

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

- **Title:** Guest-induced structural transformations in a porous halogen bonded framework.
- Authors: Leonard Barbour, Varvara Nikolayenko, Dominic Castell, and Dewald van Heerden

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201806399 Angew. Chem. 10.1002/ange.201806399

Link to VoR: http://dx.doi.org/10.1002/anie.201806399 http://dx.doi.org/10.1002/ange.201806399

WILEY-VCH

COMMUNICATION

WILEY-VCH

Guest-induced structural transformations in a porous halogen bonded framework.

Varvara I. Nikolayenko, Dominic C. Castell, Dewald P. van Heerden and Leonard J. Barbour*

Abstract: Structural evidence obtained from in situ X-ray diffraction shows that halogen bonding is responsible for the formation of a dynamic porous molecular solid. This material is surprisingly robust and undergoes reversible switching of its pore volume by activation or by exposure to a series of gases of different sizes and shapes. Volumetric gas sorption pressure-gradient differential scanning calorimetry (P-DSC) data provide further mechanistic insight into the breathing behavior.

Porous materials hold remarkable potential for gas storage^[1] and separation,^[2] drug delivery,^[3] molecular recognition^[4] and catalysis,^[5] among others. In recent years the field has been dominated by coordination polymers,^[6] metal organic frameworks (MOFs),^[7] hydrogen bonded organic frameworks (HOFs)^[8] and covalent organic frameworks (COFs).^[9] Despite the abundance of reports on these types of porous materials, the search for new and alternative methods to generate porosity in the solid-state is still a highly topical area of research.^[10]

Porous molecular solids constitute a distinct class of materials that possess intrinsic^[11] or extrinsic^[12] voids, or even both types simultaneously,^[13] that are accessible to guest molecules by means of diffusion. Intrinsic porosity occurs when host molecules contain guest-accessible cavities that preclude close-packing. Extrinsic pores consist of interstitial spaces between host molecules, and are generally due to awkward packing of the host. While many porous molecular solids contain open channels, it has been demonstrated that permanent channels are not a prerequisite for porosity.^[11a] In such systems, concerted dynamic processes occur within the host structure that facilitate diffusion of guests *via* transient channels.

The halogen bond (XB) is defined as a directional noncovalent attractive interaction between a Lewis base (XB acceptor) and a polarized halogen atom (XB donor).^[14] To date, the XB has been used to prepare a wide range of complex supramolecular assemblies and functional materials.^[15] While interesting from a structural perspective, they also have appealing chemical properties. A few examples include rotaxanes,^[16] molecular capsules,^[17] organic cages^[18] and light-responsive materials.^[19] Several separate reports^[20] have described XB molecular solids that exhibit dynamic porosity. However, in all of these cases, guest inclusion occurs via solvent exchange – i.e., exposure of a crystalline solvate to the vapor of a different solvent. None of these reports demonstrate that the host framework can survive

[a] Dr V. I. Nikolayenko, Dr D.C. Castell, Mr D. P van Heerden and Professor L. J. Barbour Department of Chemistry and Polymer Science University of Stellenbosch Stellenbosch 7600, South Africa E-mail: Ijb@sun.ac.za

Electronic Supplementary Information (ESI) available: Experimental details, SCXRD, PXRD, TGA, volumetric gas sorption analysis, P-DSC, VT-PXRD and molecular mechanics calculations. CCDC 1846617-1846624 activation in the form of a permanently porous material. Herein, we describe a flexible, permanently porous organic XB framework (Scheme 1) that survives activation without framework collapse. Moreover, the material responds to gas loading (carbon dioxide, methane, ethane, propane and butane) under pressure by adapting its guest-accessible space according to the geometry of the guest molecule.

Slow evaporation of a solution of 1,2-bis(2'-methyl-5'-(pyrid-4''-yl)thien-3'-yl)perflourocyclopentene and 1,4-di-iodotetrafluorobenzene (halogen bond acceptor **XBA** and donor **XBD**, respectively, see Scheme 1) in acetone afforded yellow crystals, one of which was subjected to single-crystal X-ray diffraction (SCD) analysis at 100 K. The asymmetric unit consists of one molecule each of **XBA**, **XBD** and acetone, which pack in the space group *Pna*2₁ to form a solvate **1**_a. Compounds **XBA** and **XBD** are arranged end-to-end as sinusoidal (**XBA**...**XBD**...)_n halogen bonded chains, involving I...N interactions (Figure S2), that propagate along [302] and [30-2].



Scheme 1 The molecular structures of XBA and XBD.

It is useful for subsequent structural discussions to consider chains aligned in a given direction as packing side-by-side to form planes parallel to (010); adjacent chains are offset relative to each other by a phase angle of 120° such that each plane consists of chains stacked in an (ABC)_n manner (Figure 1).



Figure 1 Perspective view of sinusoidal (XBA···XBD···)_n halogen bonded strands propagating along [30-2]. Neighboring strands are offset relative to each other and stack parallel to (010) in an (ABC)_n manner. Molecules are shown in spacfilling representation with A, B and C strands shown in red, green and blue, respectively.

We note that the strands comprising each layer do not form a weave (Figure S3). Successive planes alternate with respect to the direction of their strands such that a crisscross pattern is formed (Figure S4). A map^[21] of the guest-accessible surface indicates that the acetone guest molecules are located between the layers in undulating channels that extend along [010] (Figure 2, top). Two of these channels traverse a unit cell, and each has a guest-accessible volume of 247 Å³ per unit cell, as determined

COMMUNICATION

using a spherical probe of radius 1.5 Å (Figure S5). This equates to a guest-accessible volume of 124 Å³ per guest binding site (Table 1).



Figure 2 Surface maps of the guest-accessible space (probe radius = 1.5 Å) in 1_a and 1_{apo} as viewed along [010].

Table 1. Guest-accessible volumes for the as-synthesized, activated and gas-loaded structures.

Structure	Guest	Pressure / bar	Volume per guest binding site ^a / Å ³	% Guest accessible volume per HFU
1a	acetone	-	124	13.7
1 _{apo}	-	-	48	5.3
⁰ 1 _{apo}	-	2.76 x 10 ⁻²	55	6.2
²⁰ 1c	CO ₂	20	55	7.1
²⁰ 1m	CH₄	20	58	6.6
²⁰ 1e	C_2H_6	20	143	15.4
⁷ 1p	C ₃ H ₈	7	151	16.1
² 1 _b	C ₄ H ₁₀	2	156	16.4

^a Guest-accessible volume determined using Mercury^[21-22] (probe radius 1.5 Å, grid spacing 0.2 Å). Owing to the multiplicity of binding sites in *Pna*2₁, the volume per unit cell was divided by 4 in each case.

Thermogravimetric analysis (TGA) of 1_a (Figure S10) indicates that the acetone guest can be removed between 100 and 113 °C. However, attempts to activate single crystals by heating to this temperature resulted in loss of single crystallinity. Therefore, a milder activation method was employed, involving exposure of crystals to supercritical carbon dioxide (scCO₂) for 30 minutes (see ESI). Apart from the appearance of minor cracks, the crystals remained intact. SCD analysis at 100 K revealed that the acetone had been removed to yield the apohost form 1_{apo} , also in Pna21. The most notable structural change upon activation involves the shape and volume of the guest-accessible space the channels shrink to become discrete voids (Figure 2, bottom), with an overall reduction in guest-accessible volume from 124 to 48 Å³ per guest binding site. Bulk phase activation of the material was confirmed by TGA (Figure S10). The guest-accessible space is partially delimited by fluorine atoms of XBA, thus presenting a potentially interesting environment for further host-guest chemistry. Indeed, some materials with fluorine-lined guestaccessible cavities have been shown to possess several favorable sorption properties^[23] such as higher oxidative and thermal stability, $^{[24-25]}$ improved gas affinity, $^{[24]}$ and potential catalytic activity. $^{[23]}$

To the best of our knowledge, **1** represents the first example of a porous halogen bonded framework that can be activated. Comparison of **1**_a and **1**_{apo} suggests that **1**_{apo} might adapt dynamically in the presence of a range of suitable guests to regain the expanded host structure. Moreover, the material appears to tolerate significant structural contraction as a single-crystal to single-crystal (SC-SC) transformation. We are therefore presented with a rare opportunity to carry out a series of guest-loading structural studies (using an environmental gas cell during SCD analysis)^[11c] to complement sorption experiments.

To probe the porosity of 1_{apo} , a series of gas sorption experiments was carried out at 298 K using carbon dioxide, methane, ethane, propane and butane (Figures 3 and 4). The bulk sample was exposed to a maximum pressure of 20 bar (a limitation of the instrument) in the cases of carbon dioxide, methane and ethane, while maximum pressures of 7 and 2 bar were reached for propane and butane, respectively (see ESI for more detail). 1_{apo} exhibits type I sorption behavior for CO₂, absorbing one guest molecule per host formula unit (HFU) at 20 bar. Type I sorption is also observed for methane, but with only 0.3 guest molecules included per HFU at 20 bar. Negligible hysteresis upon desorption indicates minimal host-guest interactions for both CO₂ and CH₄.







Figure 4 Volumetric sorption isotherms of ⁰1_{apo} exposed to ethane (triangles), propane (squares) and butane (circles). In all cases the isotherms exhibit hysteresis, with propane and butane retained at vacuum.

WILEY-VCH

COMMUNICATION

The ethane sorption isotherm shows an inflection at approximately 1.5 bar, and reaches a total guest occupancy of half a molecule per HFU at 20 bar. This type of stepped isotherm implies a gate-opening mechanism. In the case of propane, half a guest molecule per HFU is absorbed between 0 and 1 bar, with the occupancy reaching 0.9 at the saturation pressure of 7 bar. The desorption isotherm shows hysteresis, with the material retaining 0.35 molecules per formula unit at vacuum. Butane is absorbed in a similar manner, with the inclusion of half a guest molecule at the saturation pressure limit of 2 bar. Desorption again occurs with hysteresis, with the retention of almost 0.5 molecules of butane at vacuum.

To gain structural insight into the modes of guest inclusion for the different gases at 298 K, SCD analyses were carried out for gas-loaded crystals at the same temperature. A crystal of 1_{apo} was mounted in an environmental gas cell, which was then evacuated and sealed before SCD data were recorded for the activated material under vacuum ($^{0}1_{apo}$).

The volume of each guest-binding site of ${}^{0}\mathbf{1}_{apo}$ (Figure 5a) is approximately 55 Å³, which is consistent with thermal expansion of $\mathbf{1}_{apo}$. The lengths of the two unique N···I halogen bonds are $d_{(N···I)} = 2.88(1)$ and 2.85(1) Å, which are approximately 20% shorter than the sum of the van der Waals radii^[26] of the interacting atoms. Typical of directional XB interactions,^[15] the N···I–C bond angles of 177.0(5)° and 177.5(5)°, respectively, are almost linear. Examination of intermolecular interactions using CrystalExplorer^[27] shows that there are no notable intermolecular interactions, apart from the abovementioned N···I halogen bonds (Video S1). However, there are relatively weak C–H···F hydrogen bonds with $d_{(C···F)} = 3.35(2)$ Å between layers. The wavelength of the sinusoidal chains is 53.9 Å (Figure S6).





Figure 5 Packing diagrams viewed down [001] with a) showing the C-H...F hydrogen bonding and discrete cavities in ${}^{0}1_{apo}$ and b) showing the channels in ${}^{20}1_{e}$.

Subsequent SCD experiments were undertaken as follows, starting with a new crystal of ⁰1_{apo} in each case. After backfilling the environmental cell with gas to the maximum pressure recorded for the corresponding isotherm, the system was left to equilibrate for 12 h before being sealed. SCD data were then recorded for the gas-loaded crystal x_{1g} , (x = pressure in bar, g = c, m, e, p and b for carbon dioxide, methane, ethane, propane and butane, respectively). In each case the guest molecule was either modelled crystallographically (methane and ethane), or by means of molecular mechanics (carbon dioxide, propane and butane) using Materials Studio^[28] (Figure 6 and ESI). In all cases the guest occupancy was confirmed using residual electron density analysis, as implemented by the SQUEEZE^[29a] routine of PLATON.^[29b] We note that, even when the guest cannot be modelled crystallographically, in situ gas loading diffraction data provide valuable information with regard to the guest-accessible space, as well as a reliable host model for theoretical simulations.

SQUEEZE analysis of $^{20}1_c$ indicated the presence of one molecule of CO₂ per HFU, which is consistent with the sorption data. The low guest occupancy of 0.3 molecules of methane per HFU for $^{20}1_m$ also corresponds with the gas sorption data. The structural models show that the modes of guest inclusion are similar for carbon dioxide and methane, and that little distortion of the guest-accessible space of $^{01}_{apo}$ is required to accommodate these gases. Relative to $^{01}a_{po}$, guest uptake results in only modest increases in the guest-accessible volumes by 13.6% and 4.5% in $^{20}1_c$ and $^{20}1_m$, respectively. This is likely due to excellent



Figure 6 A perspective view along [010] of the gas-loaded structures with the guest-accessible space shown as semi-transparent surfaces.^[22] Theoretically determined guest positions are shown for ²⁰¹c, ⁷¹p and ²¹b.

WILEY-VCH

COMMUNICATION

size-shape complementarity between these guest molecules and the guest-accessible pockets, as inferred from diffraction analysis and molecular mechanics calculations. The packing coefficients of CO₂ and CH₄ (i.e. ratio of molecular volume to available space) are 55% and 49%, respectively. Indeed, CO₂ is a particularly suitable van der Waals guest since its packing coefficient is strikingly consistent with that proposed by Rebek for optimal binding of guests in host capsules (albeit in solution).^[30] This implies that a larger or more awkwardly shaped guest might either not be included, or would require the host to undergo a structural change. In the cases of CO₂ and CH₄, guest diffusion occurs despite the absence of permanent pores, but the lack of a net structural transformation accounts for the smooth type I isotherms for these two gases.

Exposure of ⁰1_{apo} to 20 bar of ethane induces a SC-SC transformation^[31] to ²⁰1_e (Figures 5b). The discrete voids expand upon guest uptake to once again become open 1D channels propagating along [001]. Indeed, the host of $^{20}1_e$ reverts to a structure that is isoskeletal^[31] to that of **1**_a, with a pore volume of 143 Å³ per guest binding site (Table 1). Absorption of ethane causes adjacent layers to move apart by ca 0.83 Å and concomitantly slide laterally relative to one another by ca 2.3 Å (Video S2). An analogous translation of layers has previously been reported for a seemingly nonporous dynamic molecular solid.^[11a] Interestingly, a structural overlay (Figure S7) shows that there is little change within each (ABC)_n layer relative to that of ⁰1_{apo}; the wavelength of the sinusoidal chain is 54.3 Å, which represents an increase of only 0.7% (Figure S6). The lengths of the two unique N···I halogen bonds remain approximately the same as those of ${}^{0}\mathbf{1}_{apo},$ with $d_{(N\cdots I)}$ = 2.89(2) and 2.81(1) Å. However, lateral sliding of adjacent layers involves breaking of the weak C-H···F hydrogen bonds, as confirmed by CrystalExplorer (Video S3). Similar structural changes due to gate-opening are observed for $^71_{P}$ and $^21_{b},$ which implies that guests that are larger or less awkwardly shaped than CO2 and CH4 induce breathing in the apohost phase. The structural changes observed in the SCD correlate well with the stepped isotherms for 1e-1b. The retention of small amounts of propane and butane at vacuum indicates potential host-guest interactions

Pressure-gradient differential scanning calorimetry (P-DSC, see ESI) experiments were carried out with a view to determining the gas-specific onset pressures of the structural transformations. There are no peaks in the P-DSC thermograms for ⁰1_{apo} exposed to nitrogen pressures up to 85 bar (Figure S21), or to carbon dioxide and methane pressures up to 50 bar (Figures S22 and S23). This is consistent with the abovementioned structural transformation being guest-specific and not due only to pressure. The P-DSC thermogram for ethane in the range 0.5 to 4 bar shows an exothermic peak between 1.0 and 2.5 bar (Figure S24), which comports with the phase change of the apohost form ⁰1_{apo} to that of the enlarged structure 1e upon ethane loading. The desorption leg shows no reverse conversion, which is consistent with the gas sorption isotherm (Figure S1c). In the cases of both propane and butane the P-DSC thermograms in the range 0.1 to 0.7 bar show broad peaks with relatively low onset pressures (Figures S25 and S26). No obvious peaks occur upon lowering the pressure, and we note that the desorption isotherms for both of these gases indicate that the guests, once absorbed, are partially retained under vacuum conditions.

In summary, we have presented the first example of a porous halogen bonded framework that can be activated. Using a combination of gas sorption, in situ single-crystal X-ray diffraction and P-DSC experiments we have elucidated the dynamic behavior of this porous molecular material upon exposure to guest molecules of different sizes. Furthermore, we have provided an explanation for this dynamic behavior based on structural data. We believe that the halogen bond provides sufficient directionality such that the breathing behavior can occur by means of lateral sliding of XB layers relative to one another. To date, this type of framework flexibility has not been reported for halogen-bonded networks, and it is therefore of considerable value to use in situ SCD data to propose a mechanism for the breathing effect. Finally, diarylethenes are well known to undergo efficient photo-induced structural switching in the solid state,^[32] and our ongoing efforts are aimed at furthering this work by developing a permanently porous XB framework with light-modulated porosity.

Acknowledgements

We acknowledge the National Research Foundation of South Africa for financial support.

Keywords: halogen bonding • dynamic• single-crystal to single-crystal transformation • sorption • P-DSC

- [1] D. Yuan, W. Lu, D. Zhao, H-C, Zhou, Adv. Mater. 2011, 23, 3723-3725.
- [2] a) B. Li, Y. Zhang, R. Krishna, K. Yao, Y. Han, Z. Wu, D. Ma, Z. Shi, T. Pham, B. Space, J. Liu, P. K. Thallapally, J. Liu, M. Chrzanowski, S, Ma, *J. Am. Chem. Soc.* **2014**, *136*, 8654-8660; b) T. Hassel, M. Miklitz, A. Stephenson, M. A. Little, S. Y. Chong, R. Clowes, L. Chen, D. Holden, G. A. Tribello, K. E. Jelfs, A. I. Cooper, *J. Am. Chem. Soc.* **2016**, *138*, 1653-1659.
- [3] Q. Fang, J. Wang, S. Gu, R. B. Kaspar, Z. Zhuang, J. Zheng, H. Guo, S. Qiu, Y. Yan, J. Am. Chem. Soc. 2015, 137, 8352-8355.
- [4] R-X. Yang, T-T. Wang, W-Q. Deng, *Sci. Rep.* 2015, *5*, 10155-10164.
 [5] F. Wang, C. Li, L-D. Sun, C-H. Xu, J. Wang, J. C. Yu, C-H. Yan, *Angew. Chem. Int. Ed.* 2012, *51*, 4872-4876.
- [6] a) S-I. Noro, S. Kitagawa, M. Kondo, K. Seki, Angew. Chem. Int. Ed. 2000, 39, 2081-2084; b) S. Kitagawa, R. Kitaura, S-I. Noro, Angew. Chem. Int. Ed, 2004, 43, 2334-2375
- a) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* 2012, *112*, 1105-1125; b) J-R. Li, J. Sculley, H-C. Zhou, *Chem. Rev.* 2012, *112*, 869-932; c) K. Suminda, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T-H. Bae, J. R. Long, *Chem. Rev.* 2012, *112*, 724-781.
- [8] a) Y. He, S. Xiang, B. Chen, *J. Am. Chem. Soc.* 2011, *133*, 14570-14573;
 b) X-Z. Luo, X-J. Jia, J-H. Deng, J-L, Zhong, H-J. Liu, K-J. Wang, D-C. Zhong, *J. Am. Chem. Soc.* 2013, *135*, 11684-11687.
- a) S. Wan, J. Guo, J. Kim, H. Ihee, D. Jiang, *Angew. Chem. Int. Ed.* 2009, 48, 5439-5442; b) S-Y. Ding, J. Gao, Q. Wang, Y. Zhang, W-G. Song, C-Y. Su, W. Wang, *J. Am. Chem. Soc.* 2011, 133, 19816-19822.
- [10] S. Das, P. Heasman, T. Ben, S. Qiu, Chem. Rev. 2017, 117, 1515-1563.
- [11] a) J. L. Atwood, L. J. Barbour, A. Jerga, B. L. Schottel, *Science* 2002, 298, 1000-1002; b) P. K. Thallapally, B. P. McGrail, J. L. Atwood, *Chem. Commun.* 2007, 1521-1523; c) T. Jacobs, G. O. Lloyd, J.-A. Gertenbach, K. K. Müller-Nedebock, C. Esterhuysen, L. J. Barbour, *Angew. Chem. Int. Ed.* 2012, *51*, 4913-4916; d) V. I. Nikolayenko, A. Heyns, L J. Barbour,

COMMUNICATION

Chem. Commun. **2017**, *53*, 11306-11309; e) V. I. Nikolayenko, L. M. van Wyk, O. Q. Munro, L. J. Barbour, *Chem. Commun.* **2018**, *54*, 6975-6978; f) 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; g) C. M. Kane, A. Banisafar, T. P. Dougherty, L. J. Barbour, K. T. Holman, *J. Am. Chem. Soc.* **2016**, *138*, 4377-4392; h) A. I. Joseph, S. H. Lapidus, C. M. Kane, K. T. Holman, *Angew. Chem. Int. Ed.* **2015**, *54*, 1471-1475.

- [12] a) M. Baroncini, S. d'Agostino, G. Bergamini, P. Ceroni, A. Comotti, P. Sozzani, I. Bassanetti, F. Grepioni, T. M. Hernandez, S. Silvi, M. Venturi, A. Credi, *Nature. Chem.* 2015, *7*, 634-640; b) N. Malek, T. Maris, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.* 2005, *127*, 5910-5916; c) C. Tedesco, L. Erra, M. Brunelli, V. Cipolletti, C. Gaeta, A. N. Fitch, J. L. Atwood, P. Neri, *Chem. Eur. J.* 2010, *16*, 2371-2374; d) J. Lî, R. Cao, *Angew. Chem. Int. Ed.* 2016, *55*, 9474-9480; e) P. Sozzani, S. Bracco, A. Comotti, L. Ferretti, R. Simonutti, *Angew. Chem. Int. Ed.* 2005, *44*, 1816-1820; f) M. Mastalerz, I. M. Oppel, *Angew. Chem. Int. Ed.* 2012, *51*, 5252-5255; g) A. Comotti, S. Bracco, A. Yamamoto, M. Beretta, T. Hirukawa, N. Tohnai, M. Miyata, P. Sozzani, *J. Am. Chem. Soc.* 2014, *136*, 618-621.
- [13] a) M. Mastalerz, *Chem. Eur. J.* 2012, *18*, 10082-10091; b) H. Kim, Y. Kim, M. Yoon, S. Lim, S. M. Park, G. Seo, K. Kim, *J. Am. Chem. Soc.* 2010, *132*, 12200-12202; c) J. Tian, S. Ma, P. K. Thallapally, D. Fowler, B. P. McGrail, J. L. Atwood, *Chem. Commun.* 2011, *47*, 7626-7628; d) R. G. Harrison, O. D. Fox, M. O. Meng, N. K. Dalley, L. J. Barbour, *Inorg. Chem.* 2002, *47*, 838-843; e) M. J. Bojdys, M. E. Briggs, J. T. A. Jones, D. J. Adams, S. Y. Chong, M. Schmidtmann, A. I. Cooper, *J. Am. Chem. Soc.* 2011, *133*, 16566-16571.
- [14] G. R. Desiraju, P. S. Ho, L. Kloo, A. C. Legon, R. Marquardt, P. Metrangolo, P. Politzer, G. Resnati, K. Rissanen, *Pure. Appl. Chem.* 2013, *85*, 1711-1713
- [15] a) L. C. Gilday, S. W. Robinson, T. A. Barendt, M. J. Langton, B. R. Mullaney, P. D. Beer, *Chem. Rev.* 2015, *115*, 7118-7195; b) G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.* 2016, *116*, 2478-1601.
- [16] a) N. L. Kilah, M. D. Wise, C. J. Serpell, A. L. Thompson, N. G. White, K. E. Christensen, P. D. Beer, *J. Am. Chem. Soc.* 2010, *132*, 11893-11895;
 b) M. J. Langton, S. W. Robinson, I. Marques, V. Fèlix, P. D. Beer, *Nat. Chem.* 2014, *6*, 1039-1043; c) T. A. Barendt, A. Docker, I. Marques, V. Fèlix, P. D. Beer, *Angew. Chem. Int. Ed.* 2016, *55*, 11069-11076.
- [17] a) C. B. Aäkeroy, A. Rajbanshi, P. Metrangolo, G. Resnati, M. F. Parisi, J. Desper, T. Pilati, *CrystEngComm.* 2012, *14*, 6366-6368; b) N. K. Beyeh, F. Pan, K. Rissanen, *Angew. Chem. Int. Ed.* 2015, *54*, 7303-7307; c) L. Turunen, U. Warzok, R. Puttereddy, N. K. Beyeh, C. A. Schalley, K. Rissanen, *Angew. Chem. Int. Ed.* 2016, *55*, 14033-14036; d) O. Dumele, B. Schreib, U. Warzok, N. Trapp, C. A. Schalley, F. Diederich, *Angew. Chem. Int. Ed.* 2017, *56*, 1152-1157.
- [18] a) M. F. Roll, J. W. Kampf, R. M. Laine, *Cryst. Growth Des.* 2011, *11*, 4360-4367; b) H. Takezawa, T. Murase, G. Resnati, P. Metrangolo, M. Fujita, *Angew. Chem. Int. Ed.* 2015, *54*, 8411-8414; c) L. Turunen, A. Peuronen, S. Forsblom, E. Kalenius, M. Lahtinen, K. Rissanen, *Chem. Eur. J.* 2017, *23*, 1-6.
- [19] a) A. Priimagi, M. Saccone, G. Cavallo, A. Shishido, T. Pilati, P. Metrangolo, G. Resnati, *Adv. Mater.* 2012, *24*, OP345-OP352; b) A. Priimagi, G. Cavallo, A. Forni, M. Gorynsztejn-Leben, M. Kaivola, P. Metrangolo, R. Milani, A. Shishido, T. Pilati, G. Resnati, G. Terraneo, *Adv. Funct. Mater.* 2012, *22*, 2572-2579.
- [20] a) J. Martì-Rujas, L. Colombo, J. Lü, A. Dey, G. Terraneo, P. Metrangolo, T. Pilati, G. Resnati, *Chem. Commun.* 2012, *48*, 8207-8209; b) K. Raatikainen, K. Rissanen, *Chem. Sci*, 2012, *3*, 1235-1239. (c) P. Metrangolo, Y. Carcenac, M. Lahtinen, T. Pilati, K. Rissanen, A. Vij, G. Resnati, *Science*, 2009, *323*, 1461-1464. (d) A. Abate, M. Brischetto, G. Cavallo, M. Lahtinen, P Metrangolo, T. Pilati, S. Radice, G. Resnati, and K Rissanen, *Chem. Commun.*, 2010, *46*, 2724-2726. (e) J. Martí-Rujas, L. Meazza, G. K. Lim, G. Terraneo, T. Pilati, K. D. M. Harris, P.

Metrangolo and Giuseppe Resnati, Angew. Chem. Int. Ed. 2013, 52, 13444-13448.

- [21] a) M.L. Connoly, *Science* **1983**, *221*, 709-713; b) M. L. Connoly, *J. Mol. Graphics* **1993**, *11*, 139-141; c) C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Cryst.*, **2008**, *41*, 466-470.
- [22] L. J. Barbour, J. Supramol. Chem. 2001, 1, 189-191.
- [23] C. Yang, X. Wang, M. A. Omary, J. Am. Chem. Soc. 2007, 129, 15454-15455.
- [24] J. A. Gladysz, D. P. Curran, I. T. Horva th, Eds. Handbook of Fluorous Chemistry; Wiley/VCH: Weinheim, Germany, 2004.
- [25] a) P. T. Nyffeler, S. G. Durn, M. D. Burkart, S. P. Vincent, C. –H. Wong, Angew. Chem., Int. Ed. 2005, 44, 192-212; b) I. T. Horvath, J. Rabai, Science 1994, 266, 72-75.
- [26] A. Bondi, J. Phys. Chem, 1964, 68, 441–451.
- [27] CrystalExplorer (Version 3.1), S.K. Wolff, D.J. Grimwood, J.J. McKinnon, M.J. Turner, D. Jayatilaka, M.A. Spackman, University of Western Australia, 2012.
- [28] Dassault Systèmes BIOVIA, Materials Studio, Release 18, San Diego: Dassault Systèmes, 2017.
- [29] a) A. L. Spek, Acta Crystallogr., Sect. D, 2009, 65, 148-155.; b) A. L. Spek, Acta Crystallogr. Sect. C 2015, 71, 9-18.
- [30] S. Mecozzi, J. Rebek, Jr, Chem. Eur. J. 1998, 4, 1016-1022.
- [31] It should be noted that the space group *Pna*2₁ is preserved for all of the crystal structures investigated. However, the porous structure containing discrete pockets is easily distinguishable from that with channels by monitoring the crystallographic *b* axis. During the transformation from the apohost form ${}^{0}\mathbf{1}_{apo}$ to ${}^{x}\mathbf{1}_{y}$ (**x** = **20**,**7**,**2**, **y** = **e**, **p**, **b**, respectively) the *b* axis elongates by approximately 1.5 to 2 Å.
- [32] a) V. I. Nikolayenko, S. Herbert, L. J. Barbour, *Chem. Commun.* 2017, 53, 11142-11145; b) Y. Zheng, H. Sato, P. Wu, H. J. Jeon, R. Matsuda, S. Kitagawa, *Nat. Commun.*, DOI: 10.1038/s41467-017-00122-5; c) F. Luo, C. B. Fan, M. B. Luo, X. L. Wu, Y. Zhu, S. Z. Pu, W.-Y. Xu, G. C. Guo, *Angew. Chem., Int. Ed.*, 2014, 53, 9298-9301.

WILEY-VCH

COMMUNICATION

COMMUNICATION

In situ single crystal X-ray diffraction was used to study a robust halogen bonded framework. This material undergoes reversible switching of its pore volume by activation or by exposure to a series of gases of different sizes and shapes.



Varvara I. Nikolayenko, Dominic C. Castell, Dewald P. van Heerden and Leonard J. Barbour*

Page No. – Page No.

Guest-induced structural transformations in a porous halogen bonded framework.