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Flexible Coordination Networks with Fluorinated Backbones. Remarkable Ability for Induced-Fit Enclathration of Organic Molecules

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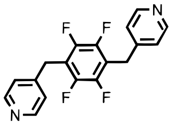
Coordination networks capable of enclathrating organic molecules have been extensively studied recently, in expectation of developing new materials such as organic zeolite analogues.[1,2] Previously reported network materials, however, enclathrate only a limited number of guest molecules due to the rigid host framework. To achieve the enclathration of a large variety of organic guests, *flexible* coordination networks are desired which can be induced-fit by guest molecules. However, if the ligands are flexible, the networks are in general constricted or interpenetrated[3] leaving no void space in the solid for enclathrating guests.

To solve this dilemma, one should develop networks which favor "hetero-recognition" (enclathration) rather than "self-recognition" (constriction or interpenetration). Thus we have designed and prepared flexible, fluorinated ligands **1**−**3**. Because of very weak intermolecular forces among fluorinated compounds,[4] networks from these ligands and metal ions are not apt to be constricted or interpenetrated, but prefer to interact with guest molecules to form clathrate compounds.[5] In these clathrate complexes, we have found that the network topologies are induced-fit by guest molecules owing to the flexibility of the ligand frameworks giving rise to 1D, 2D, and 3D structures with large cavities. Consequently, we have achieved the enclathration of a variety of organic guests with the flexible, fluorinated coordination networks.



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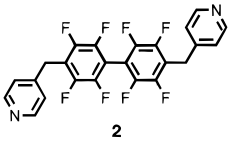

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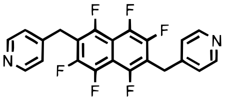

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To date, we have solved >30 crystal structures of the clathrate complexes obtained from $Cd(NO_3)_2$, fluorinated ligands (**1**−**3**), and various guest compounds. In most cases, the crystals of the clathrate complexes were easily obtained in high yields from an ethanol−water solution of $Cd(NO_3)_2$ and the fluorinated ligand (1:2 stoichiometry) in the presence of a large excess of guest compounds under homogeneous or heterogeneous conditions.[6]

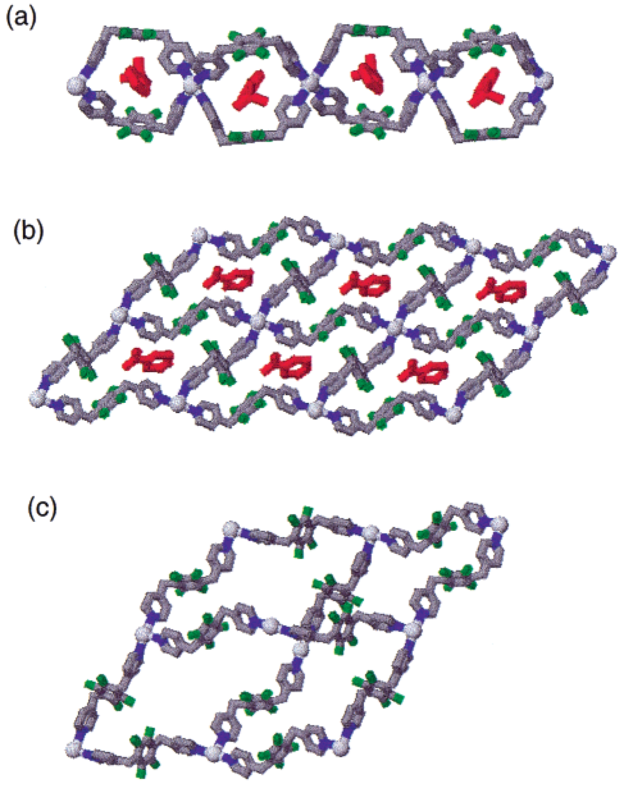

Figure 1. Crystal structure of representative 1D, 2D, and 3D clathrate complexes: (a) 1D chain complex $[Cd(\mathbf{1})_2\cdot(\textit{tert}\text{-butylbenzene})](NO_3)_2$ (guest is showin in red), (b) 2D sheet complex $[Cd(\mathbf{1})_2\cdot(\textit{N,N}\text{-dimethylaniline})](NO_3)_2$ (guest is shown in red), and (c) 3D diamond complex $[Cd(\mathbf{1})_2\cdot(\text{phenyl acetate})_2](NO_3)_2$ (guest is omitted for clarity). NO_3^- anions, which are coordinated at the apical position of Cd^{2+}, are omitted for clarity.

Interestingly, the network topologies of the host framework changed significantly depending on the small structural differences of the guest molecules. For example, ligand **1** was found to form three infinite networks: (1) a one-dimensional (1D) chain composed of a cyclic linkage with a stoichiometry of $ML_2\cdot G$; (2) a two-dimensional (2D) sheet with the same stoichiometry ($ML_2\cdot G$); and (3) a three-dimensional (3D) diamond network with a stoichiometry of $ML_2\cdot G_2$.[7]

The 1D chain structure is featured by infinite linking of boat-shaped cyclic frameworks. Figure 1a shows a typical network that was observed in the crystal structure of a clathrate complex of *tert*-butylbenzene.[8] One molecule of the guest is packed in each cyclic cavity. The distance between adjacent Cd atoms is

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(1) For reviews: (a) Iwamoto, T. *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1991; Vol. 5, Chapters 2−4, pp 177−212. (b) Janiak, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 1431.

(2) A recent review on the coordination networks: Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.

(3) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460 and references therein.

(4) For example, see: Banks, R. E.; Smart, B. E.; Tatlow, J. C., Eds. *Organofluorine Chemistry: Principles and Commercial Applications*; Plenum Press: New York, 1994.

(5) A metal-linked macrocycle assembled from $(en)Pd(NO_3)_2$ and **1** shows high molecular recognition ability for aromatic compounds: Fujita, M.; Nagao, S.; Iida, M.; Ogata, K.; Ogura, K. *J. Am. Chem. Soc.* **1993**, *115*, 1574.

(6) Experimental: See Supporting Information. We have examined each experiment at least twice and have found that the reproducibility of the experiment is good. Yields are in general in the range of 20−70% (not optimized).

(7) Examined guest compounds (network patterns) are as follows: *tert*-butylbenzene (1D), methyl benzoate (1D), cumene (1D), *N,N′*-dimethylaniline (2D), *p*-bromotoluene (2D), *p*-xylere (2D), *p*-methylaniline (2D), naphthalene (2D), phenyl acetate (3D), *N*-methylaniline (3D), toluene (3D), α-methylstyrene (3D), *m*-xylene (3D), *o*-methoxyaniline (3D), benzyl methyl ether (3D), biphenyl (3D).

(8) Crystal data for $[Cd(\mathbf{1})_2\cdot(t\text{-butylbenzene})](NO_3)_2$: triclinic, $P\bar{1}$; $a = 13.033(1)$ Å, $b = 16.865(3)$ Å, $c = 21.579(4)$ Å, $\alpha = 90.04(1)°$, $\beta = 94.19(1)°$, $\gamma = 90.137(9)°$; $V = 4730(1)$ Å^3; $Z = 4$; $d_{calc} = 1.454$ g cm^{-3}; $F(000) = 2096$; μ(Mo Kα) $= 5.47$ cm^{-1}; λ(Mo Kα) $= 0.7107$ Å; 11026 reflections measured, 6647 observed ($F > 3.00\sigma(F)$); $R = 0.150$; $R_w = 0.186$. Anal. Calcd for $C_{46}H_{38}N_6O_6F_8Cd$: C, 53.37; H, 3.70; N, 8.12. Found: C, 53.02; H, 3.95; N, 7.71.

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12.2 Å. All 1D coordination polymers in the crystal align parallel with each other, making a microchannel in which guest molecules are packed. Each cadmium atom has an octahedral geometry with four ligands at the equatorial positions. It is worthy of note that efficient edge-to-face contacts are observed between the host and the guest. These interactions agree well with the high molecular recognition ability of a related, discrete macrocycle which self-assembles from (en)Pd$(NO_3)_2$ and ligand **1**.[5]

The 2D network sheet structure is a relatively common host framework appearing throughout our experiments. As a typical example, the 2D structure of the clathrate complex with *N*,*N*-dimethylaniline is shown in Figure 1b; each network cavity is surrounded by four Cd atoms and four ligands, wherein one molecule of the guest is enclathrated.[9] Efficient edge-to-face interactions between the host and the guest are again observed in the 2D sheet structure. This 2D sheet is made up into layers stacked on each other with the interplane distance of 5.4 Å. It is worthy of note that all positional isomers of dimethoxy- and dibromobenzenes are enclathrated efficiently, in sharp contrast to the clathrate formation with a rigid Cd(II)−(4,4′-bpy) grid sheet complex[10] wherein only *o*-dibromobenzene is enclathrated. Interestingly, ligand **1** itself is enclathrated in the absence of any guest molecules, i.e., the same 2D network enclathrating one molecule of free **1**.[11]

In addition to the 1D chain and the 2D sheet structures, 3D networks with a diamond topology also have been afforded from the same metal−ligand combination, despite very small changes in guest structures. An X-ray structure is given for the clathrate complex with phenyl acetate as a typical example.[12] The 3D unit structure (Figure 1c) shows that the diamond framework is considerably deformed due to the flexibility of the ligand. The cavity in the diamond framework is very large and, in fact, the bulk of the void space is filled by the 3-folded interpenetration of the same frameworks. Nevertheless, microchannels still remain in the solid, giving clathrate complexes with $ML_2{\cdot}G_2$ composition.[13]

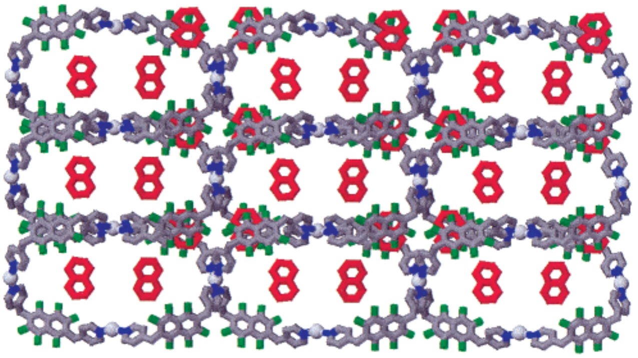

Figure 2. Crystal structure of [Cd(**3**)$_2$·(naphthalene)$_2$]$(NO_3)_2$. NO_3^- anions, which are coordinated at the apical position of Cd^{2+}, are omitted.

The important role of the tetrafluorophenylene ring in the network was demonstrated by control experiments with a nonfluorinated ligand, $PyCH_2C_6H_4CH_2Py$ (**4**). Our attempts to obtain clathrate compounds from $Cd(NO_3)_2$ and **4** with various guest molecules were unsuccessful in most cases; we obtained interpenetrated infinite ladder structures which have been previously reported.[11,14] In a few cases, clathrate complexes with aromatic guests were obtained. However, the networks were interpenetrated and guest molecules were not found in the network cavity but in the opening among the infinite ladders.[14] These results are consistent with our assumption that nonfluorinated ligands prefer "self-recognition", whereas fluorinated ligands favor "hetero-recognition".

Furthermore, the importance of the fluorinated rings was emphasized by the efficient enclathration of larger aromatic guests (e.g., biphenyl or naphthalene) with ligands **2** and **3** which possess fluorinated naphthalenyl and bipheylene cores, respectively. Both ligands gave two-dimensional networks upon complexation with $Cd(NO_3)_2$ and two enclathratied large guest molecules in each expanded cavity.[15] The clathrate complex from **3**, $Cd(NO_3)_2$, and naphthalene is shown in Figure 2 as an example.[16,17] Poor enclathration abilities have been confirmed again for their nonfluorinated counterparts.[18]

Supporting Information Available: Experimental details for the ligand syntheses and clathrate complex syntheses, and detailed X-ray crystallographic data for [Cd(**1**)$_2$·(*tert*-butylbenzene)]$(NO_3)_2$, [Cd(**1**)$_2$·(*N*,*N*-dimethylaniline)]$(NO_3)_2$, [Cd(**3**)$_2$·(naphthalene)$_2$]$(NO_3)_2$, and [Cd(**1**)$_2$·(phenyl acetate)$_2$]$(NO_3)_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] Crystal data for [Cd(**1**)$_2$·(*N*,*N*-dimethylaniline)]$(NO_3)_2$: triclinic, $P1$; $a = 10.389(5)$ Å, $b = 10.641(3)$ Å, $c = 10.269(2)$ Å, $\alpha = 108.30(2)°$, $\beta = 98.37(3)°$, $\gamma = 76.81(3)°$; $V = 1045.9(6)$ Å^3; $Z = 1$; $d_{calc} = 1.623$ g cm^{-3}; $F(000) = 516$; μ(Mo Kα) = 6.18 cm^{-1}; λ(Mo Kα) = 0.7107 Å; 3511 reflections measured, 3121 observed ($F > 3.00\sigma(F)$); $R = 0.111$; $R_w = 0.118$. Anal. Calcd for $C_{44}H_{35}N_7O_6F_8Cd$: C, 51.70; H, 3.45; N, 9.59. Found: C, 51.76; H, 3.75; N, 9.61.

[10] Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151.

[11] In the absence of guest, **1** also gave an infinite brick-wall complex with $ML_{1.5}$ composition: Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287. Note that, when $Cd(NO_3)_2$ was treated with 1.5−2.0 equiv of **1**, the infinite brick-wall was obtained. On the other hand, by treating $Cd(NO_3)_2$ with a large excess of **1**, we obtained a clathrate complex with the composition of $ML_2{\cdot}G$ (G = free **1**).

[12] Crystal data for [Cd(**1**)$_2$·(phenyl acetate)$_2$]$(NO_3)_2$: monoclinic, Cc; $a = 17.843(4)$ Å, $b = 19.036(2)$ Å, $c = 16.685(2)$ Å, $\beta = 119.171(8)°$; $V = 4948(1)$ Å^3; $Z = 4$; $d_{calc} = 1.575$ g cm^{-3}; $F(000) = 2376$; μ(Mo Kα) = 5.39 cm^{-1}; λ(Mo Kα) = 0.7107 Å; 3926 reflections measured, 3059 observed ($F > 3.00\sigma(F)$); $R = 0.081$; $R_w = 0.078$. Anal. Calcd for $C_{52}H_{40}N_6O_{10}F_8Cd$: C, 53.23; H, 3.44; N, 7.16. Found: C, 53.00; H, 3.28; N, 7.14.

[13] We attempted to remove the guest molecules from clathrate compound by extraction. When the 3D network complex enclathrating phenyl acetate, [Cd(**1**)$_2$·(phenyl acetate)$_2$]$(NO_3)_2$, was treated with hexane, the guest was removed in a few days. Powder X-ray analysis showed that the resulting material was still crystalline and the diffraction pattern was completely changed from those of the original crathrate complex. Unfortunately, we have not succeeded in the absorption of the original guest after the guest removal.

[14] Fujita, M.; Sasaki, O.; Ogura, K. *New J. Chem.* **1998**, 189.

[15] As a typical example for the clathrate complex derived from **2**, the crystal structure of [Cd(**2**)$_2$·(phenyl acetate)$_2$]$(NO_3)_2$ is shown in the Supporting Information.

[16] The network topology of Cd(**3**)$_2$ is the same as that of [Cd(**1**)$_2$·(*N*,*N*-dimethylaniline)]$(NO_3)_2$.

[17] Crystal data for [Cd(**3**)$_2$·(naphthalene)$_2$]$(NO_3)_2$: monoclinic, $P2/n$; $a = 15.583(4)$ Å, $b = 27.280(3)$ Å, $c = 13.401(2)$ Å, $\beta = 90.37(2)°$; $V = 5696(1)$ Å^3; $Z = 4$; $d_{calc} = 1.550$ g cm^{-3}; $F(000) = 2680$; μ(Mo Kα) = 4.83 cm^{-1}; λ(Mo Kα) = 0.7107 Å; 7602 reflections measured, 4585 observed ($F > 3.00\sigma(F)$); $R = 0.070$; $R_w = 0.076$. Anal. Calcd for $C_{64}H_{40}N_6O_6F_{12}Cd$: C, 57.82; H, 3.03; N, 6.32. Found: C, 57.40; H, 3.01; N, 6.00.

[18] From $PyCH_2C_6H_4C_6H_4CH_2Py$, we obtained a 2D network complex where the cavities of each layer are packed by the troughs of the adjacent layer. No enclathration has been observed with aromatic guests.