Electronic Supplementary Material (ESI) for Chemical Communications

NTCDA-TTF First Axial Fusion: Emergent Panchromatic, NIR Optical, Multi-state Redox and High Optical Contrast Photooxidation

Deepak Asthana,[a] M. R. Ajayakumar,[a] Rajendra Prasad Pant[b] and Pritam Mukhopadhyay*[a]

Supramolecular and Material Chemistry Lab, School of Physical Sciences,

Jawaharlal Nehru University,New Delhi 110067

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Experimental Details:

General: All the starting materials were obtained from Sigma Aldrich or Spectrochem India and were used as received. All solvents were made oxygen free prior to use by freeze-thaw-pump cycle. Compound **1** and **2** were prepared as described in literature.[1] Phosphite mediated cross-coupling of NTCDA and PMDA with **2** was carried out following a reported procedure.[2] Thin layer chromatography (TLC) was carried out on aluminum plates coated with silica gel mixed with fluorescent indicator having particle size of 25 μm and was sourced from Sigma Aldrich. NMR spectra were recorded in $CDCl_3$ on a Bruker spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C, DEPT-135 and APT with TMS as an internal standard. Coupling constants (*J* values) are given in terms of Hz and chemical shifts are reported in parts per million (ppm). Splitting patterns are designated as s (singlet), d (doublet), t (triplet) and merged triplets. For irradiation, a hand held UV light (365 nm, Spectroline, model ENF-280C/FE) was used. MALDI-TOF mass spectral data were obtained using a Bruker made Autoflex TOF/TOF instrument and α-Cyano-4-hydroxycinnamic acid as the matrix. Infra Red spectra were recorded in KBr pellets using a Varian 7000 FT-IR instrument. The UV-vis absorption spectra were taken using a JASCO V-600 model spectrometer. The steady state fluorescence spectra were measured using a Varian Cary Eclipse Fluorescence Spectrometer.

Electrochemistry: The electrochemical properties were studied using a computer-controlled potentiostat (CHI 650C) and a standard three electrode arrangement that consisted of both platinum working and auxiliary electrodes and a saturated calomel reference electrode. All electrochemical measurements were carried out in Ar-purged dry DCM with 0.1 M Bu_4NPF_6 as the supporting electrolyte. The scan rate for cyclic voltametry (CV) experiments was typically 200-300 mV/s. Differential Pulse Voltametry (DPV) was carried out keeping peak amplitude 50 mV, peak width 0.01 sec, pulse period 0.05 sec and increment E at 20 mV.

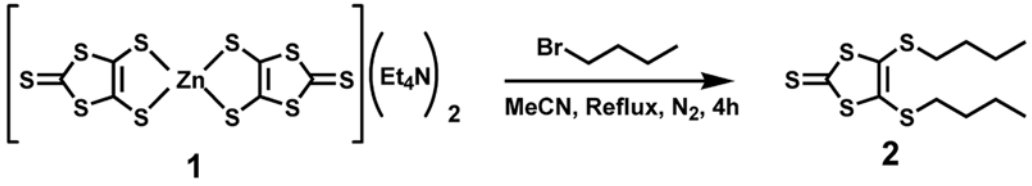
Quantum Yield: Quantum yields were calculated using cresyl violate perchlorate in MeOH (excited at 575 nm) as reference (ø = 0.54) following the relation:

$$\phi = \phi_R \left(\frac{A_R}{F_R}\frac{F}{A}\right)\left(\frac{\eta}{\eta_R}\right)^2$$

where, ϕ_R is the quantum yield of reference compound, A is absorbance at excitation wavelength, F is the area under fluorescence peak, η is refractive index of solvent and subscripts 'R' stand for the reference. [S. J. Isak et al, *J. Phys. Chem*. 1992, **96**, 1738].

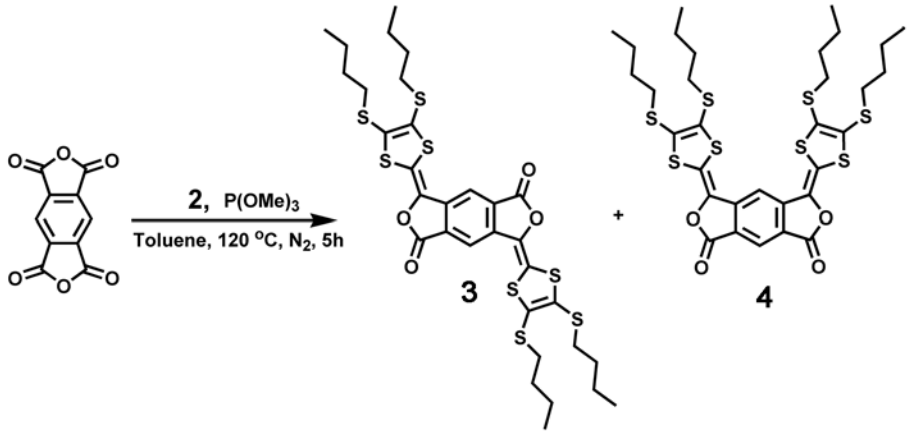
EPR: Electron Paramagnetic Resonance (EPR) spectra were recorded using Bruker EMX 1444 EPR spectrometer operating at 9.455 GHz. Diphenylpicrylhydrazyl, DPPH (*g* = 2.0037), was used for the calibration of EPR spectrometer.

Synthesis of 2:



Synthetic Procedure: In a 250 ml round bottomed (RB) flask containing 110 ml of freshly dried MeCN, **1** (6.3 g, 8.8 mmol) and n-butyl bromide (4.7 ml, 44 mmol) was refluxed for 4 hours under N_2 atmosphere. The reaction mixture was filtered and the filtrate was evaporated using a rotary evaporator. The residue was dissolved in DCM and the organic layer was washed with water (3 x 1oo ml) and dried over Na_2SO_4. The solvent was evaporated to give a viscous orange colored liquid which was purified by column chromatography (silica, n-hexane) to yield **2** as a yellow colored liquid. Yield: 87%. R_f = 0.85 (n-hexane/EtOAc, 8:2). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 2.84 (t [two triplets merged], 4H, *J* = 7.0 Hz; 7.5 Hz, SCH_2), 1.62-1.58 (m, 4H, SCH_2CH_2), 1.39-1.44 (m, 4H, $SCH_2CH_2CH_2$), 0.89 (t [two triplets merged], 6H, *J* = 7.0 Hz; 7.5 Hz, SCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 136.32, 36.50, 31.70, 21.70, 13.62.

Procedure for Synthesis of 3 and 4:

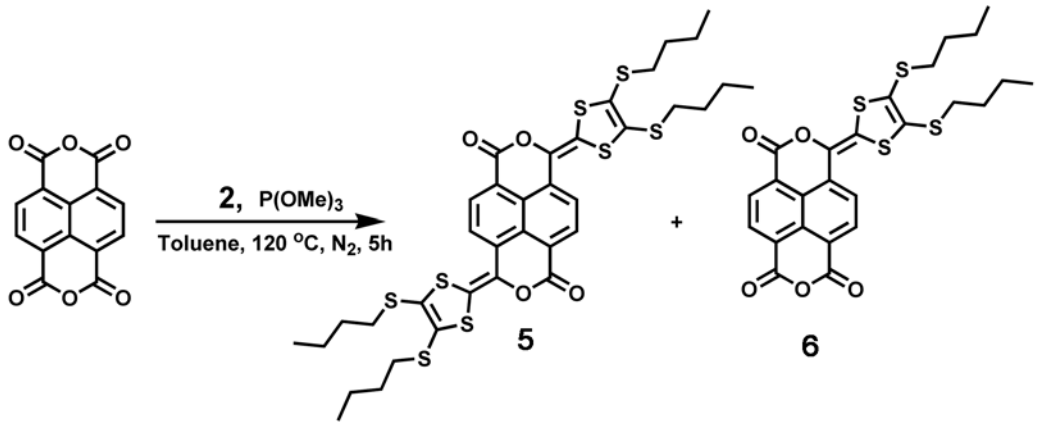


Synthetic Procedure: In a 250 ml round bottomed (RB) flask containing 120 ml freshly dried toluene, PMDA (1.12 g, 5.15 mmol) and **2** (4.00 g, 12.8 mmol) were added. Freshly distilled $P(OMe)_3$ (18.2 ml) was then added to this solution. The mixture was stirred at 120 ^{o}C under N_2 atmosphere. After 5 hours the reaction mixture was gradually brought to room temperature and filtered. Solvent was evaporated using a rotary evaporator. The crude material was purified by column chromatography (silica, n-hexane/DCM) to yield **3** (28%) as a dark brown colored solid and **4** (20%) as a reddish-brown colored solid.

Compound 3: R_f = 0.84 (7:3 DCM/n-hexane). Melting Point: 150 °C (decompose). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 7.94 (s, 2H, ArH), 2.92 (t, 4H, *J* = 7 Hz, SCH_2), 2.90 (t, 4H, *J* = 7.5 Hz, SCH_2), 1.70-1.66 (m, 8H, SCH_2CH_2), 1.51-1.44 (m, 8H, $SCH_2CH_2CH_2$), 0.95 (t, 6H, *J* = 7.0 Hz, CH_3), 0.94 (t, 6H, *J* = 7.0 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 164.36, 132.91, 130.83, 129.88, 127.55, 126.68, 123.00, 118.49, 36.20, 36.03, 31.86, 31.68, 21.69, 13.65. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): 744 (m/z). FTIR (KBr, cm^{-1}): 3422, 2957, 2928, 2872, 1784, 1601, 1491, 1437, 1360, 1234. Anal. Calcd. for $C_{32}H_{38}O_4S_8$: C, 51.72; H, 5.15; O, 8.61; S, 34.52. Anal. Found C, 51.47; H, 5.35.

Compound 4: R_f = 0.2 (7:3 DCM/n-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.41 (s, 1H, ArH), 7.23 (s, 1H, ArH), 2.93 (t [two triplets merged], 8H, *J* = 7.0 Hz, *J* = 7.5 Hz, SCH_2), 1.75-1.63 (m, 8H, SCH_2CH_2), 1.55-1.40 (m, 8H, $SCH_2CH_2CH_2$), 0.97-0.89 (t [two triplets merged], 12H, *J* = 7.0 Hz, *J* = 7.0 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 163.92, 139.44, 131.67, 131.08, 125 .59, 125.35, 120.49, 111.66, 36.37, 36.04, 33.84, 31.88, 31.70, 21.70, 13.67. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): 743.9 (m/z). FTIR (KBr, cm^{-1}): 3429, 2957, 2958, 2851, 1784, 1773, 1653, 1616, 1578, 1458, 1305, 1127. Anal. Calcd. for $C_{32}H_{38}O_4S_8$: C, 51.72; H, 5.15; O, 8.61; S, 34.52. Anal. Found: C, 51.43; H 5.53.

Procedure for Synthesis of 5 and 6:

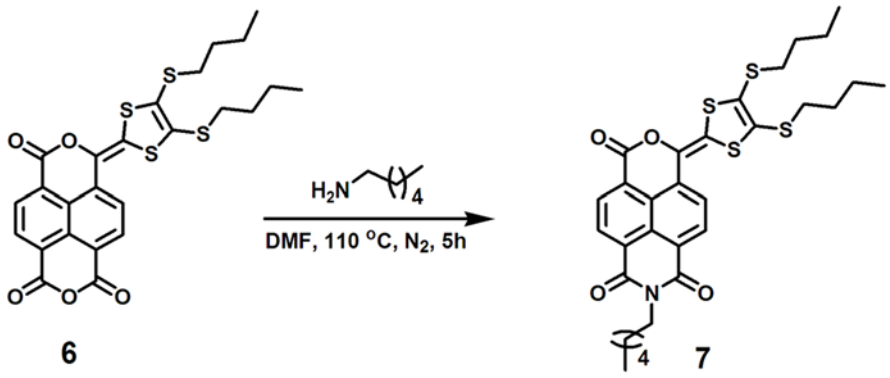


Synthetic Procedure: To a solution of NTCDA (0.175 g, 0.65 mmol) in 30 ml of freshly dried toluene, compound **2** (0.5 g, 1.6 mmol) was added. Subsequently freshly distilled $P(OMe)_3$ (2.3 ml) was added and mixture was stirred at 120 °C under N_2 atmosphere. After 5 hours, the reaction mixture was gradually brought to room temperature and filtered. The deep blue colored solution was evaporated to dryness using a rotary evaporator. The crude material was purified by column chromatography (silica, n-hexane/DCM) to yield **5** (24%) as a dark blue colored solid and **6** (26%) as a blue colored solid.

5: R_f = 0.52 (7:3 DCM/n-hexane). Melting Point: 230 °C (decompose). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.42 (d, 2H, *J* = 8 Hz, ArH), 7.39 (d, 2H, *J* = 8Hz, ArH), 2.97 (t, 4H, *J* = 7.5 Hz, SCH_2), 2.92 (t, 4H, *J* = 7.5 Hz, SCH_2), 1.71-1.65 (m, 8H, SCH_2CH_2), 1.52-1.45 (m, 8H, $SCH_2CH_2CH_2$), 0.95 (t [two triplets merged], 12H, *J* = 7.5 Hz, *J* = 7.0 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 158.91, 133.66, 133.21, 129.41, 127.56, 127.29, 126.79, 124.98, 121.41, 115.25, 36.37, 35.87, 31.86, 31.71, 21.72, 13.65. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): 794 (m/z). FTIR (KBr, cm^{-1}): 3447, 2955, 2928, 2858, 1767, 1742, 1653, 1527, 1508, 1481, 1331, 1259, 1130. Anal. Calcd. for $C_{36}H_{40}O_4S_8$: C, 54.51; H, 5.08; O, 8.07; S, 32.34. Anal. Found: C, 54.37; H, 5.25.

6: R_f = 0.16 (7:3 DCM/n-hexane). Melting Point: 210 °C (decompose). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.71 (d, 1H, *J* = 7.5 Hz, ArH), 8.63 (d, 1H, *J* = 8.5 Hz, ArH), 8.53 (d, 1H, *J* = 7.5 Hz, ArH), 7.44 (d, 1H, *J* = 8.5 Hz, ArH), 3.02 (t, 2H, *J* = 7.5 Hz, SCH_2), 2.97 (t, 2H, *J* = 7.0 Hz, SCH_2) 1.75-1.68 (m, 4H, SCH_2CH_2), 1.55-1.48 (m, 4H, $SCH_2CH_2CH_2$), 0.97 and 0.98 (t [two triplets merged], 6H, *J* = 7.5 Hz, *J* = 7.0 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 159.77, 159.43, 159.26, 157.14, 134.56, 134.10, 133.93, 133.17, 132.96, 132.80, 130.60, 127.80, 127.65, 126.65,126.48, 125.55, 122.41, 122.25, 120.40, 112.96, 36.60, 36.15, 31.80, 31.69, 21.68, 13.59, 13.40. MS (MALDI-TOF, matrix-α-cyano-4-hydroxycinnamic acid): 531 (m/z). FTIR (KBr, cm^{-1}): 3447, 2959, 2930, 2872, 1767, 1742, 1595, 1510, 1477, 1381, 1344, 1253. Anal. Calcd. for $C_{25}H_{22}O_5S_4$: C, 56.58; H, 4.18; O, 15.07; S, 24.17. Anal. Found: C, 56.73; H 4.25.

Procedure for Synthesis of 7:



Synthetic Procedure: To a solution of compound **6** in DMF was added hexyl amine. Mixture was heated at 110 °C under N_2 atmosphere for 5 hours. Solvent was removed under high vacuum. Crude solid was purified by column chromatography (silica, n-hexane/DCM) to yield **7**.

7: R_f = 0.36 (9:1 n-hexane/EtOAc). Yield = 74%. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.74 (d, 1H, *J* = 7.5 Hz, ArH), 8.68 (d, 1H, *J* = 8.0 Hz, 1H, ArH), 8.55 (d, 1H, *J* = 7.5 Hz, ArH), 7.48 (d, 1H, *J* = 8.0 Hz, ArH), 4.19 (t, 2H, *J* = 7.0 Hz, NCH_2), 2.99 (t, 2H, *J* = 7.5 Hz, SCH_2), 2.94 (t, 2H, *J* = 7.0 Hz, SCH_2), 1.74-1.66 (m, 6H, SCH_2CH_2 and NCH_2CH_2), 1.51-1.44 (m, 6H, $SCH_2CH_2CH_2$ and N $CH_2CH_2CH_2$), 1.40-1.30 (m, 4H, $NCH_2CH_2CH_2CH_2CH_2$), 0.97-0.94 (t [three triplets merged] 9H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 163.11, 163.03, 157.95, 133.87, 133.29, 131.97, 130.99, 130.89, 127.82, 127.77, 126.51, 126.29, 126.15, 125.65, 124.03, 120.61, 117.58. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): 614 (m/z). Anal. Calcd. For $C_{31}H_{35}NO_4S_4$: C, 60.65; H, 5.75; N, 2.28; O, 10.43; S, 20.89. Anal. Found: C, 60.80; H 5.95.

Optimized geometry, theoretically calculated HOMO-LUMO energy levels, dihedral angles of 3-7:

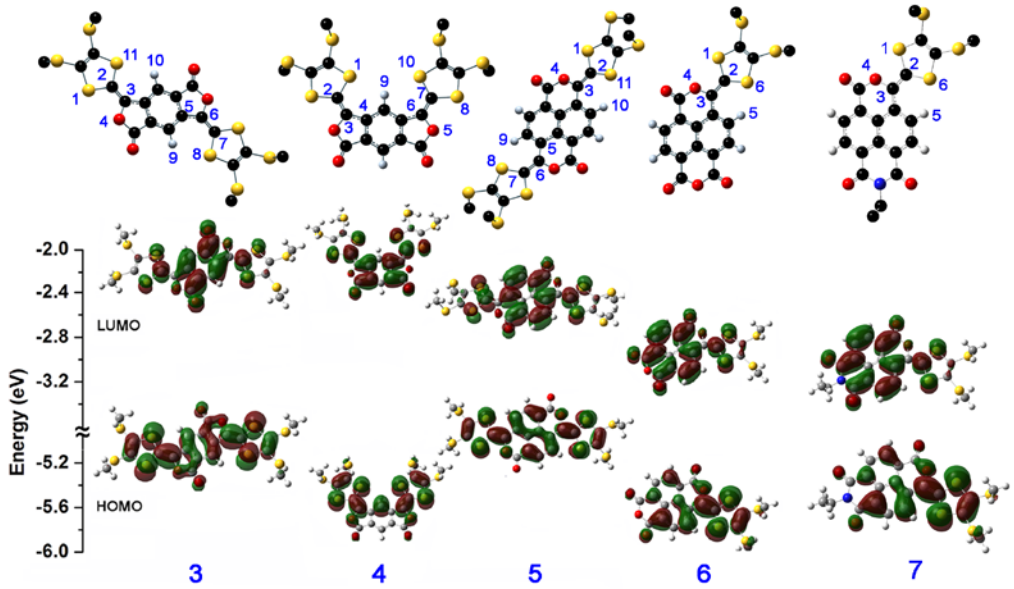


Figure S1: Theoretical HOMO-LUMO orbital and energy levels.

	HOMO ^{calc}/ HOMO ^{exp} (eV)	LUMO ^{calc}/ LUMO ^{exp} (eV)	∠1-2-3-4 (θ)	∠5-6-7-8 (θ)	S-H (A°)	μ ^{calc} (D)	β_0^{calc} (x10^{-30} esu)
3	-5.44/-5.23	-2.74/-3.07	0.455	0.870	S(11)-H(10) = 2.81 S(8)-H(9) = 2.81	-	-
4	-5.75/-5.38	-2.70/-3.17	0.143	0.604	S(1)-H(9) = 2.75 S(10)-H(9) = 2.75	11.41	24
5	-5.29/-5.12	-2.91/-3.18	0.043	0.839	S(8)-H(9) = 2.42 S(11)-H(10) = 2.41	-	-
6	-5.98/-5.33	-3.55/-3.59	0.246	-	S(6)-H(5) = 2.41	9.91	57
7	-5.75/-5.35	-3.28/-3.49	0.246	-	S(6)-H(5) = 2.41	6.30	55

Table 1: This table shows the theoretical HOMO-LUMO energy levels and their agreement with experimental data, dihedral angle formed by dithiafulvenyl groups, the S-H distances, dipole moment and static fist hyperpolarizability values.

Theoretical HOMO-LUMO levels and dipole moments (μ) were obtained by performing DFT calculations using B3LYP/dgdzvp basis set on pre-geometry optimized (HF/6-31g*) structures using G09 program.[3] The first hyperpolarizability (β) of **4**, **6** and **7** was calculated by HF/6-31g* level calculation on geometry optimized structures. The experimental HOMO-LUMO levels were obtained from CV experiments performed in DCM following equations: $E_{HOMO/LUMO} = -(4.4 + E^{1}_{ox/red})$.[4]

Cyclic Voltammetry Experiments:

Cyclic voltammetry experiments were performed in degassed DCM solutions of **3-7** (0.5 mM)**.**

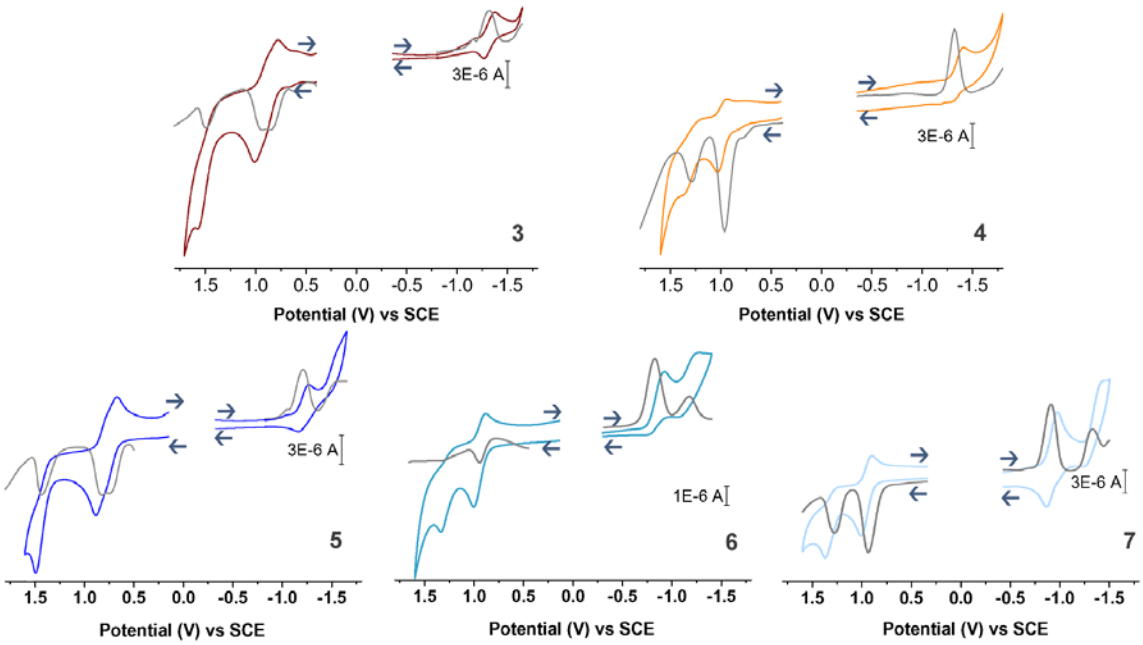


Figure S2: Cyclic Voltammogram and DPV results of **3-7** in DCM.

EPR:

a) b)

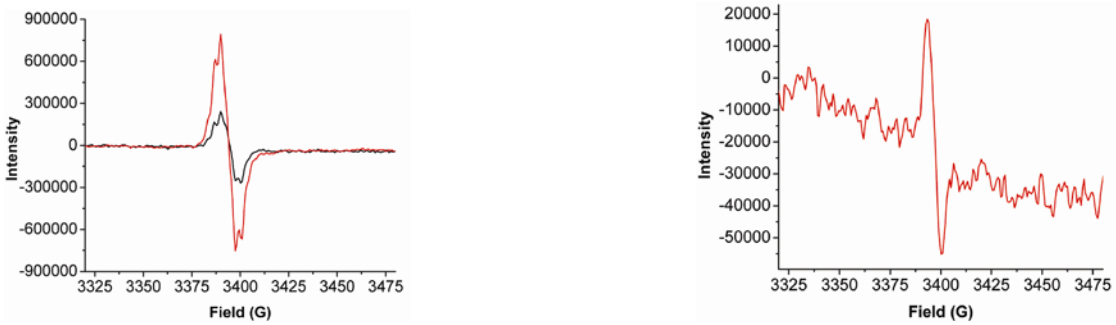


Figure S3: a) EPR spectrum of **3** with 2.0 eqv. (black) and with 4.0 eqv. (red) of Cu^{2+} and b) EPR spectrum of **5** with 2.0 eqv. of Cu^{2+}.

UV-vis-NIR absorption spectra of chemical oxidation of 3 and 4 by $FeCl_3$:

a) b)

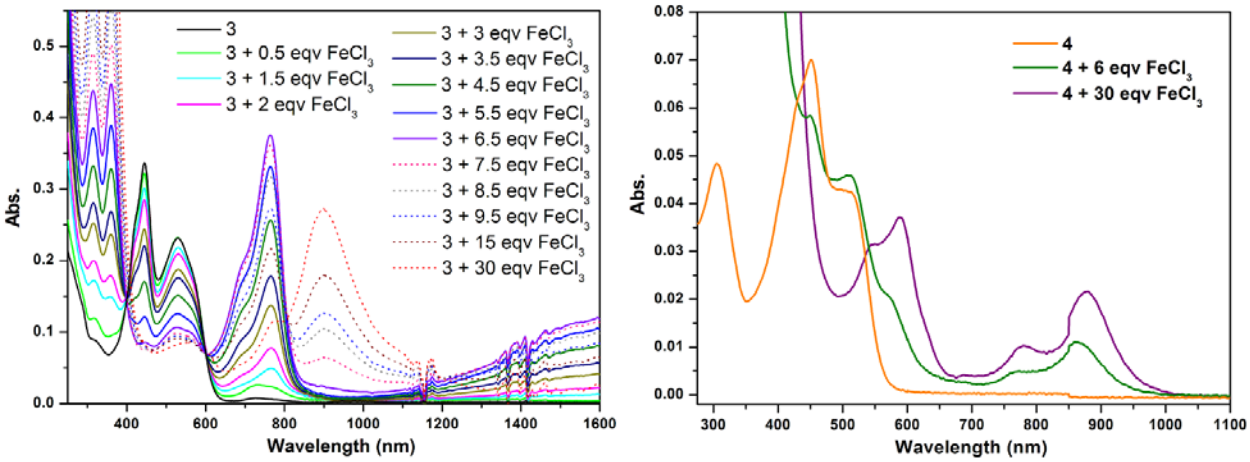


Figure S4: UV-vis-NIR titration of **3** (1 x 10-5 M) and **4** (1 x 10-5 M) against $FeCl_3$ in DCM.

UV-vis-NIR absorption spectra of chemical oxidation of 5, 6 and 7 by $FeCl_3$:

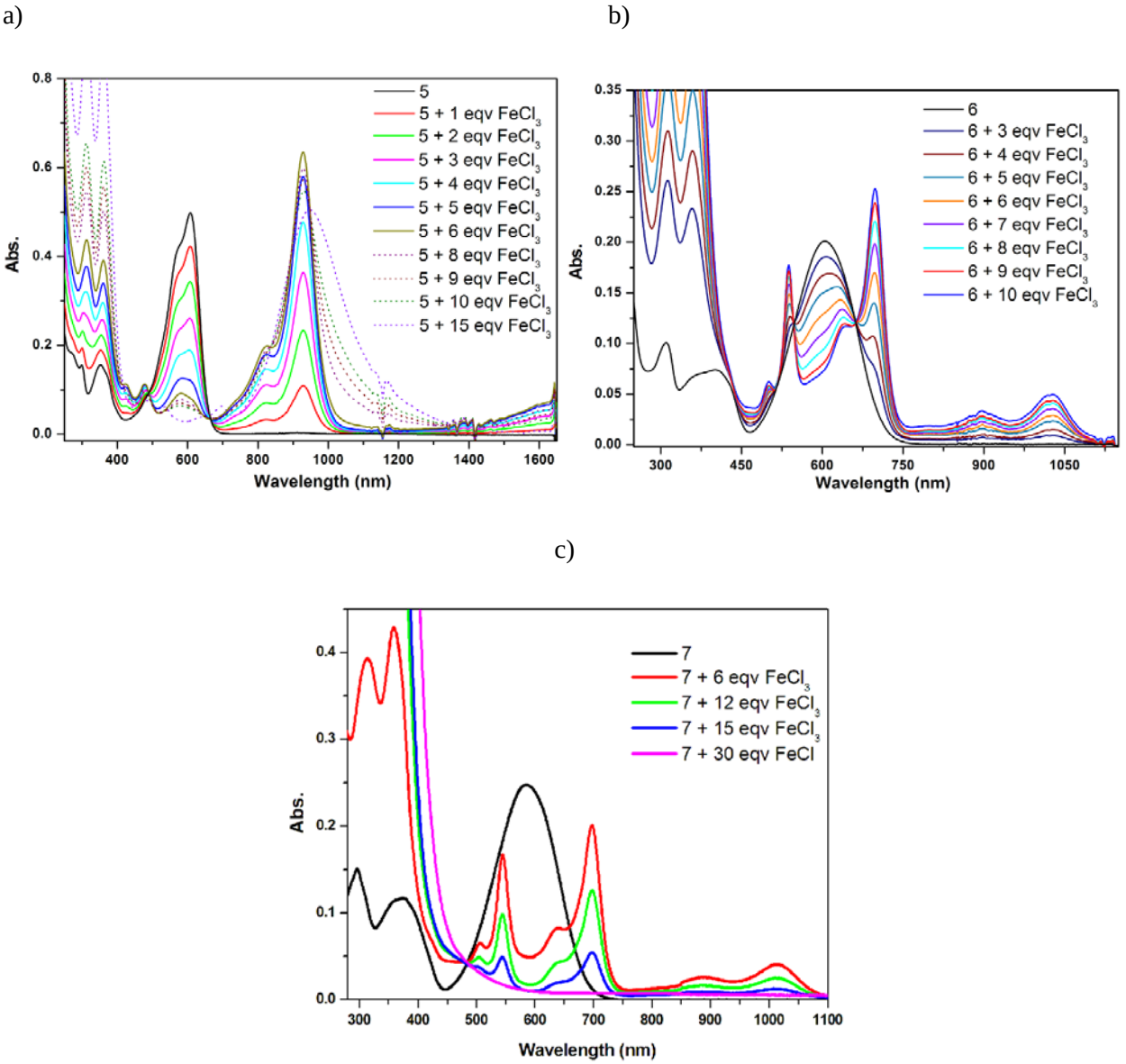


Figure S5: UV-vis-NIR titration of **5** (1 x 10^{-5} M), **6** (1 x 10^{-5} M) and **7** (1 x 10^{-5} M) against $FeCl_3$ in DCM.

Study of photooxidation of 5 and transformation to 6 by 500 MHz ^{1}H NMR Spectroscopy in $CDCl_3$:

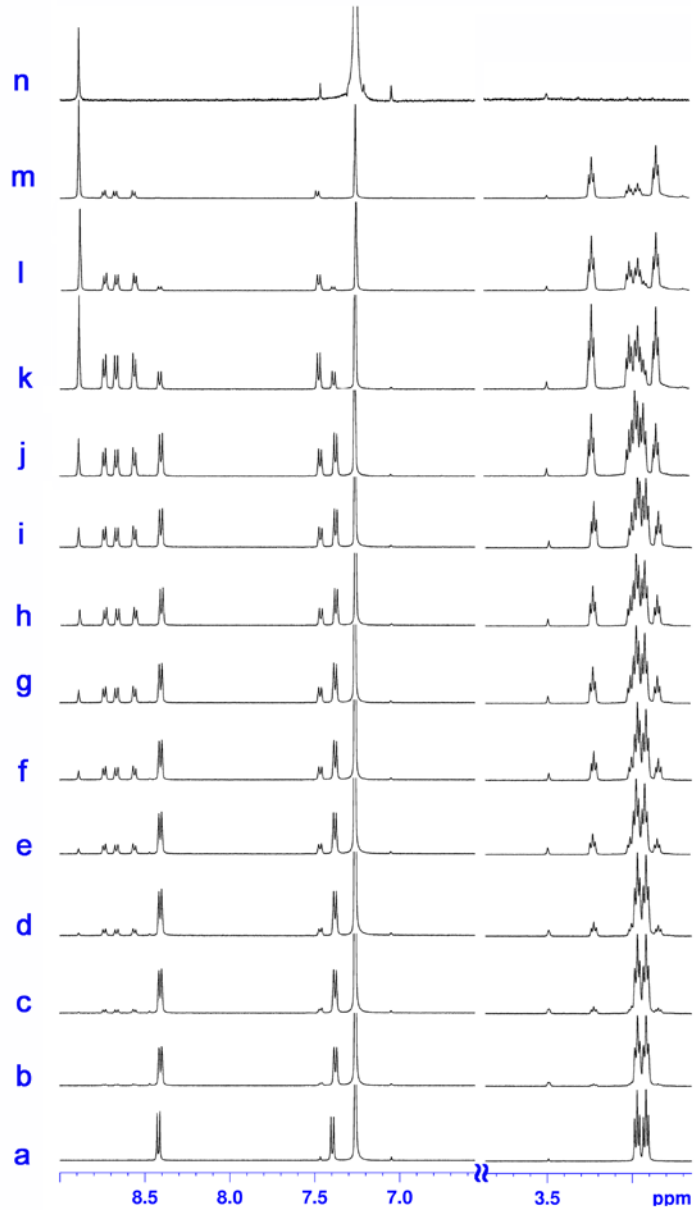


Figure S6: 500 MHz ^{1}H NMR spectra of light irradiated sample of **5** in $CDCl_3$.

^{1}H NMR spectra of **5** at different time of illumination with 365 nm light (a-m) and its comparison with NTCDA (n): a) 0 sec; b) 30 sec; c) 1 min; d) 1 min 30 sec; e) 2 min; f) 2 min 30 sec; g) 3 min; h) 4 min; i) 5 min; j) 9 min; k) 21 min; l) 30 min; m) 60 min.

Study of photooxidation of dyad 6 by 500 MHz ^{1}H NMR Spectroscopy in $CDCl_3$:

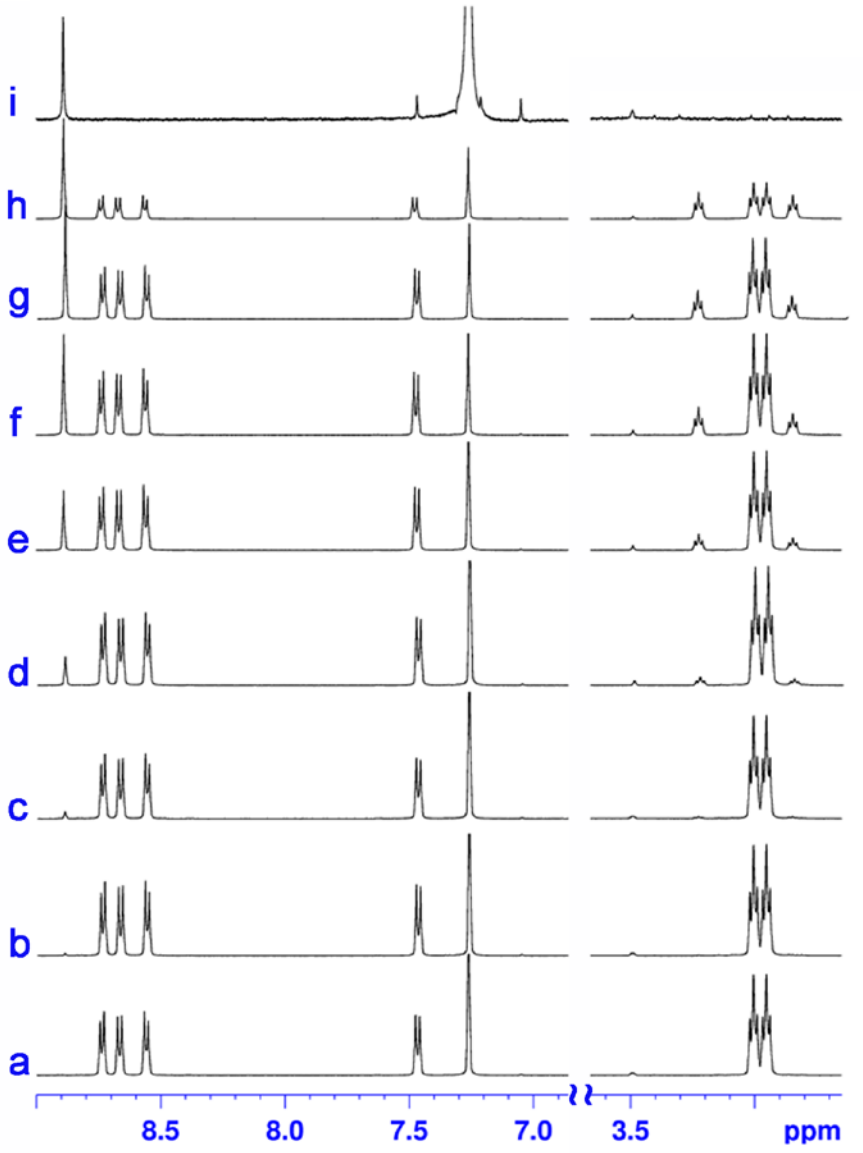


Figure S7: 500 MHz ^{1}H NMR spectra of light irradiated sample of **6** in $CDCl_3$.

^{1}H NMR spectra of **6** at different time of illumination with 365 nm light (a-h) and its comparison with NTCDA (i): a) 0 sec; b) 30 sec; c) 1 min; d) 2 min; e) 5 min; f) 10 min; g) 20 min; h) 60 min.

Study of photooxidation of 5 into 6 by MALDI-TOF Mass Spectroscopy in $CDCl_3$:

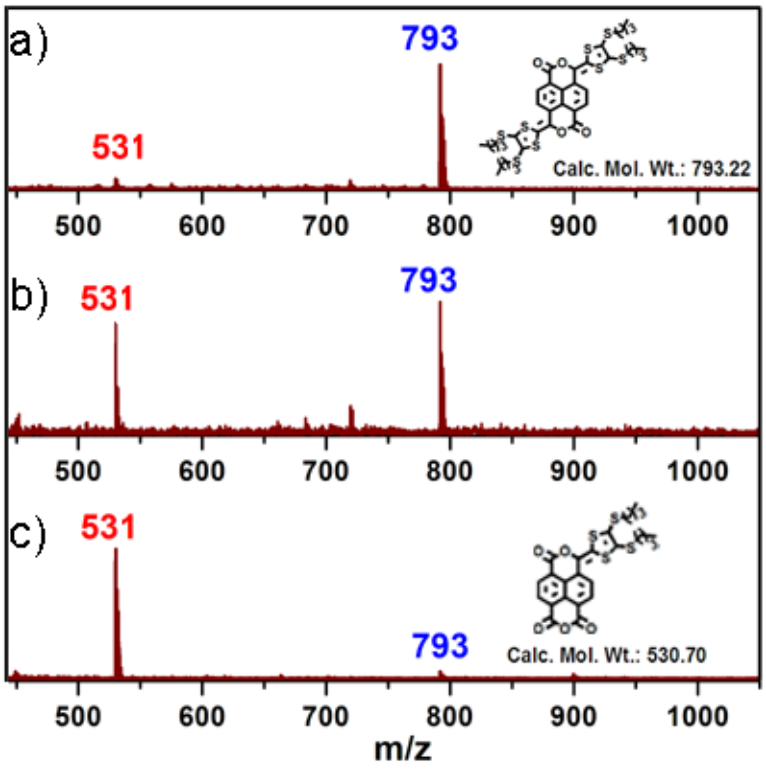


Figure S8: MALDI-TOF mass spectra of light irradiated sample of **5** in $CDCl_3$.

IR Spectra of 3-7:

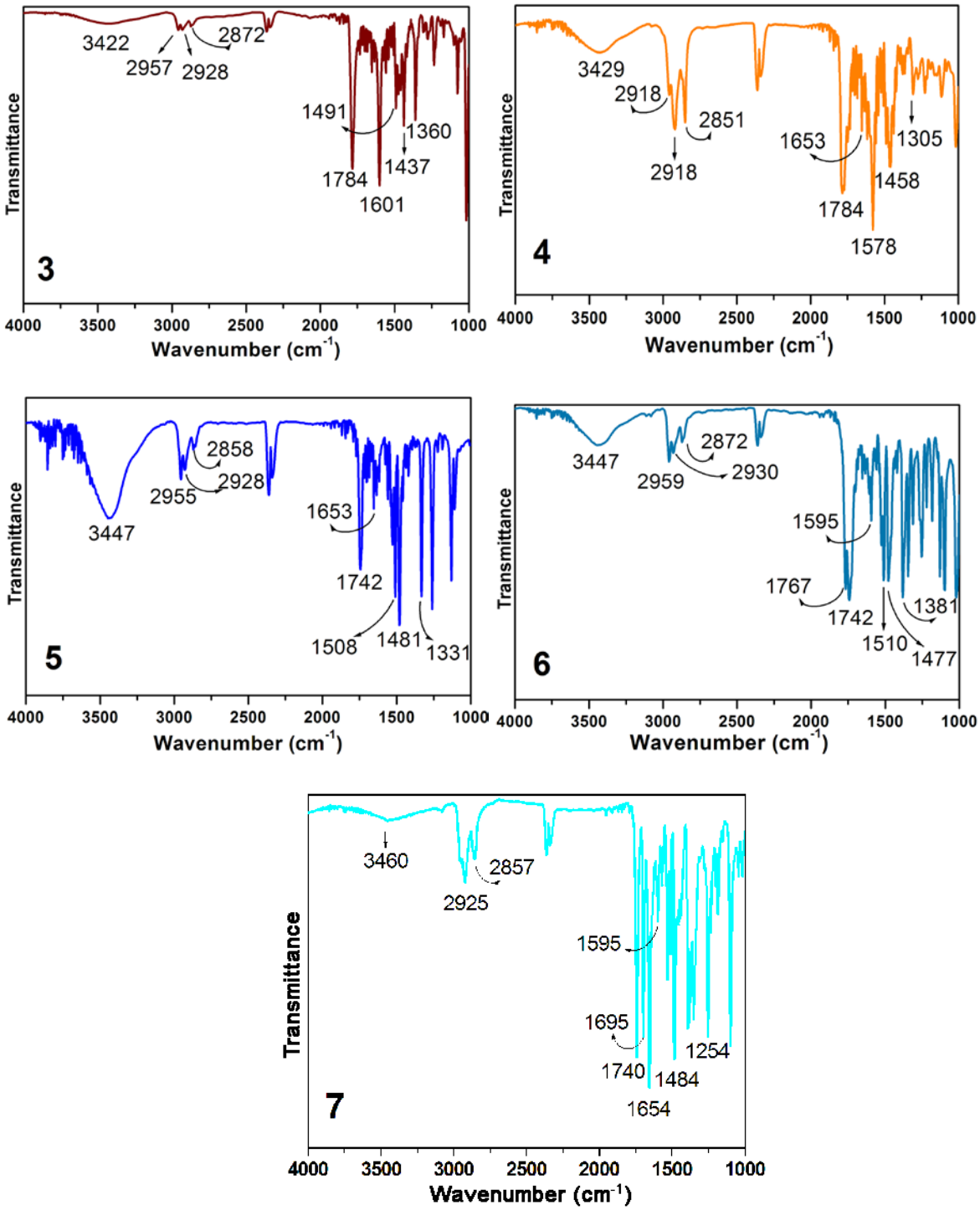


Figure S9: FT-IR spectrum of **3-7**.

MALDI-TOFF mass spectrum (α-Cyano-4-hydroxycinnamic acid) of compounds 3-7:

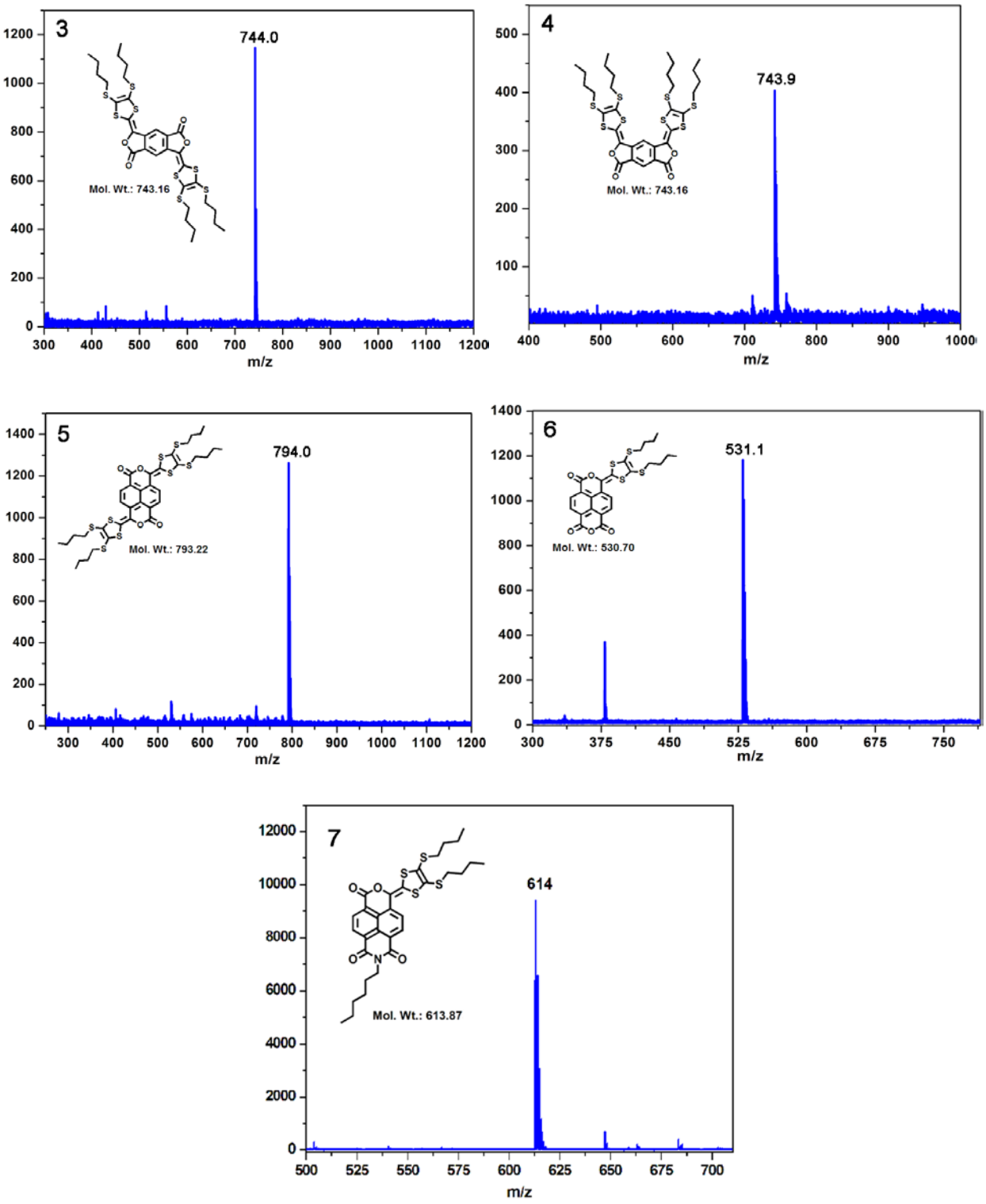


Figure S10: MALDI-TOF mass spectrum of **3-7**.

500 MHZ ^{1}H NMR Spectrum of 3 ($CDCl_3$, 300K):

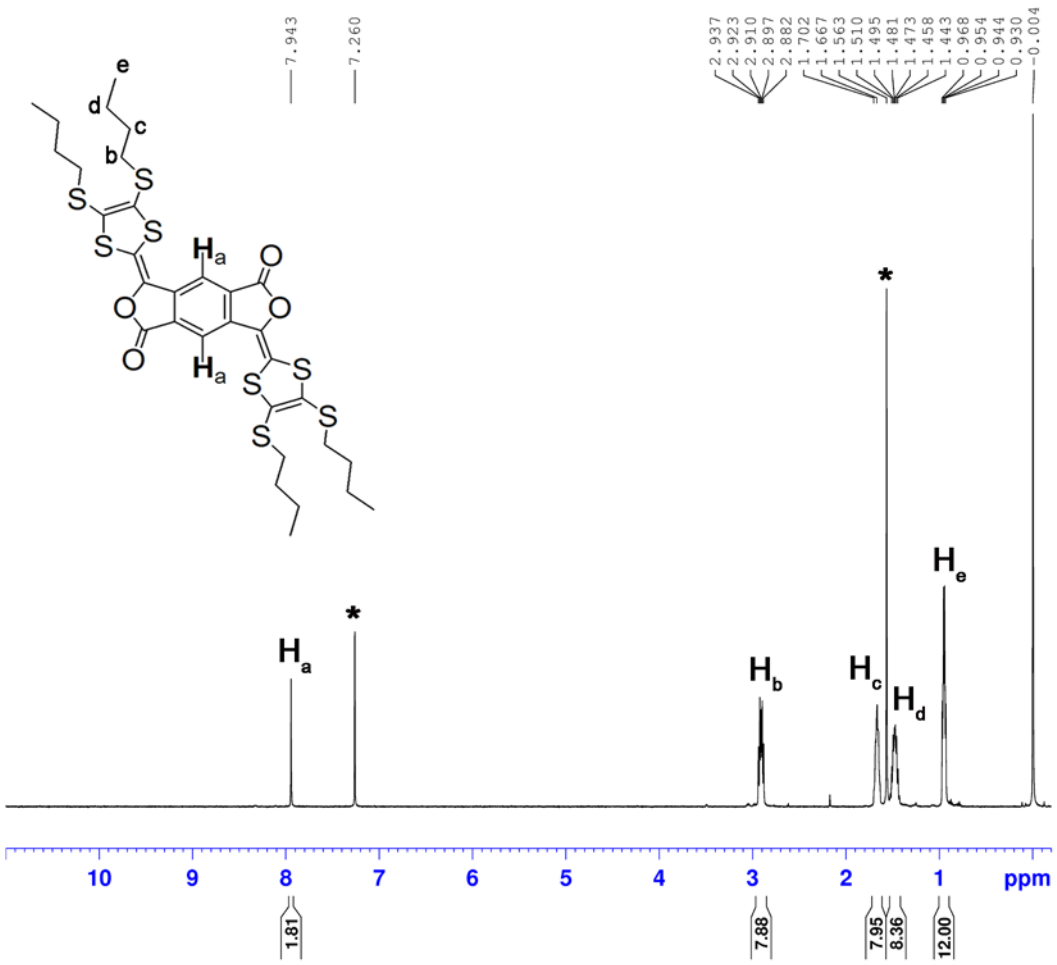


Figure S11: 500 MHz ^{1}H NMR spectrum of **3** in $CDCl_3$ at room temperature.

125 MHZ ^{13}C, DEPT 135 and APT NMR Spectrum of 3 ($CDCl_3$, 300K):

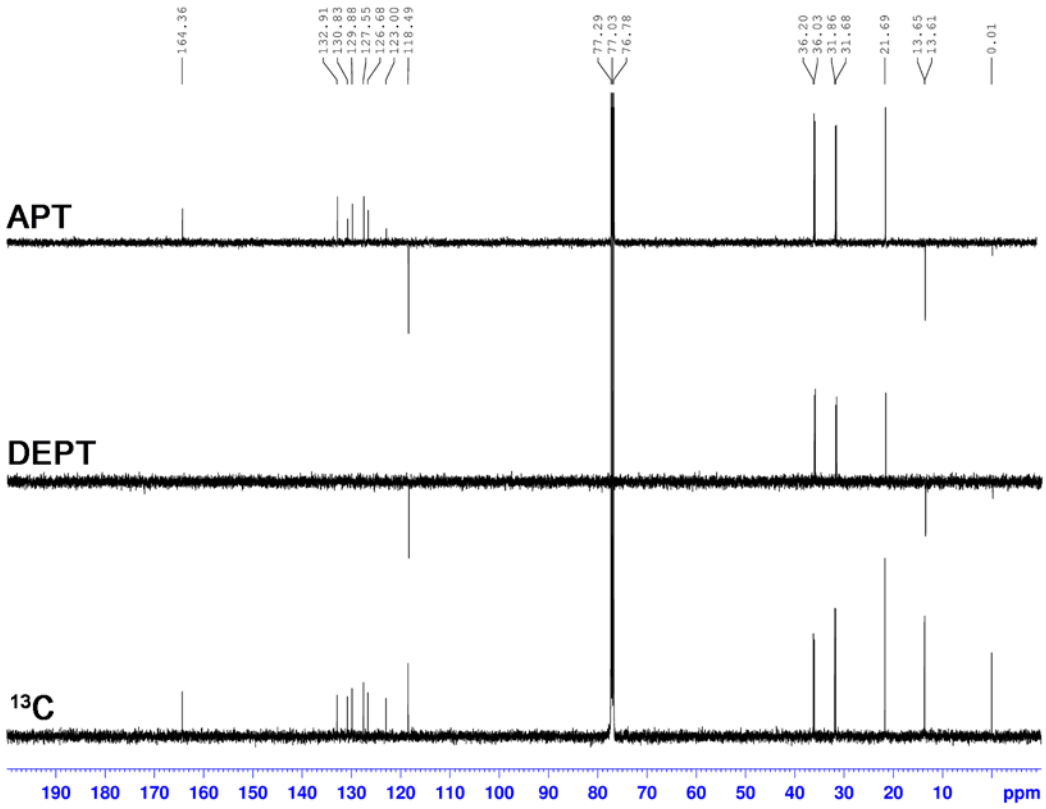


Figure S12: 125 MHz ^{13}C NMR, DEPT-135 and APT spectrum of **3** in $CDCl_3$ at room temperature.

500 MHZ ^{1}H NMR Spectrum of 4 ($CDCl_3$, 300K):

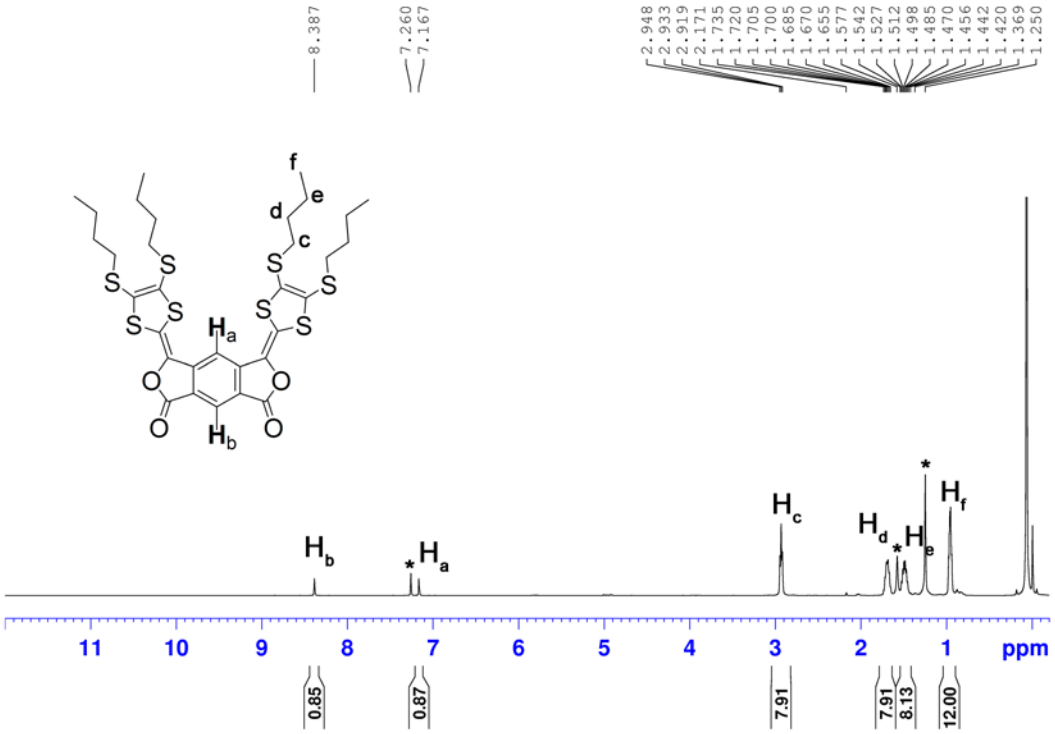


Figure S13: 500 MHz ^{1}H NMR spectrum of **4** in $CDCl_3$ at room temperature.

125 MHZ ^{13}C, DEPT 135 and APT NMR Spectrum of 4 ($CDCl_3$, 300K):

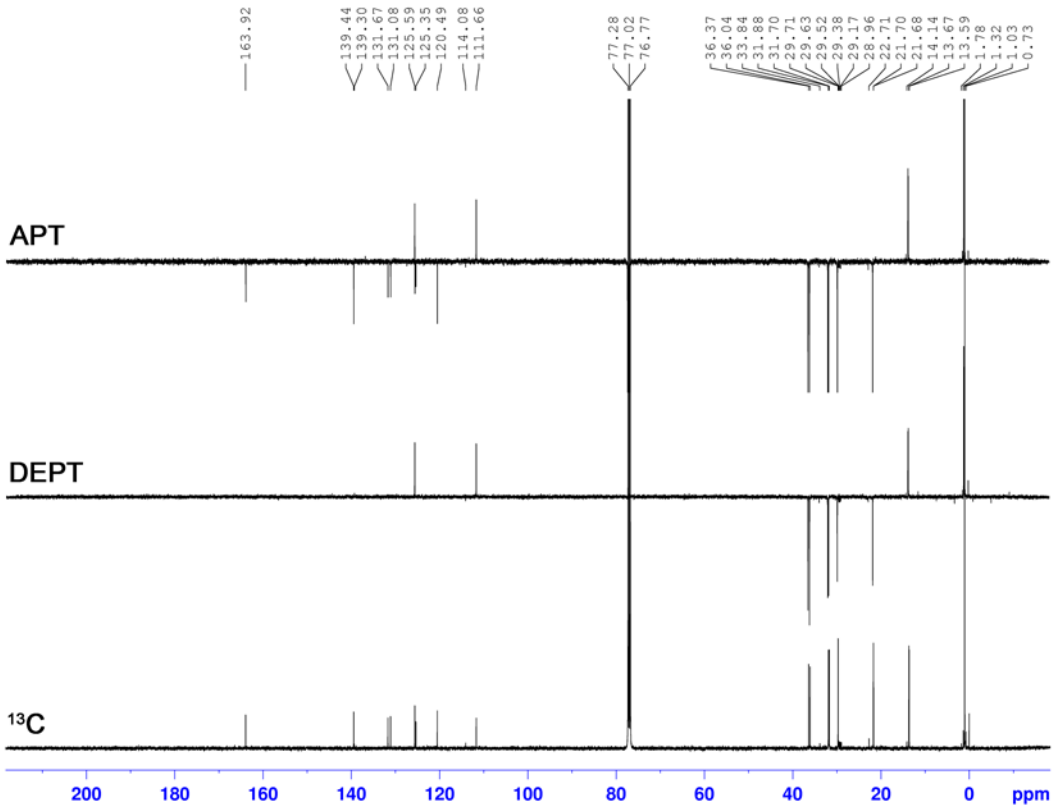


Figure S14: 125 MHz ^{13}C NMR, DEPT-135 and APT spectrum of **4** in $CDCl_3$ at room temperature.

500 MHZ ^{1}H NMR Spectrum of 5 ($CDCl_3$, 300K):

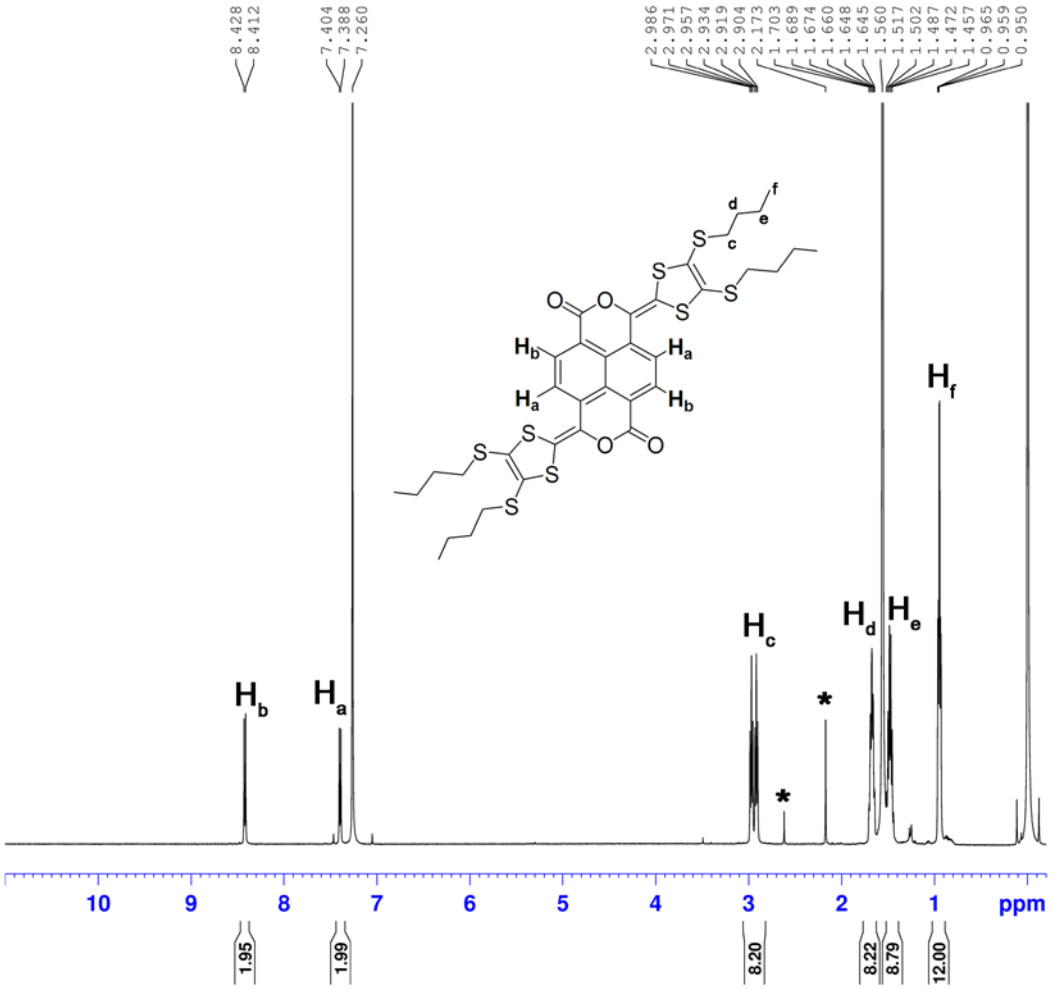


Figure S15: 500 MHz ^{1}H NMR spectrum of **5** in $CDCl_3$ at room temperature.

125 MHZ ^{13}C, DEPT 135 and APT NMR Spectrum of 5 ($CDCl_3$, 300K):

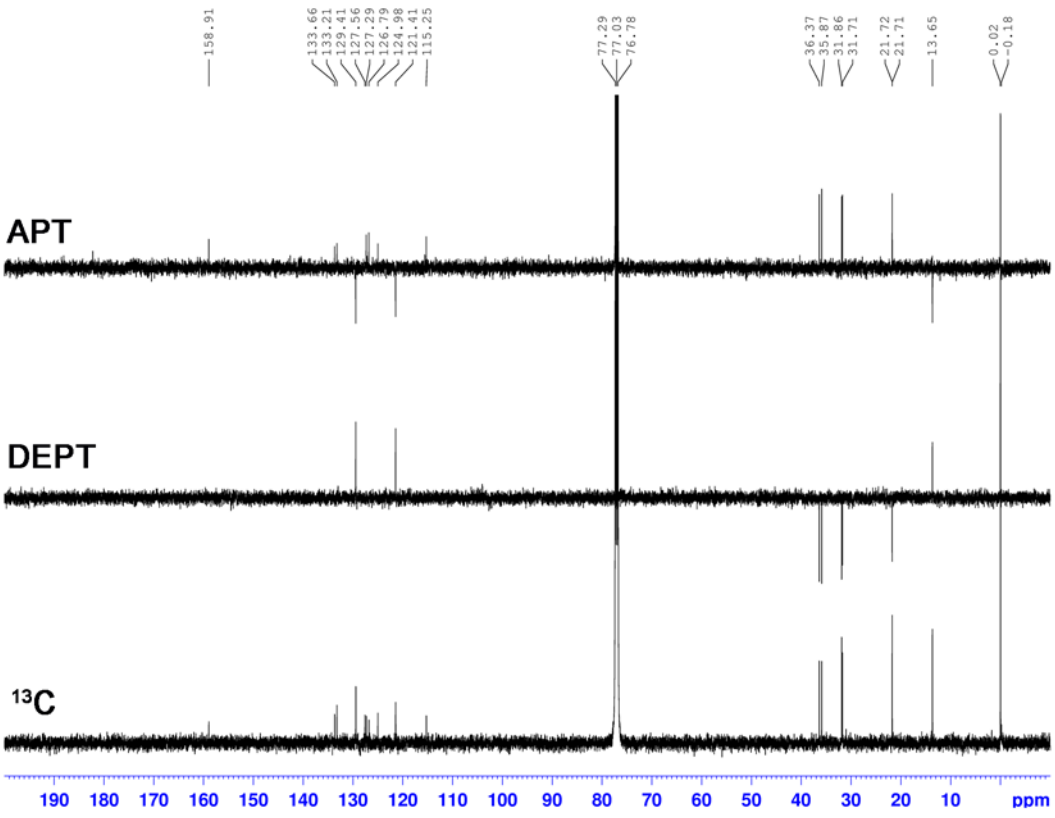


Figure S16: 125 MHz ^{13}C NMR, DEPT-135 and APT spectrum of **5** in $CDCl_3$ at room temperature.

500 MHZ ^{1}H NMR Spectrum of 6 ($CDCl_3$, 300K):

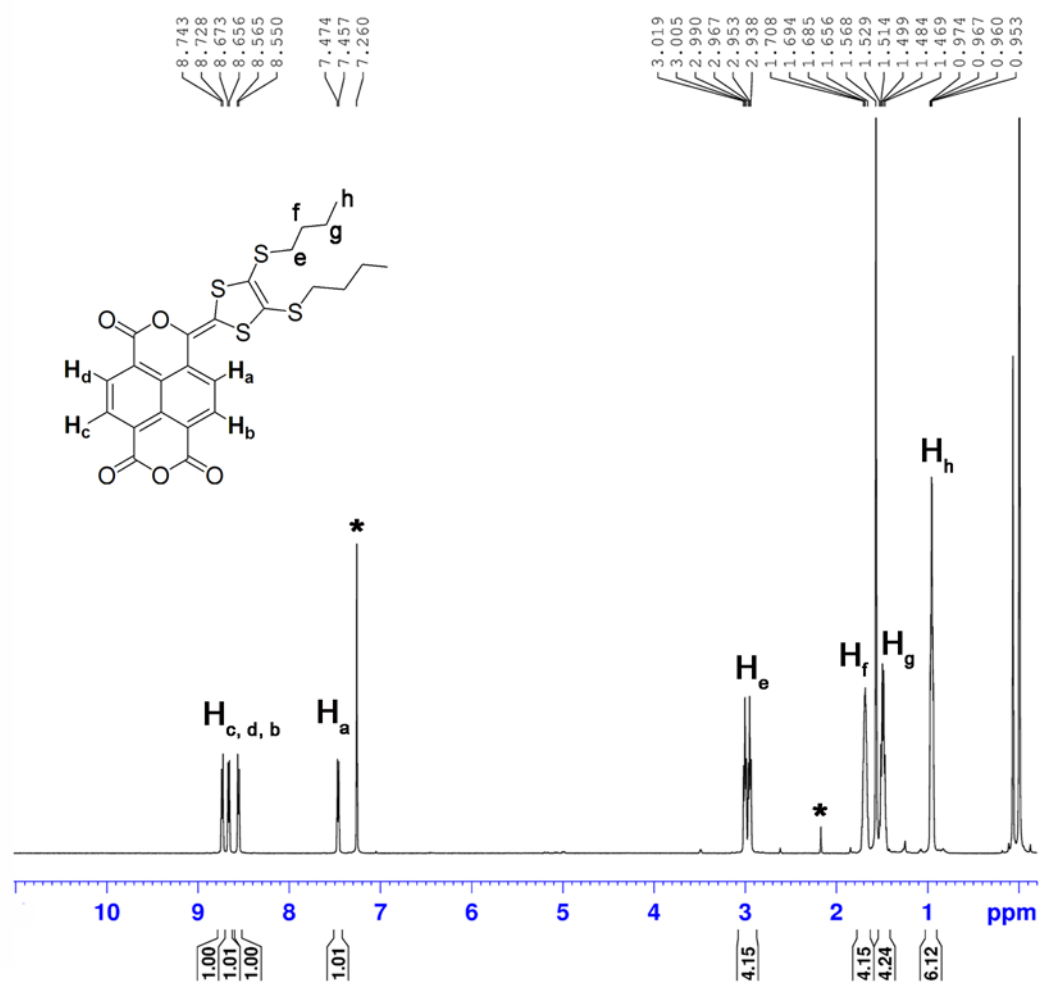


Figure S17: 500 MHz ^{1}H NMR spectrum of **6** in $CDCl_3$ at room temperature.

125 MHZ ^{13}C NMR Spectrum of 6 ($CDCl_3$, 300K):

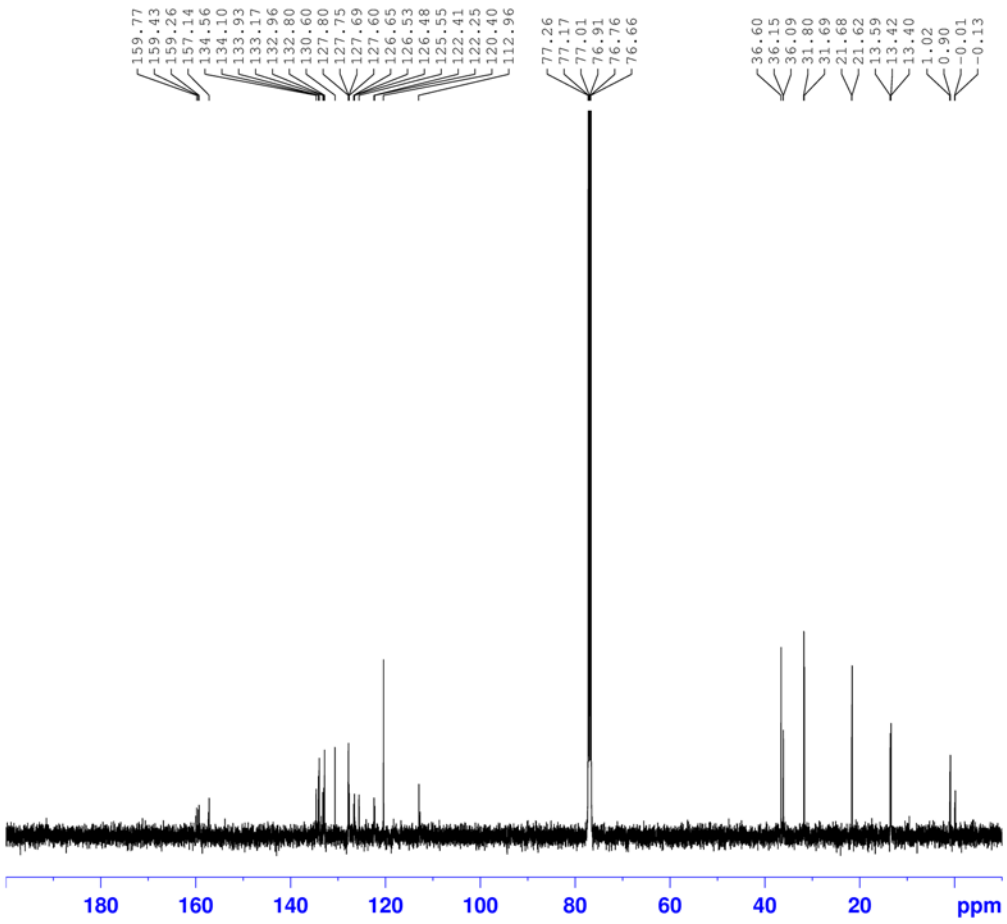


Figure S18: 125 MHz ^{13}C NMR spectrum of **6** in $CDCl_3$ at room temperature.

500 MHZ ^{1}H NMR Spectrum of 7 ($CDCl_3$, 300K):

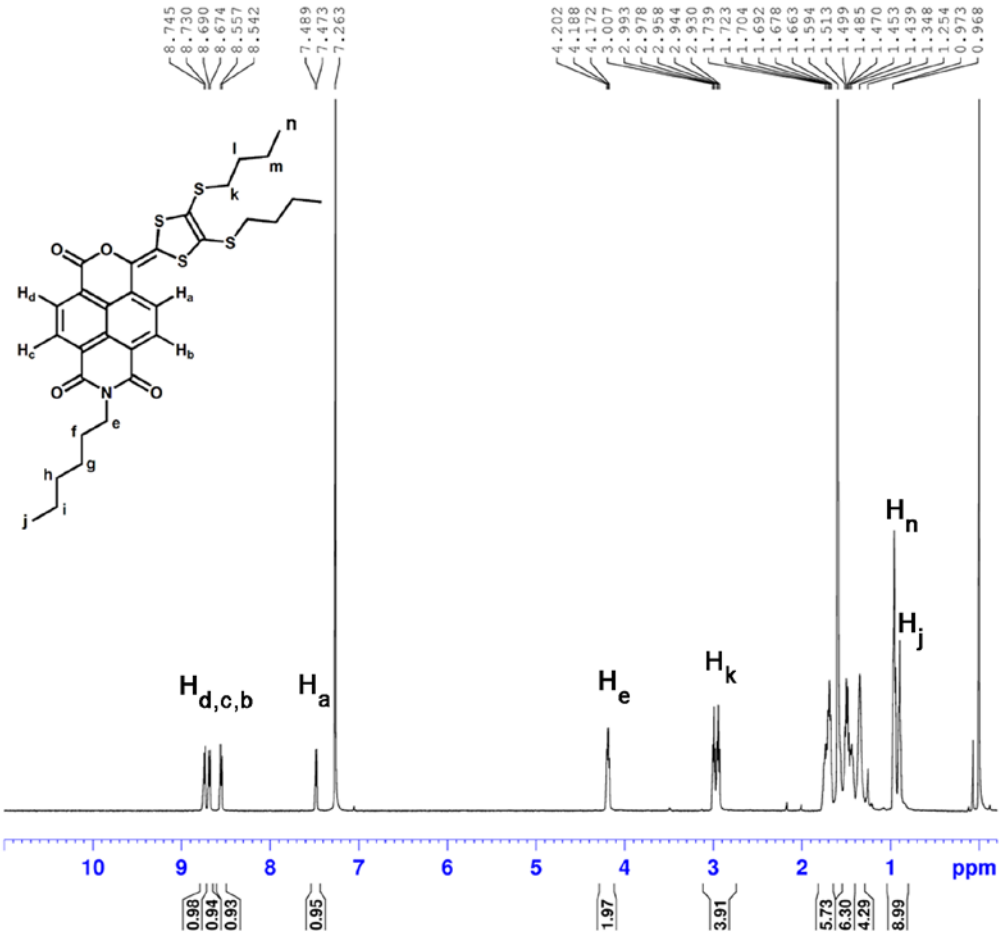


Figure S19: 500 MHz ^{1}H NMR spectrum of **7** in $CDCl_3$ at room temperature.

125 MHZ ^{13}C, DEPT 135 and APT NMR Spectrum of 7 ($CDCl_3$, 300K):

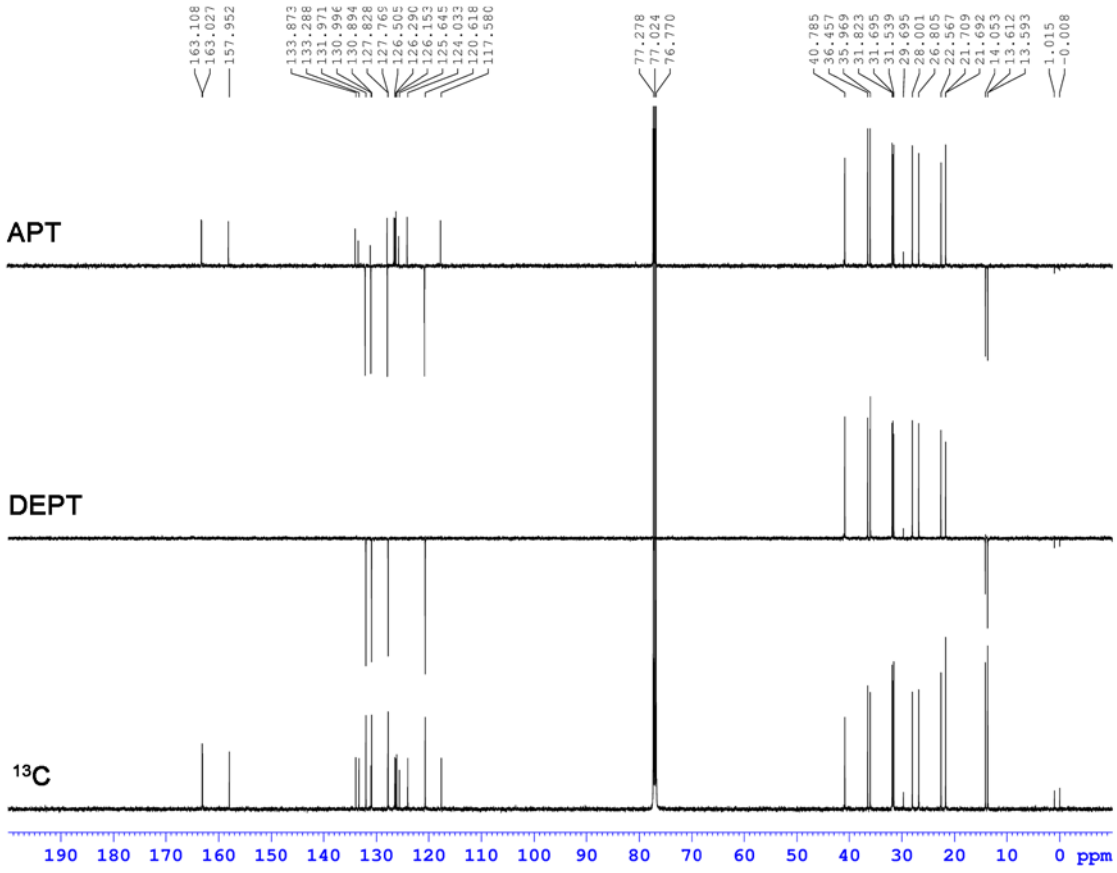


Figure S20: 125 MHz ^{13}C NMR, DEPT-135 and APT spectrum of **7** in $CDCl_3$ at room temperature.

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