Electronic supplementary information (ESI)

Zinc(II) and cadmium(II) metal-organic frameworks with 4-imidazole containing tripodal ligand: sorption and anion exchange properties[†]

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Table S1. Selected bond lengths [Å] and bond angles [9] for complexes 1 and 2

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Zn(1)-N(1)	2.008(2)	Zn(1)-N(2)#1	1.970(2)
Zn(1)-N(6)#2	1.979(2)	Zn(1)-N(4)#3	2.015(2)
N(2)#1-Zn(1)-N(6)#2	111.57(10)	N(2)#1-Zn(1)-N(1)	115.18(10)
N(6)#2-Zn(1)-N(1)	110.64(10)	N(2)#1-Zn(1)-N(4)#3	107.69(10)
N(6)#2-Zn(1)-N(4)#3	111.62(10)	N(1)-Zn(1)-N(4)#3	99.51(10)
	2		
Cd(1)-N(12)	2.337(4)		
N(12)-Cd(1)-N(12)#4	88.86(15)		

Symmetry transformations used to generate equivalent atoms: #1 -y+5/4,x+3/4,z-1/4, #2 -x+1,-y+2,-z+2, #3 -x+1/2,-y+2,z+1/2, #4 -z+1/2,-x+1,y+1/2-1.

Computational Details.

In the simulations, atomic partial charges for the frameworks are computed from the ChelpG method as Yang et al.¹ DFT calculations using the UB3LYP functional were carried out to compute the charge distributions, and the basis set LANL2DZ was used for the metal atoms Co and Zn, while $6-31+G^*$ was used for the remaining atoms. All the calculations were performed using the GAUSSIAN 03 programs.² ChelpG charge is listed by the atomic label given in Scheme 1 and Table S2.

The adsorption isotherms were simulated with grand canonical Monte Carlo (GCMC) simulations with Towhee Code.³ Detailed descriptions of the simulation method are given in the references.⁴ In the grand canonical ensemble, the chemical potential of each component, temperature, and volume are kept constant as in adsorption experiments. For the sorbate molecules as well as for the frameworks 1', 3' and 4', atomistic models were employed. Interactions beyond 0.75, 0.74 and 0.495 nm were neglected for 1', 3' and 4', respectively. The Lorentz-Berthelot (LJ) mixing rules were used to calculate mixed LJ parameters.⁵ For methane, the van der Waals interactions between the sorbate molecules themselves as well as between the sorbate molecules and the frameworks were described with the LJ potential only. Methane was described with a united atom description, with the potential parameters for methane were taken from Goodbody et. al.⁶ ($\sigma_{CH4} = 0.373$ nm, $\varepsilon_{CH4}/k_B = 148$ K). A combination of the LJ and Coulombic potentials was used to describe the van der Waals interaction for other sorbate molecules except methane. Hydrogen was treated as a diatomic molecule modeled with parameters ($\sigma_H = 0.2958$ nm, $\varepsilon_H/k_B = 36.7$ K).⁷ CO₂, N₂ were described by the TraPPE potential ($\sigma_C = 0.305 \text{ nm}$, $\varepsilon_C/k_B = 79.0 \text{ K}$, $\sigma_O = 0.280 \text{ nm}$, $\varepsilon_N/k_B = 27$ K).⁸ All the potential parameters have been successfully employed to describe the adsorption of alkanes in zeolites quantitatively. The LJ parameters for the C, H and N atoms from the frameworks were taken from the DREIDING force field,⁹ and Co atom was taken from the all-atom UFF force field,¹⁰ which is missed in DREIDING force field. The atoms of the frameworks were held fixed at their crystallographic coordinates. The excess adsorption values were conversed from absolute adsorption values, the outputs of GCMC simulations, by the method of Myers *et. al.*¹¹ Isosteric heat of adsorption is another interest in our research, which was obtained from the fluctuation theory.¹² While in the limit of zero converge, Q_{st} was derived from the (NVT) MC calculations.¹³



Scheme 1. Model systems used in the ChelpG charge calculations. The atom labels used in Table S2 are included in the figure.

	1′		3'		4'
Atom label	q/e	Atom label	q/e	Atom label	q/e
Zn1	0.864	Co1	0.864	Co1	0.834
C1	0.142	C1	0.119	C1	0.147
C2	-0.193	C2	-0.193	C2	-0.171
C3	0.119	C3	0.142	C3	0.101
C4	-0.183	C4	-0.187	C4	-0.19
C5	0.135	C5	0.135	C5	0.115
C6	-0.187	C6	-0.183	C6	-0.205
C7	0.134	C7	0.145	C7	0.215
		1			

Table S2. ChelpG charges calculation for 1', 3' and 4'

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C8	-0.023	C8	-0.008	C8	0.005
C9	0.185	С9	0.265	C9	0.308
C10	0.205	C10	0.134	C10	0.106
C11	0.041	C11	-0.023	C11	-0.002
C12	0.269	C12	0.185	C12	0.165
C13	0.145	C13	0.205	C13	0.169
C14	-0.008	C14	0.041	C14	0.015
C15	0.255	C15	0.259	C15	0.252
Н	0.349	Н	0.349	Н	0.368
H2	0.106	H2	0.106	H2	0.097
H4	0.046	H4	0.1	H4	0.143
H6	0.1	H6	0.046	H6	0.037
H8	0.101	H8	0.098	H8	0.142
H9	0.066	Н9	0.095	H9	0.144
H11	0.162	H11	0.101	H11	0.116
H12	0.149	H12	0.066	H12	0.085
H14	0.098	H14	0.162	H14	0.11
H15	0.095	H15	0.149	H15	0.091
N1	-0.471	N1	-0.532	N1	-0.498
N2	-0.536	N2	-0.545	N2	-0.603
N3	-0.545	N3	-0.536	N3	-0.529
N4	-0.532	N4	-0.471	N4	-0.463
N5	-0.594	N5	-0.494	N5	-0.544
N6	-0.494	N6	-0.594	N6	-0.56

Adsorbent	adsorbate	$Q_{\rm st}$ (kJ/mol) (sim/exp)
1′	Methane	17.43
	H ₂	7.80/ 7.32
	N_2	14.51
	CO ₂	32.69/ 33.63
3'	Methane	16.16
	H_2	7.59/ 7.27
	N_2	14.60
	CO_2	32.17/ 33.22
4'	Methane	4.31
	H ₂	3.62
	N ₂	8.38
	CO_2	22.86

 Table S3.
 Adsorption enthalpies of gases simulated by GCMC calculation



Figure S1. The coordination environment of Zn(II) atom with thermal ellipsoids at 30% probability for **1**. The free water molecules and hydrogen atoms were omitted for clarity.



Figure S2. a) The 1D helical channel formed by the coordination of Zn(II) and two imidazolyl groups. b) The 3D porous framework constructed from the connection of imidazolyl group with adjacent opposite 1D helical channels.



Figure S3. Schematic representations of the (4, 4)-connected **ecl** framework of **1** with (4 $6^3 8^2$) topology; turquiose balls represent the Zn(II) atoms, and red balls represent the centers of benzene rings of H₃L ligands.



Figure S4. The coordination environment of Cd(II) atom with thermal ellipsoids at 30% probability for **2**. The free water molecules, perchlorate ions and hydrogen atoms were omitted for clarity.



Figure S5. Schematic representations of the (3, 6)-connected **pyr** framework of **2** with $(6^3)_2(6^{12} 8^3)$ topology; green balls represent the Cd(II) atoms, and yellow balls represent the centers of benzene rings of H₃L ligands.



Figure S6. The TGA curve of complex **1**.



Figure S7. The X-ray powder diffractions of complex 1: a - simulated; b - as-synthesized; c - activated.

Calculation of CO₂/N₂ selectivity

The methods are applied to estimate the CO_2/N_2 selectivity according to the literature (*J. Am. Chem. Soc.*, 2010, **132**, 38). The ratios of these initial slopes of the CO_2 and N_2 adsorption isotherms were applied to estimate the adsorption selectivity for CO_2 over N_2 .



Figure S8. The fitting initial slope for CO_2 and N_2 isotherms collected at 273K (CO_2 : red squares; N_2 : green triangles).



Figure S9. Experimental and simulated hydrogen adsorption isotherm at 77 K



Figure S10. Experimental and simulated CO₂ adsorption isotherm at 195 K



Figure S11. Experimental and simulated N2 adsorption isotherm at 195 K.



Figure S12. Experimental and simulated CH₄ adsorption isotherm at 195 K



Figure S13. H_2 isotherm for 1' with fitting by virial method. (inlet. Isosteric heat of adsorption with mount of adsorbed H_2)



Figure S14. H_2 isotherm for **3'** with fitting by virial method. (inlet. Isosteric heat of adsorption with mount of adsorbed H_2 .)



Figure S15. CO_2 isotherm for 1' with fitting by virial method.(inlet. Isosteric heat of adsorption with mount of adsorbed CO_2 .)



Figure S16. CO_2 isotherm for **3'** with fitting by virial method.(inlet. Isosteric heat of adsorption with mount of adsorbed CO_2 .)



Figure S17. IR spectra of **2**, exchanged product **2A** and **2C** (reversed exchanged product from **2A** to **2C**).



Figure S18. IR spectra of **2**, exchanged product **2B** and **2D** (reversed exchanged product from **2B** to **2D**).



Figure S19. IR spectra of 2 and ligand H_3L .



Figure S20. The X-ray powder diffractions of complex 2: a - simulated; b - as-synthesized; and exchanged products: c - the exchanged product **2A**; d - the exchanged product **2B**.



Figure S21. IR spectra of **2A**, exchanged product **2B** and **2A** (reversed exchanged product from **2B** to **2A**).



Figure S22. IR spectra of **2B**, exchanged product **2A** and **2B** (reversed exchanged product from **2A** to **2B**).

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