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COMMUNICATION

Hydrogen and halogen bonding drive the orthogonal self-assembly of an organic framework possessing 2D channels†

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Orthogonal self-assembly of an open organic framework showing 2D channels has been obtained by combining hydrogen and halogen bonding. The framework is able to host various guest molecules with a diverse set of steric demands and substitution patterns, and survives single-crystal-to-single-crystal guest exchanges from liquid and gas phases.

Orthogonal self-assembly relying on different, noninterfering intermolecular interactions is attracting considerable interest as a strategy to obtain "smarter" stimuli-responsive materials.[1] The combination of two or more orthogonal supramolecular synthons resulted, in fact, in a range of novel materials like switchable supramolecular copolymers,[2] chiral bimetallic self-supported hydrogenation catalysts,[3] voltage-responsive vesicles,[4] and self-assembled fibrillar networks.[5] Orthogonal self-assembly has also yielded functional monolayer architectures,[6] as well as the improvement of bulk material properties.[7] Ionic interactions, metal–ligand complexation, and hydrogen bonds are most frequently combined in driving orthogonal self-assembly processes. Different complementary hydrogen bonding motifs have also been explored for this purpose.[8]

In this communication, we demonstrate that hydrogen bonding (HB) and halogen bonding (XB),[9] which most often are seen in competition, can cooperate orthogonally in building up open organic frameworks, provided that self-assembling units with optimized geometries are chosen. Organic open frameworks have found applications in, *e.g.*, gas adsorption,[10] conductivity,[11] and molecular transport.[12] Here, we report that the obtained open framework is able to host various guest molecules with a diverse set of steric demands and substitution patterns, and survives single-crystal-to-single-crystal (SCSC) guest exchanges from liquid and gas phases.

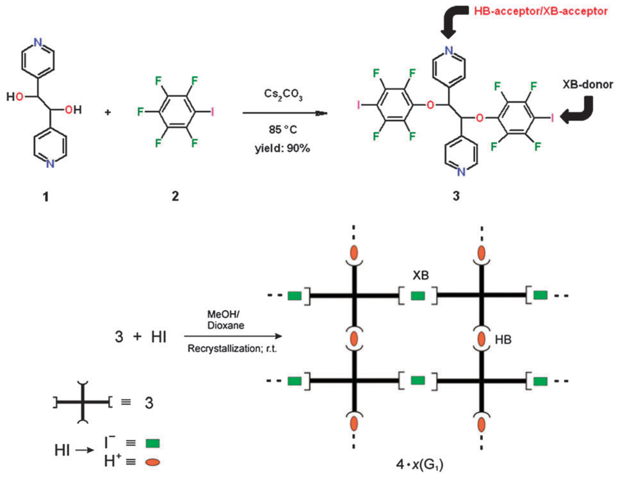

Fig. 1 Top: synthesis of ligand **3**. Bottom: cartoon showing the self-assembly of **3** (linker) with I^- and H^+ ions (nodes) through XB and HB, respectively, and the formation of the supramolecular open framework $\mathbf{4}x(\mathbf{G_1})$ (G_1 = dioxane; x = 2.5).

The ligand 4,4′-[1,2-bis(2,3,5,6-tetrafluoro-4-iodophenoxy)-ethane-1,2-diyl]dipyridine (**3**) (Fig. 1, top) has two pairs of sites for potentially orthogonal binding processes and is thus a potential candidate to be engaged in simultaneous HB and XB, in a chemically and geometrically orthogonal manner. In fact, iodotetrafluorophenyl moieties are prototypical XB-donor groups, while pyridyl residues can behave as both HB- and XB-acceptor sites. Indeed, pure ligand **3** in the crystal self-assembles by pairing the two couples of complementary binding sites, which are saturated *via* multiple XBs.[13]

In order to disrupt the tendency of ligand **3** to self-assemble *via* XB and to elicit its orthogonal HB/XB potential, a suitable partner has to be identified, which is able to involve the two pairs of complementary binding sites in two noninterfering interactions. To this purpose we selected hydrogen iodide (HI), as a source of both a strong HB-donor (H^+), for the binding of pyridine, and a strong XB-acceptor (I^-), for the binding of the iodotetrafluorophenyl ring, no more bound to the pyridine (Fig. 1).[14] An iodide anion was preferred over other halide anions due to the particular reliability of the $C–I\cdots I^-$ supramolecular synthon.[15] A straightforward formation of the hydroiodide salt of **3** from pure starting compounds was expected

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† Electronic supplementary information (ESI) available: Experimental details, crystal structure description, additional figures. CCDC 866 321 (**3**), 866 318 ($\mathbf{4} \times \mathbf{2.5(G_1)}$), 866 320 ($\mathbf{4} \times \mathbf{2(G_2)}$), 866 319 ($\mathbf{4} \times \mathbf{2(G_3)}$). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc33682k

and it was anticipated that the organization of the formed salt in the crystal was driven by the pairing of the two Lewis base sites (pyridine nitrogen and iodide anion) with the two Lewis acid sites (iodine of the iodotetrafluorophenyl ring and the proton) after the hard and soft acid–base theory (HSAB).[16]

A poorly crystalline yellow precipitate was obtained by rapid mixing of a methanol/toluene solution of **3** and excess HI dissolved in methanol. Recrystallization from methanol with slow diffusion of dioxane (**G_1**) gave large pristine pale yellow crystals.[13] Single crystal X-ray diffraction analysis showed that the open organic framework **$4x(G_1)$** (**G_1** = dioxane; x = 2.5) was obtained.‡ The crystal packing of **$4x(G_1)$** is governed mainly by HB, XB, and π–π stacking. As expected, the ion pair in HI is fully dissociated (the shortest H^+/I^- distance is 7.10 Å). The H^+ ion functions as a linear bidentate HB-donor ($N\cdots H^+\cdots N$ distances and angles are 2.657(8) Å and 172(7)°) and bridges two pyridines of two distinct and adjacent ligand **3** molecules. Analogously, the I^- ion behaves as a quasi linear bidentate XB-acceptor ($I\cdots I^-\cdots I$ angle is 146.07(1)°) and bridges the iodine atoms of other two distinct and following ligands. The $I\cdots I^-$ XB shows the standard geometric features.[17] In the network, ligand **3** adopts a cruciform shape with the four arms fully extended two-by-two to opposite sides. The above discussed HB and XB linearity translates this molecular geometry into the topology of the network which comprises a quasi-rectangular 2D grid (sides ~22 Å and 11 Å, Fig. 2a).

The 2D grid networks described above stack through π–π interactions between antiparallel tetrafluorophenyl rings [distance between centroids $(C19–C24)\cdots(C19–C24)_{1-x,1-y,1-z}$ = 3.725 Å] and residual crystal packing interactions. However, between two adjacent layers there is an offset of *ca.* 11 Å (Fig. 2b), which, upon superimposition of *n* layers, gives rise to a biporous[18] network consisting of two channels (A and B) running along the crystallographic *a*-axis and having similar dimensions (*ca.* 7 × 4 Å^2) but different shape and chemical environment (Fig. 3a). The channels are filled with dioxane molecules, which adopt a different arrangement in the channels as a likely consequence of their different shape and chemical environment (Fig. 3b).[13]

Interestingly, the packing of ligand **3** in **$4x(G_1)$** also originates channels (C) extending along the *c*-axis (Fig. 3c) having similar size but different shape from channels A and B. The two sets of channels intersect each other resulting in a 2D channel network structure (Fig. 3d), with a total solvent accessible volume of *ca.* 376 Å^3 per unit cell volume (1977 Å^3), which represents *ca.* 19% of the overall crystal lattice upon guest removal.[19]

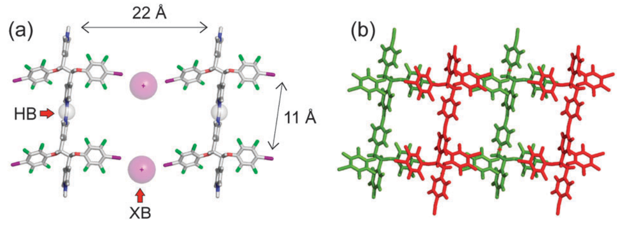

Fig. 2 Single crystal X-ray structure of **$4x(G_1)$** (**G_1** = dioxane; x = 2.5). (a) The self-assembly of ligand **3** and HI *via* orthogonal HB and XB yields a 2D grid with dimensions *ca.* 22 × 11 Å^2. The I^- and H^+ ions are shown as spheres. (b) Two adjacent layers (red and green) stack along the *a*-axis resulting in the partitioning of the void in the rectangular grids. Dioxane molecules have been omitted for clarity.

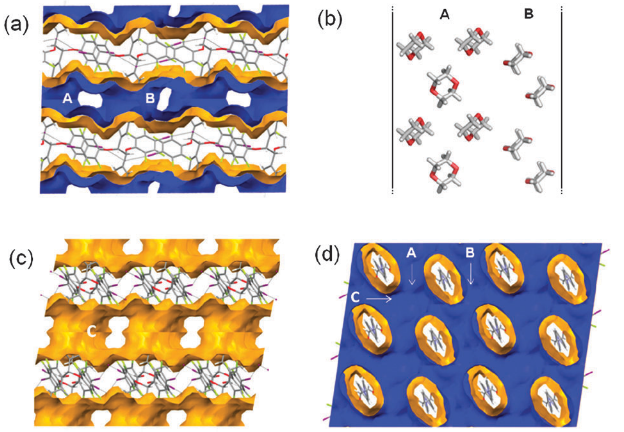

Fig. 3 Voids in **$4x(G_1)$** observed after *in silico* removal of guest molecules. Contact surface (yellow) and solvent accessible surface (blue) calculated using a 1.2 Å probe radius. (a) View along the *a*-axis showing channels A and B. (b) The different arrangement of dioxane molecules in channels A and B denotes the biporous nature of the network. (c) View along the *c*-axis of channel C which intersects A and B channels to yield an overall 2D open framework. (d) View of the network along the *b*-axis showing the intersection of the channels.

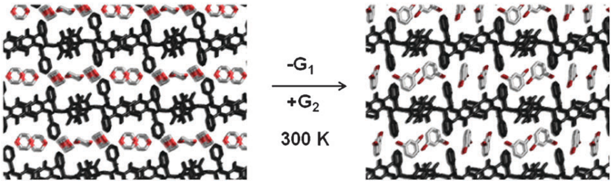

Fig. 4 Guest exchange in **$4x(G_1)$** (x = 2.5) for **G_2** to yield **$4x(G_2)$** (x = 2). The new **G_2** guest molecules are considerably well localized. Only one of the two crystallographically independent **G_2** molecules is disordered. For clarity purposes the disordered **G_2** is not shown.

The robustness of **$4x(G_1)$** is demonstrated by its ability to survive the introduction of halogenated guests which can give rise to polar host–guest interactions between the halogen atoms and the ionic 2D sheets. Immersion of a single crystal of **$4x(G_1)$** in 0.5 mL of 1,3-dibromobenzene (**G_2**) at 300 K for *ca.* 2 h yielded a good quality crystal, which, upon single crystal X-ray diffraction analysis, revealed to be the open framework **$4x(G_2)$** (**G_2** = 1,3-dibromobenzene; x = 2) (Fig. 4). Thus, **G_1** (dioxane) was neatly exchanged by **G_2** (1,3-dibromobenzene) without disrupting the framework topology.

The two crystallographically independent 1,3-dibromobenzene molecules present in **$4x(G_2)$** are involved in several contacts with the framework walls and between them.[13] Nevertheless, the framework **$4x(G_2)$** is isoreticular with **$4x(G_1)$** and shows similar geometric features for HB and XB (Fig. 4).[20] The total solvent accessible volume is *ca.* 17.1% of the unit cell volume.

Finally, we tested the ability of **$4x(G_1)$** to guest exchange in a gas/solid reaction by exposing a single crystal of **$4x(G_1)$** to vapours of **G_2**. After exposure for *ca.* 20 h at room temperature in a closed jar, the crystal was still suitable for X-ray diffraction analysis, revealing new unit cell parameters matching those of **$4x(G_2)$**, indicating that guest exchange took place.

In conclusion, XB, due to its strength and directionality, is revealing to be a promising new tool for the design of open framework materials.[21] In this communication we demonstrated that HB and XB can successfully be combined in an orthogonal manner to drive the self-assembly of a complex and functional supramolecular network. The reported results pave the way for a new design concept in orthogonal self-assembly and may also have implications for, *e.g.*, drug design.[22] The combination of pyridines and iodotetrafluorophenyl rings in the same scaffold, along with the coordination of HI may develop as a general strategy for the orthogonal self-assembly of new supramolecular co-polymers that can be tuned by various external stimuli through addressing HB and XB separately (*e.g.* pH change, or anion exchange, respectively). Current studies in our laboratory are addressing this issue as well as the synthesis of a permanently porous framework.

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Notes and references

‡ Single crystal X-ray diffraction data for (**3**), (**4** × **2.5(G$_1$)**), (**4** × **2(G$_2$)**), (**4** × **2(G$_3$)**) were recorded using Mo-Kα radiation in Bruker KAPPA APEX II diffractometer. Data were collected with ω and φ scan with the scan width 0.5. The data were reduced with empirical absorption correction. Structures were solved by a direct method using SHELXL97[23] present in the program suite WinGX (version 1.80.04).[24] The molecular diagrams were generated using Mercury.[25] The non-hydrogen atoms are refined anisotropically and hydrogen atoms were positioned geometrically. All crystallographic details are listed in Table S1 and intermolecular interactions are listed in Tables S1.1 and S1.2 in the ESI.† Single crystal X-ray diffraction data for **4** × **2.5(G$_1$)**: $C_{24}H_{11}N_2O_2F_8I_2^+$, 2.5($C_4H_8O_2$), I^-, M_r = 1112.31, triclinic, space group $P\bar{1}$, a = 9.3334(16) Å, b = 11.853(2) Å, c = 18.412(3) Å, α = 96.076(12)°, β = 96.664(12)°, γ = 99.784(13)°, V = 1977.2(6) Å^3, T = 173 K, Z = 2, ρ_{calcd} = 1.868 g cm^{-3}, 5278 unique reflections out of 7669 with $I > 2\sigma(I)$, 490 parameters, $2.25 < \theta < 26.0$, final R factors R_1 = 0.0453 and wR_2 = 0.1089. Single crystal X-ray diffraction data for **4** × **2(G$_2$)**: $C_{24}H_{11}N_2O_2F_8$ I_2^+, 2($C_6H_4Br_2$), I^-, M_r = 1363.87, triclinic, space group $P\bar{1}$, a = 9.2497(4) Å, b = 11.8502(6) Å, c = 19.1570(10) Å, α = 92.354(3)°, β = 94.750(3)°, γ = 98.469(3)°, V = 2066.76(17) Å^3, T = 93 K, Z = 2, ρ_{calcd} = 2.192 g cm^{-3}, 9168 unique reflections out of 13 288 with $I > 2\sigma(I)$, 645 parameters, $2.39 < \theta < 32.65$, final R factors R_1 = 0.0561 and wR_2 = 0.1559.

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