Supplementary Material for Chemical Communications

A Chiral, Heterometallic Metal-Organic Framework Derived from a Tris(Chelate) Coordination Complex

Electronic Supplementary Information (ESI)

Drew L. Murphy,[a] Mitchell R. Malachowski,[b] Charles F. Campana,[c] and Seth M. Cohen*[a]

[a] *Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0358, U.S.A. Fax: 858-822-5598; Tel: 858-822-5596; E-mail: scohen@ucsd.edu*

[b] *Department of Chemistry, University of San Diego, San Diego, California 92110-2492, U.S.A. Fax: 619-260-2211; Tel: 619-260-4032; E-mail: malachow@SanDiego.edu*

[c] *Single Crystal X-Ray Diffraction, Bruker AXS Inc., Madison, Wisconsin 53711-5373, U.S.A. Fax: 608-276-3006; Tel: 608-276-3042; E-mail: Charles.Campana@bruker-axs.com*

Synthesis

Tris**(5-(4'-cyanophenyl)-4,6-dipyrrinato)cobalt(III) ([Co(4-cydpm)$_3$]):** In a 500 mL round bottom flask, 1.4 g (5.69 mmol) of 5-(4'-cyanophenyl)dipyrromethane (P. D. Rao, S. Dhanalekshmi, B. J. Littler, J. S. Lindsey, *J. Org. Chem.* **2000**, *65*, 7323) was dissolved in 250 mL of chloroform. The resulting pale yellow solution was cooled over ice and stirred vigorously. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 1.37 g, 6.04 mmol) was dissolved in 250 mL benzene and added dropwise slowly via an addition funnel to the dipyrromethane solution over a period of ~2.0 h during which time the solution became intensely orange colored and then black. Once the addition was complete, the solution was stirred an additional 15 min and then the mixture was evaporated to dryness. The resulting dark brown powder was dissolved in 150 mL of acetonitrile. $Na_3Co(NO_2)_6$ (768 mg, 1.90 mmol) dissolved in 20 mL of water was added, followed by approximately 1 mL of triethylamine. The solution was heated to reflux (74 $^{\circ}$C) for 16 h. The resulting red/brown solution was evaporated to half the original volume, dried with $MgSO_4$, filtered, and the remaining solution was purified by column chromatography (SiO_2/CH_2Cl_2). The fractions containing the desired cobalt(III) complex (as determined by TLC), were combined and evaporated to dryness to get a dark solid. The solid was dissolved in 100 mL acetonitrile followed by addition of ~100 mL of hexanes to precipitate the desired product. The precipitate was isolated by vacuum filtration and rinsed with an additional ~100 mL of hexanes. Yield: 1.0 g (67%). ^{1}H NMR (400 MHz, acetone-d_6, 25 $^{\circ}$C): δ 7.95 (d, 6H, J = 8.0 Hz), 7.68 (d, 6H, J = 8.0 Hz), 6.69 (dd, 6H, J = 4.6, 1.2 Hz), 6.51 (m, 6H), 6.44 (dd, 6H, J = 4.4, 1.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25 $^{\circ}$C): δ 152.5, 143.6, 142.4, 134.9, 132.8, 131.3, 131.0, 119.5, 118.4, 112.6. APCI-MS: *m/z* 791.88 $[CoL_3+H]^+$, 547.22 $[CoL_2]^+$. HR-EIMS Calcd. for $C_{48}H_{30}N_9Co$: 791.1951. Found: 791.1956. UV-Vis (CH_2Cl_2, nm [log ε]): λ_{max} = 232 [4.9], 236 [4.9], 247 [4.4], 266 [4.4], 306 [4.4], 401 [4.2], 470 [4.7], 508 [4.6]. IR (KBr pellet): ν 2955, 2923, 2361, 2338, 2230, 1560, 1411, 1380, 1346, 1248, 1207, 1043, 1031, 998, 889, 814, 771, 728, 715 cm^{-1}.

$[Co(4\text{-cydpm})_3Ag(OTf)]$ (MOF-Co/AgOTf-2): Equal volumes of a 2.3 mM solution of $[Co(4\text{-cydpm})_3]$ in benzene were mixed with a 2.3 mM solution of $[Ag(O_3SCF_3)]$ in benzene. Reaction mixtures with total volumes of 4 mL containing 0.29 – 1.17 mM of the reactants were placed in loosely capped vials and were protected from light with aluminum foil. Slow evaporation of the reaction mixtures resulted in the formation of deep red crystals of $[Co(4\text{-cydpm})_3AgOTF]$. Thermal analysis (TGA) indicated the crystals were stable up to ~350 °C. IR (KBr pellet): ν 2931, 2847, 2358, 2333, 2225, 1563, 1380, 1346, 1252, 1203, 1030, 995, 886, 813, 768, 719, 635 cm^{-1}.

Guest Uptake/Exchange

Polycrystalline material of MOF-Co/AgOTf-2 was grown from benzene solutions of $[Co(4\text{-cydpm})_3]$ and $[Ag(O_3SCF_3)]$ (2.44 mM in each component). The material grew as clusters of dark red cubes, which were isolated from the mother liquor via vacuum filtration. The material was rinsed with 4-8 mL of ice-cold benzene-d_6 until the filter paper appeared visually dry (~1-2 min). These fresh samples were then used either as prepared or the encapsulated benzene was removed via drying in a vacuum oven at 60-75 °C for 12-15 h, which generates desolvated MOF-Co/AgOTf-2 (Figure S4). Both fresh and desolvated MOF-Co/AgOTf-2 samples were used in guest uptake studies.

In one set of experiments, fresh crystals of MOF-Co/AgOTf-2 samples were immersed in 1.0 mL of benzene-d_6 for 3.0 h at room temperature, with the benzene-d_6 solution changed every hour. The samples were then vacuum filtered and the solids were washed with 4.0 mL of ice-cold benzene-d_6. The crystalline solids were vacuum filtered until the filter paper appeared visually dry (~1-2 min). The samples were then dissolved in acetone-d_6. The resulting solution was portioned into three NMR tubes, and ^{1}H-NMR spectra were collected. The amount of benzene remaining in the framework was calculated from the integrated intensities of the respective benzene and [Co(4-cydpm)$_3$] ^{1}H-NMR signals and averaged over the three samples. These experiments demonstrated that ~80% of the benzene present in the crystals was readily exchanged with benzene-d_6 under these conditions.

MOF-Co/AgOTf-2 samples were immersed in 1.0 mL of neat aromatic guest for 1.0 h at room temperature with gentle agitation every 15-20 min. The samples were then vacuum filtered and the solids were washed with 3-5 mL of the guest solvent, followed by 4.0 mL of ice-cold benzene-d_6. The crystalline solids were vacuum filtered until the filter paper appeared visually dry (~1-2 min). The samples were then dissolved in acetone-d_6. The resulting solution was portioned into three NMR tubes, and ^{1}H-NMR spectra were collected. The ratios of aromatic guests to [Co(4-cydpm)$_3$] were calculated from the integrated intensities of their respective ^{1}H-NMR signals and averaged over the three samples (Figure S5).

X-Ray Crystallographic Analysis

Single crystals suitable for X-ray diffraction structural determination were mounted on nylon loops using Paratone oil and were cooled in a nitrogen stream on the diffractometer. Data were collected on a Bruker AXS diffractometer equipped with an area detector. Peak integrations were performed with the Siemens SAINT software package. Space group determinations were performed by the program XPREP. The structures were solved by direct methods and refined with the SHELXTL software package. Crystallographic details can be found in Table S1.

Structure of [Co(4-cydpm)$_3$]. Red plates of [Co(4-cydpm)$_3$] suitable for X-ray diffraction structural determination were grown by slow diffusion of pentane into a chloroform solution of the complex. There are two unique molecules of [Co(4-cydpm)$_3$] present in the asymmetric unit along with two co-crystallized molecules of chloroform.

Structure of [Co(4-cydpm)$_3$AgOTf] (MOF-Co/AgOTf-2). Orange-red blocks of [Co(4-pyrdpm)$_3$AgOTf] suitable for X-ray diffraction structural determination were grown from evaporation of a solution of [Co(4-cydpm)$_3$] and AgOTf dissolved in benzene. The structure was originally solved in the chiral space group *F*23; however, utilization of the program ADDSYM (A. Spek, Platon Library) identified *F*432 as the space group with which the refinement would be completed. The primary network, including the 4-cydpm ligand and the cobalt(III) and silver(I) ions, was well ordered and refined anisotropically. A substantial amount of highly disordered, residual electron density was observed, comprised of the triflate counterions and benzene solvent molecules, which was confirmed by several independent experiments (see main text). The triflate counter ions are likely coordinated to the silver(I) centers as evidenced by a large, disordered amount of electron density in the expected apical position of the trigonal pyramidal coordination sphere of the silver(I) ion (Figure S1). All of the disordered electron density was treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). Electron count/unit cell: 5580 (found). The presence of 32 triflate counter ions accounts for 2336 electrons/unit cell. A total of 77 benzene molecules/unit cell (~2.5 benzene molecules per cobalt monomer, in good agreement with ^{1}H NMR data) accounts for an additional 3234 electrons/unit cell, giving a total expected electron counts/unit cell of 5570 in excellent agreement with the SQUEEZE refinement.

Table S1. X-ray structure data for complexes [Co(4-cydpm)$_3$] and MOF-Co/AgOTf-2.

	[Co(4-cydpm)$_3$]	MOF-Co/AgOTf-2
Empirical Formula	$C_{48}H_{30}Cl_{1.5}N_9Co$	$C_{63.44}H_{44.44}N_9O_3F_3SCoAg$
Crystal System	Triclinic	Cubic
Space Group	P-1	F432
Unit Cell dimensions (Å, degrees)	a = 14.8303(8) b = 16.3535(8) c = 20.0347(10) α = 72.6680(10) β = 68.7730(10) γ = 72.6340(10)	a = 34.7494(14) b = 34.7494(14) c = 34.7494(14) α = 90 β = 90 γ = 90
Volume (Å^3), Z	4223.3(4), 4	41961(3), 32
Crystal size (mm^3)	0.35×0.30×0.15	0.40×0.39×0.18
Temperature (K)	100(2)	100(2)
Data/restraints/ parameters	18461/0/1117	4039/0/180
Goodness-of-fit on F^2	1.025	1.120
Final R indices I>2σ(I) [a]	$R1$ = 0.0682 $wR2$ = 0.1821	$R1$ = 0.0838 $wR2$ = 0.2272
R indices (all data) [a]	$R1$ = 0.0899 $wR2$ = 0.1982	$R1$ = 0.0896 $wR2$ = 0.2320
Largest diff. peak and hole	2.354 and -1.568 e Å^{-3}	2.271 and -1.737 e Å^{-3}

[a] $R_1 = \sum \left\| F_o \right| - \left| F_c \right\| / \sum \left| F_o \right|$, . $R_2 = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^4] \right\}^{1/2}$

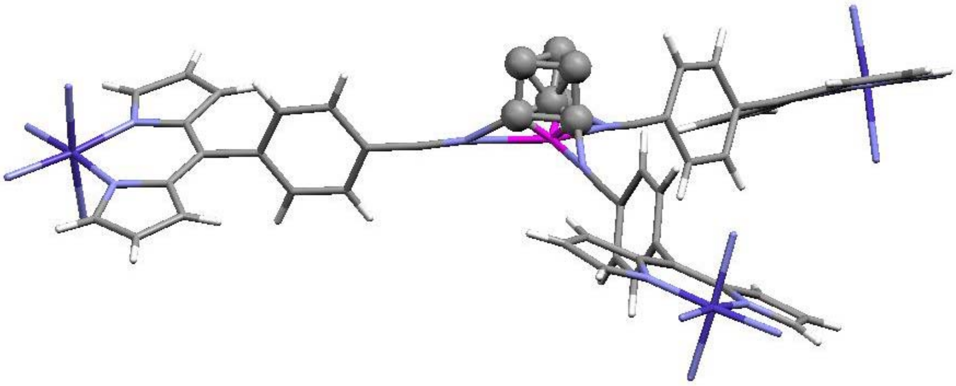

Figure S1. Figure of residual electron density in the structure of MOF-Co/AgOTf-2. Shown as spheres, the residual electron density in the crystal structure of MOF-Co/AgOTf-2 (after application of the program SQUEEZE) is located in the apical position of the silver(I) ions. This residual density is ascribed to the missing (highly disordered) triflate counterions that are in the MOF as required by charge balance and observed by IR and ^{19}F NMR spectroscopy.

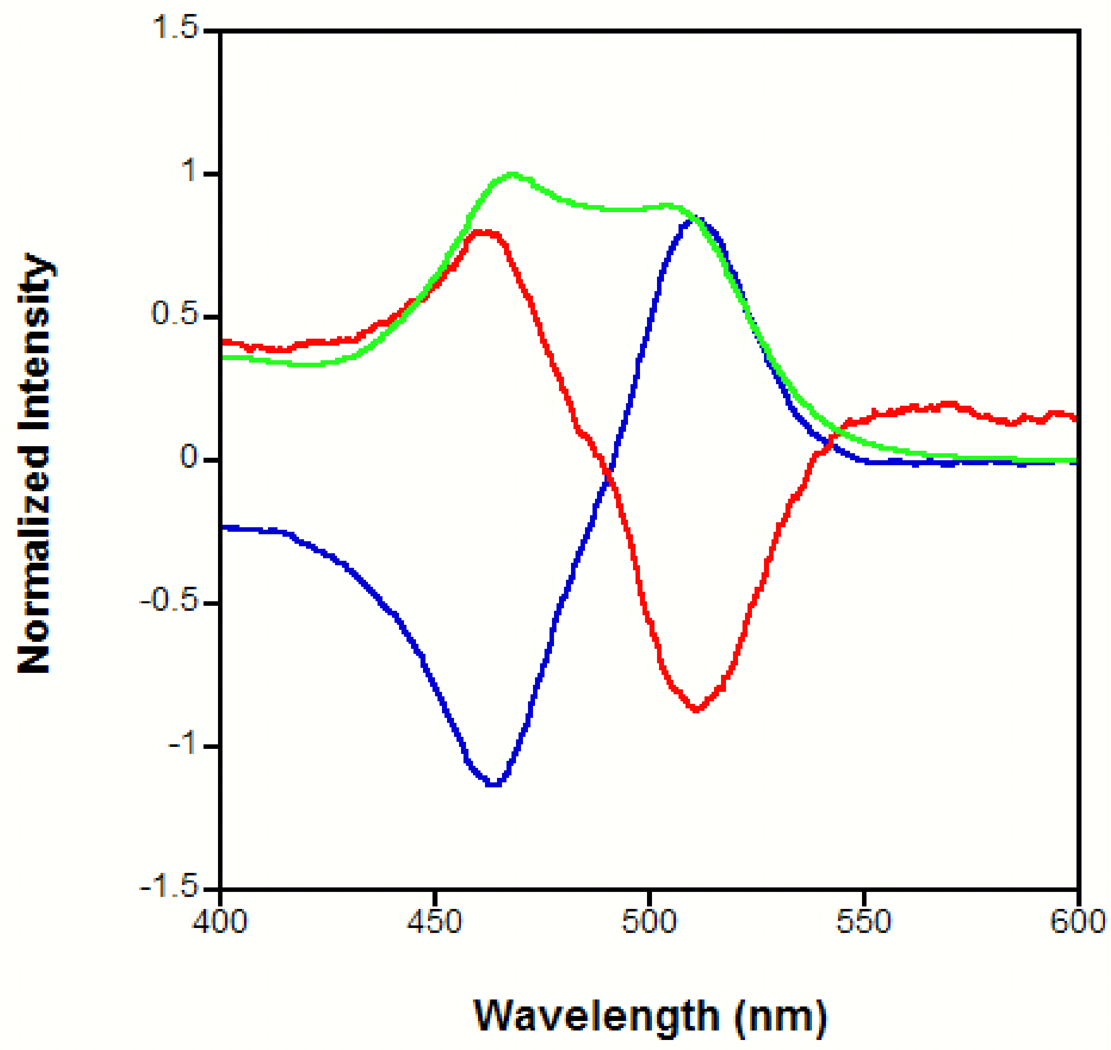

Figure S2. Normalized circular dichroism (CD) spectra of two samples of MOF-Co/AgOTf-2 (blue and red lines) and overlaid absorbance spectrum of [Co(4-cydpm)$_3$] (green line). All spectra were acquired in acetonitrile.

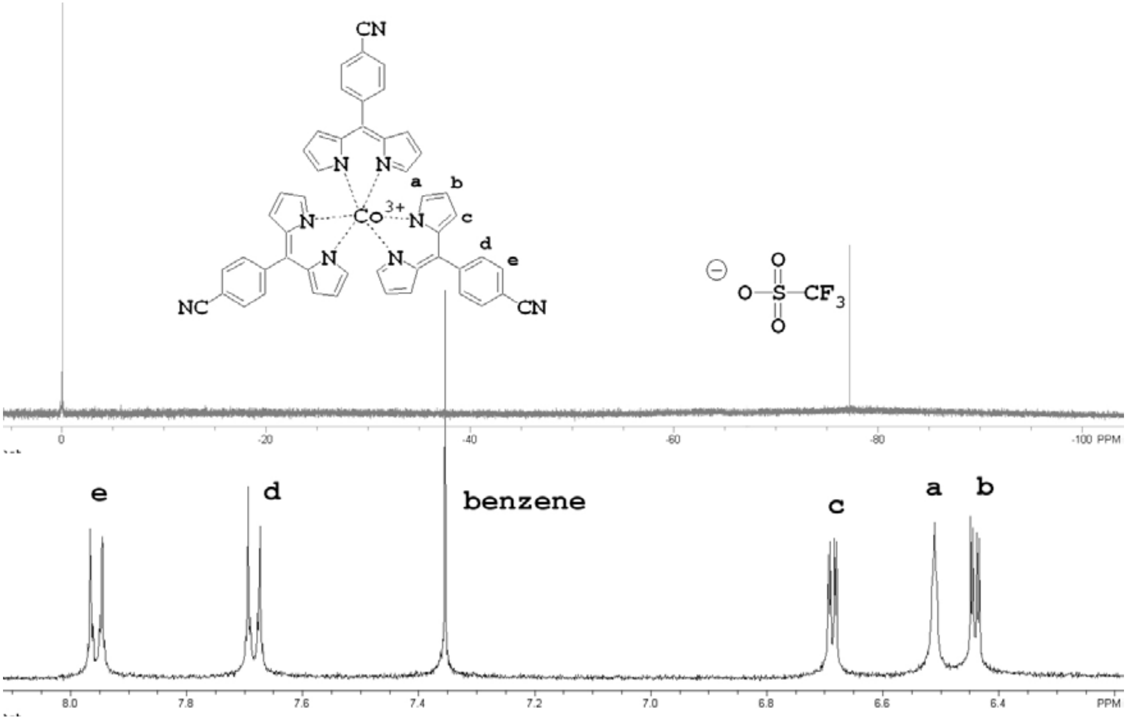

Figure S3. ^{19}F NMR (top) and ^{1}H NMR (bottom) of MOF-Co/AgOTf-2 dissolved in acetone-*d*$_6$. Crystals of MOF-Co/AgOTf-2 were isolated, washed with cold benzene, and then dissolved in acetone-*d*$_6$. A single fluorine peak at -77.8 ppm is observed, which is the same to that found for AgOTf under identical conditions.

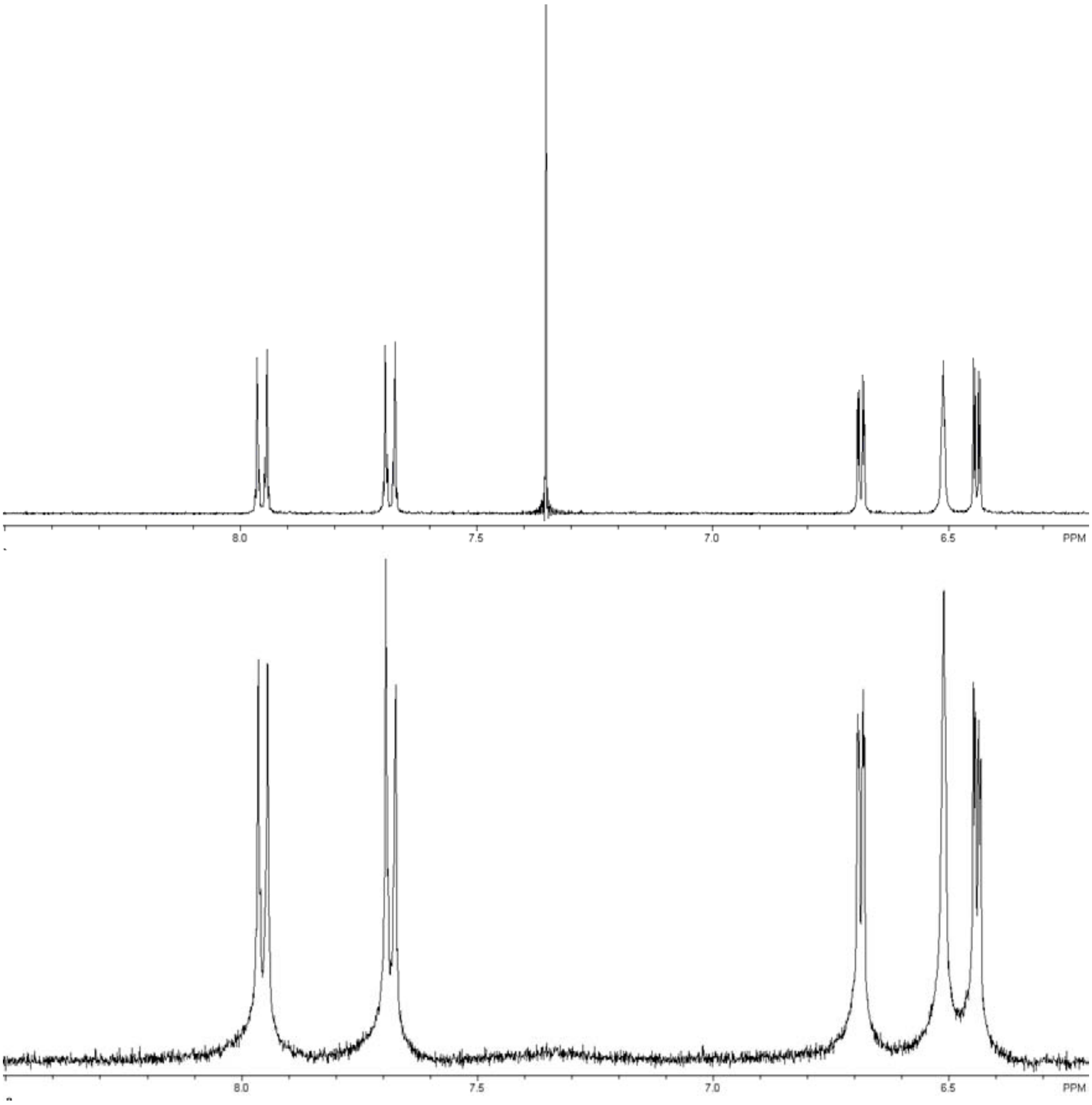

Figure S4. ^{1}H NMR spectra of fresh (top) and vacuum oven dried (bottom) crystals of MOF-Co/AgOTf-2 after dissolution in acetone-d_6. Note the complete removal of encapsulated benzene upon drying. Peak assignments are shown in Figure S3.

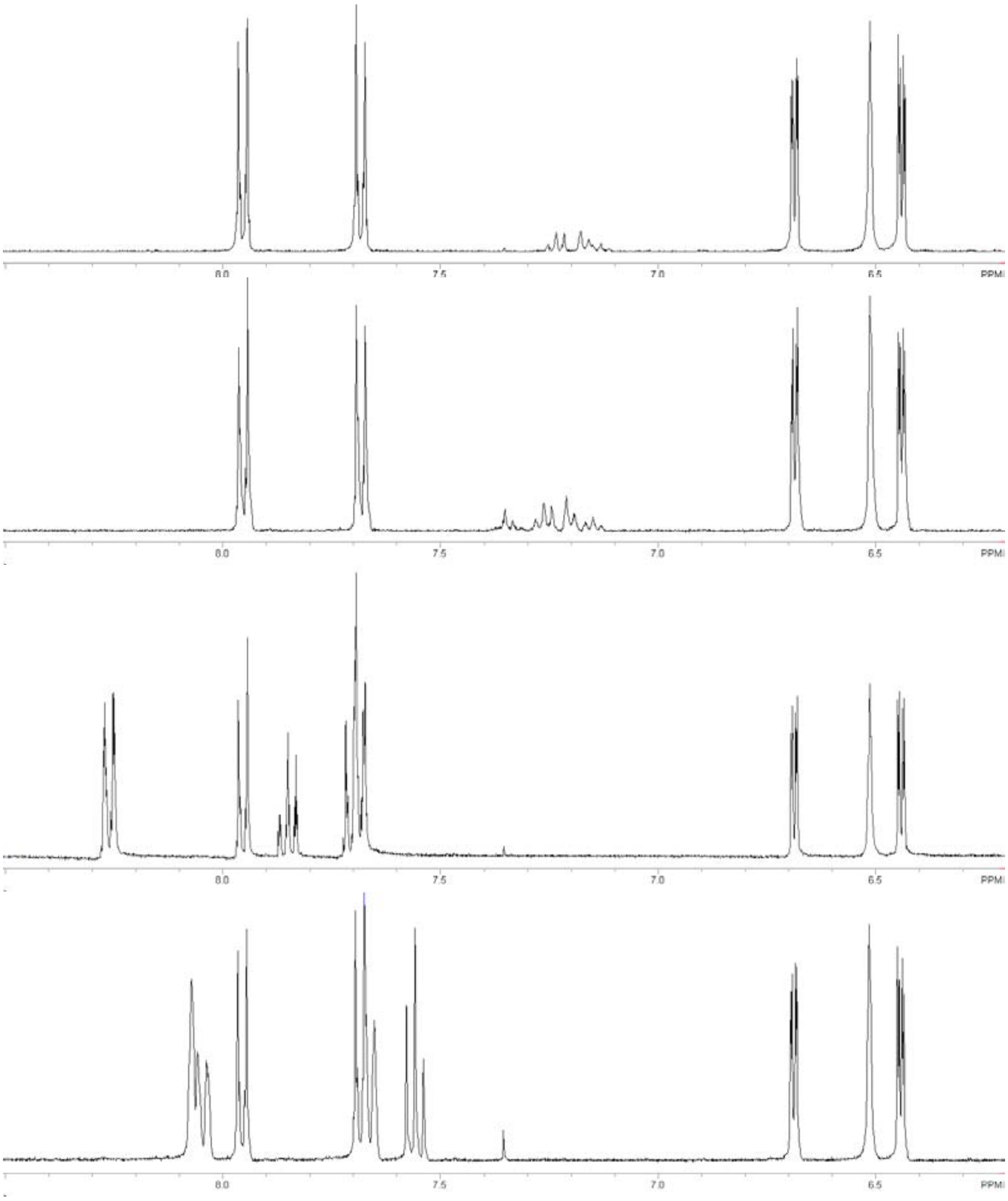

Figure S5. ^{1}H NMR spectra of crystals of MOF-Co/AgOTf-2 (dissolved in acetone-d_6) after exposure to (from top to bottom): toluene, ethylbenzene, nitrobenzene, and *m*-nitrotoluene. Extent of solvent uptake was determined by the relative integration of guest to [Co(4-cydpm)$_3$] peaks. Peak assignments are as shown in Figure S3.