Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for

Templated synthesis enhances the cobalt adsorption capacity of a porous organic polymer

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General Information

All reagents were purchased from commercial vendors and used without further purification. Elemental analyses were obtained from Galbraith Laboratories Inc. using GLI Procedure ME-14. Ultra-high purity grade (99.999% purity) gases were used for all gas adsorption measurements. Ultrapure deionized water was obtained from an Evoqua Water Technologies Reverse Osmosis Deionized (RODI) water system.

Synthesis of TPC-TAPM

In an oven-dried 250 mL round bottom flask under flowing nitrogen, tetrakis(4-aminophenyl)methane (TAPM; 0.600 g, 1.0 equiv, 1.58 mmol) and *N*,*N*-diisopropylethylamine (DIPEA; 1.10 mL, 4.0 equiv., 6.31 mmol) were dissolved in dry tetrahydrofuran (THF; 50 mL) to afford a light brown solution. In a separate flask, terephthaloyl chloride (TPC; 0.640 g, 2.0 equiv, 3.15 mmol) was dissolved in dry THF (10 mL) under flowing nitrogen to afford a clear solution. The TPC solution was added dropwise to the TAPM solution via cannula under nitrogen atmosphere over the course of 15 min. After the reaction was continuously stirred overnight at room temperature, a beige solid was isolated by vacuum filtration, washed with water (5 x 100 mL, pH adjusted to 3.3) and methanol (MeOH; 3 x 100 mL), continuously washed with THF for 24 h via Soxhlet extraction, and dried under dynamic vacuum at 120 °C for 24 h to afford a purple solid. Yield: 977 mg. Elemental Analysis: C/H/N expected: C 76.38%, H 4.83%, N 8.69%. C/H/N actual: C 71.53%, H 4.75%, N 8.02%.

Synthesis of TMC-TAPM

In an oven-dried 250 mL round bottom flask under flowing nitrogen, TAPM (0.600 g, 1.0 equiv, 1.58 mmol) and DIPEA (0.55 mL, 2.0 equiv, 3.16 mmol) were dissolved in dry THF (50 mL) to afford a light brown solution. In a separate flask, trimesoyl chloride (TMC; 0.558 g, 1.33 equiv, 2.10 mmol) was dissolved in dry THF (10 mL) under flowing nitrogen to afford a clear solution. The TPC solution was added dropwise to the TAPM solution via cannula under nitrogen atmosphere over the course of 15 min. After the reaction was continuously stirred overnight at room temperature, a beige solid was isolated by vacuum filtration, washed with water (5 x 100 mL, pH adjusted to 3.3), continuously washed with THF for 24 h via Soxhlet extraction, rinsed with ethanol (EtOH; 100 mL), and dried under dynamic vacuum at 120 °C for 24 h to afford a purple solid. Yield: 871 mg. Elemental Analysis: C/H/N expected: C 75.50%, H 4.34%, N 9.52%. C/H/N actual: C 67.03%, H 4.70%, N 8.21%.

Synthesis of tetraphenylmethane-4,4′,4″,4‴-tetraacyl chloride (TCPM)

Tetrakis(4-carboxyphenyl)methane was synthesized according to a literature procedure.[1] In an oven-dried 100 mL round bottom flask under flowing nitrogen, tetrakis(4-carboxyphenyl)methane (0.300 g, 1 equiv, 0.604 mmol) was suspended in dry THF (6.0 mL). Oxalyl chloride (0.424 mL, 8.0 equiv, 4.8 mmol) was added, followed by ~3 drops of *N*,*N*-dimethylformamide (DMF) which caused the mixture to bubble. The reaction was stirred for two hours at room temperature, after which THF, oxalyl chloride, and DMF were removed under reduced pressure. The crude product was carried on to the synthesis of TCPM-TAPM without further purification.

Synthesis of TCPM-TAPM

In an oven-dried 100 mL round bottom flask under flowing nitrogen, TAPM (0.229 g, 1.0 equiv, 0.604 mmol) and DIPEA (0.421 mL, 4.0 equiv, 2.42 mmol) were dissolved in dry THF (15 mL) to afford a light brown solution. In a separate flask under flowing nitrogen, tetraphenylmethane-4,4′,4″,4‴-tetraacyl chloride (TCPM; 0.345 g, 1.0 equiv, 0.604 mmol) was dissolved in dry THF (10 mL) to afford a brown solution. The TCPM solution was added dropwise to the TAPM solution via cannula under nitrogen atmosphere over the course of 15 min. After the reaction was continuously stirred overnight at room temperature, a beige solid was isolated by vacuum filtration, washed with water (3 x 100 mL, pH adjusted to 3.3), continuously washed with THF for 48 h via Soxhlet extraction, rinsed with EtOH (100 mL), and dried under dynamic vacuum at 115 °C for 24 h to afford a purple powder. Yield: 312 mg. Elemental Analysis: C/H/N expected: C 80.58%, H 4.51%, N 6.96%. C/H/N actual: C 72.62%, H 4.97%, N 6.82%.

Synthesis of $Co(TAPM)_{2.3}Cl_2$

In a 500 mL round bottom flask, TAPM (1.00 g, 4.0 equiv, 2.63 mmol) was dissolved in THF (75 mL) in an ambient atmosphere. A separately prepared solution of $CoCl_2{\bullet}6H_2O$ (156 mg, 1.0 equiv, 0.657 mmol) in THF (350 mL) was added dropwise over the course of 1 h to afford a light purple precipitate that was immediately isolated by vacuum filtration. Yield: 680 mg.

Synthesis of Co(II)-templated TMC-TAPM

In an oven-dried 50 mL round bottom flask under flowing nitrogen, $Co(TAPM)_{2.3}Cl_2$ (0.652 g, 1.0 equiv, 6.0 mmol amine groups) and DIPEA (1.00 mL, 0.96 equiv per amine group, 5.74 mmol) were suspended in dry THF (10 mL). In a separate flask under flowing nitrogen, TMC (534 mg, 1.0 equiv, 6.0 mmol acyl chloride groups) was dissolved in dry THF (10 mL) to afford a colorless clear solution. The TMC solution was added dropwise to the $Co(TAPM)_{2.3}Cl_2$ solution via cannula over the course of 15 min. After the reaction was continuously stirred under a N_2 atmosphere overnight at room temperature, a turquoise precipitate was isolated by vacuum filtration, stirred in acidic water (200 mL, pH adjusted to 3.0) for 1.5 h, isolated by vacuum filtration, and rinsed with water (2 x 200 mL, pH adjusted to 3.0). The solid was then continuously washed with THF for 24 h via Soxhlet extraction, and rinsed with EtOH.

To thoroughly remove any residual Co(II) template ions, the sample was placed in a 15 mL centrifuge tube with 10 mL of water (pH adjusted to 2.5), sonicated for 1 minute, and isolated by filtration. The sample was then resuspended in a fresh batch of water (pH adjusted to 2.5), and the process was repeated five times. The cobalt concentration in the filtrate was monitored by ICP-OES; see Figure S6. The following day, the solid was placed in a 50 mL centrifuge tube with 45 mL of water (pH adjusted to 2.5) and washed 5 more times. The product was then isolated by vacuum filtration, washed with 100 mL of THF and 100 mL of acetone, and dried under dynamic vacuum at 115 °C for 24 h to afford a purple solid. Yield: 544 mg. Elemental Analysis: C/H/N expected: C 68.81%, H 3.58%, N 7.90%. C/H/N actual: C 66.44%, H 4.39%, N 7.54%. We note that all reported characterization data for Co(II)-templated TMC-TAPM was obtained after the complete series of HCl washes.

Procedure for Infrared Spectroscopy Measurements

FTIR spectra were collected on a Thermo Nicolet Nexus 670 FT-IR with an ATR probe. Data was acquired with neat (solid) samples using air from the room as a blank.

Procedure for Gas Sorption Measurements

Gas adsorption isotherms were measured using a volumetric method on a Micromeritics ASAP 2020 instrument. An empty analysis tube was capped under air at room temperature and weighed. Approximately 100 mg of sample was then weighed out in air and transferred to the analysis tube, which was capped under air. The analysis tube was attached to the degas port of the

ASAP 2020 and heated to 120 °C under vacuum overnight. After activation, the tube was backfilled with N_2 and weighed to obtain the sample mass. The analysis tube was then attached to the analysis port of the ASAP 2020 for the surface area measurement. Warm and cold free spaces were measured using He. N_2 adsorption isotherms at 77 K were measured in liquid nitrogen. Brunauer-Emmett-Teller (BET) surface areas were calculated from the N_2 isotherms at 77 K using points between P/P_0 of 0.07 and 0.20.

Procedure for Preparing Ion Solutions

A buffered solution of ultrapure deionized water at pH 7 was prepared (0.1 M in HEPES). The desired amount of $MnCl_2$, $CoCl_2$, $NiCl_2$, or $ZnCl_2$ was then added to the solution, and the solution was then stirred or shaken overnight. The following day, the metal content of the solution was determined by ICP-OES, and further dilutions were performed as necessary. All HEPES-buffered solutions were wrapped in aluminum foil to reduce exposure to light and were kept in the refrigerator for long-term storage. All dilutions were done gravimetrically.

Procedure for Cobalt Adsorption Isotherms

Eight cobalt solutions were prepared at cobalt concentrations of approximately 2 ppm, 20 ppm, 50 ppm, 100 ppm, 160 ppm, 200 ppm, 300 ppm, and 400 ppm. These solutions were stored in 50 mL centrifuge tubes, wrapped in foil, and shaken overnight. Polymer samples were activated at 120 °C under vacuum on a Schlenk line overnight, backfilled with N_2, and removed from the line and exposed to air. Sample was then weighed immediately into centrifuge tubes for the adsorption experiments.

Three identical experiments were performed at each starting Co concentration. The concentration of polymer in each adsorption experiment was 2 mg polymer per gram solution. In a typical experiment, a metal cage was placed on a microanalytical balance (Mettler Toledo XPE105), into which was placed a 15 mL centrifuge tube. The tube was thoroughly deionized using a static gun. The doors to the balance were then shut and the tube was tared. The vial containing the sample and the spatula were also deionized with the static gun, and then polymer sample was added directly into the centrifuge tube on the balance. (The typical scale of an experiment was 8 mg polymer and 4 g solution.) The doors to the balance were shut and the mass was allowed to stabilize. The exact mass of polymer added was then written down and the centrifuge tube was capped.

After all the centrifuge tubes were loaded with polymer, the amount of ion solution necessary to result in a concentration of 2 mg polymer per g solution was added to each tube. The centrifuge tube was then capped, covered with foil and shaken at 580 rpm overnight. For each starting concentration, a control experiment was performed in which an aliquot of the starting solution was added to a 15 mL centrifuge tube containing no polymer and then treated identically to the polymer-containing experiments (i.e., shaken overnight, etc.).

After 16 hours, the centrifuge tubes were removed from the shaker. The solution from each tube was passed through a 0.2 micron PTFE syringe filter and then measured by ICP-OES. The control experiments (starting solution without polymer) were also filtered through the 0.2 micron PTFE filter and were later measured by ICP-OES to give an accurate value for the starting concentration.

Procedure for ICP-OES Measurements

Metal concentrations were measured using Agilent 5110 ICP-OES spectrometer in radial mode. Three characteristic wavelengths were used for each element, and the resultant concentrations from each wavelength were averaged. Data were analyzed using Agilent ICP Expert software (version 6.1). Calibration curves for concentration determination were constructed using nine standard solutions of elements in 10% HCl, along with a commercial calibration blank. All curves were fitted with rational function with error below 5% and correlation coefficient of 0.9999 or greater. A commercial 5 ppm standard was measured first and after every subsequent ~20 samples, to monitor calibration throughout the measurement. Calibration standards were diluted gravimetrically from a commercial 500 mg/L standard. Ion adsorption isotherms were fit to dual-site Langmuir models for non-templated TPC-TAPM, TMC-TAPM, and TCPM-TAPM, to account for strong binding to terminal functional groups (NH_2 and COOH) and weaker binding to other surface sites on the polymer. The dual-site models gave good fits to the experimental data and were able to minimize the fit parameters (see Table S1). For Co(II)-templated TMC-TAPM, a three-site Langmuir model was used to fit the Co(II) adsorption isotherm. The three-site model more effectively minimized the fit parameter compared to the dual-site model (see Table S1) and gave a better fit to the experimental data (Figure S8-S9).

Procedure for Thermogravimetric Analysis Measurements

Thermal stability of the reported materials was assessed using simultaneous a TGA/DSC instrument Netzsch STA 449 Jupiter J3. Samples (5-20 mg) were heated in Al_2O_3 crucibles with lids from room temperature to 700 °C at the rate 1 °C/min under flow of nitrogen (150mL/min). The data was analyzed using Proteus 8.0 package. For $Co(TAPM)_{2.3}Cl_2$ complexes, a 30-minute isotherm was performed once the sample reached a temperature of 130 °C before continuing at a heating rate of 1 °C/min.

Procedure for Powder X-ray Diffraction Measurements

Diffraction patterns were collected on a Rigaku SmartLab II diffractometer using Cu Kα1+Kα2 radiation with horizontal positioning of a sample under Parallel Beam geometry with HyPix 3000 2D detector in XRF reduction mode. Theta/2Theta continuous scans with 0.02 degree step size were used. Samples were deposited dry on onto a silicon zero-background holder. Data were analyzed using Rigaku PDXL software (version 2.6).

Procedure for Electron Microscopy Measurements

Transmission Electron Microscopy (TEM):

To prepare samples for TEM a suspension was made by vortexing the hydrated powder in excess water. A 5 μL aliquot was then taken from the cloudy supernatant and dropcast onto a copper TEM grid with an ultrathin carbon substrate. The grid was allowed to dry in order to introduce it to the high vacuum environment of the TEM. High resolution transmission electron microscopy (HRTEM) was performed on a monochromated and aberration corrected FEI Titan operating at 300 keV.

Scanning Electron Microscopy (SEM):

Room temperature scanning electron microscopy (SEM) were performed on a Scios 2 Dual Beam SEM. Dry samples were coated with 7 nm of Pt using a Leica cryo-sputter coater (ACE 600). Secondary electron imaging was performed at 5 keV/50 pA.

Cryogenic scanning electron microscopy (cryo-SEM):

Cryo-SEM experiments were performed on a Scios 2 Dual Beam SEM equipped a Leica VCT cryogenic stage cooled to -150 °C. Hydrated samples were plunge frozen in liquid nitrogen (LN2), coated with 7 nm of Pt using a Leica cryo-sputter coater (ACE 600), and transferred to the cryo-SEM cold and under vacuum using the Leica VCT500 shuttle. To protect the beam sensitive samples secondary electron imaging was performed at 5 keV/50 pA. Energy dispersive X-ray spectroscopy (XEDS) maps were taken using an EDAX Octane Elite detector.

Procedure for Solid State ^{13}C CPMAS NMR Spectroscopy

All ^{13}C CPMAS NMR spectra were obtained on a Bruker Avance III 400 NMR spectrometer using a 4 mm MAS probe, spinning at 10 kHz using a standard CP sequence with a 1 ms contact time. Chemical shifts were referenced to the external standard glycine $\delta = 176.0$ ppm wrt TMS $\delta = 0$ ppm.

Supplemental Tables

Table S1. Variables and fit parameters for Langmuir models for Co(II) adsorption data.

Langmuir model	$Q_{m,1}$ (mg/g)	$K_{L,1}$ (kg/mg)	$Q_{m,2}$ (mg/g)	$K_{L,2}$ (kg/mg)	$Q_{m,3}$ (mg/g)	$K_{L,3}$ (kg/mg)	Fit parameter
TPC-TAPM dual-site	6.2924	0.1029	4.1178	0.0008	--	--	10.63
TMC-TAPM dual-site	18.6352	0.4818	31.0871	0.0012	--	--	20.36
TCPM-TAPM dual-site	7.9924	1.1079	8.8830	0.0229	--	--	10.73
Co(II)-templated TMC-TAPM dual-site	45.2442	1.5640	19.0707	0.0254	--	--	43.27
Co(II)-templated TMC-TAPM three-site	29.2864	2.9827	27.3679	0.2083	26.1384	0.0011	26.33

Table S2. BET surface areas of polymer samples.

Porous polyamide	BET surface area (m^2/g)
TPC-TAPM	31
TMC-TAPM	78
TCPM-TAPM	215
Co(II)-templated TMC-TAPM	16

Supplemental Figures

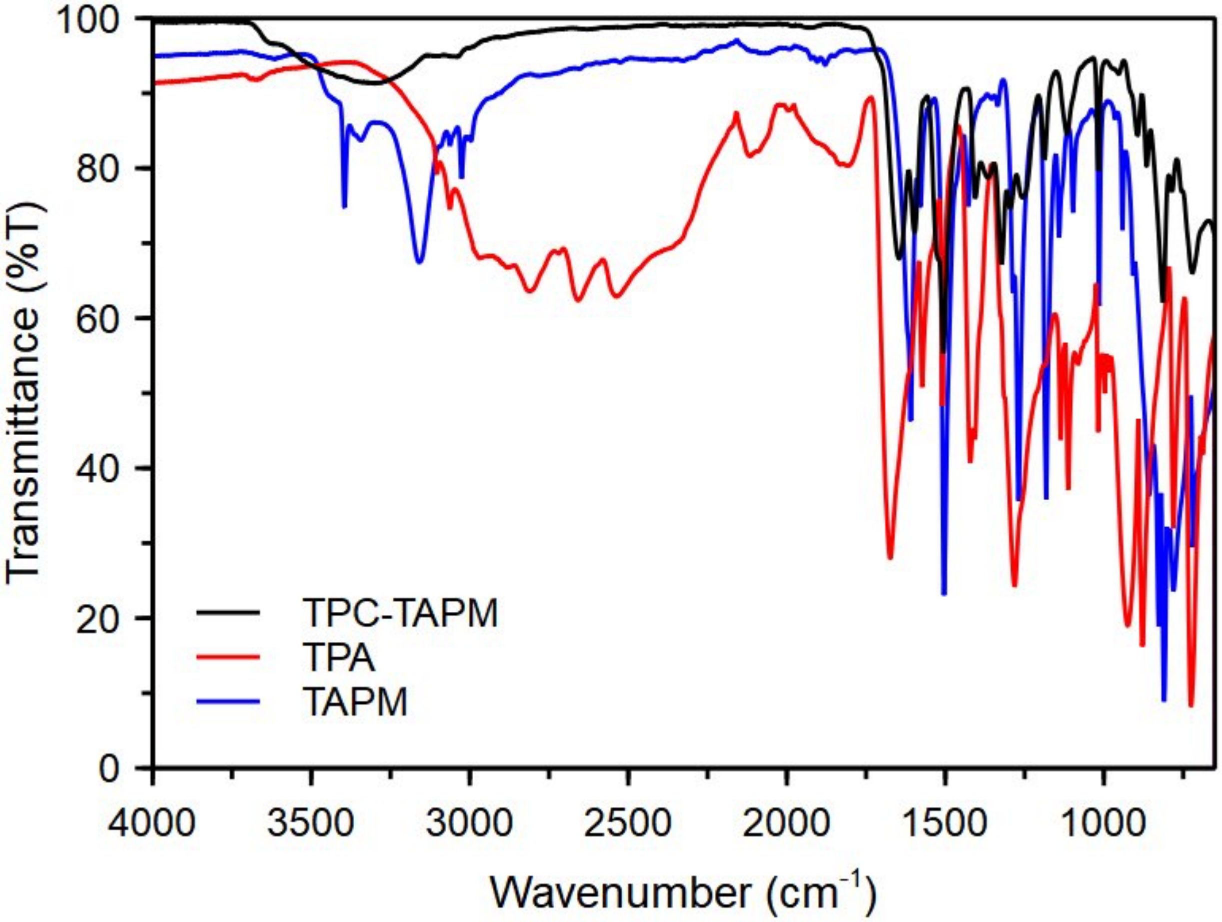

Figure S1. FTIR spectrum of terephthalic acid (TPA; red), TAPM (blue), and TPC-TAPM (black).

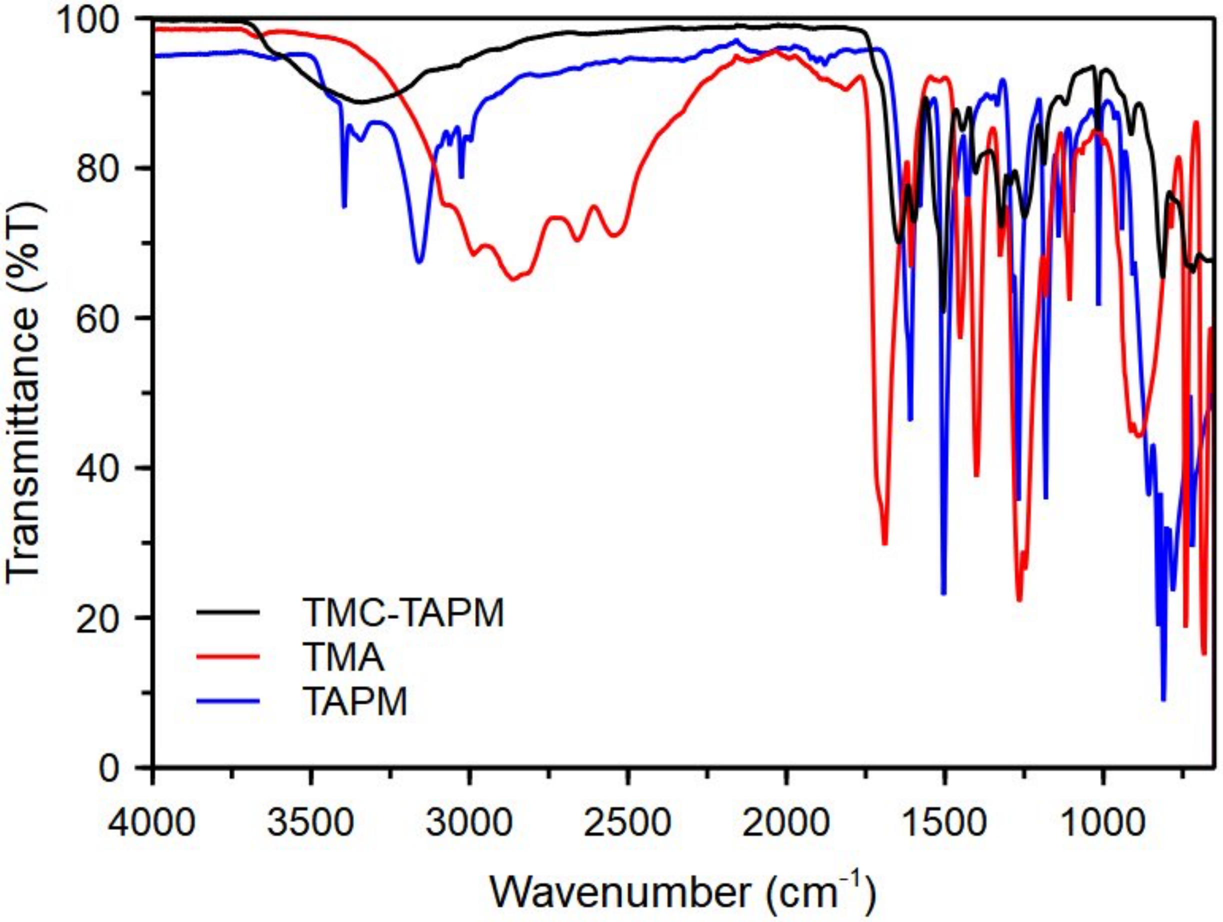

Figure S2. FTIR spectrum of trimesic acid (TMA; red), TAPM (blue), and TMC-TAPM (black).

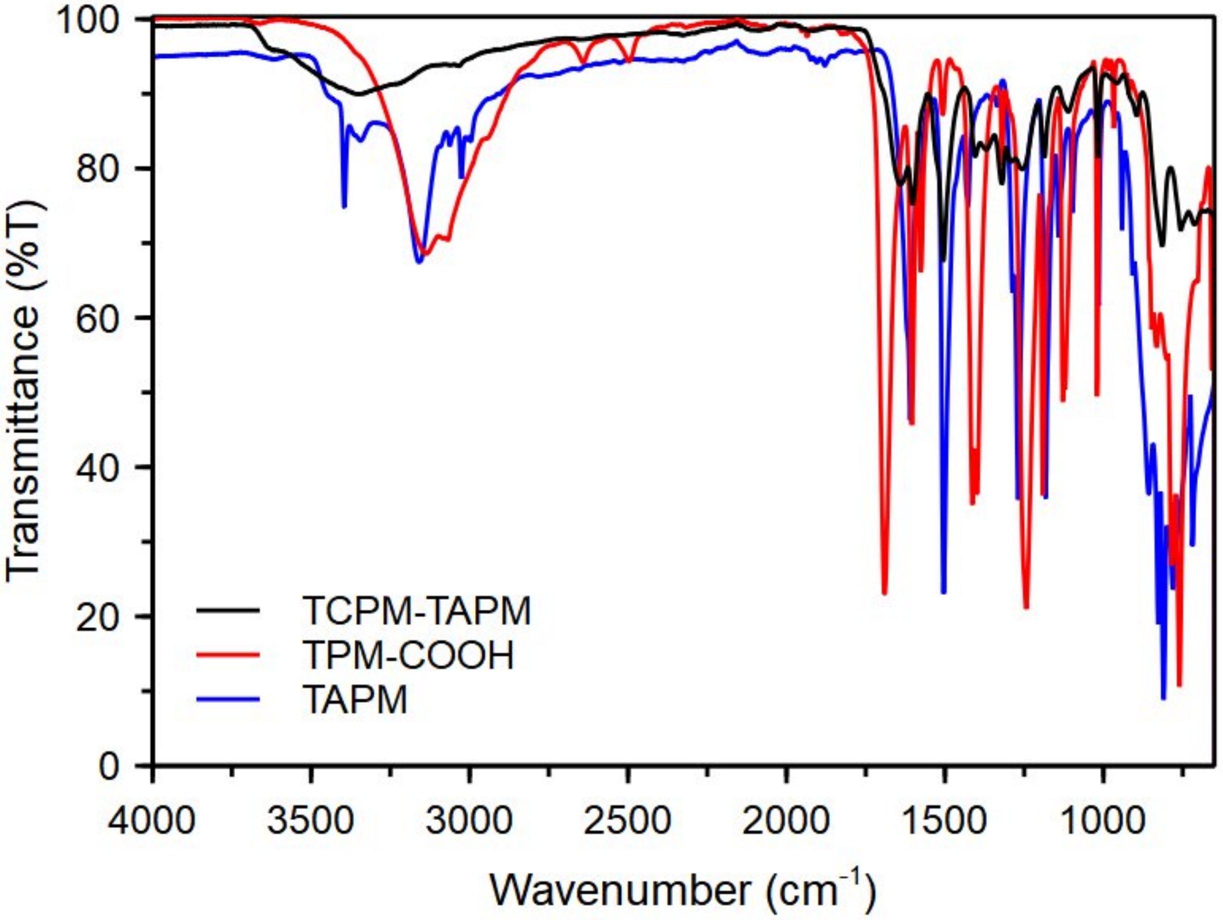

Figure S3. FTIR spectrum of tetrakis(4-carboxyphenyl)methane (TPM-COOH; red), TAPM (blue), and TCPM-TAPM (black).

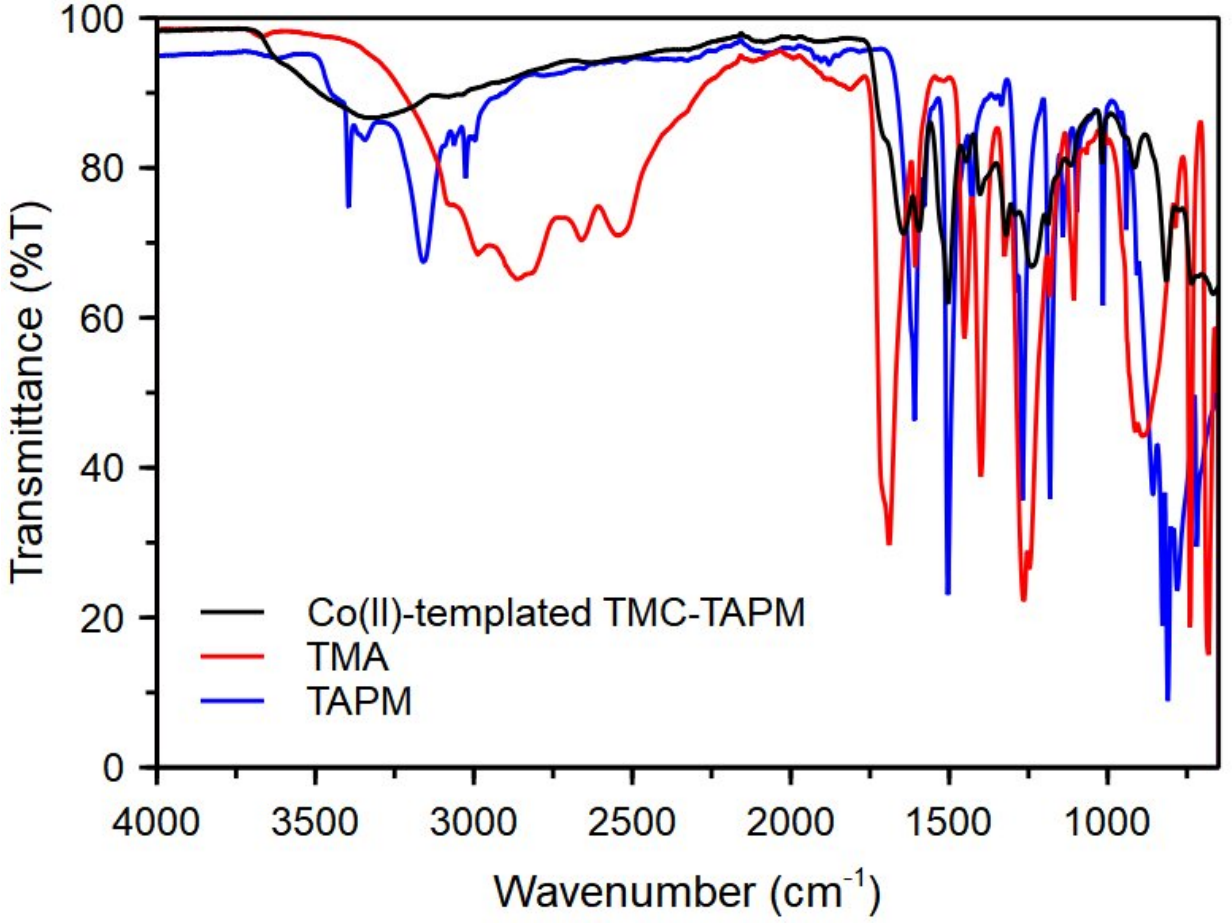

Figure S4. FTIR spectrum of TMA (red), TAPM (blue), and Co(II)-templated TMC-TAPM (black).

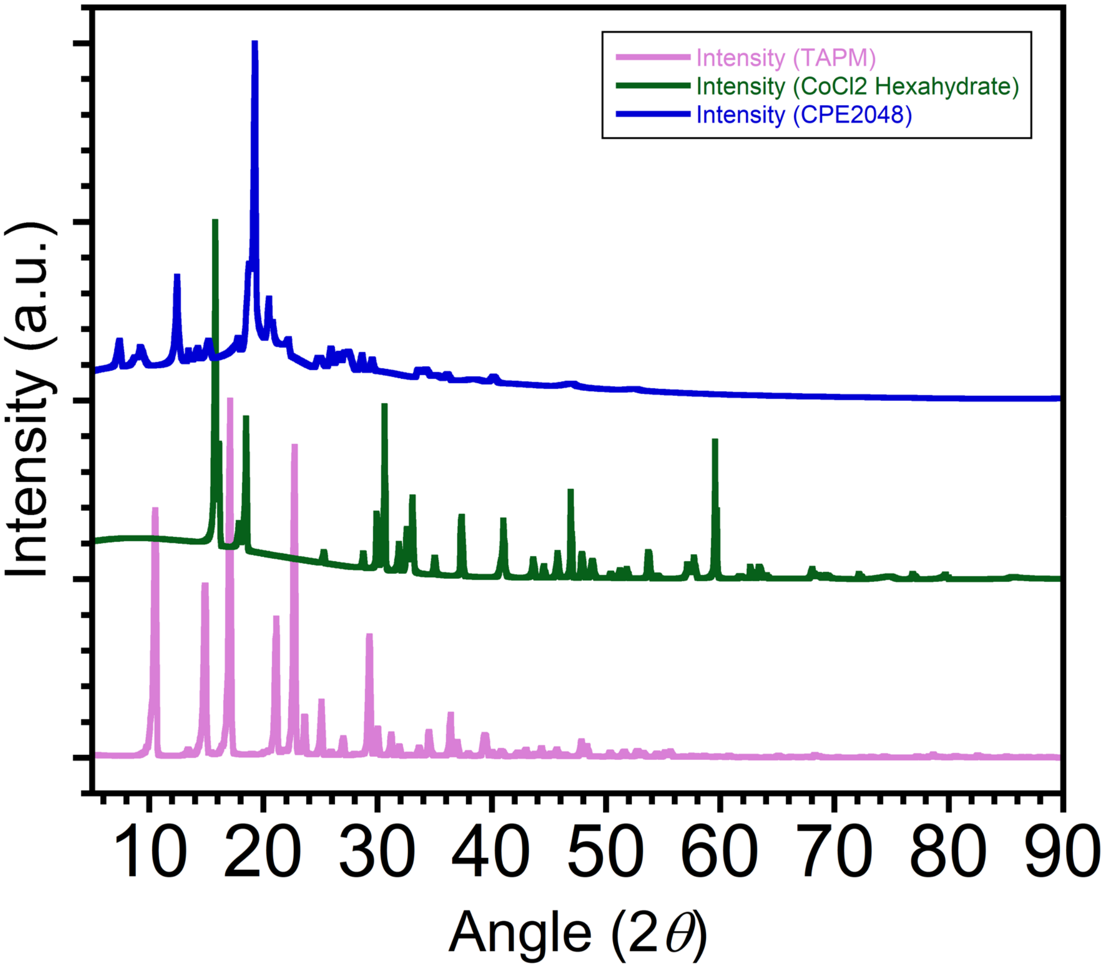

Figure S5. Powder X-ray diffraction spectra of TAPM (pink), $CoCl_2$ (green), and $Co(TAPM)_{2.3}Cl_2$ complexes (blue), indicating that $Co(TAPM)_{2.3}Cl_2$ is crystalline and structurally distinct from either of the starting materials.

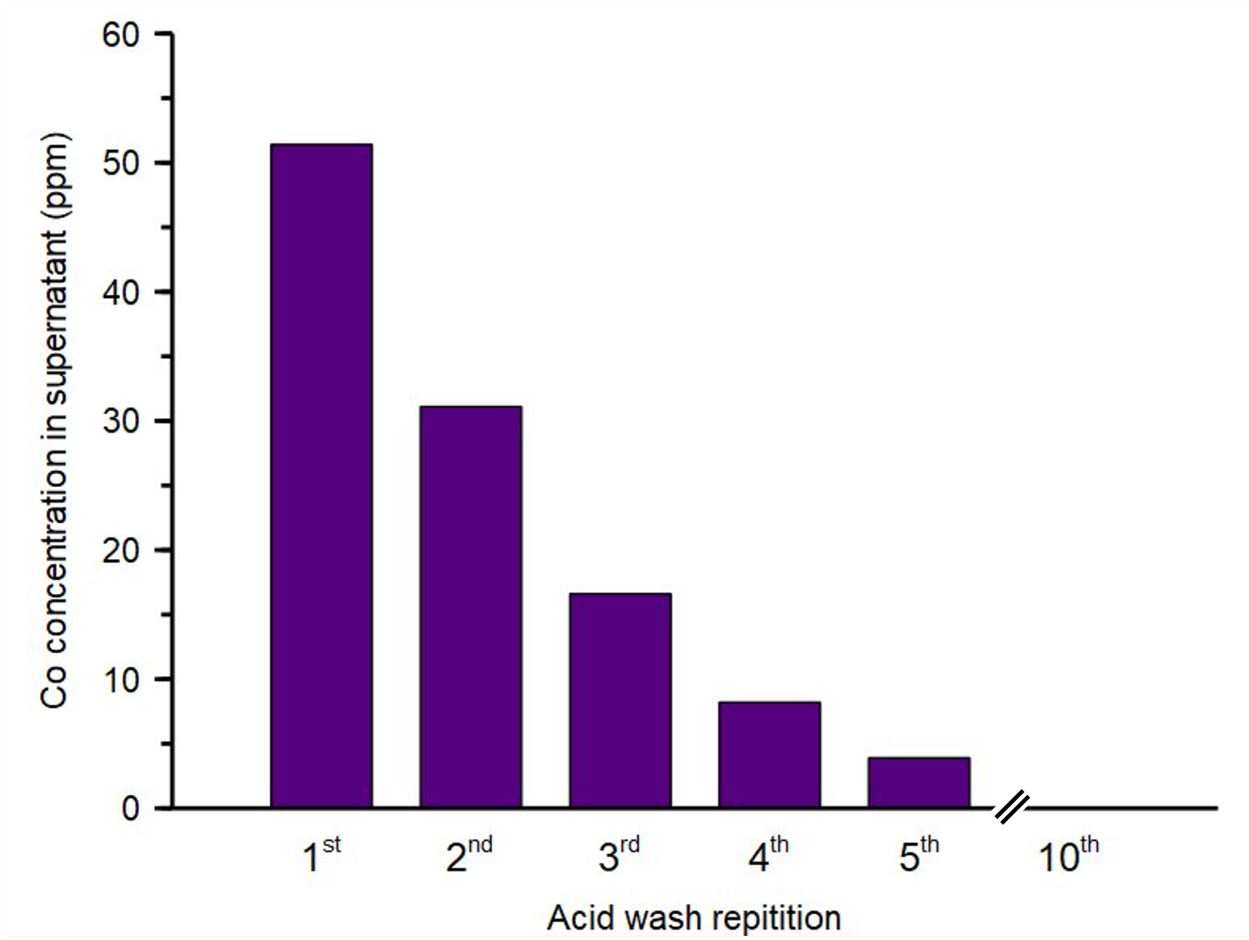

Figure S6. Cobalt concentration of the first five washes of Co(II)-templated TMC-TAPM indicated that the wash procedure was effective to remove the template ions. Washes 6-9 were not monitored by ICP-OES; however, wash 10 was measured to contain 0.04 ppm Co (below the detection limit of the instrument), indicating that the cobalt removal procedure had been successful and that the process could be used for materials recovery and reuse.

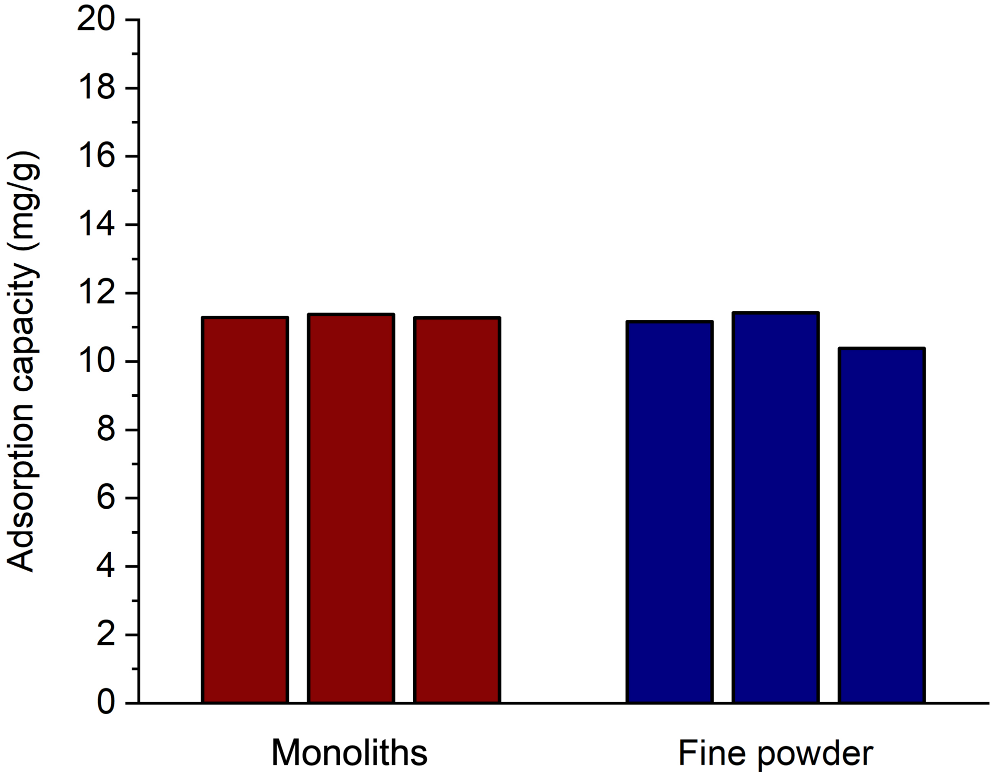

Figure S7. Co(II) adsorption capacities for monoliths (red) and micron-range powder (blue) of TMC-TAPM. Monoliths were obtained directly from TMC-TAPM synthesis and were converted to fine powder by grinding using a mortar and pestle. These adsorption experiments indicate that the macroscale morphology and particle size of TMC-TAPM do not significantly affect its Co(II) adsorption capacity.

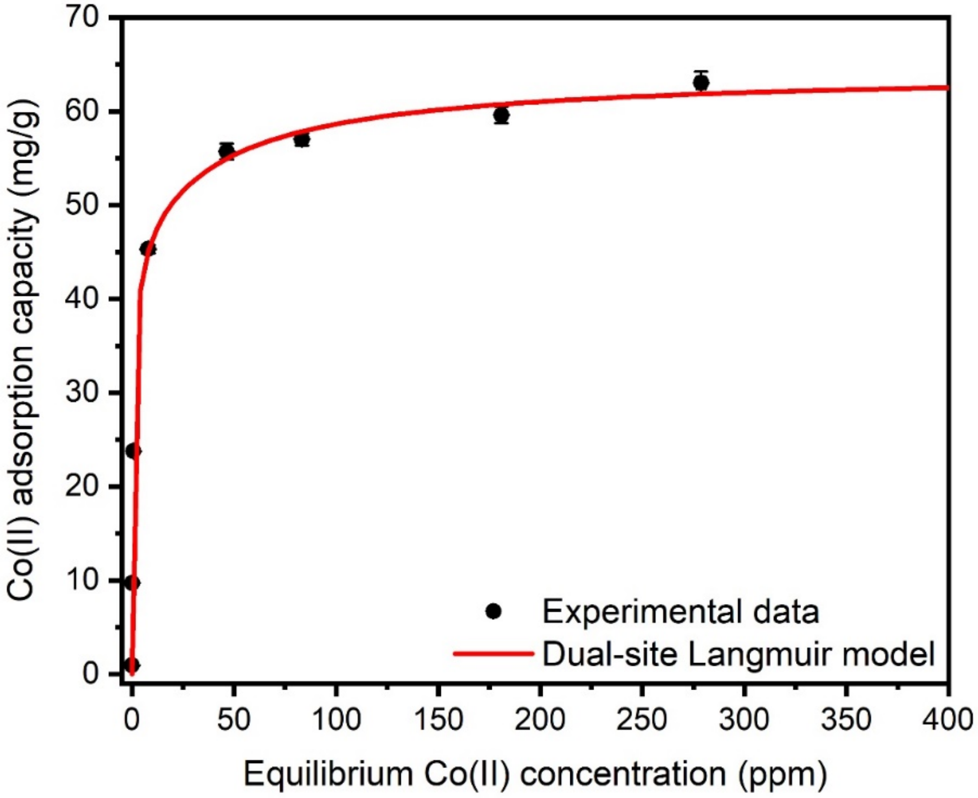

Figure S8. Co(II) adsorption data (black circles) and dual-site Langmuir model (red line) for Co(II)-templated TMC-TAPM.

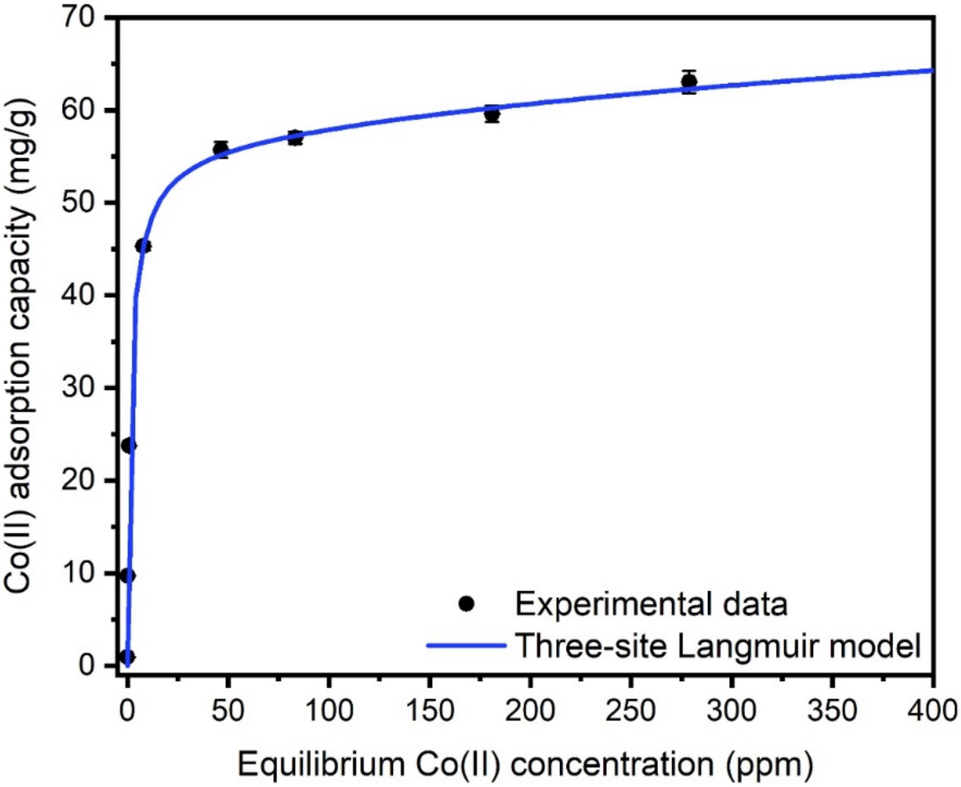

Figure S9. Co(II) adsorption data (black circles) and three-site Langmuir model (blue line) for Co(II)-templated TMC-TAPM.

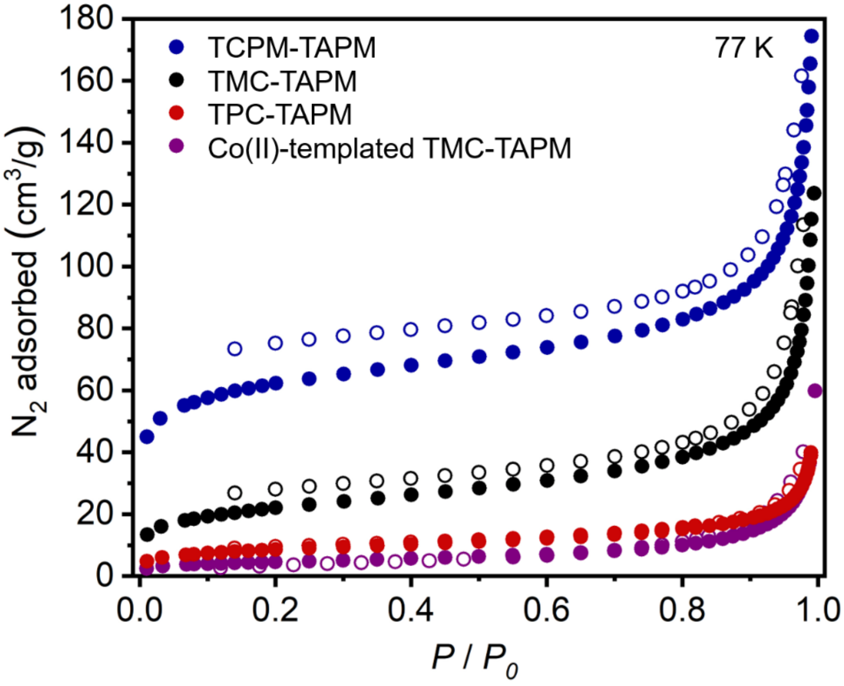

Figure S10. N_2 adsorption isotherms at 77 K for TCPM-TAPM (blue), TMC-TAPM (black), TPC-TAPM (red), and Co(II)-templated TMC-TAPM.

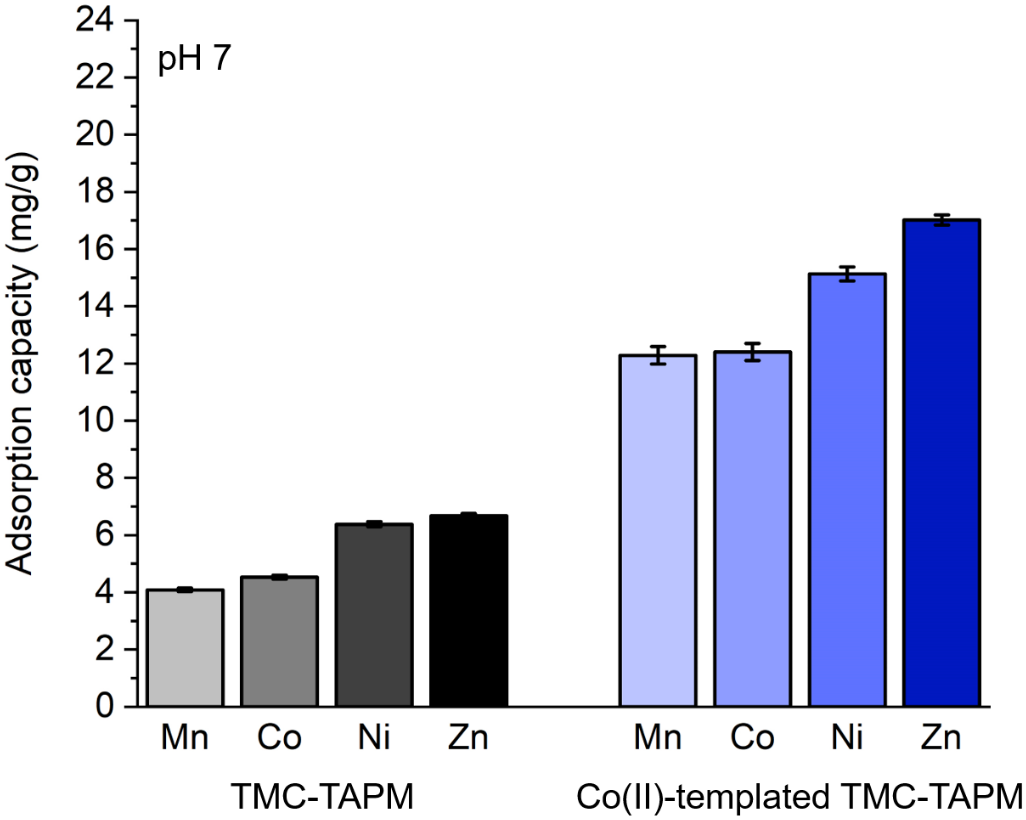

Figure S11. Competitive selectivity experiments for TMC-TAPM (left) and Co(II)-templated TMC-TAPM (right), for a multicomponent solution containing 45 ppm Mn, 45 ppm Co, 45 ppm Ni, and 45 ppm Zn (all as dichloride salts). Colors are for clarity only.

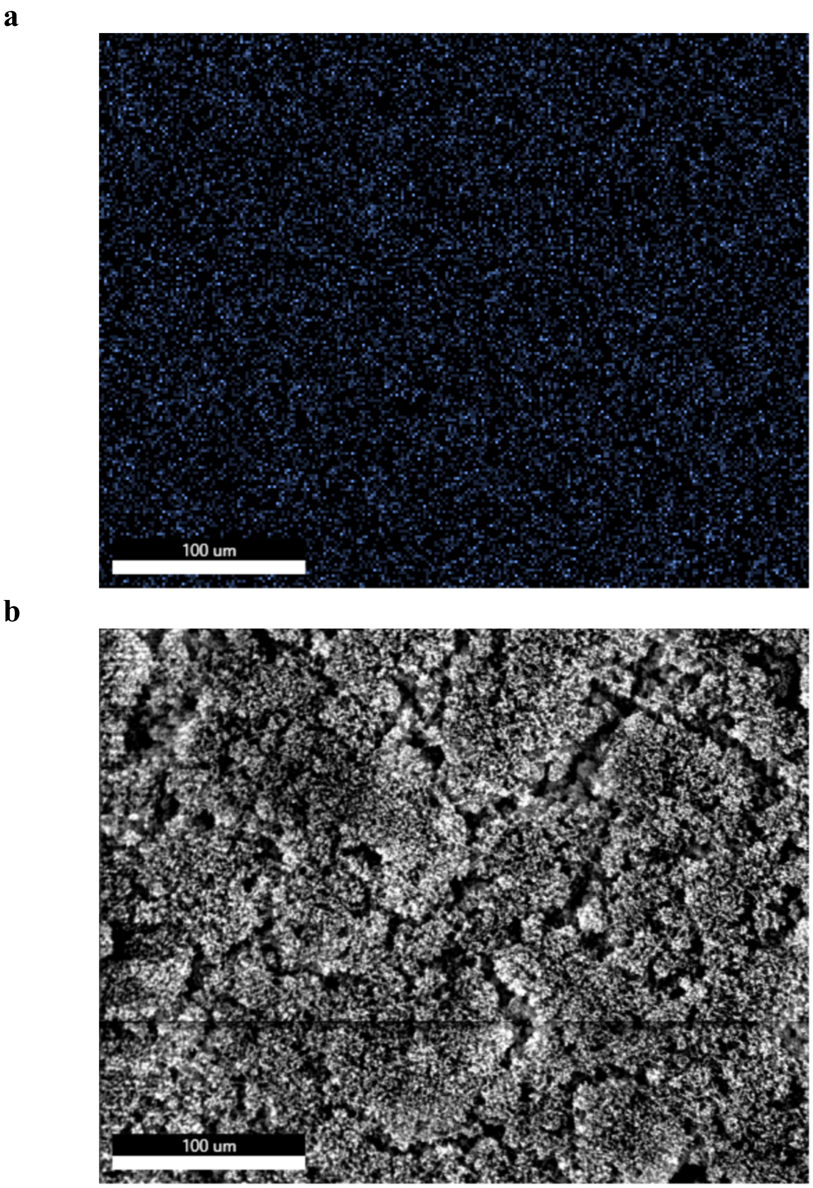

Figure S8. a) Energy dispersive X-ray spectroscopy (EDX) map of cobalt in TPC-TAPM. EDX map was taken after sample was equilibrated in an aqueous solution containing approximately 400 ppm Co and then flash frozen (vitrified) and transferred to the cryo-SEM under LN_2 (see procedure on page S7). b) Cryo-SEM image of the sample shown in a).

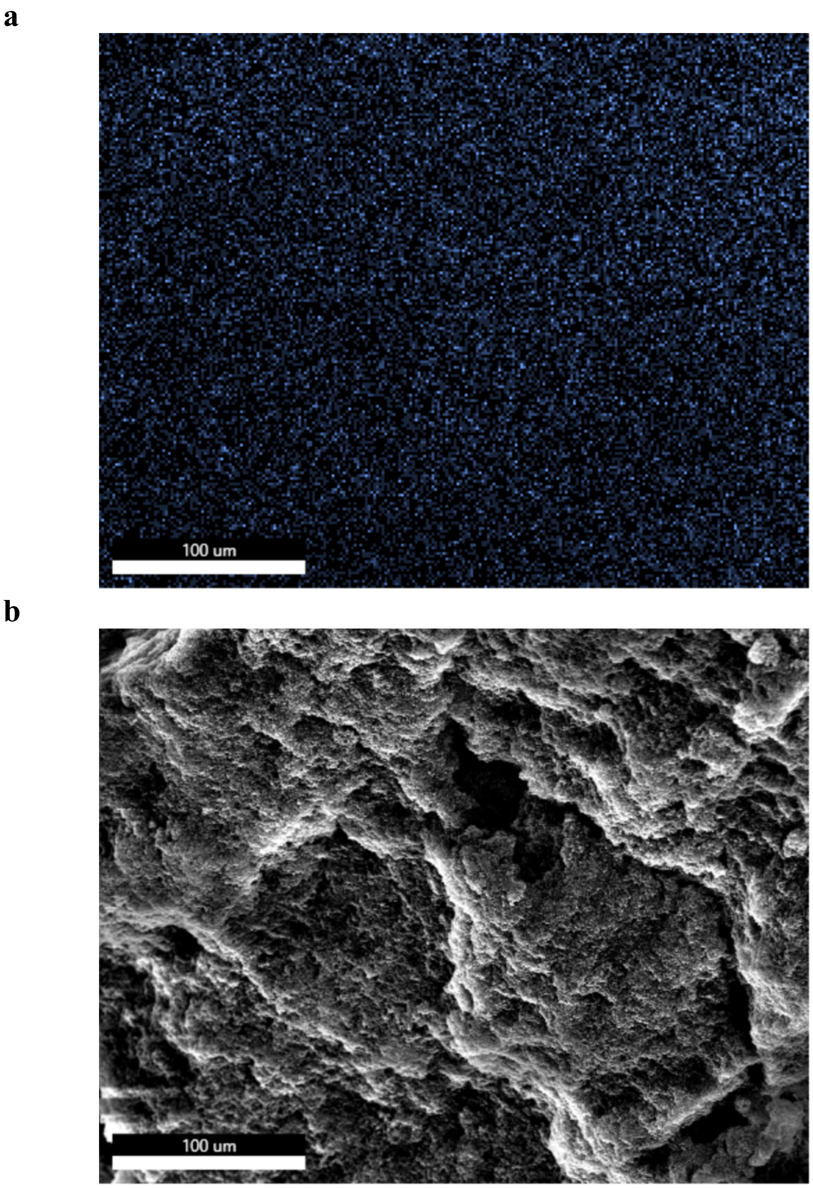

Figure S9. a) Energy dispersive X-ray spectroscopy (EDX) map of cobalt in TMC-TAPM. EDX map was taken after sample was equilibrated in an aqueous solution containing approximately 400 ppm Co and then flash frozen (vitrified) and transferred to the cryo-SEM under LN_2 (see procedure on page S7). b) Cryo-SEM image of the sample shown in a).

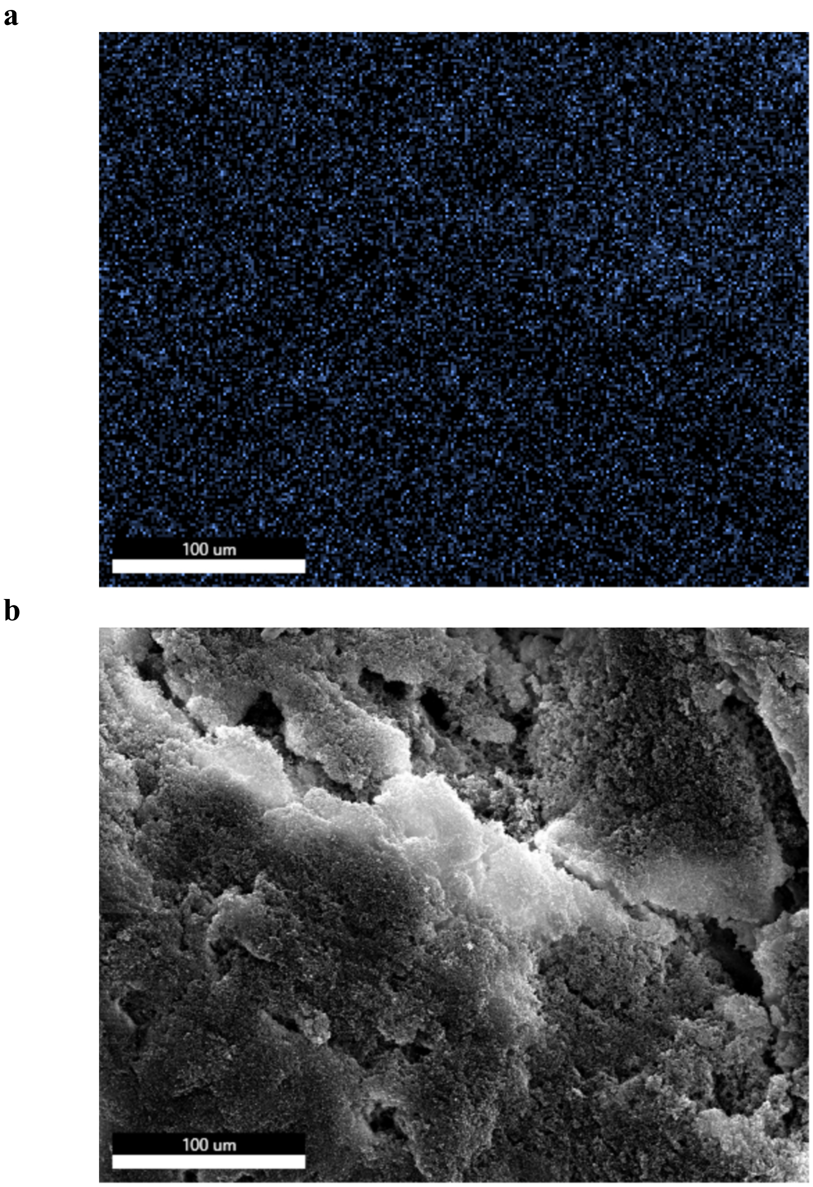

Figure S10. a) Energy dispersive X-ray spectroscopy (EDX) map of cobalt in TCPM-TAPM. EDX map was taken after sample was equilibrated in an aqueous solution containing approximately 400 ppm Co and then flash frozen (vitrified) and transferred to the cryo-SEM under LN_2 (see procedure on page S7). b) Cryo-SEM image of the sample shown in a).

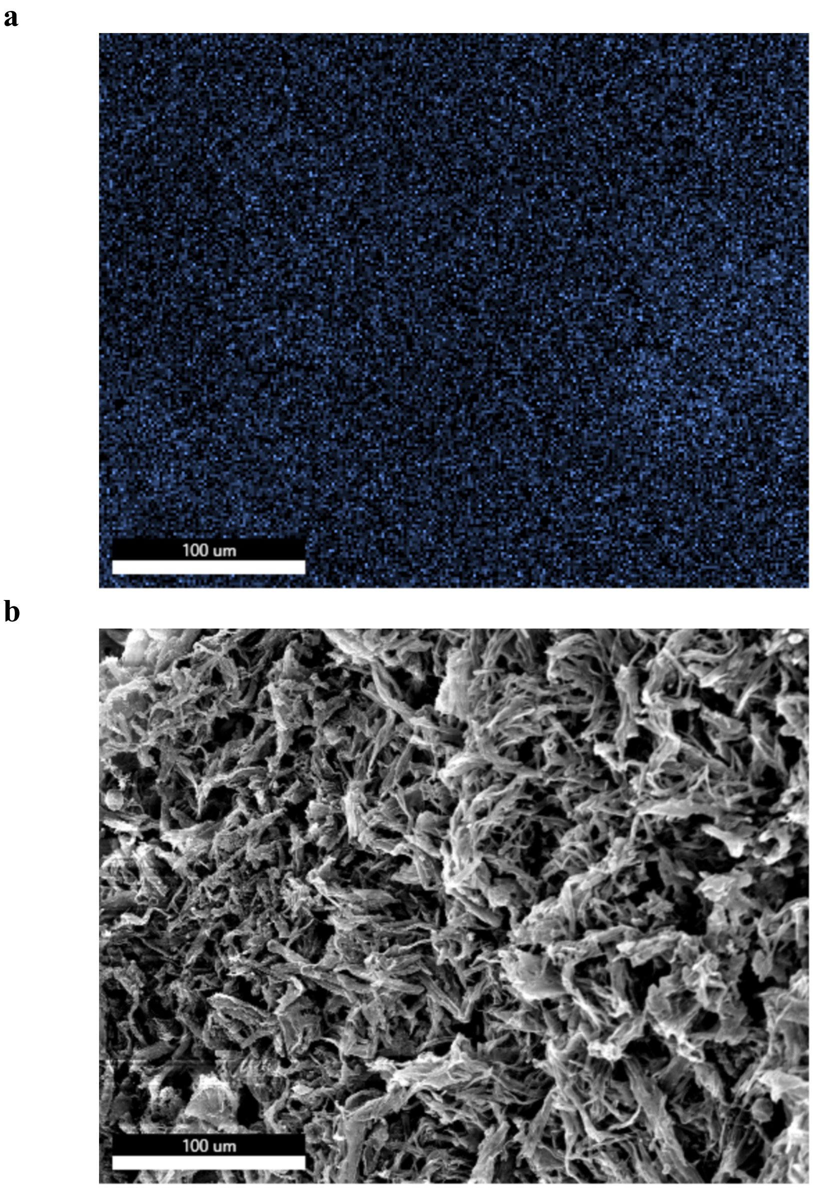

Figure S11. a) Energy dispersive X-ray spectroscopy (EDX) map of cobalt in Co(II)-templated TMC-TAPM. EDX map was taken after sample was equilibrated in an aqueous solution containing approximately 400 ppm Co and then flash frozen (vitrified) and transferred to the cryo-SEM under LN_2 (see procedure on page S7). b) Cryo-SEM image of the sample shown in a).

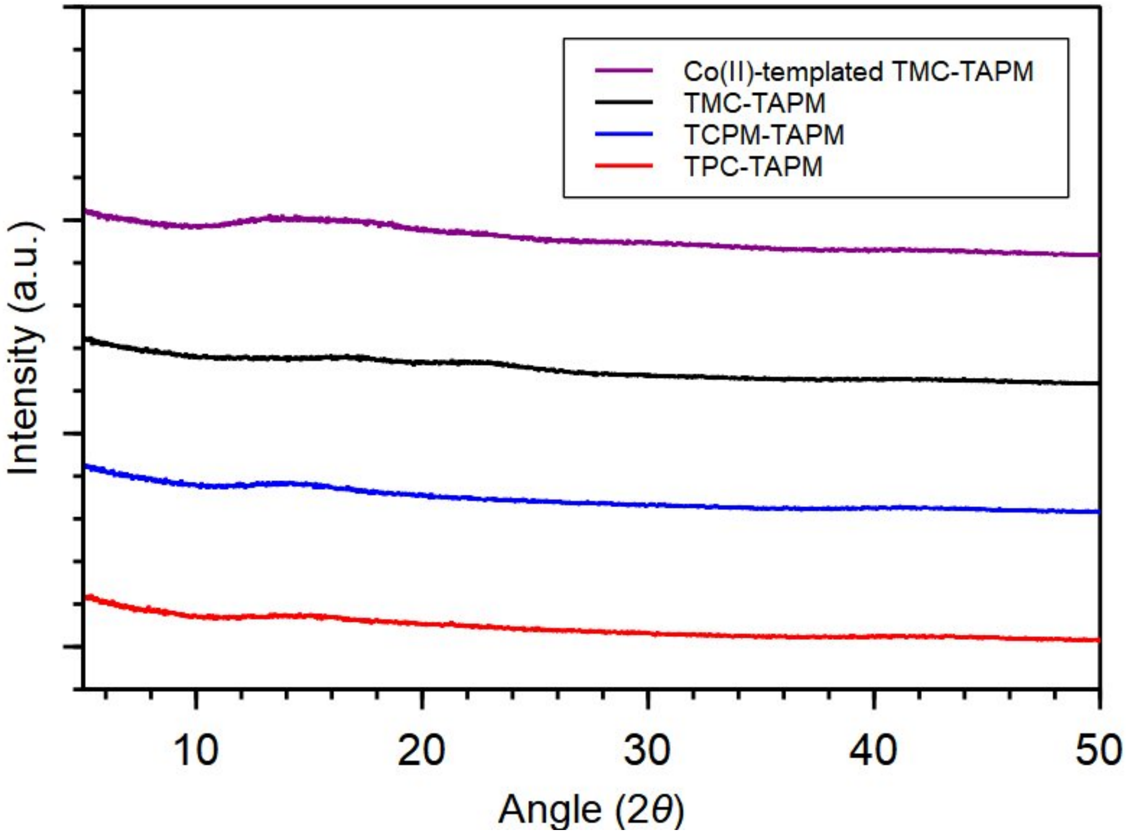

Figure S12. Powder X-ray diffraction spectra for Co(II)-templated TMC-TAPM (purple), TMC-TAPM (black), TCPM-TAPM (blue), and TPC-TAPM (red).

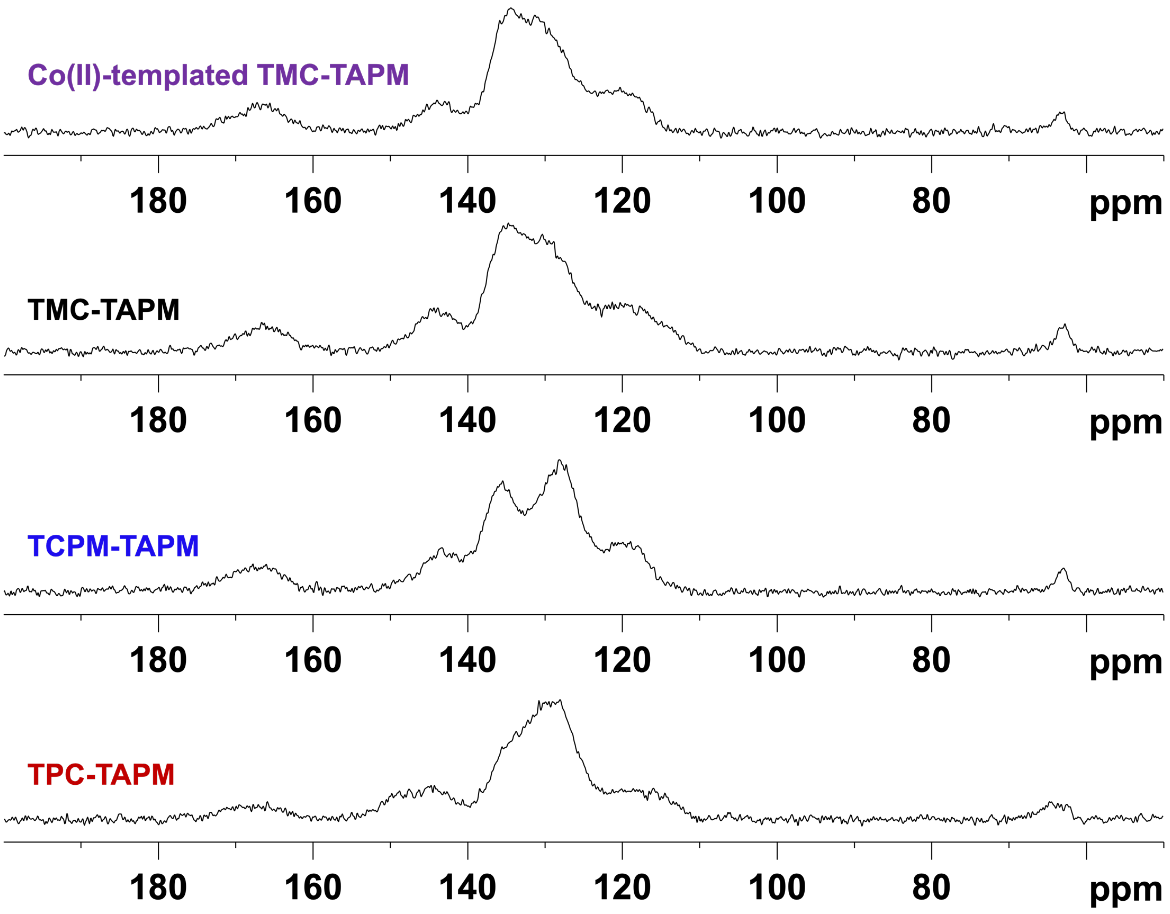

Figure S13. Solid-state ^{13}C NMR spectra for Co(II)-templated TMC-TAPM (top), TMC-TAPM (2nd from top), TCPM-TAPM (3rd from top), and TPC-TAPM (bottom). These spectra show the presence of the central tetrahedral carbon atom of tetrakis(4-aminophenyl)methane (TAPM) at approx. 65 ppm in each polymer, indicating that the TAPM monomer was incorporated into each material. The carboxylic acid peaks (approx. 170 ppm) and the amide peak (approx. 165 ppm) are overlapping; the region from 120-145 ppm comprises aromatic carbons on the phenyl rings of the monomers.

References

1) W. Jeong, M. I. Khazi, D. G. Lee, and J.-M. Kim, *Macromolecules*, 2018, **51**, 10312.