Angewandte Chemie International Edition

Host–Guest Chemistry

International Edition: DOI: 10.1002/anie.201503489
German Edition: DOI: 10.1002/ange.201503489

Host–Guest Complexation of Perethylated Pillar[5]arene with Alkanes in the Crystal State**

Tomoki Ogoshi, Ryuta Sueto, Kumiko Yoshikoshi, Yoko Sakata, Shigehisa Akine,* and Tada-aki Yamagishi*

Abstract: *Activated perethylated pillar[5]arene crystals show an unexpected alkane-shape- and -length-selective gate-opening behavior. Activated crystals were obtained upon removing solvents from perethylated pillar[5]arene crystals by heating. The activated crystals could quantitatively take up n-alkanes with carbon chains containing more than five carbon atoms as a consequence of their gate-opening pressure. As the chain length of the n-alkanes increased, the gate pressure decreased. A transformation into a herringbone structure was induced when n-hexane was used as a guest. By contrast, cyclic and branched alkanes were not taken up and could not induce a crystal transformation because they were too large to fit in the cavities of the pillar[5]arene. Alkane-shape-selective molecular recognition of pillar[5]arenes in the solution state was translated into the vapor/crystal state.*

Alkanes[1] are very important base materials for chemical engineering, and are generally obtained from petroleum processing. However, petroleum processing is an energy-demanding processes, and, thus, the development of materials for the selective inclusion of alkanes under mild conditions is highly desired. Potential candidates include macrocyclic compounds because they exhibit cavity-size-dependent host–guest interactions. However, alkanes exhibit a low electric polarization because they only have C–C and C–H groups, which makes the complexation between macrocyclic compounds and alkanes inefficient. This is also indicated by the family name of alkanes, "paraffins", which originates from the Latin parum affinis, which means "little affinity".[1] Cyclodextrins,[2,3] calix[*n*]arenes,[4–6] crown ethers,[7] cucurbit[*n*]urils,[8,9] cyclobis(paraquat-*p*-phenylene)s (blue boxes),[10] calixpyrroles,[11] and pillar[*n*]arenes,[12,13,15–17] which were introduced by our group in 2008,[12] are well-known macrocyclic molecules. However, there are only a few examples of host–guest complexes formed between these macrocyclic compounds and alkanes.[3,6,15] Among these macrocyclic compounds, pillar[5]arenes show superior shape-selective complexation abilities of alkanes in organic solvents; pillar[5]arenes can form host–guest complexes with linear *n*-alkanes in $CDCl_3$, but not with branched or cyclic alkanes.[16a,b] The driving force behind complexation would be CH/π interactions. However, because CH/π interactions are the weakest hydrogen bonds, the association constants between *n*-alkanes and pillar[5]arenes are very low in $CDCl_3$ ($K =$ ca. $10\,\text{M}^{-1}$).[16a,b] As a consequence of the low affinity, the separation of alkane mixtures by pillar[5]arenes is difficult. In the present study, we discovered that the crystal state of perethylated pillar[5]arene **1** without solvent molecules (activated crystals **1**) can quantitatively form a host–guest complex with *n*-alkanes. Furthermore, the activated crystals show an unexpected selective gate-opening behavior that depends on the alkane length and shape, with sudden uptake occurring at a given pressure. Pillar[5]arenes **1** do not exhibit strong physical interactions, and show gate-opening behavior along with a crystal transformation. In addition, the activated crystals can store *n*-alkanes even under reduced pressures. Overall, the activated crystals of **1** appear to have enhanced alkane-recognition ability over solution-state complexation.

To investigate the crystal structure of **1** with and without solvents, single crystals of **1** suitable for X-ray analysis were grown by slow evaporation of an acetone solution. The pentagonal structure of **1** formed infinite 1D channels along the *a* axis (**1α**, Figure 1b). The pillar-shaped structures of the pillar[*n*]arenes contributed to the formation of the 1D channels. Acetone molecules were included in the channels. A sample of **1α** was heated at 50 °C under reduced pressure to activate crystals of **1** (Figure 1, path I). Heating **1α** for 24 h was sufficient to desolvate all the acetone molecules from the channels. However, the powder X-ray diffraction (PXRD) pattern of the activated crystals (**1β**, Figure 1e) was different from that of the original crystals (**1α**, Figure 1d). This indicated that the removal of acetone molecules triggered a solid-state crystal transformation from **1α** into a new crystal structure, **1β**.[14] When **1β** was exposed to acetone vapor (Figure 1, path II), the PXRD pattern of **1α** was recovered (Figure S2), thus indicating that the solid-state switching between **1α** and **1β** could be reversed by the uptake and release of acetone guest molecules. This structural change did not occur in perhydroxylated pillar[5]- and pillar[6]arenes, even on removal of the solvent, because their structures were stabilized by inter-/intramolecular hydrogen bonds.[15] In contrast, the 1D channel structure of **1α** was stabilized by weak physical interactions. Therefore, the uptake and release

---

[*] Dr. T. Ogoshi, R. Sueto, K. Yoshikoshi, Dr. Y. Sakata, Prof. S. Akine, Prof. T. Yamagishi
Graduate School of Natural Science and Technology
Kanazawa University
Kakuma-machi, Kanazawa 920-1192 (Japan)
E-mail: ogoshi@se.kanazawa-u.ac.jp
akine@se.kanazawa-u.ac.jp
Dr. T. Ogoshi
PRESTO, the Japan Science and Technology Agency (JST)
4-1-8 Honcho, Kawaguchi 332-0012 (Japan) (Japan)

[**] This work was partially supported by the JSPS KAKENHI (grant number 15H00990) and Kanazawa University CHOZEN Project.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201503489.

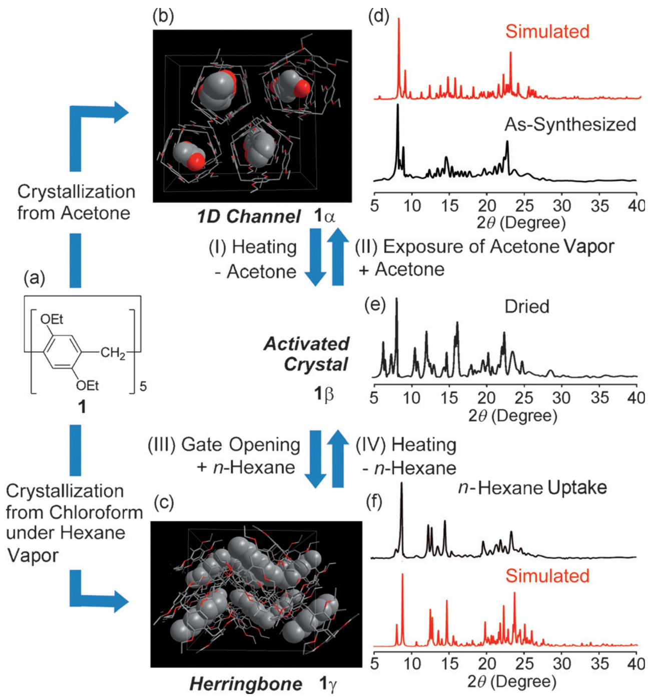

Figure 1. a) Chemical structure of perethylated pillar[5]arene (**1**). b) One-dimensional channel and c) herringbone crystal structure of **1**. PXRD patterns of d) **1α**, e) **1β**, and f) **1γ**; black lines: observed, red lines: simulated from X-ray crystal structures. In the X-ray structures, C: gray, O: red; H atoms are omitted for clarify.

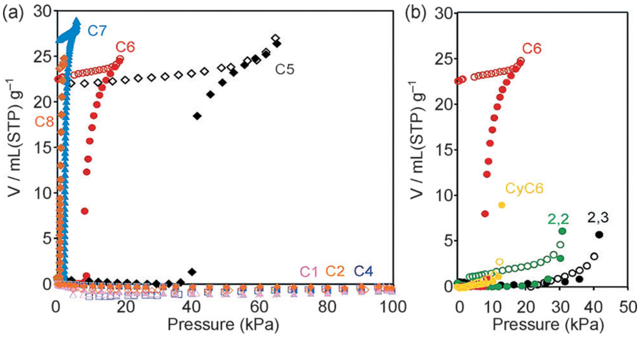

Figure 2. Sorption isotherms of activated crystals **1β** towards gases and vapors of a) linear alkanes containing methane (C1, pink triangle), ethane (C2, orange diamonds), *n*-butane (C4, purple squares), *n*-pentane (C5, black diamonds), *n*-hexane (C6, red circles), *n*-heptane (C7, blue triangles), and *n*-octane (C8, brown diamonds), and b) branched alkanes containing 2,2-dimethylbutane (2,2, green circles), 2,3-dimethylbutane (2,3, black circles), and cyclohexane (CyC6, yellow circles) at 25 °C. Solid symbols: adsorption; open symbols: desorption.

of acetone guest molecules triggered reversible solid-state switching between **1α** and **1β**.

The gas and vapor sorption ability of activated crystals of **1β** was investigated. The activated crystals **1β** adsorbed neither CO_2 nor N_2 (Figure S3). Pillar[5]arenes have pores of sufficient size to encapsulate CO_2,[15b] thus the structure of **1β** must not be suitable for the encapsulation of these gases. Pillar[5]arene can form host–guest complexes with linear alkanes in solution,[16] and thus we investigated the uptake of alkanes by **1β** (Figure 2a). **1β** took up minimal quantities of methane (C1), ethane (C2), and *n*-butane (C4). In contrast, pronounced gate-opening behaviors, followed by stepwise isotherms, were observed for *n*-pentane (C5), *n*-hexane (C6), *n*-heptane (C7), and *n*-octane (C8). The gate-opening pressure decreased as the chain length of the *n*-alkane increased. We calculated the efficiency of encapsulation from the amount of *n*-alkane taken up, ^{1}H NMR spectroscopic analysis, and thermogravimetric analysis (TGA, Table S1). Over 90 % of *n*-alkanes with more than five carbon atoms were encapsulated in the cavity of **1β**. In the desorption process, the included *n*-alkanes were not released at all, which indicated that the included *n*-alkanes were stable in the pillar[5]arene cavity. This storage ability was attributed to multiple CH/π interactions between the pillar[5]arenes and *n*-alkanes, which would also be the main driving force for the complexation in solution.[16] We could clearly monitor the encapsulation of *n*-alkanes by the gate-opening behavior, and the included *n*-alkanes could even be stored at 25 °C under reduced pressure; in contrast, the association constants between pillar[5]arenes and *n*-alkanes in solution are very low.[16] We also investigated the uptake of branched and cyclic alkanes by **1β** (Figure 2b). **1β** showed minimal uptake of branched alkanes, such as 2,3-dimethylbutane (2,3) and 2,2-dimethylbutane (2,2) or the cyclic alkane cyclohexane (CyC6). This result showed that the alkane uptake with activated crystals **1β** was alkane-shape-selective. This selectivity correlates with the host–guest properties of pillar[5]arenes in solution.[16] Therefore, the alkane-shape selectivity of pillar[5]arenes in solution was translated into the vapor/crystal state.

The host–guest complexes formed in solution by pillar[5]arenes with 1,4-dicyanobutane are more stable ($K > 10^4\,\text{M}^{-1}$) than those formed with *n*-hexane ($K = \text{ca. } 10\,\text{M}^{-1}$).[16,17] When we immersed activated crystals **1β** in 1,4-dicyanobutane and analyzed the sample by ^{1}H NMR spectroscopy, signals corresponding to 1,4-dicyanobutane were observed (Figure S4). The stoichiometry between **1** and 1,4-dicyanobutane, determined by ^{1}H NMR spectroscopy (Figure S4), was 1:1, which indicated that complexation even occurred in the solid state. The solid **1**⊃1,4-dicyanobutane complex showed minimal uptake of *n*-hexane, as compared to the activated crystals **1β** (Figure S5). This indicated that 1,4-dicyanobutane acts as a competitive guest to prevent the uptake of *n*-hexane, and that the uptake sites for *n*-hexane are the cavities in **1**.

We investigated the mechanism behind the uptake of *n*-hexane vapor by gate opening (Figure 1, path III) and the stable storage of *n*-hexane even under reduced pressures. The PXRD pattern of **1β** after *n*-hexane uptake (Figure 1 f) was completely different from that of the 1D channels in **1α** (Figure 1 d) and from that of activated crystals **1β** (Figure 1 e). These differences indicated that *n*-hexane uptake induces the formation of a new crystal structure (**1γ**). To investigate the crystal transformation, crystals of **1** were grown by slow evaporation of a solution of **1** in chloroform under *n*-hexane vapor. In the crystal structure, one *n*-hexane molecule was included in the cavity of **1**, which formed a pseudorotaxane (Figure 1 c and Figure 3 a). Neighboring **1**⊃*n*-hexane complexes were perpendicular to each other (Figure 1 c, herring-

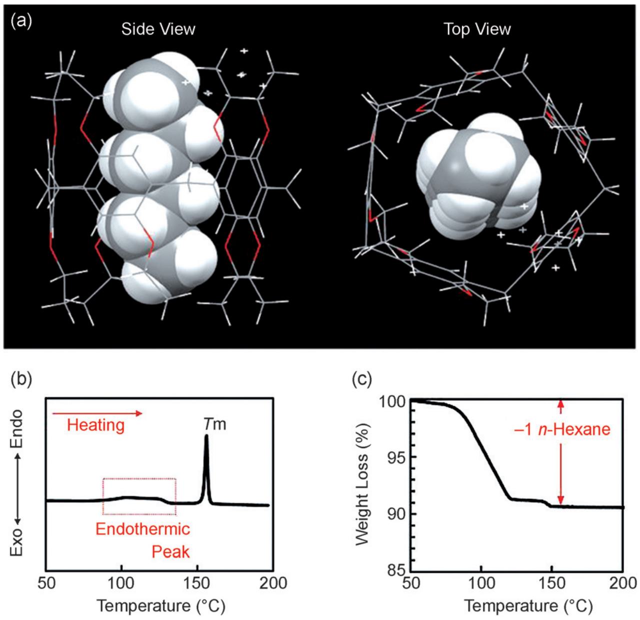

Figure 3. a) X-ray crystal structure, b) DSC heating curve, and c) TGA of **1γ** (**1**$\supset$*n*-hexane complex). In the X-ray structure, C: gray, O: red, H: white.

bone structure). The simulated PXRD pattern of the crystal was the same after the uptake of *n*-hexane (Figure 1 f), thus indicating that *n*-hexane uptake with gate opening triggered the crystal transformation from **1β** to the herringbone structure observed in **1γ**. An X-ray crystal-structure determination of the **1**$\supset$*n*-hexane complex showed that eight hydrogen atoms of the included *n*-hexane had CH/π plane distances of 2.76–3.03 Å (Figure S6), which are shorter than the longest interatomic distance in a CH/π interaction (3.05 Å),[18] thus implying the existence of CH/π interactions between **1** and *n*-hexane. These multiple CH/π interactions would result in the release of only small amounts of *n*-alkanes, even under reduced pressure at 25 °C. The release of adsorbed *n*-hexane was examined by differential scanning calorimetry (Figure 3 b, DSC) and TGA (Figure 3 c). The DSC heating trace of **1γ** (**1**$\supset$*n*-hexane complex) showed an endothermic peak from 85 to 130 °C. TGA also showed a weight loss of 10 % from 85 to 120 °C. These data indicated that release of *n*-hexane from **1γ** took place at 85–120 °C, while the boiling point of *n*-hexane is 60 °C under ordinary pressures. The data also supported the stable inclusion of *n*-hexane in the cavity of **1γ**. A similar tendency was observed for other **1**$\supset$*n*-alkane complexes (Figures S7–S9). In contrast, *n*-hexane was released from the cavity of **1** when **1γ** was dissolved in organic solvents, which was confirmed by ^{1}H NMR measurements (Figure S10). The release of *n*-hexane was also induced by immersing **1γ** in 1,4-dicyanobutane (Figure S11), because 1,4-dicyanobutane acts as a competitive guest.[19] When **1γ** was heated to remove *n*-hexane (Figure 1, path IV), the PXRD pattern of the sample returned to that of **1β** (Figure S13). Therefore, the solid-state switching between **1β** and **1γ** was completely reversible through the uptake and release of *n*-hexane guests. Reactivated crystals **1β** could take up *n*-hexane again through the gate-opening pressure (Figure S14), thus indicating that the gate-opening processes were reversible.

In conclusion, this work unveils an length- and shape-selective gate-opening behavior in the host–guest complexation of perethylated pillar[5]arene molecules with alkanes in the crystal state. The gate opening induces a crystal transformation. The results shed light on how certain guests can form host–guest complexes in the solid state. The molecular selectivity of pillar[5]arenes toward alkanes in the solution state could be translated into the crystal state because the assembled crystal structure of **1** would be flexible, and could be changed by guest inclusion. Guest-selective crystal transformations are rare in macrocyclic compounds, although there are a few examples of crystal transformations in porous organic crystals.[20b] Compared with porous organic crystals,[20] the amount of gas and organic vapors taken up using macrocyclic compounds is small.[5,9,15] However, pillar[5]arene crystals are superior adsorption materials in terms of alkane selectivity because the pore size of pillar[5]arenes is idea for *n*-alkanes.[16] The pillar[5]arene host–guest property facilitated the unexpected alkane-length- and –shape-selective gate-opening behavior in the crystal state. To the best of our knowledge, this is the first example of gate-opening behavior using organic crystals based on macrocyclic compounds, although there are reports about gate-opening behavior using molecular organic frameworks (MOFs) and porous coordination polymers (PCPs).[21] There are few examples of the gate opening of MOFs/PCPs following the adsorption of alkanes.[21c,d] Compared with the alkane-induced gate opening of PCPs/MOFs, it is clear that the gate-opening pressure depended on the length and shape of the alkanes, and this feature could be applied to separation of alkanes.

Experimental Section

1β: Evaporation of acetone from a solution of **1** in acetone afforded the one-dimensional channel **1α**. Heating powder **1α** at 50 °C under reduced pressure for 24 h afforded activated **1β**.

Keywords: alkanes · crystals · host–guest chemistry · macrocyclic compound · pillar[*n*]arenes

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 9849–9852
Angew. Chem. **2015**, *127*, 9987–9990

---

[1] A. E. Shilov, G. B. Shul′pin, *Chem. Rev.* **1997**, *97*, 2879–2932.
[2] Reviews: a) S. A. Nepogodiev, J. F. Stoddart, *Chem. Rev.* **1998**, *98*, 1959–1976; b) G. Wenz, B. H. Han, A. Müller, *Chem. Rev.* **2006**, *106*, 782–817; c) A. Harada, A. Hashidzume, H. Yamaguchi, Y. Takashima, *Chem. Rev.* **2009**, *109*, 5974–6023.
[3] I. Sanemasa, T. Osajima, T. Deguchi, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2814–2819.
[4] Reviews: a) C. D. Gutsche, *Acc. Chem. Res.* **1983**, *16*, 161–170; b) A. Ikeda, S. Shinkai, *Chem. Rev.* **1997**, *97*, 1713–1734; c) J. Rebek, Jr., *Acc. Chem. Res.* **1999**, *32*, 278–286.
[5] a) P. K. Thallapally, B. P. McGrail, J. L. Atwood, C. Gaeta, C. Tedesco, P. Neri, *Chem. Mater.* **2007**, *19*, 3355–3357; b) P. K. Thallapally, L. Dobrzańska, T. R. Gingrich, T. B. Wirsig, L. J. Barbour, J. L. Atwood, *Angew. Chem. Int. Ed.* **2006**, *45*, 6506–6509; *Angew. Chem.* **2006**, *118*, 6656–6659.

[6] a) A. Scarso, L. Trembleau, J. Rebek, Jr., *J. Am. Chem. Soc.* **2004**, *126*, 13512 – 13518; b) D. Ajami, J. Rebek, Jr., *Nat. Chem.* **2009**, *1*, 87 – 90.

[7] C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017 – 7036.

[8] Reviews: a) J. W. Lee, S. Samal, N. Selvapalam, H. J. Kim, K. Kim, *Acc. Chem. Res.* **2000**, *36*, 621 – 630; b) J. Lagona, P. Mukhopadhyay, S. Chakrabarti, L. Isaacs, *Angew. Chem. Int. Ed.* **2005**, *44*, 4844 – 4870; *Angew. Chem.* **2005**, *117*, 4922 – 4949.

[9] a) S. Lim, H. Kim, N. Selvapalam, K. J. Kim, S. J. Cho, G. Seo, K. Kim, *Angew. Chem. Int. Ed.* **2008**, *47*, 3352 – 3355; *Angew. Chem.* **2008**, *120*, 3400 – 3403; b) J. Tian, S. Ma, P. K. Thallapally, D. Fowler, B. P. McGrail, J. L. Atwood, *Chem. Commun.* **2011**, *47*, 7626 – 7628; c) H. Kim, Y. Kim, M. Yoon, S. Lim, S. M. Park, G. Seo, K. Kim, *J. Am. Chem. Soc.* **2010**, *132*, 12200 – 12202.

[10] W. R. Dichtel, O. Š. Miljanić, W. Zhang, J. M. Spruell, K. Patel, I. Aprahamian, J. R. Heath, J. F. Stoddart, *Acc. Chem. Res.* **2008**, *41*, 1750 – 1761.

[11] a) P. A. Gale, J. L. Sessler, V. Král, V. Lynch, *J. Am. Chem. Soc.* **1996**, *118*, 5140 – 5141; b) S. K. Kim, J. L. Sessler, *Acc. Chem. Res.* **2014**, *47*, 2525 – 2536.

[12] T. Ogoshi, S. Kanai, S. Fujunami, T. Yamagishi, Y. Nakamoto, *J. Am. Chem. Soc.* **2008**, *130*, 5022 – 5023.

[13] Reviews: a) T. Ogoshi, *J. Inclusion Phenom. Macrocyclic Chem.* **2012**, *72*, 247 – 262; b) T. Ogoshi, T. Yamagishi, *Eur. J. Org. Chem.* **2013**, 2961 – 2975; c) T. Ogoshi, T. Yamagishi, *Chem. Commun.* **2014**, *50*, 4776 – 4787; d) P. J. Cragg, K. Sharma, *Chem. Soc. Rev.* **2012**, *41*, 597 – 607; e) M. Xue, Y. Yang, X. Chi, Z. Zhang, F. Huang, *Acc. Chem. Res.* **2012**, *45*, 1294 – 1308; f) N. Strutt, H. Zhang, S. T. Schneebeli, J. F. Stoddart, *Acc. Chem. Res.* **2014**, *47*, 2631 – 2642.

[14] We compared the PXRD pattern of activated crystals **1β** and simulated PXRD patterns of **1α** and **1γ** without guest molecules (Figure 1S). However, the pattern of activated crystals **1β** was different from those of **1α** and **1γ** without guest molecules. Thus, **1β** formed another crystal structure.

[15] a) T. Ogoshi, R. Sueto, K. Yoshikoshi, T. Yamagishi, *Chem. Commun.* **2014**, *50*, 15209 – 15211; b) L. L. Tan, H. Li, Y. Tao, S. X. Zhang, B. Wang, Y. W. Yang, *Adv. Mater.* **2014**, *26*, 7027 – 7031.

[16] a) T. Ogoshi, K. Demachi, K. Kitajima, T. Yamagishi, *Chem. Commun.* **2011**, *47*, 10290 – 10292; b) T. Ogoshi, N. Ueshima, T. Yamagishi, *Org. Lett.* **2013**, *15*, 3742 – 3745; c) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma, F. Huang, *Angew. Chem. Int. Ed.* **2011**, *50*, 1397 – 1401; *Angew. Chem.* **2011**, *123*, 1433 – 1437.

[17] X. Shu, S. Chen, J. Li, Z. Chen, L. Weng, X. Jia, C. Li, *Chem. Commun.* **2012**, *48*, 2967 – 2969.

[18] a) H. Suezawa, T. Yoshida, M. Hirota, H. Takahashi, Y. Umezawa, K. Honda, S. Tsuboyama, M. Nishio, *J. Chem. Soc. Perkin Trans. 2* **2001**, 2053 – 2058; b) M. Nishio, Y. Umezawa, K. Honda, S. Tsuboyama, H. Suezawa, *CrystEngComm* **2009**, *11*, 1757 – 1788; c) O. Takahashi, Y. Kohno, M. Nishio, *Chem. Rev.* **2010**, *110*, 6049 – 6076.

[19] Crystal transformation was also induced by immersing **1γ** in 1,4-dicyanobutane (Figure S12).

[20] a) J. R. Holst, A. Trewin, A. I. Cooper, *Nat. Chem.* **2010**, *2*, 915 – 920; b) J. T. A. Jones, D. Holden, T. Mitra, T. Hasell, D. J. Adams, K. E. Jelfs, A. Trewin, D. J. Willock, G. M. Day, J. Bacsa, A. Steiner, A. I. Cooper, *Angew. Chem. Int. Ed.* **2011**, *50*, 749 – 753; *Angew. Chem.* **2011**, *123*, 775 – 779; c) J. T. A. Jones, T. Hasell, X. Wu, J. Bacsa, K. E. Jelfs, M. Schmidtmann, S. Y. Chong, D. J. Adams, A. Trewin, F. Schiffman, F. Cora, B. Slater, A. Steiner, G. M. Day, A. I. Cooper, *Nature* **2011**, *474*, 367 – 371; d) G. Zhang, O. Presly, F. White, I. M. Oppel, M. Mastalerz, *Angew. Chem. Int. Ed.* **2014**, *53*, 5126 – 5130; *Angew. Chem.* **2014**, *126*, 5226 – 5230; e) M. Mastalerz, *Chem. Eur. J.* **2012**, *18*, 10082 – 10091; f) P. Sozzani, S. Bacco, A. Comotti, F. Ferretti, R. Simonutti, *Angew. Chem. Int. Ed.* **2005**, *44*, 1816 – 1820; *Angew. Chem.* **2005**, *117*, 1850 – 1854; g) W. Yang, A. Greenaway, X. Lin, R. Matsuda, A. J. Blake, C. Wilson, W. Lewis, P. Hubberstey, S. Kitagawa, N. R. Champness, M. Schröder, *J. Am. Chem. Soc.* **2010**, *132*, 14457 – 14469.

[21] a) A. Kondo, H. Noguchi, S. Ohnishi, H. Kajiro, A. Tohdoh, Y. Hattori, W. C. Xu, H. Tanaka, H. Kanoh, K. Kaneko, *Nano Lett.* **2006**, *6*, 2581 – 2584; b) Y. Sakata, S. Furukawa, M. Kondo, K. Hirai, N. Horike, Y. Takashima, H. Uehara, N. Louvain, M. Meilikhov, T. Tsuruoka, S. Isoda, W. Kosaka, O. Sakata, S. Kitagawa, *Science* **2013**, *339*, 193 – 196; c) N. Nijem, H. Wu, P. Canepa, A. Marti, K. J. Balkus, T. Thonhauser, J. Li, Y. J. Chabal, *J. Am. Chem. Soc.* **2012**, *134*, 15201 – 15204; d) S. Van der Perre, T. V. Assche, B. Bozbiyik, J. Lannoeye, D. E. De Vos, G. V. Baron, J. F. M. Denayer, *Langmuir* **2014**, *30*, 8416 – 8424.

Received: April 16, 2015