Supporting Information

Construction of spin-crossover dinuclear cobalt(II) compounds based on complementary terpyridine ligand pairing

Shu-Ya Zhang,[a] Hui-Ying Sun,[b] Run-Guo Wang,[a] Yin-Shan Meng,[b] Tao Liu,*[,b] and Yuan-Yuan Zhu*[,a,b]

*E-mail: yyzhu@hfut.edu.cn; liutao@dlut.edu.cn

[a]*School of Chemistry and Chemical Engineering, Hefei University of Technology and Anhui Key Laboratory of Advanced Functional Materials and Devices, Hefei 230009, China.*

[b]*State Key Laboratory of Fine Chemicals, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China.*

Contents

SI1 Instruments and Materials

SI1.1 Instruments

Structural characterization measurements. The NMR spectra were recorded on a Bruker 400, 500 or 600 MHz spectrometer. Elemental analysis of carbon, nitrogen and hydrogen was performed using an Elementary Vario EL analyser. Mass spectrometry was performing using a Water XEVO G2Q-TOF (Waters Corporation).

Magnetic properties measurements. Magnetic susceptibility data were collected using a Quantum Design MPMS XL-5 or PPMS-9T (EC-II) SQUID magnetometer. Measurements for all the samples were performed on microcrystalline powder restrained by a parafilm and loaded in a capsule. The magnetic susceptibility data were corrected for the diamagnetism of the samples using Pascal constants and the sample holder and parafilm by corrected measurement.

X-ray Data Collection and Structure Determinations. Crystals suitable for single crystal X-ray diffraction were covered in a thin layer of hydrocarbon oil, mounted on a glass fiber attached to a copper pin, and placed under an N_2 cold stream. The single-crystal XRD data for four compounds were collected on Bruker D8 Venture CMOS-based diffractometer (Mo-$K\alpha$ radiation, λ = 0.71073 Å) using the SMART and SAINT programs. Final unit cell parameters were based on all observed reflections from integration of all frame data. The structures were solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization that implanted in Olex2. For all compounds, all non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of organic ligands were located geometrically and fixed isotropic thermal parameters. Due to the serious disorder of lattice solvents in **Co-2** and **Co-3**, unidentified Q peaks were deleted by SQUEEZE using Platon program. Some exact molecular formula and molecular weight were calculated from the real structure from elemental analyses and may unmatch with the refinement results (see Table S2).

Calorimetric Analysis. TG analysis was carried out with a TGA/DSC 1 (METTLER TOLEDO) instrument at a heating rate of 10 K min^{-1}. Differential scanning calorimetry (DSC) was carried out with a DSC 823e (Mettler Toledo) at a cooling/warming rate of 3 K min^{-1}, the sample mass was ~3 mg for each measurement.

Cyclic Voltammetry Measurements. The cyclic voltammetry curves of complexes and their corresponding ligands were measured in acetonitrile solution containing 0.001 M substrates and 0.1 M tetrabutylammonium hexafluorophosphate electrolyte. The systems were run in a three-electrode cell (10 mL working volume), using a glassy carbon as a working electrode, Ag/AgCl as a reference electrode and platinum plate as a counter electrode. The glassy carbon surface was polish by 0.05 mm alumina, then washed with DI water before using every time. The solution was degassed by bubbling nitrogen for 15 minutes before measurements and maintaining an inert nitrogen over the solution during the measurements.

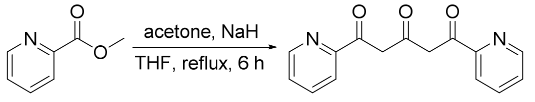
SI1.2 Materials

The ligand **L**^{5}, 2,2':6',2''-terpyridine, was purchased from Shanghai Aladdin Bio-chem Technology co., ltd. All reagents and solvents were purchased commercially and used as supplied, unless otherwise stated. THF was further dried over sodium benzophenone ketyl, distilled onto $LiAlH_4$ under nitrogen, and distilled under high vacuum just before use. Toluene was dried over anhydrous CaH_2 and distilled before use.

Caution! *Although not encountered in our experiments, perchlorate salts in the presence of organic ligands are potentially explosive. Only a small amount of the materials should be prepared and handled with care.Particularly, reducing the reaction solution of the perchlorate complexes under reduced pressure should be performed very carefully. Phosphorus pentasulfide is toxic. It should be used cautiously.*

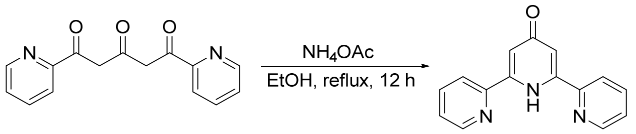
SI2 Synthesis and Characterization of Ligands and complexes

SI2.1 Synthetic Procedure for Ligands



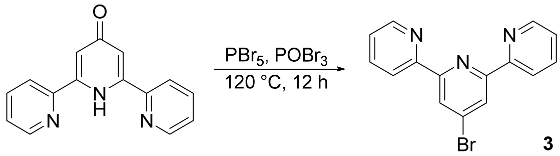
1

Synthesis of 1.[1] A mixture of sodium hydride (60% suspension in mineral oil, 5.0 g, 125 mmol) in anhydrous THF (50 mL) was vigorously stirred under a dinitrogen atmosphere at ambient temperature. Then the solution of acetone (1.45 g, 25 mmol) and pyridine-2-carboxylic acid ester (10.34 g, 75 mmol) in anhydrous THF (50 mL) was added dropwise. The mixture was vigorously stirred at ambient temperature for another 1 h, and then heated to reflux for 6 h. After cooling to ambient temperature, most of the solvent was removed under reduced pressure. Subsequently, DI water (50 mL) was added to the orange residue carefully. The resulting solution was filtered through celite, and the filtrate was adjusted to pH = 7 by adding diluted hydrochloric acid (1.0 M). The generated yellow precipitate was collected, washed with water, and recrystallized from hot ethanol, to afford the pure product as a yellow powder (2.5 g, 63%).



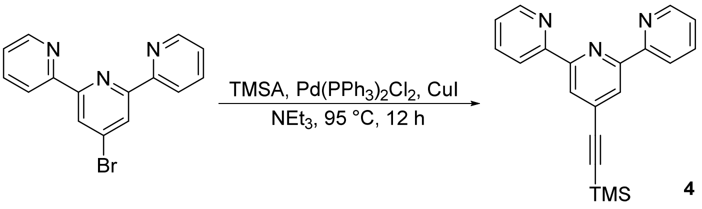
2

Synthesis of 2.[1] To a solution of **1** (4.8 g, 18 mmol) in ethanol (150 mL) was added ammonium acetate (10 g, excess equivalence). The mixture was heated to reflux for 12 h. After cooling to ambient temperature, the dark brown solution was concentrated to half of original volume. The white precipitate was generated after the solution was cooled, and it was collected and washed with diethyl ether. Recrystallization of the crude product from ethanol afforded pure **2** as a white powder (1.7 g, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.98 (s, 1 H), 8.78 (d, J = 4.6 Hz, 2 H), 7.89 (m, 4 H), 7.55 – 7.29 (m, 2 H), 7.08 (s, 2 H).

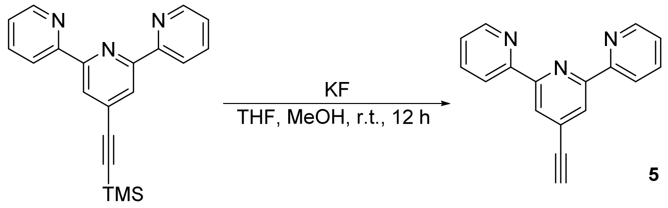


3

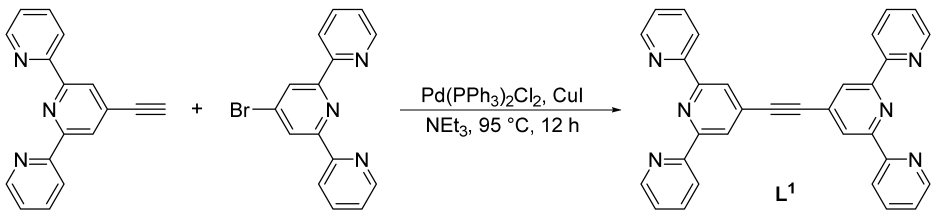
Synthesis of 3.[2] To a 100 mL flask were added **2** (1.0 g, 4 mmol), phosphorus pentabromide (2.6 g, 6 mmol) and phosphorous oxybromide (11.5 g, 40 mmol), and the mixture was heated at 120 ºC for 12 h. The brownish-black residue was carefully treated with crushed ice, and then was neutralized by adding saturated K_2CO_3 aqueous solution (~50 mL). The mixture was extracted with CH_2Cl_2 (20 mL × 2), and the combined organic phase was dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the residue was subjected to rapid column chromatography (Al_2O_3, hexane/CH_2Cl_2, 1:1) to afford **3** as a white solid (1.14 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (ddd, J_1 = 4.8 Hz, J_2 = 1.8 Hz, J_3 = 0.9 Hz, 2 H), 8.65 (s, 2 H), 8.59 (dt, J_1 = 8.0 Hz, J_2 = 1.1 Hz, 2 H), 7.93 – 7.81 (m, 2 H), 7.36 (ddd, J_1 = 7.5 Hz, J_2 = 4.8 Hz, J_3 = 1.2 Hz, 2 H).



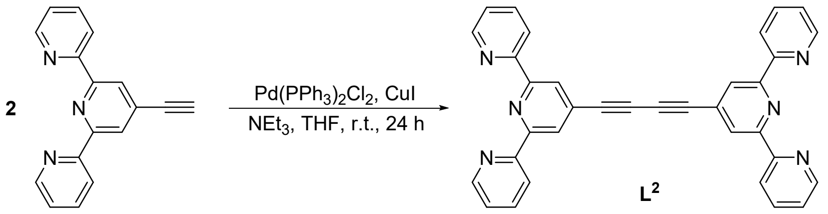
Synthesis of 4.[3] To a 25 mL Schlenk flask were added **3** (311 mg, 1.0 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol) and anhydrous triethylamine (10 mL). This solution was degassed and backfilled with N_2 for three times with the assistance of liquid nitrogen. Later (trimethylsilyl)acetylene (0.7 mL, 5 mmol) was added *via* syringe and the solution was heated to 95 ºC for 12 h. After the completion of the reaction, the resulting solution was diluted by CH_2Cl_2 (40 mL) and filtered. The filtrate was washed with DI water (20 mL × 3), brine (20 mL) and dried over anhydrous Na_2SO_4 successively. After the solvent was removed under reduced pressure, the residue was subjected to rapid column chromatography (SiO_2, CH_2Cl_2/MeOH, 20:1) to afford **4** as a white solid (286 mg, 87%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.70 (d, J = 4.4 Hz, 2 H), 8.59 (d, J = 7.9 Hz, 2 H), 8.50 (s, 2 H), 7.86 (t, J = 7.6 Hz, 2 H), 7.34 (dd, J_1 = 6.2 Hz, J_2 = 5.7 Hz, 2 H), 0.27 (s, 9 H).



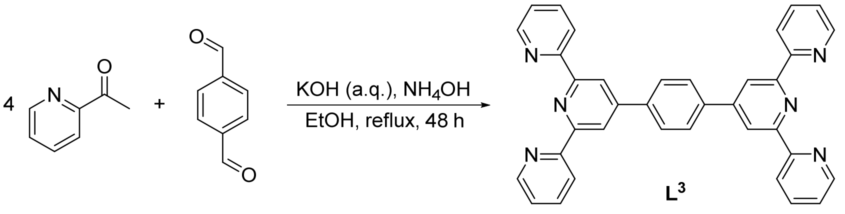
Synthesis of 5.[3] To a 50 mL flask were added **4** (286 mg, 0.87 mmol), KF (60 mg, 1.04 mmol), THF (16 mL) and MeOH (10 mL). The solution was stirred at ambient temperature for 12 h. After concentrating under reduced pressure, the residue was redissolved in CH_2Cl_2 (20 mL) and the solution was washed with water (20 mL × 3), brine (20 mL), and dried over anhydrous Na_2SO_4 successively. After the solvent was removed under reduced pressure, the residue was subjected to rapid column chromatography (SiO_2, CH_2Cl_2/MeOH, 100:1) to afford **5** as a white solid (200 mg, 84%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.71 (d, J = 4.7 Hz, 2 H), 8.59 (d, J = 7.9 Hz, 2 H), 8.54 (s, 2 H), 7.86 (td, J_1 = 7.7 Hz, J_2 = 1.7 Hz, 2 H), 7.38 – 7.31 (m, 2 H), 3.32 (s, 1 H).



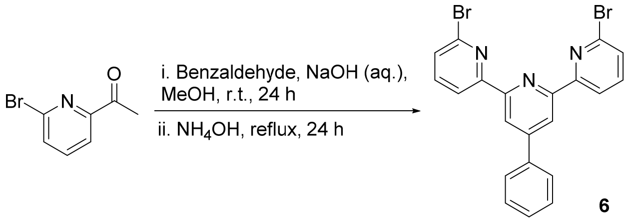
Synthesis of L^1.[3] To a Schlenk flask were added **3** (55 mg, 0.18 mmol), **5** (50 mg, 0.2 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (15 mg, 0.02 mmol), CuI (7 mg, 0.035 mmol) and anhydrous triethylamine (8 mL).This solution was degassed and backfilled with N$_2$ for three times with the assistance of liquid nitrogen. Then the solution was heated to 95 ºC for 12 h. After cooling to ambient temperature, the solution was filtered, and the filter residue was washed with CHCl$_3$. The combined organic phase was washed with water, brine and dried over anhydrous Na$_2$SO$_4$. After concentrating under reduced pressure, the residue was subjected to rapid column chromatography (SiO$_2$, CH$_2$Cl$_2$/MeOH, 15:1) to afford **L^1** as a white solid (50 mg, 51%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 8.75 (br, 4 H), 8.63 (br, 8 H), 7.88 (br, 4 H), 7.37 (br, 4 H). MS (ESI-QQQ): *m/z* 489.07 $[M + H]^+$.



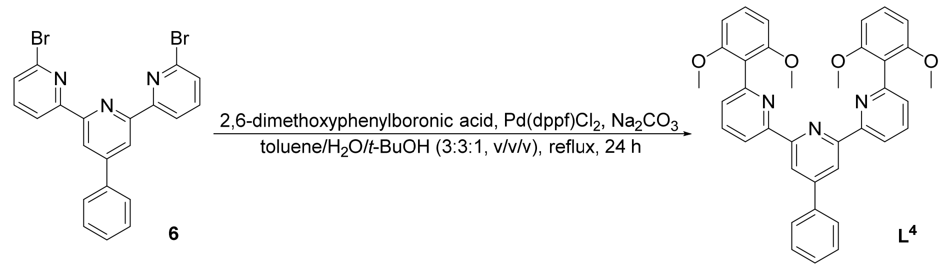
Synthesis of L^2.[3] To a 100 mL flask were added **5** (264 mg, 1.03 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (35 mg, 0.05 mmol) and CuI (10 mg, 0.05 mmol), THF (10 mL), and triethylamine (30 mL). The mixture was stirred at ambient temperature in open air for 24 h. Then the solution was filtered, and the filter residue was washed with CHCl$_3$. The combined organic phase was washed with water, brine and dried over anhydrous Na$_2$SO$_4$. After the solvent was removed, the residue was subjected to rapid column chromatography (SiO$_2$, CH$_2$Cl$_2$/MeOH, 100:1) to afford **L^2** as a pale solid (340 mg, 65%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.74 (d, $J = 4.2$ Hz, 4 H), 8.63 (s, 4 H), 8.61 (s, 4 H), 7.89 (td, $J_1 = 7.8$ Hz, $J_2 = 1.5$ Hz, 4 H), 7.38 (dd, $J_1 = 6.6$ Hz, $J_2 = 5.0$ Hz, 4 H). MS (ESI-QQQ): *m/z* 513.08 $[M + H]^+$.



Synthesis of L^3.[4] A mixture of terephthalaldehyde (0.27 g, 2.1 mmol), 2-acetylpyridine (1.00 g, 8.3 mmol) and KOH aqueous solution (15 wt %, 2.9 mL) in EtOH (50 ml) was stirred at ambient temperature for 24 h. Subsequently NH$_4$OH (28 wt %, 30 mL) was added dropwise. After the completion of addition, the resulting solution was heated to reflux for 48 h. The generated precipitate was filtrated and washed with ethanol and DI water. Recrystallization of the solid in mixed solvent of $CHCl_3$/MeOH afforded pure **L^3** as a white product (488 mg, 43%).^{1}H NMR (600 MHz, $CDCl_3$): δ 8.81 (br, 4 H), 8.77 (br, 4 H), 8.70 (d, J = 5.9 Hz, 4 H), 8.07 (s, 4 H), 7.91 (t, J = 6.9 Hz, 5 H), 7.38 (br, 4 H). MS (ESI-QQQ): *m/z* 541.06 $[M + H]^+$.



Synthesis of 6.[5] A mixture of NaOH aqueous solution (1.0 M, 12.5 mL), 2-acetyl 6-bromopyridine (2.5 g, 12.5 mmol) and benzaldehyde (0.6 g, 5.7 mmol) in methanol (50 mL) was stirred vigorously at ambient temperature for 24 h. Then an aqueous solution of NH_4OH (28 wt %, 17 mL) was added into the yellow suspension slowly. After the mixture was heated to reflux for 24 h, the solvent was removed under reduced pressure and the residue was recrystallized from $CHCl_3$/MeOH to afford **6** as a light-yellow powder (1.12 g, 42%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.69 (s, 2 H), 8.58 (d, J = 7.7 Hz, 2 H), 7.86 (d, J = 7.2 Hz, 2 H), 7.72 (t, J = 7.8 Hz, 2 H), 7.54 (t, J = 7.9 Hz, 4 H), 7.48 (t, J = 7.3 Hz, 1 H).



Synthesis of L^4.[5] A mixture of **6** (0.5 g, 1.1 mmol), 2,6-dimethoxyphenylboronic acid (480.0 mg, 2.7 mmol), $Pd(dppf)Cl_2$ (40 mg, 0.05 mmol) and Na_2CO_3 (4.5 g, 42.0 mmol) was degassed and backfilled with N_2 for three times, and then a degassed solvent mixture (45 mL) of toluene/H_2O/*t*-BuOH (3:3:1, v/v/v) was added. The resulting mixture was heated to reflux for 24 h. After cooling to ambient temperature, the reaction solution was poured into cold water (50 mL) and the mixture was extracted with CH_2Cl_2 (20 mL × 3), and the combined organic phase was washed with brine (20 mL) and dried with anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the residue was subjected to rapid column chromatography (Al_2O_3, $CHCl_3$) to afford **L^4** as a white solid (460 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 2 H), 8.61 (d, J = 7.8 Hz, 2 H), 7.91 (t, J = 7.7 Hz, 2 H), 7.80 (d, J = 7.5 Hz, 2 H), 7.43 (t, J = 7.5 Hz, 2 H), 7.40 – 7.32 (m, 5 H), 6.71 (d, J = 8.4 Hz, 4 H), 3.77 (s, 12 H).

SI2.2 Synthetic Procedure for Complexes

Synthesis of [$Co_2(L^1)(L^4)_2](ClO_4)_4$ (Co-1): In a typical solvothermal reaction, a mixture of $\mathbf{L^1}$ (12 mg, 0.025 mmol), $\mathbf{L^4}$ (30 mg, 0.05mmol), and $Co(ClO_4)_2{\cdot}6H_2O$ (18 mg, 0.05 mmol) in a mixed solvent of $CHCl_3$/MeOH (10 mL, 1:1, *v*/*v*) was sealed in a 23 mL Teflon-lined autoclave and heated at 80 °C for 2 d and then was naturally cooled to ambient temperature to afford **Co-1** as dark brown block crystals (26 mg, 60%). **Co-1**, $C_{106}H_{82}Co_2N_{12}O_8$, 4($ClO_4$), 4($CHCl_3$). Anal. Calcd. For $C_{110}H_{86}Cl_{16}Co_2N_{12}O_{24}$: C, 49.95; H, 3.28; N, 6.35. Found: C, 50.37; H, 3.06; N, 6.16. The fresh samples of **Co-1** were put in a Schlenk tube and heating in an oil bath at 127 °C under vacuum for 2 h. Then the de-solvated sample was subjected to elemental analysis. **De-solvated Co-1**, $C_{106}H_{82}Co_2N_{12}O_8$, 4($ClO_4$). Anal. Calcd. For $C_{106}H_{82}Cl_4Co_2N_{12}O_{24}$: C, 58.74, H, 3.81, N, 7.75. Found: C, 58.50, H, 3.73, N, 7.62.

Synthesis of [$Co_2(L^2)(L^4)_2](ClO_4)_4$ (Co-2): The procedure is similar to that of **Co-1** except $\mathbf{L^1}$ was replaced by $\mathbf{L^2}$ and the solvent is changed to MeOH (10 mL). The autoclave was heated to 80 °C for 5 d and to afford **Co-2** as dark brown block crystals (28 mg, 64%). **Co-2**, $C_{108}H_{82}Co_2N_{12}O_8$, 4($ClO_4$), 3($CH_3OH$), ($H_2O$). Anal. Calcd. For $C_{111}H_{96}Cl_4Co_2N_{12}O_{28}$: C, 57.82; H, 4.20; N, 7.29. Found: C, 58.21; H, 4.53; N, 7.61. **De-solvated Co-2**, $C_{108}H_{82}Co_2N_{12}O_8$, 4($ClO_4$). Anal. Calcd. For $C_{108}H_{82}Cl_4Co_2N_{12}O_{24}$: C, 59.19, H, 3.77, N, 7.67. Found: C, 59.01, H, 3.67, N, 7.48.

Synthesis of [$Co_2(L^3)(L^4)_2](ClO_4)_4$ (Co-3): The procedure is similar to that of **Co-1**, but the modification is that $\mathbf{L^1}$ was replaced by $\mathbf{L^3}$. After heating at 100 °C for 2 d, **Co-3** was afforded as dark brown block crystals (45 mg, 70%). **Co-3**, $C_{110}H_{86}Co_2N_{12}O_8$, 4($ClO_4$), 4($CHCl_3$). Anal. Calcd. For $C_{114}H_{90}Cl_{16}Co_2N_{12}O_{24}$: C, 50.77; H, 3.36; N, 6.23. Found: C, 51.12; H, 3.54; N, 6.65. **De-solvated Co-3**, $C_{110}H_{86}Co_2N_{12}O_8$, 4($ClO_4$). Anal. Calcd. For $C_{110}H_{86}Cl_4Co_2N_{12}O_{24}$: C, 59.52; H, 3.91; N, 7.57. Found: C, 59.39; H, 3.84; N, 7.49.

Synthesis of [$Co(L^4)(L^5)](ClO_4)_2$ (Co-4): To the solution of $\mathbf{L^4}$ (58 mg, 0.1 mmol) and $\mathbf{L^5}$ (23 mg, 0.1 mmol) in $CHCl_3$ (10 mL) was added the 10 mL methanol solution of $Co(ClO_4)_2{\cdot}6H_2O$ (36 mg, 0.1 mmol). This solution was stirred at ambient temperature for 10 minutes. In room temperature, the solvent was allowed to evaporate slowly for one week. **Co-4** was afforded as dark brown block crystals (78 mg, 72%). **Co-4**, $C_{52}H_{42}CoN_6O_4$, 2(ClO_4), 2($CHCl_3$), Anal. Calcd. For $C_{54}H_{44}Cl_8CoN_6O_{12}$: C, 49.45; H, 3.38; N, 6.41. Found: C, 49.82; H, 3.48; N, 6.86. **De-solvated Co-4**, $C_{52}H_{42}CoN_6O_4$, 2(ClO_4), Anal. Calcd. For $C_{52}H_{42}Cl_2CoN_6O_{12}$: C, 58.22; H, 3.95; N, 7.83. Found: C, 58.05; H, 3.89; N, 7.74.

SI3 NMR Spectra of Intermediates, Ligands, and Complexes

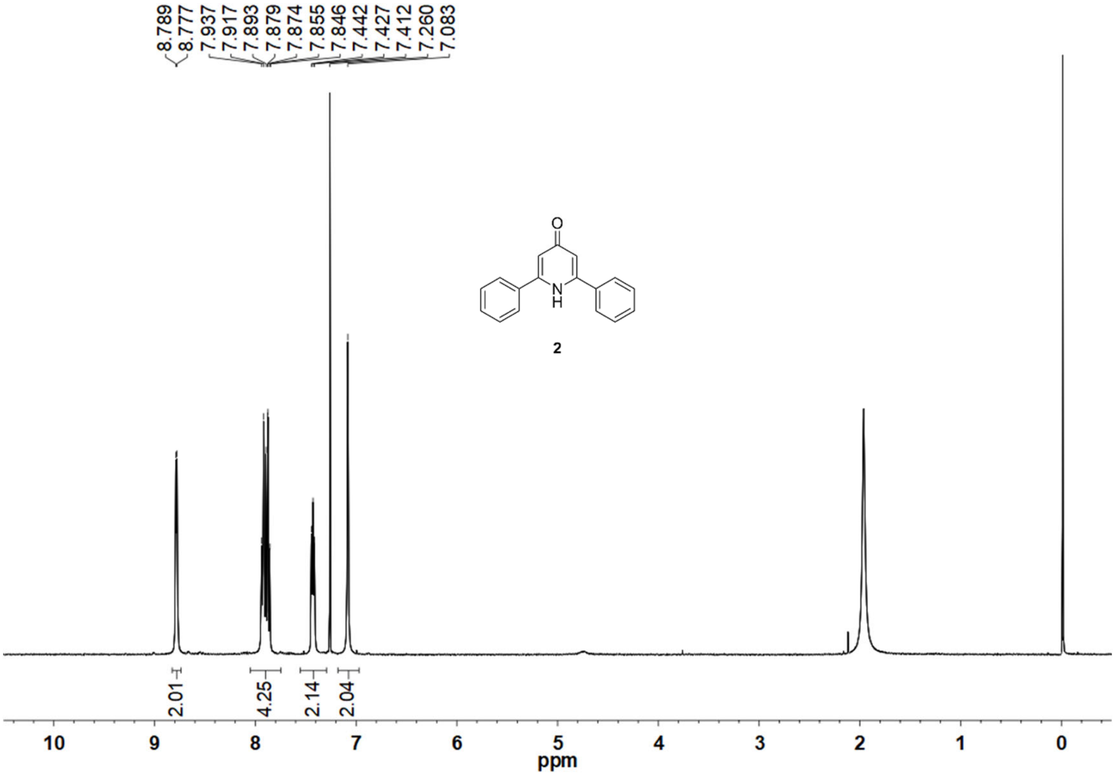


Fig. S1 ^{1}H NMR spectrum of compound **2** (400 MHz) in $CDCl_3$.

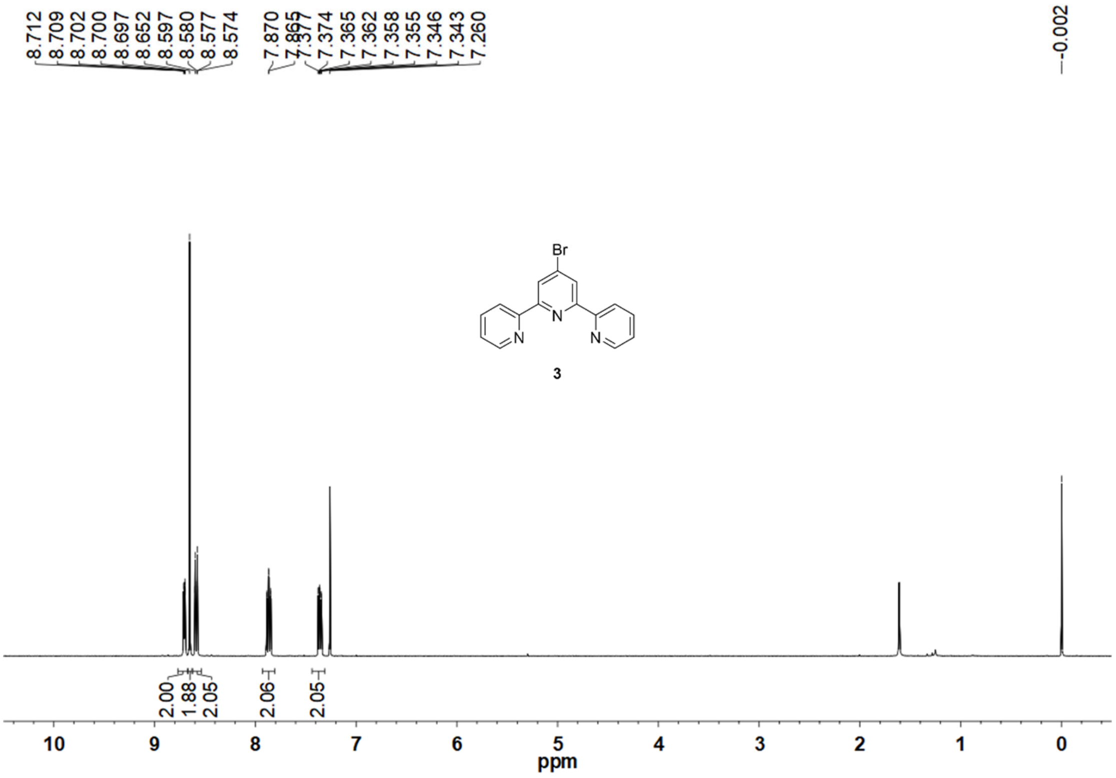


Fig. S2 ^{1}H NMR spectrum of compound **3** (400 MHz) in $CDCl_3$.

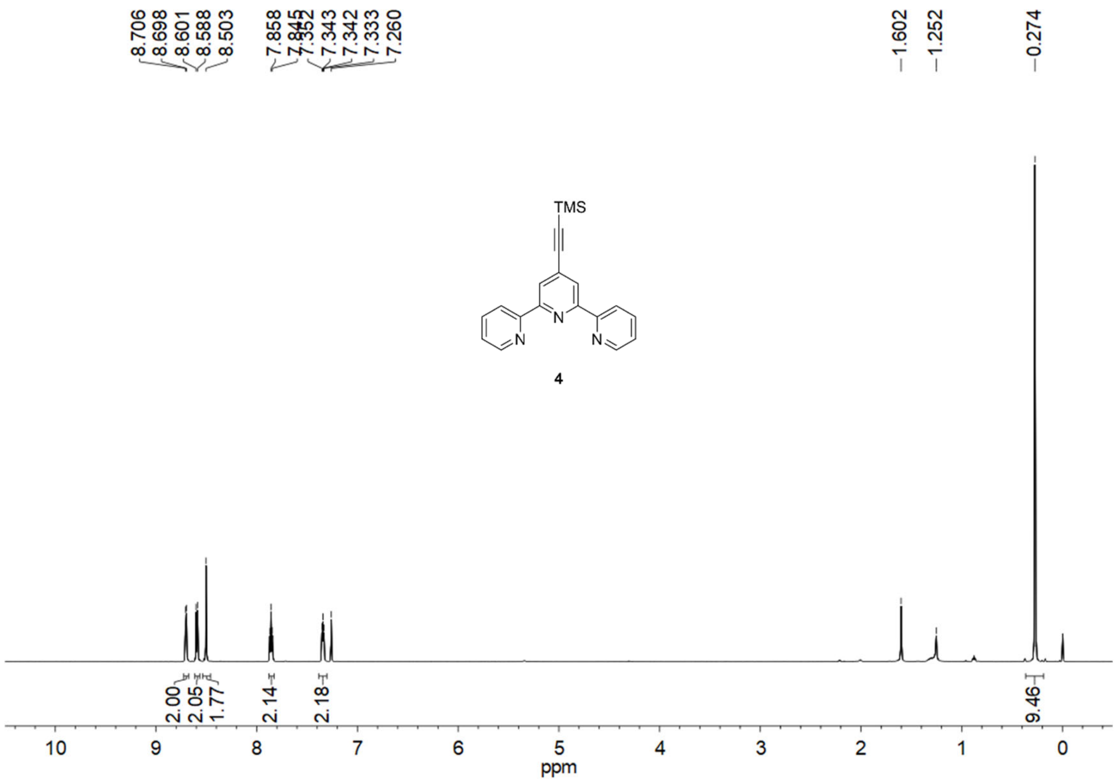


Fig. S3 ^{1}H NMR spectrum of compound **4** (600 MHz) in CDCl$_3$.

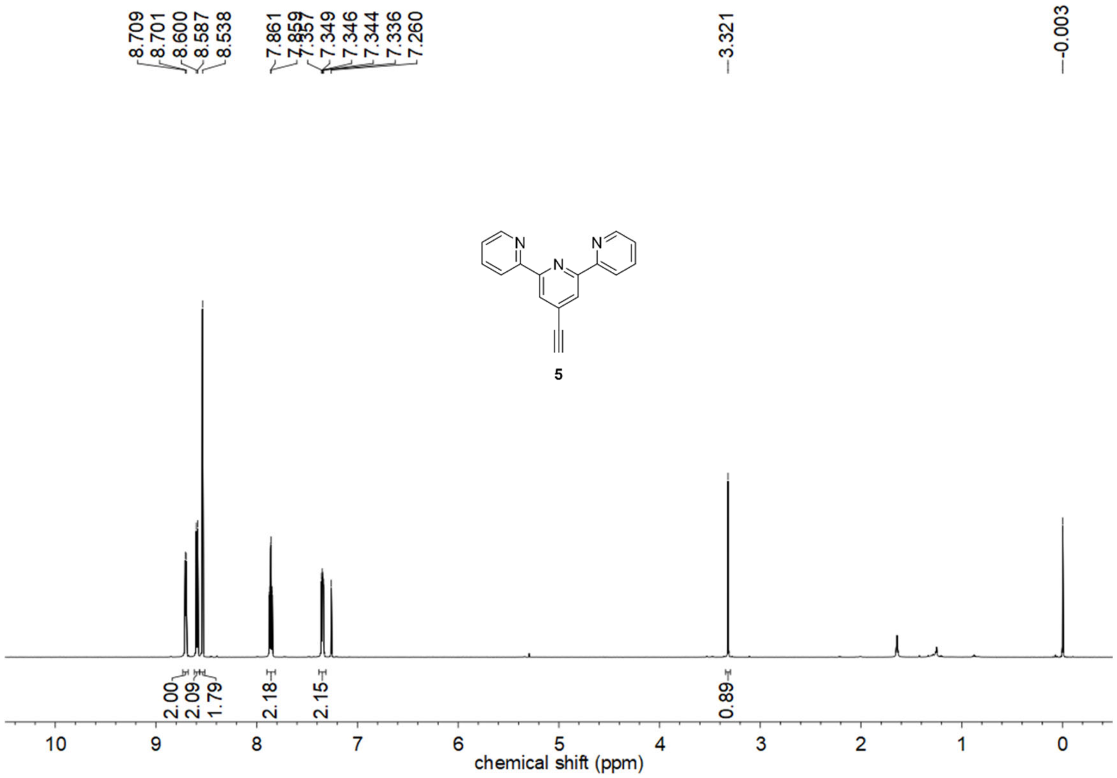


Fig. S4 ^{1}H NMR spectrum of compound **5** (600 MHz) in CDCl$_3$ (10 mM).

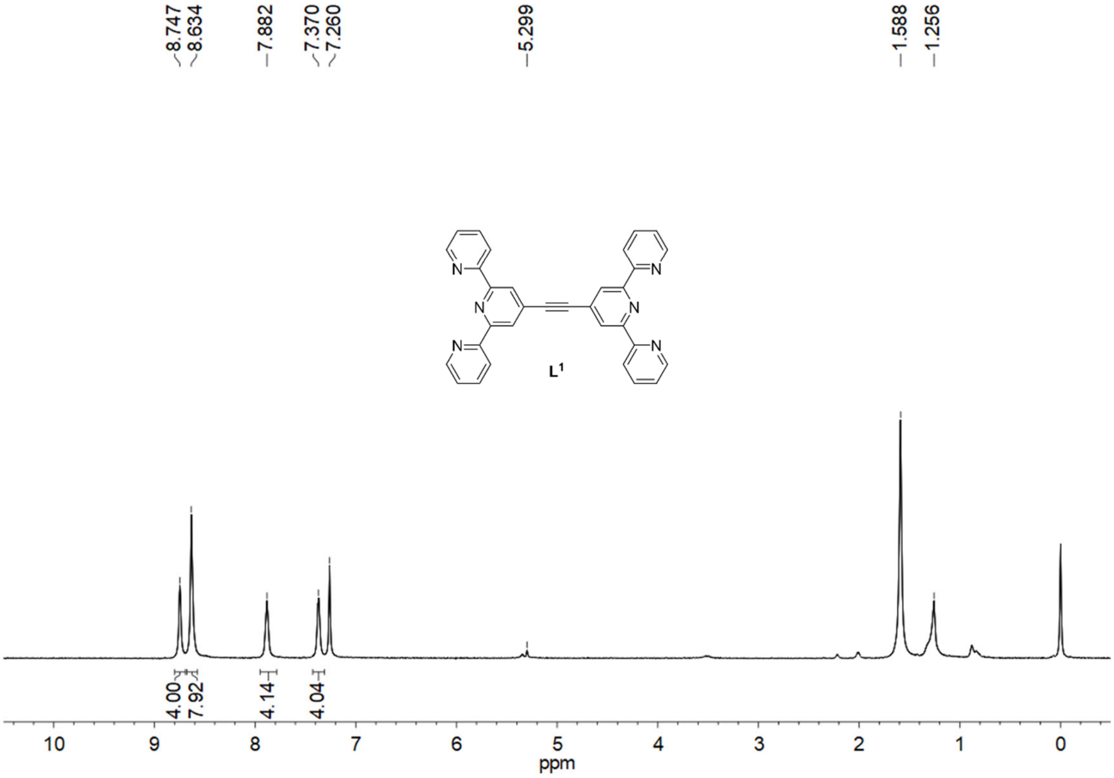


Fig. S5 ^{1}H NMR spectrum of compound **L^1** (600 MHz) in CDCl$_3$.

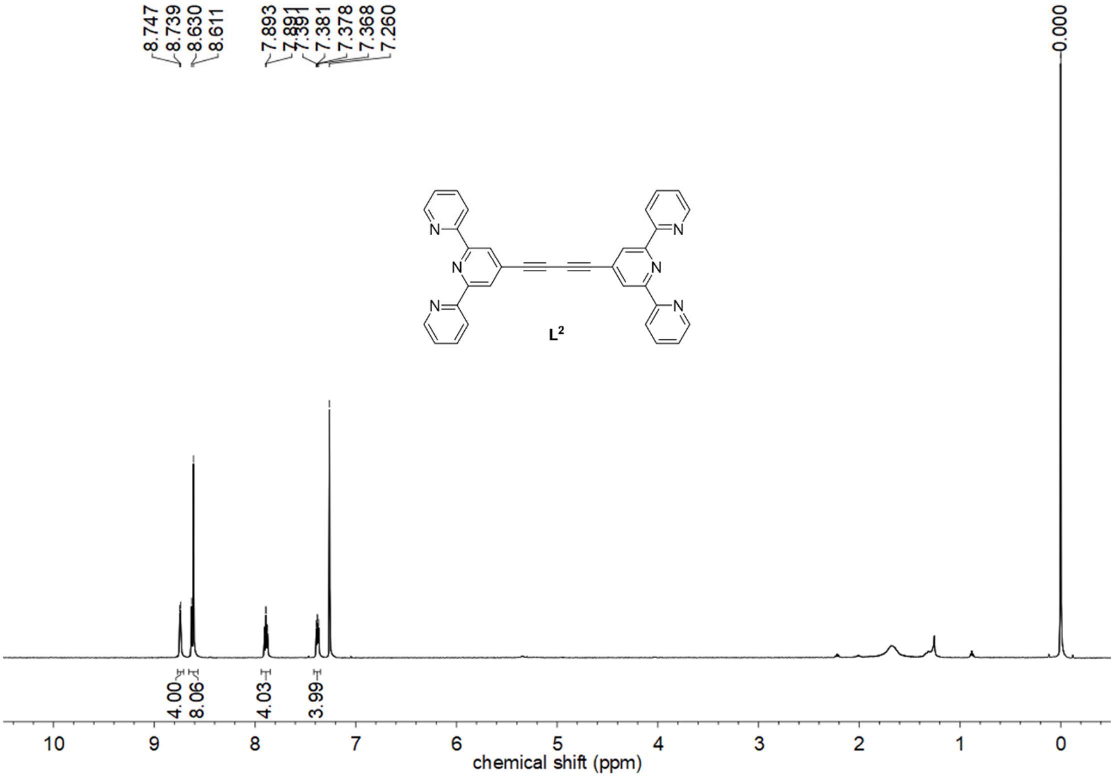


Fig. S6 ^{1}H NMR spectrum of compound **L^2** (500 MHz) in CDCl$_3$.

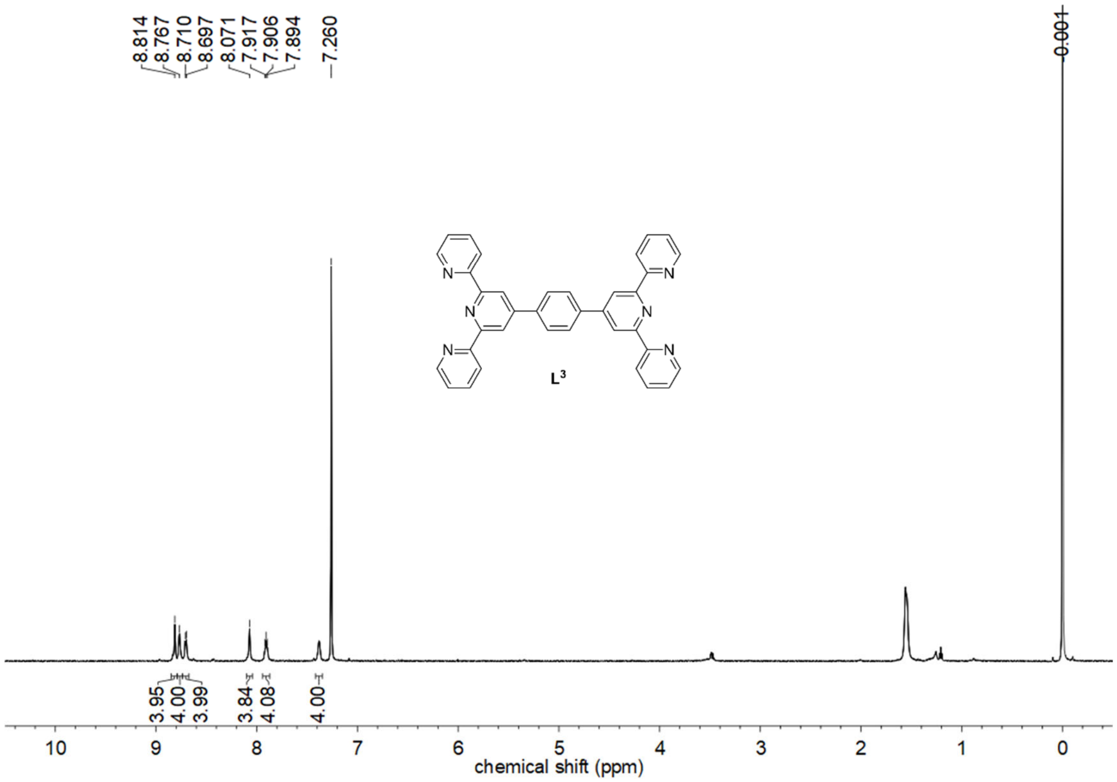


Fig. S7 ^{1}H NMR spectrum of compound **L^3** (600 MHz) in $CDCl_3$.

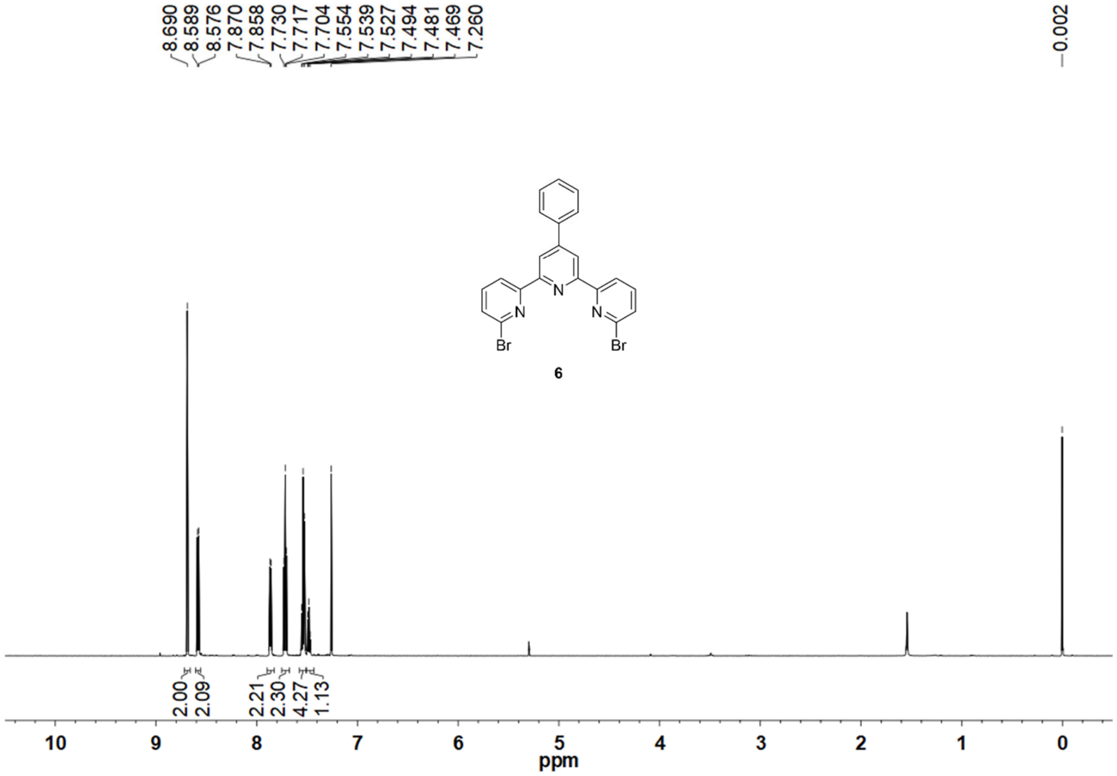


Fig. S8 ^{1}H NMR spectrum of compound **6** (600 MHz) in $CDCl_3$.

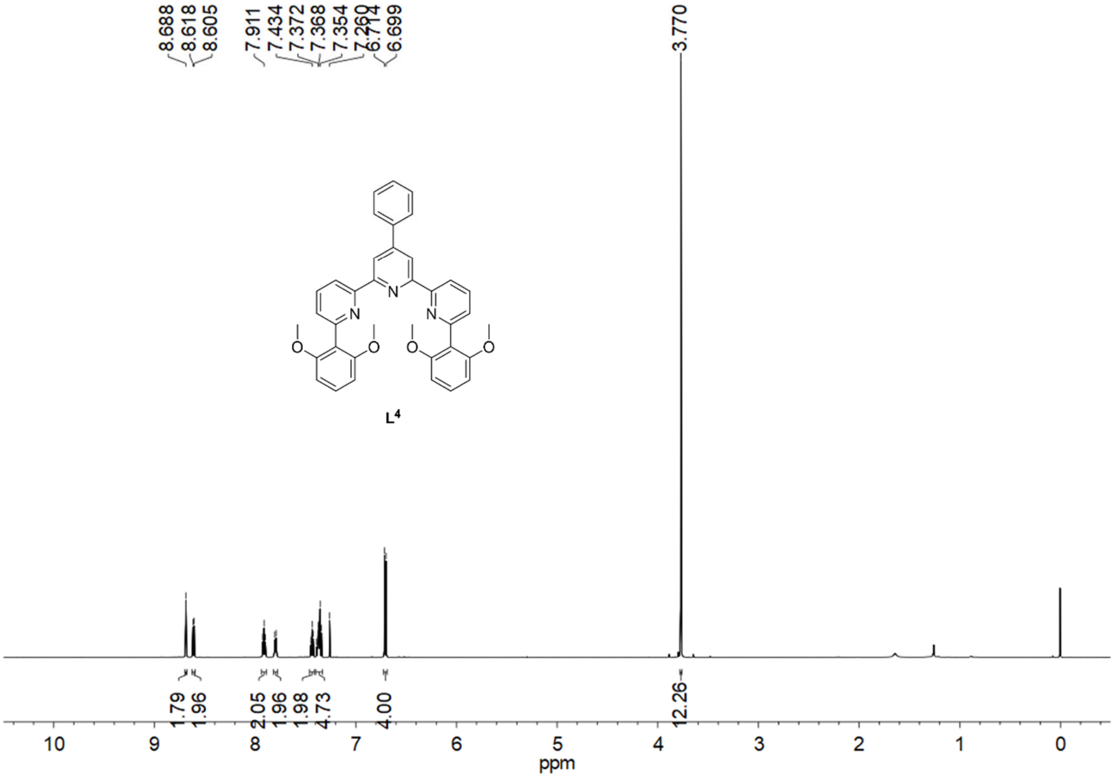


Fig. S9 ^{1}H NMR spectrum of compound **L^4** (600 MHz) in CDCl$_3$.

SI4 Structural details of the complexes

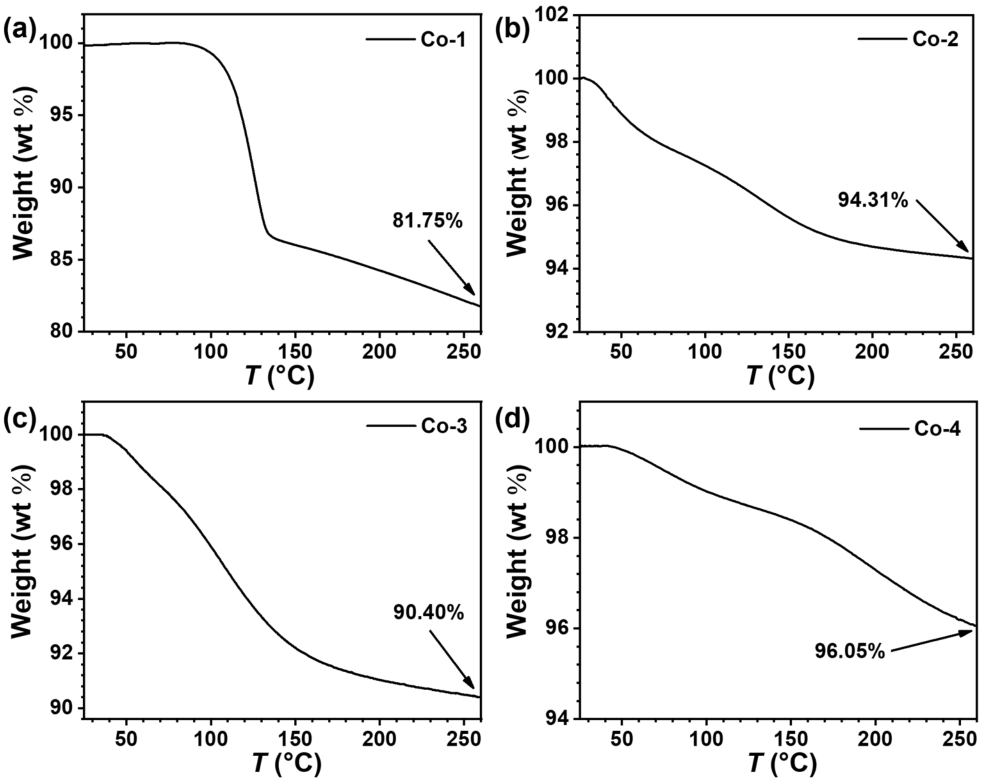


Fig. S10 The TGA traces of (a) **Co-1**, (b) **Co-2**, (c) **Co-3**, and (d) **Co-4** from ambient temperature to 260 °C. The loss in weight is due to the removal of lattice solvents. The results also indicate that the complexes are thermally stable enough below the upper limited temperature of variable-temperature magnetic susceptibility measurements.

Table S1. The comparison of theoretical mass loss of lattice solvents in four compounds and the actual loss that performed by TGA at 260 °C.

Sample	Structural Formula	Calc. Loss (wt%)	Actu. Loss (wt%)[a]
Co-1	$C_{106}H_{82}Co_2N_{12}O_8$ $4(ClO_4)$ $4(CHCl_3)$	18.05	19.25
Co-2	$C_{108}H_{82}Co_2N_{12}O_8$ $4(ClO_4)$ $3(CH_3OH)$ (H_2O)	4.95	5.69
Co-3	$C_{110}H_{86}Co_2N_{12}O_8$ $4(ClO_4)$ $4(CHCl_3)$	17.70	9.60
Co-4	$C_{52}H_{42}CoN_6O_4$ $2(ClO_4)$ $2(CHCl_3)$	18.20	3.95

[a]The actual mass loss was calculated according to the TGA value at 260 °C.

Table S2 Crystal data, data collection, solution, and refinement information of complexes in this work.

	Co-1	**Co-2**[c]	**Co-3**[d]	**Co-4**
Formula	$C_{110}H_{86}Cl_{16}Co_2N_{12}O_{24}$	$C_{108}H_{82}Cl_4Co_2N_{12}O_{24}$	$C_{110}H_{86}Cl_4Co_2N_{12}O_{24}N_{12}$	$C_{54}H_{44}Cl_8CoN_6O_{12}$
Formula weight	2644.96	2191.51	2219.56	1311.4
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2$/c
a, Å	11.7549(5)	13.540(8)	12.701(2)	15.615(3)
b, Å	14.0185(6)	13.827(8)	15.639(2)	21.483(4)
c, Å	19.0050(8)	14.657(8)	16.767(2)	16.507(3)
α, deg	98.124(2)	74.941(15)	77.673(4)	90
β, deg	94.732(2)	89.577(13)	78.057(4)	92.13(3)
γ, deg	114.218(1)	86.201(13)	66.235(4)	90
V, Å^3	2793.0(2)	2644.0(3)	2950.5(7)	5533.4(19)
Z	1	1	1	4
T, K	120.0 (2)	120.0 (2)	120.0(2)	150.0 (2)
F(000)	1348	1128	1144	2676
D_C, g cm^{-3}	1.573	1.376	1.249	1.574
μ, mm^{-1}	0.759	0.493	0.443	0.766
λ, Å	0.71073	0.71073	0.71073	0.71073
crystal size, mm^3	0.14 × 0.12 × 0.12	0.16 × 0.06 × 0.05	0.25 × 0.22 × 0.20	0.12 × 0.10 × 0.08
T_{min} and T_{max}	0.7044, 0.7456	0.9248, 0.9761	0.8968, 0.9171	0.6215, 0.7456
θ_{min}, θ_{max}, deg	2.357, 27.475	2.30, 27.17	2.45, 27.40	2.262, 26.741
no. total reflns.	57089	49803	60693	39067
no. uniq. reflns, R_{int}	12840, 0.0452	10733, 0.0414	10925, 0.0603	5252, 0.1059
no. obs. [$I \geq 2\sigma(I)$]	10194	8451	8542	3694
no. params	743	747	715	408
$R1$ [$I \geq 2\sigma(I)$]	0.0446	0.0692	0.0792	0.0546
$wR2$ (all data)	0.1210	0.1906	0.2405	0.1255
S	1.024	1.083	1.071	1.024
$\Delta\rho$,[a] e/Å^3	1.136, −0.777	0.970, −1.139	1.287, −0.770	0.443, −0.553
Max. and mean Δ/σ[b]	0.001, 0.000	0.001, 0.000	0.000, 0.000	0.000, 0.000
CCDC	2151458	2151459	2151460	2151462

[a] Max and min residual density. [b] Max and mean shift/σ. [c] The refinement showed there are 63 electrons per one **Co-2** complex, in the lattice void which belong to the seriously disordered solvent molecules, could not be modeled. These undetermined Q peaks were treated by SQUEEZE, PLATON. The 62 electrons per one complex might come from three MeOH and one H_2O molecules and were excluded in the formula. [d] Similarly, the 232 electrons per one **Co-3** complex in the lattice void might come from four $CHCl_3$ molecules and were excluded in the formula.

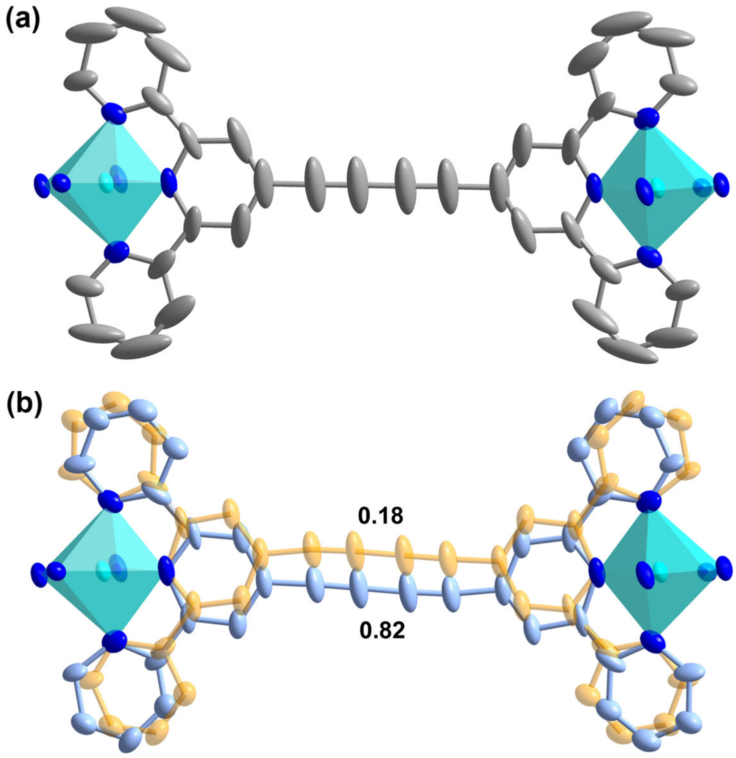


Fig. S11 The ellipsoid view of ligand **L^2** in complex **Co-2** (a) before and (b) after being splitting into two parts.

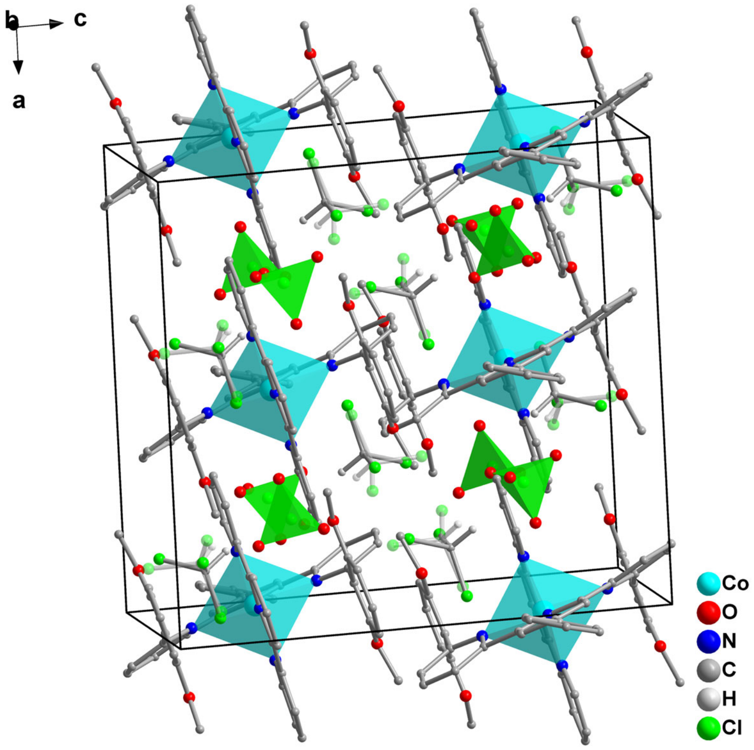


Fig. S12 Projection of the unit-cell of **Co-4** along *b* axis at 150 K.

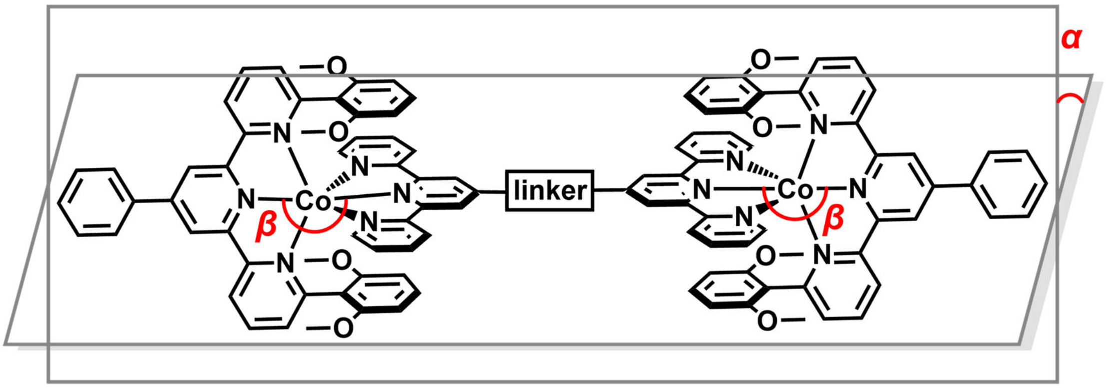
Table S3 The Selected bond lengths (Å) for the single crystal structures of Co–N bonds in four complexes.

	Co-1	**Co-2**	**Co-3**	**Co-4**
Co1–N1 (Å)	2.241(2)	2.294(3)	2.266(3)	2.280(3)
Co1–N2 (Å)	1.936(2)	1.935(3)	1.946(3)	1.924(4)
Co1–N3 (Å)	2.259(2)	2.250(3)	2.240(3)	1.955(3)
Co1–N4 (Å)	1.972(2)	1.980(3)	1.966(3)	1.856(4)
Co1–N5 (Å)	1.859(2)	1.854(3)	1.861(3)	/
Co1–N6 (Å)	1.969(2)	1.972(3)	1.957(3)	/
Avg bond length (Å)	2.039(2)	2.047(3)	2.039(3)	2.042(4)

Table S4 The summary of distances of parallelly arranged 2,6-dimethoxyphenyl and pyridine between complementary terpyridine ligands in four complexes.

Entry	**Distance of two planes (Å)**
Co-1(1)	3.383
Co-1(2)	3.501
Co-2(1)	3.448
Co-2(2)	3.597
Co-3(1)	3.420
Co-3(2)	3.416
Co-4	3.397

Table S5 The comparison of the structural parameters and spin state for cobalt(II) centers in five complexes.



Entry	T (K)	Σ (°)	α (°)	β (°)	Co−N$_{av}$ (Å)	S(O$_h$)	Spin State
Co-1	120	96.10	86.64	178.25	2.039	2.881	LS
Co-2	120	95.34	86.23	174.80	2.047	3.053	SCO
Co-3	120	91.02	89.24	176.08	2.039	2.923	SCO
Co-4	150	85.96	89.01	180.00	2.042	2.765	LS

α: the dihedral angle between the last-squares planes of the tridentate ligands and the angle;[6] β: refer to the *trans*-N(pyridine)–Fe–N(pyridine) angle;[6] Fe−N$_{av}$: the average value of the six Fe−N bond lengths in one FeN$_6$ coordination sphere; Σ: the sum of the deviations from 90° of the *cis* angles;[7, 8] S(O$_h$): the result of CShMs calculation denotes the deviation value of ideal O_h symmetry.[9]

SI5 Supplementary Magnetic and Other Physical Properties Characterization

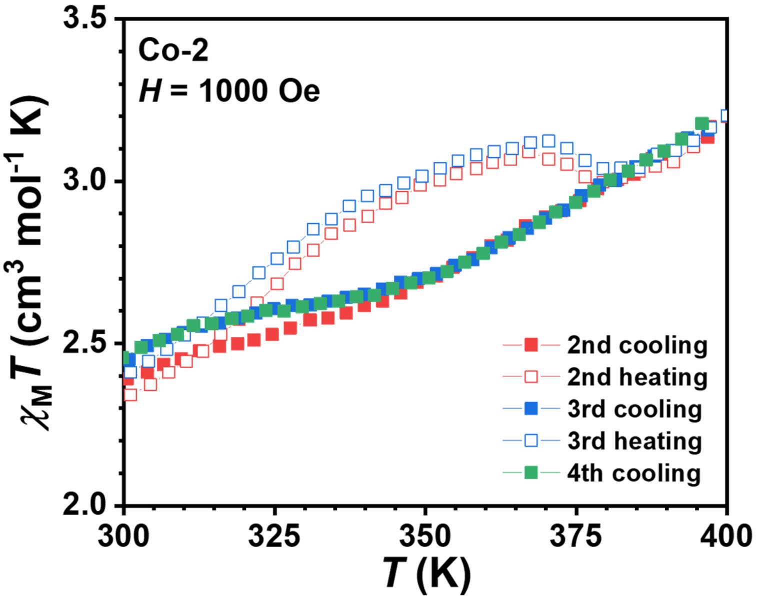


Fig. S13 The amplified thermal hysteresis loops of **Co-**2 from 322 K to 377 K in two successive scannings.

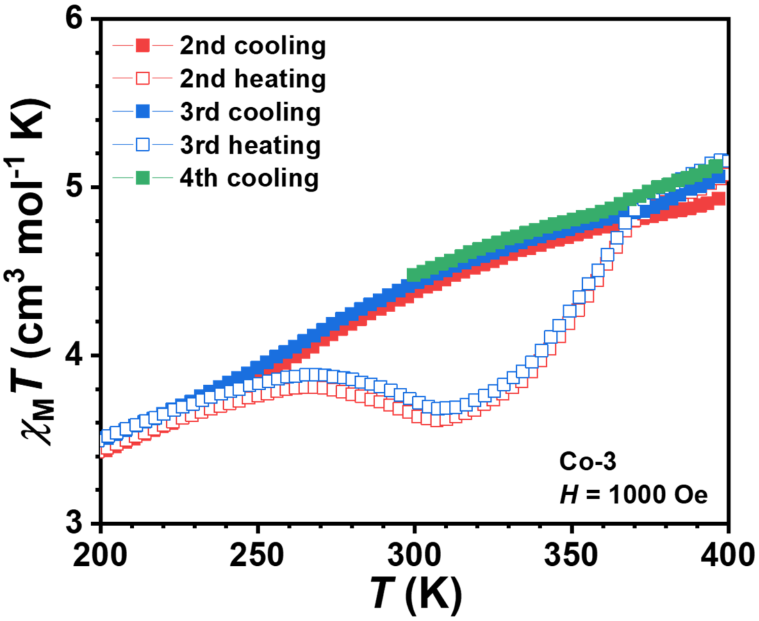


Fig. S14 The amplified thermal hysteresis loops of **Co-3** from 220 K to 370 K in two successive scannings.

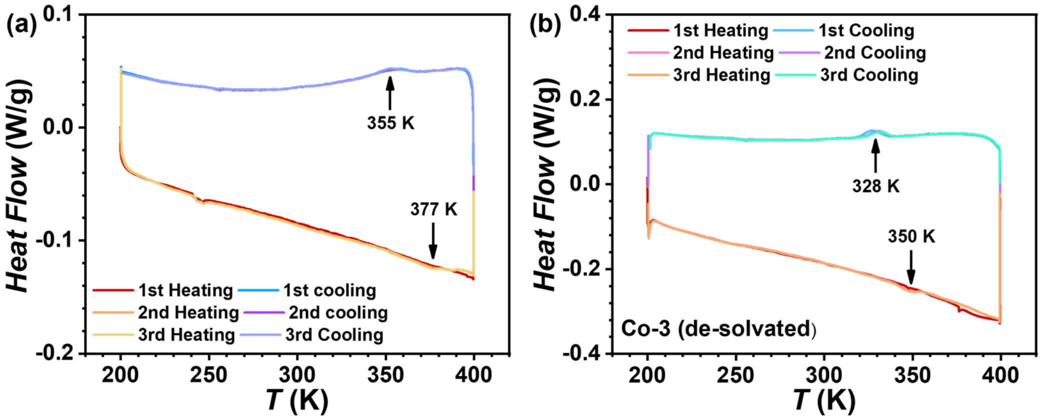


Fig. S15 Differential scanning calorimetry profile of de-solvated samples of **Co-2** and **Co-3**. The scan rate is 3 K min^{-1}.

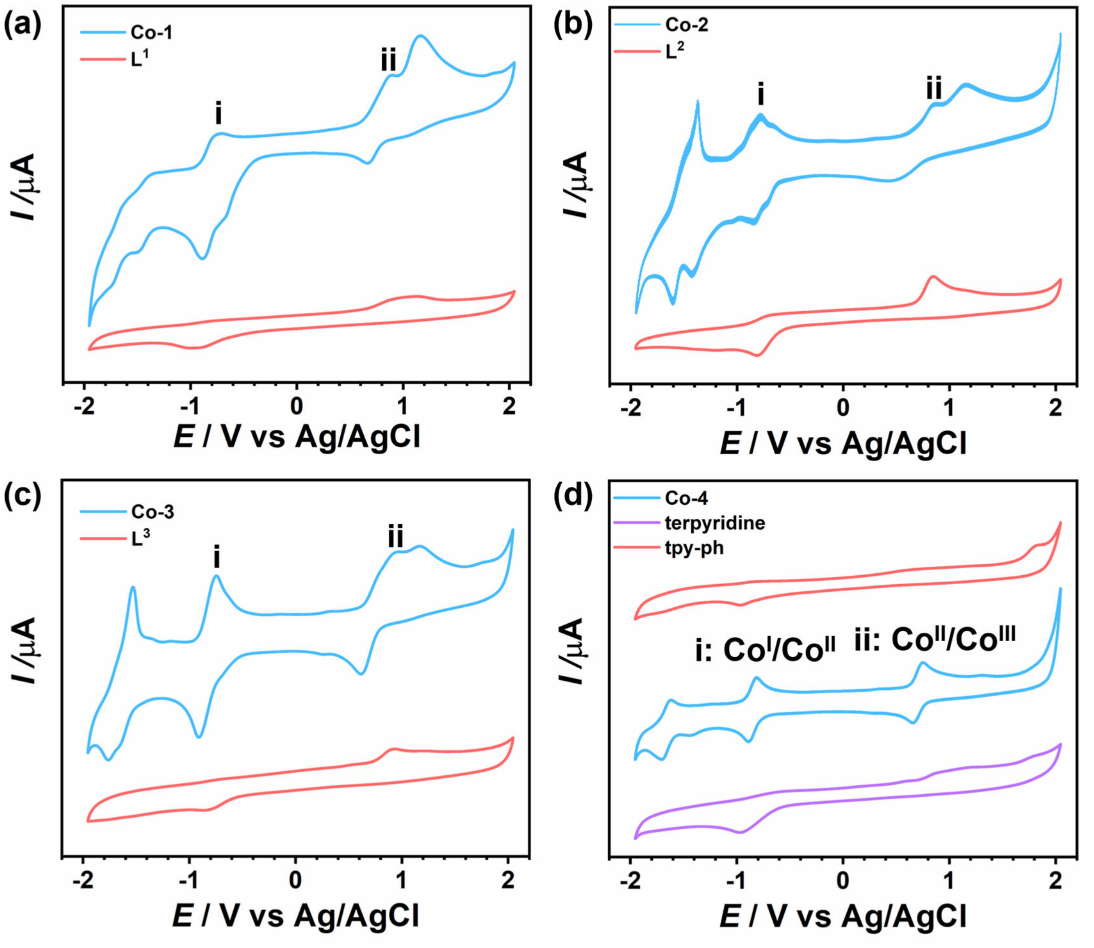


Fig S16 Cyclic voltammogram of (a) **Co-1**, (b) **Co-2**, (c) **Co-3**, (d) **Co-4** and their corresponding ligands in acetonitrile solution.

SI6 References

1. R. Akiyoshi, K. Kuroiwa, S. Alao Amolegbe, M. Nakaya, R. Ohtani, M. Nakamura, L. F. Lindoy and S. Hayami, Supramolecular architectures self-assembled using long chain alkylated spin crossover cobalt(ii) compounds, *Chem. Commun.*, 2017, **53**, 4685-4687.
2. M. L. Muro and F. N. Castellano, Room temperature photoluminescence from [Pt(4′-C CR-tpy)Cl]+ complexes, *Dalton Trans.*, 2007, DOI: 10.1039/B709886C, 4659-4665.
3. V. Grosshenny, F. M. Romero and R. Ziessel, Construction of preorganized polytopic ligands via palladium-promoted cross-coupling reactions, *J. Org. Chem.*, 1997, **62**, 1491-1500.
4. K. Bahrami and H. Targhan, A new strategy to design a graphene oxide supported palladium complex as a new heterogeneous nanocatalyst and application in carbon-carbon and carbon-heteroatom cross-coupling reactions, *Appl. Organomet. Chem.*, 2019, **33**.
5. S. Y. Wang, J. H. Fu, Y. P. Liang, Y. J. He, Y. S. Chen and Y. T. Chan, Metallo-Supramolecular Self-Assembly of a Multicomponent Ditrigon Based on Complementary Terpyridine Ligand Pairing, *J. Am. Chem. Soc.*, 2016, **138**, 3651-3654.
6. J. M. Holland, J. A. McAllister, Z. Lu, C. A. Kilner, M. Thornton-Pett and M. A. Halcrow, An unusual abrupt thermal spin-state transition in [FeL][BF] [L = 2,6-di(pyrazol-1-yl)pyridine], *Chem. Commun.*, 2001, DOI: 10.1039/B100995H, 577-578.
7. M. A. Halcrow, Structure:function relationships in molecular spin-crossover complexes, *Chem. Soc. Rev.*, 2011, **40**, 4119-4142.
8. J. K. McCusker, A. L. Rheingold and D. N. Hendrickson, Variable-Temperature Studies of Laser-Initiated 5T2 → 1A1 Intersystem Crossing in Spin-Crossover Complexes: Empirical Correlations between Activation Parameters and Ligand Structure in a Series of Polypyridyl Ferrous Complexes, *Inorg. Chem.*, 1996, **35**, 2100-2112.
9. M. Llunell, D. Casanova, J. Cirera, P. Alemany and S. Alvarez, SHAPE, version 2.0.*Journal*, 2010.