

[Electronic Supporting Information (ESI) to accompany:]
Luminescent infinite coordination polymers (CP) from metal-terpyridine ligation

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General procedures, materials, and instrumentations. All air- or water-sensitive reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Fe and Ru ICP standards were obtained from Ricca Chemicals Co. (Arlington, TX). Unless otherwise stated, all chemicals and solvents were purchased from Aldrich Chemicals Co. (Milwaukee, WI) and used without further purification. Water was obtained from a deionized water source provided by Northwestern University. Deuterated solvents were purchased from Cambridge Isotope Laboratories (Andover, MA) and used without further purification. Dry solvents were prepared by passing HPLC-grade solvents through a column packed with neutral alumina via a Dow-Grubbs solvent system^{S1} installed by Glass Contours (now SG Water USA, Nashua, NH). All dry solvents were collected under inert gases, degassed under vacuum, and stored under nitrogen in a Strauss flask prior to use. All the gases used for the adsorption and desorption measurements were Ultra High Purity Grade 5 and were obtained from Airgas Specialty Gases (Chicago, IL).

¹H and ¹³C NMR spectra were recorded on a Bruker 500 FT-NMR spectrometer (499.773 MHz for ¹H, 125.669 MHz for ¹³C). ¹H NMR data are reported as follows: chemical shift (multiplicity (b = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, t = triplet, q = quartet, and m = multiplet), integration, and peak assignments, coupling constants). ¹H and ¹³C chemical shifts are reported in ppm from TMS with the residual solvent resonances as internal standards.

Microwave experiments were performed in a Biotage (Uppsala, Sweden) SPX microwave reactor (software version 2.3, build 6250). Desired temperature was entered in the software and the reactor tuned the microwave power to obtain desired temperature and kept it stable in course of the reaction depending on the headspace available in the vial. All reactions were magnetically stirred during irradiation using the built-in magnetic stirrer.

Fourier-transformed infrared (FTIR) spectroscopy was performed on a Thermo Nicolet Nexus 870 FTIR spectrometer (Thermo Scientific, Waltham, MA), using KBr pellets for all samples. Frequencies are given in reciprocal centimeters (cm⁻¹). The FTIR spectra were analyzed using EZ Omnic software (Thermo Scientific, Waltham, MA).

Thermogravimetric analyses (TGA) were performed on a TGA/DCS 1 system (Mettler-Toledo AG, Schwerzenbach, Switzerland), which runs on a PC with STAR^c software (version 9.10). Samples placed in alumina pans were heated from 25°C to 700°C at 10°C/minute rate under N₂ flow. As synthesized Ni-CP sample (entry 9, Table 1) was collected after washing step with hot CHCl₃ for 24 hours in a Soxhlet extractor (See CP synthesis section in page S6) and subjected immediately to TGA experiment. TGA profiles for all other CPs are obtained after activation (see activation of polymers section, page S8) and CO₂ adsorption analysis of these materials. Small amount of initial mass loss (3-5% of its weight) is observed in TGA analysis of all CPS because the materials were kept in closed vials for a month after the CO₂ adsorption experiments and could absorb some moisture during this period.

Inductively coupled plasma (ICP) spectroscopy was conducted on a Varian Vista-MDX model ICP-OES spectrometer with simultaneous CCD detector (Varian, Walnut Creek, CA) that was equipped to cover the spectral range from 175 to 785 nm. The instrument was controlled by ICP expert software (version 4.1.0). Samples (1.4-3 mg) were digested in conc. H₂SO₄:H₂O₂ (35 wt% in H₂O) (3:1 v/v) at 110°C until the solution became clear and colorless and no further vapor was produced. An aliquot of this concentrated acid solution was diluted to 8.0 vol% in deionized H₂O. The instrument was calibrated using ultrapure deionized water (18.2 MΩ·cm resistivity), which was obtained from a Millipore Milli-Q Biocel A10 instrument (Millipore Inc., Billerica, MA), and mixtures containing 1, 2, 5, 10, and 20 ppm of Zn, Fe, Ni and Ru that were prepared from commercially available ICP standard solutions.

CO₂ and N₂ adsorption and desorption measurements were carried out on an Autosorb 1-MP instrument (Quantachrome Instrument, Boynton Beach, FL). Nitrogen isotherms were carried out in a liquid nitrogen bath (77K). Carbon dioxide isotherms were measured in an ice/water bath (273K). The specific surface areas for CO₂ were calculated using the NLDFT slit-pore model for CO₂ at 273 K in the Autosorb 1 software (version 1.54). Density measurements were conducted using AccuPyc 1340 pycnometer (Micromeritics, Norcross, GA). Solid sample (10-17 mg) was placed in 0.1 cm³ holder for the measurement.

Scanning electron microscope (SEM) images were gathered using a field-emission gun Nova NanoSEM 600 (FEI Co., Hillsboro, OR) microscope under an acceleration voltage of 5 kV. Samples were coated with 6 nm of osmium using an OPC-60A osmium plasma coater (Structure Probe, Inc. Supplies, West Chester, PA) prior to analysis.

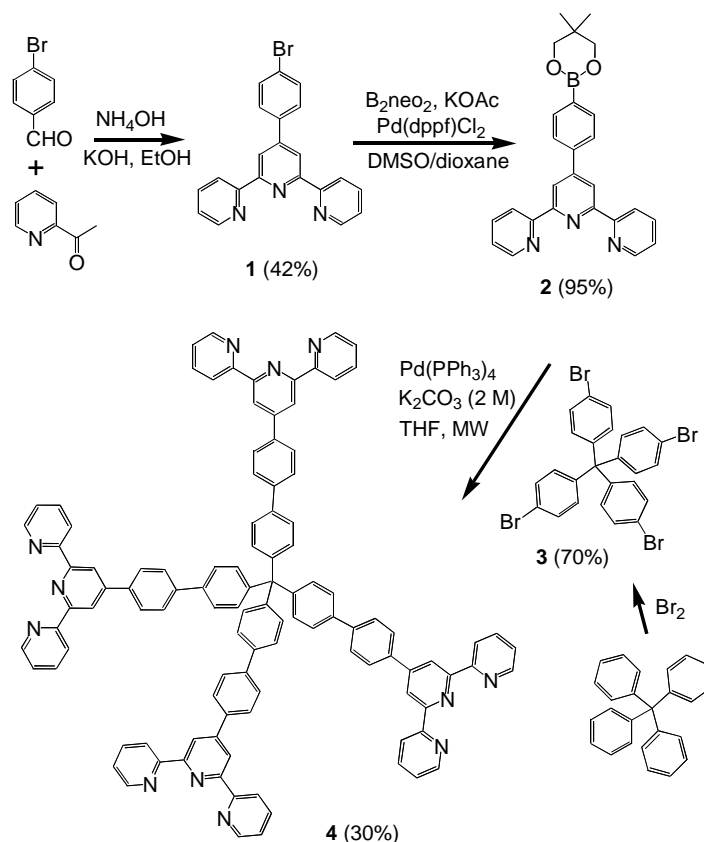
Luminescence microscope images were collected on DeltaVision PersonalDV Live Cell Imaging System (Applied Precision, Berthold Australia Pty Ltd, Bundoora, Victoria 3083, Australia). The Ru-CP sample (1 mg, Table 1, entry 15) was dispersed in EtOH (2 mL) and sonicated for 5 minutes (Fisher Scientific, Model FS60) to break up the clusters of particles. Then a couple drops of this dispersion was placed on a sample holder (Lab-Tek II Chamber #1.5 German Coverglass System, Thermal/Nalge Nunc., Rochester, NY) and dried under ambient conditions for 1 hour or more before imaging. Under these conditions, we are confident that the luminescence of our Ru-CP cannot be attributed to solvoluminescence caused by the solvent (EtOH) used in the sample preparation. To the best of our knowledge, solvoluminescence has not been reported for [Ru(tpy)₂]²⁺, either in the pure solid state or when attached to other materials. This makes sense since luminescence in [Ru(tpy)₂]²⁺ complexes is primarily attributed to their triplet MLCT states, which should not be affected by solvents.^{S2} Additionally, because the [Ru(tpy)₂]²⁺ centers are fixed in the backbone of the dense, highly catenated 3-D network of our Ru-CP, which do not swell (see discussion on page S11), we do not expect that adsorbed solvent will lead to change in their native luminescence properties or cause additional solvoluminescence.

High-resolution electrospray mass spectrometry was carried out on an Agilent 6210 Time of Flight-LC/MS mass spectrometer (Agilent, Wilmington, DE). Analyses were performed in the positive ion ESI mode using the reflectron configuration. The instrument was calibrated with the Agilent ESI low concentration tune solution. Operational parameters are as follows: mass range = 100-3000 m/z, VCap = 3806 V, drying gas (N₂) flow = 7.0 L/min, gas temperature = 315 °C, skimmer = 65 V, fragmentor = 220 V, ion focus = - 48 V. Sample was flow-injected from an Agilent 1200 HPLC system with 90% MeOH, 10% H₂O with 0.1% TFA as the carrier stream. HPLC grade solvents were used in all analysis.

Synthesis

4'-(4-Bromophenyl)-2,2';6,2''-terpyridine (1). This compound was synthesized following a modified literature procedure.^{S3} KOH (80%, 4.43 g, 63.2 mmol) and aqueous NH₄OH (100 mL of a 28 wt% solution, 80 mmol) were added to a stirring solution of 4-bromobenzaldehyde (5.84 g, 31.6 mmol) and 2-acetylpyridine (7.66 g, 63.2 mmol) in EtOH (150mL) in 500 mL round bottom flask equipped with magnetic stir bar. The resulting mixture was stirred under ambient atmosphere and temperature for 4 hours during which time a precipitate formed. The reaction content was then filtered over a Buchner funnel and the collected precipitate was washed with EtOH (50 mL) before being dried under high vacuum, giving the first crop of product **1** (3.1 g) as light yellow solid. Air was blown onto the combined filtrate solution to remove the remaining NH₃ (until all the smell disappeared) during which time more precipitate formed. The resulting mixture was filtered over a Buchner funnel and the collected precipitate was washed with EtOH (50 mL) before being dried under high vacuum to afford a second crop of product **1** (2.1 g). Total isolated product = 5.2 g (42%). ¹H NMR (CDCl₃): δ 7.36 (ddd, 2 H, 5,5''-tpyH, J₁ = 6.5 Hz, J₂ = 5.0 Hz, J₃ = 1.5 Hz), 7.65 (d, 2 H, 2,6-ArH, J = 8.5 Hz), 7.77 (d, 2 H, 3,5-ArH, J = 8.5 Hz), 7.88 (ddd, 2 H, 4,4''-tpyH, J₁ = 9.0 Hz, J₂ = 8.0 Hz, J₃ = 1.5 Hz), 8.66 (d, 2 H, 3,3''-tpyH, J = 7.5 Hz), 8.7 (s, 2 H, 3',5'-tpyH), 8.73

(d, 2 H, 6,6''-tpyH, $J = 3.6$ Hz). ^{13}C NMR (CDCl_3): δ 118.7, 121.6, 123.7, 124.1, 129.1, 132.1, 137.1, 137.6, 149.2, 149.3, 156.2, 156.3.



Scheme S1. The synthesis of tetraterpyridine **4**.

4'-(4-(Neopentyl glycolatoboron)phenyl)-2,2':6',2''-terpyridine (2). This compound was synthesized following a modified literature procedure.^{S4} $\text{Pd}(\text{dppf})\text{Cl}_2$ (240 mg, 0.33 mmol) and KOAc (3.1 g, 31.6 mmol) were added to a stirring solution comprises terpyridine **1** (4.09 g, 10.5 mmol), bis(neopentyl glycolato)diboron (B_2neo_2 , 2.5 g, 11 mmol), DMSO (50 mL), and dioxane (50 mL) in 250 mL Schlenk flask equipped with a magnetic stir bar and a rubber stopper. The resulting solution was cooled down to -78 °C in acetone/dry ice bath and subjected to three cycles of brief vacuum-degas/ N_2 back-fill with no stirring. The flask was then fitted to a water-cooled reflux condenser and stirred at 100 °C for 18 h under N_2 , after which the reaction was allowed to cool to rt. Toluene (100 mL) was added to the resulting mixture, which was then extracted with H_2O (200 mL). The aqueous layer was separated and then back-extracted with toluene (3×100 mL). All toluene layers were combined (700 mL), dried over MgSO_4 , and concentrated to give the product **2** as a brown solid, which was dried under high vacuum. Isolated yield = 4.2 g (95%). ^1H NMR (CDCl_3): δ 1.06 (s, 6 H, $\text{B}-(\text{OCH}_2-\text{C}(\text{CH}_3)_2)_2$), 3.82 (s, 4 H, $\text{B}-(\text{OCH}_2-\text{C}(\text{CH}_3)_2)_2$), 7.36 (ddd, 2 H, 5,5''-tpyH, $J_1 = 7.2$ Hz, $J_2 = 5.6$ Hz, $J_3 = 0.8$ Hz), 7.88 (ddd, 2 H, 4,4''-tpyH, $J_1 = 9.4$ Hz, $J_2 = 7.8$ Hz, $J_3 = 1.7$ Hz), 7.91 (d, 2 H, 2,6-ArH, $J = 8.2$ Hz), 7.94 (d, 2 H, 3,5-ArH, $J = 8.2$ Hz), 8.67 (d, 2 H, 3,3''-tpyH, $J = 7.9$ Hz), 8.75 (d, 2 H, 6,6''-tpyH, $J = 4.0$ Hz), 8.77 (s, 2 H, 3',5'-tpyH). ^{13}C NMR (CDCl_3): δ 22.2, 32.1, 72.55, 119.1, 121.6, 124.0, 126.7, 134.6, 137.1, 140.6, 149.3, 150.5, 156.1, 156.5.

Tetrakis(4-bromophenyl)methane (3). This compound was synthesized following a modified literature procedure.^{S5} A 150 mL round-bottom flask equipped with a magnetic stir bar and a water-cooled reflux condenser was charged with tetraphenylmethane^{S6} (10 g, 31.2 mmol). Neat bromine (11.1 mL, 194 mmol) was slowly added and the resulting solution was stirred for 20 minutes at room temperature until the solution became a viscous slurry, which was diluted with ethanol (200 mL) and further stirred for 30 minutes. The resulting mixture was then filtered; the precipitate was collected, dispersed in saturated aqueous Na_2SO_3 (200 mL), and sonicated for 15 minutes before being filtered again. The collected precipitate was dried under air and recrystallized in a mixture of $\text{EtOH}/\text{CHCl}_3$.

(500 mL, 1:1, v/v) to give the product **3**, as white solid, which was dried under high vacuum. Isolated yield = 13.9 g (70%). $^1\text{H NMR}$ (CDCl_3): δ 7.03 (d, 8 H, 3,5-BenH, $J = 8.4$ Hz), 7.39 (d, 8 H, 2,6-BenH, $J = 8.4$ Hz). $^{13}\text{C NMR}$ (CDCl_3): δ 63.8, 121.0, 131.3, 132.6, 144.6.

Tetrakis[4-(4'-phenyl-2,2':6,2''-terpyridine)phenyl]methane (4). Terpyridine **2** (620 mg, 1.47 mmol), tetrabromo compound **3** (200 mg, 0.31 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (82 mg, 0.07 mmol) were added to a 20 mL microwave reactor vial and sealed. Degassed THF (10 mL) and aqueous Na_2CO_3 (2.5 mL of a 2 M solution) were then added into the sealed reaction vial through a cannula. The mixture was cooled down to -78 °C in an acetone/dry ice bath and subjected to three cycles of brief vacuum-degas/ N_2 back-fill with no stirring and then the mixture microwave-irradiated at 140 °C for 4 hours. The aforementioned reaction procedure was repeated five times and all five reaction mixtures were combined and concentrated to give a brown paste, which was dissolved in H_2O (100 mL) and then extracted with CHCl_3 (3×100 mL). The organic layers were combined, dried over MgSO_4 , and concentrated to give a brown solid which was re-dissolved in warm CHCl_3 (70 mL, 50 °C). While this solution was kept on a warm water bath (50 °C), EtOH (50 mL) was added slowly until recrystallization started. The resulting mixture was then cooled to room temperature and the precipitate was filtered and washed with $\text{CHCl}_3/\text{EtOH}$ (30 mL, 7:5 v/v).

The aforementioned recrystallization procedure was repeated two more times with freshly obtained precipitate each time to afford the product **4** as white solid, which was dried under high vacuum. Isolated yield = 770 mg (30%). $^1\text{H NMR}$ (CDCl_3): δ 7.37 (ddd, 8 H, 5,5''-tpyH, $J_1 = 6.7$ Hz, $J_2 = 5.2$ Hz, $J_3 = 1.6$ Hz), 7.52 (d, 8 H, 3,5-BenH, $J = 8.5$ Hz), 7.68 (d, 8 H, 2,6-BenH, $J = 8.5$ Hz), 7.82 (d, 8 H, 3,5-ArH, $J = 8.4$ Hz), 7.9 (ddd, 8 H, 4,4''-tpyH, $J_1 = 9.1$ Hz, $J_2 = 7.9$ Hz, $J_3 = 1.6$ Hz), 8.03 (d, 8 H, 2,6-ArH, $J = 8.3$ Hz), 8.7 (d, 8 H, 3,3''-tpyH, $J = 8.0$ Hz), 8.76 (d, 8 H, 6,6''-tpyH, $J = 4.3$ Hz), 8.82 (s, 8 H, 3',5'-tpyH). $^{13}\text{C NMR}$ (CDCl_3): δ 64.5, 118.9, 121.6, 124.1, 126.6, 127.7, 128.0, 131.8, 137.1, 137.4, 138.2, 141.4, 146.3, 149.4, 150.0, 156.2, 156.5. HRMS (calc.): $m/z = 775.8083$ (775.809 , $[\text{M} + 2\text{H}]^{2+}$).

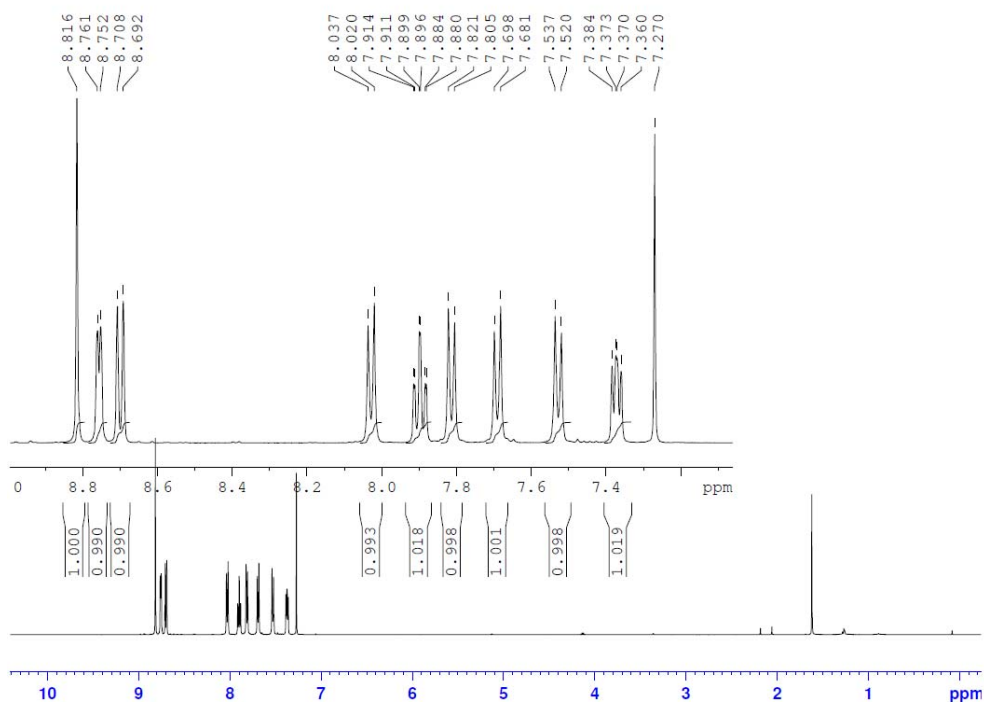


Figure S1. $^1\text{H NMR}$ spectrum of tetraterpyridine ligand **4**.

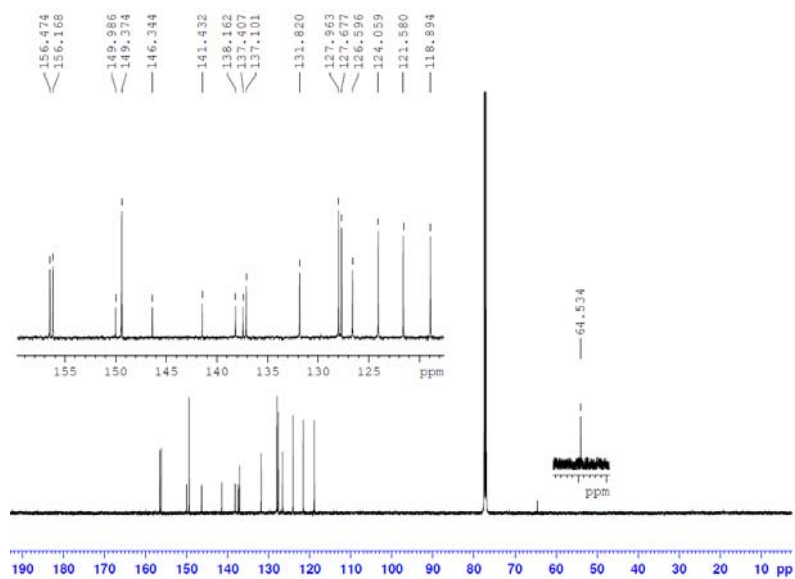


Figure S2. ^{13}C NMR spectrum of tetraterpyridine ligand **4**.

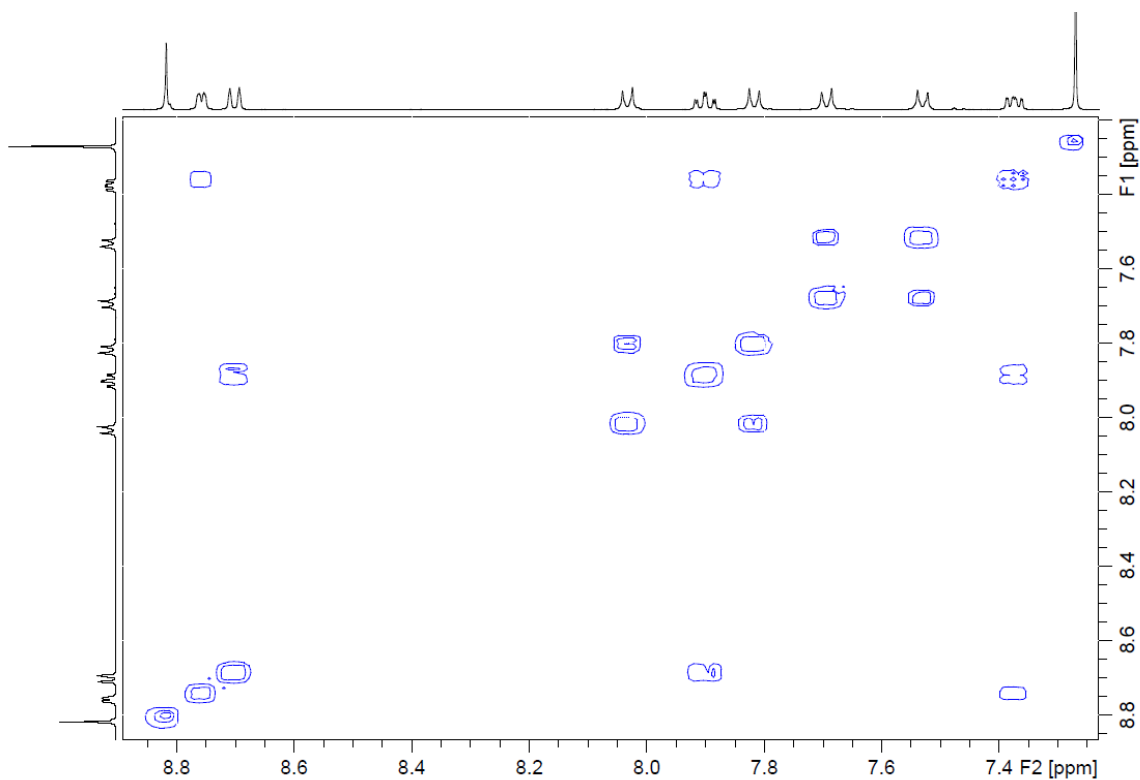


Figure S3. 2D COSY NMR spectrum of tetraterpyridine ligand (**4**).

Synthesis of CPs

Zn₂-4-(NO₃)₄ (Entry 1, Table 1). Zn(NO₃)₆H₂O (5.87 mg, 19.73 μmole) was added to a suspension of terpyridine **4** (15.3 mg, 9.87 μmole) in EtOH (2.5 mL) and MeCN (2.5 mL) in 20 mL microwave reactor vial with a magnetic stir bar. The resulting mixture was microwave-irradiated at 150 $^{\circ}\text{C}$ for 20 hours. After being cooled to rt,

the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl_3 for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 $^\circ\text{C}$ for 24 hours. Isolated yield = 18.3 mg (96%). ICP: calc. = 6.78 Zn wt%, found = 6.28 wt%.

Zn₂-4-(NO₃)₄ (Entry 2, Table 1). $\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$ (10.2 mg, 34.3 μmole) was added to a suspension of terpyridine 4 (26.7 mg, 17.6 μmole) in EtOH (4.5 mL) and MeCN (4.5 mL) in an 8-dram vial with a magnetic stir bar and the vial was capped. The resulting mixture was microwave-irradiated at 90 $^\circ\text{C}$ for 50 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl_3 for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 $^\circ\text{C}$ for 24 hours. Isolated yield = 31.1 mg (94%). ICP: calc. = 6.78 Zn wt%, found = 7.55 wt%. Density = 1.43 g/cm^3 .

Zn₂-4-(NO₃)₄ (Entry 3, Table 1). $\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$ (10.25 mg, 34.4 μmole) was added to a suspension of terpyridine 4 (26.6 mg, 17.22 μmole) in EtOH (9 mL) in an 8-dram vial with a magnetic stir bar and the vial was capped. The resulting mixture was microwave-irradiated at 90 $^\circ\text{C}$ for 50 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl_3 for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 $^\circ\text{C}$ for 24 hours. Isolated yield = 30.9 mg (91%). ICP: calc. = 6.78 Zn wt%, found = 7.36 wt%.

Zn₂-4-(NO₃)₄ (Entry 4, Table 1). $\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$ (9.75 mg, 32.8 μmole) was added to a suspension of terpyridine 4 (25.4 mg, 16.4 μmole) in EtOH (4.5 mL) and DMF (4.5 mL) in an 8-dram vial with a magnetic stir bar and the vial was capped. The resulting mixture was microwave-irradiated at 90 $^\circ\text{C}$ for 50 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl_3 for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 $^\circ\text{C}$ for 24 hours. Isolated yield = 31.1 mg (94%). ICP: calc. = 6.78 Zn wt%, found = 7.33 wt%. Density = 1.36 g/cm^3 .

Fe₂-4-Cl₄ (Entry 5 in Table 1). $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (8.6 mg, 43 μmole) was added to a suspension of terpyridine 4 (33.3 mg, 21.5 μmole) in EtOH (10 mL) in 20 mL microwave reactor vial with a magnetic stir bar. The resulting mixture was microwave-irradiated at 90 $^\circ\text{C}$ for 20 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl_3 for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 $^\circ\text{C}$ for 24 hours. Isolated yield = 32.5 mg (84%). ICP: calc. = 6.19 Fe wt%, found = 7.57 wt%. Density = 1.39 g/cm^3 .

Fe₂-4-Cl₄ (Entry 6 in Table 1). $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (5.3 mg, 26.6 μmole) was added to a suspension of terpyridine 4 (20.6 mg, 13.3 μmole) in EtOH (7 mL) in an 8-dram vial with a magnetic stir bar and the vial was capped. The resulting mixture was microwave-irradiated at 90 $^\circ\text{C}$ for 50 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl_3 for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 $^\circ\text{C}$ for 24 hours. Isolated yield = 20.1 mg (87%). ICP: calc. = 6.19 Fe wt%, found = 8.38 wt%.

Fe₂-4-Cl₄ (Entry 7 in Table 1). $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4.7 mg, 23.8 μmole) was added to a suspension of terpyridine 4 (18.3 mg, 11.8 μmole) in EtOH (3 mL) and DMF (3 mL), in an 8-dram vial with a magnetic stir bar and the vial was capped. The resulting mixture was microwave-irradiated at 90 $^\circ\text{C}$ for 50 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl_3 for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 $^\circ\text{C}$ for 24 hours. Isolated yield = 17.1 mg (85%). ICP: calc. = 6.19 Fe wt%, found = 6.01 wt%.

Fe₂-4-Cl₄ (Entry 8 in Table 1). $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (5.1 mg, 26 μmole) was added to a suspension of terpyridine 4 (20.1 mg, 13 μmole) in DMF (7 mL) in an 8-dram vial with a magnetic stir bar and the vial was capped. The resulting mixture was microwave-irradiated at 90 $^\circ\text{C}$ for 50 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl_3 for 24 hours in a

Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 °C for 24 hours. Isolated yield = 18.8 mg (81%). ICP: calc. = 6.19 Fe wt%, found = 6.37 wt%.

Ni₂-4-Cl₄ (Entry 9 in Table 1). NiCl₂·6H₂O (14.2 mg, 60 μmole) was added to a suspension of terpyridine 4 (45.5 mg, 29.35 μmole) in EtOH (14 mL) in 20 mL microwave reactor vial with a magnetic stir bar. The resulting mixture was microwave-irradiated at 150 °C for 20 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl₃ for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 °C for 24 hours. Isolated yield = 45.7 mg (86%). ICP: calc. = 6.49 Ni wt%, found = 6.82 wt%. Density = 1.37 g/cm³.

Ni₂-4-Cl₄ (Entry 10 in Table 1). NiCl₂·6H₂O (6.4 mg, 27 μmole) was added to a suspension of terpyridine 4 (21 mg, 13.5 μmole) in EtOH (7 mL) in an 8-dram vial with a magnetic stir bar an the vial was capped. The resulting mixture was microwave-irradiated at 90 °C for 50 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl₃ for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 °C for 24 hours. Isolated yield = 14.9 mg (61%). ICP: calc. = 6.49 Ni wt%, found = 7.16 wt%.

Ni₂-4-Cl₄ (Entry 11 in Table 1). NiCl₂·6H₂O (6.7 mg, 28.4 μmole) was added to a suspension of terpyridine 4 (22 mg, 14.2 μmole) in EtOH (3.5 mL) and DMF (3.5 mL), in an 8-dram vial with a magnetic stir bar an the vial was capped. The resulting mixture was microwave-irradiated at 90 °C for 50 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl₃ for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 °C for 24 hours. Isolated yield = 18.7 mg (73%). ICP: calc. = 6.49 Ni wt%, found = 6.94 wt%.

Ni₂-4-Cl₄ (Entry 12 in Table 1). NiCl₂·6H₂O (6.7 mg, 28.4 μmole) was added to a suspension of terpyridine 4 (22 mg, 14.2 μmole) in DMF (7 mL), in an 8-dram vial with a magnetic stir bar an the vial was capped. The resulting mixture was microwave-irradiated at 90 °C for 50 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl₃ for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 °C for 24 hours. Isolated yield = 23 mg (92%). ICP: calc. = 6.49 Ni wt%, found = 7.5wt%. Density = 1.41 g/cm³.

Ru₂-4-Cl₄ (Entry 13 in Table 1). RuCl₂(DMSO)₄ (26 mg, 53.4 μmole) was added to a suspension of terpyridine 4 (41.1 mg, 26.5 μmole) in EtOH (13 mL) in 20 mL microwave reactor vial with a magnetic stir bar. The resulting mixture was microwave-irradiated at 90 °C for 20 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl₃ for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 °C for 24 hours. Isolated yield = 42 mg (81%). ICP: calc. = 10.67 Ru wt%, found = 9.34 wt%. Density = 1.45 g/cm³.

Ru₂-4-Cl₄ (Entry 14 in Table 1). RuCl₂(DMSO)₄ (13 mg, 26.8 μmole) was added to a suspension of terpyridine 4 (20.7 mg, 13.4 μmole) in EtOH (7 mL), in an 8-dram vial with a magnetic stir bar an the vial was capped. The resulting mixture was microwave-irradiated at 90 °C for 50 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl₃ for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 °C for 24 hours. Isolated yield = 2 mg (8%). ICP: calc. = 10.67 Ru wt%, found = 11.84 wt%.

Ru₂-4-Cl₄ (Entry 15 in Table 1). RuCl₂(DMSO)₄ (13 mg, 26.8 μmole) was added to a suspension of terpyridine 4 (20.7 mg, 13.4 μmole) in EtOH (3.5 mL) and DMF (3.5 mL), in an 8-dram vial with a magnetic stir bar an the vial was capped. The resulting mixture was microwave-irradiated at 90 °C for 50 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl₃ for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 °C for 24 hours. Isolated yield = 17.7 mg (71%). ICP: calc. = 10.67 Ru wt%, found = 13.5 wt%.

Ru₂-4-Cl₄ (Entry 16 in Table 1). RuCl₂(DMSO)₄ (13.4 mg, 27.4 μmole) was added to a suspension of terpyridine 4 (21.3 mg, 13.7 μmole) in DMF (7 mL), in an 8-dram vial with a magnetic stir bar and the vial was capped. The resulting mixture was microwave-irradiated at 90 °C for 50 hours. After being cooled to rt, the reaction mixture was filtered over a fritted filter (por D, 10-20 μm pore size, Ace Glass Incorporation, Vineland, NJ) and washed with EtOH (50 mL). The remaining yellow precipitate was collected and washed with hot CHCl₃ for 24 hours in a Soxhlet extractor. The resulting solid was then dried in a vacuum oven (480 mtorr) at 80 °C for 24 hours. Isolated yield = 21 mg (81%). ICP: calc. = 10.67 Ru wt%, found = 13.1 wt%.

Activation of polymers. Prior to gas adsorption-desorption measurements, the coordination polymers were placed in a vacuum oven (480 mtorr) at 80 °C for 24 hours, and then under dynamic vacuum inside the Autosorb instrument for 2 hours at 50 °C.

CO₂ Adsorption analysis. The CO₂ adsorption-desorption isotherms (Figures S15-S18) for all CPs exhibited significant hysteresis. When the equilibration time for the collection of CO₂ isotherm points was changed from 3 seconds to 6 seconds for an Fe₂-4-Cl₄ sample (entry 7 in Table 1) we do not observe any change in the magnitude of the hysteresis (Figure S16, bottom panel). This leads us to think that the observed hysteresis is not caused by kinetic effects but is rather due to the chemisorption of CO₂ on open metal sites open pyridine sites.

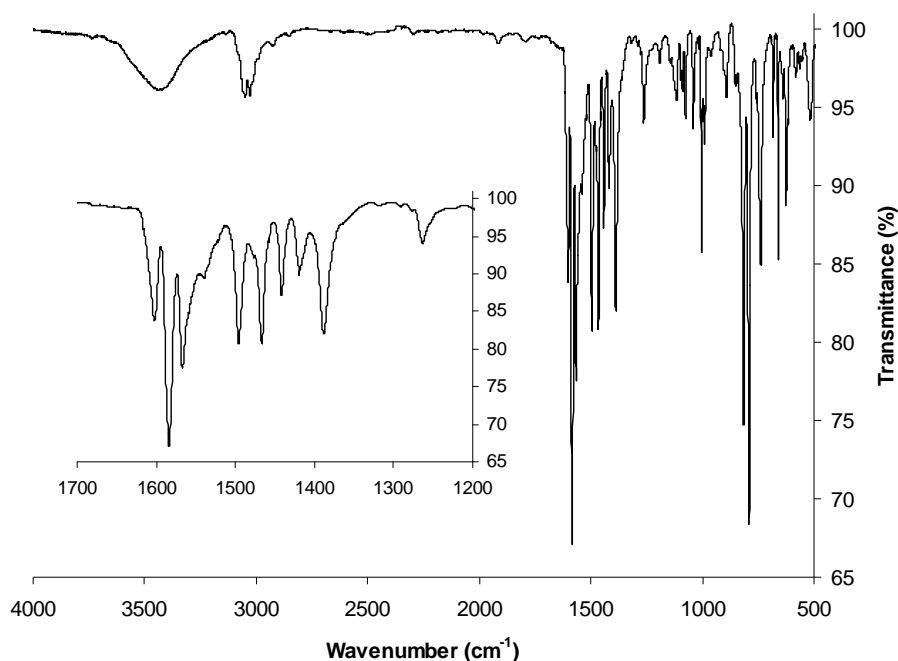


Figure S4. FT-IR spectrum of tetraterpyridine ligand 4. Inset shows the expanded region between 1200-1700 cm⁻¹.

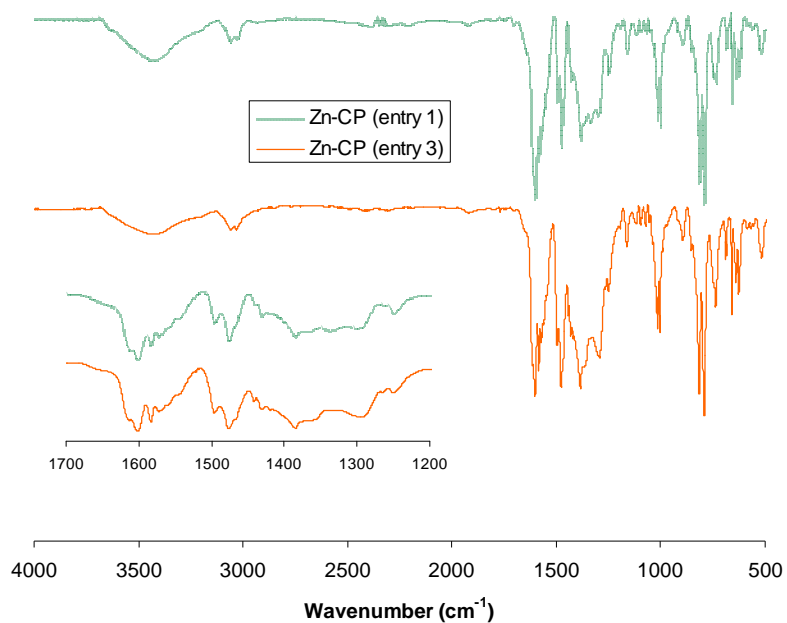


Figure S5. FT-IR spectrum of Zn₂-4-(NO₃)₄ (entries 1 and 3, Table 1). Inset shows the expanded region between 1200-1700 cm⁻¹.

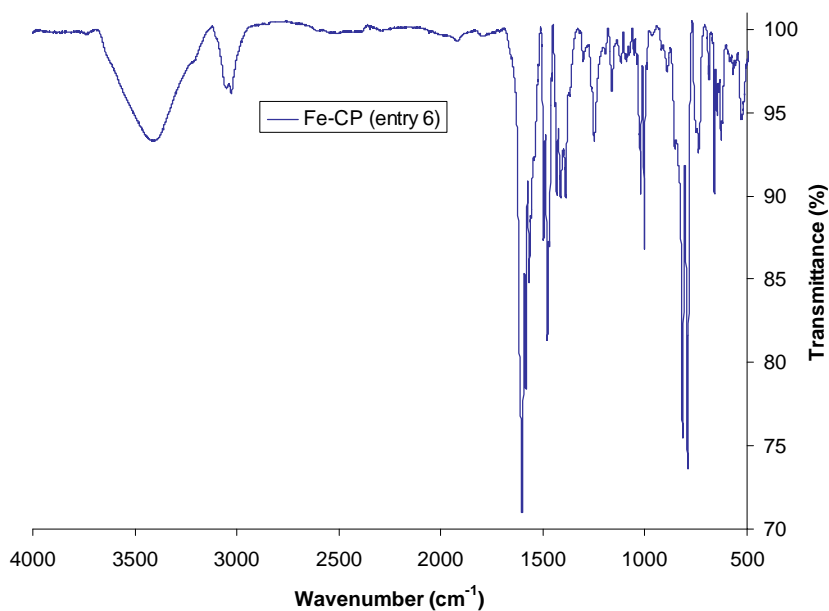


Figure S6. FT-IR spectrum of Fe₂-4-Cl₄ (entry 6 in Table 1). Inset shows the expanded region between 1200-1700 cm⁻¹.

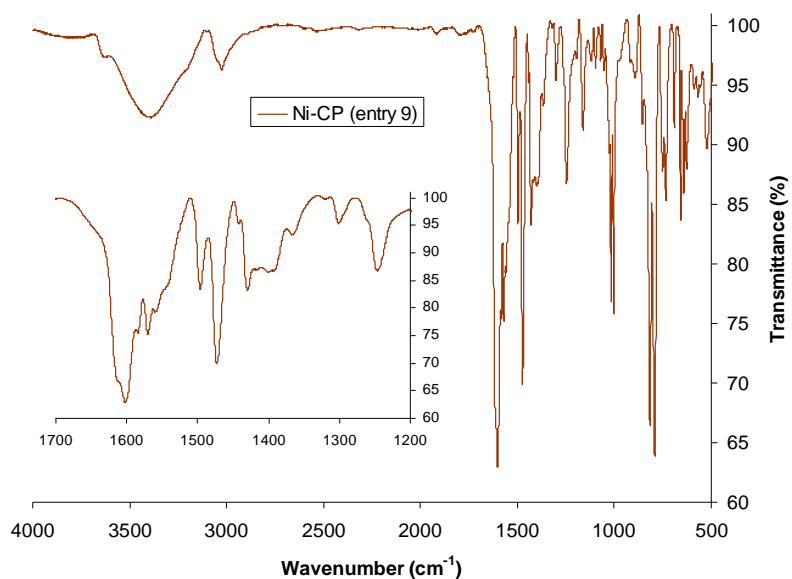


Figure S7. FT-IR spectrum of Ni₂-4-Cl₄ (entry 9 in Table 1). Inset shows the expanded region between 1200-1700 cm⁻¹.

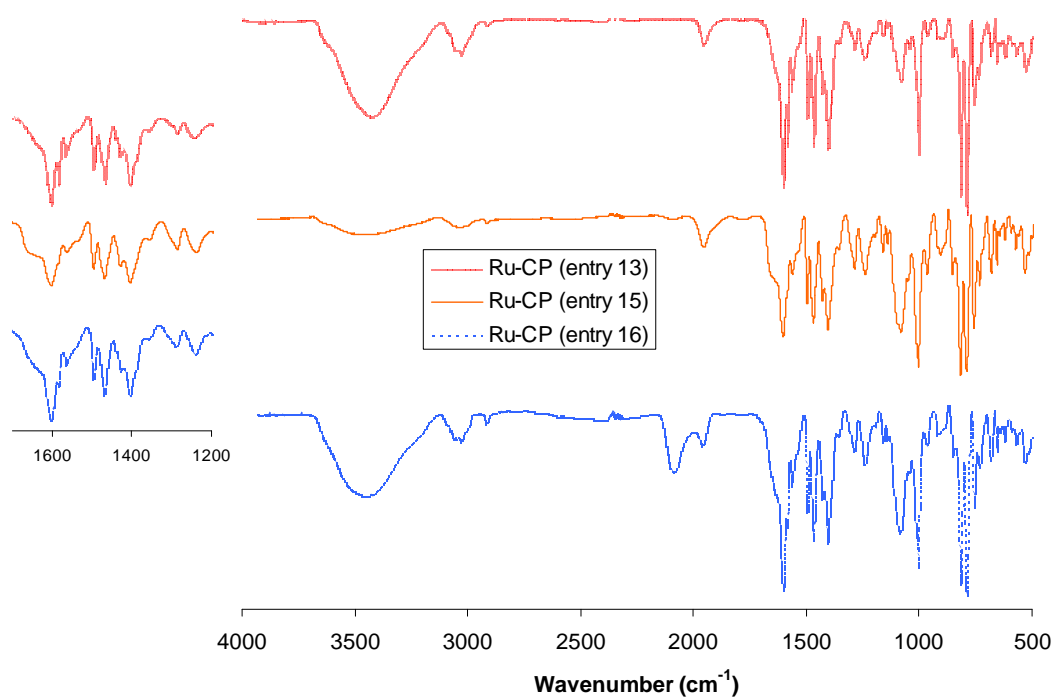


Figure S8. FT-IR spectrum of Ru₂-4-Cl₄ (entry 6 in Table 1). Inset shows the expanded region between 1200-1700 cm⁻¹.

Solvent uptake properties of terpyridine-based CPs. As mentioned in the manuscript, our materials appear to take up a moderate amount of solvent (~15% of its weight): “*Thermogravimetric analysis (TGA) of an as-synthesized Ni-CP sample (Table 1, entry 9; see also Fig. S11 in †ESI) exhibited ~15% solvent loss by weight, suggesting that the materials is moderately porous.*” For this particular as-synthesized Ni-CP sample, the solvent in question was CHCl₃ (see page S1 of this ESI for description of the sample preparation protocol) and the uptake was moderate. Unfortunately, we do not have solvent uptake data for other as-synthesized samples; most of the TGA data reported below were for “activated” materials (see page S1 of this ESI for description of the sample preparation protocol).

It is well-known that [M(tpy)₂]²⁺-based complexes are more soluble in polar solvents such as alcohols, MeCN, DMF, DMSO, and aqueous mixtures of these solvents than hexanes. Additionally, the presence of two Cl⁻ counterions for each [M(tpy)₂]²⁺ in the network makes us suspect that these materials are more hydrophilic than lipophilic. As expected for multiply catenated, highly cross-linked materials, we do not see any visible swelling of upon exposing them to various organic solvents (DMF, EtOH, CHCl₃). Unfortunately, at the present we do not have access to a vapor-phase instrument that would allow us to evaluate the solvent uptake properties of these materials.

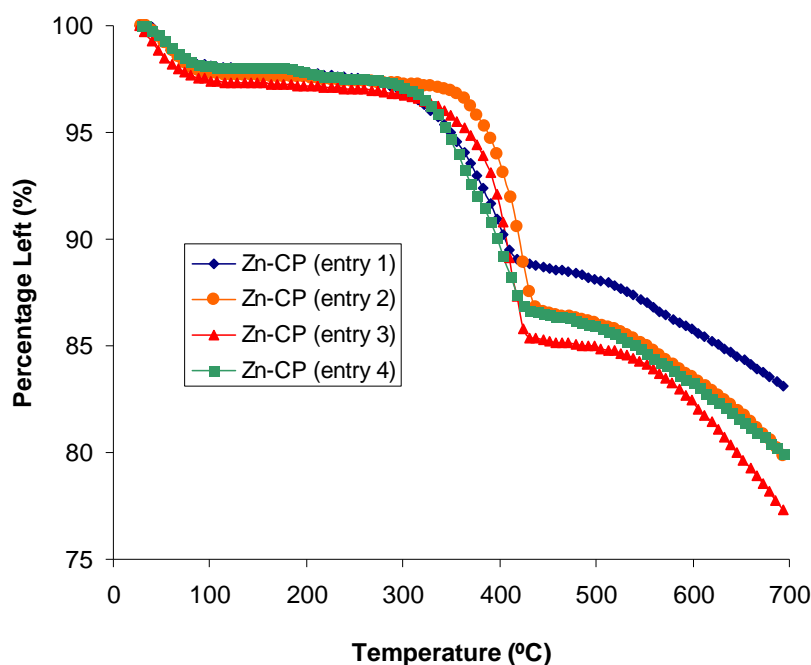


Figure S9. Thermal stability data of Zn₂-4-(NO₃)₄ (entry 1-4, Table 1) as analyzed by TGA (see page S1).

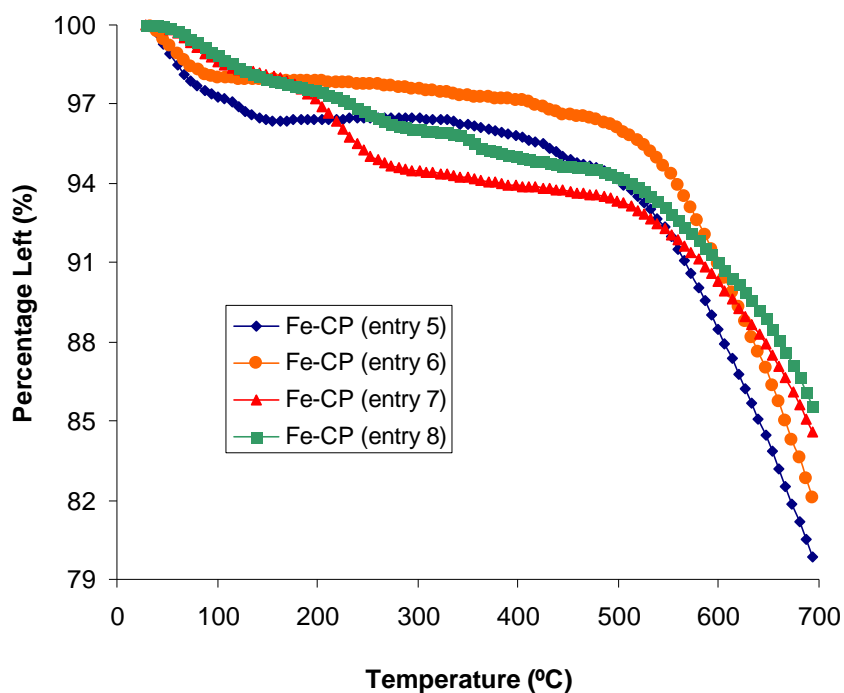


Figure S10. Thermal stability data of $\text{Fe}_2\text{-4-Cl}_4$ (entry 5-8 in Table 1) as analyzed by TGA (see page S1).

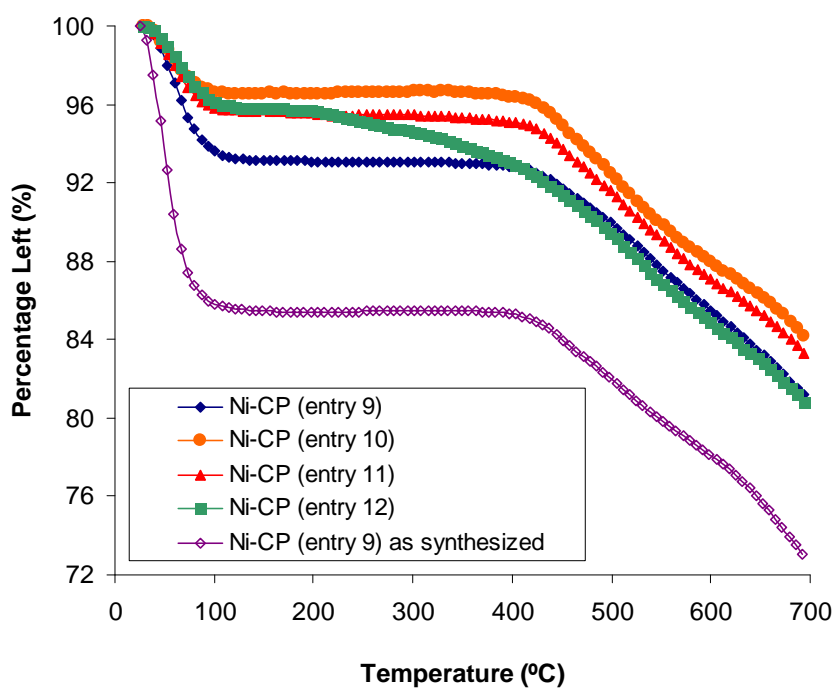


Figure S11. Thermal stability data of $\text{Ni}_2\text{-4-Cl}_4$ (entry 9-12 in Table 1) analyzed with TGA (see page S1).

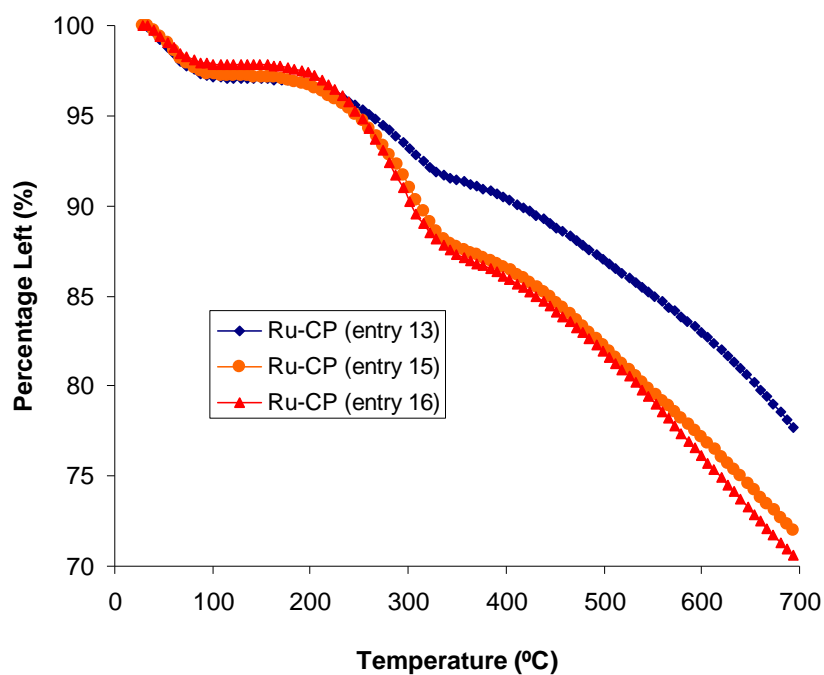


Figure S12. Thermal stability data of Ru₂-4-Cl₄ (entry 13-16 in Table 1) analyzed with TGA (see page S1).

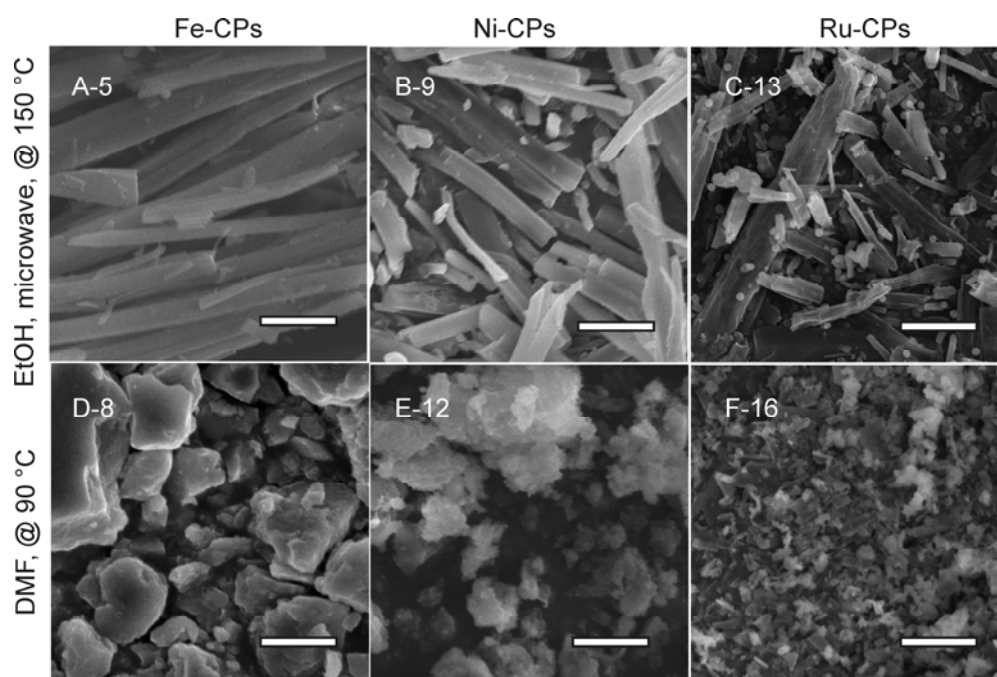


Figure S13. SEM images of Fe, Ni, and Ru-CPs that were prepared in DMF and EtOH. Numbers in each image refer to the entry number for each sample in Table 1. The scale bar in each image is 5 µm.

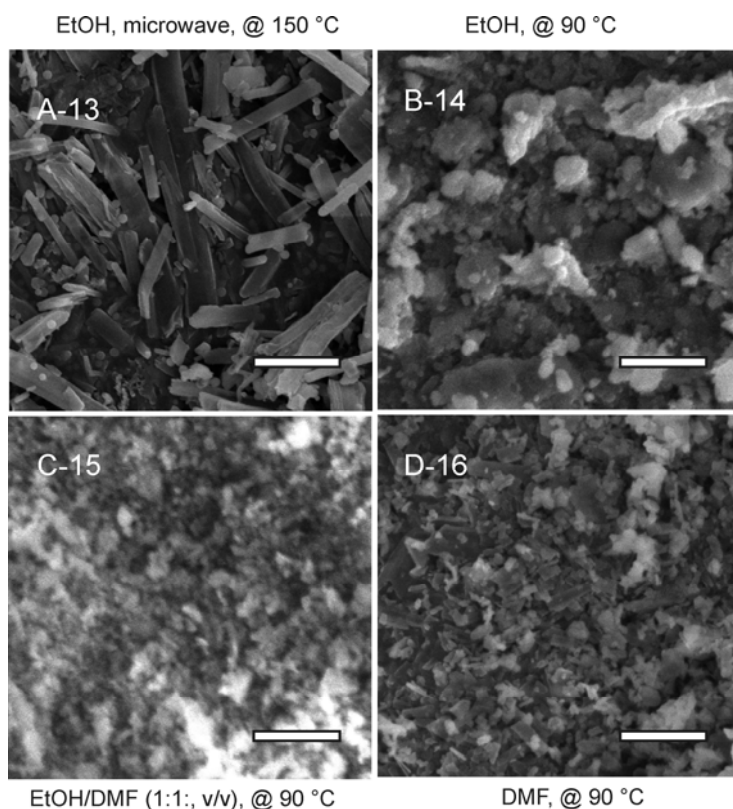


Figure S14. SEM images of Ru-CPs that were prepared under a variety of reaction conditions. Numbers in each image refer to the entry number for each sample in Table 1. The scale bar in each image is 5 μm.

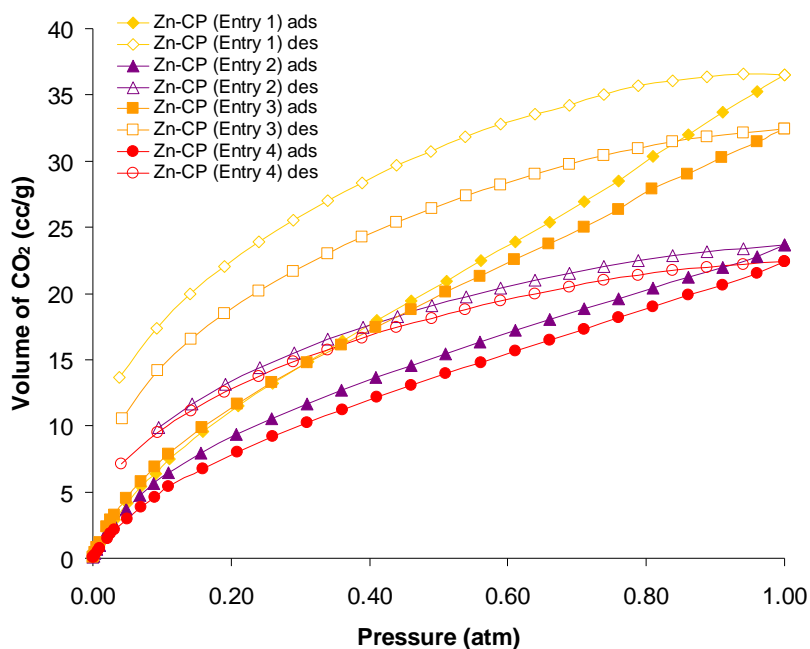


Figure S15. CO₂ adsorption-desorption isotherms of Zn₂-4-(NO₃)₄ (entries 1-4, Table 1) at 273K.

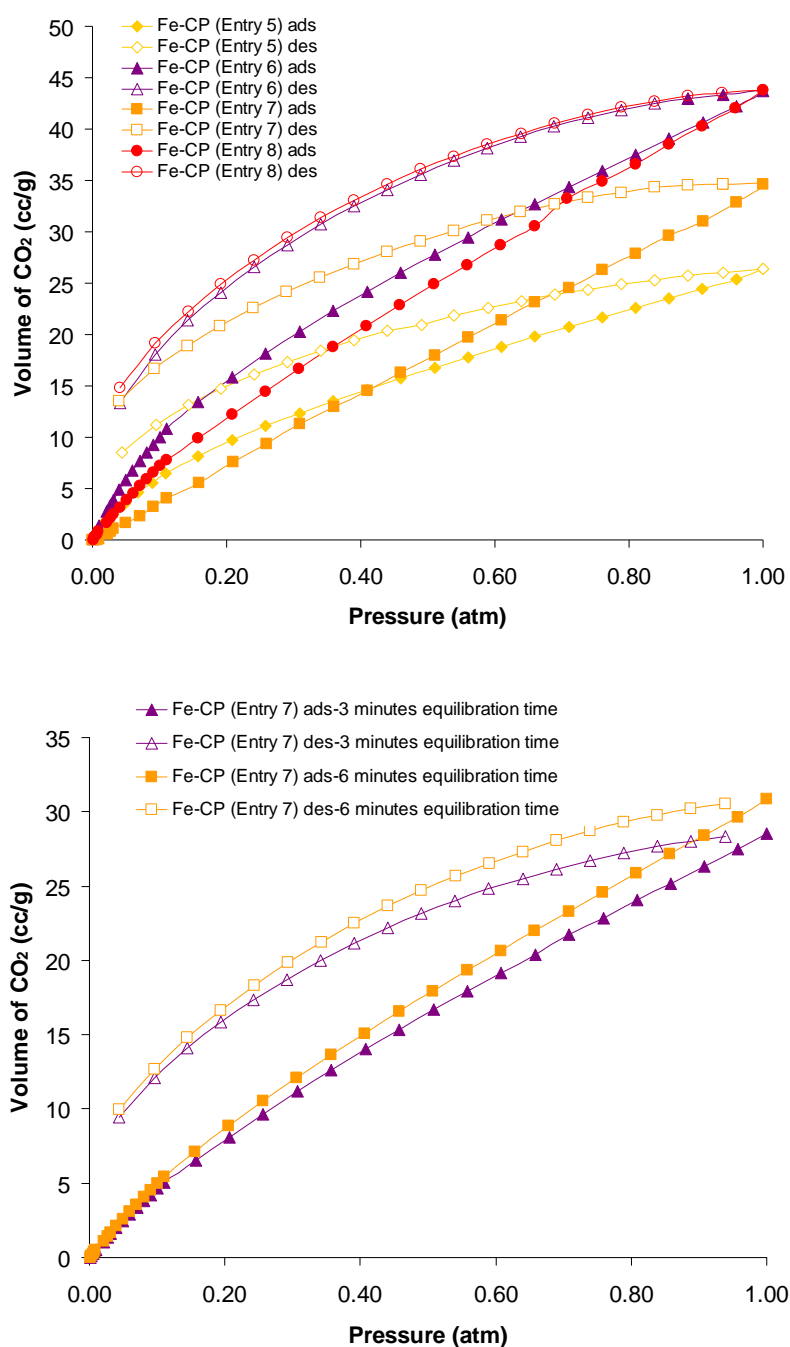


Figure S16. Top: CO₂ adsorption-desorption isotherms for Fe₂-4-Cl₄ (entry 4-8 in Table 1) at 273 K. Bottom: Two different CO₂ adsorption-desorption isotherms for a single Fe₂-4-Cl₄ sample (entry 7 in Table 1) at 273 K, where the equilibration times were set at 3 and 6 minutes. The similarities in these profiles suggest that the observed hysteresis is not due to kinetics.

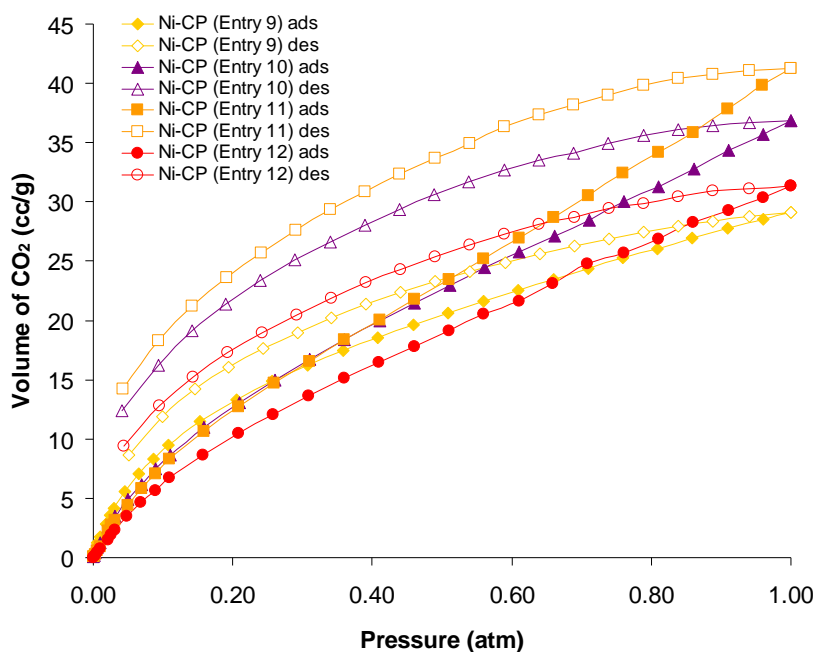


Figure S17. CO₂ adsorption-desorption isotherms of Ni₂-4-Cl₄ (entries 8-12 in Table 1) at 273K.

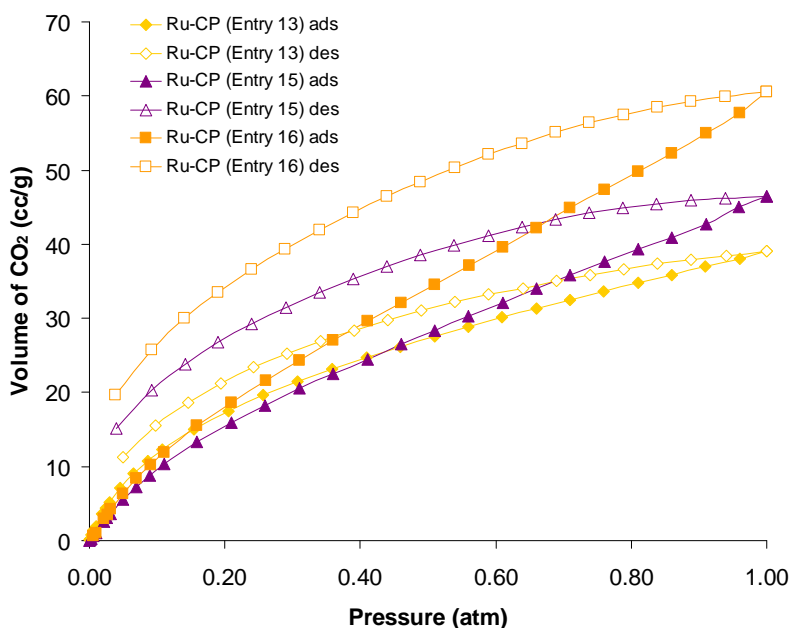


Figure S18. CO₂ adsorption-desorption isotherms of Ru₂-4-Cl₄ (entry 13-16 in Table 1) at 273K.

Growth of single crystal of ligand 4. Terpyridine **4** (20 mg) was dissolved in a mixture of CHCl₃/DMF (10 mL, 1:1, v/v) in a 20 mL disposable scintillation vial (Kimble Chase, Vineland, NJ). The mixture was kept in an C601/SD electric furnace (Cress MFG. Co., Carson City, NV) at 80 °C for overnight without a cap to afford single crystals of terpyridine **4**. Single X-ray crystallography data were collected on a Bruker APEX-II diffractometer

(Bruker AXS Inc., Madison, WI) equipped with an Apex II CCD detector using graphite monochromated CuK α radiation at a temperature of 100(2) K with a theta range of 4.03 to 50.37° and in 0.5° oscillations with 15 seconds exposures. The crystal-to-detector distance was 40.00 mm. A colorless needle crystal having approximate dimensions of 0.73 × 0.12 × 0.08 mm was mounted on a glass fiber using oil (Infiniteum V8512).

Analysis of X-ray crystallographic data for ligand 4. This structure was solved by Ms. Charlotte Stern in the IMSERC facility at Northwestern University. The solid-state structure of terpyridine **4** was solved by direct methods and expanded using Fourier techniques.^{S7} Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions but not refined. The proposed model was refined by removing contributions from DMF solvent molecules from the diffraction data using the bypass procedure in Platon.^{S8} The total potential solvent-accessible void volume was 1297.6 Å³ and the electron count/cell = 345. This corresponded to about eight DMF molecules per unit cell. The "Squeeze" data are reported in Table S1.

The final cycle of full-matrix least-squares refinement^{S9} on F² was based on 9948 reflections and 1080 variable parameters and converged (largest parameter shift was 0.000 times its esd) with unweighted and weighted agreement factors of: $R1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0736$ and $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2} = 0.1731$

The weighting scheme was calculated as: $\text{calc } w = 1 / [\sigma^2(F_o^2) + (0.0995P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2) / 3$. The standard deviation of an observation of unit weight^{S10} was 0.819.

The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots of $\sum w (|F_o| - |F_c|)^2$ vs $|F_o|$, reflection order in data collection, $\sin \theta / \lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.223 and -0.265 e⁻/Å³, respectively. Neutral atom scattering factors were taken from the compilations by Cromer and Waber.^{S11} Anomalous dispersion effects were included in Fcalc:^{S12} the values for Df' and Df'' were obtained from the compilations by Creagh and McAuley.^{S13} The values for the mass attenuation coefficients were obtained from the compilations by Creagh and Hubbell.^{S14} All calculations were performed using the Bruker SHELXTL3 crystallographic software package.

Table S1. Crystal data and structure refinement for terpyridine **4**.

Identification code	n0324
Empirical formula	C ₁₂₁ H ₁₀₀ N ₁₆ O ₄
Formula weight	1842.17
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 11.0736(8) Å α = 91.877(6)° b = 19.9537(13) Å β = 97.134(6)° c = 22.8530(14) Å γ = 92.099(6)°
Volume	5003.6(6) Å ³
Z, Calculated density	2, 1.223 mg/m ³
Absorption coefficient	0.597 mm ⁻¹
F(000)	1940
Crystal size	0.73 x 0.12 x 0.08 mm
Theta range for data collection	4.03 to 50.37°
Limiting indices	-11 ≤ h ≤ 7, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22
Reflections collected/unique	19163/9948 [R(int) = 0.0771]
Completeness to theta = 50.37	95.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9538 and 0.6706
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	9948/0/1080
Goodness-of-fit on F ²	0.819
Final R indices [I > 2sigma(I)]	R1 = 0.0736, wR2 = 0.1731
R indices (all data)	R1 = 0.1595, wR2 = 0.2047
Largest diff. peak and hole	0.223 and -0.265 e ⁻ /Å ³

Author contributions audit. I.E and O.K.F. conceived the experiments presented herein. O.K.F. synthesized and characterized tetraphenylmethane and tetrakis(4-bromophenyl)methane (**3**). I.E. synthesized and characterized ligands **1**, **2**, and **4** and all reported CPs. O.K.F. prepared the single crystals of ligand **4**. Single X-ray crystal data was collected and solved by Ms. Charlotte Stern. HRMS analysis of ligand **4** was performed by Dr. Jennifer L. Seymour (acknowledged). O.K.F. and I.E. run the CO₂ adsorption/desorption and FT-IR experiments together. I.E. conducted the TGA experiments. Digested samples for ICP was prepared by I.E. and run by Mr. Abraham Shultz (acknowledged). O.C.C. prepared the SEM samples and collected the images. Samples for fluorescence optical microscopy were prepared by I.E. and images were collected by Ms. Dan Zheng (acknowledged). J.T.H., and S. T. N. supervised the project. I.E. wrote the initial draft of the paper. O.K.F., O.C.C., and S. T. N. finalized the manuscript.

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 $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$
- S10 GooF = S = $\{\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}$ n = number of reflections; p = total number of reflections refined.
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