A three-dimensional cubic halogen-bonded network

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Electronic Supporting Information

S1. Synthesis of 1,3-di(pyridin-4-yl)propane-1,3-dione (bppdH).

5.01 g (0.041 mol) 4-acetylpyridine was dissolved at 0 °C in 100 mL dry THF under N_2. 1.81 g (0.046 mol) sodium amide was added and the resulting suspension was stirred for 10 minutes, changing in colour from white to yellow. 6.26 g (0.041 mol) Ethyl isonicotinate was dissolved in 100 mL dry THF and added dropwise over 20 minutes. The reaction was allowed to warm to room temperature before heating at reflux for 16 h. The reaction was quenched by the slow addition of 100 mL ice water. Aqueous and organic phases were separated and the aqueous phase was acidified to pH 6 with 1 M HCl before washing with chloroform (3x100 mL). The combined organic phases were dried over sodium sulfate and evaporated to dryness. The pale orange crude product was purified by recrystallization from methanol, yielding an off-white crystalline powder (4.39 g, 0.019 mol). 47% yield. ^{1}H NMR ($CDCl_3$): 6.87 (s, 1H), 7.77 (dd, 4H), 8.81 (dd, 4H), 16.15 (s, 1H). This was found to agree with known literature values.[1]

S2. Synthesis of iron(III) complex $[Fe(bppd)_3]$ (1)

This complex was prepared via established literature methods.[1-2] 0.76 g (3 mmol) bppdH was suspended in 10 mL water and dissolved via dropwise addition of 1 M NaOH. $FeCl_3 \cdot 6H_2O$ (0.2 g, 1 mmol) was dissolved in 10 mL water and added dropwise to the ligand solution. This solution was stirred at 40 °C for 2 h, leading to the formation of a red precipitate which was collected by filtration and recrystallized from dichloromethane/toluene, leading to the formation of dark red needle shaped crystals (0.55 g, 0.75 mmol). 67% yield. Selected ATR-FTIR data (cm^{-1}): 3037w, 1575m, 1516s, 1485s, 1413m, 1363s, 1318m, 1299m, 1218w, 1076w, 1060m, 994w, 943w, 850w, 781m, 716m, 692s, 616s. IR spectrum agrees with previously reported data.[1]

S3. Preparation of $[Fe(bppd)_3](1,4\text{-DITFB})_3 \cdot 0.5H_2O$ (3)

An acetone solution (5 mL) of **1** (6.5 mg, 0.009 mmol) was combined with an acetone solution (5 mL) of **2** (10.7 mg, 0.027 mmol). The solution was filtered through a cotton wool plug, then 1 mL water was added and the solution was left to stand until all acetone had evaporated, leaving large, dark red blocks on the base of the reaction vial. A single block was selected directly from the reaction vessel for single-crystal XRD. The remainder was collected by filtration, ground to a fine powder and subjected to powder XRD to confirm phase purity (see section S5). Yield 17.5 mg (0.009 mmol, 100 %).

S4. Crystallography

Crystals were coated with Paratone N oil before mounting. Single crystal X-ray data were collected at 100 K on an Oxford Diffraction GEMINI Ultra diffractometer operating with Mo Kα X-ray radiation generated from a sealed tube. Data reduction was performed using CrysAlis Pro.[3] Empirical absorption corrections were applied using CrysAlis Pro[3] and subsequent computations were carried out using the WinGX graphical user interface.[4] Structure solutions were obtained using SHELXT[5] and refinement was carried out using SHELXL-2014.[5] Reflections observed at angles greater than 50° 2θ were omitted. All non-H atoms were refined using anisotropic displacement parameters. Oxygen atom O7 was refined with an occupancy factor of 0.25 to model a partially present water molecule. All hydrogen atoms with the exception of those bonded to the partially occupied oxygen atom O7 were located in the difference Fourier map and refined isotropically without the use of restraints. Crystal data and refinement details are supplied below. The CIF file has been deposited with the CSD (CCDC reference number 1811141) and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Formula $C_{57}H_{27.50}F_{12}FeI_6N_6O_{6.25}$, M 1941.60, monoclinic, space group $P2_1/c$(#14), a 17.9257(2), b 19.9161(3), c 18.7188(2) Å, β 112.635(2) °, V 6168.06(16) Å^3, D_c 2.091 g cm^{-3}, Z 4, crystal size 0.43 by 0.20 by 0.14 mm, colour red, habit prism, temperature 100(2) K, λ(MoKa) 0.71073 Å, μ(MoKa) 3.339 mm^{-1}, T(Analytical)$_{\min,\max}$ 0.377, 0.662, $2\theta_{\max}$ 50.00, hkl range -21 21, -23 23, -22 22, N 91891, N_{ind} 10839(R_{merge} 0.0298), N_{obs} 9890($I > 2\sigma(I)$), N_{var} 910, residuals* $R1(F)$ 0.0249, $wR2(F^2)$ 0.0712, GoF(all) 1.151, D$\rho_{\min,\max}$ -1.222, 1.248 e$^-$ Å^{-3}.

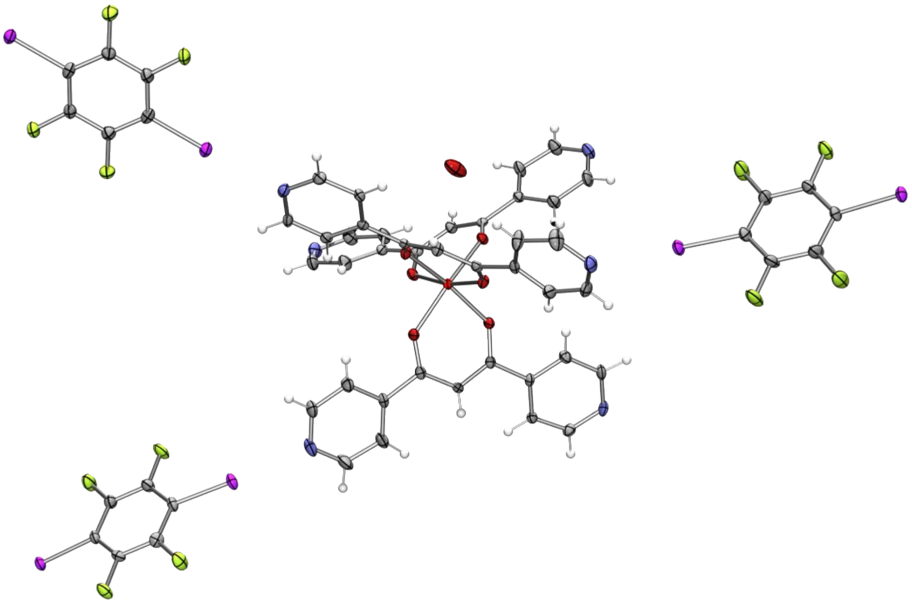

Figure S1: ORTEP[6] representation of **3** (100K). 50% probability ellipsoids are shown.

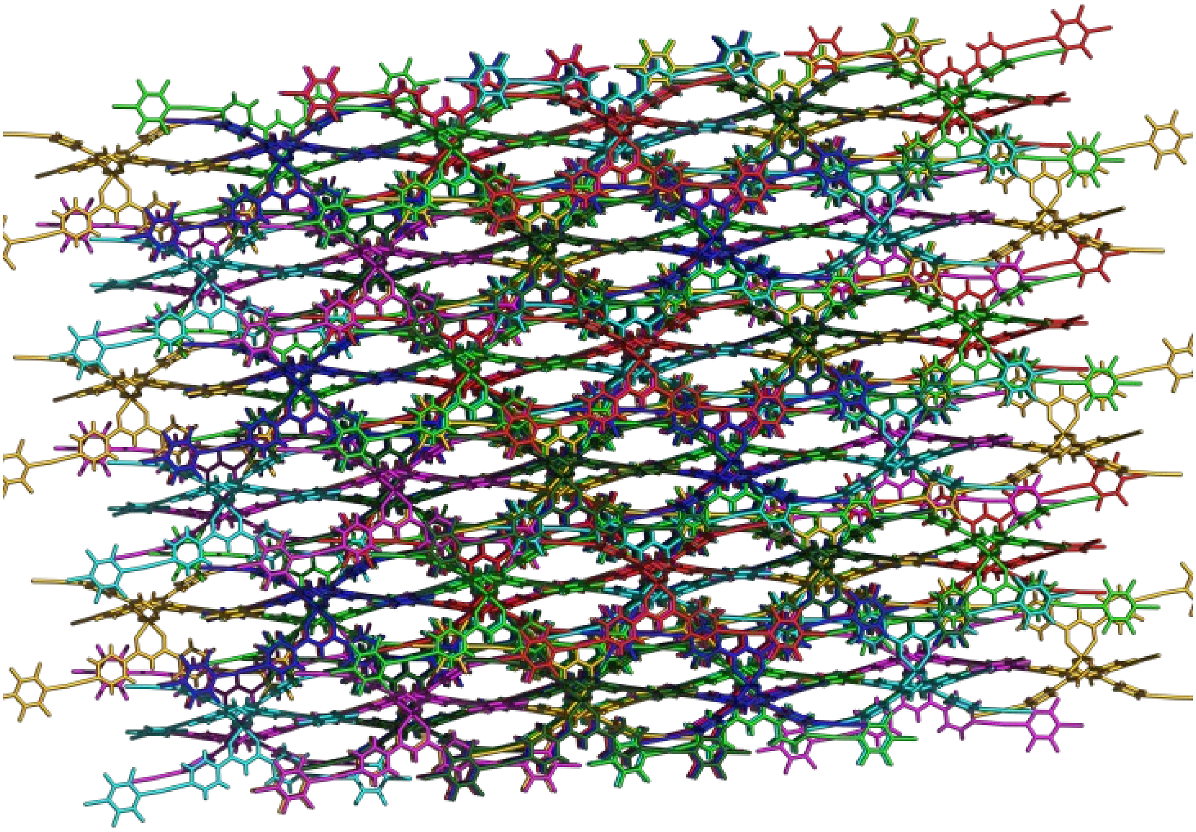

Figure S2: Seven-fold interpenetration of halogen-bonded frameworks in the crystal structure of **3**. Each individual framework is shown in a different color.

S5. Powder X-ray diffraction

Powder X-ray diffraction data were collected on a PANalytical X’Pert PRO MPD diffractometer with a beta filtered (Fe) PW3376/00 Co X-ray tube, operating at 40 kV and 40 mA, Kα1 = 1.789010 Å. A thin film of powdered sample was adhered to a piece of low diffraction silicon wafer (20 mm x 30 mm x 0.6 mm) of low-diffraction silicon wafer with an ultra-thin layer of vasoline. Diffraction data were collected in conventional Bragg-Brentano geometry using a 1D silicon strip detector (X'Celerator). Diffraction patterns were recorded from 5 to 90° 2θ with an approximate 0.047° 2θ step-length over approximately 30 minutes. Powder diffraction data were collected with a programmable divergence slit for a 20 mm irradiation length and a 15 mm axial width. A profile fit was undertaken in FullProf Suite[7] (Figure S3).

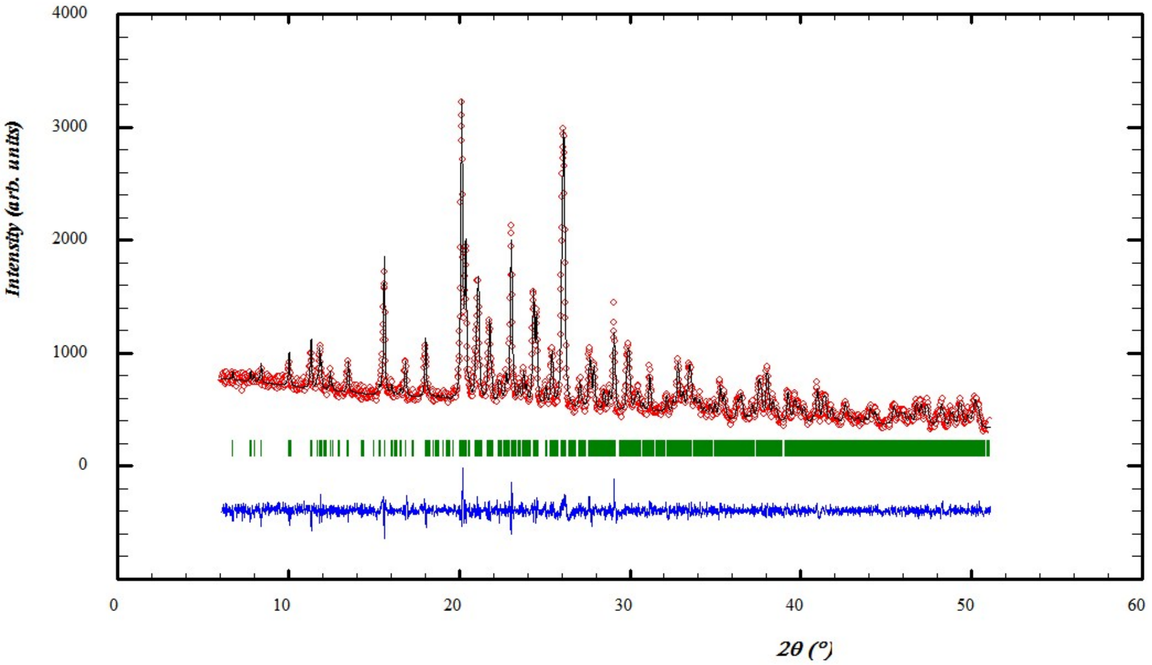

Figure S3: Experimental (red) and simulated (black) PXRD patterns for the crystal structure of **3** at 298 K. Residuals are shown in blue below. Refinement parameters: a = 17.889(10) Å b= 20.442(13) Å c = 18.691(11) Å α= 90 ° β= 112.813(13)° γ= 90 °; χ^2 = 1.73.

(1) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Visconti, M., *CrystEngComm* **2011,** *13* (19), 5891-5902.
(2) Burrows, A. D.; Mahon, M. F.; Renouf, C. L.; Richardson, C.; Warren, A. J.; Warren, J. E., *Dalton. Trans.* **2012,** *41* (14), 4153-4163.
(3) *CrysAlis RED*, Oxford Diffraction Ltd: Abingdon, Oxfordshire, England, 2007.
(4) Farrugia, L. J., *J. Appl. Crystallogr.* **2012,** *45* (4), 849-854.
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