

## **Exploring Redox Properties of a 3D Co-based Framework with Bis(triarylamine) Terphenyl as Redox-Active Linker**

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## Materials

Co(II) chloride hexahydrate (Alfa, 98%), Tri(*p*-bromophenyl)amine (TCI, 99%), pyridine-4-boronic acid (Matrix Scientific, 95%), benzene-1,4-diboronic acid (Aldrich, 95%), Pd(PPh<sub>3</sub>)<sub>4</sub> (Acros, 99%), DMF (JT baker, HPLC grade), acetonitrile (JT Baker, HPLC grade), chloroform (Merck), and 1,4-dioxane (Acros, 99.5%)

Electrochemistry: Calcium hydride (Acros, ca. 93% 10-100 mm), dichloromethane (Seedchem, 99.5%), ferrocene (Acros, 98%), tetra-*n*-butylammonium hexafluorophosphate (Alfa Aesar, 98%)-recrystallization using ethanol before use.

NMR: CDCl<sub>3</sub> (Sigma-Aldrich)

## Instrumentation

Elemental analyses (C, H, N) *via* combustion were performed using an Elementar Vario cube analyzer at the MOST Instrumental Center at National Taiwan University (NTU), Taipei, Taiwan. Thermogravimetric analysis was performed using a TA Instrument Q50 Thermogravimetric Analyzer. Measurements were carried out at the temperature of 30 °C to 900 °C with a ramp of 10 °C per min under a nitrogen atmosphere. Powder X-ray diffraction data were collected on a Bruker D8 Advance powder diffractometer at 40 kV and 40 mA operating at the Cu K<sub>α</sub> wavelength (1.5406 Å). Diffuse reflectance spectra were collected on an ultraviolet–visible (UV–vis) spectrometer JASCO V670 in the range of 300–1200 nm. Barium sulfate (BaSO<sub>4</sub>) was used to obtain a baseline spectrum. Y-axis spectra were recorded as the Kubelka-Munk transform, where  $F(R) = (1-R)^2/2R$ . IR spectra were recorded in the range of 4000-400 cm<sup>-1</sup> on a PerkinElmer Paragon 100 FT-IR spectrometer using the KBr disc technique. <sup>1</sup>H NMR spectra were obtained on a Bruker Advance 400 MHz spectrometer at 298 K.

### **Cyclic Voltammetry**

Cyclic voltammograms were obtained by using a CH Instrument 611B electrochemical analyzer. The dichloromethane was distilled over  $P_2O_5$  prior to the electrochemical experiments. Measurements were carried out in a three-electrode system. Glassy carbon was used as the working electrode, platinum wire as an auxiliary electrode and Ag/AgCl as a reference electrode. The Co compound was mounted onto the glassy carbon electrode. The electrolyte used in this work is 0.1 M [*n*-Bu<sub>4</sub>N]PF<sub>6</sub> (TBAPF<sub>6</sub>). Oxygen was removed by bubbling with Argon gas for 20 min. The voltammograms were acquired from the unstirred solution under an atmosphere of Argon gas. Ferrocene served as an internal reference and was added at the last measurement.

### **Solid State Diffuse Reflectance Spectroelectrochemical UV/Vis/NIR**

Indium tin oxide (ITO) glass (6 cm x 0.9 cm) was pretreated by washing with ethanol and acetone and purging with nitrogen. Prior to the experiment, a dry dichloromethane solvent was obtained using CaH<sub>2</sub>. The electrochemical setup employed a three-electrode system with ITO as the working electrode, Pt mesh as the counter electrode, and thin Ag wire as the reference electrode in a 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>/dichloromethane electrolyte. The three electrochemical cells were placed inside a 1 cm quartz cell, with the coated ITO sample and Pt mesh facing opposite the cell. To minimize the risk of short circuits, the compartment was separated by a hollow (0.5 cm x 2 cm) Teflon block. Samples were scanned continuously with incremental potentials using a Hokuto Denko potentiostat until a change in the spectrum was observed. The spectra were measured using the Hitachi U-4100 spectrophotometer.

### Synthesis of 4-Bromo-N, N-bis(p-(pyrid-4-yl)phenyl)aniline<sup>1</sup>

Tri(p-bromophenyl)amine (2.41 g, 5.0 mmol), pyrid-4-yl boronic acid (0.93 g, 7.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (115.6 mg, 0.10 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.66 g, 12.0 mmol) were transferred to a 50 mL two neck round bottom flask. The air was removed *via vacuo* and purged with gas argon three times. Under an inert atmosphere, 25 mL of 1,4-dioxane and 10 mL of water were injected into the flask. The reaction mixture was refluxed at 100 °C for 24 h. Further, extract with CH<sub>2</sub>Cl<sub>2</sub> to obtain the organic layer. It was transferred to column chromatography packed with silica gel. The compound was eluted out using EA/methanol as eluent to afford 1.1 g of 4-bromo-N,N-bis(p-(pyrid-4-yl)phenyl)-aniline as pale yellow solid. 46 % yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 8.62 (d, *J* = 6 Hz, 4H), δ 7.54 (d, *J* = 8.8 Hz, 4H), δ 7.45 (d, *J* = 6 Hz, 4H), δ 7.42 (d, *J* = 8.8 Hz, 2H), δ 7.19 (d, *J* = 8.8 Hz, 4H), δ 7.05 (d, *J* = 8.8 Hz, 2H).

### Synthesis of N<sup>4</sup>,N<sup>4</sup>,N<sup>4''</sup>,N<sup>4'''</sup>-tetrakis(4-(pyridin-4-yl)phenyl)-[1,1':4',1''-terphenyl]-4,4''-diamine (TPPT)<sup>2</sup>

4-Bromo-N, N-bis(p-(pyrid-4-yl)phenyl)aniline (1.05 g, 2.2 mmol), benzene-1,4-diboronic acid (165.8 mg, 1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (115.6 mg, 0.10 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.66 g, 12.0 mmol) in 1,4-dioxane/H<sub>2</sub>O (15 mL/8 mL) were prepared and transferred to a 50 mL of 2-neck round bottom flask, refluxed at 100 °C for 24 h under argon atmosphere. A greenish-yellow powder was filtered and purified with column chromatography with an eluent of CHCl<sub>3</sub>/MeOH (5%). 0.3 g, 34% yellow solid was obtained.

IR (cm<sup>-1</sup>): 3028w, 2922w, 3395s, 2360w, 1599s, 1515m, 1487s, 1407s, 1320m, 1291m, 1270sh, 1223w, 1185w, 1116w, 996w, 810s, 750w, and 515w.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 8.61 (d, *J* = 6 Hz, 8H), δ 7.67 (s, 4H), δ 7.57-7.61 (m, 12H), δ 7.48 (d, *J* = 6.4 Hz), δ 7.24-7.27 (m, 12H).

MS (ESI): *m/z* calculated for C<sub>62</sub>H<sub>44</sub>N<sub>6</sub> [M+H]<sup>+</sup>: 873.36, found 873.36

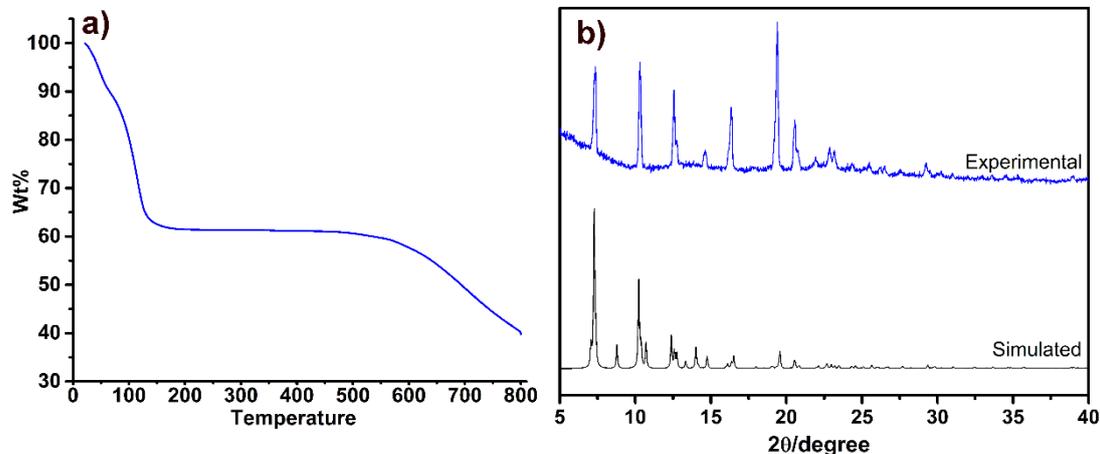
Elemental analysis calculated for C<sub>62</sub>H<sub>44</sub>N<sub>6</sub> (%): C 85.29, H 5.08, N 9.63; found (%) C 83.46, H 5.08, N 9.28.

### Synthesis of [Co(TPPT)Cl<sub>2</sub>] $\cdot$ 10MeOH $\cdot$ 7DMF $\cdot$ 10H<sub>2</sub>O (**1**)

The diffusion method is adopted to obtain a quality single crystal for single-crystal X-ray diffraction. A glass tube with a diameter of 1.5 cm and a height of 15 cm was chosen. The bottom part consists of **TPPT** ligand (0.01 mmol, 8.72 mg) dissolved in 2 mL of CHCl<sub>3</sub>, followed by a buffer layer consisting of DMF solvent 4 mL, and finally, the top part consists of CoCl<sub>2</sub> (0.02 mmol, 4.8 mg) dissolved in 2 mL of MeOH. Brown green color crystals were observed on the buffer layer after one week. Yield: 14 mg, 80.2 % (Based on **TPPT**)

IR (cm<sup>-1</sup>): 2921w, 1660s, 1595s, 1520m, 1487s, 1411m, 1383m, 1324s, 1294s, 1225m, 1182w, 1094m, 1063w, 1038w, 1003m, 814s, 756m, 659m, 515m.

**Elemental analysis** calculated for [Co(TPPT)Cl<sub>2</sub>] $\cdot$ 10MeOH $\cdot$ 7DMF $\cdot$ 10H<sub>2</sub>O (**1**) (%): C 57.82, H 6.87, N 10.44; found (%) C 58.72, H 6.738, N 10.54.



## Crystal Structure Data Collection and Description

A green, plate-like specimen of  $[\text{Co}(\text{TPPT})\text{Cl}_2]\cdot 10\text{MeOH}\cdot 7\text{DMF}\cdot 10\text{H}_2\text{O}$  (**1**) with approximate dimensions of 0.200 mm x 0.200 mm x 0.340 mm was selected for the X-ray crystallographic analysis. The X-ray intensity data were measured ( $\lambda = 1.54184 \text{ \AA}$ ). The exposure time is  $8 \text{ s/}^\circ$  to  $32 \text{ s/}^\circ$  and the frame width is  $0.3^\circ$ . A total of 6305 frames were collected. The total exposure time was 13.06 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 121372 reflections to a maximum  $\theta$  angle of  $74.64^\circ$  ( $0.80 \text{ \AA}$  resolution). The final cell constants of  $a = 11.9310(11) \text{ \AA}$ ,  $b = 25.018(2) \text{ \AA}$ ,  $c = 27.747(2) \text{ \AA}$ , volume =  $8282.2(17) \text{ \AA}^3$ , are based upon the refinement of the XYZ-centroids of 8863 reflections above  $20 \sigma(I)$  with  $7.066^\circ < 2\theta < 133.4^\circ$ . Data were corrected for absorption effects using the Multi-Scan method (SADABS) and APEX4.<sup>3</sup> The ratio of minimum to maximum apparent transmission was 0.723.

The structures were solved using SHELXT<sup>4</sup> and refined by full-matrix least-squares against  $F^2$  with all reflections using Shelxl2018.<sup>3</sup> Hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms. The structure contains additional solvent-accessible voids. The structure factors were instead augmented via reverse Fourier transform methods using the SQUEEZE/PLATON<sup>5</sup>. Solvents were determined from the elemental analysis (EA) and thermal gravimetric analysis (TGA).

Crystal structure (CCDC 2265792) has been deposited in the CCDC.

At 100 K (**1**): C8, C9, C10, and C11 were found disordered and assigned to be 50 % occupancy; C19, C20, C21, and C22 were found disordered and assigned to be 43.6 % and 56.4 % occupancy, respectively and C30, C31, C32, and C33 were found disordered and assigned to be 47.6 % and 52.4 % occupancy, respectively.

After careful inspection from Figure S3 and Figure S6 below, we observed that the terphenyl ring is nearly coplanar; however, the middle ring existed with two conformations. The middle benzene ring is either in P- or M-conformation. The center ring behaves like a propeller, a common characteristic in a bis(triarylamine) system.

This phenomenon clearly explained the existence of conformation isomerism or stereoisomerism with degenerate potential wells.

The middle benzene ring behaves like a "free rotor" with random conformations, coexisting as a stereoisomerism (Figure S6). The first and third benzene rings are nearly coplanar, with the middle benzene ring behaving like a propeller with degenerated energetic potential wells. Measurement of torsion angles we observed as 47.0° (Figure S6b) and -42.3° (Figure S6a) (or dihedral angle), respectively.

Responses to check CIF alerts:

PLAT094\_ALERT\_2\_B Ratio of Maximum / Minimum Residual Density .... 7.11 Report

**Author Response: This is caused by unaccounted twinning.**

PLAT097\_ALERT\_2\_B Large Reported Max. (Positive) Residual Density 2.90 eA-3

**Author Response: This is caused by unaccounted twinning.**

Table S1. Crystal data for [Co(TPPT)Cl<sub>2</sub>]·10MeOH·7DMF·10H<sub>2</sub>O (1)

Empirical formula	C <sub>93</sub> H <sub>153</sub> Cl <sub>2</sub> CoN <sub>13</sub> O <sub>27</sub>
Formula weight	2015.10
Crystal system	Orthorhombic
Space group	<i>Pcca</i>
<i>a</i> (Å)	25.018(2)
<i>b</i> (Å)	11.9310(11)
<i>c</i> (Å)	27.747(2)
<i>V</i> (Å <sup>3</sup> )	8282.1(13)
<i>Z</i>	4
$\rho_{calcd}$ (Mg/m <sup>3</sup> )	0.804
<i>F</i> (000)	2076
$\lambda$ (Å)	1.54178
<i>T</i> (K)	100(2)
Crystal size (mm)	0.340 x 0.200 x 0.2

Theta range °	3.53 to 66.70
Reflections measured	121372
independent reflections	8863 [R(int) = 0.1161]
Completeness to theta = 67.679°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.7234
Diffractometer	Bruker AXS D8 VENTURE, PhotonIII_C28
Data/restraints/parameters	8863/768/413
Goodness-of-fit on $F^2$	1.862
Final R indices [ $I > 2\sigma(I)$ ]	0.1252
$wR_2 (F^2)$ indices (all data)	0.3534
Largest diff. peak and hole ( $e \cdot \text{\AA}^{-3}$ )	2.900 and -0.408

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR_2 = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

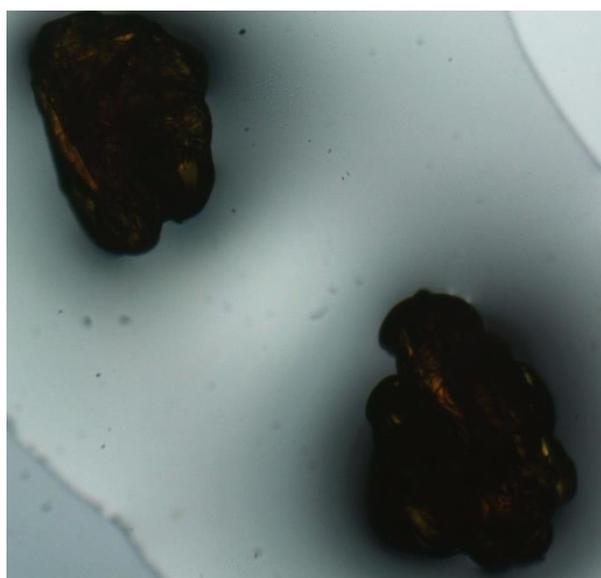


Figure S2. Crystals of **1** were obtained from the diffusion method.

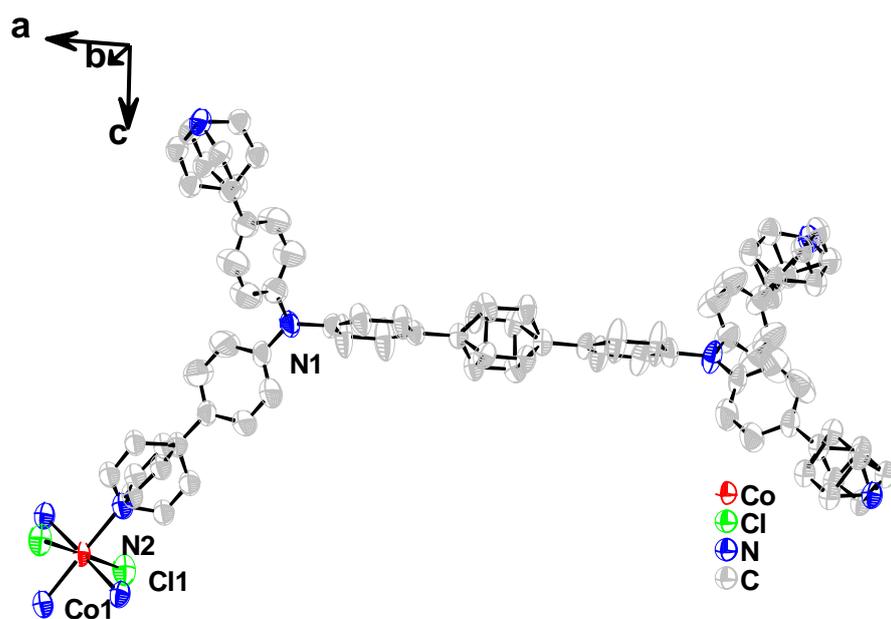


Figure S3. Coordination environments of **1** at 100 K with thermal ellipsoids at 50 % probability. Hydrogen atoms have been omitted for clarity.

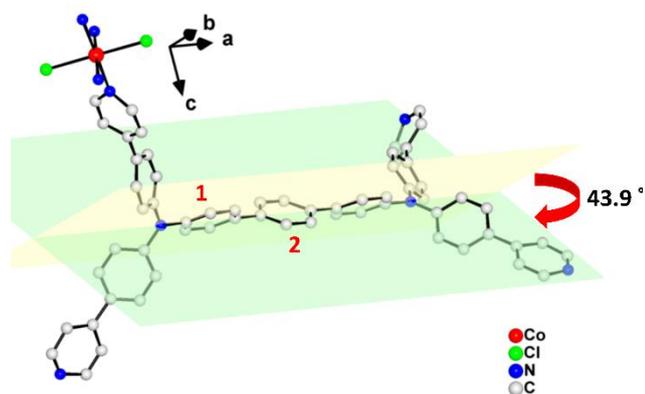


Figure S4. Measured angles between phenyl ring 1 and phenyl ring 2. Hydrogen atoms have been omitted for clarity.

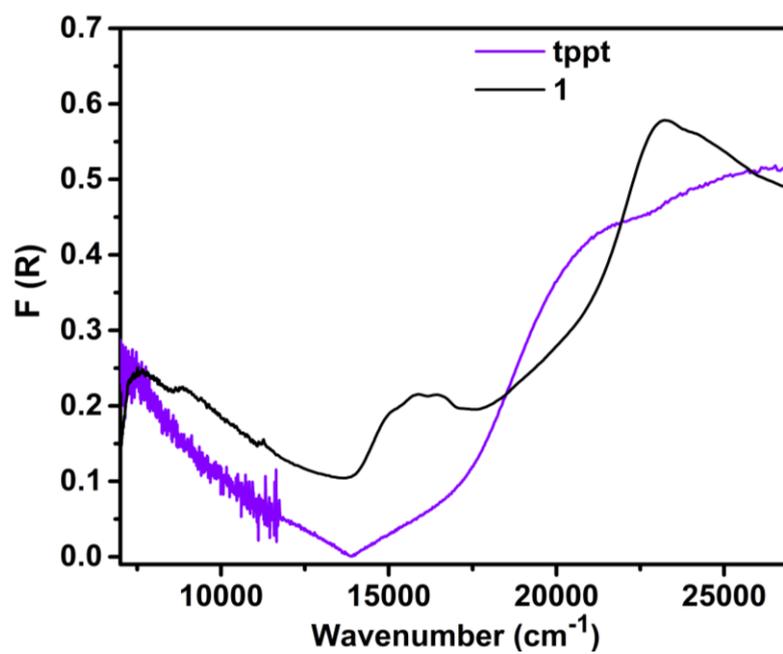


Figure S5. Solid state diffuse reflectance spectra of TPPT and 1.

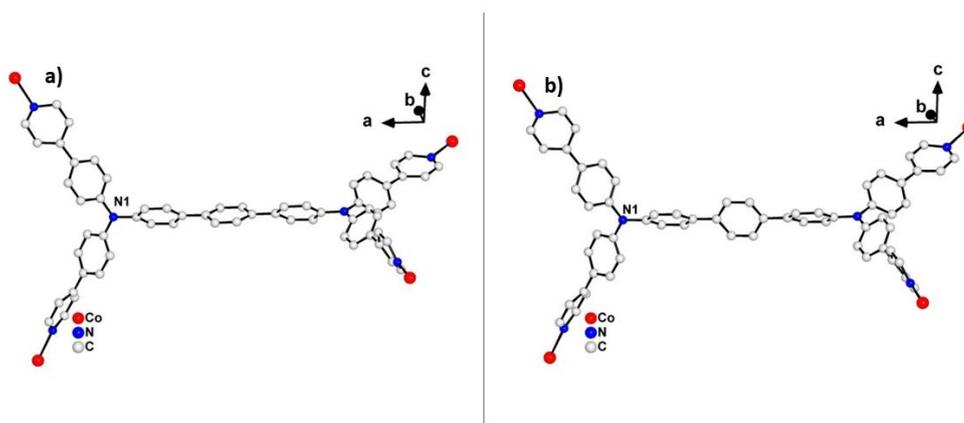


Figure S6 depicts the two orientations of the center phenyl rings.

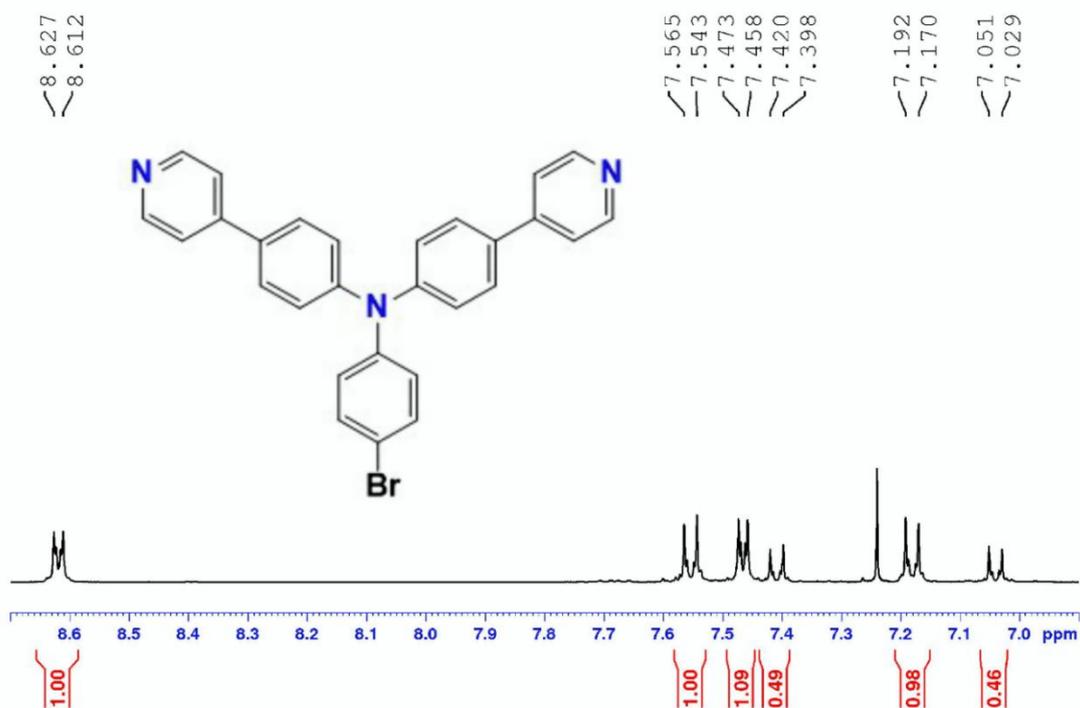


Figure S7. <sup>1</sup>H NMR (CDCl<sub>3</sub>) of 4-Bromo-N,N-bis(p-(pyridin-4-yl)phenyl)aniline.

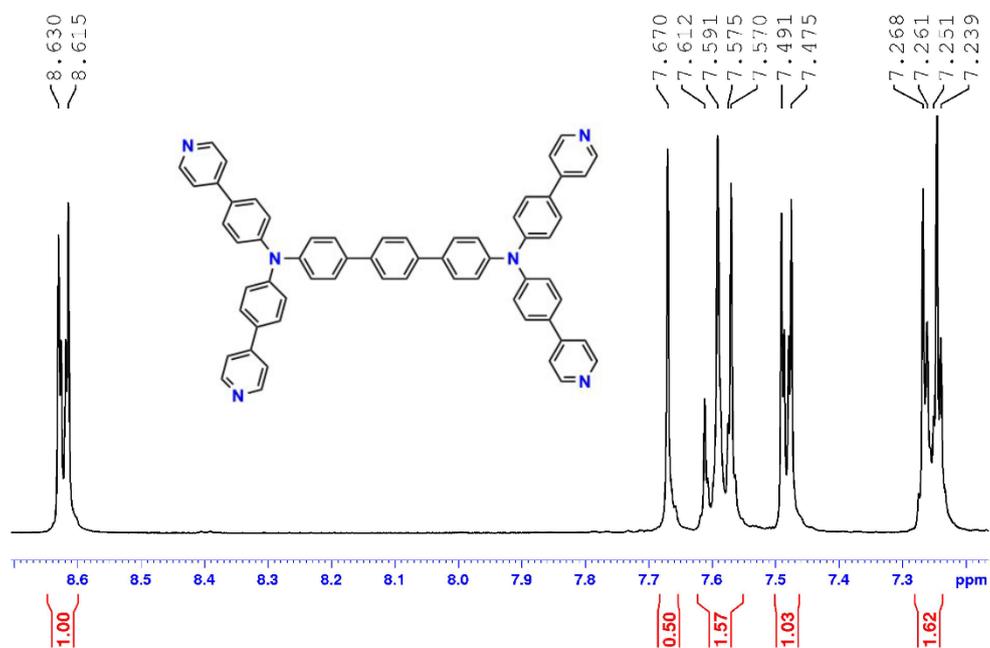


Figure S8. <sup>1</sup>H NMR (CDCl<sub>3</sub>) of N<sup>4</sup>,N<sup>4</sup>,N<sup>4'</sup>,N<sup>4''</sup>-tetrakis(4-(pyridin-4-yl)phenyl)-[1,1':4',1''-terphenyl]-4,4''-diamine.

## References:

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