Topological Control in Heterometallic Metal-Organic Frameworks by Anion Templating and Metalloligand Design

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Crystallographic Details

MOF-Co/AgBF$_4$-1. The asymmetric unit contains 2 formula units and 2 disordered BF$_4^-$ anions in general positions. The anions were restrained to approximately tetrahedral geometry, and the sum of the occupancies for each anion was constrained to unity. The major positions refined to occupancies of 58.4(8) % and 51.1(1) %. The anions were left isotropic. The crystal was twinned by rotation about the 1 0 0 direct lattice direction. Twin law: 1 0 0 0 -1 0 0 0 -1; BASF refined to 2.31(6)%. The structure included disordered acetonitrile and benzene solvent molecules. Satisfactory atomic positions could not be identified, so the disordered solvent was treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 4647.3 Å^3 void space per unit cell and 996.8 electrons; 13 molecules of acetonitrile and 17 molecules of benzene require 1000 electrons per unit cell.

MOF-Fe/AgOTf-1. There are three [Fe(4-pyrdpm)$_3$][AgOTf] formula units per asymmetric unit, giving Z' = 3 for the main residue. The asymmetric unit includes two half Fe(dipyrrin) complexes with Fe atoms (Fe3 and Fe4) on special positions (50% occupancy) and two Ag atoms (Ag3 and Ag4) on special positions (50% occupancy). Other atoms in the main residues that reside on special positions at 50% occupancy include C103, C104, C125, C126, N23, and N24. The pyridyl group that includes C13 and C14 appears to be slightly disordered, but the data was not strong enough to resolve the disorder. The asymmetric unit also includes two full acetonitrile molecules and four full benzene molecules, as well as half of a benzene molecule with two atoms (C160 and C163) on special positions (50% occupancy). An additional benzene molecule was detected, but was partially occupied and disordered. This disordered solvent was treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 1906.9 Å^3 void space per unit cell and 165 electrons; 4 molecules of benzene require 168 electrons per unit cell. The crystal diffracted very poorly, which led to a high R_{int} of 0.150.

MOF-FeCo/AgBF₄-1. The BF_4^- anion is disordered. This anion was modeled as having two positions with assumed 50 % occupancy for each F atom. The disorder was too great to refine the occupancies. Each part was restrained to approximately tetrahedral geometry. Only one [M(4-pyrdpm)₃] complex was found. On the basis of spectroscopic data, the metal was set as Co1 and Fe1 sharing a position, with the occupancy of each set to 50%. The asymmetric unit thus contains 0.5 of a formula unit (Z' = 0.5). A benzene molecule and three acetonitrile molecules were detected, but were partially occupied and disordered. These solvent molecules were treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 4208.4 Å^3 void space per cell and 1027 electrons; 30 molecules of acetonitrile and 10 molecules of benzene require 1080 electrons per unit cell.

MOF-FeCo/AgOTf-1. The triflate anion is disordered over two independent positions, with the S atoms sharing a position. The two orientations were constrained to a total occupancy of 1. The major orientation refined to an occupancy of 65.8(5)%. Only one [M(4-pyrdpm)₃] complex was found. On the basis of spectroscopic data, the metal was set as Co1 and Fe1 sharing a position, with the occupancy of each set to 50%. The asymmetric unit thus contained 0.5 of a formula unit (Z' = 0.5). A benzene molecule and three acetonitrile molecules were detected, but were partially occupied and disordered. These solvent molecules were treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 4208.4 Å^3 void space per cell and 1101.7 electrons; 30 molecules of acetonitrile and 10 molecules of benzene require 1080 electrons per unit cell.

MOF-Co/AgPF₆-1. The asymmetric unit includes two half occupied PF_6^- anions. One anion resides on a special position for atom P1, and the other (containing atom P2) is disordered by proximity to a special position and shares its location with a benzene molecule having an assumed occupancy of 50%. Because of the anion/solvent disorder, the benzene molecule was treated as a rigid group. Additional partially occupied and/or disordered solvent molecules (benzene, acetonitrile) were also found, but

satisfactory atomic positions could not be determined. These disordered solvent molecules were treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 899.6 Å^3 void space per unit cell and 248.6 electrons; 4 molecules of acetonitrile and 2 molecules of benzene require 244 electrons per unit cell, giving 2 additional acetonitrile molecules and 1 additional benzene per formula unit.

MOF-Fe/AgPF$_6$-1. The asymmetric unit contains two independent PF$_6^-$ anions. One is situated on an inversion center with the P atom on the special position at 50% occupancy. The second anion is disordered by proximity to an inversion center, and was set to 50% occupancy. The asymmetric unit includes three disordered and partially occupied benzene molecules and seven disordered and partially occupied acetonitrile molecules. All of the partially occupied solvent molecules were set at 50% assumed occupancy. The H atoms for C58, C62, C72, and C74 of four acetonitrile molecules were not included because they could not be located in the difference map. Atom C61 is isotropic.

MOF-Co/AgSbF$_6$-1. One pyridyl ring had a two-fold disorder with 50% occupancy for atoms C39 to H46. The asymmetric unit includes three independent, partially occupied positions for the SbF$_6^-$ anions (Sb1, Sb2, and Sb3). Two anions, containing atoms Sb1 and Sb2, lie on special positions for the Sb atoms. The third, which includes atom Sb3, occupies a general position that is shared with a partially occupied benzene. The total occupancy of the Sb atoms refined to 96% after adjusting for special position occupancy. The final occupancies of the anions were set to 32%, 38%, and 30%, respectively, for a charge balance of one SbF$_6^-$ per formula unit. The asymmetric unit also includes an acetonitrile molecule and two benzene molecules; one of the latter is partially occupied and shares a position with a partially occupied anion. Additional acetonitrile molecules were observed in the electron density map, but satisfactory atomic positions could not be identified. These disordered solvent molecules were treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 998.4 Å^3 void space per unit cell and 216.2 electrons; 10 molecules of acetonitrile require

220 electrons per unit cell, giving 2.5 additional acetonitrile molecules per formula unit. All H atoms were located in a difference map, placed calculated positions and treated with a riding model, with the exception of the methyl group (C48 to H48C) of an acetonitrile solvent molecule, which was treated as a rigid group. The formula has non-integer C and H stoichiometry because of the partially occupied (70%) benzene molecule.

MOF-Fe/AgSbF$_6$-1. One pyridyl ring has a two-fold disorder with 59(3)% refined occupancy for the major orientation. The asymmetric unit includes three independent, partially occupied positions for the SbF$_6^-$ anions. These anions contain atoms Sb1, Sb2, and Sb3. Two anions were disordered over special positions, with the Sb atoms (Sb1 and Sb2) located on the special positions. These two anions had assumed relative occupancies of 50% for the disordered F atom positions. The third anion (Sb3) occupies a general position, which is shared with a partially occupied benzene. The total occupancy of the Sb atoms refined to 97% after adjusting for special position occupancy. The final occupancies of the anions were set to 38%, 26%, and 36%, respectively, for a charge balance of one SbF$_6^-$ per formula unit. Because of the anion disorder and partial occupancy, the anions were restrained to be approximately octahedral. The asymmetric unit also includes an acetonitrile molecule and two benzene molecules; one of the latter is partially occupied and shares a position with a partially occupied anion. Additional acetonitrile molecules were observed in the electron density map, but satisfactory atomic positions could not be identified. These additional, disordered solvent molecules were treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 846.5 Å^3 void space per unit cell and 182 electrons; 8 molecules of acetonitrile require 176 electrons per unit cell, giving 2 additional acetonitrile molecules per formula unit. All H atoms were placed in calculated positions and treated with a riding model, with the exception of the methyl group (C48 to H48C) of an acetonitrile solvent molecule, which was treated as a rigid group. A weak data set and the aforementioned disorder resulted in final R-values greater than 10%.

MOF-Co/Ag×BF$_4$-1. The structure contains a disordered BF$_4^-$ anion with two positions for three of the fluorine atoms. Atom F5 is isotropic. The major orientation refined to 62(2)%. The minor orientation was restrained to approximately tetrahedral geometry. The asymmetric unit contains disordered benzene and acetonitrile solvent molecules whose positions could not be satisfactorily determined. These solvent molecules were treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 4599.4 Å^3 void space per unit cell and 1129.0 electrons; 28 molecules of acetonitrile and 12 molecules of benzene require 1120 electrons per unit cell. Weak high angle diffraction led to an R_{int} of 0.1194.

MOF-Co/Ag×PF$_6$-1. The asymmetric unit contains a disordered PF$_6^-$ anion. The major orientation refined to 67.7(6)% occupancy. The asymmetric unit contains disordered and partially occupied solvent molecules (benzene and acetonitrile) whose positions could not be satisfactorily determined. These solvent molecules were treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 4678.2 Å^3 void space per unit cell and 970.3 electrons; 12 molecules of acetonitrile and 16 molecules of benzene require 936 electrons per unit cell.

[Co(4-quindpm)$_3$]. The asymmetric unit contains 1/3 of a [Co(4-quindpm)$_3$] molecule for a Z' = 1/3. A grossly disordered pentane molecule was also detected. This disordered molecule was treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 2636.8 Å^3 void space per unit cell and 511.3 electrons; 12 molecules of pentane require 504 electrons per unit cell.

[Fe(4-quindpm)$_3$]. The asymmetric unit contains 1/3 of a [Fe(4-quindpm)$_3$] molecule for a Z' = 1/3. A solvent region containing grossly disordered and partially occupied pentane and benzene molecules was also detected. The disordered solvent was treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 2597.6 Å^3 void space per unit cell and

544.7 electrons; 13 mixed molecules of pentane and benzene require 546 electrons per unit cell (42 el. per molecule).

MOF-Fe/AgOTf-3. One quinoline (with atom N5) is disordered with respect to a glide plane. The group was set at 50% occupancy and treated as a rigid group. The occupancies of N5 and C24 were left unchanged because they occupied special positions on the glide plane and were included in both orientations. Atoms C25 and C26 were generated from atoms C32 and C27, respectively, and are symmetry equivalents of the latter atoms. This manipulation was performed so that H atoms could be placed on the disordered quinoline. Atoms Ag1, Fe1, C23, C24 and N5 are located on special positions (glide plane), and have 50% occupancy by special position constraint. The crystal was of poor quality and had very weak high angle data. Thus, R_{int} was high (0.1179) and Ratio Observed/Unique Reflections was low (40%). As a result of the poor crystal quality, the positions of solvent molecules and triflate (OTf$^-$) anions could not reliably be determined. As such, the solvent and anions were treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 11357.3 Å^3 void space per unit cell and 3294.8 electrons; 16 OTf$^-$ anions, 32 benzene molecules, and 32 acetonirile molecules require 3216 electrons. Because the OTf$^-$ could not be located, the calculated density is low (< 1).

[Co(4-papyrdpm)$_3$]. The pyridyl group containing N15 has considerable thermal motion; however, independent disordered positions could not be found. The asymmetric unit contains two major residues, two hexane molecules, and a chloroform molecule. An additional chloroform was detected, but was grossly disordered and partially occupied. This additional chloroform was treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 378.3 Å^3 void space per unit cell and 87.3 electrons; 1.5 molecules of chloroform require 87 electrons per unit cell.

MOF-Co/AgOTf-4. The asymmetric unit includes 4 fully occupied benzene molecules and a fully occupied acetonitrile molecule. The acetonitrile molecule was treated as a rigid group. Additional partially occupied and disordered solvent molecules were detected, but acceptable atomic positions could not be determined. These partially occupied and disordered solvent molecules were treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 423.2 Å^3 void space per unit cell and 64 electrons; 1 molecule of acetonitrile and 1 molecule of benzene require 64 electrons per unit cell.

MOF-Co/AgBF$_4$-4. The structure contains a rotationally disordered BF_4^- anion. Two positions were located for atoms F2, F3, and F4. The major orientation has a refined occupancy of 65(2)%. The structure contains a disordered phenyl ring (C55, C56, C58, and 59). The major orientation had a refined occupancy of 64.1(7)%. The asymmetric unit includes a fully occupied benzene molecule and a fully occupied acetonitrile molecule. Four additional molecules of benzene and two additional molecules of acetonitrile were detected, but were partially occupied and disordered. These additional solvent molecules were treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 1171.9 Å^3 void space per cell and 424 electrons; 4 molecules of acetonitrile and 8 molecules of benzene require 424 electrons per unit cell.

MOF-Co/AgPF$_6$-4. The asymmetric unit includes four fully occupied and ordered benzene molecules. An additional benzene molecule and two acetonitrile molecules were detected, but were partially occupied and disordered. These additional solvent molecules were treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). SQUEEZE calculated 608.9 Å^3 void space per cell and 176.4 electrons; 4 molecules of acetonitrile and 2 molecules of benzene require 424 electrons per unit cell. Residual electron density in the vicinity of Co1 and Ag1 results from a truncation error.
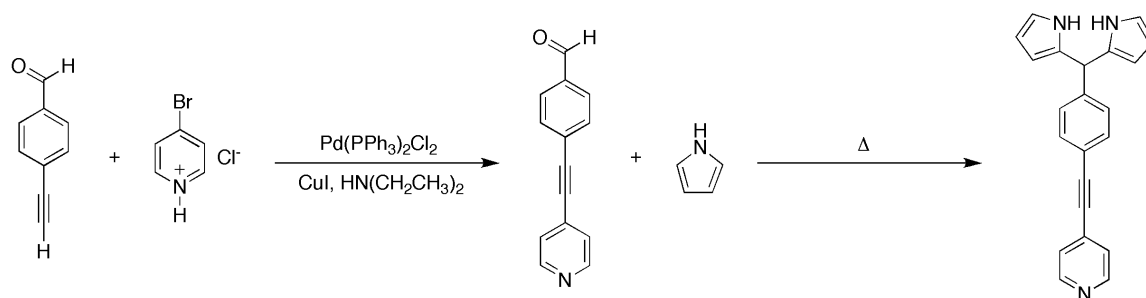
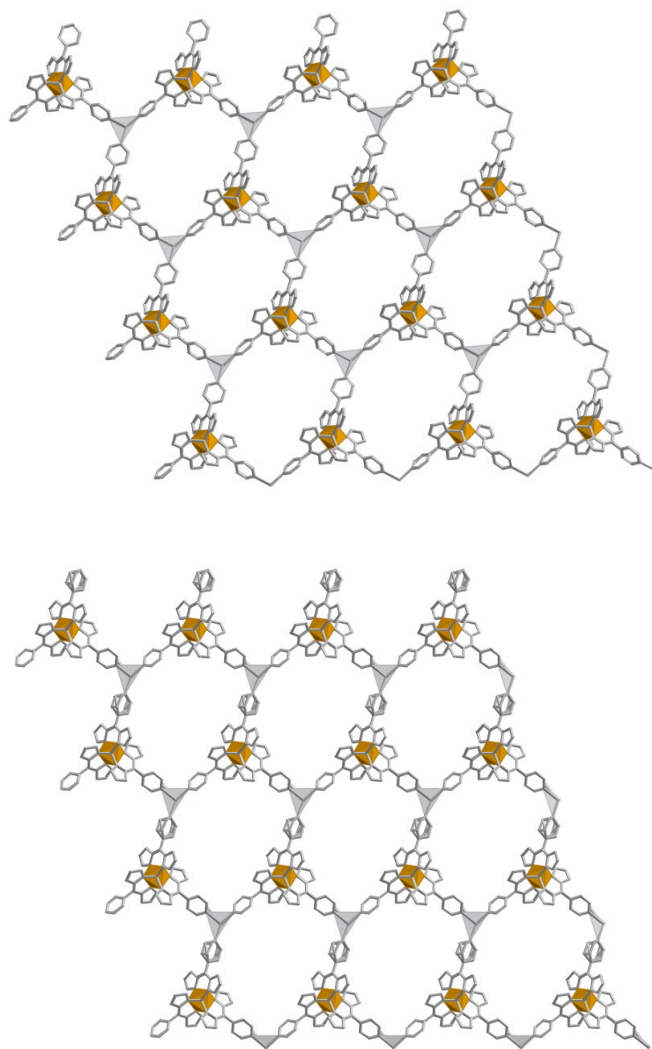**Scheme S1.** Synthesis of 5-(4-pyridin-4-ylethynylphenyl)dipyrromethane (precursor to the 4-papyrdpm ligand).

Figure S1. X-ray structure of (6,3) nets MOF-Fe/AgPF$_6$-1 (top) and MOF-Co/AgSbF$_6$-1 (bottom). Iron(III) and silver(I) centers are represented by gold and gray polyhedra, respectively. MOF-Fe/AgPF$_6$-1 is viewed along the crystallographic *a*-axis and MOF-Fe/AgSbF$_6$-1 (some disorder shown) is viewed along the crystallographic *b*-axis. Hydrogen atoms, anions, and solvent molecules have been omitted for clarity.
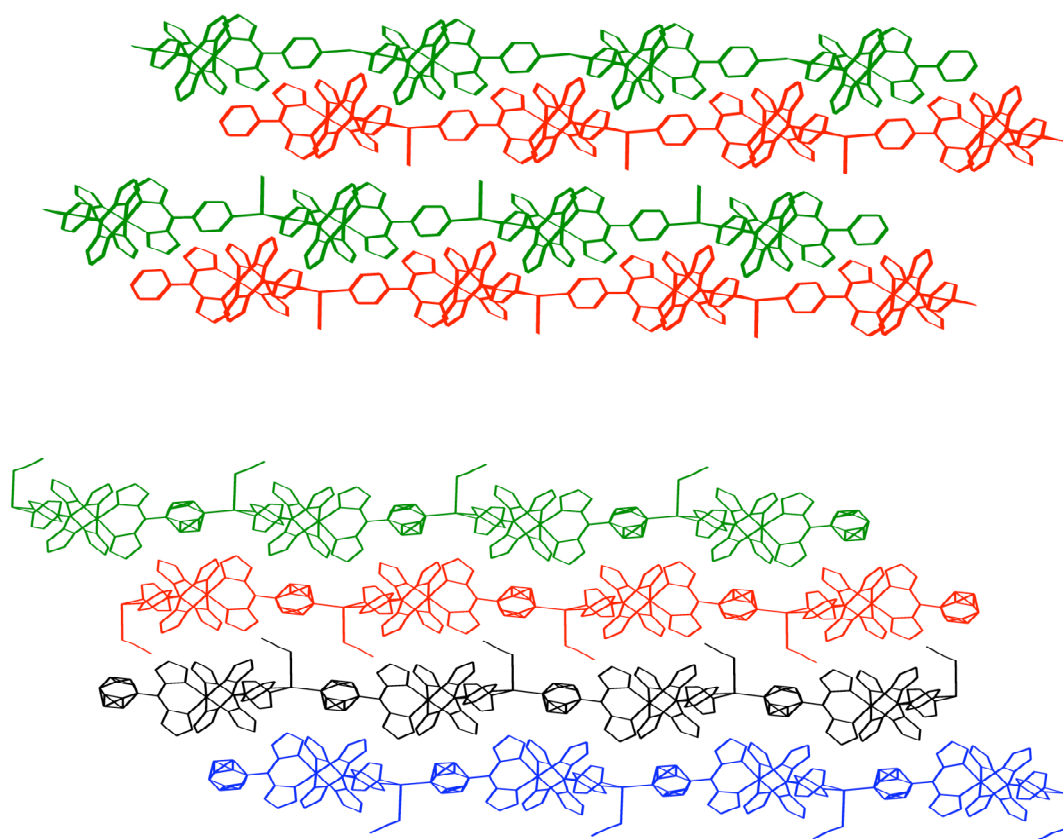
Figure S2. Structural diagram of the 2-dimensional (6,3) nets MOF-Fe/AgPF$_6$-1 (top) and MOF-Fe/AgSbF$_6$-1 (bottom) colored to emphasize the *AB* and *ABCD* layered structures, respectively. The isostructural nets MOF-Co/AgPF$_6$-1 (top) and MOF-Co/AgSbF$_6$-1 (bottom) show identical layering patterns as the iron analogues shown. Hydrogen atoms, anions, and most solvent molecules have been omitted for clarity.
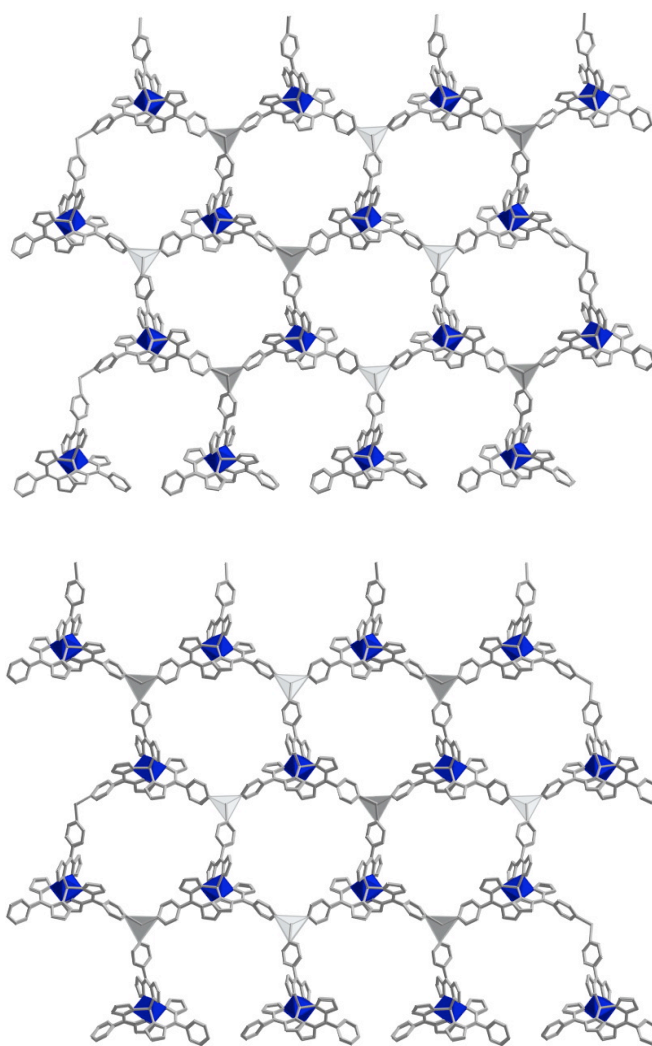
Figure S3. X-ray structure of the anion exchanged, 3-dimensional (10,3) nets MOF-Co/Ag×BF$_4$-1 (top) and MOF-Co/Ag×PF$_6$-1 (bottom) viewed along the crystallographic *b*-axis. Cobalt(III) and silver(I) centers are represented by blue and gray polyhedra, respectively. These compounds are isostructural with the parent MOF-Co/AgOTf-1. Hydrogen atoms, anions, and solvent molecules have been omitted for clarity.
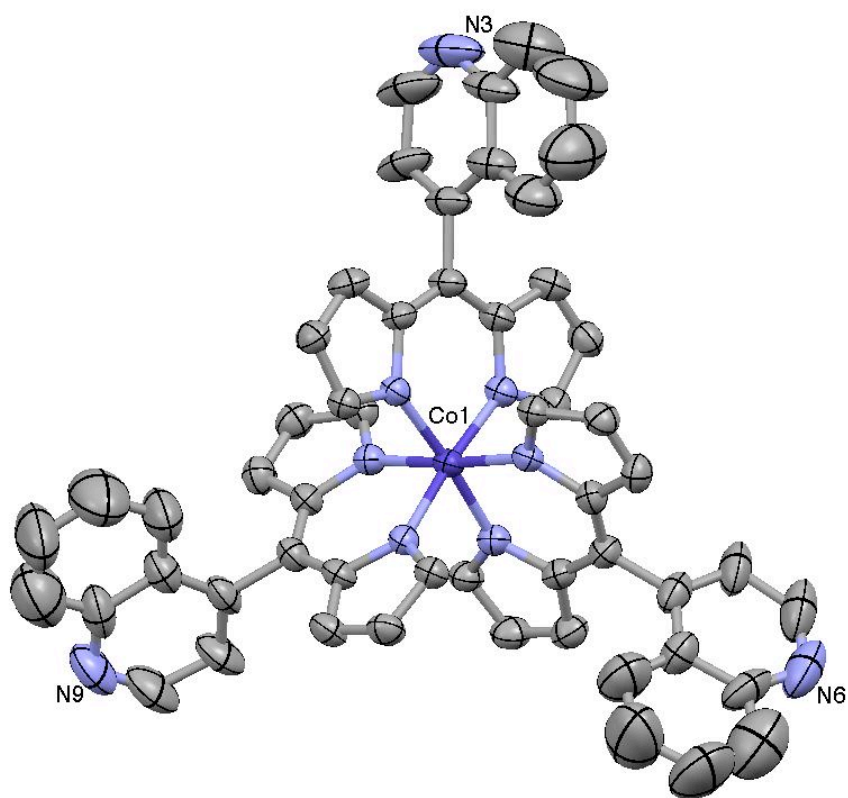
Figure S4. Structural diagram of [Co(4-quindpm)₃] with partial atom numbering scheme (ORTEP, 50% probability ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity.
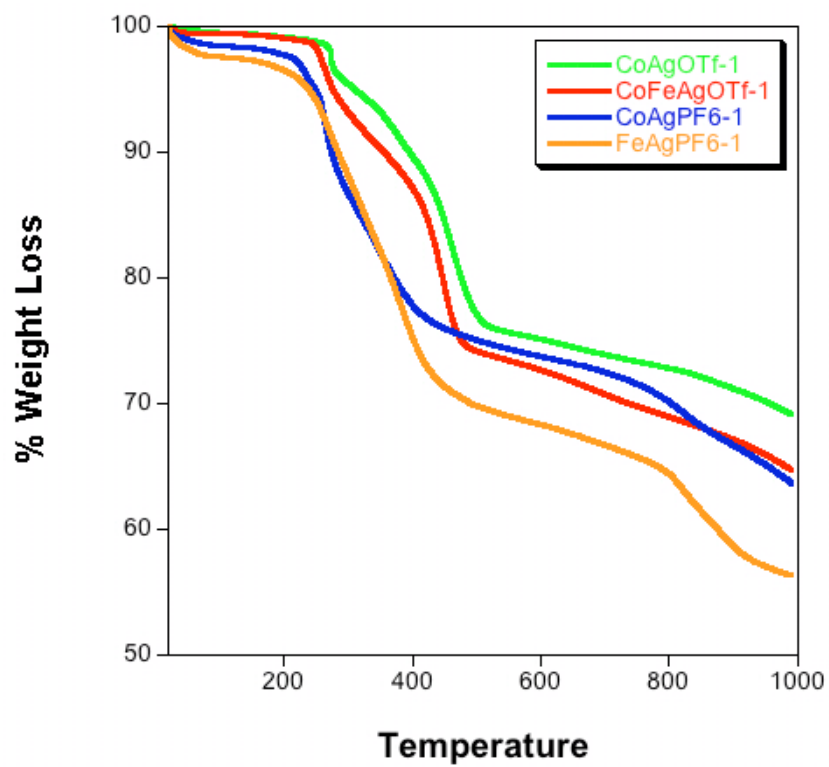
Figure S5. Representative thermal gravimetric analysis (TGA) traces for four of the MOFs: MOF-Co/AgOTf-1 (green), MOF-CoFe/AgOTf-1 (red), MOF-Co/AgPF$_6$-1 (blue), and MOF-Fe/AgPF$_6$-1 (orange). Rate = 20 °C/min.
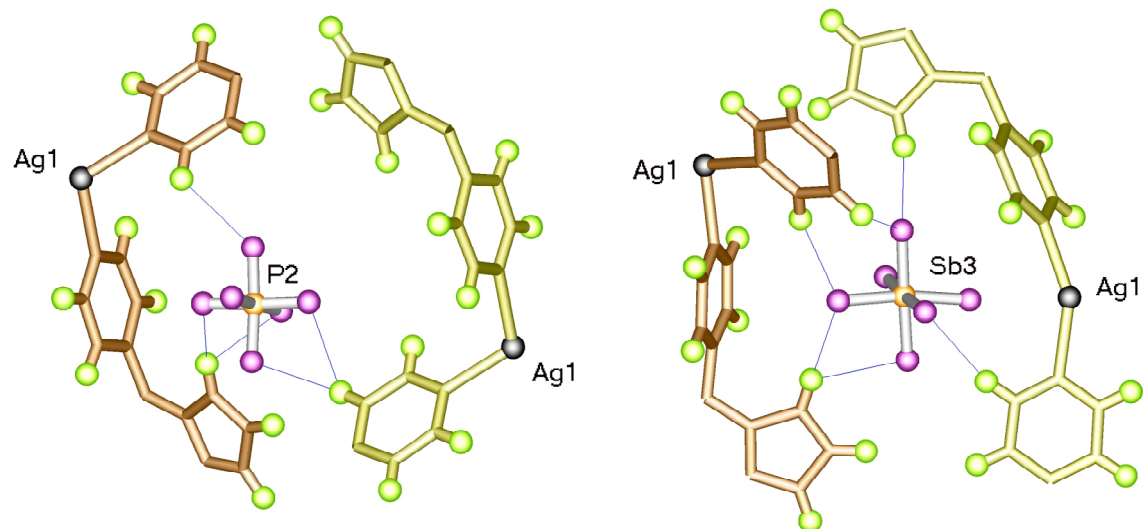
Figure S6. X-ray structures of MOF-Co/AgPF$_6$-1 (left) and MOF-Co/AgSbF$_6$-1 (right), highlighting the possible C-H⋯F interactions (thin gray lines) between adjacent network sheets (one shown in brown and one shown in yellow). C-H⋯F distances range from ~2.28 – 2.78 Å.
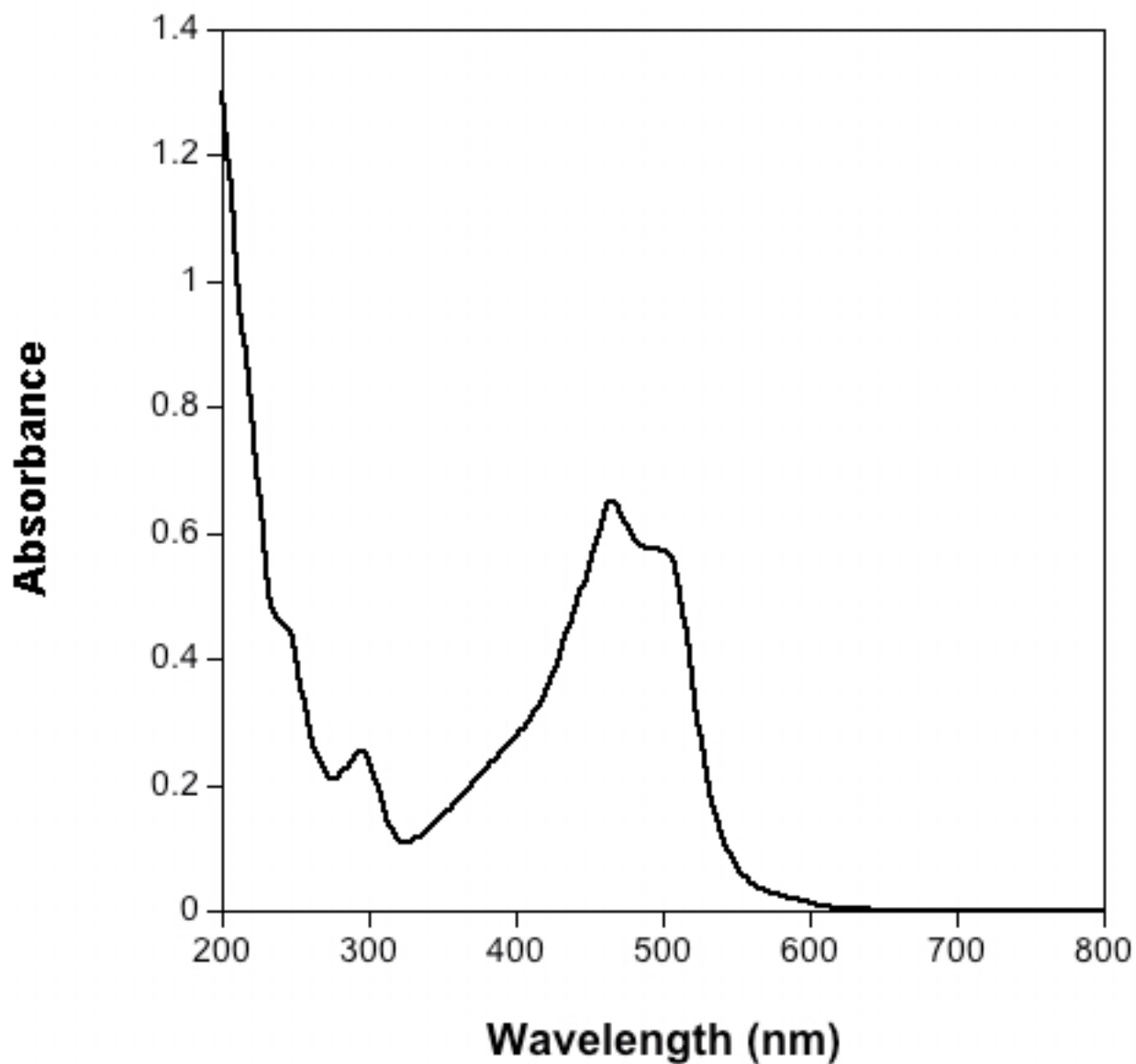
Figure S7. UV-visible spectra of MOF-CoFe/AgBF$_4$-1 crystals dissolved in acetonitrile. The spectra show characteristic spectra features of [Fe(4-pyrdpm)$_3$] (shoulder at ~444 nm) and [Co(4-pyrdpm)$_3$] (peaks at ~469, 506 nm).

Table S1. Summary of decomposition temperatures (5% and 25% weight loss) as determined by thermogravimetric analysis (TGA) for nine MOFs. Rate = 20 °C/min.

MOF	T_5 (°C)	T_{25} (°C)	Topology
MOF-Co/AgOTf-1	310	610	(10,3)-d
MOF-Fe/AgOTf-1	275	473	(10,3)-b
MOF-Fe/AgOTf-3	263	481	(10,3)-b
MOF-CoFe/AgOTf-1	276	476	(10,3)-d
MOF-CoFe/AgBF$_4$-1	245	607	(10,3)-d
MOF-Co/AgPF$_6$-1	249	504	(6,3)
MOF-Fe/AgPF$_6$-1	238	403	(6,3)
MOF-Fe/AgSbF$_6$-1	216	414	(6,3)
MOF-Co/AgBF$_4$-4	289	605	(6,3)