

A Novel Coordination Polymer, $[\text{Ag}_4^{\text{I}}(\text{bpdc})(\text{H}_2\text{bpdc})(\text{Hbpdc})_2]_n$ (bpdc = 2,2'-bipyridyl-3,3'-dicarboxylate): Coordination Models of bpdc Ligands

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A novel coordination polymer, $[\text{Ag}_4(\text{bpdc})(\text{H}_2\text{bpdc})(\text{Hbpdc})_2]_n$ (bpdc = 2,2'-bipyridyl-3,3'-dicarboxylate), was hydrothermally synthesized at 403 K and structurally characterized by single crystal X-ray diffraction analysis. The compound crystallizes in the monoclinic space group *C2/c* with $a=1.9516(4)$ nm, $b=1.9503(4)$ nm, $c=1.2566(3)$ nm, and $\beta=112.48(3)^\circ$. In the two-dimensional crystal structure, Ag^{I} center is coordinated, in a scarce coordination environment, double-capped tetrahedron, by one bpdc ligand to form N—Ag—N chelate bond via two pyridyl N atoms, and other two bpdc ligands to form two O—Ag—O chelate bonds, respectively, via two carboxyl O atoms. The bpdc ligands are present in one non-protonated form, bpdc, and two protonated forms, Hbpdc and H_2bpdc , which all act as μ_3 -ligand in a hexadentate fashion (N, N'; O, O'; O, O') to coordinate with three Ag centers, respectively, through the three chelate bonds. This coordinated fashion of bpdc ligand is first found in the title compound. UV-Vis-NIR reflectance spectroscopy study revealed insulator nature for the crystal with an optical energy gap of 3.1 eV.

Keywords coordination polymer, silver, 2,2'-bipyridyl-3,3'-dicarboxylate, crystal structure

Introduction

Transition metal coordination polymers of one-, two- and three-dimensional infinite frameworks have been an attractive research area because of their diverse structures and useful properties.^{1,2} Polydentate ligands, which are used as bridges in constructing the coordination polymers are quite important in the crystal engineering of supramolecular architecture organized by coordinate covalent or hydrogen bonding.³ 2,2'-Bipyridyl-3,3'-dicarboxylate (bpdc) is a potential bridging ligand in various coordination models as a result of its multi-functional groups. However, it usually acts as an (N,N') bidentate ligand to form a chelate with one metal center in the corresponding discrete complex molecules.⁴⁻⁷ Only a few transition metal coordination polymers of bpdc ligands have been reported up to date. In $[\text{Mn}(\text{bpdc})(\text{H}_2\text{O})_4]_n$, the bpdc acts as an (O,O') bidentate μ_2 -ligand to bridge two metal centers via one oxygen atom of its two carboxyl groups, respectively, as shown in the model **I**.⁸ The monoprotonated bpdc, in $[\text{Ag}(\mu_3\text{-Hbpdc})(\text{H}_2\text{O})]_n$, coordinates with Ag^+ as an (N, N', O) tridentate ligand (model **II**) to form three bridges, N—Ag, N'—Ag and O—Ag bonds.⁹ The bpdc ligand is also in a tridentate fashion (N, N', O), but behaves as a

μ_2 -ligand to link two Cu^{2+} ions through one N—Cu—N' chelating system and one O—Cu bond in $[\text{Cu}(\mu_2\text{-bpdc})(\text{H}_2\text{O})_2]_n$, as shown in model **III**.^{10,11} We have recently demonstrated that bpdc acted as a μ_2 -ligand in a tetradentate fashion (N, N'; O, O') to form two chelate bridges, respectively, with two bivalent d-block transition metal ions to construct 1-D coordination polymer, as shown in model (**IV**).¹² Herein, we report the synthesis, structure and properties of a novel coordination polymer, $[\text{Ag}_4^{\text{I}}(\text{bpdc})(\text{H}_2\text{bpdc})(\text{Hbpdc})_2]_n$, of the bpdc ligand in two unprecedented coordination models (**V** and **VI**).

Experimental

Synthesis

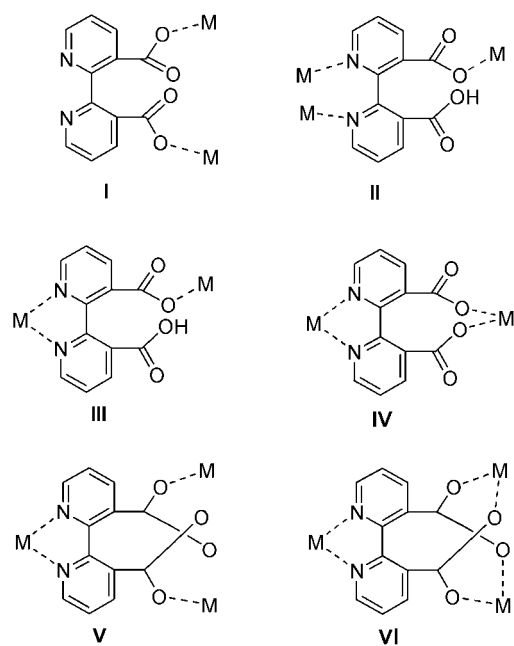
All the chemicals and solvents used in the syntheses were of reagent grade without further purification. 2,2'-Bipyridyl-3,3'-dicarboxylate acid (H_2bpdc) was prepared according to the reported method.¹³

A mixture of AgNO_3 (0.0849 g, 0.5 mmol) and H_2bpdc (0.1220 g, 0.5 mmol) in 1 : 1 molar ratio was sealed in a 25 mL Teflon-lined stainless steel Parr bomb containing H_2O (12 mL), heated at 403 K for 3 d and

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then cooled down to room temperature. Light yellow block crystals were isolated and washed with water. Yield 0.0883 g, *ca.* 50% based on AgNO₃. Elemental analyses of C, H, N for the crystal were performed by an Elementar Vario EL III. Calcd for C₂₄H₁₄Ag₂N₄O₈: C 41.06, H 2.01, N 7.99; found C 41.10, H 2.18, N 8.04. The infrared spectra were recorded from a KBr pellet on a Nicolet 750 FT IR spectrometer in the 600–4000 cm⁻¹ region: 3079 w, 1724 s, 1583 m, 1568 s, 1353 w, 1424 w, 1309 m, 1272 m, 1147 w, 1085 m, 1055 w, 954 w, 844 m, 828 w, 799 m, 773 m, 765 m, 745 w, 679 w, 661 w.

X-ray crystallographic analysis

A single crystal with dimensions of 0.10 mm × 0.10 mm × 0.10 mm was selected for the X-ray diffraction experiment. The intensity data were collected on a Rigaku R-Axis RAPID image plate diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.071069$ nm) at 293(2) K. A total of 18225 reflections in the range of $3.08^\circ \leq 2\theta \leq 55.04^\circ$, were measured, including 5042 unique reflections with $R_{\text{int}} = 0.0433$ and 2513 observed reflections having $I \geq 2\sigma(I)$. An absorption correction was applied by the correction of symmetry-equivalent reflections using the ABSCOR program.¹⁴ The structure was solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELX 97 programs.¹⁵ All the non-H atoms were refined anisotropically. H atoms of carboxyl groups were located from a Fourier difference map and the other H atoms were placed at their calculated positions on the relevant atoms. The final R indices are $R_1 = 0.0403$, $wR_2 = 0.0686$ for the observed reflections and $R_1 = 0.0912$, $wR_2 = 0.0752$ for all data. The crystal structure belongs to monoclinic space group $C2/c$ with unit cell dimensions, $a = 1.9516(4)$ nm, $b = 1.9503(4)$

nm, $c = 1.2566(3)$ nm, and $\beta = 112.48(3)^\circ$. The crystal drawings were produced with the program SCHAKAL92.¹⁶ The atomic coordinates are listed in Table 1, selected bond lengths in Table 2, bond angles in Table 3, and hydrogen bonds in Table 4.

Table 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{nm}^2 \times 10^5$)

| Atoms | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq}^a |
|-------|----------|----------|----------|-------------------|
| Ag(1) | 87(1) | -637(1) | 7510(1) | 58(1) |
| Ag(2) | 5000 | 567(1) | 7500 | 52(1) |
| Ag(3) | 5000 | -1846(1) | 7500 | 65(1) |
| O(1) | 5764(2) | -56(1) | 6468(2) | 38(1) |
| O(2) | 5103(1) | -1020(1) | 6041(2) | 37(1) |
| O(3) | 5911(2) | -232(1) | 9067(3) | 39(1) |
| O(4) | 6426(2) | -1189(1) | 8754(3) | 43(1) |
| O(5) | 4683(2) | -4582(1) | 8557(2) | 38(1) |
| O(6) | 5758(2) | -5135(1) | 9037(3) | 39(1) |
| O(7) | 4948(2) | 3870(1) | 8932(2) | 37(1) |
| O(8) | 5865(2) | 3270(2) | 8755(3) | 43(1) |
| N(1) | 7866(2) | 72(2) | 7790(3) | 37(1) |
| N(2) | 7690(2) | -1288(2) | 7145(3) | 34(1) |
| N(3) | 5764(2) | -2849(2) | 7847(3) | 35(1) |
| N(4) | 4395(2) | 1564(2) | 7807(3) | 35(1) |
| C(1) | 8077(2) | 637(2) | 8423(4) | 41(1) |
| C(2) | 7757(2) | 865(2) | 9143(4) | 42(1) |
| C(3) | 7195(2) | 484(2) | 9250(3) | 35(1) |
| C(4) | 6972(2) | -119(2) | 8631(3) | 25(1) |
| C(5) | 7312(2) | -299(2) | 7875(3) | 25(1) |
| C(6) | 7106(2) | -917(2) | 7114(3) | 25(1) |
| C(7) | 6379(2) | -1094(2) | 6418(3) | 26(1) |
| C(8) | 6273(2) | -1696(2) | 5770(4) | 36(1) |
| C(9) | 6875(2) | -2083(2) | 5812(4) | 45(1) |
| C(10) | 7572(2) | -1862(2) | 6510(4) | 38(1) |
| C(11) | 5713(2) | -675(2) | 6300(3) | 28(1) |
| C(12) | 6409(2) | -564(2) | 8825(3) | 29(1) |
| C(21) | 6488(2) | -2804(2) | 8502(4) | 42(1) |
| C(22) | 6876(2) | -3318(2) | 9226(4) | 43(1) |
| C(23) | 6500(2) | -3903(2) | 9294(4) | 36(1) |
| C(24) | 5746(2) | -3963(2) | 8630(3) | 26(1) |
| C(25) | 5402(2) | -3421(2) | 7899(3) | 26(1) |
| C(26) | 5339(2) | -4595(2) | 8744(3) | 30(1) |
| C(31) | 3969(2) | 1524(2) | 8417(4) | 42(1) |
| C(32) | 3898(2) | 2037(2) | 9101(4) | 41(1) |
| C(33) | 4295(2) | 2627(2) | 9170(4) | 35(1) |
| C(34) | 4757(2) | 2686(2) | 8573(3) | 26(1) |
| C(35) | 4775(2) | 2144(2) | 7864(3) | 24(1) |
| C(36) | 5241(2) | 3307(2) | 8763(3) | 30(1) |

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Diffuse reflectance spectra

Optical diffuse reflectance measurement for the title compound was made with a Shimadzu UV 3100 recording spectrophotometer with $\Phi 60$ mm integrating sphere from 250 to 2500 nm at room temperature. Initially, the 100% line flatness of the spectrophotome-

Table 2 Selected bond lengths

| Bonds | Bond lengths/nm |
|--------------|-----------------|
| Ag(1)—N(1) | 0.2398(3) |
| Ag(1)—N(2) | 0.2378(3) |
| Ag(1)—O(7)#1 | 0.2481(3) |
| Ag(1)—O(6)#2 | 0.2616(3) |
| Ag(1)—O(5)#3 | 0.2695(3) |
| Ag(1)—O(8)#4 | 0.2890(3) |
| Ag(2)—N(4) | 0.2382(3) |
| Ag(2)—O(3) | 0.2605(3) |
| Ag(2)—O(1) | 0.2619(3) |
| Ag(3)—N(3) | 0.2397(3) |
| Ag(3)—O(2) | 0.2505(3) |
| Ag(3)—O(4) | 0.2917(3) |
| O(1)—C(11) | 0.1223(4) |
| O(2)—C(11) | 0.1297(5) |
| O(7)—Ag(1)#3 | 0.2481(3) |
| O(8)—C(36) | 0.1224(4) |
| N(1)—C(1) | 0.1328(5) |
| N(1)—C(5) | 0.1339(5) |

Table 3 Selected bond angles

| Bond angles | Bond angle data/(°) |
|---------------------|---------------------|
| N(2)-Ag(1)-N(1) | 70.49(11) |
| N(2)-Ag(1)-O(7)#1 | 116.03(11) |
| N(1)-Ag(1)-O(7)#1 | 130.33(10) |
| N(4)#2-Ag(2)-N(4) | 70.47(16) |
| N(3)#2-Ag(3)-N(3) | 70.57(15) |
| N(3)#2-Ag(3)-O(2)#2 | 116.09(10) |
| N(3)-Ag(3)-O(2)#2 | 127.60(10) |
| N(3)#2-Ag(3)-O(2) | 127.60(10) |
| N(3)-Ag(3)-O(2) | 116.09(10) |
| O(2)#2-Ag(3)-O(2) | 99.95(13) |
| C(11)-O(2)-Ag(3) | 118.3(2) |
| C(36)-O(7)-Ag(1)#3 | 123.4(2) |
| C(1)-N(1)-C(5) | 118.3(4) |
| C(1)-N(1)-Ag(1) | 119.2(3) |
| C(5)-N(1)-Ag(1) | 112.0(3) |

ter was set by using barium sulfate (BaSO₄). A powder sample of the title compound was mounted on the sample holder. The thickness of the sample was approxi-

mately 2.00 mm, which was much greater than the size of the individual crystal particles.¹⁷

Results and Discussions

Description of the crystal structure

The title compound, [Ag₄(bpdc)(H₂bpdc)(Hbpdc)₂]_n, crystallizes in monoclinic space group *C2/c*. The crystal structure determination reveals a new layered structure as shown in Figure 1.

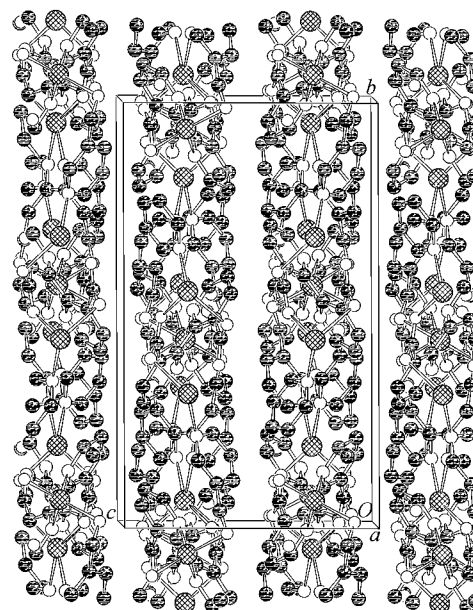


Figure 1 A packing view along the *a*-axis direction for [Ag₄(bpdc)(H₂bpdc)(Hbpdc)₂]_n with double shaded circles for Ag, partly shaded circles for N, open circles for O and solid circles for C atoms. The H atoms are left out. The unit cell is outlined.

The layer in (001) plane consists of a structural unit, [Ag(1)₂(bpdc)(H₂bpdc)][Ag(2)Ag(3)(Hbpdc)₂] with a twofold axis passing through Ag(2) and Ag(3) atoms (Figure 2). The structural unit is built up with two subunits [Ag(1)₂(bpdc)(H₂bpdc)] and [Ag(2)Ag(3)(Hbpdc)₂] through an N(3)-Ag(3)-N(3A) chelate bridge. In the first subunit, two Ag atoms, Ag(1) and Ag(1A), two nicotinic acid group anions of the non-protonated bpdc, and two nicotinic carboxyl groups of the double-protonated H₂bpdc are symmetrically related, respectively. In the second subunit, Ag(2) and Ag(3) are on the twofold axis. Two mono-protonated Hbpdc ligands are symmetrically related.

All the Ag atoms are tetrahedrally coordinated, in the main, by two pyridyl N atoms from one bpdc ligand and two carboxyl O atoms, respectively, from two bpdc ligands, as shown in Figure 3.

Table 4 Hydrogen bonds

| D—H···A | <i>d</i> (D—H)/nm | <i>d</i> (H···A)/nm | <i>d</i> (D···A)/nm | ∠(DHA)/(°) |
|---------------------|-------------------|---------------------|---------------------|------------|
| O(6)—H(41)···O(7)#4 | 0.997(19) | 1.49(2) | 2.474(4) | 168(5) |
| O(3)—H(42)···O(2)#2 | 0.988(19) | 1.48(2) | 2.468(4) | 176(5) |

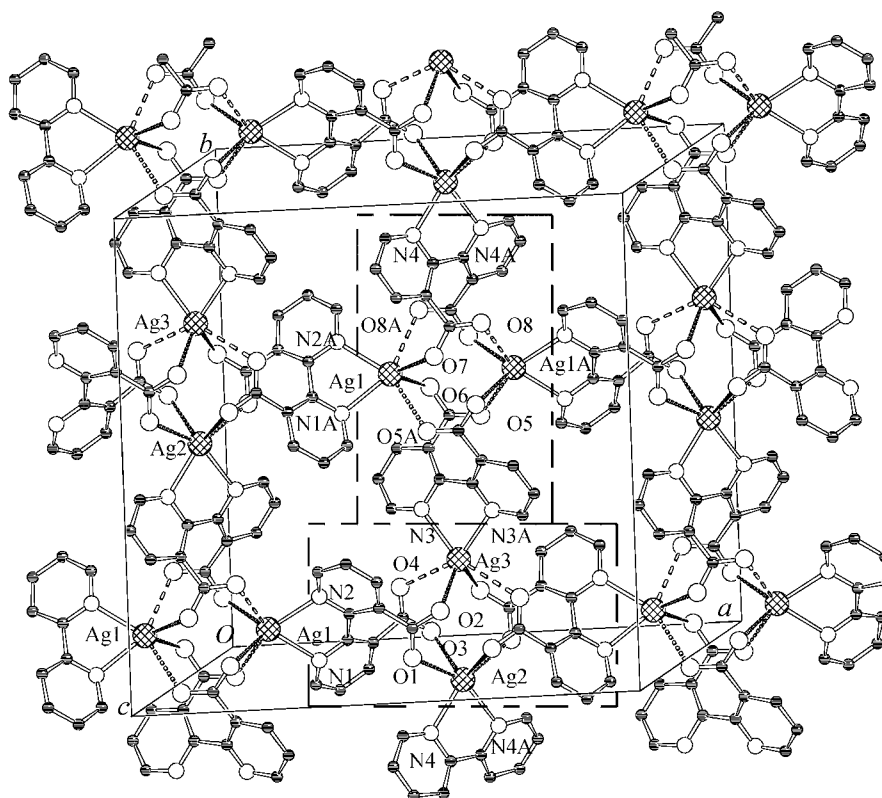


Figure 2 Structure of the layer. The structural unit $[\text{Ag}(1)_2(\text{bpdc})(\text{H}_2\text{bpdc})][\text{Ag}(2)\text{Ag}(3)(\text{Hbpdc})_2]$ is outlined by dotted line.

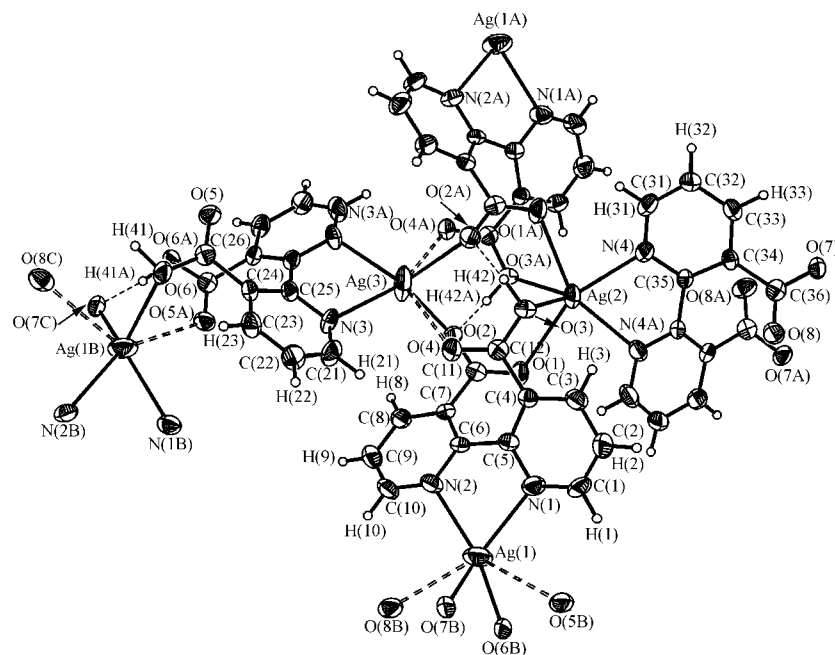


Figure 3 The coordination environments of $\text{Ag}^{\text{I}}(1)$, $\text{Ag}^{\text{I}}(2)$, and $\text{Ag}^{\text{I}}(3)$ atoms with the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

For $\text{Ag}(1)$ center in the first subunit, the coordinated $\text{N}(1)$ and $\text{N}(2)$ are two pyridyl N atoms of one Hbpdc ligand of the second subunit and the coordinated $\text{O}(6)$ and $\text{O}(7)$, are from one carboxyl group of H_2bpdc and one carboxylate of bpdc of the first subunit, respectively. $\text{Ag}(2)$ in the second subunit is coordinated by pyridyl $\text{N}(4)$ and $\text{N}(4\text{A})$ from one bpdc of the first sub-

unit, and carboxyl $\text{O}(3)$ and $\text{O}(3\text{A})$, respectively, from two Hbpdc ligands of the second subunit. In a similar way to $\text{Ag}(2)$, $\text{Ag}(3)$ is coordinated by $\text{N}(3)$, $\text{N}(3\text{A})$ and $\text{O}(2)$, $\text{O}(2\text{A})$.

The coordination tetrahedron around $\text{Ag}(1)$ center, however, is considerably distorted with the $\text{Ag}(1) - \text{N}(1)$, 0.2398(3) nm, $\text{Ag}(1) - \text{N}(2)$, 0.2378(3) nm; $\text{Ag}(1)$

—O(7)^{#1}, 0.2481(3) nm; N(1)-Ag(1)-N(2), 70.49°; N(1)-Ag(1)-O(7)^{#1}, 130.33°; and N(2)-Ag(1)-O(7)^{#1}, 116.03°. The distortion results from a weak coordination of another carboxyl of H₂bpdc, [-C(26A)O(5A)O(6A)H], to the Ag(1) center via O(5A) outside-in [N(1A)O(6)-O(7)] triangle plane of the coordination tetrahedron to form Ag(1)—O(5A) bond (0.2695 nm), and another weak coordination from carboxylate of bpdc, [-C(36A)O(7A)O(8A)], via O(8A) outside-in [N(2)-O(6)O(7)] triangle plane to form Ag(1)—O(8A) bond (0.2890 nm). By considering the weak coordinations, Ag(1) center, therefore, is coordinated by two N and four O atoms in a quasi-double-capped tetrahedral geometry. Similarly, the Ag(3)-centred coordination tetrahedron, [Ag(2)O(3)O(3A)N(4)N(4A)], is considerably distorted and capped, in the same way as above, by O(1) and O(1A), from the carboxylates of two symmetrically related Hbpdc ligands, respectively. The Ag(2)—O(1) distance is 0.2619(3) nm comparable with a normal Ag—O bond length. Ag(2) atom is coordinated by two N and four O atoms in a truly double-capped tetrahedron. The coordination tetrahedron of Ag(3), [Ag(3)N(3)N(3A)O(2)O(2A)], is also capped by two O atoms, O(4) and O(4A) (Ag—O, 0.2917 nm) to form a quasi-double-capped tetrahedral geometry.

The coordination polyhedra around Ag(1), Ag(2) and Ag(3) centers are quite similar, and especially, each Ag center is coordinated by two pyridyl N and four carboxyl O atoms of bpdc ligands in a scarce coordination environment, double-capped tetrahedron.

The bpdc ligands are present in three forms, one deprotonated bpdc, and two protonated Hbpdc and H₂bpdc. All the bpdc ligands in the compound act as tetradentate μ_3 -ligands in an (N, N'; O, O') fashion with the unprecedented coordination model **V**, only considering the strong interactions between Ag center and bpdc ligand. Each ligand bridges three Ag centers to form one chelate bond, N-Ag-N', and two Ag—O bonds, respectively, through its two carboxyl groups.

If the coordinations of capping O atom is considered, bpdc ligands are hexadentate, in (N, N'; O, O'; O, O') coordination fashion, still bridging three Ag centers, respectively, through one N-Ag-N and two O-Ag-O chelating systems in another new coordination model **VI**. The model **VI** is the strongest one of the bpdc ligand so found up to date.

There are two intra-layered hydrogen bonds between two bpdc ligands in each subunit as shown in Figure 2. In the first subunit, two carboxyl groups of H₂bpdc form two symmetrically related hydrogen bonds involving H(41) and H(41A) atoms, respectively, with two carboxyl groups of bpdc, O(6)—H(41)···O(7A) and O(6A)—H(41A)···O(7). Similarly, two symmetric hydrogen bonds, O(3)—H(42)···O(2A) and O(3A)—H(42A)···O(2) are formed in the second subunit.

The structural units are connected through N(1)-Ag(1)-N(2) chelating bridges extending along the *a*-axis direction, and N(4)-Ag(2)-N(4A) chelating bridges along the *b*-axis direction to form the layer par-

allel to (001) plane. The layers are packed along the *c*-axis direction by inter-molecular forces to construct the whole crystal structure (Figure 1).

Supporting Information Available

The X-ray crystallographic files in CIF format for this paper are available free charge via internet at www.ccdc.cam.ac.uk/conts/retrieving (CCDC-211869).

Optical band gap

In order to explore the conductivity of the title compound, the measurement of diffuse reflectivity for a powder sample was used to obtain its band gap E_g , which agrees rather well with that obtained by absorption measurement from a single crystal.¹⁸ The band gap E_g was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in a plot of Kubelka-Munk function F against energy E .¹⁹ Kubelka-Munk function, $F=(1-R)^2/2R$, was converted from the recorded diffuse reflectance data, where R is the reflectance of an infinitely thick layer at a given wavelength.²⁰ The F versus E plot for the title compound is shown in Figure 4, where a steep absorption edge is displayed and the E_g can be assessed at 3.1 eV.

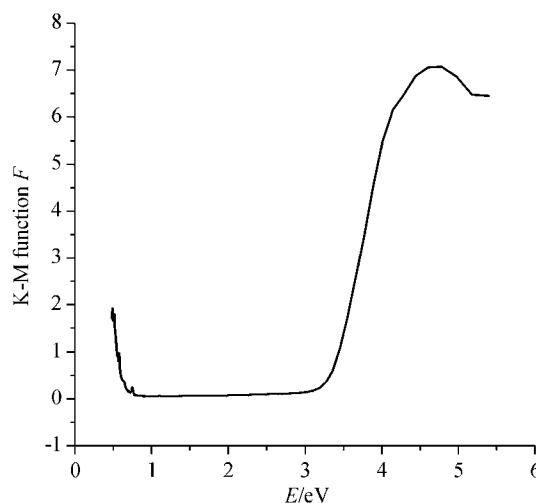


Figure 4 K-M Function F -Energy E curve of [Ag₄(bpdc)(H₂bpdc)(Hbpdc)₂]_n.

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