Angewandte Chemie
International Edition

Supramolecular Chemistry

DOI: 10.1002/anie.201208153

Dynamically Deformable Cube-like Hydrogen-Bonding Networks in Water-Responsive Diamondoid Porous Organic Salts**

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Porous host frameworks with well-defined void spaces are of great importance for storage and as carriers for gases and organic molecules, such as hydrogen,[1] reactive substances,[2] and pharmacological agents.[3] One of the most intriguing challenges for these materials is the regulation of the release of the guest molecules by external stimuli; this regulation would lead to potential applications as easy-to-use controlled transport systems.[4] One possible way to achieve stimuli-responsive frameworks is by the incorporation of supramolecules. Noncovalently formed assemblies are inherently sensitive enough to amplify a local response as alteration of their structures, aggregations, and characteristics through transformation of the molecular arrangement.[5] Furthermore, such transformability also enables the response even if individual components do not have any stimuli-responsive sites.[6] Thus far, there has been a large number of examples of inorganic host frameworks combined with stimuli-responsive supramolecular units to achieve controlled release of the guest molecules.[7] On the other hand, there have been no such examples involving organic frameworks, even though their structures are generally flexible enough to show strong responses to external stimuli.[8]

In this context, we previously reported tetrahedral supramolecular clusters constructed of aromatic sulfonic acid derivatives and triphenylmethylamine (TPMA; Figure 1 a–c).[9] In the clusters, aromatic groups surround a cube-like hydrogen-bonding-network (H-bonding) core, thus shielding the structure. Recently, we also fabricated diamondoid porous organic salts (d-POSs) by using these clusters as building blocks (Figure 2).[10] The flexible host frameworks of these d-POSs are formed through π–π interactions between the clusters. Therefore, we expected that the clusters could also serve as stimuli-responsive supramolecular units in the d-POS frameworks.

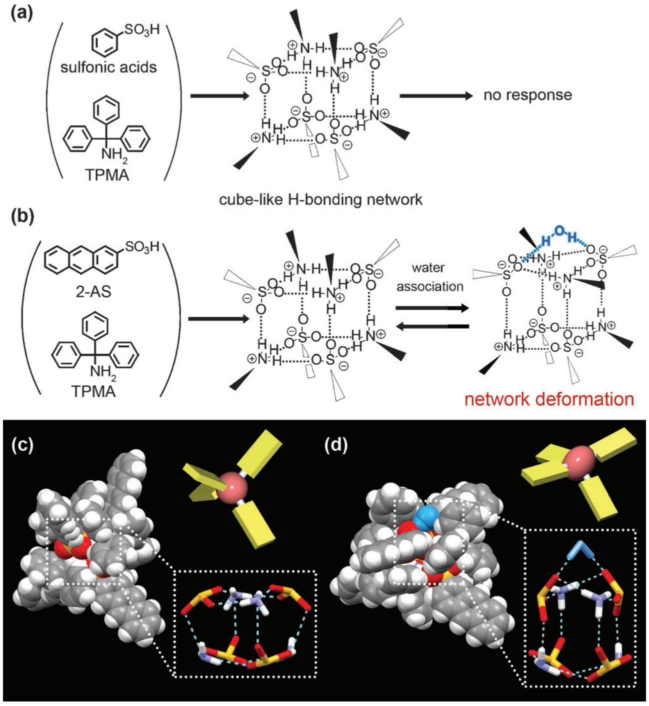

Figure 1. a) Static cube-like H-bonding network in a supramolecular cluster comprised of standard monosulfonic acids, such as benzenesulfonic acid, and TPMA. White wedges: phenyl groups; black wedges: triphenylmethyl groups. b) Deformable H-bonding network comprised of 2-AS and TPMA. White wedges: anthracenyl groups; black wedges: triphenylmethyl groups. c) Tetrahedral cluster comprised of 2-AS and TPMA and having a highly symmetrical cube-like H-bonding network. d) Distorted cluster containing a H-bonded water molecule.

Herein, we demonstrate that the cluster comprising anthracene-2-sulfonic acid (2-AS) and TPMA changes its conformation in the d-POSs triggered by moisture (Figure 1 b and d). The conformational change originates from the well-controlled deformation of the core by addition of a water molecule. The perturbation of the core is amplified through the dynamic transformation of the host frameworks and these conformational changes result in remarkable guest-molecule exclusion and fluorescent modulation (Figure 2). The transformation of the core leading to a dynamic response has not been demonstrated previously owing to the high symmetrical geometry of Platonic solids and cube-like networks in stable porous materials.[11] The coinstantaneous response of the

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[**] This work was financially supported by research fellowships of the Japan Society for the Promotion of Science (JSPS) for Young Scientists and Grants-in-Aid for Scientific Research on Innovative Areas "Coordination Programming" (area 2107, No. 24108723) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) (Japan). The synchrotron radiation experiments were performed at BL38B1 in the Spring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Proposal No. 2007B1988, 2007B2005, 2007B2039, 2008A1422, and 2012A1580)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201208153.

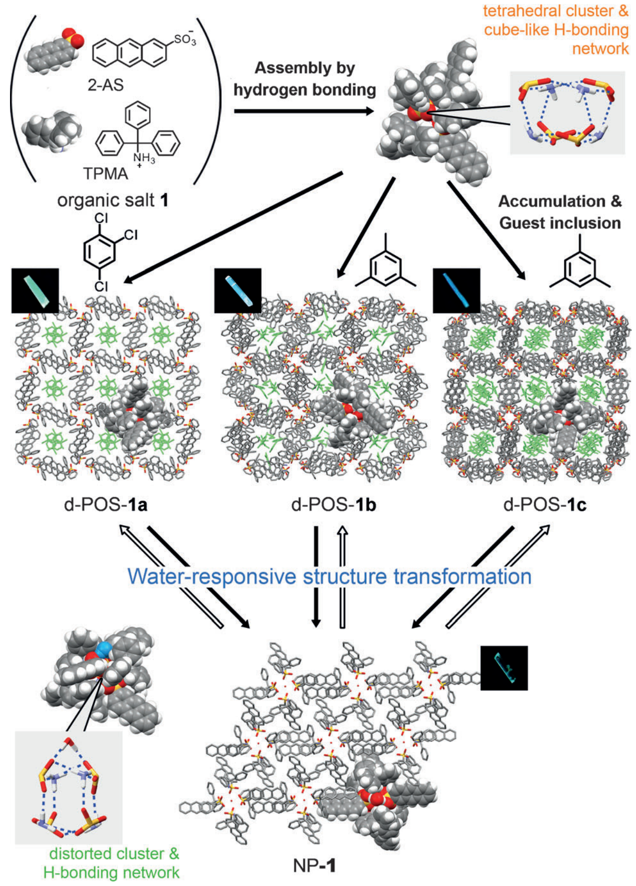

Figure 2. Guest-dependent construction and water-responsive transformation of d-POSs.

framework and fluorescence suggests potential applications such as drug delivery systems that enable medical treatment and detection concurrently without further labeling and time lag.

As previously reported, organic salt **1** comprised of 2-AS and TPMA formed three guest-dependent d-POSs (d-POS-**1a**–**c**), based on highly symmetrical tetrahedral clusters (Figure 1c and 2).[10,12] The d-POSs entrap the guest molecules at room temperature. Notably, however, the guest molecules undergo distinct exclusion dynamics under high humidity conditions (Figure 3, and Figures S1 and S2 in the Supporting Information). As shown in Figure 3, d-POS-**1a** shows remarkable weight loss upon exposure to the air saturated with water vapor (ca. 7.4 kPa) and only slight weight loss at ambient moisture. Upon exposure to the air saturated with water vapor the total weight loss is 33 %, which corresponds to the loss of almost all the guest molecules (35 %). It should be also noted that powder X-ray diffraction (PXRD) measurements provide the assumption that all the *d*-POSs transform to the same structure upon the exposure.

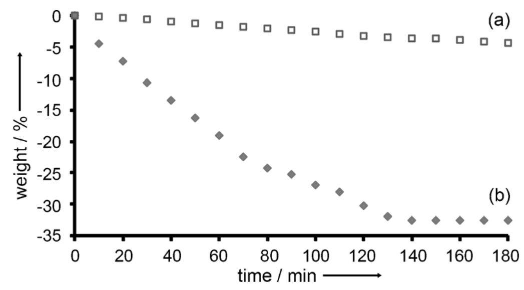

Figure 3. Guest-release profile of d-POS-**1a** at 40 °C in the absence (a) and presence (b) of air saturated with water vapor.

As expected, the PXRD pattern after the transformation is in good agreement with that of crystals containing water molecules (Figure S3 in the Supporting Information). The crystals were reproducibly obtained by recrystallization from a mixture of ethanol, aromatic solvents, and addition of a small amount of water.[12] Single-crystal X-ray analysis revealed that the crystal has a nonporous structure, NP-**1**, (Figure 2 and Figure S5a in the Supporting Information).[13] In NP-**1**, as d-POS-**1a**–**c**, a cluster contains four 2-AS molecules and four TPMA molecules (Figure 1d and Figure S5b in the Supporting Information). However, it is particularly noticeable that one water molecule is inserted in the core in NP-**1**. Two of four sulfonate anions rotate to accommodate a water molecule on one face of the core through additional hydrogen bonding (Figure 1c and d, and Figure S5b in the Supporting Information). After the addition, the core is deformed to provide a distorted cluster in which two of four anthracene moieties are in an almost linear arrangement. This conformational change is accompanied by more effective shielding of the other faces by the aromatic groups, thus preventing further approach and uncontrolled addition of water molecules and maintaining the distorted cluster.

The conformational change clearly affects the resultant packing structures through a domino effect (Figure S6 in the Supporting Information). In d-POS-**1a**–**c**, the clusters are assembled into diamondoid networks through π–π interactions between tetrahedral anthracene moieties and then subsequent interpenetration of the diamondoid networks to give the porous host frameworks (Figure S6a in the Supporting Information). In contrast, the distorted clusters in NP-**1** are linked in only one direction to yield chain networks (Figure S6b in the Supporting Information). Bundling of the chain networks yields the nonporous structures. Figure 4 shows a schematic representation of the dynamic effect starting from addition of a water molecule. First, upon exposure to moisture, a water molecule is specifically added to the H-bonded core. Upon addition of the water molecule, the core undergoes a conformational change. This effect is successively propagated to dynamically rearrange the network. Finally, the rearrangement results in the transformation of the framework through interdigitation of the chain networks (Figure S7 in the Supporting Information).

These phenomena seem to mimic the allosteric regulation of enzymes. A water molecule can be considered as an effector molecule and the H-bonding core as an allosteric site. It is striking that only one small water molecule can regulate the conformation of a cluster that has a total molecular weight of over 2000, thus bringing about the dynamic transformation of the host frameworks and guest release through a heterotropic effect. This allosteric effect also has a large influence on the crystallization process. When NP-**1** was dissolved in solvent and recrystallized, NP-**1** was obtained even without

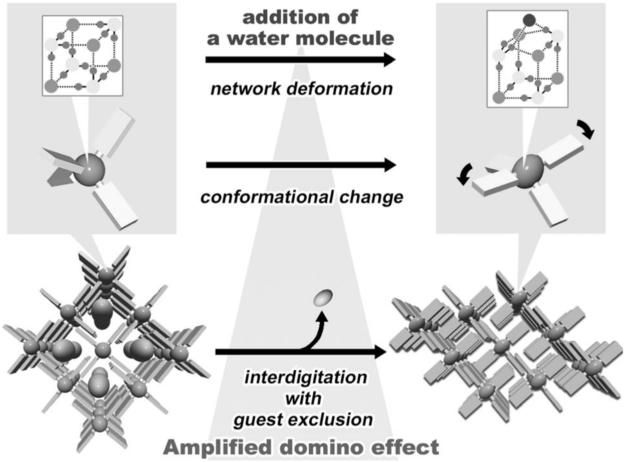

Figure 4. Schematic representation of the dynamic domino effect involving the addition of a water molecule and resulting in the transformation of the host frameworks.

addition of water; this result indicates that the distorted cluster is retained in solution and can reassemble into NP-**1**. However, when NP-**1** was recrystallized after being heated to 100 °C, thus removing water molecules, d-POS-**1a–c** were obtained from the solution.[12] These allosteric-like responses are significantly attractive in terms of efficient stimuli transduction and sensitivity.

Interestingly, the dynamic transformation also provides unique fluorescent modulations. As shown in Figure 5, d-POS-**1a** displays green fluorescence with a band at 535 nm, whereas d-POS-**1b** and **1c** show blue fluorescence with bands at 454 nm. The green fluorescence reflects strong interactions that originate from large π-overlapping of the anthracene moieties in the dimer structures (43 % overlap) and CH−Cl interaction between the guest molecules and the host framework (Figure S8a in the Supporting Information). In contrast, d-POS-**1b** and **1c** have small π-overlapping dimer structures (20 % and 36 % overlap, respectively), thus leading to weak interactions and the blue fluorescence (Figure S8b and c in the Supporting Information). However, after the transformation all the d-POSs show the same fluorescence profile as that of the single crystal of NP-**1**, which displays a band at 525 nm. Notably the fluorescence of d-POS-**1a** is blue-shifted whereas those of d-POS-**1b** and **1c** are red-shifted to result in the same profile. The same terminal state, which is achieved independent of each initial state, is favorable for fluorescent tracking by stationary measurements. These unique modulations are derived from dynamic changes of the π-stacked arrangements. In NP-**1**, two of four anthracene moieties form large π-overlapping dimers (51 % overlap) similar to those in d-POS-**1a** (Figure S8d in the Supporting Information). Thus, NP-**1** provides red-shifted fluorescence compared to d-POS-**1b** and **1c**. On the other hand, there is no host–guest interaction in NP-**1** owing to the guest exclusion. Consequently, NP-**1** exhibits relatively blue fluorescence compared to d-POS-**1a**. The combination of dynamic fluorescent modulation and guest release in response to a single external stimulus can potentially lead to useful applications in not only chemical sensing but also polyphasic molecular containers and drug-delivery systems. The dual response should allow concurrent treatment and detection without further labeling of drugs.

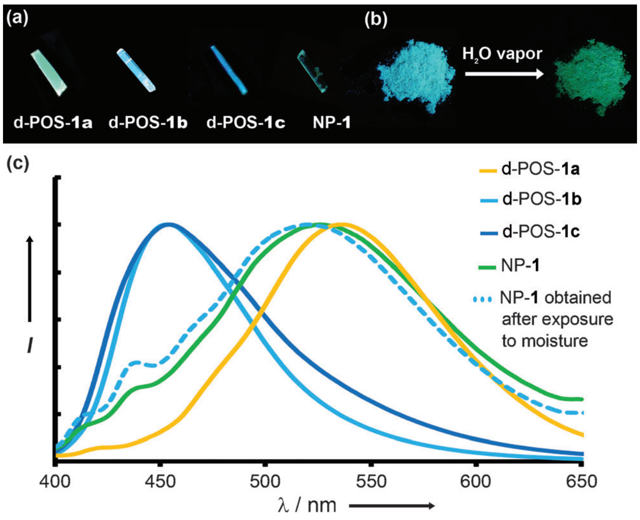

Figure 5. a) Images of d-POS-**1a–c** and NP-**1**. b) Dynamic fluorescent modulation from d-POS-**1b** to NP-**1** by exposure to saturated vapor at 40 °C for 3 h. c) Normalized fluorescent spectra of d-POS-**1a–c** and NP-**1**. The excitation wavelength was 365 nm.

In summary, we have demonstrated that a supramolecular cluster undergoes a dynamic conformational change in d-POSs upon exposure to moisture. This change is attributed to controlled deformation of the cube-like H-bonding network by addition of only one water molecule. The conformational change results in the dynamic transformation of the host frameworks and the associated controlled guest release and fluorescent modulation. To the best of our knowledge, this is the first example in which organic frameworks have been combined with a stimuli-responsive supramolecular unit to achieve controlled release and fluorescent modulation at the same time. The simultaneous responses to chemical stimuli provide potential applications for both smart sensing and release systems. Furthermore, the use of organic salts makes it possible to finely tune building blocks and host frameworks as observed in our previous work and some other successful examples.[9,14] Therefore, this work will provide useful strategy for designing organic porous structures with a variety of stimuli-responsiveness.

Experimental Section

Single-crystal X-ray diffraction data of NP-**1** was measured on a Rigaku R-AXIS RAPID diffractometer with a 2D area detector using graphite-monochromated CuKα radiation ($\lambda = 1.54187$ Å). See the Supporting Information for more experimental details.

Received: October 10, 2012

Keywords: dynamic deformation · hydrogen bonds · organic salts · porous structures · supramolecular chemistry

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[12] More experimental details are described in the Supporting Information.

[13] CCDC 880742 (d-POS-**1a**), 881390 (d-POS-**1b**), 881391 (d-POS-**1c**), and 901019 (NP-**1**) 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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