

Selective incorporation of functional dicarboxylates into zinc metal-organic frameworks

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Supplementary information

Synthesis of 2-iodo-1,4-benzenedicarboxylic acid

2-Iodo-1,4-benzenedicarboxylic acid (H_2bdc-I) was prepared from 2-amino-1,4-benzenedicarboxylic acid *via* the diazonium salt.^{S1}

Synthesis of $[Zn_4O(bdc-I)_3]$

2-Iodo-1,4-benzenedicarboxylic acid (0.100 g, 0.34 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.300 g, 1.0 mmol) were dissolved in DEF (20 cm³) in an Ace pressure tube (Aldrich Chemical Co.) and heated at 95 °C for 72 hours. The resulting pale yellow cubic crystals (0.200 g, 59 %) were separated by filtration and washed with fresh DEF. Found: C, 36.5; H, 4.44; N, 4.89 %. Calc. for $C_{54}H_{75}I_3N_6O_{19}Zn_4$ ($[Zn_4O(bdc-I)_3] \cdot 6DEF$): C, 37.0; H, 4.31; N, 4.79 %.

Powder diffraction patterns showed samples of $[Zn_4O(bdc-I)_3]$ to have limited crystallinity, with the observed peaks matching those simulated from the X-ray crystal structure of $[Zn_4O(bdc-Br)_3]$ (IRMOF-2). Single crystals did not diffract well enough for a complete structural determination to be carried out. However, determination of the unit cell confirmed the crystals were isostructural with $[Zn_4O(bdc-Br)_3]$ (IRMOF-2).

The TGA trace for $[Zn_4O(bdc-I)_3]$ is shown in Figure S1, alongside the trace for $[Zn_4O(bdc-Br)_3]$. The mass loss of approximately 30 % between room temperature and 350 °C is consistent with the loss of 5DEF molecules (calc. 30.6 %).

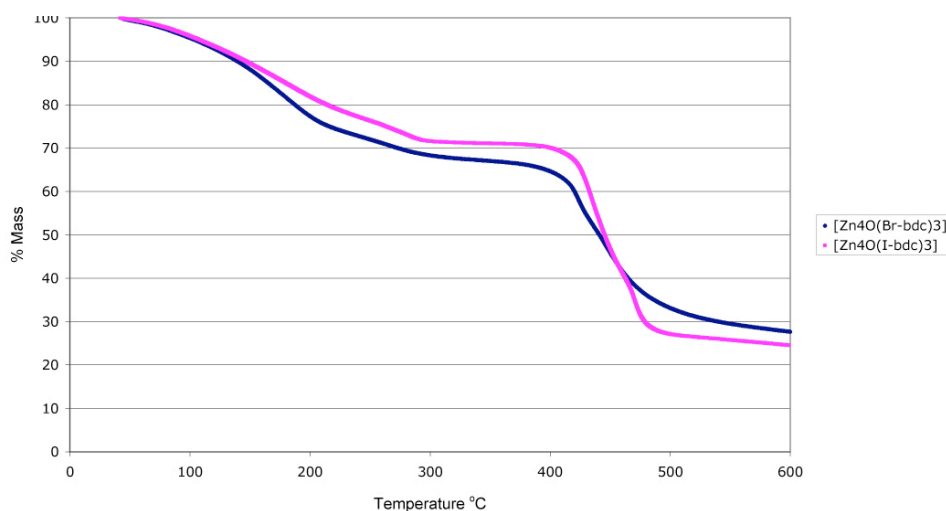


Fig. S1. Thermogravimetric analyses for $[Zn_4O(bdc-I)_3]$ and $[Zn_4O(bdc-Br)_3]$.

The nitrogen adsorption/desorption isotherm for an activated samples of $[\text{Zn}_4\text{O}(\text{bdc-I})_3]$ is shown in Figure S2. The BET surface area for $[\text{Zn}_4\text{O}(\text{bdc-I})_3]$, calculated using the standard BET range ($0.05 < P/P_0 < 0.3$) is $1096 \text{ m}^2 \text{ g}^{-1}$.

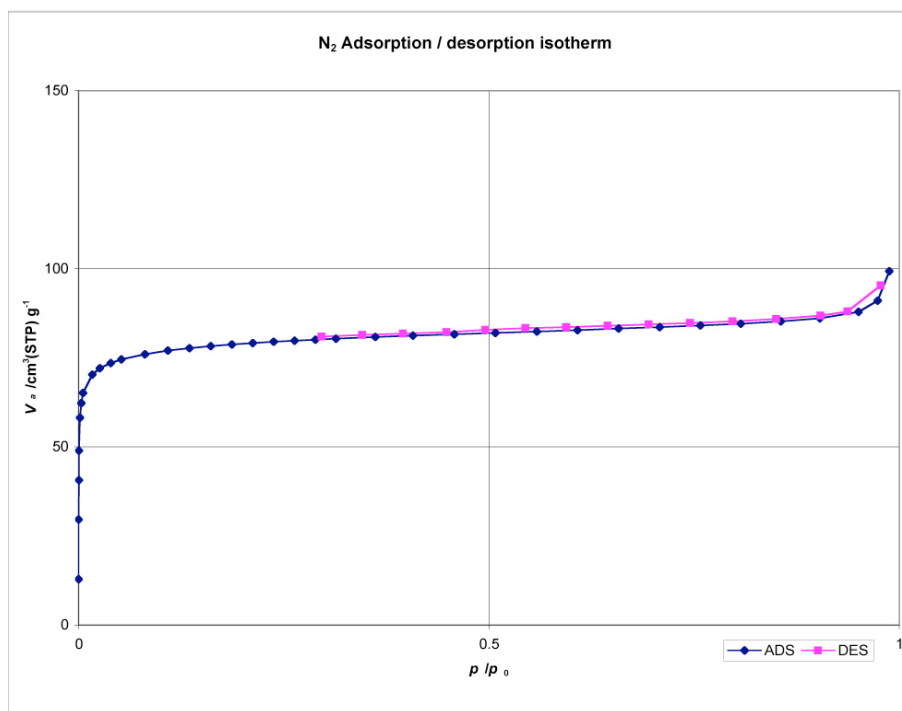


Fig. S2. Nitrogen adsorption/desorption isotherm for $[\text{Zn}_4\text{O}(\text{bdc-I})_3]$.

Synthesis of $[\text{Zn}_4\text{O}(\text{bdc})_{3-x}(\text{bdc-I})_x]$

2-Iodo-1,4-benzenedicarboxylic acid and 1,4-benzenedicarboxylic acid were combined in different ratios (total 0.112 mmol) with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.100 g, 0.34 mmol), dissolved in DEF (5 cm^3) in an Ace pressure tube (Aldrich Chemical Co.) and heated at $95 \text{ }^\circ\text{C}$ for 170 hours. The resulting pale yellow cubic crystals were separated by filtration and washed with fresh DEF. Yield 49-61 %.

The MOFs were digested by sonication in 1.5 cm^3 of a solution of $\text{DMSO-}d_6$ and 0.2 cm^3 of a DCI solution prepared by dissolving 0.023 cm^3 of 35 % DCI/ D_2O solution in 1 cm^3 DMSO. This solution was used directly for ^1H NMR, and was diluted by a factor of 10 in ethanol for mass spectrometry. In the ^1H NMR spectra, the ratio of the dicarboxylic acids was determined through a comparison of the integrals for the doublet observed at δ 7.75 ppm (1H, $\text{H}_2\text{bdc-I}$) and the singlet observed at δ 8.05 ppm (4H, H_2bdc).

ESI-MS (negative mode): m/z 165.0183 (calc. 165.0188 for $[\text{Hbdc}]^-$), 290.9151 (calc. 290.9154 for $[\text{Hbdc-I}]^-$).

Representative X-ray powder diffraction patterns from this series of MC-MOFs are shown in Figure S3.

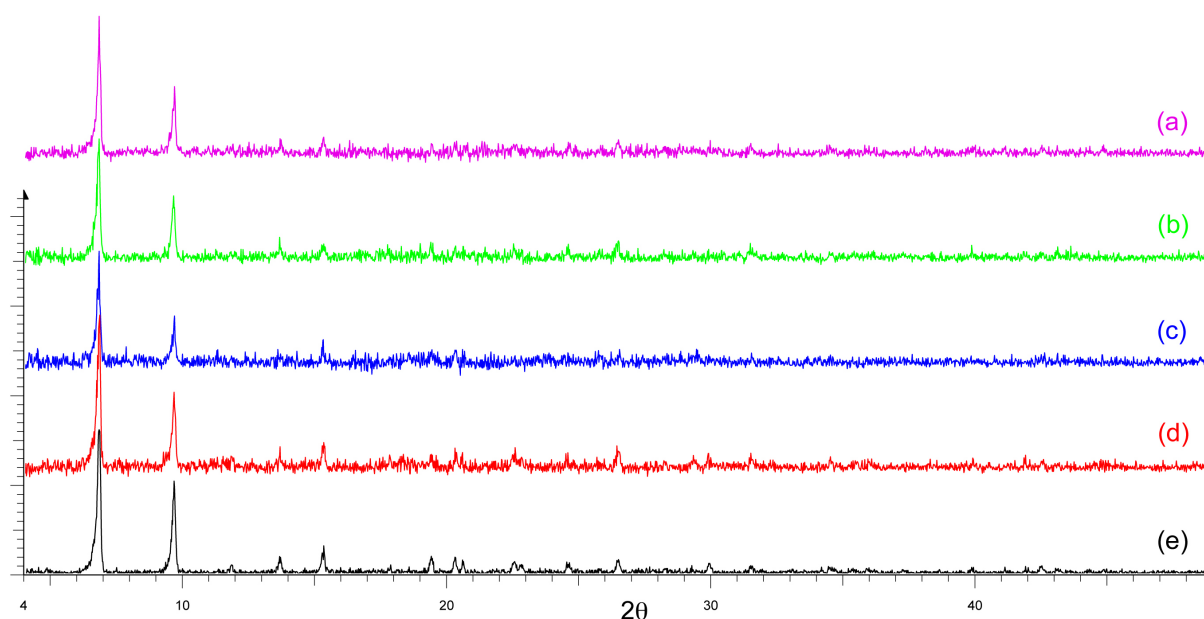


Fig. S3. Powder X-ray diffraction patterns for (a) $[\text{Zn}_4\text{O}(\text{bdc})_{1.19}(\text{bdc-I})_{1.81}]$, (b) $[\text{Zn}_4\text{O}(\text{bdc})_{1.78}(\text{bdc-I})_{1.22}]$, (c) $[\text{Zn}_4\text{O}(\text{bdc})_{0.72}(\text{bdc-I})_{2.28}]$, (d) $[\text{Zn}_4\text{O}(\text{bdc})_{1.57}(\text{bdc-I})_{1.43}]$ and (e) $[\text{Zn}_4\text{O}(\text{bdc})_{2.53}(\text{bdc-I})_{0.47}]$.

Synthesis of $[\text{Zn}_4\text{O}(\text{bdc})_{3-x}(\text{bdc-Br})_x]$

2-Bromo-1,4-benzenedicarboxylic acid and 1,4-benzenedicarboxylic acid were combined in different ratios (total 0.112 mmol) with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.100 g, 0.34 mmol), dissolved in DEF (5 cm³) in an Ace pressure tube (Aldrich Chemical Co.) and heated at 95 °C for 170 hours. The resulting colourless cubic crystals were separated by filtration and washed with fresh DEF. Yield 42-59 %.

The MOFs were digested by sonication in 1.5 cm³ of a solution of $\text{DMSO-}d_6$ and 0.2 cm³ of a DCI solution prepared by dissolving 0.023 cm³ of 35 % DCI/D₂O solution in 1 cm³ DMSO. This solution was used directly for ¹H NMR, and was diluted by a factor of 10 in ethanol for mass spectrometry. In the ¹H NMR spectra, the ratio of the dicarboxylic acids was determined through a comparison of the integrals for the doublet observed at δ 7.83 ppm (1H, H₂bdc-Br) and the singlet observed at δ 8.05 ppm (4H, H₂bdc).

ESI-MS (negative mode): *m/z* 165.0191 (calc. 165.0188 for $[\text{Hbdc}]^-$), 242.9293 (calc. 242.9275 for $[\text{Hbdc-Br}]^-$).

Representative X-ray powder diffraction patterns from this series of MC-MOFs are shown in Figure S4.

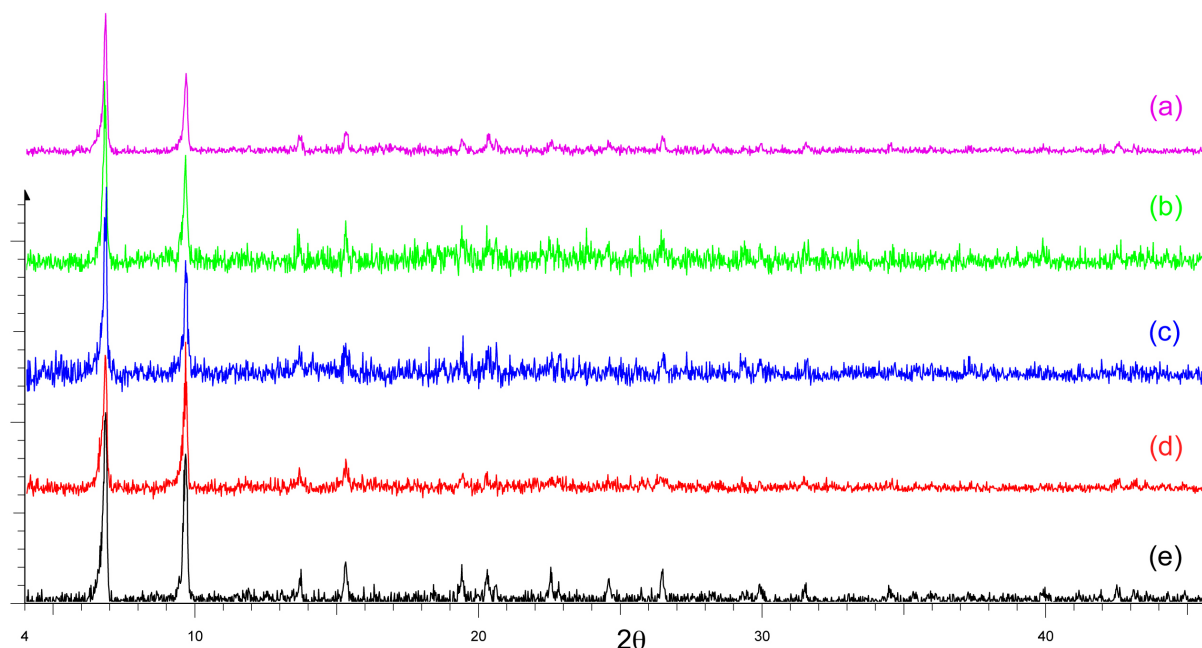


Fig. S4. Powder X-ray diffraction patterns for (a) $[\text{Zn}_4\text{O}(\text{bdc})_{1.45}(\text{bdc-Br})_{1.55}]$, (b) $[\text{Zn}_4\text{O}(\text{bdc})_{2.15}(\text{bdc-Br})_{0.85}]$, (c) $[\text{Zn}_4\text{O}(\text{bdc})_{1.13}(\text{bdc-Br})_{1.87}]$, (d) $[\text{Zn}_4\text{O}(\text{bdc})_{1.87}(\text{bdc-Br})_{1.13}]$ and (e) $[\text{Zn}_4\text{O}(\text{bdc})_{2.78}(\text{bdc-Br})_{0.22}]$.

Synthesis of $[\text{Zn}_4\text{O}(\text{bdc-Br})_{3-x}(\text{bdc-I})_x]$

2-Bromo-1,4-benzenedicarboxylic acid and 2-iodo-1,4-benzenedicarboxylic acid were combined in different ratios (total 0.112 mmol) with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.100 g, 0.34 mmol), dissolved in DEF (5 cm³) in an Ace pressure tube (Aldrich Chemical Co.) and heated at 95 °C for 170 hours. The resulting pale yellow cubic crystals were separated by filtration and washed with fresh DEF. Yield 41-51 %.

The MOFs were digested by sonication in 1.5 cm³ of a solution of DMSO-*d*₆ and 0.2 cm³ of a DCI solution prepared by dissolving 0.023 cm³ of 35 % DCI/D₂O solution in 1 cm³ DMSO. This solution was used directly for ¹H NMR, and was diluted by a factor of 10 in ethanol for mass spectrometry. In the ¹H NMR spectra, the ratio of the dicarboxylic acids was determined through a comparison of the integrals for the doublet observed at δ 7.83 ppm (1H, H₂bdc-Br) and the doublet observed at δ 7.78 ppm (1H, H₂bdc-I).

ESI-MS (negative mode): *m/z* 242.9279 (calc. 242.9293 for $[\text{Hbdc-Br}]^-$), 290.9154 (calc. 290.9145 for $[\text{Hbdc-I}]^-$).

Representative X-ray powder diffraction patterns from this series of MC-MOFs are shown in Figure S5.

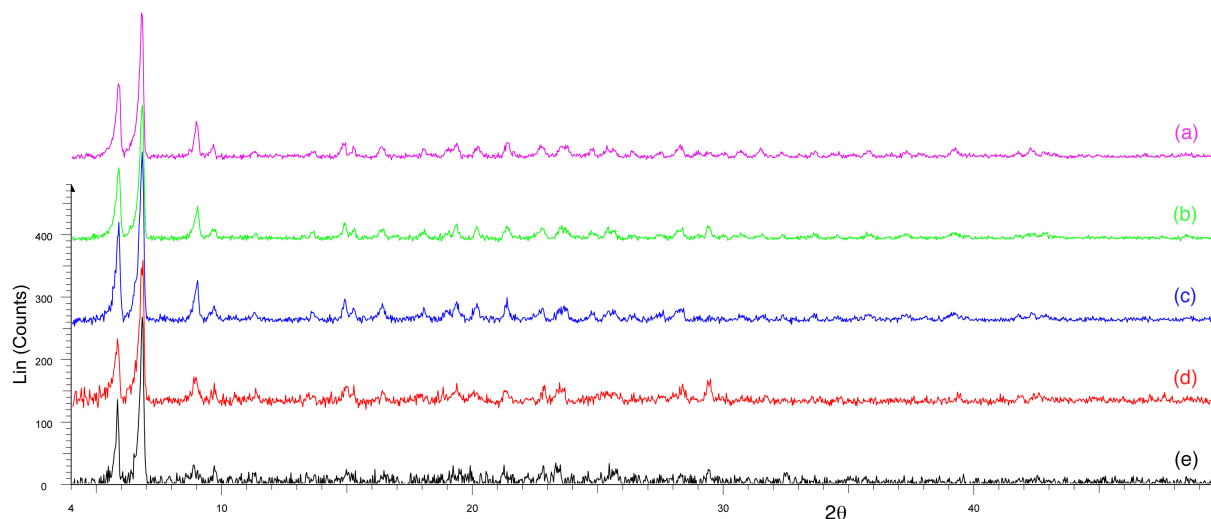


Fig. S5. Powder X-ray diffraction patterns for (a) $[\text{Zn}_4\text{O}(\text{bdc-Br})_{2.58}(\text{bdc-I})_{0.42}]$, (b) $[\text{Zn}_4\text{O}(\text{bdc-Br})_{2.13}(\text{bdc-I})_{0.87}]$, (c) $[\text{Zn}_4\text{O}(\text{bdc-Br})_{1.47}(\text{bdc-I})_{1.53}]$, (d) $[\text{Zn}_4\text{O}(\text{bdc-Br})_{0.93}(\text{bdc-I})_{2.07}]$ and (e) $[\text{Zn}_4\text{O}(\text{bdc-Br})_{0.45}(\text{bdc-I})_{2.55}]$.

Reference

- S1. A. Kommreddy, M. S. Bowsher, M. R. Gunna, K. Botha and T. K. Vinod, *Tetrahedron Lett.*, 2008, **49**, 4378.