**Supplementary Information for**

# A Cyclic Octithiophene Containing β,β′-Linkages

Kengo Asai,[a] Aiko Fukazawa,*[a] and Shigehiro Yamaguchi*[ab]

[a]*Department of Chemistry, Graduate School of Science and* [b]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Furo, Chikusa, Nagoya 464-8602, Japan*

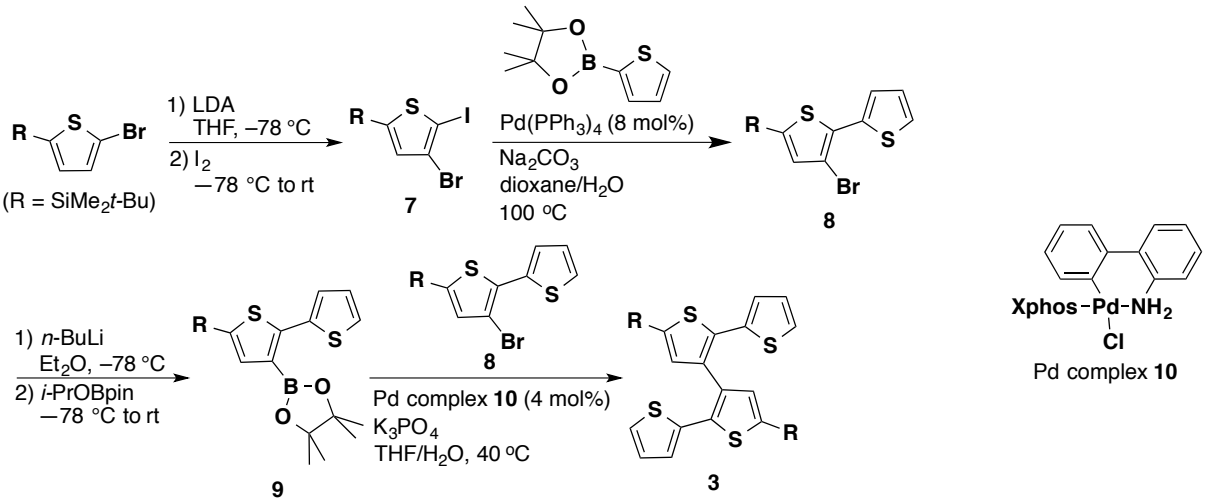
## *Contents*

## 1. Experimental Details

**General.** Melting points (mp) were determined with a Yanaco MP-S3 instrument (MP-S3). Thermal gravimetric analyses (TGA) for the determination of the 5% weight loss temperature ($T_{d5}$) were conducted using a SII TGA6200 instrument. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were recorded with a JEOL AL-400 spectrometer in $CDCl_3$, $CD_2Cl_2$ or $C_2D_2Cl_4$ (400 MHz for $^{1}H$ and 100 MHz for $^{13}C$). The chemical shifts in $^{1}H$ NMR spectra are reported in $\delta$ ppm using the residual proton of the solvents, $CHCl_3$ (7.26 ppm), $CH_2Cl_2$, (5.32 ppm), and $C_2H_2Cl_4$ (6.00 ppm) as an internal standard. The chemical shifts in $^{13}C$ NMR spectra are reported in $\delta$ ppm using the solvent signals of $CDCl_3$ (77.16 ppm) as an internal standard. Electron paramagnetic resonance (EPR) spectrum was measured with a JEOL JES-FA 200 ESR spectrometer in a sealed tube in $CH_2Cl_2$. Mass spectra were measured with a Bruker micrOTOF Focus spectrometer with the ionization method of APCI. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thickness of silica gel $60F_{254}$ (Merck). Column chromatography was performed using PSQ100B (Fuji Silysia Chemicals). Anhydrous THF, $CH_2Cl_2$, toluene, and *i*-$Pr_2NH$ were purchased from Kanto Chemicals and further purified by Glass Contour solvent systems. 5-(*t*-butyldimethylsilyl)-2-bromothiophene,[1] 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene,[2] 5,5′-dibromo-2,2′-bithiophene,[3] and Pd complex **10**[4] were prepared according to the literature methods. All reactions were preformed under a nitrogen or argon atmosphere, unless stated otherwise.

## *Synthesis of Compound 3*

### *Scheme S1*




**5-(*t*-Butyldimethylsilyl)-3-bromo-2-iodothiophene (7).** To a solution of *i*-$Pr_2NH$ (6.28 mL, 4.84 g, 47.5 mmol) in THF (14.4 mL) was added a hexane solution of *n*-BuLi (1.60 M, 29.7 mL, 47.5 mmol) at –78 °C, and the mixture was stirred for 1 h at –78 °C. The LDA solution thus prepared was added dropwise to a solution of 5-(*t*-butyldimethylsilyl)-2-bromothiophene (12.0 g, 43.3 mmol) in THF (54 mL) at –78 °C. The reaction mixture was stirred at the same temperature for 2 h and transferred into a solution of $I_2$ (16.4 g, 64.8 mmol) in THF (65 mL). The reaction mixture was allowed to warm to ambient temperature and stirred for 26 h. After addition of water (100 mL), the aqueous layer was extracted with $Et_2O$. The combined organic layer was washed with a 10wt% $Na_2SO_3$ solution, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane, $R_f$ = 0.75) to afford **7** as light yellow oil (15.1 g, 37.5 mmol, 87%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.27 (s, 6H), 0.92 (s, 9H), 6.98 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ –5.1, 17.0, 26.3, 81.9, 121.8, 137.5, 146.1. HRMS (APCI): *m/z* Calcd. for $C_{10}H_{16}{}^{79}BrISSi$: 401.8965 ($[M]^+$). Obsd. 401.8978.

**5-(*t*-Butyldimethylsilyl)-3-bromo-2,2′-bithiophene (8).** To a solution of **7** (16.3 g, 40.4 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (9.34 g, 44.5 mmol), and $Pd(PPh_3)_4$ (3.74 g, 3.24 mmol) in degassed dioxane (420 mL) was added a degassed 2M $Na_2CO_3$ aqueous solution (70

mL). The reaction mixture was stirred at 100 °C for 22 h. After addition of water (100 mL), the aqueous layer was extracted with $CHCl_3$ and washed with brine. The combined organic layer was dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane, $R_f$ = 0.50) to afford **8** as white solids (9.24 g, 25.7 mmol, 64%). Mp: 76.2–77.2 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.30 (s, 6H), 0.95 (s, 9H), 7.08 (dd, $J$ = 4.8, 4.0 Hz 1H), 7.10 (s, 1H), 7.35 (d, $J$ = 4.8 Hz, 1H), 7.45 (d, $J$ = 4.0 Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ −5.1, 17.1, 26.4, 109.0, 126.2, 126.7, 127.4, 134.7, 137.1, 137.3, 139.3. HRMS (APCI): $m/z$ Calcd. for $C_{14}H_{19}{}^{79}BrS_2Si$: 357.9875 ($[M]^+$). Obsd. 357.9892.

**5-(*t*-Butyldimethylsilyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene (9).** To a solution of **8** (4.49 g, 12.5 mmol) in $Et_2O$ (90 mL) was added a hexane solution of *n*-BuLi (1.65 M, 7.60 mL, 12.5 mmol) dropwise at –78 °C. The reaction mixture was stirred at the same temperature for 1.5 h, and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.80 mL, 2.55 g, 13.7 mmol) was added to the solution. The reaction mixture was warmed gradually to ambient temperature and stirred for 18 h. After addition of water (20 mL), the aqueous layer was extracted with $Et_2O$. The combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The crude product was recrystallized from MeOH to afford **9** as white solids (4.03 g, 9.91 mmol, 79%). Mp: 111.0–112.0 °C. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 0.31 (s, 6H), 0.95 (s, 9H), 1.33 (s, 12H), 7.05 (dd, $J$ = 5.2, 3.6 Hz 1H), 7.31 (dd, $J$ = 5.2, 1.2 Hz, 1H), 7.43 (s, 1H), 7.45 (dd, $J$ = 3.6, 1.2 Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ –4.6, 17.0, 25.0, 26.6, 83.8, 125.8, 127.2, 127.4, 136.8, 137.2, 143.1, 151.6. HRMS (APCI): $m/z$ Calcd. for $C_{20}H_{31}BO_2S_2Si$: 406.1622 ($[M]^+$). Obsd. 406.1637.

**5′,5″-Bis(*t*-butyldimethylsilyl)-2,2′:3′,3″:2″,2‴-quaterthiophene (3).** To a solution of **8** (1.62 g, 4.51 mmol), **9** (2.01 g, 4.94 mmol), and Pd complex **10** (71.1 mg, 0.090 mmol) in THF (45 mL) was added a 0.5 M $K_3PO_4$ aqueous solution (18 mL). The reaction mixture was stirred at 40 °C for 2 h. After addition of water (15 mL), the aqueous layer was extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure.

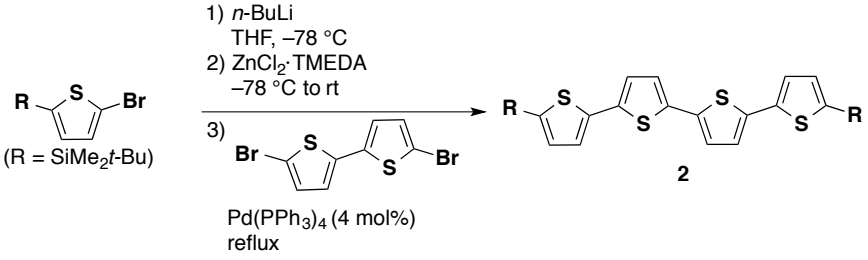
The crude product was purified by column chromatography (hexane, $R_f$ = 0.18) to afford **3** as white solids (2.41 g, 4.31 mmol, 96%). Mp: 110.0–111.0 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.29 (s, 12H), 0.94 (s, 18H), 6.85 (dd, $J$ = 5.2, 4.0 Hz, 2H), 7.00 (d, $J$ = 4.0, 0.8 Hz, 2H), 7.03 (s, 2H), 7.07 (d, $J$ = 5.2, 0.8 Hz, 2H). $^{13}$C{$^1$H} NMR ($CDCl_3$, 100Hz): $\delta$ –4.9, 17.1, 26.5, 125.1, 125.6, 127.0, 133.6, 135.7, 136.3, 138.7, 140.2. HRMS (APCI): $m/z$ Calcd. for $C_{28}H_{38}S_4Si_2$: 558.1389 ([$M$]$^+$). Obsd. 558.1390.

### *Synthesis of Compound 1*

**Cyclic octithiophene (1).** To a solution of **3** (534 mg, 0.955 mmol) in THF (7 mL) was added a hexane solution of *n*-BuLi (1.65 M, 1.25 mL, 2.06 mmol) at –78 °C. After the reaction mixture was stirred at the same temperature for 1.5 h, $Me_3SnCl$ (398 mg, 2.00 mmol) in THF (1.8 mL) was added to the solution. The reaction mixture was warmed gradually to ambient temperature and stirred for 1.5 h. After addition of water (10 mL), the aqueous layer was extracted with EtOAc. The combined organic layer was dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The resulting mixture was dissolved in THF (240 mL) and Pt(cod)$Cl_2$ (358 mg, 0.957 mmol) was added to the solution. The reaction mixture was stirred at reflux temperature for 3 days. The reaction mixture was cooled to ambient temperature and the precipitates were collected by filtration and washed with hexane. The obtained solid was dissolved in $CH_2Cl_2$ (160 mL) and 1,1′-bis(diphenylphosphino)ferrocene (530 mg, 0.956 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 15 h. The solvent was removed under reduced pressure and the resulting mixture was dissolved in toluene (160 mL) and then $PPh_3$ (2.51 g, 9.57 mmol) was added to the solution. The reaction mixture was stirred at 95 °C for 20 h and cooled to ambient temperature. The precipitates were collected by filtration and washed with hexane and $CH_2Cl_2$. The crude product was recrystallized from chlorobenzene to afford **1** as yellow solids (361 mg, 0.324 mmol, 68%). TGA: $T_{d5}$ = 434.6 °C. $^1$H NMR (400 MHz, $C_2D_2Cl_4$, 130 °C): $\delta$ 0.45 (s, 24H), 1.11 (s, 36H), 6.30 (d, $J$ = 3.6 Hz, 4H), 6.82 (d, $J$ = 3.6 Hz, 4H), 7.37 (s, 4H). $^{13}$C NMR spectrum was not obtained due to the poor solubility. HRMS (APCI): $m/z$ Calcd. for $C_{56}H_{73}S_8Si_4$: 1113.2550 ([$M$+H]$^+$). Obsd. 1113.2501.

### *Synthesis of Compound 2*

***Scheme S2***



**5′,5‴-Bis(*t*-butyldimethylsilyl)-2,2′:5′,2″:5″,2‴-quaterthiophene (2).** To a solution of 5-(*t*-butyldimethylsilyl)-2-bromothiophene (157 mg, 0.566 mmol) in THF (2.7 mL) was added a hexane solution of *n*-BuLi (1.65 M, 0.370 mL, 0.610 mmol) at –78 °C. After stirring at the same temperature for 1.5 h, $ZnCl_2$(tmeda) (152 mg, 0.602 mmol) was added. The reaction mixture was allowed to warm to ambient temperature and stirred for 1.5 h. The mixture was transferred into a solution of 5,5′-dibromo-2,2′-bithiophene (80.7 mg, 0.249 mmol) and $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol) in THF (1.3 mL). The reaction mixture was stirred at reflux temperature for 13.5 h. After addition of a saturated aqueous $NH_4Cl$ solution (5 mL), the aqueous layer was extracted with $Et_2O$. The combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane, $R_f$ = 0.15) and recrystallized from hexane to afford to **2** as yellow solids (39.7 mg, 0.071 mmol, 29 %). Mp: 197.8–198.5 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.31 (s, 12H), 0.95 (s, 18H), 7.07 (d, $J$ = 3.6 Hz, 2H), 7.10 (d, $J$ = 3.6 Hz, 2H), 7.14 (d, $J$ = 3.6 Hz, 2H), 7.24 (d, $J$ = 3.6 Hz, 2H). $^{13}$C{$^1$H} NMR ($CDCl_3$, 100Hz): $\delta$ –4.8, 17.1, 26.5, 124.4, 124.6, 125.0, 136.1, 136.1, 136.5, 137.4, 142.3. HRMS (APCI): *m*/*z* Calcd. for $C_{28}H_{38}S_4Si_2$: 558.1389 ($[M]^+$). Obsd. 558.1386.

**Chemical oxidation of 1.** To a solution of **1** (5.6 mg, 5.0 μmol) in degassed and dehydrated $CH_2Cl_2$ (5 mL) was added tris(*p*-bromophenyl)aminium hexachloroantimonate (4.6 mg, 5.6 μmol) under an argon atmosphere. The mixture was stirred at ambient temperature for 1 h. The resuting solution of $\mathbf{1}^{\bullet+}$ (ca. $1.0 \times 10^{-3}$ M) was directly used for the EPR measurement. UV-vis-NIR measurement was carried out using a diluted solution of $\mathbf{1}^{\bullet+}$ (ca. $1.0 \times 10^{-4}$ M).

**Chemical oxidation of 2.** To a solution of **2** (2.8 mg, 5.0 μmol) in degassed and dehydrated $CH_2Cl_2$ (5 mL) was added tris(*p*-bromophenyl)aminium hexachloroantimonate (4.6 mg, 5.6 μmol) under argon atmosphere. The mixture was stirred at ambient temperature for 1 h. The solution of $\mathbf{2}^{\bullet+}$ (ca. $1.0 \times 10^{-3}$ M) was directly used for the for EPR measurement. UV-vis-NIR measurement was carried out using the diluted solution of $\mathbf{2}^{\bullet+}$ (ca. $1.0 \times 10^{-4}$ M).

## 2. X-ray Crystallographic Analysis

**X-ray Data Collection of 1.** Single crystals of **1** suitable for X-ray crystallographic analysis were obtained by recrystallization from 1-methylnaphthalene. Intensity data were collected at 123 K on a Rigaku X-ray diffractometer equipped with a molybdenum FR-X microfocus generator, VariMax-Mo optics, and a PILATUS 200K detector. Total of 29857 reflections were measured with the maximum $2\theta$ angle of 55.0°, of which 6967 were independent reflections ($R_{int}$ = 0.0566). The structure was solved by direct methods (SHELXS-2013) and refined by the full-matrix least-squares on $F^2$ (SHELXL-2013). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{56}H_{72}S_8Si_4$; FW = 1113.98, crystal size 0.14 × 0.02 × 0.01 mm$^3$, monoclinic, *C2/c*, $a$ = 43.196(17) Å, $b$ = 6.377 (2) Å, $c$ = 24.5113(10) Å, $\beta$ = 115.408(5)°, $V$ = 6099(3) Å$^3$, $Z$ = 4, $D_c$ =1.213 g cm$^{-3}$, $\mu$ = 0.406 mm$^{-1}$, $R_1$ = 0.0617 ($I > 2\sigma(I)$), $wR_2$ = 0.2189 (all data), GOF = 1.115. CCDC 1043632.

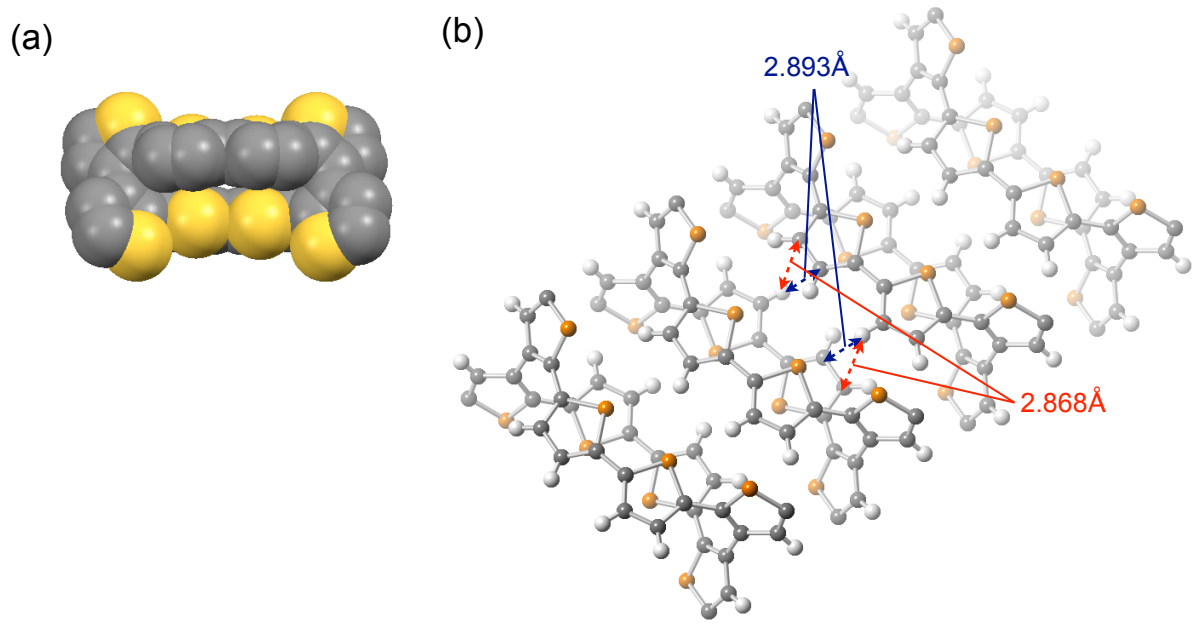



***Fig. S1*** X-ray crystal structure of **1**: (a) space filling model and (b) packing structure, where silyl groups are omitted for clarity.

## 3. Photophysical Properties

UV-vis absorption spectra were measured with a Shimadzu UV-3150 spectrometer with a resolution of 0.5 nm using dilute sample solutions in spectral grade solvents in a 1 cm or 1 mm-thickness quartz cuvette. Emission spectra were measured with a Hitachi F-4500 spectrometer with a resolution of 1 nm. For the fluorescence measurement, the sample solutions were excited at 370 nm for **1** and 400 nm for **2**. Absolute fluorescence quantum yields were determined with a Hamamatsu Photonics C-9920-02 calibrated integrating sphere system. The PMMA films were prepared on the surface of a quartz cell by casting a $CHCl_3$ solution (2 mL) of the sample (0.5 mg) and PMMA (50 mg, WAKO Chemicals).

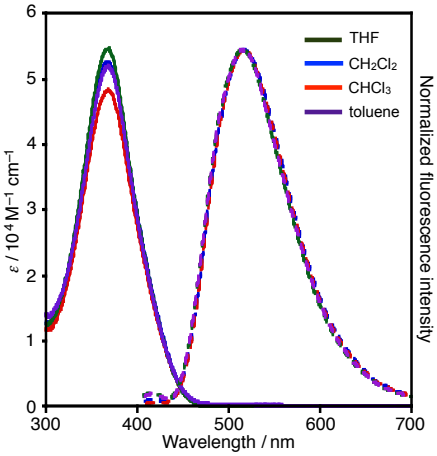



***Fig. S2*** Absorption (solind line) and fluorescence (broken line) spectra of **1** in various solvents.

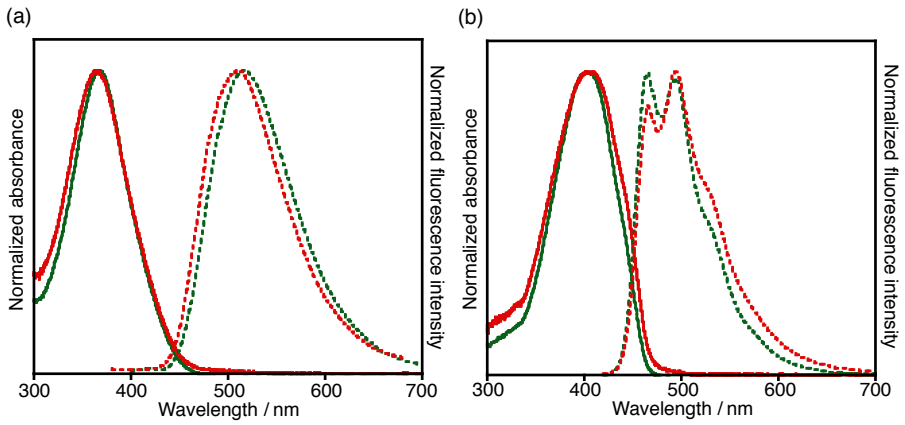



***Fig. S3*** Absorption (solid line) and fluorescence (broken line) spectra of (a) **1** and (b) **2** in $CH_2Cl_2$ (green) and in the PMMA film (red). The PMMA film contains the sample in a 1.0wt% concentration.

## 4. Electrochemical Properties

**Cyclic Voltammetry and Differential Pulse Voltammetry.** Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed on an ALS/chi-617A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ reference electrode. The measurements were carried out under an argon atmosphere using $CH_2Cl_2$ solution of sample with a concentration of 0.1 mM (**1**) and 1 mM (**2**), and 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. The oxidation potentials were calibrated with ferrocene/ferrocenium ion couple.

**Electrochemical Absorption Spectroscopy.** Electrochemical absorption spectra of **1** and **2** (Fig. S5) were measured with a Shimadzu UV-3150 spectrometer with a resolution of 0.5 nm by cooperating with ALS/chi-617A electrochemical analyzer. The electrochemical cell consisted of 1 mm of thin layer quartz cell, a Pt mesh working electrode, a Pt wire counter electrode, and a $Ag/AgNO_3$ reference electrode. The measurements were carried out under flow of nitrogen gas using $CH_2Cl_2$ solution of sample with a concentration of ca. 0.1 mM (**1**) and 1 mM (**2**), and 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. The oxidation potentials were calibrated with ferrocene/ferrocenium ion couple. Electrochemical absorption spectra of **1** and **2** were recorded during oxidation at each oxidation potential.

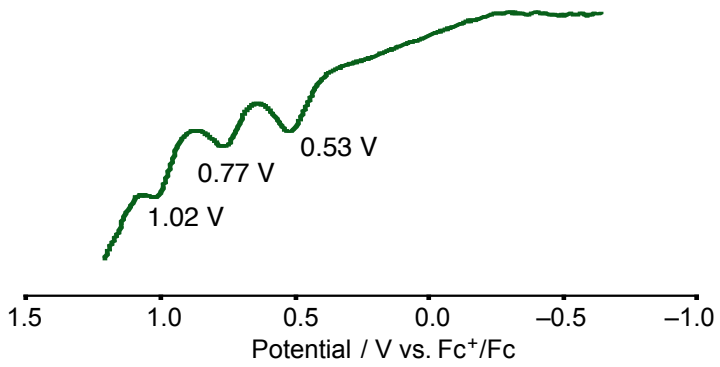



***Fig. S4*** Differential pulse voltammogram of **1** at a scan rate of 0.1 V $s^{-1}$ in $CH_2Cl_2$ with $Bu_4NPF_4$ as the supporting electrolyte. All oxidation potentials are referenced by $Fc/Fc^+$.

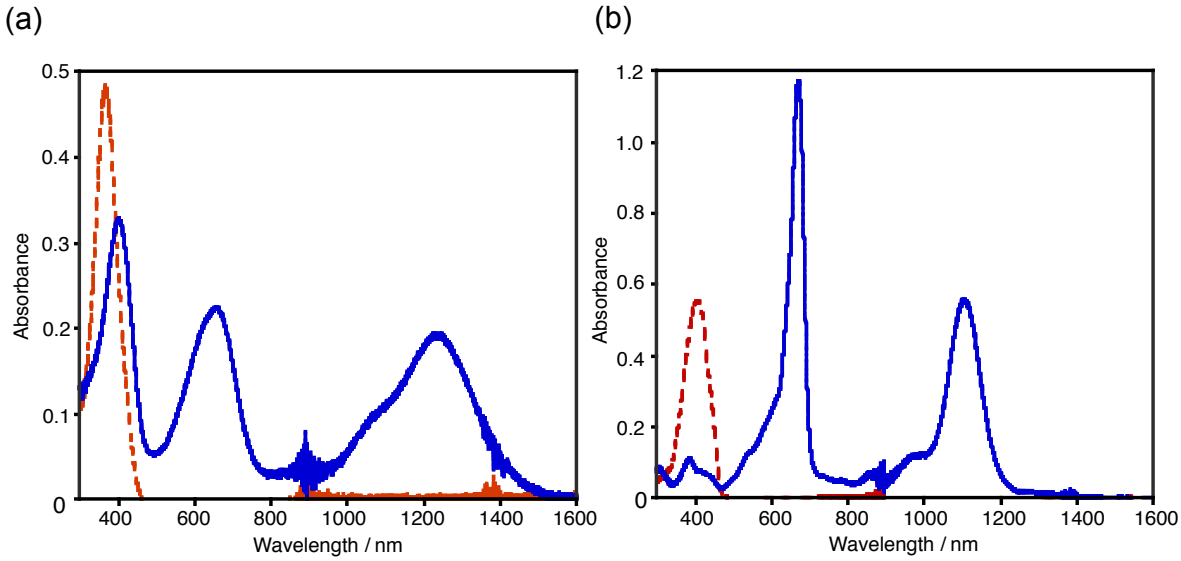



***Fig. S5*** Electrochemical absorption spectra of (a) **1** at 0 V (broken line) and at 0.64 V (solid line) and (b) **2** at 0V (broken line) and 0.67 V (solid line).

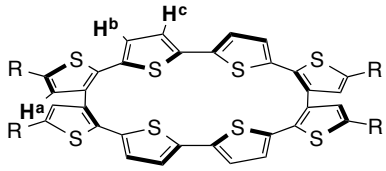
***Table S1***. Electrochemical Absorption in $CH_2Cl_2$

| cmpd | potential [V] | $\lambda_{abs}$ [nm] |
|---|---|---|
| **1** | 0.0 | 366 |
| | + 0.64 | 401, 654, 1229 |
| **2** | 0.0 | 406 |
| | +0.67 | 671, 1103 |

## 5. EPR Measurements

**Sample Preparation.** The ca. $1.0 \times 10^{-3}$ M solutions of **1** and **2** in $CH_2Cl_2$ with tris(*p*-bromophenyl)aminium hexachloroantimonate were prepared. The solutions were charged into a quartz EPR tube under an argon atmosphere and degassed by freeze-pump-thaw cycles. The tubes were sealed off under vacuum.

**Analyses of the EPR Spectra.** The obtained spectra were simulated with Lorentz functions. The spin densities of the carbon atoms adjacent to protons are estimated from McConnell's equation ($a_H = Q\rho$).[5] The splitting pattern of $\mathbf{2}^{\bullet+}$ can be explained by the presence of four kinds of hydrogen nuclei. The best-fit simulated spectrum was obtained by the hyperfine coupling constants $|a_H|$ of 0.259 mT (2H), 0.228 mT (2H), 0.105 mT (2H), and 0.089 mT (2H) (Fig. 6d and Table S2). On the other hand, the chemically generated $\mathbf{1}^{\bullet+}$ showed a broad EPR signal without hyperfine structures, which is totally different from that of $\mathbf{2}^{\bullet+}$. In light of the spin densities derived from DFT calculations (Fig. S22), we assumed that the delocalization of spin density over the entire cyclic π framework might be responsible for the line broadening. Therefore, taking the results of DFT calculations into account, we assumed that $\mathbf{1}^{\bullet+}$ has three kinds of nonequivalent protons on the thiophene rings, i.e., $H^a$, $H^b$, and $H^c$, and their coupling constants were simulated with Lorenz functions. As a result, the best-fit simulated spectrum was obtained with a major contribution of the hyperfine coupling constant $|a_H|$ of 0.126 mT (4H) together with two minor coupling constants (0.015 mT and 0.013 mT), although the latter two values have less accuracy because they are too small compared to the line width of the major signal (0.12 mT). Since these values are much smaller than those of $\mathbf{2}^{\bullet+}$, the corresponding spin densities in $\mathbf{1}^{\bullet+}$ are likely smaller than those of $\mathbf{2}^{\bullet+}$, supporting the effective delocalization of spin densities over the cyclic octithiophene framework.




**Determination of the Spin Concentration.** The concentration of radical cation of $\mathbf{1}^{\bullet+}$ was determined using a standard curve obtained by the plot of the concentration of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) versus the corresponding peak area ($R^2 = 0.995$). The peak area was determined using double integration.

***Table S2.*** Hyperfine Coupling Constants of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$

| cmpd | coupling constant (spin density)[a] |
|---|---|
| $\mathbf{1}^{\bullet+}$ | 0.126 mT (0.048)<br>0.015 mT (0.006)<br>0.013 mT (0.005) |
| $\mathbf{2}^{\bullet+}$ | 0.259 mT (0.098)<br>0.228 mT (0.086)<br>0.105 mT (0.040)<br>0.089 mT (0.034) |

[a]Estimated with McConnell's equation: $a_H = Q\rho$, ($Q$ = –2.64 mT)[5].

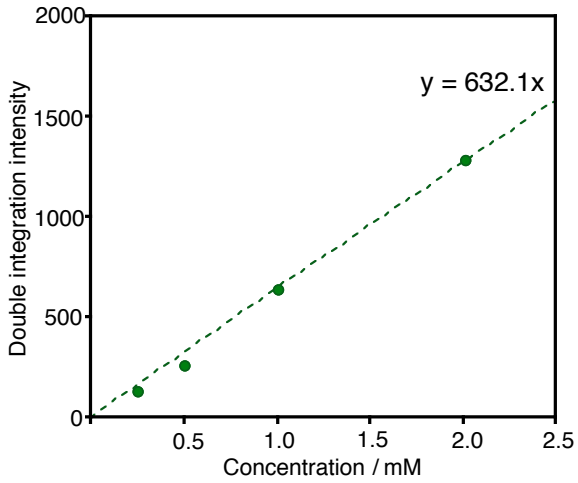



***Fig. S6*** A plot of the EPR signal integration of TEMPO as a function of concentration in $CH_2Cl_2$. The obtained standard curve was used for the determination of spin concentration of $\mathbf{1}^{\bullet+}$.

***Table S3.*** Estimated Concentration of $\mathbf{1}^{\bullet+}$ after Addition of $(p\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$

| cmpd | Amount of $(p\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$ [equivalent] | Ideal concentration of radical cation [mM] | Estimated concentration of radical cation [mM] |
|---|---|---|---|
| $\mathbf{1}^{\bullet+}$ | 1.1 | 1.0 | 0.53 |
| | 2.0 | 1.0 | 0.90 |

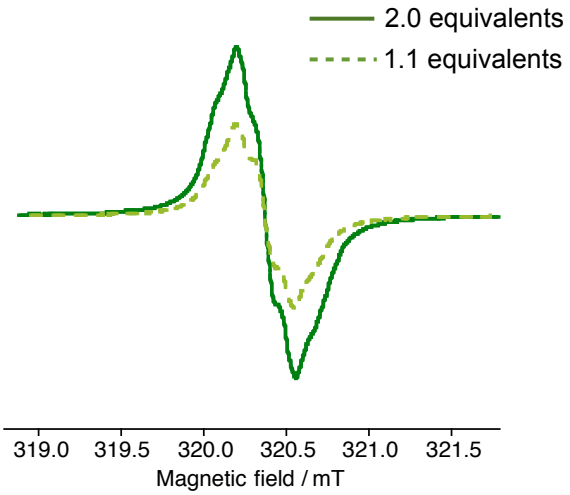



***Fig. S7*** EPR spectra of **1** in $CH_2Cl_2$ after addition of 1.1 and 2.0 equivalents of $(p\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$.

## 6. Theoretical Calculations

**Computational Method.** The geometry optimizations of **1′** and **2′** in the ground state ($S_0$) were performed using PBE0 (Gaussian keyword: PBE1PBE) hybrid exchange-correlation functional[6] with the 6-31G(d) basis set[7] implemented in the Gaussian 09 program.[8] For the geometry optimizations, a stationary point was optimized without any symmetry assumptions and characterized by frequency analysis at the same level of theory (the number of imaginary frequencies, NIMAG, was 0.) The energy calculations and geometry optimizations of **1′** and **2′** in the first excited singlet state ($S_1$) were performed using the time-dependent PBE0 method implemented in the Gaussian 09 program. The Cartesian coordinates for **1′** and **2′** in $S_0$ and $S_1$ are given in Tables S6–S9. The Kohn-Sham molecular orbitals of **1′** and **2′** in $S_0$ are illustrated in Fig. S10. TD-DFT vertical excitation calculations of **1′** and **2′** were performed using the optimized geometry at the PBE0/6-31G(d) level, implemented in the Gaussian 09 program. The geometry optimizations of $\mathbf{1'}^{+}$ and $\mathbf{2'}^{+}$ were performed using UB3LYP functional[9] with 6-31G(d) basis set implemented in the Gaussian 09 program and the obtained structures were compared with those of the neutral state optimized with the B3LYP functional. The Kohn-Sham molecular orbitals of $\mathbf{1'}^{+}$ and $\mathbf{2'}^{+}$ are illustrated in Fig. S19 and S20. TD-DFT vertical excitation calculations of $\mathbf{1'}^{+}$ and $\mathbf{2'}^{+}$were performed using the optimized geometry at the UB3LYP/6-31G(d) level, implemented in the Gaussian 09 program. The Cartesian coordinates for **1′** and **2′** in the neutral state and in the radical cation state are given in Tables S10–S13. The spin density distributions in $\mathbf{1'}^{+}$ and $\mathbf{2'}^{+}$ are also illustrated in Figs. S21–S23.

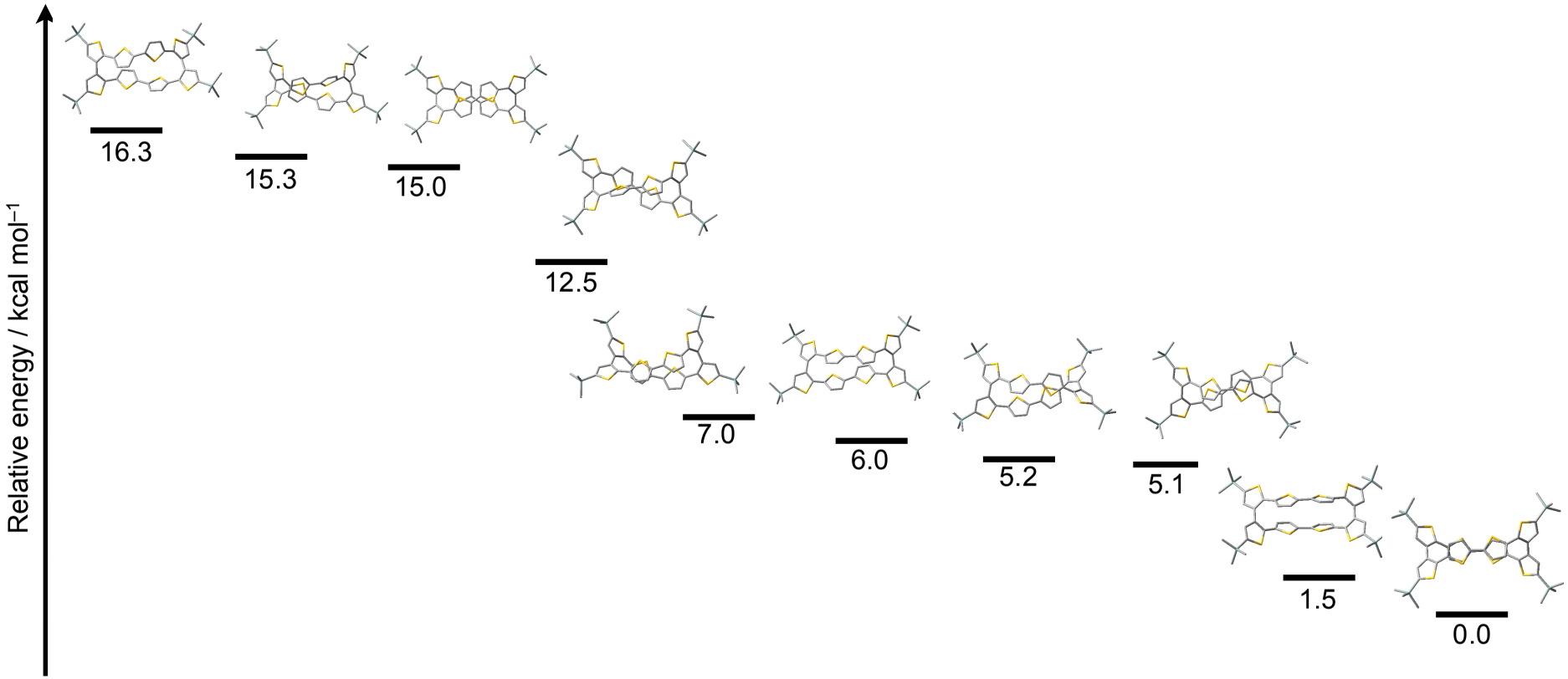



***Fig. S8*** Energy diagram of the various conformers of **1′** optimized at the PBE0/6-31G(d) level. Hydrogen atoms are omitted for clarity.

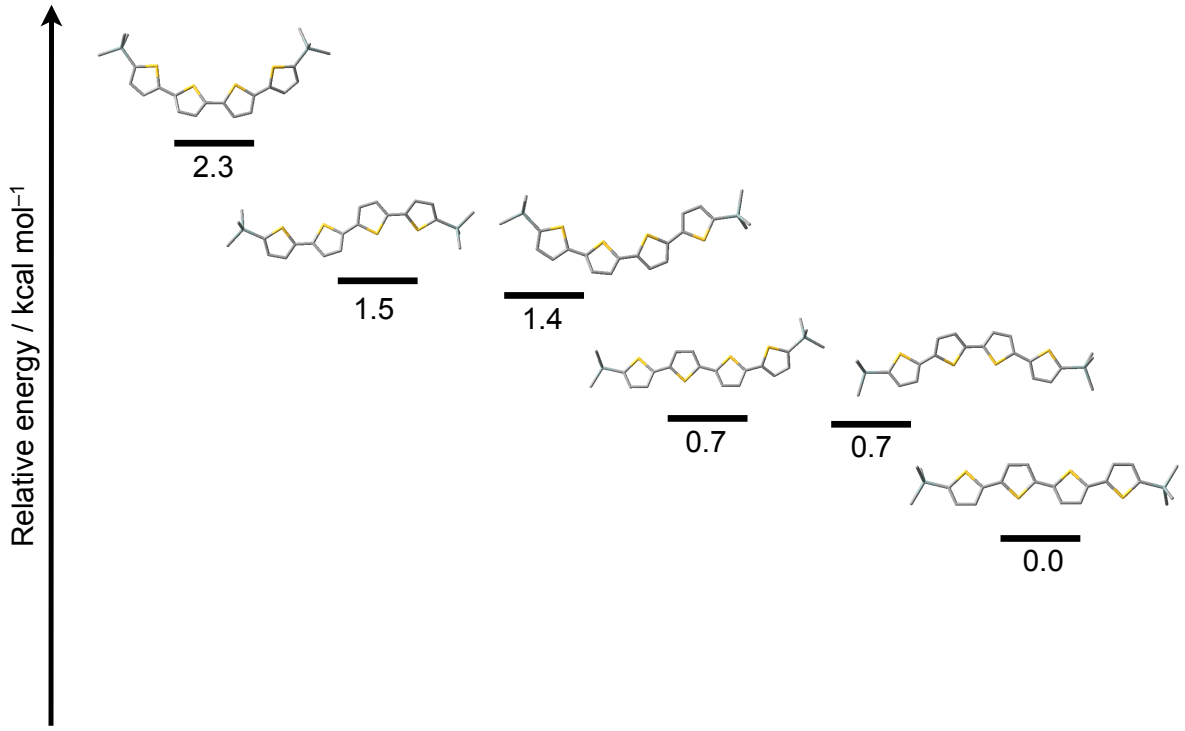



***Fig. S9*** Energy diagram of the various conformers of **2′** optimized at the PBE0/6-31G(d) level. Hydrogen atoms are omitted for clarity.

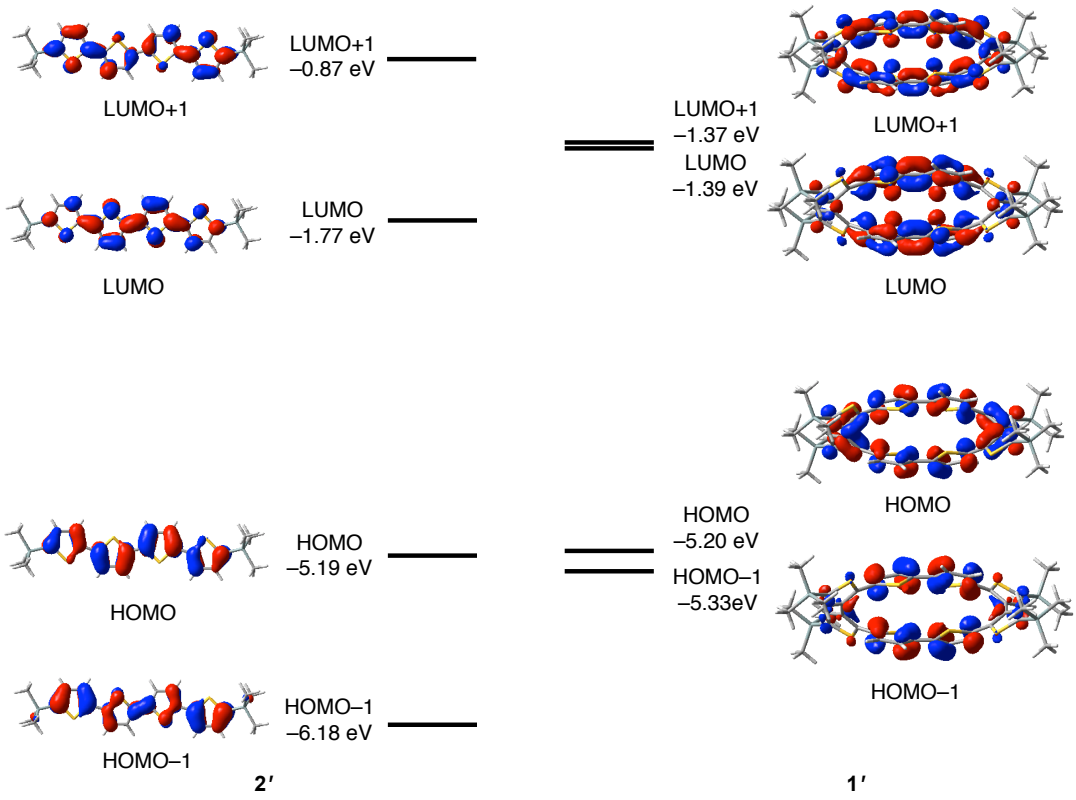



***Fig. S10*** Kohn-Sham molecular orbitals of **1′** and **2′** in the neutral state calculated at the PBE0/6-31G(d) level. Hydrogen atoms are omitted for clarity.

***Table S4***. Excitation Energies of **1′** Calculated at the PBE0/6-31G(d) Level

| excited state | transition energy [eV] (wavelength [nm]) | main CI coefficient | oscillator strength *f* |
|---|---|---|---|
| 1 | 3.05 (406) | –0.20871 (HOMO-1→LUMO) | 0.0531 |
| | | 0.66683 (HOMO→LUMO+1) | |
| 2 | 3.17 (391) | 0.33167 (HOMO-1→LUMO+1) | 0.1698 |
| | | 0.62021 (HOMO→LUMO) | |
| 3 | 324 (382) | 0.67134 (HOMO-1→LUMO) | 0.0272 |
| | | 0.21215 (HOMO→LUMO+1) | |
| 4 | 3.40 (365) | 0.61841 (HOMO-1→LUMO+1) | 1.6735 |
| | | –0.32946 (HOMO→LUMO) | |
| 5 | 3.71 (335) | 0.22751 (HOMO-2→LUMO+1) | 0.0431 |
| | | 0.66002 (HOMO→LUMO+2) | |

***Table S5.*** Excitation Energies of **2′** Calculated at the PBE0/6-31G(d) Level

| excited state | transition energy [eV] (wavelength [nm]) | main CI coefficient | oscillator strength *f* |
|---|---|---|---|
| 1 | 2.95 (421) | 0.70485 (HOMO→LUMO) | 1.5779 |
| 2 | 3.72 (333) | –0.39778 (HOMO-1→LUMO) | 0.0004 |
| | | 0.57309 (HOMO→LUMO+1) | |
| 3 | 4.01 (309) | 0.57723 (HOMO-1→LUMO) | 0.0042 |
| | | 0.39497 (HOMO→LUMO+1) | |
| 4 | 4.51 (275) | –0.22431 (HOMO-6→LUMO) | 0.0068 |
| | | 0.19080 (HOMO-3→LUMO) | |
| | | 0.60446 (HOMO→LUMO+2) | |
| | | –0.15662 (HOMO→LUMO+4) | |
| 5 | 4.63 (268) | 0.14271 (HOMO-4→LUMO) | 0.0026 |
| | | 0.66738 (HOMO-2→LUMO) | |
| | | 0.10705 (HOMO→LUMO+3) | |

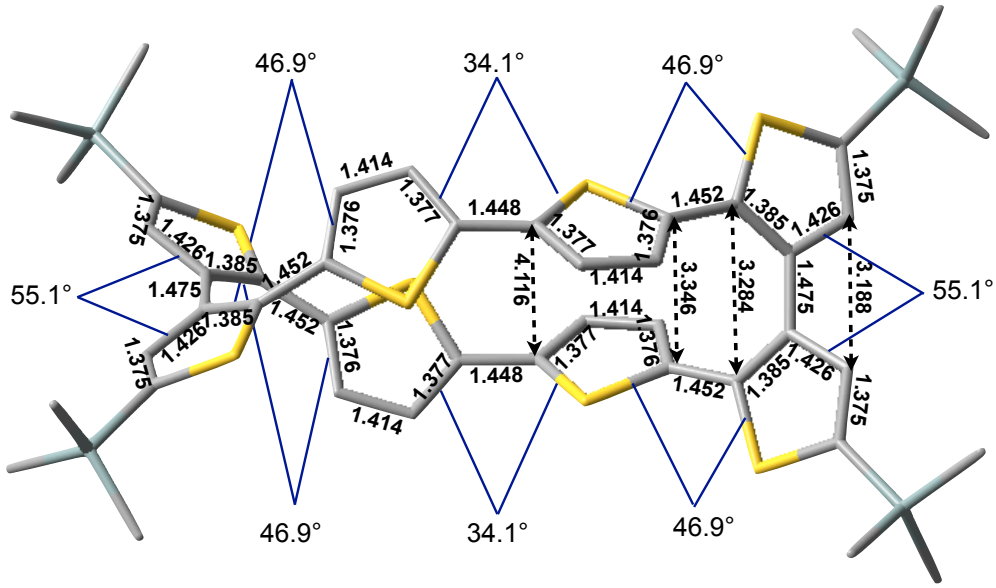



***Fig. S11*** Selected bond lengths, interatomic distances, and dihedral angles for the optimized structure of **1′** in $S_0$ calculated at the PBE0/6-31G(d) level. The distances are shown in Å. Hydrogen atoms are omitted for clarity.

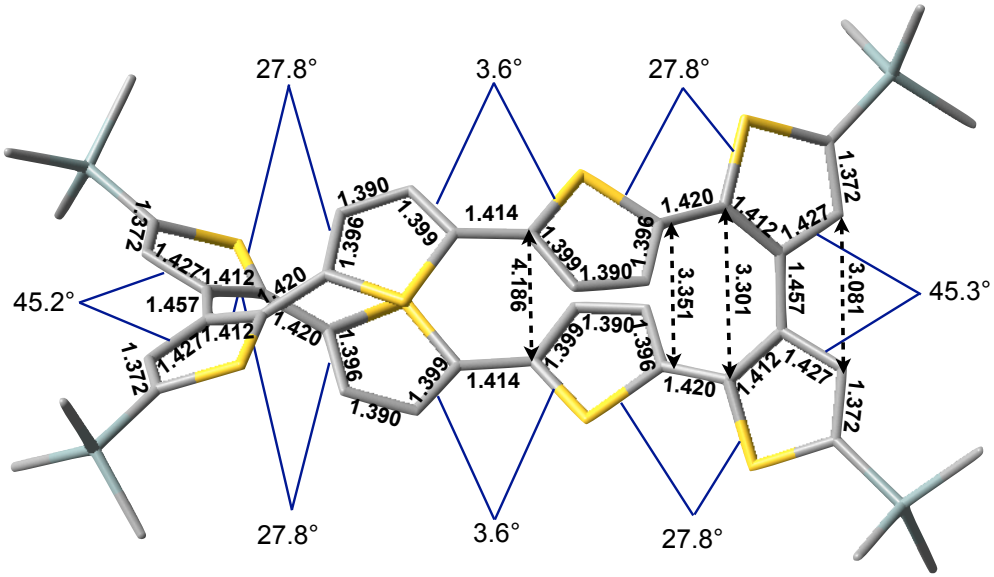



***Fig. S12*** Selected bond lengths, interatomic distances, and dihedral angles for the optimized structure of **1′** ($S_1$) calculated at the PBE0/6-31G(d) level. The distances are shown in Å. Hydrogen atoms are omitted for clarity.

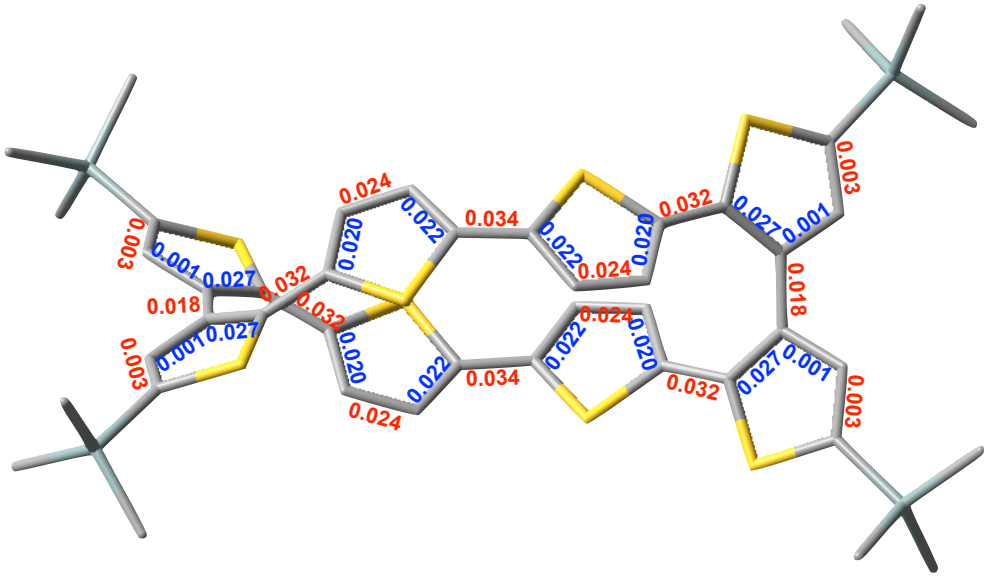



***Fig. S13*** Differences of bond lengths between **1′** ($S_0$) and **1′** ($S_1$) calculated at the PBE0/6-31G(d) level. The elongated bond length and shortened bond length from $S_0$ to $S_1$ are displayed in blue and red colors, respectively. The distances are shown in Å. Hydrogen atoms are omitted for clarity.

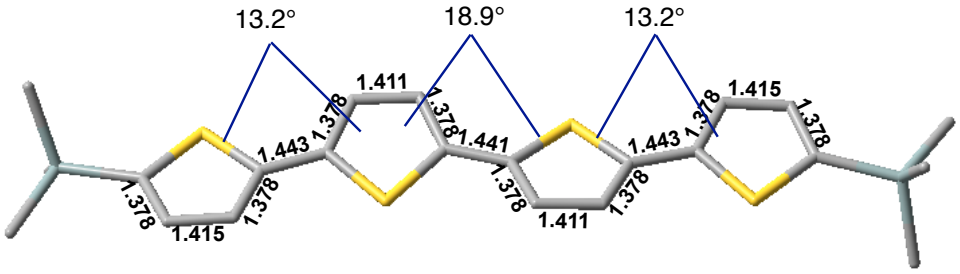



***Fig. S14*** Selected bond lengths and dihedral angles for the optimized structure of **2′** in $S_0$ calculated at the PBE0/6-31G(d) level. The distances are shown in Å. Hydrogen atoms are omitted for clarity.

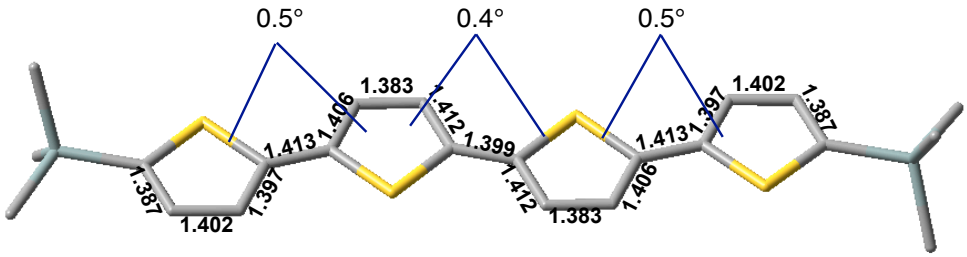



***Fig. S15*** Selected bond lengths and dihedral angles for the optimized structure of **2′** in $S_1$ calculated at the PBE0/6-31G(d) level. The distances are shown in Å. Hydrogen atoms are omitted for clarity.

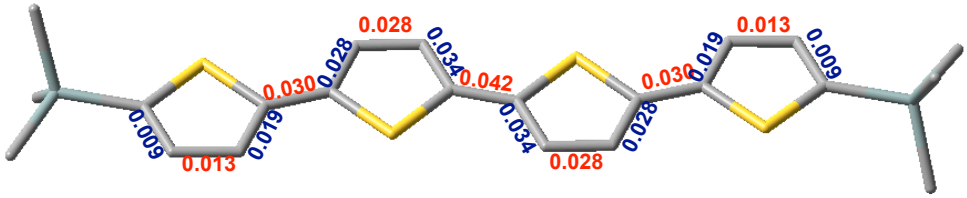



***Fig. S16*** Differences of bond lengths between **2′** ($S_0$) and **2′** ($S_1$) calculated at the PBE0/6-31G(d) level. The elongated and shortened bond lengths from $S_0$ to $S_1$ are displayed in blue and red colors, respectively. The distances are shown in Å. Hydrogen atoms are omitted for clarity.

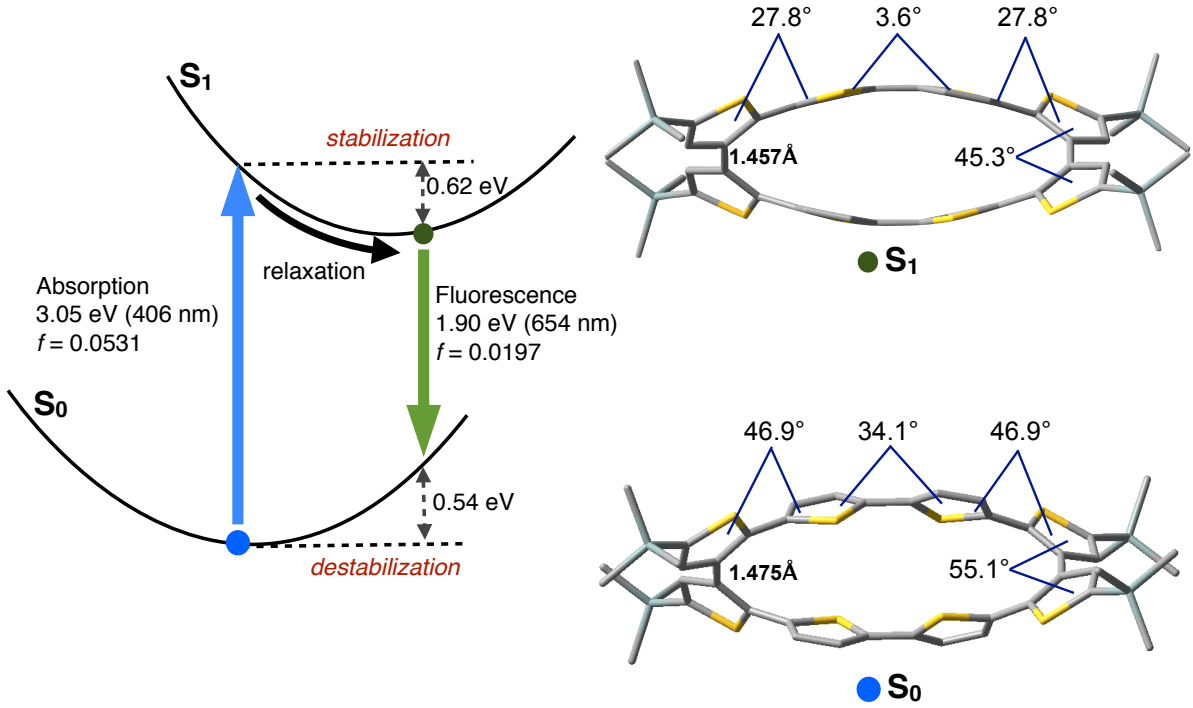



***Fig. S17*** Optimized structures of **1′** in $S_0$ and $S_1$ calculated at the PBE0/6-31G(d) level. TD-DFT vertical excitation in $S_0$ and vertical transition in $S_1$ with relative energies of the $S_0$ and $S_1$ states are shown. Hydrogen atoms are omitted for clarity.

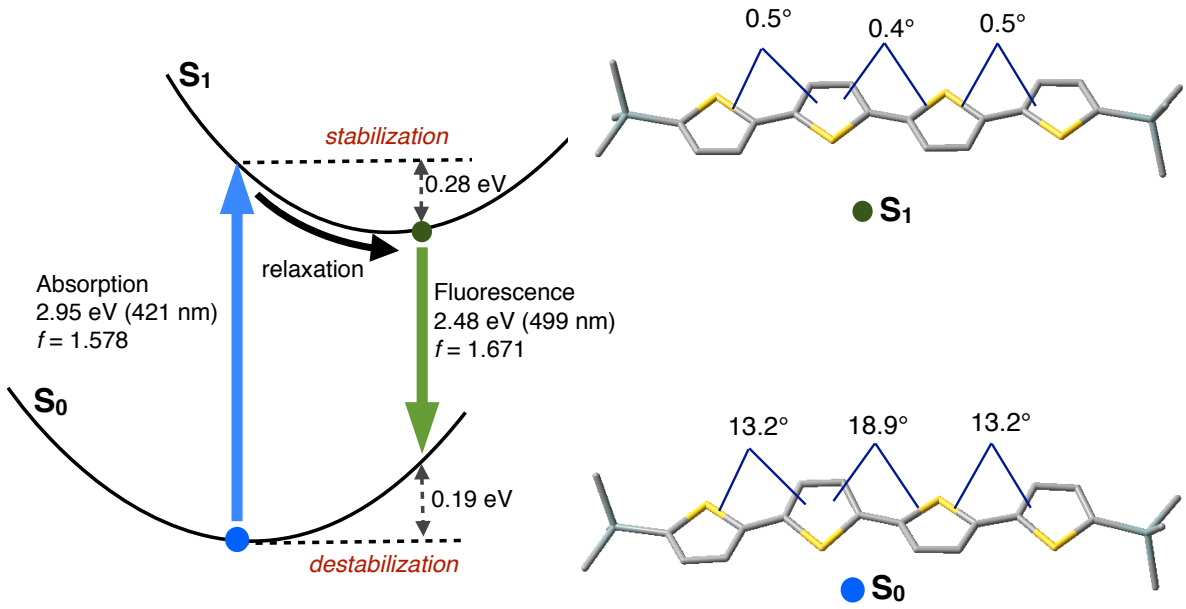



***Fig. S18*** Optimized structures of **2′** in $S_0$ and $S_1$ at PBE0/6-31G(d) level. Hydrogen atoms are omitted for clarity. TD-DFT vertical excitation in $S_0$ and vertical transition in $S_1$ with relative energies of the $S_0$ and $S_1$ states are shown.

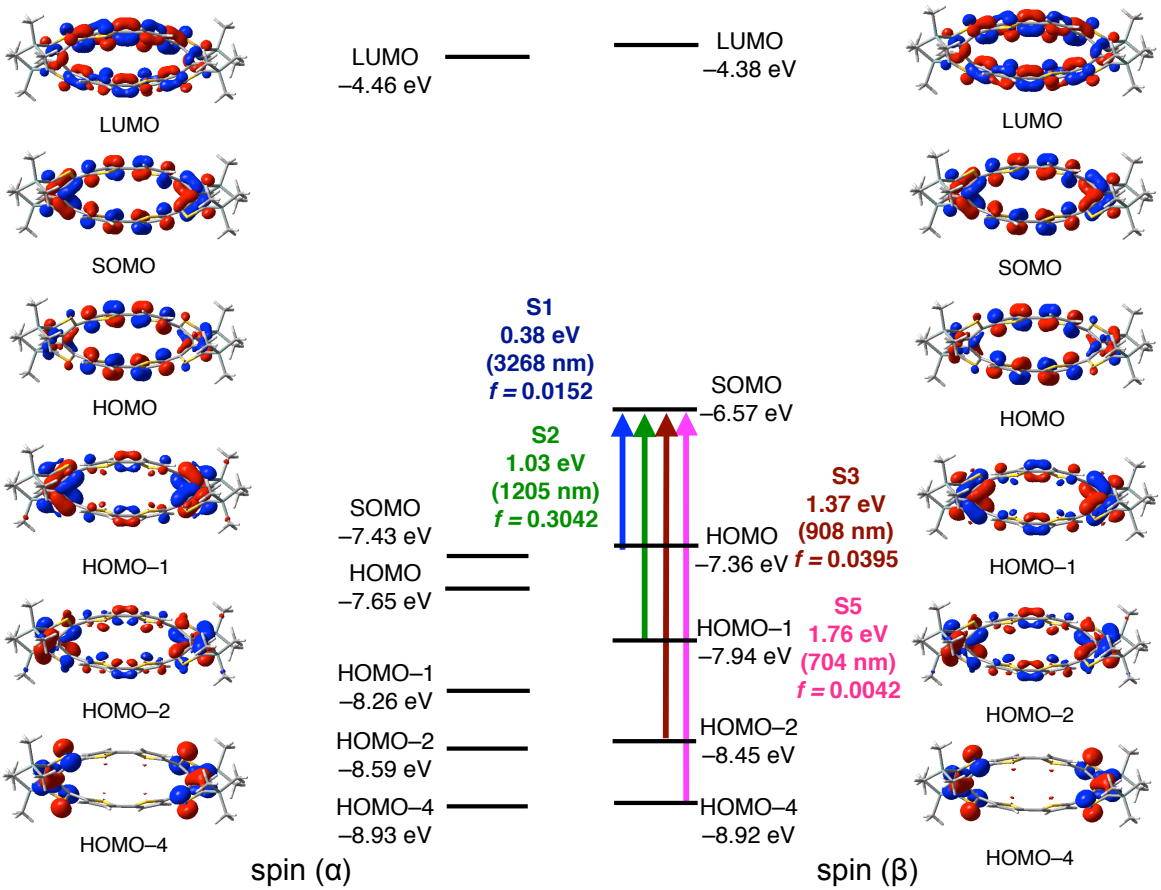



***Fig. S19*** Kohn-Sham molecular orbitals of $\mathbf{1}^{\bullet+}$ calculated at the UB3LYP/6-31G(d) level. TD-DFT vertical excitation in $\mathbf{1}^{\bullet+}$ calculated at the UB3LYP/6-31G(d) level. Hydrogen atoms are omitted for clarity.

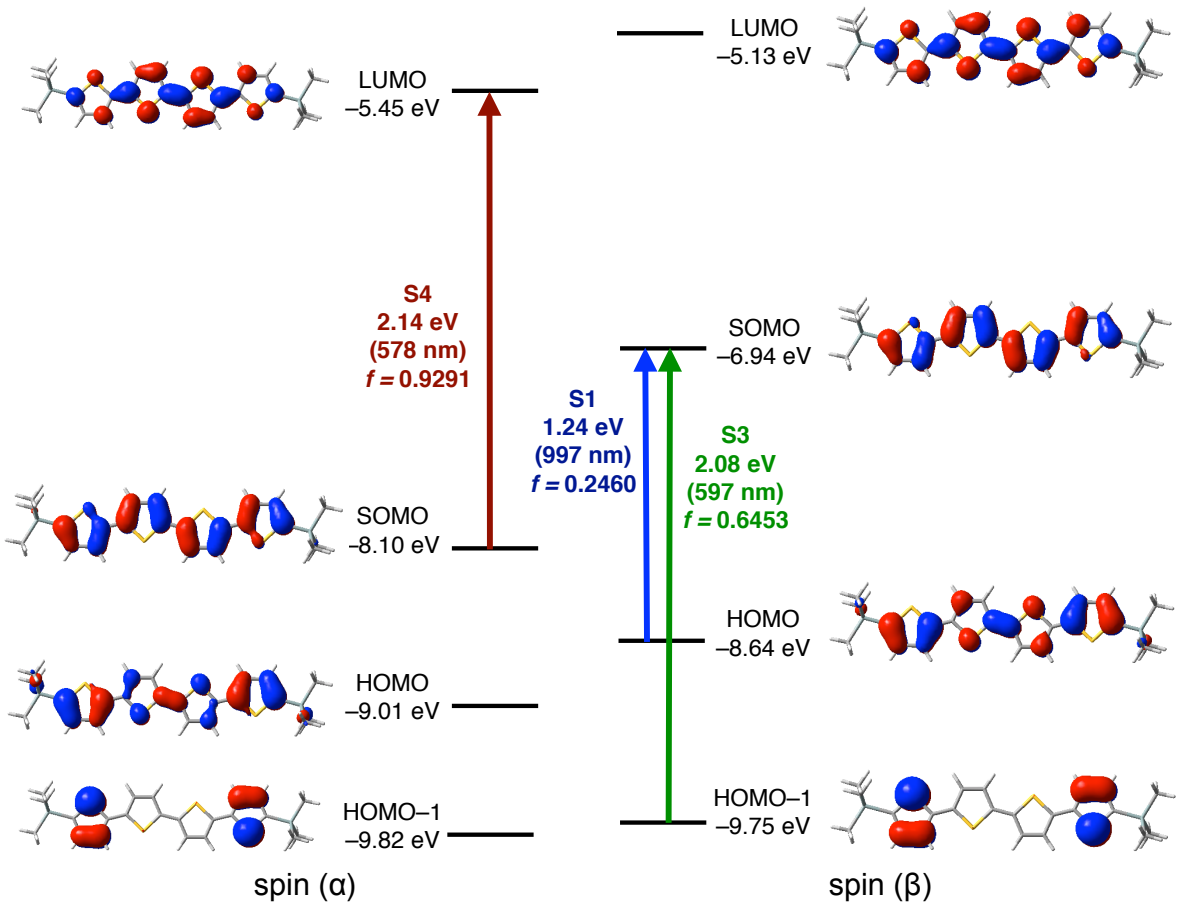



***Fig. S20*** Kohn-Sham molecular orbitals of $\mathbf{2}^{\bullet+}$ calculated at the UB3LYP/6-31G(d) level. TD-DFT vertical excitation in $\mathbf{2}^{\bullet+}$ calculated at the UB3LYP/6-31G(d) level. Hydrogen atoms are omitted for clarity.

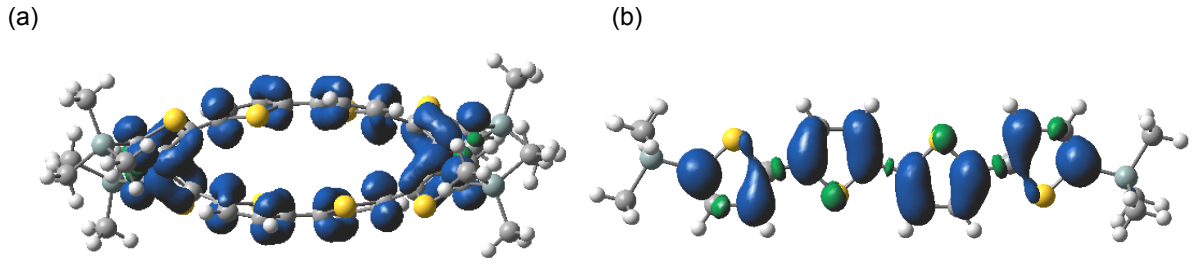



***Fig. S21*** Spin density distribution of compounds (a) $\mathbf{1}^{\bullet+}$ and (b) $\mathbf{2}^{\bullet+}$, calculated at the UB3LYP/6-31G(d) level (isovalue = 0.001).

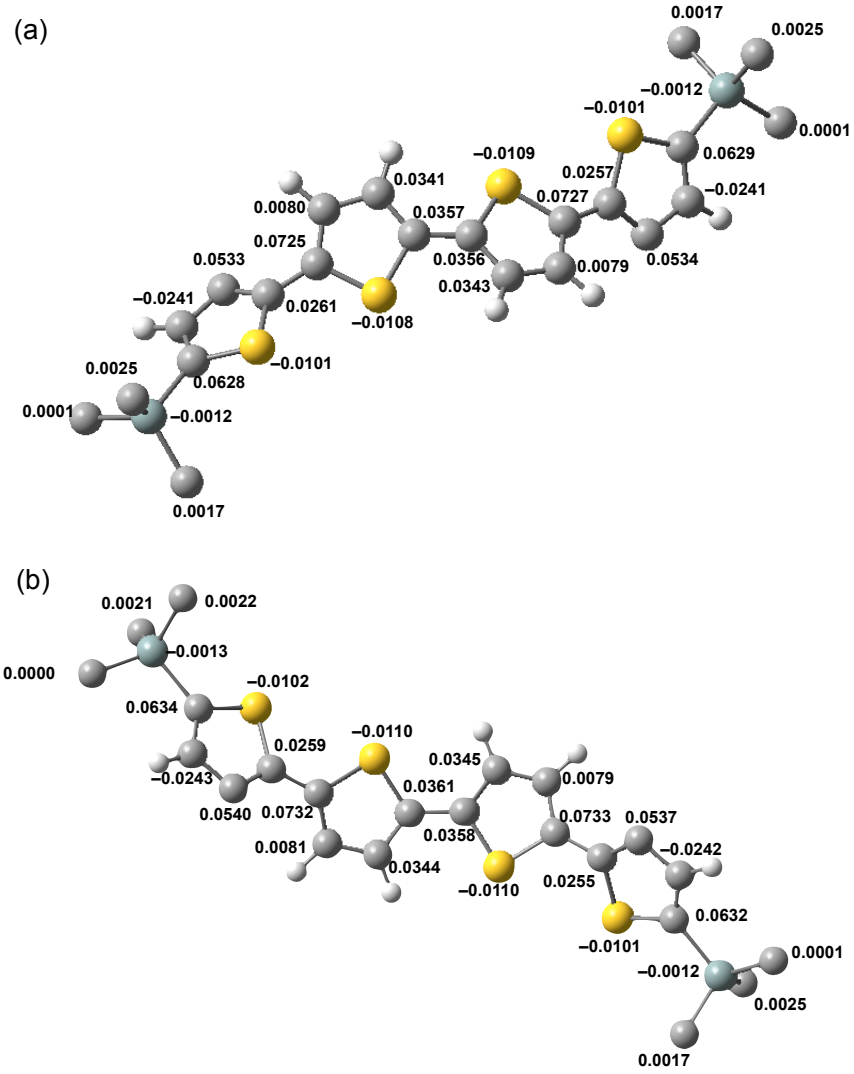



***Fig. S22*** Spin densities of $\mathbf{1}^{\bullet+}$ calculated at the UB3LYP/6-31G(d) level: (a) one of the quaterthiophene substructures and (b) the other quaterthiophene. Hydrogen atoms on $Me_3Si$ groups are omitted for clarity.

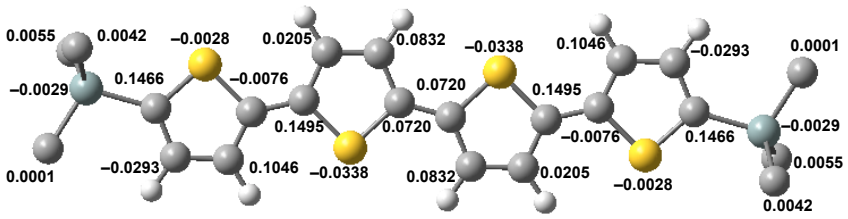



***Fig. S23*** Spin densities of $\mathbf{2}^{\bullet+}$ calculated at the UB3LYP/6-31G(d) level. Hydrogen atoms on $Me_3Si$ groups are omitted for clarity.

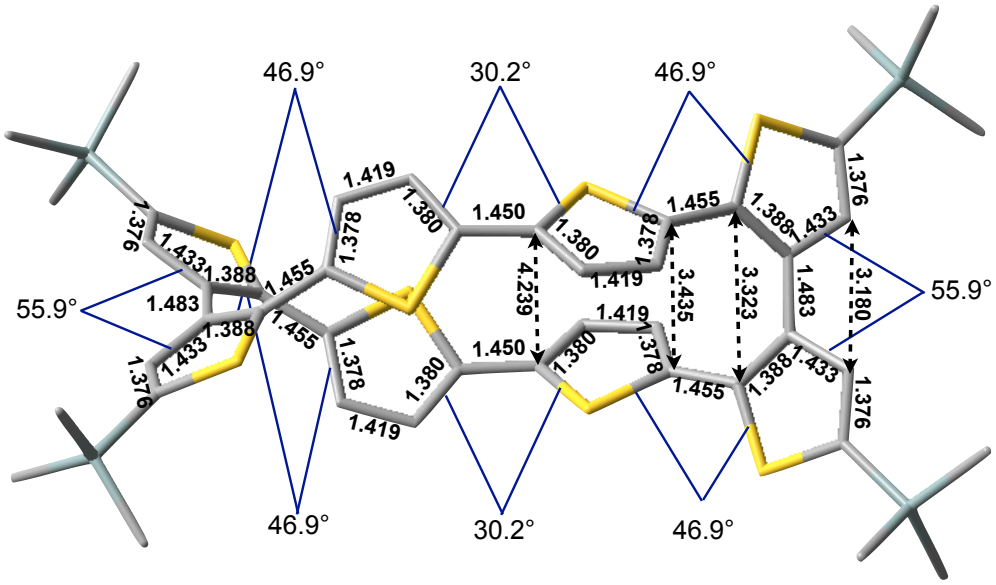



***Fig. S24*** Selected bond lengths, interatomic distances, and dihedral angles for the optimized structure of neutral **1′** calculated at the B3LYP/6-31G(d) level. The distances are shown in Å. Hydrogen atoms are omitted for clarity.

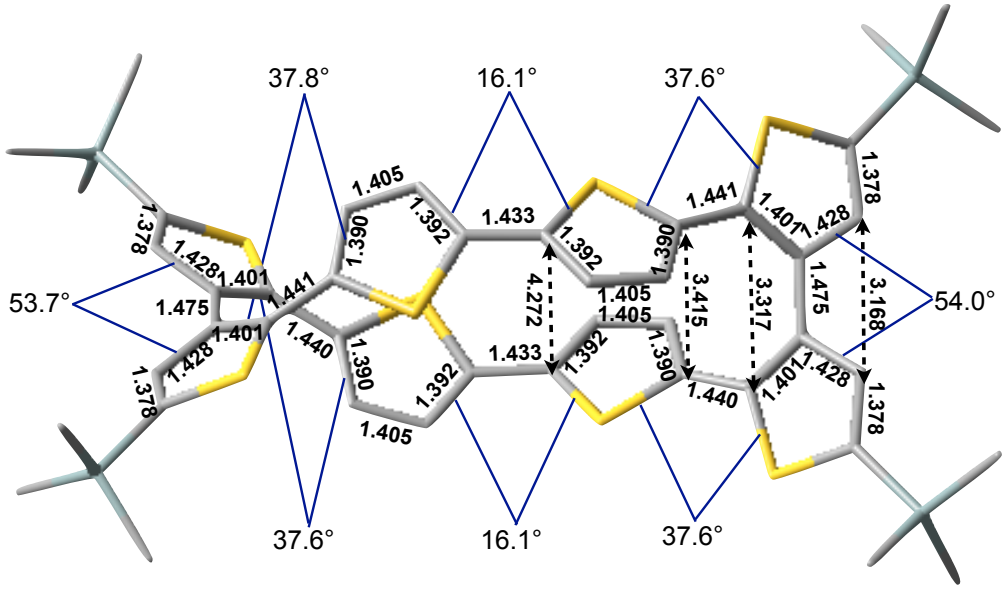



***Fig. S25*** Selected bond lengths, interatomic distances, and dihedral angles for the optimized structure of radical cation of $\mathbf{1'}^{+}$ calculated at UB3LYP/6-31G(d) level. The distances are shown in Å. Hydrogen atoms are omitted for clarity.

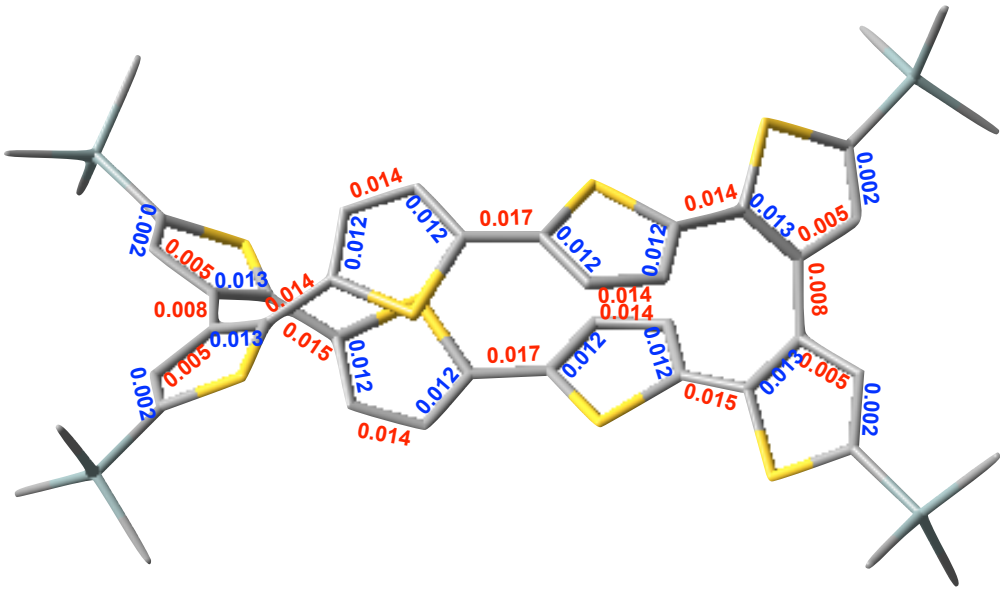



***Fig. S26*** Differences of bond lengths between $\mathbf{1'}^{\bullet+}$ and **1′** calculated at the UB3LYP/6-31G(d) and B3LYP/6-31G(d) level, respectively. The elongated and shortened bond lengths by the one-electron oxidation are displayed in blue and red colors, respectively. The distances are shown in Å. Hydrogen atoms are omitted for clarity.

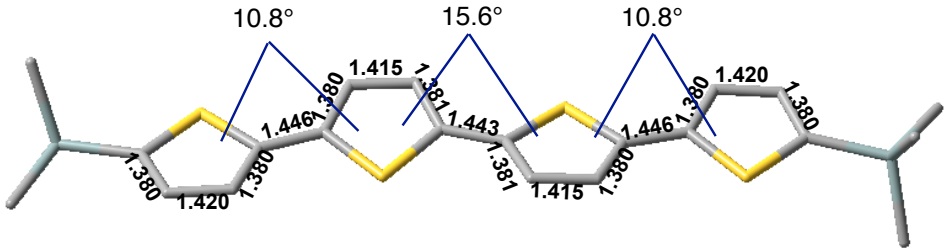



***Fig. S27*** Selected bond lengths and dihedral angles for the the optimized structure of neutral **2′** calculated at the B3LYP/6-31G(d) level. The distances are shown in Å. Hydrogen atoms are omitted for clarity.

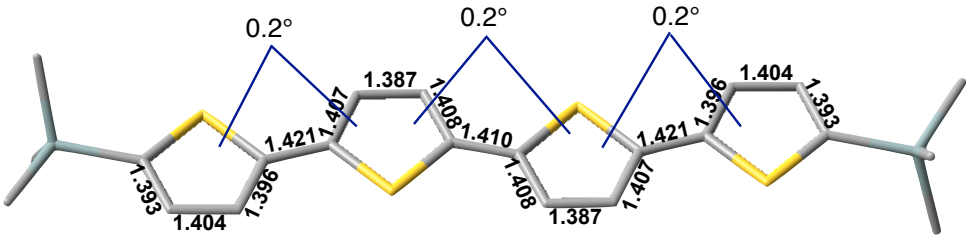



***Fig. S28*** Selected bond lengths and dihedral angles for the optimized structure of radical cation of $\mathbf{2'}^{\bullet+}$ calculated at the UB3LYP/6-31G(d) level. The distances are shown in Å. Hydrogen atoms are omitted for clarity.

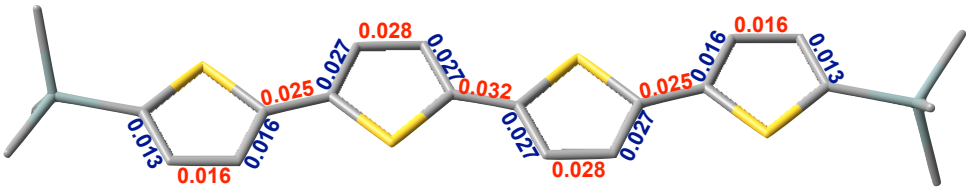



***Fig. S29*** Differences of bond lengths between $\mathbf{2'}^{+}$ and $\mathbf{2'}$ calculated at the UB3LYP/6-31G(d) and B3LYP/6-31G(d) level, respectively. The elongated and shortened bond lengths upon the oxidation are displayed in blue and red colors, respectively. The distances are shown in Å. Hydrogen atoms are omitted for clarity.

***Table S6***. Cartesian Coordinates (Å) of the Optimized Structure of **1′** ($S_0$) at the PBE0/6-31G(d) Level

| atom | *x* | *y* | *z* | atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| C | -1.57334958 | 1.07667263 | 2.28997149 | Si | -7.43442297 | 4.24872298 | -0.86575401 |
| H | -1.22286358 | 2.04319684 | 2.63701729 | H | -6.15393447 | 5.62853803 | 0.77728045 |
| C | -0.72382761 | 0.01782771 | 2.05779728 | C | -6.51647798 | 5.77349688 | -0.24631251 |
| C | -2.9298056 | 0.77542848 | 2.02865982 | H | -5.64859465 | 5.99929454 | -0.87655009 |
| H | -3.74613364 | 1.47780561 | 2.15436827 | H | -7.16886145 | 6.65474343 | -0.25170915 |
| C | -3.1266893 | -0.5142341 | 1.59213978 | C | -8.87513999 | 3.8348268 | 0.27456917 |
| S | -1.614999 | -1.36378161 | 1.50570115 | H | -9.42022791 | 2.9490054 | -0.070175 |
| C | -5.35000183 | -0.65604577 | 0.33686742 | H | -9.58697865 | 4.66778561 | 0.30863869 |
| C | -4.36161564 | -1.1508226 | 1.17140857 | H | -8.53635993 | 3.64687872 | 1.29943067 |
| C | -6.422974 | -1.58343547 | 0.18432359 | C | -8.05159001 | 4.54992637 | -2.62056472 |
| C | -6.26753888 | -2.77493009 | 0.85197822 | Si | 7.43447261 | 4.24861644 | 0.86577929 |
| S | -4.77065609 | -2.74519818 | 1.71853079 | Si | 7.43469216 | -4.24849011 | -0.86594586 |
| C | -6.4229386 | 1.58345665 | -0.18429013 | Si | -7.43453278 | -4.24866955 | 0.86580058 |
| C | -6.26748104 | 2.77494211 | -0.85195609 | C | 6.51665065 | 5.77342057 | 0.24623075 |
| C | -5.34998828 | 0.65604191 | -0.33683473 | H | 5.64880478 | 5.99935153 | 0.87647208 |
| C | -4.36159379 | 1.15079259 | -1.17138159 | H | 6.15406692 | 5.62840574 | -0.77734001 |
| S | -4.77063143 | 2.74514824 | -1.71856394 | H | 7.16911483 | 6.65460796 | 0.25153337 |
| C | -2.92980195 | -0.77550225 | -2.02856567 | H | 8.53649709 | 3.64666994 | -1.29933385 |
| H | -3.74613486 | -1.47788088 | -2.15423451 | C | 8.87522699 | 3.83459557 | -0.2744516 |
| C | -3.12667455 | 0.51417988 | -1.59209885 | H | 9.58713655 | 4.66749552 | -0.30848029 |
| C | -1.57334837 | -1.07676885 | -2.28986588 | H | 9.42021987 | 2.94873105 | 0.07033185 |
| H | -1.22287022 | -2.0433121 | -2.6368667 | C | 8.0515625 | 4.54984875 | 2.62061242 |
| C | -0.72381882 | -0.01791738 | -2.05774857 | H | 7.16954351 | -6.65454292 | -0.25185806 |
| S | -1.61498108 | 1.36372887 | -1.50573043 | C | 6.51704521 | -5.77338215 | -0.24635734 |
| C | 1.5732859 | 1.0765213 | -2.29027974 | H | 6.15464669 | -5.62847035 | 0.77729367 |
| H | 1.22278204 | 2.04302709 | -2.63735945 | H | 5.64909033 | -5.99929242 | -0.87645596 |
| C | 0.72376291 | 0.01772545 | -2.05787459 | C | 8.05165764 | -4.54963058 | -2.62083928 |
| C | 2.92975795 | 0.77528503 | -2.02903487 | H | 9.58746914 | -4.6672404 | 0.30815569 |
| H | 3.74608126 | 1.47765212 | -2.15482897 | C | 8.87551116 | -3.83438002 | 0.27417185 |
| C | 3.12664152 | -0.51430927 | -1.59230645 | H | 9.42042937 | -2.94848945 | -0.07066249 |
| S | 1.61498869 | -1.36392736 | -1.50599289 | H | 8.53684814 | -3.64646165 | 1.29907752 |
| C | 5.34986282 | -0.65606368 | -0.33681418 | C | -8.8752625 | -3.8347182 | -0.27448674 |
| C | 4.36154191 | -1.15085499 | -1.17143288 | H | -9.58711184 | -4.66766722 | -0.30857358 |
| C | 6.42288764 | -1.58339554 | -0.18428934 | H | -8.53649624 | -3.64673966 | -1.29934722 |
| C | 6.26754703 | -2.77487157 | -0.85199745 | H | -9.42033412 | -2.94890181 | 0.070296 |
| S | 4.77053266 | -2.7453225 | -1.71832358 | H | -8.73465222 | -5.40703603 | 2.65473976 |
| C | 6.42282758 | 1.58341881 | 0.18428726 | C | -8.05166976 | -4.5498539 | 2.62062531 |
| C | 6.26744357 | 2.77490481 | 0.85196777 | H | -7.22169441 | -4.75865135 | 3.30532143 |
| C | 5.3498507 | 0.65604005 | 0.33686239 | H | -8.5877524 | -3.6759792 | 3.0068421 |
| C | 4.36152404 | 1.15080739 | 1.17148791 | C | -6.5166579 | -5.7734755 | 0.24633455 |
| S | 4.77054425 | 2.74522978 | 1.71848857 | H | -7.22162154 | 4.75867921 | -3.30528278 |
| C | 2.9297475 | -0.7753812 | 2.02899057 | H | -8.58772452 | 3.67607521 | -3.00676288 |
| C | 3.12662784 | 0.51424018 | 1.59234149 | H | -8.73453183 | 5.40714128 | -2.65466777 |
| C | 1.57327783 | -1.07663147 | 2.29023416 | H | -6.15416731 | -5.62854264 | -0.7772809 |
| H | 1.22277664 | -2.04315861 | 2.63725713 | H | -5.64874472 | -5.99928194 | 0.87652797 |
| C | 0.72375382 | -0.01781945 | 2.05790687 | H | -7.16906111 | -6.65470707 | 0.25178231 |
| S | 1.61497382 | 1.36386202 | 1.50608835 | H | 7.22162381 | -4.75851273 | -3.30543883 |
| H | 3.74607115 | -1.47775819 | 2.15472813 | H | 8.73471794 | -5.40674784 | -2.65502655 |
| H | 7.28211068 | 1.36852681 | -0.44444931 | H | 8.58761228 | -3.67570755 | -3.00712424 |
| H | -7.28223276 | 1.36860732 | 0.44444607 | H | 8.58765371 | 3.67599292 | 3.00686008 |
| H | 7.28219736 | -1.36846023 | 0.4443959 | H | 8.73452686 | 5.40704534 | 2.65472585 |
| H | -7.28227107 | -1.36855913 | -0.44439921 | H | 7.22156698 | 4.75864385 | 3.30528493 |

***Table S7***. Cartesian Coordinates (Å) of the Optimized Structure of **1′** ($S_1$) at the PBE0/6-31G(d) Level

| atom | *x* | *y* | *z* |
|---|---|---|---|
| C | -1.51534021 | 1.16389531 | 1.94268421 |
| H | -1.11623476 | 2.1721012 | 1.98307724 |
| C | -0.70629768 | 0.03248027 | 2.09268038 |
| C | -2.84469189 | 0.87326865 | 1.65927724 |
| H | -3.60665963 | 1.62315308 | 1.4838276 |
| C | -3.12325403 | -0.49346768 | 1.60130591 |
| S | -1.68422285 | -1.41576048 | 1.98147198 |
| C | -5.37219029 | -0.61071468 | 0.39710372 |
| C | -4.33846125 | -1.11758196 | 1.21466338 |
| C | -6.49617906 | -1.49062108 | 0.38880456 |
| C | -6.33737641 | -2.66926235 | 1.07240433 |
| S | -4.76967489 | -2.69733106 | 1.82482748 |
| C | -6.49618689 | 1.4906134 | -0.38872009 |
| C | -6.33739456 | 2.66925772 | -1.0723164 |
| C | -5.37219648 | 0.61070961 | -0.39703528 |
| C | -4.33847791 | 1.11758214 | -1.21460489 |
| S | -4.76970058 | 2.69733426 | -1.82475448 |
| C | -2.84471243 | -0.87326284 | -1.65925896 |
| H | -3.60667816 | -1.62315011 | -1.48381258 |
| C | -3.12327427 | 0.49347271 | -1.60126588 |
| C | -1.51536325 | -1.16388532 | -1.94268306 |
| H | -1.1162577 | -2.17209059 | -1.98309306 |
| C | -0.70632273 | -0.03246787 | -2.092673 |
| S | -1.68424772 | 1.41577077 | -1.98143651 |
| C | 1.51534588 | 1.16391809 | -1.94268313 |
| H | 1.11624008 | 2.17212432 | -1.98306312 |
| C | 0.70630226 | 0.03250471 | -2.09268511 |
| C | 2.84469828 | 0.87328865 | -1.65928398 |
| H | 3.60666639 | 1.6231711 | -1.4838284 |
| C | 3.12325899 | -0.49344856 | -1.60132151 |
| S | 1.68422892 | -1.41573698 | -1.98150246 |
| C | 5.3721914 | -0.61070933 | -0.39711138 |
| C | 4.33846369 | -1.1175672 | -1.21468012 |
| C | 6.49617996 | -1.49061616 | -0.38882118 |
| C | 6.33737551 | -2.66925264 | -1.07242845 |
| S | 4.76967901 | -2.69730882 | -1.82486271 |
| C | 6.49618785 | 1.49060802 | 0.38873768 |
| C | 6.3373934 | 2.66924799 | 1.07234068 |
| C | 5.37219769 | 0.61070379 | 0.39704409 |
| C | 4.33848046 | 1.11756707 | 1.21462271 |
| S | 4.76970554 | 2.69731095 | 1.82479221 |
| C | 2.84471862 | -0.87328305 | 1.65926572 |
| C | 3.12327922 | 0.49345338 | 1.60128215 |
| C | 1.5153688 | -1.16390824 | 1.94268223 |
| H | 1.11626277 | -2.17211382 | 1.98307899 |
| C | 0.70632728 | -0.03249239 | 2.09267819 |
| S | 1.68425389 | 1.41574713 | 1.98146776 |
| H | 3.60668463 | -1.62316836 | 1.48381303 |
| H | 7.38758925 | 1.26990168 | -0.19146041 |
| H | -7.38758978 | 1.26989967 | 0.19147302 |
| H | 7.38758888 | -1.26991379 | 0.19136684 |
| H | -7.3875893 | -1.2699114 | -0.19137877 |

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Si | -7.55040148 | 4.09918177 | -1.2028983 |
| H | -6.38901882 | 5.5997283 | 0.42351501 |
| C | -6.70386912 | 5.67972932 | -0.62272931 |
| H | -5.81222572 | 5.89753359 | -1.22181663 |
| H | -7.37856916 | 6.5398383 | -0.70738233 |
| C | -9.02561647 | 3.69340687 | -0.10488289 |
| H | -9.52771201 | 2.77397202 | -0.42631878 |
| H | -9.7639978 | 4.50267612 | -0.14509174 |
| H | -8.72692041 | 3.5691307 | 0.94187165 |
| C | -8.10099247 | 4.295472 | -2.99461051 |
| Si | 7.55039402 | 4.09917695 | 1.20292499 |
| Si | 7.550372 | -4.0991831 | -1.20303636 |
| Si | -7.55037835 | -4.09918876 | 1.20300806 |
| C | 6.7038542 | 5.67972318 | 0.62276279 |
| H | 5.81221212 | 5.89752285 | 1.22185368 |
| H | 6.38900056 | 5.5997237 | -0.42348065 |
| H | 7.37855149 | 6.53983433 | 0.70741566 |
| H | 8.7269139 | 3.56914406 | -0.94184918 |
| C | 9.02560959 | 3.69341298 | 0.10490633 |
| H | 9.76398923 | 4.50268346 | 0.14512124 |
| H | 9.52770704 | 2.77397676 | 0.42633535 |
| C | 8.10098644 | 4.29546336 | 2.99463715 |
| H | 7.37852751 | -6.53984497 | -0.70755024 |
| C | 6.70383319 | -5.67973297 | -0.6228825 |
| H | 6.38898929 | -5.59974328 | 0.42336465 |
| H | 5.81218503 | -5.89752433 | -1.22196744 |
| C | 8.10094923 | -4.2954534 | -2.99475505 |
| H | 9.76397462 | -4.50270662 | -0.14525554 |
| C | 9.025598 | -3.69343412 | -0.10502616 |
| H | 9.52769577 | -2.77399629 | -0.42645026 |
| H | 8.72691168 | -3.56917472 | 0.94173314 |
| C | -9.02560324 | -3.69342923 | 0.10500022 |
| H | -9.76398209 | -4.50269996 | 0.14522433 |
| H | -8.72691623 | -3.56916397 | -0.94175818 |
| H | -9.52769857 | -2.77399208 | 0.42642999 |
| H | -8.80671494 | -5.12830488 | 3.09845751 |
| C | -8.10095537 | -4.29546417 | 2.99472625 |
| H | -7.24902567 | -4.49631434 | 3.65422361 |
| H | -8.59476231 | -3.38775985 | 3.35857944 |
| C | -6.70384552 | -5.67973911 | 0.62284727 |
| H | -7.24906827 | 4.49633071 | -3.65411233 |
| H | -8.5947994 | 3.38776961 | -3.35846832 |
| H | -8.80675521 | 5.1283116 | -3.09832896 |
| H | -6.38900294 | -5.59974666 | -0.42340007 |
| H | -5.81219725 | -5.89753566 | 1.22193011 |
| H | -7.3785426 | -6.5398492 | 0.70751288 |
| H | 7.24901895 | -4.49629669 | -3.65425382 |
| H | 8.80670489 | -5.12829701 | -3.09848943 |
| H | 8.59476067 | -3.38774985 | -3.35860402 |
| H | 8.59479972 | 3.38776263 | 3.35849054 |
| H | 8.8067441 | 5.12830701 | 3.09835784 |
| H | 7.24906202 | 4.496314 | 3.65414111 |

***Table S8***. Cartesian Coordinates (Å) of the Optimized Structure of **2′** ($S_0$) at the PBE0/6-31G(d) Level

| atom | *x* | *y* | *z* | atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| C | 1.27978704 | 1.41437863 | -0.49044774 | S | -1.92133842 | 1.03476705 | -0.06821344 |
| H | 0.70199835 | 2.31407371 | -0.67508446 | Si | 8.92611278 | 0.09700941 | 0.25580674 |
| C | 0.69857435 | 0.17676989 | -0.31934738 | Si | -8.92611363 | -0.09702388 | 0.25578058 |
| C | 2.68953821 | 1.38480065 | -0.44172748 | C | -9.17565266 | -1.17241189 | 1.78302091 |
| H | 3.31496802 | 2.26047596 | -0.58083788 | H | -8.85475265 | -0.64992691 | 2.69086268 |
| C | 3.20713326 | 0.12550559 | -0.23217585 | H | -8.60086235 | -2.10333696 | 1.71596002 |
| S | 1.92133623 | -1.03474628 | -0.06817141 | H | -10.2312829 | -1.44301147 | 1.90434634 |
| C | 5.11719974 | -1.55525552 | -0.15827603 | C | -9.86749053 | 1.52482472 | 0.43138871 |
| H | 4.50926479 | -2.44673834 | -0.27670383 | H | -9.73823063 | 2.16609314 | -0.44768914 |
| C | 4.58786036 | -0.28357407 | -0.1344638 | H | -9.53865984 | 2.08634294 | 1.31278957 |
| C | 6.52676011 | -1.57184056 | -0.03247287 | H | -10.94068168 | 1.33103486 | 0.54258066 |
| H | 7.10993667 | -2.48762858 | -0.03397757 | C | -9.50358481 | -1.02922321 | -1.27712758 |
| C | 7.10298757 | -0.3262814 | 0.08630456 | H | -9.37273542 | -0.4231943 | -2.18031366 |
| S | 5.86124854 | 0.88287465 | 0.05398387 | H | -10.5645101 | -1.29533103 | -1.19950473 |
| C | -6.52676037 | 1.57183977 | -0.03241113 | H | -8.93668066 | -1.9569374 | -1.4154686 |
| H | -7.1099391 | 2.48762648 | -0.03389697 | C | 9.17570473 | 1.17212418 | 1.78323036 |
| C | -7.10298804 | 0.32627458 | 0.0863048 | H | 8.60089389 | 2.10305025 | 1.71636147 |
| C | -5.11720038 | 1.55526055 | -0.15821545 | H | 10.23133572 | 1.44271987 | 1.90455739 |
| H | -4.5092665 | 2.44674696 | -0.2766211 | H | 8.85485451 | 0.64946981 | 2.69099217 |
| C | -4.58785952 | 0.28357867 | -0.1344406 | C | 9.86751382 | -1.52486217 | 0.43107447 |
| S | -5.86124092 | -0.88287377 | 0.05402308 | H | 10.94070851 | -1.33108338 | 0.54225019 |
| C | -2.68953385 | -1.38479067 | -0.44171592 | H | 9.73821301 | -2.16596136 | -0.44812055 |
| H | -3.31496037 | -2.2604716 | -0.58080572 | H | 9.5387335 | -2.08655189 | 1.31238481 |
| C | -3.2071323 | -0.12549594 | -0.23217137 | C | 9.50349511 | 1.02949653 | -1.27696022 |
| C | -1.27978257 | -1.41436577 | -0.49043499 | H | 8.93656816 | 1.95722703 | -1.4151 |
| H | -0.70199176 | -2.31406367 | -0.67505101 | H | 9.37260466 | 0.42363131 | -2.18025007 |
| C | -0.69857267 | -0.17675385 | -0.31935025 | H | 10.56441983 | 1.29560854 | -1.19934726 |

***Table S9***. Cartesian Coordinates (Å) of the Optimized Structure of **2′** ($S_1$) at the PBE0/6-31G(d) Level

| atom | *x* | *y* | *z* | atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| C | -1.27915161 | 1.44192141 | 0.02018044 | S | 1.91822338 | 1.08581143 | 0.01140886 |
| H | -0.69284777 | 2.35482507 | 0.02448025 | Si | -8.92245331 | 0.0966102 | -0.00942295 |
| C | -0.68022517 | 0.16377153 | 0.0174381 | Si | 8.92245384 | -0.09661294 | -0.00924688 |
| C | -2.66191136 | 1.40690983 | 0.01714955 | C | 9.30168512 | -1.25706702 | -1.44620041 |
| H | -3.28988196 | 2.29175009 | 0.01769221 | H | 9.06567174 | -0.78696482 | -2.40707574 |
| C | -3.20165847 | 0.10883647 | 0.01118435 | H | 8.71840373 | -2.18257122 | -1.37755424 |
| S | -1.91822274 | -1.08580657 | 0.01153095 | H | 10.36287701 | -1.53351393 | -1.45626797 |
| C | -5.10080966 | -1.56869889 | -0.01596952 | C | 9.87153392 | 1.51967254 | -0.19873596 |
| H | -4.48688284 | -2.46374528 | -0.02629741 | H | 9.67528801 | 2.20530349 | 0.63318558 |
| C | -4.55961132 | -0.28142735 | 0.00290586 | H | 9.6107078 | 2.03264302 | -1.1310164 |
| C | -6.50309139 | -1.57596726 | -0.02466709 | H | 10.9504087 | 1.32596856 | -0.2178618 |
| H | -7.09007718 | -2.48936259 | -0.04198681 | C | 9.38006394 | -0.94006305 | 1.61430486 |
| C | -7.09259902 | -0.32001171 | -0.01191906 | H | 9.18352788 | -0.28467059 | 2.46976042 |
| S | -5.85526371 | 0.89660513 | 0.0104204 | H | 10.44347092 | -1.20790075 | 1.63022803 |
| C | 6.50309398 | 1.57596511 | -0.02491225 | H | 8.80226689 | -1.85966529 | 1.76119678 |
| H | 7.0900821 | 2.48935982 | -0.04218774 | C | -9.30145963 | 1.25710492 | -1.44640433 |
| C | 7.09259987 | 0.32001011 | -0.01202395 | H | -8.71818899 | 2.18260736 | -1.37764169 |
| C | 5.10081173 | 1.56869858 | -0.01628954 | H | -10.36264967 | 1.5335531 | -1.45663104 |
| H | 4.48688661 | 2.46374591 | -0.02663743 | H | -9.06529576 | 0.7870289 | -2.40725554 |
| C | 4.55961125 | 0.28142878 | 0.00264398 | C | -9.87150191 | -1.51967133 | -0.19910721 |
| S | 5.85526048 | -0.89660785 | 0.01001234 | H | -10.95037388 | -1.32596829 | -0.21840252 |
| C | 2.66191015 | -1.4069058 | 0.01692902 | H | -9.67538998 | -2.20532444 | 0.6328277 |
| H | 3.28988 | -2.29174662 | 0.0174084 | H | -9.61052492 | -2.03261698 | -1.13135908 |
| C | 3.20165812 | -0.10883284 | 0.01097809 | C | -9.38032001 | 0.94001334 | 1.61407949 |
| C | 1.27915066 | -1.44191627 | 0.02004735 | H | -8.80254984 | 1.85961399 | 1.76108669 |
| H | 0.69284632 | -2.35481952 | 0.02436225 | H | -9.18391577 | 0.28459856 | 2.46954824 |
| C | 0.68022512 | -0.16376586 | 0.01738377 | H | -10.44373069 | 1.20784543 | 1.62984229 |

***Table S10***. Cartesian Coordinates (Å) of the Optimized Structure of Neutral **1′** at the B3LYP/6-31G(d) Level

| atom | *x* | *y* | *z* | atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| C | -1.56856447 | -1.09836908 | -2.3120683 | Si | -7.51696018 | -4.21173139 | 0.9741024 |
| H | -1.2126144 | -2.07313249 | -2.6289195 | H | -6.25462256 | -5.65303783 | -0.6433411 |
| C | -0.72484657 | -0.02338651 | -2.11932835 | C | -6.6189167 | -5.76908227 | 0.3838848 |
| C | -2.93160239 | -0.80831432 | -2.04706911 | H | -5.75378466 | -5.99755677 | 1.01756915 |
| H | -3.73345395 | -1.53113114 | -2.14502069 | H | -7.2854365 | -6.64017063 | 0.4072367 |
| C | -3.15199435 | 0.49125786 | -1.64563904 | C | -8.9620254 | -3.81012355 | -0.17781142 |
| S | -1.63989952 | 1.37922954 | -1.60517124 | H | -9.50014939 | -2.91143531 | 0.14516526 |
| C | -5.37088978 | 0.64775202 | -0.36054796 | H | -9.68171254 | -4.63768483 | -0.19048354 |
| C | -4.39415851 | 1.12234844 | -1.22537944 | H | -8.62653088 | -3.64969936 | -1.20888219 |
| C | -6.45544982 | 1.57401107 | -0.22538841 | C | -8.14384646 | -4.47290461 | 2.74009922 |
| C | -6.32881961 | 2.74873534 | -0.93127807 | Si | 7.51725789 | -4.21154013 | -0.97419665 |
| S | -4.82925402 | 2.70939871 | -1.82657133 | Si | 7.51695467 | 4.21173119 | 0.97414279 |
| C | -6.45541934 | -1.57403421 | 0.22541088 | Si | -7.51721275 | 4.21156986 | -0.9741999 |
| C | -6.32887618 | -2.74863985 | 0.93151498 | C | 6.61940306 | -5.76929045 | -0.38477535 |
| C | -5.37088708 | -0.64774454 | 0.36055567 | H | 5.754938 | -5.99818739 | -1.01921814 |
| C | -4.39422011 | -1.12222956 | 1.22552328 | H | 6.25414413 | -5.65337105 | 0.6421225 |
| S | -4.82936483 | -2.70920386 | 1.82688667 | H | 7.28633357 | -6.64007966 | -0.40749891 |
| C | -2.93155476 | 0.80842734 | 2.0471248 | H | 8.62625476 | -3.65021847 | 1.20928034 |
| H | -3.73335678 | 1.53129951 | 2.14508208 | C | 8.96197327 | -3.80998088 | 0.17818028 |
| C | -3.15203975 | -0.49114478 | 1.645765 | H | 9.68201909 | -4.63723407 | 0.19052889 |
| C | -1.56848847 | 1.09841726 | 2.31204781 | H | 9.49976002 | -2.91089892 | -0.14426322 |
| H | -1.21247808 | 2.07317258 | 2.62885635 | C | 8.14465319 | -4.47191481 | -2.74013462 |
| C | -0.72483794 | 0.02337775 | 2.11932237 | H | 7.28552456 | 6.6401938 | 0.40732916 |
| S | -1.63997898 | -1.37919099 | 1.60519444 | C | 6.61903285 | 5.76909 | 0.38375903 |
| C | 1.56848948 | -1.09844188 | 2.31199953 | H | 6.25501569 | 5.65308445 | -0.64356988 |
| H | 1.21248547 | -2.07320822 | 2.6287825 | H | 5.75372507 | 5.99751169 | 1.01722219 |
| C | 0.72483417 | -0.02339912 | 2.11931404 | C | 8.14363198 | 4.47295957 | 2.74020617 |
| C | 2.93155012 | -0.80844716 | 2.04705855 | H | 9.68185865 | 4.63756958 | -0.19020941 |
| H | 3.73334987 | -1.53132707 | 2.14497973 | C | 8.9621433 | 3.81003211 | -0.17758408 |
| C | 3.1520318 | 0.49113579 | 1.64573054 | H | 9.50019845 | 2.91134028 | 0.14549687 |
| S | 1.6399669 | 1.37918479 | 1.60520874 | H | 8.62676727 | 3.64957372 | -1.20868828 |
| C | 5.37086263 | 0.64777296 | 0.36049048 | C | -8.96217187 | 3.80980232 | 0.17779779 |
| C | 4.3941893 | 1.1222405 | 1.22546058 | H | -9.68198882 | 4.63725006 | 0.19049253 |
| C | 6.4553896 | 1.57406924 | 0.22536474 | H | -8.62663767 | 3.64940024 | 1.20885752 |
| C | 6.32883538 | 2.74867047 | 0.93147808 | H | -9.50016347 | 2.91104309 | -0.14520278 |
| S | 4.82927863 | 2.70925076 | 1.82676711 | H | -8.83879314 | 5.32007622 | -2.78881744 |
| C | 6.45548591 | -1.57395688 | -0.22544583 | C | -8.14422159 | 4.47216403 | -2.74025777 |
| C | 6.32888565 | -2.74868708 | -0.93133026 | H | -7.32015921 | 4.67927586 | -3.43322011 |
| C | 5.3708974 | -0.64773075 | -0.36059851 | H | -8.67158032 | 3.5852765 | -3.10999219 |
| C | 4.39416658 | -1.12236223 | -1.22541415 | C | -6.61952493 | 5.76928119 | -0.38445459 |
| S | 4.82927163 | -2.70942879 | -1.82654829 | H | -7.31973619 | -4.67997165 | 3.43301801 |
| C | 2.93158073 | 0.80828013 | -2.04709295 | H | -8.67141845 | -3.58623147 | 3.11004912 |
| C | 3.15199107 | -0.49128936 | -1.64566528 | H | -8.83821898 | -5.32099006 | 2.7884994 |
| C | 1.56853599 | 1.09832157 | -2.31207553 | H | -6.25527683 | 5.65366607 | 0.64283701 |
| H | 1.21257219 | 2.07307823 | -2.62893091 | H | -5.75437728 | 5.99769007 | -1.01814538 |
| C | 0.72483371 | 0.02332671 | -2.11933027 | H | -7.28617391 | 6.64025995 | -0.40815549 |
| S | 1.63990186 | -1.37927196 | -1.60516161 | H | 7.31944059 | 4.68008511 | 3.43301157 |
| H | 3.73342367 | 1.53110517 | -2.14505349 | H | 8.83802398 | 5.32102631 | 2.78865386 |
| H | 7.30252618 | -1.36619915 | 0.42123762 | H | 8.67112878 | 3.58628727 | 3.11026476 |
| H | -7.30241897 | -1.36637843 | -0.4213607 | H | 8.67218406 | -3.58501593 | -3.10959744 |
| H | 7.30241256 | 1.36641085 | -0.42137505 | H | 8.83916907 | -5.31987529 | -2.7886769 |
| H | -7.30247495 | 1.3662925 | 0.42132688 | H | 7.32075342 | -4.67883773 | -3.43334619 |

***Table S11***. Cartesian Coordinates (Å) of the Optimized Structure of $\mathbf{1}^{\bullet+}$ at the UB3LYP/6-31G(d) Level

| atom | *x* | *y* | *z* |
|---|---|---|---|
| C | 1.55698828 | -1.12993558 | 2.1815769 |
| H | 1.19754171 | -2.12937701 | 2.402522 |
| C | 0.71576346 | -0.02153074 | 2.13568558 |
| C | 2.90108372 | -0.83465712 | 1.89779127 |
| H | 3.69415365 | -1.57243752 | 1.88810018 |
| C | 3.13095502 | 0.50957424 | 1.62936894 |
| S | 1.64234215 | 1.42663639 | 1.77773787 |
| C | 5.34669421 | 0.64920046 | 0.35021948 |
| C | 4.34778136 | 1.14791895 | 1.19686994 |
| C | 6.43225763 | 1.56823711 | 0.21894255 |
| C | 6.28446281 | 2.76425563 | 0.88731818 |
| S | 4.76703394 | 2.75644878 | 1.74983054 |
| C | 6.43209003 | -1.56945524 | -0.21687078 |
| C | 6.28460685 | -2.7650094 | -0.88622164 |
| C | 5.34695303 | -0.65002061 | -0.34870697 |
| C | 4.34888159 | -1.14794871 | -1.196782 |
| S | 4.76801712 | -2.75633824 | -1.75014782 |
| C | 2.90382081 | 0.83586511 | -1.89743121 |
| H | 3.69731579 | 1.57316522 | -1.88697959 |
| C | 3.13283995 | -0.50877121 | -1.62986153 |
| C | 1.56001376 | 1.13208502 | -2.18108321 |
| H | 1.20107766 | 2.131894 | -2.40119191 |
| C | 0.7181603 | 0.02403509 | -2.13595066 |
| S | 1.64394592 | -1.4249782 | -1.77922535 |
| C | -1.55537012 | -1.1266183 | -2.1814096 |
| H | -1.19602006 | -2.12590409 | -2.40319156 |
| C | -0.71410025 | -0.01811422 | -2.13545354 |
| C | -2.89907228 | -0.83158176 | -1.89649128 |
| H | -3.69216783 | -1.56931548 | -1.88672244 |
| C | -3.12878805 | 0.5126282 | -1.6271739 |
| S | -1.64046795 | 1.42989589 | -1.77621242 |
| C | -5.34666839 | 0.64850337 | -0.35192281 |
| C | -4.34580032 | 1.15020083 | -1.19475241 |
| C | -6.43591535 | 1.56390317 | -0.22629591 |
| C | -6.28829675 | 2.76071812 | -0.89326919 |
| S | -4.76756261 | 2.75732556 | -1.74988516 |
| C | -6.43174723 | -1.56987516 | 0.21577862 |
| C | -6.28454081 | -2.76508481 | 0.88563962 |
| C | -5.34635839 | -0.65050972 | 0.34710246 |
| C | -4.34825778 | -1.14830605 | 1.19536492 |
| S | -4.7679087 | -2.75627565 | 1.74955451 |
| C | -2.90215344 | 0.83414474 | 1.89860377 |
| C | -3.13179495 | -0.50981188 | 1.62877945 |
| C | -1.55809289 | 1.12934132 | 2.18276674 |
| H | -1.19879666 | 2.12861365 | 2.40471781 |
| C | -0.71670268 | 0.02111228 | 2.13572922 |
| S | -1.64306513 | -1.42681619 | 1.77632486 |
| H | -3.69530533 | 1.57185089 | 1.88962778 |
| H | -7.29215817 | -1.35190469 | -0.40842729 |
| H | 7.29251187 | -1.35134355 | 0.4072712 |
| H | -7.30055891 | 1.34134964 | 0.39047055 |
| H | 7.29318292 | 1.3494754 | -0.40427803 |

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Si | 7.48557965 | -4.241324 | -0.92557046 |
| H | 6.19717804 | -5.64721905 | 0.70370567 |
| C | 6.56288535 | -5.77446527 | -0.32154147 |
| H | 5.70099917 | -6.00687146 | -0.95810687 |
| H | 7.22383572 | -6.6495677 | -0.33252639 |
| C | 8.92028686 | -3.81271112 | 0.22237271 |
| H | 9.45871841 | -2.91837488 | -0.11174523 |
| H | 9.6423734 | -4.6376375 | 0.2446445 |
| H | 8.58547731 | -3.64410501 | 1.25227288 |
| C | 8.08355444 | -4.48484634 | -2.6994506 |
| Si | -7.4859968 | -4.24094571 | 0.9260077 |
| Si | -7.48701245 | 4.23874735 | -0.92502102 |
| Si | 7.48582683 | 4.24022811 | 0.92611983 |
| C | -6.56381659 | -5.77482856 | 0.32309259 |
| H | -5.70185327 | -6.00684516 | 0.95969895 |
| H | -6.19829953 | -5.64859533 | -0.70234299 |
| H | -7.22496763 | -6.64976556 | 0.33503129 |
| H | -8.58587456 | -3.64490524 | -1.25219491 |
| C | -8.92064416 | -3.81267981 | -0.22214614 |
| H | -9.64296904 | -4.63741787 | -0.24377063 |
| H | -9.45880334 | -2.91796139 | 0.11138549 |
| C | -8.08410134 | -4.48295133 | 2.70006025 |
| H | -7.35280992 | 6.55305223 | -0.0065547 |
| C | -6.68680564 | 5.68161044 | -0.00548583 |
| H | -6.47592332 | 5.42622521 | 1.03921018 |
| H | -5.74349502 | 5.98758972 | -0.47273605 |
| C | -7.81722614 | 4.70208615 | -2.72471449 |
| H | -9.80033752 | 4.5000237 | -0.05503916 |
| C | -9.06992024 | 3.68216285 | -0.06191402 |
| H | -9.53617424 | 2.83178298 | -0.57233279 |
| H | -8.89201122 | 3.39735658 | 0.98159717 |
| C | 8.92016044 | 3.81076671 | -0.22200957 |
| H | 9.6427788 | 4.63522368 | -0.2443845 |
| H | 8.58515451 | 3.64230795 | -1.25187106 |
| H | 9.45808853 | 2.91610637 | 0.11206831 |
| H | 8.7866677 | 5.32491497 | 2.75493163 |
| C | 8.08446086 | 4.48416784 | 2.69972141 |
| H | 7.25543866 | 4.70233676 | 3.38298078 |
| H | 8.60104692 | 3.5939089 | 3.07576536 |
| C | 6.56348157 | 5.77346418 | 0.32185147 |
| H | 7.25428707 | -4.7030112 | -3.38241948 |
| H | 8.59988638 | -3.59447235 | -3.07556639 |
| H | 8.78583001 | -5.32550754 | -2.75507927 |
| H | 6.19642714 | 5.64563284 | -0.70283968 |
| H | 5.70253887 | 6.00700915 | 0.95928399 |
| H | 7.22503875 | 6.64812591 | 0.33130357 |
| H | -6.89875928 | 4.99437509 | -3.24733383 |
| H | -8.50971834 | 5.55072368 | -2.78051716 |
| H | -8.26572349 | 3.86983097 | -3.27879322 |
| H | -8.60041371 | -3.59218977 | 3.0753015 |
| H | -8.78645682 | -5.32349418 | 2.75641175 |
| H | -7.25492039 | -4.7005196 | 3.38332133 |

***Table S12***. Cartesian Coordinates (Å) of the Optimized Structure of Neutral **2′** at the B3LYP/6-31G(d) Level

| atom | *x* | *y* | *z* | atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| C | 1.28740027 | 1.41752414 | -0.40086076 | S | -1.93587999 | 1.05635024 | -0.05250883 |
| H | 0.71304681 | 2.3252278 | -0.55294262 | Si | 8.98604581 | 0.09375394 | 0.2071857 |
| C | 0.69989507 | 0.17548052 | -0.2612461 | Si | -8.98602088 | -0.09371482 | 0.2074029 |
| C | 2.70144036 | 1.38834189 | -0.36089834 | C | -9.27082053 | -1.18828653 | 1.72428922 |
| H | 3.31983676 | 2.27224697 | -0.47565698 | H | -8.96751482 | -0.67752314 | 2.64537046 |
| C | 3.23000056 | 0.12470002 | -0.18940541 | H | -8.69958423 | -2.12211481 | 1.66100562 |
| S | 1.93585722 | -1.05644843 | -0.05273995 | H | -10.33039436 | -1.45548489 | 1.82183954 |
| C | 5.15040121 | -1.55395058 | -0.12934181 | C | -9.93716862 | 1.53108553 | 0.38596539 |
| H | 4.54454659 | -2.44914846 | -0.22650777 | H | -9.79424293 | 2.18544701 | -0.48178348 |
| C | 4.61512064 | -0.28180476 | -0.11027726 | H | -9.62808349 | 2.08403603 | 1.28034048 |
| C | 6.5663804 | -1.57123616 | -0.02580235 | H | -11.01242176 | 1.33380652 | 0.47447912 |
| H | 7.14267009 | -2.49117553 | -0.02792114 | C | -9.54691813 | -1.01143448 | -1.3497204 |
| C | 7.15404857 | -0.32684998 | 0.07240675 | H | -9.4013049 | -0.39809075 | -2.24632126 |
| S | 5.90295904 | 0.89938508 | 0.04617058 | H | -10.61081798 | -1.2729349 | -1.29063078 |
| C | -6.56640866 | 1.57121978 | -0.02649539 | H | -8.98399959 | -1.94167036 | -1.4906889 |
| H | -7.14271417 | 2.49114827 | -0.02888828 | C | 9.27116339 | 1.18901383 | 1.72351461 |
| C | -7.15405354 | 0.32685349 | 0.07211641 | H | 8.69981712 | 2.12276124 | 1.66003404 |
| C | -5.1504367 | 1.55392202 | -0.13015432 | H | 10.33073896 | 1.45634874 | 1.82066259 |
| H | -4.54459974 | 2.44908925 | -0.22770697 | H | 8.96816872 | 0.67857399 | 2.64487906 |
| C | -4.61514152 | 0.281789 | -0.11072325 | C | 9.93720662 | -1.53096791 | 0.3864073 |
| S | -5.90294507 | -0.89936892 | 0.04620204 | H | 11.01246462 | -1.33364109 | 0.47476517 |
| C | -2.70146012 | -1.38830778 | -0.36172382 | H | 9.79422912 | -2.18573873 | -0.48102226 |
| H | -3.31986373 | -2.27214928 | -0.47693147 | H | 9.62817922 | -2.08349446 | 1.28106478 |
| C | -3.23001904 | -0.12472115 | -0.1898341 | C | 9.54663301 | 1.01069324 | -1.35050717 |
| C | -1.28741428 | -1.41748959 | -0.40155276 | H | 8.98374452 | 1.9409027 | -1.49176415 |
| H | -0.71305527 | -2.32513901 | -0.55393872 | H | 9.40074122 | 0.3969397 | -2.24678211 |
| C | -0.69990925 | -0.17550792 | -0.26138353 | H | 10.61056747 | 1.27214238 | -1.29181322 |

***Table S13***. Cartesian Coordinates (Å) of the Optimized Structure of **2′**$^{\bullet+}$ at the UB3LYP/6-31G(d) Level

| atom | *x* | *y* | *z* | atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| C | 1.29102137 | 1.42870584 | 0.01205978 | S | -1.92333027 | 1.0991482 | 0.00857698 |
| H | 0.71615052 | 2.34843253 | 0.01392771 | Si | 8.97888498 | 0.1075982 | -0.00643615 |
| C | 0.6872922 | 0.15692844 | 0.01143329 | Si | -8.97889864 | -0.10749621 | -0.00662475 |
| C | 2.67759015 | 1.39256714 | 0.01002485 | C | -9.30457416 | -1.28370102 | -1.44511425 |
| H | 3.30203372 | 2.27878376 | 0.01004433 | H | -8.73157849 | -2.21377529 | -1.35237112 |
| C | 3.21312762 | 0.09136548 | 0.00738963 | H | -9.04850804 | -0.82605844 | -2.40717509 |
| S | 1.92332089 | -1.09928296 | 0.00847456 | H | -10.3664388 | -1.55573534 | -1.47891881 |
| C | 5.12461887 | -1.57853202 | -0.00311924 | C | -9.38267257 | -0.92918897 | 1.64339247 |
| H | 4.51894804 | -2.47917593 | -0.00368123 | H | -9.16361859 | -0.26741588 | 2.48872853 |
| C | 4.58078155 | -0.2926995 | 0.00295199 | H | -8.81523395 | -1.85599082 | 1.78641986 |
| C | 6.52892857 | -1.58518192 | -0.01040593 | H | -10.44824939 | -1.18488596 | 1.68853008 |
| H | 7.11573074 | -2.49704691 | -0.01787456 | C | -9.90910873 | 1.51822848 | -0.21585976 |
| C | 7.11461126 | -0.32146294 | -0.0091506 | H | -9.71982256 | 2.21196086 | 0.61130436 |
| S | 5.87795038 | 0.89738847 | -0.00111618 | H | -10.98873568 | 1.32764058 | -0.2378641 |
| C | -6.52883925 | 1.58531418 | -0.01049977 | H | -9.64831156 | 2.02316596 | -1.15287041 |
| H | -7.11555944 | 2.49723166 | -0.01813025 | C | 9.38300765 | 0.9299653 | 1.64312932 |
| C | -7.11463878 | 0.32165989 | -0.00921227 | H | 8.81594718 | 1.85704341 | 1.78582252 |
| C | -5.12453365 | 1.57853992 | -0.00303456 | H | 10.44869511 | 1.18528152 | 1.68786677 |
| H | -4.51879379 | 2.47913835 | -0.00350478 | H | 9.16392747 | 0.26869273 | 2.48885081 |
| C | -4.58079742 | 0.29266401 | 0.00314375 | C | 9.9089413 | -1.51828906 | -0.21522916 |
| S | -5.87807559 | -0.89732075 | -0.00102345 | H | 10.98850057 | -1.3275948 | -0.23931544 |
| C | -2.67766066 | -1.39268213 | 0.0102963 | H | 9.646593 | -2.02423564 | -1.15126799 |
| H | -3.3021309 | -2.27888035 | 0.01039676 | H | 9.72111825 | -2.21114928 | 0.61298938 |
| C | -3.21316782 | -0.09146692 | 0.00760244 | C | 9.3046701 | 1.28312026 | -1.44549057 |
| C | -1.29109226 | -1.4288538 | 0.01223606 | H | 8.73130597 | 2.21304618 | -1.35355086 |
| H | -0.71623706 | -2.34859059 | 0.01410936 | H | 9.04912776 | 0.82476918 | -2.40735239 |
| C | -0.68733281 | -0.1570896 | 0.01149391 | H | 10.36645001 | 1.55552706 | -1.47907745 |

## 7. References


(1) M. Ishikawa, H. Teramura, K. K. Lee, W. Schneider, A. Naka, H. Kobayashi, Y. Yamaguchi, M. Kikugawa, J. Ohshita, A. Kunai, H. Tang, Y. Harima, T. Yamabe and T. Takeuchi, *Organometallics,* 2001, **20**, 5331.

(2) Y. Dienes, S. Durben, T. Kárpáti, T. Neumann, U. Englert, L. Nyulászi and T. Baumgartner, *Chem. Eur. J.*, 2007, **13**, 7487.

(3) Y. A. Getmanenko and R. J. Twieg, *J. Org. Chem.*, 2008, **73**, 830.

(4) T. Kinzel, Y. Zhang and S. L. Buchwald, *J. Am. Chem. Soc.*, 2010, **132**, 14073.

(5) J. R. Smith, P. A. Cox, S. A. Campbell and N. M. Ratcliffe, *J. Chem. Soc. Fraday Trans.*, 1995, **91**, 2331.

(6) C. Adamo and V. Barone, *J. Chem. Phys.,* 1999, **110**, 6158.

(7) (*a*) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724; (*b*) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; (*c*) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta.*, 1973, **28**, 213; (*d*) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, *J. Chem. Phys*., 1982, **77**, 3654.

(8) Gaussian 09 (Revision C.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken,; C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, **2010**.

(9) (*a*) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; (*b*) C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (*c*) A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648.

## 8. NMR Spectra

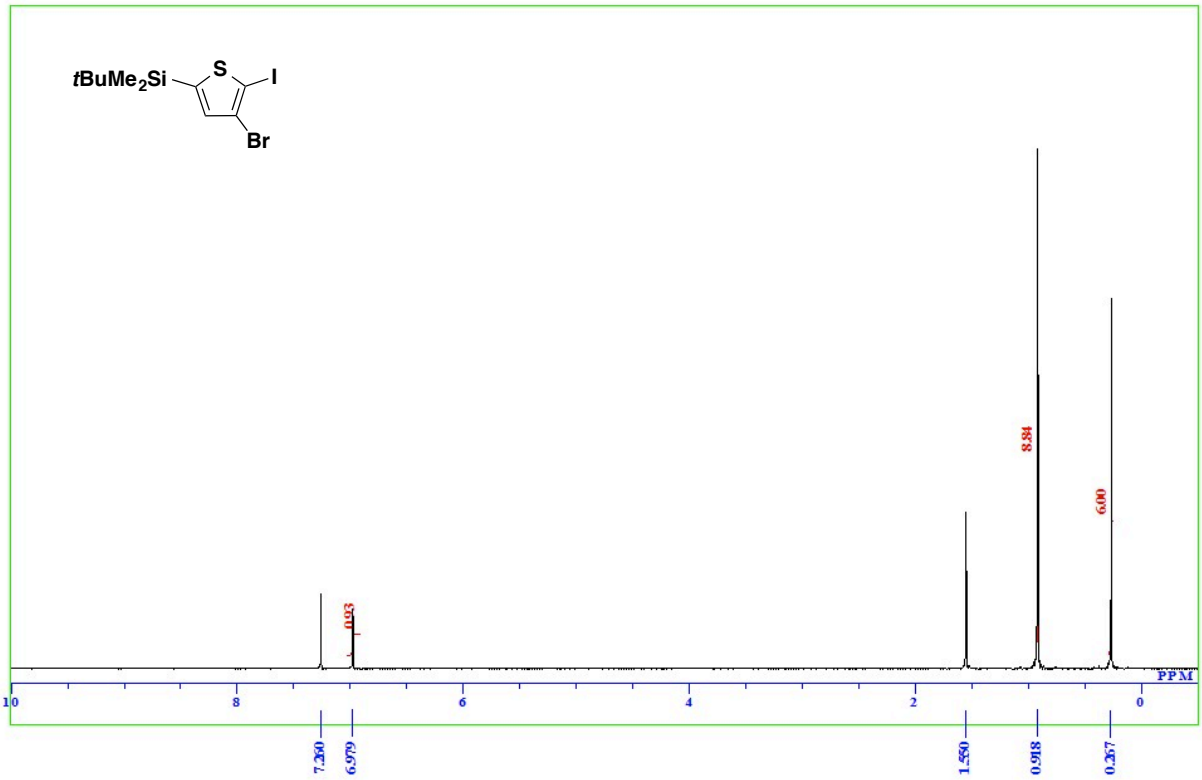



***Fig. S30*** $^{1}$H NMR spectrum of **7** (400 MHz, $CDCl_3$).

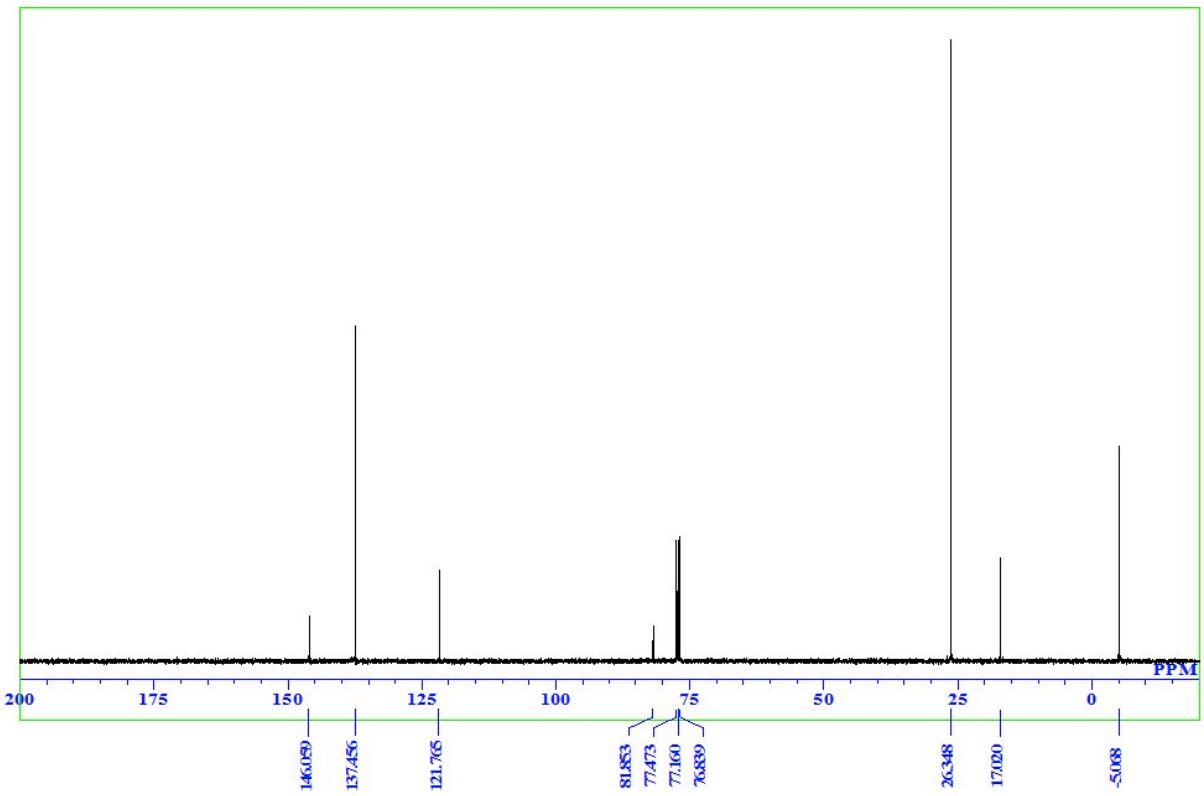



***Fig. S31*** $^{13}C\{^{1}H\}$ NMR spectrum of **7** (100 MHz, $CDCl_3$).

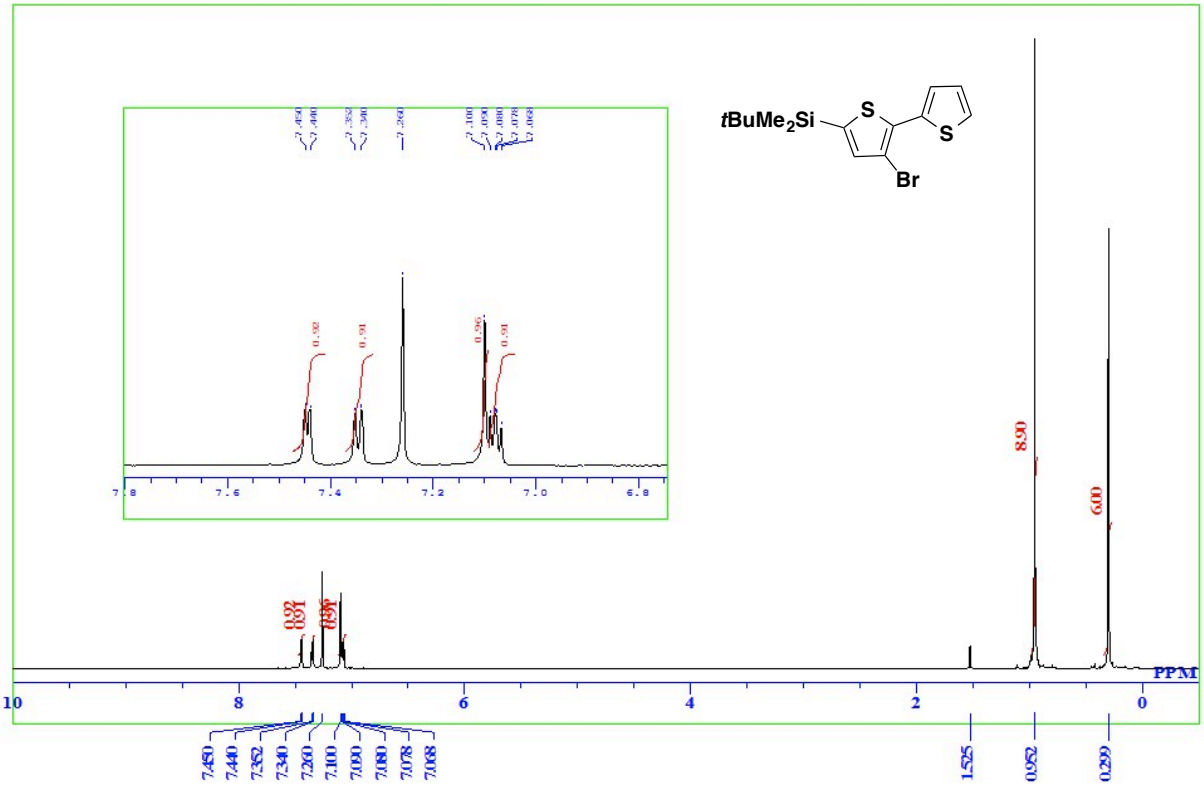



***Fig. S32*** $^{1}$H NMR spectrum of **8** (400 MHz, $CDCl_3$).

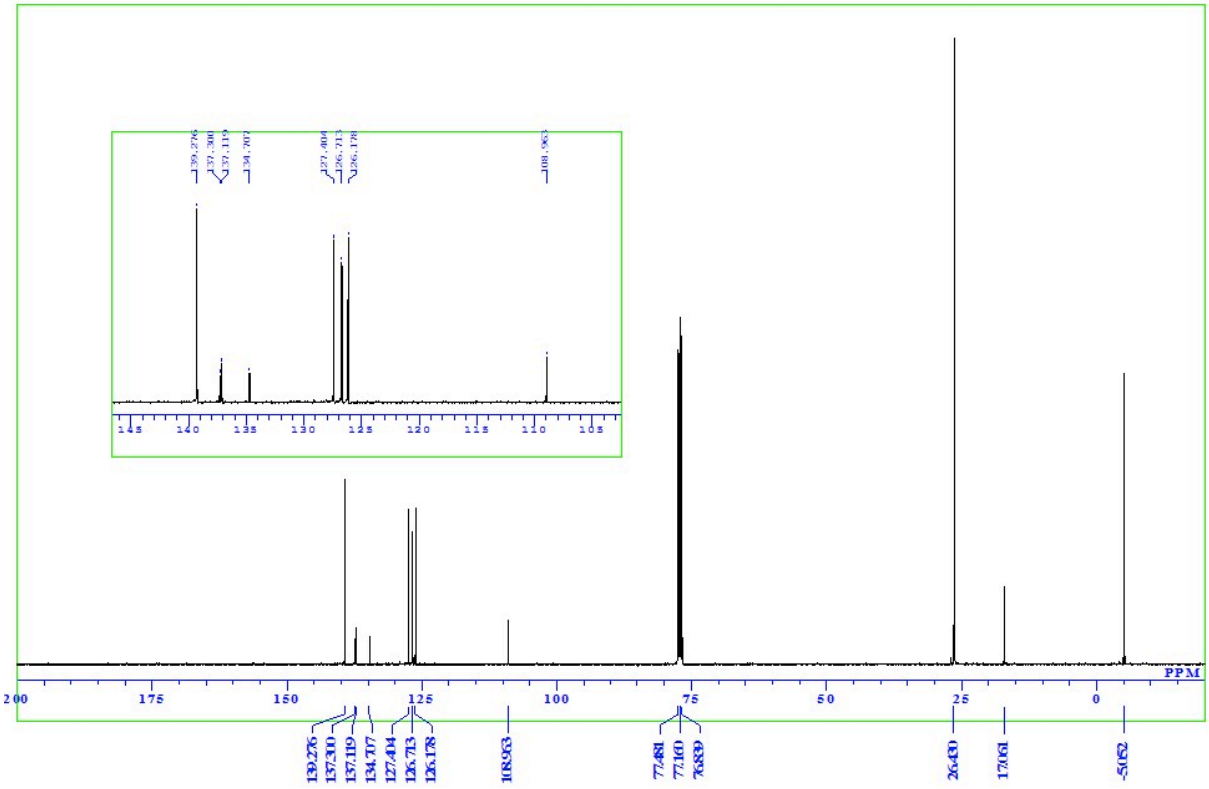



***Fig. S33*** $^{13}$C{$^{1}$H} NMR spectrum of **8** (100 MHz, $CDCl_3$).

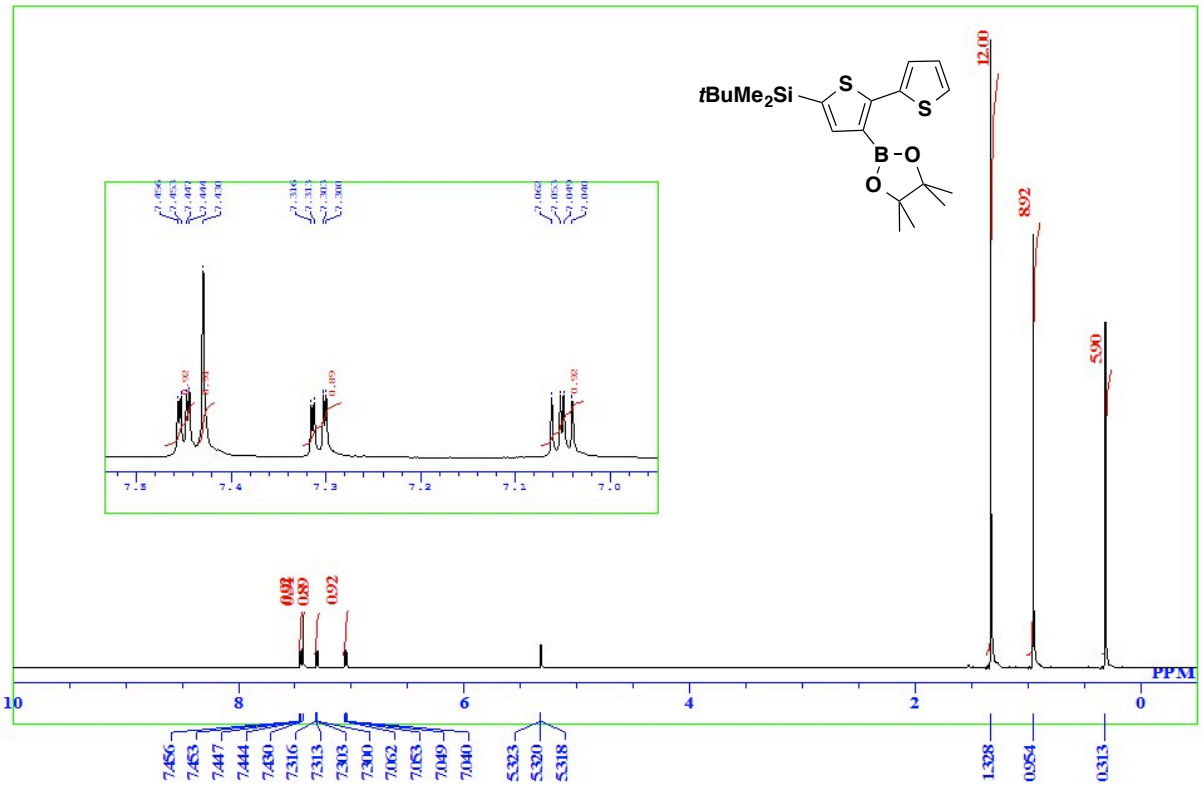



***Fig. S34*** $^{1}$H NMR spectrum of **9** (400 MHz, $CD_2Cl_2$).

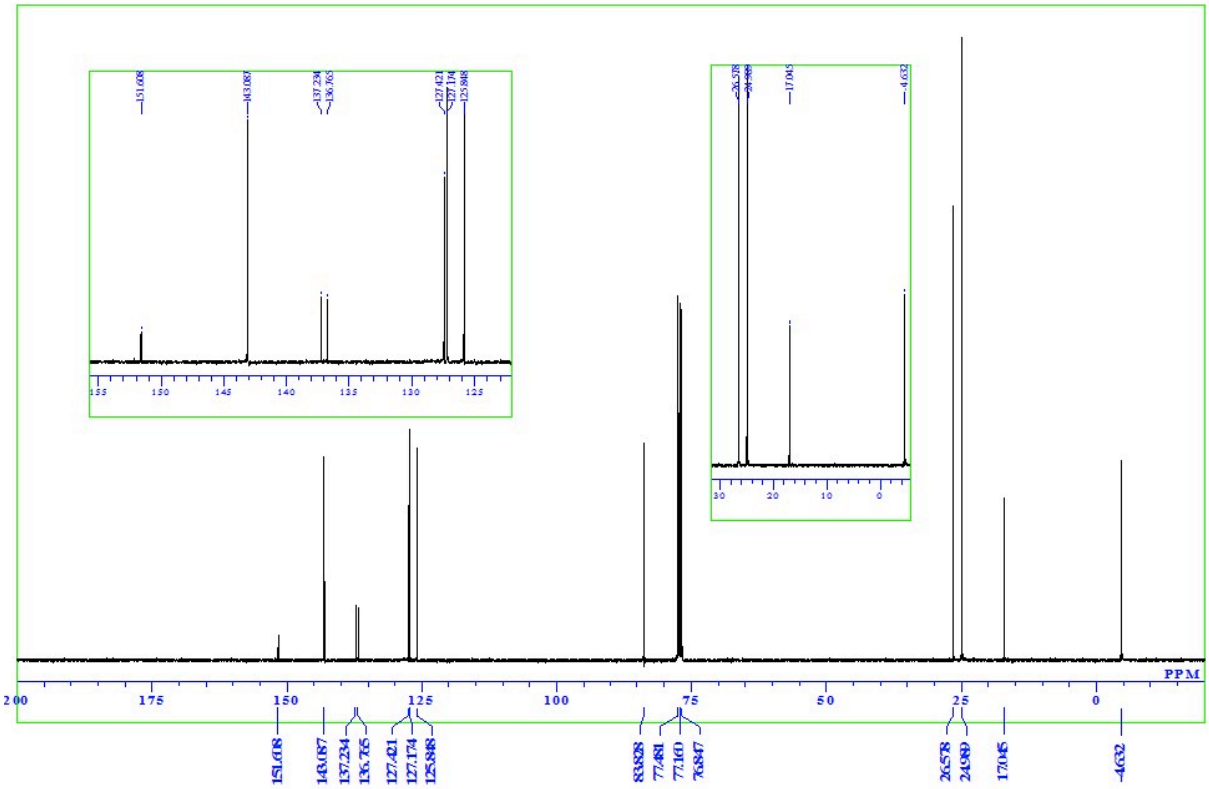



***Fig. S35*** $^{13}$C{$^{1}$H} NMR spectrum of **9** (100 MHz, $CDCl_3$).

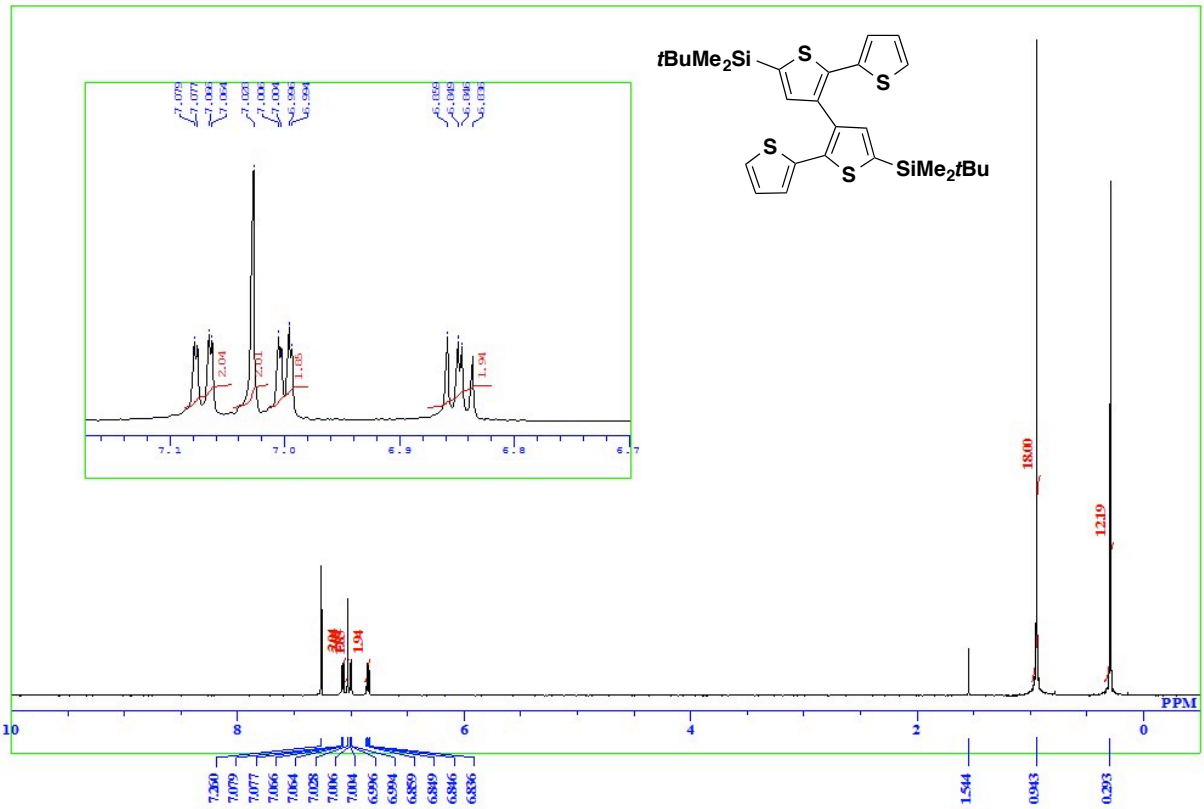



***Fig. S36*** $^{1}$H NMR spectrum of **3** (400 MHz, $CDCl_3$).

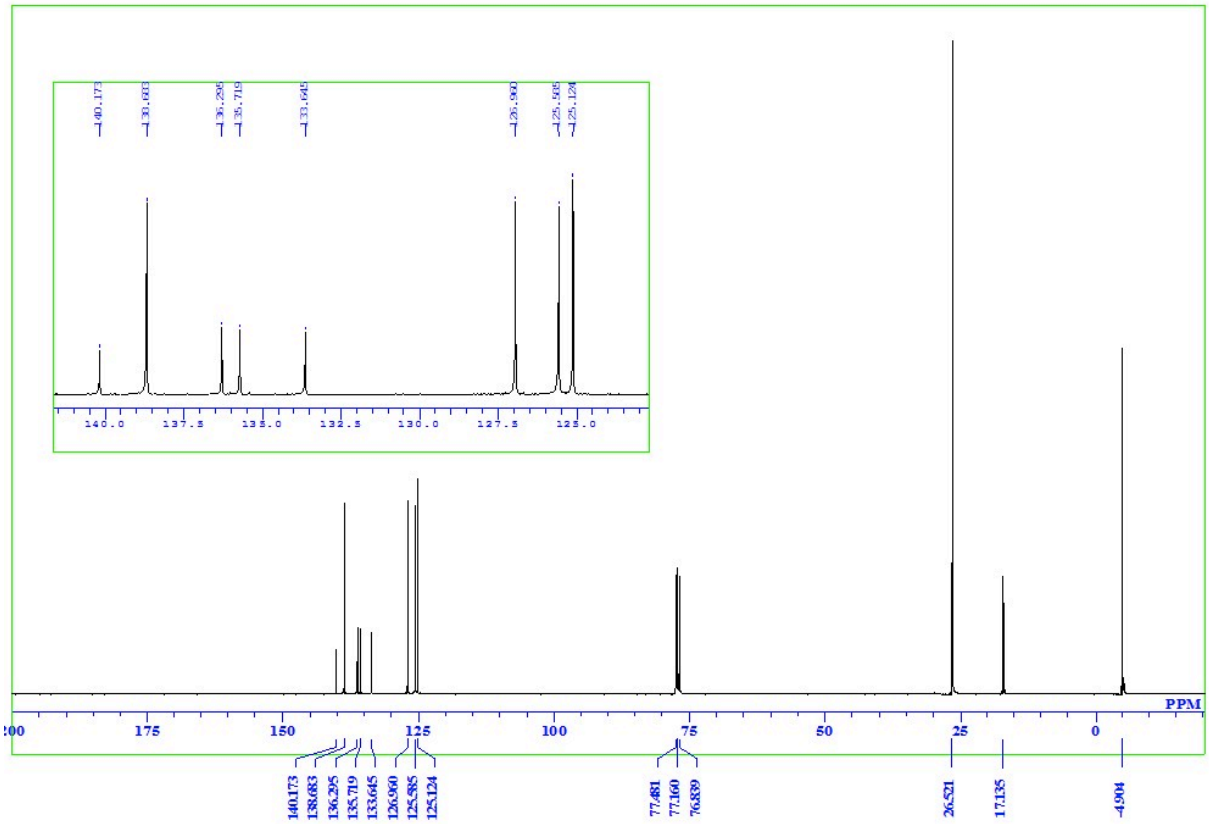



***Fig. S37*** $^{13}C\{^{1}H\}$ NMR spectrum of **3** (100 MHz, $CDCl_3$) .

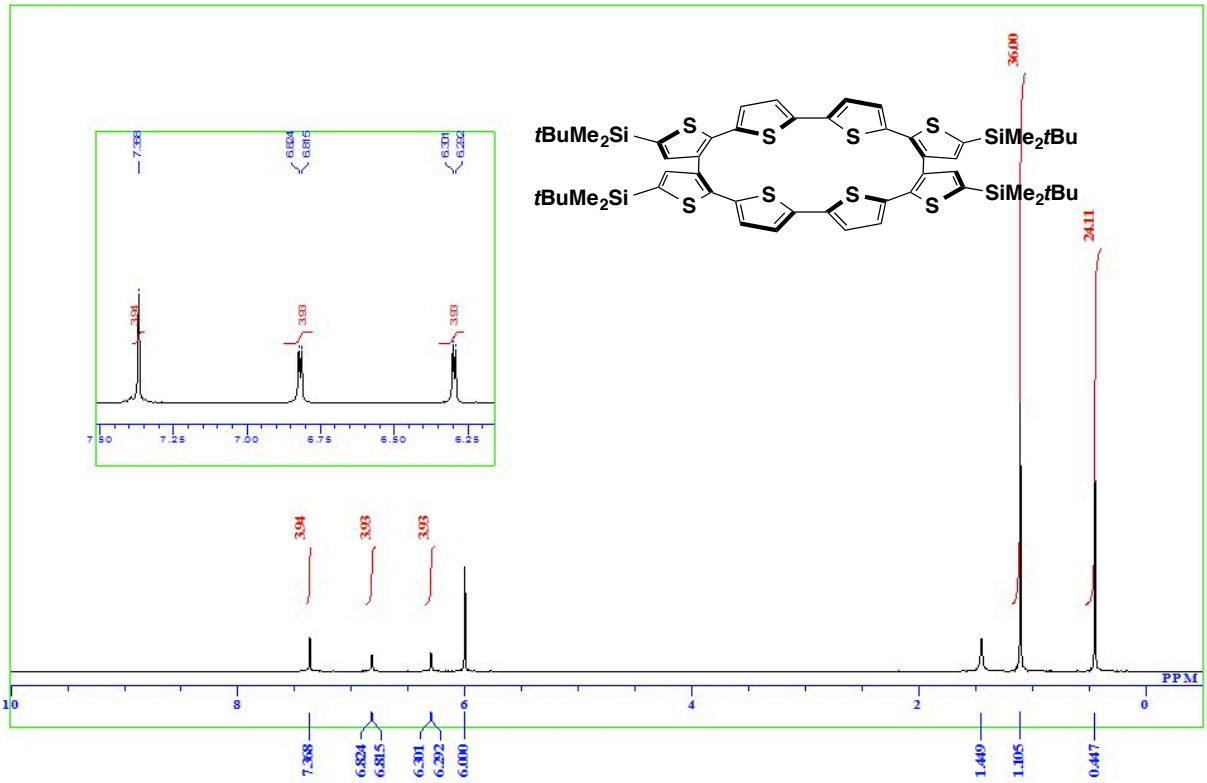



***Fig. S38*** $^{1}$H NMR spectrum of **1** (400 MHz, $C_2D_2Cl_4$, VT130 °C).

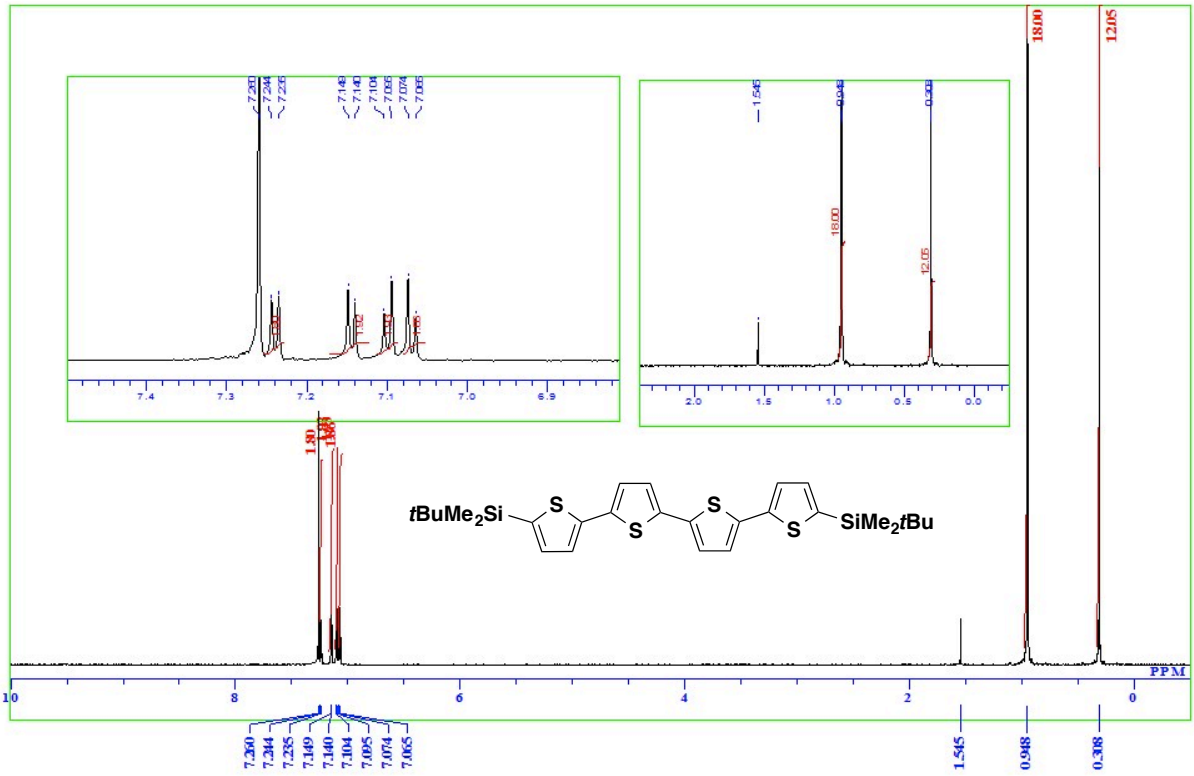



***Fig. S39*** $^{1}$H NMR spectrum of **2** (400 MHz, $CDCl_3$) .

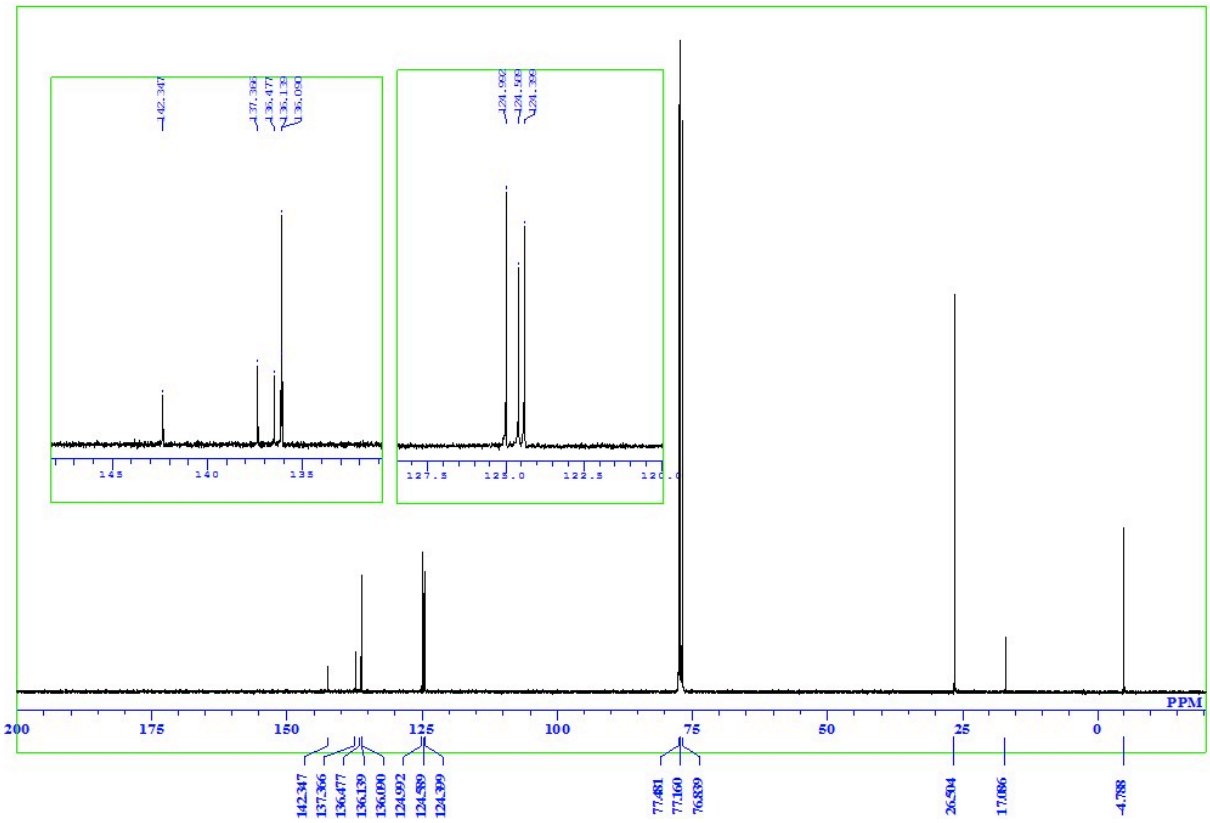



***Fig. S40*** $^{13}C\{^{1}H\}$ NMR spectrum of **2** (100 MHz, $CDCl_3$).

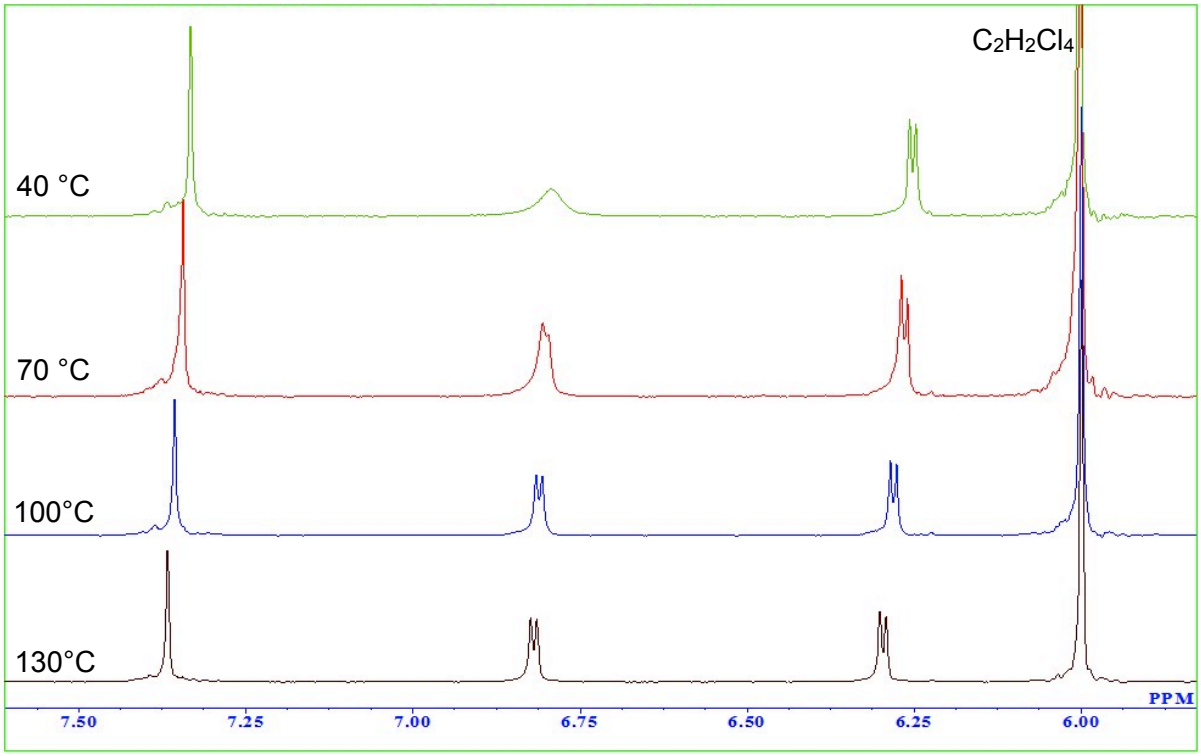



***Fig. S41*** $^{1}H$ NMR spectrum of **1** (400 MHz, $C_2D_2Cl_4$,) on various temperatures ranged from 6.0 ppm to 7.5 ppm.