Supporting Information for

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Ligand Symmetry Modulation for Designing Mixed-ligand Metal−Organic Frameworks: Gas Sorption and Luminescence Sensing Properties

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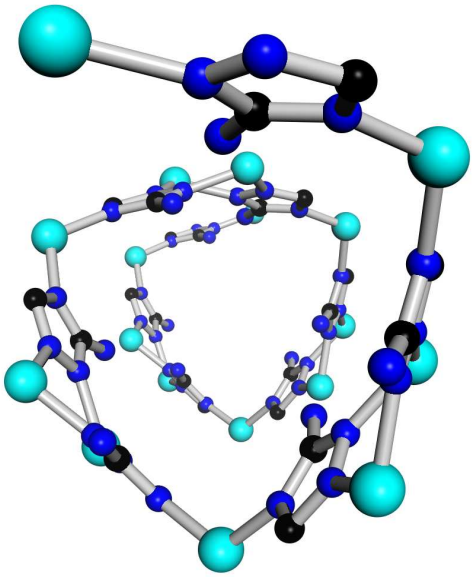


Figure S1. View of the 1D right-handed helical chain building unit along *c* axis.

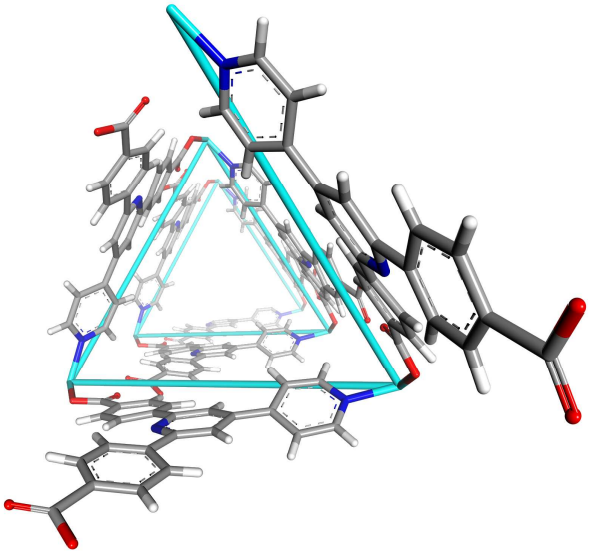


Figure S2. View of the 1D right-handed helical channel along *c* axis.

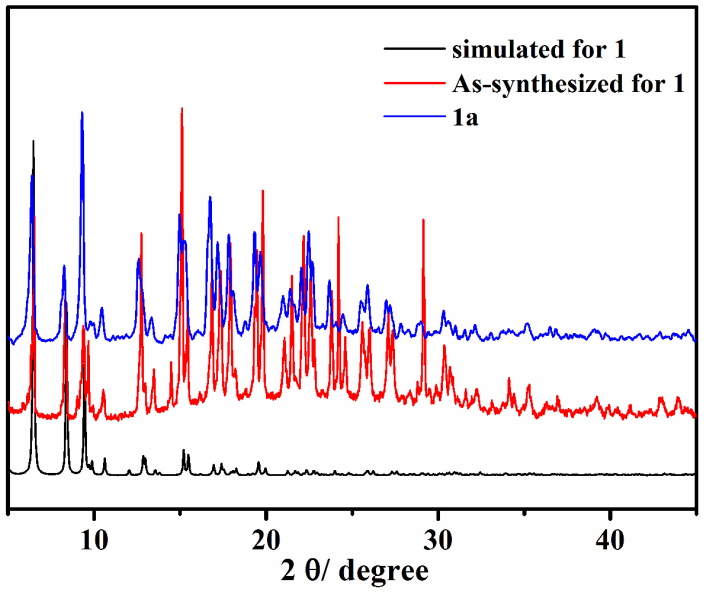
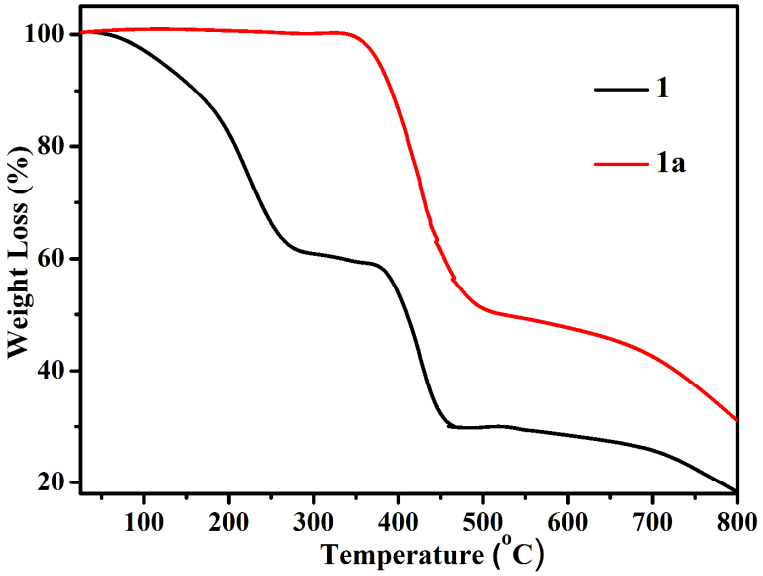


Figure S3. PXRD patterns of **1** and **1a**.



FigureS4. Thermogravimetric curves of **1** and **1a**.

Analysis of H_2 Adsorption Isotherms using Clausius-Clapeyron equation:

The H_2 adsorption isotherms of **1a**are fitted to the Langmuir-Freundlich according to the literature. An accurate fit was obtained by using this equation which results a precise prediction over the quantity of gas adsorbed at saturation. A variant of the Clausius-Clapeyron equation was used to calculate enthalpy of adsorption.

$$ln\frac{P_1}{P_2} = \Delta H_{ads} \times \frac{T_2 - T_1}{R \times T_2 \times T_1} \quad \text{(I)}$$

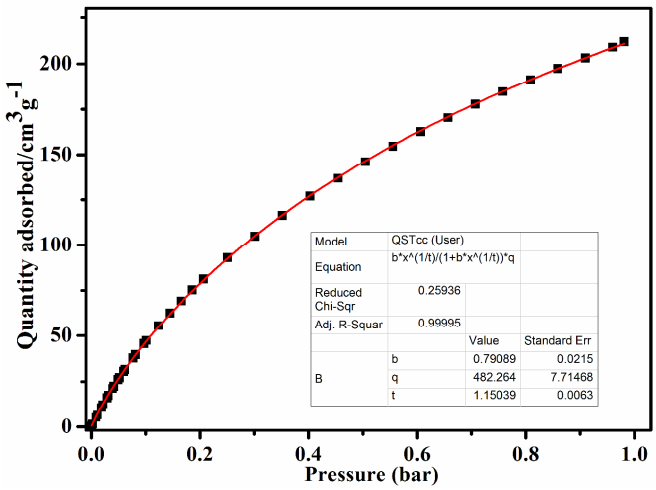
where T_1 and T_2 are the two isotherm temperatures (77 and 87 K), P_1 and P_2 are pressures at T_1 and T_2, respectively, for a given uptake, and R is the universal gas constant (R = 8.3147 J/(K·mol)). Pressure as a function of the amount of gas adsorbed was determined using the Langmuir-Freundlich fit for the isotherms.

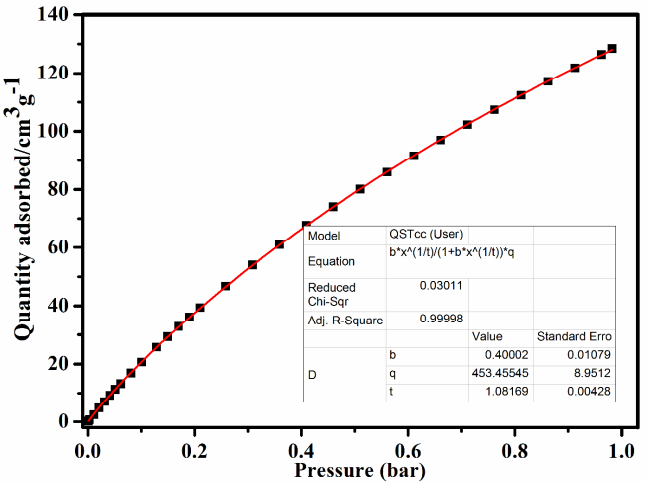
$$\frac{q_i}{q} = \frac{bp^{(1/t)}}{1 + bp^{(1/t)}} \quad \text{(II)}$$

Where q_i= the amount adsorbed, q = the amount adsorbed at saturation, p = pressure, b and t = constants. The equation (II) rearranges to:

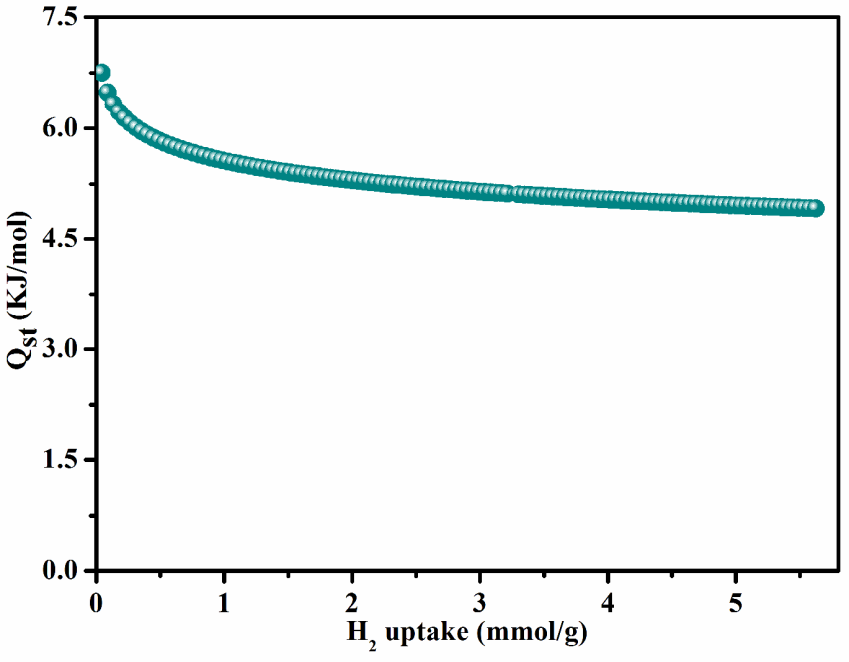
$$p = \left(\frac{\frac{q_i}{q}}{b - b\frac{q_i}{q}}\right)^t \quad \text{(III)}$$

$$\Delta H_{ads} = \frac{RT_1T_2}{T_2 - T_1} \times ln\left(\frac{P_1}{P_2}\right) \quad \text{(IV)}$$





FigureS5. H_2 isotherms at 77 and 87 K (symbols) and Langmuir-Freundlich equation fits (line) for **1a**.

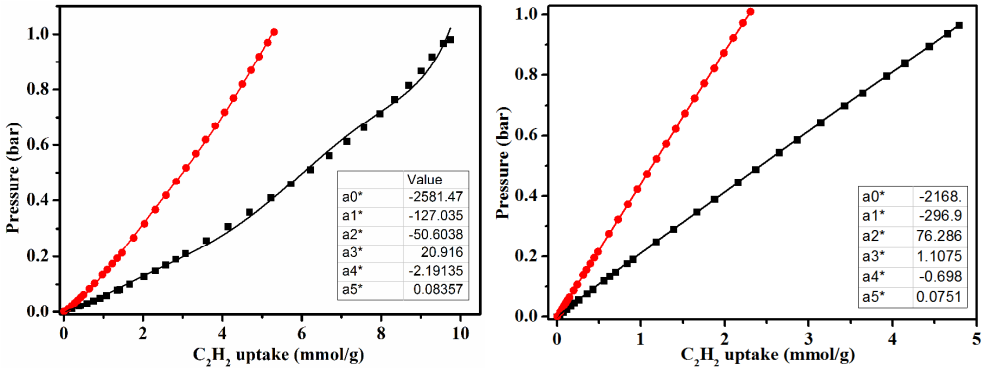


FigureS6. Thecalculated H_2 adsorption heats of **1a**.

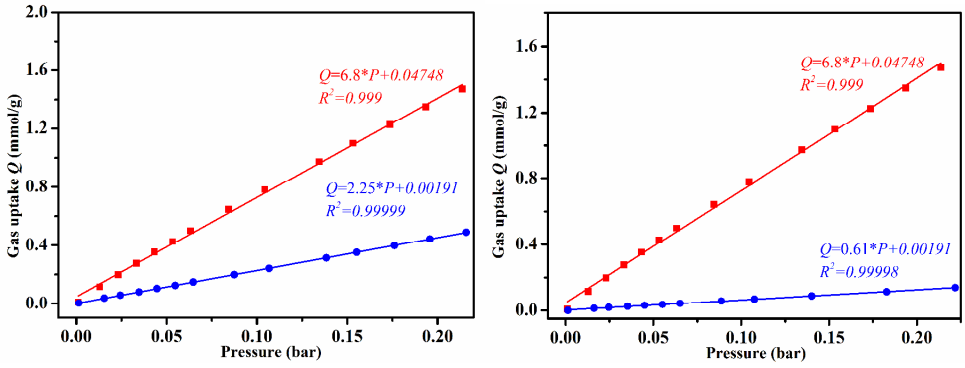
Calculation of Sorption Heat for CO_2 and C_2H_2 Uptake Using Virial.

$$\ln P = \ln N + 1/T\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad\qquad Q_{st} = -R\sum_{i=0}^{m} a_i N^i$$

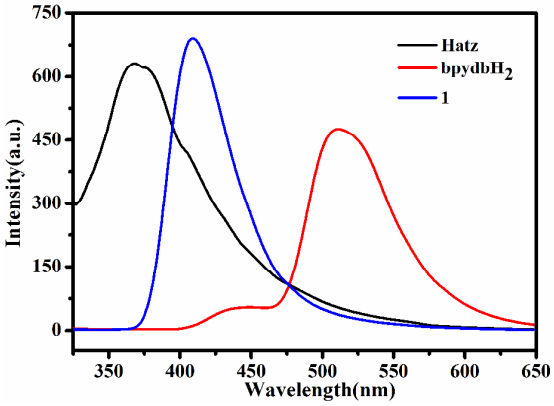
The above virial expression was used to fit the combined isotherm data for **1a** at 273and 298 K, where P is the pressure, N is the adsorbed amount, T is the temperature, ai and bi are virial coefficients, and m and N are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and R is the universal gas constant.



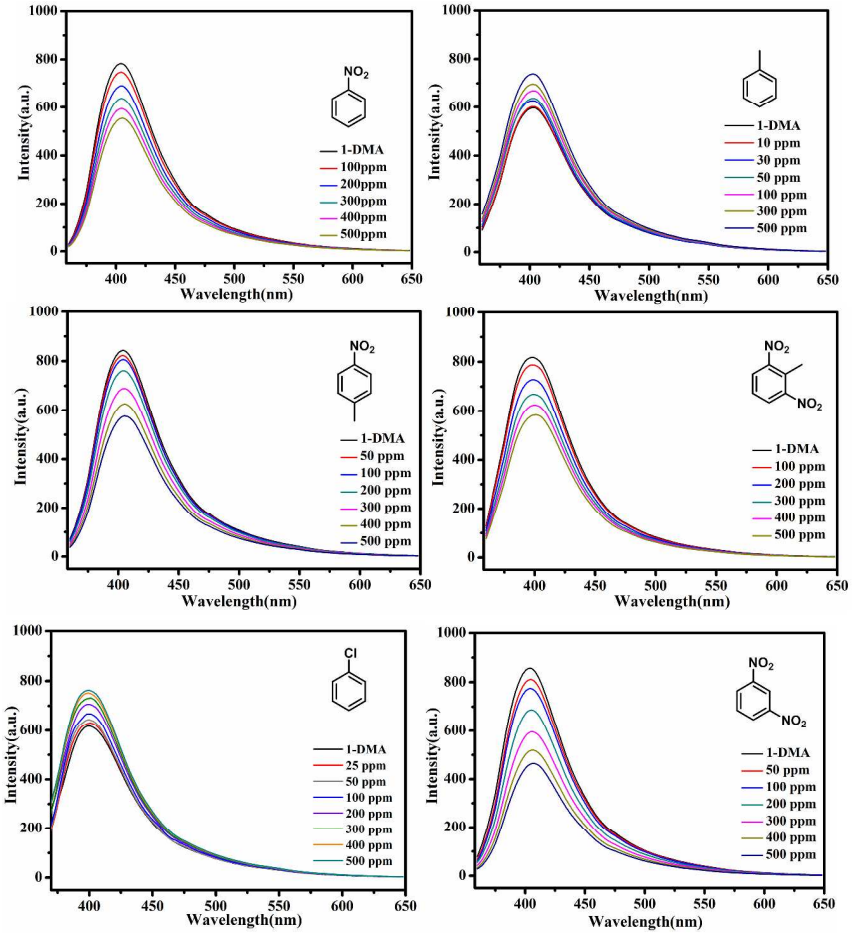
FigureS7. The virial fitting of the adsorption isotherms of C_2H_2 (left) and CO_2 (right) at 273 and 298 K.



FigureS8. Linear fitting of the low-pressure region of C_2H_2, CO_2, and CH_4 adsorption isotherms measured at 298 K.



FigureS9. The solid-state excitation and emission spectra of Hatz, bpydbH_2, and **1** at room temperature.



FigureS10. The emission spectra of **1-DMA** after adding different amount of substituted benzene compounds.

Table S1. Selected bond lengths (Å) for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	O1	1.945(7)	C9	C10	1.382(13)
Zn1	O1[1]	1.945(7)	N1	Zn2[5]	2.053(8)
Zn1	N3	2.012(5)	N1	C23	1.277(13)
Zn1	N3[1]	2.012(5)	N1	C22	1.336(12)
Zn2	O4[2]	2.005(7)	C5	C8	1.511(13)
Zn2	N4	2.002(4)	C5	C4	1.383(15)
Zn2	N5[3]	2.020(14)	C5	C6	1.322(17)
Zn2	N1[4]	2.053(8)	C23	C24	1.361(17)
Zn2	O3[2]	2.396(10)	C11	C12	1.389(15)
Zn2	C17[2]	2.508(13)	C11	C10	1.394(14)
O1	C1	1.289(15)	O3	Zn2[2]	2.396(10)
N2	C12	1.324(11)	O3	C17	1.242(13)
N2	C8	1.387(13)	C12	C13	1.478(14)
O4	Zn2[2]	2.005(7)	C22	C21	1.280(15)
O4	C17	1.251(14)	C24	C20	1.419(15)
N3	C25	1.357(4)	C15	C16	1.339(15)
N3	C26	1.357(4)	C15	C14	1.397(15)
C25	N4	1.357(4)	C19	C13	1.373(16)
N4	N5	1.357(4)	C19	C18	1.452(16)
N5	Zn2[3]	2.020(6)	C10	C20	1.433(15)
N5	C26	1.357(4)	C3	C4	1.416(14)
C26	N6	1.311(8)	C17	Zn2[2]	2.508(13)
C2	C1	1.555(14)	C17	C16	1.496(16)
C2	C3	1.381(17)	C20	C21	1.393(14)
C2	C7	1.301(15)	C16	C18	1.315(15)
C1	O2	1.209(15)	C13	C14	1.378(14)
C9	C8	1.349(16)	C7	C6	1.394(14)

Symmetry transformations used to generate equivalent atoms: [1]-Y+X,-Y,5/3-Z; [2]-Y+X,-Y,2/3-Z;

[3]-X,-X+Y,4/3-Z; [4]+Y,-1+X,1-Z; [5]1+Y,+X,1-Z.

Table S2. Selected bond Angles (°) for **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Zn1	O1[1]	103.4(5)	C23	N1	Zn2[5]	121.7(7)
O1[1]	Zn1	N3[1]	100.6(3)	C23	N1	C22	114.9(9)
O1	Zn1	N3	100.6(3)	C22	N1	Zn2[5]	123.0(7)
O1[1]	Zn1	N3	117.4(3)	C4	C5	C8	117.3(11)
O1	Zn1	N3[1]	117.4(3)	C6	C5	C8	121.7(10)
N3	Zn1	N3[1]	117.5(4)	C6	C5	C4	121.0(10)
O4[2]	Zn2	N5[3]	100.7(5)	N1	C23	C24	125.5(11)
O4[2]	Zn2	N1[4]	99.0(3)	C12	C11	C10	122.6(9)
O4[2]	Zn2	O3[2]	58.6(3)	C17	O3	Zn2[2]	80.4(8)
O4[2]	Zn2	C17[2]	29.6(3)	N2	C12	C11	121.4(9)
N4	Zn2	O4[2]	138.4(4)	N2	C12	C13	116.9(10)
N4	Zn2	N5[3]	104.4(4)	C11	C12	C13	121.6(9)
N4	Zn2	N1[4]	105.9(3)	C21	C22	N1	125.8(10)
N4	Zn2	O3[2]	89.5(2)	C23	C24	C20	118.9(11)
N4	Zn2	C17[2]	116.3(3)	C16	C15	C14	122.5(10)
N5[3]	Zn2	N1[4]	104.9(6)	C13	C19	C18	118.3(10)
N5[3]	Zn2	O3[2]	157.9(5)	N2	C8	C5	112.7(11)
N5[3]	Zn2	C17[2]	130.2(5)	C9	C8	N2	122.1(9)
N1[4]	Zn2	O3[2]	87.2(4)	C9	C8	C5	125.2(10)
N1[4]	Zn2	C17[2]	90.9(4)	C9	C10	C11	114.0(11)
O3[2]	Zn2	C17[2]	29.2(3)	C9	C10	C20	123.4(10)
C1	O1	Zn1	113.2(8)	C11	C10	C20	122.3(8)
C12	N2	C8	117.1(9)	C2	C3	C4	119.5(11)
C17	O4	Zn2[2]	98.1(8)	O4	C17	Zn2[2]	52.3(6)
C25	N3	Zn1	120.0(3)	O4	C17	C16	118.5(11)
C25	N3	C26	108.0	O3	C17	Zn2[2]	70.4(7)
C26	N3	Zn1	131.7(3)	O3	C17	O4	122.0(12)
N3	C25	N4	108.0	O3	C17	C16	119.3(12)
C25	N4	Zn2	127.8(3)	C16	C17	Zn2[2]	164.2(9)
C25	N4	N5	108.0	C24	C20	C10	122.7(10)
N5	N4	Zn2	124.1(3)	C21	C20	C24	113.1(11)
N4	N5	Zn2[3]	121.8(3)	C21	C20	C10	124.2(10)
C26	N5	Zn2[3]	129.7(3)	C15	C16	C17	119.6(10)

Symmetry transformations used to generate equivalent atoms: [1]-Y+X,-Y,5/3-Z; [2]-Y+X,-Y,2/3-Z;

[3]-X,-X+Y,4/3-Z; [4]+Y,-1+X,1-Z; [5]1+Y,+X,1-Z.