

# A chiral, heterometallic metal-organic framework derived from a tris(chelate) coordination complex†

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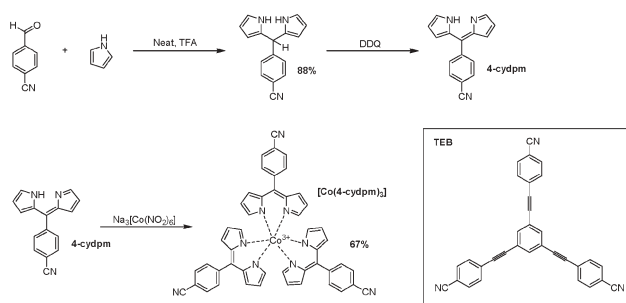
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A novel tris(chelate) metalloligand has been used to synthesize a chiral, heterometallic metal-organic framework that is robust to solvent removal and shows selective uptake of nitroaromatic compounds.

Metal-organic frameworks (MOFs) have been presented as a new class of rationally designed porous materials.<sup>1–5</sup> Carefully selected organic ligands have been combined with metal ions to generate MOFs with a wide range of structures. Some of these MOF architectures are extremely robust to temperature and solvent loss, and show remarkably high surface areas and porosities.<sup>6</sup> To add functionality to these materials, metalloligands have been proposed as a route to prepare MOFs with desirable catalytic, storage, separation, and sensory properties.<sup>5</sup> A strategy to prepare metalloligands that possess high structural homology to organic ligand systems described in the MOF literature would allow for the preparation of MOFs with predetermined architectures and physical properties. The ability to duplicate recognized MOF structures would provide a route to materials of demonstrated porosity, topology, and robustness, while introducing enhanced functionality *via* a second metal center (*e.g.* chirality, optical absorption, paramagnetism). Herein, we report a modified coordination complex with peripheral binding groups that generates a MOF which is structurally similar to that of a known MOF; however, the metalloligand-derived MOF possesses strong optical absorption, as well as chirality, originating from the metalloligand building block. The ability to perform processes such as catalysis or sensing enantioselectively has generated significant interest in homochiral MOFs. A number of homochiral MOFs have been reported recently,<sup>7,8</sup> many of which use a chiral organic ligand to direct the growth of the homochiral network.<sup>9–16</sup> In the present case, the homochirality of the MOF is derived from the  $\Delta$  or  $\Lambda$  handedness of the tris(chelate) coordination complex. When compared with earlier reported examples of such homochiral systems,<sup>17–19</sup> the metalloligand described here is more synthetically versatile, such that routes to homochiral analogues of many important MOF structure types can be realized.<sup>6,20</sup>

A tris(dipyrrinato) coordination complex was designed as the synthon for construction of a (10,3) net MOF. We recently reported the use of tris(dipyrrinato) compounds in the construction of achiral, heterometallic MOFs.<sup>21</sup> Our approach uses a tandem, or ‘two-step’, synthetic strategy.<sup>5,22,23</sup> The synthesis of the complex utilized in this study is shown in Fig. 1. The nitrile functionalized 4-cydpdm ligand (4-cydpdm = 5-(4'-cyanophenyl)dipyrromethene) was prepared and combined with a labile cobalt(III) salt to obtain the desired building block [Co(4-cydpdm)<sub>3</sub>] in modest yield (Fig. 1). [Co(4-cydpdm)<sub>3</sub>] was designed to reproduce the structure and symmetry of a class of silver(I)-N donor atom networks extensively investigated in the literature by Lee and co-workers,<sup>16,24–26</sup> which utilize 3-fold symmetric 1,3,5-tris(4-ethynylbenzonitrile)benzene bridging ligands (Fig. 1, TEB, in raised box). The TEB ligand, when combined with AgOTf (OTf<sup>−</sup> = trifluoromethanesulfonate, triflate), generates a (10,3)-b net that is 6-fold interpenetrated.<sup>20</sup> This MOF, designated [Ag(TEB)OTf], was shown to readily exchange guest solvent molecules.<sup>20,27</sup> It was anticipated, based on the similar structure and linking motif of TEB and [Co(4-cydpdm)<sub>3</sub>], that the latter would also generate a porous (10,3) net with good stability toward guest exchange.

The single crystal structure of the air and moisture stable [Co(4-cydpdm)<sub>3</sub>] was determined (Fig. 2).† The complex displays a distorted octahedral coordination geometry (Co–N ~ 1.94 Å) and, as anticipated, the three nitrile groups are poised in a pseudo-3-fold symmetric fashion about the cobalt(III) metal center.<sup>21,28</sup> The diamagnetic compound shows the expected 3-fold symmetry in solution, generating only one set of NMR resonances for the three dipyrrin ligands attached to the cobalt center. The pyrrolic protons nearest the cobalt are shifted 0.3–1.2 ppm downfield relative to the free dipyrrin ligand in solution, while the phenyl protons remain essentially unperturbed in the metal complex (7.7–8.0 ppm).



**Fig. 1** Scheme for the synthesis of [Co(4-cydpdm)<sub>3</sub>]. The complex has a similar geometry to the 1,3,5-tris(4-ethynylbenzonitrile)benzene ligand (TEB, in raised box) used to make a (10,3)-b net MOF in combination with silver(I) ions ([Ag(TEB)OTf]).

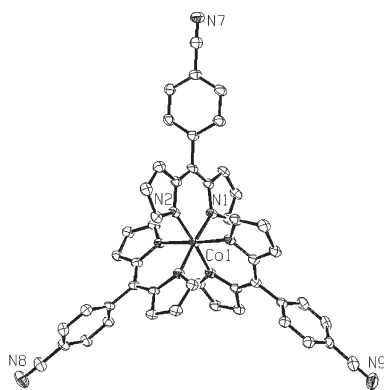
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† Electronic supplementary information (ESI) available: synthetic, guest exchange, and crystallographic details, Table S1, and Figures S1–S5. See DOI: 10.1039/b510915a



**Fig. 2** Structural diagram of  $[\text{Co}(4\text{-cydpdm})_3]$  with partial atom numbering schemes (ORTEP, 50% probability ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity.

The metalloligand  $[\text{Co}(4\text{-cydpdm})_3]$  was combined with one equivalent of  $\text{AgOTf}$  in benzene solution at concentrations ranging from 0.29–1.17 mM. The solutions were shielded from light and upon slow evaporation, the most concentrated solutions (0.88 and 1.17 mM) generated large crystals after  $\sim 13$  days. The deep, red-orange color of the crystals indicated that the  $[\text{Co}(4\text{-cydpdm})_3]$  complex was present in the material. The IR spectrum of the crystals showed several features clearly indicative of the dipyrin complex ( $1563, 1380, 1252 \text{ cm}^{-1}$ ).<sup>†</sup>

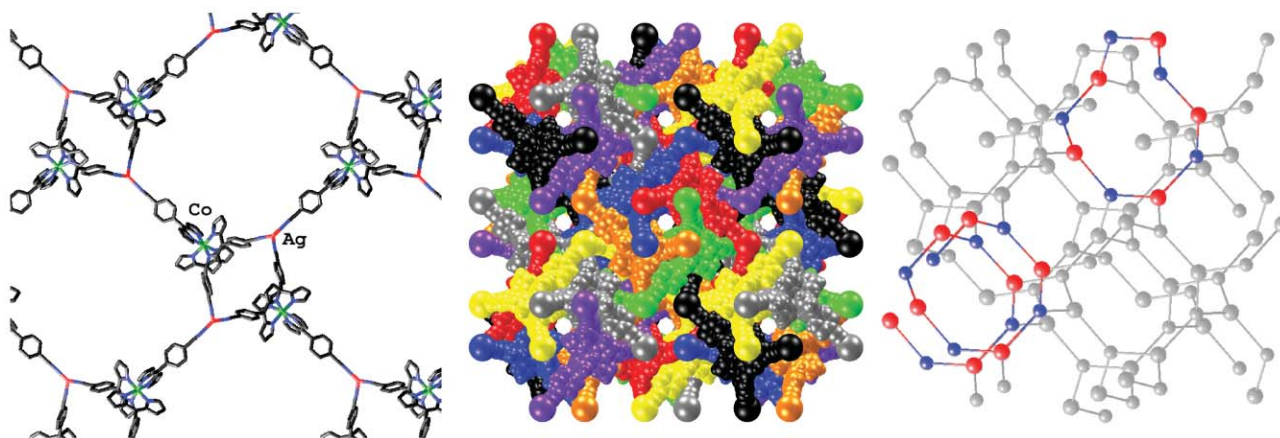
A single crystal X-ray diffraction study of the red crystals revealed the formation of an extended solid, MOF-Co/AgOTf-2 (Fig. 3).<sup>‡</sup> The  $[\text{Co}(4\text{-cydpdm})_3]$  complexes are linked to the silver(I) centers *via* the nitrogen atoms of the nitrile groups. Each silver(I) ion is bound by three nitrile groups in a trigonal pyramidal coordination geometry from three different cobalt(III) complexes. The apical position of the trigonal pyramidal silver(I) center is likely occupied by a triflate counterion, although this ion was too disordered to conclusively identify in the structure (Figure S1<sup>†</sup>). The Ag–N bond length of  $\sim 2.16 \text{ \AA}$  is nearly identical to those found in  $[\text{Ag}(\text{TEB})\text{OTf}]$  ( $\sim 2.2 \text{ \AA}$ ).<sup>20</sup> The geometry of the

cobalt(III) coordination sphere possesses crystallographic 3-fold symmetry as the metal ion lies on a special position in the crystal lattice. The Co–N bond lengths (Co–N  $\sim 1.93 \text{ \AA}$ ) are essentially unchanged from the  $[\text{Co}(4\text{-cydpdm})_3]$  starting material.

Among the most interesting features of MOF-Co/AgOTf-2 is that the complex was found to crystallize in the chiral space group *F*432. As expected, inspection of the cobalt(III) centers in the structure show them to be of all the same handedness ( $\Lambda$  as solved). Although synthesis of the MOF began from a racemic mixture of  $\Delta$ - and  $\Lambda$ - $[\text{Co}(4\text{-cydpdm})_3]$ , spontaneous resolution occurs during the growth of the crystals. Examination of the network topology reveals the structure to be a (10,3)-a network,<sup>29–31</sup> comprised of eight interpenetrated frameworks (Fig. 3). Crystals of MOF-Co/AgOTf-2 can be dissolved in polar, organic solvents (*e.g.* acetone, acetonitrile), which allowed for the use of spectroscopic methods in solution. Therefore, the homochirality of the MOF-Co/AgOTf-2 was confirmed by dissolution of the crystals in acetonitrile and acquisition of their circular dichroism (CD) spectra. As expected, frameworks of opposite handedness were identified by CD spectroscopy (Figure S2<sup>†</sup>).

Due to the fact that the triflate counterions could not be conclusively located in the crystal structure, further experiments were performed to fully characterize the material. Infrared difference spectra of  $[\text{Co}(4\text{-cydpdm})_3]$  and MOF-Co/AgOTf-2 clearly show features that are indicative of the triflate counterion (data not shown).<sup>32</sup> Upon dissolution of the MOF in acetone- $d_6$ , the proton signals of the  $[\text{Co}(4\text{-cydpdm})_3]$  building block are clearly observed in the proton spectrum, and the triflate counterions were readily detected by using  $^{19}\text{F}$  NMR (Figure S3<sup>†</sup>). The  $^{19}\text{F}$  NMR spectrum of dissolved MOF-Co/AgOTf-2 shows a single resonance at  $-77.8 \text{ ppm}$ , which is identical to the  $^{19}\text{F}$  NMR spectrum of silver(I) triflate in acetone- $d_6$  (Figure S3<sup>†</sup>).

As described above, the MOF is comprised of eight interpenetrated networks (Fig. 3), akin to the 6-fold interpenetration observed in  $[\text{Ag}(\text{TEB})\text{OTf}]$ .<sup>20</sup> The MOF-Co/AgOTf-2 lattice displays channels about the 4-fold axis that parallel the crystal axes. The solvent accessible space in the structure was calculated using the program SOLV which is included in the Platon software



**Fig. 3** Diagram of one network of MOF-Co/AgOTf-2 (sticks, left). Complete packing diagram (spacefilling, middle) of the eight interpenetrating nets of MOF-Co/AgOTf-2 viewed down the crystallographic *a*-axis; each of the eight interpenetrated networks is shown in a different color. An off-axis view of MOF-Co/AgOTf-2 showing only the cobalt(III) (blue) and silver(I) (red) ions (right), emphasizing the 10-membered rings and homochiral helices, which are characteristic of a (10,3)-a net.

package (A. Spek, Platon Library). A free volume of  $\sim 12823 \text{ \AA}^3$  was determined, which corresponds to  $\sim 31\%$  of the total cell volume. This value represents an upper limit for the free volume as only the atoms of the network were used in the calculation, and did not include the highly disordered triflate counterions that are present in the structure (*vide supra*). Crystals of MOF-Co/AgOTf-2 were generally robust to loss of guest molecules, in contrast to earlier studies with [Ag(TEB)OTf].<sup>20</sup> The proton NMR spectrum of freshly prepared crystals dissolved in acetone-*d*<sub>6</sub> shows the presence of benzene (7.35 ppm;  $\sim 2.4$  benzene/[Co(4-cydp<sub>m</sub>)<sub>3</sub>]), but upon overnight drying of MOF-Co/AgOTf-2 in a vacuum oven ( $\sim 60$ – $75$  °C) benzene is no longer observed in the NMR spectrum (Figure S4†). Furthermore, drying of MOF-Co/AgOTf-2 crystals under these conditions showed no apparent change in bulk morphology, and indexing of dried crystals by X-ray diffraction gave essentially identical cell parameters ( $a = b = c = 34.6546(9) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ) as found in the single crystal structure determination. § Decomposition of the framework was not observed until  $350$  °C, as determined by thermal gravimetric analysis. †

With evidence that MOF-Co/AgOTf-2 was robust to heat and solvent removal, the ability of the framework to exchange and uptake various guest molecules was examined. † By using proton NMR, freshly isolated crystals were found to contain benzene that could be exchanged for toluene, ethylbenzene, and *p*-xylene. Solvent-evacuated crystals were also examined for the uptake of aromatic guests. The oven dried material could absorb a number of guests including, toluene, ethylbenzene, nitrobenzene, and *m*-nitrotoluene (Figure S5†). Toluene and ethylbenzene exhibited the poorest uptake ( $\sim 1$  guest/[Co(4-cydp<sub>m</sub>)<sub>3</sub>]), while nitrobenzene and *m*-nitrotoluene showed consistently more efficient uptake ( $\sim 3$  and  $5$  guests/[Co(4-cydp<sub>m</sub>)<sub>3</sub>], respectively). The selectivity for *m*-nitrotoluene was also observed when the crystals were exposed to a 1 : 1 (v : v) mixture of *m*-nitrotoluene and toluene solvents; in these experiments the *m*-nitrotoluene:toluene ratio found in MOF-Co/AgOTf-2 was 6 : 1.

In summary, a 3-fold symmetric octahedral coordination complex based on a ditopic dipyrin ligand has been used to construct a homochiral, heterometallic MOF. The metalloligand [Co(4-cydp<sub>m</sub>)<sub>3</sub>] produced a MOF with a related architecture to that found with the analogous organic ligand TEB. Like [Ag(TEB)OTf], MOF-Co/AgOTf-2 demonstrates the ability to absorb a variety of aromatic guest molecules, and moreover is robust to heat and solvent loss. In addition, MOF-Co/AgOTf-2 is homochiral, with the chirality originating from the handedness at the octahedral tris(chelate) metal centers. Continued efforts to investigate and apply this metalloligand design strategy to other established MOF architectures are presently underway and will be reported in due course.

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## Notes and references

‡ Crystal data for [Co(4-cydp<sub>m</sub>)<sub>3</sub>]: Data were collected on a Bruker AXS diffractometer equipped with an area detector. C<sub>48</sub>H<sub>30</sub>C<sub>11.5</sub>N<sub>9</sub>Co,  $T = 100(2)$ , triclinic, space group  $P\bar{1}$ ,  $a = 14.8303(8) \text{ \AA}$ ,  $b = 16.3535(8) \text{ \AA}$ ,  $c = 20.0347(10) \text{ \AA}$ ,  $\alpha = 72.6680(10)^\circ$ ,  $\beta = 68.7730(10)^\circ$ ,  $\gamma = 72.6340(10)^\circ$ ,  $V = 4223.3(4) \text{ \AA}^3$ ,  $Z = 4$ , final  $R$  indices [ $I > 2\sigma(I)$ ]:  $R1 = 0.0682$ ,  $wR2 = 0.1821$ ,  $R$  indices (all data):  $R1 = 0.0899$ ,  $wR2 = 0.1982$ . CCDC 281272. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b510915a

§ Crystal data for MOF-Co/AgOTf-2: Data were collected on a Bruker AXS diffractometer equipped with an area detector. C<sub>63.44</sub>H<sub>44.44</sub>C<sub>11.5</sub>N<sub>9</sub>O<sub>3</sub>F<sub>3</sub>SCoAg,  $T = 100(2)$ , cubic, space group  $F432$ ,  $a = b = c = 34.7494(14) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 41961(3) \text{ \AA}^3$ ,  $Z = 32$ , final  $R$  indices [ $I > 2\sigma(I)$ ]:  $R1 = 0.0838$ ,  $wR2 = 0.2272$ ,  $R$  indices (all data):  $R1 = 0.0896$ ,  $wR2 = 0.2320$ . CCDC 281273. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b510915a

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