

Article

Synthesis and Characterization of Novel Copper(II) 2D Coordination Polymers from a Fluorinated Flexible Ligand with Remarkable Clathration Ability

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Abstract: Two-dimensional (2D) grid coordination polymers were prepared by the reaction of 1,4-bis(4-pyridylmethyl)tetrafluorobenzene (bpf) with $\text{Cu}(\text{NO}_3)_2$ in the presence of aromatic compounds. Crystal structures of $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)_2] \cdot (\text{biphenyl})_2\}_n$ (**1**), $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)_2] \cdot (m\text{-C}_6\text{H}_4(\text{OMe})_2)_2\}_n$ (**2**), $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)_2] \cdot \text{Ph}^t\text{Bu}\}_n$ (**3**) and $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)(\text{H}_2\text{O})]\text{NO}_3 \cdot (\text{bpf})_{0.5}\}_n$ (**4**) were determined. The grid networks were held together by $\text{C-H} \cdots \text{O}$ and $\text{C-H} \cdots \text{F}$ hydrogen bonds via the NO_3^- anions and the tetrafluorophenylene rings of bpf, respectively. Biphenyl, *m*-dimethoxybenzene, *t*-butylbenzene, and bpf molecules were clathrated in cyclic cavities of the grid networks through arene-perfluoroarene interactions. These coordination networks have remarkable clathration ability for aromatic compounds.

Keywords: porous coordination networks; metal-organic frameworks; X-ray crystal structure

1. Introduction

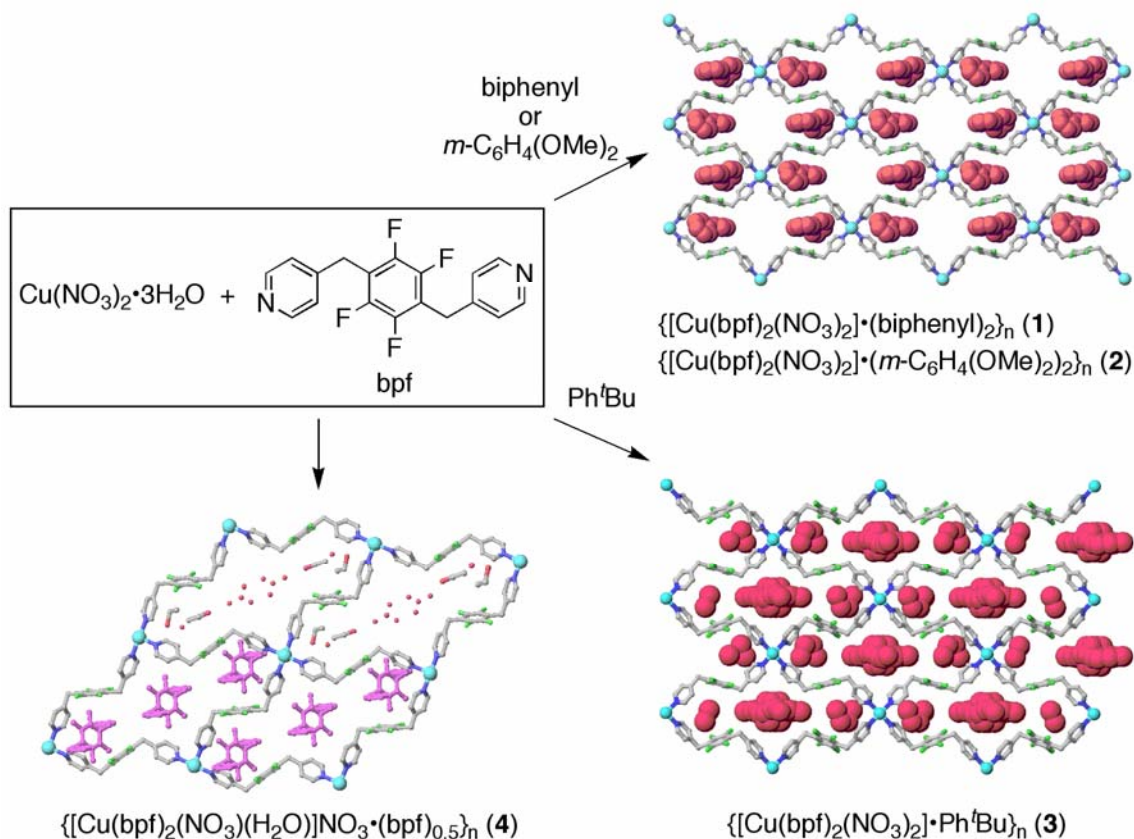
Coordination networks with inner cavities and channels constructed from metal ions and bridging ligands [1–4] have attracted much attention owing to their potential functionalities such as molecular adsorption [5–8], ion-exchange [9,10], and heterogeneous catalysis [11,12]. Rational design of porous

coordination networks with specific functions has been achieved by well-planned organic ligands and metal ions of various coordination geometries and oxidation states. We have reported the preparation of a series of clathrate coordination networks with $\text{Cd}(\text{NO}_3)_2$ and fluorinated flexible ligands $\text{Py}-\text{CH}_2-\text{X}-\text{CH}_2-\text{Py}$ (Py = 4-pyridyl; X = C_6F_4 , $\text{C}_6\text{F}_4\text{C}_6\text{F}_4$ or C_{10}F_6) [13–16]. These networks have remarkable clathration ability for guest aromatic compounds whose structures and topologies differ significantly depending on the size, shape, and number of the guest to afford one-dimensional (1D) cyclic chains, two-dimensional (2D) grids, or three-dimensional (3D) diamond networks. Fluorine atoms contained in the flexible ligands are mainly responsible for the clathration ability through $\text{C}-\text{H}\cdots\text{F}$ and/or arene-perfluoroarene interactions [14]. The authors report here the structures and characterizations of a new number of this family with $\text{Cu}(\text{NO}_3)_2$, the flexible fluorinated ligand 1,4-bis(4-pyridylmethyl)tetrafluorobenzene (bpf) and guest aromatic molecules.

2. Results and Discussion

The reaction of $\text{Cu}(\text{NO}_3)_2$ and bpf in the presence of biphenyl, *m*-dimethoxybenzene and *t*-butylbenzene resulted in the clathrate 2D grid networks $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)_2]\cdot(\text{biphenyl})_2\}_n$ (**1**), $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)_2]\cdot(m\text{-C}_6\text{H}_4(\text{OMe})_2)_2\}_n$ (**2**) and $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)_2]\cdot\text{Ph}^t\text{Bu}\}_n$ (**3**), respectively. The reaction of $\text{Cu}(\text{NO}_3)_2$ and bpf in the absence of aromatic molecules resulted in a similar 2D grid network, $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)(\text{H}_2\text{O})]\text{NO}_3\cdot(\text{bpf})_{0.5}\}_n$ (**4**), in which bpf molecules were clathrated as guests (Scheme 1). Single crystal X-ray analysis of **1–4** confirms that these are 2D grid networks with [4,4] topology based on distorted octahedral Cu(II) centers.

Scheme 1. Structures of the clathrate 2D grid networks from $\text{Cu}(\text{NO}_3)_2$ and bpf.



2.1. Description of Crystal Structure of $\{[Cu(bpf)_2(NO_3)_2] \cdot (biphenyl)_2\}_n$ (**1**)

The asymmetric unit of **1**, as illustrated by the labeled unprimed atoms of Figure 1(a), consists of half of $Cu(NO_3)_2$, a bpf molecule with *trans* conformation, a biphenyl molecule, and half of the EtOH solvent molecule. The copper ion adopts a distorted octahedral geometry with four bpf pyridine rings at the equatorial positions and two monodentate NO_3^- anions at the axial positions. Some selected bond lengths and angles around the Cu center are listed in Table 1. The extended structure forms a 2D rhombus grid and the shape of the cavity is an accurate rhombus. The diagonal-to-diagonal distances are 16.05×28.10 Å, corresponding to the dimensions of the b and c axes, and the grid dimensions are 16.18 Å. Each cavity is surrounded by four Cu(II) ions and four ligands in which two guest molecules of biphenyl are clathrated [Figure 1(b)]. Each guest molecule is packed between the perfluoroaromatic rings of the host framework with arene-perfluoroarene face-to-face interactions [17–20]. The shortest intermolecular contact $C10 \cdots C27$ is 3.530 Å [Figure 1(c)]. A side view of the stacking of **1** is shown in Figure 1(d). Interestingly, the adjacent sheets are enantiomers of each other and stacked alternately. The same enantiomers are eclipsed whereas the opposite enantiomers are staggered with an interplane distance of 6.2 Å. Each layer is linked by two types of hydrogen bonds [Figure 1(e)]. An oxygen atom of the nitrate anion binds to both the methylene group and pyridine ring of the neighboring layer ($N3-O3 \cdots H4A$ (pyridine): 2.376 Å; $N3-O3 \cdots H6B$ (CH_2): 2.518 Å), whereas fluorine atoms of the perfluorophenylene ring bind to pyridine rings of the neighboring layer ($H1A \cdots F2$: 2.698 Å; $H3A \cdots F4$: 2.435 Å; $H15A \cdots F3$: 2.474 Å) [18,21]. Moreover, the guest molecules are linked by a $C-H \cdots F$ hydrogen bond with the neighboring layer ($H27A \cdots F4$: 2.772 Å).

Figure 1. Crystal structure of **1**. **(a)** ORTEP view around the metal center. Thermal ellipsoids are shown at 50% probability. **(b)** Top view of the 2D sheet structure. Hydrogen atoms, solvent EtOH molecules and nitrate anions are omitted for clarity. **(c)** Top view of the cyclic cavity with guest molecules linked by arene-perfluoroarene face-to-face interactions. **(d)** Side view of the stacking layers linked by hydrogen bonds. **(e)** Side view of the stacking layers linked by hydrogen bonds.

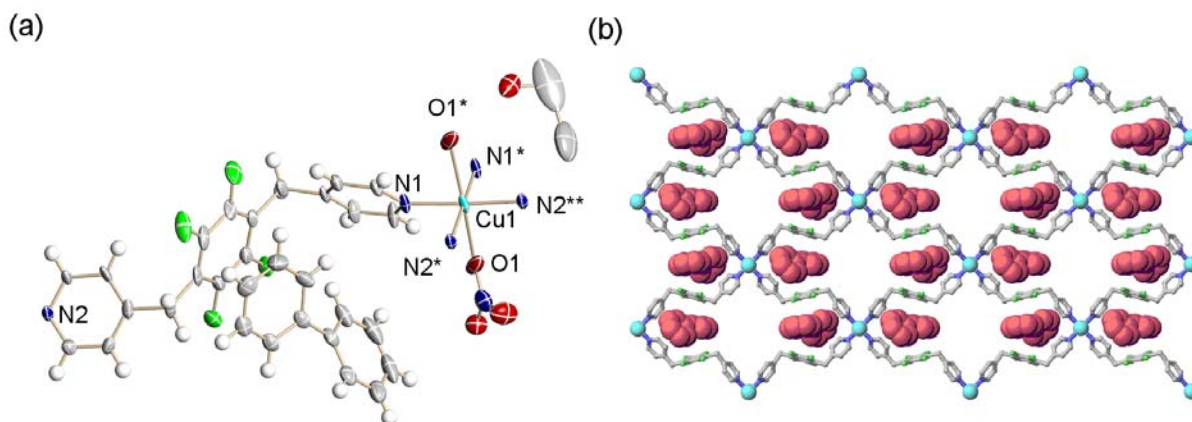
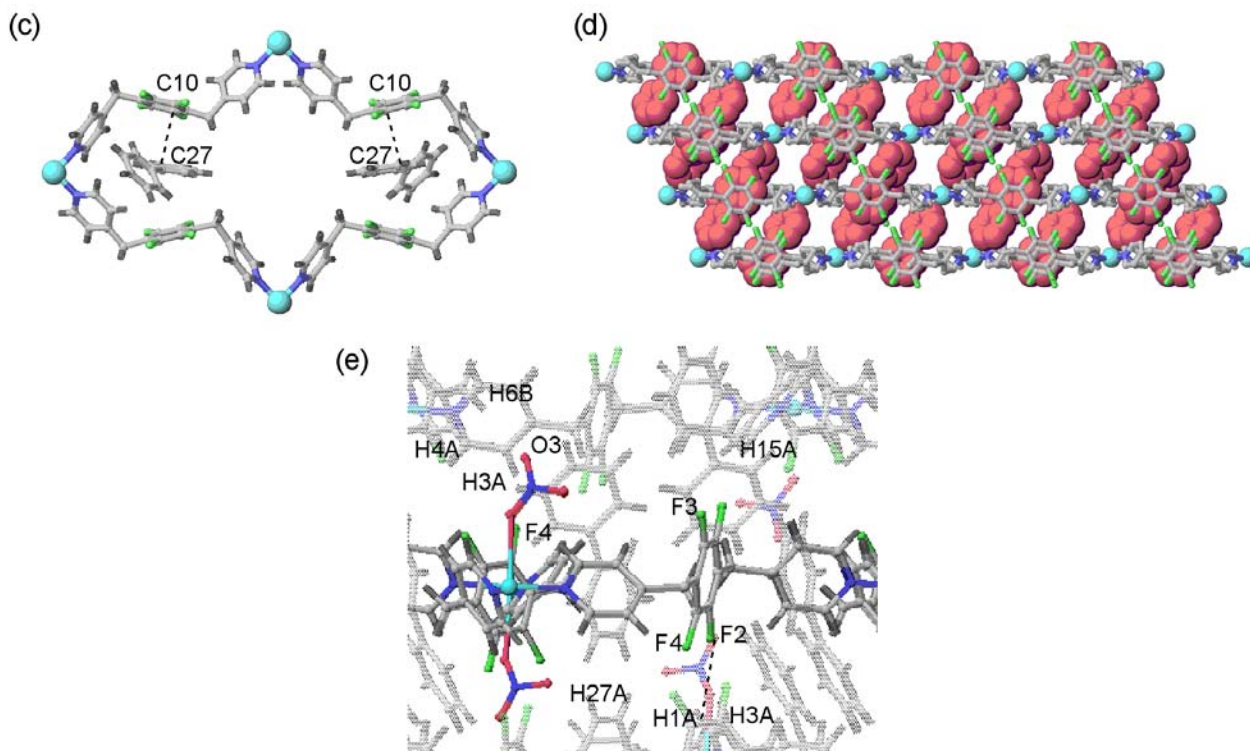


Figure 1. Cont.

**Table 1.** Selected bond lengths (Å) and angles (°) of **1**.

Cu1–N1	2.026(3)	Cu1–N2	2.011(3)
Cu1–O1	2.538(4)		
N1–Cu1–N1*	88.45(19)	N1–Cu1–N2*	90.11(13)
N1–Cu1–N2**	176.98(15)	N1*–Cu1–N2**	90.11(13)
N1*–Cu1–N2*	176.98(15)	N2*–Cu1–N2**	91.45(19)
N1–Cu1–O1	89.33(14)	N1*–Cu1–O1	87.82(13)
N2*–Cu1–O1	89.51(13)	N2**–Cu1–O1	93.26(13)

2.2. Description of Crystal Structure of $\{[Cu(bpf)_2(NO_3)_2] \cdot (m-C_6H_4(OMe)_2)_2\}_n$ (**2**)

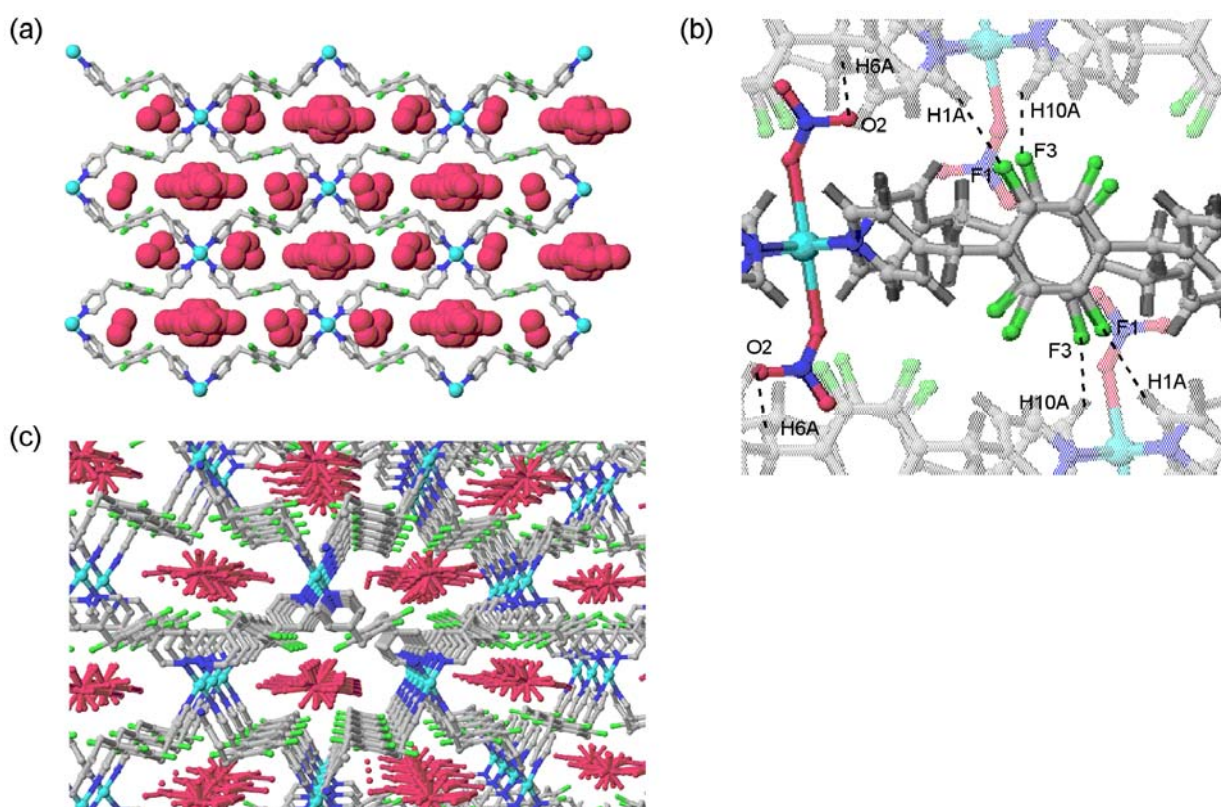
The structure of **2** is identical to that of **1** with the same space group $C2/c$ and similar unit cell dimensions. The diagonal-to-diagonal distances of the cyclic cavity are 15.16×28.48 Å, corresponding to the dimensions of the b and c axes, and the grid dimensions are 16.13 Å. Two guest molecules are clathrated in a cavity through arene-perfluoroarene interactions with the shortest intermolecular contact $C7 \cdots C24$ of 3.462 Å.

2.3. Description of Crystal Structure of $\{[Cu(bpf)_2(NO_3)_2] \cdot Ph^tBu\}_n$ (**3**)

When *t*-butylbenzene is used, which contains a bulky group, only one guest molecule is clathrated in each cavity to afford **3**. Figure 2(a) shows that the disordered *t*-butylbenzene molecules are clathrated at the cavity centers in the 2D grid network. The cavity is not exactly a rhombus but a quadrangle in which the two pairs of adjacent sides are the same (15.80 and 16.12 Å), and the diagonal-to-diagonal distances are 15.00×28.18 Å. This 2D sheet is relatively flat, and is made up of

layers stacked on each other with an interplane distance of 5.8 Å. These layers are linked by two types of hydrogen bonds [Figure 2(b)]. An oxygen atom of the nitrate anion binds to both the methylene group and pyridine ring of the neighboring layer (N3–O2···H6A (pyridine): 2.446 Å), whereas fluorine atoms of the perfluorophenylene ring bind to pyridine rings of the neighboring layer (H1A···F1: 2.547 Å; H10A···F3: 2.468 Å). Consequently, microchannels still remain in the solid along the *a* axis [Figure 2(c)].

Figure 2. Crystal structure of **3**. (a) Top view of the 2D sheet structure. Hydrogen atoms, solvent EtOH molecules and nitrate anions are omitted for clarity. (b) side view of the stacking layers linked by hydrogen bonds. (c) Top view of the stacking layers.



2.4. Description of Crystal Structure of $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)(\text{H}_2\text{O})]\text{NO}_3 \cdot (\text{bpf})_{0.5}\}_n$ (**4**)

The coordination environment of **4** is different from those of the other networks. Instead of an uncoordinated NO_3^- anion bonding to a water molecule through a hydrogen bond, the oxygen atom of a water molecule coordinates to the copper ion, while the other NO_3^- anion coordinates to the copper ion in a monodentate mode [Figure 3(a)]. Some selected bond lengths and angles around the Cu center are listed in Table 2. The grid sheet structure of **4** is shown in Figure 3(b). There are two cavities with alternate linking of alignments: cavity A clathrates three molecules of bpf, while cavity B apparently contains water and EtOH molecules. While these cavities are accurately classified as rhomboids, the shape is almost a rhombus. The diagonal-to-diagonal distances are 15.31×28.20 and 15.46×28.07 Å and the grid dimensions are 16.16×15.93 and 16.16×15.88 Å in cavities A and B, respectively. In cavity A, pyridine rings of bpf molecules are packed between perfluoroaromatic rings of the host framework with arene-perfluoroarene face-to-face interactions at both ends of the cavity. The shortest

intermolecular contact $C34 \cdots C38$ is 3.404 Å [Figure 3(c)]. The middle bpf molecule is held in place by edge-to-face interactions between guest F atoms and host pyridine rings with $F \cdots$ centroid distances of 3.417 and 3.441 Å. This 2D sheet is relatively flat, and is made up into layers stacked and eclipsed on each other along the a axis with an interplane distance of 5.9 Å [Figure 3(d)]. It is clear that the bpf molecules in the cavities (colored with pink) are clathrated across the three sheets. These layers are linked by $C-H \cdots F$ interactions. The distances of $H1A \cdots F5$, $H18A \cdots F1$, $H20A \cdots F4$, and $H28A \cdots F7$ are 2.392, 2.568, 2.627, and 2.597 Å, respectively [Figure 3(e)]. Consequently, microchannels are formed along the a axis [Figure 3(f)].

Figure 3. Crystal structure of **4**. (a) ORTEP view around the metal center. Thermal ellipsoids are shown at 50% probability. (b) Top view of the 2D sheet structure. Hydrogen atoms and nitrate anions are omitted for clarity. (c) Top view of the cyclic cavity with guest molecules linked by arene-perfluoroarene face-to-face interactions. (d) Side view of the stacking sheets. (e) Side view of the stacking layers linked by hydrogen bonds. (f) Top view of the stacking layers.

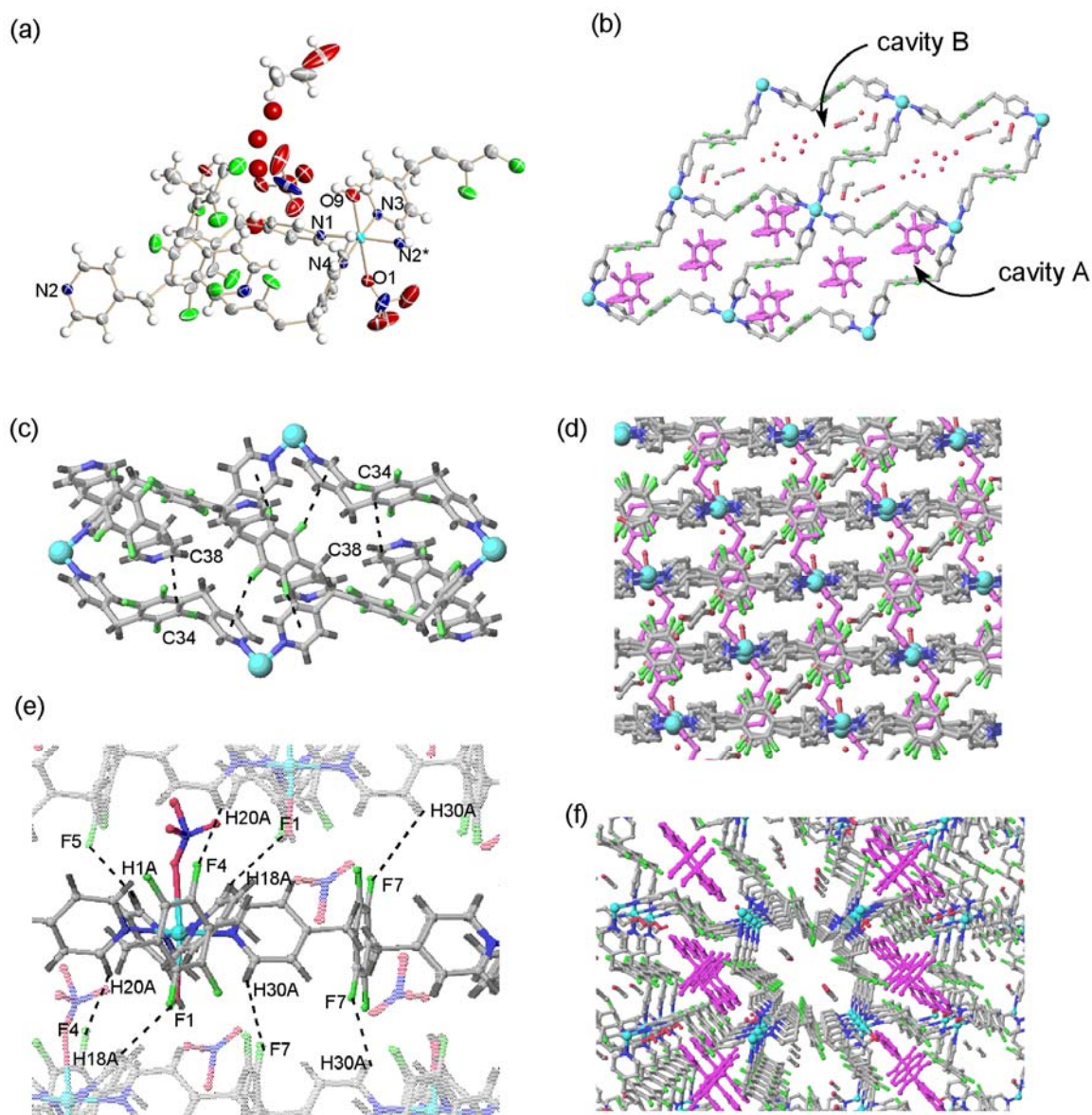


Table 2. Selected bond lengths (Å) and angles (°) of **4**.

Cu1–N1	2.037(4)	Cu1–N2*	2.025(4)
Cu1–N3	2.034(4)	Cu1–N4	2.021(4)
Cu1–O1	2.571(4)	Cu1–O9	2.327(4)
N1–Cu1–N2*	175.54(18)	N1–Cu1–N3	89.74(16)
N1–Cu1–N4	89.75(17)	N2*–Cu1–N3	91.03(17)
N2*–Cu1–N4	89.21(17)	N3–Cu1–N4	176.51(19)
N1–Cu1–O1	84.48(16)	N2*–Cu1–O1	91.21(16)
N3–Cu1–O1	84.73(15)	N4–Cu1–O1	91.79(15)
N1–Cu1–O9	92.59(16)	N2*–Cu1–O9	91.81(16)
N3–Cu1–O9	89.60(15)	N4–Cu1–O9	93.87(16)
O1–Cu1–O9	173.62(13)		

3. Experimental Section

3.1. Materials

Ligand bpf was prepared in a similar manner as described in the literature [14]. Coordination networks were prepared in air. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and biphenyl were purchased from Kanto Chemical Co., Ltd. *m*-Dimethoxybenzene and *t*-butylbenzene were purchased from Tokyo Chemical Industry Co., Ltd.

Synthesis of $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)_2] \cdot (\text{biphenyl})_2\}_n$ (1**).** A solution of bpf (80 mg, 0.24 mmol) in ethanol (16 mL) was added to a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (29 mg, 0.12 mmol) in H_2O (4 mL) with stirring. After filtration, a saturated ethanol solution of biphenyl (2 mL) was added slowly. The mixture was allowed to stand for 48 h at room temperature to give blue prism shaped crystals (yield: 111 mg, 77%). Anal. Calcd for $\text{C}_{62}\text{H}_{50}\text{O}_7\text{N}_6\text{CuF}_8$ $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)_2] \cdot (\text{biphenyl})_2 \cdot \text{EtOH}\}$: C, 61.71; H, 4.18; N, 76.96. Found: C, 61.88; H, 4.18; N, 7.19%.

Synthesis of $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)_2] \cdot (m\text{-C}_6\text{H}_4(\text{OMe})_2)_2\}_n$ (2**).** A solution of bpf (20 mg, 0.06 mmol) in ethanol (4 mL) was added to a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (7.2 mg, 0.03 mmol) in H_2O (1 mL) with stirring. After filtration, *m*-dimethoxybenzene (0.25 mL, 1.9 mmol) was added slowly. The mixture was allowed to stand for 48 h at room temperature to give blue prism shaped crystals (yield: 7.2 mg, 20%). Anal. Calcd for $\text{C}_{54}\text{H}_{54}\text{O}_{13}\text{N}_6\text{CuF}_8$ $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)_2] \cdot (m\text{-C}_6\text{H}_4(\text{OMe})_2)_2 \cdot (\text{EtOH}) \cdot (\text{H}_2\text{O})_2\}$: C, 53.58; H, 4.50; N, 6.94. Found: C, 53.42; H, 4.36; N, 7.06%.

Synthesis of $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)_2] \cdot \text{Ph}^t\text{Bu}\}_n$ (3**).** A solution of bpf (20 mg, 0.06 mmol) in ethanol (4 mL) was added to a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (7.2 mg, 0.03 mmol) in H_2O (1 mL) with stirring. After filtration, *t*-butylbenzene (0.29 mL, 1.9 mmol) was added slowly. After standing for 48 h at room temperature, the title compound was obtained as blue prism shaped crystals (yield: 13 mg, 42%). Anal. Calcd for $\text{C}_{47}\text{H}_{45}\text{O}_{8.5}\text{N}_6\text{CuF}_8$ $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)_2] \cdot \text{Ph}^t\text{Bu} \cdot (\text{EtOH})_{0.5} \cdot (\text{H}_2\text{O})_2\}$: C, 54.00; H, 4.34; N, 8.04. Found: C, 54.12; H, 4.24; N, 8.21%.

Synthesis of $\{[\text{Cu}(\text{bpf})_2(\text{NO}_3)(\text{H}_2\text{O})]\text{NO}_3 \cdot (\text{bpf})_{0.5}\}_n$ (4**).** A solution of bpf (25 mg, 0.075 mmol) in ethanol (4 mL) was added to a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (7.2 mg, 0.03 mmol) in H_2O (1 mL)

with stirring. After filtration and standing for 48 h at room temperature, the title compound was obtained as blue prism shaped crystals (yield: 11 mg, 32%). Anal. Calcd for $C_{48}H_{43}O_{9.5}N_7CuF_{10}$ $\{[Cu(bpf)_2(NO_3)(H_2O)]NO_3 \cdot (bpf)_{0.5} \cdot (EtOH)_{1.5} \cdot (H_2O)_{1.5}\}$: C, 50.91; H, 3.92; N, 8.66. Found: C, 50.79; H, 4.02; N, 8.57%.

3.2. Crystallographic Data Collection and Refinement

Crystal data for all the structures were collected with a Bruker SMART/CCD diffractometer (MoK_{α} radiation, $\lambda = 0.71073 \text{ \AA}$) by the ω -2 θ scan technique using frames of 0.3° oscillation ($1.92 \leq 2\theta \leq 28.01^\circ$ for **1**; $2.54 \leq 2\theta \leq 28.02^\circ$ for **2**; $1.90 \leq 2\theta \leq 27.56^\circ$ for **3**; and $2.02 \leq 2\theta \leq 28.02^\circ$ for **4**). An empirical absorption correction was applied using the SADABS program. The structures were solved by the direct method (SIR 97 [22] for **1**, **2**, and **4** and SHELXS 97 [23] for **3**) and refined by full-matrix least-squares against F^2 of all data using the SHELXL 97 program package [24]. The positions of the hydrogen atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective parent atoms before the final cycle of least-squares refinements. Crystallographic data for the four structures are listed in Table 3. CCDC-282151–CCDC-282154 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystallographic data for **1–4**.

	1	2	3	4
Formula	$C_{62}H_{50}CuF_8N_6O_7$	$C_{54}H_{54}CuF_8N_6O_{13}$	$C_{47}H_{45}CuF_8N_6O_{8.5}$	$C_{48}H_{44}CuF_{10}N_7O_{10}$
M	1,206.62	1,210.57	1,045.43	1,132.44
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$P2_1/c$ (No. 13)	$P1$ (No. 2)
a (Å)	28.104(3)	28.476(6)	10.7067(15)	10.1918(8)
b (Å)	16.0488(16)	15.156(2)	15.089(2)	11.6258(9)
c (Å)	14.1585(14)	15.346(2)	15.475(2)	22.3500(19)
α (°)				84.796(2)
β (°)	116.884(2)	121.965(4)	98.769(4)	83.948(2)
γ (°)				84.632(2)
V (Å ³)	5,695.8(10)	5,618.5(16)	2,470.8(6)	2,613.1(4)
Z	4	4	2	2
T (K)	153(2)	153(2)	200(2)	153(2)
D_c (g cm ^{−3})	1.407	1.431	1.405	1.439
μ (mm ^{−1})	0.469	0.483	0.531	0.516
$F(000)$	2,484	2,500	1,076	1,160
Reflections collected	13,835	10,182	22,146	17,746
Unique reflections (R_{int})	6,682 (0.0512)	5,675 (0.0914)	5,624 (0.0368)	12,237 (0.0523)
Parameters	393	434	407	723
goodness-of-fit	0.950	0.864	1.005	0.889
R_1 indices [$I > 2\sigma(I)$]	0.0710 (3,418)	0.0679 (1,901)	0.0556 (4,076)	0.0732 (4,299)
wR_2 (all data)	0.2318	0.2040	0.1626	0.2113

4. Conclusions

Assembly of Cu(II) with flexible fluorinated ligand bpf in the presence of aromatic compounds affords 2D grid coordination networks. The guest molecules are clathrated in cyclic cavities of the grid networks. The grid networks are held together by C–H $\cdots$ O and C–H $\cdots$ F hydrogen bonds via the NO₃[−] anions and tetrafluorophenylene rings of bpf, respectively. The guest aromatic rings are held in the cavity by arene-perfluoroarene interactions. Even in the absence of aromatic compounds, the combination of Cu(NO₃)₂ and bpf can afford a 2D grid network which clathrates the ligand as a guest molecule. These coordination networks have remarkable clathration ability for aromatic compounds.

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