Supporting Information

N-rich zeolite-like metal-organic framework with sodalite topology: high CO_2 uptake, selective gas adsorption and efficient drug delivery

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S1. Materials and Measurements

The starting material H_3L was synthesized according to modified procedure of the reported literature.[1] All other chemicals were obtained from commercial sources, and were used without further purification. Elemental analyses (C, H and N) were measured on a Perkin-Elmer 2400 CHN elemental analyzer; Zn was determined with a Plasma-SPEC(I) ICP atomic emission spectrometer. IR spectrum was performed in the range 4000–400 cm^{-1} using KBr pellets on an Alpha Centaurt FT/IR spectrophotometer. Powder X-ray diffraction measurement was recorded radiation ranging from 5 to 50° at room temperature on a Siemens D5005 diffractometer with Cu-Kα (λ = 1.5418 Å). Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer TG-7 analyzer heated from room temperature to 900 °C under nitrogen at the heating rate of 5 $°C\cdot min^{-1}$.

S2. Gas Sorption Experiments

The N_2, H_2 and CO_2 sorption measurements were performed on automatic volumetric adsorption equipment (Belsorp mini II). Before gas adsorption measurements, the sample was immersed in methanol for 24 h, and the extract was decanted. Fresh methanol was subsequently added, and the crystals were allowed to stay for an additional 24 h to remove the nonvolatile solvates (DMA). The sample was collected by decanting and treated with dichloromethane similarly to remove methanol solvates. After the removal of dichloromethane by decanting, the sample was activated by drying under a dynamic vacuum at room temperature overnight. Before the measurement, the sample was dried again by using the 'outgas' function of the surface area analyzer for 12 h at 90 °C.

S3. The Isosteric Heats of Adsorption

The isosteric heat of adsorption represents the average binding energy of an adsorbing gas molecule at a specific surface coverage, which is calculated by employing the Clausius-Clapeyron equation:

$$Q_{st} = RT^2(\partial \ln P/\partial \mathrm{T})_q$$

where P is pressure, T is temperature, q is the amount adsorbed, R is the gas constant, and Q_{st} denotes the heat of adsorption.

S4. The Selectivity for Gases Adsorption

The selectivity (S) for adsorption of CO_2 over N_2 of **IFMC-1** was calculated from the single-component isotherm data. For CO_2 capture, this value typically reports the ratio of the adsorbed amount of CO_2 at 0.15 bar to the adsorbed amount of N_2 at 0.75 bar; the value is normalized for the pressures chosen, according to equation:

$$S = (qCO_2/qN_2)/(pCO_2/pN_2)$$

where q is the amount adsorbed and P is pressure.

S5. The computational simulation studies of gases adsorption

All the GCMC simulations were performed with the Monte Carlo simulation suite of the MUSIC[2] code and included a 5×10^6 step equilibration period followed by a 5×10^6 step production run. The framework and the gas molecules were considered to be rigid. Lennard-Jones (LJ) interactions were implored to describe the van der Waals interaction with a cutoff distance of 10.0 Å

$$V_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

where i and j are atoms of gases and the **IFMC-1**; r is the distance between two atoms; and ε and σ are LJ well depth and diameter, respectively. Lorentz-Berthelot mixing rules were used to calculate the ε and σ between different atomic species. For Nitrogen, three different types of Monte Carlo trials were used in the simulations: insertion of a new adsorbate molecule at a random position in the adsorbent, removal of a randomly chosen adsorbed molecule from the adsorbent, and translation of a randomly chosen adsorbate molecule within the adsorbent. For the models of CO_2, an additional Monte Carlo trial was needed: rotation of a randomly chosen adsorbate molecule within the adsorbent. Additionally, the Ewald sum method was used to compute the Coulombic interactions for the CO_2 adsorption and the partial charges for atoms of the **IFMC-1** were derived from QEq method. The partial charges on the carbon and oxygen atoms of CO_2 molecules were 0.70e and -0.35e, respectively. The LJ parameters used for **IFMC-1** are taken from UFF[3] and listed together with the parameters of gases in the following table.

		ε/k_B(kcalmol^{-1})	σ(Å)	q(e)
ZIF	C	52.84	3.43	
	H	22.14	2.57	
	N	34.72	3.26	
	Zn	62.40	2.46	
CO_2	C	27.00	2.80	0.70
	O	79.00	3.05	-0.35
N_2	N_2	95.20	3.75	0.00

S6. Drug Loading and Release

Dissolving 5-Fluorouracil (5-FU) (25 mg) and desolvated **IFMC-1** (25 mg) in methanol (5 mL) three days yielded heterogeneous light yellow solution. Then the mixture was centrifuged (12000 r/min for 20 min) and then the solid was washed with methanol. The 5-FU content was calculated through UV/Vis results ($\lambda = 266$ nm).

15 mg of drug-loaded **IFMC-1** was dissolved into 1.5 mL of PBS buffer solution (pH = 7.4), and loaded into a dialysis bag, which was dialyzed against 3 mL of deionized water at 37°C. During each time interval, ca. 1 mL of the solution was pulled out to test, and then decanted back when the test was over. The content of 5-FU in the samples taken out was monitored by fluorometry, in which the detection wavelength was 453 nm ($\lambda_{ex} = 374$ nm).

Reference:

1 M. Dincă, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 16876–16883.

2 A. Gupta, S. Chempath, M. J. Sanborn, L. A. Clark and R. Q. Snurr, *Mol. Simul.*, 2003, **29**, 29–46.

3 A. K. Rappié, C. J. Casewit, K. S. Colwell, W. A. Goddard III and W. M. Skid, *J. Am. Chem. Soc.*, 1992, **114**, 10024–10035.

S7. The Supporting Figures

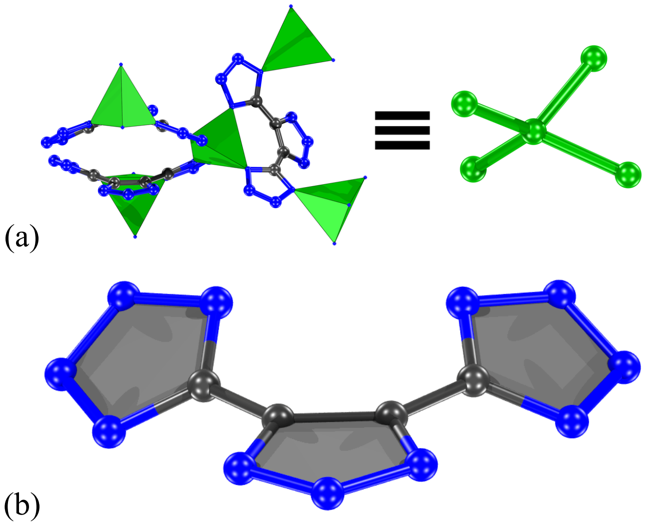

Fig. S1 (a) The structure of **IFMC-1** comprised of four-coordinated ZnN_4 that can be regarded as a 4-connected node; (b) The dihedral angles between triazolate ring and tetrazolate rings is ca. 30º.

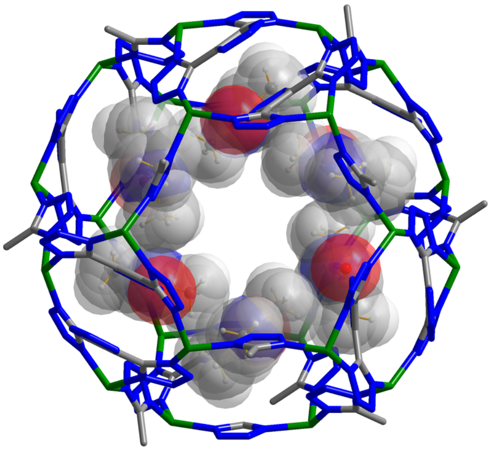

Fig. S2 In **IFMC-1**, six structurally ordered DMA solvent molecules occupied one **sod** cage.

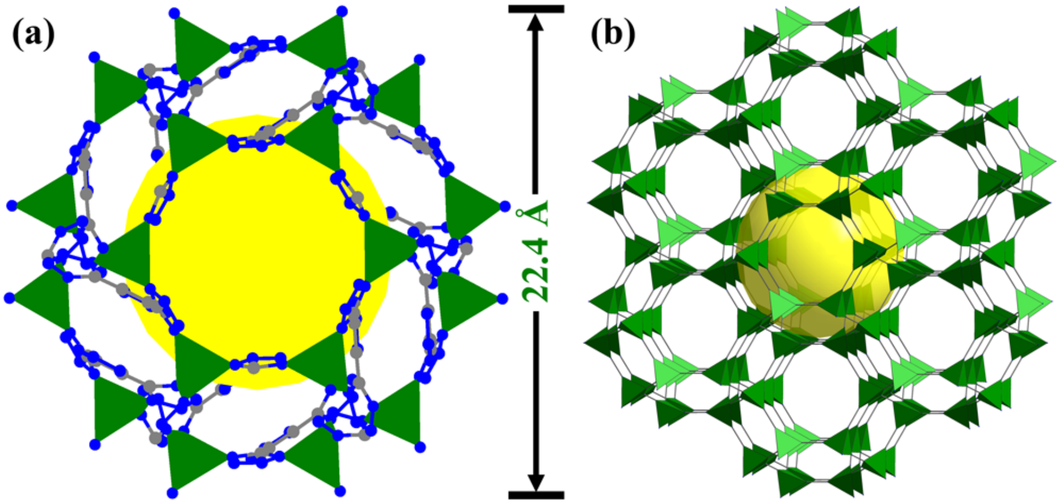

Fig. S3 A sphere of 12 Å in diameter can fit into the cavity without touching the internal van der Waals surface of the cage in **IFMC-1**.

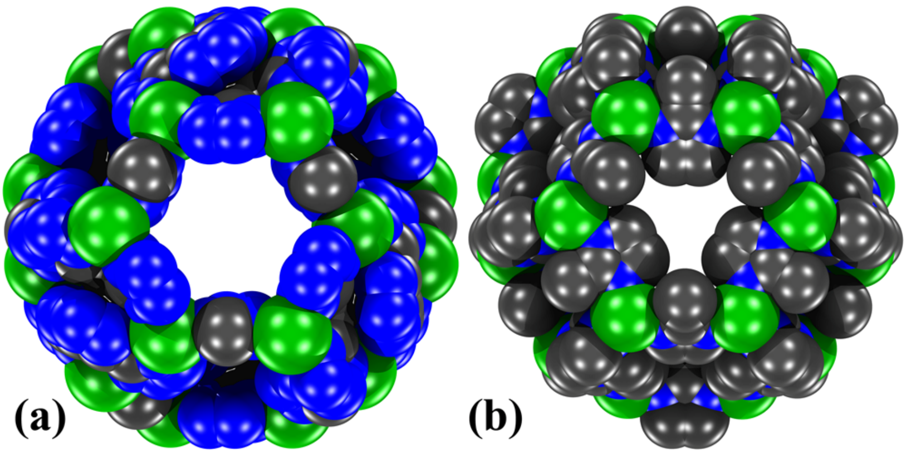

Fig. S4 The spacefill representation of the **sod** cage in **IFMC-1** (a, aperture, 6.4 Å) and ZIF-8 (b, aperture, 3.4 Å). All hydrogen atoms are omitted for clarity.

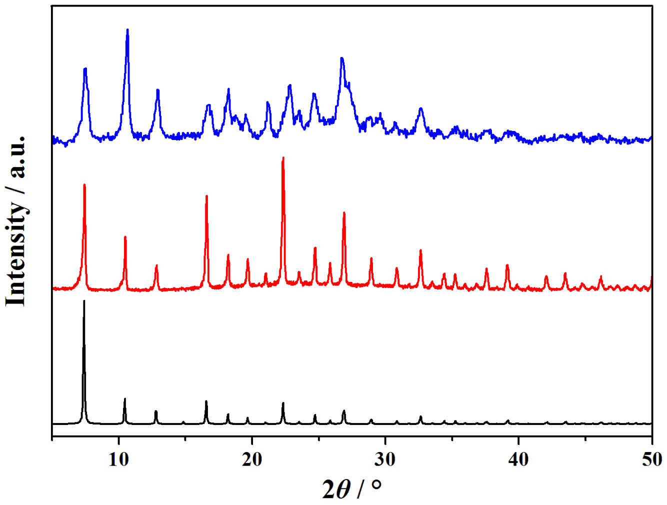

Fig. S5 The XRPD pattern (red) and simulated pattern (black) of **IFMC-1**, and the pattern (blue) of activated **IFMC-1a**, respectively.

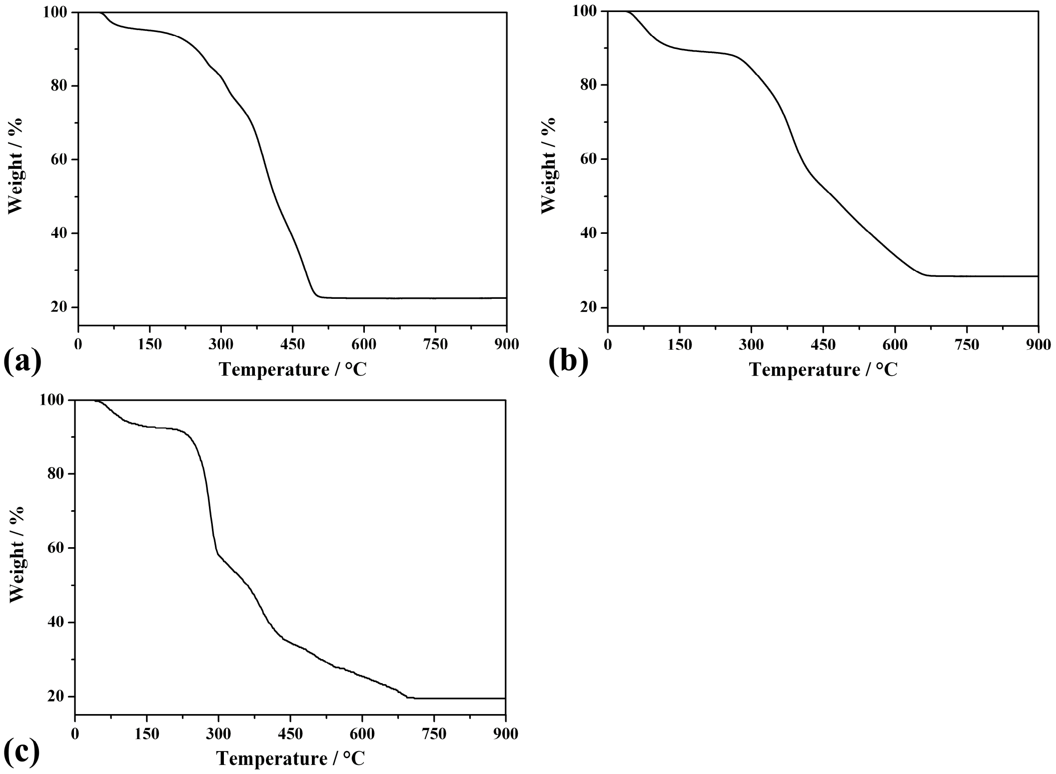

Fig. S6 The TGA curves of **IFMC-1** (a), **IFMC-1a** (b) and **IFMC-1a** after drug loaded (c) measured under N_2 atmosphere from room temperature to 900 °C at the heating rate of 5 °C·min^{-1}.

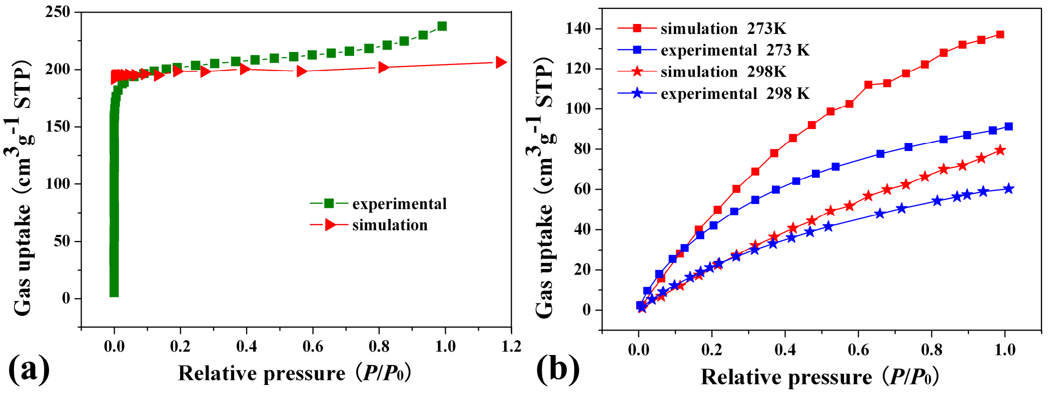

Fig. S7 (a) Comparison of nitrogen isotherms at 77K in **IFMC-1**: experimental data (*green*) and simulated isotherm (*red*). (b) Comparison of CO_2 isotherms at 273 and 298 K in **IFMC-1**: experimental data (*blue*) and simulated isotherm (*red*).

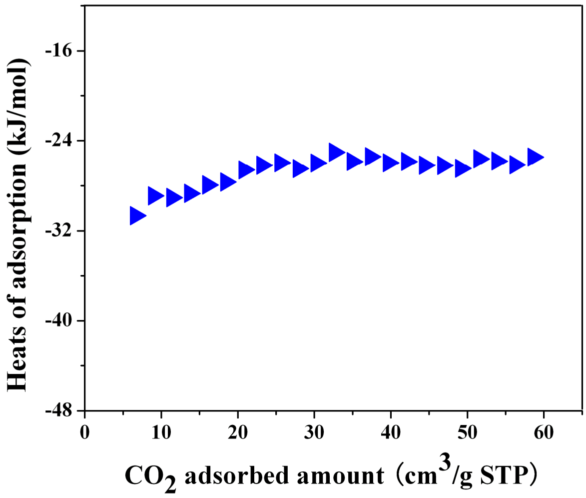

Fig. S8 Isosteric heats of adsorption for CO_2 in **IFMC-1a** as obtained from fits to the gas adsorption data collected at 273 K and 298 K.

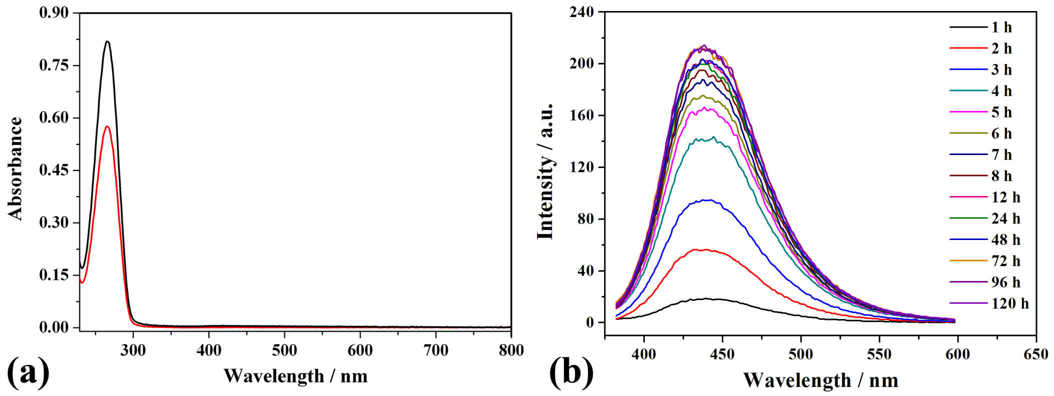

Fig. S9 (a) The UV/Vis absorption spectra of 5-FU methanol solution before (*black*) and after (*red*) drug loaded when diluted 300 times; (b) Luminescence spectra of 5-FU releasing from **IFMC-1a** in PBS (pH 7.4).

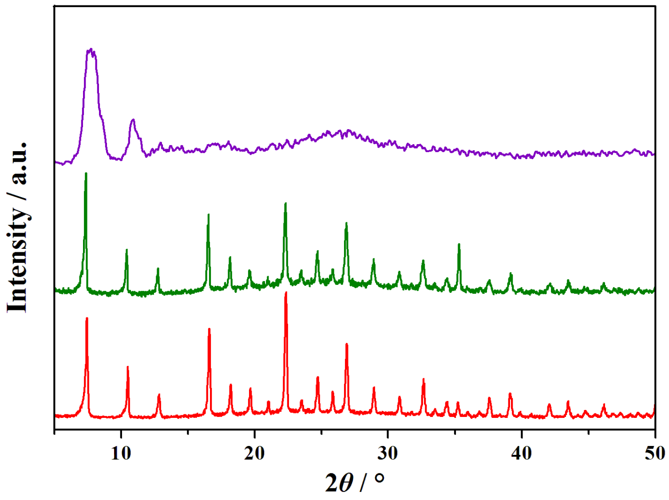

Fig. S10 The XRPD pattern (red) of **IFMC-1** and patterns after drug loaded (green) and after drug delivery (purple) of **IFMC-1**, respectively.

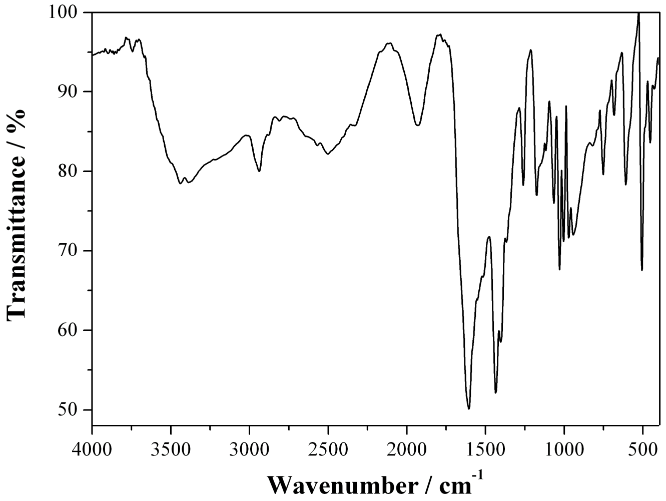

Fig. S11 The IR spectrum of **IFMC-1** in KBr pellets from 4000 cm^{-1} to 400 cm^{-1}.

S7. The Supporting Tables

Table S1. The relevant data of gases adsorption for ZMOFs with **sod** topology

Compound	surface area (m^2 g^{-1})	CO$_2$ uptake (1 atm)		Ref.
		195 K	273 K	
[Zn(HL)]·DMA **(IFMC-1)**	780, BET 932, Langmuir	166.8 cm^3·g^{-1} 7.4 mmol·g^{-1}	91.4 cm^3·g^{-1} 4.1 mmol·g^{-1}	This work
MAF-7	1870 Langmuir	——[b]	62.5 cm^3·g^{-1}	*Adv. Mater.* **2011**, *23*, 1268
Cd(mim)$_2$	2420 Langmuir	——[b]	48 cm^3·g^{-1} 2.2 mmol·g^{-1}	*Chem. Eur. J.* **2010**, *16*, 1137
[LiB(mim)$_4$] (BIF-3-Li)	726.5 Langmuir	——[[b]	34.5 cm^3·g^{-1}	*Angew. Chem., Int. Ed.* **2009**, *48*, 2542
MAF-4	1870 Langmuir	——[b]	29.3 cm^3·g^{-1}	*Adv. Mater.* **2011**, *23*, 1268
[CuB(mim)$_4$] (BIF-3-Cu)	182.3 Langmuir	——[b]	21.9 cm^3·g^{-1}	*Angew. Chem., Int. Ed.* **2009**, *48*, 2542
nZIF-8	1264 BET	——[b]	35 wt% 30 bar	*Chem. Commun.* **2010**, *46*, 4878
HZIF-1Mo	342 BET	77.3 cm^3·g^{-1}	——[b]	*Angew. Chem. Int. Ed.* **2011**, *50*, 450
HZIF-1W	288 BET	70.2 cm^3·g^{-1}	——[b]	*Angew. Chem. Int. Ed.* **2011**, *50*, 450
ZIF-8	1947	——[b]	——[b]	*PNAS* **2006**, *103*, 10186.
Zn(mim)$_2$·2H$_2$O	1030, BET 1400, Langmuir	——[b]	——[b]	*Angew. Chem. Int. Ed.* **2006**, *45*, 1557.
ZIF-90	1270, BET 1320, Langmuir	——[b]	——[b]	*J. Am. Chem. Soc.* **2008**, *130*, 12626.
ZIF-91	1010, BET 1070, Langmuir	——[b]	——[b]	*J. Am. Chem. Soc.* **2008**, *130*, 12626.
Co(nIM)2 ZIF-65	——[a]	——[b]	——[b]	*Science*, **2008**, *319*, 939.
Co(mIM)2 ZIF-67	——[a]	——[b]	——[b]	*Science*, **2008**, *319*, 939.
sod-ZMOF	——[a]	——[b]	——[b]	*Chem. Commun.* **2006**, 1488

[a] No available data for surface area; [b] No available data for the gas sorption.

Table S2. The relevant data of gases adsorption for ZMOFs

ZMOF	zeolite code	surface area m^2 g^{-1}	CO_2 uptake (1 atm)		Ref.
			298 K	273 K	
[Zn(HL)]·DMA **(IFMC-1)**	SOD	780, BET 932, Langmuir	60.3 $cm^3 \cdot g^{-1}$ 2.7 $mmol \cdot g^{-1}$ 66.8 $L \cdot L^{-1}$	91.4 $cm^3 \cdot g^{-1}$ 4.1 $mmol \cdot g^{-1}$ 101.3 $L \cdot L^{-1}$	This work
ZIF-68	GME	1220, Langmuir	37.6 $cm^3 \cdot g^{-1}$ 39.9 $cm^3 \cdot cm^{-3}$	——^{d}	*Acc. Chem. Res.*, **2010**, *43*, 58
ZIF-69	GME	1070, Langmuir	40.6 $cm^3 \cdot g^{-1}$ 49.2 $cm^3 \cdot cm^{-3}$	82.6 $L \cdot L^{-1}$	*Acc. Chem. Res.*, **2010**, *43*, 58; *Science* **2008**, *319*, 939
ZIF-78	GME	620, BET	51.5 $cm^3 \cdot g^{-1}$ 60.2 $cm^3 \cdot cm^{-3}$	——^{d}	*Acc. Chem. Res.*, **2010**, *43*, 58
ZIF-79	GME	810, BET	33.5 $cm^3 \cdot g^{-1}$ 36.1 $cm^3 \cdot cm^{-3}$	——^{d}	*Acc. Chem. Res.*, **2010**, *43*, 58
ZIF-81	GME	760, BET	38.2 $cm^3 \cdot g^{-1}$ 49.3 $cm^3 \cdot cm^{-3}$	——^{d}	*Acc. Chem. Res.*, **2010**, *43*, 58
ZIF-82	GME	1300, BET	52.7 $cm^3 \cdot g^{-1}$ 49.3 $cm^3 \cdot cm^{-3}$	——^{d}	*Acc. Chem. Res.*, **2010**, *43*, 58
ZIF-20	LTA	800, Langmuir	——^{d}	71 $cm^3 \cdot g^{-1\ a}$	*Nat. Mater.* **2007**, *6*, 501
ZIF-71	RHO	652, BET	0.65 $mmol \cdot g^{-1\ b}$	——^{d}	*J. Am. Chem. Soc.* **2010**, *132*, 11006
ZIF-25	RHO	1110, BET	1.09 $mmol \cdot g^{-1\ b}$	——^{d}	*J. Am. Chem. Soc.* **2010**, *132*, 11006
ZIF-93	RHO	864, BET	1.65 $mmol \cdot g^{-1\ b}$	——^{d}	*J. Am. Chem. Soc.* **2010**, *132*, 11006
ZIF-95	POZ	1050, BET	19.7 $cm^3 \cdot g^{-1}$ 19.2 $cm^3 \cdot cm^{-3}$	——^{d}	*Acc. Chem. Res.*, **2010**, *43*, 58
ZIF-96	RHO	960, BET	2.18 $mmol \cdot g^{-1[b]}$	——^{d}	*J. Am. Chem. Soc.* 2010, **132**, 11006
ZIF-97	RHO	564, BET	1.06 $mmol \cdot g^{-1\ b}$	——^{d}	*J. Am. Chem. Soc.* 2010, **132**, 11006
ZIF-100	MOZ	595, BET	0.96 $mmol \cdot g^{-1}$	32.6 $cm^3 \cdot g^{-1}$ 28.2 $cm^3 \cdot cm^{-3}$ 1.7 $mmol \cdot g^{-1}$	*Nature* **2008**, *453*, 207
ZIF-70	GME	1970, Langmuir	55.0 $cm^3 \cdot g^{-1}$ 45.4 $cm^3 \cdot cm^{-3}$	——^{d}	*Acc. Chem. Res.* **2010**, *43*, 58
ZIF-14	ANA	40.8, Langmuir	——^{d}	——^{d}	*Angew. Chem. Int. Ed.* **2006**, *45*, 1557
rho-ZMOF	RHO	1067, Langmuir	——^{d}	——^{d}	*Chem. Commun.* **2006**, 1488
ZIF-64	BCT	——^{c}	——^{d}	——^{d}	*Science* **2008**, *319*, 939
ZIF-1	BCT	——^{c}	——^{d}	——^{d}	*PNAS* **2006**, *103*, 10186
ZIF-2	BCT	——^{c}	——^{d}	——^{d}	*PNAS* **2006**, *103*, 10186

ZIF-6	GIS	——[c]	——[d]	——[d]	*PNAS* **2006**, *103*, 10186
ZIF-74	GIS	——[c]	——[d]	——[d]	*Science* 2008, *319*, 939
ZIF-75	GIS	——[c]	——[d]	——[d]	*Science* 2008, *319*, 939
TIF-5Zn	GIS	——[c]	——[d]	——[d]	*Chem. Mater.* **2008**, *20*, 7377
TIF-5Co	GIS	——[c]	——[d]	——[d]	*Chem. Mater.* **2008**, *20*, 7377
ZIF-80	GME	——[c]	——[d]	——[d]	*J. Am. Chem. Soc.* **2009**, *131*, 3875
ZIF-76	LTA	——[c]	——[d]	——[d]	*Science* **2008**, *319*, 939
ZIF-21	LTA	——[c]	——[d]	——[d]	*Nat. Mater.* **2007**, *6*, 501
ZIF-22	LTA	——[c]	——[d]	——[d]	*Nat. Mater.* **2007**, *6*, 501
ZIF-60	MER	——[c]	——[d]	——[d]	*Science* **2008**, *319*, 939
ZIF-10	MER	——[c]	——[d]	——[d]	*Science* **2008**, *319*, 939
TIF-3	ACO	——[c]	——[d]	——[d]	*Chem. Mater.* **2008**, *20*, 7377
ZIF-11	RHO	——[c]	——[d]	——[d]	*PNAS* **2006**, *103*, 10186
ZIF-12	RHO	——[c]	——[d]	——[d]	*PNAS* **2006**, *103*, 10186

[a] the data was obtained from the Figure 4c in the paper (*Nat. Mater.* **2007**, *6*, 501);

[b] the data were obtained from the Figure 2 in the paper (*J. Am. Chem. Soc.* **2010**, *132*, 11006);

[c] No available data for surface area; [d] No available data for the gas sorption.