Host–Guest Systems

A Two-in-One Crystal: Uptake of Two Different Guests into Two Distinct Channels of a Biporous Coordination Network

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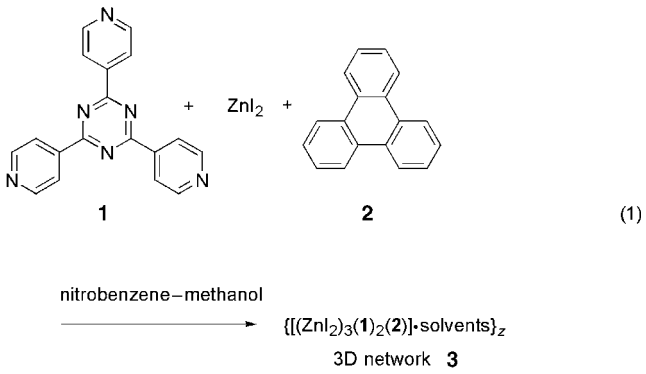
Coordination networks with well-defined microchannels hold great promise for a number of applications owing to guest adsorption, removal, and exchange behaviors in the channels.[1,2] In general, the channels formed in crystals are uniform and therefore inclusion phenomena in all the channels are identical. However, if two (or more) distinct channels exist in a crystal, they may take up two (or more) guests independently. Such biporous materials[3] make, for example, the simultaneous isolation or transportation of two different guests possible. Herein, we report the formation of two distinct large channels within a three-dimensional coordination network. These channels adsorb their own preferred guests from a mixture of two guests to form two independent columnar arrays of guests in the crystal. Since the guest uptake proceeds in a single-crystal-to-single-crystal fashion, we can observe all the processes by X-ray crystallographic analysis.

The coordination network discussed herein is composed of the tris(4-pyridyl)triazine ligand **1** and ZnI_2. Single crystals of $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2})]\cdot x\,(\text{nitrobenzene})\cdot y\,(\text{methanol})\}_z$ –(**3**; $x \approx 4$, $y \approx 2$) were grown from a triple-layered solution with a methanol solution (0.5 mL) of ZnI_2 (0.03 mmol) as the top layer, methanol (0.5 mL) as the middle layer, and a nitrobenzene/methanol solution (4:1, 5 mL) of ligand **1** (0.02 mmol) and triphenylene (**2**, 0.1 mmol) as the bottom layer. The crystals were isolated in 54% yield [Eq. (1)].



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Crystallographic analysis showed that the network has an interpenetrated structure (Figure 1a), in which triphenylene is tightly intercalated between two triazine ligands ($\mathbf{1}_A$ and $\mathbf{1}_B$; Figure 1b). An infinite aromatic stacking is observed, which presumably stabilizes the solid structure.

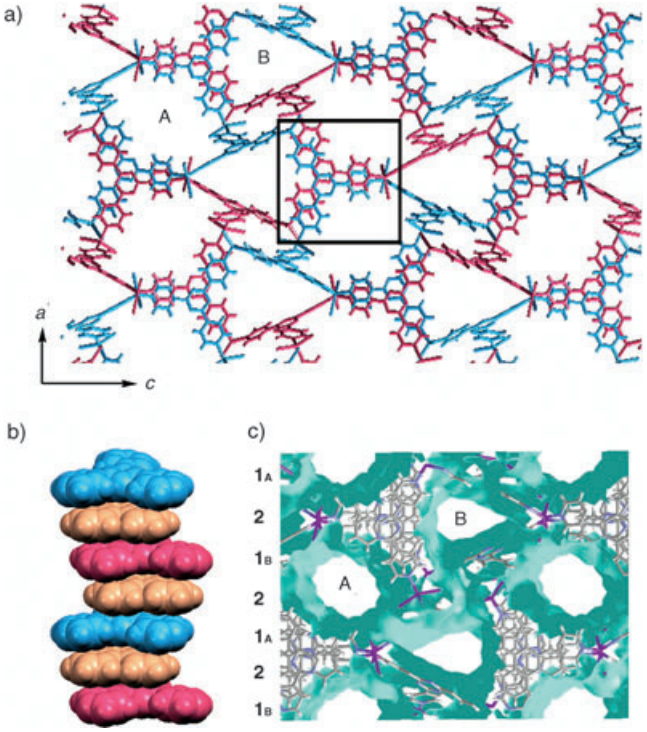

Figure 1. Crystal structure of **3**: a) view of the interpenetrated networks along the *b* axis; b) the infinite aromatic stacking between the ligands ($\mathbf{1}_A$ and $\mathbf{1}_B$) and triphenylene (**2**) at the inserted square in (a); c) a free-volume drawing showing the two distinct channels **A** and **B**.

Intercalated triphenylene is not replaced by common aromatic compounds under guest-exchange conditions because of this strong stacking. Therefore, triphenylene is best regarded as forming part of the host framework rather than being a guest. The strong binding of triphenylene is ascribed to a charge-transfer (CT) interaction between the layers. A broad CT absorption band was observed in the range 400–600 nm in the UV/Vis spectrum. Furthermore, calculations predicted an efficient in-phase overlap between the triphenylene HOMO and ligand LUMO (Figure 2).[4] In the absence of triphenylene, a 3D coordination network with a

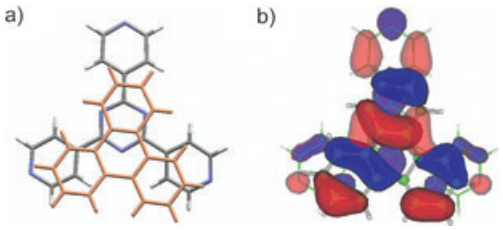

Figure 2. Structures showing a) π-π stacking between ligand **1** and triphenylene (**2**) in **3** (occupancy: 84%); b) superposition of the HOMO and the LUMO.

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different network topology is obtained,[2c,5] which is not converted to complex **3** under guest-exchange conditions with triphenylene.

The structure of complex **3** contains two distinct channels (**A** and **B**) within the framework. Channel **A** is roughly cylindrical and is mainly surrounded by the hydrogen atoms of infinitely stacked **1** and **2**. Channel **B**, however, is roughly trigonal prismatic, where two of the three walls are the π faces of ligand **1** and the third is the edges of **1** and **2** (Figure 1a,c). The approximate dimensions of the channels are 7.4 × 5.5 Å (channel A) and 7.3 × 5.5 Å (channel B). Their void occupancies are almost identical (ca. 20% for each).[6]

Surprisingly, the two channels take up their own preferred guests from a mixture: channels **A** of as-synthesized **3** are filled with nitrobenzene and methanol, which are considerably disordered and could not be fully located by crystallographic analysis, whereas channels **B** are filled with nitrobenzene (Figure 3a). Dipping crystals of **3** into a saturated cyclohexane solution of naphthalene at room temperature for two days caused channels **A** and **B** to be selectively filled with naphthalene and cyclohexane, respectively, to give guest-exchanged crystals of $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2})]\cdot x\,(\text{cyclohexane})\cdot y\,(\text{naphthalene})\}_z$ (**4**, $x \approx 1.3$ and $y \approx 2.3$; Figure 3b). Even after this guest exchange, high-quality diffraction data could be collected, and the structure converged to a final R_1 value of 0.052. The crystallographic analysis revealed the formation of columnar arrays of naphthalene (100% occupancy) and cyclohexane (82% occupancy) in channels **A** and **B**, respectively (Figure 3b). The geometry of the host framework, including intercalated triphenylene, remained almost unchanged despite the dramatic replacement of large molecules in the channels. The uptake of two different guests by the two channels was also observed for the azulene/cyclohexane pair: channels **A** and **B** selectively adsorbed azulene (100% occupancy) and cyclohexane (100% occupancy), respectively, to give **5** (Figure 3c).

Guest-exchange experiments with each individual guest showed the preference of the two channels for a specific guest: channel **A** prefers naphthalene whereas channel **B** prefers cyclohexane. Channel **A** was 50% filled with naphthalene to form a naphthalene/nitrobenzene 1:1 column when only naphthalene (nitrobenzene solution) was used, whereas channel **B** remained intact (**6**; Figure 3d). In contrast, guest exchange with cyclohexane led to the complete filling of channel **B** with cyclohexane (occupancy 100%) but only partial filling of channel **A** in compound **7** (occupancies: cyclohexane 64% and nitrobenzene 36%; Figure 3e).

Thermogravimetric (TG) analysis of a crystalline sample of **4** showed the release of guest molecules in three steps. The guest molecules, the weight loss observed (%; calcd (%)), and the temperature (°C) are as follows: cyclohexane, 4.55 (4.93), 50–160; naphthalene, 12.87 (13.31), approximately 200; triphenylene, 10.31 (10.31), approximately 420. These results agree with the elemental and crystallographic analyses. Note that crystals of pure triphenylene undergo a weight loss at a much lower temperature (below 330 °C). This fact indicates that the coordination network holds triphenylene strongly.

In conclusion, we have prepared a biporous coordination network where two guests are separately included into two channels by guest exchange. Two compounds which cannot

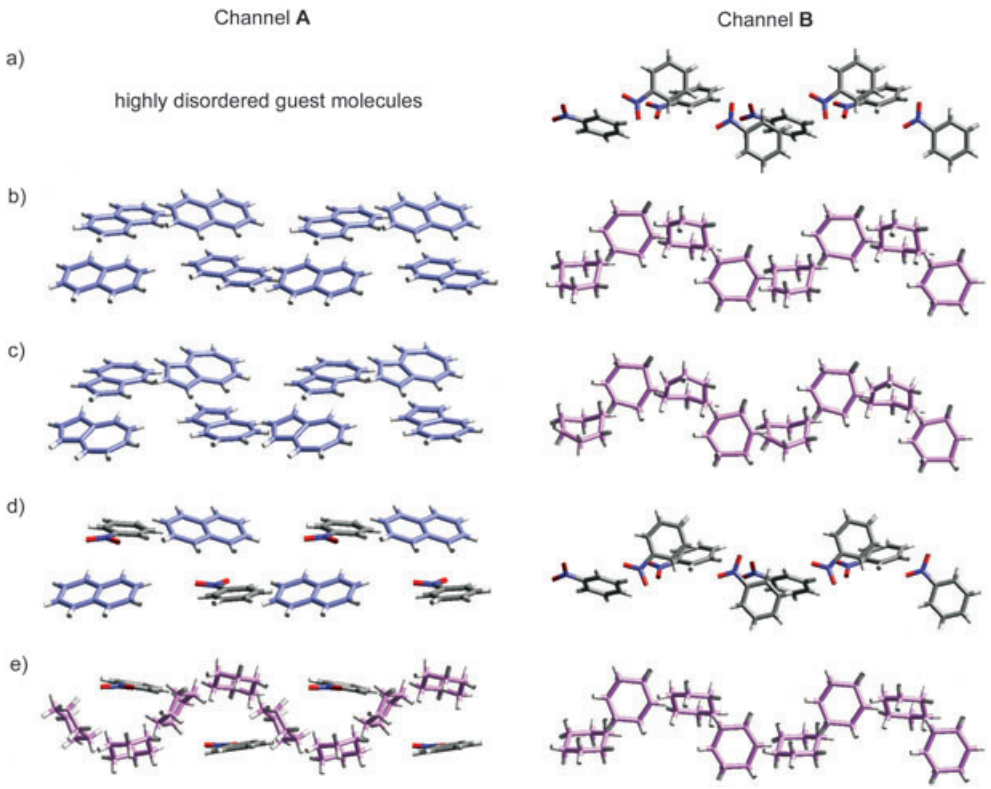

Figure 3. Columnar arrays of guest molecules in channels **A** (left) and **B** (right) in: a) **3** before guest exchange; b) **4**, c) **5**, d) **6**, and e) **7** after guest exchange. Partially disordered molecules have been omitted for clarity. The crystallographic details are given in the Supporting Information.

coexist can, therefore, be stored within the same crystal (for example, an acid/base or an oxidizing/reducing agent pair) as they are separated from each other by a rigid host framework. A variety of scientific and technological applications are likely to be possible for such a "two-in-one" crystal.

Experimental Section

Elemental analyses for **3**–**7**: $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2})]\cdot 3.9\,(\text{nitrobenzene})\cdot 1.8\,(\text{methanol})\}_z$ (**3**): calcd C 40.51, H 2.69, N 9.48; found C 40.89, H 2.60, N 9.49. $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2})]\cdot 1.3\,(\text{cyclohexane})\cdot 2.3\,(\text{naphthalene})\}_z$ (**4**): calcd C 45.99, H 3.19, N 7.59; found C 45.71, H 2.92, N 7.29. $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2})]\cdot 1.4\,(\text{cyclohexane})\cdot 2\,(\text{azulene})\}_z$ (**5**): calcd C 45.30, H 3.17, N 7.69; found C 45.50, H 2.88, N 7.41. $-\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2})]\cdot 2.4\,(\text{nitrobenzene})\cdot(\text{naphthalene})\}_z$ (**6**): calcd C 42.15, H 2.53, N 9.03; found C 41.85, H 2.67, N 8.94. $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2})]\cdot 2.0\,(\text{cyclohexane})\cdot 0.4\,(\text{nitrobenzene})\}_z$ (**7**): calcd C 40.51, H 3.08, N 8.56; found C 40.51, H 3.03, N 8.18. The cyclohexane and nitrobenzene in **7** could be completely removed by heating the crystals at 250 °C under N_2 for 20 min. $[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2})]_z$: calcd C 35.82, H 2.00, N 9.28; found C 36.12, H 2.17, N 9.02. Part of the guest molecules escaped at room temperature.

Crystallographic data for **3**–**7. 3**: $C_{79.33}H_{55.56}I_6N_{15.91}O_{9.68}Zn_3$, $M_r = 2344.00$, orthorhombic, space group *Pbca*, $a = 27.268(3)$, $b = 13.6992(16)$, $c = 45.888(5)$ Å, $V = 17141(3)$ Å^3, $T = 80$ K, $Z = 8$, $\rho_{calcd} = 1.817$ g cm^{-3}, 15876 unique reflections out of 21251 with $I > 2\sigma(I)$, 1025 parameters, $1.72 < \theta < 28.92°$, final R factors $R_1 = 0.0821$ and $wR_2 = 0.1478$; **4**: $C_{85.38}H_{71.07}I_6N_{12}Zn_3$, $M_r = 2222.62$, orthorhombic, space group *Pbca*, $a = 27.6479(19)$, $b = 13.7500(9)$, $c = 45.714(3)$ Å, $V = 17379(2)$ Å^3, $T = 80$ K, $Z = 8$, $\rho_{calcd} = 1.854$ g cm^{-3}, 15905 unique reflections out of 21663 with $I > 2\sigma(I)$, 1057 parameters, $1.72 < \theta < 28.75°$, final R factors $R_1 = 0.0517$ and $wR_2 = 0.1174$; **5**: $C_{86}H_{76}I_6N_{12}Zn_3$, $M_r = 2235.10$, orthorhombic, space group *Pbca*, $a = 27.787(3)$, $b = 13.7247(12)$, $c = 45.881(4)$ Å, $V = 17498(3)$ Å^3, $T = 80$ K, $Z = 8$, $\rho_{calcd} = 1.697$ g cm^{-3}, 14824 unique reflections out of 21598 with $I > 2\sigma(I)$, 904 parameters, $1.71 < \theta < 28.71°$, final R factors $R_1 = 0.0783$ and $wR_2 = 0.1636$; **6**: $C_{82}H_{59}I_6N_{15}O_6Zn_3$, $M_r = 2307.95$, orthorhombic, space group *Pbca*, $a = 27.5680(18)$, $b = 13.7285(9)$, $c = 45.836(3)$ Å, $V = 17347(2)$ Å^3, $T = 80$ K, $Z = 8$, $\rho_{calcd} = 1.767$ g cm^{-3}, 14715 unique reflections out of 21416 with $I > 2\sigma(I)$, 1005 parameters, $1.71 < \theta < 28.84°$, final R factors $R_1 = 0.0776$ and $wR_2 = 0.1678$; **7**: $C_{77.13}H_{77.65}I_6N_{12.66}O_{1.32}Zn_3$, $M_r = 2307.95$, orthorhombic, space group *Pbca*, $a = 27.873(2)$, $b = 13.7073(10)$, $c = 45.852(3)$ Å, $V = 17518(2)$ Å^3, $T = 80$ K, $Z = 8$, $\rho_{calcd} = 1.638$ g cm^{-3}, 15437 unique reflections out of 21619 with $I > 2\sigma(I)$, 1086 parameters, $1.71 < \theta < 28.84°$, final R factors $R_1 = 0.0739$ and $wR_2 = 0.1323$.

CCDC-251671 (**3**), -251672 (**4**), -251675 (**5**), -251673 (**6**), and -251674 (**7**) 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.

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