Electronic Supplementary Material (ESI) for ChemComm.

Photoinduced radical Formation in Hydrogen-bonded Organic Frameworks

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Experimental

General procedures

All chemicals were obtained from commercial suppliers, (Alfa Aesar, Fisher Scientific, Sigma-Aldrich, or VWR international) and used without further purification. The synthesis of **2**, which is sensitive to air and moisture, was performed using a standard Schlenk line, with nitrogen as the inert gas. Glassware was flame dried under vacuum and backfilled with dinitrogen.

^{1}H and ^{13}C NMR experiments were carried out using Bruker DPX (400 MHz), Bruker AV(III)400hd (400 MHz), Bruker AV(III) 400 or AV(III) 500 MHz instrument at room temperature. Chemical shifts are reported with respect to the $CDCl_3$ residual peak at 7.26 ppm (^{1}H) and 77.00 ppm (^{13}C) or DMSO-d_6 residual peak at 2.50 ppm. For ^{1}H spectroscopy, splitting patterns are described in brackets after the chemical shift as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, or qd = quartet of doublets.

Electrospray ionisation (ESI) spectra were recorded on a Bruker MicroTOF II spectrometer operating in Flow Injection mode, using methanol or acetonitrile as the solvent. Nominal mass matrix-assisted laser desorption/ionisation (MALDI) spectra were recorded with a Bruker Ultraflex III mass spectrometer using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) as the matrix.

UV-vis reflection spectra were recorded on a Cary 50 UV/Vis spectrometer. The solid sample was sandwiched between two quartz slides for analysis. The absorption spectra were recorded at wavelengths ranging from 230 to 1000 nm.

Powder X-ray diffraction (PXRD) data were collected using The Panalytical Empyrean. The data was collected at room temperature equipped with Cu Kα radiation ($\lambda = 1.54178$ Å) operating at 40 kV and 40 mA and on a diffracted-beam graphite monochromator and in the 2θ range from 3 to 50° with a step size of 0.02°. The data were corrected for background noise by subtracting the background using HighScore Plus software.[S1]

Electron Paramagnetic Resonance

EPR studies were conducted using a Bruker EMX Plus instrument operating at X-Band at room temperature. Standard field calibration off-set was measured with reference to a BDPA standard (g = 2.0003).[S2] In Short; the samples were loaded in to a capillary tube before being irradiated with LEDs at 390 nm – 400 nm for 30 minutes. Followed by spectra acquisition at 2.00 mW using a modulation frequency of 100 kHz and modulation amplitude of 1.0000 G.

Thermogravimetric analysis (TGA)

Data were collected using PerkinElmer TGA8000. The sample was heated to 1000°C under the flow of N_2, at a rate of 10°C/min from room temperature.

X-ray Crystallography

Data was collected on a ROD, Synergy Custom system, HyPix diffractometer. The crystal was mounted in Fomblin oil and kept at 293(2) K or 100(2) K and using monochromated (Cu Kα) irradiation (λ = 1.54178 Å); or at the UK Diamond Light Source I19-1 3-circle diffractometer4 (λ = 0.6889 Å). Using Olex2,[S3] the structure was solved with the ShelXT[S4] structure solution program using Intrinsic Phasing and refined with the ShelXL[S5] refinement package using Least Squares minimisation. Atoms other than hydrogen were refined anisotropically, hydrogen atoms were incorporated as constants according to geometric calculations. When necessary, a solvent mask was applied. The number of electrons in voids were calculated per unit cell and this figure related to the number of disordered molecules. Further details of the refinement are given in the relevant cif.

Molecular Hirshfeld Surfaces

CrystalExplorer[S6] was used to generate the molecular Hirshfeld surfaces at a standard (high) surface resolution The 3D d_{norm} surfaces were mapped over a fix color scale of -0.680 (red) to 4.030 a.u. (blue). The short contacts on the d_{norm} surface are highlighted in red, the longer contacts in blue, and the contacts around the sum of Van der Waals radii are displayed in white.

Synthesis

The synthesis of **1**[S7] and **2**[S8] were carried out according to literature procedures.

Synthesis of HOF ***A***. **1** (14.5 mg, 0.024 mmol) was dissolved in a mixture of 1M NaOH (0.1 mL) and 3.90 mL H_2O in a vial. Separately, **2** (8.5 mg, 0.036 mmol) was dissolved in 4 mL distilled water and a third solution of **1** (14.5 mg, 0.024 mmol) in 4 mL of hot DMF was prepared. The solution of **2** was layered on top of the basic solution of **1**. Finally, the solution of **1** in DMF was layered on top of the solution of **2** and the layers were allowed to mix slowly. The vial containing the mixture was sealed and stored at room temperature with no disturbance. Within a day, a brown ring appears on top of the solution mixture and after two weeks, honey-coloured, plate-like crystals were formed and separated either manually or by filtration (4mg, 27.6%).

Crystal Data for **A**. $C_{23}H_{32}N_5O_{14.5}$ (M = 610.53 g/mol): triclinic, space group P-1 (no. 2), a = 7.08760(10) Å, b = 9.07010(10) Å, c = 22.17710(10) Å, α = 93.4340(10)°, β = 95.1770(10) °, γ = 94.8900(10) °, V = 1411.39(3) Å^3, Z = 2, T = 293(2) K, μ(CuKα) = 1.043 mm^{-1}, $Dcalc$ = 1.437 g/cm^3, GooF = 1.039, 5703 reflections measured (4.01° ≤ 2Θ ≤ 150.288°), 5071 unique

(R_{int} = 0.0360) which were used in all calculations. The final R_1 was 0.0558 (I > 2σ(I)) and wR_2 was 0.1670 (all data).

*Synthesis of HOF **B***. **1** (14.5 mg, 0.024 mmol) was dissolved in a mixture of 1M NaOH (0.1 mL) and 3.90 mL H_2O in a vial. Separately, **2** (45 mg, 0.192 mmol) was dissolved in 8 mL distilled water and then this solution was layered on top of the basic solution of **1**. The vial containing the mixture was sealed and stored at room temperature with no disturbance. Within a day, a yellow cloudy precipitate was observed at the meeting point between the two solutions. After keeping the system for three months a few crystals of honey-coloured plates were formed which were separated manually.

Crystal Data for **B**. $C_{27}H_{29}N_6O_{11}$ (M =613.56 g/mol): triclinic, space group P-1 (no. 2), a = 7.13610(10) Å, b = 9.06550(10) Å, c = 20.9919(3) Å, α = 88.4100(10) °, β = 87.4730(10) °, γ = 83.4320(10) °, V = 1347.44(3) $Å^3$, Z = 2, T = 99.98(10) K, μ(CuKα) = 1.014 mm^{-1}, $Dcalc$ = 1.512 g/cm^3, GooF = 1.051, 56339 reflections measured (8.43° ≤ 2Θ ≤ 158.17°), 5728 unique (R_{int} = 0.0300) which were used in all calculations. The final R_1 was 0.0384 (I > 2σ(I)) and wR_2 was 0.1048 (all data).

*Synthesis of HOF **C***. A solution containing (7.14 mg, 0.012 mmol) of **1** and 0.1 ml of NaOH and 4.7 ml of H_2O was prepared. In a second vial, (5.75 mg, 0.048 mmol) of **2** was dissolved in 9.83 ml of H_2O. The solution of **2** was layered onto the solution of **1** and allowed to mix slowly. Within a day, a yellow cloud begins to appear at the meeting point between the two solutions. It takes about a year for two to three crystals to form.

Crystal Data for **C**. $C_{54}H_{78}N_{13}O_{36}$ (M = 1485.29 g/mol): triclinic, space group P-1 (no. 2), a = 7.8430(4) Å, b = 19.3052(12) Å, c = 23.3588(7) Å, α = 88.568(5) °, β = 81.294(4) °, γ = 86.534(5) °, V = 3489.2(3) $Å^3$, Z = 2, T = 293(2) K, μ(0.6889) = 0.112 mm^{-1}, $Dcalc$ = 1.414 g/cm^3, GooF = 0.8027, 14538 reflections measured (1.71° ≤ 2Θ ≤ 48.416°), 8715 unique (R_{int} = 0.1969) which were used in all calculations. The final R_1 was 0.1372 (I > 2σ(I)) and wR_2 was 0.3727 (all data).

Additional Figures

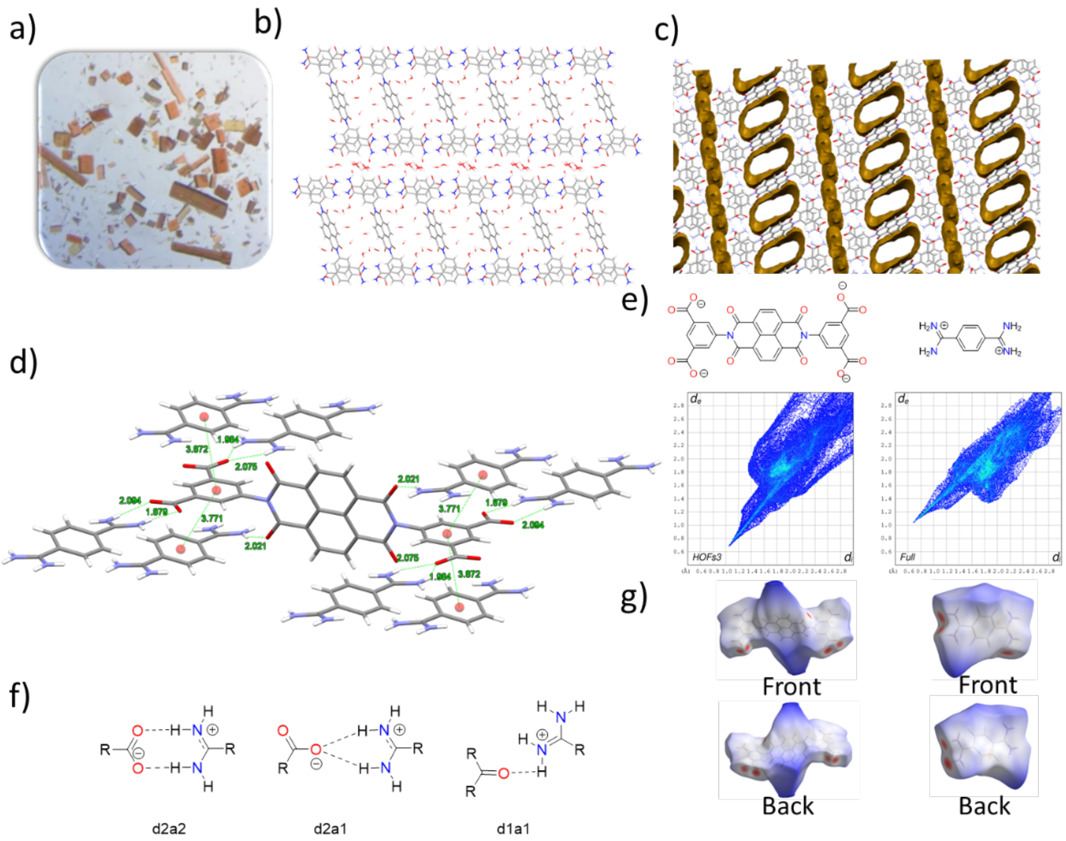

Figure S1. a) Honey-coloured plate crystals of HOF **A** ; b) crystal structure of HOF **A** showing the bilayer structure and guest water molecules; c) two different voids seen in the structure of **A** both between bilayers and forming channels within the framework (voids are visualised in bronze); d) illustration of the different interactions between **1** and **2**; e) the full fingerprint of the Hirshfeld surfaces for **1** and **2**; g) views of the d_{norm} surface for **1** and **2**; and f) the various H-bond geometries observed in **A**.

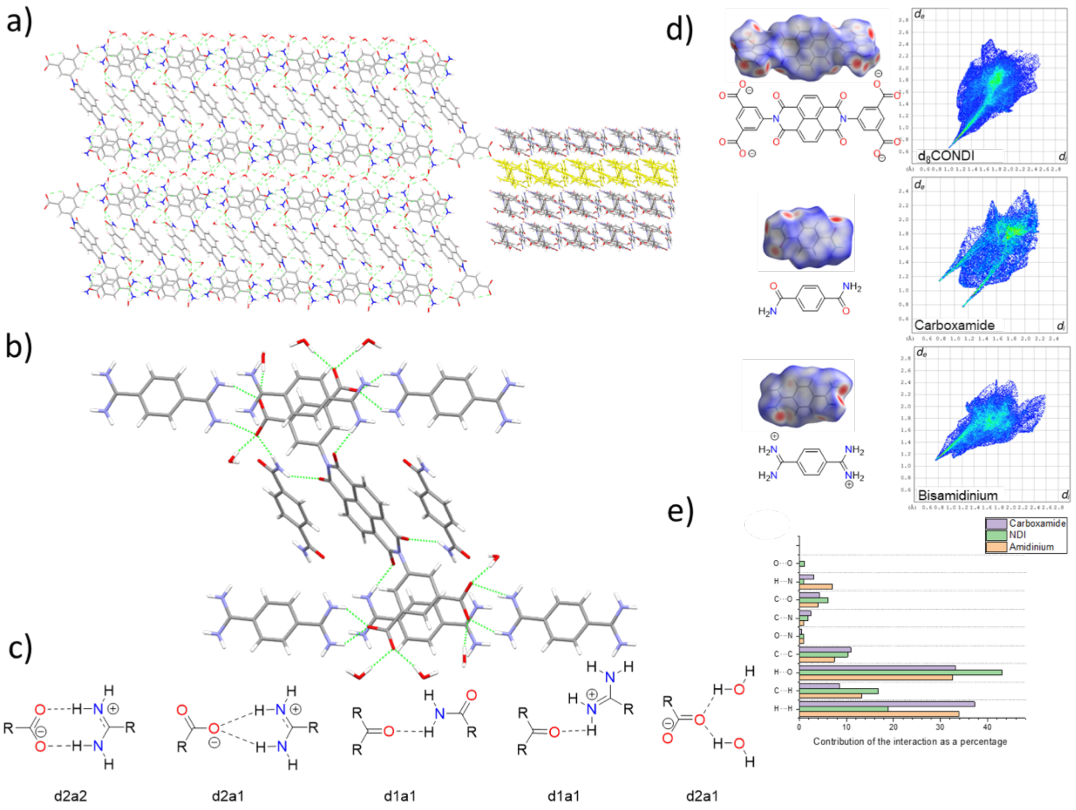

Figure S2. A) Views of the crystal structure of HOF **B** showing the layers of the sheet; b) the H-bonding interactions in the structure of **B**; c) H-bonding interactions observed in **B**; d) d_{norm} surface and 2D figure print plots of **1**, **2** and **3** in **B**; and e) a comparison of the proportions of non-covalent interactions between the different components of **B**.

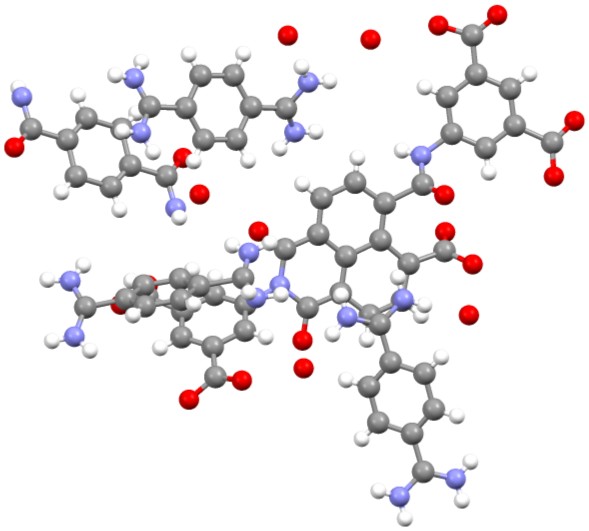

Figure S3. View of the asymmetric unit of the crystal structure of HOF **C**.

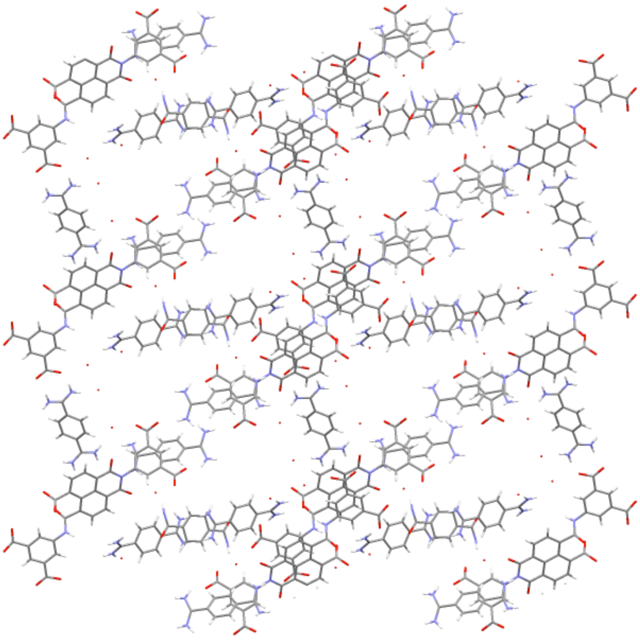

Figure S4. View of the extended structure of **C** formed as a result of a wide variety of hydrogen bonds and π-π interactions.

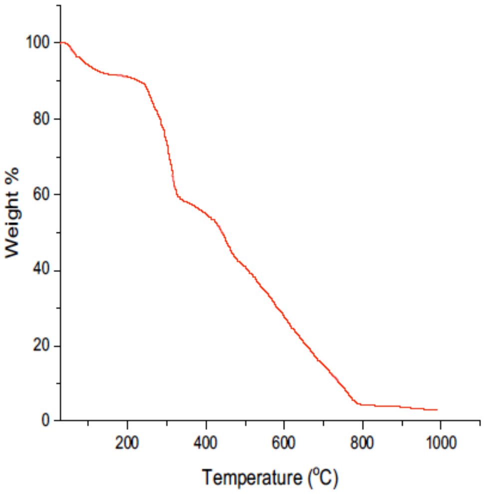

Figure S5. TGA plot for HOF **A** performed under a N_2 environment at a temperature from 25°C to 1000°C.

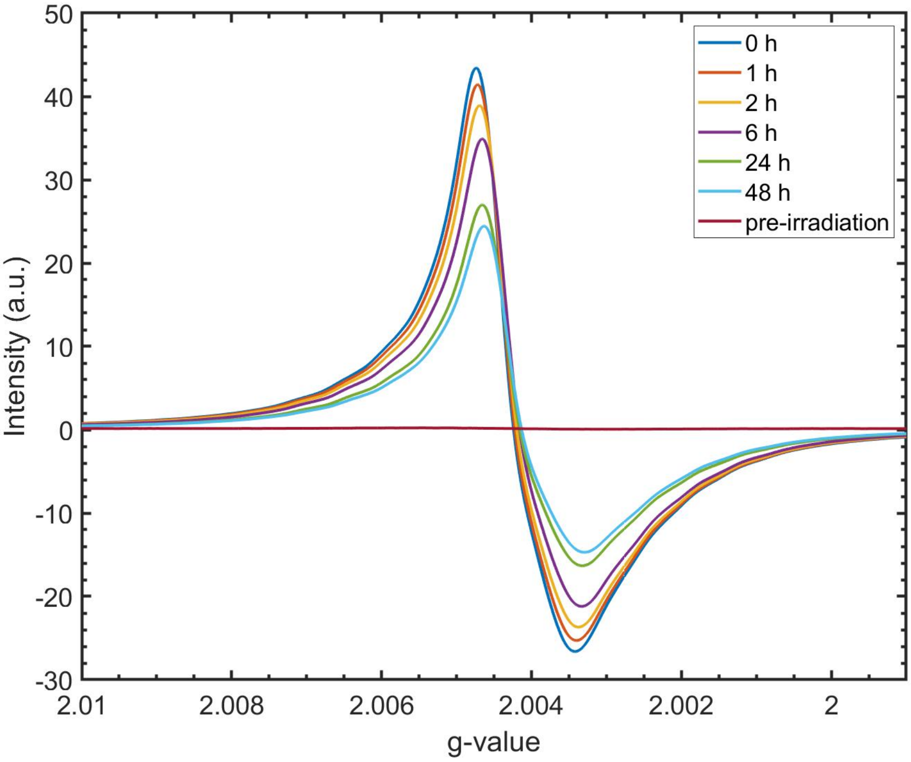

Figure S6. EPR spectra of HOF **A** after irradiating the sample for five minutes under 369 nm light and spectra recorded at regular intervals over a 48 hour period.

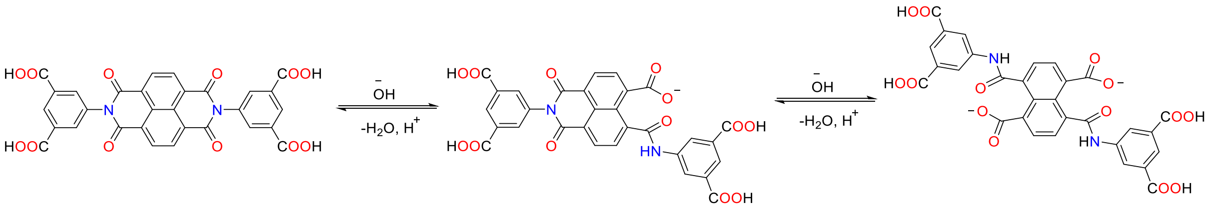

Figure S7. Hydrolysis of **1** with ring-opening of the imide group as observed in HOF **C**.

References

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