Supplementary Information

Three metal-organic framework isomers of different pore sizes for selective CO_2 adsorption and isomerization studies

Rui Zhang,[a] Jv-Hua Huang,[a] De-Xian Meng,[a] Fa-Yuan Ge,[b] Li-Fei Wang,[a] Yong-Kai Xv,[a] Xing-Gui Liu,[a] Mei-Mei Meng,[a] Zhen-Zhong Lu,*[a] He-Gen Zheng,*[b] Wei Huang*[a,c]

a. Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211800, China.

b. State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, P. R. China.

c. Institute of Flexible Electronics (IFE), Northwestern Polytechnical University (NPU), 127 West Youyi Road, Xi'an 710072, China

Table 1. Crystal and Structure Refinement Data for compound **1, 2 and 3**

	1	**2**	**3**
Empirical formula	$C_{20}H_{12}CdN_6O_4$, $0.5[C_3H_7NO]$	$C_{20}H_{12}CdN_6O_4$	$C_{20}H_{12}CdN_6O_4$
Formula weight	549.30	512.76	512.76
Temp. (K)	290	290	293
MoK_α	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Hexagonal
Space group	*Pcca*	*Pbam*	*P6/m*
a (Å)	14.374(2)	21.073(1)	25.357(1)
B (Å)	15.700(2)	13.611(1)	25.357(1)
C (Å)	20.961(3)	15.691(1)	15.796(1)
a (°)	90	90	90.00
β (°)	90	90	90.00
γ (°)	90	90	120.00
V ($Å^3$)	4730.6(9)	4500.8(6)	8795.6(9)
Z	8	4	6
ρ_{calc} (g/cm^3)	1.542	0.757	0.581
μ (mm^{-1})	0.966	0.503	0.386
Final R indices(R1)	0.0414	0.0378	0.0331
[I>2σ(I)] wR2	0.1159	0.1175	0.0595
GOOF	1.078	1.030	1.056

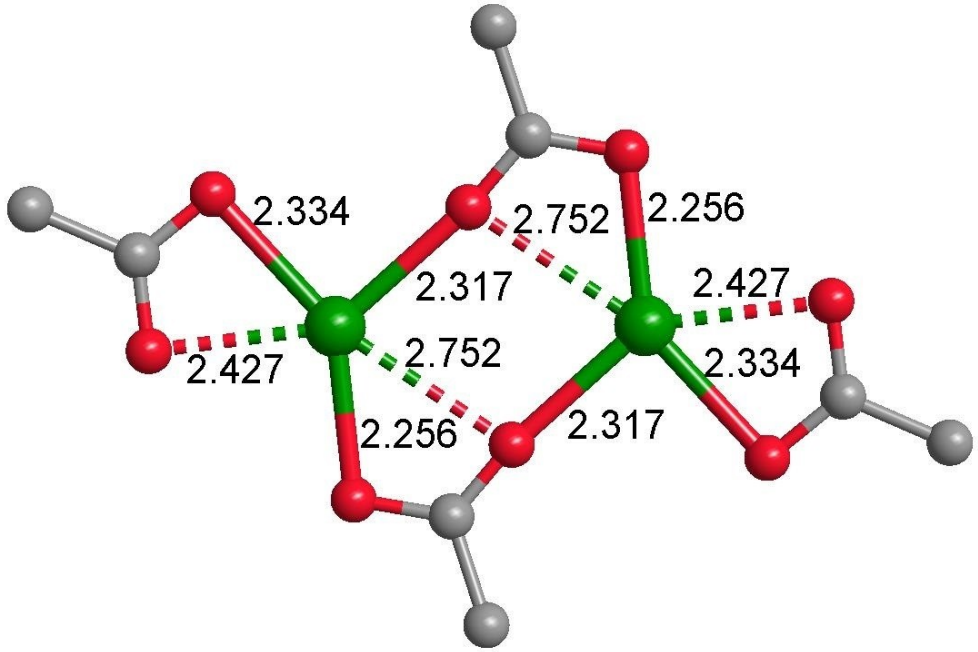

Figure S1. The coordination environment of Cd(II) and the Cd-O bond lengh (Å) in **1** (nitrogen atoms are omitted for clarity, Cd, green; C, dark grey; O, red).

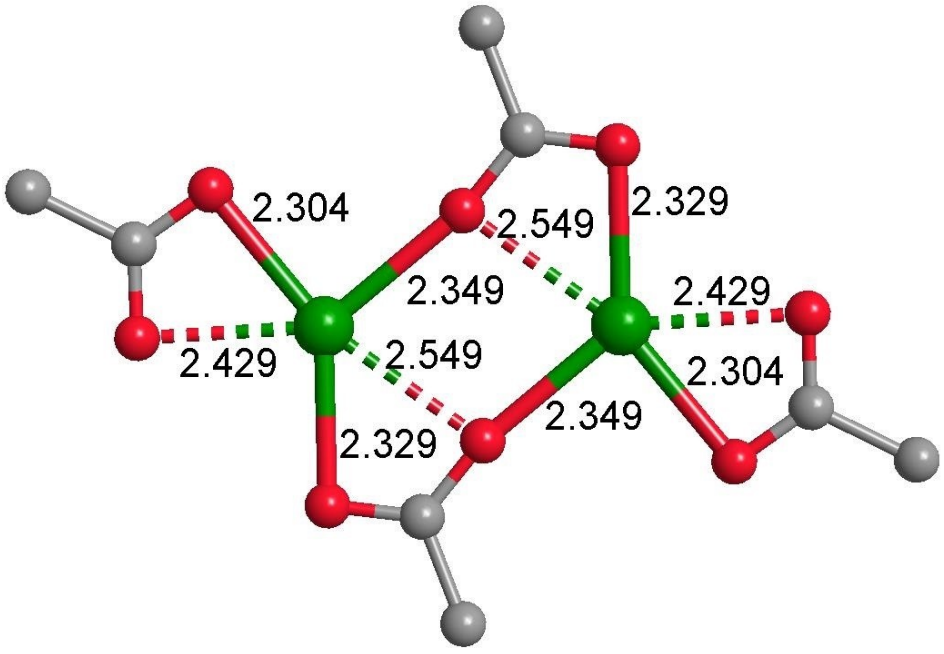

Figure S2. The coordination environment of Cd(II) and the Cd-O bond lengh (Å) in **2** (nitrogen atoms are omitted for clarity, Cd, green; C, dark grey; O, red).

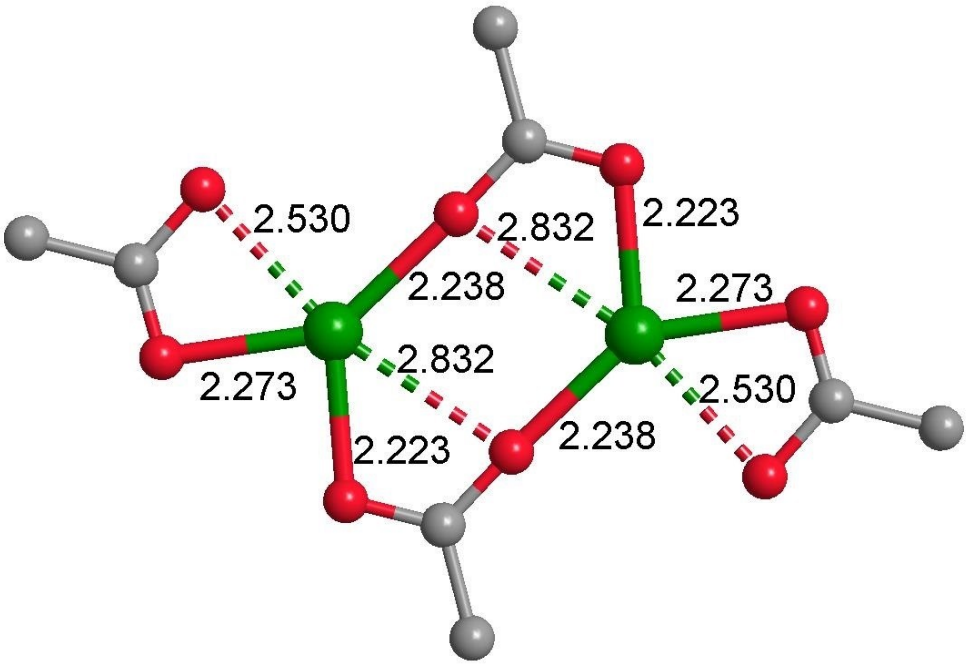

Figure S3. The coordination environment of Cd(II) and the Cd-O bond lengh (Å) in **3** (nitrogen atoms are omitted for clarity, Cd, green; C, dark grey; O, red).

Table S1. The comparison of the Cd-O bond lengths and the acute and obtuse angles of the '**X**' unit[§] in **1**, **2** and **3**.

MOF	Cd-O bond length involving chelating carboxylate group (Å)		Cd-O bond length involving chelating and bridging carboxylate group (Å)			Acute angle of "**X**"[§] (°)	Obtuse angle of "**X**"[§] (°)
1	2.334(1)	2.427(1)	2.256(1)	2.317(1)	2.752(1)	69	111
2	2.304(1)	2.429(1)	2.329(1)	2.349(1)	2.549(1)	66	114
3	2.530(1)	2.273(1)	2.223(1)	2.238(1)	2.832(1)	60	120

[§] The $Cd_2(carboxylate)_4$ units are simplified schematically as red "**X**" (see Figure 2 in main text).

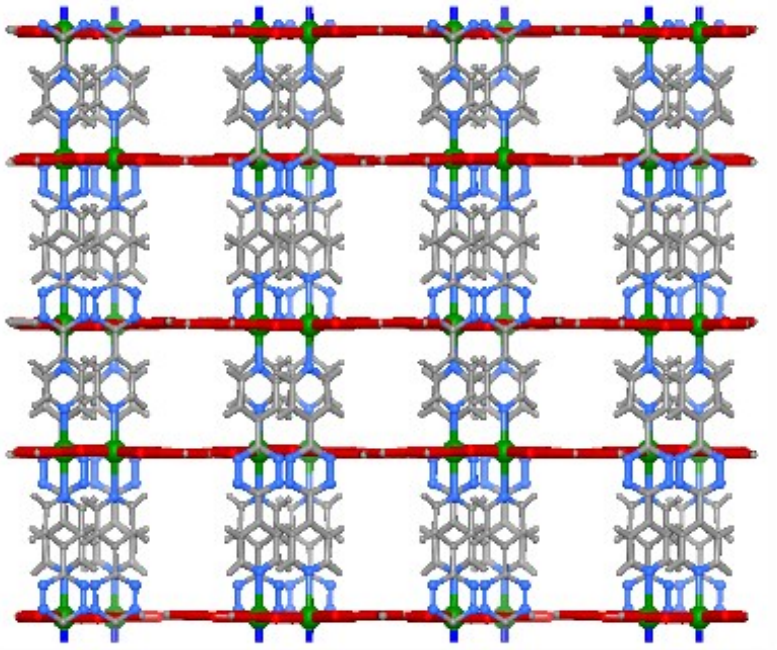

Figure S4. Side view showing the pore structures of **1** ($Cd_2(tp)_2$ layer, red; Cd, green; C/H, grey; N, light blue).

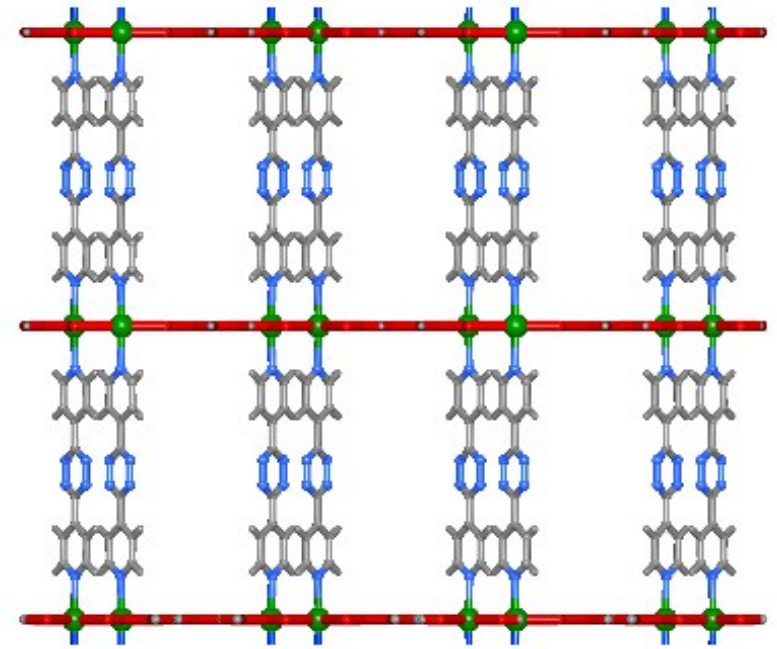

Figure S5. Side view showing the pore structure of **2** ($Cd_2(tp)_2$ layer, red; Cd, green; C/H, grey; N, light blue).

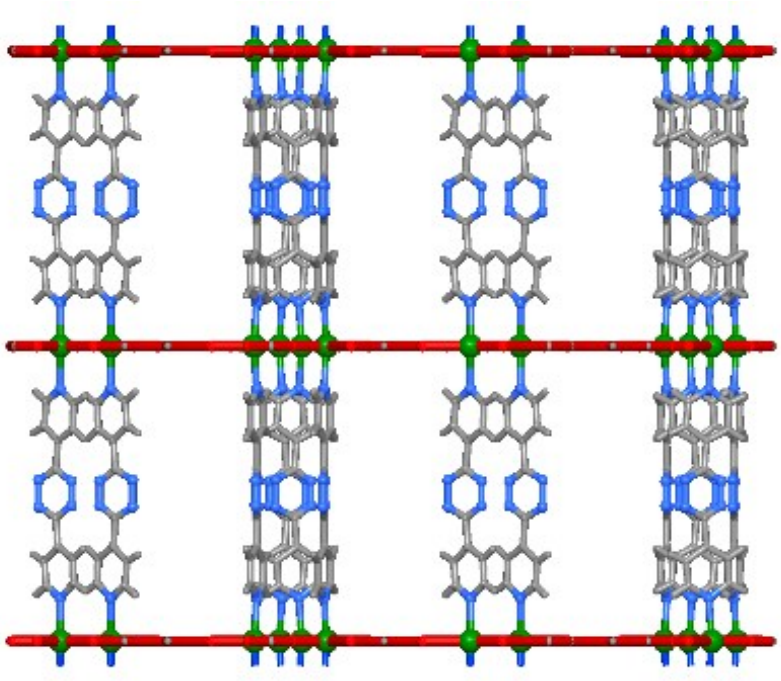

Figure S6. Side view showing the pore structure of **3** ($Cd_2(tp)_2$ layer, red; Cd, green; C/H, grey; N, light blue).

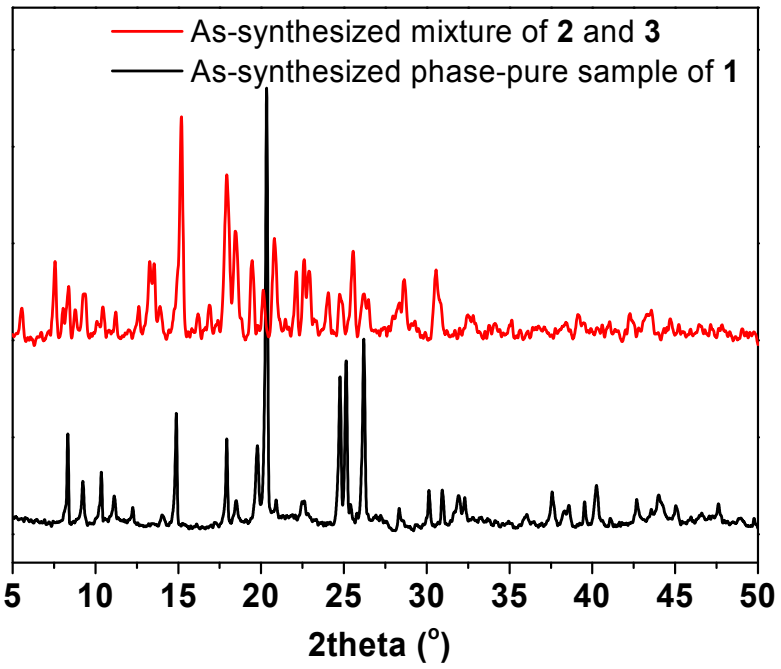

Figure S7. Collected PXRD of as-synthesized phase-pure sample of **1** and as-synthesized mixture of **2** and **3**.

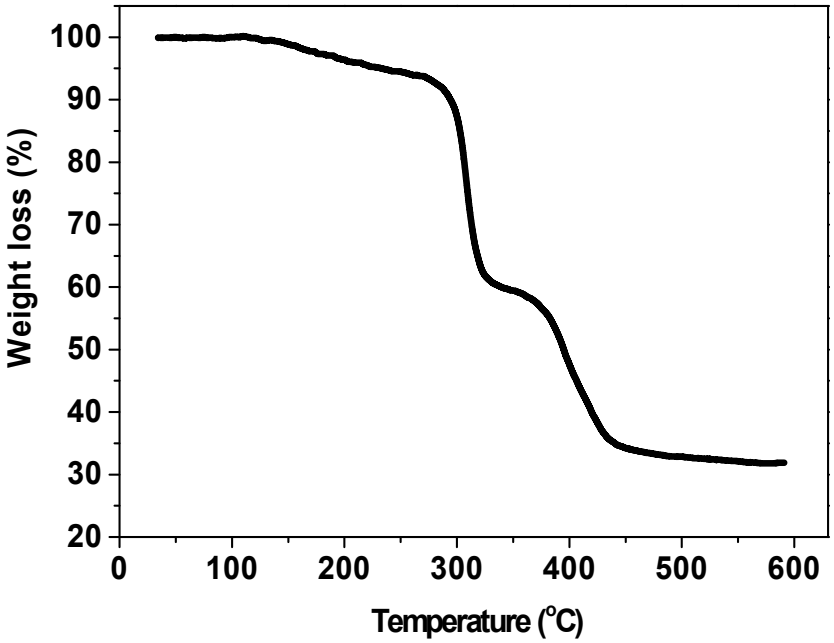

Figure S8. TG result of **1**.

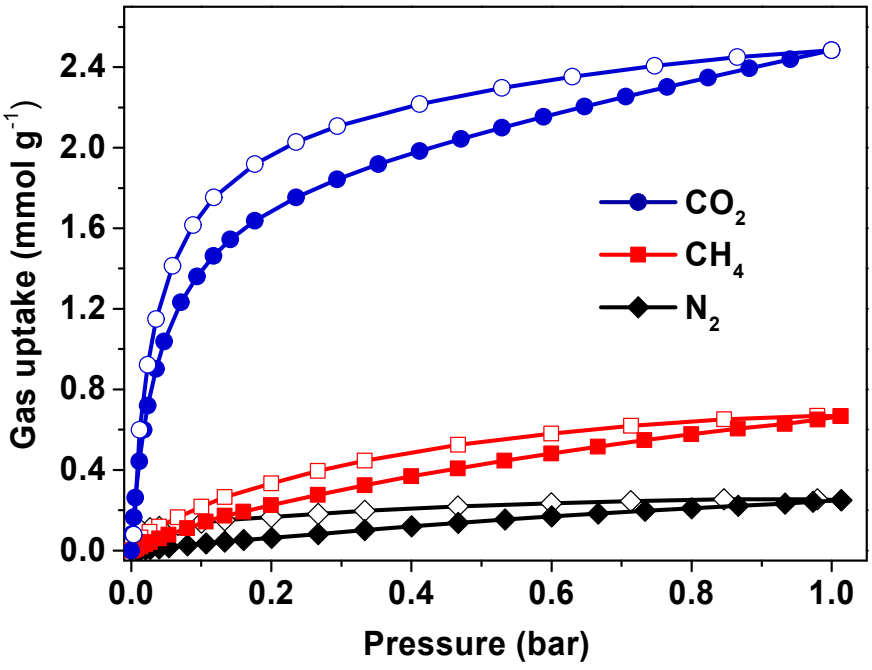

Figure S9. Isotherms of CO_2, CH_4 and N_2 for **1** at 273K**.**

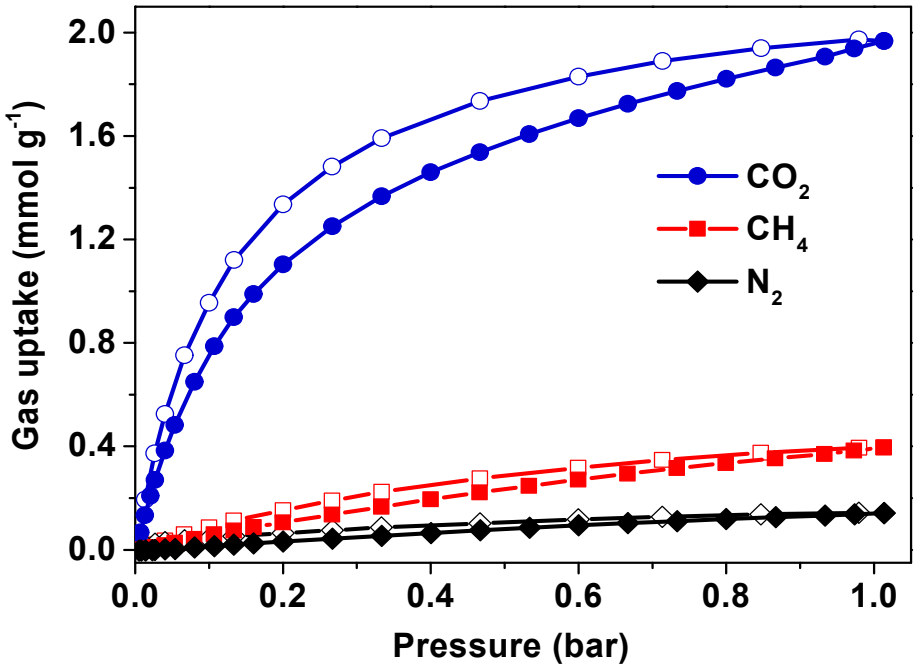

Figure S10. Isotherms of CO_2, CH_4 and N_2 for **1** at 298K**.**

IAST Analysis of the selectivity data in 1.

Ideal adsorbed solution theory (IAST)[1] was used to determine the selectivity factor, *S*, for binary mixtures using pure component isotherm data. The selectivity factor, *S*, is defined according to Equation 1 where *xi* is the amount of each component adsorbed as determined from IAST and *yi* is the mole fraction of each component in the gas phase at equilibrium. The IAST adsorption selectivities were calculated for CO_2/N_2 binary mixtures of compositions (50:50) at 273 K and a total pressure of 1.0 bar.

$$S = \frac{x_1/y_1}{x_2/y_2} \qquad (1)$$

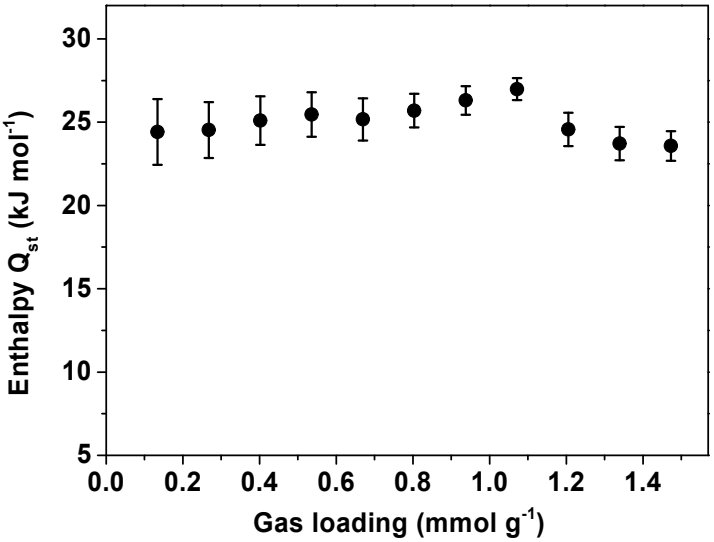

Figure S11. Variation of isosteric heat of adsorption of CO_2 for **1**.

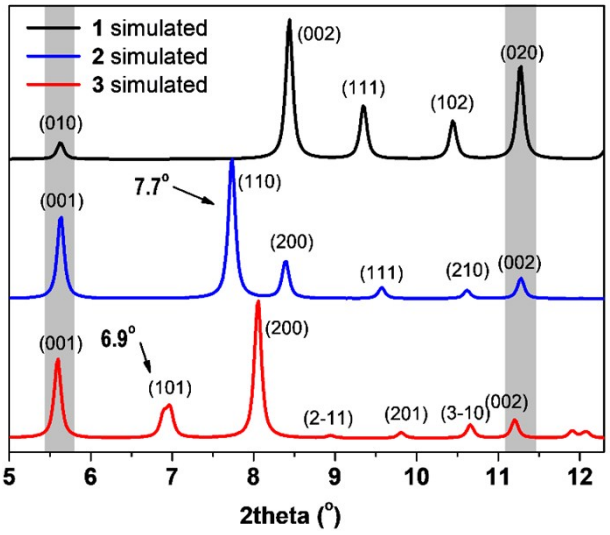

Figure S12. Comparison of simulated PXRD patterns of **1**, **2** and **3** with peaks indexed.

References

1 A. L. Myers and J. M. Prausnitz, *AIChE J.* ,1965, **11**, 121.