Crystal Engineering

A Structurally Variable Porous Organic Salt Based on a Multidirectional Supramolecular Cluster

Tetsuya Miyano, Naoki Okada, Ryunosuke Nishida, Atsushi Yamamoto, Ichiro Hisaki, and Norimitsu Tohnai^{*[a]}

Abstract: A porous organic salt (POS) composed of 2-sulfophenyl anthracene (2-SPA) and triphenylmetylamine (TPMA) forms five types of porous crystals, POS-a–e, by recognizing subtle differences in the molecular structure of incorporated guest molecules. This structurally variable POS was hierarchically designed on the basis of a supramolecular cluster with a directionally flexible linker formed by the organic salt. Xray crystallographic analysis reveals that the salt forms six conformers attributable to rocking and rotational motions of

Introduction

Nanometer-sized porous materials have attracted much attention because of their potential for many applications.^[1] Over the past couple of decades, metal organic frameworks (MOFs)^[2] have been studied and advanced because of their permanent porosity. Moreover, there are many types of porous networks in MOFs because of the diverse range of secondary building units that act as building blocks of porous structures, which provides high designability. As a result, a variety of functional materials have been reported that can be used, for example, for storage and separation of gasses,^[3] chemical and gas sensors,^[4] catalysts,^[5] and platforms for polymerization.^[6] Meanwhile, the number of reported covalent organic frameworks (COFs)^[7] have grown rapidly because they can offer the same advantages. Porous networks of MOFs and COFs have been constructed by using strong bonds such as coordination bonds or covalent bonds, to yield permanent porosity with open channels in crystalline materials. However, these methods have limitations in terms of processability, because of the strong interactions. On the other hand, noncovalent organic frameworks (NCOFs) or supramolecular frameworks that are constructed through hydrogen bonds,^[8] halogen bonds,^[9] and the others^[10] have gained interest because of their easy solution-based fabrication and reassembly, recyclability, dynamic

 [a] T. Miyano, N. Okada, R. Nishida, Dr. A. Yamamoto, Dr. I. Hisaki, Prof. Dr. N. Tohnai
 Department of Material and Life Science
 Graduate School of Engineering, Osaka University
 2-1 Yamadaoka, Suita, Osaka 565-0871 (Japan)
 E-mail: tohnai@mls.eng.osaka-u.ac.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201602233. the phenylene group in 2-SPA. The clusters form POS crystals through different porous networks according to the conformers. The POS crystals show a wide range of fluorescence spectra that are responsive to differences in the molecular and electronic structure of the guest molecule. This remarkable behavior has potential application in sensitive chemical sensors that are responsive to slight differences in molecular structures.

structural conversion, and so on. Cooper and Mastalerz designed porous crystals by using the self-assembly of permanent porous organic cages with large surface area.^[12] Meanwhile, Ward utilized salts composed of guanidinium and sulfonate groups to yield large supramolecular cages containing a large guest and flexible hydrogen-bonded frameworks showing single-crystal-single-crystal transformation through guest exchange.^[13] The groups of Credi and Comotti reported stimuli-sensitive porous materials that show adsorption and release of gas upon photoirradiation.^[14] In this way, organic porous frameworks assembled by noncovalent interactions become suitable for constructing robust and flexible porous structures with dynamic structural behavior and solvent-induced adaptation that is reminiscent of a living system. Especially, porous materials composed of hydrogen-bonding organic frameworks were investigated because the robust or flexible porous structures keeping permanent porosity.^[8]

Previously, our group reported that various sulfonic acids and triphenylmethylamine (TPMA) specifically formed [4+4] supramolecular clusters through charge-assisted hydrogenbonded networks.^[14] Subsequently, these clusters were connected by CH- π interactions, π - π interactions, or neutral hydrogen bonds to yield porous structures through the formation and interpenetration of diamondoid networks.^[15] The hierarchical method used to construct these crystals, which we termed diamondoid porous organic salts (d-POSs), are illustrated in Figure 1 a. By using this approach, we designed porous crystals with dynamic structural behavior that were responsive to guest absorption-desorption processes and moisture.^[16] However, the clusters only form diamondoid networks irrespective of the guest molecules used as template. Having a directionally diverse in-cluster linker is important for constructing structurally variable porous materials with various functions. In previous

Chem. Eur. J. 2016, 22, 1-8

Wiley Online Library

These are not the final page numbers! 77





Figure 1. a) Previous method of construction for a diamondoid porous network based on a rigid tetrahedral supramolecular cluster. b) New design of multidirectional supramolecular cluster forming various types of porous networks.

studies, a sulfo group was directly bonded to polyaromatic groups, acting as a linker that connected the clusters. In these cases, the directions of polyaromatic groups were limited to tetrahedral because of the steric hindrance of TPMA, which prevents the clusters from forming other networks. Therefore, some of their organic salts form only one porous structure, irrespective of the molecular structure of the template. In other words, these organic salts have low molecular recognition. Resolving the problem of limited networks opens up the possibility of using POS crystals as novel functional organic materials.

In this work, we designed a multidirectional supramolecular cluster composed of TPMA and 2-sulfophenyl anthracene (2-SPA) having a phenylene group between anthracene and sulfonic acid, as shown in Figure 1b. The phenylene group enables the cluster to be connected in a multidirection manner. Then, the cluster forms various types of porous networks, in addition to the diamondoid network noted in the previous work, according to the direction of the linkers. As a result, the salt forms appropriate porous crystals in accordance with the molecular structure of the template. In other words, the salt precisely recognizes differences in the molecular structures of the template. Moreover, the fluorescence spectra were highly sensitive to the structure of the template, because of the flexible dihedral angle between the phenylene group and anthracene moiety as well as the interactions between fluorophores. These results strongly suggest that introduction of directional

flexibility in the linker plays a very important role in forming structurally variable porous crystals with fluorescence modulation. To our knowledge, this POS constitutes the first report of a multicomponent porous material formed by noncovalent interactions that forms various porous crystals with fluorescence modulations.

Results and Discussion

Preparation and crystallization of a salt composed of 2-SPA and TPMA

The synthetic route used to prepare 2-SPA is shown in Scheme 1. According to an established procedure,^[17] 2-SPA was synthesized by Suzuki coupling of 2-anthraceneboronic acid and neopentyl 4-bromobenzenesulfonate followed by hydrolysis of the 2-SPA precursor. Then 2-SPA was mixed with TPMA at a ratio of 1:1 in methanol and evaporated to yield an organic salt. Subsequently, single crystals suited to various measurements were prepared by recrystallization from chloroform mixed with various guest molecules used as template, as described in Scheme 2.

Single-crystal X-ray structural analysis revealed that the organic salt composed of 2-SPA and TPMA molecules formed five types of porous structures, POS-a–e, depending on the template molecules and recrystallization conditions, as shown



Scheme 1. Synthesis of 2-SPA.

Chem. Eur. J. 2016, 22, 1–8

www.chemeurj.org

2

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

FR These are not the final page numbers!



Scheme 2. Chemical structures of organic salt and template molecules.

Table 1. Recrystallization conditions for preparing POS crystals.			
Crystal	Template	Recrystallization method ^[a]	<i>Т</i> [°С]
POS-a (Ben)	benzene	solvent evaporation	RT
POS-b (Ben) POS-b (<i>m</i> -Xy)	m-xylene	solvent evaporation	0 RT
POS-b (Ani)	N,N-dimethylaniline	solvent evaporation	RT
POS-c (p-Xy) POS-c	<i>p</i> -xylene benzene/decane	solvent evaporation solvent evaporation	RT
(Ben/Dec)			
POS-d (Mes)	mesitylene	solvent evaporation	RT
POS-d (EtAc) POS-e (Ben)	ethyl acetate benzene	solvent evaporation solvent evaporation	RT 0
[a] Recrystallized from mixture of chloroform and template molecule.			





Figure 2. [4+4] Supramolecular clusters composed of 2-SPA and TPMA. a) Hydrogen-bonding networks of the clusters and an example of 2-SPA conformational isomers. Conformers of supramolecular clusters formed in b) POS-a: C_a ; c) POS-b: C_b ; d) POS-c: C_c ; e,f) POS-d: C_{d-i} and $C_{d-i\nu}$ and g) POS-e: C_c :

Chem. Eur. J. 2016, 22, 1-8

www.chemeurj.org

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers! 77

in Table 1. Recrystallization from chloroform with various template molecules by slow evaporation at room temperature yielded POS-a-d crystals. In addition, recrystallization from chloroform with benzene at low temperature yielded POS-b and POS-e crystals, whereas a POS-a crystal was obtained from the same solvent mixture at room temperature.

Conformers and porous networks of supramolecular clusters

Surprisingly, four 2-SPA molecules and TPMA molecules always formed a [4+4] supramolecular cluster in all POS crystals. On the other hand, conformations of the cluster differed (Figure 2), owing to the introduction of a phenylene group between the sulfonic acid and anthracene. There are several factors that determine the conformers, which are attributable to not only rotational motion but also rocking motion of the 2-SPA molecules in the cluster (Figure 2a). These conformers affect the directions of the anthracene moieties acting as a linker. As a result, the cluster formed various porous networks as shown in Figure 3. The precise network structures are completely different, whereas the structures of the conformers are similar. For example, conformations C_c

and C_{d-i} are similar from the viewpoint of linker direction, however, networks formed by these conformers are clearly different (Figure 3-c,d). Subsequently, the networks of the various clusters interpenetrated each other to yield POS crystals. According to authoritative topological descriptions of porous networks,^[18] interpenetrated networks of C_{a^\prime} C_{b^\prime} C_{c^\prime} $C_{d\text{-}i\prime}$ $C_{d\text{-}ii\prime}$ and C_e were described by dia-c4, sql, dia-c4, dia-c4, dia-c, and dia-c4, respectively. These findings show that slight differences in the connection direction and dihedral angle strongly affect the structure of the porous networks. In other words, increasing the flexibility of the direction of the cluster linker enhances the diversity of the porous networks.



Figure 3. Porous networks composed of supramolecular clusters in each POS crystals a) network of C_a in POS-a; b) network of C_b in POS-b; c) network of C_c in POS-c; d) network of C_{d-i} in POS-d; e) network of C_{d-i} in POS-d; f) network of C_{d-i} in POS-d;

The structures of POS-a-e crystals

In the POS-a crystal, which belongs to the space group C_2/c , C_a clusters were connected by π - π interaction to form the network (Figure 3a) as in previous studies. Subsequently, the networks interpenetrated each other to yield the POS-a crystal with 0D closed voids (Figure 4a). In the POS-b crystal (space group: *Pban*), C_{b} clusters were connected by CH- π interactions to form the network shown in Figure 3b. The two networks then interpenetrated and laminated to yield POS-b with two types of voids: 0D closed and 1D bottle-neck voids (Figure 4b). In POS-c (space group: C2/c), C_c clusters were connected by CH- π and π - π interactions to form the network (Figure 3-c). The networks then interpenetrated to yield POS-c with channels (Figure 4-c). In POS-d (space group: C2/c), two conformationally different clusters, $\boldsymbol{C}_{d\text{-}i}$ and $\boldsymbol{C}_{d\text{-}ii}$ were constructed, each of which formed a different network. $\boldsymbol{C}_{d\text{-}i}$ clusters were arranged to form the network shown in Figure 2 d, whereas C_{d-ii} clusters were connected by $CH-\pi$ interactions to form a similar network to that seen in POS-b. Subsequently, two different networks interpenetrated in an intricate manner to yield POS-d with 0D closed and 1D channel voids (Figure 4d). POS-e (space group: Pc) was obtained by recrystallization at low temperature. In this crystal, $\boldsymbol{C}_{\!\!e}$ clusters were connected by CH- $\!\pi$ and π - π interactions to form a network (Figure 2 f) that was distinct from the other networks of POSs. The network then interpenetrated to yield POS-e with 0D closed and 1D void spaces (Figure 4 e).

To summarize, in the crystal structures of POSs composed of 2-SPA and TPMA, the salt assembled into conformers of supramolecular clusters with different connecting directions to form various types of porous networks classifiable into four types. These networks then interpenetrated to yield porous crystals in response to differences in template molecular structures.

Correlation between POS crystals and template molecules

Different types of POS crystals were obtained by recrystallization at room temperature depending on differences in the molecular size and shape of the template. For example, when benzene molecules were used as template, the salt yields POSa. On the other hand, use of slightly larger template molecules such as toluene, m-xylene, and N,N-dimethylaniline yielded POS-b. In POS-a, benzene occupied the 0D void spaces (Figure S1), but larger template molecules could not do so. Thus, recrystallization with such template molecules yielded POSb with larger 0D and 1D bottle-neck void spaces. In POS-b, the template molecules occupied the 0D and 1D channel void spaces (Figure S2). POS-c with 1D channels was obtained by using the longer template molecule p-xylene (Figure S3). The inclusion of benzene with decane also yielded POS-c. However, bulky template molecules such as mesitylene could not be incorporated into the narrow channels in POS-c. Thus, larger template molecules yielded POS-d with large 0D and 1D channel voids (Figure S4). These results indicate that the salt forms different types of POS crystals by recognizing subtle differences in template molecular structure; for example, the presence and position of a methyl group. That is, the salt had high molecular recognition ability, yielding different POS structures depending on the template molecule. It is very likely that the clusters with directionally flexible linker increased the diversity of the porous crystal structure.

Fluorescence modulation depending on the template molecules

POS crystals displayed a wide range of emission from blue to yellow-green, depending on the template molecule (Figure 5 a). Figure 5-c shows fluorescence spectra of these crystals excited at 365 nm. The spectra of POS-a,c,d were observed in

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Void: 21% per U.C.

Figure 4. Crystal structures and void spaces. a) POS-a; b) POS-b; c) POS-c; d) POS-d; e) POS-e. Guest molecules included in the void spaces are omitted for clarity.

a longer wavelength region (from 436 to 477 nm) than those of POS-b(m-Xy) (429 nm). In POS-a,c,d, porous networks were formed by $\pi\text{-}\pi$ or CH- π interactions between anthracene moieties or between anthracene and a phenylene group. On the other hand, the sheet network in POS-b was formed by only $CH-\pi$ interactions between anthracene moieties. The type of interaction has an influence on the fluorescence modulations. In addition, the dihedral angle between the anthracene moiety and phenylene group significantly alters the fluorescence. In the present POSs, there were some conformers of 2-SPA and different interactions between fluorophores, even in the isostructures. Thus, POS crystals with templates displayed different fluorescence spectra in response to slight differences in



uropean Journal

Full Paper

Figure 5. (a) Photographs of POSs crystals containing various template molecules under UV irradiation (λ = 365 nm). Normalized b) excitation and c) fluorescence spectra of each POS crystal excited at 365 nm.

template molecular structure, even though all crystal structures were nearly the same. However, it is difficult to determine the precise correlation between fluorescence modulations and the interactions or dihedral angles of fluorophores because of the many factors affecting the fluorescence spectra. The maximum wavelength of the fluorescence emission spectra shifted from 429 to 515 nm in POS-b(m-Xy) and POS-b(Ani), whereas their excitation spectra were not redshifted at all (Figure 5b). This suggests that there are no interactions in the ground state between template molecules and fluorophores. The fluorescence lifetime of POS-b(Ani) (67 ns (Figure S7)) was clearly longer than that of POS-b(m-Xy) (0.34 nm (Figure S6)). These results suggest that interactions between the template molecules and the fluorophores occurred to provide redshifted exciplex fluorescence. Consequently, fluorescence spectra of the organic salt depended sensitively on differences in electronic structures as well as molecular structures of the template molecule. These results indicate that the introduction of a phenylene group between the sulfonic acid and anthracene increases the sensitivity for template molecules, leading to the emission of different fluorescence for different template molecules.

Finally, we performed guest exchange experiments for POSb(m-Xy) by vapor exposure to benzene or N,N-dimethylaniline for one day at 50°C. Fluorescence spectra were drastically changed by vapor exposure (Figure S9), whereas their PXRD patterns were not shifted (Figure S8). In the fluorescence spec-

Chem. Eur. J. 2016, 22, 1-8 www.chemeurj.org These are not the final page numbers! **77** 5



trum of POS-b(*m*-Xy) exposed to benzene (Figure S9b), the peak around 490 nm increased and it corresponded to excimer emission of anthracene reported in a previous study.^[19] In this case, anthracene moieties became rotatable because the size of benzene is smaller than *m*-xylene. As a result, anthracene moieties tend to interact with each other in the excited state to increase excimer emission. In addition, the fluorescence spectrum of POS-b(*m*-Xy) exposed to *N*,*N*-dimethylaniline (Figure S9c) corresponded to POS-b(Ani) (Figure 5-c). These results strongly suggest that *m*-xylene molecules were exchanged to other volatile solvents by vapor exposure while maintaining the porous crystal structure.

Conclusion

We have prepared multidirectional supramolecular clusters composed of triphenylmethylamine (TPMA) and 2-sulfophenyl anthracene (2-SPA) having a phenylene group between the sulfonate and anthracene. The organic salt formed [4+4] supramolecular clusters with various conformers, and these clusters formed different porous networks according to their conformation. Subsequently, the clusters interpenetrated each other to yield porous crystals with different void spaces, POS-a-e, by recognizing the different template molecular structures. The salt also showed a wide range of fluorescence from 429 to 515 nm in response to the molecular shapes and chemical properties of the template molecules, because of the different interactions between fluorophores or fluorophores and template molecules. The present study demonstrates that the introduction of flexibility to the building blocks of porous networks yields guest-sensitive porous materials based on supramolecular clusters. We believe that these results may lead to useful new approaches to constructing statically flexible and dynamically transformable porous materials with fluorescent modulations. Such materials may be applied as sensitive chemical sensors that are responsive to slight differences in molecular structures.

Experimental Section

All chemicals and solvents were commercially available and used without any purification.

Synthesis of neopentyl 4-bromobenzenesulfonate: Neopentyl alcohol dissolved in chloroform (10 mL) was added to solution of 4bromobenzenesulfonyl chloride (10.2 g, 40.0 mmol) in chloroform (20 mL) and pyridine (11.7 mL, 40.0 mmol) at -5 °C for 1 h. The solution was then stirred overnight at RT. Chloroform (100 mL) was added and the mixture was washed with 0.1 \times HCl, water, brine, dried over anhydrous NaSO₄ and concentrated. Recrystallization from hexane gave the product (10.1 g, 98%) as colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ = 7.78 (d, J = 8.8 Hz, 2 H; Ar-H), 7.71 (d, J = 8.8 Hz, 2 H; Ar-H), 3.69 (s, 2 H; CH₂), 0.93 ppm (s, 9 H; CH₃).

Synthesis of 2-sulfophenyl anthracene precursor: 2-Sulfophenyl anthracene precursor was synthesized according to an established procedure. Toluene (200 mL), ethanol (50 mL), and $2 \, \text{mK}_2 \text{CO}_3$ solution (50 mL) were added to a mixture of neopentyl 4-bromobenzenesulfonate (5.53 g, 18.1 mmol), 2-anthraceneboronic acid (4.02 g, 18.1 mmol) and tetrakis(triphenylphosphane)palladium (0) (0.65 g,

0.562 mmol) under N₂ atmosphere. The reaction mixture was heated at 115 °C and stirred for 6 h. The mixture was then concentrated in vacuo, extracted with chloroform, washed with water and brine, and dried over anhydrous Na₂SO₄. The product was purified with column chromatography (silica gel; chloroform/hexane=4:1 v/v) to give 2-sulfophenyl anthracene precursor (6.68 g, 91%) as a pale-yellow solid. ¹H NMR (400 MHz, CDCI₃): δ = 8.52 (s, 1 H; Ar-H), 8.48 (s, 1 H; Ar-H), 8.27 (s, 1 H; Ar-H), 8.13 (d, *J* = 8.8 Hz, 1 H; Ar-H), 8.04 (m, 4H; Ar-H), 7.94 (d, *J* = 8.0 Hz, 2 H; Ar-H), 7.74 (dd, *J*₁ = 9.2 Hz, *J*₂ = 1.2 Hz, 1 H; Ar-H), 7.51 (m, 2 H; Ar-H), 3.76 (s, 2 H; CH₂), 0.95 ppm (s, 9 H; CH₃).

Preparation of the organic salt composed of 2-SPA and TPMA: 2-SPA was obtained by hydrolysis of 2-SPA precursor. 2-SPA precursor, dioxane, ethanol, and 0.5 M HCl was added to a pressure bottle and stirred at 160 °C for 18 h. The reaction mixture was concentrated in vacuo and dissolved in methanol. This operation was repeated several times to remove HCl. Subsequently, 2-SPA and TPMA were mixed in methanol in a 1:1 molar ratio. The solution was evaporated to give a pale-yellow powder of the crude salt.

Preparation of single crystals: The crude salt was dissolved in chloroform and various template solvents were added to the solution. Slow evaporation of the solvent at RT gave each single crystal with template except for POS-b-Ben and POS-e-Ben. POS-b-Ben crystal was obtained by vapor diffusion method with benzene at 0 °C and POS-e-Ben crystal was obtained by slow evaporation at 0 °C.

Fluorescence spectroscopy measurements: Fluorescence spectra were measured with a FP-6500 spectrofluorometer (Jasco). Samples for the measurements in the solid state were encapsulated in a quartz cell $(30 \times 30 \times 0.3)$. The excitation wavelength was 365 nm.

Fluorescence lifetime measurements: Fluorescence lifetime measurements for the crystals were undertaken with a TemPro Fluorescence Lifetime System (Horiba Jobin Yvon) equipped with an LED excitation source of 352 nm with a pulse-duration full width at half maximum (FWHM) of approximately 1 ns.

Molecular graphics and calculations: The inclusion space volumes filled by the solvent molecules in the crystal structures were calculated from the atomic coordinates by using the PLATON program. The atomic radii (Å) were adopted as follows: H 1.20, C 1.70, O 1.60, N 1.65, and S 1.80. The probe radius was fixed at 0.7 Å.

Crystallographic analysis of single crystals: X-ray diffraction data of POS-a(Ben) and POS-d(Mes) were collected with a Rigaku R-AXIS RAPID diffractometer with a 2D area detector by using graphitemonochromatized CuK α radiation ($\lambda = 1.54187$ Å). The data of POS-b(Ben) were recorded with a Rigaku XtaLAB P-200 system by using graphite monochromatic CuK α radiation ($\lambda = 1.54187$ Å). The other X-ray diffraction data were collected with a CCD with synchrotron radiation ($\lambda = 0.8000$ Å) monochromated by the fixed exit Si (111) double crystal. The cell refinements were performed with HKL2000 software.^[20] Direct methods (SIR-2004,^[21] SIR-2008,^[22] ShelexIS^[23] and Superflip^[24]) were used for the structure solution. All calculations were performed with the observed reflections [1> $2\sigma(l)$ by using the CrystalStructure crystallographic software pack $age^{\scriptscriptstyle [23]}$ except for refinement, which was performed using SHELXL.^[25] All non-hydrogen atoms were refined with anisotropic displacement parameters, placed in idealized positions, and refined as rigid atoms with the relative isotropic displacement parameters. The data were also refined by using the SQUEEZE routine function in PLATON to solve the structures without the influence of the disordered guest molecules.[26]

Chem. Eur. J. 2016, 22, 1–8 wv

www.chemeurj.org

6

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Powder diffraction X-ray analysis: Powder X-ray diffraction (PXRD) patterns were measured with a Rigaku Ultima IV using graphite monochromatized Cu K α radiation ($\lambda = 1.54187$ Å) at RT.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number JP25288036 and JSPS KAKENHI Grant Number JP16H01027 in "Precisely Designed Catalysts with Customized Scaffolding". We thank Dr. K. Aburaya and Dr. H. Sato (Rigaku Corporation) for crystal structure analysis. We also thank Professor Dr. M.Miyata (Osaka University) for his support. T. M. thanks the Interactive Materials Science Cadet Program in Osaka University. The synchrotron radiation experiments were performed at BL38B1 in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal nos. 2014A1648 and 2015A1776). We deeply appreciate the referee's constructive comments regarding topology.

Keywords: cluster compounds · crystal engineering · fluorescence · host–guest systems · supramolecular chemistry

- [1] a) K. B. Yoon, Acc. Chem. Res. 2007, 40, 29; b) A. Thomas, Angew. Chem. Int. Ed. 2010, 49, 8328-8344; Angew. Chem. 2010, 122, 8506-8523.
- [2] a) S. Kitagawa, R. Kitaura, S. Noro, Angew. Chem. Int. Ed. 2004, 43, 2334–2375; Angew. Chem. 2004, 116, 2388–2430; b) O. K. Farha, J. T. Hupp, Acc. Chem. Res. 2010, 43, 1166–1175; c) O. M. Yaghi, M. O Keeffe, N. W. Ockwing, H. K. Chae, M. Eddaoudi, J. Kim, Nature 2003, 423, 705–714.
- [3] a) J. R. Li, Y. Mab, M. C. McCarthyb, J. Sculleya, J. Yub, H. K. Jeongb, P. B. Balbuenab, H. C. Zhoua, *Coord. Chem. Rev.* 2011, *255*, 1791–1823; b) T. Rodenas, I. Luz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, F. X. L. Xamena, J. Gascon, *Nat. Mater.* 2014, *14*, 48–55.
- [4] a) N. Yanai, K. Kitayama, Y. Hijikata, H. Sato, R. Matsuda, Y. Kubota, M. Takata, M. Mizuno, T. Uemura, S. Kitagawa, *Nat. Mater.* 2011, *10*, 787–793; b) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. V. Duyne, J. T. Hupp, *Chem. Rev.* 2012, *112*, 1105–1125; c) J. He, M. Zha, J. Cui, M. Zeller, A. D. Hunter, S. M. Yiu, S. T. Lee, Z. Xu, *J. Am. Chem. Soc.* 2013, *135*, 7807–7810; d) Z. Xie, L. Ma, K. E. Krafft, A. Jin, W. Lin, *J. Am. Chem. Soc.* 2010, *132*, 922–923.
- [5] a) P. Hu, J. V. Morabito, C. K. Tsung, ACS Catal. 2014, 4, 4409-4419;
 b) A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkovc, F. Verpoort, Chem. Soc. Rev. 2015, 44, 6804-6849; c) P. Z. Li, X. J. Wang, J. Liu, J. S. Lim, R. Zou, Y. I. Zhao, J. Am. Chem. Soc. 2016, 138, 2142-2145.
- [6] a) G. Distefano, H. Suzuki, M. Tsujimoto, S. Isoda, S. Bracco, A. Comotti, P. Sozzani, T. Uemura, S. Kitagawa, *Nat. Chem.* **2013**, *5*, 335–341; b) T. Ishiwata, Y. Furukawa, K. Sugikawa, K. Kokado, K. Sada, J. Am. Chem. Soc. **2013**, *135*, 5427–5432.
- [7] a) A. P. Cote, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O. M. Yaghi, *Science* 2005, *310*, 1166–1170; b) X. Feng, X. Dinga, D. Jiang, *Chem. Soc. Rev.* 2012, *41*, 6010–6022; c) S. Ding, W. Wang, *Chem. Soc. Rev.* 2013, *42*, 548–568.
- [8] a) P. Sozzani, S. Bracco, A. Comotti, L. Ferretti, R. Simonutti, Angew. Chem. Int. Ed. 2005, 44, 1816–1820; Angew. Chem. 2005, 117, 1850–1854; b) I. Hisaki, S. Nakagawa, N. Tohnai, M. Miyata, Angew. Chem. Int. Ed. 2015, 54, 3008–3012; Angew. Chem. 2015, 127, 3051–3055; c) J. Lü, C. Perez-Krap, M. Suyetin, N. H. Alsmail, Y. Yan, S. Yang, W. Lewis, E. Bichoutskaia, C. C. Tang, A. J. Blake, R. Cao, M. Schroder, J. Am. Chem. Soc. 2014, 136, 12828–12831; d) M. Mastalerz, I. M. Oppel, Angew. Chem. Int. Ed. 2012, 51, 5252–5255; Angew. Chem. 2012, 124, 5345–5348; e) H. Wang, B. Li, H. Wu, T. Hu, Z. Yao, W. Zhou, S. Xiang, B. Chen, J. Am. Chem. Soc. 2015, 137, 9963–9970; f) S. A. Dalrymple, G. K. H. Shimizu, J. Am. Chem. Soc. 2011, 133, 14570–14573; h) P. Li, Y. He, J. Guang, L.

Weng, J. C. Zhao, S. Xiang, B. Chen, J. Am. Chem. Soc. 2014, 136, 547–549; i) P. Li, Y. He, Y. Zhao, L. Weng, H. Wang, R. Krishna, H. Wu, W. Zhou, M. O'Keeffe, Y. Han, B. Chen, Angew. Chem. Int. Ed. 2015, 54, 574–577; Angew. Chem. 2015, 127, 584–587; j) J. Tian, P. K. Thallapally, S. J. Dalgarno, J. L. Atwood, J. Am. Chem. Soc. 2009, 131, 13216–13217; k) W. Yang, A. Greenaway, X. Lin, R. Matsuda, A. J. Blake, C. Wilson, W. Lewis, P. Hubberstey, S. Kitagawa, N. R. Champness, M. Schroder, J. Am. Chem. Soc. 2010, 132, 14457–14469; l) X. Luo, X. Jia, J. Deng, J. Zhong, H. Liu, K. Wang, D. Zhong, J. Am. Chem. Soc. 2013, 135, 11684–11687; m) R. Natarajan, L. Bridgland, A. Sirikulkajorn, J. Lee, M. F. Haddow, G. Magro, B. Ali, S. Narayanan, P. Strickland, J. P. H. Charmant, A.. Orpen, N. B. McKeown, C. G. Bezzu, A. P. Davis, J. Am. Chem. 2015, 127, 6288–6293; Angew. Chem. Int. Ed. 2015, 54, 6190–6195.

- [9] a) K. Raatikainen, K. Rissanen, *Chem. Sci.* **2012**, *3*, 1235–1239; b) J. Syssa-Magalé, K. Boubekeur, J. Leroy, L. Chamoreau, C. Favec, B. Schollhorn, *CrystEngComm* **2014**, *16*, 10380–10384; c) J. Martí-Rujas, L. Colombo, J. Lu, A. Dey, G. Terraneo, P. Metrangolo, T. Pilatib, G. Resnati, *Chem. Commun.* **2012**, *48*, 8207–8209.
- [10] T. Chen, I. Popov, W. Kaveevivitchai, Y. Chuang, Y. Chen, O. Daugulis, A. J. Jacobson, O. S. Miljanic, *Nat. Commun.* **2013**, *4*, 5131.
- [11] a) A. G. Slater, A. I. Cooper, *Science* 2015, *348*, 8075; b) T. Hase, M. Miklitz, A. Stephenson, M. A. Little, S. Y. Chong, R. Clowes, L. Chen, D. Holden, G. A. Tribello, Kim. E. Jelfs, A. I. Cooper, *J. Am. Chem. Soc.* 2016, *138*, 1653–1659; c) G. Zhang, O. Presly, F. White, I. M. Oppel, M. Mastalerz, *Angew. Chem. Int. Ed.* 2014, *53*, 1516–1520; *Angew. Chem.* 2014, *126*, 1542–1546; d) G. Zhang, M. Mastalerz, *Chem. Soc. Rev.* 2014, *43*, 1934–1947.
- [12] a) Y. Liu, C. Hu, A. Comotti, M. D. Ward, Science 2011, 333, 436–440;
 b) W. Xiao, C. Hu, M. D. Ward, J. Am. Chem. Soc. 2014, 136, 14200–14206.
- [13] M. Baroncini, S. Agostino, G. Bergamini, P. Ceroni, A. Comotti, P. Sozzani, I. Bassanetti, F. Grepioni, T. M. Hernandez, S. Silvi, M. Venturi, A. Credi, *Nat. Chem.* **2015**, *7*, 634–640.
- [14] N. Tohnai, Y. Mizobe, M. Doi, S. Sukata, T. Hinoue, T. Yuge, I. Hisaki, Y. Matsukawa, M. Miyata, Angew. Chem. Int. Ed. 2007, 46, 2220–2223; Angew. Chem. 2007, 119, 2270–2273.
- [15] A. Yamamoto, S. Uehara, T. Hamada, M. Miyata, I. Hisaki, N. Tohnai, *Cryst. Growth Des.* 2012, *12*, 4600–4606.
- [16] a) A. Yamamoto, T. Hasegawa, T. Hamada, T. Hirukawa, I. Hisaki, M. Miyata, N. Tohnai, *Chem. Eur. J.* **2013**, *19*, 3006–3016; b) A. Yamamoto, T. Hamada, I. Hisaki, M. Miyata, N. Tohnai, *Angew. Chem. Int. Ed.* **2013**, *52*, 1709–1712; *Angew. Chem.* **2013**, *125*, 1753–1756.
- [17] K. Ito, T. Suzuki, Y. Sakamoto, D. Kubota, Y. Inoue, F. Sato, S. Tokito, Angew. Chem. Int. Ed. 2003, 42, 1159–1162; Angew. Chem. 2003, 115, 1191–1194.
- [18] a) M. O'Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi, Acc. Chem. Res. 2008, 41, 1782–1789; b) M. O'Keeffe, O. M. Yaghi Chem. Rev. 2012, 112, 675–702; c) M. Li, D. Li, M. O'Keeffe, O. M. Yaghi, Chem. Rev. 2014, 114, 1343–1370.
- [19] M. Sugino, Y. Araki, K. Hatanaka, I. Hisaki, M. Miyata, N. Tohnai, Cryst. Growth Des. 2013, 13, 4986–4992.
- [20] Z. Otwinowski, W. Minor, Methods Enzymol. 1997, 276, 307-326.
- [21] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, J. Appl. Crystallogr. 2005, 38, 381–388.
- [22] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna, J. Appl. Crystallogr. 2007, 40, 609–613.
- [23] G. M. Sheldrick, Acta Crystallogr. Sect. A 2008, 64, 112-122.
- [24] L. Palatinus, G. Chapuis, J. Appl. Crystallogr. 2007, 40, 786-790.
- [25] Rigaku (2015). CrystalStructure. Version 4.2. Rigaku Corporation, Tokyo, Japan.
- [26] a) P. van der Sluis, A. L. Spek, Acta Crystallogr. Sect. A 1990, 46, 194–201;
 b) A. L. Spek, Acta Crystallogr. Sect. D 2009, 65, 148–155.

Received: May 11, 2016 Published online on

Chem. Eur. J. **2016**, 22, 1–8

www.chemeurj.org

7

These are not the final page numbers! **77**



FULL PAPER

Crystal Engineering

T. Miyano, N. Okada, R. Nishida, A. Yamamoto, I. Hisaki, N. Tohnai*

A Structurally Variable Porous Organic Salt Based on a Multidirectional Supramolecular Cluster



Flexible crystals: A flexible supramolecular cluster composed of an organic salt provides structurally variable porous crystals with high molecular recognition ability. The structures and fluorescence

properties of the porous crystals differ in response to differences in the molecular structures of incorporated molecules (see scheme).

CHEMISTRY A European Journal

Full Paper

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

8