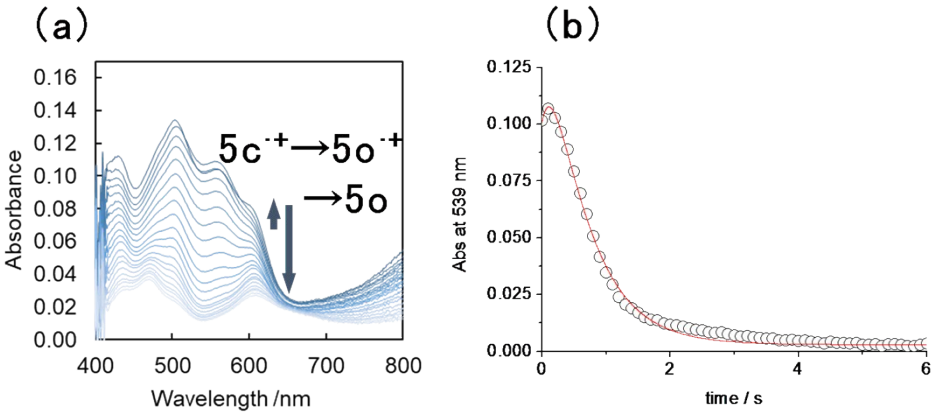


Fig. S17 (a) Stopped-flow absorption spectral changes after mixing solutions of **5c** (1.1 x 10^{-5} M) and TBPA$^{\cdot+}$ solution (1.1 × 10^{-5} M). Time intervals are 0.1 s. The recording of spectra started 5 ms after the injection of both solutions and stopped after 10 s; (b) Deacay of absorbance at 539 nm (circles) and curve fitting (red line) for the evolution of kinetic parameters, k_2 and k_3 for **5c**$^{\bullet+}$/**5o**$^{\bullet+}$/**5o** based on the sequential reaction model with the parameters of Table S2.[3]

Table S2 Kinetic parameters of radical cation species determined by the electron transfer stopped-flow experiments of Figures S13 and S14

substances	k_2 /s^{-1} [a]	k_3 /s^{-1} [a]	k_2/k_3
1c/1o	3.6	1.9 x 10^{-2}	1.9 x 10^{2}
5c/5o	1.7	5.0	0.034

[a] k_2 and k_3 are defined with following reaction scheme.
The cascade reaction was suppressed under the equimolar condition

$$c \xrightarrow{k_1} c^{+\bullet} \xrightarrow{k_2} o^{+\bullet} \xrightarrow{k_3} o$$

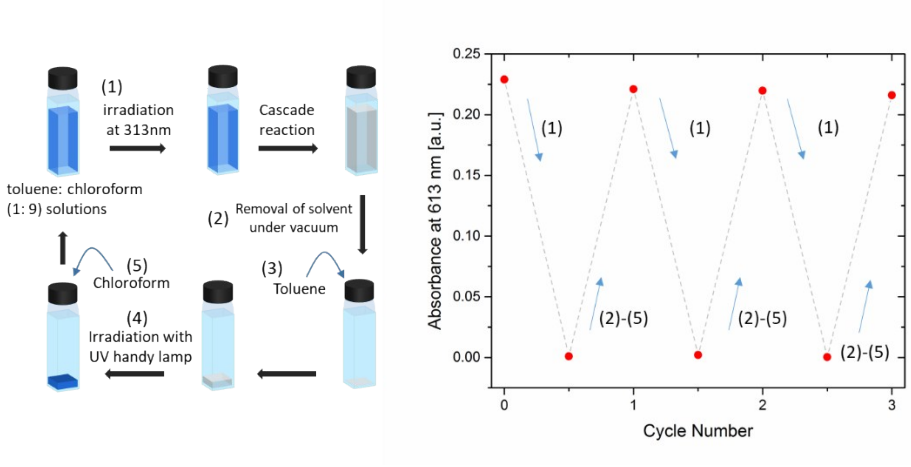


Fig. S18 UV-induced bleaching–coloration cycles by irradiation with UV.
Experimental procedure: (1) Toluene-chloroform (v/v = 1/9) solutions of **4o**/**4c** (concentration of c forms = 2.0 x 10^{-5} M, 3 mL) was irradiated with UV (313 nm) for 60 sec. After cascade bleaching reaction finished in 10 min, the absorbance of fully bleached solution was measured confirming Abs_{613nm} < 0.01; (2) The solution was removed under vacuum; (3) Toluene (0.3 mL) was added into the cuvette; (4) The toluene solution was irradiated with UV (365 nm) for 300 sec; (5) the irradiated toluene solution was diluted by chloroform (2.7 mL) and the absorbance was measured observing Abs_{613nm} > 0.20.

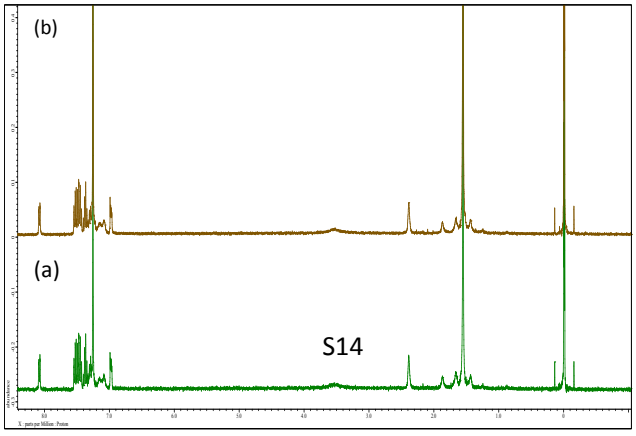


Fig. S19 ^{1}H NMR spectra of (a) **4o**, (b) after UV induced fading reaction (400 MHz, $CDCl_3$, 25 °C, TMS); After NMR measurement for **4o**/$CDCl_3$ solution (a), solvent was removed under vacuum and toluene was added followed by UV light irradiation (365nm) for 60 sec. Toluene was then removed under vacuum and $CDCl_3$ was introduced. The **4o**/**4c** sample in the ^{1}H NMR tube was irradiated with UV (313 nm) to obtain fully bleached solution after about 20 min. Then, ^{1}H NMR spectrum (b) was obtained. No significant changing was observed in ^{1}H NMR spectra.

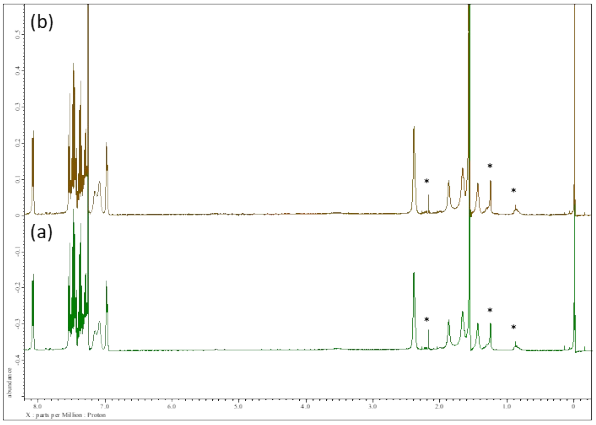


Fig. S20 ^{1}H NMR spectra of (a) **4o**, (b) after X-ray induced fading reaction (400 MHz, $CDCl_3$, 25 °C, TMS) Experimental procedure: after ^{1}H NMR measurement of **4o**/$CDCl_3$ solution (a), solvent was removed under vacuum and toluene was added followed by UV light irradiation (365nm) for 60 sec. Toluene was then removed under vacuum and $CDCl_3$ was introduced again. The **4o**+**4c**/$CDCl_3$ solution in the NMR tube was irradiated with X-ray (100 mGy). ^{1}H NMR spectrum (b) was obtained at the fully bleached steady state, about 20 min later. No significant changing of ^{1}H NMR spectra was observed. As marked with *, the solution indicated small amount of acetone (δ = 2.17 ppm) and hexane (δ = 0.87, 1.26 ppm).

Table S3. Blank experiment to measure σ_{blank} of 4c

run#	Abs^0_{613nm} (1)	Abs_{613nm} (1),(2)	X_{cyclo} (%) (3)
1	0.37645	0.36884	2.023
2	0.39380	0.38592	2.001
3	0.43275	0.42389	2.048
4	0.30769	0.30143	2.034
5	0.45280	0.44364	2.022
6	0.40266	0.39467	1.986
7	0.32215	0.31559	2.036
8	0.57182	0.55977	2.107
9	0.46331	0.45391	2.029
10	0.42328	0.41458	2.056
11	0.38512	0.37729	2.033
12	0.36817	0.36065	2.045
13	0.31491	0.30840	2.067

14	0.44276	0.43375	2.035
15	0.31945	0.31290	2.052
		σ_{blank} (%)[4]	*0.028*
		LOD	*0.34*

(1) Absorbance was measured with a UV-vis spectrometer in 6 digits after the decimal point.

(2) Abs^0_{613nm} and Abs_{613nm} are absorbance of **4o**/**4c** (concentration of **4c=** 2.7-5.1 x 10^{-5} M in toluene) solution measured before and after an interval of 600 sec at dark condition without X-ray irradiation.

(3) X_{cyclo} (%) denotes decrease in absorbance due to the spontaneous cycloreversion, X_{cyclo} (%) = Abs^0_{613nm} - $Abs^t_{613nm}{}^*$/ Abs^0_{613nm} x 100 .

(4) Standard division of X_{cyclo}

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