

Supporting Information

The Crystalline Sponge Method: MOF Terminal Ligand Effects

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Experimental Details

Crystal growth and guest inclusion

The synthesis of crystals **1b** and **1c** is based upon a derivative of a previously reported procedure,¹ where 0.03 M ZnBr₂ / MeOH for **1b** or 0.03 M ZnCl₂ / MeOH for **1c** was used instead of 0.03 M ZnI₂ / MeOH. The crystallization time was extended to 7 days at room temperature, and the same established workup procedure was employed to afford clear crystals of **1b** (yield: 52%) and **1c** (yield: 20%), which were directly used for guest inclusion. The unit cell dimensions for **1b** measured on an in-house diffractometer are $a = 33.69(1) \text{ \AA}$, $b = 14.579(3) \text{ \AA}$, $c = 30.590(9) \text{ \AA}$, $\beta = 101.13(2)^\circ$, $V = 14742(7) \text{ \AA}^3$ (monoclinic $C2/c$) and for **1c** is $a = 32.81(2) \text{ \AA}$, $b = 14.419(5) \text{ \AA}$, $c = 30.55(1) \text{ \AA}$, $\beta = 100.52(2)^\circ$, $V = 14211(11) \text{ \AA}^3$ (monoclinic $C2/c$). The crystals were kept in CHCl₃ and can be stored short-term at -20 °C. For inclusion of guest molecule **2** the same procedure as previously reported was employed,¹ where crystals of **1b** or **1c** were pipetted into a smaller vial, the CHCl₃ solvent was carefully removed, and enough of neat **2** was added to submerge the crystals, which were then left to soak for 2 d at ambient temperature.

Crystallographic procedures

Prismatic crystals of **1b2** and **1c2** were picked in NVH immersion oil and mounted on polyimide loops. The loops were mounted on a Bruker D8 three-circle fixed chi goniometer with an APEX II CCD detector and a 100 K liquid nitrogen cold stream generated by an Oxford Cryostream at the ChemMatCARS sector 15 beamline (experimental station ID-B) of the Advanced Photon Source at Argonne National Laboratory. An irradiation wavelength of $\sim 0.41 \text{ \AA}$ was used with 0.3 s exposure times, and data were collected with multiple ϕ scans at 0.5° increments with ω offsets and ω scans at 0.5° increments with ϕ offsets. Data were processed in the Bruker APEX2 software suite,² where SAINT was used for data integration,³ and multi-scan absorption correction was performed in SADABS.⁴ Intrinsic phasing (SHELXTL XT-2014)⁵ was used to solve the data and SHELXL-2014 was used to perform least-squares refinement on F^2 .⁶ Hydrogen atoms were added through the riding model, and anomalous dispersion and absorption coefficients (f' and f'') were calculated for the wavelength used for data collection and applied during refinement. Absolute configuration parameters (Flack x and Hooft y) were determined using PLATON/BIJVOETPAIR.⁷ Specific procedures and guidelines for refinement of the crystalline sponge systems were performed as previously reported.¹ Void spaces were determined using the CalcVoid tool in Olex2.⁸ Before running the tool, all guest and solvent molecules were deleted. The CalcVoid tool was run using a resolution of 0.2 \AA and using no additional distance (0 \AA) from the Van der Waals surface.

Unit cell determinations of blank **1b** and **1c** crystals (solvent: CHCl_3) were performed on a Bruker SMART APEX II in-house diffractometer equipped with I μ S microfocus $\text{MoK}\alpha$ and $\text{CuK}\alpha$ sealed tube sources and Triumph monochromator, Bruker D8 three-circle fixed chi goniometer, and an APEX II CCD detector. Measurements were performed at 100 K using a liquid nitrogen cold stream generated by an Oxford Cryostream 700 series low temperature device, and a $\text{MoK}\alpha$ radiation source was used. For data processing, the resolution cutoffs recommended by SAINT were used for integration.

Table S1. Crystallographic details for **1b2**

	znbr2menthylacetate-chiralfrc_b
Crystal data	
Chemical formula	C ₇₂ H ₄₈ Br _{11.98} N ₂₄ Zn _{5.99} ·1.71(C ₁₂ H ₂₂ O ₂)·0.62(CHCl ₃)
<i>M_r</i>	3012.07
Crystal system, space group	Monoclinic, <i>C2</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	33.964 (3), 14.5897 (14), 33.787 (3)
β (°)	104.9361 (14)
<i>V</i> (Å ³)	16176 (3)
<i>Z</i>	4
Radiation type	Synchrotron, λ = 0.40651 Å
μ (mm ⁻¹)	2.08
Crystal size (mm)	0.2 × 0.04 × 0.03
Data collection	
Diffractometer	Bruker D8 goniometer diffractometer
Absorption correction	Multi-scan <i>SADABS2014/4</i> was used for absorption correction. <i>wR</i> ₂ (int) was 0.1490 before and 0.0816 after correction. The Ratio of minimum to maximum transmission is 0.7885. The λ/2 correction factor is 0.00150.
<i>T</i> _{min} , <i>T</i> _{max}	0.716, 0.908
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	163312, 28563, 20713
<i>R</i> _{int}	0.100
(sin θ/λ) _{max} (Å ⁻¹)	0.596
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.071, 0.230, 1.06
No. of reflections	28563
No. of parameters	1432
No. of restraints	95
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.1378P)^2 + 29.0441P]$ where $P = (F_o^2 + 2F_c^2)/3$
Δ _{max} , Δ _{min} (e Å ⁻³)	1.60, -0.95
Absolute structure	Flack <i>x</i> determined using 7739 quotients [(<i>I</i> ₊)-(<i>I</i> ₋)]/[(<i>I</i> ₊)+(<i>I</i> ₋)] (S. Parsons, H. D. Flack and T. Wagner, <i>Acta Cryst.</i> , 2013, B69 , 249).
Absolute structure parameter	0.054 (19)

Table S2. Crystallographic details for **1c2**

	znc12menthylacetate_a
Crystal data	
Chemical formula	C ₇₂ H ₄₈ Cl ₁₂ N ₂₄ Zn ₆ ·1.89(C ₁₂ H ₂₂ O ₂)·0.44(CHCl ₃)
<i>M_r</i>	2493.49
Crystal system, space group	Monoclinic, <i>C2</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	33.391 (2), 14.3975 (10), 33.897 (2)
β (°)	105.2725 (12)
<i>V</i> (Å ³)	15720.2 (19)
<i>Z</i>	4
Radiation type	Synchrotron, λ = 0.40656 Å
μ (mm ⁻¹)	0.61
Crystal size (mm)	0.15 × 0.04 × 0.03
Data collection	
Diffractometer	Bruker D8 goniometer diffractometer
Absorption correction	Multi-scan <i>SADABS2014/4</i> was used for absorption correction. <i>wR</i> ₂ (int) was 0.1134 before and 0.0812 after correction. The Ratio of minimum to maximum transmission is 0.8879. The λ/2 correction factor is 0.00150.
<i>T</i> _{min} , <i>T</i> _{max}	0.870, 0.980
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	158634, 27736, 19831
<i>R</i> _{int}	0.098
(sin θ/λ) _{max} (Å ⁻¹)	0.596
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.085, 0.273, 1.06
No. of reflections	27736
No. of parameters	1373
No. of restraints	80
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.1777P)^2 + 14.8349P]$ where $P = (F_o^2 + 2F_c^2)/3$
Δ _{max} , Δ _{min} (e Å ⁻³)	1.74, -0.88
Absolute structure	Flack <i>x</i> determined using 6818 quotients [(<i>I</i> ₊)-(<i>I</i> ₋)]/[(<i>I</i> ₊)+(<i>I</i> ₋)] (S. Parsons, H. D. Flack and T. Wagner, <i>Acta Cryst.</i> , 2013, B69 , 249).
Absolute structure parameter	0.05 (2)

References

- 1) T. R. Ramadhar, S.-L. Zheng, Y.-S. Chen and J. Clardy, *Acta Cryst.*, 2015, **A71**, 46.
- 2) Bruker, APEX2 (V2014.9), Bruker AXS Inc., Madison, Wisconsin, USA, 2014.
- 3) Bruker, SAINT (8.34A), Bruker AXS Inc., Madison, Wisconsin, USA, 2013.
- 4) Bruker, SADABS-2014/4, Bruker AXS Inc., Madison, Wisconsin, USA, 2014.
- 5) G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3.
- 6) G. M. Sheldrick, *Acta Cryst.*, 2015, **A64**, 112.
- 7) A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148.
- 8) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.