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Supplementary Information for:

Investigations into oxidation induced ring openings of terarylenes containing π-extended thieno[b]thiophene units

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Experimental details

^{1}H and ^{13}C NMR (400 and 600 MHz) spectra were recorded on, *JEOL* JNM-ECP400 and *JEOL* JNMECA600 spectrometers, respectively. High-resolution mass spectrometry were performed on matrix assisted laser desorption/ionization (MALDI) time of Flight (TOF) – MS spectra (*Bruker* Autoflex II or *JEOL* spiralTOF JMS-S3000). Recycling preparative GPC were performed on *Japan Analytical Industry* LC-9110NEXT. UV/Vis spectra, quantum yields of photochromic reactions ($\phi_{o\text{-}c}$ and $\phi_{c\text{-}o}$) and photo-induced fading reactions were measured using a *JASCO* V-660, V-760 spectrophotometer and a *Shimadzu* QYM-01 set-up. All illuminations were performed in the dark at room temperature in high grade HPLC solvents that were stored under argon, used without further purification and pre-bubbled with nitrogen gas for 30 minutes before solid dissolution where necessary.

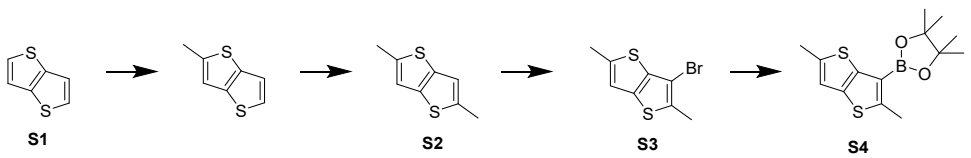
UV-induced cycloreversion experiments were performed on the photo stationary state (PSS) generated in toluene through irradiation with a LED-UV light at 365 nm followed by dilution with chloroform, monitoring the evolution of absorbance at λ_{max} with constant stirring to avoid the effect of diffusion on the electron transfer. Oxidative cycloreversion experiments were performed by mixing the requisite amounts of the oxidizing agent tris(4-bromophenyl)ammonium hexachloroantimonate (TBPA) with a photogenerated PSS in acetonitrile and monitoring the evolution of absorbance at λ_{max}, with constant stirring to avoid the effect of diffusion on the electron transfer. Cyclic voltammetry measurements were performed with an ALS electrochemical analyser Model 630DA at room temperature working under an argon atmosphere, equipped with a 3 mm diameter glassy carbon working electrode, a Pt wire counter electrode and Ag/Ag^{+} reference electrode at a scan rate of 100 mV s^{-1} at 20°C. Samples were run in HPLC grade acetonitrile deoxygenated by argon bubbling for at least 20 min, containing 0.1 M $TBAPF_6$ as supporting electrolyte at initial concentrations of 1 mmol in a standard one-component cell; the obtained values were converted into those of Fc/Fc^{+} based on the measured redox potential of ferrocene. $TBAPF_6$ used as electrolyte was recrystallized from ethanol and dried under reduced pressure for 12 h at 100°C. Ferrocene was sublimated under reduced pressure at 80°C. PSS Solutions for voltammetry were generated via illumination of the open form at 365 nm in 20 mL of high-grade toluene. The mass of solid present was such that upon removal of toluene and redissolution in 5 mL of electrolyte a 1 mmol PSS (open + closed) was formed.

Calculations were performed with the Gaussian09 package.[1] We worked at the B3LYP 6-31+G(d,p) level of theory in vacuo. The open form as drawn with the reactive carbons relatively close to each other were used as input structures. Frequency calculation showed no negative frequencies confirming that resulting structures were in the absolute minima of the potential map. Kinetic curve fittings were carried out, with calculated values for [**C**], [$\mathbf{C}^{\cdot+}$], [**O**] and [$\mathbf{O}^{\cdot+}$] generated using an initial experimental concentration of $5.59\text{x}10^{-6}$ M along with the kinetic parameters and equations show in

Figure 11. These were then used to generate a calculated decay in absorption over time (A_{calc}) using the experimentally estimated absorption coefficient of 9090 $M^{-1}cm^{-1}$ at the absorption maximum, this was then compared to the measured decay (A_{exp}). The residual square difference $R_s = (A_{exp}-A_{Calc})^2$ between the calculated and experimental absorption was calculated for each data point and then all values of R_s summed to give a residual sum of squares (R). R was then minimised computationally, with constant values of k_1, k_2, k_5 and k_6 determined as described in the main text, in a three variable ([C]: [$C^{+\cdot}$], k_3 and k_4) optimisation using the SOLVER software, adjusting the kinetic parameters to give a minimum value for R.

General Synthesis

All reagents and solvents were purchased at the highest commercial quality available and used without further purification, unless otherwise stated. Compounds **S4, S11** and **1o-4o** were prepared according to the routes depicted in Schemes S1 to S6. Compounds **5o,**[2] **6o,**[2] **S12,**[3] **S13,**[4] **S15**[2] and **S16**[2] were synthesized as previously reported and compounds **S1** and **S5** were commercially available. The final structures of **1o**-**4o** have all been successfully characterised using NMR and HR-MS which are shown in Figures S1-S12.



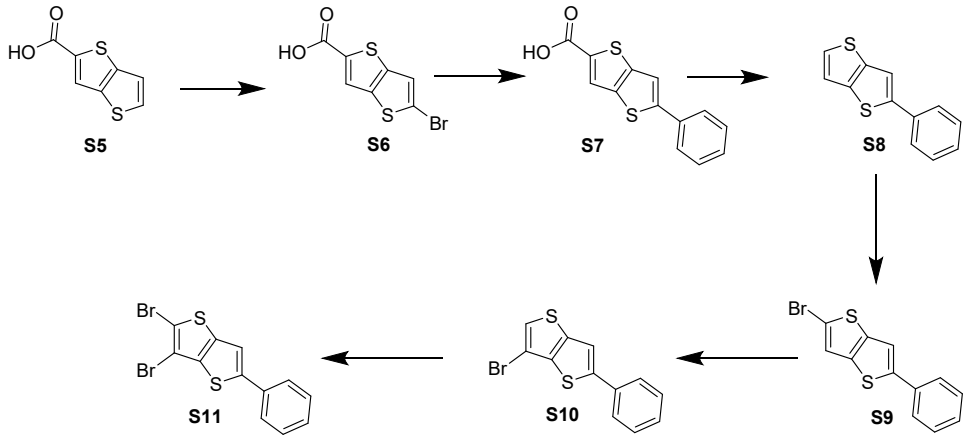
Scheme S1. *Synthesis of key intermediate* ***S4****.*

S2: 2,5-dimethylthieno[3,2-b]thiophene: Thieno[3,2-b]thiophene **S1** (3.50 g, 24.96 mmol) was dissolved in tetrahydrofuran (200 mL) and cooled to -40°C. To this solution n-butyllithium (2.5 M, 12.98 mL, 32.45 mmol) was added dropwise and the solution was stirred for 45 min at -40°C. To this, methyl iodide (2.02 mL, 32.45 mmol) was added dropwise over 20 min and the solution warmed to room temperature. Water was added and the solution extracted with ethyl acetate, dried over magnesium sulfate and solvent removed under vacuum. The solid was dissolved in hexane and passed through a short silica column (1st spot Rf = 0.8) to give intermediate 2-methylthieno[3,2-b]thiophene that was then dissolved in tetrahydrofuran (200 mL) and cooled to -40°C. To this solution n-butyllithium (2.5 M, 12.98 mL, 32.45 mmol) was added dropwise and the solution was stirred for 45 min at -40°C. To this, methyl iodide (2.02 mL, 32.45 mmol) was added dropwise over 20 min and the solution warmed to room temperature. Water was added and the solution extracted with ethyl acetate, dried over magnesium sulfate and solvent

removed under vacuum. The solid was dissolved in hexane and passed through a short silica column (1st spot Rf = 0.8) to give pure white crystals. **Yield:** 3.07 g, 18.24 mmol, 73% over two steps. **^{1}H-NMR** (400 MHz, $CDCl_3$, 25°C) δ: 6.87 (m, 2H), 2.59 (d, 6H, J = 1.3).

S3: 3-bromo-2,5-dimethylthieno[3,2-b]thiophene: To a solution of **S2** (1.5 g, 8.91 mmol) in a 1:1 mix of glacial acetic acid: chloroform (160 mL) was added n-bromosuccinimide (1.75 g, 9.81 mmol) and the solution stirred for 16 hours. Then 2 M aqueous potassium hydroxide was added until the solution reached a pH of 5 and then a saturated aqueous solution of sodium thiosulfate was added. The solution was extracted into dichloromethane, washed with water, dried over magnesium sulfate, filtered and solvent removed. Silica gel column chromatography (1st spot, Rf = 0.9 in hexane) gave the product as a white solid. **Yield:** 1.74 g, 7.08 mmol, 79%. **^{1}H-NMR** (400 MHz, $CDCl_3$, 25°C) δ: 6.92 (q, 1H, J = 1.2 Hz), 2.60 (d, 3H, J = 1.2 Hz), 2.51 (s, 3H).

S4: 2-{2,5-dimethylthieno[3,2-b]thiophen-3-yl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: To a solution of **S3** (900 mg, 3.64 mmol) in tetrahydrofuran (30 mL) under inert atmosphere, n-butyl lithium (1.6 M, 2.50 mL, 4.01 mmol) was added dropwise at –78°C and the mixture stirred for 2 hours at that temperature. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.89 mL, 4.37 mmol) was then added dropwise and the system was stirred for another 2 hours at –78°C. The reaction mixture was allowed to warm to room temperature over 3 hours and then methanol (40 mL) added and the solution extracted with ethyl acetate. The combined organic fraction was washed with water, dried over anhydrous magnesium sulfate, and concentrated to a yellow oil. Silica gel column chromatography (3rd spot Rf = 0.6 in 2:1 hexane: dichloromethane) gave the product as a yellow solid. **Yield:** 835 mg, 2.84 mmol, 78%. **^{1}H-NMR** (400 MHz, $CDCl_3$, 25°C) δ: 6.82 (q, 1H, J = 1.3 Hz), 2.74 (s, 3H), 2.54 (d, 3H, J = 1.3 Hz), 1.35 (s, 12H).



Scheme S2. *Synthesis of key intermediate **S9**.*

S6: 5-bromothieno[3,2-b]thiophene-2-carboxylic acid: Thieno[3,2-b]thiophene-2-carboxylic

acid **S5** (5.0 g, 27.13 mmol) was dissolved in dimethylformamide (50 mL) at 0°C. n-Bromosuccinimide (4.927 g, 27.66 mmol) was added and the reaction mixture stirred for 3 hours. Water (50 mL) was added and the mixture stirred for 30 min as a white precipitate formed. The precipitate was filtered off and recrystallized from water. This was dried in a desiccator in the presence of phosphorous pentoxide to give a white solid that was used crude in the next step. **Yield:** 4.31 g.

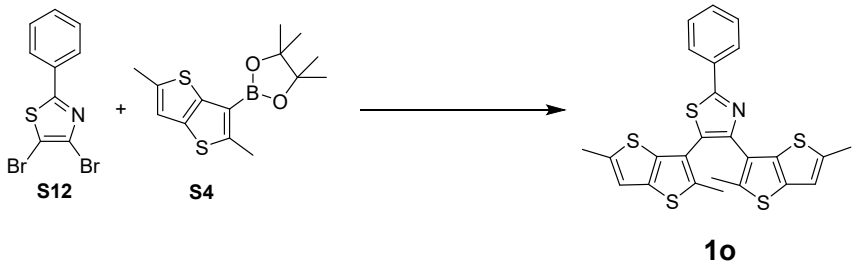
S7: 5-phenylthieno[3,2-b]thiophene-2-carboxylic acid: Under an inert atmosphere, **S5** (4.285 g, 16.29 mmol) and phenyl boronic acid (2.085 g, 17.1 mmol) were dissolved in tetrahydrofuran (190 mL). Tetrakis(triphenyphosphine) palladium 0 (376 mg, 0.326 mmol), potassium carbonate (6.752 g, 48.86 mmol) and water (60 mL) were added and the solution refluxed for 24 hours. Upon cooling to room temperature more water (200 mL) was added. All solvents except water were removed under vacuum and the solution cooled at 0°C giving a white precipitate which was dissolved in hot water, acidified by addition of 1M aqueous hydrochloric acid and cooled again to give a solid that was collected by filtration. This was dried in a desiccator in the presence of phosphorous pentoxide to give the product as a white solid. **Yield:** 3.61 g, 13.87 mmol, 85%. **^{1}H-NMR** (400 MHz, d-DMSO, 25°C) δ: 13.30 (br-s, 1H), 8.12 (s, 1H), 7.95 (s, 1H), 7.73 (m, 2H), 7.48 (m, 2H), 7.39 (m, 1H).

S8: 2-phenylthieno[3,2-b]thiophene: Under an inert atmosphere, **S7** (1.90 g, 7.30 mmol) was dissolved in quinoline (25 mL), copper powder (232 mg, 3.65 mmol) was added and the resulting mixture was heated to 225°C for 3 hours. Quinoline was distilled off under reduced pressure and the residue dissolved in ethyl acetate and filtered through celite. The resulting solution was washed three times with dilute aqueous hydrochloric acid (1 M), and then washed three times with water. After drying over anhydrous magnesium sulfate, the solvent was evaporated to give a yellow solid. Silica gel column chromatography (1st spot Rf = 0.3 in hexane) followed by recrystallization from ethanol gave the product as a yellow solid. **Yield:** 1.154 g, 5.335 mmol, 73%. **^{1}H-NMR** (400 MHz, $CDCl_3$, 25°C) δ: 7.68 (m, 2H), 7.53 (d, 1H, J = 0.6 H), 7.48-7.38 (m, 3H), 7.35 (tt, 1H, J = 9.8 and 1.7 Hz), 7.29 (dd, 1H, J = 7.0 and 0.6 Hz).

S9: 2-bromo-5-phenylthieno[3,2-b]thiophene: S8 (1.154 g, 5.335 mmol) was dissolved in dimethylformamide (11 mL) at 0°C. n-Bromosuccinimide (969 mg, 5.441 mmol) was added and the reaction mixture stirred for 3 hours. Water (20 mL) was added and the mixture extracted with dichloromethane, washed three times with water, dried over anhydrous magnesium sulfate and concentrated to a yellow oil. This was dissolved in 1:1 hexane: dichloromethane and passed through a short silica column (1st spot Rf = 0.8) to give the product as a yellow solid. **Yield:** 1.24 g, 4.20 mmol, 79%. **^{1}H-NMR** (400 MHz, $CDCl_3$, 25°C) δ: 7.64 (m, 2H), 7.44 (m, 3H), 7.35 (tt, 1H, J = 9.7 and 1.8 Hz), 7.29 (d, 1H, J = 4.0 Hz).

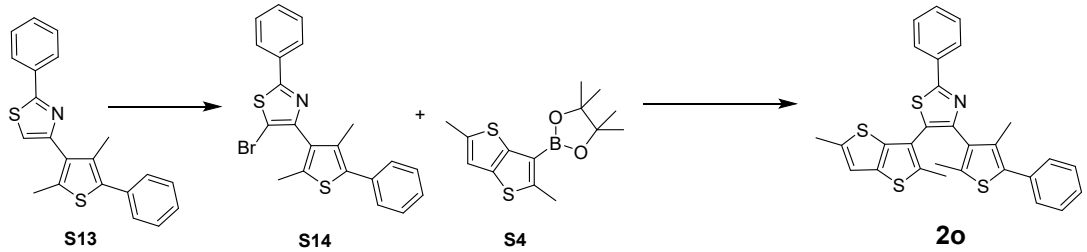
S10: 6-bromo-2-phenylthieno[3,2-b]thiophene: Freshly prepared lithium diisopropylamide (2.07 mmol) in tetrahydrofuran (9 mL) at 0°C was added dropwise over 30 minutes to a solution of **S9** (1.24 g, 4.20 mmol) in tetrahydrofuran (16 mL) cooled to –78°C and then stirred for 90 min at –78°C. Methanol (7 mL) was added and the solution stirred 30 min at –78°C followed by 16 hours at room temperature. Water was added and the solution extracted with chloroform, washed with brine, then with water, dried over anhydrous magnesium sulfate and concentrated to an orange solid. This was dissolved in chloroform and passed through a short silica column (1st spot Rf = 0.8) to give the product as a yellow solid. **Yield:** 1.08 g, 3.66 mmol, 87%. **^{1}H-NMR** (400 MHz, $CDCl_3$, 25°C) δ: 7.69-7.62 (m, 2H), 7.51 (s, 1H), 7.49-7.34 (m, 4H).

S11: 2,3-dibromo-5-phenylthieno[3,2-b]thiophene: S10 (1.08 g, 3.66 mmol) and n-bromosuccinimide (977 mg, 5.488 mmol) were dissolved in chloroform (40 mL) and refluxed for 16 hours. An aqueous sodium thiosulfate solution was added and the mixture extracted with chloroform. The organic layer was washed with water, dried over anhydrous magnesium sulfate and concentrated to an orange solid. This was dissolved in chloroform and passed through a short silica column (1st spot Rf = 0.8) to give the product as an off white solid. **Yield:** 1.151 g, 3.077 mmol, 84%. **^{1}H-NMR** (400 MHz, $CDCl_3$, 25°C) δ: 7.67-7.62 (m, 2H), 7.49-7.33 (m, 4H).



Scheme S3. *Synthesis of compound **1o**.*

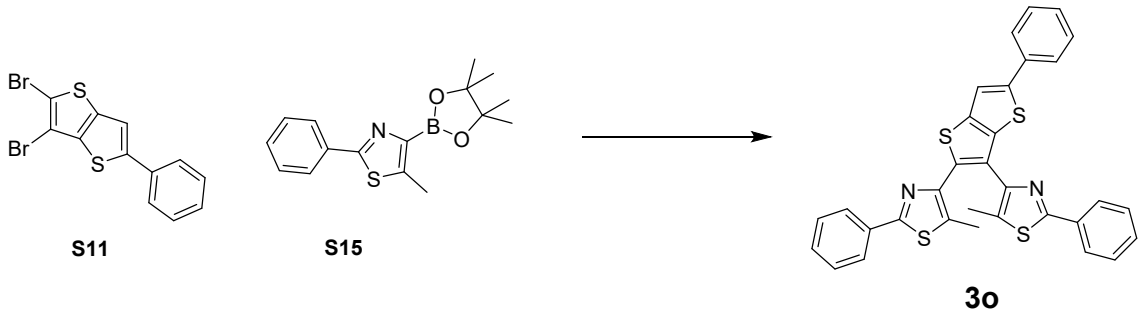
1o: To a solution of **S12**[3] (500 mg, 1.567 mmol), **S4** (968 mg, 3.291 mmol) and triphenylphosphine (206 mg, 0.784 mmol), in 2M aqueous tripotassium phosphate (75 mL) and 1,4-dioxane (75 mL) was added tetrakis(triphenyphosphine) palladium 0 (181 mg, 0.157 mmol) and the solution refluxed at 100°C for 3 days. The solution was quenched with 2M aqueous hydrochloric acid and extracted to ethyl acetate, washed three times with water, dried over anhydrous magnesium sulfate and concentrated to a yellow solid. Silica gel column chromatography (1st spot Rf = 0.7 in 9:1 hexane: ethyl acetate) gave the product as a white solid that turned blue under UV light. **Yield:** 480 mg, 0.972 mmol, 62%. **^{1}H-NMR** (600 MHz, $CDCl_3$, 25°C) δ: 8.06 (m, 2H), 7.45 (m, 3H), 6.84 (m, 1H), 6.82 (m, 1H), 2.53 (m, 6H), 2.05 (s, 3H), 2.02 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$, 25°C) δ: 166.8, 147.7, 141.1, 138.7, 138.4, 138.3, 138.1, 134.8, 134.6, 133.6, 130.3, 129.0, 127.4, 127.0, 126.6, 125.3, 121.0, 117.6, 117.1, 16.5, 16.4, 15.4, 15.2. **HRMS:** m/z 439.0112 ($[M]^+$) (calc. 439.0116).



Scheme S4. *Synthesis of compound* ***2o****.*

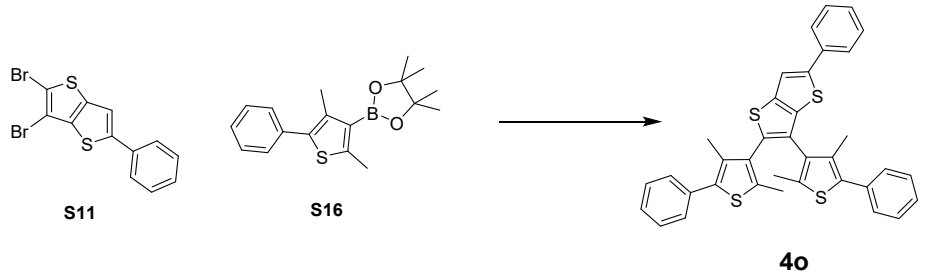
S14: S13[4] (780 mg, 2.25 mmol) was dissolved in a mixture of chloroform (70 ml) and glacial acetic acid (7 mL). To this n-bromosuccinimide (479 mg, 2.69 mmol) was added and the solution heated under reflux at 60°C for 16 hours. The solution was quenched with water and extracted into chloroform, washed with brine and then water, dried over dried over anhydrous magnesium sulfate and concentrated to a yellow solid. This was dissolved in dichloromethane and passed through a short silica column (1st spot Rf = 0.8) to give the product as a yellow solid. **Yield:** 347 mg, 0.814 mmol, 36%. **^{1}H-NMR** (400 MHz, $CDCl_3$, 25°C) δ: 7.97 (m, 2H), 7.55-7.40 (m, 7H), 7.35 (tt, 1H, J = 9.7 and 1.2 Hz), 2.44 (s, 3H), 2.19 (s, 3H).

2o: S14 (347 mg, 0.814 mmol), **S4** (311 mg, 1.058 mmol) and tripotassium phosphate (259 mg, 1.221 mmol) were cycled between argon and vacuum 3 times. Then tetrakis(triphenyphosphine) palladium 0 (28 mg, 0.024 mmol) was added and the system cycled between argon and vacuum 3 more times. 1,2-dimethoxyethane (40 mL) and water (20 mL) were then added and the solution heated to 70°C for 24 hours. The mixture was cooled to room temperature and water added followed by extraction into ethyl acetate, washed with brine then with water, dried over anhydrous magnesium sulfate and concentrated to give a yellow solid. Silica gel column chromatography (2nd spot Rf = 0.6 in 20:1 hexane: ethyl acetate) gave a solid that was further purified by GPC in chloroform to give a white solid that turned blue under UV light. **Yield:** 290 mg, 0.564 mmol, 69%. **^{1}H-NMR** (600 MHz, $CDCl_3$, 25°C) δ: 8.04 (m, 2H), 7.49-7.35 (m, 7H), 7.28 (dt, 1H, J = 6.9 and 1.8 Hz), 6.84 (q, 1H, 1.2 Hz), 2.53 (d, 3H, J = 1.2 Hz), 2.14 (s+s, 6H), 2.04 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$, 25°C) δ: 166.4, 149.4, 141.1, 138.7, 138.0, 137.3, 135.2, 135.0, 134.7, 134.0, 133.7, 133.0, 130.3, 129.3, 129.0, 128.5, 128.2, 127.0, 126.6, 121.0, 117.5, 16.4, 15.0, 14.9, 14.3. **HRMS:** m/z 513.0707 ($[M]^+$) (calc. 513.0708).



Scheme S5. *Synthesis of compound* ***3o****.*

3o: S11 (296 mg, 0.79 mmol), **S15**[2] (500 mg, 1.66 mmol), triphenylphosphine (104 mg, 0.395 mmol) and tripotassium phosphate (587 mg, 2.765 mmol) were dissolved in a mixture of 1,4-dioxane (70 mL) and water (30 mL). Then tetrakis(triphenyphosphine) palladium 0 (91 mg, 0.079 mmol) was added and the solution refluxed at 110°C for 72 hours. The mixture was cooled to room temperature and quenched with 1M aqueous hydrochloric acid followed by extraction into ethyl acetate, washed with brine then with water, dried over anhydrous magnesium sulfate and concentrated to give an orange solid. Silica gel column chromatography (1st spot Rf = 0.8 in 20:1 hexane: ethyl acetate) gave a solid that was further purified by GPC in chloroform to give a white solid that turned blue under UV light. **Yield:** 121 mg, 0.215 mmol, 27%. **^{1}H-NMR** (600 MHz, $CDCl_3$, 25°C) δ: 8.02 (m, 2H), 7.94 (m, 2H), 7.68 (m, 2H), 7.53 (s, 1H), 7.48-7.38 (m, 8H), 7.30 (m, 1H), 2.05 (s, 3H), 2.01 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$, 25°C) δ: 164.9, 164.7, 147.1, 146.7, 146.5, 140.2, 138.9, 135.0, 134.7, 133.7, 133.5, 131.2, 131.1, 130.1, 130.0, 129.1, 129.0, 129.0, 127.9, 126.6, 126.5, 126.4, 126.1, 115.5, 12.5, 12.3. **HRMS:** m/z 562.0662 ($[M]^+$) (calc. 562.0660)



Scheme S6. *Synthesis of compound* ***4o****.*

4o: S11 (284 mg, 0.76 mmol), **S16**[2] (500 mg, 1.59 mmol), triphenylphosphine (104 mg, 0.397 mmol) and tripotassium phosphate 563 mg, 2.653 mmol) were dissolved in a mixture of 1,4-dioxane (70 mL) and water (30 mL). Then tetrakis(triphenyphosphine) palladium 0 (91 mg, 0.079 mmol) was added

and the solution refluxed at 110°C for 72 hours. The mixture was cooled to room temperature and quenched with 1M aqueous hydrochloric acid followed by extraction into ethyl acetate, washed with brine then with water, dried over anhydrous magnesium sulfate and concentrated to give a yellow solid. Silica gel column chromatography (1st spot Rf = 0.8 in 4:1 hexane: ethyl acetate) gave a solid that was further purified by GPC in chloroform to give a white solid that turned blue under UV light. **Yield:** 126 mg, 0.214 mmol, 28%. **^{1}H-NMR** (600 MHz, $CDCl_3$, 25°C) δ: 7.65 (m, 2H), 7.54 (s, 1H), 7.47-7.36 (m, 10H), 7.34-7.27 (m, 3H), 2.32-2.00 (m, 12 H, CH_3 signals broadened by conformational isomers). **^{13}C-NMR** (151 MHz, $CDCl_3$, 25°C) δ: Signals split by isomerization. **HRMS:** m/z 588.1069 ($[M]^+$) (calc. 588.1068).

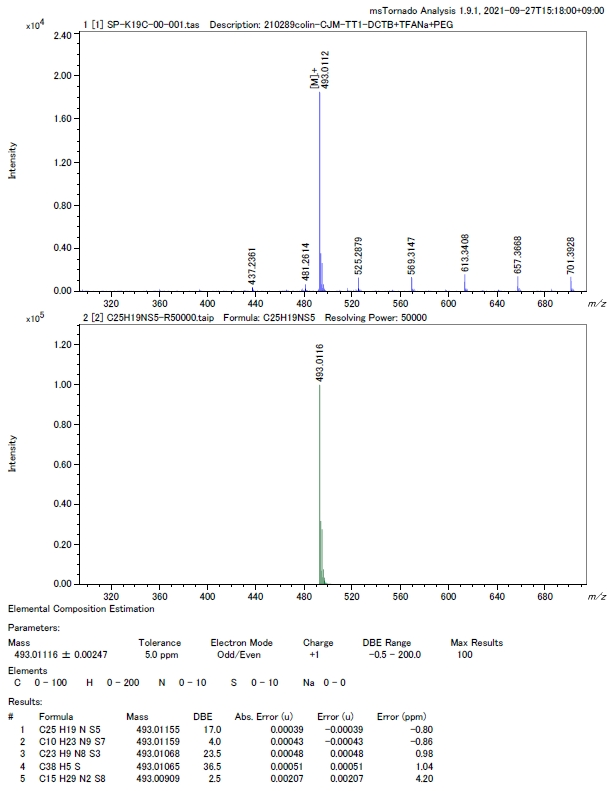


Figure S1. HR-MS data measurement (top) and calculation result (bottom) of **1o**. MALDI-Spiral-TOF system with polyethylene glycol as internal standard.

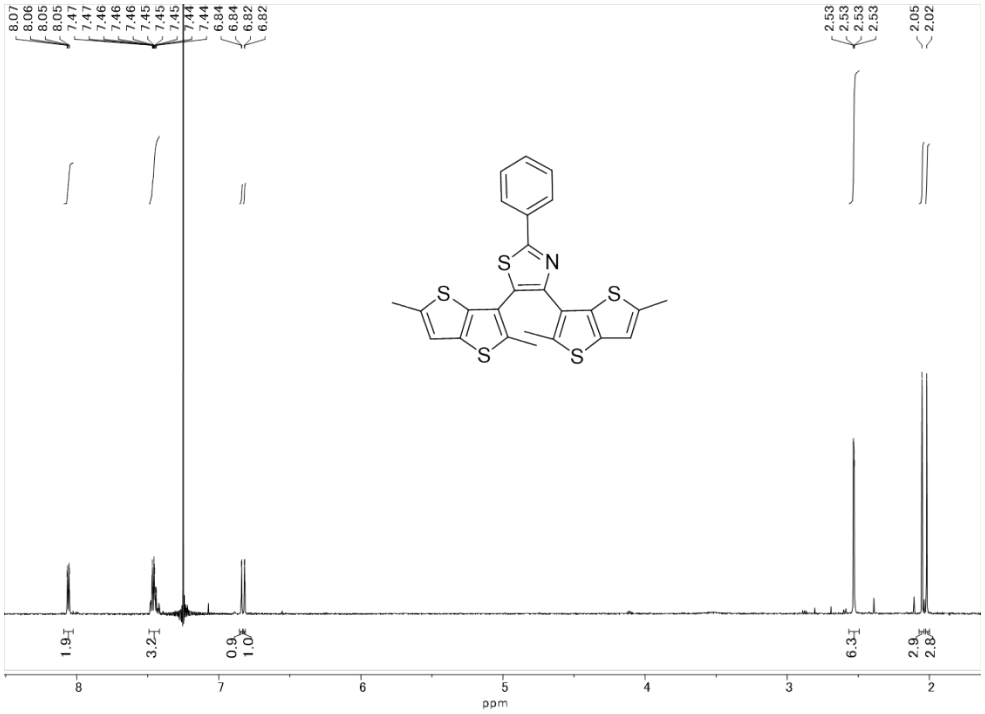


*Figure S2. ^{1}H NMR spectrum of **1o** (600 MHz, $CDCl_3$, TMS, 25°C).*

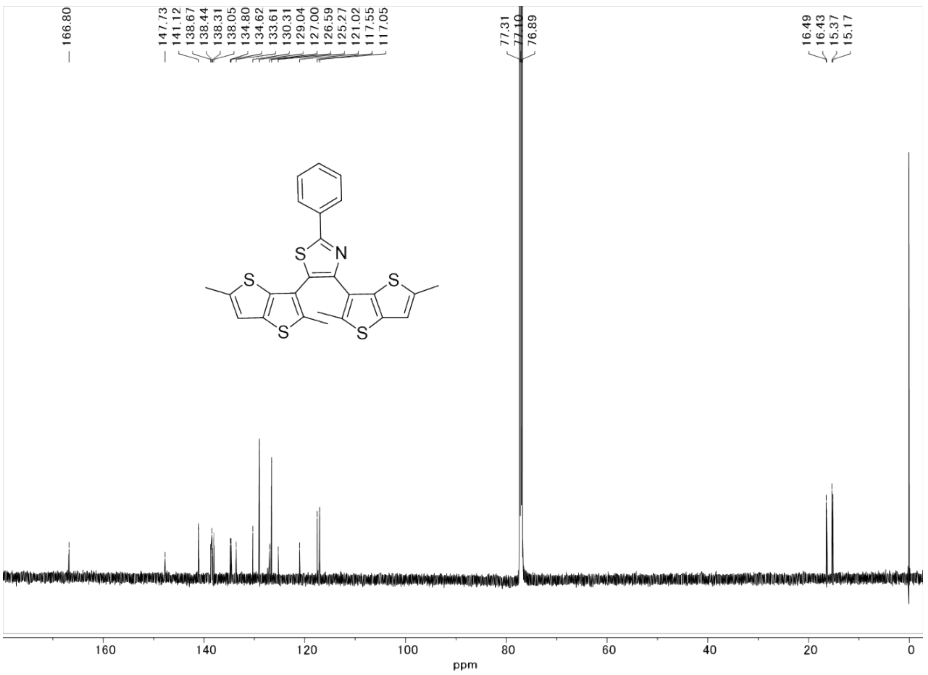


*Figure S3. ^{13}C NMR spectrum of **1o** (151 MHz, $CDCl_3$, TMS, 25°C).*

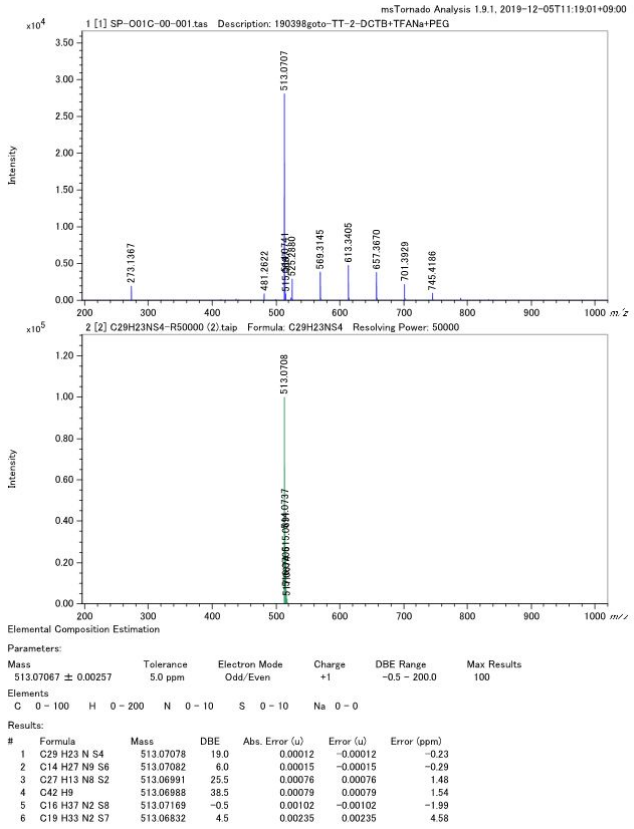


*Figure S4. HR-MS data measurement (top) and calculation result (bottom) of **2o**. MALDI-Spiral-TOF system with polyethylene glycol as internal standard.*

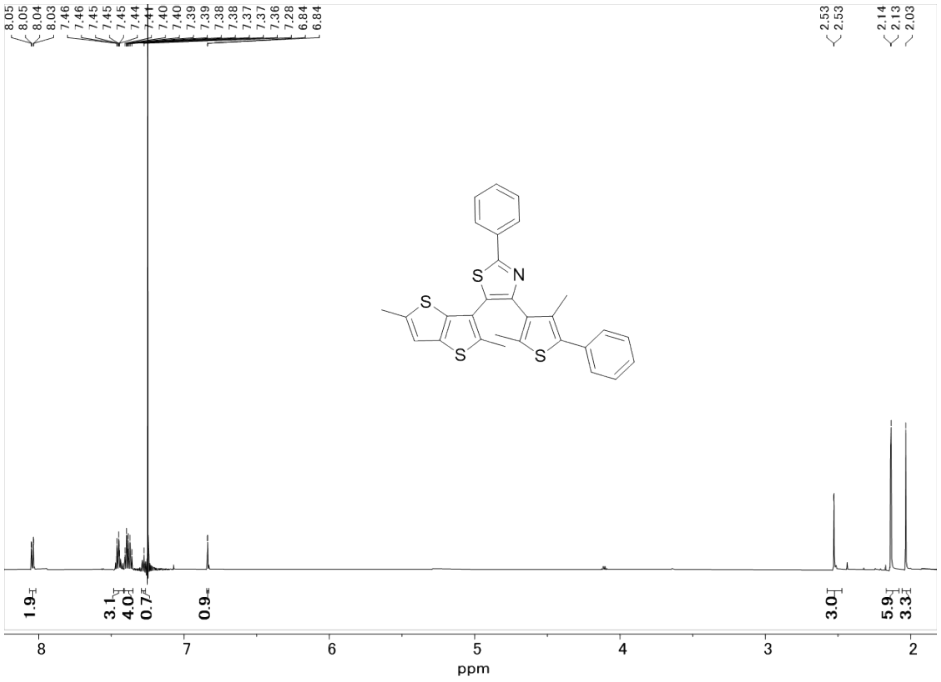


*Figure S5. ^{1}H NMR spectrum of **2o** (600 MHz, $CDCl_3$, TMS, 25°C).*

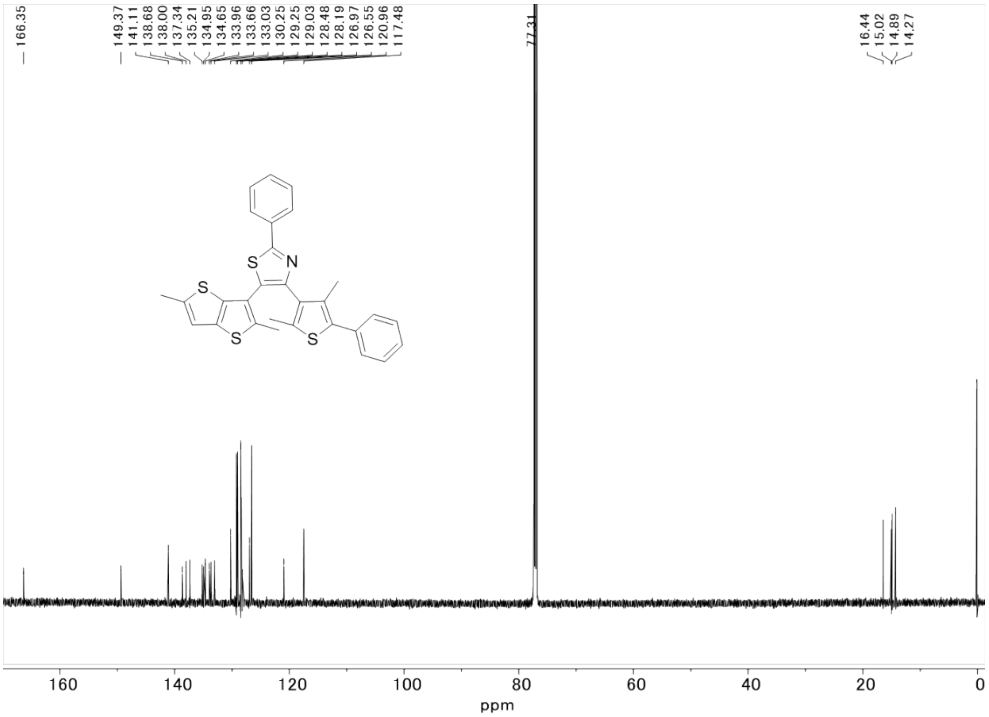


*Figure S6. ^{13}C NMR spectrum of **2o** (151 MHz, $CDCl_3$, TMS, 25°C).*

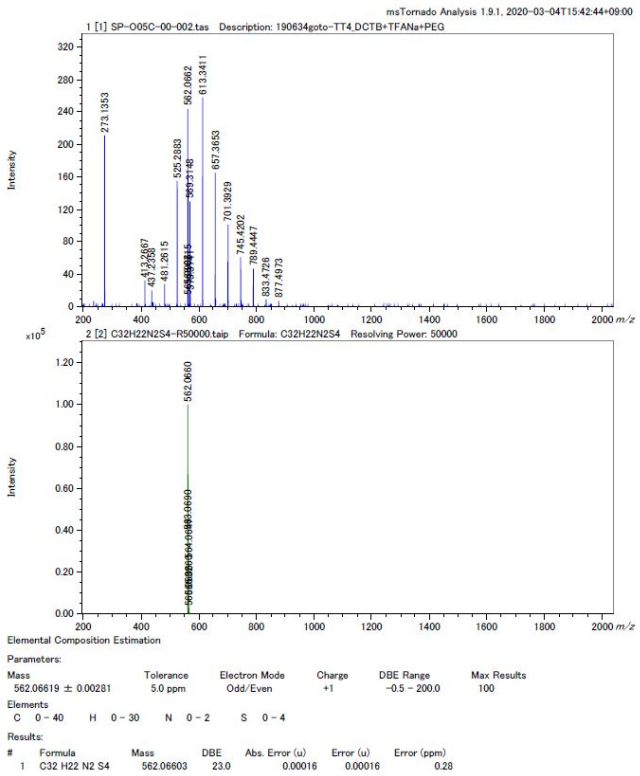


*Figure S7. HR-MS data measurement (top) and calculation result (bottom) of **3o**. MALDI-Spiral-TOF system with polyethylene glycol as internal standard.*

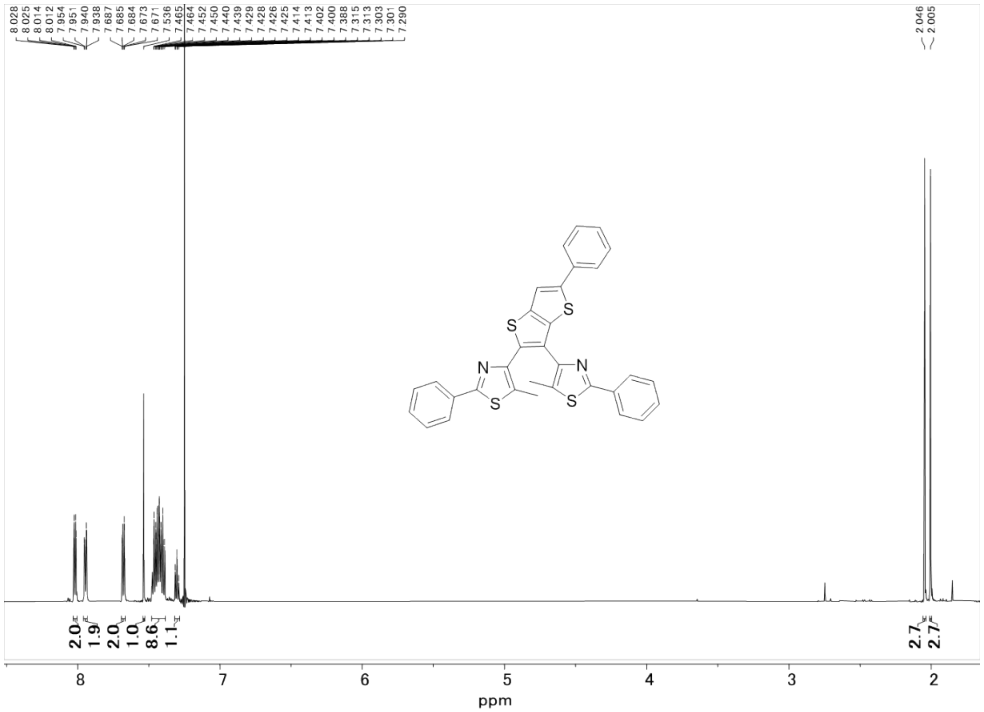


*Figure S8. ^{1}H NMR spectrum of **3o** (600 MHz, $CDCl_3$, TMS, 25°C).*

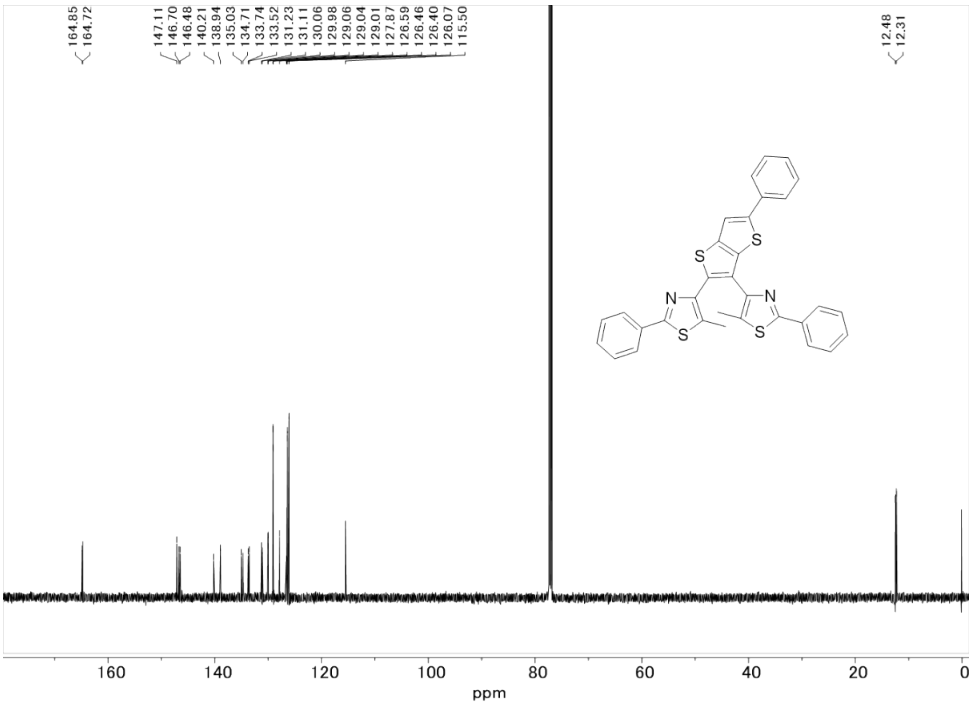


*Figure S9. ^{13}C NMR spectrum of **3o** (151 MHz, $CDCl_3$, TMS, 25°C).*

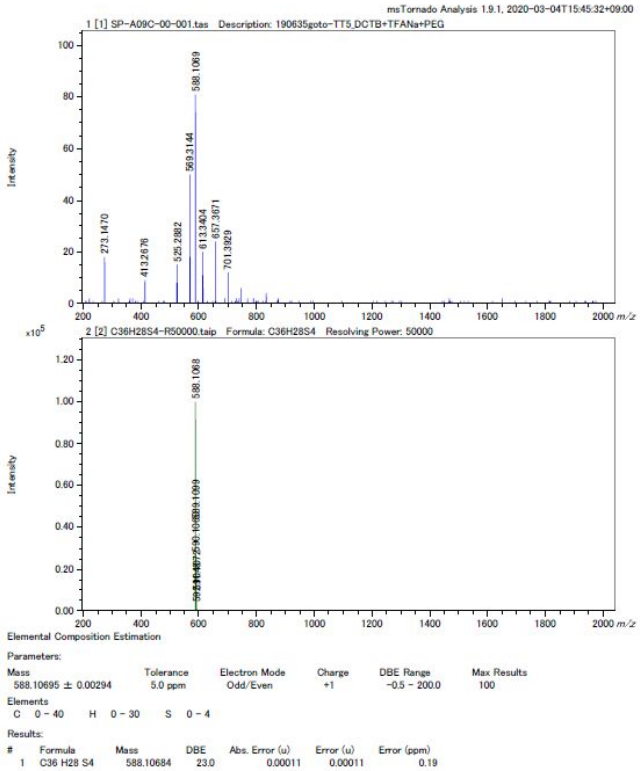


*Figure S10. HR-MS data measurement (top) and calculation result (bottom) of **4o**. MALDI-Spiral-TOF system with polyethylene glycol as internal standard.*

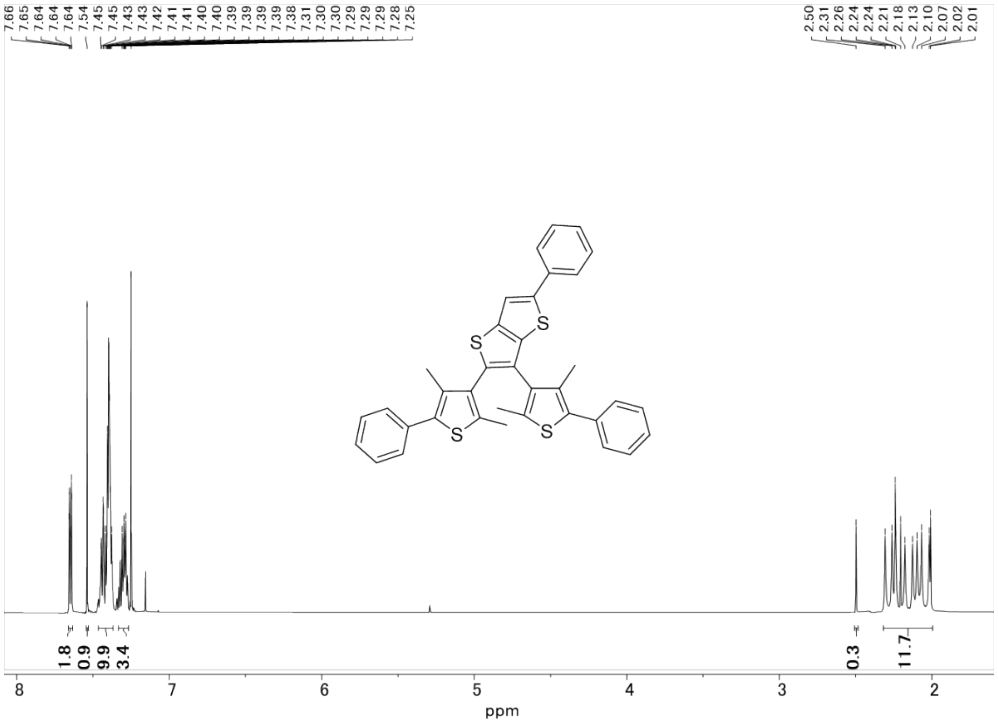


*Figure S11. ^{1}H NMR spectrum of **4o** (600 MHz, $CDCl_3$, TMS, 25°C).*

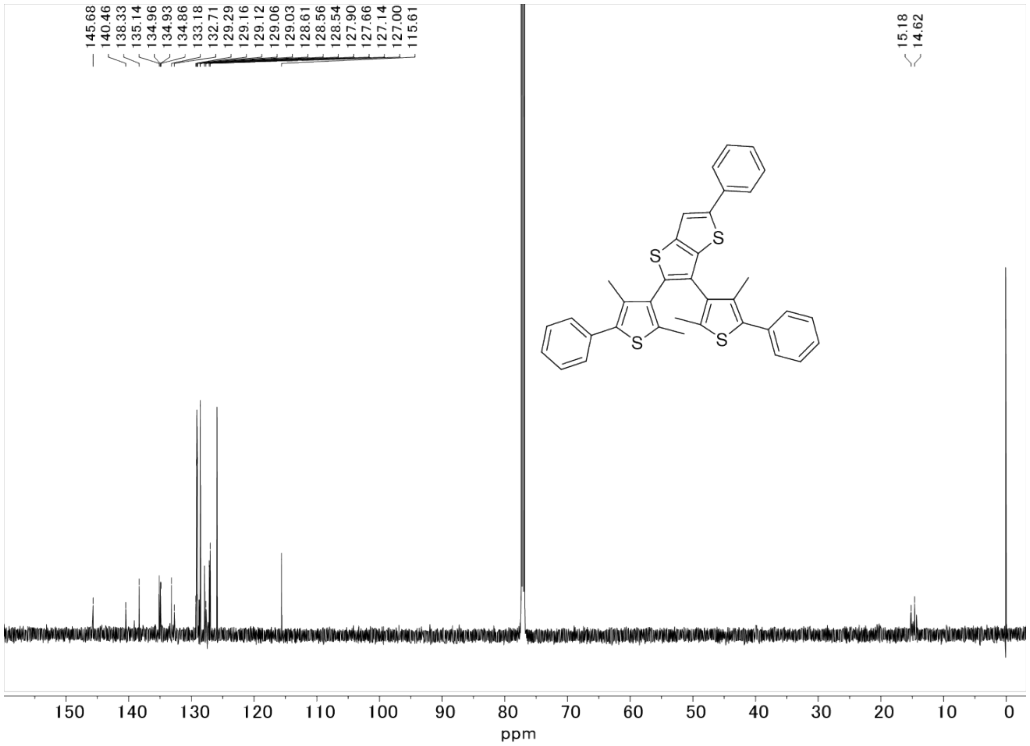


*Figure S12 ^{13}C NMR spectrum of **4o** (151 MHz, $CDCl_3$, TMS, 25°C).*

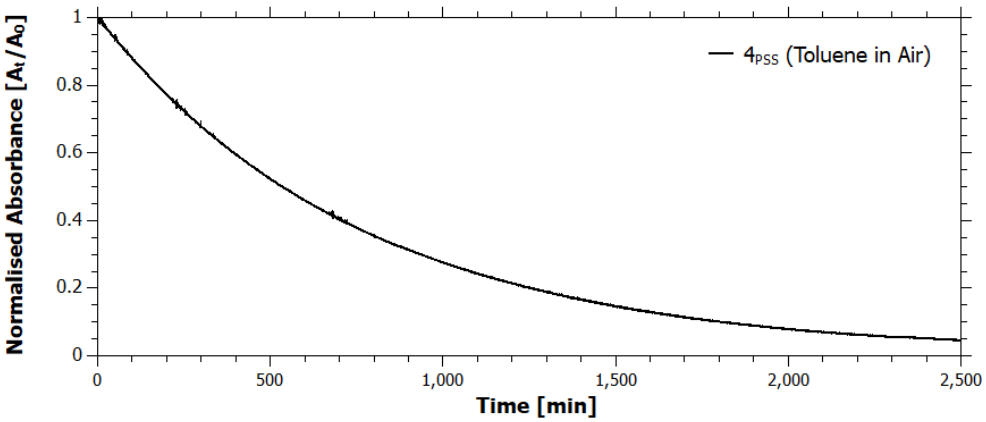


*Figure S13. Thermal decay in absorbance at λ_{max} of a PSS solution of **4** in toluene under air.*

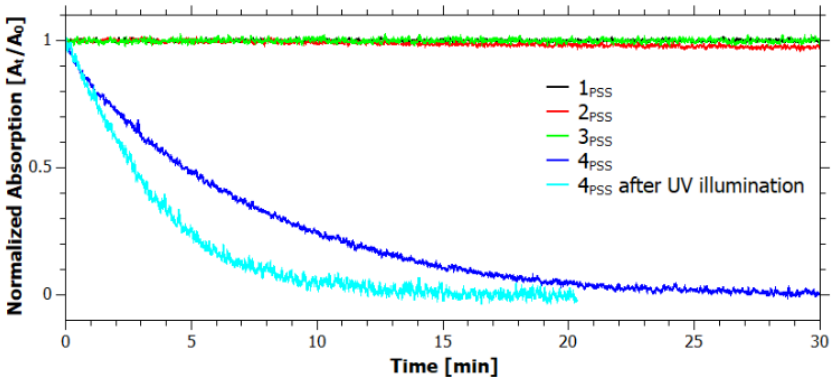


*Figure S14. Thermal decay in absorbance at λ_{max} of PSS solutions of **1**-**4** in 9:1 chloroform: toluene.*

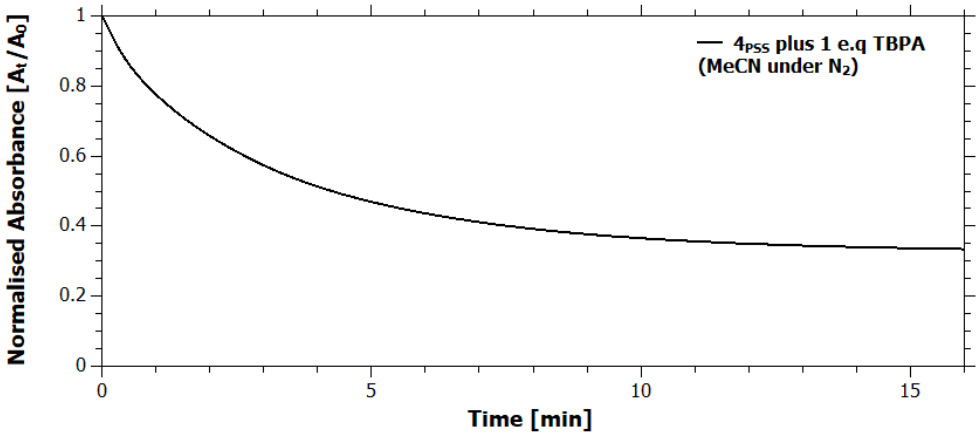


*Figure S15. Decay in absorbance at λ_{max} of a PSS solution of **4** in acetonitrile upon addition of 1 eq. of TBPA, showing the decay of a 100% **C**$^{\cdot+}$ solution.*

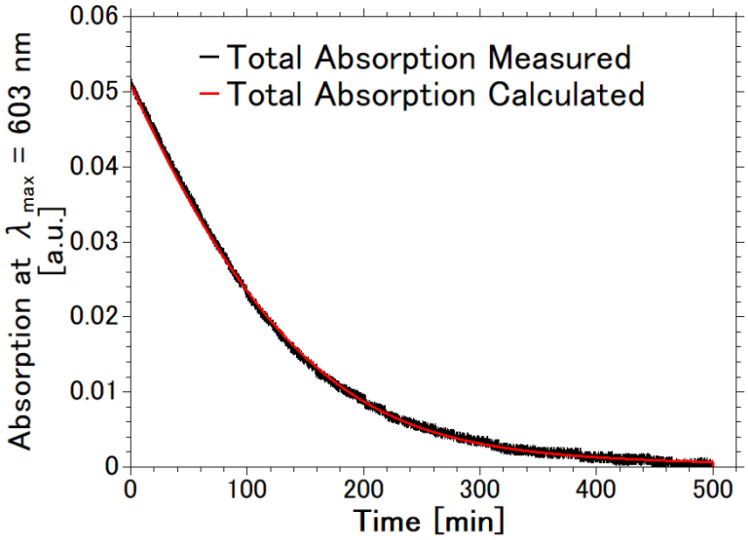


*Figure S16. Experimental (black) and calculated thermal decays at λ_{max} of a PSS solution of **4** in acetonitrile showing the optimised kinetic fitting.*

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