**Functional Versatility of a Series of Zr MOFs Probed by Solid-State Photoluminescence Spectroscopy**

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**SUPPORTING INFORMATION**

Data can be accessed by Bruker TopSpin v3.2 NMR software (NMR data) 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, Maybridge, 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°. Variable temperature PXRD measurements were collected on the same diffractometer but equipped with an Anton Paar HTK 1200N high temperature oven chamber under a trickle flow of Argon. PXRD patterns were calculated from the structure determined from single crystal data using Mercury 3.5.1.[S1] (University of Glasgow)

**Single Crystal X-Ray Diffraction (SCXRD):** Data for L1-Me2, L2-Me2 and**Hf-L5** were collected using a Bruker ApexII CCD kappa goniometer with a Mo sealed tube source and equipped with an Oxford Cryosystems n-Helix device. (University of Glasgow) Data were collected using Bruker Apex2[S2] and processed using *SAINT* v8.34A.[S3]

Data for L3-Me2, L4-Me2 and L5-Me2 were collected using a Nonius KappaCCD with a Mo sealed tube source and equipped with an Oxford Cryosystems cryostream device. (University of Glasgow) Data were collected using Collect[S4] and processed using *SAINT* v8.34A.[S3]

Data for L4-H2, **Zr-L3**, **Hf-L3**, **Zr-L4**, **Hf-L4**, **Zr-L5**, **Zr-L6**, **Hf-L6**, **Zr-L7** and **Hf-L7** 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 were collected using *CrystalClear*-SM Expert 3.1 b27[S5] and processed with *CrysAlisPro* 1.171.38.41.[S6]

Data for **Zr-L2** were collected using a Rigaku OD SuperNova goniometer equipped with a micro-focus Cu sealed tube source and a Pilatus 200K detector equipped with an Oxford Cryosystems cryostream device. (Rigaku OD UK applications laboratory) Data were collected and processed using *CrysAlisPro* 1.171.38.42t.[S6]

The structures were solved using ShelxT[S7] except for L1-Me2, L3-Me2 and L4-H2 which were solved using Superflip.[S8] L2-Me2 and L4-Me2 which were solved using direct methods in ShelxS.[S9]

The structures were refined against *F*2 using full-matrix least-squares refinement using Shelxl2015/16[S10] within OLEX2.[S11] Positional and anisotropic displacement parameters were refined for all non-hydrogen atoms unless stated in the text below each structure given. Hydrogen atoms were placed in geometrically calculated positions and refined as part of a riding model except the OH hydrogen atoms of the MOF clusters which were not included explicitly in the model but are included in the cell contents and all values derived from them.

With the exception of **Zr-L2** all the MOFs crystallise in the space group *Fd-3m* and the asymmetric unit consists of a metal site (Zr or Hf) 0.25 crystallographic occupancy on a *2mm* special position (Wyckoff letter f), 2 oxygen sites in the cluster (Wyckoff letter e, *3m*, 1/6 crystallographic occupancy); a third oxygen site (carboxylate) in a general position and overall a quarter of the linker is crystallographically unique.

**Thermogravimetric Analysis (TGA):** Measurements were carried out using a TA Instruments Q500 Thermogravimetric Analyser. Measurements were collected from room temperature to 800 °C with a heating rate of 10 °C / min under an air atmosphere. (University of Glasgow)

**Nuclear Magnetic Resonance Spectroscopy (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. Measurements were carried out at room temperature unless stated otherwise. (University of Glasgow)

**Gas Uptake:** N2 adsorption and desorption 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 hours 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)

**Pore-Size Distribution (PSD):** Pore size distributions were calculated using the N2 at 77 K on carbon (slit pore, QSDFT, equilibrium model) calculation model within the Quantachrome ASiQwin operating software. (University of Glasgow)

**UV-Vis Spectroscopy:** UV-vis spectra were recorded using a Shimadzu UV-1800 spectrophotometer. (University of Glasgow)

**Solid-State UV-Vis Spectroscopy:** Solid-state UV-vis spectra were recorded using a Shimadzu UV-2600 spectrophotometer. Samples were prepared by evenly distributing small amounts of solid samples across a thin layer of BaSO4. Spectra were recorded over the range  = 250-700 nm. (University of Glasgow)

**Solid-State Photoluminescence Spectroscopy:** Fluorescence emission measurements were carried out using an Edinburgh Instruments FS5 Fluorescence Spectrometer. An SC-10 Front Face Sample Holder was used along with a solid-state cuvette. Solid-state quantum yields (QY) were also performed with the FS5, equipped with a standard xenon lamp (150 W) and a standard PMT detector (R928P, Hamamatsu). QY measurements were performed using SC-30 Integrating Sphere module, and reported values based on triple independent measurements. Excitation wavelengths are noted with each spectrum. (University of Kent, Canterbury)

**Contact Angle Measurements:** Contact angle measurements were performed using an Attension-Theta optical tensiometer (Biolin Scientific), at room temperature. Using a glass microscope slide with a thin recess, powdered sample was loaded into the recess and packed flat until level with the slide. Analysis was performed using the One-Attension software package. (University of Kent, Canterbury)