Supramolecular Two-dimensional Arrays with Phenyl/Perfluorophenyl Interactions Constructed from One-dimensional Coordination Polymers

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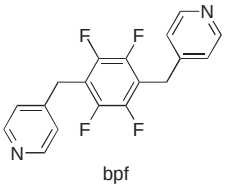
Supramolecular assembly of $Cd(NO_3)_2$, aniline derivatives and fluorinated ligand 1,4-bis(4-pyridylmethyl)-2,3,5,6-tetrafluorobenzene (bpf) afforded one-dimensional coordination polymers $[Cd(bpf)(aniline)_2(NO_3)_2]_n$ (**1**), $[Cd(bpf)(p\text{-toluidine})_2(NO_3)_2]_n$ (**2**), and $\{[Cd(bpf)(p\text{-bromoaniline})_2(NO_3)_2]\cdot(p\text{-bromoaniline})_2\}_n$ (**3**). The 1D polymers of **1** and **2** were connected through phenyl/perfluorophenyl interaction to give supramolecular two-dimensional arrays while no such interaction in **3** due to the bulky Br group.

The design and synthesis for supramolecular polymeric architectures in the crystal engineering[1] through noncovalent motifs, such as hydrogen bonding[2] and metal–ligand coordination,[3] have lately been achieved by well-designed building blocks due to novel solid-state materials with desired structures, properties, and functions. We have reported a series of clathrate-coordination networks whose structures are dependent on guest organic molecules using fluorinated flexible ligands such as 1,4-bis-(4-pyridylmethyl)-2,3,5,6-tetrafluorobenzene (bpf)(Scheme 1).[4] The topologies and structures of the host frameworks can vary depending on the size, shape, and number of the guest molecules to afford one-dimensional cyclic chains, two-dimensional grid, or three-dimensional diamond networks, and so on. In this system, the construction of the infinite frameworks have been achieved not only by the coordination between nitrogen atoms of pyridine rings and metal ions but also hydrogen bonding between anions and hydrogen atoms of ligands linking with adjacent frameworks.[4b] It is clear that a suitable combination of several supramolecular interactions causes the successful crystal engineering.

Recently, the phenyl/perfluorophenyl interactions, stabilized by quadrupole–quadrupole interaction between electron-rich and electron-deficient aromatic rings, have been used as supramolecular motifs in the crystal engineering and effective face-to-face interactions have been observed in the solid-state materials.[5] The perfluorophenylene ring of the fluorinated ligand bpf can be potentially utilized as a supramolecular synthon to achieve a novel polymeric architecture. To the best of my knowledge, the combination of coordination bonding and phenyl/perfluorophenyl interactions as supramolecular motifs is very rare.[6] Aniline derivatives are expected to be appropriate tools for the phenyl/perfluorophenyl interactions to bind coordination polymers because those amino groups can coordinate to metal ions of the polymers.[7] Here, I report two-dimensional arrays with phenyl/perfluorophenyl interactions constructed from one-dimensional coordination polymers composed of $Cd(NO_3)_2$, aniline derivatives, and fluorinated ligand bpf.



Scheme 1.

The reaction of bpf and $Cd(NO_3)_2$ in the presence of aniline, *p*-toluidine, or *p*-bromoaniline afforded one-dimensional coordination polymers, in which adjacent cadmium ions are bridged by one ligand and two molecules of aniline derivatives coordinate to a Cd(II) ion. Usage of aniline and *p*-toluidine gave $[Cd(bpf)(aniline)_2(NO_3)_2]_n$ (**1**) and $[Cd(bpf)(p\text{-toluidine})_2(NO_3)_2]_n$ (**2**), respectively, while usage of *p*-bromoaniline gave $\{[Cd(bpf)(p\text{-bromoaniline})_2(NO_3)_2]\cdot(p\text{-bromoaniline})_2\}_n$ (**3**).[8,9]

The structure of **1** is shown in Figure 1 as a typical example. Each cadmium ion has an octahedral geometry and is coordinated by four nitrogen atoms at the equatorial positions, in which two pyridine rings of ligands with *trans* conformation and two molecules of aniline are in *cis* positions, respectively, and by two oxygen atoms of monodentate NO_3^- anions at the axial positions. In consequence, a zig-zag polymeric structure in which adjacent cadmium ions are bridged by linear ligand bpf is formed. Interestingly, these polymers are connected through two kinds of effective π–π interaction. One is the phenyl/perfluorophenyl interaction between benzene ring of aniline and tetrafluorophenylene ring of bpf with a centroid–centroid

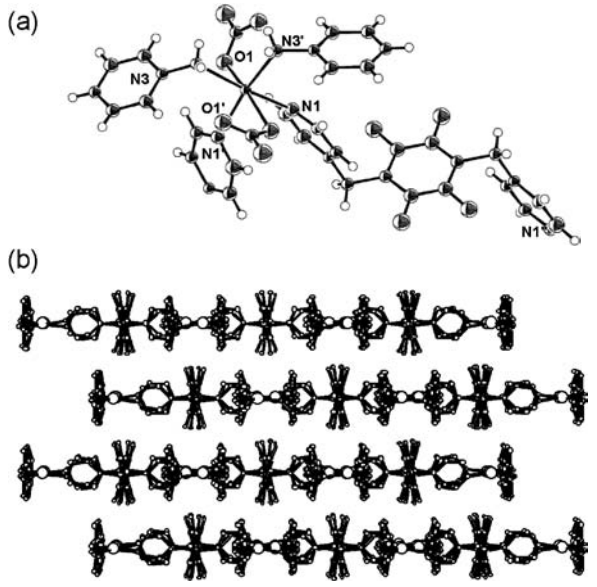


Figure 1. Crystal structure of **1**. (a) ORTEP view around the metal center. Thermal ellipsoids are shown in 50% probability. (b) Side view of packing of 2D alignment between *a* and *c* axes. Hydrogen atoms and nitrate anions are omitted for clarify.

separation of 3.95 Å, and the other is the offset-staking of the adjacent aniline rings with the shortest interplanar C–C distance of 3.52 Å as shown in Graphical Abstract. The resulting two-dimensional sheets are stacked in an alternating fashion with an interlayer separation of 5.9 Å (Figure 1b). Moreover, the adjacent sheets are held each other through hydrogen bonding between a hydrogen atom of pyridine ring, methylene group and an oxygen atom of a monodentate nitrate anion (O(3)···H(3) (py) 2.867 and O(3)···H(5) (CH_2) 2.540 Å). That is, the supramolecular architecture is constructed by the combination of coordination bonding to form one-dimensional coordination polymers, phenyl/perfluorophenyl interaction to form two-dimensional layers, and hydrogen bonding to form three-dimensional networks. Although **2** has an equivalent structure with the same space group and similar unit cell dimensions to **1**, the corresponding interplanar C–C distance between adjacent aniline rings is increased to 3.81 Å due to the methyl group.

The structure of **3** is entirely different from **1** and **2** as shown in Figure 2. Each cadmium ion has an octahedral geometry and is coordinated by four nitrogen atoms at the equatorial positions, in which two pyridine rings of ligands with *trans* conformation and two molecules of *p*-bromoaniline are in *trans* positions, respectively, and by two oxygen atoms of monodentate NO_3^- anions at the axial positions. Consequently, the polymeric structure form is relatively straight compared with the zig-zag structure of **1**. Moreover, one molecule of *p*-bromoaniline is intercalated with coordinating *p*-bromoaniline through hydrogen bonding between a hydrogen atom of coordinating amino group and a nitrogen atom of uncoordinating amino group (NH···N 2.43 Å). These polymers are aligned parallel to each other along the *b* axis, leading to a 2D structural motif in the *ab* plane. These 2D sheets are stacked in an alternating fashion with an interlayer separation of 9.2 Å. Instead of phenyl/perfluorophenyl interaction between adjacent 1D polymers in **1** and **2**, bromine atoms both of two anilines coordinating a metal ion interact with a perfluoroaromatic ring (Br–centroid separation 4.10 Å).[5c] It appears that the electronegative Br group blocks the alignment of 1D coordination polymers to a 2D sheet through phenyl/perfluorophenyl interactions such as **1** and **2**.

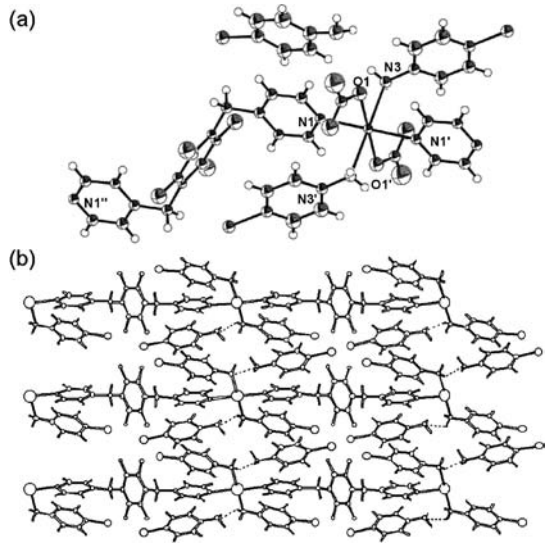


Figure 2. Crystal structure of **3**. (a) ORTEP view around the metal center. Thermal ellipsoids are shown in 50% probability. (b) Top view of 2D alignment of linear polymeric frameworks along *c* axis. The dotted lines show NH···N hydrogen bonding between the coordinating and uncoordinating aniline molecules.

In summary, I have demonstrated well-defined supramolecular architectures in 1D coordination polymers composed of $Cd(NO_3)_2$, aniline derivatives and fluorinated ligand bpf. The structures of **1** and **2** were constructed by the combination of coordination bonding (1D), phenyl/perfluorophenyl interaction (2D), and hydrogen bonding (3D), which are key processes in the crystal engineering. The phenyl/perfluorophenyl interaction was influenced by substituents of aniline derivatives; no such interactions were observed in **3** due to the Br groups.

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8 **1**: (Yield 51%) Anal. Calcd. for $C_{30}H_{26}O_6N_6CdF_4$: C, 47.73; H, 3.47; N, 11.13. Found: C, 47.64; H, 3.27; N, 11.26. **2**: (Yield 43%) Anal. Calcd. for $C_{32}H_{30}O_6N_6CdF_4$: C, 49.09; H, 3.86; N, 10.73. Found: C, 48.82; H, 3.87; N, 10.73. **3**: (Yield 54%) Anal. Calcd. for $C_{42}H_{36}O_6N_8Br_4CdF_4$: C, 40.14; H, 2.89; N, 8.92. Found: C, 40.20; H, 3.10; N, 8.86.

9 Crystal data for **1**: fw = 754.97, monoclinic, $C2/c$, $a = 25.409(4)$, $b = 11.1328(17)$, $c = 11.7739(17)$ Å, $\beta = 115.883(2)^\circ$, $V = 2996.4(8)$ Å^3, $Z = 4$, $T = 173$ K, $D_{calcd} = 1.674$ g cm^{-3}, 3518 unique reflections, the final R and R_w were 0.0210 and 0.0517 (3203 reflections [$(I > 2\sigma(I))$]). For **2**: fw = 783.02, monoclinic, $C2/c$, $a = 26.480(4)$, $b = 10.9279(15)$, $c = 11.8813(16)$ Å, $\beta = 114.300(2)^\circ$, $V = 3133.4(7)$ Å^3, $Z = 4$, $T = 173$ K, $D_{calcd} = 1.660$ g cm^{-3}, 3679 unique reflections, the final R and R_w were 0.0233 and 0.0614 (3428 reflections [$(I > 2\sigma(I))$]). For **3**: fw = 1256.83, monoclinic, $P2_1/c$, $a = 16.775(2)$, $b = 7.5581(10)$, $c = 18.294(3)$ Å, $\beta = 96.568(2)^\circ$, $V = 2304.3(5)$ Å^3, $Z = 2$, $T = 173$ K, $D_{calcd} = 1.811$ g cm^{-3}, 5399 unique reflections, the final R and R_w were 0.0304 and 0.0570 (3602 reflections [$(I > 2\sigma(I))$]).

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