Supplementary Information for:

Size-Matching Ligand Insertion in MOF-74 for Enhanced CO_2 Capture under Humid Conditions

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Table S1. Binding energies (in kJ/mol) for guest molecules in MOFs.

CO_2	tpt-Mg-MOF-74		tpt-Zn-MOF-74		Mg-MOF-74		Zn-MOF-74	
	DFT	Classical	DFT	Classical	DFT	Classical	DFT	Classical
None					-45.24	-46.6	-35.18	-35.65
100%	-57.89	-57.34	-40.77	-46.68				
50%		-55.25		-44.39				
Cross		-63.05		-47.93				

Table S2. Binding energies (in kJ/mol) for guest molecules in MOFs.

H_2O	tpt-Mg-MOF-74		tpt-Zn-MOF-74		Mg-MOF-74		Zn-MOF-74	
	DFT	Classical	DFT	Classical	DFT	Classical	DFT	Classical
None					-69.48	-78.08	-51.68	-46.49
100%	-85.51	-85.03	-69.96	-60.42				
50%		-90.06		-69.05				
Cross		-93.48		-73.48				

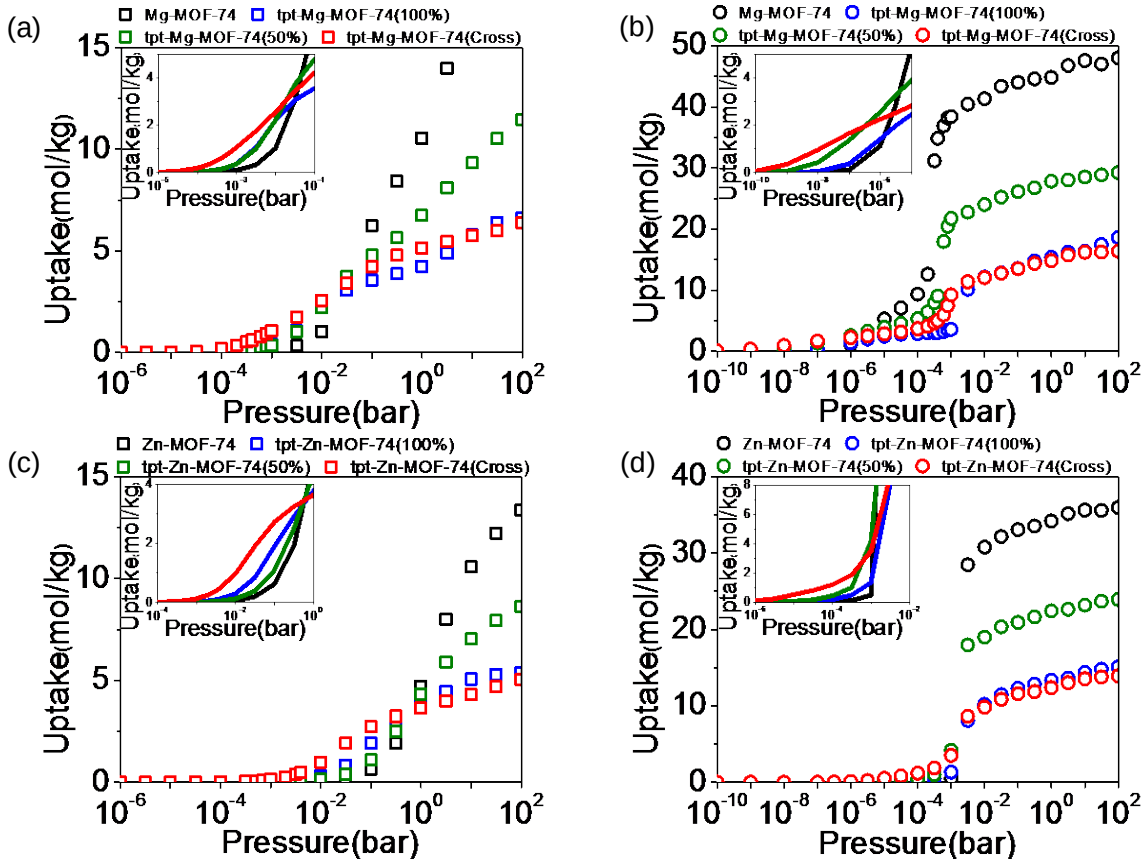

Figure S1. At 313K, (a) CO_2 adsorption isotherm in Mg-MOF-74, tpt-Mg-MOF-74 (50%), tpt-Mg-MOF-74 (100%) and tpt-Mg-MOF-74 (100%, crossed) represented by black, green, blue, and red squares, respectively. (b) Same as (a) except for H_2O with circle representations. (c) Same as (a) but in Zn-MOF-74 and tpt-Zn-MOF-74. (d) Same as (b) but in Zn-MOF-74 and tpt-Zn-MOF-74. In (a) - (d), the inset figures show the zoomed in part at the low pressure region of the isotherms.

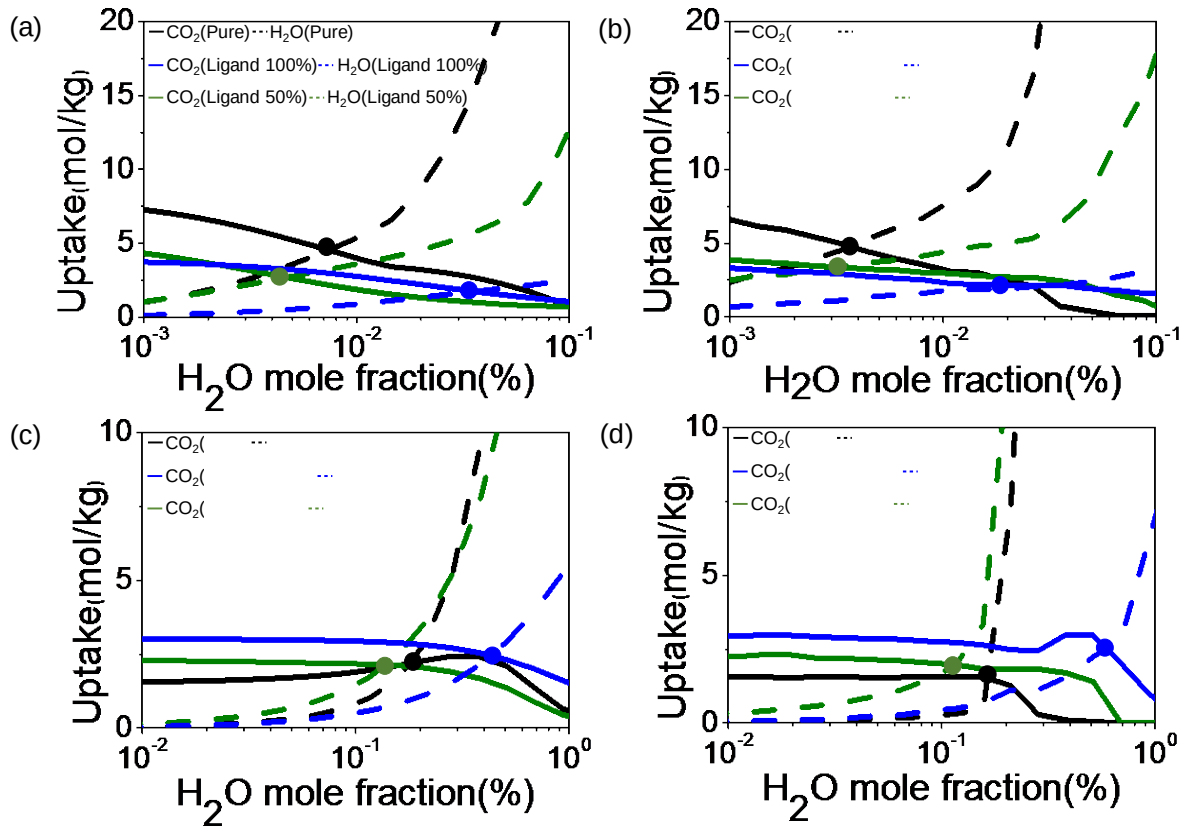

Figure S2. Binary mixture inside (a) the IAST code result in Mg-MOF-74 and tpt-Mg-MOF-74. (b) same as (a) but mixture GCMC simulation result are used. (c) the IAST code result in Zn-MOF-74 and tpt-Zn-MOF-74. (d) same as (c) but mixture GCMC simulation result are used. *y*-axis: simulated binary mixture uptake of CO_2 (solid lines) and H_2O (dot line) as a function of H_2O mole fraction at total pressure of 0.15 bar and temperature of 298 K.

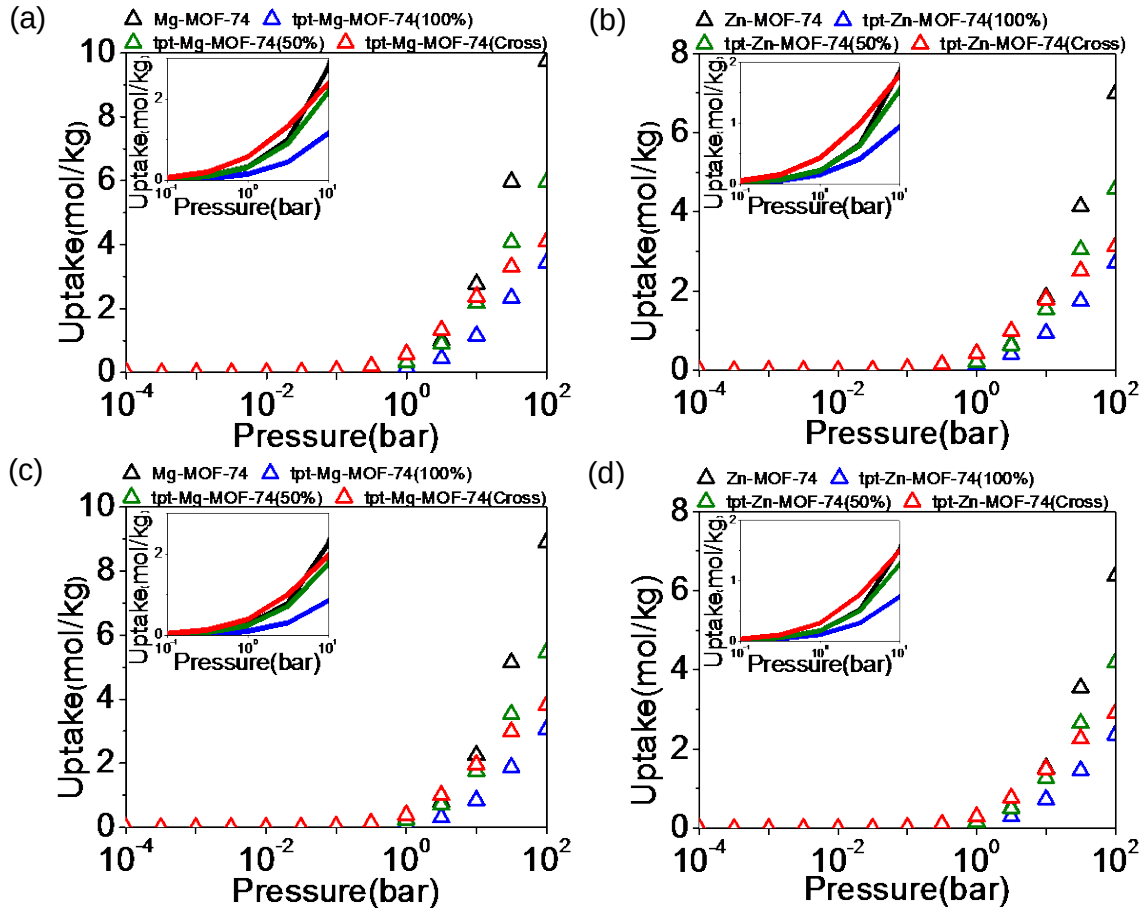

Figure S3. At 298K, (a) N_2 adsorption isotherm in Mg-MOF-74, tpt-Mg-MOF-74 (50%), tpt-Mg-MOF-74 (100%) and tpt-Mg-MOF-74 (100%, crossed) represented by black, green, blue, and red triangles, respectively. (b) Same as (a) but in Zn-MOF-74 and tpt-Zn-MOF-74. (c) Same as (a) but at 313K. (d) Same as (b) but at 313K. In (a) - (d), the inset figures show the zoomed in part at the low pressure region of the isotherms.

Section S4

CO_2/N_2 selectivity using IAST

The selectivity of CO_2/N_2 binary mixture was predicted using the IAST code. By assuming that the binary mixture of CO_2/N_2(15/85) is identical to the composition of flue gas in post-combustion CO_2 capture. The adsorption selectivity is defined as:

$$S = \frac{x_1 / x_2}{y_1 / y_2}$$

where x is the in the molar fraction in the adsorbed phase and y is the molar fraction in the gas phase.

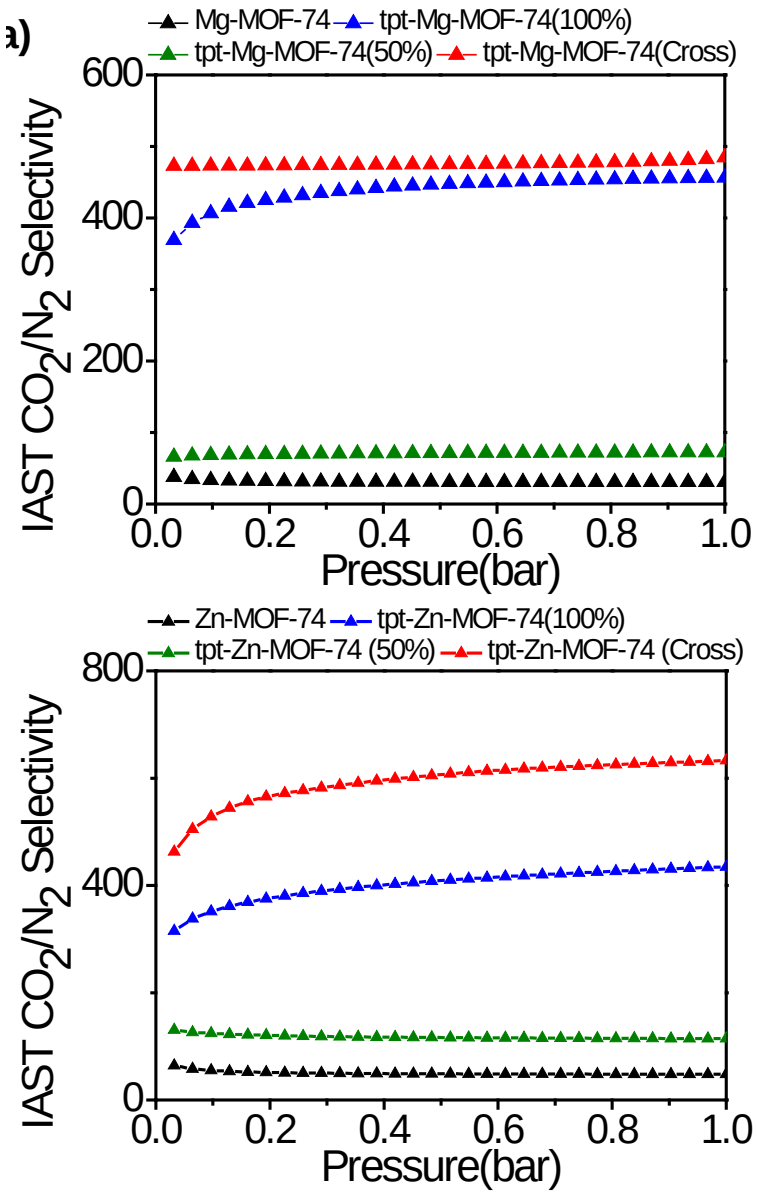

Figure S4. IAST-predicted selectivity for CO_2/N_2 (15:85) mixtures at 298K: (a) Mg-MOF-74(black), tpt-Mg-MOF-74 (50%) (green), tpt-Mg-MOF-74 (100%) (blue) and tpt-Mg-MOF-74 (100%, crossed) (red). (b) Same as (a) but with Zn-MOF-74.

The selectivity of CO_2/N_2 mixtures exhibits on the calculated samples at 298K(Figure S4). The CO_2/N_2 selectivity of tpt-M-MOF-74 (M=Mg, Zn) was significantly higher than that of the parent material, especially within the low-pressure region. The selectivity of CO_2/N_2 of

Mg-MOF-74 was 30.74 at 1bar. Whereas, that of tpt-Mg-MOF-74s was as high as 484.42(100%, crossed), 456.11(100%, non-crossed) and 72.06(50%), respectively. Similar results obtained for tpt-Zn-MOF-74s. The Zn-MOF-74 shows selectivity of 48.10. On the other hand, the CO_2/N_2 selectivity is also high in tpt-Zn-MOF-74(100%, crossed), tpt-Zn-MOF-74(100%, non-crossed), and tpt-Zn-MOF-74(50%), with values of 632.80, 434.70 and 114.36, respectively. It can be concluded that the tpt-M-MOF-74(M=Mg, Zn) not only had a CO_2 adsorption, but also had high CO_2/N_2 selectivity, which would be a promising material for CO_2 capture. Breakthrough simulations were also performed for the four materials, demonstrating the superior performance of tpt-Zn-MOF-74(100%, crossed) over tpt-Zn-MOF-74(50%) and Zn-MOF-74 (See Fig.S5). It can be concluded that the tpt-M-MOF-74(M=Mg, Zn) not only had a CO_2 adsorption, but also had high CO_2/N_2 selectivity, which would be a promising material for CO_2 capture.

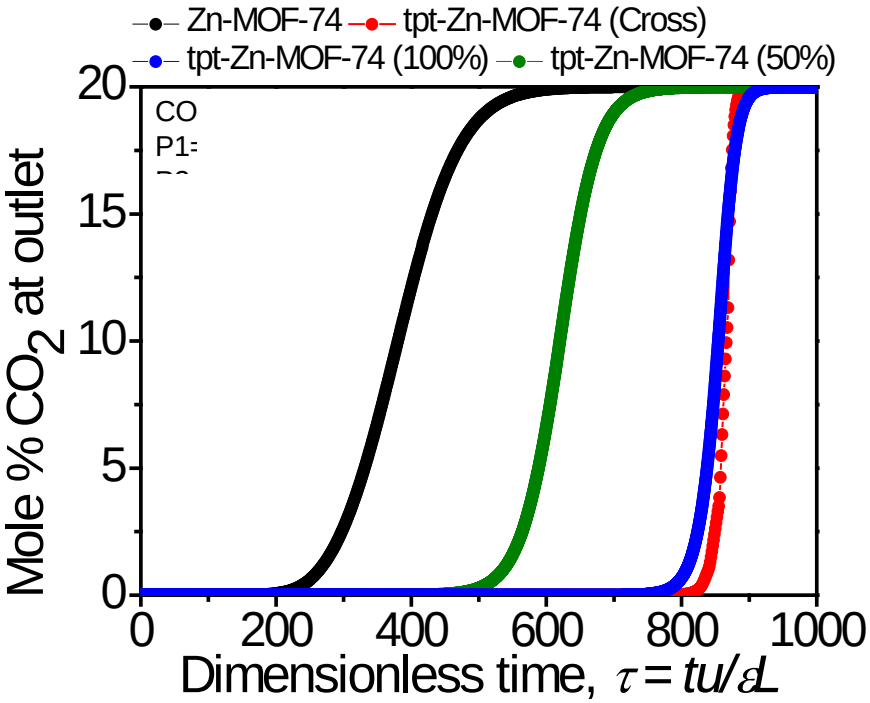

Figure S5. Breakthrough curves representing the mole % CO_2 in the outlet with step-input 15/85 CO_2/N_2 mixture at a total pressure of 1 bar and 298K.