

Supporting Information for:

Quinoxaline-Based Cross-Conjugated Luminophores: Charge Transfer, Piezofluorochromic, and Sensing Properties

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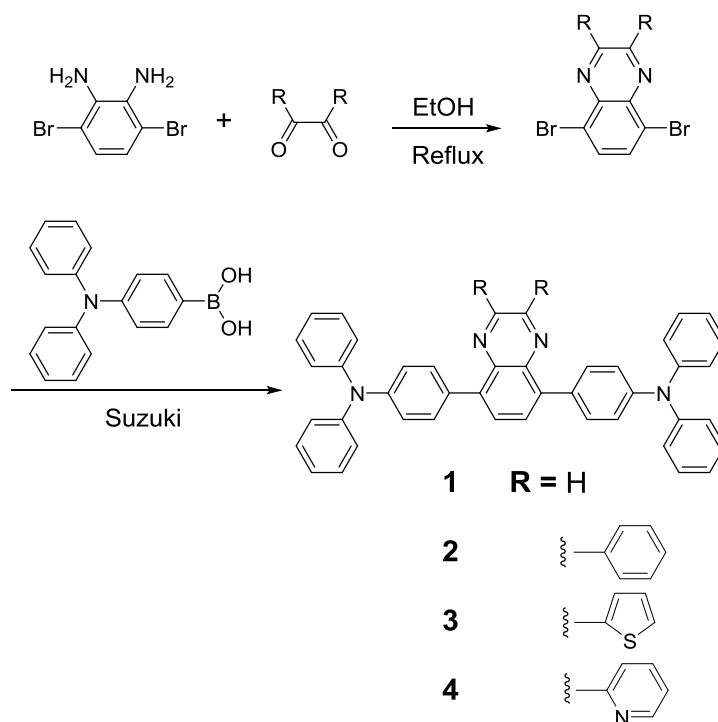
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Experimental section

Materials and reagents.

All the chemicals and reagents were purchased from commercial sources and used as received. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques. The Schlenk flasks and tubes were capped by rubber septa, and the reactions were conducted under nitrogen or argon. Anhydrous toluene and toluene were distilled from sodium benzophenone ketyl. Other anhydrous solvents were distilled according to standard procedures. The synthesis of luminophores **1** has been published elsewhere.^{S1}

Synthesis.



Scheme S1 Synthetic route for luminophores **1-4**.

Synthesis of 2,3-diaryl-5,8-dibromoquinoxaline:

A mixture of 3,6-dibromo-1,2-phenylenediamine (1 g, 9.6 mmol) and diaryldione (9.6 mmol) were added to the 500 mL one neck round-bottom flask followed by 250 mL of ethanol and 3 drops of triethylamine. The mixture was refluxed overnight, and the reaction mixture was allowed to cool to room temperature. Yellow precipitate was filtered and washed with 20 mL of ethanol two times. Then the crude product was purified by recrystallization.

Synthesis of luminophores 2, 3, and 4:

Under a nitrogen atmosphere, a solution of 2,3-diaryl-5,8-dibromoquinoxaline (0.5 mmol), 4-diphenylaminophenylboronic acid (373mg, 1.25 mmol), $(\text{PPh}_3)_2\text{PdCl}_2$ (35 mg, 0.05 mmol) in 20 mL toluene and K_2CO_3 (3.6 g, 26 mmol) in 10 mL H_2O were mixed together in a 100 mL Schlenk flask. The mixture was stirred and heated at 85 °C overnight. Then the mixture was poured into water and extracted with dichloromethane twice. The combined organic solution was washed by brine and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was purified by flash column chromatography (silica gel, DCM/PE = 1/2) to afford the desired product.

4,4'-(2,3-Diphenylquinoxaline-5,8-diyl)bis(N,N-diphenylaniline) (2).

Yield: 58% (220 mg), greenyellow solid. ^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.88 (s, 2H), 7.79 (d, 2H, $J = 8$ Hz), 7.61 (d, 4H, $J = 8$ Hz), 7.30 (m, 12H), 7.21 (d, 12H, $J = 8$

Hz), 7.06 (t, 4H, $J = 8$ Hz). ^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 151.2, 148.0, 147.6, 139.4, 138.8, 138.6, 132.4, 131.9, 130.3, 129.6, 129.5, 129.0, 128.4, 124.9, 123.2, 123.0. HRMS (ESI, m/z): $[(\text{M}+\text{Na})^+]$ calcd for $\text{C}_{56}\text{H}_{40}\text{N}_4\text{Na}$, 791.3145; found, 791.3154.

4,4'-(2,3-Di(thiophen-2-yl)quinoxaline-5,8-diyl)bis(N,N-diphenylaniline) (3).

Yield: 87% (340 mg), orange solid. ^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.85 (s, 2H), 7.78 (d, 2H, $J = 8$ Hz), 7.45 (m, 4H), 7.30 (t, 8H, $J = 8$ Hz), 7.23 (t, 12H, $J = 8$ Hz), 7.06 (t, 8H, $J = 8$ Hz), 7.00 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 148.0, 147.6, 144.4, 142.9, 138.3, 138.1, 132.1, 132.0, 129.6, 129.5, 129.4, 129.2, 127.7, 124.8, 123.16, 123.1. HRMS (ESI, m/z): $[(\text{M}+\text{H})^+]$ calcd for $\text{C}_{52}\text{H}_{37}\text{N}_4\text{S}_2$, 781.2454; found, 781.2463.

4,4'-(2,3-Di(pyridin-2-yl)quinoxaline-5,8-diyl)bis(N,N-diphenylaniline) (4).

Yield: 86% (330 mg), yellow solid. ^1H NMR (400 MHz, CDCl_3 , δ ppm): 8.24 (d, 2H, $J = 8$ Hz), 8.20 (s, 2H), 7.84 (t, 2H, $J = 8$ Hz), 7.77 (d, 4H, $J = 8$ Hz), 7.30 (t, 8H, $J = 8$ Hz), 7.23 (t, 12H, $J = 8$ Hz), 7.06 (t, 4H, $J = 8$ Hz). ^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 157.9, 150.9, 148.2, 147.9, 147.7, 138.7, 138.7, 137.1, 132.1, 131.9, 130.1, 129.5, 125.0, 124.3, 123.3, 123.1, 123.0. HRMS (ESI, m/z): $[(\text{M}+\text{H})^+]$ calcd for $\text{C}_{54}\text{H}_{39}\text{N}_6$, 771.3231; found, 771.3230.

Characterizations.

Proton nuclear magnetic resonance (^1H NMR, 400 MHz) and carbon nuclear magnetic resonance (^{13}C NMR, 100 MHz) spectra were measured on a Varian Mercury Plus-400 spectrometer. (Ultraviolet-visible) UV-vis absorption spectra were recorded on a Shimadzu UV-2550 UV-vis spectrophotometer. Photoluminescence (PL) spectra were measured on a Shimadzu RF-5301PC spectrometer. Differential scanning calorimetry (DSC) curves were obtained with a DSC Q2000-TA at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under N_2 atmosphere. Wide-angle X-ray diffraction (WAXD) measurements were carried out using an X-ray powder diffractometer (D8 ADVANCE, Bruker) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$).

Piezofluorochromic and stimulus-recovering experiments.

Ground samples were prepared by grinding the luminophore powders using a mortar and pestle. Thermal annealing experiments were done in a vacuum oven whose temperature was 20 $^{\circ}\text{C}$ higher than corresponding T_{cc} for 5 min. For the solvent fuming, the ground sample was filled on a glass culture dish, which was placed in a large beaker saturated with cyclohexane vapors for 10 s.

Metal ions sensing experiments.

The THF solutions of luminophores **1-4** (10^{-5} M) were prepared by successive dilution. The saturate CH_3CN solutions of metal ions were prepared by dissolving excess cationic perchlorate salts or cationic nitrate salts in CH_3CN .

Then 0.1 mL of cation solution was added into 2 mL of the prepared luminophore solutions. THF was further added to acquire 10 mL of solutions. The solutions were ultrasonically treated for 1 min prior to measuring the UV-vis absorption and fluorescence spectra.

References:

[S1]X. Lu, S. Fan, J. Wu, X. Jia, Z.-S. Wang, G. Zhou, *J. Org. Chem.* **2014**, *79*, 6480–6489.

Fig. S1 PL spectra of the luminophores powders.

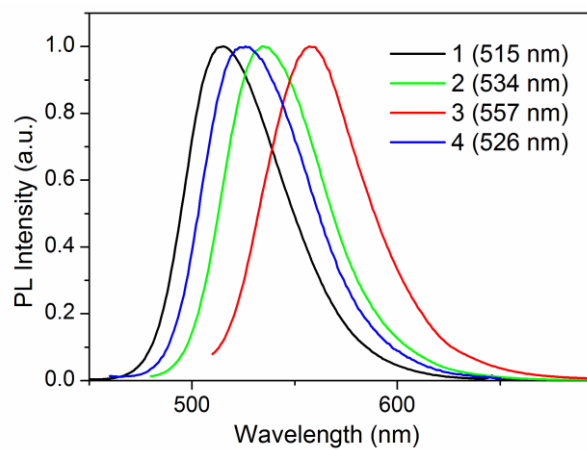


Fig. S2 UV-vis absorption spectra changes of the luminophores in the presence of different metal ions.

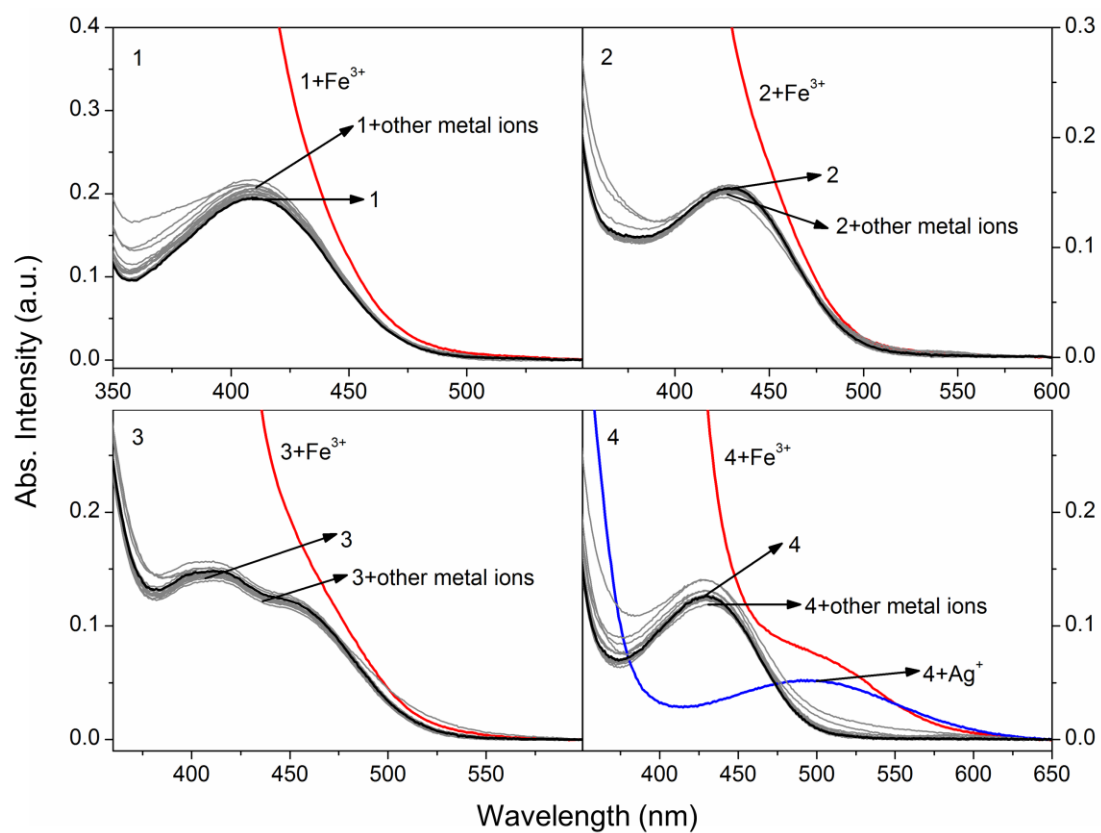


Fig. S3 PL spectra of the luminophores in THF solutions upon addition of Fe^{3+} ions and $\text{NH}_3 \cdot \text{H}_2\text{O}$.

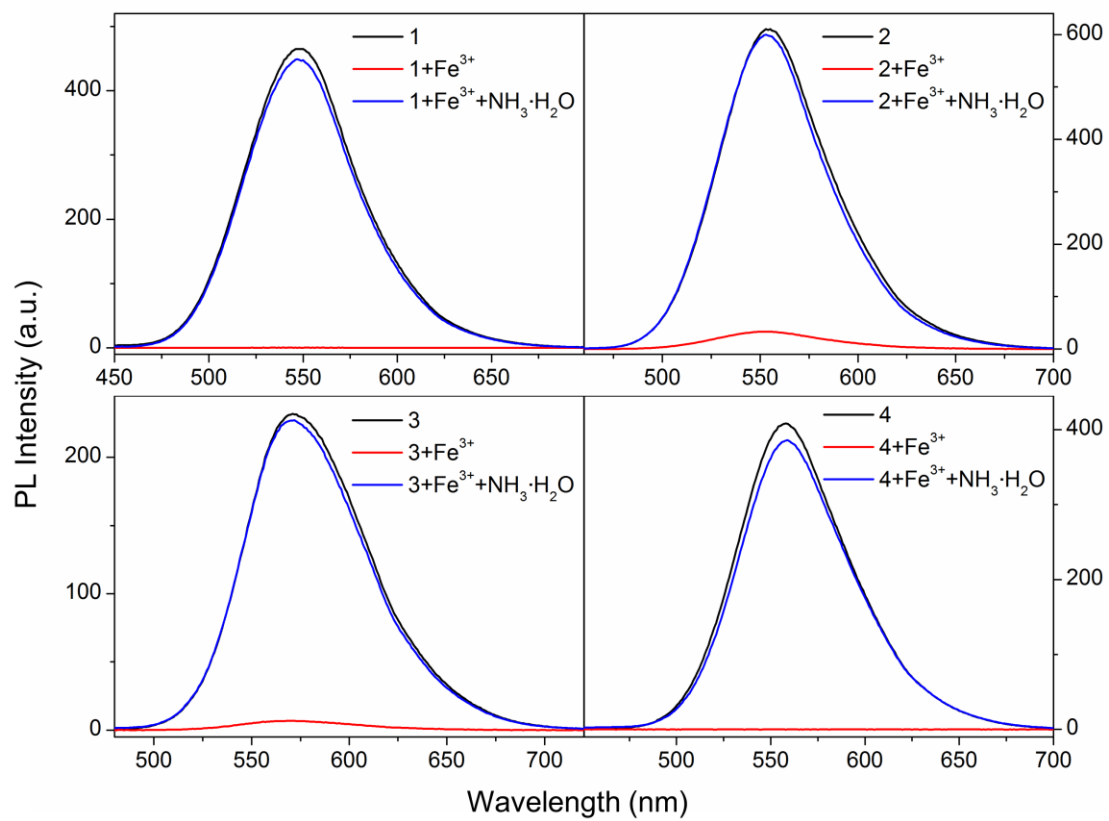


Fig. S4 ^1H NMR spectrum of compound **2** in CDCl_3 .

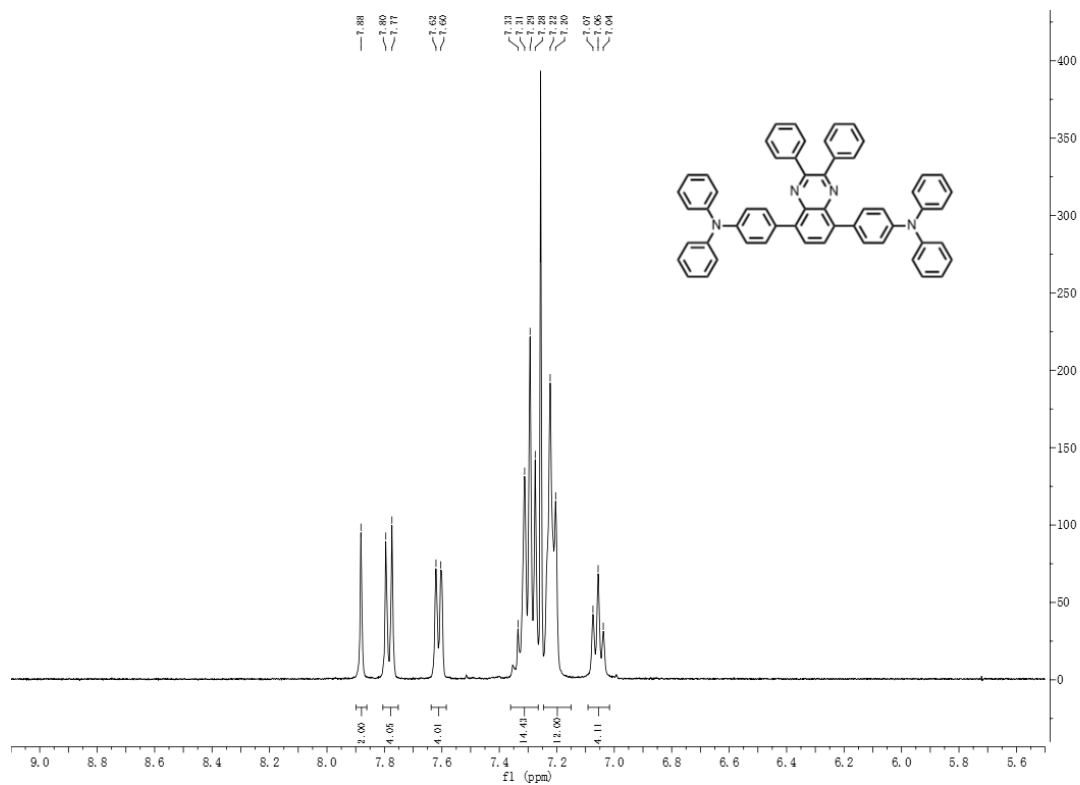


Fig. S5 ^{13}C NMR spectrum of compound **2** in CDCl_3 .

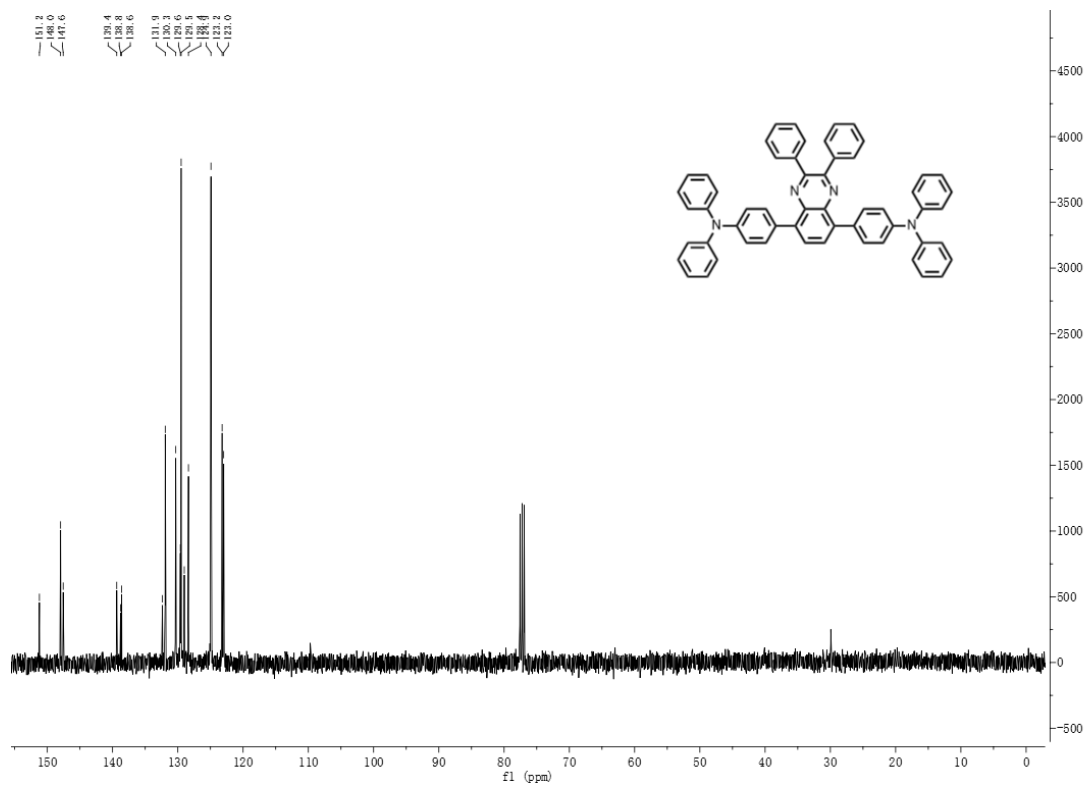


Fig. S6 ^1H NMR spectrum of compound **3** in CDCl_3 .

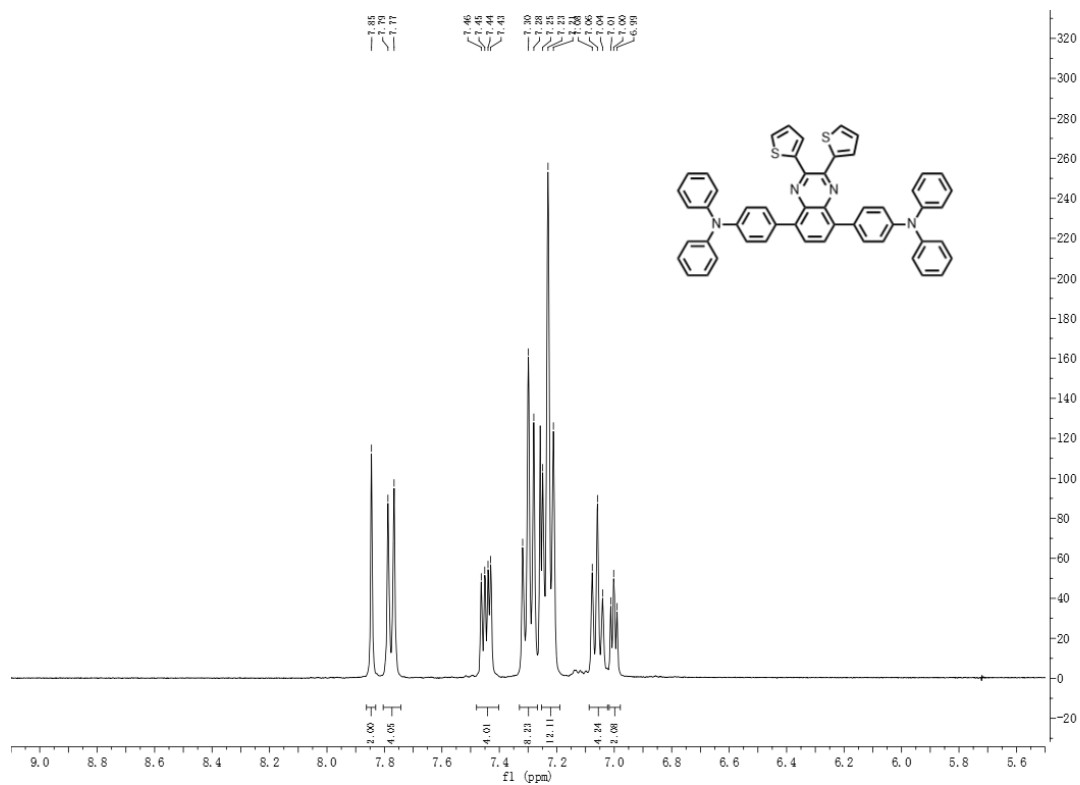


Fig. S7 ^{13}C NMR spectrum of compound **3** in CDCl_3 .

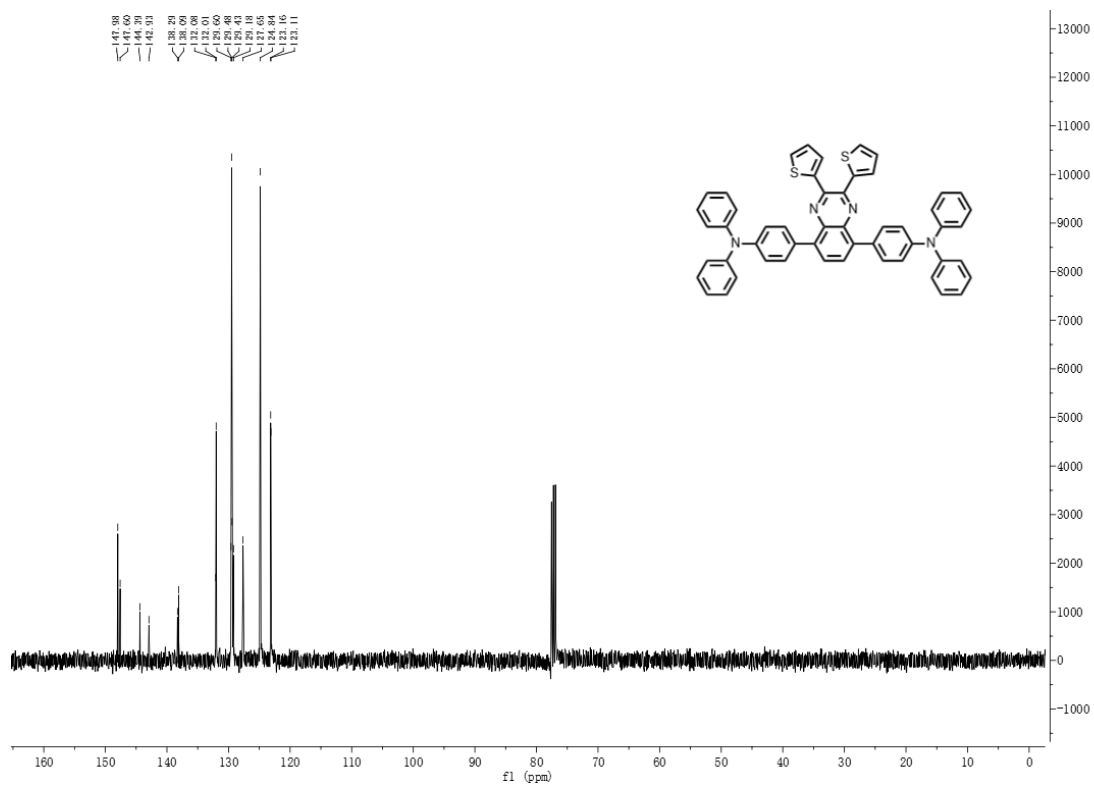


Fig. S8 ^1H NMR spectrum of compound **4** in CDCl_3 .

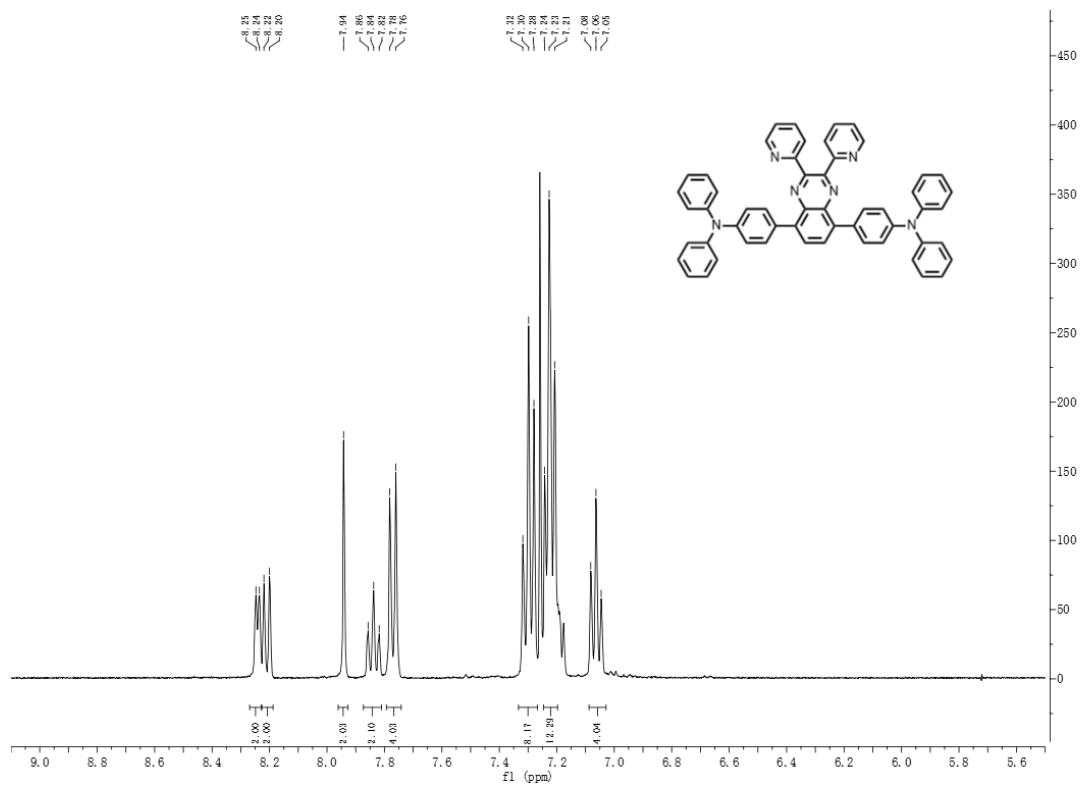


Fig. S9 ^{13}C NMR spectrum of compound **4** in CDCl_3 .

