

Supplementary information for

**Carbonyl-rich porous organic polymers for cobalt adsorption from water**

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## General Information

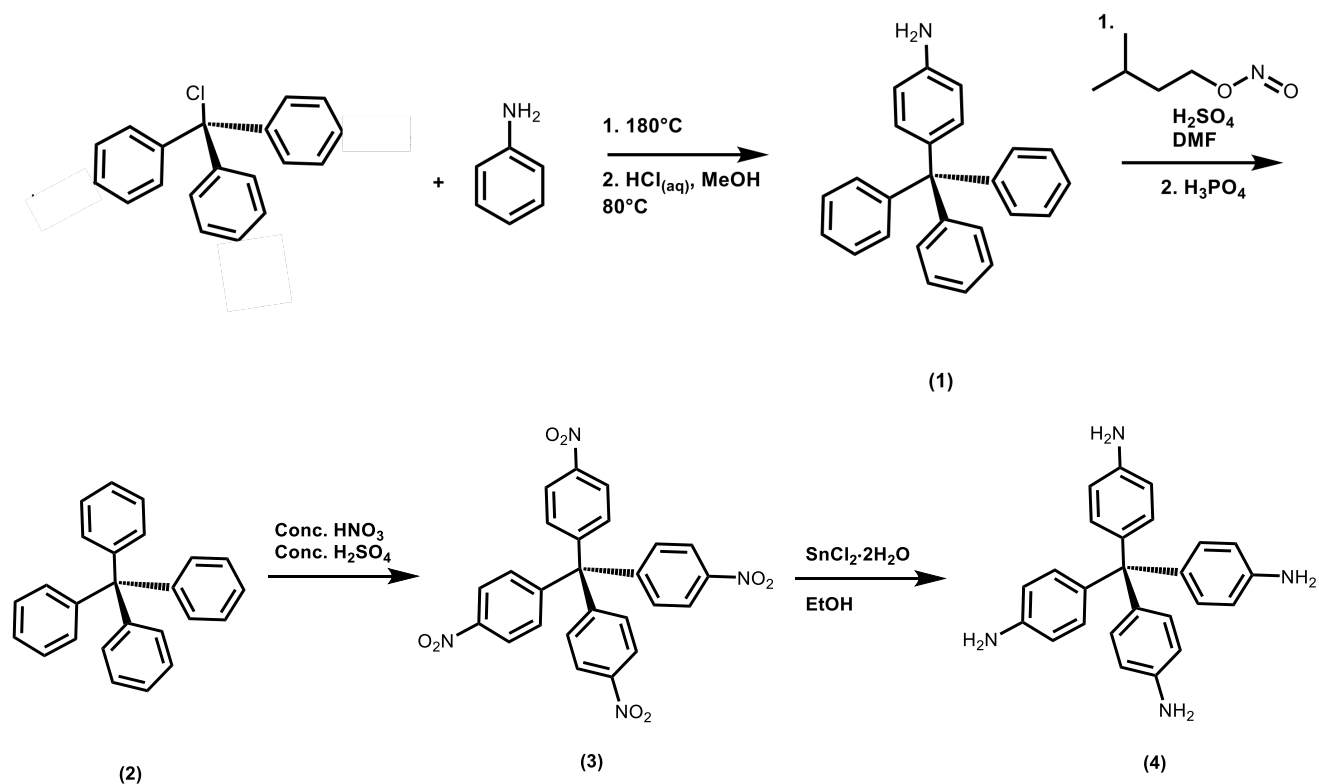
All reagents were purchased from commercial vendors and used without further purification.

Ultra-high purity grade (99.999% purity) gases were used for all gas adsorption measurements.

Ultrapure deionized water was obtained from a Sartorius Arim Mini water filtration system.

## Synthetic Procedures

### Scheme 1. Synthesis of tetrakis(4-aminophenyl)methane (TAPM)



### Synthesis of 4-Tritylaniline (1)

The synthesis of 4-tritylaniline was adapted from literature procedures.<sup>1,2</sup> In a round-bottom flask equipped with a stir bar and a reflux condenser, trityl chloride (10 g, 1 eq.) and aniline (8.4 mL, 2.7 eq.) were added together and heated to 180 °C with vigorous stirring, leading to the formation

of a purple solid. The reaction mixture was held at 180 °C for 10 mins and then cooled to room temperature. The solid was broken up and suspended in a 1:1 volume ratio of methanol (50 mL) and 2 M HCl (50 mL). The resulting suspension was heated to 80 °C for 30 min and then cooled to room temperature. The resulting light purple solid was isolated by vacuum filtration and washed with water. The solid product (4-tritylaniline) was dried under vacuum and carried forward without additional purification.

### **Synthesis of Tetraphenylmethane (2)**

In a round-bottom flask equipped with a stir bar, 4-tritylaniline (12.009 g, 1 eq.) was suspended in 100 mL *N,N*-dimethylformamide (DMF), and the mixture was cooled to -10 °C through an acetone/ice bath. When the temperature reached -10 °C, 96% H<sub>2</sub>SO<sub>4</sub> (11 mL, 5.53 eq.) was slowly added to the reaction mixture followed by isopentyl nitrite (8.6 mL, 1.79 eq.). The reaction mixture was stirred at -10 °C for 1 hour, after which H<sub>3</sub>PO<sub>2</sub> (17 mL, 4.57 eq.) was added dropwise. The reaction mixture was heated to 50 °C and stirred for 2 hours at that temperature. The reaction mixture was cooled to room temperature and then isolated by vacuum filtration. The solid was then washed with DMF (2x), water (1x), and ethanol (1x) to give pure tetraphenylmethane in a 72.4% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ = 7.33-7.29 (t, 8H), 7.22-7.19 (t, 4H), 7.16-7.14 (d, 8H).

### **Synthesis of tetrakis(4-nitrophenyl)methane (3)**

In a small vial cooled to 0 °C, 70% HNO<sub>3</sub> (31.9 mL, 20.1 eq) and 96% H<sub>2</sub>SO<sub>4</sub> (15.9mL, 11.5 eq) were carefully combined. In a separate round-bottom flask equipped with a stir bar, tetraphenylmethane (7.94 g, 1 eq.) was cooled to 0 °C. To the tetraphenylmethane, the acid mixture was carefully added dropwise. The reaction mixture was warmed to room temperature and stirred

for 6 hours. The reaction mixture was cooled to 0 °C and carefully diluted with 79.7 mL of H<sub>2</sub>O. The mixture was passed through a fritted glass funnel and washed with H<sub>2</sub>O. The crude solid was recrystallized from tetrahydrofuran (a second crop may be collected by placing the filtrate in the freezer overnight) to yield pure tetrakis(4-nitrophenyl)methane in a 24.7% yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ = 8.25-8.23 (d, 8H), 7.62-7.60 (d, 8H).

### **Synthesis of tetrakis(4-aminophenyl)methane (4)**

The synthesis of tetrakis(4-aminophenyl)methane was adapted from a literature procedure.<sup>3</sup> In a round-bottom flask equipped with a stir bar, tetrakis(4-nitrophenyl)methane (3.3 g, 1 eq.) was dissolved in ethanol (180 mL). SnCl<sub>2</sub>·2H<sub>2</sub>O (32 g, 20 eq.) was added into the solution and stirred for 2.5 hours at reflux. The solution was then cooled to room temperature, and ethanol was removed under reduced pressure. Water was added to the resulting residue, and the mixture was cooled to 0 °C. 10% aq. NaOH (w/w) was added until the system reached pH ~10. The solution was then stirred overnight in order to hydrolyze the tin salts. The resulting solid was collected through vacuum filtration and washed with water. The isolated solids were heated in 1,4-dioxane in order to selectively dissolve tetrakis(4-aminophenyl)methane. The remaining residue was removed by vacuum filtration and washed with hot 1,4-dioxane. The 1,4-dioxane was removed from the filtrate under reduced pressure. The resulting solid was washed with water by adding to the flask and swirling. The solid was collected by vacuum filtration and washed with more water followed by ethanol to yield pure tetrakis(4-aminophenyl)methane in a 25.5% yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ = 6.68-6.66 (d, 8H), 6.39-6.37 (d, 8H), 4.85 (s, 8H).

### **General synthesis of trimesoyl-tetrakis(4-aminophenyl) methane (TMC-TAPM) materials<sup>4</sup>**

In an oven-dried round-bottom flask under flowing argon, tetrakis(4-aminophenyl)methane (TAPM) (1 eq.) and *N,N*-diisopropylethylamine (DIPEA) (4 eq.) were dissolved in dry tetrahydrofuran (THF) to afford a clear brown solution. In a separate flask, the desired equivalents of trimesoyl chloride (TMC; see Table S1) were dissolved in dry THF under flowing argon to afford a clear solution. The TMC solution was added dropwise to the TAPM solution via cannula under an argon atmosphere over the course of 15 minutes, leading to the immediate formation of a beige precipitate. The reaction was stirred at room temperature overnight under an argon atmosphere. The beige solid was then isolated by vacuum filtration and washed with aqueous HCl (pH=3.3). Afterward, the solid was continuously washed with THF for 24 hrs via Soxhlet extraction. Finally, the solid was washed with ethanol (EtOH; 100 mL) on a Buchner funnel and dried under dynamic vacuum at 120 °C for 24 hours to afford a purple solid.

### **Example synthetic procedure for TMC-TAPM materials: TMC(1.5)-TAPM**

In an oven-dried round-bottom flask under flowing argon, tetrakis(4-aminophenyl)methane (TAPM) (292.8 mg) and *N,N*-diisopropylethylamine (DIPEA) (0.55 mL) were dissolved in dry tetrahydrofuran (THF) (24 mL) to afford a clear brown solution. In a separate flask, trimesoyl chloride (TMC) (422.1 mg) were dissolved in dry THF (6 mL) under flowing argon to afford a clear solution. The TMC solution was added dropwise to the TAPM solution via cannula under an argon atmosphere over the course of 15 minutes, leading to the immediate formation of a beige precipitate. The reaction was stirred at room temperature overnight under an argon atmosphere. The beige solid was then isolated by vacuum filtration and washed with aqueous HCl (pH=3.3). Afterward, the solid was continuously washed with THF for 24 hrs via Soxhlet

extraction. Finally, the solid was washed with ethanol (EtOH; 100 mL) on a Buchner funnel and dried under dynamic vacuum at 120 °C for 24 hours to afford a purple solid in 74.4% yield (430.7 mg).

### **Synthesis of benzanilide for amide stability testing**

Aniline (2 mL, 1.23 eq.) was dissolved in an aqueous solution containing 10% NaOH (30 mL, 4.4 eq. of NaOH) in a round-bottom flask with magnetic stirring applied. Benzoyl chloride (3 mL, 1 eq.) was then slowly added into the aniline solution. Solid appeared soon after addition of benzoyl chloride. The reaction mixture was stirred for 1 hour to ensure completion. Cold water was added to the mixture, and crude product was collected through vacuum filtration and washed with cold water. The crude product was recrystallized from ethanol to yield a colorless solid in 20% yield.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  = 8.00-7.00 (m, 10H), 10.25 (s, 1H).

### **Procedure for Gas Sorption Measurements**

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  $\text{N}_2$  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.  $\text{N}_2$  adsorption isotherms at 77 K were measured in liquid  $\text{N}_2$ . Brunauer-Emmett-Teller (BET) surface areas were calculated from the  $\text{N}_2$  isotherms at 77 K using points between  $P/P_0$  of 0.005 and 0.3

following the Rouquerol criteria. Pore size distributions were calculated using the NLDFT(SD3), N2-77-Carbon Slit Pores model while minimizing error of fit and roughness of distribution.

### **Procedure for Infrared Spectroscopy Measurements**

Fourier transform infrared (FTIR) spectra were collected on Thermo Nicolet Nexus 670 FT-IR E.S.P. with an ATR probe. Data were obtained with solid samples using air from the room as a blank.

### **Procedure for Solid-State NMR Measurements**

Solid-state  $^{13}\text{C}$  and  $^{15}\text{N}$  cross-polarization magic-angle spinning (CPMAS) NMR spectra of TMC-TAPM polymers were collected on a Bruker Advance NEO solid-state 500m MHz NMR spectrometer with a double resonance H/F-X probe. Carbon-13 chemical shifts were referenced with respect to TMS by setting  $\delta(^{13}\text{C}) = 0$  ppm and nitrogen-15 chemical shifts were referenced with respect to  $\alpha$ -glycine by setting  $\delta(^{15}\text{N}) = 33.4$  ppm. TMC-TAPM polymers were packed in a 3.2-mm outer diameter zirconia rotor with Kel-F endcap spinning at 8k Hz ( $^{15}\text{N}$ ) and 11k Hz ( $^{13}\text{C}$ ). Proton-carbon matched cross polarization ramp was at 50 kHz with 2-ms contact time. The proton dipolar decoupling was achieved by applying continuous wave spinal64 on the  $^1\text{H}$  channel during acquisition. The  $\pi/2$  pulse length was  $2.5 \mu\text{s}$  for  $^1\text{H}$  and the recycle delay was 5 s. Each  $^{13}\text{C}$  spectrum was collected with 2048 scans, and the line broadening for the spectrum was 50 Hz. Each  $^{15}\text{N}$  spectrum was collected with 15360 scans and the line broadening for the spectrum was 100 Hz.



### **Procedure for Solution $^1\text{H}$ NMR measurement**

Solution-state  $^1\text{H}$  NMR spectra were collected on a Bruker AV NEO 400 MHz (NMR400). Solid samples were dissolved in DMSO- $d_6$ . Proton chemical shifts were referenced with respect to TMS by setting  $\delta(^1\text{H}) = 0$  ppm.

### **Procedure for Preparing Ion Solutions**

A buffered solution of ultrapure deionized water at pH 7 was prepared (0.1 M in HEPES buffer). The desired amount of  $\text{MCl}_2$  ( $\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{or Zn}$ ) 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 or MP-AES, 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 Experiments (Figures 3a-3b)**

Cobalt solutions were prepared as described above. The 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 argon, and removed from the line and exposed to air. Polymer samples were then weighed immediately into 15 mL 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. 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 24 hours, the centrifuge tubes were removed from the shaker. The solution from each tube was passed through a 0.2 micron PES syringe filter and then measured by ICP-OES or MP-AES. The control experiments (without polymer) were also filtered through the 0.2 micron PES filter and were later measured by ICP-OES or MP-AES to give an accurate value for the starting concentration. Ion adsorption isotherms were fit to dual-site Langmuir models to account for strong binding to terminal functional groups ( $\text{NH}_2$  and  $\text{COO}^-$ ) and weaker binding to other surface sites on the polymer.

### **Procedure for ICP-OES Measurements**

Metal concentrations were measured using an Agilent 5110 inductively coupled plasma optical emission spectrometer (ICP-OES) 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.

### **Procedure for MP-AES Measurements**

Metal concentrations were measured using an Agilent Technologies 4210 microwave plasma atomic emission spectrometer (MP-AES). Three characteristic wavelengths were used for each element. The resultant concentration was based on the selected wavelength that gave the best fit with control samples. Data were analyzed using Agilent MP Expert software (version 1.6.1). Calibration curves for concentration determination were constructed using two standard solutions of elements in 10% nitric acid, 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. Calibration standards were diluted gravimetrically from a commercial 1000 mg/L standard.

### **Procedure for SEM imaging**

Scanning electron microscopy (SEM) was performed on a Tescan XEIA FEG instrument. Dry powders were deposited onto carbon tape and coated with carbon. The non-conductive powder samples required a conductive carbon coating to achieve high quality images.

### **Procedure for Adsorbent Regeneration**

Following a 400-ppm cobalt adsorption experiment, adsorbents were washed 3 times with ~15 mL water and then soaked in ~12 mL of 1M HCl for 3 hours. Afterward, the solid was washed with water and activated under 120°C vacuum. Re-activated material was used to perform cobalt adsorption experiments (see **Procedure for Cobalt Adsorption Experiments**), and cobalt uptake was measured.

### **Procedure for Amide Stability Testing**

To determine the hydrolytic stability of the amide bonds in the porous organic polymers under our acidic regeneration conditions, we used the molecular analog benzanilide for hydrolysis tests (Figure S15). Benzanilide (~15 mg) was placed inside a solution NMR tube filled with ~1 mL of a 1 M DCl in D<sub>2</sub>O solution. Like the porous polyamides studied herein, benzanilide is insoluble in 1 M DCl. Hydrolysis of the amide bond in benzanilide liberates aniline, which is soluble in 1 M DCl and visible by <sup>1</sup>H NMR. No aniline peaks were observed to appear over the course of a 72-hour test, indicating amide bond stability under the regeneration conditions.

### **Procedure for Multicomponent Adsorption Experiments**

A mixed-metal solution containing 40 ppm Mn, 40 ppm Co, 40 ppm Ni, and 40 ppm Zn was prepared as described above. The solution was stored in a 50 mL centrifuge tubes, wrapped in foil, and shaken overnight. A TMC(1.5)-TAPM sample was activated at 120 °C under vacuum on a Schlenk line overnight, backfilled with argon, and removed from the line and exposed to air. The sample was then weighed immediately into 15 mL centrifuge tubes for the adsorption experiments. Three identical experiments were performed, with a polymer concentration of 2 mg polymer per gram solution. 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 tubes were then capped, covered with foil and shaken at 580 rpm overnight. 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 24 hours, the centrifuge tubes were removed from

the shaker. The solution from each tube was passed through a 0.2 micron PES syringe filter and then measured by MP-AES. The control experiment (without polymer) was also filtered through the 0.2 micron PES filter and were later measured by MP-AES to give an accurate value for the starting concentrations of each metal ion.

### **Procedure for Time-Dependent Adsorption Measurements**

Ten grams of a 0.1 M HEPES aqueous solution and 10 grams of a 380 ppm Co(II) solution were prepared separately. A sample of TMC(1.5)-TAPM was activated at 120 °C under vacuum on a Schlenk line overnight, backfilled with argon, and removed from the line and exposed to air. 40 mg of the activated polymer sample was then weighed immediately into a 50 mL centrifuge tube for the time-dependent adsorption experiment. Approximately 1 g of the 0.1 M HEPES solution was removed from the original 10 g HEPES solution and used to wet the polymer sample. The remaining HEPES solution was combined with the 380 ppm Co(II) solution, shaken at 580 rpm for 30 minutes, and subsequently added to the wetted polymer sample. As soon as the cobalt-containing solution was added to the wetted polymer sample, we began timing the experiment. We remove 1 mL aliquots of the supernatant after 0.5, 1, 1.5, 2, 5, 10, 20, 30, 40, 60, 120, 180, and 240 minutes. In between the removal of aliquots, the centrifuge tube was capped and shaken at 80 rpm on a shaker plate. All aliquots were passed through a 0.2 micron PES syringe filter and then measured by MP-AES.

### **Procedure for C/H/N Combustion Analysis**

C/H/N combustion analysis was performed by Galbraith Laboratories, Inc., for all polymer samples, according to the following procedure. Samples, standards, and blanks were prepared in tin capsules and crimped. Blanks and conditioners were run to evaluate system suitability. The instrument was calibrated using known standards. Samples were then analyzed with bracketing QC standards run at least every ten samples. Samples were burned in a PerkinElmer 2400 Series II CHNS/O Analyzer in pure oxygen at 920 – 980°C under static conditions to produce combustion products of CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>. The results were then calculated based on the amount of carbon, hydrogen, and/or nitrogen are detected accounting for sample mass used.

## Supplementary Tables

**Table S1.** Stoichiometric ratios of acyl chloride- and amine-based monomers used in the synthesis of porous organic polymer samples.

Sample	Trimesoyl chloride (equivalents)	Tetrakis(4-aminophenyl)methane (equivalents)
TMC (2)- TAPM	2.7	1
TMC (1.75)- TAPM	2.33	1
TMC (1.5)- TAPM	1.99	1
TMC (1.25)- TAPM	1.67	1
TMC (1.1)- TAPM	1.47	1
TMC (1)- TAPM	1.33	1
TMC(0.67) – TAPM	0.89	1

**Table S2.** Results of C/H/N combustion analysis.

<b>Sample</b>	<b>Carbon (C%)</b>	<b>Hydrogen (H%)</b>	<b>Nitrogen (N%)</b>	<b>C%:N% ratio</b>
TMC (2)- TAPM	66.94	4.66	7.79	8.59
TMC (1.75)- TAPM	66.89	4.93	7.90	8.46
TMC (1.5)- TAPM	67.07	4.06	7.67	8.74
TMC (1.25)- TAPM	66.17	4.88	7.83	8.45
TMC (1.1)- TAPM	66.94	4.39	8.08	8.28
TMC(0.67) – TAPM	68.75	4.69	9.04	7.61

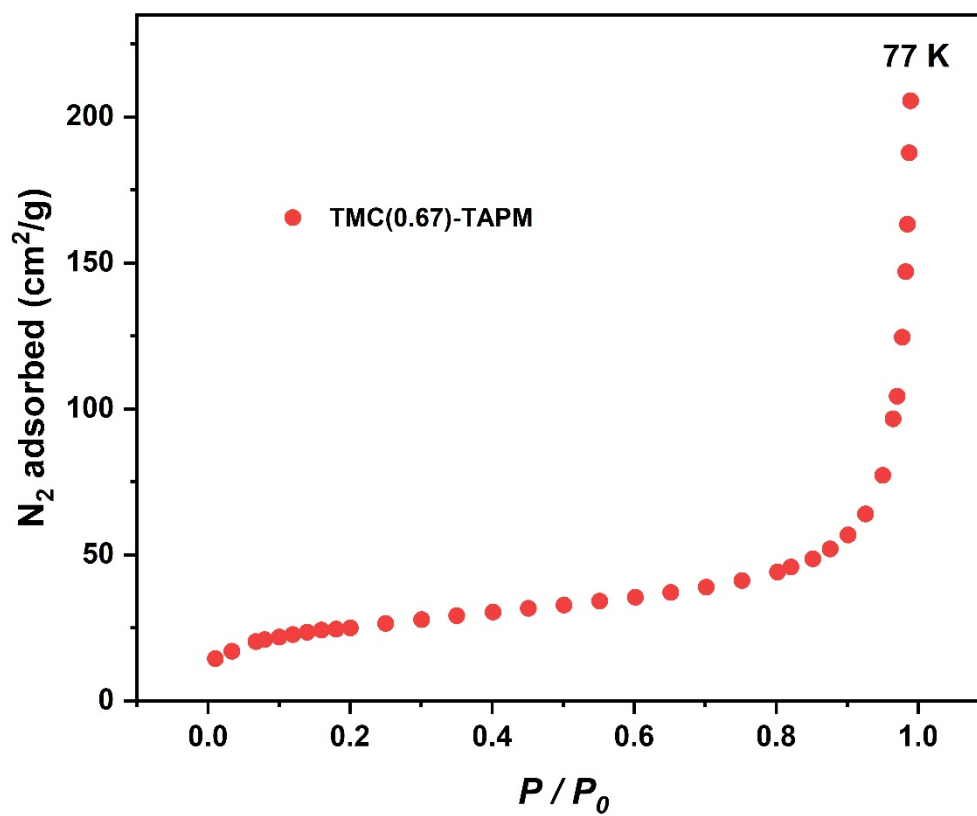


**Table S3.** Predicted C/H/N weight percentages and C:N ratios under two scenarios: a) an assembly of monomers with no linkages between them (after aqueous work-up), and b) an entirely crosslinked network with no end groups (after aqueous work-up).

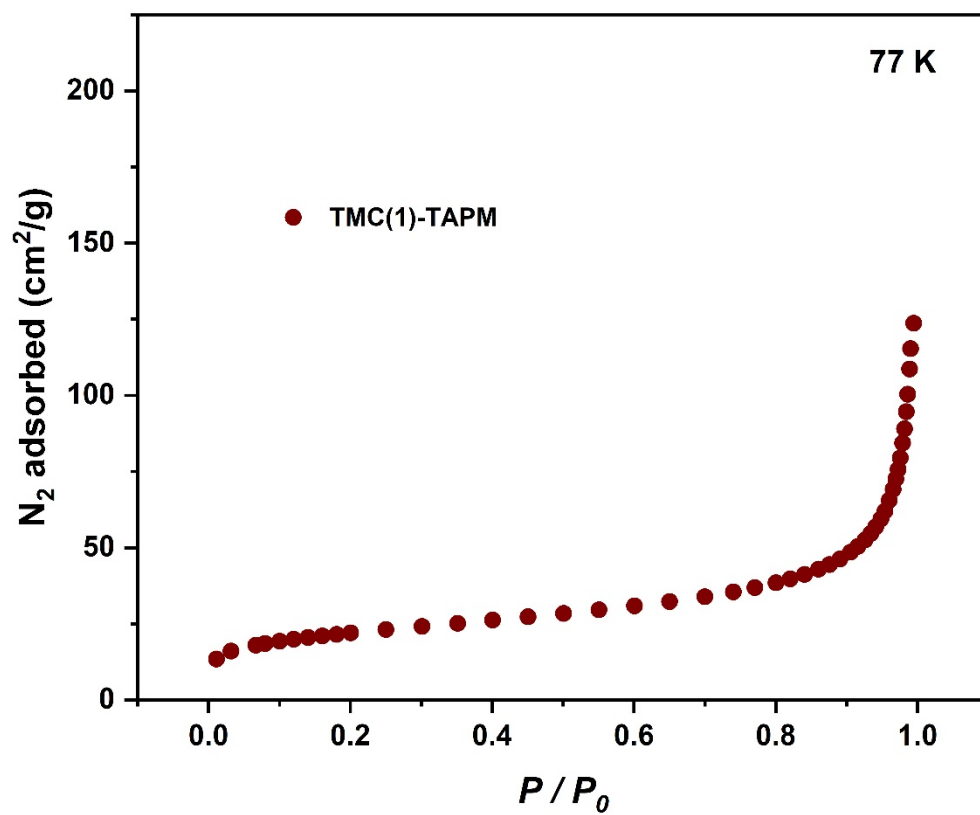
<b>Sample</b>	<b>Predicted % C/H/N under scenario a)</b>	<b>Predicted % C/H/N under scenario b)</b>
TMC(2)-TAPM  a) $(C_9H_6O_6)_{2.67}(C_{25}H_{24}N_4)$ b) $(C_9H_3O_3)_{2.67}(C_{25}H_{20}N_4)$	C: 62.54%  H: 4.28%  N: 5.95%  Resulting C:N ratio: <b>10.51</b>	C: 73.49%  H: 3.52%  N: 6.99%  Resulting C:N ratio: <b>10.51</b>
TMC(1.75)-TAPM  a) $(C_9H_6O_6)_{2.33}(C_{25}H_{24}N_4)$ b) $(C_9H_3O_3)_{2.33}(C_{25}H_{20}N_4)$	C: 63.46%  H: 4.4%  N: 6.44%  Resulting C:N ratio: <b>9.85</b>	C: 73.89%  H: 3.64%  N: 7.5%  Resulting C:N ratio: <b>9.85</b>
TMC(1.5)-TAPM  a) $(C_9H_6O_6)_2(C_{25}H_{24}N_4)$ b) $(C_9H_3O_3)_2(C_{25}H_{20}N_4)$	C: 64.5%  H: 4.53%  N: 7%  Resulting C:N ratio: <b>9.21</b>	C: 74.34%  H: 3.77%  N: 8.07%  Resulting C:N ratio: <b>9.21</b>
TMC(1.25)-TAPM  a) $(C_9H_6O_6)_{1.67}(C_{25}H_{24}N_4)$ b) $(C_9H_3O_3)_{1.67}(C_{25}H_{20}N_4)$	C: 65.73%  H: 4.69%  N: 7.66%	C: 74.87%  H: 3.93%  N: 8.72%

	Resulting C:N ratio: <b>8.58</b>	Resulting C:N ratio: <b>8.58</b>
TMC(1.1)-TAPM a) $(C_9H_6O_6)_{1.47}(C_{25}H_{24}N_4)$ b) $(C_9H_3O_3)_{1.47}(C_{25}H_{20}N_4)$	C: 66.61% H: 4.8% N: 8.13% Resulting C:N ratio: <b>8.19</b>	C: 75.23% H: 4.03% N: 9.18% Resulting C:N ratio: <b>8.19</b>
TMC(1)-TAPM a) $(C_9H_6O_6)_{1.33}(C_{25}H_{24}N_4)$ b) $(C_9H_3O_3)_{1.33}(C_{25}H_{20}N_4)$	C: 67.28% H: 4.88% N: 8.49% Resulting C:N ratio: <b>7.92</b>	C: 75.51% H: 4.11% N: 9.53% Resulting C:N ratio: <b>7.92</b>
TMC(0.67)-TAPM a) $(C_9H_6O_6)_{0.89}(C_{25}H_{24}N_4)$ b) $(C_9H_3O_3)_{0.89}(C_{25}H_{20}N_4)$	C: 69.86% H: 5.21% N: 9.87% Resulting C:N ratio: <b>7.08</b>	C: 76.53% H: 4.41% N: 10.81% Resulting C:N ratio: <b>7.08</b>

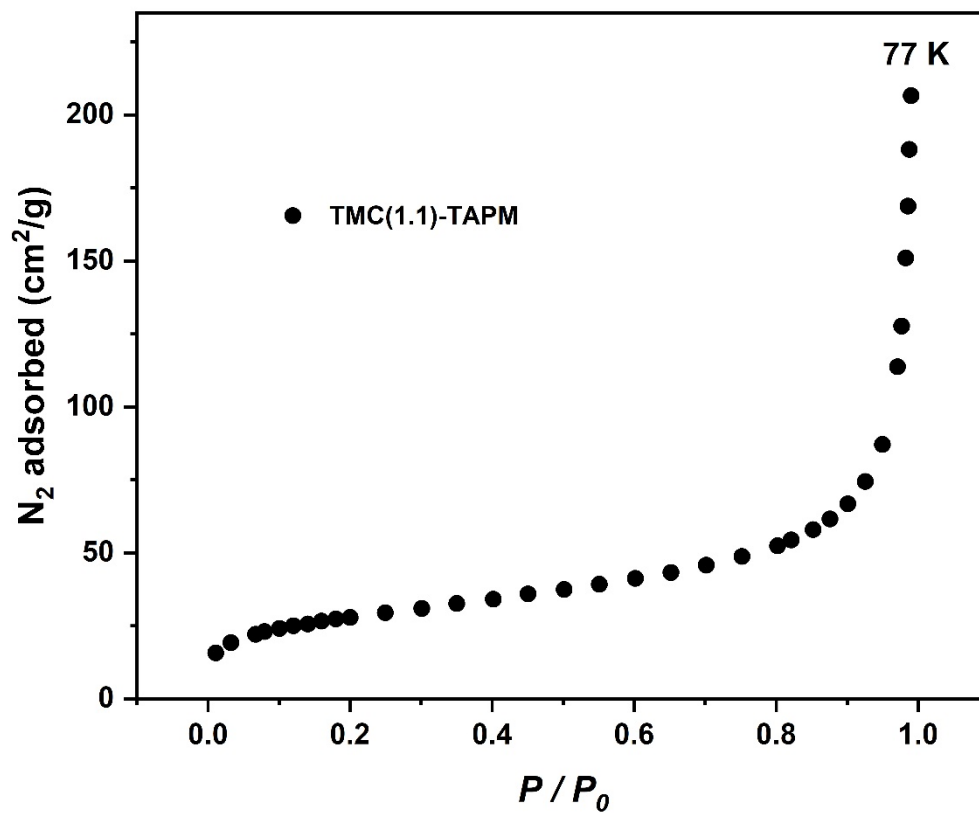
Supplementary Figures



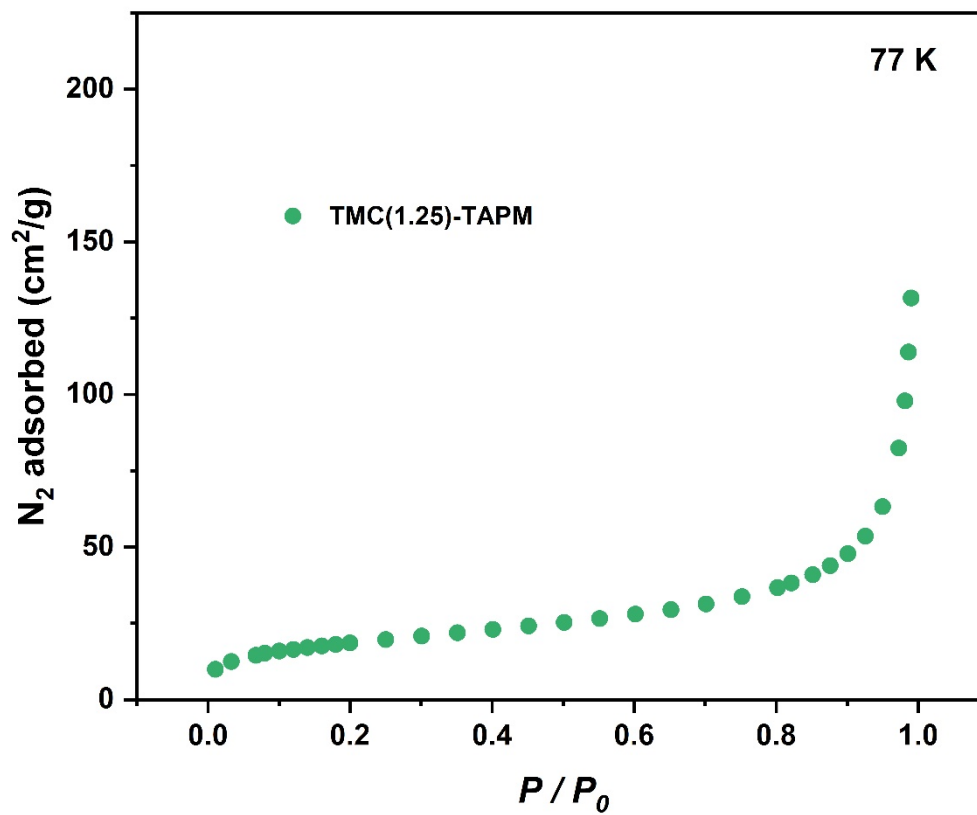
**Figure S1.** N<sub>2</sub> adsorption isotherm at 77 K for TMC(0.67)-TAPM.



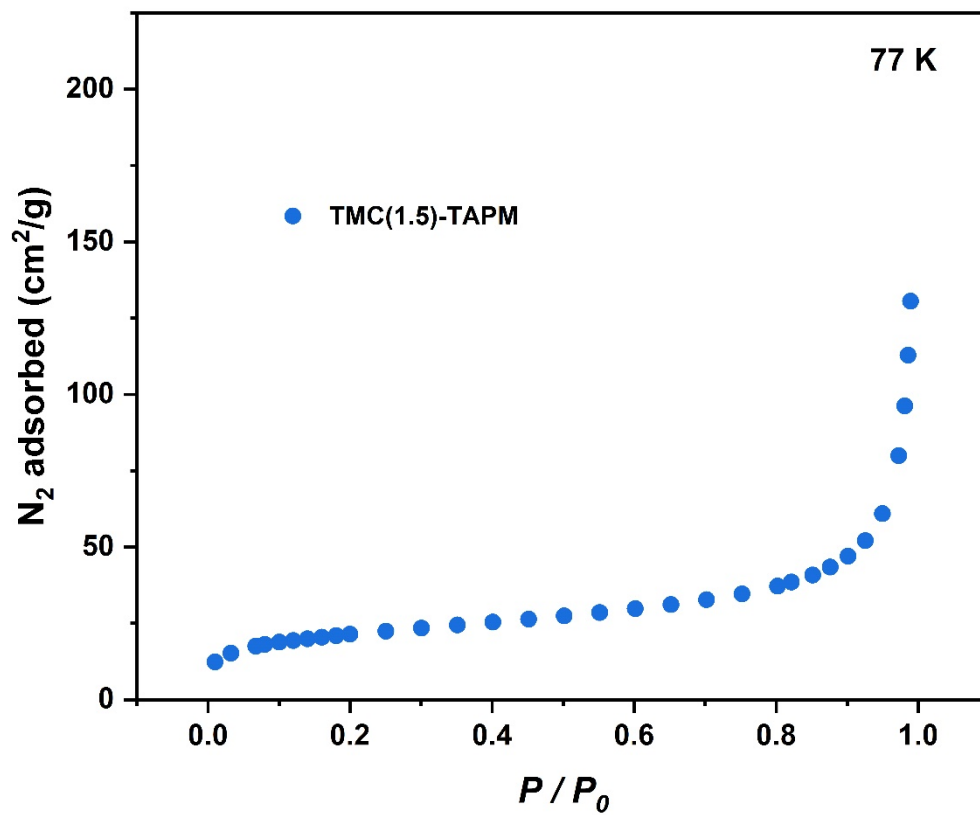
**Figure S2.**  $N_2$  adsorption isotherm at 77 K for TMC(1)-TAPM. This data was published by us in previous work.<sup>4</sup>



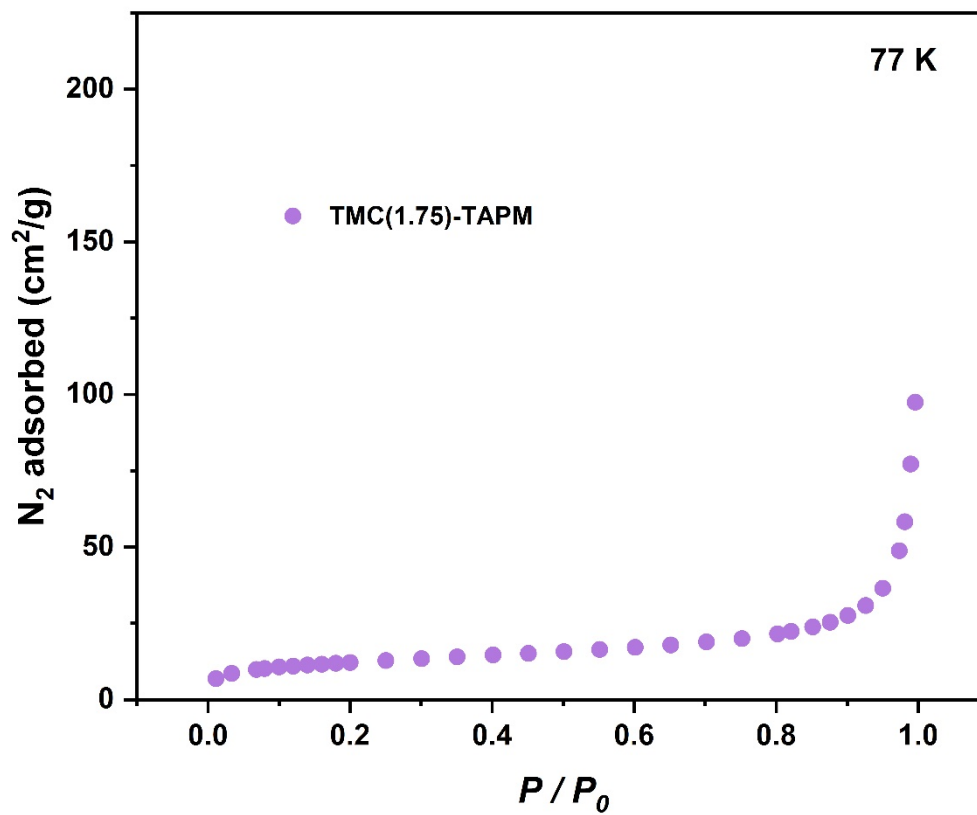
**Figure S3.**  $N_2$  adsorption isotherm at 77 K for TMC(1.1)-TAPM.



**Figure S4.**  $N_2$  adsorption isotherm at 77 K for TMC(1.25)-TAPM.

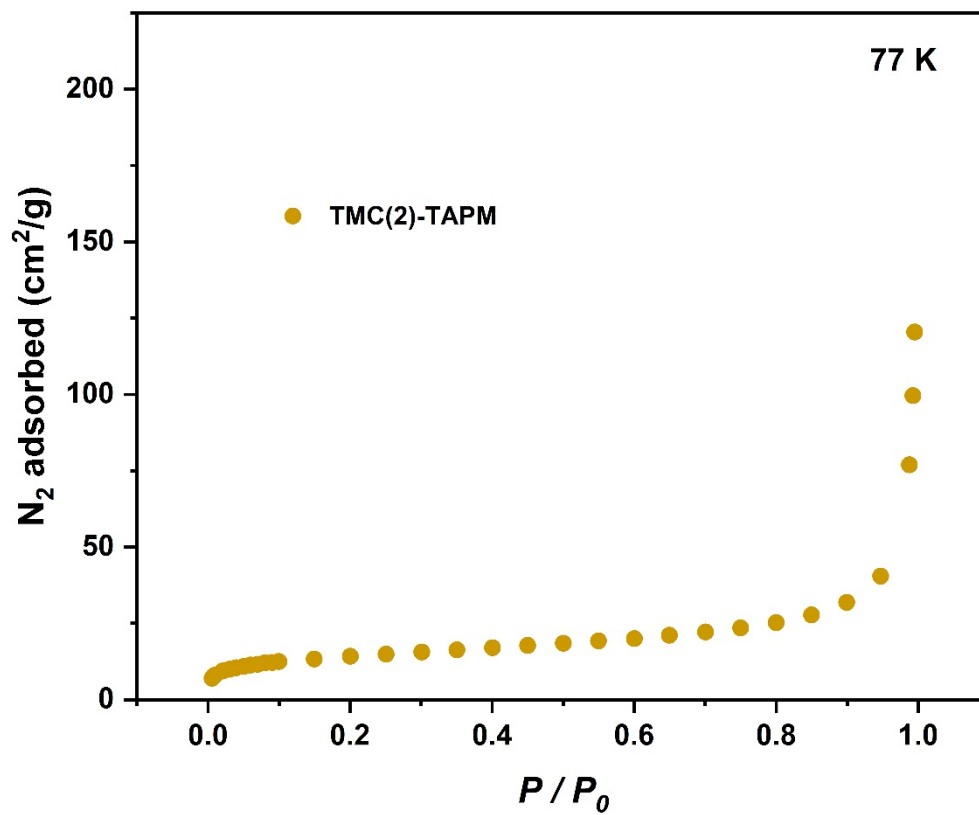


**Figure S5.**  $N_2$  adsorption isotherm at 77 K for TMC(1.5)-TAPM.

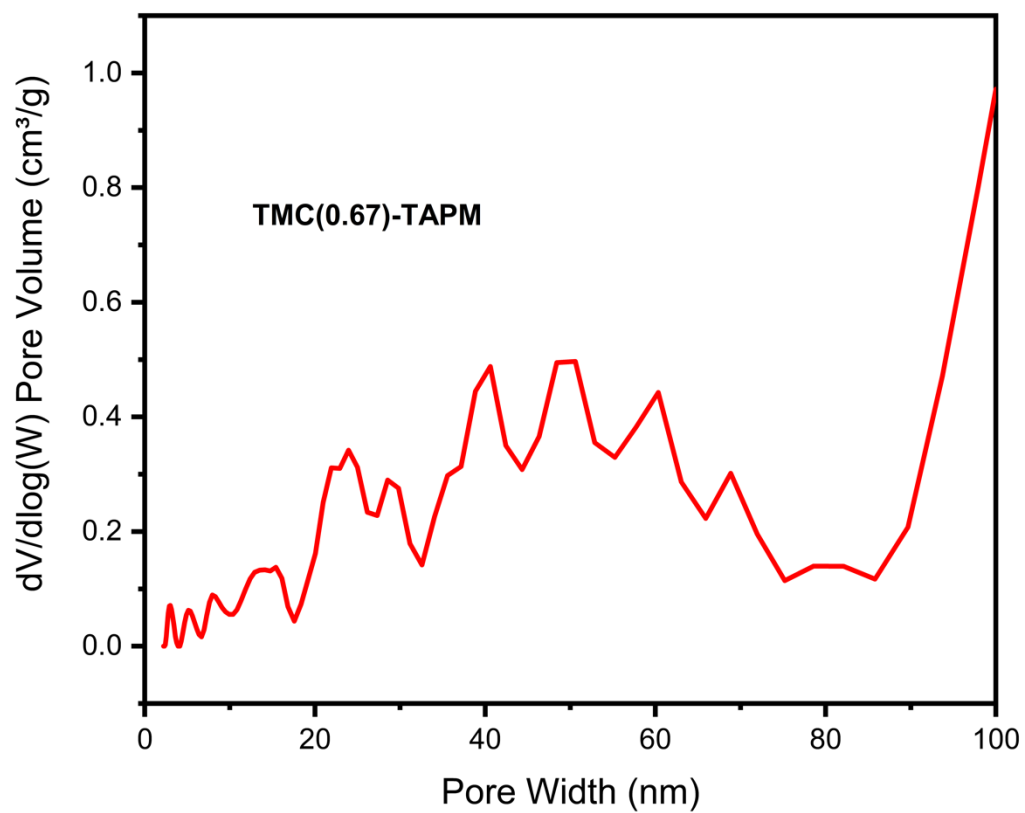


**Figure S6.**  $N_2$  adsorption isotherm at 77 K for TMC(1.75)-TAPM.

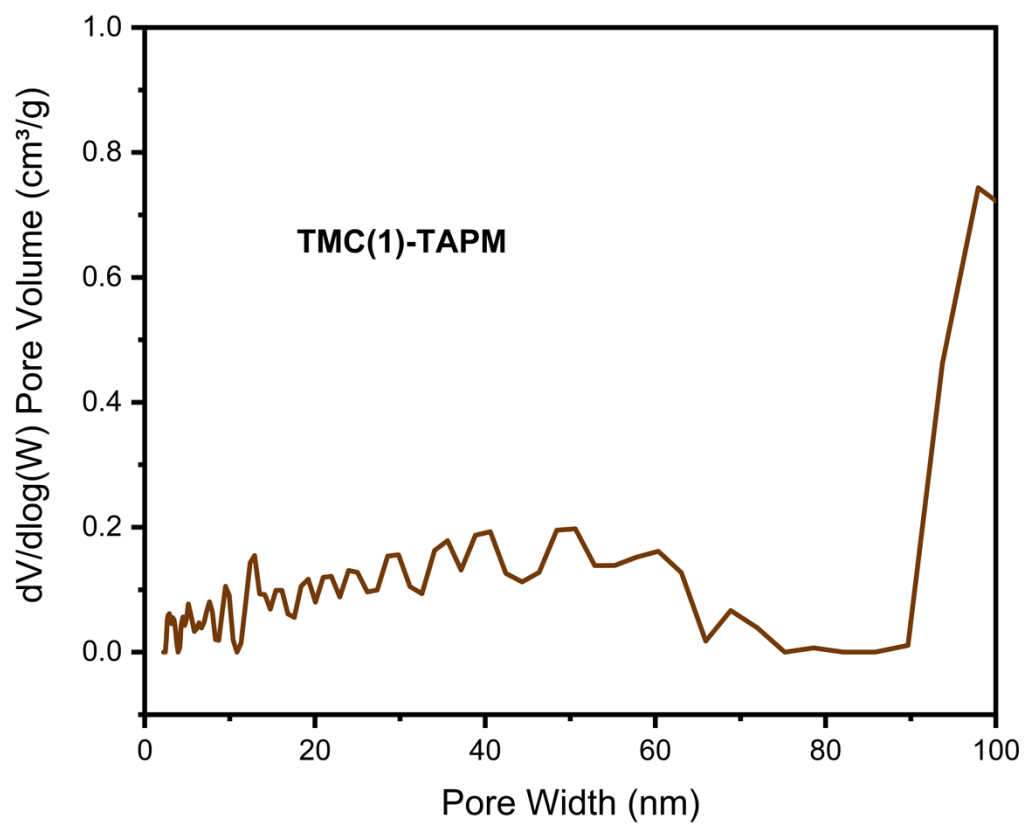




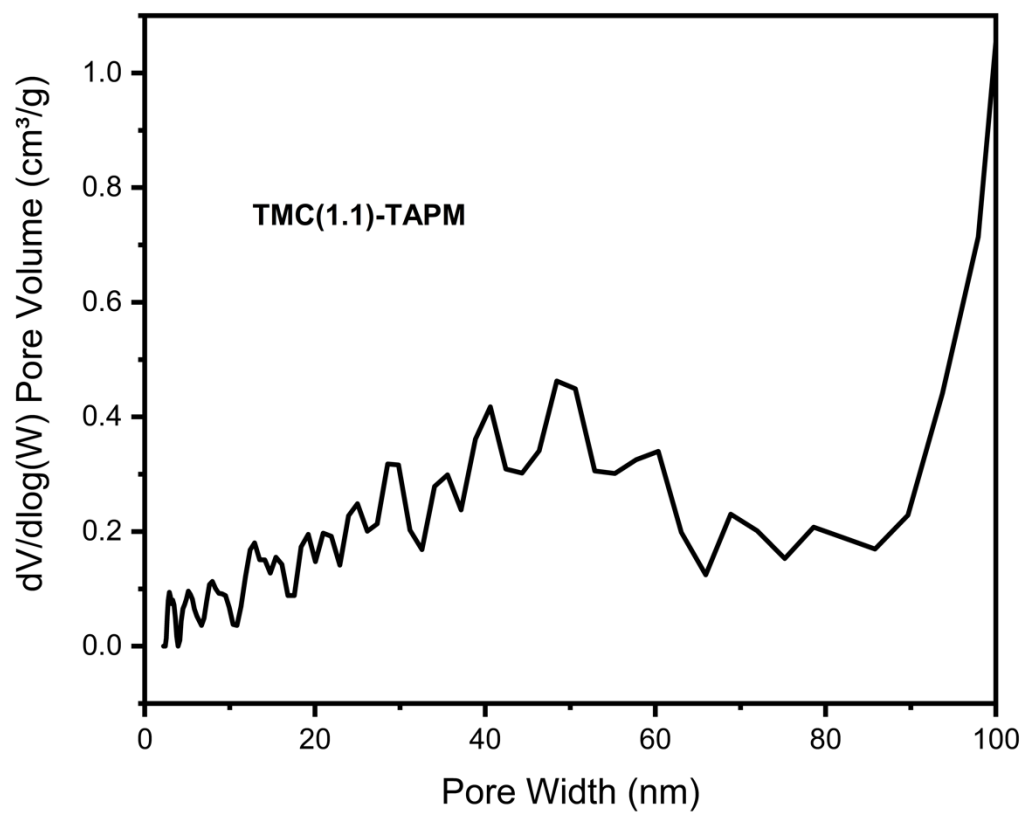
**Figure S7.**  $N_2$  adsorption isotherm at 77 K for TMC(2)-TAPM.



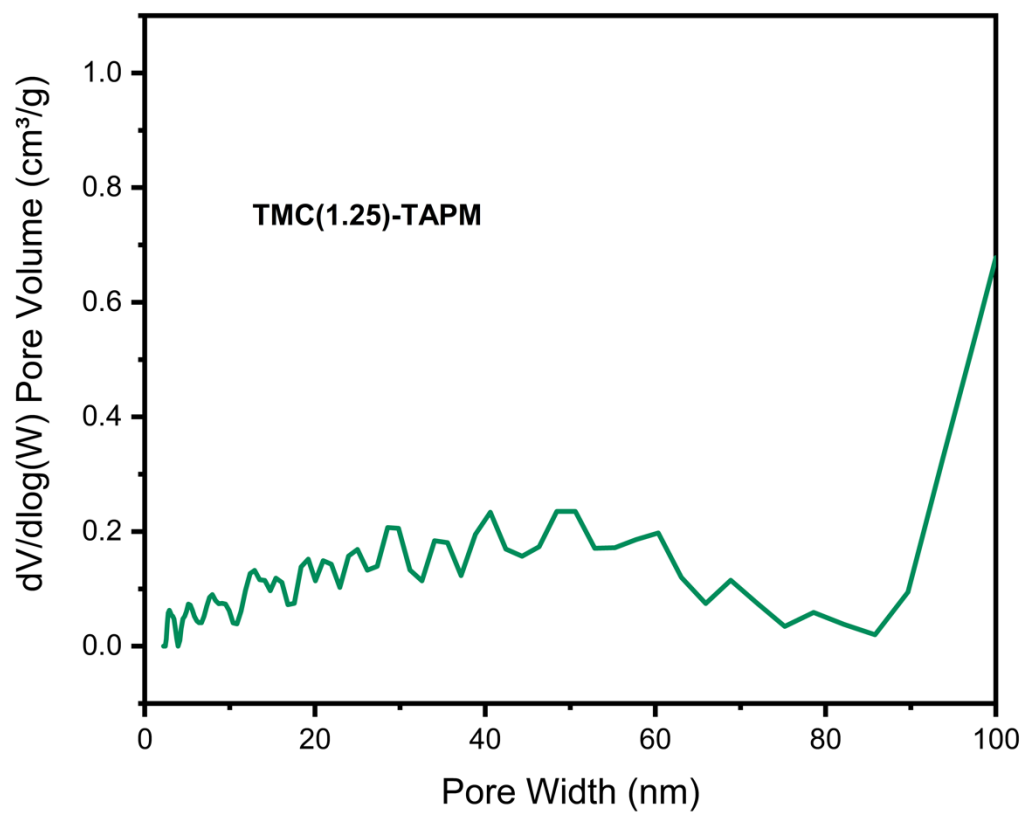
**Figure S8.** Pore size distribution for TMC(0.67)-TAPM.



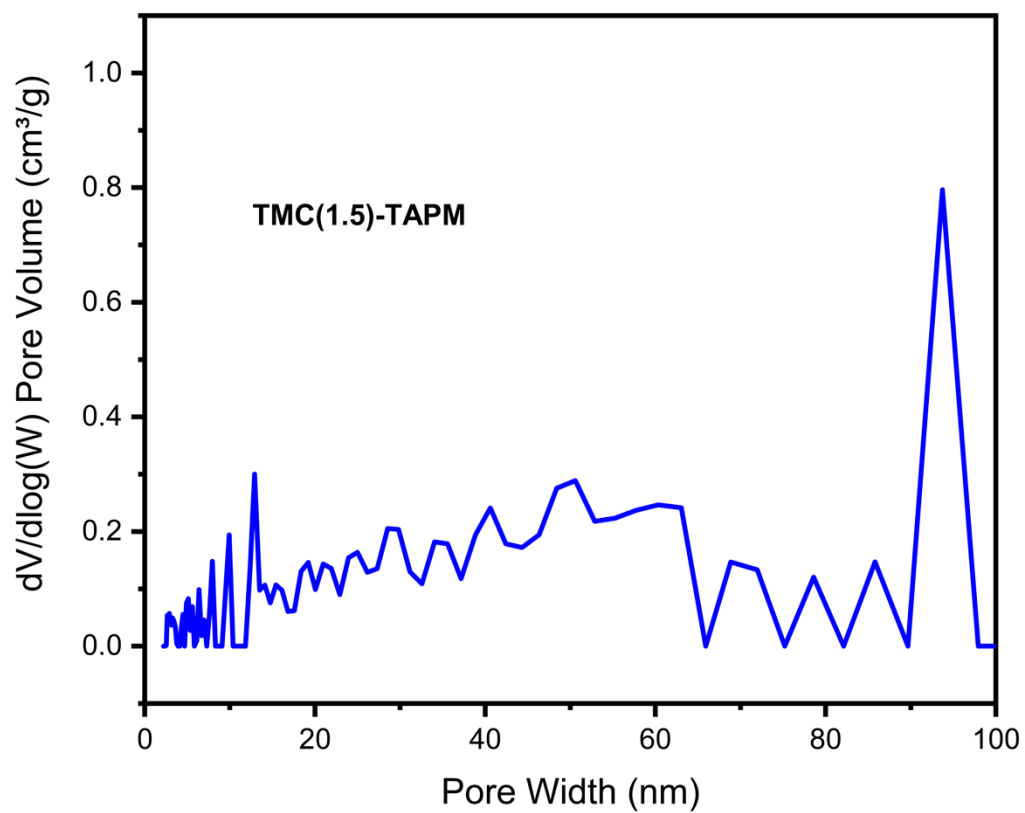
**Figure S9.** Pore size distribution for TMC(1)-TAPM.



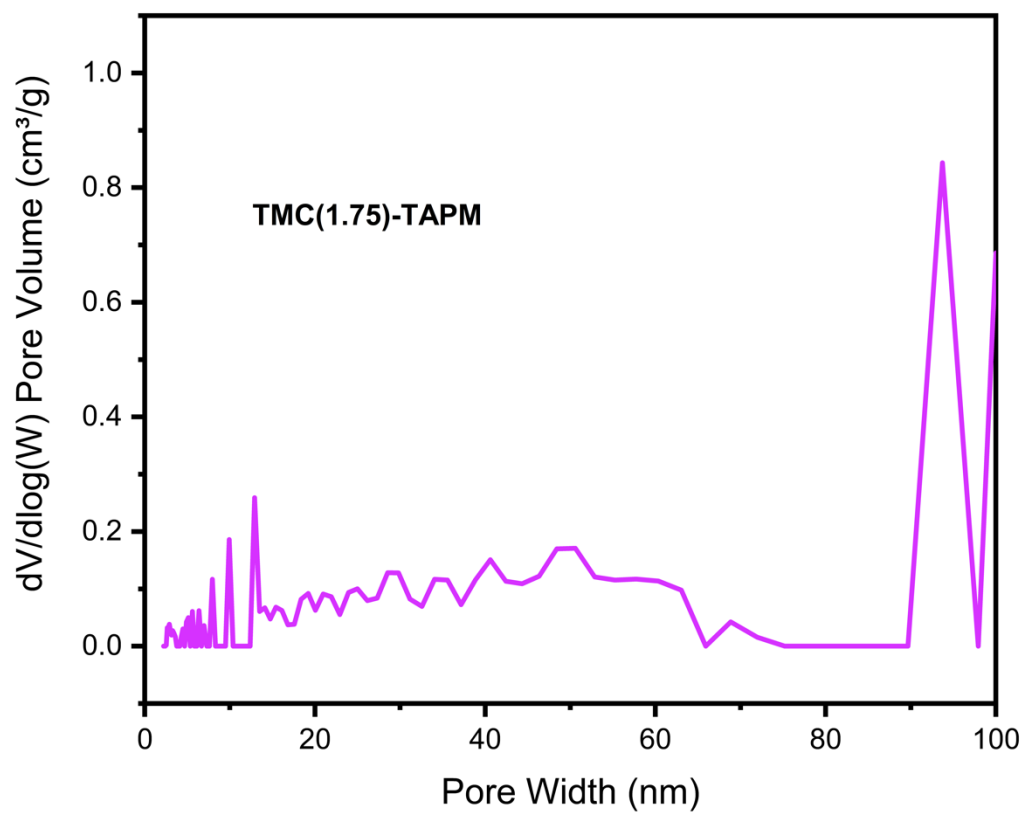
**Figure S10.** Pore size distribution for TMC(1.1)-TAPM.



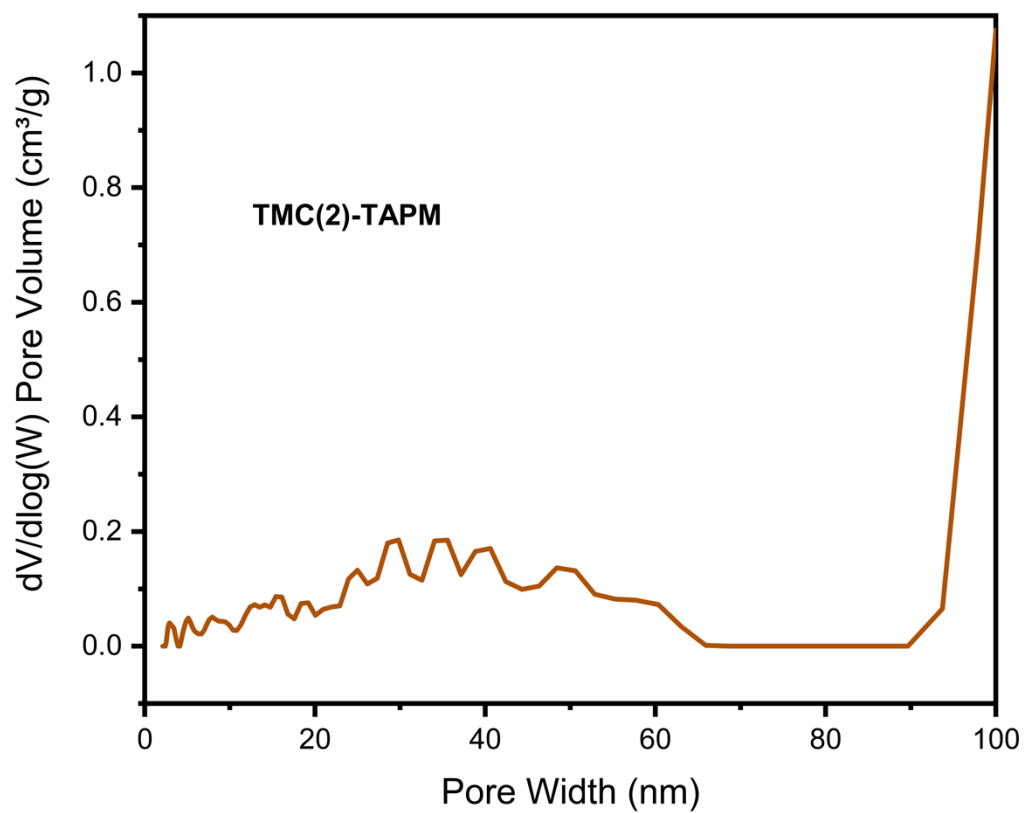
**Figure S11.** Pore size distribution for TMC(1.25)-TAPM.



**Figure S12.** Pore size distribution for TMC(1.5)-TAPM.

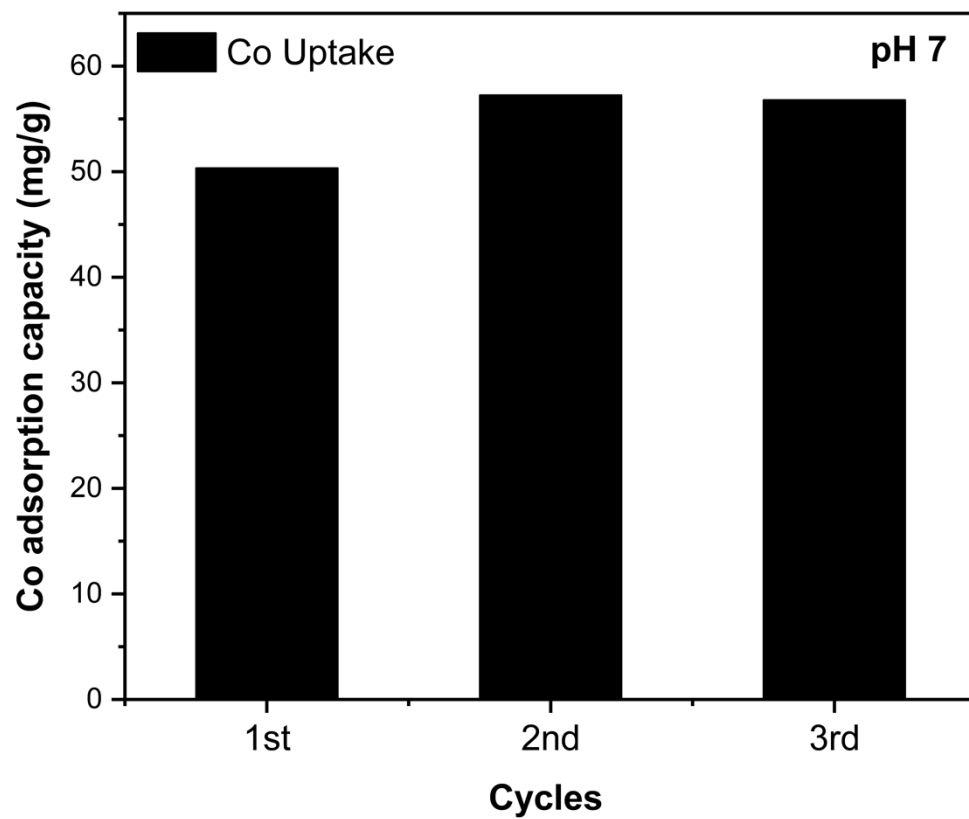


**Figure S13.** Pore size distribution for TMC(1.75)-TAPM.

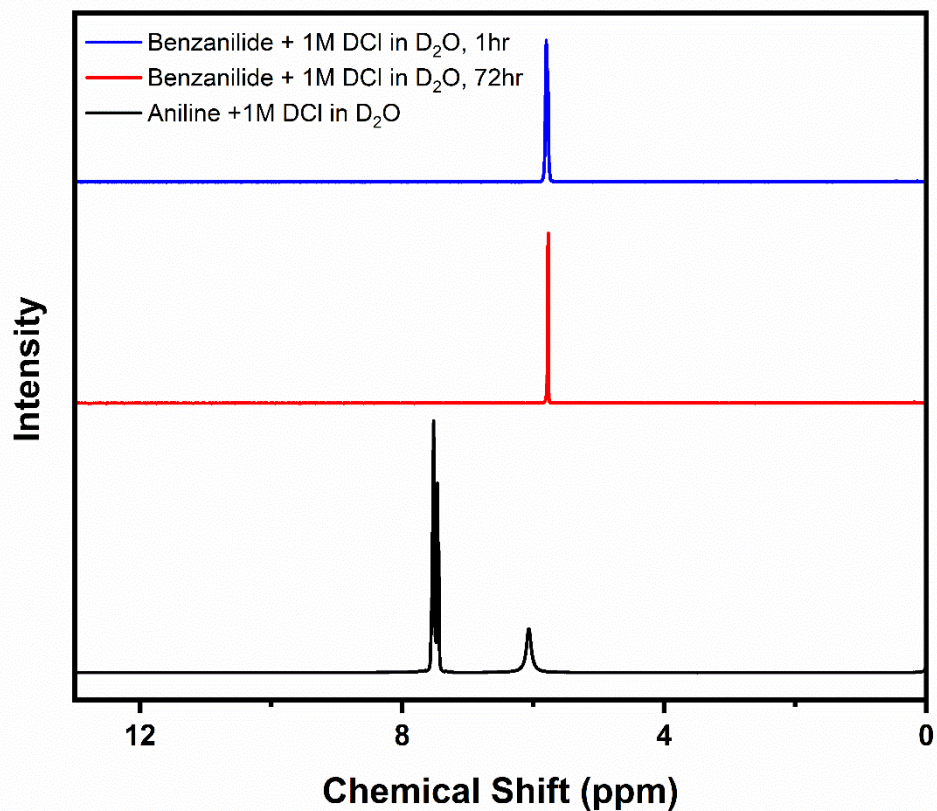


**Figure S14.** Pore size distribution for TMC(2)-TAPM.

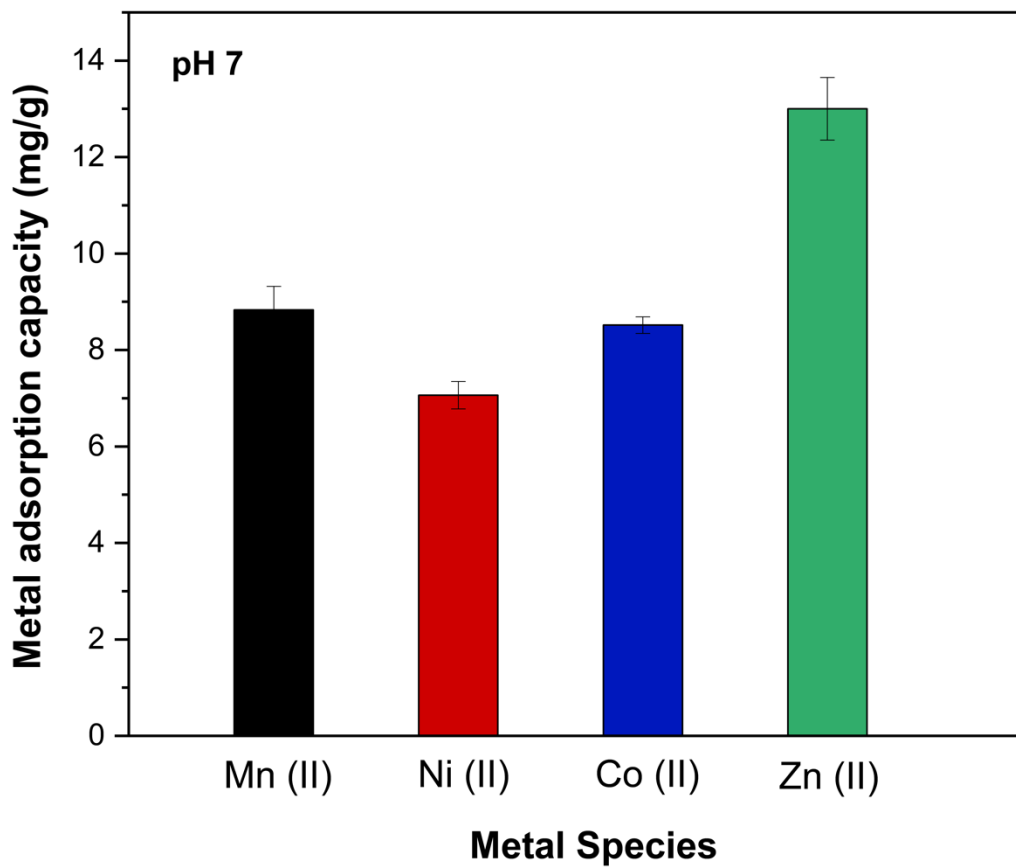




**Figure S15.** Cobalt adsorption cycles for TMC(1.75)-TAPM.



**Figure S16.** Hydrolytic stability testing for molecular analog (benzanilide). Benzanilide in 1 M DCl in D<sub>2</sub>O over 1 hour (blue spectrum) and 72 hours (red spectrum) showed no appearance of aniline (black spectrum) by <sup>1</sup>H NMR. The peak at ~5 ppm in all three spectra is the solvent peak.



**Figure S17.** Results of multicomponent adsorption experiments for TMC(1.5)-TAPM in a solution containing 40 ppm Mn(II), 40 ppm Ni(II), 40 ppm Co(II), and 40 ppm Zn(II).

## References

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