

Electronic Supplementary Information (ESI)

Organic double D- π -A sensitizers based on 2,2'-(2,2 diphenylethene-1,1-diyl)dithiophene: π -conjugation fragment effect on the photovoltaic properties

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1. Materials and instrumentations

All chemical reagents and solvents were used as received from commercial suppliers without further purification. The toluene solvent was dried and distilled from sodium under a nitrogen atmosphere. Compound $C_6S_2TPAB(OH)_2$ was synthesized according to the previously reported literature^{S1}. 1H NMR and ^{13}C NMR spectra were obtained on a 400 MHz or 600 Hz spectrometer at room temperature. Chemical shifts (δ) were reported in ppm relative to internal TMS in $CDCl_3$ (7.26 ppm for 1H and 77.16 ppm for ^{13}C). Mass spectra data were obtained on a MALDI-TOF mass spectrometer (Bruker). HRMS data were obtained with an APCI ion source. The absorption spectra of the dyes in solution and adsorbed on TiO_2 film were measured with Lambda-950 (PerKin-Elmer) spectrometer or Shimadzu UV-3600 spectrometer. IR spectra were measured by a fourier infrared spectrometer from the German Bruker company. The current–density voltage (J - V) characteristics curves of the DSSCs were recording on a Keithley 2400 source meter under the illumination of AM 1.5G simulated solar light (94022A, Newport Co., USA equipped with a 300 W Xe lamp). The incident light intensity was calibrated to 100 mW cm^{-2} with a standard silicon solar cell. The spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for solar cells were recorded on a commercial setup (QTest Station 2000 IPCE Measurement System, Crowntech, USA). Electrical impedance spectra (EIS) for DSSCs under dark conditions with bias -0.7 V were measured with CHI760E Electrochemical Workstation at frequencies of 0.1-100 KHz.

2. Measurement of the amounts of dye adsorption

The amounts of dyes adsorbed on the TiO₂ films were measured by Lambda-950 (PerKin-Elmer) spectrometer. The sensitized electrodes were immersed into a 0.01 g mL⁻¹ NaOH solution in a mixed solvent (H₂O/CH₃CH₂OH/THF = 1:1:1, v/v/v), which was used to desorption of the dyes, and absorption data of the obtained solutions were used for calculating the amounts of dye adsorption on TiO₂.

Table S1 The dye loading amount of the dyes

Dye	λ_{\max} (nm)	concentration (10 ⁻⁵ mol L ⁻¹)	dye loading (10 ⁻⁷ mol cm ⁻²)
A6	426	0.26	0.51
A8	419	0.38	0.74
A9	426	0.47	0.91
AZ6	440	0.43	0.84

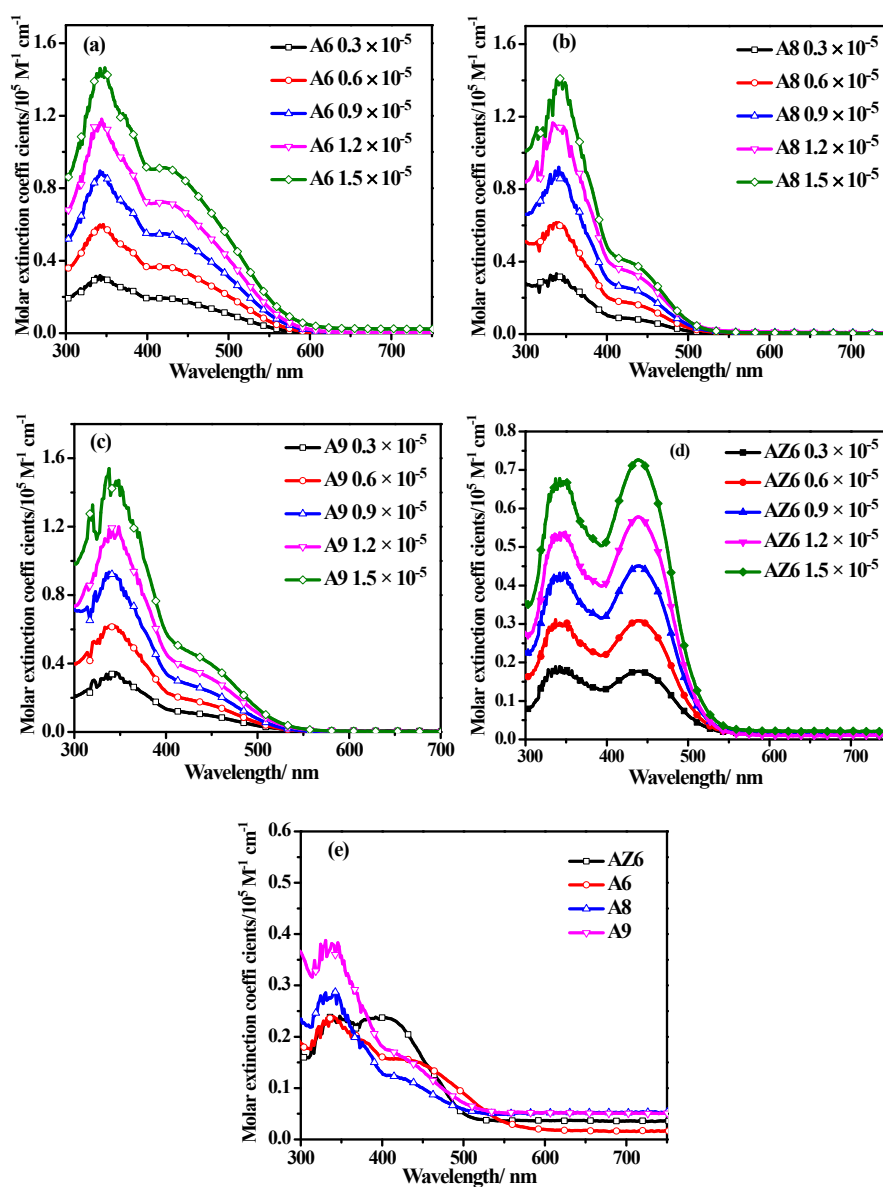


Fig. S1 The UV-Vis absorption spectra of (a) **A6**; (b) **A8**; (c) **A9**; (d) **AZ6** in 0.01 g mL⁻¹ NaOH solution (H₂O/CH₃CH₂OH/THF = 1:1:1, v/v/v) for various concentration. (e) Desorption of the dyes **AZ6**, **A6**, **A8** and **A9** in 7 mL 0.01 g mL⁻¹ NaOH solution.

3. FT-IR spectra of pristine dyes and dyes adsorbed on the TiO₂ film

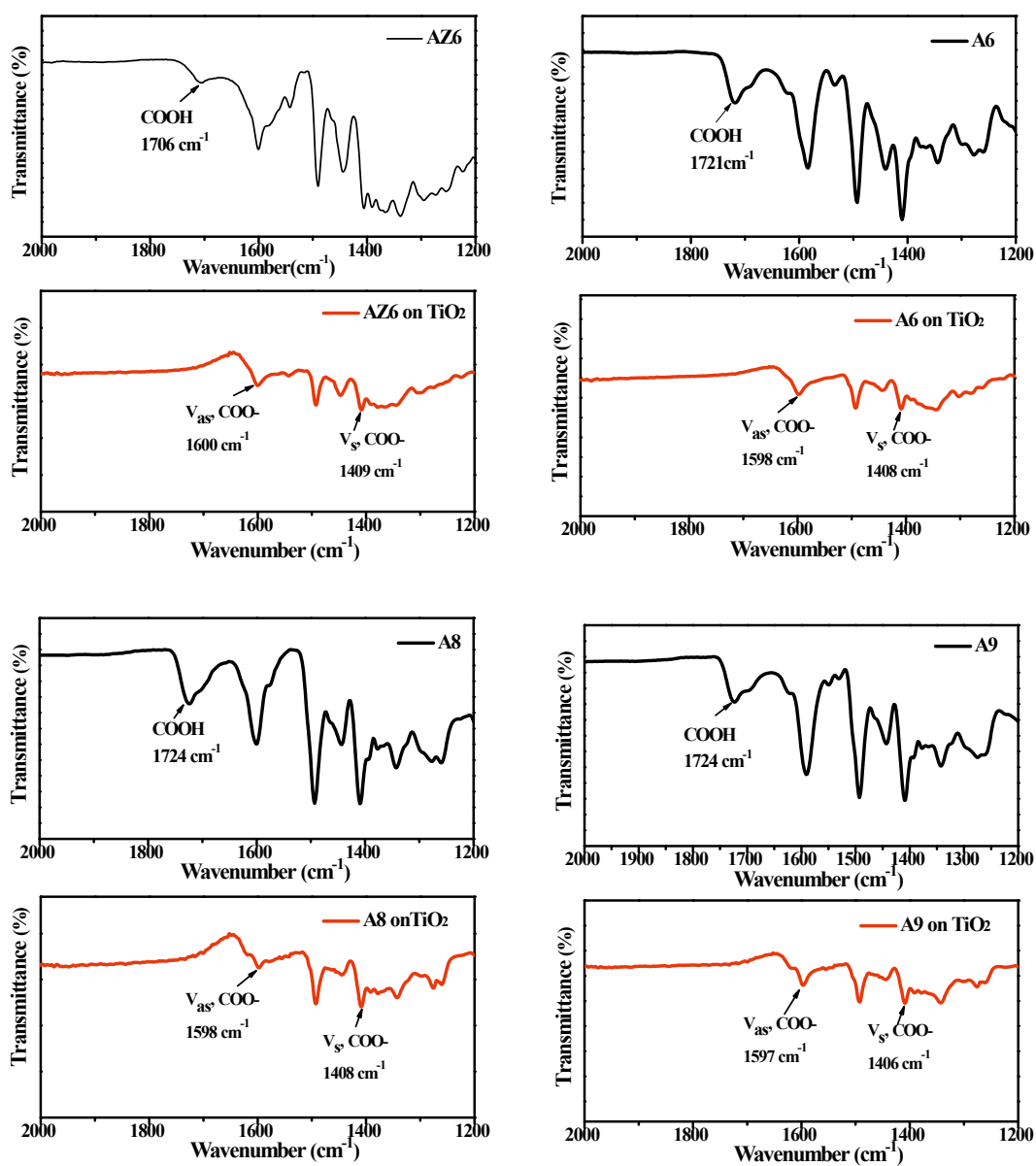


Fig. S2 FT-IR spectra of the pure dyes and dyes adsorbed on the TiO₂ film.

4. UV-vis absorption spectra of the dyes on TiO₂ film in an alkaline solution

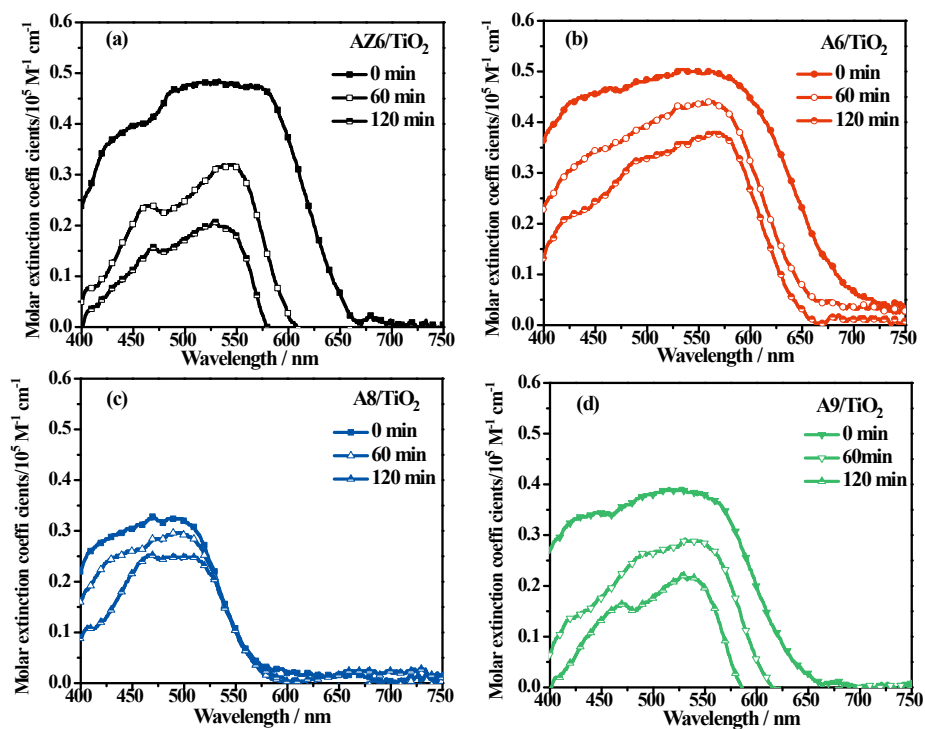


Fig. S3 UV-vis absorption spectra of the dyes on TiO₂ film after soaking in an alkaline solution for 0 min, 60 min, 120 min (saturated KOH in ethanol) (a) AZ6; (b) A6; (c) A8; (d) A9.

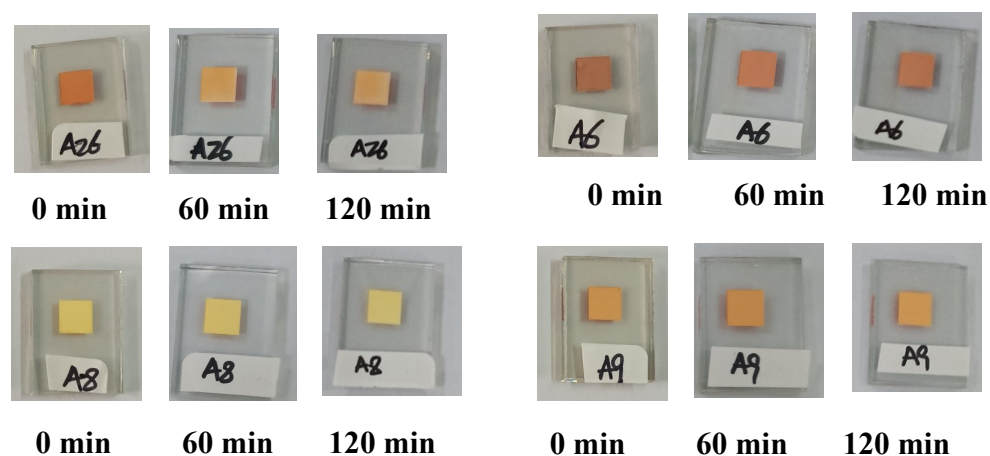


Fig. S4 The color change of the dyes on TiO₂ film in an alkaline leaching solution (saturated KOH in ethanol).

5. DFT and TD-DFT calculation data of the dyes

All calculations were carried out via Gaussian 09, geometry optimization, energy levels, and frontier molecular orbitals of the dyes HOMO, HOMO-1, LUMO and LUMO+1, LUMO+2 levels were calculated at the B3LYP/6-311G (d, p) level.

Table S2 Energy level data of dyes by DFT calculation

Dye	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
A6	-5.21	-3.16	2.05
A8	-5.12	-3.10	2.02
A9	-5.17	-3.17	2.00
AZ6	-5.26	-2.97	2.29

Table S3 Main electron transitions, oscillator strengths (f), and absorption bands in the UV-vis regions at the CAM-B3LYP/6-31G (d) level for all the organic dyes in CH_2Cl_2 (H = HOMO, L+2 = LUMO+2).

Dyes	excited energy (eV)	λ (nm)	f	main composition
A6	2.55	485.7	1.0967	H→L (60%)
A8	3.01	412.5	0.8574	H→L+2 (78%)
A9	2.99	414.8	0.9444	H→L+2 (70%)

6. Electrochemical properties

Cyclic voltammograms (CV) of dyes were conducted on a CHI760E Electrochemical Workstation at a scan rate 100 mV s^{-1} in a typical three-electrode electrochemical system (working electrode: glassy carbon; counter electrode: Pt; reference electrode:

Ag/Ag⁺ in 10 M AgNO₃ solution). The redox potentials were calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as the internal reference, 0.1 M tetrabutylammoniumhexafluorophosphate (Bu₄NPF₆) as electrolyte under oxygen-free atmosphere in DCM/MeCN (2:1, v/v) solutions.

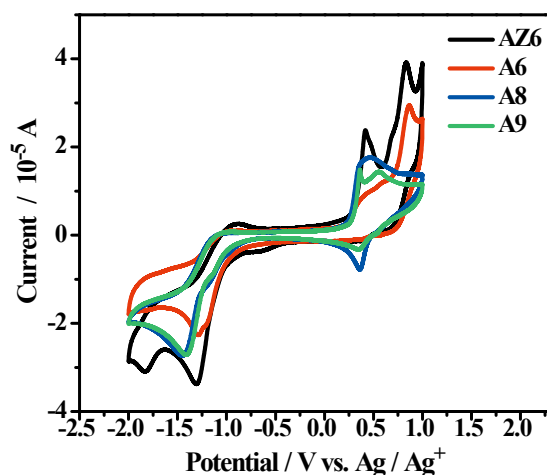


Fig. S5 Cyclic voltammograms of AZ6, A6, A8 and A9.

7. Fabrication of cells

Anatase TiO₂ film photoanode was purchased from Yingkou OPV Tech new energy company (active area: 0.25 cm²) and without further treatment, which was immersed in a 0.4 mM (AZ6) or 0.3 mM (A6, A8, A9) dye sensitized solution (DCM/t-BuOH = 1:1, v/v) under dark for 24 h at room temperature. The dye-adsorbed TiO₂ working electrodes were sandwiched together with Pt-counter electrodes using a hot-melt (Surllyn, 25 μm thick) and then the electrolyte was injected into the inter-electrode space. The iodine liquid electrolyte was composed of 0.12 M I₂, 0.1 M LiI, 1.0 M DMPII and 0.5 M 4-tert-butylpyridine (tBP) in acetonitrile /3-methoxypropionitrile (1:3, v/v) solution.

8. Stability measurements

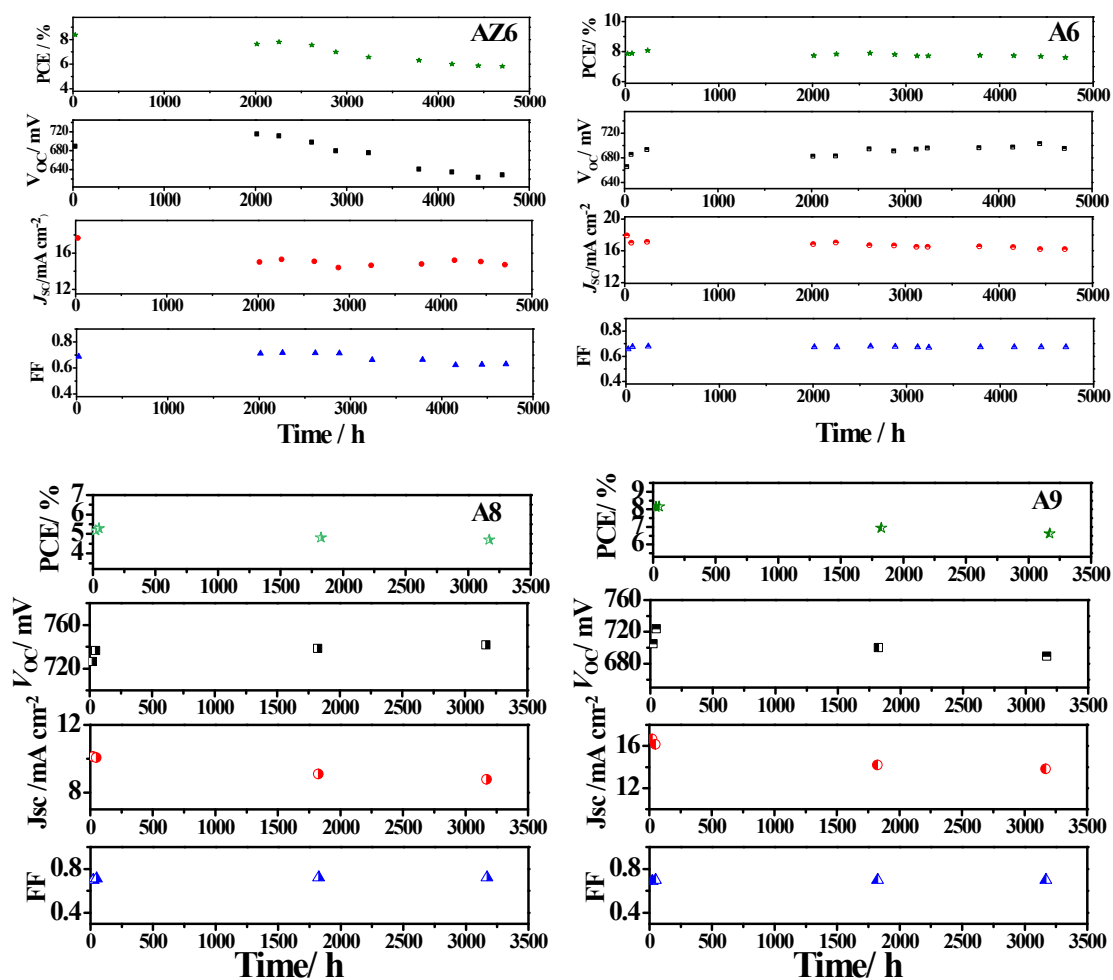
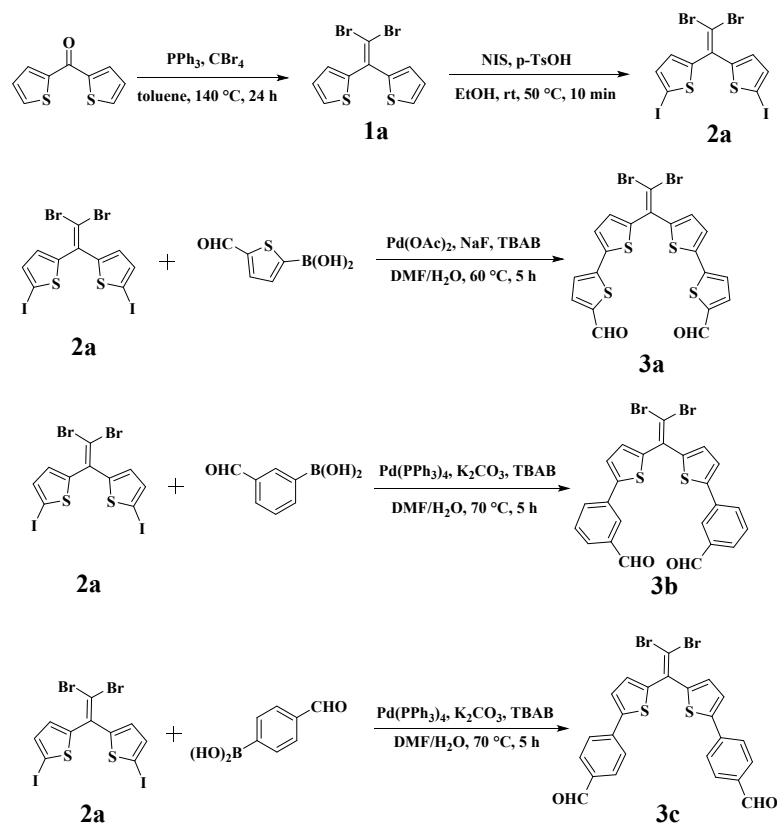


Fig. S6 Long-term stability of the solar cells based on AZ6, A6, A8, and A9, respectively, using iodine-based electrolyte under irradiation of simulated solar light (AM 1.5 G, 100 mW cm⁻²).

9. Synthesis procedures

Scheme S1 Synthetic routes of the intermediate products.



2,2'-(2,2-dibromoethene-1,1-diyl)dithiophene (1a): An oven-dried sealable 100 mL pressure vessel was charged with di(thiophen-2-yl)methanone (1.16 g, 6 mmol), carbon tetrabromide (3.98 g, 12 mmol), triphenylphosphine^{S2} (6.3 g, 24 mmol). The vessel was purged with nitrogen gas, 30 mL of anhydrous toluene was added, and the vessel was sealed. The reaction mixture was heated at 140°C for 24 h in a silicone oil bath with vigorous stirring. The vessel was cooled to room temperature before opening, and the mixture was rinsed into a round-bottom flask with toluene. The mixture was filtered and the filtrate was collected, washed with water. The organic layer was separated, dried with Na_2SO_4 , and then the solvent was removed by a rotary

evaporator. The residue was purified by silica gel column chromatography using hexane as the eluent to obtain the product as a pale yellow liquid (1.47 g, 4.2 mmol, Yield: 70%). ¹H NMR (400 MHz, CDCl₃): δ 7.41-7.39 (dd, *J* = 5.2, 1.2 Hz, 2H), 7.11-7.10 (dd, *J* = 3.6, 1.2 Hz, 2H), 7.02-7.00 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 142.0, 134.1, 129.9, 127.5, 126.7, 92.1. IR (KBr) 3108, 3060, 1407 cm⁻¹. HR-MS (APCI) *m/z* calcd for C₁₀H₇Br₂S₂ [M+H]⁺: 350.8330; found: 350.8331.

5,5'-(2,2-dibromoethene-1,1-diyl)bis(2-iodothiophene) (2a): This reaction was carried out under the air atmosphere. To a stirred solution of **1a** (7.0 g, 20 mmol) in 90 mL ethanol, N-iodosuccinimide^{S3} (9.45 g, 42 mmol, 2.1 eq) and *p*-toluenesulfonic acid (0.76 g, 4 mmol, 20 mol %) were added at 25 °C. The reaction mixture was stirred for 10 min at 50 °C. After cooling to room temperature, a saturated solution of sodium thiosulfate (50 mL) was added. The mixture was extracted with ethyl acetate and the organic phase was washed with a 1 M solution of sodium carbonate (40 mL). The organic phase was dried over magnesium sulfate, filtered. After removing the solvent under vacuum, the residue was purified by column chromatography on silica gel using hexane as eluent to obtain the product as gray solid (10.22 g, 17 mmol, Yield: 85%). ¹H NMR (400 MHz, CDCl₃): δ 7.16 (d, *J* = 4.0 Hz, 2H), 6.73 (d, *J* = 4.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 147.0, 136.7, 132.6, 131.5, 93.7, 77.0. IR (KBr) 3085, 1395 cm⁻¹. HR-MS (APCI) *m/z* calcd for C₁₀H₅Br₂I₂S₂ [M+H]⁺: 602.6263; found: 602.6266.

5',5'''-(2,2-dibromoethene-1,1-diyl)bis([2,2'-bithiophene]-5-carbaldehyde)

(3a): A mixture of compound **2a** (3 g, 5 mmol), Pd(OAc)₂ (56 mg, 0.25 mmol), NaF (840 mg, 20 mmol), TBAB (323 mg, 1 mmol), (5-formylthiophen-2-yl)boronic acid (2.34 g, 15 mmol) was added in batches in the solution of DMF (50 mL) and H₂O (20 mL). The reaction mixture was heated at 60 °C for 5 h under a nitrogen atmosphere. After the reaction finished, the water was added to the reaction mixture and extracted three times with CH₂Cl₂. The combined organic layer was washed with H₂O and brine, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using PE/EA (5:1, v/v) as the eluent. The target product was obtained as a black-brown solid (1.14 g, 2 mmol, Yield: 40%). ¹H NMR (400 MHz, CDCl₃): δ 9.87 (s, 2H), 7.68 (d, *J* = 4.0 Hz, 2H), 7.28 (d, *J* = 4.0 Hz, 4H), 7.11 (d, *J* = 3.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 182.7, 146.2, 142.5, 142.4, 138.1, 137.4, 132.8, 131.4, 125.7, 124.9, 94.4. IR (KBr) 1648, 1426 cm⁻¹. HR-MS (APCI) *m/z* calcd for C₂₀H₁₁Br₂O₂S₄ [M+H]⁺: 570.7983; found: 570.7980.

5',5'''-(2,2-bis(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5yl)amino)phenyl)ethene-1,1-diyl)bis([(2,2'-bithiophene]-5-carbaldehyde)) (4a):
To a mixture of compound C₆S₂TPAB(OH)₂ (970 mg, 1.26 mmol), compound **3a** (342 mg, 0.6 mmol), Pd(PPh₃)₄ (35 mg, 0.03 mmol), K₂CO₃ (332 mg, 2.4 mmol), TBAB (58 mg, 0.18 mmol), DMF (20 mL) and H₂O (8 mL) was heated at 75 °C for 4 h under nitrogen. After cooling to room temperature, the reaction was quenched by water, extracted three times with CH₂Cl₂, dried over anhydrous Na₂SO₄, After removing the solvent under reduced pressure, the crude product was purified by

column chromatography on silica gel using PE/EA (10:1, v/v) as eluent. **4a** was obtained as a dark red solid (782 mg, 0.42 mmol, Yield: 70%). ¹H NMR (400 MHz, CDCl₃): δ 9.87 (s, 2H), 7.67 (d, *J* = 2.8 Hz, 2H), 7.20 (d, *J* = 4.0 Hz, 2H), 7.16 (d, *J* = 3.6 Hz, 2H), 7.08-7.03 (m, 8H), 6.98-6.85 (m, 14H), 4.27-4.12 (m, 16 H), 1.83-1.64 (m, 16 H), 1.42-1.18 (m, 48 H), 0.89-0.77 (m, 24H). ¹³C NMR (100 MHz, CDCl₃): δ 182.4, 169.5, 148.1, 147.8, 147.0, 144.1, 143.1, 141.8, 137.5, 136.6, 135.4, 133.2, 133.1, 132.1, 131.2, 128.9, 125.4, 124.0, 123.8, 121.1, 120.6, 109.7, 106.2, 45.0, 44.8, 31.6, 31.5, 28.0, 27.9, 26.7, 26.6, 22.6, 22.5, 14.1. IR (KBr) 2925, 2852, 1664, 1592, 1491, 1440, 1411 cm⁻¹. HR-MS (APCI) *m/z* calcd for C₁₀₈H₁₃₅N₁₀O₂S₈ [M+H]⁺: 1860.8563; found: 1860.8567.

(2E,2'E)-3,3'-((2,2-bis(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5-yl)amino)phenyl)ethene-1,1-diyl)bis([2,2'-bithiophene]-5',5'-diyl))bis(2-cyanoacrylic acid) (A6): A mixture of aldehyde compound **4a** (595 mg, 0.32 mmol), cyanoacetic acid (136 mg, 1.6 mmol) and piperidine (13.6 mg, 0.16 mmol) was dissolved in chloroform under a nitrogen atmosphere and heated to reflux for 5 h. After the completion of the reaction, the mixture was washed with a water solution, extracted with dichloromethane, dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography on silica gel with CH₂Cl₂/CH₃OH (10:1, v/v) as eluent to yield the desired sensitizer **A6** as a dark red solid (447 mg, 0.224 mmol, Yield: 70%). ¹H NMR (400 MHz, CDCl₃): δ 8.32 (s, 2H), 7.66 (d, *J* = 3.2 Hz, 2H), 7.23-7.21 (m, 4H), 7.06-6.83 (m, 22H), 4.27-4.13 (m, 16H), 1.81-1.67 (m, 16H), 1.41-1.20 (m, 48H), 0.89-0.77 (m, 24H). ¹³C NMR (150 MHz, CDCl₃): δ

168.7, 166.0, 148.0, 147.6, 147.3, 146.4, 144.1, 142.0, 139.4, 135.2, 134.0, 133.3, 132.3, 131.1, 130.4, 128.1, 125.3, 123.2, 122.5, 119.9, 119.4, 114.9, 108.7, 105.6, 95.9, 44.1, 43.8, 30.6, 30.5, 27.1, 27.0, 25.7, 25.6, 21.7, 21.6, 13.2. IR (KBr) 3436, 2925, 2858, 2219, 1721, 1583, 1496, 1438, 1406 cm^{-1} . MS (MALDI-TOF) m/z calcd for $\text{C}_{114}\text{H}_{137}\text{N}_{12}\text{O}_4\text{S}_8$ $[\text{M}+\text{H}]^+$: 1994.8679; found: 1994.3871.

3,3'-((2,2-dibromoethene-1,1-diyl)bis(thiophene-5,2-diyl))dibenzaldehyde

(3b): A mixture of compound **2a** (1.8 g, 3 mmol), (3-formylphenyl)boronic acid (1.35 g, 9 mmol), $\text{Pd}(\text{PPh}_3)_4$ (347 mg, 0.3 mmol) and K_2CO_3 (1.66 g, 12 mmol) was dissolved in a mixed solvent DMF/ H_2O (50 mL, 15 mL). The reaction mixture was stirred under a nitrogen atmosphere at 70 °C for 5 h. After cooling to room temperature, the mixture was extracted with 30 mL dichloromethane three times. The organic portion was collected and dried over magnesium sulfate then removed solvent by rotary evaporation. The residue was purified by using column chromatography silica gel with $\text{CH}_2\text{Cl}_2/\text{EA}$ (10:1, v/v) as eluent to yield a yellow solid (1.0 g, 1.8 mmol, Yield: 60%). ^1H NMR (400 MHz, CDCl_3): δ 10.06 (s, 2H), 8.11 (t, $J = 1.6$ Hz, 2H), 7.88-7.80 (m, 4H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.34 (d, $J = 3.6$ Hz, 1H), 7.19 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 192.1, 144.6, 141.8, 137.1, 134.9, 133.5, 131.6, 131.3, 129.9, 129.4, 126.6, 123.7, 93.1. IR (KBr) 3081, 3051, 2820, 2730, 1703, 1594 cm^{-1} . HR-MS (APCI) m/z calcd for $\text{C}_{24}\text{H}_{15}\text{Br}_2\text{O}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 558.8854; found: 558.8864.

4,4'-((2,2-dibromoethene-1,1-diyl)bis(thiophene-5,2-diyl))dibenzaldehyde (3c):

Compound **2a** (1.2 g, 2 mmol), (4-formylphenyl)boronic acid (0.9 g, 6 mmol),

Pd(PPh₃)₄ (231.3 mg, 0.2 mmol) and K₂CO₃ (1.11 g, 8 mmol) were added in a mixed solvent DMF/ H₂O (50 mL, 15 mL). The reaction mixture was stirred under a nitrogen atmosphere at 70 °C for 5 h. The experiment treatment procedure was similar to that of **3b**. The product was obtained with a yellow solid (0.6 g, 1.2 mmol, Yield: 60%). ¹H NMR (400 MHz, CDCl₃): δ 10.01 (s, 2H), 7.90 (d, *J* = 8.0 Hz, 4H), 7.77 (d, *J* = 8.0 Hz, 4H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 4.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 191.5, 144.6, 142.7, 139.5, 135.5, 133.4, 131.5, 130.6, 126.1, 124.7, 93.7. IR (KBr) 2922, 2832, 1690, 1600, 1564 cm⁻¹. HR-MS (APCI) *m/z* calcd for C₂₄H₁₅Br₂O₂S₂ [M+H]⁺: 558.8854, found: 558.8865.

3,3'-((2,2-bis(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5-yl)amino)phenyl)ethene-1,1-diyl)bis(thiophene-5,2-diyl))dibenzaldehyde (4b):
A mixture of compound C₆S₂TPAB(OH)₂ (1.62 g, 2.1 mmol), aldehyde compound **3b** (558 mg, 1mmol), Pd(PPh₃)₄ (115 mg, 0.1 mmol) and K₂CO₃ (552 mg, 4 mmol) was added in a mixed solvent DMF/H₂O (20 mL, 8 mL). The reaction mixture was stirred under a nitrogen atmosphere at 80 °C for 4 h. After cooling to room temperature, the mixture was extracted with 30 mL dichloromethane three times. The organic portion was collected and dried over anhydrous sodium sulfate and then removed the solvent by rotary evaporation. The residue was purified by column chromatography silica gel using CH₂Cl₂/EA (10:1, v/v) as the eluent to yield a red solid (1.39 g, 0.75 mmol, Yield: 75 %). ¹H NMR (600 MHz, CDCl₃): δ 10.04 (s, 2H), 8.04 (s, 2H), 7.80 (dd, *J* = 25.8, 7.8 Hz, 4H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.21 (s, 2H), 7.11 (d, *J* = 7.8 Hz, 4H), 6.99-6.86 (m, 18H), 4.25-4.08 (m, 16H), 1.80-1.78 (m, 16H),

1.42-1.20 (m, 48H), 0.89-0.78 (m, 24H). ¹³C NMR (150 MHz, CDCl₃): δ 191.8, 169.5, 147.6, 146.7, 143.2, 142.9, 142.6, 137.1, 135.9, 135.4, 133.1, 132.0, 131.0, 129.7, 129.4, 128.7, 125.3, 124.9, 123.4, 121.0, 120.4, 109.6, 106.1, 44.9, 44.7, 31.5, 31.4, 28.0, 27.8, 26.6, 26.5, 22.6, 22.5, 14.1, 14.0. IR (KBr) 2927, 2855, 1695, 1600, 1490, 1438, 1410 cm⁻¹. HR-MS (APCI) m/z calcd for C₁₁₂H₁₃₉N₁₀O₂S₆ [M+H]⁺: 1848.9435; found: 1848.9419.

(2E,2'E)-3,3'-(((2,2-bis(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5-yl)amino)phenyl)ethene-1,1-diyl)bis(thiophene-5,2-diyl)bis(3,1-phenylene))bis(2-cyanoacrylic acid)(A8): Aldehyde compound **4b** (370 mg, 0.2 mmol), cyanoacetic acid (85 mg, 1 mmol) and piperidine (8.5 mg, 0.1 mmol) were dissolved in chloroform in a Schlenk tube under a nitrogen atmosphere and heated under reflux reaction conditions for 5 h. After the completion of the reaction, the residue was washed with water, extracted three times with dichloromethane, dried over anhydrous sodium sulfate. The crude product was purified by using column chromatography silica gel with CH₂Cl₂/CH₃OH (10:1, v/v) as eluent to yield the desired sensitizer **A8** as a yellow solid (277 mg, 0.14 mmol, Yield: 70%). ¹H NMR (400 MHz, CDCl₃): δ 8.30 (s, 4H), 7.83-7.71 (m, 4H), 7.53-7.49 (m, 2H), 7.30-7.21 (m, 2H), 7.11 (d, *J* = 8.8 Hz, 4H), 7.01-6.86 (m, 18H) 4.26-4.09 (m, 16H), 1.81-1.67 (m, 16H), 1.42-1.21 (m, 48H), 0.89-0.79 (m, 24H). ¹³C NMR (150 MHz, CDCl₃): δ 169.3, 166.2, 155.7, 147.5, 146.9, 143.3, 142.7, 142.6, 136.1, 135.7, 133.1, 132.1, 132.0, 131.1, 130.3, 130.0, 128.7, 127.2, 124.8, 123.7, 121.1, 120.5 115.2, 109.6, 106.2, 103.6, 45.0, 44.7, 31.6, 31.5, 28.0, 27.9, 26.6, 26.5,

22.6, 22.5, 14.1. IR (KBr) 3436, 2931, 2859, 2227, 1724, 1604, 1484, 1448, 1406 cm⁻¹.

¹. HR-MS (APCI) m/z calcd for C₁₁₈H₁₄₀N₁₂O₄S₆ [M]⁺: 1981.9473; found: 1981.9483.

4,4'-((2,2-bis(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5-yl)amino)phenyl)ethene-1,1-diyl)bis(thiophene-5,2-diyl))dibenzaldehyde (4c):

To a 100 mL flask was added a mixture of compound C₆S₂TPAB(OH)₂ (1.62 g, 2.1 mmol), aldehyde compound **3c** (558 mg, 1 mmol), Pd(PPh₃)₄ (115 mg, 0.1mmol) and K₂CO₃ (0.55g, 4 mmol). The 20 mL DMF and 8 mL H₂O were added as the mixed solvent. The reaction mixture was heated to 80 °C and stirred for 4 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was extracted with 30 mL dichloromethane three times. The organic portion was collected and dried over magnesium sulfate then removed by rotary evaporation. The residue was purified by column chromatography using CH₂Cl₂/EA (10:1, v/v) as eluent to obtain a red solid (1.30 g, 0.7 mmol, Yield: 70 %). ¹H NMR (400 MHz, CDCl₃): δ 10.00 (s, 2H), 7.88 (d, *J* = 7.2 Hz, 4H), 7.70 (d, *J* = 8.4 Hz, 4H), 7.28 (d, *J* = 4.0 Hz, 4H), 7.11 (d, *J* = 7.6 Hz, 4H), 6.94-6.85 (m, 16H), 4.25-4.08 (m, 16H), 1.80-1.66 (m, 16H), 1.41-1.21 (m, 48H), 0.88-0.79 (m, 24H). ¹³C NMR (100 MHz, CDCl₃): δ 191.2, 169.5, 148.0, 147.8, 143.3, 143.1, 142.9, 140.0, 135.8, 135.2, 133.2, 132.1, 131.3, 130.6, 128.8, 125.5, 124.6, 120.9, 120.5, 109.6, 106.1, 45.0, 44.7, 31.6, 31.5, 28.0, 27.9, 26.7, 26.6, 22.7, 22.6, 14.2. IR (KBr) 2925, 2851, 1700, 1594, 1496, 1406 cm⁻¹. HR-MS (APCI) m/z calcd for C₁₁₂H₁₃₉N₁₀O₂S₆ [M+H]⁺: 1848.9435; found: 1848.9431.

(2E,2'E)-3,3'-(((2,2-bis(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5-yl)amino)phenyl)ethene-1,1-diyl)bis(thiophene-5,2-

diyl))bis(4,1-phenylene))bis(2-cyanoacrylic acid) (A9): Aldehyde compound **4c** (370 mg, 0.2 mmol), cyanoacetic acid (85 mg, 1 mmol) and piperidine (8.5 mg, 0.1 mmol) were dissolved in chloroform under a nitrogen atmosphere and heated to reflux for 5 h. After cooling to room temperature, the residue was washed with water, extracted three times with dichloromethane, dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography on a silica gel column using CH₂Cl₂/CH₃OH (10:1, v/v) as eluent to obtain the desired sensitizer **A9** as a red solid (258 mg, 0.13 mmol, Yield: 65%). ¹H NMR (600 MHz, CDCl₃): δ 8.26 (s, 2H), 8.05 (d, *J* = 7.8 Hz, 4H), 7.67 (d, *J* = 8.4 Hz, 4H), 7.29 (s, 2H), 3.78 (d, *J* = 8.4 Hz, 4H), 7.00-6.85 (m, 18H), 4.25-4.10 (m, 16H), 1.80-1.65 (m, 16H), 1.41-1.19 (m, 48H), 0.89-0.78 (m, 24H). ¹³C NMR (150 MHz, CDCl₃): δ 169.5, 167.0, 155.1, 148.4, 147.9, 143.8, 143.1, 142.8, 139.4, 135.7, 133.2, 132.3, 132.2, 131.4, 130.2, 128.9, 125.7, 124.9, 124.4, 120.6, 115.6, 109.7, 106.3, 101.4, 45.0, 44.8, 31.6, 31.5, 28.1, 27.9, 26.7, 26.6, 22.7, 22.6, 14.1. IR (KBr) 3428, 2925, 2854, 2223, 1722, 1592, 1492, 1448, 1408 cm⁻¹. MS (MALDI-TOF) *m/z* calcd for C₁₁₈H₁₄₁N₁₂O₄S₆ [M+H]⁺: 1982.9551; found: 1982.8967.

10. Characterization spectra for the compounds

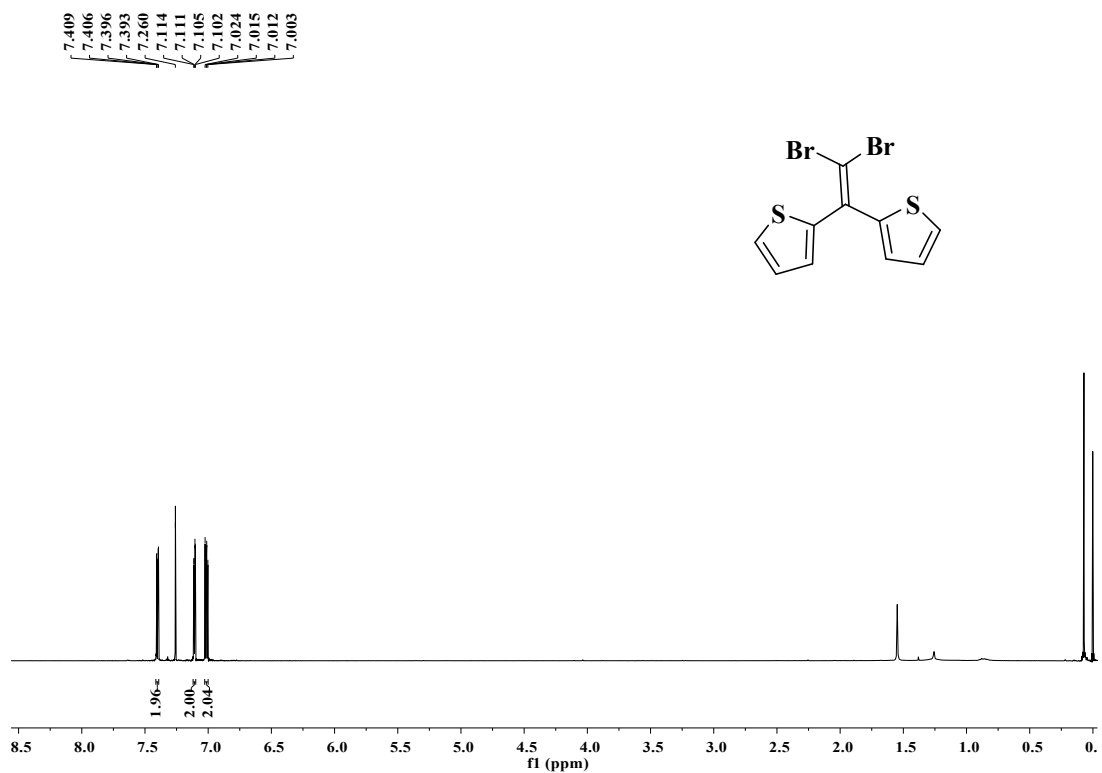


Fig. S7 The ¹H NMR spectrum of **1a** in CDCl₃.

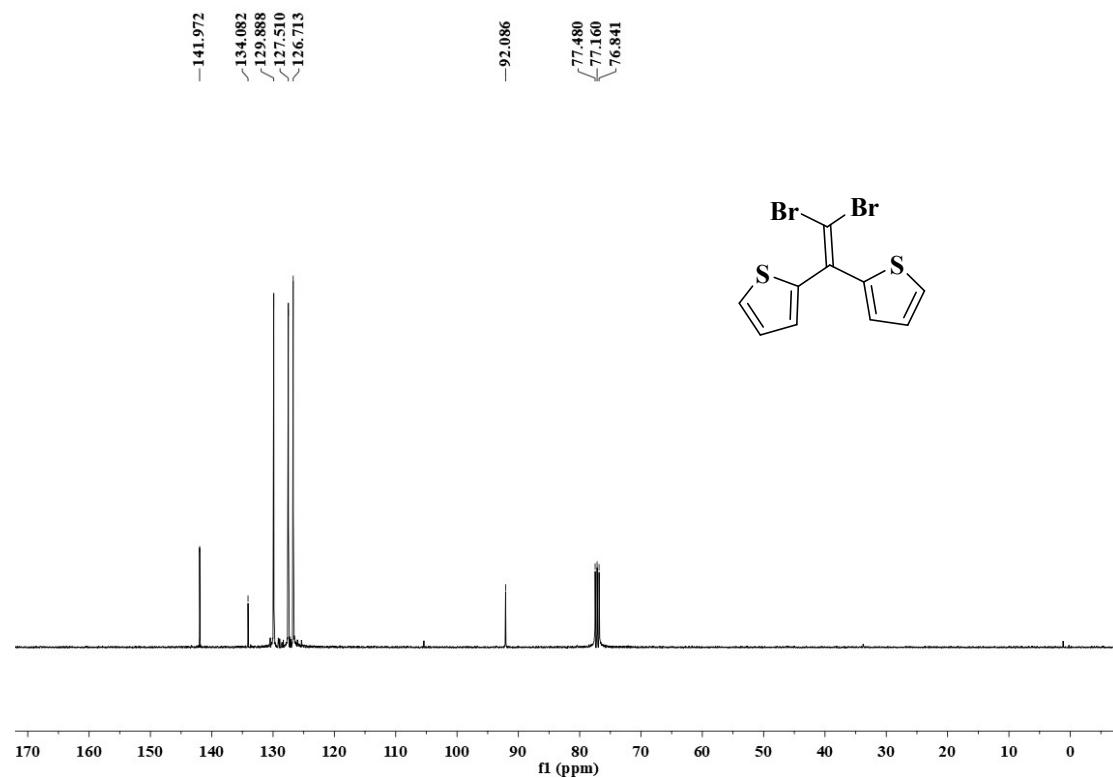


Fig. S8 The ¹³C NMR spectrum of **1a** in CDCl₃.

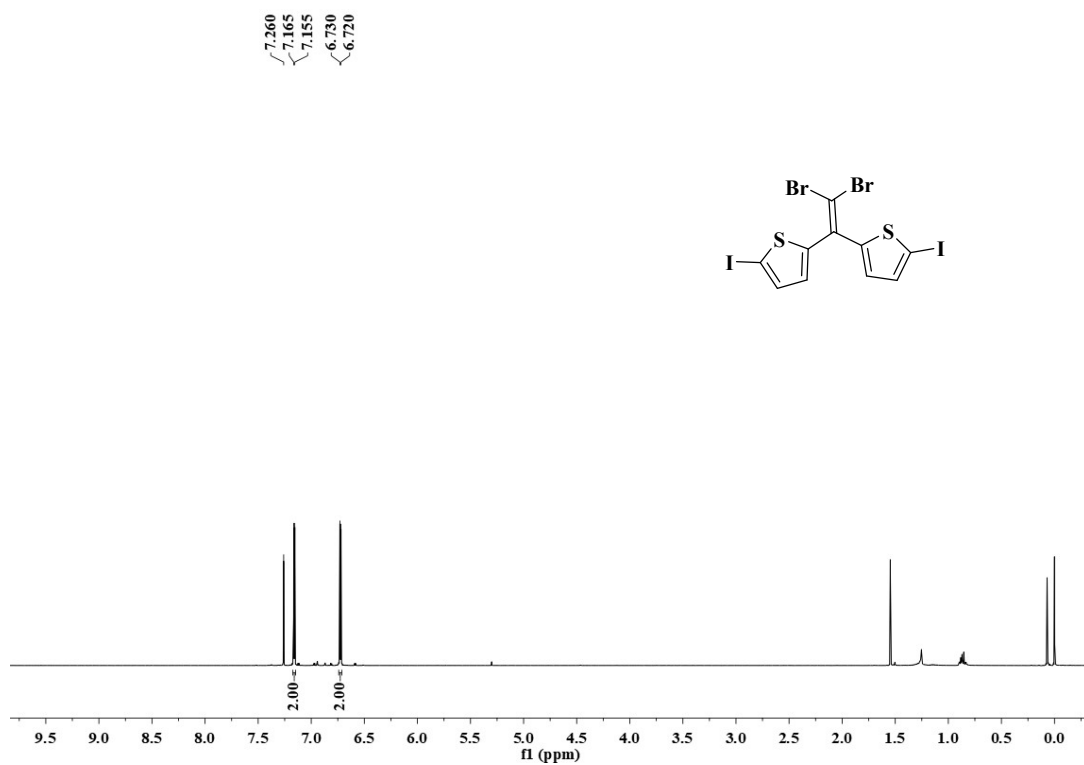


Fig. S9 The ¹H NMR spectrum of **2a** in CDCl₃.

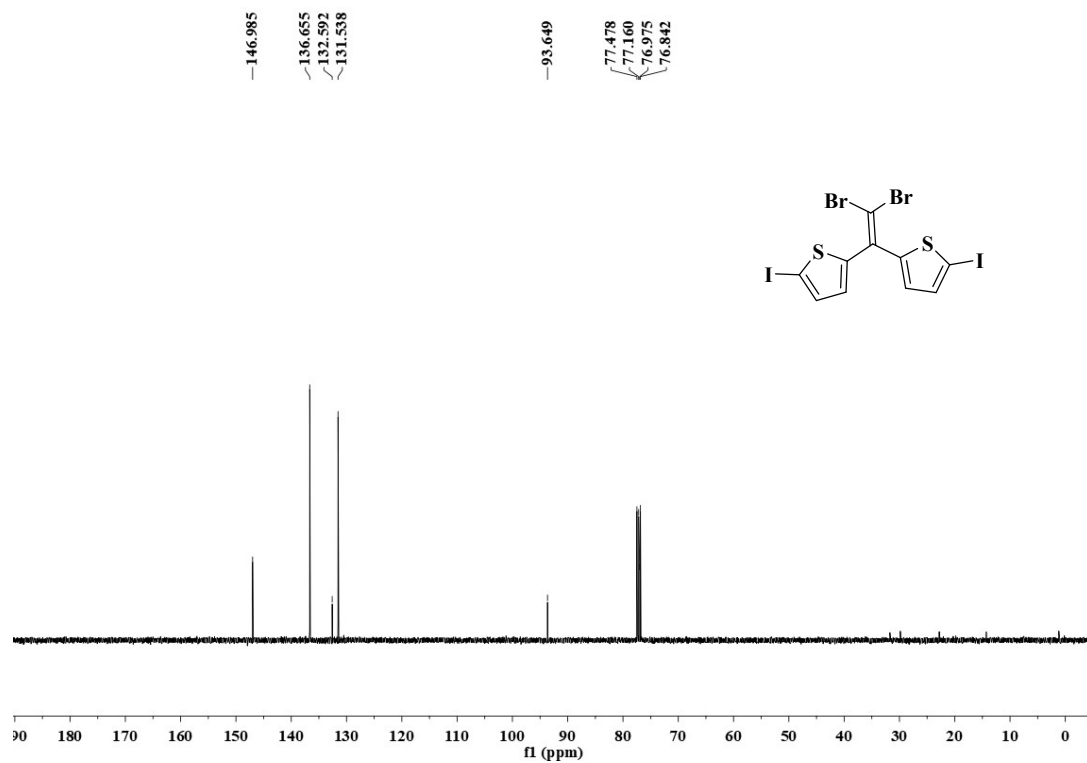


Fig. S10 The ¹³C NMR spectrum of **2a** in CDCl₃.

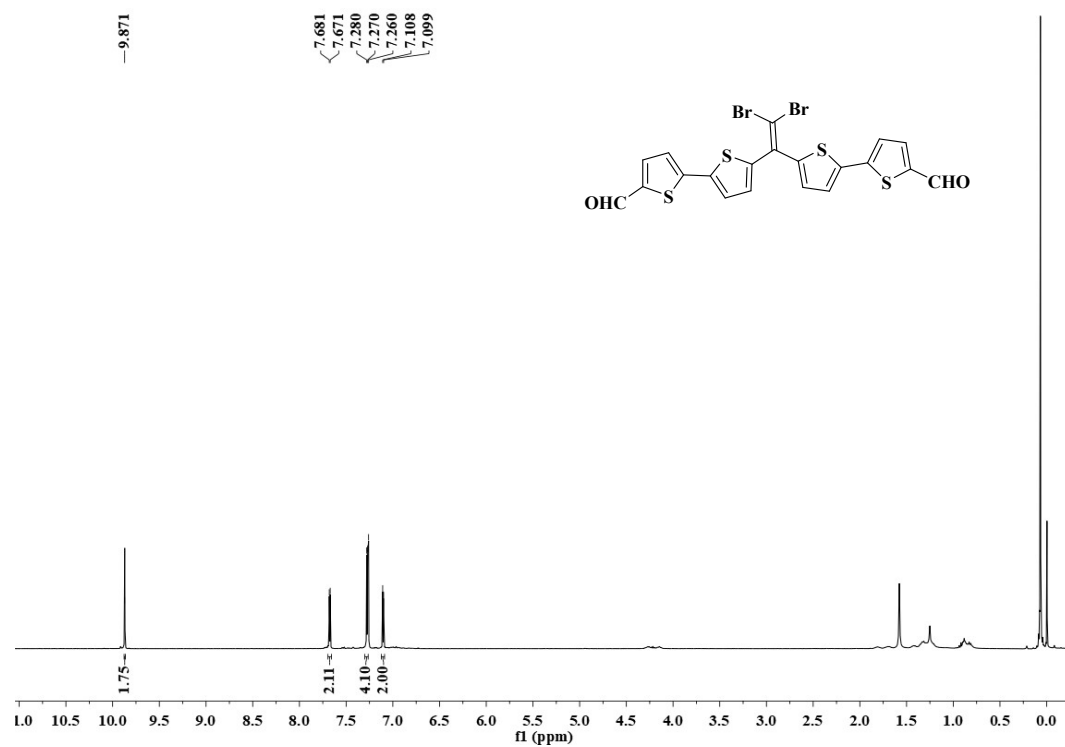


Fig. S11 The ¹H NMR spectrum of **3a** in CDCl₃.

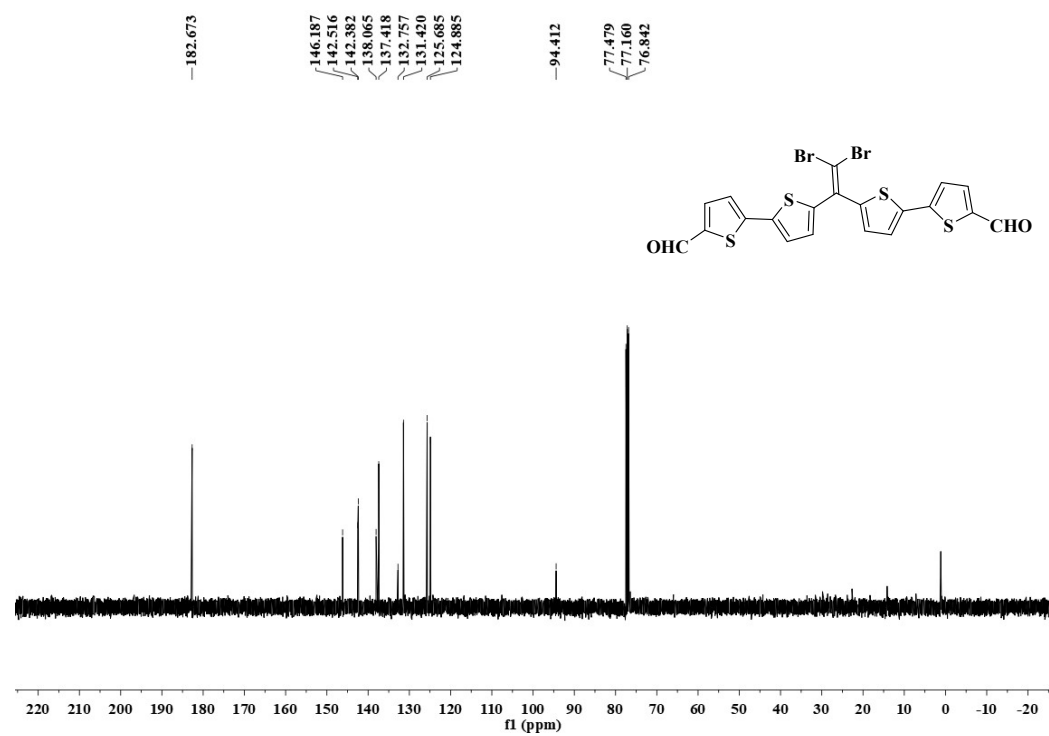


Fig. S12 The ¹³C NMR spectrum of **3a** in CDCl₃.

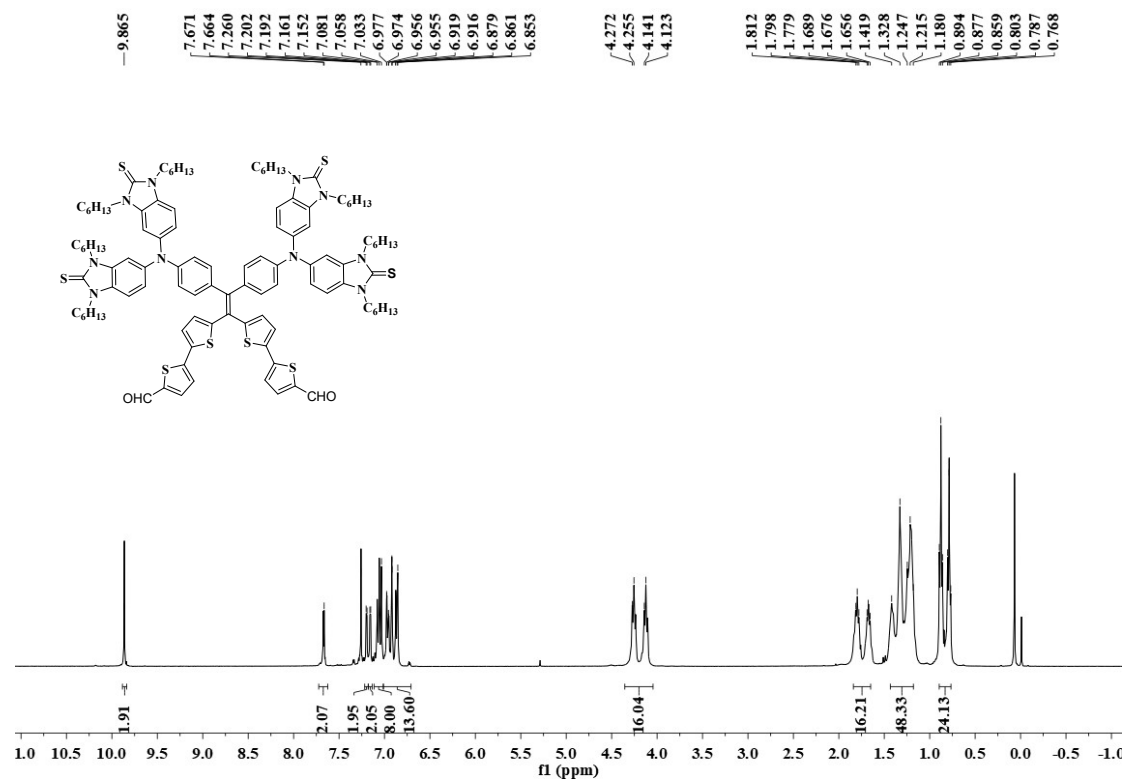


Fig. S13 The ¹H NMR spectrum of **4a** in CDCl₃.

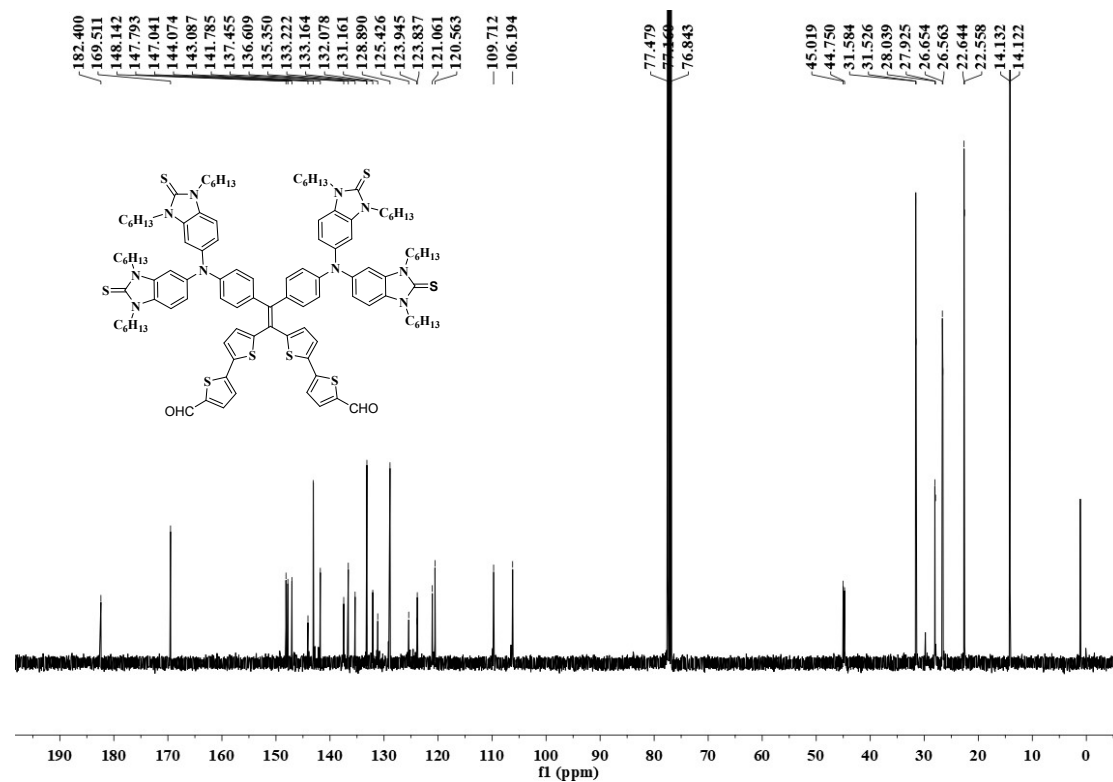


Fig. S14 The ¹³C NMR spectrum of **4a** in CDCl₃.

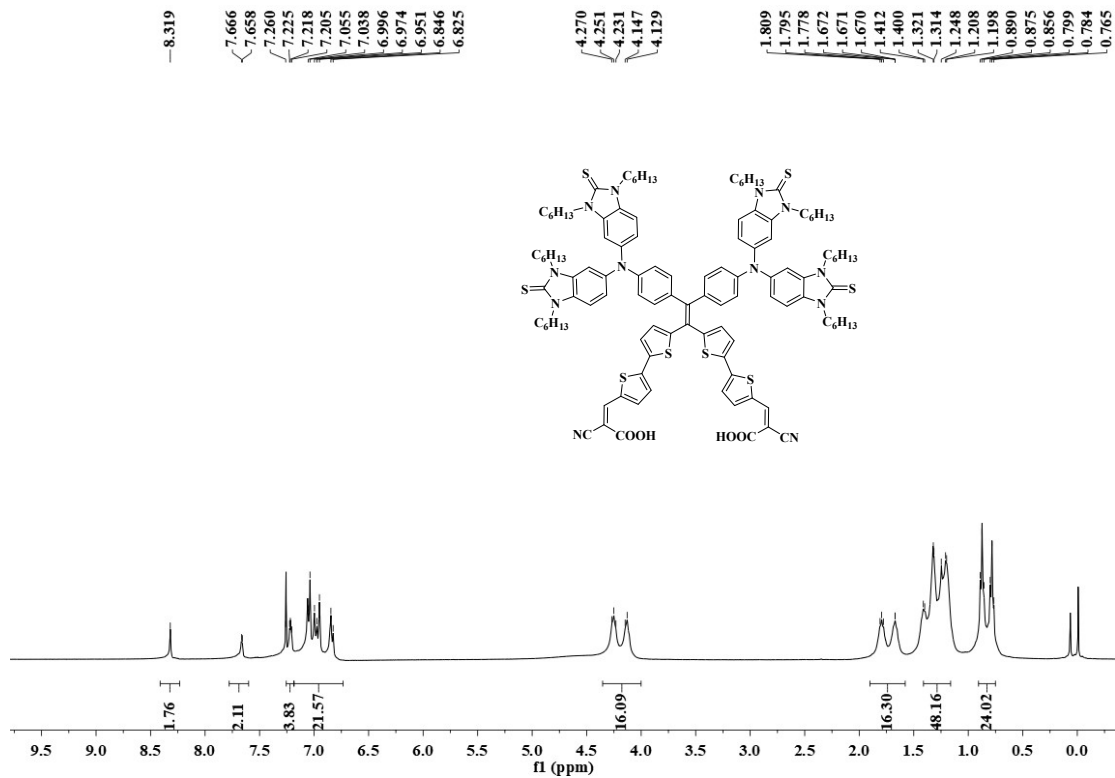


Fig. S15 The ¹H NMR spectrum of A6 in CDCl₃.

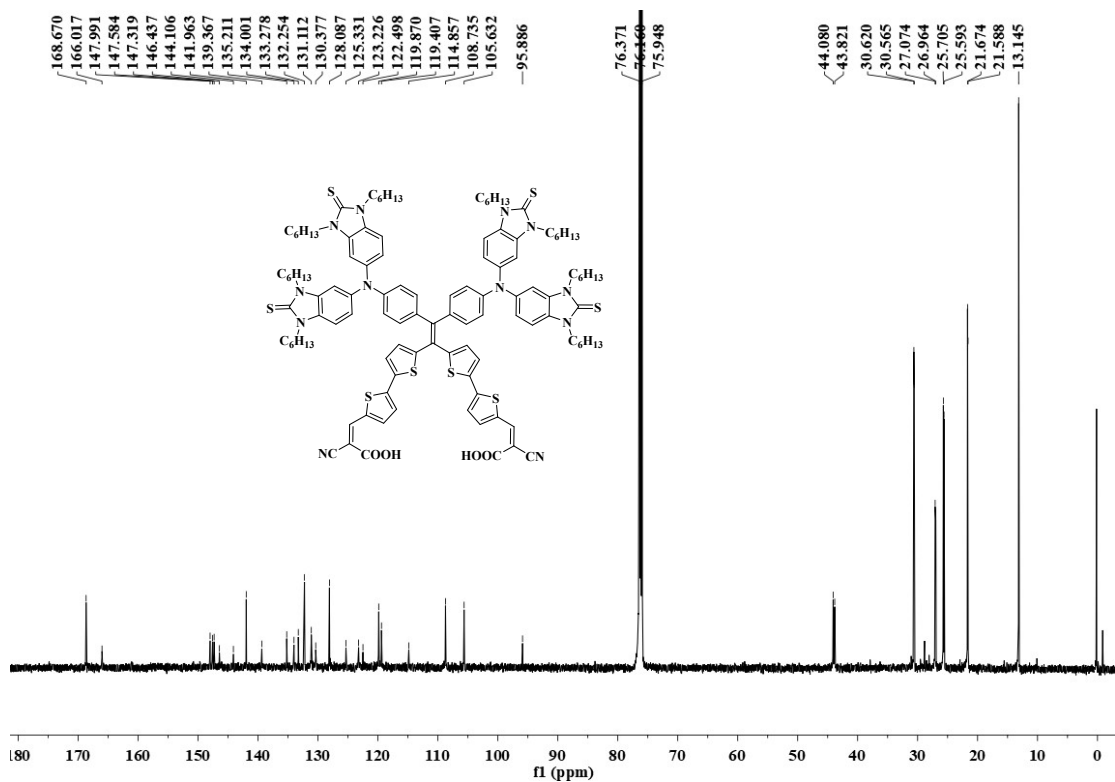


Fig. S16 The ¹³C NMR spectrum of A6 in CDCl₃.

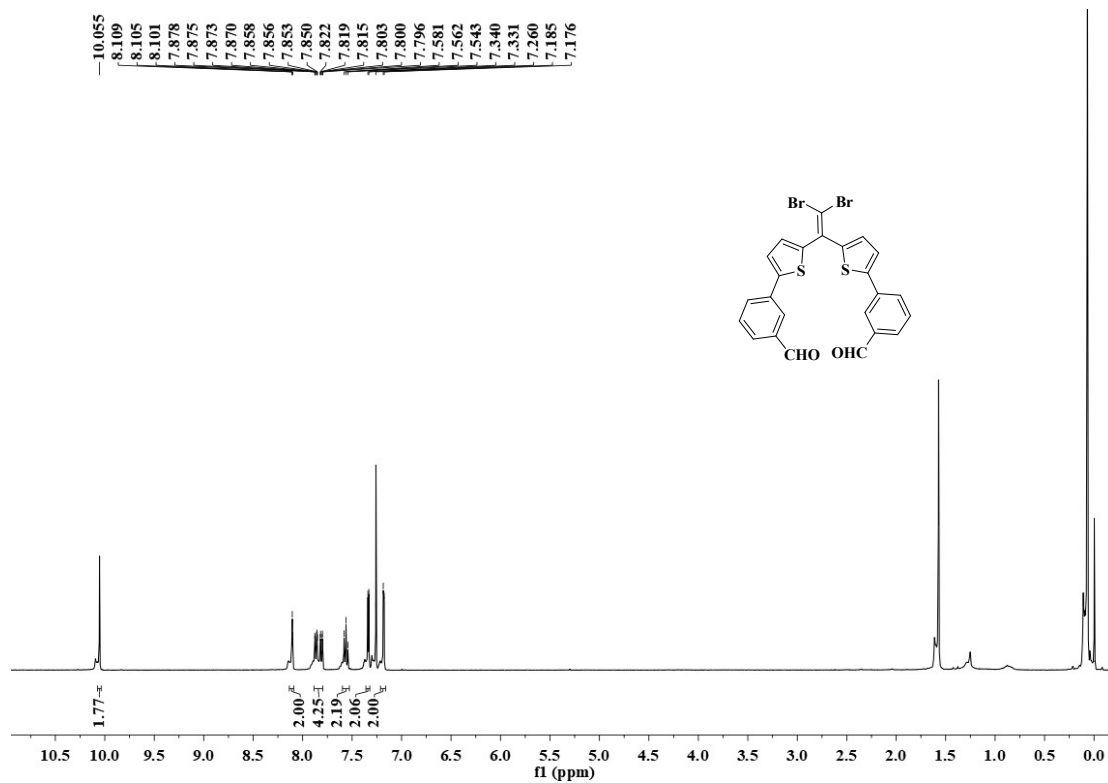


Fig. S17 The ¹H NMR spectrum of **3b** in CDCl₃.

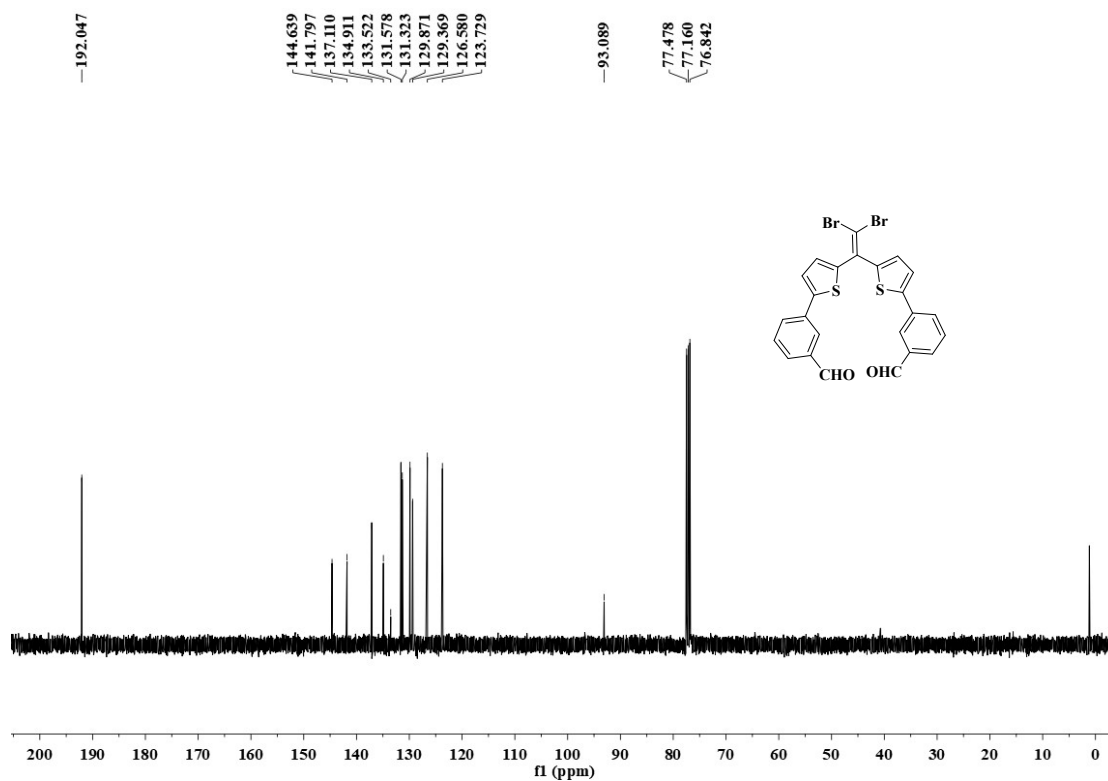


Fig. S18 The ¹³C NMR spectrum of **3b** in CDCl₃.

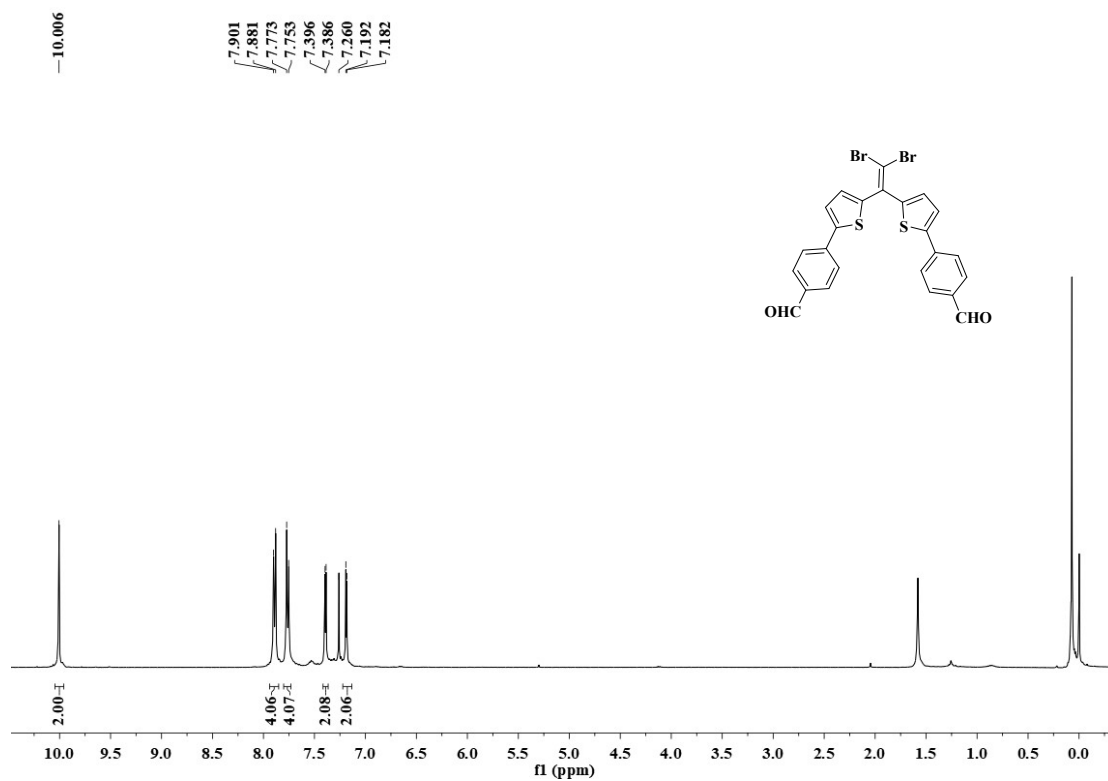


Fig. S19 The ¹H NMR spectrum of **3c** in CDCl₃.

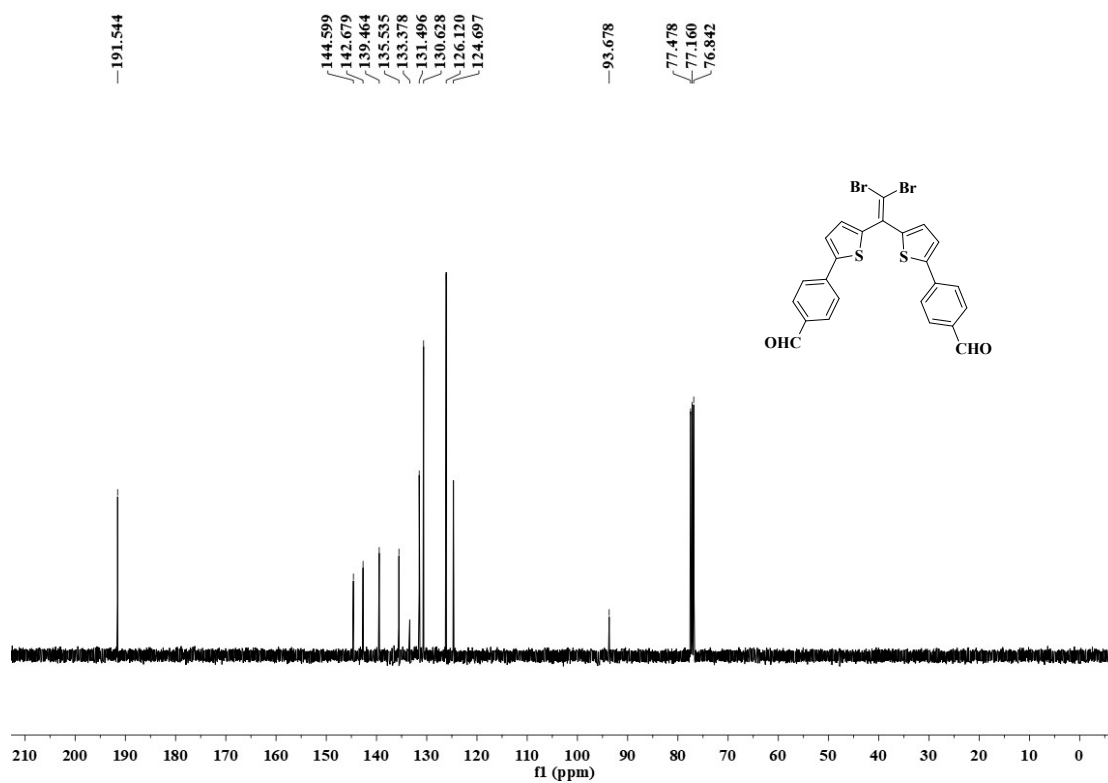


Fig. S20 The ¹³C NMR spectrum of **3c** in CDCl₃.

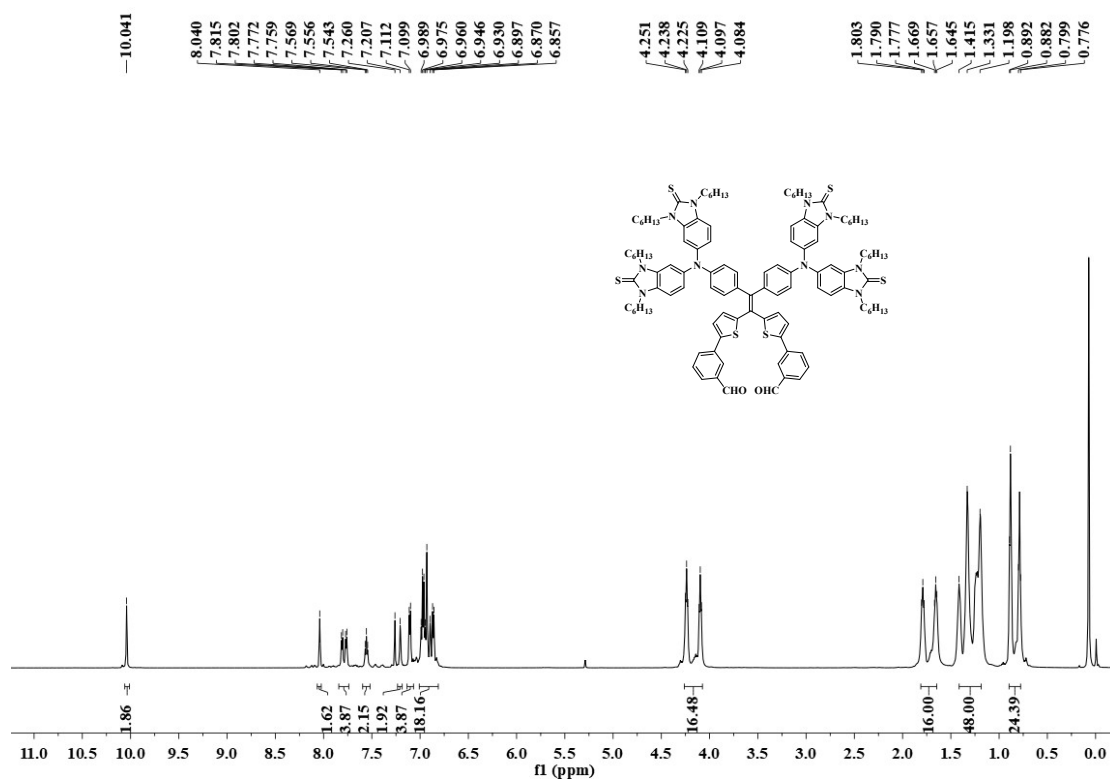


Fig. S21 The ¹H NMR spectrum of **4b** in CDCl₃.

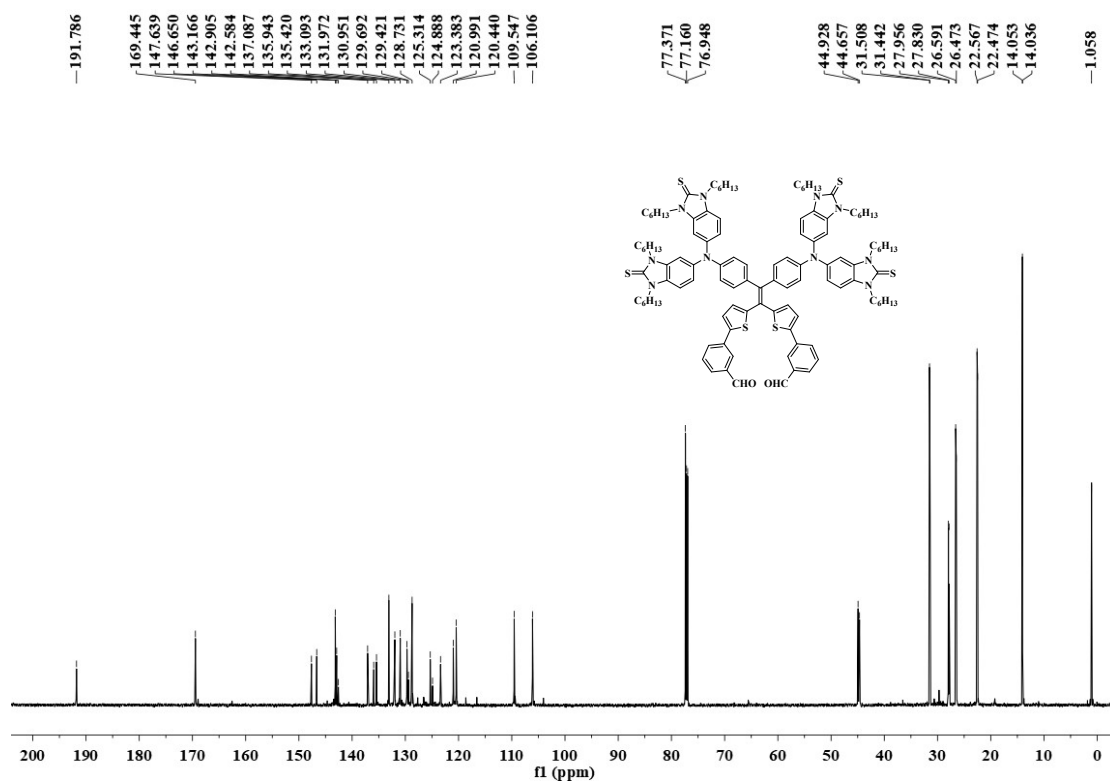


Fig. S22 The ¹³C NMR spectrum of **4b** in CDCl₃.

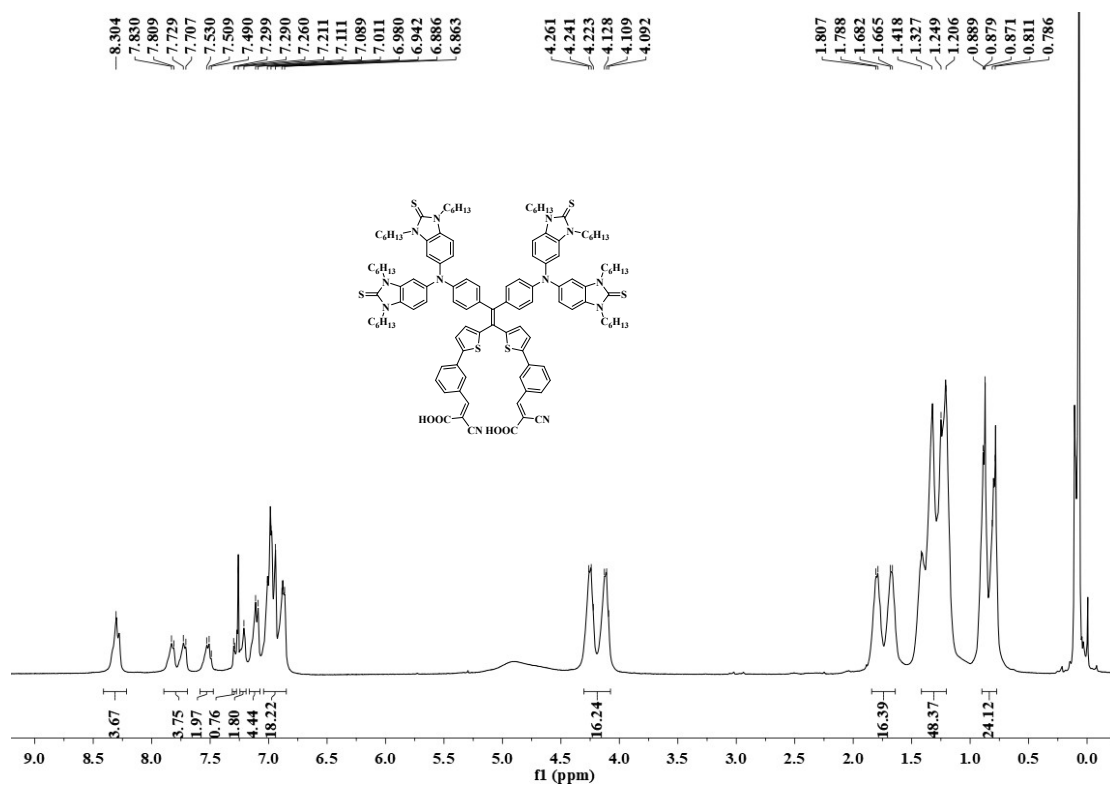


Fig. S23 The ¹H NMR spectrum of **A8** in CDCl₃.

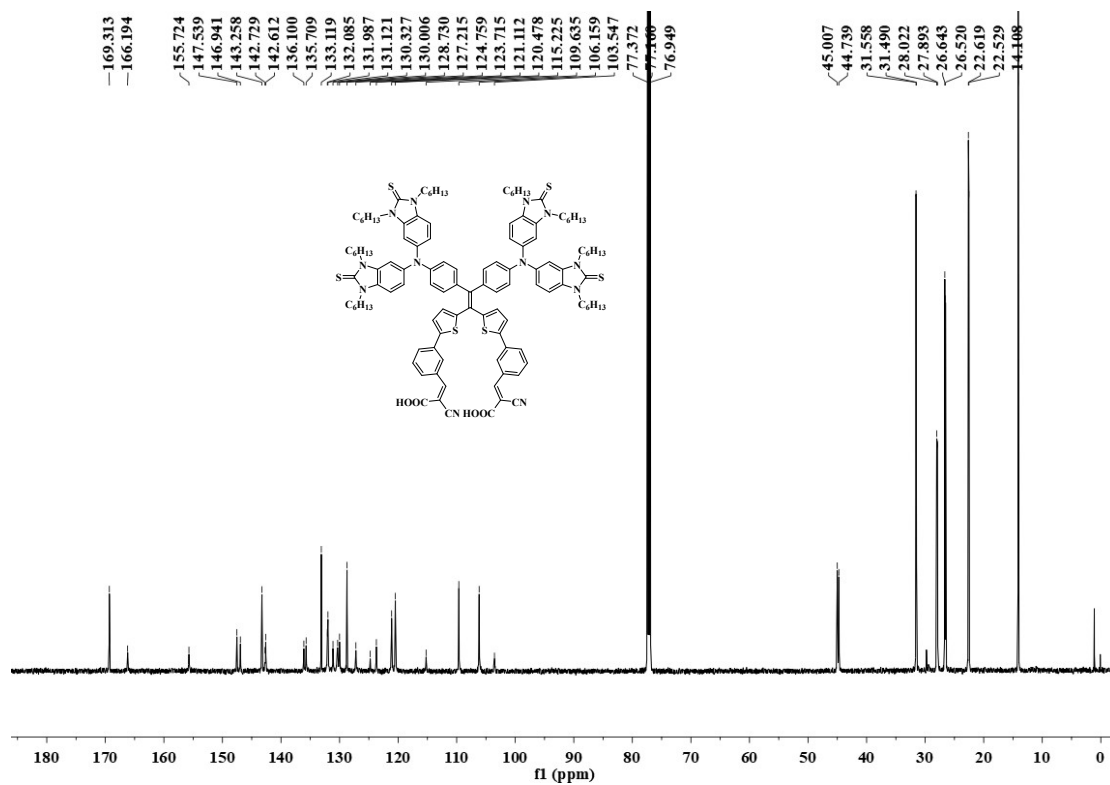


Fig. S24 The ¹³C NMR spectrum of **A8** in CDCl₃.

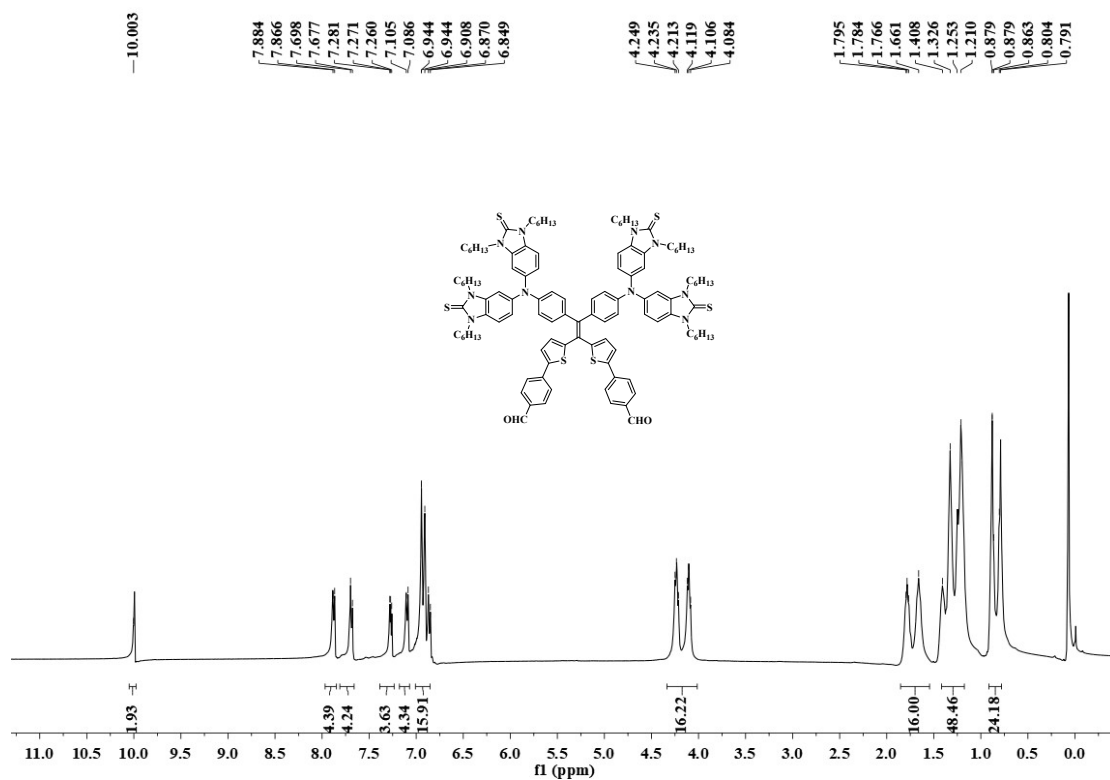


Fig. S25 The ¹H NMR spectrum of **4c** in CDCl₃.

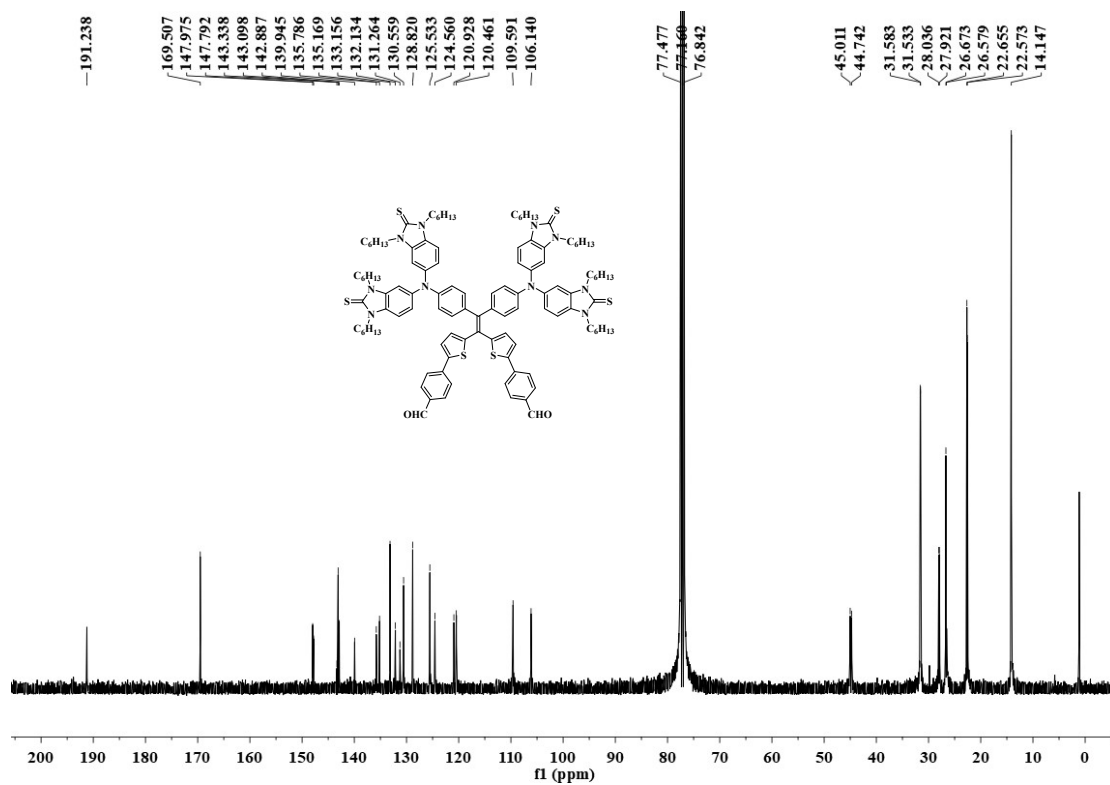


Fig. S26 The ¹³C NMR spectrum of **4c** in CDCl₃.

11. References

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