Electronic Supplementary Information for

Ternary gradient metal-organic frameworks

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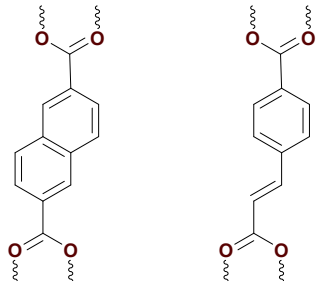
bMOF-110 characterization



bMOF-101 **bMOF-110**

Fig. S1 Comparison of the ditopic linkers of bMOF-101[1] which is based on 2,6-naphthalenedicarboxylate (left), and bMOF-110 which is based on CCA (right).

Table S1 Comparison of unit cell parameters of bMOF-101[1] and bMOF-110

	Space Group	a = b = c (Å)	α = β = γ (°)
bMOF-101	*Ia-3d*	62.0387(51)	90
bMOF-110	*Ia-3d*	62.0887(5)	90

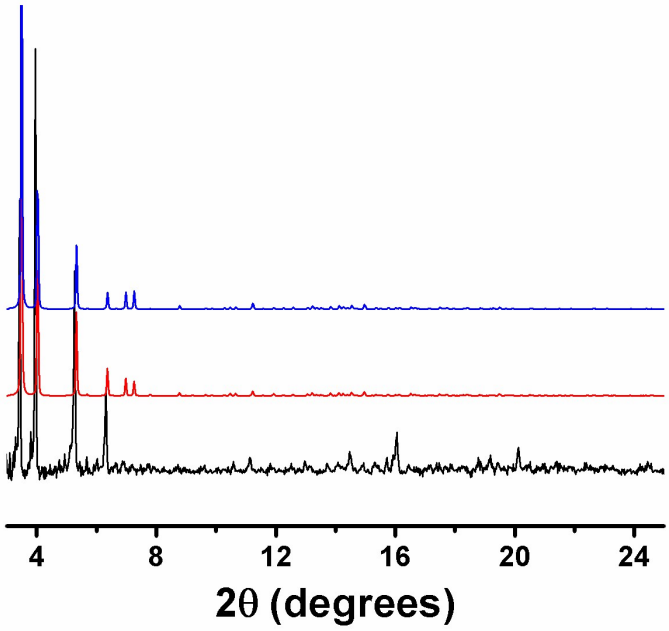


Fig. S2 PXRD comparison of experimental bMOF-110 (black) with simulated patterns of bMOF-101 (blue) and bMOF-110 (red).

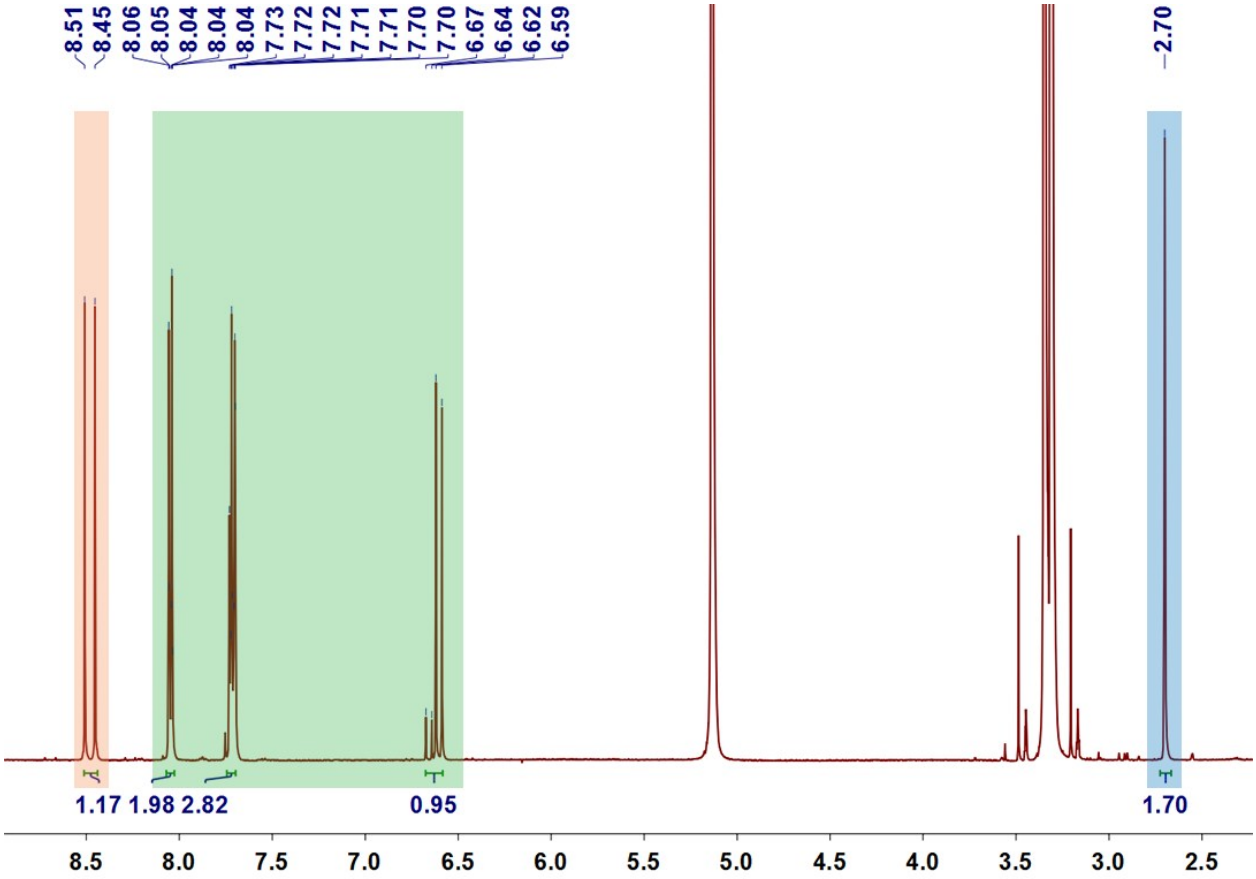


Fig. S3 ^{1}H NMR spectrum of dissolved bMOF-110 crystals in methanol-d_4 and DCl/D_2O. Peak assignment: beige-adenine; green-CCA; blue-dimethylammonium.

bMOF-100/102 binary gradient MOFs

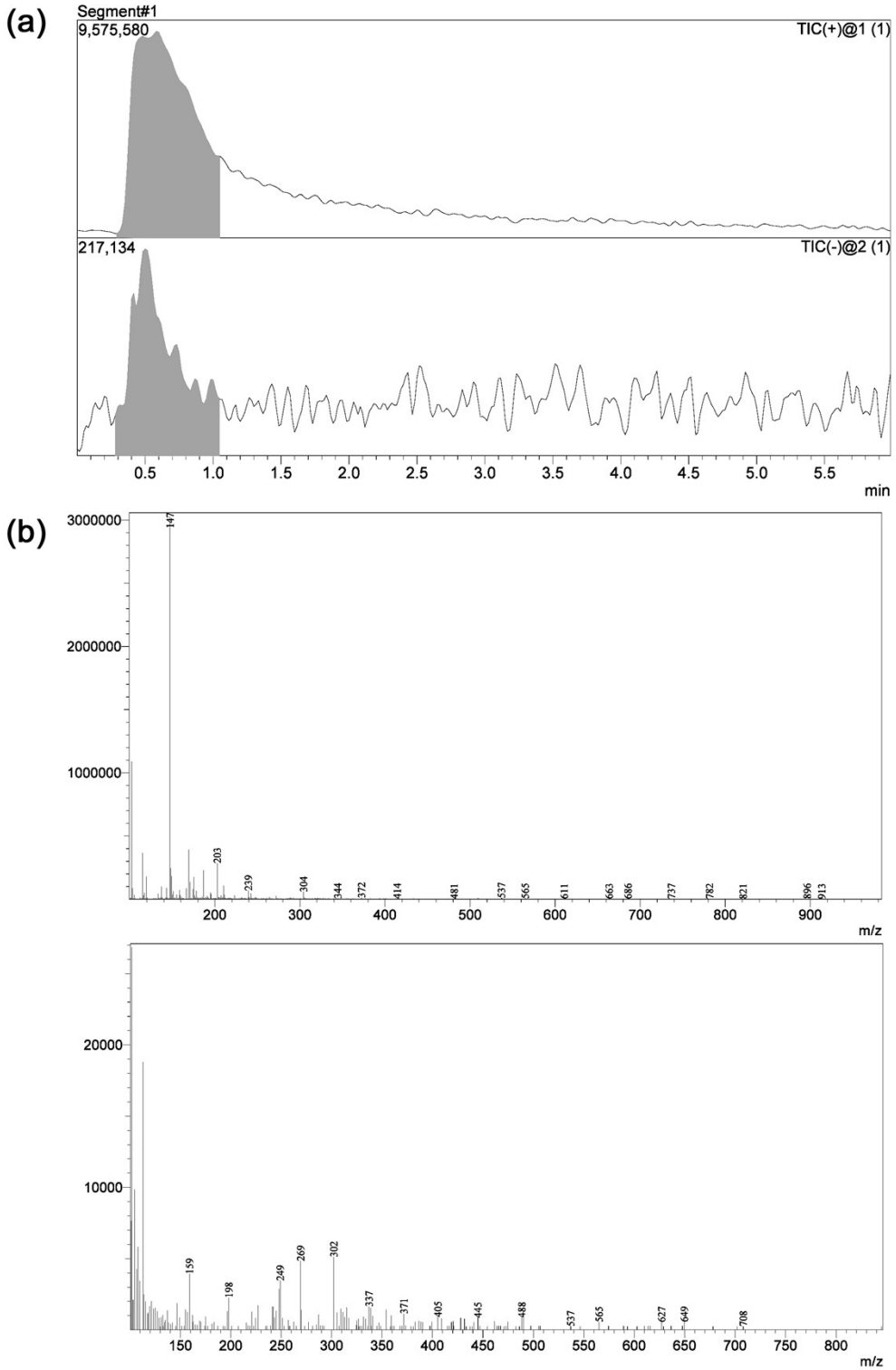


Fig. S4. (a): total ion chromatogram (top: positive mode; bottom: negative mode) of the final supernatant, shadowed area indicates time range in which the average mass spectra were obtained; (b): mass spectra of the corresponding time ranges (top: positive mode; bottom: negative mode). The positive peak with m/z = 147 is $[2DMF+H]^+$, from the solvent. The negative peak with m/z = 269 is $[H_2\text{-ABDC-H}]^-$, with intensity close to background noise, indicating adequate removal.

Table S2 Comparison of unit cell parameters of two different bMOF-100/102 binary gradient MOFs

Sample	Space Group	a = b = c (Å)	Average a = b = c (Å)	α = β = γ (°)
bMOF-100/102-a	*Ia-3d*	70.4982(138)	70.1720 ± 0.4523*	90
		70.3715(58)		
		70.4726(88)		
		70.9532(131)		
		69.8512(63)		
		70.1711(191)		
		69.7256(68)		
		69.9820(106)		
		70.3186(108)		
		69.3755(50)		
bMOF-100/102-b	*Ia-3d*	73.6121(40)	73.2314 ± 0.5540†	90
		72.8372(60)		
		72.5443(40)		
		73.4423(65)		
		74.1049(30)		
		72.5836(95)		
		72.6949(50)		
		73.8068(50)		
		73.5870(70)		
		73.1011(77)		

* Sample standard deviation

† Sample standard deviation

bMOF-100/102/106 ternary gradient MOFs

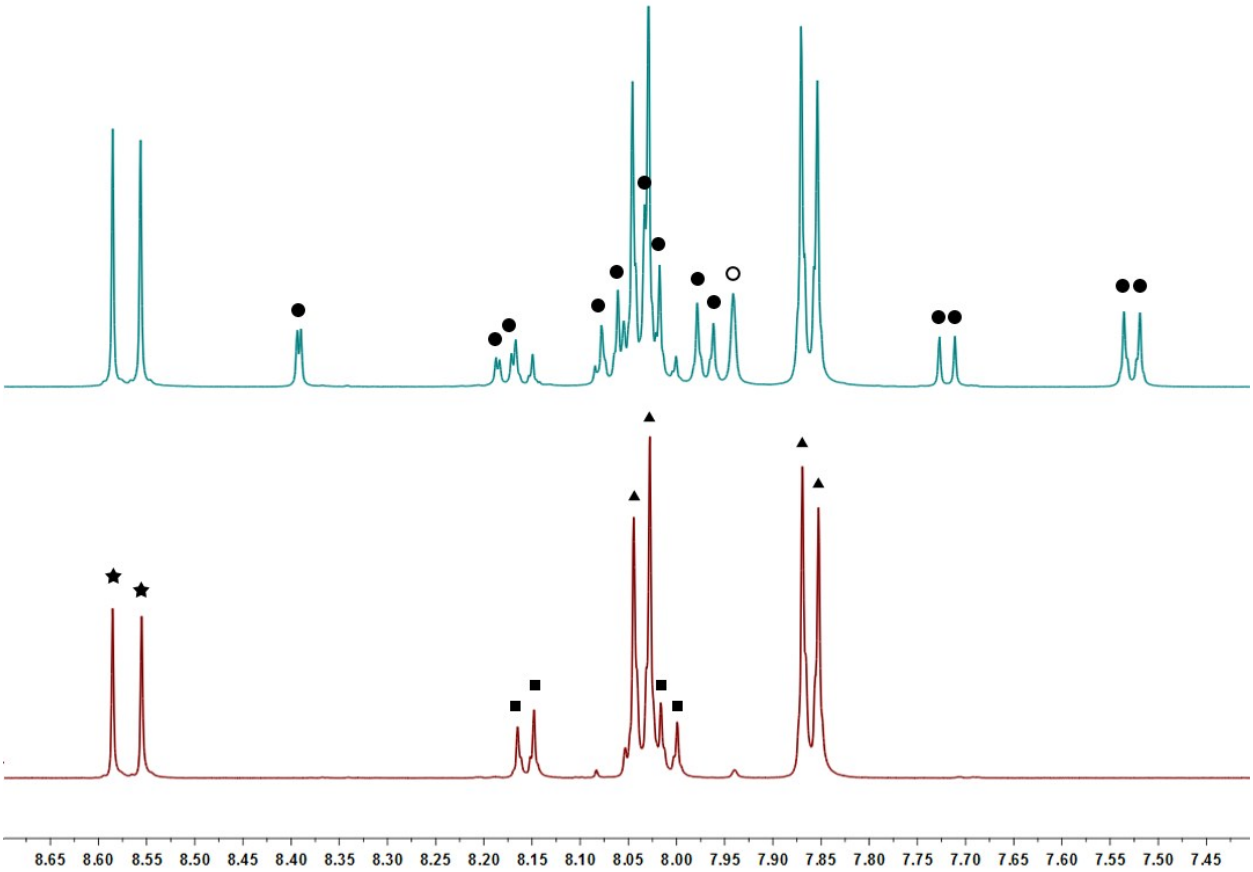


Fig. S5. ^{1}H NMR spectra of dissolved crystals from reactions in Fig. 3a. Bottom: bMOF-100/102-c; top: bMOF-100/102/106-c. Peak assignment: star-adenine, square-ABDC, triangle-BPDC, solid circle-NO_2-TPDC, circle-DMF. Composition was calculated by comparing peak integrations of dicarboxylate ligands present, as shown in Fig. 3b. Top: total ion chromatogram of the final supernatant, shadowed area indicates time range in which the ligands should be eluted; bottom: mass spectrum of the shadowed time range.

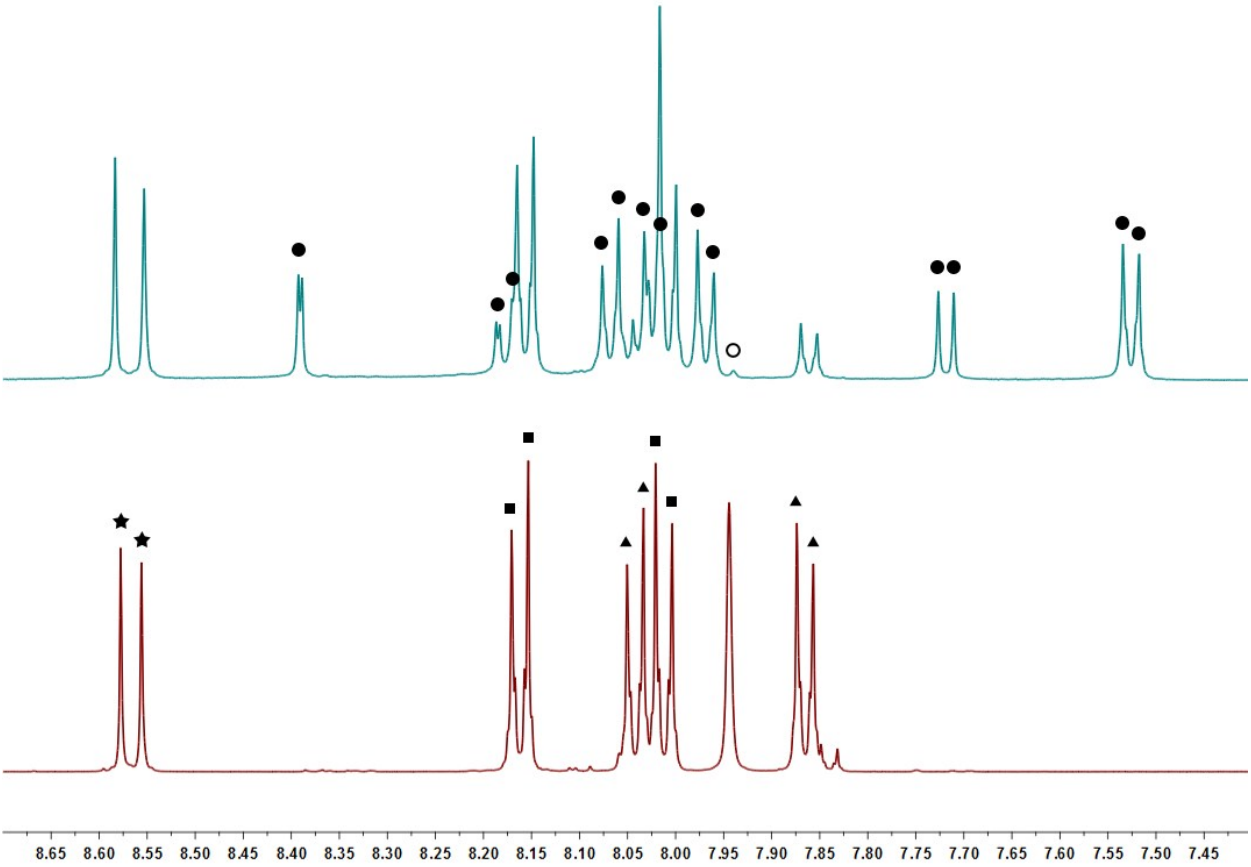


Fig. S6. ^{1}H NMR spectra of dissolved crystals from reactions in Fig. 3a. Bottom: bMOF-100/102-d; top: bMOF-100/102/106-d. Peak assignment: star-adenine, square-ABDC, triangle-BPDC, solid circle-NO_2-TPDC, circle-DMF. Composition was calculated by comparing peak integrations of dicarboxylate ligands present, as shown in Fig. 3b.

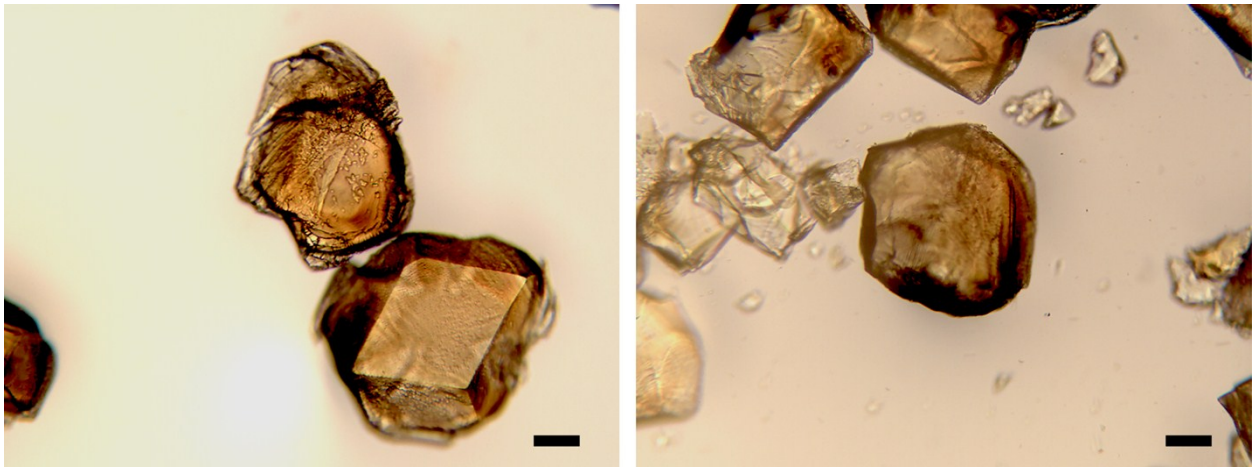


Fig. S7. Optical microscopic images of ternary gradient MOF bMOF-100/102/106-c crystals. Scale bar: 100 μm.

Table S3 Comparison of unit cell parameters for ternary bMOF-100/102/106-c system

Sample	Space Group	a = b = c (Å)	α = β = γ (°)
Unexchanged core	*Ia-3d*	70.333(15)	90
Intact bMOF-100/102/106-c		77.003(31)	
Partially exchanged shell		80.009(33)	
Pure bMOF-100		69.1286(20)[2]	
Pure bMOF-102		75.2350(10)[2]	
Pure bMOF-106		81.7060(32)[2]	

bMOF-110/100/102 ternary gradient MOFs

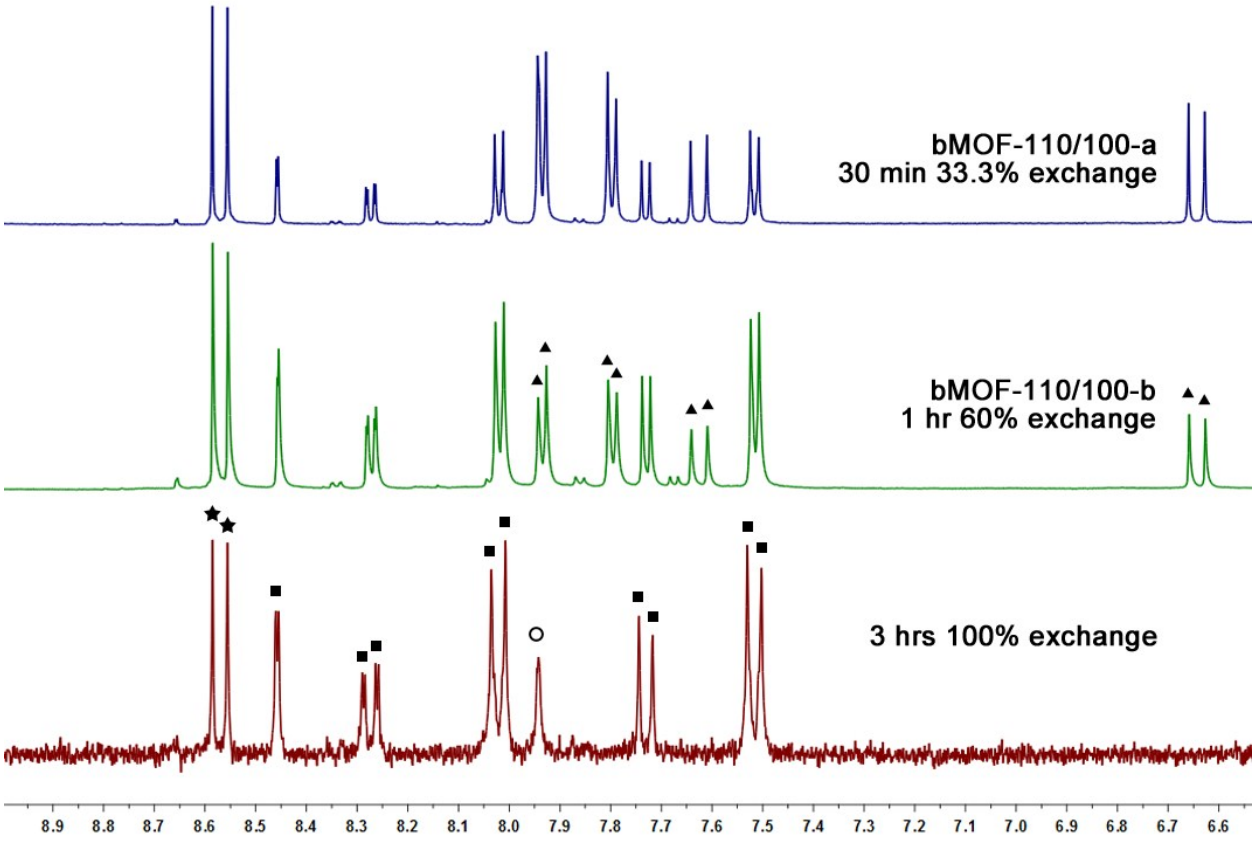


Fig. S8. ^{1}H NMR spectra of dissolved crystals from ligand exchange reactions of bMOF-110 with H_2-NO_2-BPDC for different periods of time. Peak assignment: star-adenine, square-NO_2-BPDC, triangle-CCA, circle-DMF. Exchange percentage was calculated by comparing peak integrations of NO_2-BPDC and CCA.

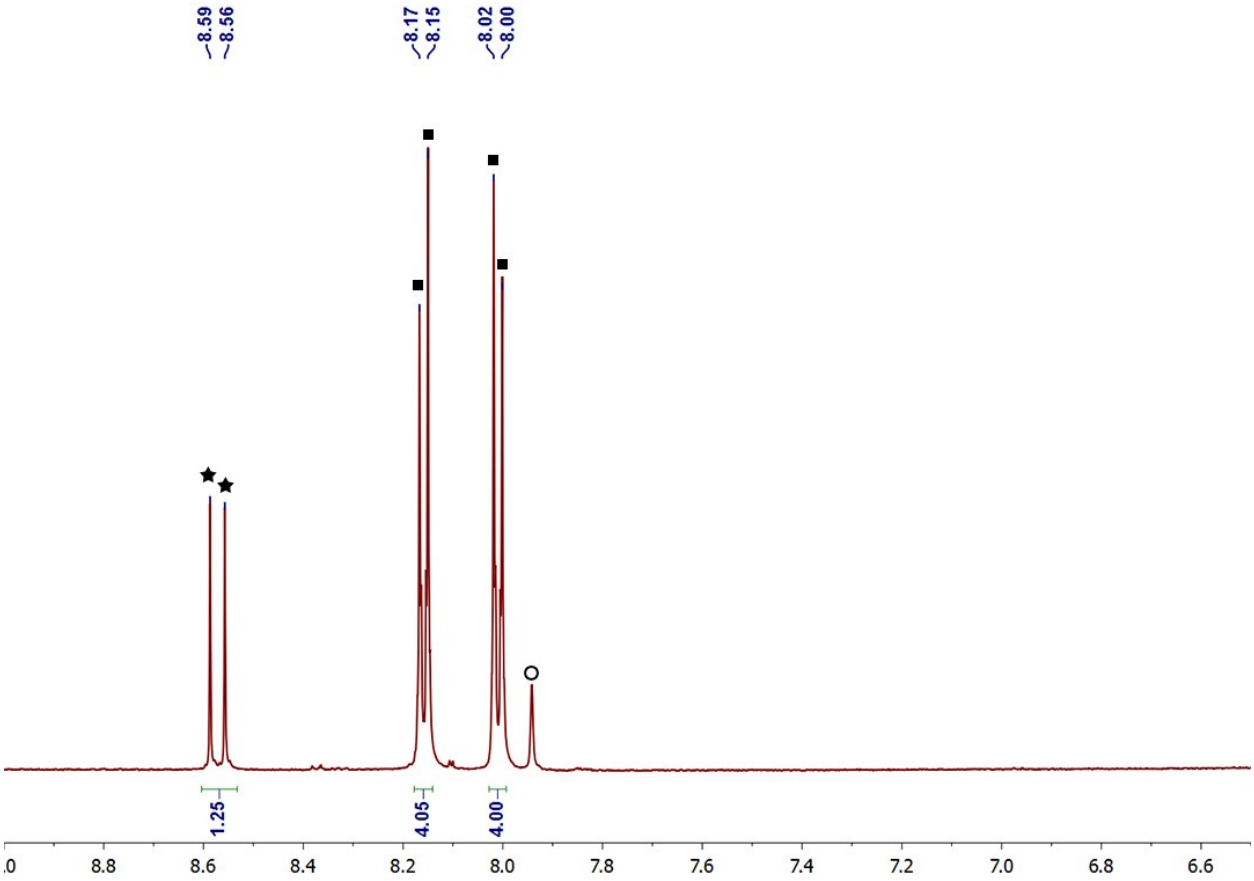


Fig. S9. ^{1}H NMR spectrum of dissolved crystals from a 15-hour ligand exchange reaction of bMOF-110 with H_2-ABDC. Peak assignment: star-adenine, square-ABDC, circle-DMF. No peak from CCA was observed.

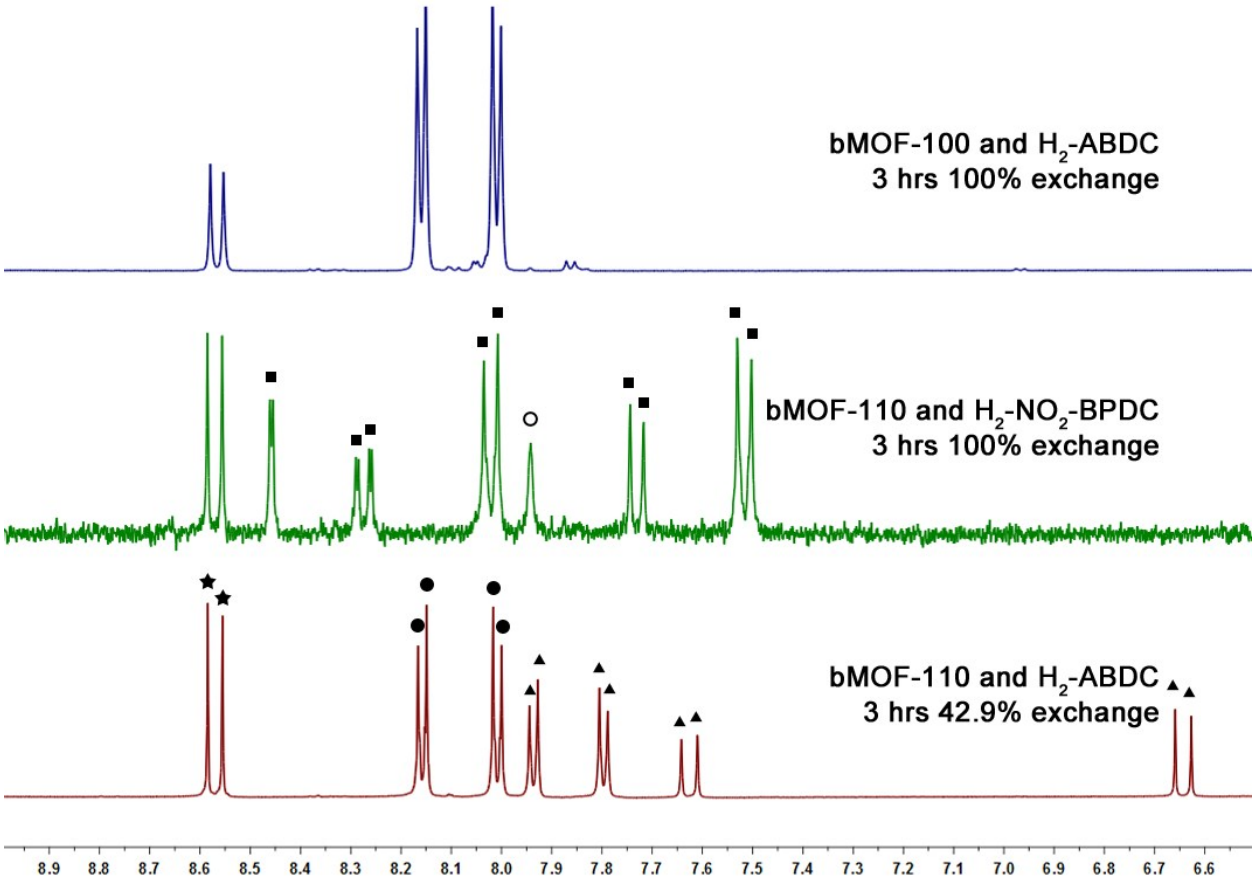


Fig. S10. ^{1}H NMR spectra of dissolved crystals from three different ligand exchange reactions for the same period of time (3 hours). Peak assignment: star-adenine, square-NO_2-BPDC, triangle-CCA, solid circle-ABDC, circle-DMF. For the bottom spectrum, exchange percentage was calculated by comparing peak integrations of ABDC and CCA.

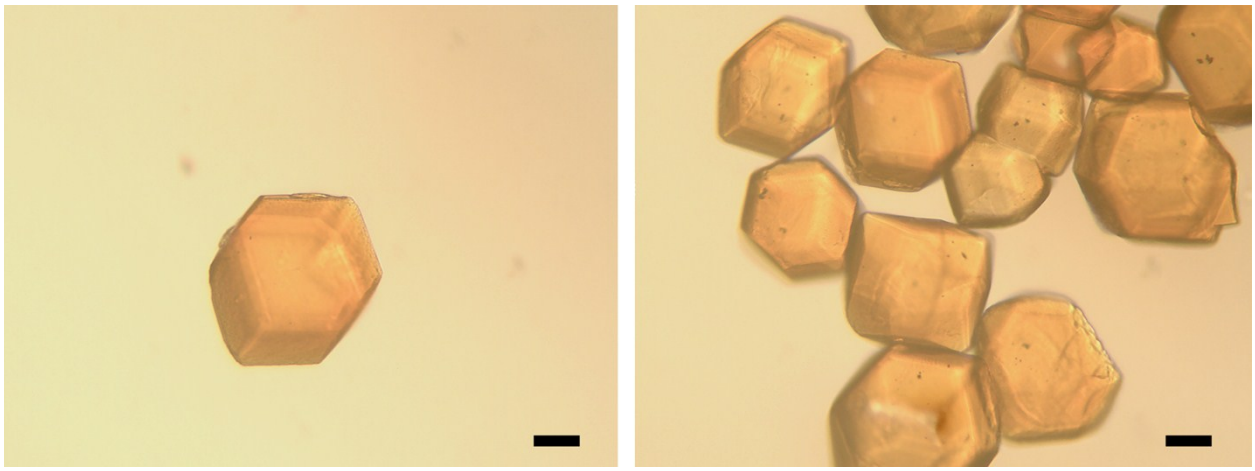


Fig. S11. Optical microscopic images of bMOF-110/102 crystals prepared by reacting bMOF-110 with H_2-ABDC for 3 hours. Scale bar: 100 μm.

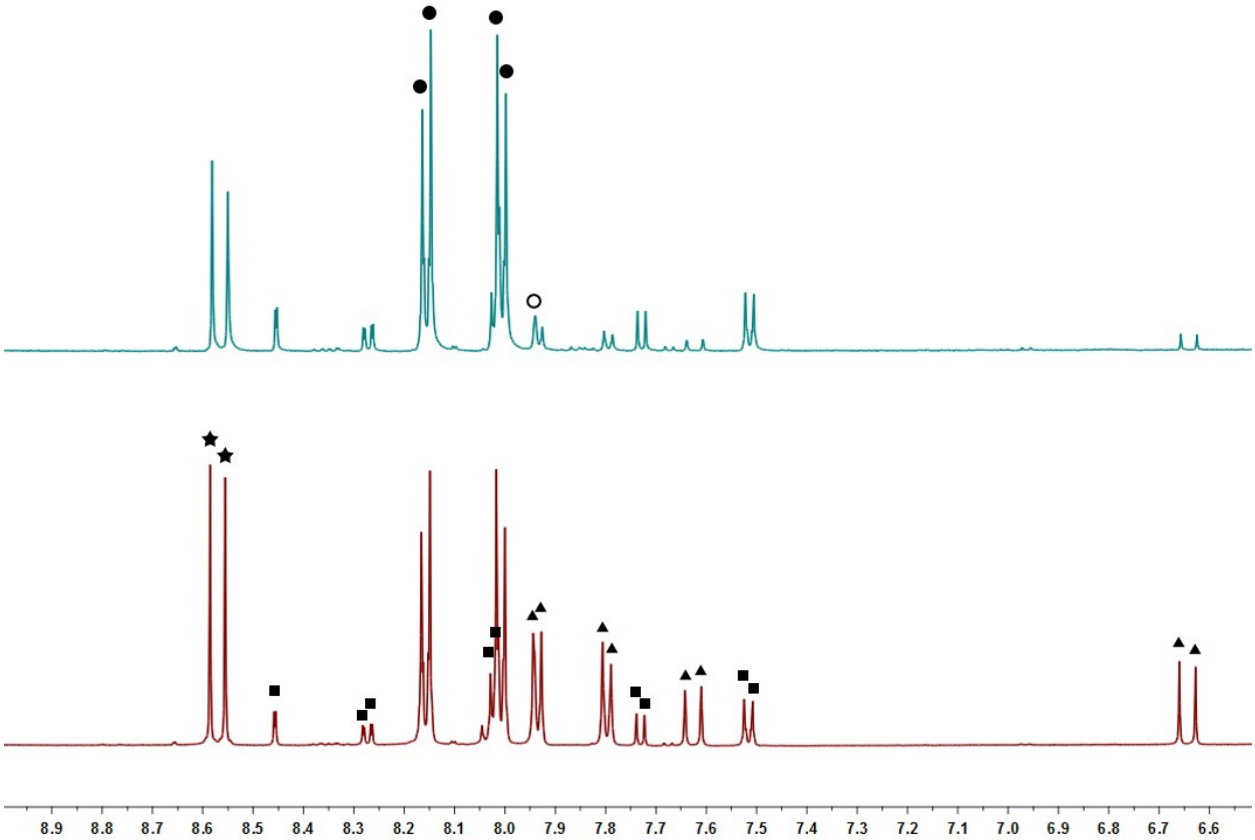


Fig. S12. ^{1}H NMR spectra of dissolved ternary gradient MOF crystals from reactions in Fig. 4a. Bottom: bMOF-110/100/102-a; top: bMOF-110/100/102-b. Peak assignment: star-adenine, square-NO_2-BPDC, triangle-CCA, solid circle-ABDC, circle-DMF. Composition was calculated by comparing peak integrations of dicarboxylate ligands present, as shown in Fig. 4b.

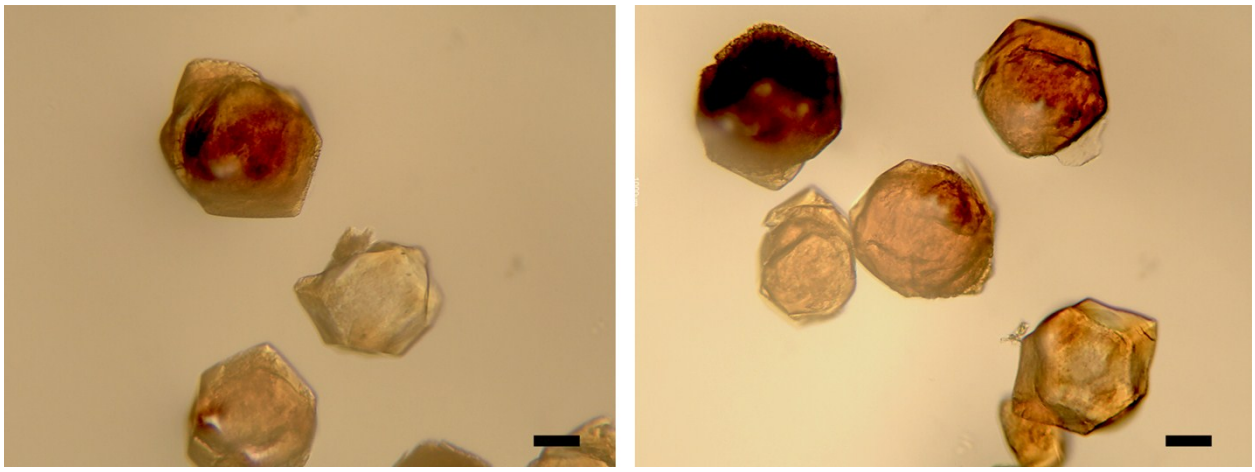


Fig. S13. Optical microscopic images of bMOF-110/100/102-a crystals. Scale bar: 100 μm.

References:

1 T. Li, M. T. Kozlowski, E. A. Doud, M. N. Blakely, N. L. Rosi. *J. Am. Chem. Soc.*, **2013**, *135*, 11688-11691.
2 C. Liu, C. Zeng, T. -Y. Luo, A. D. Merg, R. Jin, N. L. Rosi. *J. Am. Chem. Soc.*, **2016**, *138*, 12045-12048.