Directed synthesis of a halogen-bonded open porphyrin network†

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A strategy for the elaboration of a halogen-bonded porphyrin network is reported. The progressive introduction of geometric constraints via the modulation of building blocks and self-assembly via strong and directional halogen bonding led 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 systematically alter 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 and 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 tool in crystal engineering.4,5 The resulting materials promise interesting potential applications in shape- and size-selective sorption (storage and molecular sieves), chemical sensing or catalysis.4 A recent IUPAC recommendation6 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 the XB donor, and the involved Lewis base the corresponding XB acceptor. A striking characteristic of this particular interaction is its unambiguous unidirectionality rendering crystal engineering more predictable in the absence of other competitive strong interactions. Only a 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 to solvents. Relatively weak type II XB between halogen atoms (C–X⋯X–C) afforded hexagonal channel clathrates.8,9 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 Metrangolo11 involved the alignment of cyclophane 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 study by Goldberg12,13 on halogen-bonded porphyrin assemblies have revealed any porous inclusion compounds. Taking into account these results, we chose a more directed approach 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.

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 I2-PFB and various
We extended the nature of the XB donor by a tritopic (I₃-PFB)¹⁶ 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 structures 2–3 were found to be monoclinic.

The bidentate tectons I₂-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⋯A⋯]ₙ with alternating XB donor (D) and acceptor (A) modules (Fig. 1). The particularly short intermolecular I⋯N distance of 2.77 Å and the large bond angle (α_{C—I⋯N} = 174°) close to linearity suggest strong halogen bonding (Table 1).⁴ By replacing I₂-PFB with the tridentate I₃-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⋯N} = 2.87 Å) (Scheme 2b). This feature was observed for all three compounds 2a–c containing I₃-PFB. Employing HMTA instead of DABCO yielded 2b, composed of arcade-like chains due to the geometry of tetramine (Fig. 1), with only two of the four HTMA nitrogens being XB acceptors.

A striking similarity of the first three systems 1, 2a and 2b is the fact that the corresponding structures displayed similar packing arrangements with one-dimensional ribbons aligned to form distinct two-dimensional sheets interconnected by a multitude of short C–H⋯F contacts (d_{H⋯F} = 2.4–2.8 Å, interatomic contacts calculated from the C⋯F distance) (Fig. 2). The layers are stacked in the third dimension, hydrocarbons and perfluorocarbons being segregated and certainly contributing

### Table 1: Halogen bond geometry in the crystal structure of compounds 1 and 2a–c: interatomic distances d (Å) and angles ψ (°)

<table>
<thead>
<tr>
<th>Compound</th>
<th>C—I⋯N—C</th>
<th>d_{I⋯N}</th>
<th>ψ_{C—I⋯N}</th>
<th>d_{C—I}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₁—I₁⋯N₁</td>
<td>2.764(8)</td>
<td>173.21(13)</td>
<td>2.114(6)</td>
</tr>
<tr>
<td>2a</td>
<td>C₁—I₁⋯N₁</td>
<td>2.774(8)</td>
<td>174.08(11)</td>
<td>2.111(6)</td>
</tr>
<tr>
<td>2b</td>
<td>C₁—I₁⋯N₁</td>
<td>2.866(5)</td>
<td>166.11(14)</td>
<td>2.105(4)</td>
</tr>
<tr>
<td>2c</td>
<td>C₁—I₁⋯N₁</td>
<td>2.874(5)</td>
<td>166.05(14)</td>
<td>2.108(5)</td>
</tr>
<tr>
<td></td>
<td>C₁—I₁⋯N₁</td>
<td>—</td>
<td>—</td>
<td>2.089(7)</td>
</tr>
<tr>
<td>2b</td>
<td>C₁—I₁⋯N₁</td>
<td>2.864(7)</td>
<td>171.72(15)</td>
<td>2.112(7)</td>
</tr>
<tr>
<td>2c</td>
<td>C₁—I₁⋯N₁</td>
<td>2.879(7)</td>
<td>170.53(14)</td>
<td>2.108(5)</td>
</tr>
<tr>
<td>2c</td>
<td>C₁—I₁⋯N₁</td>
<td>—</td>
<td>—</td>
<td>2.082(11)</td>
</tr>
</tbody>
</table>

### Scheme 1: XB donors, 1,4-diodo-perfluorobenzene (I₂-PFB), 1,3,5-triiodo-perfluorobenzene (I₃-PFB) and tetrakis(4-iodo-perfluoro-phenyl) porphyrin (I₄-PFTPP), and XB acceptors, 1,4-diazeato[2.2.2]octane (DABCO), hexamethylenetetramine (HMTA) and 4,4′-bipyridyl (bipy), used in adduct formation.

### Scheme 2: Schematic representation of the XB donor coordination sites of I₂-PFB (a), I₃-PFB (b) and I₄-PFTPP (c) in the respective co-crystal structures.
to the driving force for the observed self-assembly process. The layers of DABCO-containing compounds 1 and 2a are completely planar, whereas I$_2$-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 but no comment was made on its interpenetrated network structure shown in Fig. 3. The parallel polymeric halogen-bonded chains (horizontal) are interconnected by short C–H⋯F contacts ($d_{C-H-F} = 2.77$ Å, calculated from $d_{C-F} = 3.64$ Å). Obviously, the increasing constraints combined with D and A which are different in size lead to a more complex structure.

We finally employed the porphyrin I$_4$-PFTP, 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 Fig. 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 iodides bonded to the same porphyrin (layer A: I1 to I4 and layer B: I5 to I8) as shown in Fig. 5 for the B layer. Within each layer, infinite N⋯I halogen-bonded ladder-type chains (Fig. 1) can be distinguished, with the XB involving three of the four iodines of the porphyrin (I5, I7, I8 for the 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 ($d_{I-I}$ 2.4% and 4.8% shorter than the sum of the van der Waals radii, Table 2). In both layers the orthogonal C⋯I⋯I angles of 92–93° and the almost linear C–I⋯I angles of 170–174° suggest type II halogen bonding (Scheme 2) due to the anisotropic electron density of the involved electron-poor iodides. It is worth noting that I1 (like I5) is simultaneously involved in a N⋯I...
and I⋯I interaction being an XB donor as well as an acceptor. In summary, all iodine atoms are involved in XB (N⋯I and/or I⋯I).

The alternating layers A and B are stacked in the crystallographic 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 calculated21 void volume was found to be 31.4%. The volume of pores with a mean diameter of 8 Å were observed. The total calculated21 void volume was found to be 31.4%. The volume of pores with a mean diameter of 8 Å were observed. The total calculated21 void volume was found to be 31.4%. The volume of pores with a mean diameter of 8 Å were observed. The total

The present guest molecules derived from the solvent mixture consisting of porphyrins in the direction perpendicular to b were totally disordered in the large channels. Changing the nature of the solvent molecules present in the interporphyrin voids of compound 3 was attempted 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 in 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.

Another interesting feature of the porphyrin network is the presence of a linear helical structure pattern exclusively consisting of porphyrins 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 overall crystal structure is not chiral because of the presence of enantionic left- and right-handed helices. It is also worth noting the position of the non-coordinated nitrogen of HMTA, which is situated close to one side of the macrocyclic 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 catalysts as shown in other supported porphyrinic systems.24

In summary, we report herein a strategy for the elaboration of a halogen-bonded open porphyrin network. 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 straightforward modulation of the building blocks and self-assembly via strong and directional halogen bonding led successfully to the construction of an extended porphyrin network with nano-sized linear channels. The system is a remarkable example of the strength of halogen bonding, ruling out steric constraints and thus opening access to new materials with potential catalytic or optical properties considering the use of porphyrins and their metal complexes.

### Acknowledgements

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### Notes and references

‡ 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 I₈PFTHP and HMTA in a mixture of chloroform and acetone. Single crystal X-ray analysis: intensity data were collected using a NONIUS Kappa-CCD four-circle diffractometer at room temperature by using graphite monochromated Mo-Kα radiation. The structures were solved by direct methods with SHELXL-97, refined by full least-squares on F² and completed with SHELXL-97 (G. M. Sheldrick, Acta Cryst. B 1990, 46, 1). 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!


