

A variety of one-, two- and three-dimensional copper(I) and silver(I) co-ordination polymers assembled by 1,4-bis(4-pyridyl)butadiyne and 1,4-bis(2-pyridyl)butadiyne †

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Four copper(I) and six silver(I) novel co-ordination polymers linked by 1,4-bis(4-pyridyl)butadiyne (4-bpbd) or 1,4-bis(2-pyridyl)butadiyne (2-bpbd) were prepared and seven structures crystallographically characterized, in order to illustrate the structural versatility of co-ordination polymers assembled by the Group 11 metal ions and rod-like nitrogen bidentate ligands with long spacers. Reaction of appropriate copper(I) and silver(I) salts with the 4-bpbd ligand affords 2-D interwoven copper(I) co-ordination polymers $\{[\text{Cu}_2(4\text{-bpbd})_3(\text{CH}_3\text{CN})_2]\text{X}_2\}_n$ ($\text{X} = \text{PF}_6$ **1a**·2H₂O or BF₄ **1b**) and 1-D straight chain silver(I) co-ordination polymers $\{[\text{Ag}(4\text{-bpbd})]\text{X}\}_n$ ($\text{X} = \text{NO}_3$ **2a**·CH₃CN, ClO₄ **2b**·(CH₃)₂CO or CF₃SO₃ **2c**·(CH₃)₂CO), respectively. On the other hand, reaction of suitable salts with the 2-bpbd ligand provides a 3-D diamondoid copper(I) co-ordination polymer $\{[\text{Cu}(2\text{-bpbd})_2]\text{BF}_4\}_n$ **3b**, a 1-D zigzag chain silver(I) co-ordination polymer $\{[\text{Ag}(2\text{-bpbd})(\text{NO}_3)]\}_n$ **4a** and a 2-D braid sheet silver(I) co-ordination polymer $\{[\text{Ag}(2\text{-bpbd})(\text{CF}_3\text{SO}_3)]\}_n$ **4c**, respectively. On the basis of these structural studies, the unique structural features and the dimensionality of the copper(I) and silver(I) co-ordination polymers are revealed.

Introduction

The construction of solid-state architectures and crystal engineering are rapidly developing areas of research,^{1,2} implicated in potential applications of materials to host–guest chemistry,³ catalysis,⁴ and the evolution of optical, magnetic and electron properties.^{5,6} During the past ten years, many researchers have attempted to prepare extensive co-ordination polymers with various dimensionalities, sizes, cavities and shapes.^{1,2} It has been considered that their structural versatility greatly relates to the nature of the metal center and ligand:^{7,8} (1) the oxidation state and co-ordination predisposition of the metal, (2) the ligand geometry including relative orientation of the donor groups and the spacing between donor groups and (3) the influence of the co-ordination anions. To generate multi-dimensional arrays or networks,^{1h,9–11} one of the simplest approaches is to use a bifunctional rod-like diatomic anion such as CN[−], or bidentate N,N′-donor linking groups such as pyridine- and pyrazine-based ligands with a preference for binding metals at each end in a linear fashion. Organic building blocks of various connectivities and geometries have been proposed in the preparation of co-ordination polymers.⁷ In particular, the 4,4′-bipyridine ligand (4,4′-bpy) is a highly investigated ligand, which has produced a number of 1-D co-ordination polymers^{12,13a} in zigzag chain, straight chain and stair-step structures, together with 2-D^{12c,13b–d} and 3-D¹³ co-ordination polymers in the shape of layers and networks. It is suggested that a degree of structural control may be introduced by manipulation of the disposition of 4-pyridyl groups of the parent 4,4′-bipyridine ligand. Linear rod-like ligands with

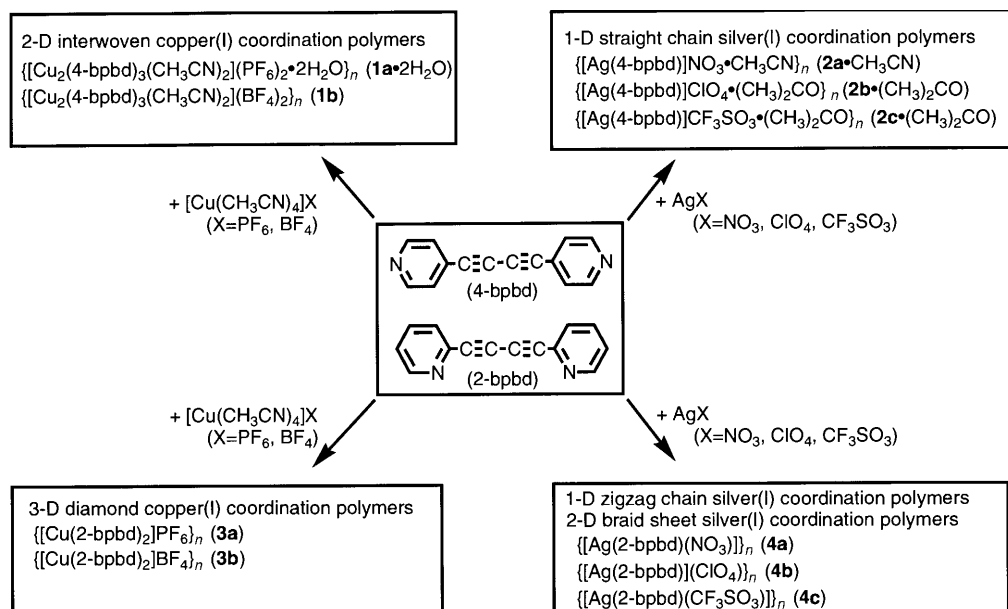
varying spacer lengths are represented by 1,4-bis(4-pyridyl)benzene, 1,4-bis(4-pyridyl)butadiyne¹⁴ and 2,7-diazapyrene.¹⁵ The relative orientations of the pyridyl donors should be modified by introduction of appropriate fixed spacers as in 1,2-*trans*-bis(4-pyridyl)ethene,^{12b,14a,16} and 4,4′-azobis(pyridine),^{16i,17} or by conformationally flexible tethers as in 1,2-bis(4-pyridyl)ethane¹⁸ and 1,3-bis(4-pyridyl)propane.¹⁹ Thus, systematic investigations of co-ordination polymers with 4,4′-bpy and related compounds are expected to provide useful knowledge, regarding the production of new crystal phases² with one-, two-, and three-dimensional motifs such as diamondoid, grid, ladder, brick and railroad. The aim of this study is to illustrate the structural versatility of co-ordination polymers that are built by the Group 11 metal ions (Cu^I and Ag^I) and rod-like nitrogen bidentate ligands with long spacers. According to Scheme 1, using 1,4-bis(4-pyridyl)butadiyne (4-bpbd) and 1,4-bis(2-pyridyl)butadiyne (2-bpbd), we prepared four copper(I) and six silver(I) novel co-ordination polymers and the versatile dimensionality of seven of them was demonstrated crystallographically.

Experimental

General procedures and reagents

All operations were carried out using usual Schlenk techniques under an argon atmosphere. $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{X}$ ($\text{X} = \text{PF}_6$ or BF₄) were prepared according to the literature.²⁰ AgNO₃, AgClO₄ and AgCF₃SO₃ were purchased from Aldrich and used without further purifications. The 4-bpbd and 2-bpbd ligands were synthesized according to the literature.²¹ All organic solvents were dried by usual methods and distilled before use. Infrared spectra were recorded with a JASCO 8000 spectrometer as KBr pellets.

† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/b0/b005006g/>



Scheme 1

Preparation of silver(I) and copper(I) co-ordination polymers

(a) $\{[\text{Cu}_2(4\text{-bpbd})_3(\text{CH}_3\text{CN})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}\}_n$ **1a**·2H₂O. A CH₃CN solution (1 ml) of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (37.2 mg, 0.10 mmol) was mixed with a (CH₃)₂CO solution (9 ml) of 4-bpbd (20.4 mg, 0.10 mmol) for 30 min under Ar. The resultant orange suspension was sealed in a 5 mm diameter glass tube and warmed in hot water (*ca.* 90 °C) to form a clear yellow solution. This was slowly cooled to room temperature in a thermobottle over 3 days and red crystals were obtained. Calc. for C₄₆H₃₂Cu₂F₁₂N₈O₂: C, 48.13; H, 2.99; N, 9.76. Found: C, 48.97; H, 3.06; N, 9.38%.

(b) $\{[\text{Cu}_2(4\text{-bpbd})_3(\text{CH}_3\text{CN})_2](\text{BF}_4)_2\}_n$ **1b**. Complex **1b** was prepared in the same manner as **1a**·2H₂O, using $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ (31.4 mg, 0.10 mmol). Red crystals were collected, which were not suitable for single-crystal X-ray analysis. Calc. for C₂₃H₁₅BCuF₄N₄: C, 55.50; H, 3.04; N, 11.26. Found: C, 57.03; H, 3.43; N, 10.49%.

(c) $\{[\text{Ag}(4\text{-bpbd})]\text{NO}_3 \cdot \text{CH}_3\text{CN}\}_n$ **2a**·CH₃CN. A CH₃CN solution (5 ml) of AgNO₃ (8.5 mg, 0.05 mmol) and a THF solution (5 ml) of 4-bpbd (10.2 mg, 0.05 mmol) were prepared in Schlenk tubes under Ar. The AgNO₃ solution was introduced into one compartment of a 5 mm diameter h-shaped glass tube and the 4-bpbd solution into the second compartment under Ar. These solutions were bridged by *n*-pentane and the h-shaped glass tube was sealed. It was allowed to stand at 5 °C for 6 months and colorless crystals were obtained. Calc. for C₁₆H₁₁AgN₄O₃: C, 46.29; H, 2.67; N, 13.50. Found: C, 45.06; H, 2.51; N, 12.39%.

(d) $\{[\text{Ag}(4\text{-bpbd})]\text{ClO}_4 \cdot (\text{CH}_3)_2\text{CO}\}_n$ **2b**·(CH₃)₂CO. A (CH₃)₂CO solution (5 ml) of AgClO₄ (10.3 mg, 0.05 mmol) and a CH₂Cl₂ solution (5 ml) of 4-bpbd (10.2 mg, 0.05 mmol) were prepared in Schlenk tubes under Ar. 2 ml samples of the 4-bpbd solution, (CH₃)₂CO solvent and the AgClO₄ solution were triply layered in a 5 mm diameter glass tube. The glass tube was sealed and allowed to stand at 5 °C for 3 days. Colorless crystals were obtained. Calc. for C₁₇H₁₄AgClN₂O₅: C, 43.48; H, 3.00; N, 5.79. Found: C, 42.27; H, 2.76; N, 7.10%.

(e) $\{[\text{Ag}(4\text{-bpbd})]\text{CF}_3\text{SO}_3 \cdot (\text{CH}_3)_2\text{CO}\}_n$ **2c**·(CH₃)₂CO. AgCF₃SO₃ (12.8 mg, 0.05 mmol) in CH₃CN solution (5 ml) was mixed with 4-bpbd (5.1 mg, 0.025 mmol) in (CH₃)₂CO solution (5 ml) for 30 min under Ar. The reaction solution was filtered and the

filtrate introduced into one compartment of a 5 mm diameter h-shaped glass tube. Diethyl ether was introduced into the second compartment. The glass tube was sealed and allowed to stand at 5 °C for 3 days. Colorless crystals were obtained. Calc. for C₁₈H₁₄AgF₃N₂O₄: C, 41.64; H, 2.72; N, 5.39. Found: C, 40.09; H, 2.51; N, 6.04%.

(f) $\{[\text{Cu}(2\text{-bpbd})_2]\text{PF}_6\}_n$ **3a**. $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (37.2 mg, 0.10 mmol) was treated with 2-bpbd (20.4 mg, 0.10 mmol) in CH₃CN–(CH₃)₂CO (10 ml, 1:9 v/v). After stirring for 30 min, the solution was filtered. The filtrate was introduced into a 5 mm glass tube and layered with *n*-pentane. The glass tube was sealed and allowed to stand at 5 °C for 1 week. The orange crystals were collected, but were not suitable for single-crystal X-ray analysis. Calc. for C₂₈H₁₆CuF₆N₄P: C, 54.51; H, 2.61; N, 9.08. Found: C, 53.34; H, 2.73; N, 9.35%.

(g) $\{[\text{Cu}(2\text{-bpbd})_2]\text{BF}_4\}_n$ **3b**. Complex **3b** was prepared in the same manner as **3a**, using $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ (31.4 mg, 0.10 mmol). Orange crystals were collected. Calc. for C₂₈H₁₆BCuF₄N₄: C, 60.18; H, 2.89; N, 10.03. Found: C, 59.64; H, 3.00; N, 10.07%.

(h) $\{[\text{Ag}(2\text{-bpbd})(\text{NO}_3)]\}_n$ **4a**. AgNO₃ (17.0 mg, 0.10 mmol) was mixed with 2-bpbd (20.4 mg, 0.10 mmol) in CH₃CN–CH₂Cl₂ (10 ml, 1:1 v/v). After stirring for 30 min the solution was filtered. The filtrate was introduced into a 5 mm glass tube and layered with *n*-pentane. The glass tube was sealed and allowed to stand at 5 °C for 3 days. Pale yellow crystals were collected. Calc. for C₁₄H₈AgN₃O₃: C, 44.95; H, 2.16; N, 11.23. Found: C, 44.31; H, 2.21; N, 11.16%.

(i) $\{[\text{Ag}(2\text{-bpbd})]\text{ClO}_4\}_n$ **4b**. Complex **4b** was prepared in the same way as **4a**, using AgClO₄ (20.6 mg, 0.10 mmol). Pale yellow crystals were collected, but were not suitable for single-crystal X-ray analysis. Calc. for C₁₄H₈AgClN₂O₄: C, 40.86; H, 1.96; N, 6.81. Found: C, 40.78; H, 2.12; N, 6.92%.

(j) $\{[\text{Ag}(2\text{-bpbd})](\text{CF}_3\text{SO}_3)]\}_n$ **4c**. 5 ml (CH₃)₂CO solutions of AgCF₃SO₃ (6.4 mg, 0.025 mmol) and 2-bpbd (5.1 mg, 0.025 mmol) were prepared in Schlenk tubes under Ar. A 2 ml sample of each solution was layered in a 5 mm diameter glass tube, sealed and allowed to stand at 5 °C for 3 days. Colorless crystals were obtained. Calc. for C₁₅H₈AgF₃N₂O₃S: C, 39.07; H, 1.75; N, 6.07. Found: C, 40.27; H, 1.77; N, 5.91%.

Crystal structure determinations

X-Ray measurement of complex **1a**·2H₂O was made with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) at 23 °C on a Quantum CCD area detector coupled with a Rigaku AFC-7 diffractometer. The data were corrected for Lorentz and polarization effects. **2a**·CH₃CN, **2b**·(CH₃)₂CO, **2c**·(CH₃)₂CO, **3b**, **4a** and **4c** were attached to ends of glass fibers and mounted on a Rigaku AFC-7R automated diffractometer equipped with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). The structures were solved by direct methods (SAPI 91^{22a} for **1a**·2H₂O, **2a**·CH₃CN, **2c**·(CH₃)₂CO and **4c**; SIR 88^{22b} for **2b**·(CH₃)₂CO, **3b** and **4a**) and expanded using Fourier techniques.^{22c} The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically for **4a** and included but not refined for other complexes. The F atom of the PF₆ and BF₄ anion for **1a**·2H₂O and **3b** and the O atom of solvated H₂O molecule of **1a**·2H₂O are disordered. Atomic scattering factors and anomalous dispersion terms were taken from ref. 23. All calculations were performed using TEXSAN.²⁴ Crystal data and details of the structure determination are summarized in Table 1. CCDC reference number 186/2192.

See <http://www.rsc.org/suppdata/dt/b0/b005006g/> for crystallographic files in .cif format.

Results and discussion

2-D interwoven copper(i) co-ordination polymer: **1a**·2H₂O

The reaction of the 4-bpbd ligand with [Cu(CH₃CN)₄]X afforded red-brown crystals of {[Cu₂(4-bpbd)₃(CH₃CN)₂]X₂}_n (X = PF₆ **1a**·2H₂O or BF₄ **1b**). The crystal structure of **1a**·2H₂O was characterized crystallographically. It shows an undulating polycatenated molecular ladder involving fully interwoven 2-D sheets. The whole structural motif bears a close resemblance to that described for {[Cu₂(pybut)₃(CH₃CN)₂][PF₆]₂·0.5MeCN·0.5Et₂O}_n (pybut = 1,4-bis(4-pyridyl)butadiyne), which was prepared by another procedure.^{2f,14e} The structural difference is that the PF₆⁻ anion and two H₂O molecules are interposed between the fourfold interpenetrated 2-D sheets. The molecular structure of **1a**·2H₂O was deposited as ESI, together with the bond distances and angles. Recently the features of ordered interpenetrating networks were reviewed by Batten and Robson.^{2g} Molecular ladders have been observed for relatively few related systems and the metal junction of the ladder is pseudo-octahedral in {[Co₂(4,4'-bpy)₃(NO₃)₄]_n²⁵ and {[Cd₂(L)₃(NO₃)₄]_n (L = 1,4-bis(4-methylpyridyl)benzene).²⁶ It was indicated that the 2-D ladder structure with linkage of the tetrahedral metal centers can be produced by combination of copper(i) ion and a rod-like ligand with a long spacer.

1-D straight chain silver(i) co-ordination polymers: **2a**·CH₃CN, **2b**·(CH₃)₂CO and **2c**·(CH₃)₂CO

A series of 1-D straight chain silver(i) co-ordination polymers {[Ag(4-bpbd)]X}_n (X = NO₃ **2a**·CH₃CN, ClO₄ **2b**·(CH₃)₂CO or CF₃SO₃ **2c**·(CH₃)₂CO) were obtained by reaction of appropriate silver(i) salts with the 4-bpbd ligand. Similar co-ordination polymers {[Ag(pybut)]X}_n (X = PO₂F₂ or NO₃) were reported as unpublished data in a recent report.^{2f} The fragment structure of **2a**·CH₃CN, **2b**·(CH₃)₂CO and **2c**·(CH₃)₂CO is shown in Fig. 1, together with the atomic labeling scheme. Selected bond distances and angles are listed in the caption. In Fig. 1(b) complex **2b**·(CH₃)₂CO has an inversion center of symmetry on the Ag(1) atom. Each Ag is co-ordinated by two N atoms of the 4-bpbd ligand in a completely linear geometry to form a 1-D straight chain structure of alternating silver(i) ions and 4-bpbd ligands. The ClO₄ anion is not co-ordinated, the Ag(1)···O(2) distance being 2.840(1) Å. Similarly, complexes **2a**·CH₃CN and **2c**·(CH₃)₂CO afforded 1-D straight chain structures, although they are slightly wavy at the N–Ag–N angles of 169.5(1) and

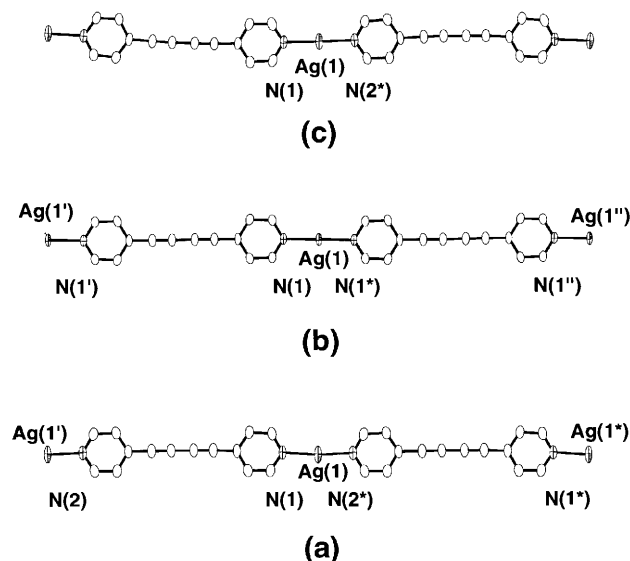


Fig. 1 The fragment structure of complexes **2a**·CH₃CN (a), **2b**·(CH₃)₂CO (b) and **2c**·(CH₃)₂CO (c). Selected bond distances (Å) and bond angles (°): **2a**·CH₃CN Ag(1)–N(1) 2.174(3) and Ag(1)–N(2*) 2.172(3); N(1)–Ag(1)–N(2*) 169.5(1); **2b**·(CH₃)₂CO Ag(1)–N(1) 2.162(2) and Ag(1)–N(1*) 2.162(2); N(1)–Ag(1)–N(1*) 180.0; **2c**·(CH₃)₂CO Ag(1)–N(1) 2.160(4) and Ag(1)–N(2*) 2.171(4); N(1)–Ag(1)–N(2*) 178.9(2).

178.9(2)°, respectively. The Ag(1)···O(1)(NO₃) 2.706(4) Å and Ag(1)···O(4) (CF₃SO₃) 2.869(8) Å distances are not indicative of co-ordination of the counter anion. In all of the silver(i) 4-bpbd complexes the two pyridyl groups of the co-ordinating 4-bpbd ligand are coplanar through the diyne portion. These 1-D straight chain co-ordination polymers assembled by the linkage of two-co-ordinate metal centers are structurally significant, since it seems that 1-D co-ordination polymers are generally assembled by linkage of square-planar and octahedral metal centers.^{2d,e}

The molecular structures of complexes **2a**·CH₃CN and **2b**·(CH₃)₂CO are depicted in Figs. 2 and 3, and that of **2c**·(CH₃)₂CO is deposited as ESI. As mentioned above, the parallel 1-D straight chains constructed alternately by Ag atoms and 4-bpbd ligands are *ca.* 7.64 Å apart in **2a**·CH₃CN. The counter anion NO₃⁻ and the CH₃CN molecule lie between these chains. Similarly, the 1-D straight chains are *ca.* 7.94 and 8.91 Å apart in **2b**·(CH₃)₂CO and **2c**·(CH₃)₂CO. The counter anion and solvent molecule {ClO₄⁻ and (CH₃)₂CO and CF₃SO₃⁻ and (CH₃)₂CO} are situated between the 1-D co-ordination chains for **2b**·(CH₃)₂CO and **2c**·(CH₃)₂CO, respectively. Incidentally, Schröder and co-workers recently reported the effect of ligand functionality and anion functionality on 1-D silver(i) co-ordination polymers.^{2f} In {[Ag(4,4'-bpy)]BF₄]_n 1-D linear chains of alternating silver(i) ions and 4,4'-bpy ligands lie parallel within the crystal structure but are staggered, minimizing Ag···Ag contacts and π – π interactions between adjacent chains. The structure of {[Ag(pybut)](PO₂F₂)_n contains pairs of 1-D linear chains of alternating silver(i) ions and bipyridyl ligands, resembling a ladder structure with π – π interactions of 3.394 Å and Ag···Ag interactions of 3.1929(10) Å. A similar ladder-like motif has been found in {[Ag(4-pyzt)]X}_n (4-pyzt = 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine, X = BF₄⁻ or PF₆⁻)^{13a} and {[Ag(3-pyzt)]CF₃SO₃]_n^{2f} with Ag···Ag interactions of 3.312(1), 3.230(1) and 3.2199(13) Å, respectively. In {[Ag(pybut)](NO₃)_n the Ag···Ag and π – π interactions are also replaced by weak interactions involving the NO₃⁻ anion. The 1-D linear chains no longer link pairwise to form ladders with Ag···Ag interactions. The weakly co-ordinating NO₃⁻ anions bridge between adjacent chains so as to form staggered pairs of chains. On the other hand, the side views of **2a**·CH₃CN, **2b**·(CH₃)₂CO and **2c**·(CH₃)₂CO reveal that the

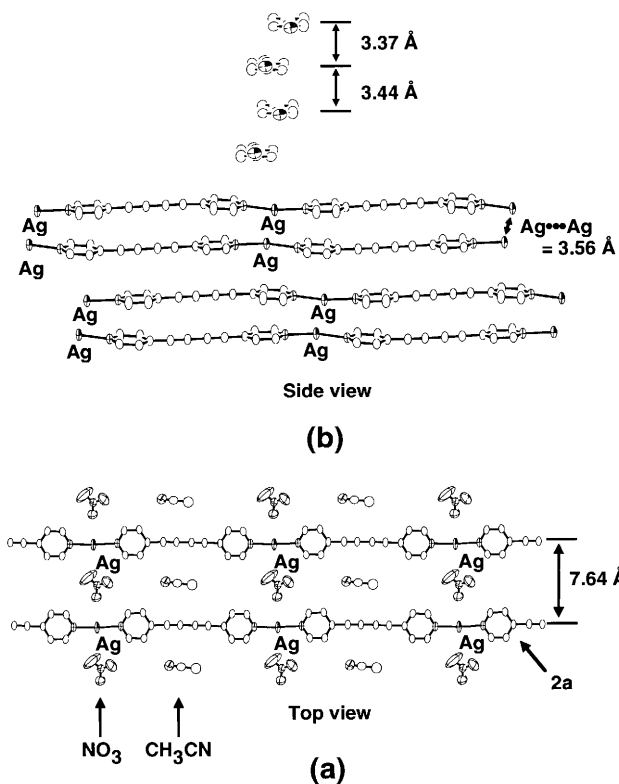


Fig. 2 The molecular structure of complex **2a**·CH₃CN. Top view (a) and side view (b).

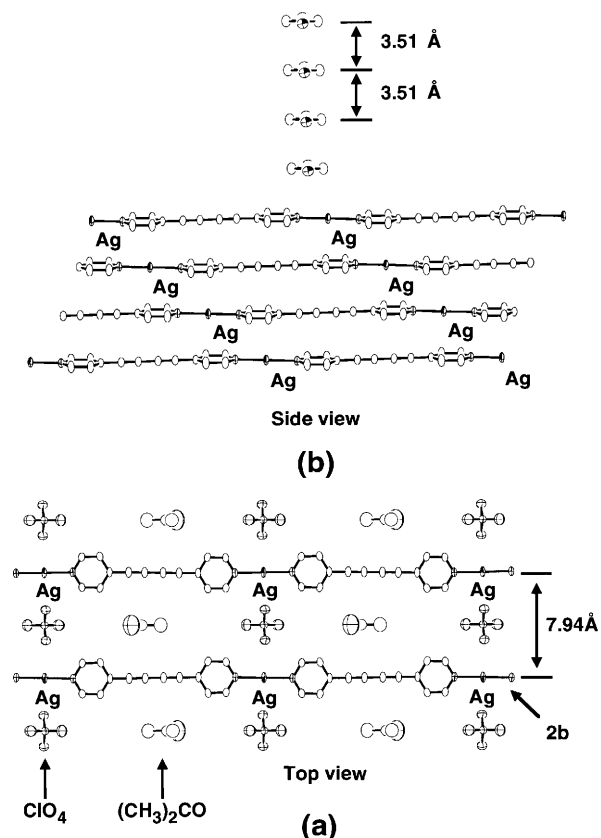


Fig. 3 The molecular structure of complex **2b**·(CH₃)₂CO. Top view (a) and side view (b).

parallel 1-D straight chains of **2a**·CH₃CN are nearly overlapping at *ca.* 3.37 and 3.44 Å, and the Ag···Ag separation of 3.56 Å is not bridged by the NO₃⁻ anions. Moreover, the parallel 1-D straight chains of **2b**·(CH₃)₂CO and **2c**·(CH₃)₂CO are not ladder-like motifs but are staggered at *ca.* 3.51 and 3.33 Å, respectively. Thus, structural differences with {[Ag(pybut)]X}_n

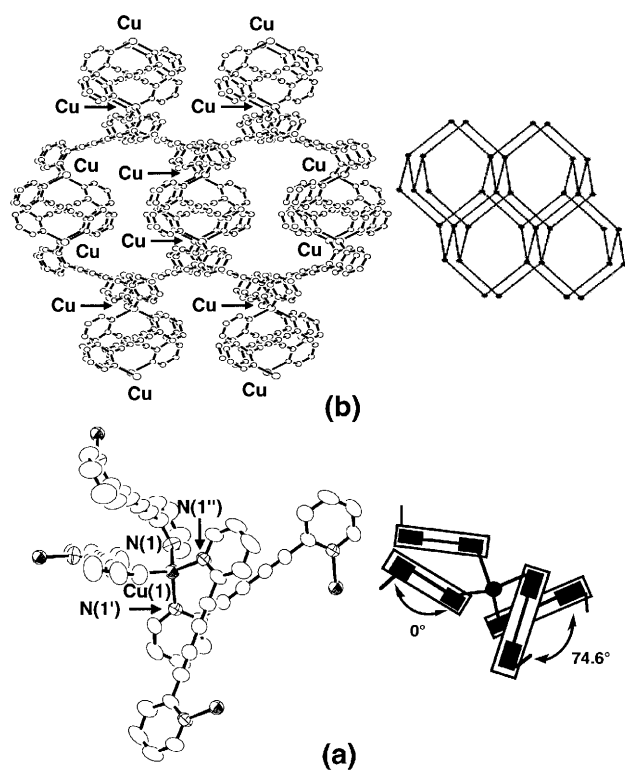


Fig. 4 The fragment structure (a) and the molecular structure (b) of complex **3b**. Selected bond distances (Å) and angles (°): Cu(1)–N(1) 2.070(6), Cu(1)–N(1') 2.070(6), Cu(1)–N(1'') 2.070(6) and Cu(1)–N(1*) 2.070(6); N(1)–Cu(1)–N(1') 105.7(1), N(1)–Cu(1)–N(1'') 105.7(1), N(1)–Cu(1)–N(1*) 117.4(3), N(1')–Cu(1)–N(1'') 117.4(3), N(1')–Cu(1)–N(1*) 105.7(1), N(1'')–Cu(1)–N(1*) 105.7(1), Cu(1)–N(1)–C(1) 122.4(5) and Cu(1)–N(1)–C(5) 122.4(5).

(X = PO₂F₂ or NO₃)^{2f} are probably derived from the occurrence of solvent molecules between the 1-D straight chains. It was demonstrated that the accommodation of solvent molecules is greatly related to an essential factor in the construction of longer-range silver(I) arrays, in addition to the effects of ligand functionality and anion functionality.^{2f}

3-D diamondoid copper(I) co-ordination polymer: **3b**

On the basis of the above crystallographic studies, it was obvious that the 4-bpbd ligand can provide a remarkable 2-D interwoven and 1-D straight chain structure for Cu^I and Ag^I, respectively. The 2-bpbd ligand is expected to produce an even more attractive co-ordination structure, since it can be co-ordinated in a *cisoid* or *transoid* conformation, similar to the 3,3'-dicyanodiphenylacetylene ligand.²⁷ According to the Experimental section, the reaction of [Cu(CH₃CN)₄]BF₄ with 2-bpbd afforded a 3-D diamondoid copper(I) co-ordination polymer {[Cu(2-bpbd)₂]BF₄}_n **3b**. The fragment structure and the molecular structure of **3b** are shown in Fig. 4. Selected bond distances and angles are listed in the caption. Each Cu atom is co-ordinated by four equivalent N atoms from the 2-bpbd ligand in a tetrahedral geometry. The Cu–N distance of 2.070(6) Å and the N–Cu–N angles of 105.7(1) and 117.4(3)° are almost equal to those of typical tetrahedral copper(I) complexes.²⁸ The pyridyl groups of the 2-bpbd ligands are coplanar through the diyne portion. The dihedral angle between the planes defined by two 2-bpbd ligands is *ca.* 74.6° *via* the Cu atom. The tetrahedral copper centers are in helices joined by the 2-bpbd ligands in a *transoid* conformation. The most remarkable feature is that the framework of the linkage of Cu atoms reveals a 3-D diamondoid structure with a Cu^I···Cu^I separation of 8.34 Å, which is not indicative of an attractive intermolecular interaction. The BF₄⁻ counter anions occupy vacant space in the crystal packing, which is not concurrent with interpenetration and π–π stacking.

Several co-ordination polymers with diamondoid and related frameworks have recently been reported.^{2b,g,29} In particular, the copper(I) and silver(I) ions having d¹⁰ electronic configuration are suitable for tetrahedral geometries in a diamondoid framework. Diamond-related frameworks have been constructed by combination of a tetrahedral metal ion and a bridging ligand, e.g. pyrazine,³⁰ 4,4'-bipyridine,^{13d-f} bisnitrile ligand^{27,31} and related compounds,^{15,16a} which in many cases generates a π - π interaction (stacking) and an interpenetrated structure. For instance, pyrazine (pz) and its derivatives are the shortest bridging ligands. The copper(I) ion in [Cu(2,5-Me₂pz)₂]₂PF₆³⁰ has a tetrahedral geometry with co-ordination of four N atoms of 2,5-dimethylpyrazine (2,5-Me₂pz). Coordination of the other N atoms of each 2,5-Me₂pz to other copper(I) ions results in the formation of a diamondoid framework with the shortest Cu^I...Cu^I separation of 6.99 Å. The presence of the PF₆⁻ counter anion and methyl groups in 2,5-Me₂pz prevents interpenetration of any other framework. On the other hand, 4,4'-bipyridine provided fourfold interpenetrated diamondoid frameworks for both Cu^I and Ag^I. The copper(I) compound [Cu(4,4'-bpy)₂]₂PF₆^{13d} exists as four independent concatenated diamondoid frameworks with Cu...Cu separations of 11.16 Å, in which the PF₆⁻ counter anions occupy channels. The silver(I) compound [Ag(4,4'-bpy)₂]₂CF₃SO₃^{13e} contains four interpenetrating diamondoid frameworks with a Ag^I...Ag^I intraframework separation of ca. 11.6 Å. The copper(I) complex [Cu(4,4'-bpy)_{1.5}]₂NO₃·1.25H₂O^{13f} showed sixfold interpenetrated frameworks with an interconnection of trigonal copper(I) centers through 4,4'-bpy by hydrothermal synthesis. A 1,2-*trans*-bis(4-pyridyl)ethene (4-bpe) ligand with a long spacer and a specific directionality afforded the copper(I) compound [Cu(4-bpe)₂]₂BF₄·0.5CH₂Cl₂^{16a} with fivefold interpenetrated diamondoid frameworks. The Cu...Cu distances bridged by 4-bpe ranged from 13.33 to 13.82 Å to create large cavities within the diamondoid framework. All five independent frameworks are polycatenated with channels throughout the structure, and these channels accommodate BF₄⁻ counter anions and CH₂Cl₂ solvent molecules. A *transoid* conformation of 3,3'-dicyanodiphenylacetylene (3,3'-dcpa) afforded the silver(I) compound [Ag(3,3'-dcpa)₂]₂ClO₄·H₂O with eightfold interpenetrated diamondoid frameworks,²⁷ which possessed the long Ag^I...Ag^I distance of ca. 17.0 Å. A majority of the large amount of void space created in a single diamondoid framework is filled through interpenetration. The remaining space within the lattice is filled by perchlorate ions and water. Thus, in many cases interpenetration and accommodation of solvent molecules or counter anions fill the vacant space in crystal packing. It has been suggested that the degree of interpenetration in a diamondoid structure is strongly correlated with the bridging M...M distance, counter anion size and π - π stacking distance. This is supported by a model study; it was found that the longer the M...M distance, the greater is the degree of interpenetration.^{29c} In contrast, in our crystallographic study, it is remarkable that complex **3b** did not display interpenetration and π - π stacking, regardless of the use of the 2-bpbd ligand with a rigid long spacer and a specifically co-ordinative orientation. Although the Cu^I...Cu^I separation of 8.34 Å is longer than that (6.99 Å) of 3-D interpenetrated copper(I) co-ordination polymers of 2,5-Me₂pz,³⁰ the separation is rather shorter than those of the 3-D interpenetrated copper(I) and silver(I) co-ordination polymers^{13d-f,16a,27} of 4,4'-bpy, 4-bpe and 3,3'-dcpa mentioned above. This result is in good agreement with the above suggestions. It was proposed that the specifically co-ordinative orientation of 2-bpbd and the favorable counter anion size of BF₄⁻ might prevent interpenetration of other frameworks.^{29c}

1-D zigzag chain silver(I) co-ordination polymer: **4a**

The reaction of AgNO₃ with the 2-bpbd ligand provided an

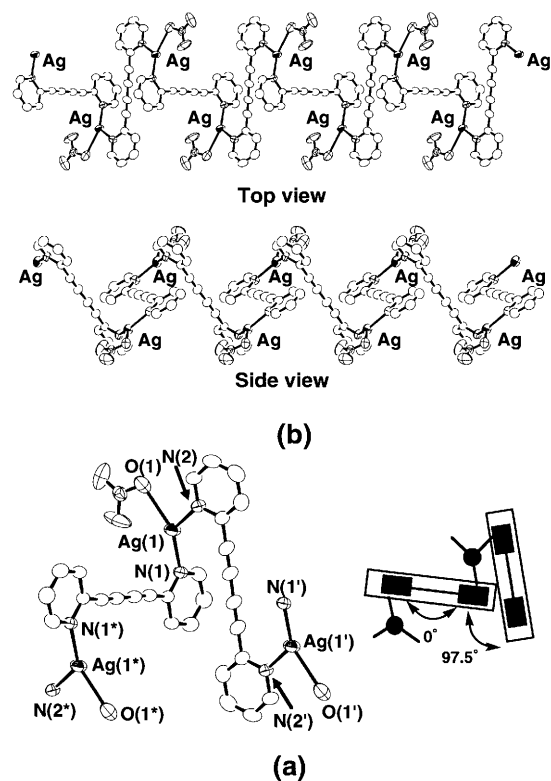


Fig. 5 The fragment structure (a) and the molecular structure (b) of complex **4a**. Selected bond distances (Å) and angles (°): Ag(1)–O(1) 2.532(1), Ag(1)–N(1) 2.240(2) and Ag(1)–N(2) 2.274(2); O(1)–Ag(1)–N(1) 139.69(6), O(1)–Ag(1)–N(2) 88.30(6), N(1)–Ag(1)–N(2) 130.81(5), Ag(1)–O(1)–N(3) 103.1(1), Ag(1)–N(1)–C(1) 120.6(2), Ag(1)–N(1)–C(5) 122.3(1), Ag(1)–N(2)–C(10) 121.2(1) and Ag(1)–N(2)–C(14) 120.9(1).

interesting 1-D zigzag chain silver(I) co-ordination polymer {[Ag(2-bpbd)(NO₃)]_n **4a**, in contrast to the 1-D straight chain co-ordination polymer **2a**·CH₃CN provided by AgNO₃ and the 4-bpbd ligand. The fragment structure of **4a** is shown in Fig. 5(a). Selected bond distances and angles are listed in the caption. Each Ag atom is co-ordinated by two N atoms of the 2-bpbd ligand and the O atom of the NO₃⁻ anion in a Y-shaped trigonal geometry.³² The Ag(1)–O(1) distance of 2.532(1) Å is longer than other distances of Ag(1)–N(1) 2.240(2) and Ag(1)–N(2) 2.274(2) Å, whereas the O(1)–Ag(1)–N(2) angle of 88.30(6)° is smaller than other angles of N(1)–Ag(1)–N(2) 130.81(5) and O(1)–Ag(1)–N(1) 139.69(6)°. The silver center is linked by 2-bpbd ligands in a *transoid* conformation to provide a 1-D zigzag chain structure. The pyridyl groups of the 2-bpbd ligands are coplanar through the diyne portions. The dihedral angle between the planes defined by the two 2-bpbd ligands is 97.5° through each Ag atom. Therefore, the ligands intersect at nearly right angles to each other.

The molecular structure is shown in Fig. 5(b). The 1-D zigzag chains are completely separated and no intermolecular interaction was found between them. It has recently been reported that the 1-D silver(I) co-ordination polymer {[Ag(2-bpbd)(NO₃)]_n,³³ which has the same components and the two pyridine rings attached to each tetrahedral Ag approximately coplanar, has a ribbon-like metallopolymeric structure. It resembles the structural motif in the 1-D silver(I) co-ordination polymer {[Ag(2,2'-dcpa)(CF₃SO₃)]_n³⁴ of 2,2'-dicyanodiphenylacetylene (2,2'-dcpa), in which 2,2'-dcpa co-ordinates to a distorted trigonal Ag atom in a *transoid* conformation, resulting in a half-bow-tie motif for chains and a flat 1-D silver(I) infinite chain constructed by the alternate arrangement of Ag atoms and 2,2'-dcpa. In contrast, the 2-bpbd ligands of **4a** in our crystallographic study are not coplanar to each Ag atom but intersect at nearly right angles to each other. Consequently,

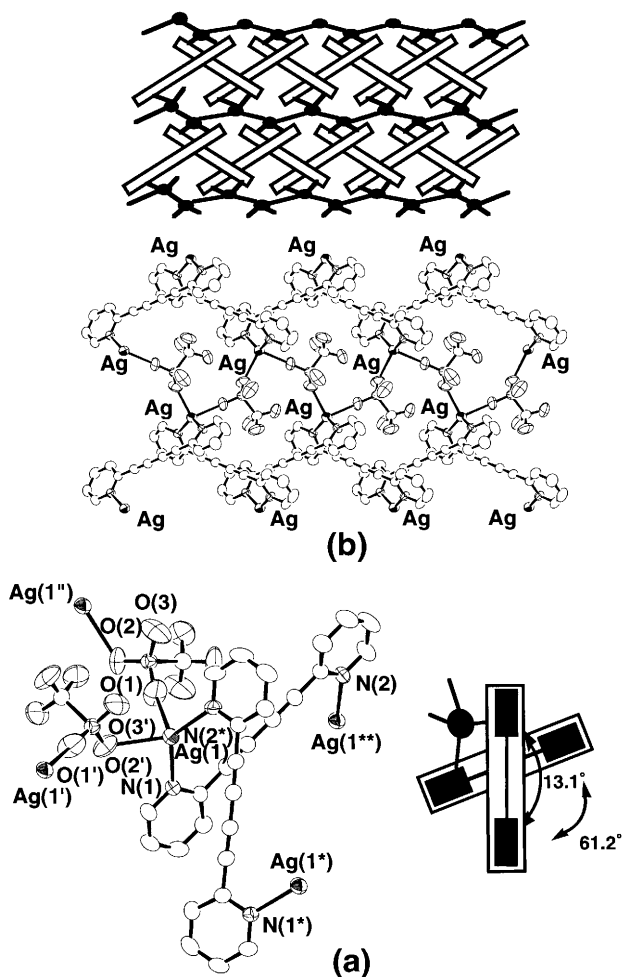


Fig. 6 The fragment structure (a) and the molecular structure (b) of complex **4c**. Selected bond distances (Å) and angles (°): Ag(1)–O(2') 2.572(4), Ag(1)–O(1) 2.445(4), Ag(1)–N(1) 2.258(3) and Ag(1)–N(2*) 2.239(3); O(2')–Ag(1)–O(1) 86.6(1), O(2')–Ag(1)–N(1) 88.1(1), O(2')–Ag(1)–N(2*) 136.2(1), O(1)–Ag(1)–N(1) 106.5(2), O(1)–Ag(1)–N(2*) 98.4(2), N(1)–Ag(1)–N(2*) 130.6(1), Ag(1)–O(2')–S(1') 111.4(2), Ag(1)–O(1)–S(1) 164.2(4); Ag(1)–N(1)–C(1) 123.8(3), Ag(1)–N(1)–C(5) 118.6(2), Ag(1)–N(2*)–C(10*) 119.5(3) and Ag(1)–N(2*)–C(14*) 122.4(3).

the whole motif of **4a** is greatly different from those found in $\{[\text{Ag}(2\text{-bpbd})(\text{NO}_3)]\}_n$ ³³ and $\{[\text{Ag}(2,2'\text{-dcpa})(\text{CF}_3\text{SO}_3)]\}_n$ ³⁴. Thus the structural differences are probably attributable to conditions of preparation, *i.e.* the solvents used and the reaction temperature.

2-D braid sheet silver(I) co-ordination polymer: **4c**

It is known that a counter anion such as NO_3 , ClO_4 or CF_3SO_3 can act as a useful bridging ligand. The 2-D braid sheet silver(I) co-ordination polymer $\{[\text{Ag}(2\text{-bpbd})(\text{CF}_3\text{SO}_3)]\}_n$ **4c** was constructed by the use of AgCF_3SO_3 (instead of AgNO_3), compared with the 1-D zigzag chain silver(I) co-ordination polymer formed by AgNO_3 and the 2-bpbd ligand. The fragment structure of **4c** is shown in Fig. 6(a). Selected bond distances and angles are listed in the caption. Each Ag atom is co-ordinated by two N atoms of the 2-bpbd ligand and two O atoms of CF_3SO_3 in a distorted tetrahedral geometry. The tetrahedral silver centers are connected by 2-bpbd ligands in a *transoid* conformation. The pyridyl groups of the 2-bpbd ligand are slightly twisted through the diyne portions at 13.1° , and this structural feature is unique among the copper(I) and silver(I) co-ordination polymers of 2-bpbd and 4-bpbd in this study. The dihedral angle between the mean planes defined by each 2-bpbd ligand is 61.2° *via* the Ag atom. Consequently, a 1-D braid chain structure is formed by the alternating Ag atoms and

Table 1 Crystallographic data and details of the structure determination

	1a ·2H ₂ O	2a ·CH ₃ CN	2b ·(CH ₃) ₂ CO	2c ·(CH ₃) ₂ CO	3b	4a	4c
Formula	C ₄₆ H ₃₄ Cu ₂ F ₁₂ N ₈ O ₈ P ₂	C ₁₆ H ₁₁ AgN ₄ O ₃	C ₁₇ H ₁₄ AgClN ₂ O ₅	C ₁₈ H ₁₄ AgF ₃ N ₂ O ₄ S	C ₂₈ H ₁₆ BCuF ₄ N ₄	C ₃₈ H ₁₆ Ag ₂ N ₆ O ₆	C ₁₅ H ₁₀ AgF ₃ N ₂ O ₃ S
Formula weight	11147.85	415.16	469.63	519.24	558.81	748.2	461.16
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Tetragonal	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>m</i>	<i>P</i> ₂ / <i>c</i>	<i>I</i> ₄ / <i>a</i>	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>c</i>
<i>a</i> /Å	12.639(2)	14.739(6)	5.296(2)	11.399(3)	10.626(3)	9.918(3)	15.870(4)
<i>b</i> /Å	15.558(2)	7.644(4)	15.876(6)	17.818(1)	10.626(3)	10.625(3)	10.912(4)
<i>c</i> /Å	16.5787(5)	7.582(5)	10.889(3)	10.157(3)	25.718(3)	7.398(3)	9.457(5)
<i>a</i> /°	113.349(1)	75.66(5)	100.47(4)	104.98(2)		95.33(2)	99.32(3)
<i>b</i> /°	91.187(2)	89.36(5)	900.3(6)	1992(1)		102.96(3)	161.6(1)
<i>c</i> /°	106.020(1)	80.00(4)	2	4		113.84(2)	4
γ /°	284.5(3)	814.7(8)	12.95	11.68		680.0(4)	14.22
<i>Z</i>	8, 84	2	296	296	4	1	296
μ (Mo–K α)/cm ⁻¹	296	12.55	4004	4824	7.99	14.91	296
<i>T</i> /K	12379	296	1829	2583	296	296	296
Measured reflections	6748	2644	1424	701	1853	3308	3943
Observed reflections (<i>I</i> > 2 σ (<i>I</i>))	0.111	0.041	0.024	0.055	701	2529	2578
<i>R</i>	0.111	0.041	0.024	0.055	0.093	0.029	0.041
<i>R</i> _w	0.358	0.123	0.071	0.180	0.297	0.073	0.103

2-bpbd ligands. The 1-D braid chains are further bridged by CF_3SO_3 anions to provide a quite interesting 2-D braid sheet structure. The molecular structure is shown in Fig. 6(b). So far, various motifs of 2-D copper(I) and silver(I) co-ordination polymers have been reported,² including hexagonal, helical (spiral), zigzag, square grid, rectangular grid, ladder (railroad-like), rhombic and honeycomb grid. However, to the best of our knowledge, complex **4c** is the first 2-D co-ordination polymer having a braid sheet structure. It is considered that the specifically co-ordinative direction of functional groups and the rigid long spacer in the rod-like 2-bpbd ligand greatly contributed to the formation of the 2-D braid sheet structure.

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