

Supporting Information

Switching of the π -Electronic Conjugations in the Reductions of a Dithienylethene-Fused *p*-Benzoquinone

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1. Materials

Unless otherwise noted, reagents and solvents were used as received from Kishida Chemical Co., Ltd. [CH_2Cl_2 (>98%), AcOEt (>99%), toluene (>99%) and *n*-hexane (>95%)], Nakarai Tesuque, Inc. [KBr (>99%), AcOH (>99%), Na_2CO_3 (>99%), CuI (>95%) and tributyltin chloride (>97%)], Wako Pure Chemical Industries, Ltd. [NBS (>98%), Na_2SO_4 (>99%), 18-crown-6 (>98%), Ag_2O (>99%), AlCl_3 (>98%) and cyclohexane for spectroscopic analysis (>99.8%)], Sigma-Aldrich [Na (>99.5%) and 2,3-dimethylhydroquinone (>97%)], Kanto Chemical Co., Inc. [THF dehydrated stabilizer free, CH_2Cl_2 dehydrated stabilizer free and 1.6 M *n*-BuLi hexane solution], Tokyo Chemical Industry Co., Ltd. (TCI) [2,5-dimethylthiophene (>97%), Br_2 (>98%), ferrocene (>95%), $\text{Pd}(\text{PPh}_3)_4$ (>97%), KF (>98%), NaBH_4 (>95%), tetrabutylammonium perchlorate (>98%) and tetramethyl-1,4-benzoquinone (>98%)] and Cambridge Isotope Laboratories, Inc. (CIL) [CDCl_3 (D, 99.8%) + 0.05% V/V TMS + Silver foil]. Dry toluene was prepared through dehydration with Type 4A molecular sieve. For column chromatography, Wakogel C-300HG (particle size 40–60 μm , silica) was used.

2. Measurements

^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 and 500 spectrometers, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane as the internal standard. Absorption spectra were recorded on a JASCO V-670 UV/VIS/NIR spectrometer equipped with a JASCO ETC-717 temperature/stirring controller. Fourier transform infrared spectra were performed on a JASCO FT/IR 4200. Fourier transform

mass spectrometry was performed on a Thermo Fisher Scientific LTQ Orbitrap Discovery. X-ray diffraction data was collected on a Bruker APEX II Ultra CCD diffractometer. Elemental analysis was performed on a YANACO MT-5 CHN recorder.

3. Methods

Cyclic voltammetry. Electrochemical measurements were made with an ALS 1210A electrochemical analyzer using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag⁺ [0.01 M AgNO₃, 0.1 M Bu₄NClO₄ (MeCN)] reference electrode. The scan rate was 50–50 mV s⁻¹. The CV curves were calibrated using the ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an external standard, which was measured under the same conditions before and after the measurement of samples.

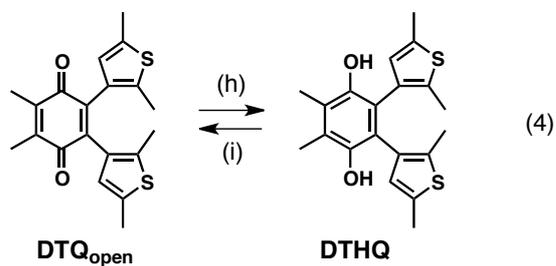
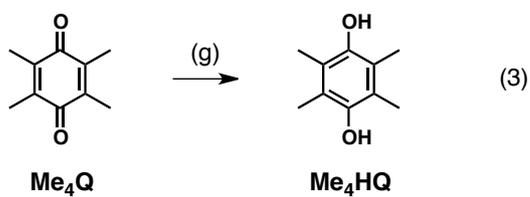
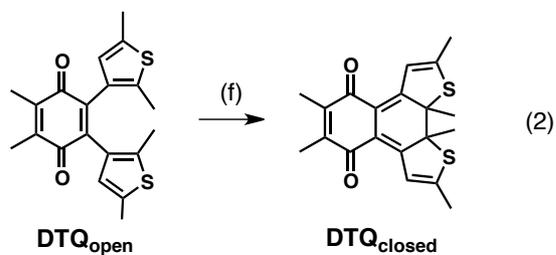
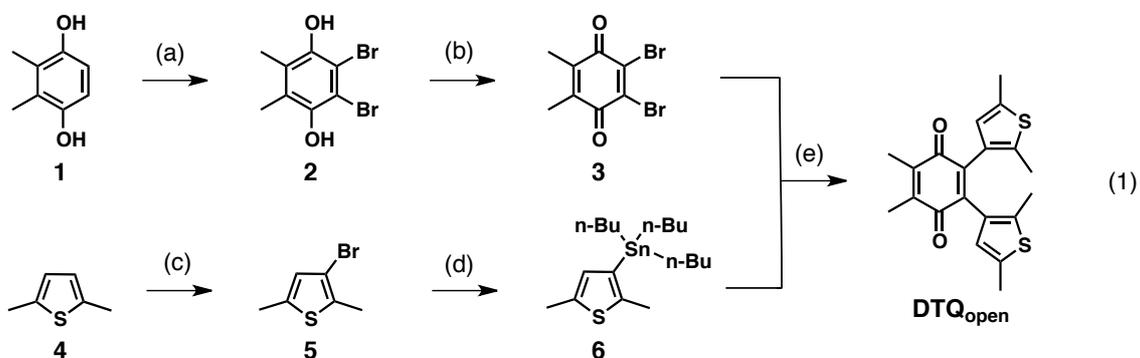
EPR measurements. The EPR spectra were recorded on a Bruker EMXPlus system. EPR spectra were measured under nonsaturating microwave power conditions. The amplitude of modulation (0.4 gauss) was chosen to optimize the resolution and the signal-to-noise (S/N) ratio of the observed spectra. The g values were calibrated with a 1,3-bisdiphenylene-2-phenylallyl (BDPA) complex with benzene (1:1) marker. Simulations of EPR signals were performed with WINEPR Simfonia program. The sample was prepared upon mixing **DTQ** and metallic sodium (1 eq.) and 18-crown-6 (1.5 eq.) in CH₂Cl₂ under nitrogen atmosphere in a glove box, and then, the sample solution was degassed by freeze-pump-thaw cycle three times.

Theoretical calculations. For calculations of molecular orbitals and the orbital energy of **DTQ**, the density functional theory (B3LYP/6-311G(d,p) and UB3LYP/6-311+G(d,p), respectively) was employed as implemented in the Gaussian 09 set of programs.¹

Photo-irradiation. Photo-irradiation for the sample solution was demonstrated with a 500 W xenon lamp (USHIO SPAX INC., SX-UID502XAM) equipped with a monochromator (JASCO CT-10T).

4. Synthesis

4.1. Synthetic Scheme



Scheme S1. Reagents and conditions: (a) Br_2 (b) Ag_2O (c) NBS (d) (i) $n\text{-BuLi}$, (ii) tributyltin chloride (e) $\text{Pd}(\text{PPh}_3)_4$, reflux (f) AlCl_3 (g) and (h) NaBH_4 (i) Ag_2O

4.2. Synthetic procedures

Compounds **2**, **3**, **5**, **6** and **Me₄HQ** were prepared by procedures analogous to those reported previously, and unambiguously characterized by means of ¹H NMR spectroscopy.²⁻⁶ **DTQ_{open}** was prepared through modifications of the literature methods.⁵

2,3-Bis(2,5-dimethylthiophen-3-yl)-5,6-dimethylbenzoquinone (DTQ_{open}):

2,5-Dimethyl-3-(tri-*n*-butylstannyl)thiophen **6** (1.81 g, 4.5 mmol) was added to a solution of 2,3-dibromo-5,6-dimethylbenzoquinone (588 mg, 2 mmol) with Pd(PPh₃)₄ (60 mg) and CuI (10 mg) in 40 mL dried toluene. After stirring under Ar at reflux overnight, the reaction mixture was cooled to room temperature and the solvent was evaporated under vacuum. The residue was dissolved in EtOAc, and concentrated KF aqueous solution (20 mL) was added. After vigorously stirring for 1 h, the precipitate (Bu₃SnF) was filtered and washed with EtOAc. The aqueous layer was back extracted with EtOAc and the organic layers were combined, dried over Na₂SO₄ and evaporated under vacuum. The crude product was purified by silica gel chromatography (CH₂Cl₂ : hexane = 1 : 1) and reprecipitation (CH₂Cl₂ / hexane) in 69 % yield. ¹H NMR (500 MHz, CDCl₃): 6.26 (s, 2H), 2.34 (s, 6H), 2.10 (s, 6H), 1.90 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): 186.77, 140.86, 139.44, 136.69, 135.06, 129.69, 127.26, 15.09, 14.49, 12.66; IR (cm⁻¹, in KBr pellet) 3269, 2966, 2918 2857, 1649, 1609; HRMS: m/z calculated for [M+H]⁺ (C₂₀H₂₀O₂S₂) 357.0982, found for 357.0982.

2,5,6,9,10a,10b-Hexamethylnaphtho[2,1-*b*:3,4-*b'*]dithiophene-4,7(10a*H*,10b*H*)-

dione (DTQ_{closed}): AlCl₃ (42 mg, 0.3 mmol) was added to the solution of compound DTQ_{open} (36 mg, 0.1 mmol) in CH₂Cl₂ (5 ml) at room temperature in the dark. After 10 min, the reaction was complete and water was added to quench the reaction. The organic layer was washed with water, dried over Na₂SO₄ and evaporated under vacuum. The crude product was purified by silica gel chromatography with EtOAc/hexane in 71% yield. ¹H NMR (500 MHz, CDCl₃): 7.46 (q, *J* = 1.5 Hz, 2H), 2.29 (d, *J* = 1.0 Hz, 6H), 2.09 (s, 6H), 1.96 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): 181.83, 163.11, 160.36, 145.89, 122.24, 118.30, 69.07, 25.44, 18.90, 13.48; IR (cm⁻¹, in KBr pellet) 3108, 2970, 2924, 2859, 1632, 1611; HRMS: *m/z* calculated for [M+H]⁺ (C₂₀H₂₀O₂S₂) 357.0982, found for 357.0982.

2,3-bis(2,5-dimethylthiophen-3-yl)-5,6-dimethylhydroquinone(DTHQ): To a suspension of DTQ_{open} (107 mg, 0.3 mmol) in THF (1 mL) and MeOH (2 mL), was slowly added NaBH₄ (15 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 30 min and then cooled to 0°C. Additional MeOH was slowly added until no more gas evolution was observed. A small amount of water was added and the aqueous layer was back extracted with EtOAc, and the organic layers were combined, dried over Na₂SO₄ and evaporated under vacuum. Its purity was sufficient for various measurements without any purification and the yield was 76%. ¹H NMR (500 MHz, CDCl₃): 6.24 (q, *J* = 1 Hz, 2H), 4.78 (s, 2H), 2.33(s, 6H), 2.26 (s, 6H), 2.05 (s, 6H) and 6.16 (q, *J* = 1 Hz, 2H), 4.75(s, 2H), 2.30 (s, 6H), 2.25 (s, 6H), 2.13 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): 144.73, 144.67, 136.73, 136.70, 135.25, 135.01, 131.61, 131.41, 127.58, 126.98, 123.35, 123.24, 119.29,

119.26, 15.17, 15.12, 13.81, 13.58, 12.40 12.40; IR (cm^{-1} , in KBr pellet) 3508, 3461, 3216, 2943, 2917, 2859, 1440; elemental analysis: calculated for C:67.00%, H:6.19%, found for C:66.70%, H:6.27%; HRMS: m/z calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{20}\text{H}_{22}\text{O}_2\text{S}_2$) 359.1139, found for 359.1135.

5. X-ray crystal structure analysis of DTQ_{open}

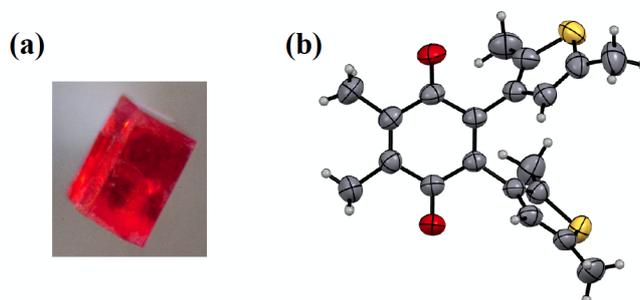


Fig. S1 (a) The crystal of DTQ_{open} (b) ORTEP diagram of DTQ_{open}, using 50% probability ellipsoids. X-ray diffraction data were collected on a Bruker APEX II Ultra CCD diffractometer using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298 K. The structure was resolved by direct methods and refined by full-matrix least-squares on F^2 (SHELXL97).⁷ The positions of all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at ideal positions and included in the refinement. CCDC 1508336 contain the supplementary crystallographic data for this paper.

Table 1 Crystal data and structure refinement for compound **DTQ_{open}**.

Identification code	Shelxl
Empirical formula	C ₂₀ H ₂₀ O ₂ S ₂
Formula weight	356.48
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	$a = 8.8493(14)$; $\alpha = 90^\circ$ $b = 11.2288(18)$; $\beta = 90.450(2)^\circ$ $c = 18.574(3)$; $\gamma = 90^\circ$
Volume	1845.6(5) Å ³
Z	4
Calculated density	1.283 g/cm ³
Absorption coefficient	0.297 mm ⁻¹
F(0 0 0)	752
Crystal size	0.2 × 0.1 × 0.1 mm
Theta range for data collection	2.847–27.548°
Limiting indices	$-11 \leq h \leq 8$, $-14 \leq k \leq 12$, $-24 \leq l \leq 21$,
Reflections collected/unique	10339/4245
Goodness-of-fit on F^2	0.883
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0439, wR2 = 0.1321
R indices (all data)	R1 = 0.0592, wR2 = 0.1500

6. ^1H and ^{13}C NMR spectra of DTQ_{open} and $\text{DTQ}_{\text{closed}}$

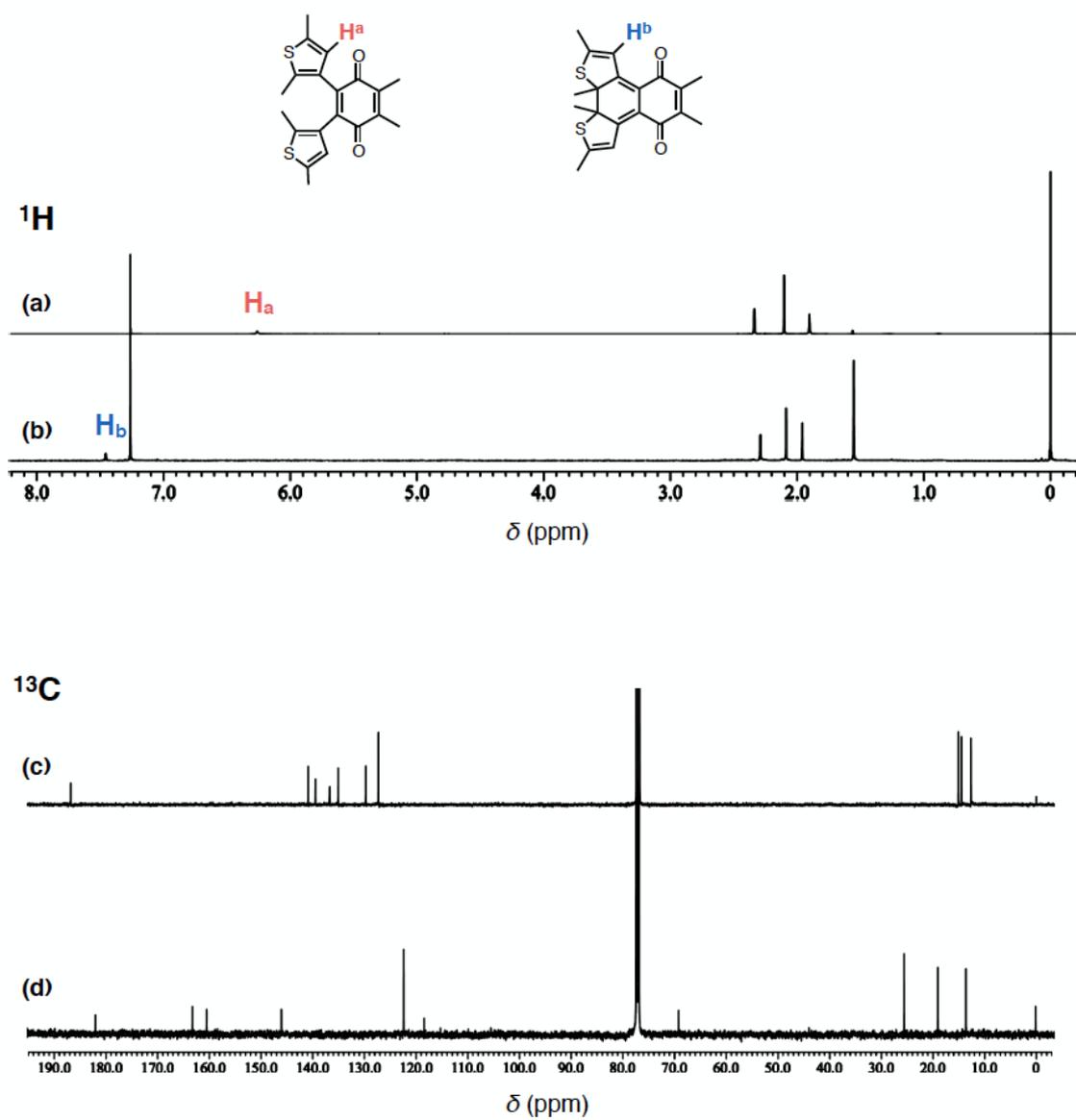


Fig. S2 ^1H and ^{13}C NMR spectra (500 MHz and 125 MHz, respectively) of DTQ_{open} (a, c) and $\text{DTQ}_{\text{closed}}$ (b, d) in CDCl_3 at room temperature.

7. Absorption spectral changes of DTQ_{open} upon photoirradiation with UV light

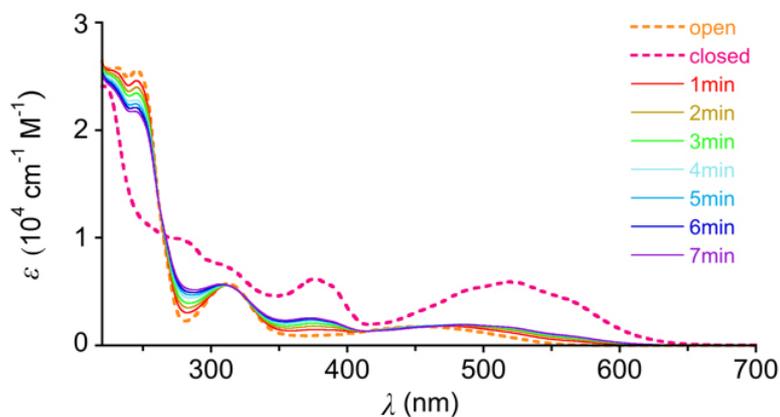


Fig. S3 Absorption spectral changes of cyclohexane solutions of DTQ_{open} upon photoirradiation with 320 nm light at 20 °C. The spectra were taken on the concentration at 4.0×10^{-5} M.

8. ¹H NMR spectral changes of DTQ_{closed} upon photoirradiation with visible light

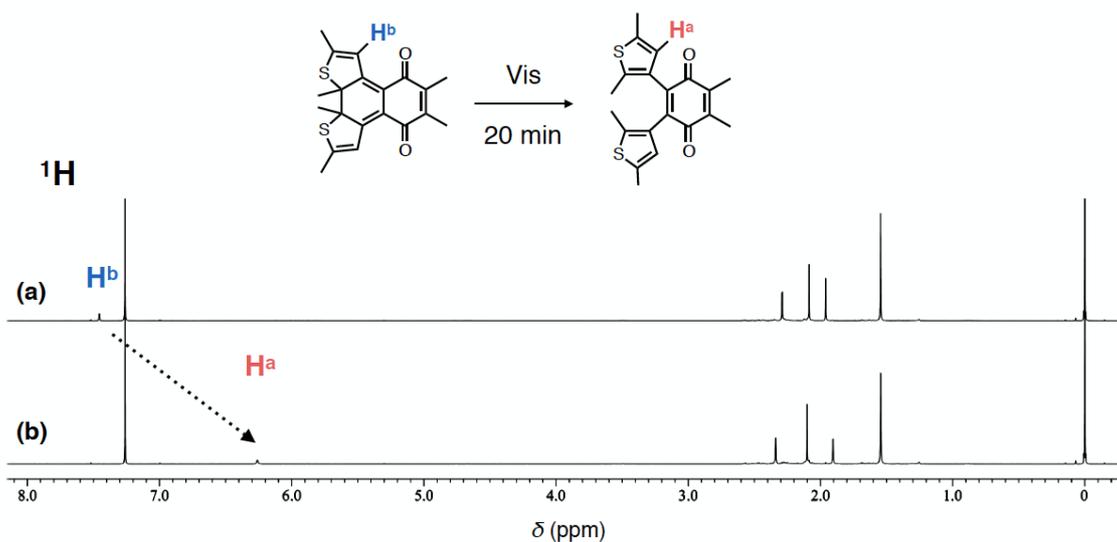


Fig. S4 ¹H NMR spectral (400 MHz) changes of DTQ_{closed} after photoirradiation with visible light ($\lambda > 380$ nm) for 20 min in CDCl₃ at room temperature.

9. ^1H NMR spectrum of $\text{DTQ}_{\text{closed}}$ after standing for 14 days

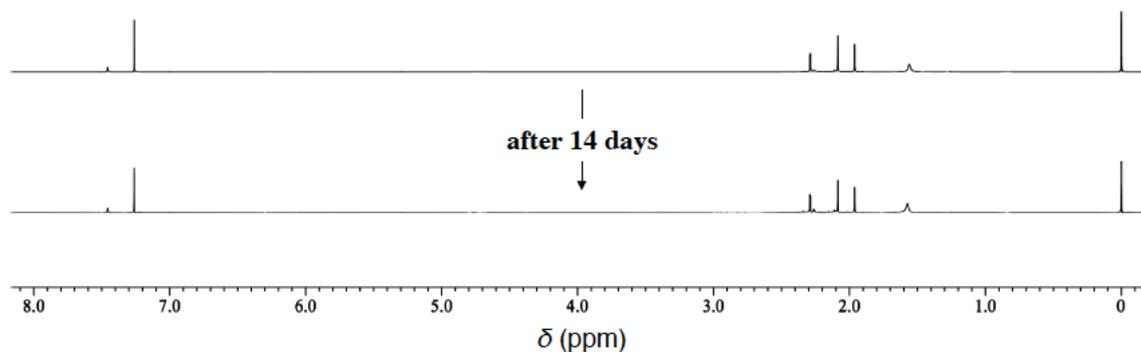


Fig. S5 ^1H NMR spectra of a CDCl_3 solution of $\text{DTQ}_{\text{closed}}$ before and after standing for 14 days in the dark at room temperature.

10. Reversible changes of the photoisomerization in absorption spectroscopy

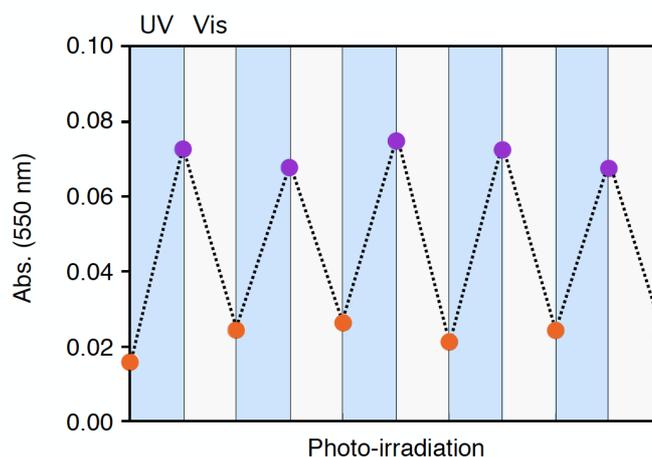
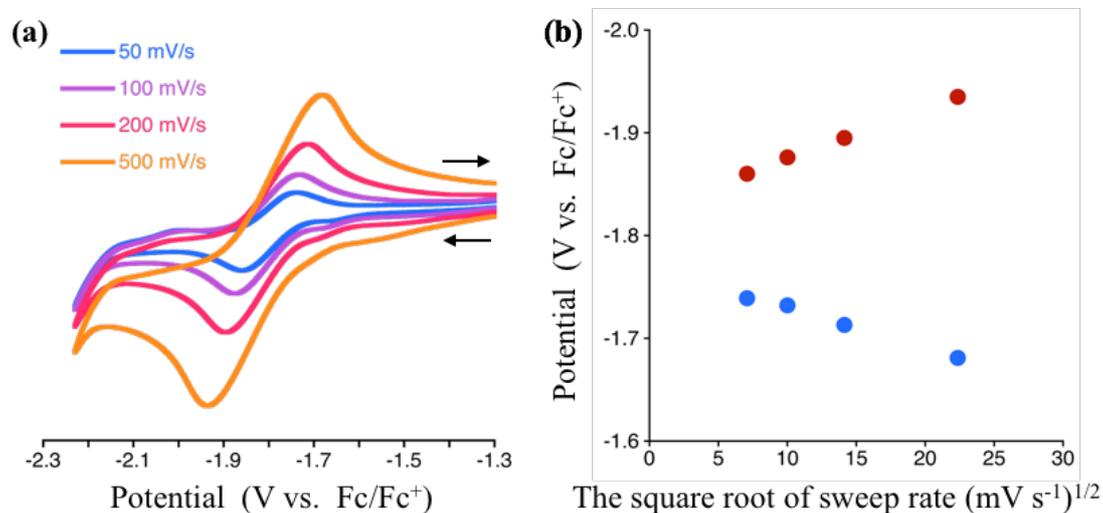


Fig. S6 Reversible changes of the absorbance of DTQ at 550 nm through sequential 3 min photo-irradiations with UV ($\lambda = 320$ nm) and visible light ($\lambda = 550$ nm) at 20°C . $[\text{DTQ}] = 8.0 \times 10^{-5}$ M.

11. Cyclic voltammetry of DTQ_{closed}



The Cathode's liner plot; $y = -0.0049x - 1.8263$ ($R^2 = 0.99949$)

The Anode's liner plot; $y = 0.0039x - 1.7684$ ($R^2 = 0.99497$)

$$\Delta E_p = E_{pa} - E_{pc} = -176.84 - (-182.63) = 57.9 \text{ (mV)}$$

$$= 2.3 \frac{RT}{nF} = \frac{59}{n} (25^\circ\text{C})^8$$

$$n \text{ (= electron number)} = 1.02 \approx 1$$

Fig. S7 Estimation of electron number (n) in cyclic voltammogram of DTQ_{closed} from (a) variable scan rate (50-500 mV/s) of cyclic voltammograms, and (b) plots of E_{pa} and E_{pc} values (blue and red circle, respectively) with respect to the square root of scan rate.

12. Spin densities of $\text{DTQ}_{\text{open}}^{\cdot-}$ and $\text{DTQ}_{\text{closed}}^{\cdot-}$ in DFT calculations

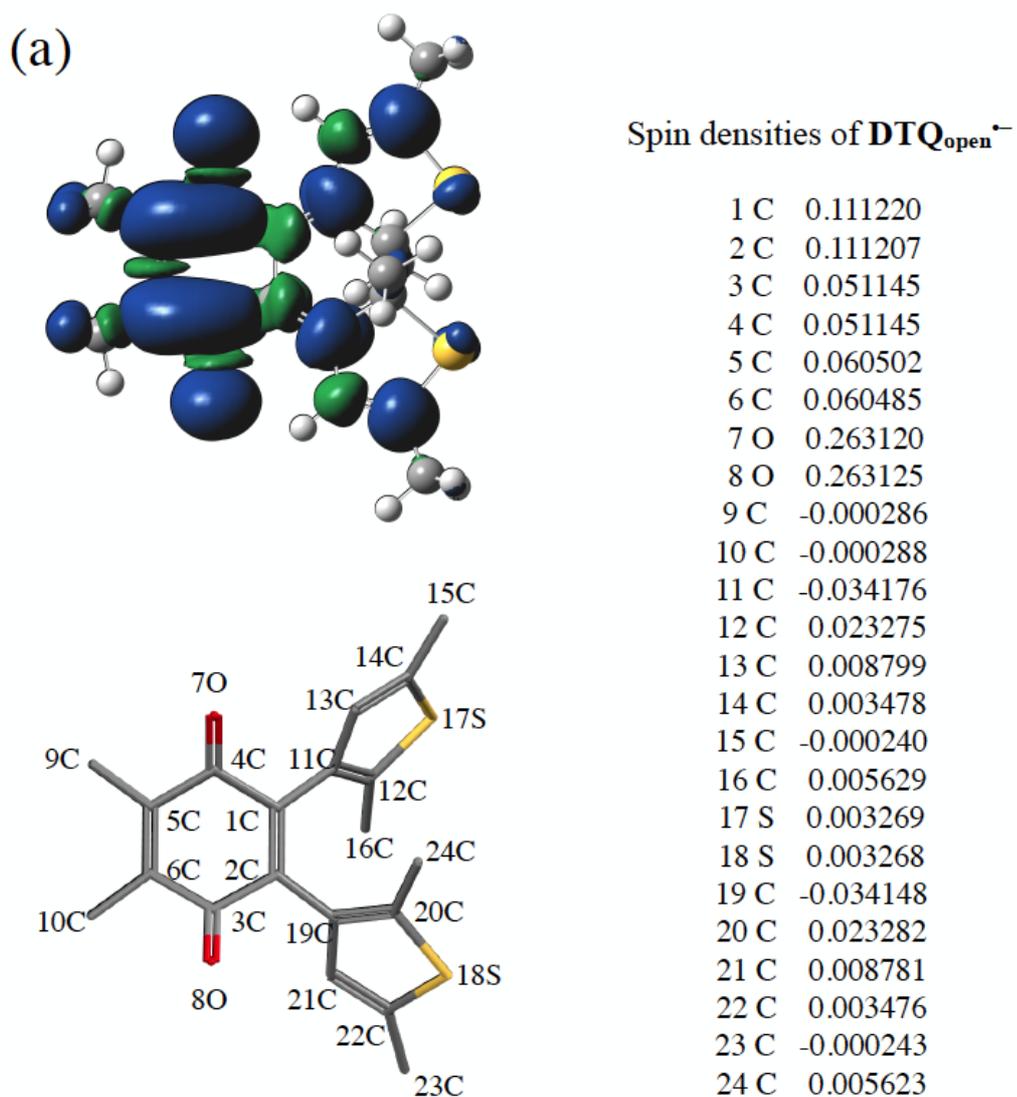


Fig. S8 Calculated spin densities of (a) $\text{DTQ}_{\text{open}}^{\cdot-}$ and (b) $\text{DTQ}_{\text{closed}}^{\cdot-}$ in DFT with UB3LYP/6-311+G(d,p) level.

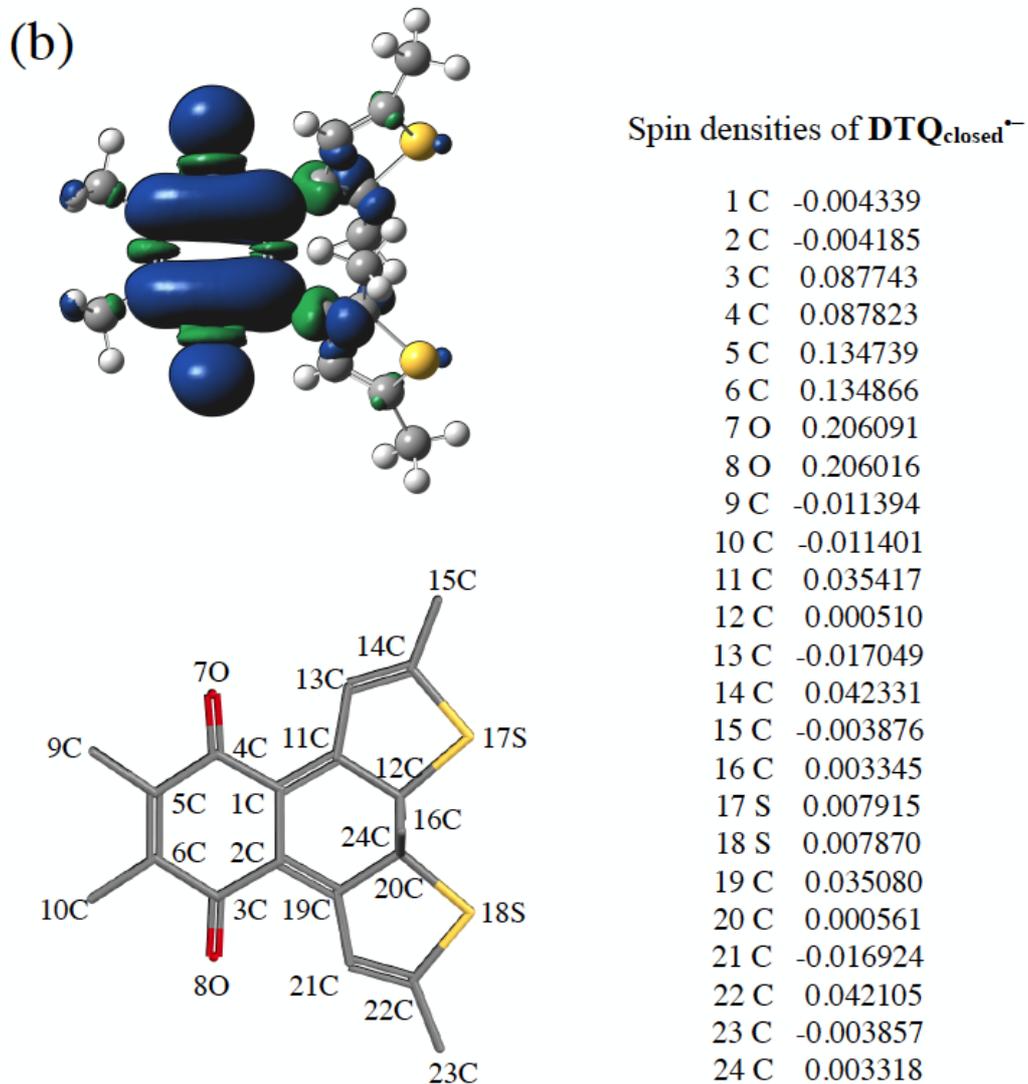


Fig. S8 (continued) Calculated spin densities of (a) $\text{DTQ}_{\text{open}}^{\bullet-}$ and (b) $\text{DTQ}_{\text{closed}}^{\bullet-}$ in DFT with UB3LYP/6-311+G(d,p) level.

13. Cyclic voltammetry of Me₄Q

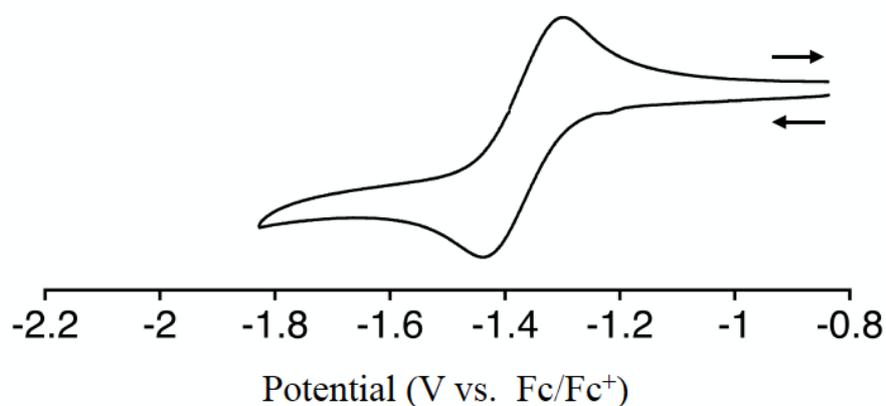


Fig. S9 A redox profile in cyclic voltammetry (V vs Fc/Fc⁺) of Me₄Q in CH₂Cl₂. Scan rate, 100 mV s⁻¹; working electrode, Pt; supporting electrolyte, 0.1 M Bu₄NClO₄.

14. ¹H NMR spectral changes of DTQ_{open} upon mixing with Me₄HQ

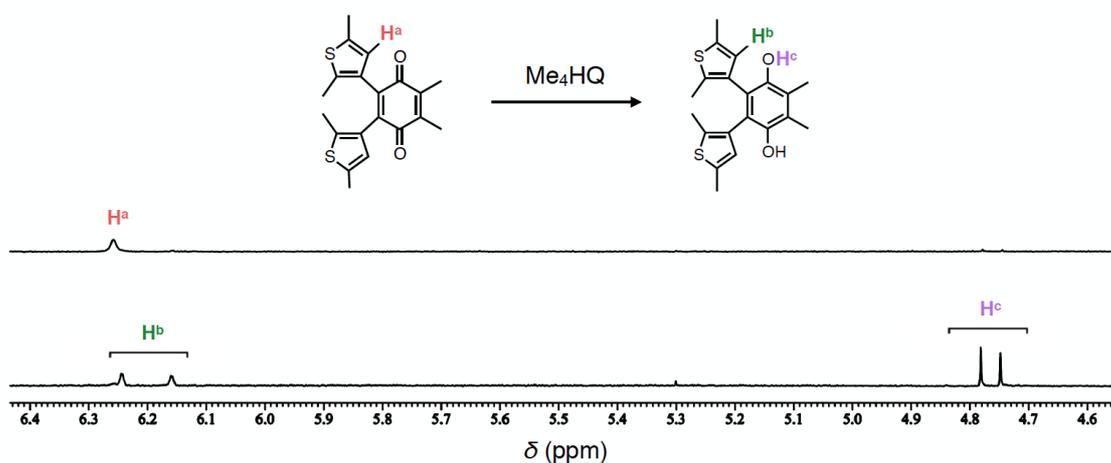


Fig. S10 ¹H NMR spectral (400 MHz) changes of DTQ_{open} upon mixing with 10 equiv. amounts of Me₄HQ after stirring for 4 h in the dark at room temperature.

15. H-H NOESY spectrum of DTHQ

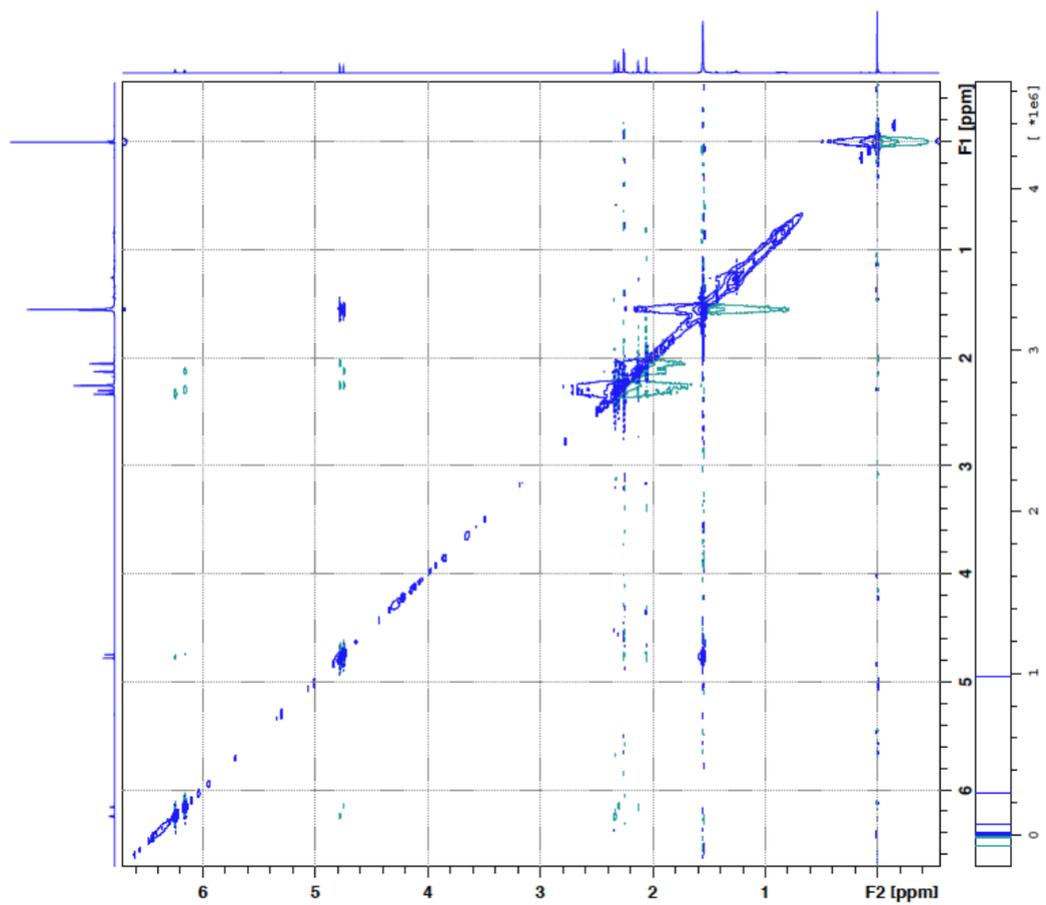


Fig. S11 H-H NOESY spectrum (400 MHz) of **DTHQ** in CDCl₃ at room temperature.

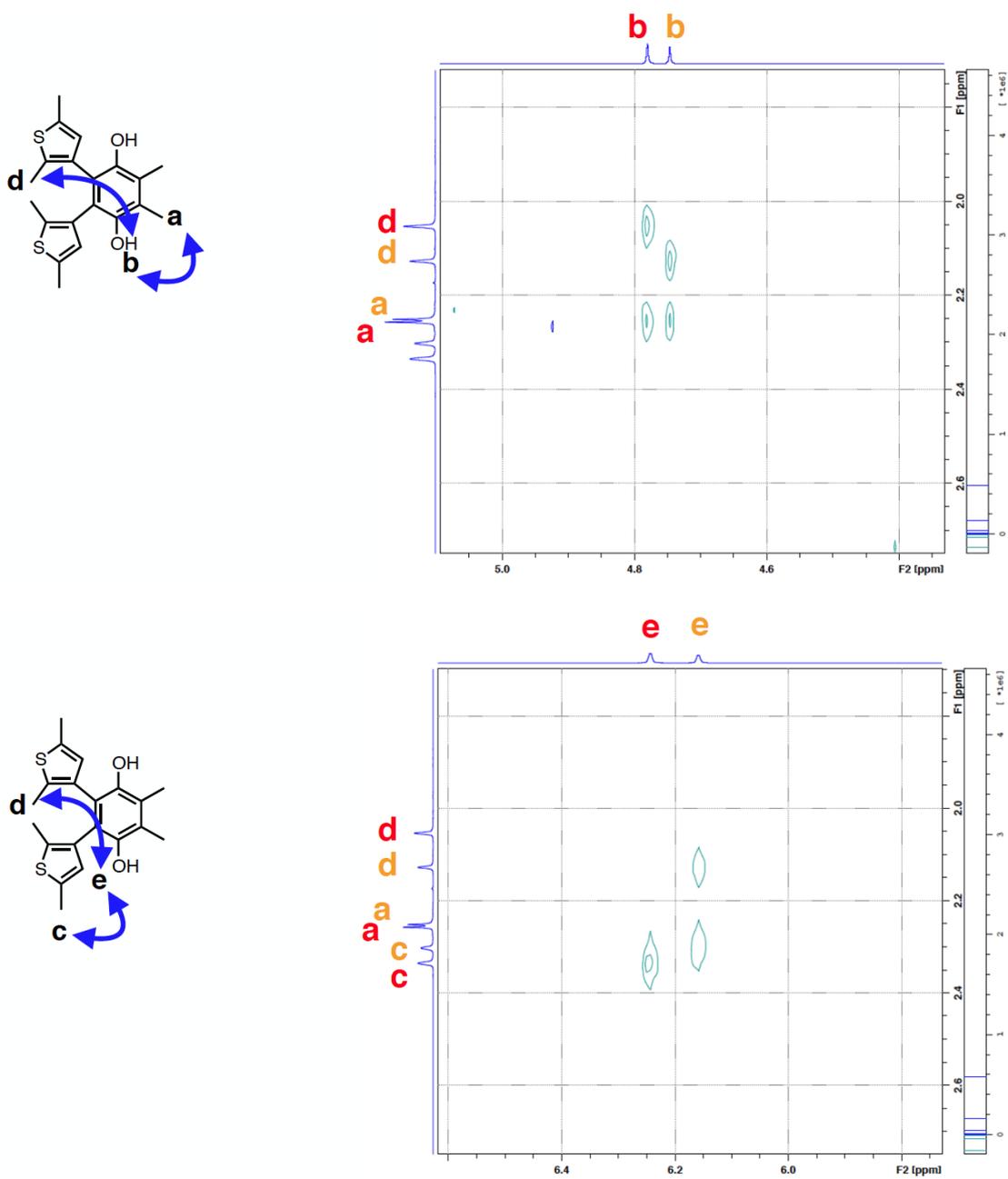


Fig. S11 (continued) Magnified H-H NOESY spectrum (400 MHz) of **DTHQ** in CDCl₃ at room temperature.

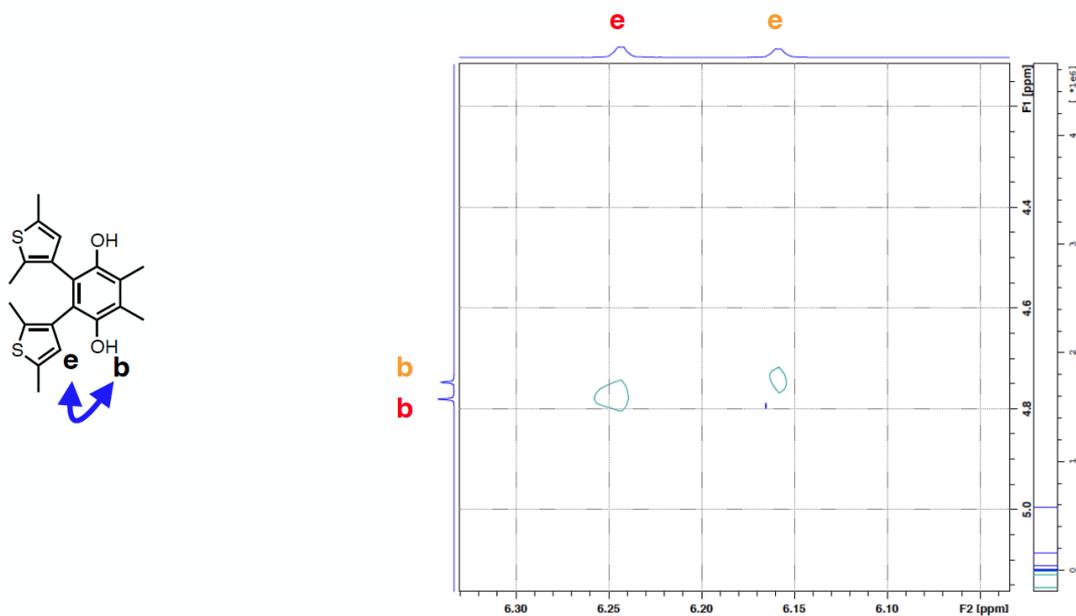


Fig. S11 (continued) Magnified H-H NOESY spectrum (400 MHz) of **DTHQ** in CDCl_3 at room temperature.

16. ESI-FT-MS of DTHQ

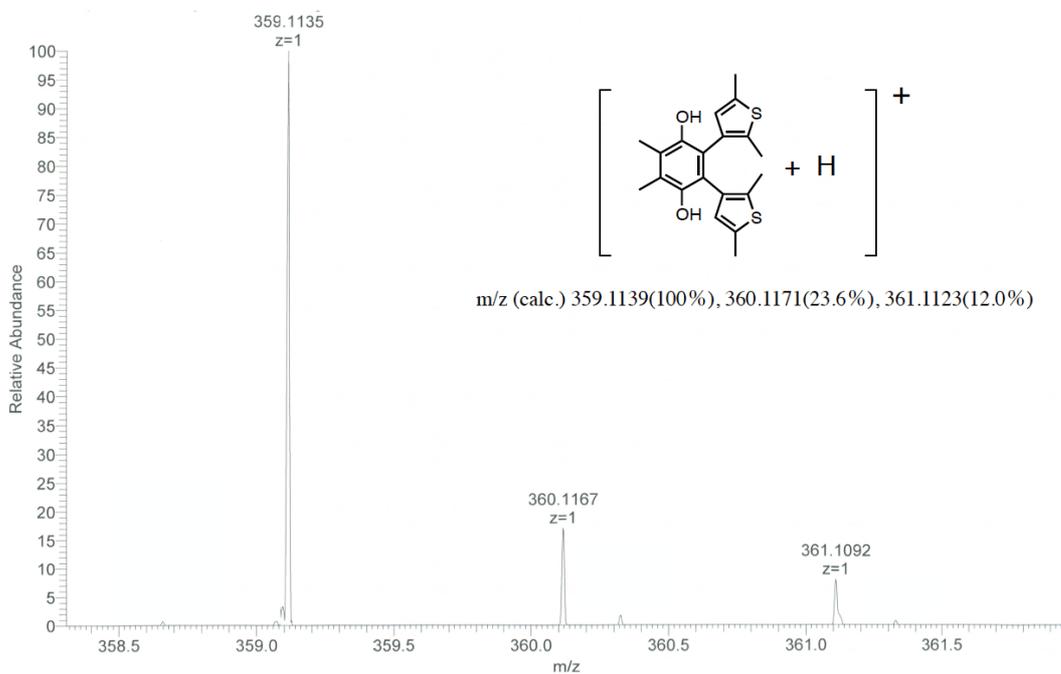


Fig. S12 Electrospray fourier transform mass spectral profile of a methanol solution of **DTHQ**.

17. ^1H NMR spectral changes of DTHQ upon mixing with Ag_2O

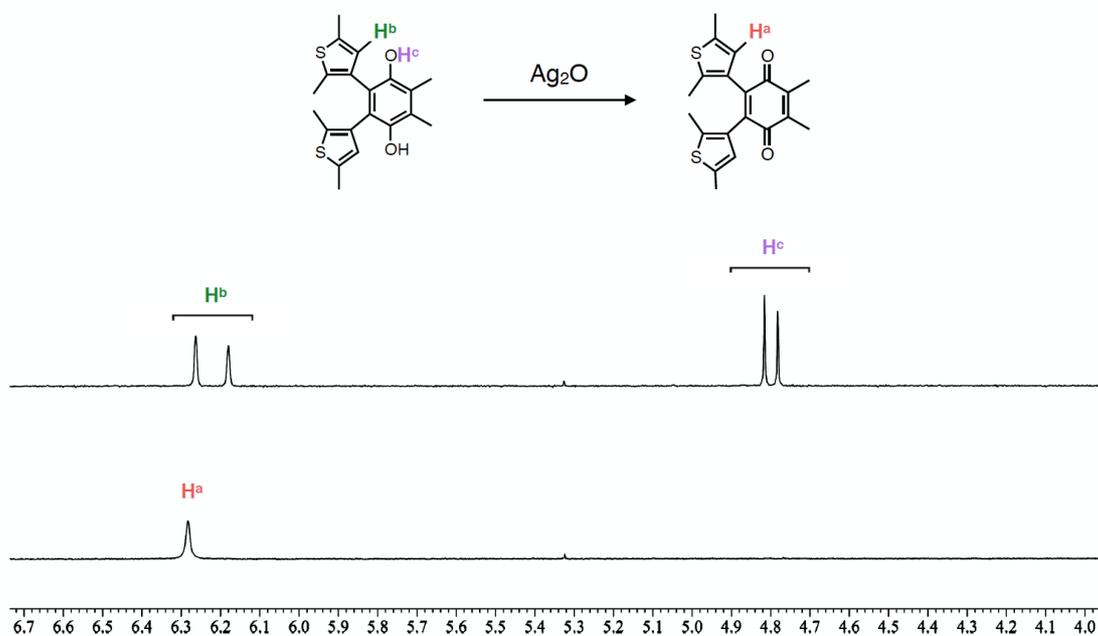


Fig. S13 ^1H NMR spectral (400 MHz) changes of **DTHQ** upon mixing with 1.2 equiv. amounts of Ag_2O after stirring for 3 h at room temperature.

18. ^1H and ^{13}C NMR spectra and H–H COSY spectra

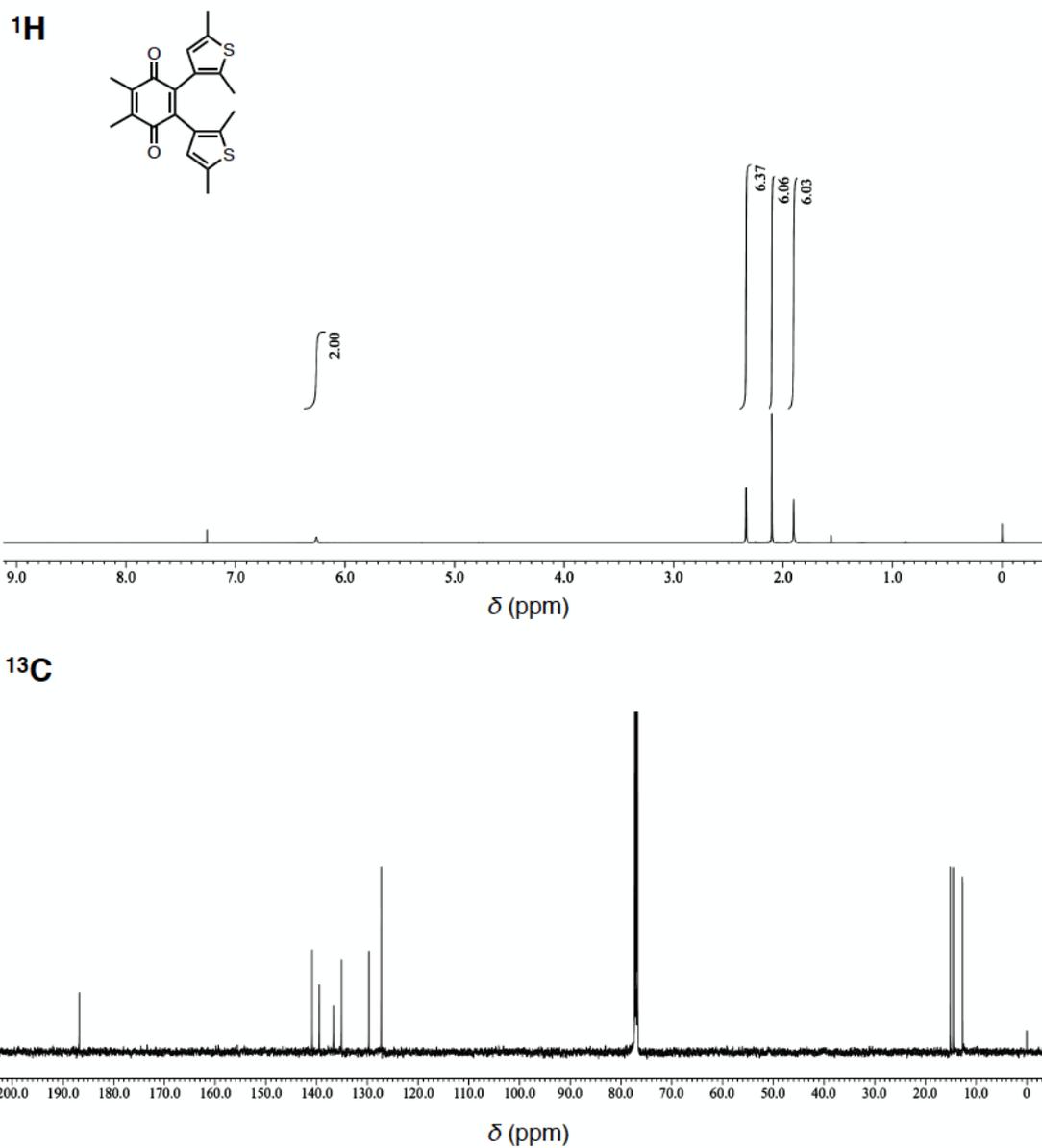


Fig. S14 ^1H and ^{13}C NMR spectra (500 MHz and 125 MHz, respectively) of DTQ_{open} in CDCl_3 at room temperature.

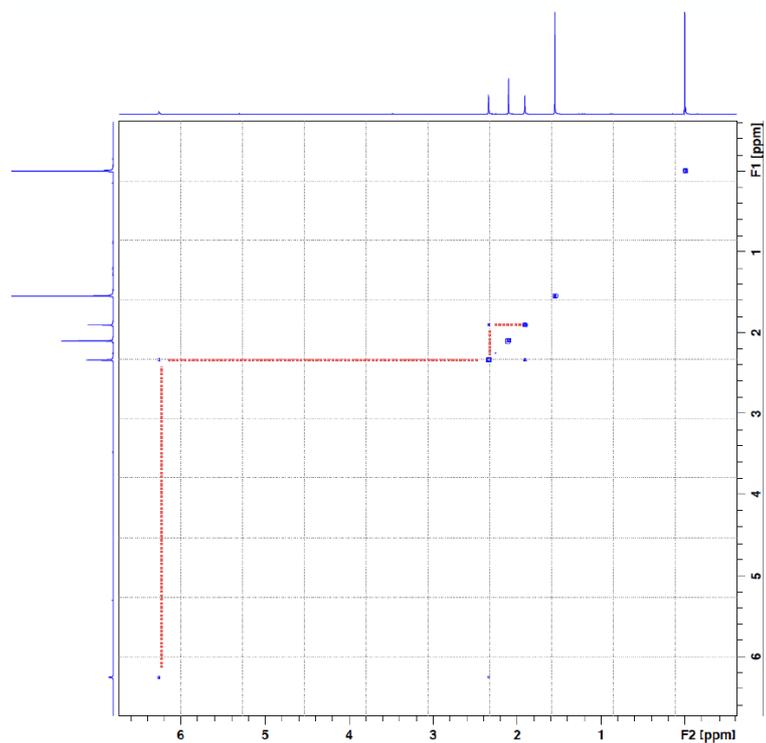


Fig. S15 H-H COSY spectrum (400 MHz) of **DTQ_{open}** in CDCl₃ at room temperature.

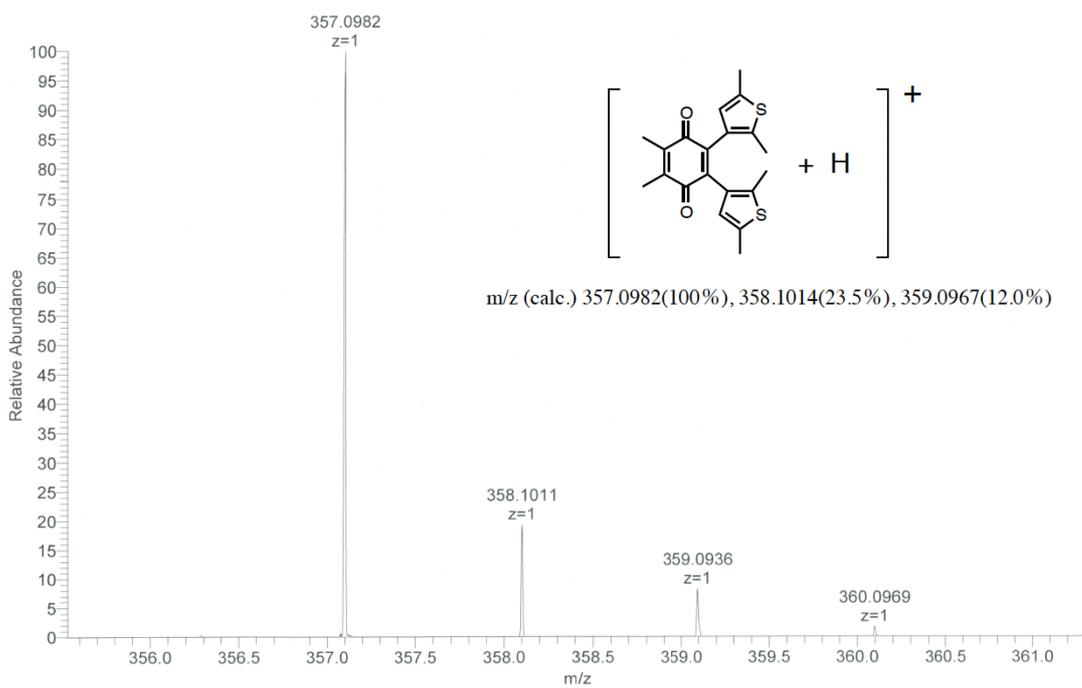


Fig. S16 Electrospray fourier transform mass spectral profile of a methanol solution of **DTQ_{open}**.

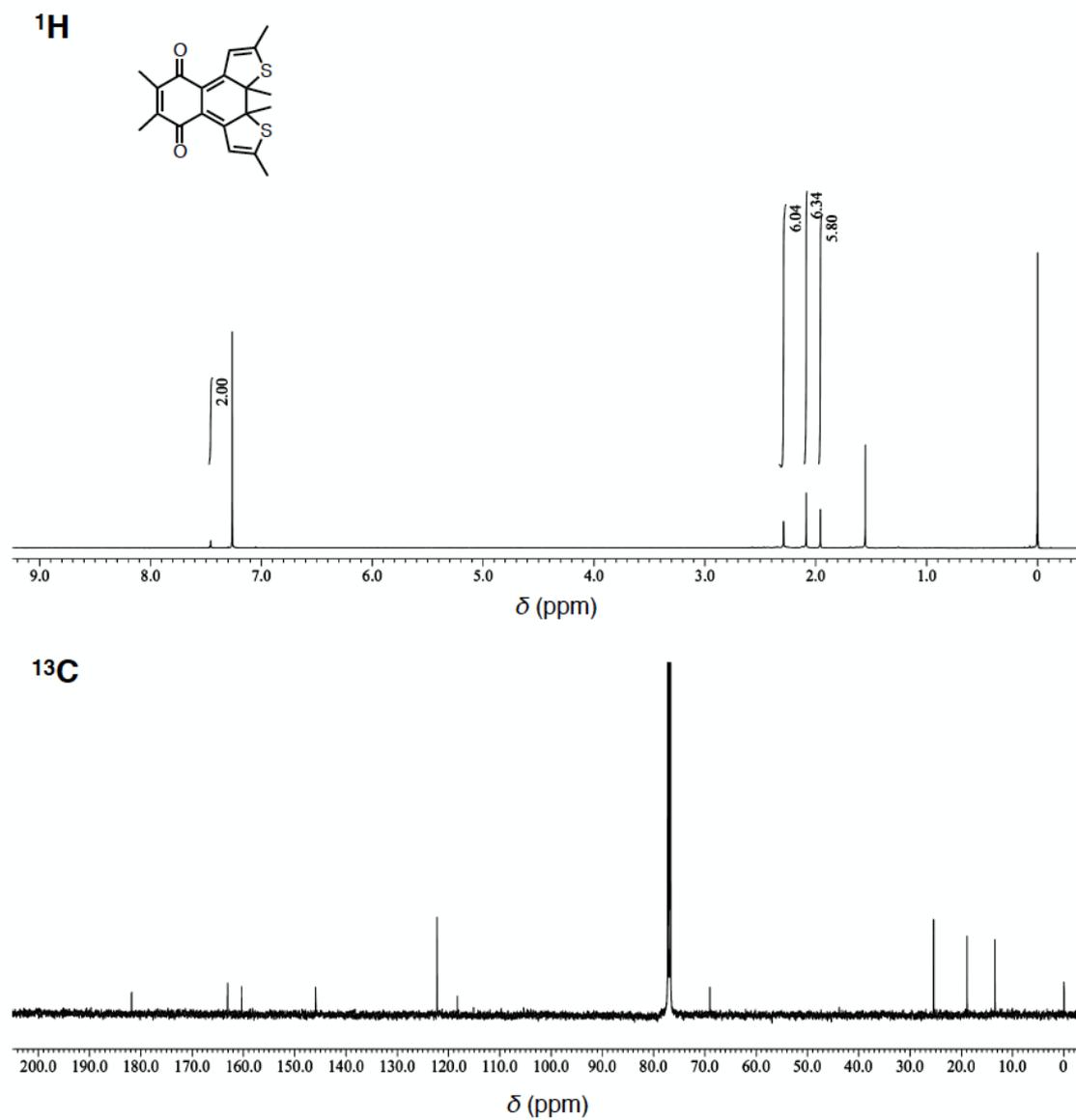


Fig. S17 ¹H and ¹³C NMR spectra (500 MHz and 125 MHz, respectively) of **DTQ_{closed}** in CDCl₃ at room temperature.

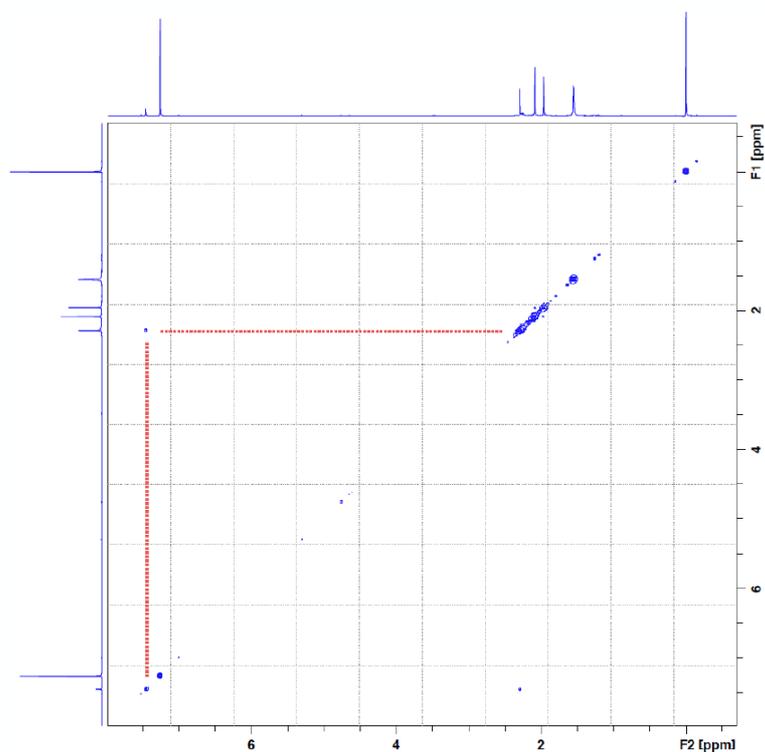


Fig. S18 H-H COSY spectrum (400 MHz) of **DTQ_{closed}** in CDCl_3 at room temperature.

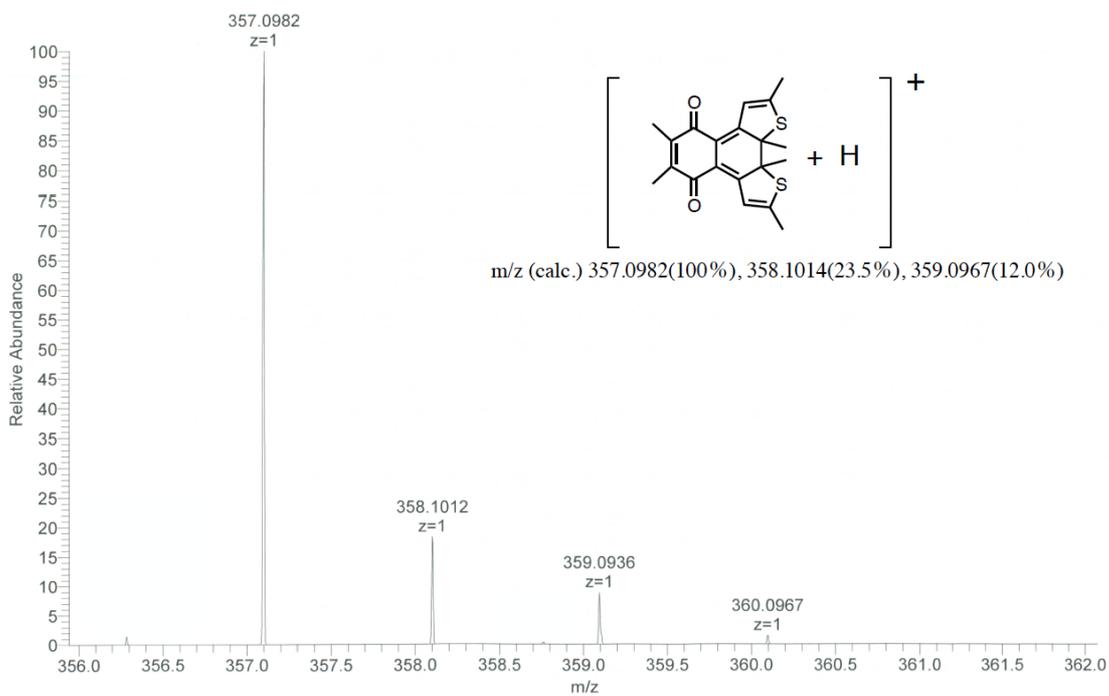


Fig. S19 Electrospray fourier transform mass spectral profile of a methanol solution of **DTQ_{closed}**.

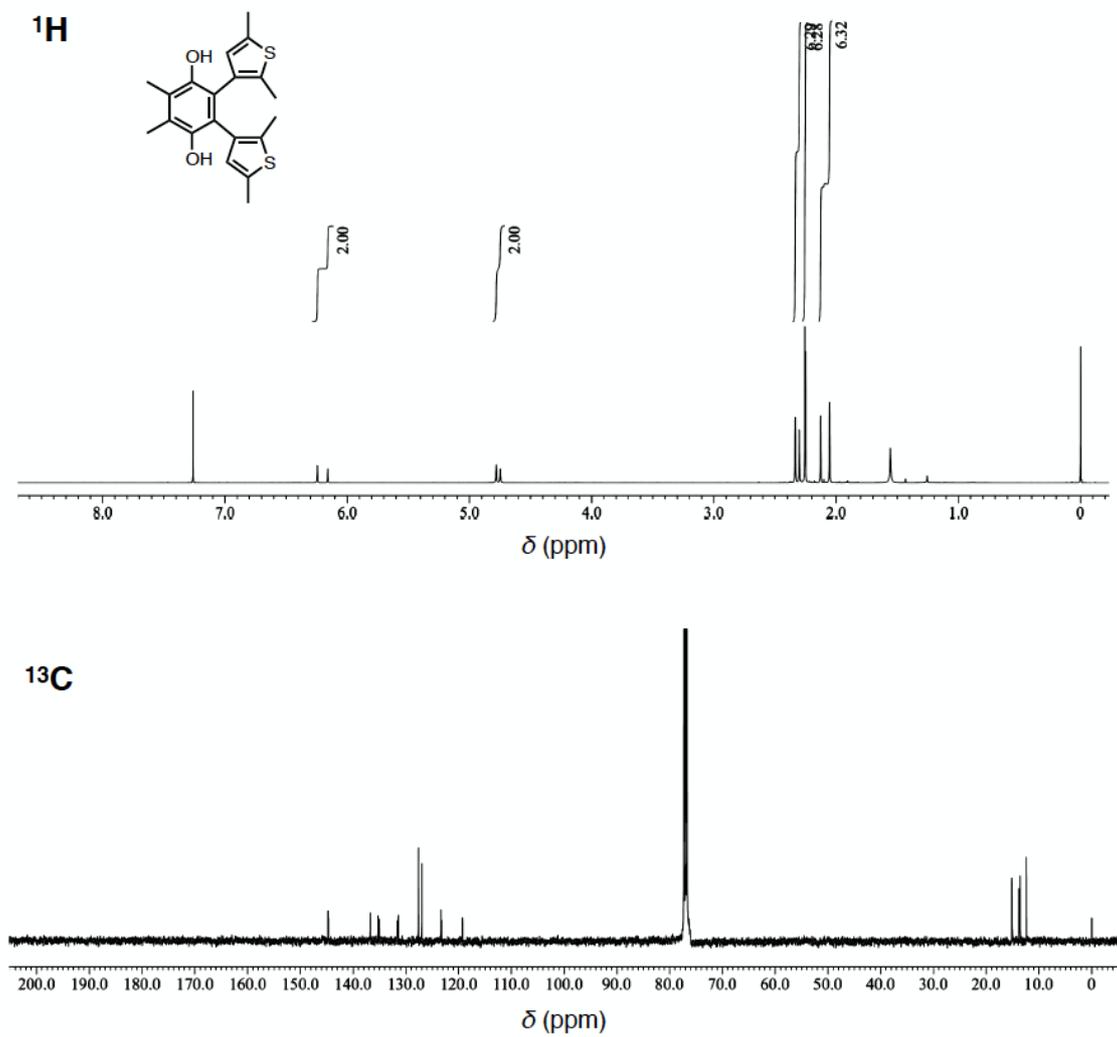


Fig. S20 ¹H and ¹³C NMR spectra (500 MHz and 125 MHz, respectively) of **DTHQ** in CDCl₃ at room temperature.

19. References

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