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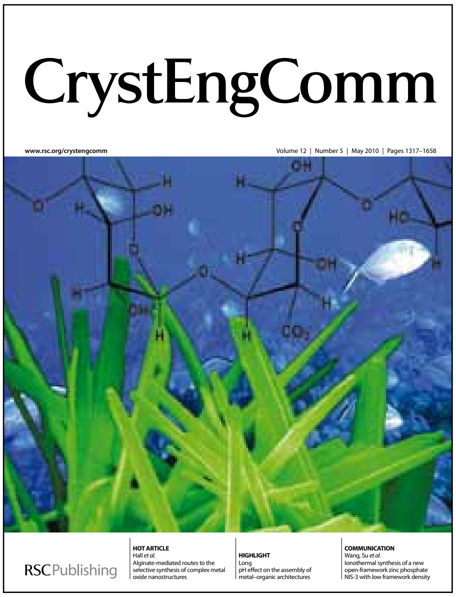

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Three cobalt(II) coordination polymers based on V-shaped aromatic polycarboxylates and rigid bis(imidazole) ligand: Syntheses, crystal structures, physical properties and theoretical studies

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Abstract

To investigate the effect of organic anions on the coordination frameworks, we synthesized three new complexes, namely, Co(SDBA)(BIMB) (**1**), $Co_2(SA)(BIMB)_{1.5}(H_2O)$ (**2**) and $Co(FBA)(BIMB)_{0.5}{\cdot}H_2O$ (**3**) (H_2SDBA = 4,4'-dicarboxybiphenylsulfone, H_4SA = 3,3',4,4'-diphenylsulfonetetracarboxylate acid and H_2FBA = 4,4'-(hexafluoroisopropylidene)bis(benzoic acid)), which were obtained by the reactions of 4,4′-bis(1-imidazolyl)biphenyl (BIMB), and three V-shaped aromatic polycarboxylates as organic anions with $Co(NO_3)_2{\cdot}6H_2O$. Single crystal structure analysis shows that complex **1** features a 3-fold interpenetrating three-dimensional (3D) framework with $CdSO_4$-type topology. Complex **2** has an previously unknown 3D trinodal (4,4,6)-connected framework with Schläli symbol of $(4.6^4.8)_2(4^3.6^3)_2(4^4.6^{10}.8)$. Complex **3** exhibits a three-dimensional 2-fold interpenetrating pillared helical-layer open framework of α-Po topology based upon binuclear paddlewheel units. The results reveal that the carboxylic building blocks with different conformations play a significant role in promoting the diversity of the observed structural motifs. The magnetic properties of three complexes as well as SHG and ferroelectric properties for **1** have also been investigated. Finally, theoretical calculations were carried about the conformation of the BIMB ligand in three complexes.

Keywords: cobalt(II) coordination polymer; magnetic property; nonlinear optical property; ferroelectric property; theoretical calculation

Introduction

Crystal engineering to synthesis rationally coordination polymers attract much interest because of their potential applications as functional materials in the field of heterogeneous catalysis porosity, luminescence, conductivity, molecular magnetism, nonlinear optics and chirality.[1-4] Their fascinating architectures and topological networks also account for their wide interest.[5-8] In order to build novel molecular architectures, much effort has been devoted to modify the building blocks and to control the assembled motifs for required products *via* selecting different organic ligands.[9,10] Besides that, several factors also influence the construction of molecular architecture, such as pH value, template, reaction temperature, the solvent system, metal ions and counterions.[11-13] Among these factors, the selection of organic ligands is one of the most important aspects.[14] The configuration, rigidity, substituent and coordination modes of organic ligands have an important effect on the final structures. Generally, polycarboxylate ligands feature prominently in the construction of coordination polymers, and the reported coordination polymers are mostly constructed by rigid polycarboxylate ligands.[15] Recently, more and more attention has been paid to the flexible polycarboxylate ligands,[16] but studies of semirigid V-shaped polycarboxylate ligands are relatively few.[17]

Up to now, a number of pyridyl-containing ligands have been widely employed as the second ligands for meeting the requirement of coordination geometries of metal ions or tuning the fine structure.[18] Compared with rigid bridging pyridyl ligands, 4,4′-bis(1-imidazolyl)biphenyl (BIMB) possesses a similar rigid structure but a more flexible coordination fashion and an excellent coordination ability, and has the potential to construct porous MOFs. BIMB has two coordination fashions (Scheme 1), *cis*-configuration and *trans*-configuration, while free rotation of the imidazolyl ring and benzene ring makes its style more diverse.[19] In the progress of linking metal ions, terminal nitrogen atoms from the five-membered ring units of imidazolyl ligands have a weaker steric hindrance than those from six-membered ring units of pyridyl ligands. Inspired by those ideas, we successfully obtained three new three-dimensional (3D) MOFs, namely, Co(SDBA)(BIMB) (**1**), $Co_2(SA)(BIMB)_{1.5}(H_2O)$ (**2**) and $Co(FBA)(BIMB)_{0.5}\cdot H_2O$ (**3**). They are characterized by elemental analysis and X-ray crystallography. The crystal structures as well as topological analysis of these complexes will be represented and discussed in detail. In addition, their physical properties are also studied.

Experimental section

Materials and general methods

All the reagents and solvents for syntheses and analyses were purchased from Sigma or TCI and employed as received without further purification. The BIMB ligand was prepared according to the reported method.[20] Elemental analyses (C, H and N) were performed on a Vario EL III elemental analyzer. Infrared spectra were performed on a Nicolet AVATAR-360 spectrophotometer with KBr pellets in the 4000 - 400 cm^{-1} region. The second-order nonlinear optical intensity was estimated by measuring a powder sample relative to urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate a SHG signal from powder samples. The backscattered SHG light was collected by a spherical concave mirror and passed through a filter that transmits only 532 nm radiation. The ferroelectric property of the solid-state sample was measured by the Premier II ferroelectric tester at room temperature. Variable-temperature susceptibilities were measured using a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.[21]

Preparation of Co(SDBA)(BIMB) (1). A mixture containing $Co(NO_3)_2{\cdot}6H_2O$ (29.6mg, 0.1 mmol), H_2SDBA (30.6 mg, 0.1 mmol), BIMB (28.6 mg, 0.1 mmol) and NaOH (8.0 mg, 0.2 mmol) in 15 ml deionized water was sealed in a 25 ml Teflon lined stainless steel container and heated at 160 ºC for 3 days. Purple pillar crystals of **1** were collected by filtration and washed with water and ethanol several times with a yield of 64%. Anal. calcd for $C_{32}H_{22}N_4O_6SCo$: C 59.17; H 3.41; N 8.63; Found: C 59.12; H 3.38; N 8.60%. IR(KBr pellet, cm^{-1}): 3443(br), 3151(m), 1634(s), 1603(s), 1564(m), 1519(s), 1361(s), 1300(m), 1253(w), 1158(m), 1095(s), 958(m), 833(m), 751(s), 690(w), 626(w), 561(w).

Preparation of $Co_2(SA)(BIMB)_{1.5}(H_2O)$ (2). A mixture containing $Co(NO_3)_2{\cdot}6H_2O$ (59.2 mg, 0.2 mmol), H_4SA (39.4 mg, 0.1 mmol), BIMB (57.2 mg, 0.2 mmol) and $LiOH{\cdot}H_2O$ (16.8 mg, 0.4 mmol) in 15 ml deionized water was sealed in a 25 ml Teflon lined stainless steel container and heated at 140 ºC for 3 days. Purple platelet crystals of **2** were collected by filtration and washed with water and ethanol several times with a yield of 41%. Anal. calcd for $C_{43}H_{29}N_6O_{11}SCo_2$: C 54.04; H 3.06; N 8.79;

Found: C 54.02; H 3.04; N 8.76%. IR(KBr pellet, cm^{-1}): 3447(br), 3157(m), 1620(s), 1580(s), 1520(m), 1407(s), 1366(s), 1325(m), 1244(w), 1101(m), 1067(m), 969(m), 818(m), 796(m), 745(w), 715(w), 644(w), 532(w).

Preparation of Co(FBA)(BIMB)$_{0.5}$·H$_2$O (3). A mixture containing Co(NO$_3$)$_2$·6H$_2$O (59.2mg, 0.2 mmol), H$_2$FBA (39.2 mg, 0.1 mmol), BIMB (28.6 mg, 0.1 mmol) and LiOH·H$_2$O (8.4 mg, 0.2 mmol) in 15 ml deionized water was sealed in a 25 ml Teflon lined stainless steel container and heated at 140 ºC for 3 days. Purple pillar crystals of **3** were collected by filtration and washed with water and ethanol several times with a yield of 46%. Anal. calcd for $C_{26}H_{17}F_6N_2O_5Co$: C 51.16; H 2.81; N 4.59; Found: C 51.13; H 2.77; N 4.55%. IR (KBr pellet, cm^{-1}): 3442(br), 3139(w), 1605(s), 1517(m), 1391(s), 1259(s), 1208(m), 1167(s), 1116(m), 1066(m), 964(w), 933(w), 832(m), 781(m), 740(m), 720(m), 648(w), 577(w).

X-Ray crystallography

Crystallographic data collections for complexes **1 - 3** were carried out on a Bruker Smart Apex II CCD with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K using the ω-scan technique. The data were integrated by using the SAINT program,[22] which was also used for the intensity corrections for the Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program.[23] The structures were solved by direct methods using the program SHELXS-97 and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package. The hydrogen atoms of the water molecules were located in a difference

Fourier map, and the other hydrogen atoms were generated geometrically. All calculations were performed on a personal computer with the SHELXL-97 crystallographic software package.[24] The details of the crystal parameters, data collection and refinement for the complexes are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are listed in Table 2. CCDC-893724 (**1**), 893725 (**2**) and 893726 (**3**) contain the crystallographic data for this paper.

<Table 1 and Table 2 here>

Results and discussion

IR spectra

The absence of such bands at around 1700 cm^{-1} in the IR spectrum of three complexes indicates the complete deprotonation of H_2SDBA, H_4SA and H_2FBA. The characteristic bands of carboxyl groups are shown in the range of 1540 - 1620 cm^{-1} for antisymmetric stretching and 1360 - 1460 cm^{-1} for symmetric stretching. The separations (Δ) between ν_{asym} (CO_2) and ν_{sym} (CO_2) bands indicate the presence of different coordination modes. The bands in the region 640 -1310 cm^{-1} are attributed to the -CH- in-plane or out-of-plane bend, ring breathing, and ring deformation absorptions of benzene ring, respectively. Weak absorptions observed at 3139 – 3159 cm^{-1} can be attributed to $\nu_{C\text{-}H}$ of benzene ring.. The IR spectra exhibit the characteristic peaks of imidazole groups at *ca*. 1520 cm^{-1}.[25]

Crystal structure of Co(SDBA)(BIMB) (1)

Single-crystal X-ray structural analysis reveals that complex **1** crystallizes in the acentric group *Cc* with Flack parameter of 0.025(10). The asymmetry unit contains one independent cobalt ion, one SDBA dianion, and one BIMB ligand. The Co(II) ion is coordinated by two oxygen atoms from two adjacent SDBA dianions and two nitrogen atoms from BIMB linkers to give the CoO_2N_2 tetrahedral geometry (Fig. 1a). The Co-O/N bond lengths are in the range of 1.9538(19) - 2.052(2) Å, which are comparable to those reported in other relative Co(II) polymers.[26] The completely deprotonated SDBA ligand shows a bi(monodentate) coordination manner, while the BIMB adopts a *trans*-conformation. The Co(II) cations are bridged by SDBA to form a 1D zigzag chain, as shown in Fig. 1b. These chains are further connected by bridging BIMB linkers to give rise to a complicated 3D network with the small solvent-accessible void space (equal to 4.2% of the cell volume) (Fig. 1c). Better insight into the elegant framework of **1** can be accessed by the topology method. In this analysis, the metal center can be viewed as 4-connect node. In this way, this net can be simplified as $CdSO_4$ topology (Fig. 1d).[27] Moreover, the occurrence of 3-fold interpenetration and polycatenane character are also observed, as exhibited in Fig. 1e and 1f.

<Figure 1 here>

Crystal structure of $Co_2(SA)(BIMB)_{1.5}(H_2O)$ (2)

To investigate the influence of the carboxylate ligand on the structure of the complexes, the reaction of BIMB and H_4SA with $Co(NO_3)_2$•$6H_2O$ was carried out, and a new complex **2** was obtained. As illustrated in Fig. 2a, although all the Co(II) centers have octahedral geometries, the two unique metal centers exhibit different coordination environments: Co1 lies in a distorted octahedral coordination sphere, the equatorial plane of which comprises three carboxylate oxygen atoms (O1, O2, and O4A) from two distinct SA^{4-} anions and one BIMB nitrogen atom (N5); another imidazole nitrogen atom (N1) and one coordinated water molecule (O1W) occupy the axial coordination site. Co2 is surrounded by five carboxylate oxygen atoms from three inequivalent SA^{4-} ainions and one BIMB nitrogen atom in a distorted octahedron sphere. In **2**, the Co-O bond lengths range between 2.041(3) and 2.343(3) Å, and the Co-N distances are 2.064(4) and 2.152(3) Å, both of which are in the normal range.[28]

Two Co2 atoms are double bridged by two carboxylate groups with Co2···Co2 separations of 3.612 Å to from a dinuclear Co_2 unit. The fully deprotonated SA^{4-} ligand coordinates to five Co atoms with four carboxylate groups adopting four different coordination fashions: μ_1-η^1:η^0-monodentate, μ_1-η^1:η^1-chelating, μ_2-η^1:η^1-bridging and μ_2-η^2:η^1-bridging fashion.[25] The SA^{4-} ligand thus links cobalt ions to form a 1D chain structure (Fig. 2b). In addition, it should be noted that there are two independent sets of BIMB spacers adopting *cis*- and *trans*-conformations, respectively, which establish a physical bridge between Co atoms with Co···Co separations of 17.28 and 17.36 Å, and one of them resides at a crystallographic inversion center, resulting in the formation of a complicated 3D structure (Fig. 2c).

A better insight into the nature of this intricate framework can be acquired by using topological analysis. In **2**, each SA^{4-} anion is four-connected by linking to two Co atoms and two dinuclear Co_2 units; the BIMB groups can be simplified to be linear connectors. Co1 and dinuclear Co_2 unit were also considered as distinct nodes; therefore, the combination of nodes and connectors suggests an uncommon trinodal (4,4,6)-connected network with a Schäfli symbol of $(4.6^4.8)_2(4^3.6^3)_2(4^4.6^{10}.8)$ for $(Co1)_2(SA)_2(Co_2)$ (Fig. 2d).[29] As far as we know, this topology is completely new within coordination polymer chemistry. The discovery of this new topology is useful at the basic level in the crystal engineering of coordination networks.

<Figure 2 here>

Crystal structure of $Co(FBA)(BIMB)_{0.5}\cdot H_2O$ (3)

Single-crystal X-ray analysis revealed that complex **3** displays a 3D 2-fold interpenetrated polymeric structure with 1D helical channels. The asymmetric unit contains one cobalt ion, one FBA dianion, and half of the BIMB ligand (Fig. 3a) with the metal-based building unit comprising a binuclear Co(II)-tetracarboxylate paddlewheel cluster.[30] In this binuclear unit (Fig. 3b), each Co(II) ion resides in a square pyramidal coordination geometry with the apical position occupied by one nitrogen atom from the BIMB ligand, while the basal plane consists of four carboxylate oxygen atoms. The intradimer Co···Co separation is 2.9177(11) Å, within the normal range found in other reported bimetallic paddlewheel units of type

$[M_2(O_2CR)_4]$.[31] In **3**, each paddlewheel unit connects to four neighboring paddlewheel clusters via bridging FBA^{2-} dianions, which adopt a bridging tetradentate mode to form a 2D undulating (4,4) net with large rhomb-like windows (Fig. 3c). The dimensions of the rhombic window are 14.24×14.24 Å^2 as measured between the centroids of the binuclear Co(II) subunits at the corners of the window. As depicted in Fig. 3d, the skeleton of this 2D sheet can also be described as a unique helical layer in which the left and right helical chains appear alternatively by sharing the paddlewheel clusters. The pitch of helix is double the *b* parameter (14.393 Å).

Most strikingly, the two diagonals of the rhombic window are equal to unit cell parameters *b* and *c*, respectively. Two closest identical helical layers shift by *b* so that the paddlewheel units from one layer fall in the center of the window of the other layer, and interpenetrate each other in a parallel 2D→2D fashion, resulting in an interwoven bilayer with 1D double helical channels. The FBA^{2-} ligand presents a dihedral angle of 77.98° between the two benzene rings, and this configuration contributes to the parallel 2D→2D interpenetration. The skeleton of these 2D layers can also be viewed as a unique helical tubular double layer, which is similar to the previously reported Co-FBA sheets in the compound $[Co(FBA)(py)]_n$.[32] These helical interpenetrated double layers are extended to a 3D framework with the aid of the pillar BIMB ligand (Fig. 3e). The BIMB ligand connects the two paddle wheels of two different double layers with a separation of 17.92 Å in a regular *trans*-conformation. The connectivity pattern of linker BIMB forms 1D chains through the crystallographic *c* axis connecting the double layers in the *ab* plane. The two imidazole rings in the BIMB ligand twist from the phenyl ring plane by a torsion angle of 75.89°. If the paddle-wheel dimer can be topologically viewed as an octahedral node, meanwhile the FBA^{2-} and BIMB bridges can be viewed as linkers, the topology of single net for **3** can be best described as an uninodal six-connected distorted primitive cubic (α-Po) net (Fig. 3f).[30] Two identical nets interpenetrate each other, giving rise to a 2-fold interpenetrating framework.

<Figure 3 here>

It is well known that the organic anions play an important role in determining the final structures of the compounds. By varying the anions under similar synthetic conditions three related Co(II) complexes with different structures were successfully synthesized. The roles played by the carboxylate anions in complexes **1-3** can be explained in terms of their differences in the positions and numbers of the carboxylate groups. It is a feasible method to introduce ligands to construct coordination polymers with different structural types.

SHG activity and ferroelectric properties of complex 1

Second-order non-linear optical (NLO) materials have attracted more and more attention in fields such as laser frequency conversion and optical parameter oscillators. Among them, new NLO materials made from metal-organic coordination polymers have been a major point of focus in recent years because of their advantages over pure inorganic or organic compounds. It is well-known that only a non-centrosymmetric structure may have second-order NLO effects.[33] Therefore, it is believed that complex **1** with *Cc* space group has a NLO response, and a quasi-Kurtz second-harmonic-generation (SHG) measurement was carried out to evaluate their potential application as a second-order NLO material. The preliminary experimental results revealed that complex **1** exhibits modest powder SHG activity with a response of 0.8 times of that for urea, which indicates that the complex **1** can be used as a potential optical material.

Recently, a prevalent research have focused on developing ferroelectric materials based on metal-organic frameworks (MOFs) and have reported some such materials.[34] However, the reported ferroelectric materials are mostly built upon chiral organic tectons, whereas the proper use of achiral ligands by spontaneous are scarce.[35] Herein, we describe the preliminary investigation of the possible ferroelectric property of complex **1**. Complex **1** crystallizes in the acentric space group *Cc*, which belongs to the polar point group *Cs*, which falls in one of the 10 polar point groups (*C*1, *Cs*, *C*2, *C*2*v*, *C*4, *C*4*v*, *C*3, *C*3*v*, *C*6, *C*6*v*) required for ferroelectric materials. Therefore, the ferroelectric behavior of **1** was examined. Fig. 4 clearly shows that there is an electric hysteresis loop that is a typical ferroelectric feature with a remanent polarization (*Pr*) of *ca*. 0.051 μC cm^{-2} and coercive field (*Ec*) of *ca*. 3.38 kV cm^{-1}. The saturation spontaneous polarization (*Ps*) of **1** is *ca*. 0.238 μC cm^{-2}. Furthermore, we also studied the behavior of permittivity (ε) = $\varepsilon_1(\omega) - i\varepsilon_2(\omega)$, where $\varepsilon_1(\omega)$ and $i\varepsilon_2(\omega)$ are the real (dielectric constant) and imaginary (dielectric loss) parts, respectively. The results reveal that the frequency dependence of the dielectric constant ε_1 at room temperature

(20 ºC) indicates that ε_1 rapidly decreases with the increase of frequency, while dielectric loss remains unchanged.

<Figure 4 here>

Magnetic properties

The variable-temperature magnetic susceptibility measurements of complexes **1** - **3** were performed on the Quantum Design SQUID MPMS XL-7 instruments in the temperature range of 2-300 K under a field of 1000 Oe. Temperature dependence of $\chi_M T$ and χ_M for complexes **1-3** as displayed in Fig. 5. Magnetic susceptibility data of per Co(II) ion of **1** shows the $\chi_M T$ value of 2.16 cm^3 K mol^{-1} at room temperature, which is much higher than the expected value of 1.875 cm^3 K mol^{-1} for one magnetism-isolated Co(II) ion with S = 3/2 and g = 2.0, they are common values for high-spin complexes in tetrahedral Co(II) centers (4.30-5.20 μ_B). The magnetic behavior should be due to a larger orbital contribution arising from the $^4A_{2g}$ ground-state of Co(II).[36] The $\chi_M T$ value increases gradually with decreasing temperature and move up to a maximum value of 3.257 cm^3 K mol^{-1} at ca. 36.1 K, which suggests ferromagnetic behavior, and then decrease sharply down to a minimum value of 1.49 cm^3 K mol^{-1} at 2 K, such behavior is possibly due to ZFS (zero-field splitting) and/or antiferromagnetic interactions.[31] From the structure of complex **1**, though the magnetic centers separated by the long BIMB and SDBA ligands are weakly magnetic coupled (17.298 and 13.758 Å), the nearest Co···Co distance between adjacent chains is about 7.659 Å which should make a contribution to the ferromagnetic behavior *via* intermolecular interactions. The plot of $1/\chi_M$ versus T can be fitted by the Curie-Weiss law [$\chi_M = C/(T-\theta)$] above 18 K, giving the Curie constant value C = 2.75 cm^3 K mol^{-1} and Weiss constant θ = +6.12 K. The Curie constant value is consistent with the $\chi_M T$ value at room temperature. The positive value of θ further conforms the ferromagnetic behavior.

As for **2**, the $\chi_M T$ value at room temperature is 4.44 cm^3 K mol^{-1} per two Co(II) ions, which is much higher than the calculated spin-only value (3.87 cm^3 K mol^{-1}) for two uncoupled high-spin Co(II) ion (S = 3/2, g = 2). This is as expected for octahedral high-spin cobalt(II) ions, which have a large first-order orbital contribution to the magnetic moment.[36] Upon cooling the $\chi_M T$ value decreases smoothly to reach a value of 1.125 cm^3 K mol^{-1} at 26 K and slightly shifts the curve and then decreases to a minimum value of 0.280 cm^3 K mol^{-1} at 2 K. The results show that the complex shows overall antiferromagnetic interactions and also spin-orbit coupling interactions between the adjacent Co(II) ions.

Complex **3** is essentially a Co-dimer with four carboxyl ligands coordinating to two Co(II) ions that form a typical paddle wheel SBU, which is further connected through the axial site by the BIMB ligand. The $\chi_M T$ value at the room temperature is 2.22 cm^3 K mol^{-1}, which is little lager than the calculated spin-only value of 1.875 cm^3 K mol^{-1} for one isolated Co(II) ion (S = 3/2), with octahedral geometry, indicating the orbital contribution of Co(II) ions. The plot of $1/\chi_M$ versus T can be fitted by the Curie-Weiss law above 2 K, giving the Curie constant value C = 2.93 cm^3 K mol^{-1} and

Weiss constant θ = -3.81 K. The negative θ value is indicative of a dominant antiferromagnetic interaction between Co(II) centers. According to the structure of complex **3**, it could be presumed that the main magnetic interactions are between the paddle-wheel unit metal center, while the superexchange interactions between Co(II) ions through the BIMB bridge can be ignored due to the length of the BIMB ligands. The results indicates the typical antiferromagnetic and spin-orbit coupling interactions present in the complex.

<Figure 5 here>

Theoretical calculations

To compare the stability of the BIMB ligand in their different conformations in three complexes, theoretical calculations have been performed. The molecular geometries of only the ligands were taken from the CIF files, generated during the crystal structure determination of the complexes, and are optimized. Single point energy calculations have been carried out by using B3LYP with 6-311g** basis set. It is a common practice in the field of polymeric metal complexes to compute the energies, using a model structure that very closely resembles the particular moiety to reduce mainly the computational time.[37] In the present study, we have considered only the BIMB ligand geometries in the complexes without considering coordination for the computational simplification as model structures. These considerations are adopted in these calculations only to compare the energies of the particular conformations. It has been shown, however, that these considerations can have a significant consequence on the absolute values, and therefore, only a qualitative comparison could be expected. From the literature, the energy calculations of the crystal structures have been performed by optimizing the crystal structures through various optimization procedures (Dreiding force field) using density functional theory (DFT) methods.[38] The optimized energy of the BIMB ligand in three complexes show almost the same energy (kcal/mol) in all its conformers, −452463.3423 (−452381.345) for **1**, −452617.4654 (−452589.452) and -452477.8070 (−452436.275) for **2** and −452471.7657 (−452461.842) for **3**. The values in the parentheses indicate single point energies. From the optimized energy values, all the conformations of the BIMB ligand converge to global minima in the potential energy surface (which corresponds to energies of stable conformations). A qualitative comparison of single point energy calculations reveals a slight difference in the energy values of the conformers. The results indicate that the BIMB ligands can show stable *cis*- and *trans*-conformations, and the energy difference between these conformations are very less, so that the ligand can exist in different conformations depending upon the coordination requirements.

Conclusions

In this work, we have successfully fabricated three novel coordination polymers under hydrothermal condition. Complex **1** features a 3-fold interpenetrating three-dimensional (3D) framework with $CdSO_4$-type topology. Complex **2** has an previously unknown 3D trinodal (4,4,6)-connected framework with Schläli symbol of $(4.6^4.8)_2(4^3.6^3)_2(4^4.6^{10}.8)$. Complex **3** exhibits a three-dimensional 2-fold interpenetrating pillared helical-layer open framework of α-Po topology based upon binuclear paddlewheel units. The results reveal that the carboxylic building blocks with different conformations play a significant role in promoting the diversity of the observed structural motifs. The magnetic properties of three complexes indicate the typical antiferromagnetic interactions and spin-orbit coupling interactions between the adjacent Co(II) ions. Complex **1** has modest power SHG activity and ferroelectric properties. Moreover, theoretical calculations indicate that the BIMB ligands can show stable *cis*- and *trans*-conformations, and the energy difference between these conformations are very less.

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Table 1 X-ray crystallographic data for complexes **1** - **3**

Complex	**1**	**2**	**3**
Formula	$C_{32}H_{22}N_4O_6SCo$	$C_{43}H_{29}N_6O_{11}SCo_2$	$C_{26}H_{17}F_6N_2O_5Co$
Formula weight	649.53	955.64	610.35
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*Cc*	*C*2/*c*	*P*2/*c*
a (Å)	22.707(3)	49.698(4)	14.909(3)
b (Å)	10.2165(11)	7.2513(6)	7.1963(15)
c (Å)	15.1394(16)	21.8865(19)	24.592(5)
α (°)	90	90	90
β (°)	124.5430(10)	93.5130(10)	104.312(2)
γ (°)	90	90	90
V (Å^3)	2892.9(5)	7872.6(12)	2556.5(9)
Z	4	8	4
D_{calc} (Mg/m^3)	1.491	1.613	1.586
μ (mm^{-1})	0.719	0.969	0.756
F(000)	1332	3896	1232
θ range (°)	2.27-25.50	2.41-25.50	2.47-26.00
Reflections collected	10927	30070	19735
Independent reflections (R_{int})	5274 (0.0184)	7325 (0.0598)	5025 (0.0138)
Data/restraints/parameters	5274 / 2 / 397	7325 / 14 / 576	5025 / 2 / 359
Goodness-of-fit	1.022	1.039	1.025
R indices $[I > 2\sigma(I)]^{a,b}$	$R_1 = 0.0283$	$R_1 = 0.0510$	$R_1 = 0.0468$
	$wR_2 = 0.0723$	$wR_2 = 0.1237$	$wR_2 = 0.1152$
R indices (all data)	$R_1 = 0.0299$	$R_1 = 0.0772$	$R_1 = 0.0570$
	$wR_2 = 0.0735$	$wR_2 = 0.1390$	$wR_2 = 0.1165$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1-3**[a]

Co(SDBA)(BIMB) (**1**)			
Co(1)-O(1)	1.9538(19)	Co(1)-O(3)#1	1.975(2)
Co(1)-N(4)#2	2.046(2)	Co(1)-N(1)	2.052(2)
O(1)-Co(1)-O(3)#1	112.59(10)	O(1)-Co(1)-N(1)	103.26(9)
O(1)-Co(1)-N(4)#2	123.64(9)	O(3)#1-Co(1)-N(1)	96.42(9)
O(3)#1-Co(1)-N(4)#2	112.85(9)	N(4)#2-Co(1)-N(1)	102.97(9)
$Co_2(SA)(BIMB)_{1.5}(H_2O)$ (**2**)			
Co(1)-O(4)#3	2.057(3)	Co(2)-O(6)#4	2.041(3)
Co(1)-N(5)	2.076(4)	Co(2)-N(4)#5	2.064(4)
Co(1)-O(1)	2.092(3)	Co(2)-O(5)#6	2.063(3)
Co(1)-O(1W)	2.115(3)	Co(2)-O(8)	2.144(3)
Co(1)-N(1)	2.152(3)	Co(2)-O(7)	2.188(3)
Co(1)-O(2)	2.238(3)	Co(2)-O(7)#4	2.343(3)
O(4)#3-Co(1)-N(5)	90.51(13)	O(6)#4-Co(2)-N(4)#5	98.52(13)
O(4)#3-Co(1)-O(1)	101.80(12)	O(6)#4-Co(2)-O(5)#6	94.57(11)
N(5)-Co(1)-O(1)	167.51(14)	N(4)#5-Co(2)-O(5)#6	102.54(14)
O(4)#3-Co(1)-O(1W)	85.53(14)	O(6)#4-Co(2)-O(8)	155.52(11)
N(5)-Co(1)-O(1W)	89.99(16)	N(4)#5-Co(2)-O(8)	105.72(13)
O(1)-Co(1)-O(1W)	88.86(14)	O(5)#6-Co(2)-O(8)	83.62(11)
O(4)#3-Co(1)-N(1)	93.35(12)	O(6)#4-Co(2)-O(7)	94.58(10)
N(5)-Co(1)-N(1)	91.13(14)	N(4)#5-Co(2)-O(7)	161.04(13)
O(1)-Co(1)-N(1)	90.28(13)	O(5)#6-Co(2)-O(7)	89.96(12)
O(1W)-Co(1)-N(1)	178.42(16)	O(8)-Co(2)-O(7)	61.08(10)
O(4)#3-Co(1)-O(2)	158.40(12)	O(6)#4-Co(2)-O(7)#4	84.46(10)
N(5)-Co(1)-O(2)	107.17(13)	N(4)#5-Co(2)-O(7)#4	93.22(12)
O(1)-Co(1)-O(2)	60.36(11)	O(5)#6-Co(2)-O(7)#4	164.17(11)
O(1W)-Co(1)-O(2)	82.25(13)	O(8)-Co(2)-O(7)#4	90.73(10)
N(1)-Co(1)-O(2)	98.48(12)	O(7)-Co(2)-O(7)#4	74.40(12)
$Co(FBA)(BIMB)_{0.5}{\cdot}H_2O$ (**3**)			
Co(1)-O(3)#7	2.012(2)	Co(1)-N(1)	2.058(3)

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Co(1)-O(1)	2.013(2)	Co(1)-O(2)#9	2.122(3)
Co(1)-O(4)#8	2.045(2)		
O(3)#7-Co(1)-O(1)	93.47(10)	O(4)#8-Co(1)-N(1)	92.40(10)
O(3)#7-Co(1)-O(4)#8	160.82(10)	O(3)#7-Co(1)-O(2)#9	86.96(10)
O(1)-Co(1)-O(4)#8	86.65(10)	O(1)-Co(1)-O(2)#9	160.50(10)
O(3)#7-Co(1)-N(1)	105.85(11)	O(4)#8-Co(1)-O(2)#9	86.66(11)
O(1)-Co(1)-N(1)	106.91(10)	N(1)-Co(1)-O(2)#9	91.66(11)

[a] Symmetry transformations used to generate equivalent atoms: #1 x+1/2, y-1/2, z+1; #2 x+1/2, -y+1/2, z-1/2; #3 x, y-1, z; #4 -x, -y+3, -z+1; #5 -x, y+3, -z+3/2; #6 x, y+1, z; #7 x, -y+2, z+1/2; #8 -x+1, y+1, -z+1/2; #9 -x+1, -y+3, -z+1.

Captions for Scheme and Figures:

Scheme 1 Two coordination fashions of BIMB: *trans*-configuration (top) and *cis*-configuration (bottom).

Fig. 1 (a) Coordination environment of Co(II) ions in **1** with the ellipsoids drawn at the 30% probability level; hydrogen atoms were omitted for clarity. Symmetry codes: A x+1/2, y-1/2, z+1; B x+1/2, -y+1/2, z-1/2. (b) A zigzag chain directed by Co(II) ions and SDBA dianions. (c) The 3D micropous metal-organic framework. (d) Schematic diagram of $CdSO_4$ topology. (e) View of 3-fold interpenetrating net. (f) Schematic diagram of polycatenane motif in **1**.

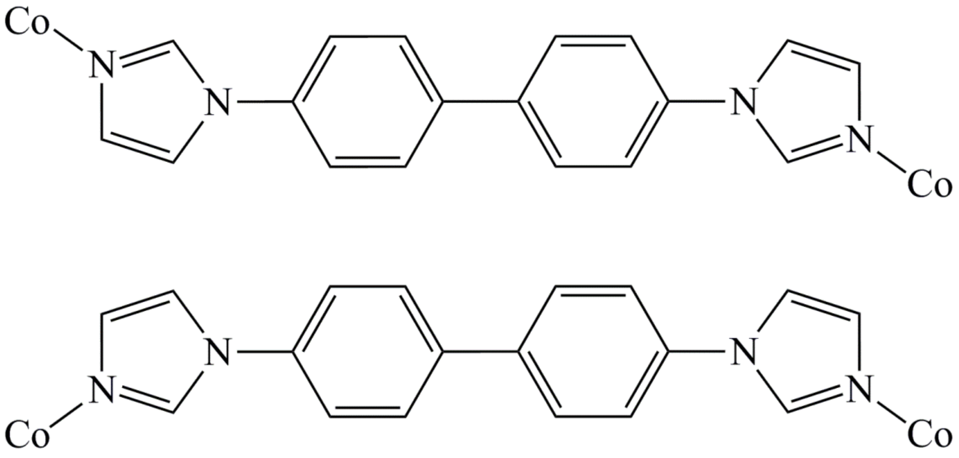
Fig. 2 (a) Coordination environment of Co(II) ions in **2** with the ellipsoids drawn at the 30% probability level; hydrogen atoms and water molecule were omitted for clarity. Symmetry codes: A x, y-1, z; B -x, -y+3, -z+1; C -x, y+3, -z+3/2; D x, y+1, z; E 1/2-x, -1/2-y, 2-z. (b) 1D chain constructed from SA^{4-} ligands and Co(II) ions. (c) The complicated 3D structure of **2**. (d) A schematic representation of the trinodal 4-connected network structure of **2**: cyan spheres represent Co1 nodes, purple spheres represent dinuclear Co_2 nodes, yellow spheres represent SA^{4-} nodes, and BIMB bridges are shown as green bonds.

Fig. 3 (a) Coordination environment of Co(II) ions in **3** with the ellipsoids drawn at the 30% probability level; hydrogen atoms were omitted for clarity. Symmetry codes: A x, -y+2, z+1/2; B -x+1, y+1, -z+1/2; C -x+1, -y+3, -z+1; D 2-x, 1-y, 1-z. (b) Dinuclear Co_2 paddlewheel building unit observed for **3**. (c) Paddlewheel clusters in **3** linked by FBA^{2-} ligands to form a helical (4,4)-net with large rhombic pores. (d) The

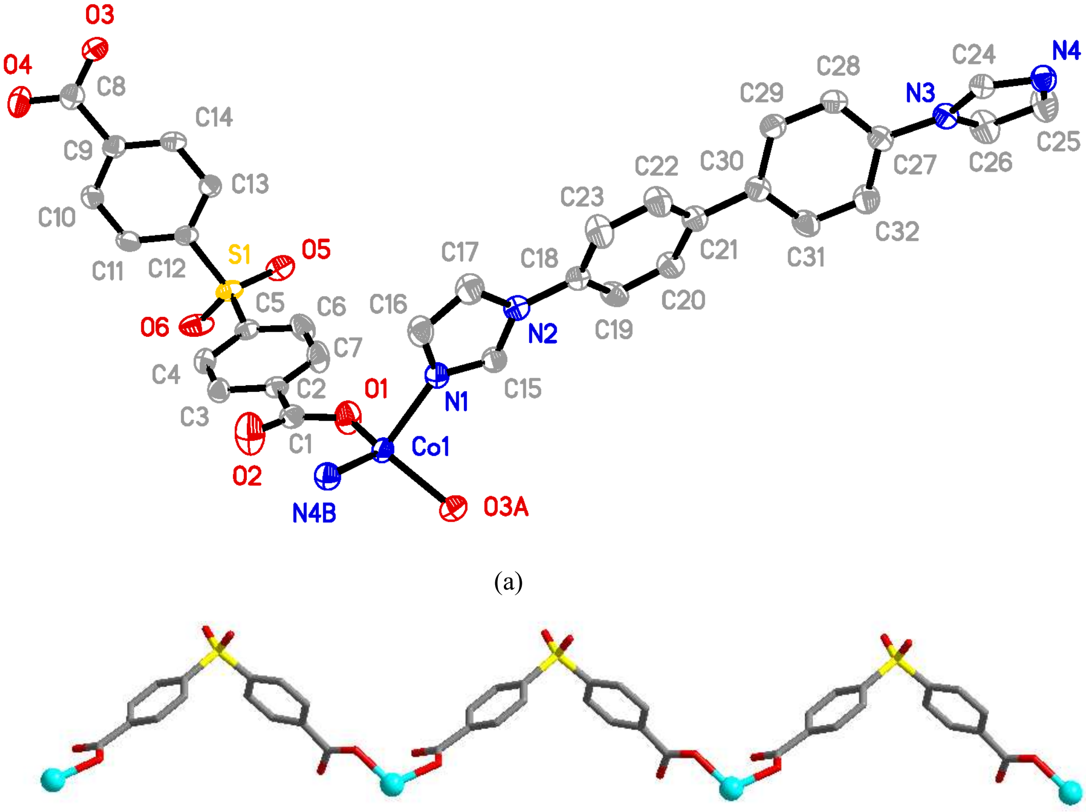
2-fold parallel 2D→2D interpenetration resulting in 1D double helical channels in **3**. (e) The 3D pillar-layered framework in **3** (viewed along the *b* axis). (f) Schematic representation of the 2-fold interpenetrating network in **3**.

Fig. 4 Electric hysteresis loops of complex **1** under different voltages at room temperature.

Fig. 5 Temperature dependence of $\chi_M T$ and χ_M for complexes **1-3**.


Co
N
N
N
N
Co
Co
N
N
N
N
Co

Scheme 1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O4
C8
C14
C9
C13
C10
C11
C12
S1
O5
O6
C5
C6
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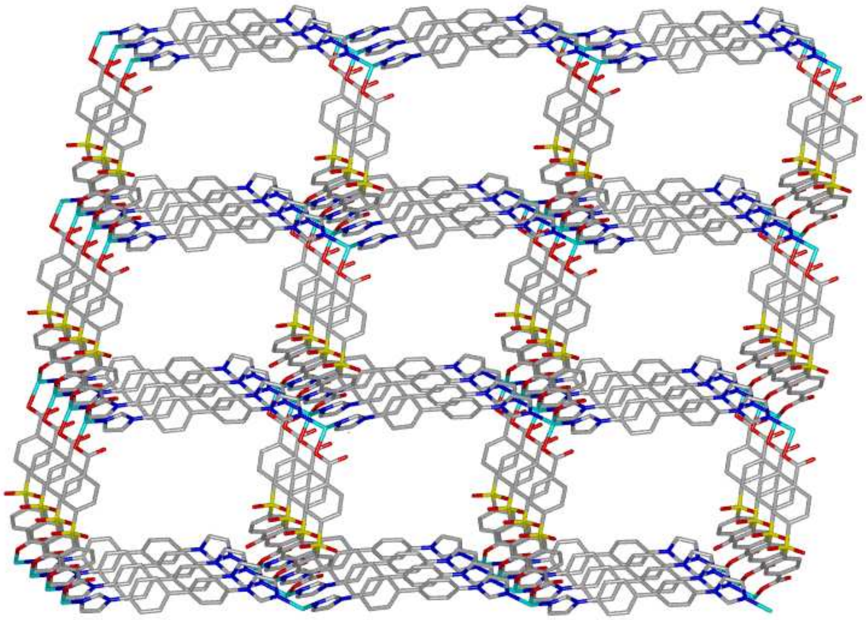
C4
C3
C2
C1
O1
O2
N4B
Co1
O3A
N1
C15
C16
C17
N2
C18
C19
C20
C21
C22
C23
C30
C29
C28
C31
C32
C27
N3
C24
N4
C25
C26

(a)

(b)



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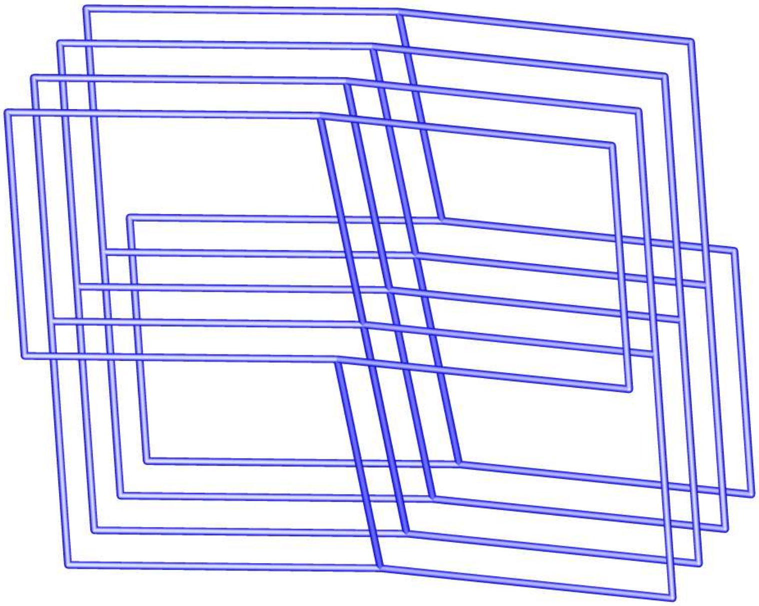

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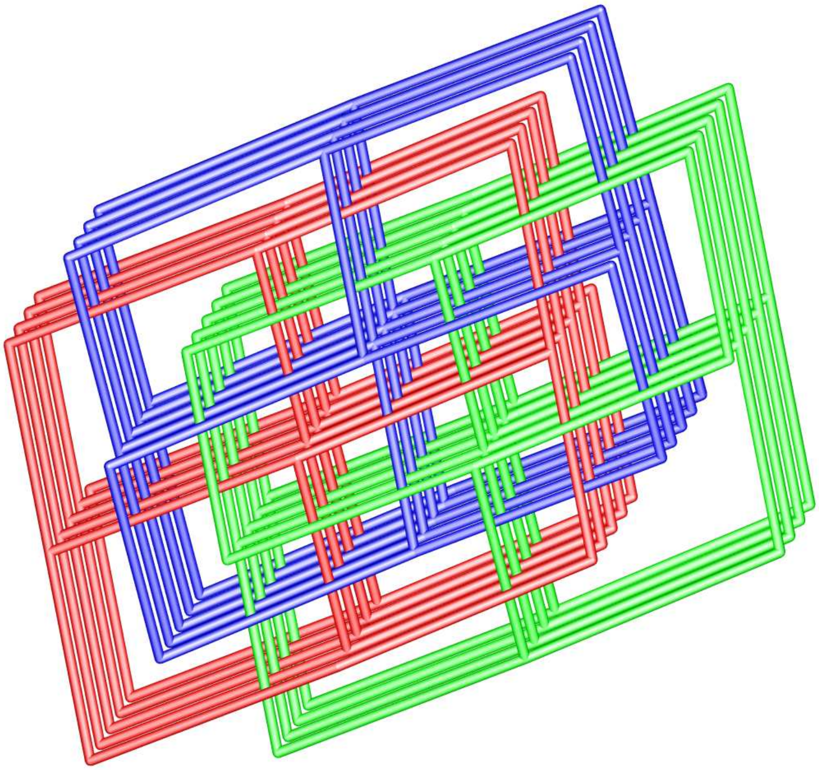
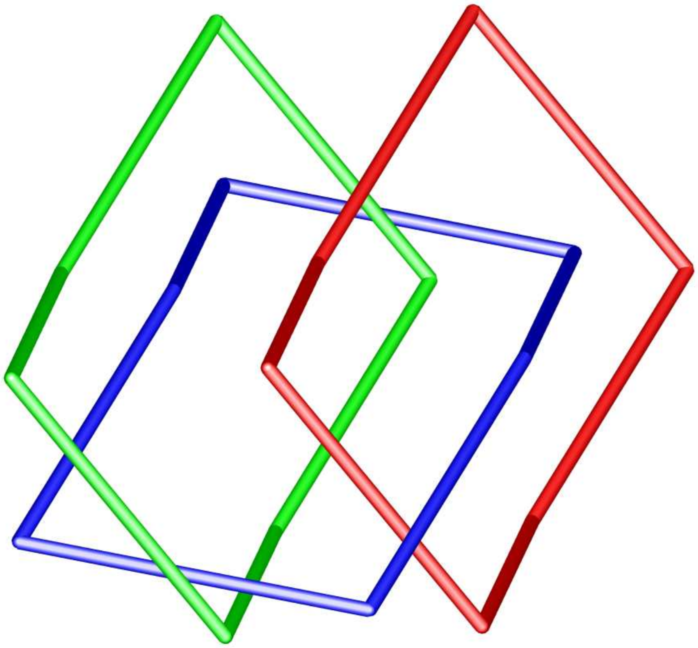
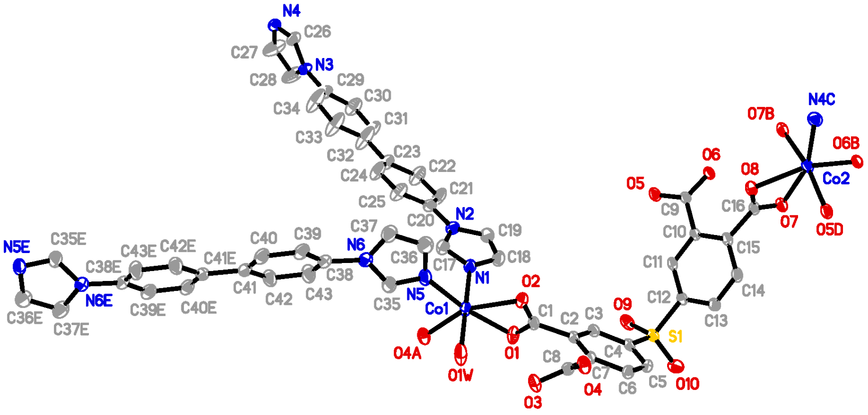


(e)

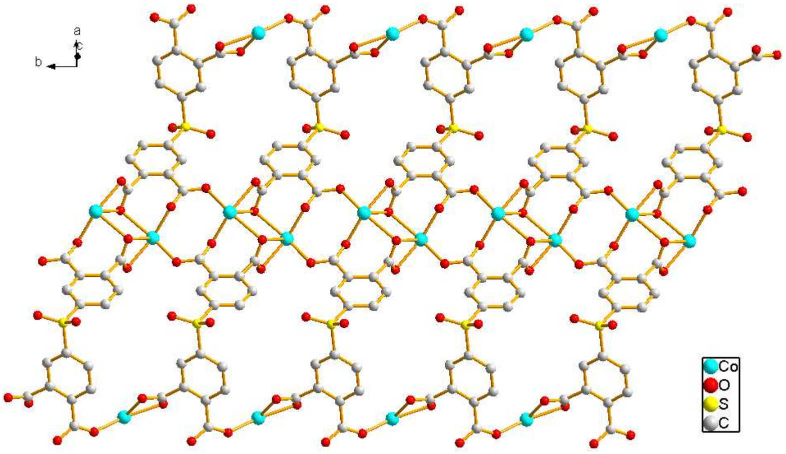


(f)

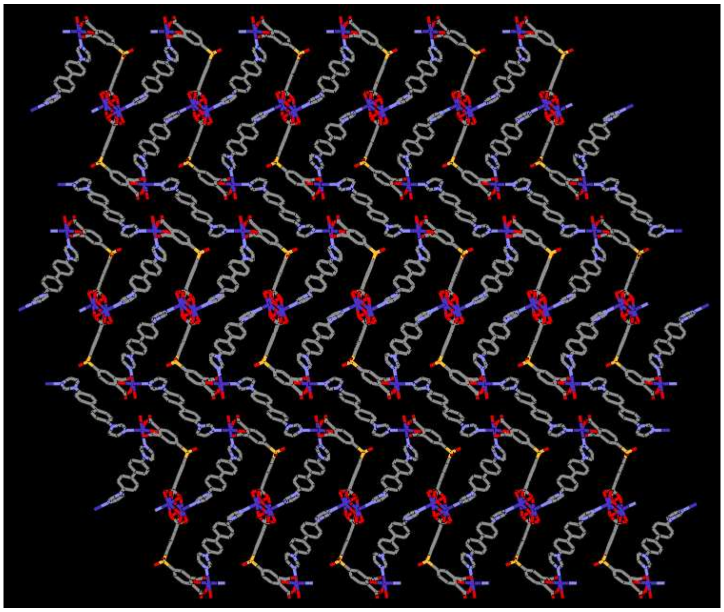
Figure 1.


N4
C26
C27
C28
N3
C29
C30
C34
C31
C33
C32
C23
C22
C24
C21
C25
C20
N2
C19
C37
N6
C36
C17
C18
N5E
C35E
C43E
C42E
C38E
C41E
C40
C39
N6E
C41
C42
C43
C38
N1
N5
C35
C39E
C40E
C36E
C37E
Co1
O2
C1
C2
C3
O4A
O1W
O1
C8
C4
O9
S1
O3
O4
C7
C6
C5
O10
O5
O6
C9
C10
C11
C12
C13
C14
C15
C16
O8
O7
O7B
N4C
O6B
Co2
O5D

(a)


a
c
b
Co
O
S
C

(b)



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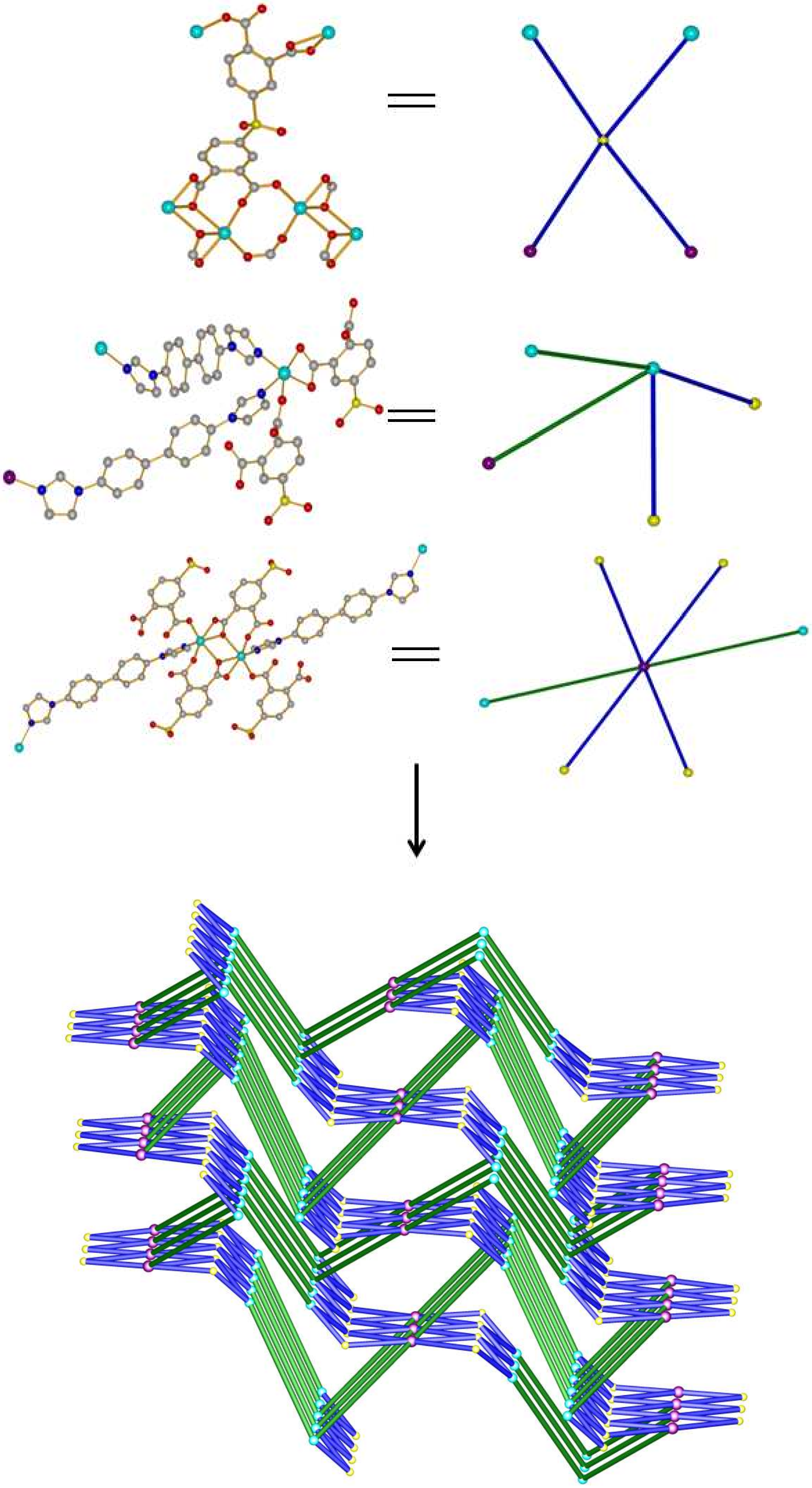
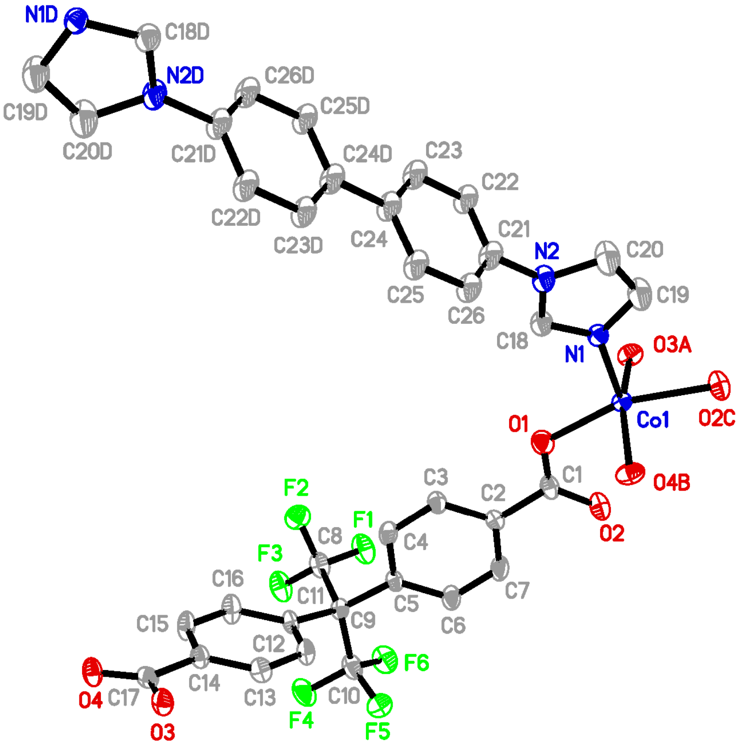
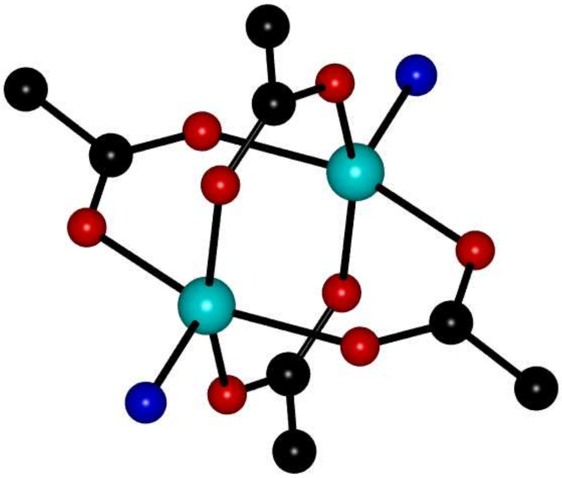


(d)

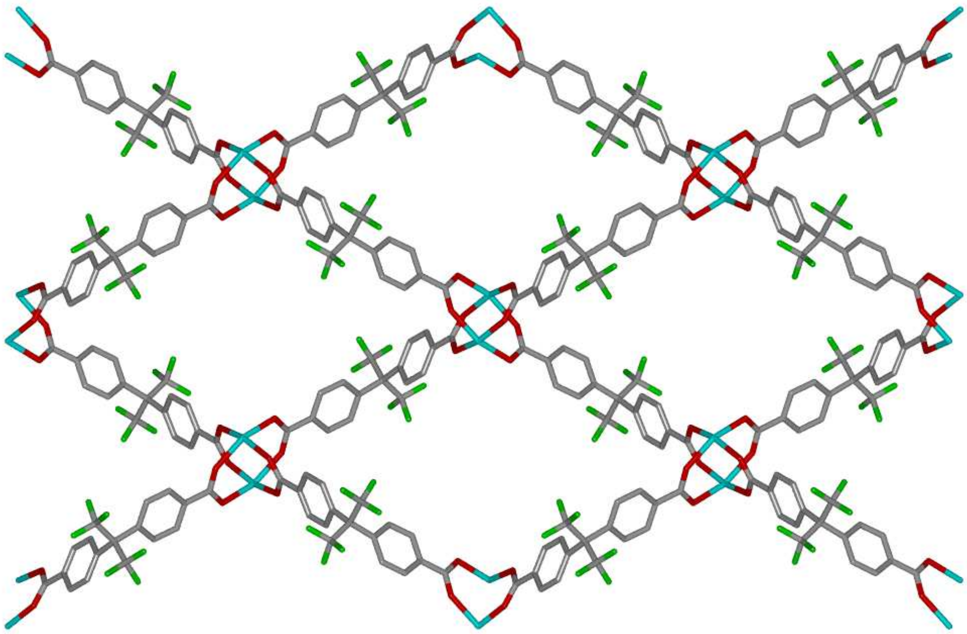
Figure 2.


N1D
C18D
N2D
C26D
C25D
C19D
C20D
C21D
C24D
C23
C22
C22D
C23D
C24
C21
N2
C20
C19
C25
C26
C18
N1
O3A
O2C
Co1
O1
O4B
C1
C2
C3
O2
F2
F1
C8
C4
F3
C16
C11
C5
C6
C7
C15
C9
C12
F6
O4
C17
C14
C13
C10
O3
F4
F5

(a)



(b)



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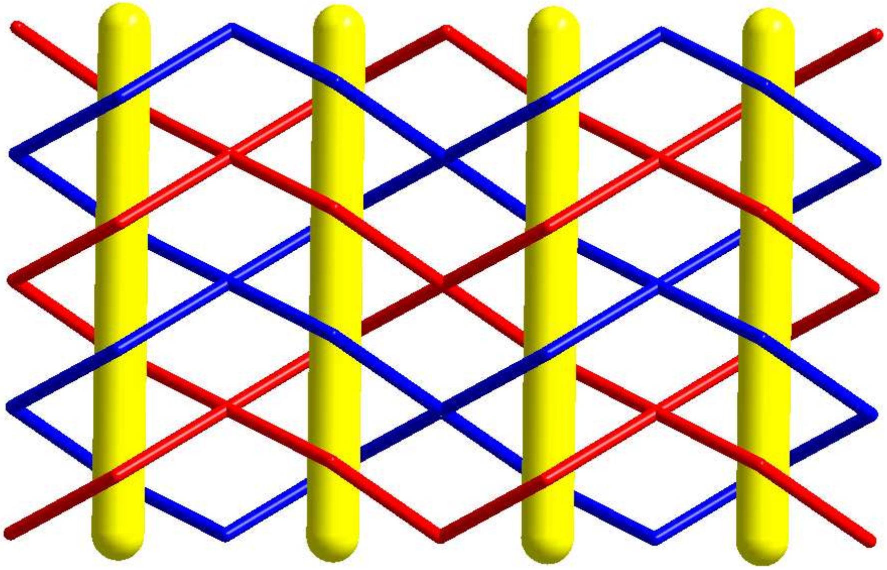
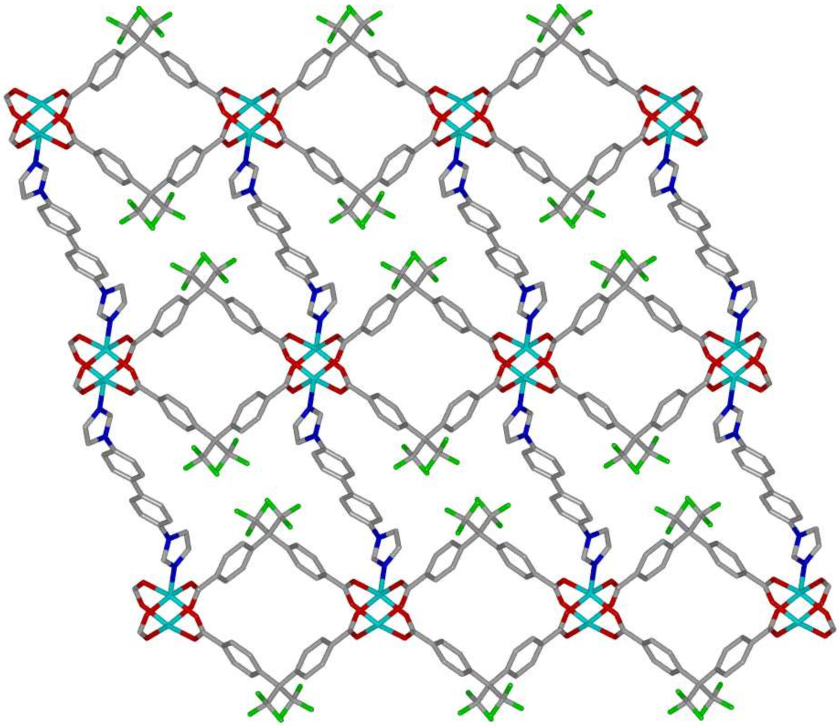
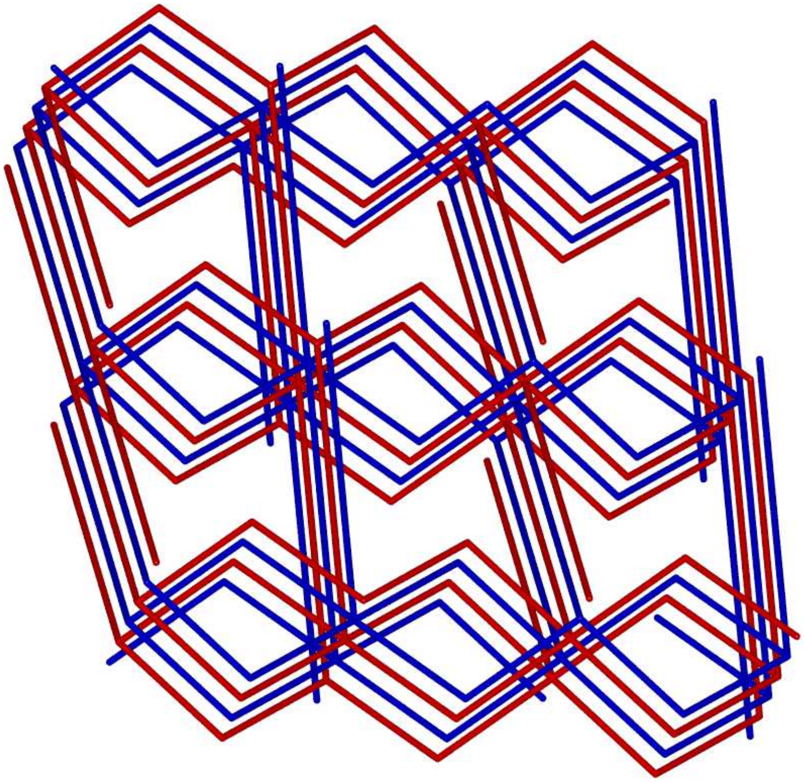


(d)



(e)



(f)

Figure 3.

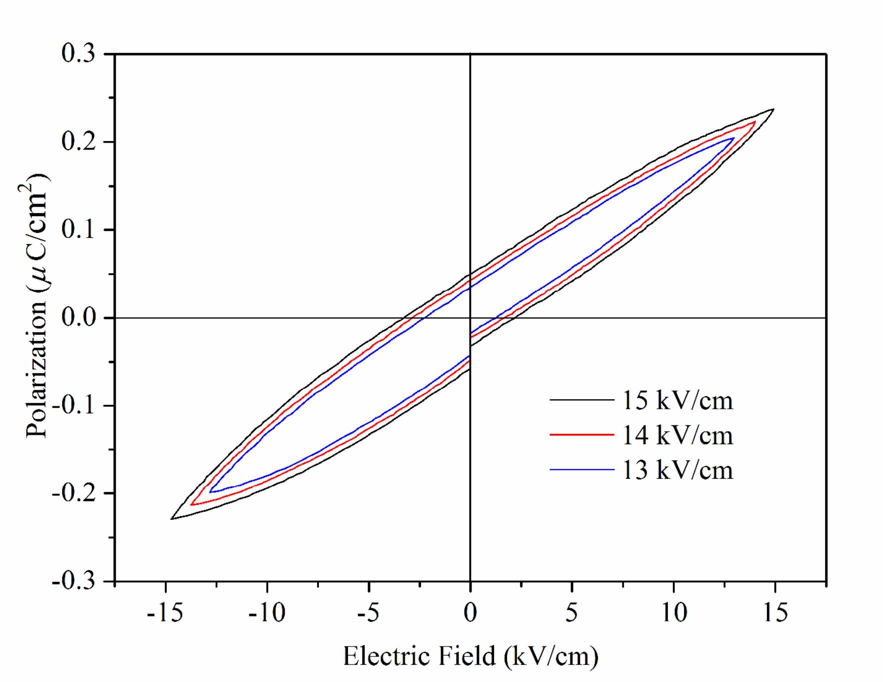
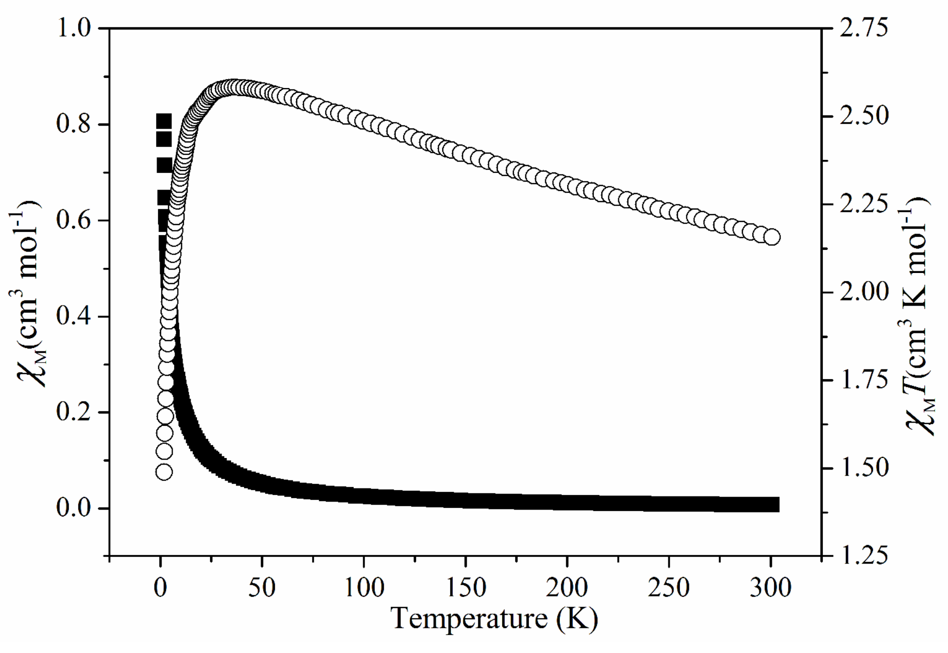
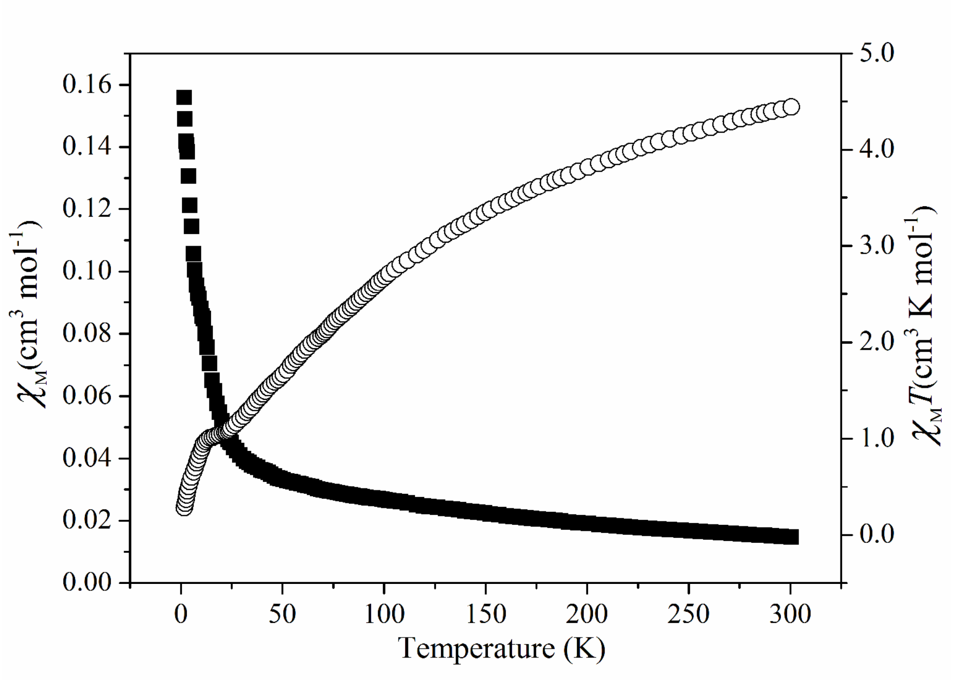

0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
Polarization (μC/cm^2)
-15
-10
-5
0
5
10
15
Electric Field (kV/cm)
15 kV/cm
14 kV/cm
13 kV/cm

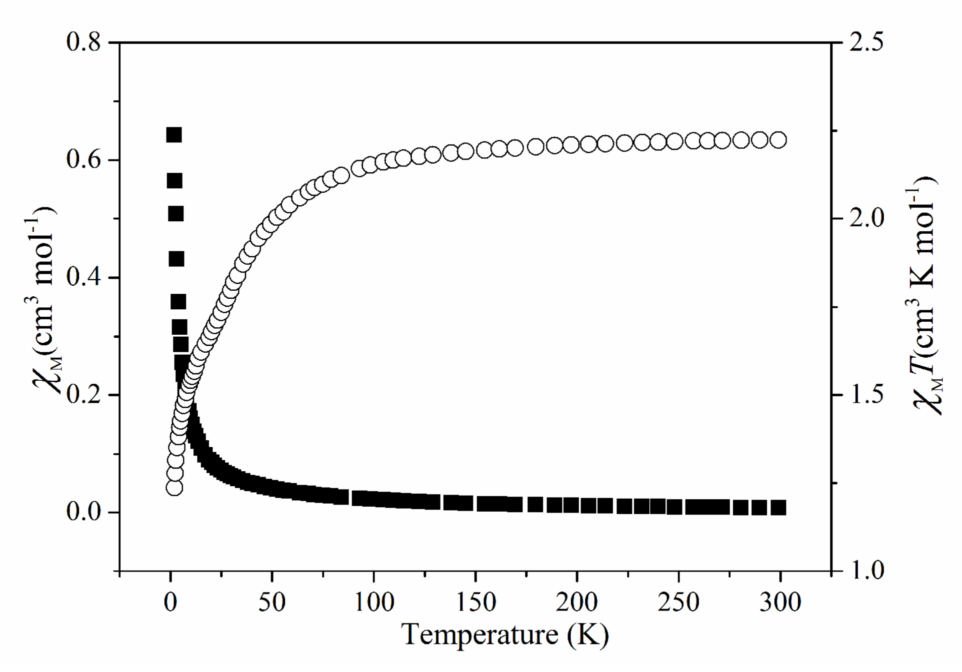
Figure 4.


1.0
0.8
0.6
0.4
0.2
0.0
χ_M(cm^3 mol^{-1})
2.75
2.50
2.25
2.00
1.75
1.50
1.25
$\chi_M T$(cm^3 K mol^{-1})
0
50
100
150
200
250
300
Temperature (K)

(a)


0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
χ_M(cm^3 mol^{-1})
0.0
1.0
2.0
3.0
4.0
5.0
$\chi_M T$(cm^3 K mol^{-1})
0
50
100
150
200
250
300
Temperature (K)

(b)


0.0
0.2
0.4
0.6
0.8
χ_M(cm^3 mol^{-1})
1.0
1.5
2.0
2.5
$\chi_M T$(cm^3 K mol^{-1})
0
50
100
150
200
250
300
Temperature (K)

(c)

Figure 5.

***Graphical Abstract*:**

Three cobalt(II) coordination polymers, based on V-shaped aromatic polycarboxylates and rigid bis(imidazole) ligand, are obtained, indicating that mixed-ligands are applied to expand the structural diversity.