

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

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Supporting Information

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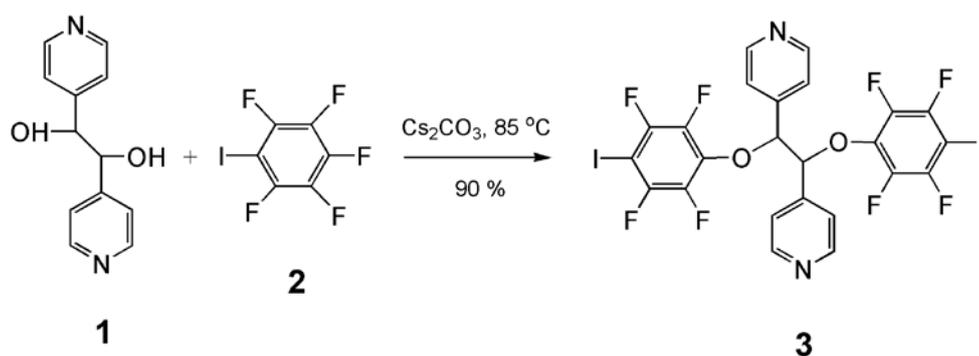
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Materials and Methods

The starting materials were purchased from Sigma-Aldrich and Apollo Scientific and used without further purification. Commercial HPLC-grade solvents were used without further purification. ^1H and ^{19}F NMR spectra were recorded on a Bruker AV500 spectrometer, using $\text{d}^6\text{-DMSO}$ as solvent. TMS and CFCl_3 were used as internal standards for ^1H and ^{19}F NMR spectra, respectively; chemical shifts were referenced to traces of protium containing solvent. Melting points were determined with DSC analysis using a Mettler Toledo DSC 823e. X-ray powder diffraction experiments were measured on a Bruker D8 Advance diffractometer operating in reflection mode with Gemonochromated $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) and a linear position-sensitive detector. Single crystal X-ray analysis were collected on a Bruker KAPPA APEX II diffractometer with $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) equipped with a CCD detector. The low temperature data were collected using a Bruker KRYOFLEX device. The mass spectra of **3** and its hydroiodide derivative were recorded on a BRUKER Esquire 3000 PLUS.

Preparation of 4,4'-[1,2-bis(2,3,5,6-tetrafluoro-4-iodophenoxy)ethane-1,2-diyl]dipyridine (**3**):



1,2-Bis(4-pyridyl)-1,2-ethanediol monohydrate (**1**) (0.75 mmol, 0.160 g), iodopentafluorobenzene (**2**) (19 mmol, 5.6 g) and Cs_2CO_3 (2.42 mmol, 0.787 g) were mixed in a flask and kept at 85°C for three days under N_2 atmosphere with magnetic stirring. After cooling at room temperature, water was added to the crude reaction mixture, and organic compounds were extracted (3 times) with AcOEt. Combined organic layers were dried with anhydrous sodium sulphate and the residue was purified using column chromatography (AcOEt/*n*-hexane, 5:1) to give 424 mg (90% yield) of a pale yellow solid. Elemental Analysis: Calcd for $\text{C}_{24}\text{H}_{10}\text{F}_8\text{I}_2\text{N}_2\text{O}_2$: C, 37.72; H, 1.32; N, 3.67; Found: C, 38.0; H, 1.3; N, 3.7.

ESI-Mass: calcd exact mass for **3** [$\text{C}_{24}\text{H}_{10}\text{F}_8\text{I}_2\text{N}_2\text{O}_2$] 763.87. Ion polarity: positive; m/z found $[\text{M}+\text{H}]^+$ 764.9.

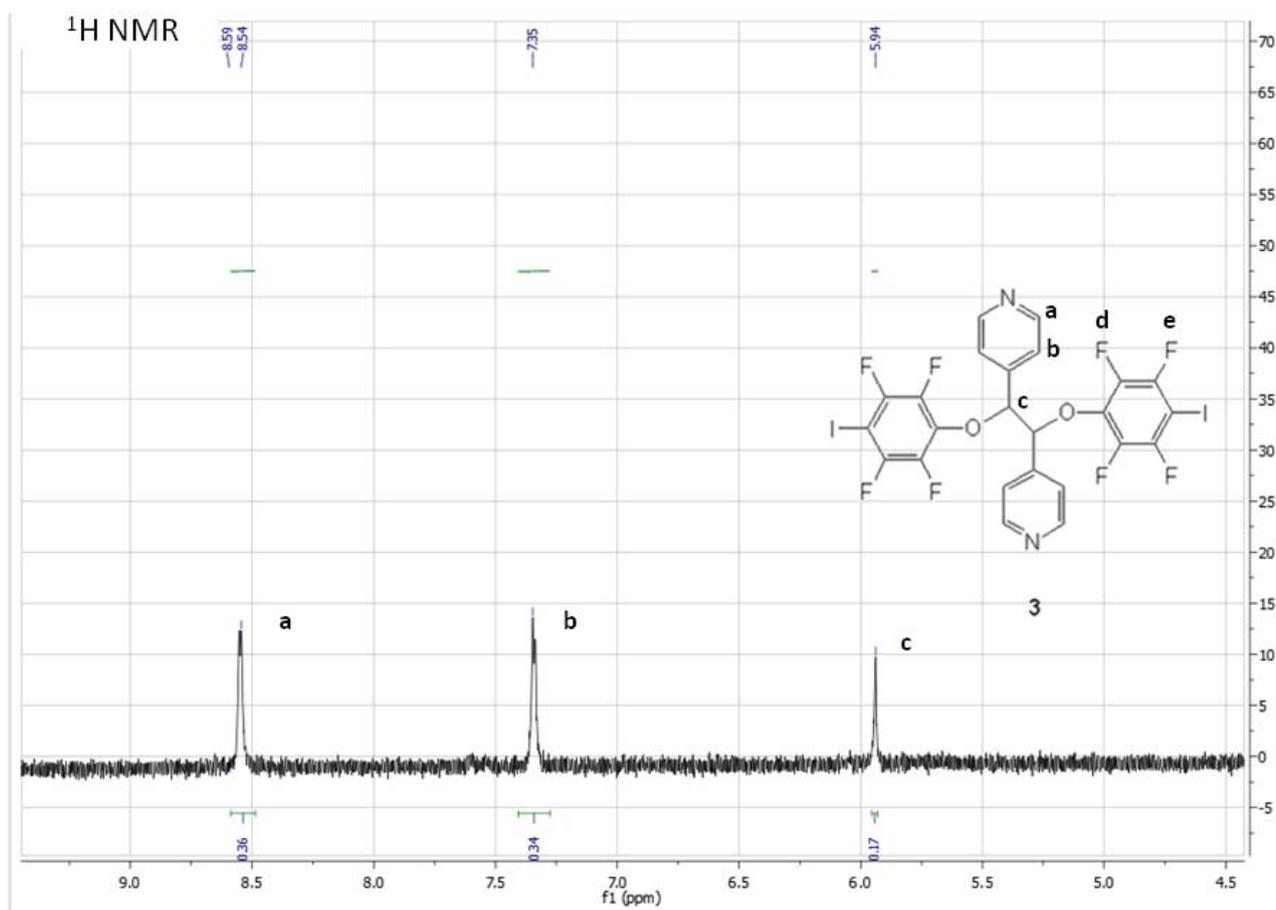


Figure S1. ¹H NMR spectrum of the ligand 3.

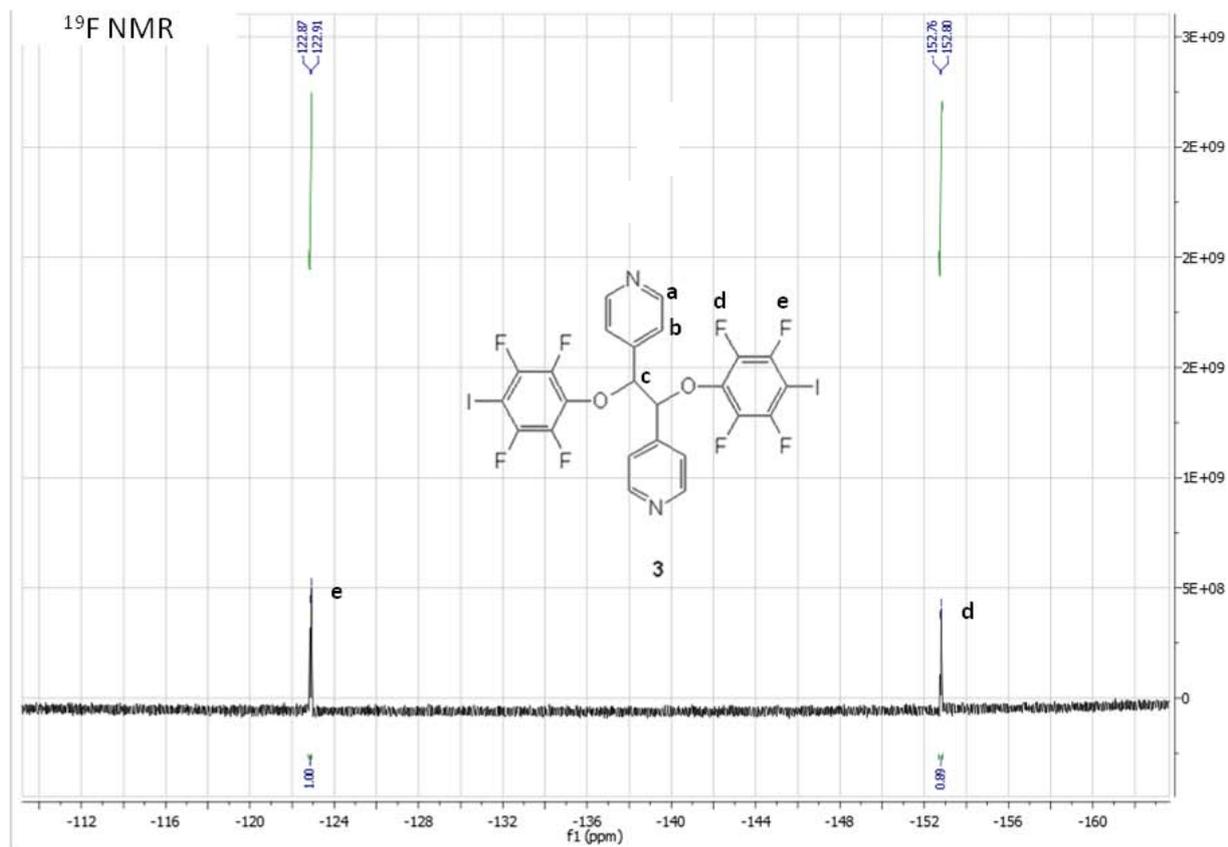


Figure S2. ^{19}F NMR spectrum of the ligand **3**.

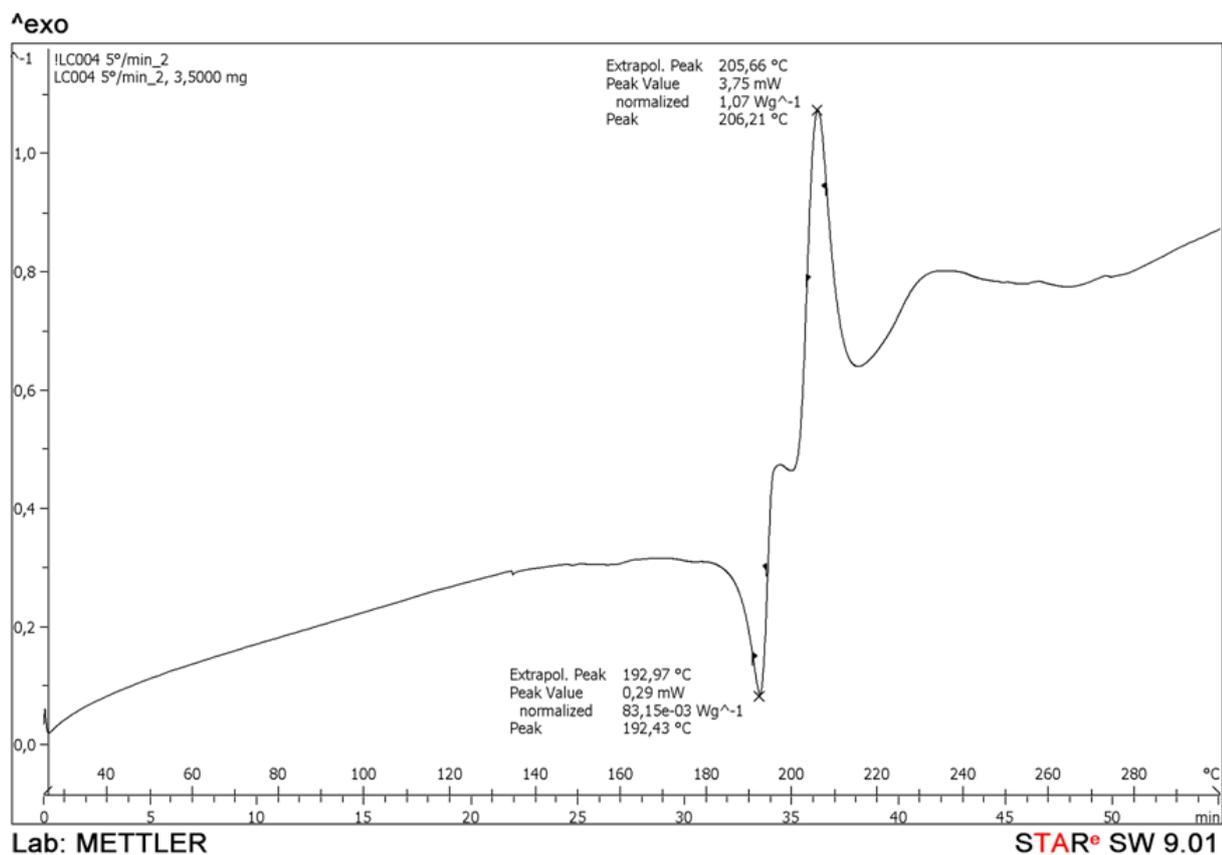


Figure S3. DSC Thermograph (5 °C/min) of the ligand **3** showing that melting occurs at *ca.* 193 °C then decomposition occurs at 206 °C.

Single crystal X-ray diffraction data for the ligand **3**:

Single crystals of **3** were grown from a solution of ethyl acetate on evaporation for 5 days at RT. $C_{24}H_{10}F_8I_2N_2O_2$, Mr = 764.14, triclinic, space group $P-1$, $a = 9.3175(6)\text{\AA}$, $b = 10.3237(6)\text{\AA}$, $c = 13.5796(7)\text{\AA}$, $\alpha = 68.372(2)^\circ$, $\beta = 74.546(3)^\circ$, $\gamma = 85.996(3)^\circ$, $V = 1169.78(12)\text{\AA}^3$, $T = 103\text{ K}$, $Z = 2$, $\rho_{\text{calcd}} = 2.169\text{ g cm}^{-3}$, 4438 unique reflections out of 5060 with $I > 2\sigma(I)$, 343 parameters, $2.12 < \theta < 28.67$, final R factors $R_1 = 0.0468$ and $wR_2 = 0.1299$.

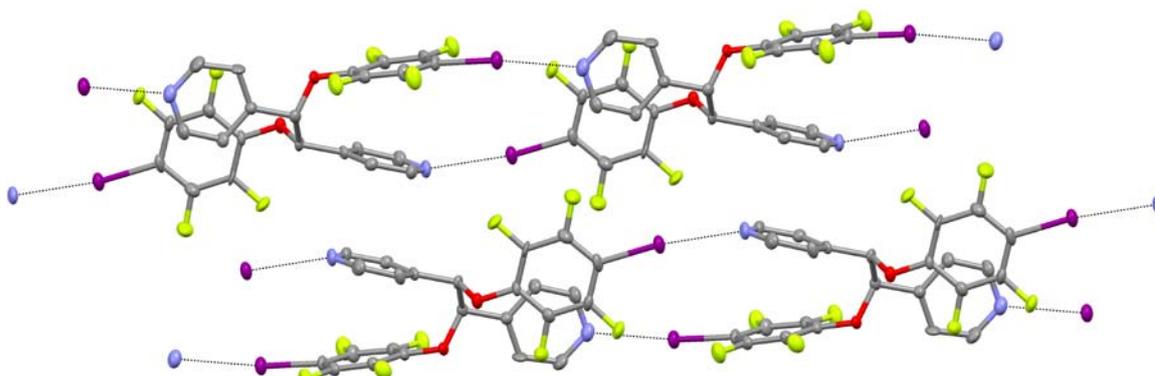


Figure S4. Partial view (ellipsoid representation) of the crystal packing of ligand **3**. Dashed lines indicate halogen bonding. Colour code: Carbon: gray; Nitrogen: blue; Oxygen: red; Fluorine: yellow; Iodine: purple; Hydrogen: light gray. For detailed geometrical information regarding hydrogen and halogen bonding see the Crystallographic section.

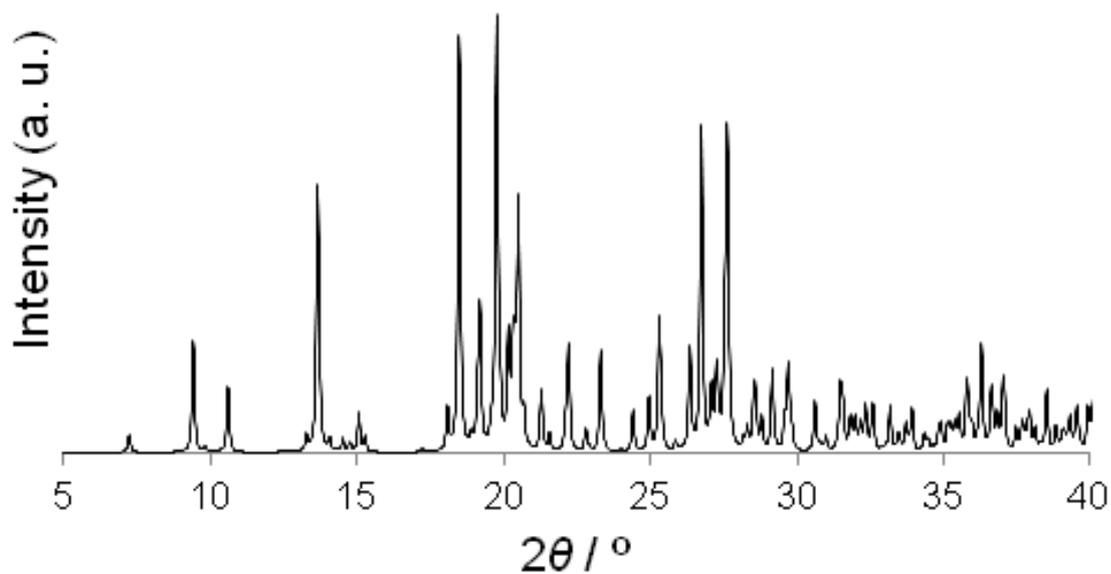


Figure S5. Simulated PXRD pattern of **3** (obtained from single crystal X-ray diffraction data).

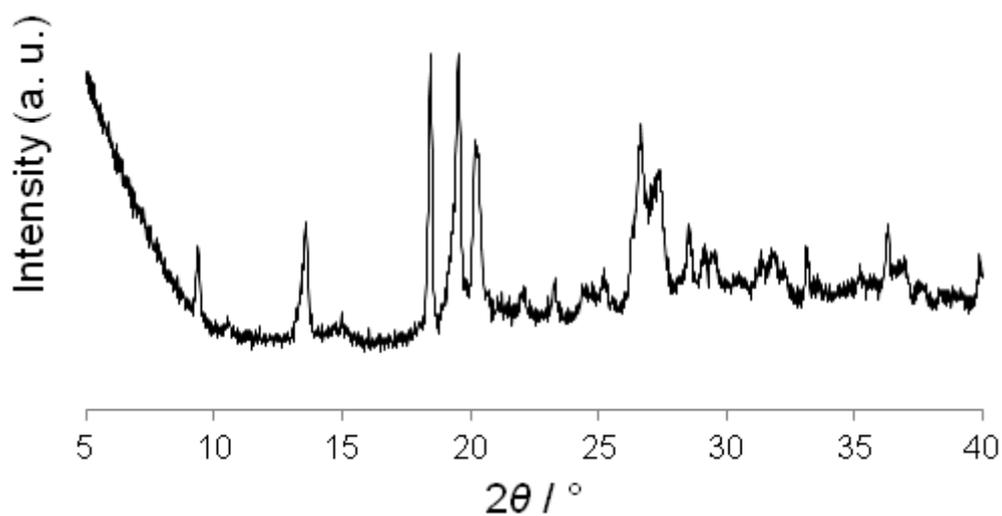


Figure S6. Experimental PXRD pattern of **3** (obtained from the powder after column chromatography).

Preparation of a methanol solution of HI.

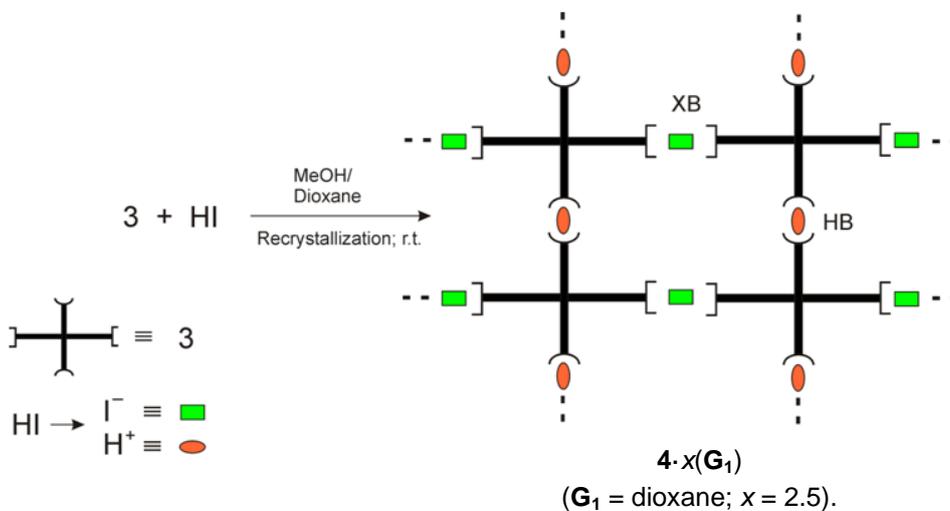
1 mL of a water solution of HI (55%, Aldrich) and 15 mL of MeOH were mixed. Excess sodium sulphate was added (to remove water). Filtration of the resulting system afforded a clear solution containing HI. This solution was immediately used to prepare the hydroiodide salt of **3**.

Preparation of crude hydroiodide of ligand 3.

0.5 mL of a freshly prepared solution of HI methanol solution (prepared as described above) were added dropwise and under vigorous stirring to a solution of 34 mg of the ligand **3** in 6 mL of a 2:1 mixture of MeOH and toluene. The solution turned dark brown and stirring was continued. After *ca.* 30 min., a fine yellow solid began to form and it was filtered after 3 hours.

ESI-Mass: calcd exact mass for **3**·HI [C₂₄H₁₀F₈I₂N₂O₂ HI] 891.78. Ion polarity: negative; *m/z* found [M+I]⁻ 890.8.

Preparation of $4 \cdot x(\mathbf{G}_1)$ ($\mathbf{G}_1 \equiv$ dioxane; $x = 2.5$).



The crude hydroiodide of **3** (18 mg) was dissolved in MeOH (4 mL) at room temperature and the solution was exposed to vapours of dioxane in a sealed jar. Large block crystals were obtained after 3 days.

$4 \cdot x(\mathbf{G}_1)$ ($x=2.5$) was kept at 0.1 mmHg for 24h for solvent removal. Elemental analysis of $4 \cdot x(\mathbf{G}_1)$ ($x=2.5$) after complete evacuation of the guest solvent: Calcd for $\text{C}_{24}\text{H}_{10}\text{F}_8\text{I}_2\text{N}_2\text{O}_2 \cdot \text{HI}$: C, 32.31, H, 1.24; N, 3.14; Found: C, 32.4; H, 1.3; N, 3.1.

Single crystal X-ray diffraction data for organic framework 4·x(G₁):

C₂₄H₁₁N₂O₂F₈I₂⁺Γ·2.5(C₄H₈O₂), Mr=1112.31, triclinic, space group *P*-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) Å³, *T* = 173 K, *Z* = 2, ρ_{calcd} = 1.868 g cm⁻³, 5278 unique reflections out of 7669 with *I* > 2σ(*I*), 490 parameters, 2.25 < θ < 26.0, final *R* factors *R*₁ = 0.0453 and *wR*₂ = 0.1089.

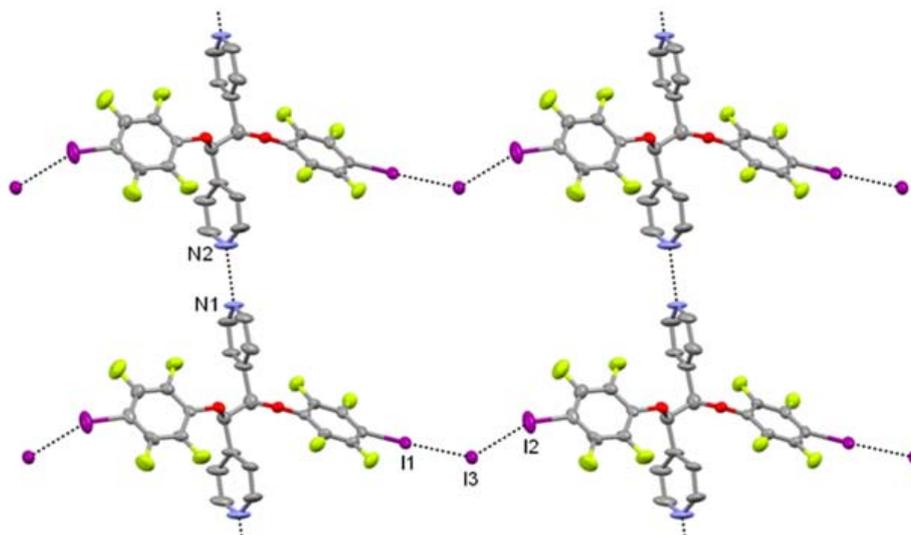


Figure S7. Partial view (ellipsoid representation) of the crystal packing of the organic framework 4·2.5(G₁) showing the approximately rectangular 2D grid formed by halogen and hydrogen bonding (dotted lines). The dioxane guest molecules have been omitted for clarity. Colour codes as in Figure S4. For details on bond and angle geometries see the Crystallographic section.

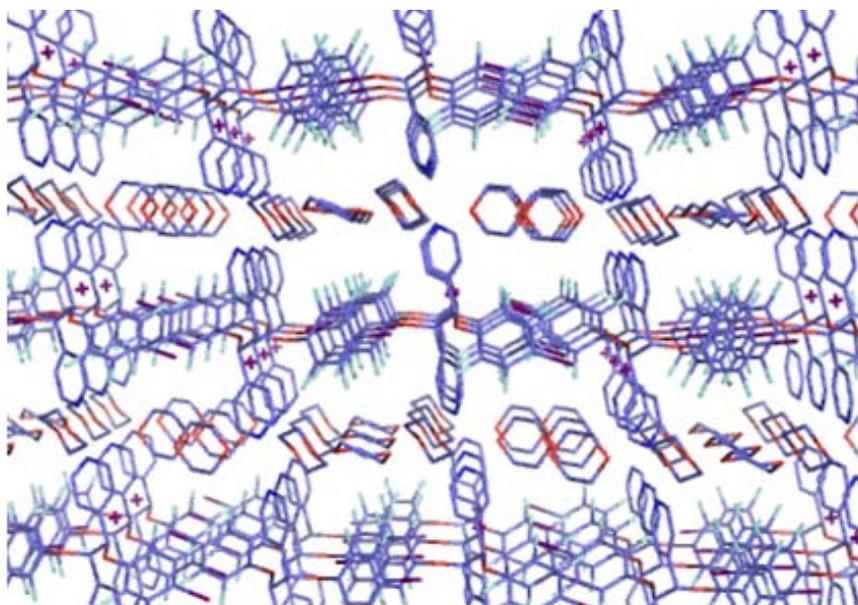


Figure S8. Perspective view of the crystal packing of the organic framework 4·2.5(G₁) along *a* axis (*z*+90°). Guest molecules G₁ (dioxane) fill in the channels. Colour code: Carbon: light blue; Nitrogen: blue; Oxygen: red; Fluorine: light green; Iodine: purple. Hydrogen atoms omitted for clarity.

Guest Exchange Reaction of G_1 for G_2 in $4 \cdot 2.5(G_1)$.

A rectangular single crystal of $4 \cdot 2.5(G_1)$ was immersed in 0.5 mL of 1,3-dibromobenzene for *ca.* 2 h at room temperature. Upon immersion the single crystal turned slightly brown, but maintained single crystallinity allowing for single crystal X-ray analysis. The data collection was carried out at 90 K.

Single crystal X-ray diffraction data for $4 \cdot 2(G_2)$:

$C_{24}H_{11}N_2O_2F_8 I_2^+ \Gamma^- \cdot 2(C_6H_4Br_2)$, Mr = 1363.87, triclinic, space group $P-1$, $a = 9.2497(4) \text{ \AA}$, $b = 11.8502(6) \text{ \AA}$, $c = 19.1570(10) \text{ \AA}$, $\alpha = 92.354(3)^\circ$, $\beta = 94.750(3)^\circ$, $\gamma = 98.469(3)^\circ$, $V = 2066.76(17) \text{ \AA}^3$, $T = 93 \text{ K}$, $Z = 2$, $\rho_{\text{calcd}} = 2.192 \text{ g cm}^{-3}$, 9168 unique reflections out of 13288 with $I > 2\sigma(I)$, 645 parameters, $2.39 < \theta < 32.65$, final R factors $R_1 = 0.0561$ and $wR_2 = 0.1559$.

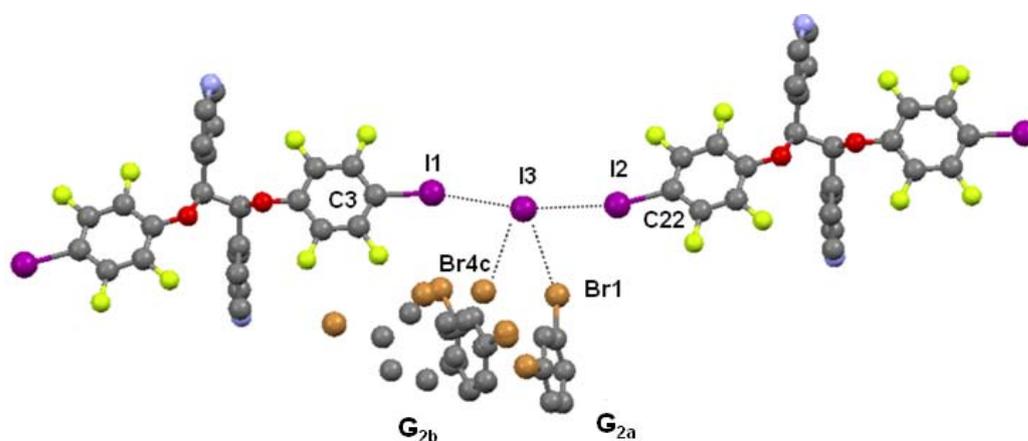


Figure S9. Partial view (ball and stick representation) of the crystal packing of the organic framework $4 \cdot 2(G_2)$. Halogen bonds in black dotted lines. Colour codes: Bromine: light brown; other atoms as in Figure S4. Hydrogen atoms have been omitted for clarity. One guest molecule of 1,3-dibromobenzene is ordered (G_{2a}) while the other is disordered (G_{2b}). Halogen bond distances and angles between guest molecules and iodide anion are: C–Br1 \cdots I3 $^-$ 3.689(2) Å and 156.7(2) $^\circ$; C–Br4c \cdots I3 $^-$ 3.665(3) Å and 156.3(3) $^\circ$.

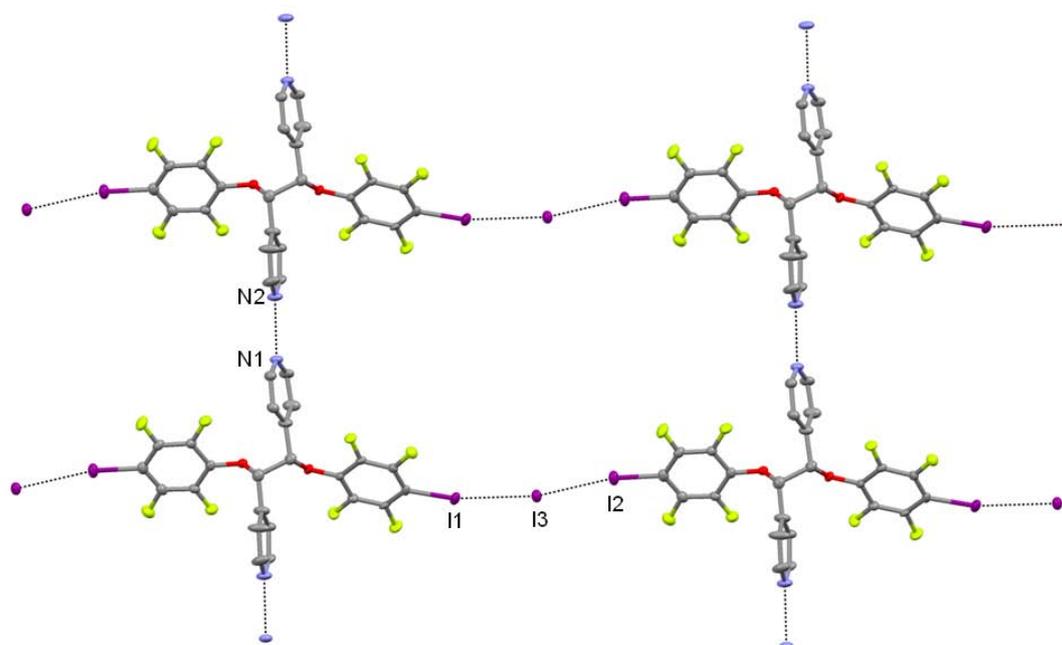


Figure S10. Partial view (ellipsoid representation) of the crystal packing of the organic framework **4·2(G₂)** showing the approximately rectangular 2D grid formed by halogen and hydrogen bonding (dotted lines). The dibromobenzene guest molecules have been omitted for clarity. Colour codes as in Figure S4. For details on bond and angle geometries see the Crystallographic section. Note the similarity in the packing of **4·2.5(G₁)** (Figure S10) and **4·2(G₂)**. Note also that halogen and hydrogen bonds and the architecture thereof are robust enough to allow for substituting the new guest (**G₂**) for the old guest (**G₁**) in a single-crystal-to-single-crystal process.

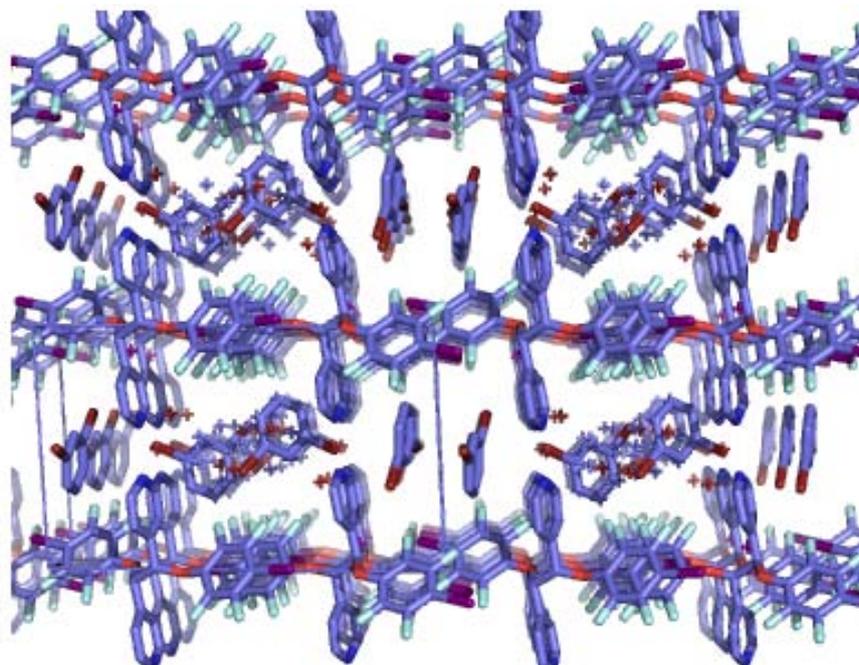


Figure S11. Perspective view of the crystal packing of the organic framework **4·2(G₂)** along *a* axis ($z+90^\circ$). Guest molecules **G₂** (1,3-dibromobenzene) fill in the channels. Colour code: bromine: brown; other atoms as in Figure S8. Hydrogen atoms omitted for clarity.

Guest Exchange Reaction of G_1 for G_3 in $4 \cdot 2.5(G_1)$

A single crystal of $4 \cdot 2.5(G_1)$ was immersed in 2 mL of nitrobenzene for 12 h at room temperature. Then it was mounted in the goniometer for single crystal X-ray analysis. Interestingly, the single crystal maintained integrity and diffracted well.

Single crystal X-ray diffraction data for $4 \cdot 2(G_3)$:

$C_{24}H_{11}N_2O_2F_8I_2^+ \Gamma^- \cdot 2(C_6H_5NO_2)$, $M_r = 1138.27$, triclinic, space group $P-1$, $a = 9.004(2) \text{ \AA}$, $b = 11.872(2) \text{ \AA}$, $c = 19.283(4) \text{ \AA}$, $\alpha = 94.51(2)^\circ$, $\beta = 91.37(2)^\circ$, $\gamma = 107.65(2)^\circ$, $V = 1955.7(7) \text{ \AA}^3$, $T = 103 \text{ K}$, $Z = 2$, $\rho_{\text{calcd}} = 1.933 \text{ g cm}^{-3}$, 3504 unique reflections out of 4332 with $I > 2\sigma(I)$, 627 parameters, $2.38 < \theta < 24.41$, final R factors $R_1 = 0.0830$ and $wR_2 = 0.1941$.

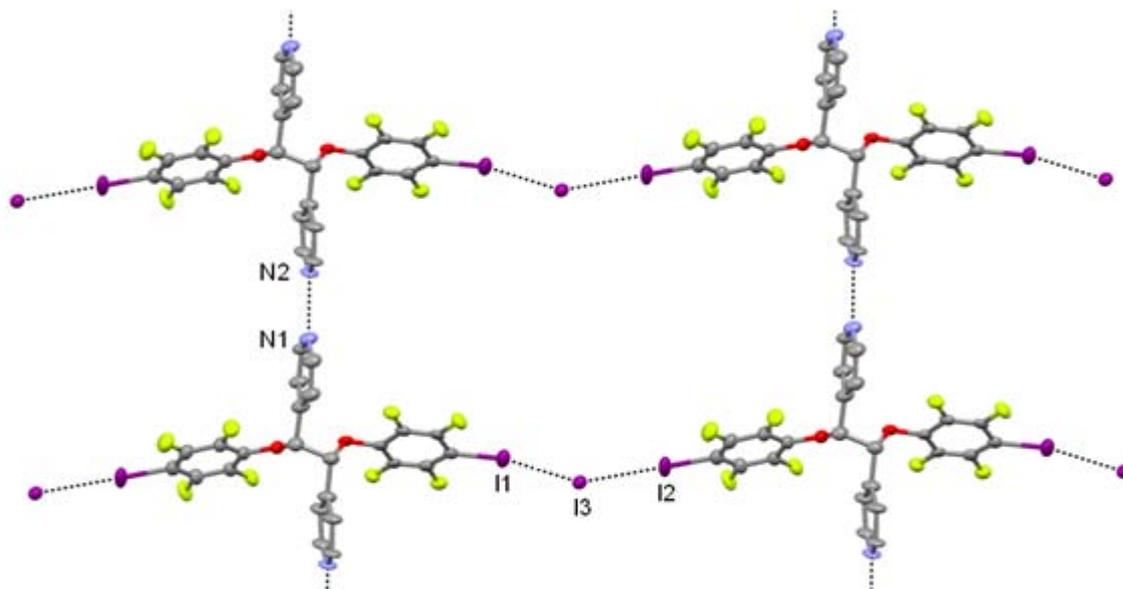


Figure S12. Partial view (ellipsoid representation) of the crystal packing of the organic framework in $4 \cdot 2(G_3)$ showing the approximately rectangular 2D grid formed by halogen and hydrogen bonding (dotted lines). For details on bond and angle geometries see the Crystallographic section. The nitrobenzene guest molecules have been omitted for clarity. Colour codes as in Figure S4. Note the similarity in the packing of $4 \cdot 2.5(G_2)$, $4 \cdot 2(G_2)$, and $4 \cdot 2(G_3)$. Note also that once again halogen and hydrogen bonds and the architecture thereof are robust enough to allow for substituting the new guest (G_3) for the old guest (G_1) in a single-crystal-to-single-crystal process.

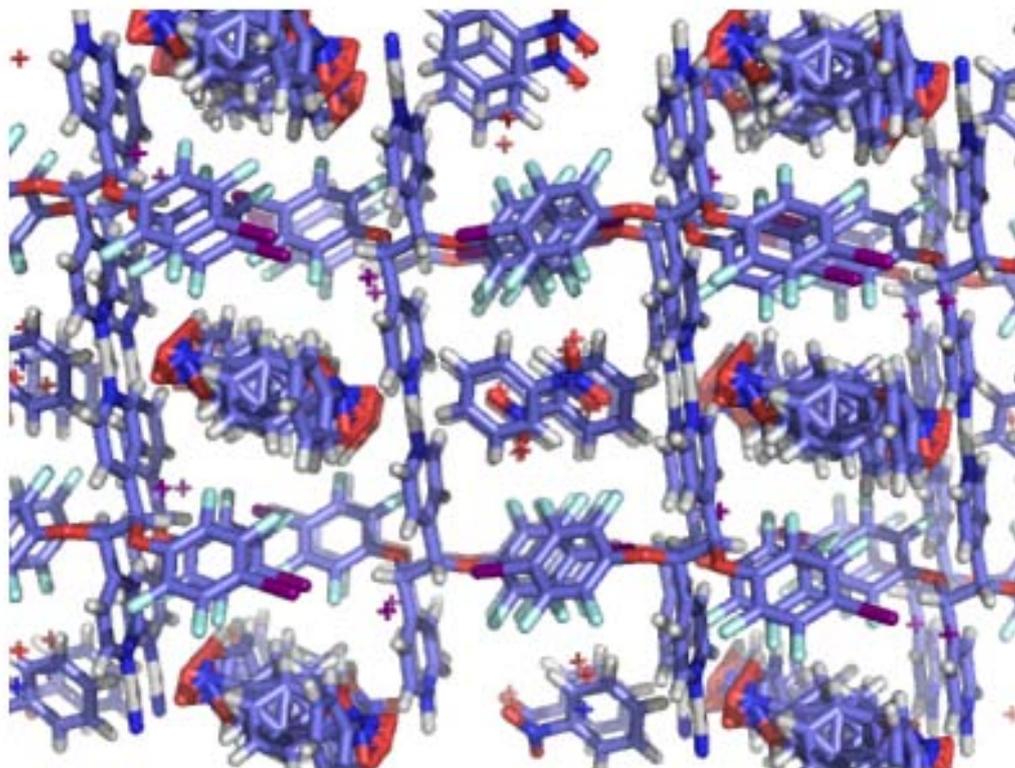


Figure S13. Perspective view of the crystal packing of the organic framework **4·2(G₃)** along *a* axis ($z+90^\circ$). Nitrobenzene molecules are severely disordered while the host framework is not. Colour code as in Figure S8.

Crystallographic Section

Table S1. Crystallographic Information

	3	4·2.5(G₁)	4·2(G₂)	4·2(G₃)
Formula	C ₂₄ H ₁₀ F ₈ I ₂ N ₂ O ₂	C ₂₄ H ₁₁ N ₂ O ₂ F ₈ I ₂ ⁺ , 2.5(C ₄ H ₈ O ₂),I ⁻	C ₂₄ H ₁₁ N ₂ O ₂ F ₈ I ₂ ⁺ , 2(C ₆ H ₄ Br ₂),I ⁻	C ₂₄ H ₁₁ N ₂ O ₂ F ₈ I ₂ ⁺ , 2(C ₆ H ₅ NO ₂),I ⁻
Formula weight	764.14	1112.31	1363.87	1138.27
Temperature K	103(2)	173(2)	93(2)	103(2)
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
a (Å)	9.3175(6)	9.3334(16)	9.2497(4)	9.004(2)
b (Å)	10.3237(6)	11.853(2)	11.8502(6)	11.872(2)
c (Å)	13.5796(7)	18.412(3)	19.1570(10)	19.283(4)
α (°)	68.372(2)	96.076(12)	92.354(3)	94.51(2)
β (°)	74.546(3)	96.664(12)	94.750(3)	91.37(2)
γ (°)	85.996(3)	99.784(13)	98.469(3)	107.65(2)
Volume (Å³)	1169.78(12)	1977.2(6)	2066.76(17)	1955.7(7)
Z	2	2	2	2
Dimension [mm³]	0.10 x 0.16 x 0.18	0.17 x 0.18 x 0.36	0.6 x 0.12 x 0.24	0.13 x 0.16 x 0.18
Density (gcm⁻³)	2.169	1.868	2.192	1.933
μ (mm⁻¹)	2.780	2.456	6.206	2.485
F (000)	724	1072	1272	1088
Tmin, Tmax	0.6037, 0.7458	0.3789, 0.4619	0.2764, 0.3649	0.4629, 0.5694
θ_{min, max} (°)	2.12, 28.67	2.25, 26.0	2.39, 32.65	2.38, 24.41
h_{min, max}	-11, 12	-10, 11	-13, 13	-10, 10
k_{min, max}	-11, 13	-14, 13	-17, 17	-12, 13
l_{min, max}	0, 18	-22, 22	-27, 27	-21, 15
No. of reflections meas.	5060	7669	13288	4332
No. unique reflections.	4438	5278	9168	3504
No of parameters	343	490	645	627
No of restraints	-	1	691	658
R_{all}, R_{obs}	0.0536, 0.0468	0.0833, 0.0453	0.0926, 0.0561	0.1049, 0.0830
wR_{2-all}, wR_{2-obs}	0.1299, 0.1232	0.1089, 0.0929	0.1559, 0.1404	0.1941, 0.1806
Δρ_{max, min} (eÅ⁻³)	-1.806, 2.285	-1.368, 1.379	-1.941, 3.454	-1.563, 1.275
G.o.F	1.014	1.076	1.059	1.254
CCDC No.	866321	866318	866320	866319

G₁: dioxane; G₂: 1,3-dibromobenzene; G₃: nitrobenzene

Table S1.1. HB parameters

	N...H ⁺ ...N	
	Distance D...A (Å)	Angle D...H...A (°)
4·2.5(G₁)	2.657(8)	172(7)
4·2(G₂)	2.665(8)	165(2)
4·2(G₃)	2.6759(17)	176(7)

Table S1.2. XB geometrical parameters

	I...I...I		
	Distance I...I (Å)	Angle C-I...I (°)	Angle I...I...I (°)
4·2.5(G₁)	3.3601(8) I1...I3	173.80(20) C3-I1...I3	146.07(1) I1...I3...I2
	3.6012 (9) I2...I3	156.89(23) C22-I2...I3	
4·2(G₂)	3.4596(6) I1...I3	166.40(17) C3-I1...I3	167.81(2) I1...I3...I2
	3.4172(6) I2...I3	166.61(19) C22-I2...I3	
4·2(G₃)	3.5022(21) I1...I3	160.49(46) C3-I1...I3	140.33(5) I1-I3-I2
	3.4159(19) I2...I3	177.94 (58) C22-I2...I3	

Description of the channels

Shortest contacts along the channels. All short contacts are through centres of symmetry; F...F contacts are nearly perpendicular to C...C and H...H.

Table S1.3 Channel B (x,1,1)

Mean x	Atom1	Equiv. position	Atom2	Equiv. position	d_{ij}	dr_{ij}^{\S}
0	F2	x,y,x	F2	-x,-y,2-z	8.37	5.43
0	H10	x,y,x	H10	2-x,2-y,2-z	7.02	4.62
0	C10	x,y,x	C10	2-x,2-y,2-z	8.59	5.19
0.5	F4	x,y,x	F4	1-x,2-y,2-z	8.09	5.17
0.5	C10	x,y,x	C10	1-x,2-y,2-z	8.43	5.03

Table S1.4 Channel A (x,0,0.5)

0	C16	x,y,x	C16	-x,-y,1-z	11.42	8.02
0	F7	-1+x,-1+y,x	F7	1-x,1-y,1-z	6.92	3.98
0	H16	-1+x,y,x	H16	1-x,-y,1-z	9.83	7.43
0.5	F4	x,y,x	F4	1-x,-y,-z	8.09	5.17
0.5	C11	x,-1+y,x	C11	1-x,1-y,1-z	9.10	5.70
0.5	H11	x,-1+y,x	H11	1-x,1-y,1-z	7.93	5.53

Table S1.5 Channel C (0,0,z)

0.5	F7	x,y,x	F7	2-x,2-y,1-z	6.92	3.98
0.442	F7	x,y,x	F8	2-x,2-y,1-z	6.71	3.77
0.754	C10	x,y,x	H16	1+x,1+y,z	8.03	4.63
0.0	F4	x,y,x	F4	1-x,-y,-z	8.09	5.17

$$^{\S} dr_{ij} = d_{ij} - RvdW_i - RvdW_j$$