

Supplementary Material for:

Structural Investigation into Magnesium Based MOFs Derived from Aliphatic Linkers

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S1. Thermogravimetric analysis (TGA)

Following material synthesis, the mother liquor was exchanged with fresh DMF thrice and fresh DCM thrice, with each solvent exchange occurring over half a day. Following solvent exchange the crystals were air dried to afford desolvated MOF material for TGA analysis.

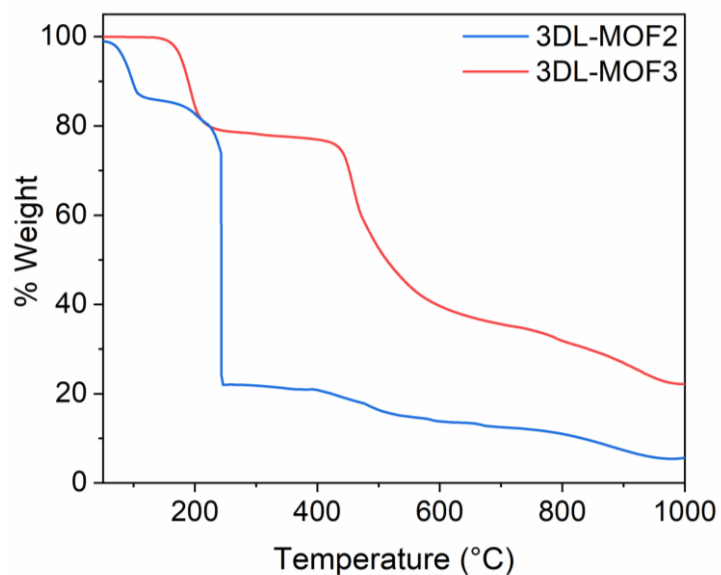


Figure S1. Thermogravimetric analysis plot of 3DL-MOF-2 and 3DL-MOF-3 performed under a N₂ atmosphere at a thermal ramping rate of 5 °C min⁻¹.

S2. Gas adsorption

Following material synthesis, the mother liquor was exchanged with fresh DMF thrice and fresh DCM thrice, with each solvent exchange occurring over half a day. Following solvent exchange, approximately 60 mg of dried, DCM exchanged sample was weighed in a pre-dried and weighed Quartz BET tube. The MOF was activated at 120 °C under dynamic vacuum at 10^{-6} Torr for at least 24 h to remove any solvent molecules. An accurate weight of the degassed sample was measured prior to analysis. Nitrogen adsorption isotherms were recorded at low pressure (0 – 1.2 bar) by a volumetric method using a Micromeritics 3Flex instrument. Gas adsorption measurements were performed using ultra-high purity N_2 .

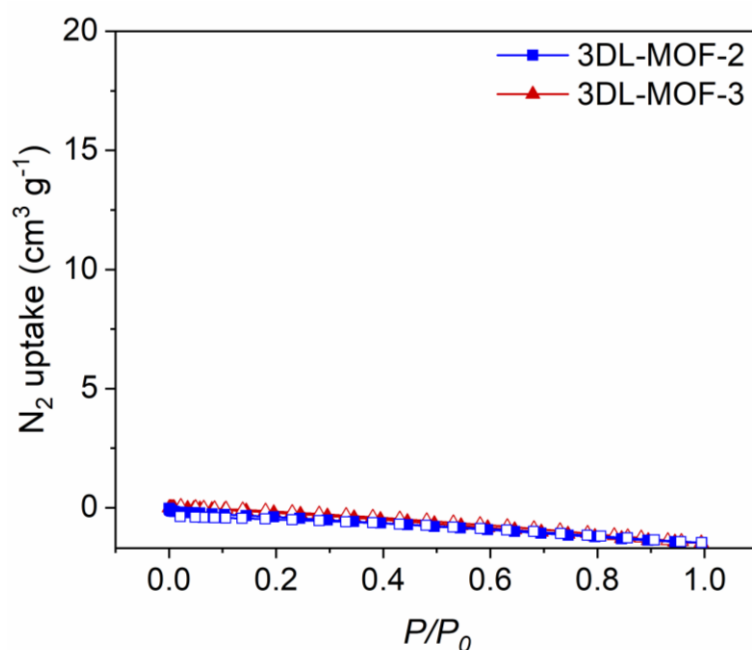


Figure S2. N_2 adsorption isotherm of 3DL-MOF-2 and 3DL-MOF-3.

S3. Powder X-ray diffraction

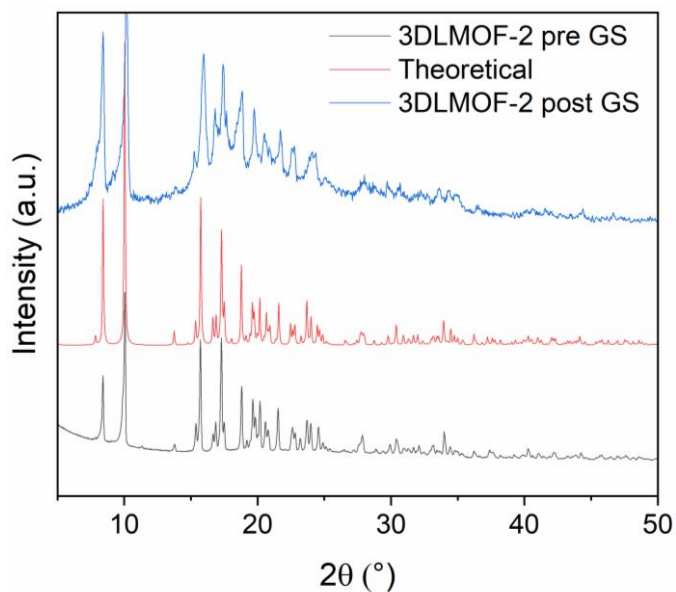


Figure S3. Powder X-ray diffraction (PXRD) plot of 3DL-MOF-2 pre-activation and post-activation. Post-activation shows the development of an amorphous MOF. GS = gas-sorption.

S4. ATR-IR

3DL-MOF-1 was activated at 120 °C for 24 hours and then analysed using ATR-IR, along with DMAc to confirm the removal of solvent from the MOF.

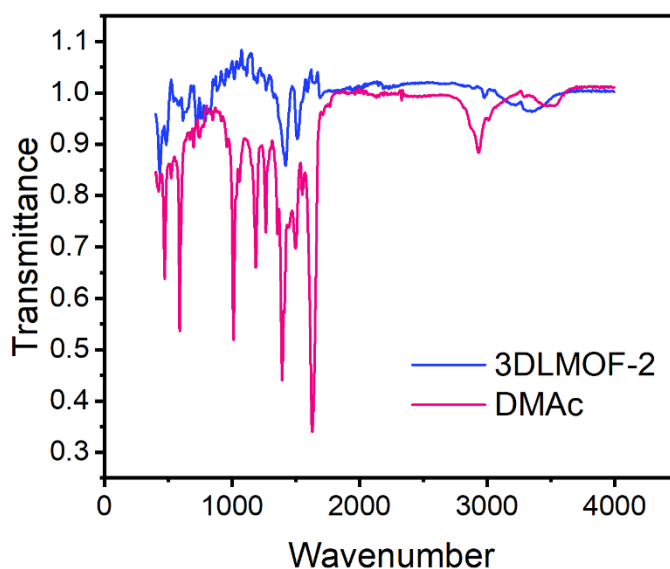


Figure S4. ATR (attenuated total reflectance)-IR plot of 3DL-MOF-2 post-activation and DMAc. Post-activation shows the loss of DMAc from the MOF.

S5. Single crystal X-ray diffraction

X-ray diffraction data were collected at 100 K on the MX2 Macromolecular Crystallography beamline at the Australian Synchrotron at a wavelength of 0.71073 Å.^[1] The data collection and integration were performed within the Blu-Ice^[1] and XDS^[2] software programs. The solutions were obtained by direct methods using SHELXT^[3] followed by successive refinements using full matrix least squares method against F^2 using SHELXL-2018/3.^[4] The program OLEX2^[5] was used as a graphical SHELX interface.

The data completeness for these samples was less than ideal despite multiple attempts on the same crystal. However, the completeness was sufficient that the connectivity was unambiguous.

Table S1. Crystal and data refinement parameters for the X-ray studies.

| MOF | 3DL-MOF-2 | 3DL-MOF-3 |
|--|---|--|
| CCDC Deposition number | 21103591 | 21103590 |
| Formula | C ₂₄ H ₂₃ Mg ₂ NO ₁₀ | C ₁₄ H ₂₆ Mg ₃ O ₁₆ |
| Formula weight | 534.05 | 523.28 |
| Temperature/K | 100(2) | 100(2) |
| Crystal system | triclinic | orthorhombic |
| Space group | <i>P</i> -1 | <i>Prma</i> |
| <i>a</i> (Å) | 5.4120(11) | 12.454(3) |
| <i>b</i> (Å) | 11.660(2) | 12.910(3) |
| <i>c</i> (Å) | 18.358(4) | 13.289(3) |
| α (°) | 78.38(3) | 90 |
| β (°) | 86.38(3) | 90 |
| γ (°) | 79.66(3) | 90 |
| Volume (Å ³) | 1115.9(4) | 2136.6(7) |
| <i>Z</i> | 2 | 4 |
| $\rho_{\text{calc}}/\text{g cm}^{-3}$ | 1.589 | 1.627 |
| μ (mm ⁻¹) | 0.173 | 0.223 |
| <i>F</i> (000) | 556.0 | 1096.0 |
| Reflections collected | 18556 | 25573 |
| Independent reflections | 5642 [$R_{\text{int}} = 0.1012$, $R_{\text{sigma}} = 0.0900$] | 3096 [$R_{\text{int}} = 0.0681$, $R_{\text{sigma}} =$ 0.0339] |
| Data/restraints/parameters | 5642/1/362 | 3096/0/204 |
| GooF | 1.093 | 1.138 |
| Final <i>R</i> indexes [$I \geq 2\sigma(I)$] | $R_1 = 0.0950$, $wR_2 = 0.2714$ | $R_1 = 0.0524$, $wR_2 = 0.1475$ |
| Final <i>R</i> indexes [all data] | $R_1 = 0.1150$, $wR_2 = 0.2894$ | $R_1 = 0.0549$, $wR_2 = 0.1496$ |
| Largest diff. peak/hole / e Å ⁻³ | 0.83/-0.86 | 0.88/-0.45 |

S5.1 Details of structure determination

3DL-MOF-2

Single crystal X-ray data were collected on a colourless block-like crystal of 3DL-MOF-2. Elucidation of the data revealed the crystal possessed triclinic symmetry and a satisfactory solution was obtained in the space group $P-1$. All non-hydrogen framework atoms were clearly defined and refined with anisotropic displacement parameters. All hydrogen framework atoms were placed in geometrically estimated positions. The coordinated DMAc molecule is disordered over two positions that share the same position for their oxygen atom and methyl groups. Each methyl group was split and subsequently constrained with EADP and EXYZ. C21, N1 and the methyl carbons C22a, C23b and C24b were placed in PART 1 and their site occupation refined. C25, N2 and the methyl carbons C22b, C23b and C24b were placed in PART 2 their site occupation refined to 1- the site occupation of PART 1. The primary site occupation of the DMAc molecule was refined to 81.3%. The Two orientations of the DMAc molecule is shown in **Figure S2**.

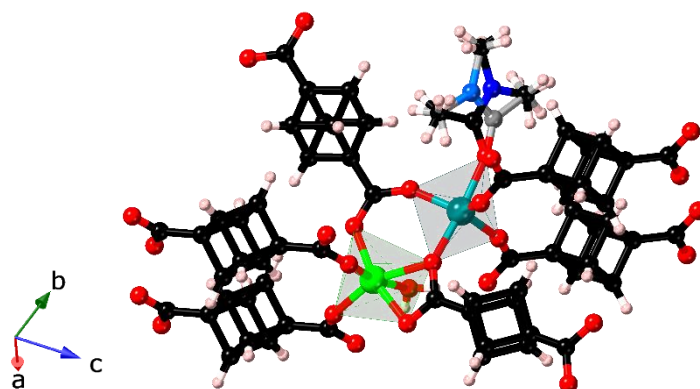


Figure S5. The dinuclear Mg cluster in 3DL-MOF-2 highlighting the disordered nature of the coordinated DMAc molecule. The secondary ~20% occupancy orientation of the molecule is represented with grey carbon atoms and a light blue nitrogen atom. The two orientations share the same position for their oxygen atom and methyl groups.

3DL-MOF-3

Single crystal X-ray data were collected on a colourless prism-like crystal of 3DL-MOF-3. Elucidation of the data revealed the crystal possessed orthorhombic symmetry and a satisfactory solution was obtained in the space group $Pnma$. All non-hydrogen framework atoms were clearly defined and refined with anisotropic displacement parameters. All hydrogen framework atoms were placed in geometrically estimated positions, besides two hydroxide hydrogen atoms (H3, H8). The carbon atoms of the [1.1.1]bicyclopentane units (C1 – C6) are

only partially present in the asymmetric unit, as seen in **Figure S3**. The [1.1.1]bicyclopentanes have been modelled over two orientations, each at 50% occupancy. The atoms have been placed in separate PARTs to prevent interactions from “adjacent” carbon atoms.

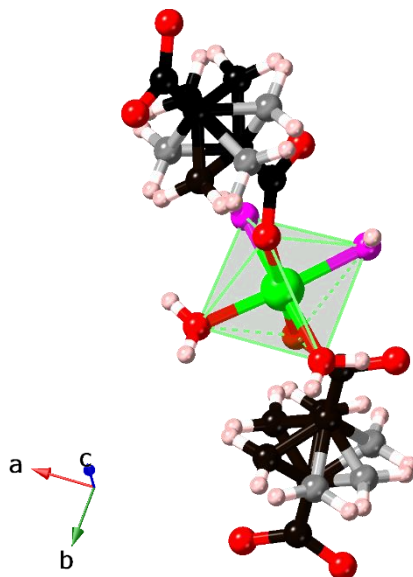


Figure S6. The Mg(2) coordination sphere in 3DL-MOF-3 highlighting the disordered nature of the coordinated pdc^{2-} ligand. The symmetry generated atoms of the pdc^{2-} ligand are highlighted in grey. Hydroxide atoms are shown in pink.

S6. References

- [1] T. M. McPhillips, S. E. McPhillips, H.-J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis and P. Kuhn, *J. Synchrotron Radiat.*, **2002**, 9, 401. doi:10.1107/S0909049502015170
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