Supporting Information

Structure modulation from unstable to stable MOFs by regulating secondary N-donor ligands

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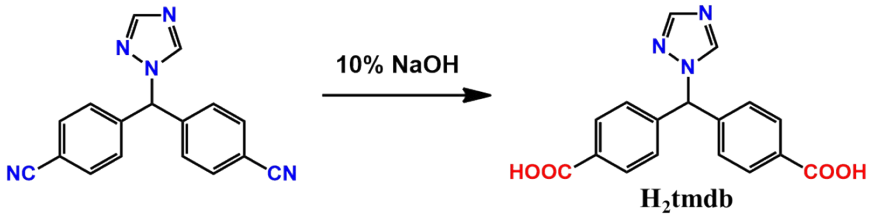
1. Synthesis and Structures.

Preparation of H_2tmdb

8.56 g (0.03 mol) of 4,4'-((1*H*-1,2,4-triazol-1-yl)methylene)dibenzonitrile was charged into a three-necked flask equipped with a magnetic stir bar and 10% sodium hydroxide (50 mL) was added. The resulting mixture was stirred at reflux for 6 h (monitored by TLC). After cooling to ambient temperature, the reaction mixture was extracted with ethyl acetate. Then the water layer was acidified with concentrated hydrochloric acid, and a white precipitate formed which was filtered and washed with distilled water, and then further dried in vacuum. 9.21 g of 4,4'-((1*H*-1,2,4-triazol-1-yl)methylene)dibenzoic acid was obtained without further purification (Yield: 94.9%). 1H NMR (DMSO-d6, 400 MHz) δ 13.06 (s, 2 H), 8.69 (s, 1 H), 8.12 (s, 1 H), 7.96 (d, J = 8.0 Hz, 4 H), 7.36 (d, J = 8.0 Hz, 4 H), 7.33 (s, 1 H); 13C NMR (DMSO-d6, 100 MHz) δ 166.8, 152.1, 144.7, 143.0, 130.6, 129.6, 128.3, 64.6.



Scheme S1. Preparation procedure of H_2tmdb ligand

Synthesis of the $[Cd(tmdb)(DMA)]_n$ (YZ-3)

A mixture of H_2tmdb (16.1 mg, 0.05 mmol), $Cd(NO_3)_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol), DMA (4 mL) and water (1 mL) was sealed in a 20 mL glass vial, which was then ultrasound-treated for 10 min and placed in a 100℃ oven for 96 h. Colorless block crystals were obtained through filtration, DMA washed and air dried (yield 60.3% based on Cd). Elemental analysis for $C_{21}H_{19}N_4O_5Cd$: calcd. (%): C 48.52, H 6.48, N 10.78; found (%): C 48.57, H 6.41, N 10.82.

Structure description of $[Cd(tmdb)(DMA)]_n$ (YZ-3)

X-ray diffraction analysis revealed that **YZ-3** crystallizes in *C*2/*c* space group of monoclinic system with a two dimensional (2D) structure. As shown in Fig. S1a, the asymmetric unit of YZ-3 contains one crystallographic independent Cd^{2+} ion, which is six-coordinated by four carboxylic O atoms from three different $tmdb^{2-}$ ligands, one O atom from DMA molecule and one N atom from another $tmdb^{2-}$ ligand. The Cd-O bonds are around 2.2050(3)-2.59(3) Å, Cd-N bond is 2.259(2) Å

and the Cd^{2+} ion centers based angles are around 78.97(9)-156.38(11)°. In the structure of YZ-3, $tmdb^{2-}$ links four Cd^{2+} ions in a $\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\mu_4$ mode (Fig. S1b) and form a 2D layer structure along *bc* plane (Fig. S1c). Moreover, the coordination of solvent DMA molecules up and down the layers for restricting the dimension generation of structure.

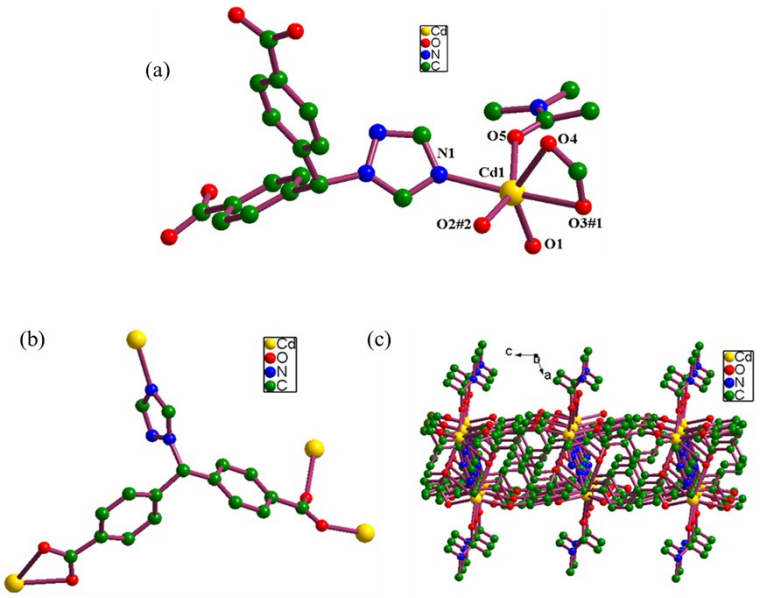


Fig. S1. Structures of YZ-3.

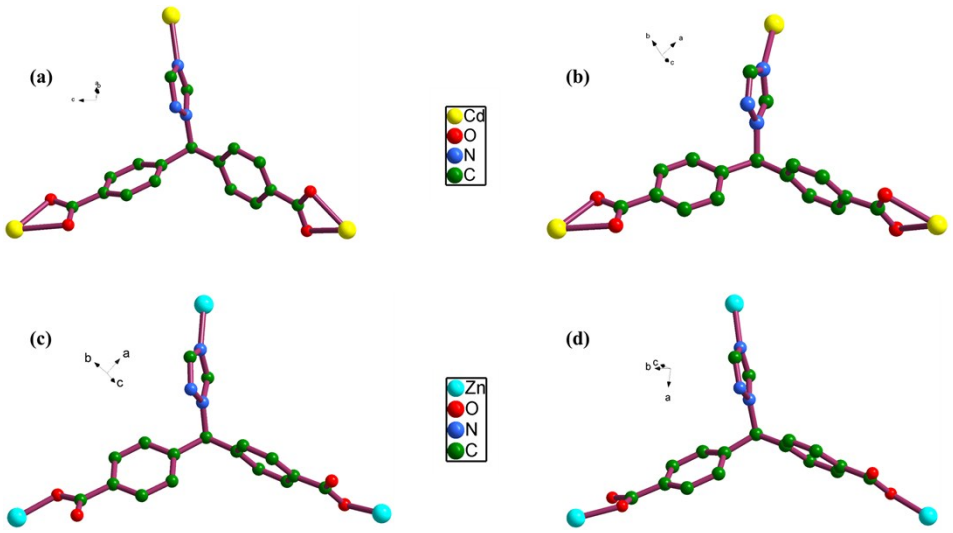


Fig. S2. Coordination modes of H_2tmdb ligand in YZ-7 (a), YZ-8 (b), YZ-9 (c) and YZ-10 (d).

Table S1

Compound	YZ-7	YZ-8	YZ-9	YZ-10
Empirical formula	$C_{23}H_{16}CdN_5O_4$	$C_{24}H_{18}CdN_5O_4$	$C_{48}H_{37}N_{10}O_8Zn_2$	$C_{45}H_{36}N_{10}O_8Zn_2$
Formula weight	538.81	552.83	1012.61	975.58
Crystal system	*monoclinic*	*monoclinic*	*triclinic*	*orthorhombic*
Space group	*C2/c*	*P2/c*	*P*-1	$P2_12_12$
Unit cell dimensions				
a (Å)	34.226(18)	12.292(4)	11.733(4)	17.8890(10)
b (Å)	16.245(9)	20.108(7)	19.916(6)	22.857(2)
c (Å)	14.643(8)	19.807(7)	20.326(7)	9.176(3)
α (deg)	90	90.000(6)	95.447(6)	90
β (deg)	99.029(10)	104.488(6)	102.611(5)	90
γ (deg)	90	90	95.538(6)	90
Volume (A^3)	8041(8)	4740(3)	4580(3)	3752.2(13)
Z	8	4	2	2
Calculated density (g/cm^3)	0.890	0.775	0.734	0.863
F(000)	2152.0	1108.0	1038.0	1000.0
θ range for data collection (°)	3.822 to 49.67	2.026 to 49.694	2.068 to 56.668	2.89 to 55.15
Goodness-of-fit on F^2	1.000	0.956	0.904	0.834
Final R indices [I>2σ(I)]	R1 = 0.0455, wR2 = 0.1164	R1 = 0.0569, wR2 = 0.1592	R1 = 0.0511, wR2 = 0.1242	R1 = 0.0420, wR2 = 0.0877
R indices (all data)	R1 = 0.0848, wR2 = 0.1319	R1 = 0.0982, wR2 = 0.1860	R1 = 0.1284, wR2 = 0.1478	R1 = 0.0728, wR2 = 0.0946
Largest diff. peak and hole ($e.A^{-3}$)	0.56 and -0.38	1.09 and -1.04	0.35 and -0.49	0.25 and -0.16

Table S2

YZ-7			
Cd1-O1#1	2.309(4)	Cd1-O3(2)	2.411(4)
Cd1-O4#2	2.301(4)	Cd1-O2#1	2.404(4)
Cd1-N3	2.270(5)	Cd1-N4	2.249(4)
O1#1-Cd1-O3#2	129.47(14)	O1#1-Cd1-O2#1	55.25(14)
O4#2-Cd1-O1#1	90.13(15)	O4#2-Cd1-O3#2	55.44(15)
O4#2-Cd1-O2#1	100.33(16)	O2#1-Cd1-O3#2	152.15(15)
N3-Cd1-O1#1	88.41(16)	N3-Cd1-O3#2	95.32(15)
N3-Cd1-O4#2	138.42(17)	N3-Cd1-O2#1	112.52(15)
N4-Cd1-O1#1	140.13(15)	N4-Cd1-O3#2	90.22(16)
N4-Cd1-O4#2	114.67(17)	N4-Cd1-O2#1	88.50(16)

N4-Cd1-N3	91.69(18)		
Symmetry codes #1: 3/2-X, 1/2+Y, 3/2-Z; #2: 3/2-X, 1/2+Y, 1/2-Z; #3: 3/2-X, -1/2+Y, 3/2-Z; #4 3/2-X, -1/2+Y, 1/2-Z; #5: 1-X, 1-Y, 1-Z;			
YZ-8			
Cd1-O1#1	2.373(4)	Cd1-O2#2	2.348(4)
Cd1-O3	2.320(4)	Cd1-O4	2.338(5)
Cd1-N1	2.258(5)	Cd1-N4	2.219(6)
O2#2-Cd1-O1#1	108.40(16)	O3-Cd1-O1#1	54.64(15)
O3-Cd1-O2#2	91.28(17)	O3-Cd1-O4	98.48(17)
O4-Cd1-O1#1	150.58(18)	O4-Cd1-O2#2	55.34(14)
N1-Cd1-O1#1	95.80(18)	N1-Cd1-O2#2	85.22(17)
N1-Cd1-O3	147.34(19)	N1-Cd1-O4	105.91(18)
N4-Cd1-O1#1	97.3(2)	N4-Cd1-O2#2	152.84(19)
N4-Cd1-O3	96.7(2)	N4-Cd1-O4	97.71(19)
N4-Cd1-N1	101.1(2)		
Symmetry codes #1: 1+X, +Y, +Z; #2: +X, -Y, -1/2+Z; #3: -1+X, +Y, +Z; #4 +X, -Y, 1/2+Z; #5: 1-X, 1-Y, 1-Z;			
YZ-9			
Zn1-O3	2.036(2)	Zn1-N24#1	2.036(2)
Zn1-O1	1.959(2)	Zn1-N1	2.061(3)
Zn2-O6#2	2.009(2)	Zn2-O7	1.954(2)
Zn2-N3	2.070(3)	Zn2-N5	2.030(2)
O3-Zn1-N1	94.87(11)	N24#1-Zn1-O3	109.75(10)
N24#1-Zn1-N1	100.21(11)	O1-Zn1-O3	110.73(10)
O1-Zn1-N24#1	127.18(12)	O1-Zn1-N1	108.61(12)
O6#2-Zn2-N3	102.37(11)	O6#2-Zn2-N5	110.45(10)
O7-Zn2-O6#2	109.98(10)	O7-Zn2-N3	104.89(11)
O7-Zn2-N5	125.31(10)	N5-Zn2-N3	100.72(11)
Symmetry codes #1: -1+X, +Y, +Z; #2: -1+X, +Y, -1+Z; #3: 1+X, +Y, 1+Z; #4 1+X, +Y, +Z; #5: 1-X, 2-Y, 1-Z; #6: 1-X, -Y, 2-Z;			
YZ-10			
Zn1-N3#1	2.011(3)	Zn1-O3#2	1.929(3)
Zn1-O1	1.968(3)	Zn1-N4	2.016(5)
N3#1-Zn1-N4	110.91(14)	O3#2-Zn1-N3#1	108.19(13)
O3#2-Zn1-O1	97.89(14)	O3#2-Zn1-N4	108.07(17)
O1-Zn1-N3#1	114.49(14)	O1-Zn1-N4	116.04(19)
Symmetry codes #1: 1/2+X, 3/2-Y, 2-Z; #2: 1/2-X, 1/2+Y, 1-Z; #3: -1/2+X, 3/2-Y, 2-Z; #4 1/2-X, -1/2+Y, 1-Z; #5: -X, 2-Y, +Z.			

2. Characterization.

IR spectra

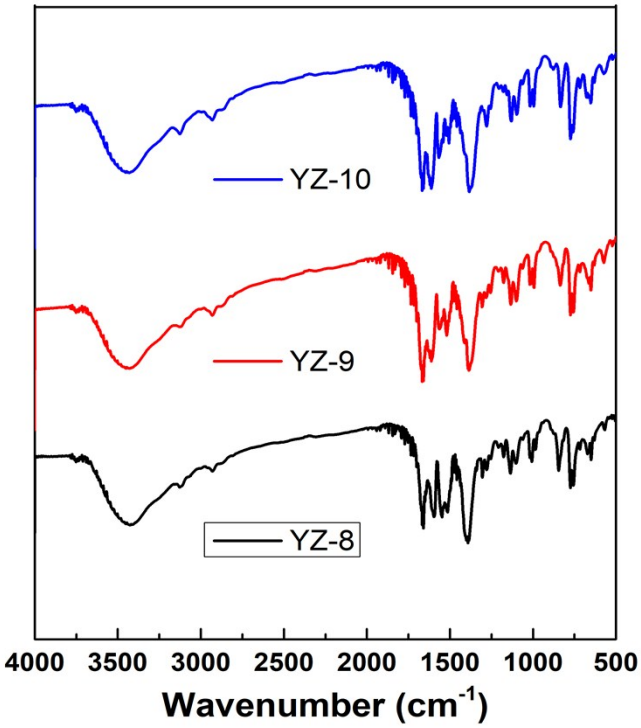
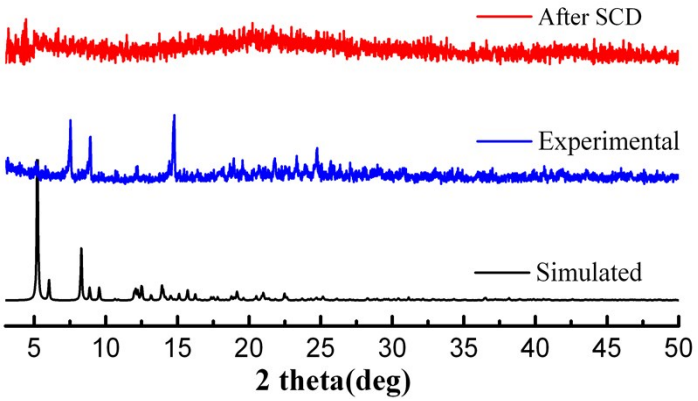
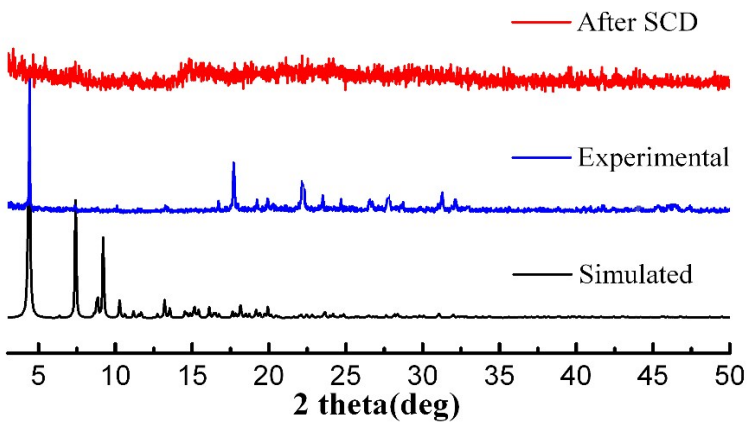


Fig. S3. IR spectrum of YZ-8−YZ-10

PXRD



(a)



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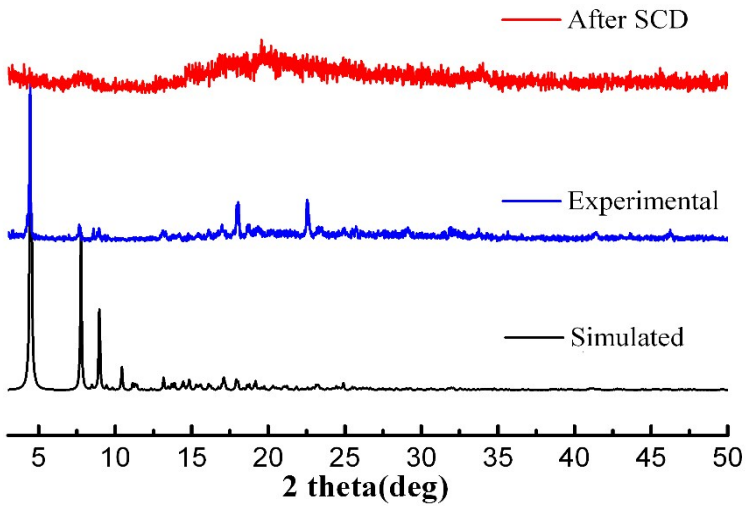

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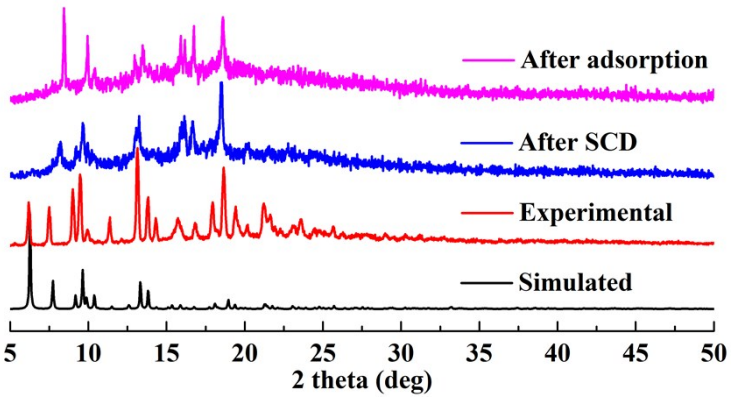

(d)

Fig. S4. PXRD patterns of YZ-7 (a), YZ-8 (b), YZ-9 (c) and YZ-10 (d).

3. Gas Adsorption Properties.

Q_{st} Calculation

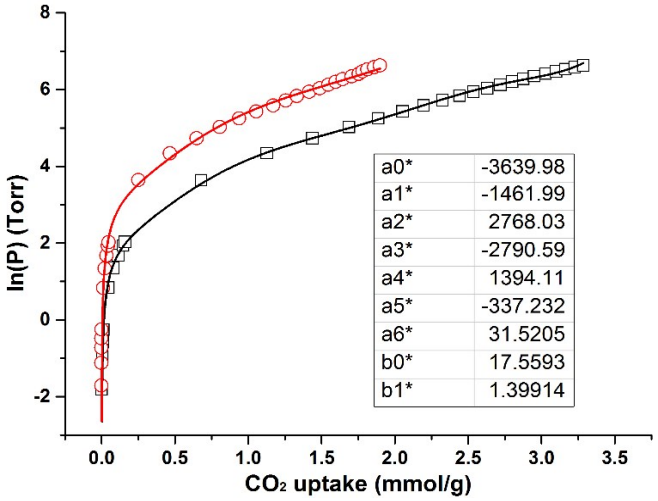

Fig. S5. The CO_2 isotherms at 273 K and 298 K (symbols) and the virial equation fits (lines) for YZ-10.

Calculation of Gas Upatake Selectivity

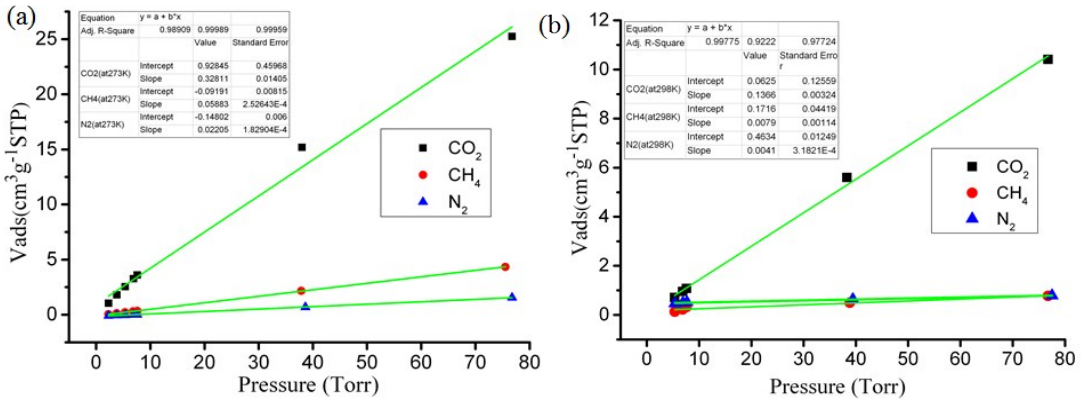

Fig. S6. The fitting initial slopes for CO_2, CH_4, N_2 at 273 K (a) and 298 K (b) for YZ-10.

Prediction of the Gases Adsorption Selectivity by IAST

IAST (ideal adsorption solution theory) was used to predict binary mixture adsorption from the experimental pure-gas isotherms. In order to perform the integrations required by IAST, the single component isotherms should be fitted by a proper model. In practice, several methods to do this are available. We found for this set of data that the dual-site Langmuir-Freundlich equation was successful in fitting the data.

$$q = \frac{q_{m,1} b_1 p^{1/n_1}}{1 + b_1 p^{1/n_1}} + \frac{q_{m,2} b_2 p^{1/n_2}}{1 + b_2 p^{1/n_2}}$$

Here, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mmol/g), $q_{m,1}$ and $q_{m,2}$ are the saturation capacities of sites 1 and 2 (mmol/g), b_1 and b_2 are the affinity coefficients of sites 1 and 2 (1/kPa), and n_1 and n_2 represent the deviations from an ideal homogeneous surface. The fitted parameters were then used to predict multicomponent adsorption with IAST.

The selectivity $S_{A/B}$ in a binary mixture of components A and B is defined as (x_A/y_A) / (x_B/y_B),

where x_i and y_i are the mole fractions of component i (i = A, B) in the adsorbed and bulk phases, respectively.

Table S3.

	CO_2	CH_4	N_2
Kinetic diameter (Å)	3.3	3.8	3.6
Quadrupole moment $10^{40}\ \theta$ (cm^2)	13.4	0	4.7
Dipole moment (D)	0	0	0