

Supplementary Information

Donor-Acceptor Coupling Unit Modulates the Spin

Coupling Effect of Stable Diradical

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Contents:

1. Experimental details
2. Materials
3. Synthesis of the target compounds
4. UV-vis Spectra

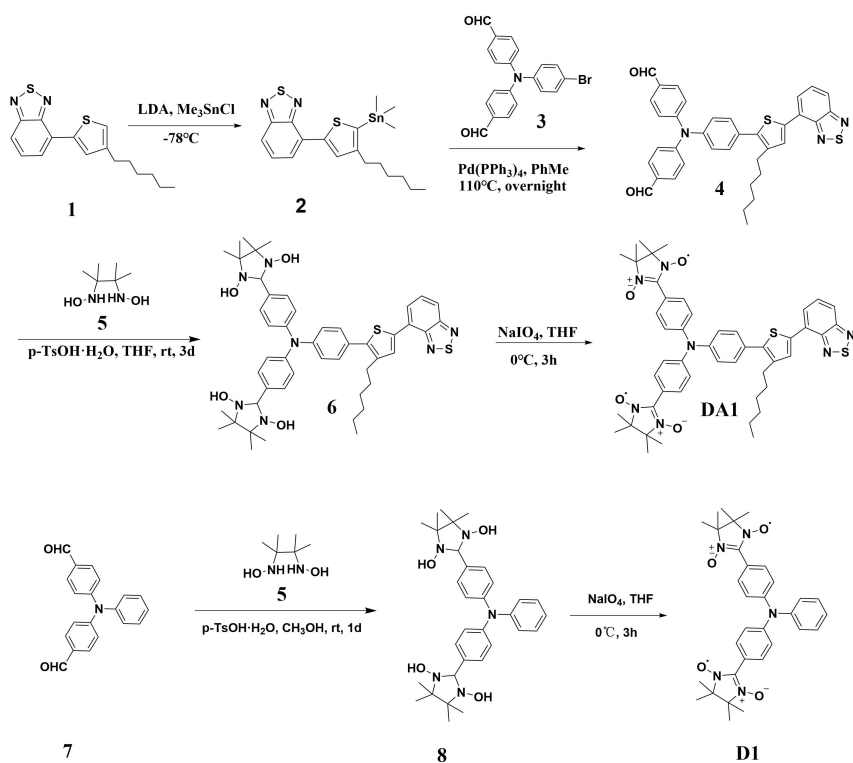
1. Experimental details

^1H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded on a Bruker Avance II DMX 400 MHz NMR spectrometer in CDCl_3 or DMSO-d_6 . Tetramethylsilane was used as an internal reference. The GCT instrument of high performance liquid time-of-flight mass spectrometry produced by Waters Company and Bruker Daltonics Biflex MalDI-TOF analyzer produced by Bruker Company. A SHIMADZU UV-3600 spectrometer was used for measuring UV-Vis-NIR absorptions. Toluene was used as the test solvent, and a 1 cm cuvette was used as the absorption pool. Circulating voltammetric (CV) measurements were carried out on a ZIVE SP1 Electrochemical Workstation. A three-electrode setup was used with platinum wires both as working electrode and counter electrode, and Ag/Ag^+ was used as reference electrode calibrated with ferrocene/ferrocenyl couple (Fc/Fc^+). A 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous acetonitrile was used as supporting electrolyte. ESR spectroscopy measurement was conducted by a Bruker EMX plus X-band spectrometer with 9.8 GHz microwave frequency. The sample for ESR measurement with a concentration of 0.1 mmol/L in anhydrous toluene or solid solution.

2. Materials

Unless otherwise stated, all chemicals and solvents were purchased from commercial sources and were used without further purification. $\text{Pd}(\text{PPh}_3)_4$ catalyst was in house prepared. Anhydrous solvents were obtained from an anhydrous solvent system.

3. Synthesis of target compounds



Scheme S1 Synthetic routes of the molecules **D1** and **DA1**.

Compound 2 Compound **1** (5.0 g, 16.5 mmol) was added into a 100 mL single-necked containing 40 mL anhydrous tetrahydrofuran (THF). Under a nitrogen atmosphere, the mixture was cooled down to -78 °C. While stirring, the freshly prepared lithium diisopropylamide (LDA) (20 mL, 2M, 33.0 mmol) was added dropwise to the mixture and stirred for 2 h at -78 °C. Then, trimethyltin chloride (SnMe₃Cl) (24 mL, 1M, 41.0 mmol) was then added in one portion. The reaction was stirred for 1 h at -78 °C before warming to room temperature. Then, 20 mL deionized water was added to quench the reaction, 40 mL saturated potassium fluoride (KF) solution was added to the reaction, after stirring for 1 h, the mixture was filtered. The filtrate was extracted by petroleum ether (PE) (3×50 mL), and washed with deionized water (3×50 mL), the organic phase was collected and dried with anhydrous Na₂SO₄. The solvent was removed by vacuum distillation after filtration, and the crude product was purified by column chromatography using petroleum ether and dichloromethane (15/1 v/v) as eluent to obtain a yellow liquid. Yield: 2.5 g, 33%. ¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.96 (s, 1H), 7.75-7.70 (m, 2H), 7.02 (s, 1H), 2.71-2.67 (t, J = 7.7 Hz, 2H), 1.32-1.26 (m, 6H), 0.88(s, 5H), 0.45 (s, 9H). ¹³C NMR (101 MHz, CDCl₃, δ/ppm): 161.2, 151.4, 144.4, 139.4, 137.6, 136.7, 129.3, 127.5, 124.7, 121.4, 31.9, 30.8, 30.6, 29.2, 22.8, 14.3. ESI-HRMS m/z calculated for C₁₉H₂₆N₂S₂Sn: 467.0637; found: 467.0646.

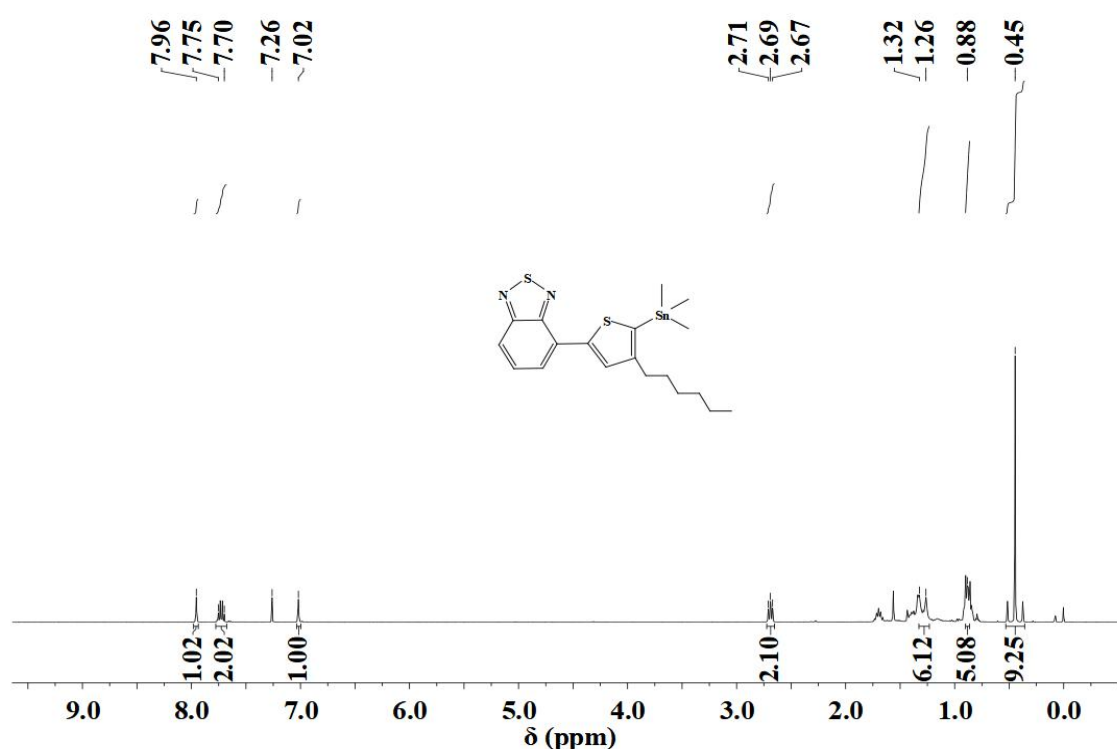


Figure S1 ¹H NMR spectrum for compound **2**

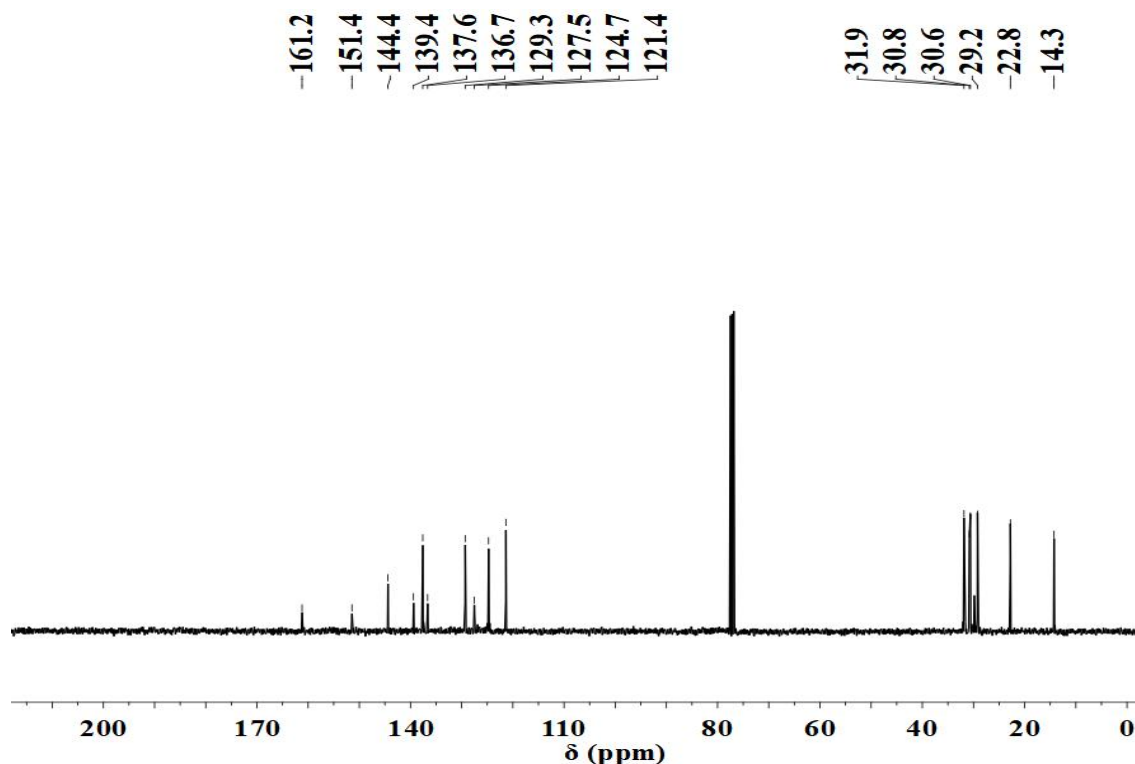


Figure S2 ^{13}C NMR spectrum for compound **2**

Compound 4 Compound **2** (2.5 g, 5.4 mmol) and compound **3** (1.5 g, 4.1 mmol) were added to a 100 mL single-necked round bottom flask and dissolved in 30 mL toluene (PhMe). Then $\text{Pd}(\text{PPh}_3)_4$ (0.1 g, 0.1 mmol) was added. After stirring at 110 °C under a nitrogen atmosphere for 12 h, the reaction was cooled down to room temperature, the reaction mixture was extracted with dichloromethane (DCM) (3×30 mL), and washed with deionized water (3×50 mL). The organic phase was collected and dried with anhydrous MgSO_4 . The solvent was removed under reduced pressure and the crude product was purified by column chromatography using petroleum ether and ethyl acetate (10/1 v/v) as eluent to obtain a bright orange solid, Yield: 0.43 g, 17%. ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 9.93 (s, 2H), 8.03-8.01 (m, 3H), 7.94-7.92 (d, $J = 7.5$ Hz, 1H), 7.83-7.81 (d, $J = 8.6$ Hz, 4H), 7.76-7.74 (t, $J = 7.7$ Hz, 1H), 7.33-7.31 (d, $J = 8.6$ Hz, 2H), 7.30-7.28 (d, $J = 8.6$ Hz, 4H), 7.07 (s, 1H), 2.71 (d, $J = 8.6$ Hz, 2H), 1.34-1.27 (m, 8H), 0.85-0.90 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3 , δ/ppm): 190.6, 153.9, 152.9, 152.0, 145.6, 144.6, 138.9, 134.9, 131.7, 131.5, 131.3, 130.8, 129.5, 128.2, 127.1, 126.7, 125.6, 123.4, 121.9, 31.8, 30.8, 30.6, 29.8, 29.2, 22.8. ESI-HRMS m/z calculated for $\text{C}_{36}\text{H}_{31}\text{N}_3\text{O}_2\text{S}_2$: 602.1936; found: 602.1941.

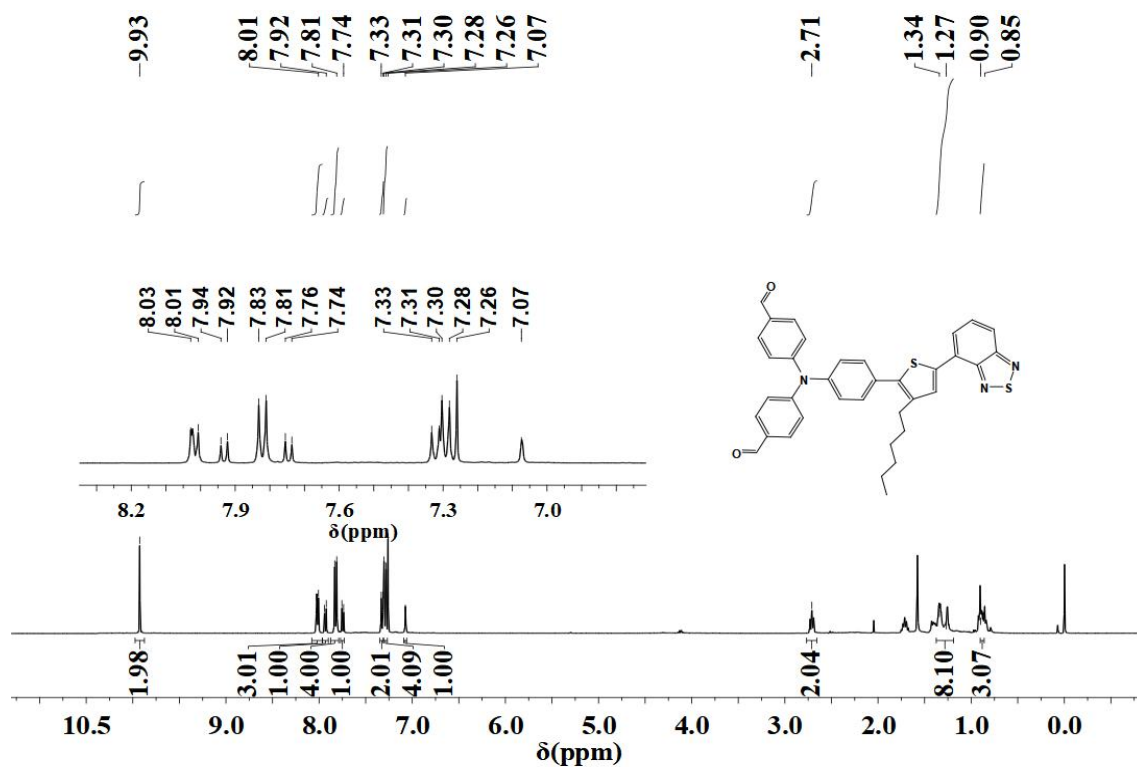


Figure S3 $^1\text{H NMR}$ spectrum for compound 4

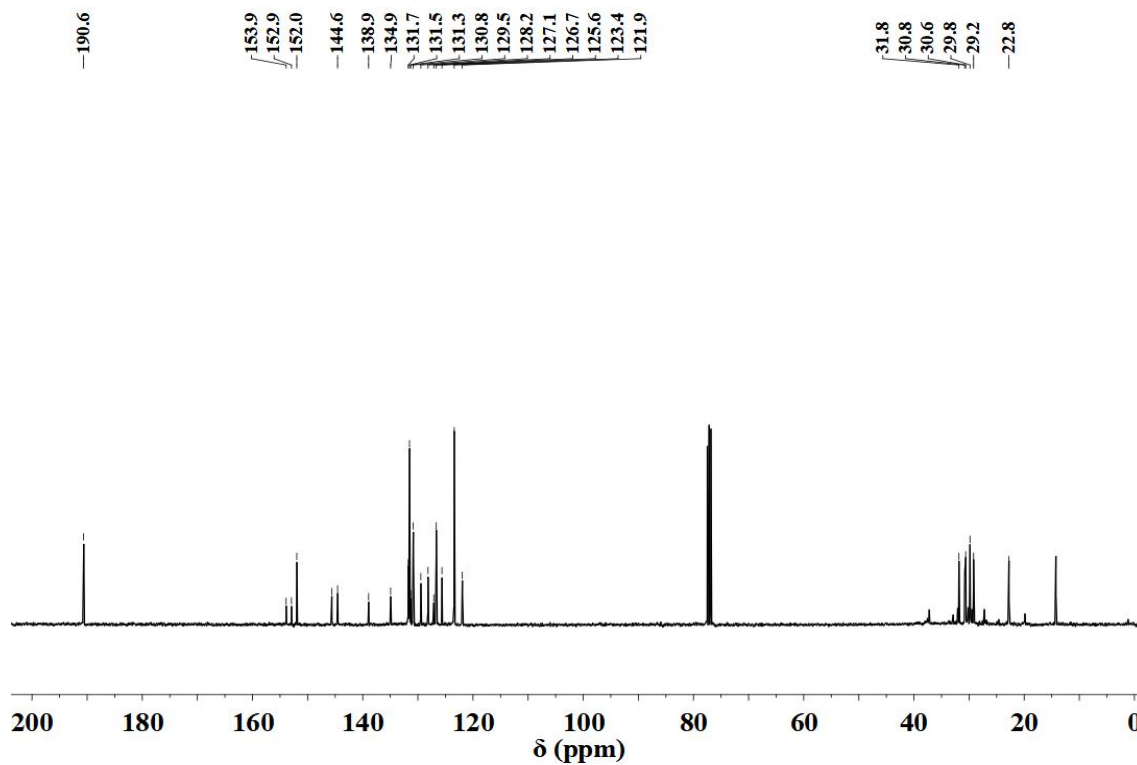


Figure S4 $^{13}\text{C NMR}$ spectrum for compound 4

Compound 6 Compound **4** (0.4 g, 0.7 mmol), p-toluene sulfonic acid monohydrate (p-TsOH·H₂O) (0.8 g, 4.0 mmol), compound **5** (0.4 g, 2.7 mmol), and 20 mL tetrahydrofuran (THF) were added to a 50 mL single-neck flask, the reaction mixture was stirred under a nitrogen atmosphere for 3 days at room temperature. Then, the solvent was removed under reduced pressure, and 30 mL deionized water was added. The mixture was extracted with ethyl acetate (EA) (3×10 mL), then the organic phase was washed with deionized water (3×10 mL), and the organic phase was collected and dried with anhydrous MgSO₄. After filtration, the solvent was removed by vacuum distillation. 10mg pure orange-red product was obtained by recrystallization with chloroform (CHCl₃), and 0.23 g mixture was obtained which was used for the following reaction without further purification. Yield: 0.23g, 40%. ¹H NMR (400 MHz, d₆-DMSO, δ/ppm): 8.10-8.08 (d, J = 7.5 Hz, 1H), 8.04 (s, 1H), 7.98-7.95 (d, J = 8.6 Hz, 2H), 7.88-7.86 (d, J = 7.6 Hz, 1H), 7.78 (s, 4H), 7.47-7.45 (d, J = 8.3 Hz, 4H), 7.34 (s, 1H), 7.09-7.04 (m, 6H), 4.50 (s, 2H), 2.67-2.64 (m, 2H), 1.37-1.23 (m, 8H), 1.08(s, 12H), 1.05 (s, 12H), 0.89-0.86 (m, 3H). ¹³C NMR (101 MHz, d₆-DMSO, δ/ppm): 153.2, 152.0, 147.8, 146.05, 143.5, 138.2, 137.4, 131.2, 130.0, 129.7, 128.5, 127.2, 125.7, 125.0, 124.0, 122.6, 121.4, 90.0, 66.0, 54.9, 31.1, 30.0, 27.2, 24.5, 22.1, 17.1, 13.9. ESI-HRMS m/z calculated for C₄₈H₅₉N₇O₄S₂: 862.4148; found: 862.4149.

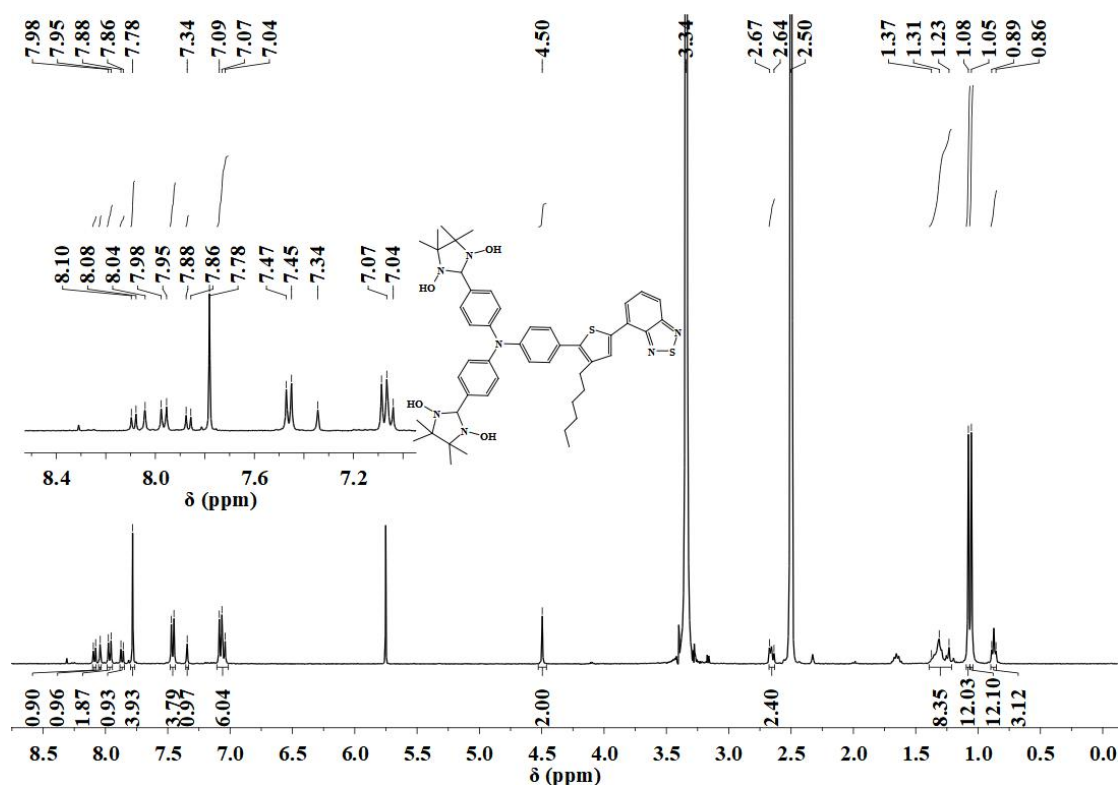


Figure S5 ¹H NMR spectrum for compound **6**

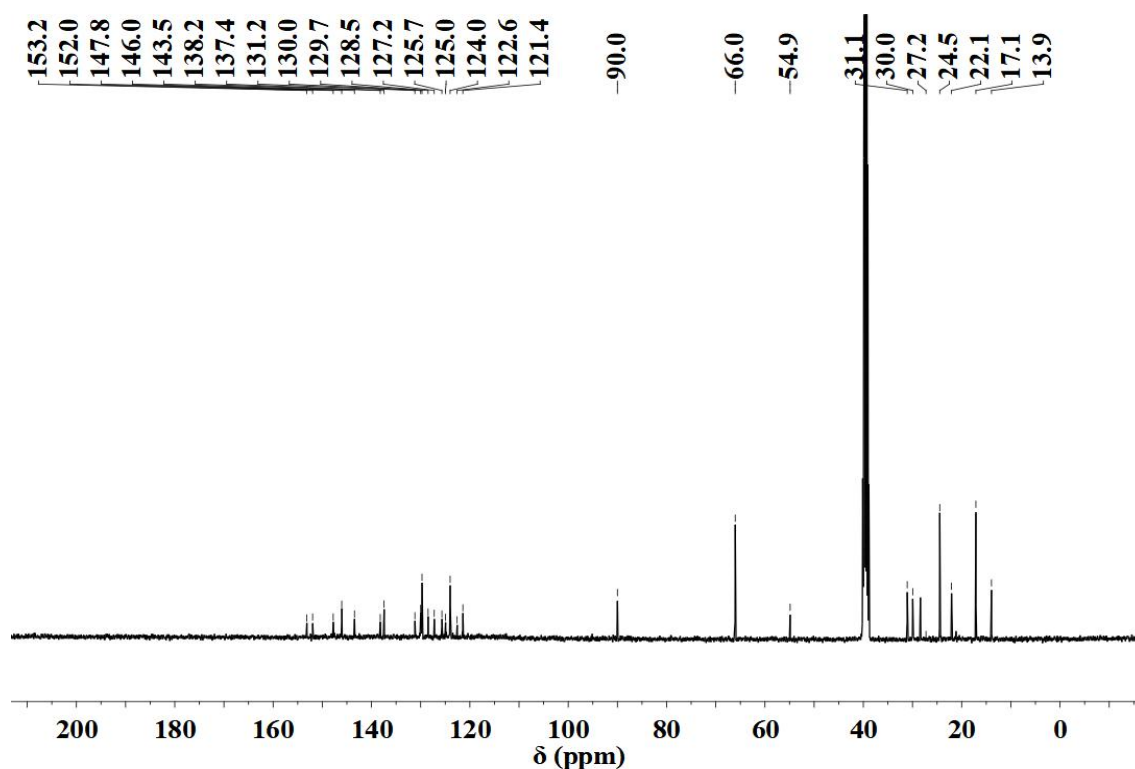


Figure S6 ^{13}C NMR spectrum for compound **6**

DA1 Compound **6** (0.23 g, 0.27 mmol) and 50 mL tetrahydrofuran (THF) were added into a 100 mL flask protected from light. The reaction was cooled to 0 °C with an ice bath, then a solution of NaIO_4 (1.14 g, 5.34 mmol) was added dropwise for 15 min. After stirring at 0 °C for 3 h, the reaction was quenched with saturated ammonium chloride solution (NH_4Cl) (20 mL). Then, 30 mL deionized water was added to the reaction mixture. The mixture was extracted with methylene chloride (DCM) (3×20 mL) and washed with deionized water (3×20 mL). The organic phase was collected and dried with anhydrous MgSO_4 . After filtration, the organic phase was concentrated under reduced pressure. The crude product was obtained by column chromatography using petroleum ether and ethyl acetate (1/1 v/v) as eluent and **DA1** was obtained as a brown-black solid. Yield: 35 mg, 15%. ESI-HRMS m/z calculated for $\text{C}_{48}\text{H}_{53}\text{N}_7\text{O}_4\text{S}_2^{2-}$: 856.3678; found: 856.3682.

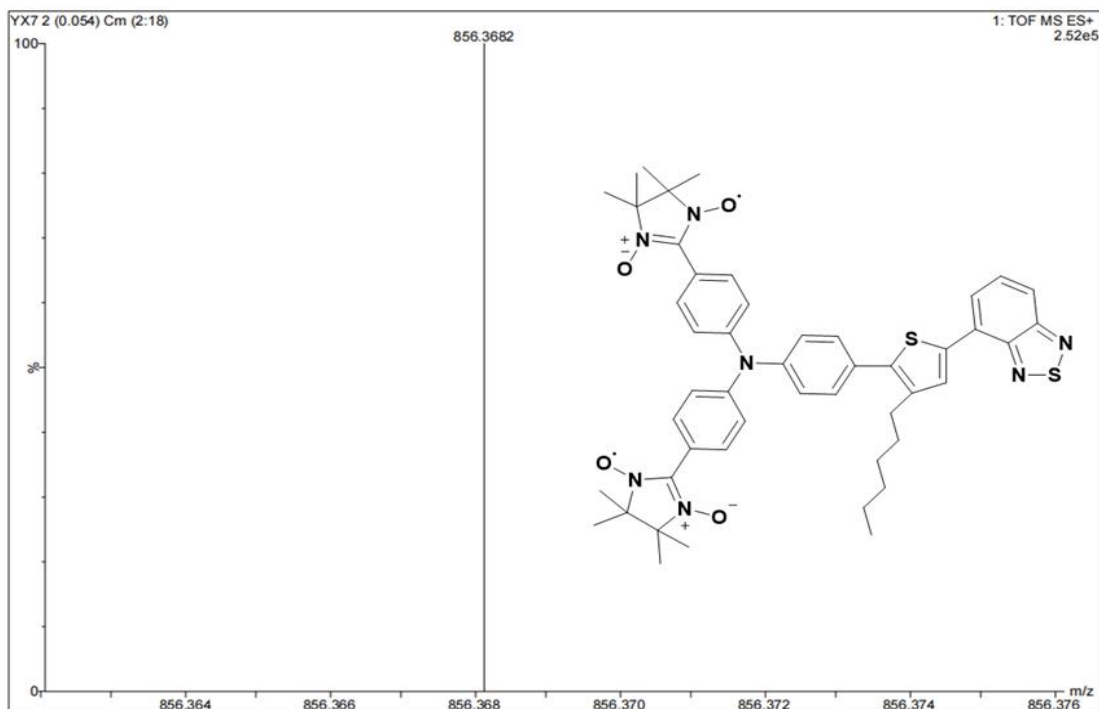


Figure S7 HRMS spectrum for compound **DA1**

Compound 8 Compound **7** (1.0 g, 3.3 mmol), compound **5** (2.0 g, 13.3 mmol), p-toluene sulfonic acid monohydrate (p-TsOH·H₂O) (3.8 g, 20.0 mmol) and 20 mL methanol (MeOH) were added into a 50 mL flask, then the reaction was stirred under a nitrogen atmosphere for 1 day at room temperature. Then, the solution was neutralized by adding triethylamine (Et₃N) until the color changed from yellow to milky white. Milky white precipitate was precipitated immediately when distilled water (50 mL) was added. The precipitate was then filtered and washed with methanol (MeOH) (3×20 mL) to obtain white solid. Yield: 1.68 g, 94%. ¹H NMR (400 MHz, d₆-DMSO, δ/ppm): 7.74 (s, 4H), 7.40-7.38 (d, J = 8.4 Hz, 4H), 7.30-7.26 (t, J = 7.9 Hz, 2H), 7.01-6.99 (d, J = 7.4 Hz, 1H), 6.96 – 6.93 (m, 6H), 4.46 (s, 2H), 1.07(s, 12H), 1.04 (s, 12H). ¹³C NMR (101 MHz, d₆-DMSO, δ/ppm): 147.6, 146.5, 136.7, 129.6, 129.4, 123.3, 122.8, 122.2, 90.0, 66.0, 24.5, 17.1. ESI-HRMS m/z calculated for C₃₂H₄₃N₅O₄: 562.3393; found: 562.3382.

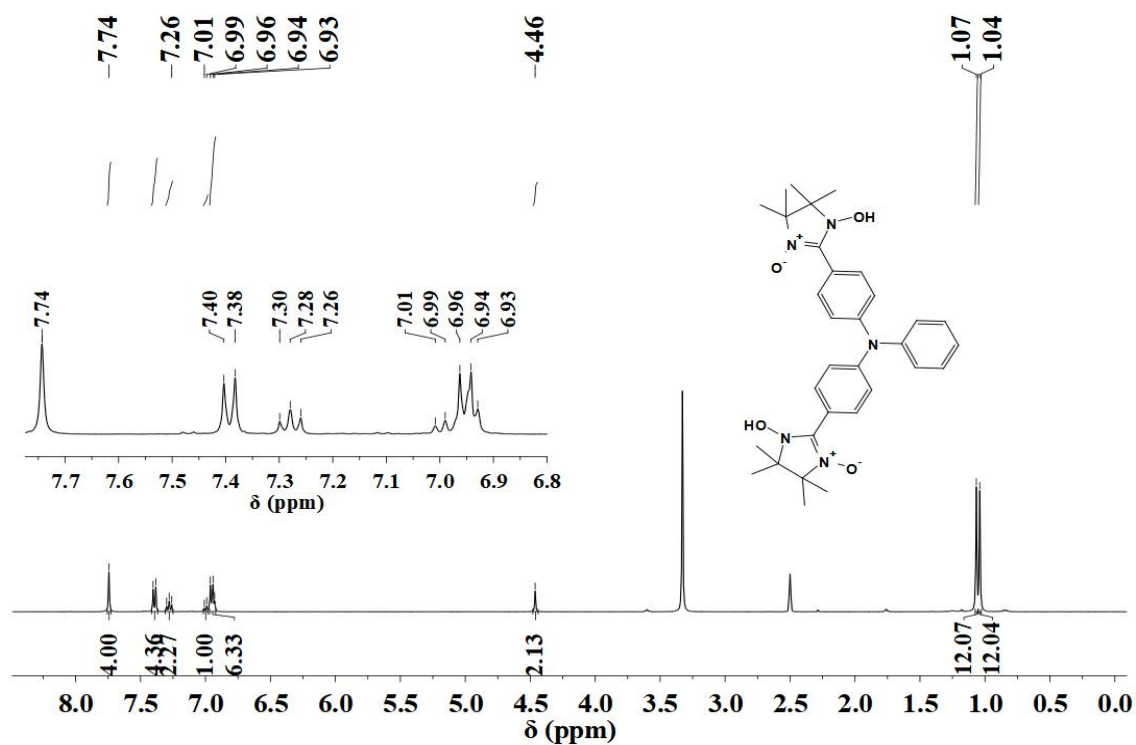


Figure S8 ¹H NMR spectrum for compound 8

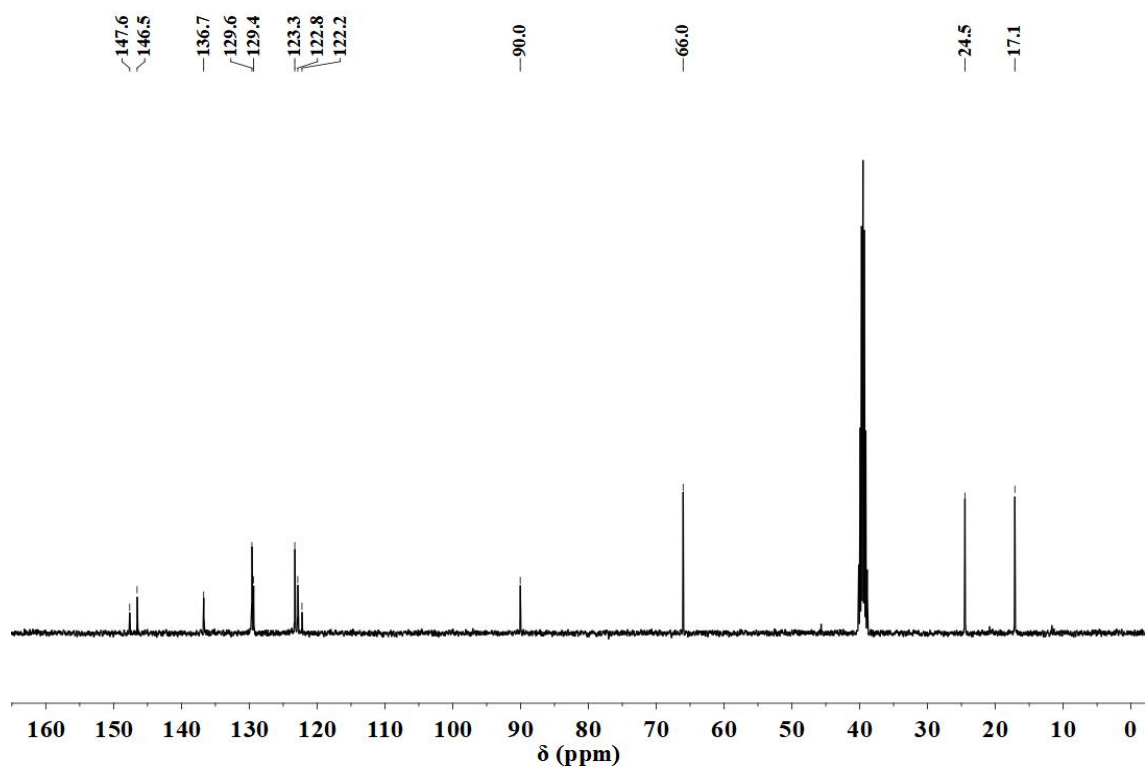


Figure S9 ¹³C NMR spectrum for compound 8

D1 Compound **8** (0.5 g, 0.9 mmol) and 70 mL tetrahydrofuran (THF) were added into a 250 mL reaction flask. The reaction was cooled to 0 °C with an ice bath, then a solution of NaIO₄ (3.8 g, 17.8 mmol) was added dropwise for 15 min. After stirring at 0 °C for 3 h, the reaction was quenched with saturated ammonium chloride solution (NH₄Cl) (50 mL). Then, the reaction mixture was extracted with methylene chloride (DCM) (3×10 mL) and washed with deionized water (3×10 mL). The organic phase was collected and dried with anhydrous MgSO₄. After filtration, the organic phase was concentrated under reduced pressure. The crude product was obtained by column chromatography using petroleum ether and ethyl acetate (1/1 v/v) as eluent to obtain a dark blue solid. Yield: 0.26 g, 52%. ESI-HRMS m/z calculated for C₃₂H₃₇N₅O₄²⁺: 556.2924; found: 556.2917.

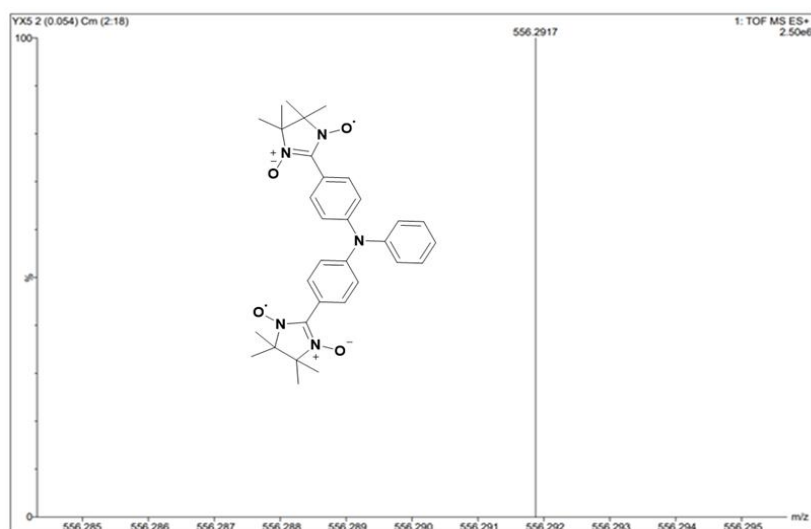


Figure S10 HRMS spectrum for compound **D1**

4. UV-vis Spectra

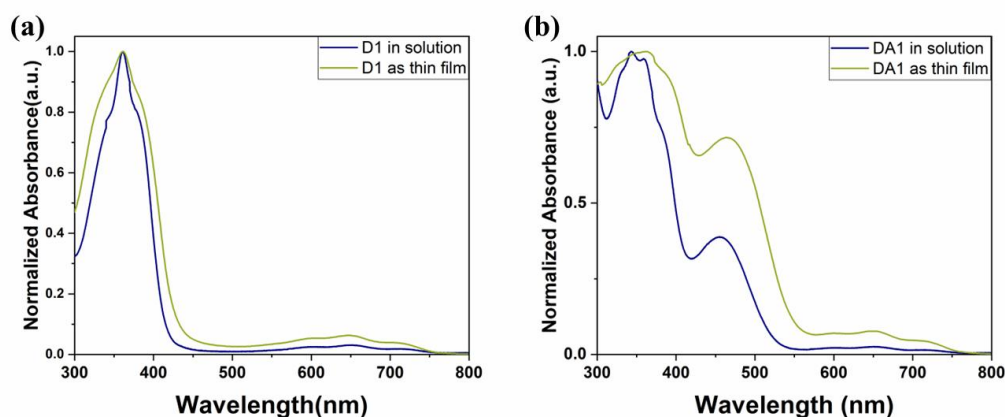


Figure S11 Normalized UV-vis-NIR spectra for **D1** and **DA1**