**Stereoselective Halogenation of Integral Unsaturated C-C Bonds in Chemically and Mechanically Robust Zr and Hf MOFs**

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The data comprise experimental synthesis and characterisation of a number of Zr and Hf metal-organic frameworks, and their postsynthetic modification by bromination reported. The ability to sequester iodine is also detailed.

Data can be accessed by Bruker TopSpin v3.2 NMR software (NMR data), Avogadro 1.1.1 molecular modelling software or by OriginPro v8.5 (all other data). Images can be opened by any imaging software.

**S1. General Experimental Remarks**

All chemicals and solvents were purchased from Alfa Aesar, Fisher Scientific, Fluorochem, Merck Millipore, Sigma-Aldrich, Strem Chemicals and VWR and used without further purification.

**Powder X-ray Diffraction (PXRD):** PXRD measurements were carried out at 298 K using a PANalytical X’Pert PRO diffractometer (λ (CuKα) = 1.4505 Å) on a mounted bracket sample stage. Data were collected over the range 3–45 °. PXRD patterns were predicted from single crystal data using Mercury 3.5.1.[S1] (University of Glasgow)

**Single Crystal Diffraction (SCXRD):** Data for **(3)**, **(3-Br4)**, **(4)**, **(4-Br4)** and **(5-Br4)** were collected using a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator with VHF Varimax optics (70 μm focus) equipped with an Oxford Cryosystems cryostream device. (EPSRC UK National Crystallography Service)

Data for **(5)** and *trans*,*trans*-peb-I4-H2 were collected using a Bruker ApexII CCD kappa goniometer with a Mo sealed tube source and equipped with an Oxford Cryosystems n-Helix device. Data for *trans*,*trans*-bdb-I4-H2 were collected using a Nonius KappaCCD with a Mo sealed tube source and equipped with an Oxford Cryosystems cryostream device. (University of Glasgow)

**Bromine Analysis:** Carried out by MEDAC Ltd, analytical and chemical consultancy services, Surrey, UK.

**Thermal Gravimetric Analysis (TGA):** Measurements were carried out using a TA Instruments Q500 Thermogravimetric Analyser. Measurements were collected from room temperature to 1000 °C with a heating rate of 10 °C / min under an air atmosphere. (University of Glasgow)

**Nuclear Magnetic Resonance (NMR):** NMR spectra were recorded on either a Bruker AVIII 400 MHz spectrometer or a Bruker AVI 500 MHz Spectrometer and referenced to residual solvent peaks unless stated otherwise. (University of Glasgow)

**Raman Spectroscopy:** Raman spectra were collected on a LabRAM HR system using a Ventus 532 laser system (λ = 532 nm, 100 mW), equipped with a Synapse CCD detection system. The brominated materials were sensitive to the Raman laser (λ = 532 nm, 100 mW), and so the spectra have lower resolution than those of the parent materials. (University of Glasgow)

**Gas Uptake:** N2 adsorption isotherms were carried out at 77 K on a Quantachrome Autosorb iQ gas sorption analyser. Samples were degassed under vacuum at 120 °C for 20 h using the internal turbo pump. BET surface areas were calculated from the isotherms using the Micropore BET Assistant in the Quantachrome ASiQwin operating software. (University of Glasgow)

**Molecular Dynamics:** Minimisation of bdb-Br4-H4 was carried out using the UFF forcefield in a steepest descent, four step update protocol, using the auto-optimisation tool in Avogadro 1.1.1 software suite, with a planar structure imported from Chemdraw Prime version 15 as an input file. (University of Glasgow)