CrystEngComm

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/crystengcomm

CrystEngComm RSCPublishing

COMMUNICATION

Directed synthesis of a halogen bonded open porphyrin network †

Cite this: DOI: 10.1039/x0xx00000x

Jean-Laurent Syssa-Magalé,[a] Kamal Boubekeur,[b] Jacques Leroy,[a] Lise-Marie Chamoreau,[b] Claire Fave[c] and Bernd Schöllhorn[c,]*

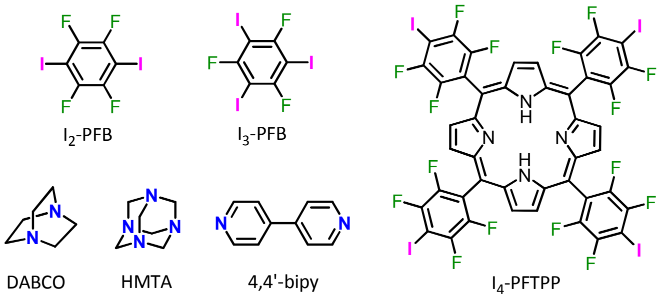
Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Abstract: A strategy for the elaboration of a halogen bonded porphyrin network is reported. The progressive introduction of geometric constraints via the modulation of the building blocks and self-assembly via strong and directional halogen bonding was leading successfully to the construction of an open porphyrin network with nano-sized tubular channels.

Based on the chemical and structural diversity of molecular building blocks one can nowadays control to a certain degree the self-assembly process in order to alter systematically the composition, topology and functionality of molecular materials. However, the search for porous solids remains an important topic and new strategies for the construction of extended framework architectures are longed for.[1,2] Porphyrins and their metal complexes are particularly useful building blocks because of their thermal and chemical stability, their square planar geometry and multidentate functionality. Since 1990 many groups have been working successfully on the development of porphyrin framework solids.[3] These assemblies are mainly based on thermodynamically labile interactions such as metal coordination, hydrogen bonding or **π-π** stacking. More recently non-covalent halogen bonding (XB) has proven to be an alternative powerful and tool in crystal engineering.[4,5] Resulting materials promise interesting potential applications such as shape and size selective sorption (storage and molecular sieves), chemical sensing or catalysis.[4] A recent IUPAC recommendation[6] defines XB, a special case of σ-hole bonding,[7] as a non-covalent attractive interaction involving halogens as electron density acceptors. In analogy to hydrogen bonding the halogenated binding partner is designated being the XB donor and the involved Lewis Base the corresponding XB acceptor. A striking characteristic of this particular interaction is its unambiguous uni-directionality rendering crystal engineering more predictable in the absence of other competitive strong interactions. Only few examples of porous supramolecular materials are known that are based on XB as the predominant interaction. Besides cage structures[8] particularly interesting and challenging is certainly the elaboration of open networks containing channels accessible for solvents. Relatively weak XB of type II between halogen atoms (C-X···X-C) afforded hexagonal channel clarthrates.[8a,9] In more recent approaches the self-assembly process was mainly governed by strong and linear C-X···A interactions (A = Lewis base).[10,11] The strategy of Rissanen and Metrangolo[11] involved the alignment of cyclophanes cavities capable of complexing small solvent molecules such as chloroform or methanol. In previous work we have also used less rigid ferrocenophanes for the self-assembly directed by XB.[12] Neither our structure nor the more recently published work of Goldberg[3c,13] on halogen bonded porphyrin assemblies have revealed any porous inclusion compounds. Taking account of these results a more directed approach was chosen for the present study.[14] We systematically varied the topicity, geometry and size of conformationally rigid XB acceptor (A) and donor (D) modules with the aim of creating voids through geometric constraints.



Scheme 1. XB donors 1,4-diiodo-perfluorobenzene (I$_2$-PFB), 1,3,5-triiodo-perfluorobenzene (I$_3$-PFB) and tetrakis(4-iodo-perfluoro-phenyl) porphyrin (I$_4$-PFTPP) and XB acceptors 1,4-diazabicyclo[2.2.2]octane (DABCO), hexamethylen-tetramine (HMTA) and 4,4'-bipyridyl (bipy) used in adduct formation.

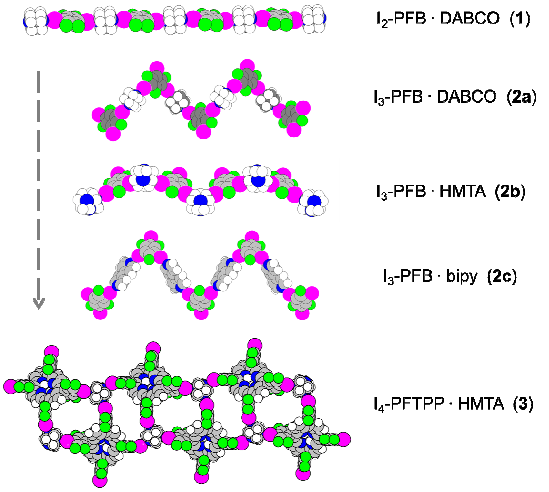


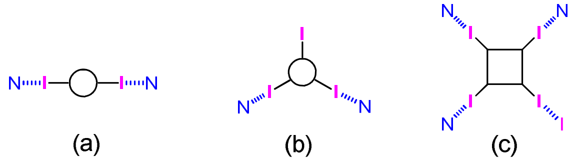
Figure 1. Space-filling representation of the polymeric chain fragments of compounds **1**-**3** with alternating donor and acceptor molecules. C (grey), H (white), F (green), I (pink), N (blue).

In the present work we have studied the self-assembly of various tertiary amines with multidentate XB donors (Scheme 1). It is well known that electron withdrawing groups such as fluorine atoms considerably enhance the XB donor (Lewis acid) properties of iodo-arenes affording particularly strong interactions.[4c-d] In this study perfluoro-iodides have been chosen because of their particularly high XB donor strength compared to the corresponding bromo or chloro derivatives.[4c-e] Among other groups we have been studying in the past the self-assembly of I_2-PFB and various nitrogen and oxygen containing XB acceptors.[12,15] We extended the nature of the XB donor by a tritopic (I_3-PFB)[16] and a tetratopic (I_4-PFTPP)[17] derivative the latter being a porphyrin carrying four iodo-perfluorophenyl groups in the *meso* positions. The respective donor and acceptor molecules have been co-crystallized and the resulting adduct structures were resolved by single crystal x-ray diffraction as described in the footnote (Table S1).[‡] Only compound **1** crystallized in the triclinic system. The crystal systems of all other structures **2**-**3** were found to be monoclinic.

Table 1 Halogen bond geometry in the crystal structure of compounds **1** and **2a-c**: inter atomic distances [Å] and angles [°].

Compnd	**C-I···N-C**	I···N	∠ C-I···N	C-I
1	C1-**I1**···N1	2.764(8)	173.21(13)	2.114(6)
	C4-**I2**···N2	2.774(8)	174.08(11)	2.111(6)
2a	C1-**I1**···N1	2.866(5)	172.55(14)	2.114(5)
	C5-**I3**···N2	2.874(5)	166.11(14)	2.105(4)
	C3-**I2**	-	-	2.089(7)
2b	C1-**I1**···N6	2.864(7)	171.72(15)	2.112(7)
	C5-**I3**···N1	2.879(7)	170.53(16)	2.108(5)
	C3-**I2**	-	-	2.082(11)
2c	C1-**I1**···N1	2.934(16)	164.67(36)	2.108(16)
	C3-**I2**···N2	2.853(15)	170.69(34)	2.095(13)
	C5-**I3**	-	-	2.081(9)

The bidentate tectons I_2-PFB and DABCO co-crystallize in a classic and previously described 1:1 stoichiometry.[18] The structure of compound **1** contains linear one dimensional polymeric chains $[D\cdots A\cdots]_n$ with alternating XB-donor (D) and acceptor (A) modules (Fig. 1). The particularly short[19] intermolecular I···N distance of 2.77 Å and the large bond angle ($\alpha_{C\text{-}I\cdots N}$ = 174°) being close to linearity are suggesting strong halogen bonding (Table 1).[4] Replacing I_2-PFB by the tridentate I_3-PFB an angle of approximately 120° could be imposed, resulting in a polymeric zigzag chain (**2a** in Fig. 1). In **2a** only two of the three iodine atoms are involved in XB interactions ($d_{I\cdots N}$ = 2.87 Å) (Scheme 2b). This feature was observed for all three compounds **2a-c** containing I_3-PFB. Employing HMTA instead of DABCO yielded in **2b** composed of arcade like chains due to the geometry of the tetramine (Fig. 1) with only two of the four HTMA nitrogens being XB acceptors.



Scheme 2. Schematic representation of the XB donors coordination sites of I_2-PFB (a), I_3-PFB (b) I_4-PFTPP (c) in the respective co-crystal structures.

A striking similarity of the first three systems **1**, **2a** and **2b** is the fact that the corresponding structures displayed similar packing arrangements with 1-dimensional ribbons aligned to form distinct two-dimensional sheets interconnected by a multitude of short C-H···F contacts ($d_{H\cdots F}$ = 2.4-2.8 Å, interatomic contacts calculated from C···F distance) (Fig. 2). The layers are stacked in the third dimension, hydrocarbons and perfluorocarbons being segregated and certainly contributing to the driving force for the observed self-assembly process.[4d] The layers of the DABCO containing compounds **1** and **2a** are completely planar whereas I_3-PFB●HMTA (**2b**) displays undulated sheets. Pursuing the systematic variation of the precursor compounds via the introduction of the longer but still rigid 4,4'-bipy spacer afforded I_3-PFB●4,4'-bipy (**2c**) (Fig. 1). The crystal structure of this compound has already been reported[20] but no comment was made on its interpenetrated network structure shown in Figure 3. The parallel polymeric halogen bonded chains (horizontal) are interconnected by short C-H···F contacts ($d_{H\cdots F}$ = 2.77 Å, calculated from $d_{C\cdots F}$ = 3.64 Å). Obviously the increasing constraints combined with D and A different in size is leading to a more complex structure.

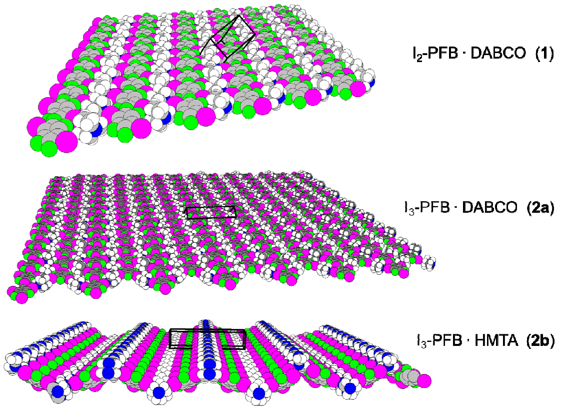


Figure 2. Space-filling representation of the 2D assembled polymeric halogen bonded chains forming layers of compounds **1**, **2a** and **2b**. C (grey), H (white), F (green), I (pink), N (blue).

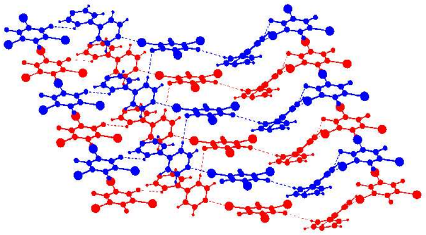
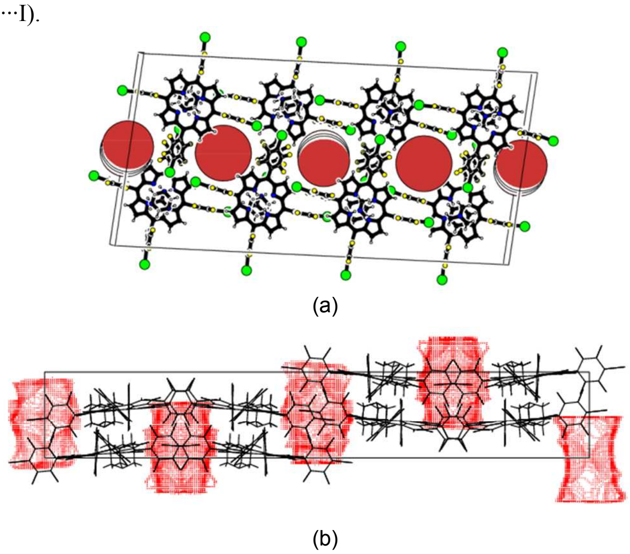


Figure 3. Crystal packing in I_3-PFB●bipy (**2c**), displaying the interpenetrated network formed by parallel polymeric XB donor acceptor chains (horizontal) interconnected through short C-H···F contacts.

We finally employed the porphyrin I_4-PFTPP,[17] a considerably longer and bulkier tecton. Its perfect square planar and tetradentate XB-donor properties are due to the four peripheral 4-iodo-perfluoro-phenyl groups in the meso positions of the porphyrin macrocycle. Co-crystallisation with HMTA afforded an extended porous porphyrin framework as shown in Figure 4. The AB layered structure (A and B layers in the a,c plane) of compound **3** involves eight crystallographically different iodine atoms (I1 to I8). Each homologous layer contains 4 of iodides bond to the same porphyrin (layer A: I1 to I4 and layer B: I5 to I8) as shown in Figure 5 for the B layer. Within each layer infinite N···I halogen bonded ladder-type chains (Fig. 1) can be distinguished, the XB involving three of the four iodines of the porphyrin (I5, I7, I8 for B layer) and three of the four nitrogens of HMTA (Fig. 6a, Scheme 2c). The halogen bonds within the ladders show relatively long interatomic I···N distances of 2.85 to 3.17 Å and C-I···N bond angles of 151.3-170.7° (Table 2) which is probably due to the geometric constraints within this framework. These ladders are interconnected to each other via short I···I interactions ($d_{I\cdots I}$ 2.4 and 4.8% shorter than the sum of the van der Waals radii, Table 2). In the both layers the orthogonal C-I···I angles of 92-93° and the almost linear C-I···I angles of 170-174° are suggesting type II halogen bonding (Scheme 2) due to the anisotropic electron density of the involved electron poor idodides.[4c-d] It is noteworthy that I1 (like I5) is simultaneously involved in a N···I and I···I interaction being XB donor as well as acceptor. In summary all iodine atoms are involved in XB (either N···I or/and I···I).


(a)

(b)

Figure 4. Crystal packing in compound **3** displaying the void space (red) forming parallel linear channels in b direction and the alternating layers parallel to the a,c plane. View on the a,c (a) and on the a,b (b) plane.

Table 2 Halogen bond geometry in the crystal structure of compound **3**: inter atomic distances (d [Å]) and angles (∠ [°]).

C-I···X-C *	d **I···X** *	∠ **C-I···X** *	d **C-I**	d **I-C**	∠ **I···I-C**
C24-**I1**···N5	2.852(5)	170.94(18)	2.128(6)	-	-
C24-**I1**···**I3**-C42	3.766(1)	93.17(19)	id.	2.095(7)	174.13(20)
C30-**I2**···N6	3.010(6)	160.92(21)	2.100(7)	-	-
C36-**I4**···N8	3.149(5)	151.81(18)	2.107(6)	-	-
C74-**I5**···N13	2.869(5)	170.70(18)	2.143(6)	-	-
C74-**I5**···**I6**-C80	3.863(1)	92.12(19)	id.	2.061(8)	170.04(23)
C86-**I7**···N14	3.170(5)	152.28(24)	2.103(8)	-	-
C92-**I8**···N16	2.972(6)	163.30(24)	2.098(8)	-	-

* X=N,I

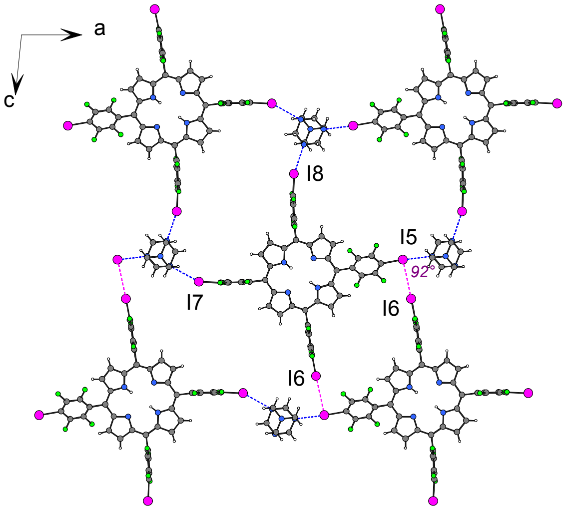


Figure 5. Compound **3**. Representative cut-out of the B layer showing the N···I and I···I XB within the a,c layer. C (grey), H (white), F (green), I (pink), N (blue).

The alternating layers A and B are stacked in the crystallographical b direction leaving cavities in the form of tubular parallel channels (Fig. 4). Two different channel shaped pores with a mean diameter of 8 Å were observed. The total calculated[21] void volume was found to be 31.4%. The volume of the cavities represented in Figure 4b is about 258 $Å^3$. Conclusively small molecules such as toluene or adamantane (approximate van der Waals volumes in the range of 100-150 $Å^3$)[22] are potential guests susceptible to penetrate the porphyrin framework. The present guest molecules deriving from the solvent mixture chloroform/acetone are totally disordered in the large channels. It was attempted to change the nature of the solvent molecules present in the interporphyrin voids of compound **3** by simple immersion of the crystals in cyclohexane. The resulting unit-cells were approximately identical to the initial structure suggesting the absence of any significant change of the porphyrin network. Unfortunately a complete structure resolution was impossible because of the low quality of the collected data probably due to the fading of the crystals during immersion.

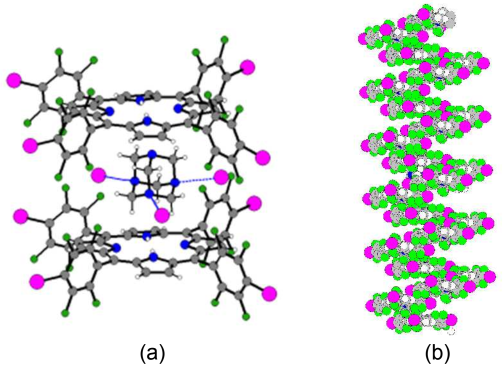

(a) (b)

Figure 6. Structure elements in compound **3** with C (grey), H (white), F (green), I (pink), N (blue). a) Coordination sites and relative position of the non-coordinated HMTA nitrogen. b) Helical structure of porphyrins forming a channel in the b direction.

Another interesting feature of the porphyrin network is the presence of a linear helical structure pattern exclusively consisting of pophyrins in the b direction perpendicular to the AB layers (Fig. 6b). Within a helix the macrocycles are linked via short C-H…F contacts. However the all over crystal structure is not chiral because of the presence of enantiomeric left and right handed helices. Noteworthy is also the position of the non-coordinated nitrogen of HMTA which is situated close to one side of the macrocycle cavity of the porphyrin (Fig. 6a). This would be a perfect arrangement for an axial ligand in the presence of a metalloporphyrin leading to similar networks while leaving vacant the second axial coordination position.[23] Work is in progress to verify this hypothesis envisioning the elaboration of size selective biomimetic catalyst as shown for other supported porphyrinic systems.[24]

In summary, we report herein a strategy for the elaboration of a halogen bonded open porphyrin network. Starting with a simple case geometric constraints, such as topicity and size of the precursor molecules, were progressively introduced aiming for more complex structures such as interpenetrated networks, clathrates or porous networks. A straight forward modulation of the building blocks and self-assembly via strong and directional halogen bonding was leading successfully to the construction of an extended prophyrin network with nano-sized linear channels. The system is a remarkable example for the strength of halogen bonding out ruling steric constraints and thus opening the access to new materials with potential catalytic or optical properties considering the use of porphyrins and their metal complexes.

Acknowledgements

We gratefully acknowledge the financial support of Université Paris Diderot - Sorbonne Paris Cité (IDEX, project HalBond), Université Pierre et Marie Curie and the CNRS.

Notes and references

[a] *Ecole Normale Supérieure, Département de Chimie, UMR 8640 CNRS "PASTEUR", 24 rue Lhomond, 75005 Paris, France.*
[b] *Institut Parisien de Chimie Moleculaire – UMR CNRS 8232 UPMC Université Paris 6, 4 place Jussieu, 75252 Paris Cedex 5, France ;*
[c] *Laboratoire d'Electrochimie Moléculaire, UMR 7591 CNRS, Université Paris Diderot, Sorbonne Paris Cité, 15 rue Jean-Antoine de Baïf, 75205 Paris cedex, France. E-mail : bernd.schollhorn@univ-paris-diderot.fr; tel : (+33 01) 5727 8791*

† Electronic Supplementary Information (ESI) available: crystallographic data. CCDC 1018108-1018112. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

‡ The co-crystals **1** and **2a-c** were obtained by exposing equimolar solutions of the respective XB donor (0.10 mmol) and acceptor molecules (0.10 mmol) in chloroform to a saturated *n*-hexane atmosphere at room temperature. Compound **3** was obtained by slow evaporation of an equimolar solution of I_4-PFTPP and HMTA in a mixture of chloroform and acetone. *Single crystal X-ray analysis:* Intensity data were collected on an NONIUS Kappa-CCD four-circle diffractometer at room temperature by using a graphite monochromated Mo-K_α radiation. The structures were solved by direct methods with SHELXS-86, refined by full least-squares on F^2 and completed with SHELXL-97 (G. M. Sheldrick, Acta Crystallogr., Sect. A, 2008, **64**, 112-122). Graphics were generated using DIAMOND (Crystal Impact GbR). All non-H atoms were refined with anisotropic displacement parameters and H atoms were simply introduced at calculated positions (riding model with isotropic temperature factors fixed at 1.2-times that of the parent atom). All crystallographic details are listed in Table S1 in the ESI.†

1 (a) X. Zhao, *J. Mat. Chem.*, 2006, **16**, 623-625; (b) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273–282.
2 (a) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319–330; (b) T. Ohmura, A. Usuki, K. Fukumori, T. Ohta, M. Ito and K. Tatsumi, *Inorg. Chem.*, 2006, **45**, 7988–7990.
3 (a) K. S. Suslick, P. Bhyrappa, J.-H. Chou, M. E. Kosal, S. Nakagaki, D. W. Smithenry and S. R. Wilson, *Acc. Chem. Res.*, 2005, **38**, 283–291; (b) I. Goldberg, *Chem. Commun.*, 2005, **10**, 1243–1254; (c) I. Goldberg, *CrystEngComm*, 2008, **10**, 637–645; (d) Q. Zha, X. Rui, T. Wei and Y. Xie, *CrystEngComm,* 2014, **16**, 7371–7384. And references therein.
4 (a) H. A. Bent, *Chem. Rev.,* 1968, **68**, 587–648; (b) O. Hassel, *Science,* 1970, **170**, 497–502; (c) P. Metrangolo, F. Meyer, T. Pilati, G. Resnati and G. Terraneo, *Angew. Chem. Int. Ed.*, 2008, **47**, 6114–6127; (d) P. Metrangolo and G. Resnati, *Halogen Bonding: Fundamentals and Applications (Structure and Bonding)*, Springer: Berlin, Heidelberg, 2008, vol. 126; (e) P. Metrangolo and G. Resnati, *Crystal Growth & Design*, 2012, **12**, 5835–5838; (f) M. Fourmigué, *Curr. Opin. Solid State Mater. Sci.* 2009, **13,** 36-45.
5 (a) P. Auffinger, F. Hays, E. Westhof and P. S. Ho, *Proceedings of the National Academy of Sciences of the United States of America*, 2004, **101**, 16789–16794; (b) P. Metrangolo and G. Resnati, *Science*, 2008, **321**, 918–919.
6 G. R. Desiraju, P. S. Ho, L. Kloo, A. C. Legon, R. Marquardt, P. Metrangolo, P. Politzer, G. Resnati and K. Rissanen, *Pure Appl. Chem.*, 2013, **85/8**, 1711-1713.
7 (a) A. Karpfen, *Theor. Chem. Acc.* 2003, **110**, 1–9; (b) P. Politzer, P. Lane, M. C. Concha, Y. Ma and J. S. Murray, *J. Mol. Model.*, 2007, **13**, 291-296.
8 (a) B. K. Saha, R. K. R. Jetti, L. S. Reddy, S. Aitipamula and A. Nangia, *Cryst. Growth Des.*, 2005, **5**, 887-889; (b) P. Metrangolo, F. Meyer, T. Pilati, G. Resnati and G. Terraneo, *Chem. Commun.*, 2008, **14**, 1635-1637; (c) P. Metrangolo, Y. Carcenac, M. Lahtinen, T. Pilati, K. Rissanen, A. Vij and G. Resnati, *Science*, 2009, **322**, 1461-1464.
9 (a) R. K. R. Jetti, F. Xue, T. C. W. Mak and A. Nangia, *Cryst. Eng.*, 1999, **2**, 215-224; (b) R. K. R. Jetti, P. K. Thallapally, F. Xue, T. C. W. Mak and A. Nangia, *Tetrahedron*, 2000, **56**, 6707-6719.
10 (a) F. C. Pigge, V. R. Vangala and D. C. Swenson, *Chem. Commun.*, 2008, **39**, 4726-4728; (b) K. Raatikainen and K. Rissanen, *CrystEngComm*, 2011, **13**, 6972-6977; (c) K. Raatikainen and K. Rissanen, *Chem. Sci.*, 2012, **3**, 1235–1239.
11 (a) K. Raatikainen, J. Huuskonen, M. Lahtinen, P. Metrangolo and K. Rissanen, *Chem. Commun.*, 2009, **16**, 2160–2162; (b) K. Raatikainen and K. Rissanen, *Cryst. Growth Des.*, 2010, **10**, 3638-3646.
12 J.-L. Syssa-Magalé, K. Boubekeur, P. Palvadeau, A. Meerschaut and B. Schöllhorn, *J. Mol. Str.*, 2004, **691**, 79–84.
13 H.M. Titi, R. Patra and I. Goldberg, *Chem. Eur. J.*, 2013, **19**, 14941-14949.
14 B. Schöllhorn, Symposium on Halogen Bonding, Washington DC, *Abstracts of Papers of the Am. Chem. Soc.,* **238**, 56-ORGN, AUG 16 2009.
15 (a) J.-L. Syssa-Magal, K. Boubekeur, P. Palvadeau, A. Meerschaut and B. Schöllhorn, *CrystEngComm*, 2005, **7**, 302-308; (b) J.-L. Syssa-Magalé, K. Boubekeur and B. Schöllhorn, *J. Mol. Str.*, 2005, **737**, 103–107; (c) K. Boubekeur, J.-L. Syssa-Magalé, P. Palvadeau and B. Schöllhorn, *Tetrahedron Letters*, 2006, **47**, 1249–1252.
16 H. H. Wenk and W. Sander, *Eur. J. Org. Chem.*, 2002, **23**, 3927–3935.
17 J. Leroy, B. Schöllhorn, J.-L. Syssa-Magalé, K. Boubekeur and P. Palvadeau, *J. Fluorine Chem.*, 2004, **125**, 1379–1382.
18 D. Cincic, T. Friscic and W. Jones, *Chem. -Eur. J.,* 2008, **14,** 747-753.
19 (a) S. C. Nyburg and C. H. Faerman, *Acta Cryst. B*, 1985, **41**, 274-279; (b) R. S. Rowland and R. Taylor, *J. Phys. Chem.*, 1996, **100**, 7384-7391.
20 A. C. B. Lucassen, A. Karton, G. Leitus, L. J. W. Shimon, J. M. L. Martin and M. E. van der Boom, *Cryst. Growth Des.,* 2007*,* **7**, 386-392.
21 (a) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 2001; (b) P. van der Sluis and A. L. Spek, *Acta Crystallogr.,* 1990, **A46**, 194-201.
22 (a) A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441-451 ; (b)Y. H. Zhao, M. H. Abraham and A. M. Zissimos, *J. Org. Chem.*, 2003, **68**, 7368-7373.
23 A. M. Shultz, O. K. Farha, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.*, 2009, **131**, 4204–4205.
24 For example: (a) D. Deniaud, B. Schöllhorn, D. Mansuy, P. Battion, B. Bujoli and J. Rowel, *Chem. Mater.*, 1995, **7**, 995–1000; (b) P. Battioni, E. Cardin, M. Louloudi, B. Schöllhorn, G. A. Spyroulias, D. Mansuy and T. G. TrayIor, *Chem. Commun.*, **17**,. 1996, 2037–2038.