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Hierarchical Guest Exchange and Step-by-Step Activation of a Biporous Coordination Framework

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Supporting Information

ABSTRACT: A unique step-by-step activation of the biporous material via formation of the intermediate host–guest complex with a labile ligand has been presented on the example of the metal–organic framework $[Zn_4(ur)_2(ndc)_4]$. The difference in the chemical environment of channels allows highly selective separation of the mixture of S_4N_4 and benzene.

Metal–organic frameworks (MOFs) are one of the most intensively investigated objects in modern chemical science. The reason for such interest lies in the intrinsic porosity, great surface area, and virtually infinite functionality of such materials, which plays a critical role in any heterogeneous process such as adsorption or catalysis.[1] In many cases, the pores or channels demonstrate geometrical and chemical uniformity; i.e., there is only one type of pore/channel in the structure. A rarer case is the so-called biporous materials (the term is put forward by Fujita and co-workers), which have two distinct isolated cages or 1D channels with different chemical interfaces.[2] The coexistence of the different channels broadens the host–guest chemistry of such porous compounds because distinctions between the chemical nature of the pores allow selective sorption governed by the chemical affinity. Such a circumstance makes these materials prominent for separation purposes.

Recently, we reported an interesting porous compound, $[Zn_4(dmf)(ur)_2(ndc)_4]\cdot 5DMF\cdot H_2O$ (**1d**·5DMF·H$_2$O; ndc^{2-} = 2,6-naphthalenedicarboxylate and ur = urotropin, where the letter "d" in the compound index indicates a coordinated *N*,*N*-dimethylformamide (DMF) ligand), and its guest-selective luminescence properties.[3] According to the single-crystal X-ray diffraction data, this framework $[Zn_4(ur)_2(ndc)_4]$ (**1**) has a complicated structure containing two types of channels (Figure 1). The first ones (channels α) are hexagonal channels with characteristic dimensions 9.5 × 11 Å, and the second ones (channels β) are ellipsoidal with characteristic dimensions 4 × 5 Å. The channels have no obvious cross intersections or connections. The most important difference between the α and β channels, however, lies in their functional environment and chemical nature. The α channels are lined with aromatic naphthalene rings and urotropine fragments, which encrust the surfaces by unsaturated nitrogen atoms bearing lone-electron pairs. These channels have basic nature (in terms of the Lewis theory). On the contrary, the surface of the β channels contains unsaturated Zn^{2+} cations and should be regarded as Lewis acidic. We should note here that the simultaneous existence of centers of opposite reactivity, such as basic and acidic, in the same compound is impossible unless these sites are spatially separated, as takes place in the biporous MOF **1d**. Such materials often demonstrate a unique reactivity, particularly in multistep tandem catalytic reactions.[4]

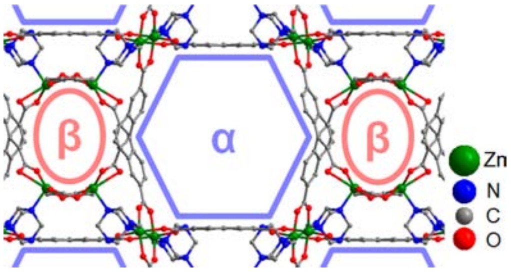

Figure 1. View of the section of the MOF **1**. The α and β channels are highlighted.

Both types of channels in the as-synthesized crystals **1d**·5DMF·H$_2$O are filled with DMF/H$_2$O solvent molecules: five guest DMF molecules and one H$_2$O in the α channels and one DMF in the β channels having relatively long Zn–O(dmf) coordination interaction (2.282 Å). Common thermal activation of **1d**·5DMF·H$_2$O at low pressure removes the solvent molecules from the α channels only, resulting in a permanently porous **1d**, the sorption properties of which were described earlier.[3] Further treatment destroys the framework, making it impossible to obtain fully activated **1** at higher temperature. This paper reports serendipitous, yet successful step-by-step activation of both types of channels in **1**, meditated by S_4N_4 guest molecules. As could be expected, the total pore volume and surface area of **1** are gradually increased compared to **1d**. More strikingly, the truly biporous nature of **1** was demonstrated by selective adsorption experiments through quantative separation of the molecular mixtures onto the corresponding channels with appropriate functionality. Simultaneous separation and storage of the distinct guest molecules in different compartments of biporous hosts is highly unusual and could be used, e.g., for multicomponent storage of reactive chemicals.

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Soaking of **1d** in the acetone solution S_4N_4 (**1d**:S_4N_4 = 1:1) turns the colorless crystals orange. Single-crystal X-ray analysis reveals complete substitution of coordinated DMF ligands in β channels to S_4N_4 molecules, resulting in the formula $[Zn_4(S_4N_4)(ur)_2(ndc)_4]\cdot x Me_2CO$ (**1s**·$x$$Me_2CO$, where index "s" is after S_4N_4). The substitution of DMF to S_4N_4 in **1** virtually does not affect the structure of the $[Zn_4(ur)_2(ndc)_4]$ framework; however, the crystallographic symmetries in **1d** and **1s** are different as a result of minor distortions. The shapes of the α and β channels in both structures are also similar. In spite of lone-electron pairs on nitrogen atoms of the S_4N_4 molecule, it has no obvious interactions with zinc cations of the framework (Figure 2a).

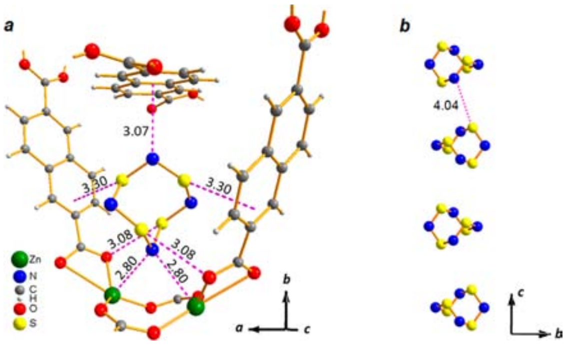

Figure 2. (a) Interactions of S_4N_4 molecules with β channels in **1s** (perspective view). (b) Arrangement of S_4N_4 molecules in **1s**. The shortest intermolecular contacts (Å) are marked by dotted lines.

The interatomic Zn–N(S_4N_4) distances (2.80 Å) found are too long even for a weak coordination bond. Indeed, the S_4N_4 molecule is a quite poor electron donor; nevertheless, there are a few S_4N_4 complexes known with Lewis acids, such as BF_3, $FeCl_3$, $SbCl_5$, SO_3, AsF_5, $TaCl_5$, and $SnCl_4$.[5] Such coordination commonly results in a significant flattening of the S_4N_4 ring, contrary to our case, where inclusion of the S_4N_4 molecule does not change its geometry or conformation. This also indirectly proves the absence of any S_4N_4 coordination to Zn^{2+} cations; therefore, **1s** should be more properly described as a host–guest complex between the host framework **1** and S_4N_4 molecules. The intermolecular contacts between the S_4N_4 molecules in the β channels are relatively long and slightly exceed the van der Waals distances (Figure 2b). To our best knowledge, this is the first example of the successful structural characterization of a S_4N_4 inclusion compound, which could be interesting when taking into account its known polymerization into superconducting chains $(SN)_x$.[6]

The S_4N_4 molecules reside in the tight pocket between the Zn_2 unit (d_{N-Zn} = 2.80 Å) and the naphthalene groups ($d_{S-ndc} \approx 3.30$ Å; $d_{N-ndc} \approx 3.08$ Å). Its orientation favors host–guest complementary Coulomb interactions between atoms of opposite charge, i.e., $O^{\delta-}\cdots S^{\delta+}$ or $Zn^{\delta+}\cdots N^{\delta-}$ (Figure 2). These relatively weak but numerous intermolecular interactions between the S_4N_4 guest and β-channel host probably explain the facile substitution of DMF by S_4N_4 but not by other organic solvent molecules, such as acetone or benzene, whose shape and functionality does not fit the environment of β channels. On the other hand, the absence of strong coordination bonds between S_4N_4 and the host framework in **1s** suggests the possibility of further substitution of S_4N_4 or even its complete removal from the β channels. Indeed, after **1s** crystals were washed in acetone, their orange color, attributed to S_4N_4, was gone. It would be reasonable to assume the formula $[Zn_4(Me_2CO)(ur)_2(ndc)_4]\cdot x Me_2CO$ (**1a**·$x$$Me_2CO$, where "a" stands for acetone) for that acetone-exchanged intermediate. Subsequent heating in a vacuum (45 °C, 3 days) gave rise the fully activated framework **1**, with both α and β channels being unoccupied. The quality of the crystals did not allow us to carry out single-crystal X-ray diffraction analysis; however, the stability of the porous framework was confirmed by the powder X-ray diffraction (PXRD) data. Elemental analysis and IR data also support the bulk formula of **1** (see the Supporting Information). More importantly, the successful activation and permanent porosity of the biporous framework **1** were confirmed by the N_2 adsorption measurements.

The extensive host–guest chemistry of biporous framework **1** is summarized in Figure 3. In general, the solvent guest molecules in roomy α channels are relatively labile and could be easily substituted or removed. On the contrary, the activation or guest exchange in tighter β channels is tricky. As was already pointed, the removal of DMF ligands in **1d** at elevated temperatures could not be performed and so goes the substitution by acetone or benzene. However, these DMF molecules in the β channels could gradually be substituted to S_4N_4 and then to acetone. Therefore, the compound **1s** is an important intermediate in the β-channel activation scheme because the S_4N_4 molecules mediate DMF exchange. We should note here that substitution of DMF by S_4N_4 in **1d** takes place in an acetone solution but not in benzene. Apparently, much better solubility of S_4N_4 in benzene does not favor its inclusion into β channels, while in acetone, the solution–solid distribution of S_4N_4 is shifted toward the formation of **1s**. In turn, the substitution of S_4N_4 could be performed in acetone but not in benzene because the single-crystal X-ray diffraction data of benzene-washed **1s** reveal the composition $[Zn_4(S_4N_4)(ur)_2(ndc)_4]\cdot 6C_6H_6$ (**1s**·$6C_6H_6$). Nevertheless, the incorporation of benzene molecules into the β channels could be successfully achieved by guest exchange of the intermediate **1a**, as was proven by determination of the corresponding crystal structure $[Zn_4(^1/_2C_6H_6 + {}^1/_2H_2O)(ur)_2(ndc)_4]\cdot 6C_6H_6$ (**1b**·$6C_6H_6$, where index "b" is after benzene) for benzene-washed crystals **1a**. We should point out that the studied compounds retain their structure and composition during the solvent-exchange reactions, as was confirmed by PXRD and ^1H NMR data. More importantly, the single-crystal-to-single-crystal manner of these processes allows

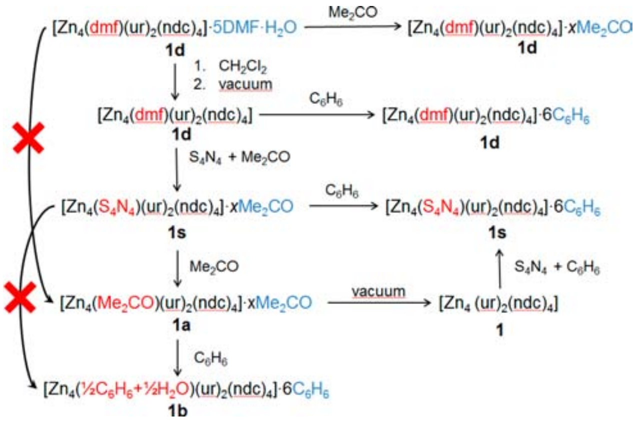

Figure 3. Host–guest chemistry and step-by-step activation of **1d**·$5DMF\cdot H_2O$. Red and blue colors highlight the guest molecules in the α and β channels, respectively.

us to precisely characterize and elucidate the locations of the guest molecules for all compounds by X-ray crystallography.

The two types of channels in compound **1** have quite distinct host−guest chemistry, which results from both their structural and functional differences. The larger α channels are omnivorous with no distinct preferences for the size or type of guest. On the other hand, the affinity of smaller β channels toward different molecules could be arranged in the following order: DMF $\geq$ S_4N_4 > acetone > benzene. Moreover, the host−guest interaction energy differences and, therefore, the equilibrium constants for the guest-exchange reactions appear to be quite significant. It is only possible to shift the equilibrium state by solvent washing between the particular intermediates, in a step-by-step manner. As in the above example, the DMF guest molecules could be substituted to S_4N_4 and then to acetone, but direct DMF-to-acetone solvent exchange does not take place. Such pronounced hierarchical host−guest substitution is unusual for porous materials.

The unique biporous nature of **1** and the remarkable difference in the host affinity between the α and β channels were demonstrated by the highly selective separation of S_4N_4 and benzene. The saturation of fully activated **1** in a 0.05 M S_4N_4 solution in benzene resulted in the formation of orange crystals, the structure of which was determined by single-crystal X-ray crystallography. These data clearly reveal compound **1s**·$6C_6H_6$, described above, where each component of the S_4N_4−C_6H_6 mixture is accommodated in the particular compartment of the biporous structure. The β channels selectively absorb S_4N_4 molecules from the mixture, following the above-mentioned preference. The benzene molecules, in turn, ended up in the indiscriminating α channels simply because of the great excess of C_6H_6 in the solution mixture. To our best knowledge, this is the only second example of simultaneous adsorption and selective spatial separation of different types of molecules by porous structures.[7]

Host−guest compounds, such as **1s**·$6C_6H_6$, could be regarded as solutions of two guest components in the host matrix; however, there is a very important difference here. Even though these guest species are mixed on the molecular level, there is no direct contact between the different types of guests, contrary to the conventional multicomponent solutions or many other porous materials, filled with molecular mixtures. Such a unique feature is only possible for biporous compounds with distinct size and/or functionality of the isolated channels. This opens new application and synthetic possibilities, e.g., the simultaneous storage and release of reactive species (acid and base, oxidizer and reducer, etc.) in the same material.

In summary, we have reported the unique hierarchical guest exchange and activation of biporous coordination framework **1**, mediated by S_4N_4 molecules. The biporous compound possesses two types of channels with different geometries and opposite functionality. It demonstrates a highly discriminating sorption of the molecular mixtures with simultaneous size and functional recognition; therefore, each component of the mixture is selectively accommodated in the particular channel type of the biporous structure.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format (CCDC 924319−924321), experimental details, single-crystal, PXRD, and sorption data, FT-IR and NMR spectra, and fragments of structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Special issue, *Chem. Soc. Rev.* **2009**, *38*, 1213−1504. (b) Special issue, *Chem. Rev.* **2012**, *2*, 673−1268.

(2) (a) Abrahams, B. F.; Moylan, M.; Orchard, S. D.; Robson, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1848−1851. (b) Ohmori, O.; Kawano, M.; Fujita, M. *CrystEngComm* **2005**, *7*, 255−259. (c) Kawano, M.; Kawamichi, T.; Haneda, T.; Kojima, T.; Fujita, M. *J. Am. Chem. Soc.* **2007**, *129*, 15418−15419. (d) Haneda, T.; Kawano, M.; Kawamichi, T.; Fujita, M. *J. Am. Chem. Soc.* **2008**, *130*, 1578−1579.

(3) Sapchenko, S. A.; Samsonenko, D. G.; Dybtsev, D. N.; Melgunov, M. S.; Fedin, V. P. *Dalton Trans.* **2011**, *40*, 2196−2203.

(4) Srirambalaji, R.; Hong, S.; Natarajan, R.; Yoon, M.; Hota, R.; Kim, Y.; Ko, Y.; Kim, K. *Chem. Commun.* **2012**, *48*, 11650−11652.

(5) (a) Drew, M. G. B.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1967**, *6*, 1906−1910. (b) Thewalt, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 855−859. (c) Neubauer, D.; Weiss, J. *Z. Anorg. Allg. Chem.* **1960**, *303*, 28−38. (d) Gieren, A.; Dederer, B.; Roesky, H. W.; Amin, N.; Petersen, O. *Z. Anorg. Allg. Chem.* **1978**, *440*, 119−129. (e) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Acta Crystallogr., Sect. B: Struct. Sci.* **1980**, *B36*, 655−657. (f) Thewalt, U.; Albrecht, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1098−1100. (g) Martan, H.; Weiss, J. *Z. Anorg. Allg. Chem.* **1984**, *514*, 107−114.

(6) (a) Rawson, J. M.; Longridge, J. J. *Chem. Soc. Rev.* **1997**, *26*, 53−61. (b) Banister, A. J.; Gorrell, I. B. *Adv. Mater.* **1998**, *17*, 1415−1429.

(7) Ohmori, O.; Kawano, M.; Fujita, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1962−1964.