Electronic Supplementary Information

Smoothing the single-crystal to single-crystal conversions of a two-dimensional metal–organic framework via the hetero-metal doping of the linear trimetallic secondary building unit

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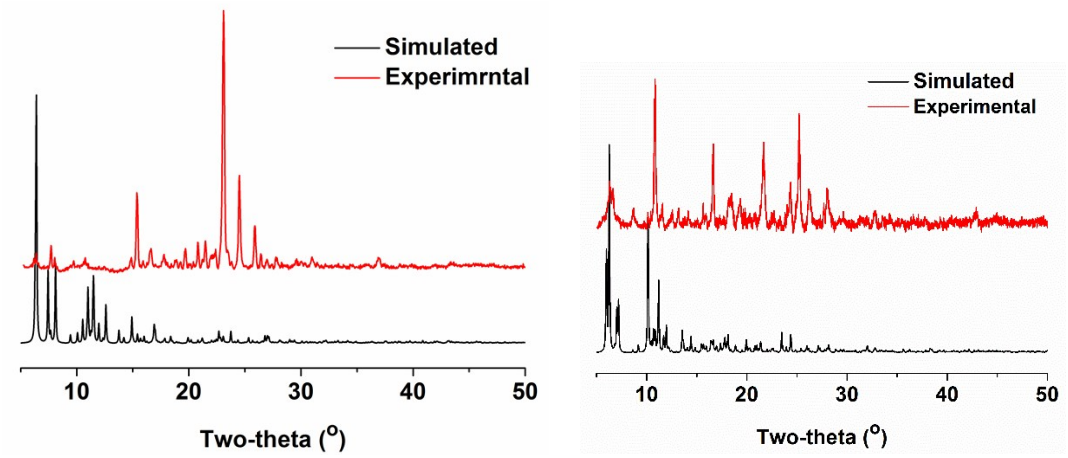
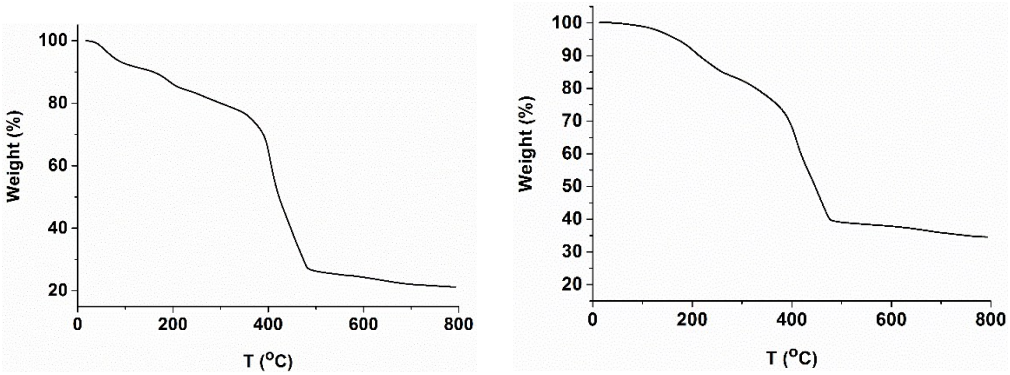


(a) (b)

Fig. S1 PXRD patterns of $[Cd_{2.25}Co_{0.75}(BTB)_2(DPDS)_2]\cdot x$Sol (**3**, a) and $[Cd_{2.25}Co_{0.75}(BTB)_2(BIPY)(H_2O)_2]\cdot x$Sol (**4**, b).



(a) (b)

Fig. S2 TGA curves of $[Cd_{2.25}Co_{0.75}(BTB)_2(DPDS)_2]\cdot x$Sol (**3**, a) and $[Cd_{2.25}Co_{0.75}(BTB)_2(BIPY)(H_2O)_2]\cdot x$Sol (**4**, b).

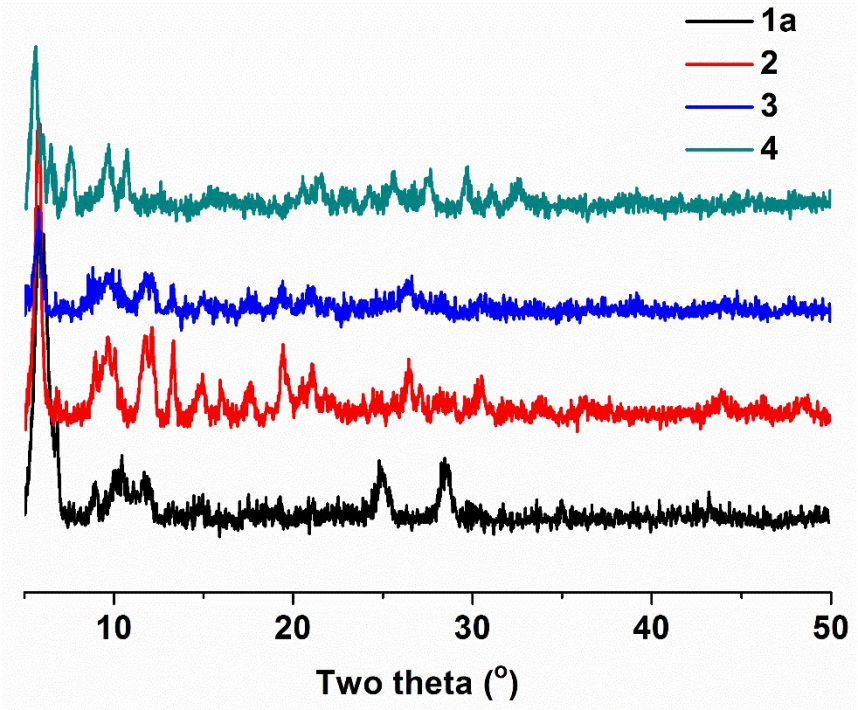


Fig. S3 The PXRD patterns for samples by heating **1a**, **2**–**4** at 380 °C under N_2 for 30 min, showing the retention of some crystallinity.

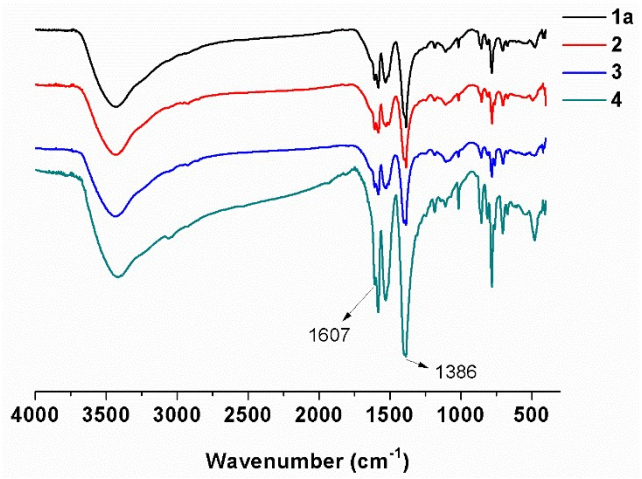


Fig. S4 The FT-IR spectra of the samples by heating **1a**, **2**–**4** at 380 °C under N_2 for 30 min, showing the generation of the same product (likely $[Cd_{2.25}Co_{0.75}(BTB)_2]\cdot xH_2O$). Peaks at wave numbers of 1607 cm^{-1} and 1386 cm^{-1} are characteristic asymmetric and symmetric stretching vibrations of the carboxylate.

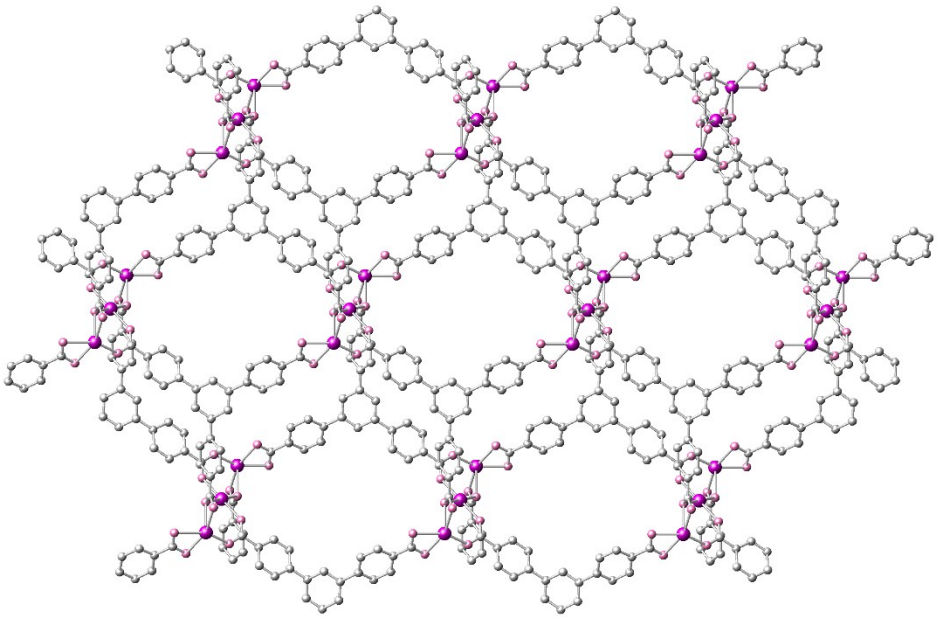
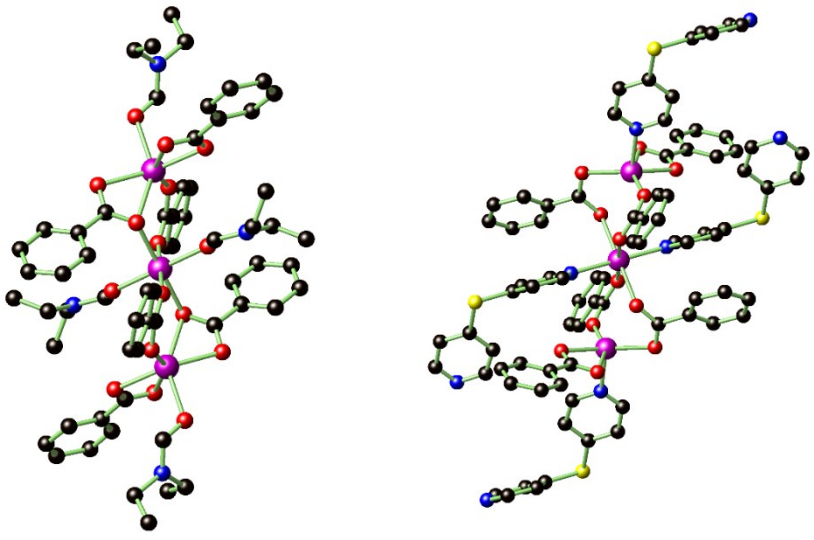
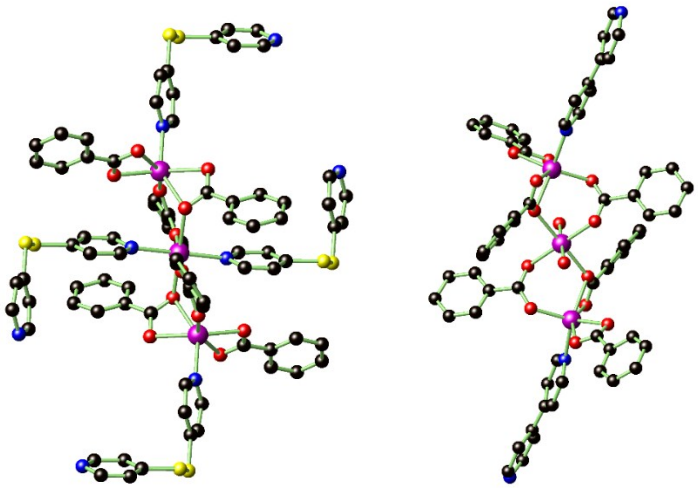


Fig. S5 The structure of 1a showing the double-layered structure with honeycomb-shaped cavities as supported by $Cd_{2.25}Co_{0.75}$-BTB associations.

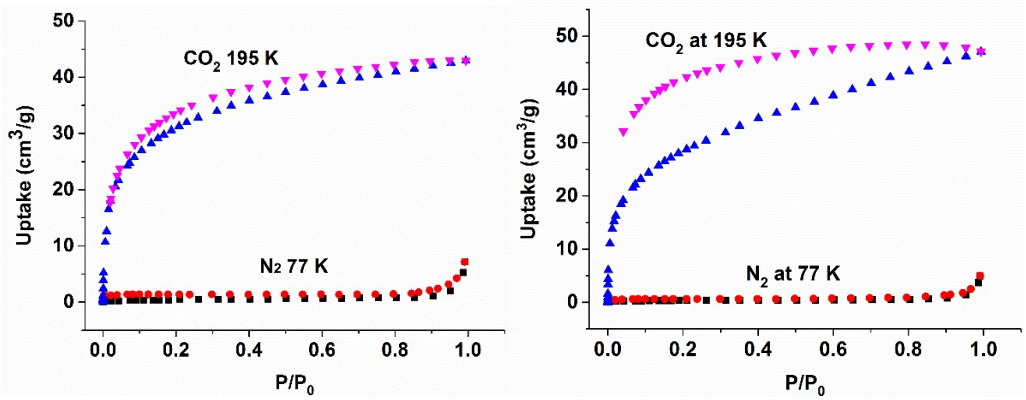


(a) (b)



(c) (d)

Fig. S6 The Cd_3 coordination environments of $[Cd_{2.25}Co_{0.75}(BTB)_2(DEF)_4]\cdot 2(DEF)_{0.5}$ (**1a**, a), $[Cd_{2.25}Co_{0.75}(BTB)_2(DPS)_2]\cdot x$Sol (**2**, b), $[Cd_{2.25}Co_{0.75}(BTB)_2(DPDS)_2]\cdot x$Sol (**3**, c) and $[Cd_{2.25}Co_{0.75}(BTB)_2(BIPY)(H_2O)_2]\cdot x$Sol (**4**, d). Color legend: Cd (dark magenta), C (black), O (red), N (blue), S (yellow).



(a) (b)

Fig. S7 N_2 (77 K) and CO_2 (195 K) sorption isotherms of $[Cd_{2.25}Co_{0.75}(BTB)_2(DPDS)_2]\cdot x$Sol (**3**, a), $[Cd_{2.25}Co_{0.75}(BTB)_2(BIPY)(H_2O)_2]\cdot x$Sol (**4**, b), with pressures of up to 1 bar. The black square and red circle represent N_2 absorption and desorption at 77 K, while the blue and pink triangles represent CO_2 absorption and desorption at 195 K. P_0 is the saturated vapor pressure of the adsorbates at the measurement temperatures.

Table S1 The ICP analysis showing the different metal distribution in the products.

Starting ratio (Cd:Co)	m (mg)	Cd		Co		Product ratio ($Cd:Co_)$
		c (ppm)	w%	c (ppm)	w%	
1:1	7.21	16.58	11.50	6.83	4.74	5:4
2:1	7.24	21.42	14.79	3.79	2.62	3:1
3:1	7.08	20.89	14.76	3.83	2.71	3:1
3:2	7.16	19.37	13.53	5.18	3.62	2:1
4:1	7.05	23.58	16.72	2.55	1.81	5:1
4:3	7.14	17.46	12.23	5.24	3.67	5:3
5:1	7.20	24.21	16.81	2.38	1.65	5:1
5:2	7.25	21.14	14.58	3.38	2.33	3:1
5:3	7.13	20.40	14.31	4.27	2.99	5:2
5:4	7.29	17.93	12.30	6.26	4.30	3:2