Supporting information

Controllable synthesis of isoreticular pillared-layer MOFs: gas adsorption, iodine sorption and sensing small molecules

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S1. Materials and measurements

All chemical materials were purchased from commercial sources and used without further purification. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer. XRPD patterns were recorded on a Siemens D5005 diffractometer with Cu K α (λ = 1.5418 Å) radiation in the range of 3–60° at a rate of 5°/min. The UV-Vis absorption spectra were examined on a Shimadzu UV-2550 spectrophotometer in the wavelength range of 200-800 nm. The C, H, and N elemental analyses were conducted on a Perkin-Elmer 2400CHN elemental analyzer. TG curves were performed on a Perkin–Elmer TG-7 analyzer heated from room temperature to 1000 °C at a ramp rate of 5 °C/min under nitrogen. The photoluminescence spectra were measured on a Perkin-Elmer FLS-920 Edinburgh Fluorescence Spectrometer.

S2. X-ray crystallography

Single-crystal X-ray diffraction data for 1–5 were recorded by using a Bruker Apex CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) at 293 K. Absorption corrections were applied by using a multi-scan technique. All the structures were solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program within WINGX. Non-hydrogen atoms were refined with anisotropic temperature parameters.

The detailed crystallographic data and structure refinement parameters for 1–5 are summarized in Table S1.

S3. Gas sorption experiments

The N₂ and CO₂ sorption measurements were performed on automatic volumetric adsorption equipment (Belsorp mini II). Before gas adsorption measurements, the samples **1-5** were immersed in CH₂Cl₂ for 24 h, and the extracts were decanted. Fresh CH₂Cl₂ was subsequently added, and the crystals were allowed to stay for an additional 24 h to remove the nonvolatile solvates (DMA). After the removal of dichloromethane by decanting, the samples were activated by drying under a dynamic vacuum at room temperature overnight. Before the measurement, the samples were dried again by using the 'outgas' function of the surface area analyzer for 12 h at 90 °C. Meanwhile, the activated samples **1a** were immersed in water, HCl (pH = 2) and NaOH (pH = 12) solutions. After the removal of water by decanting, the samples **1a** were tested N₂ sorption measurements. The results show water and acid/alkaline solutions destroyed the framework in a certain degree, although XRPD patterns keep the same.

S4. Heat of adsorption calculation for gas uptake

The isosteric heat of adsorption values were calculated using the Clausius–Clapeyron equation:

 $\ln(P_1/P_2) = \Delta H_{abs} \times (T_2 - T_1) / R T_1 T_2(1)$

Where P_i = pressure for isotherm i

 T_i = temperature for isotherm i

$$R = 8.315 \text{ J} / (\text{K*mol})$$

The equation can be applied to calculate the enthalpy of adsorption of a gas as afunctionofthequantityofgasadsorbed.



Fig. S1 Representations of the crystal structures of 1 (a), 2 (b) and 5 (c).



Fig. S2 X-ray powder diffraction patterns of simulated (black), as-synthesized (red) and activated samples (blue) of 1 (a), 2 (b), 3 (c), 4 (d) and 5 (e), respectively.



Fig. S3 TG curves of 1 (a), 2 (b), 3 (c), 4 (d) and 5 (e).



Fig. S4 XRPD patterns of **1-5**: as-synthesized (red), and treated in ambient temperature (yellow) and boiling water (green) of a) **1**, b) **2**, c) **3**, d) **4**, e) **5**.



Fig. S5 XRPD patterns of **1-5**: as-synthesized (red), after soaking in acid (pH = 2, blue), alkaline solutions (pH = 12, green) and exposed in air (purple) of a) **1**, b) **2**, c) **3**, d) **4**, e) **5**.



Fig. S6 The nitrogen sorption isotherms of **1a** after (a) water, (b) HCl (pH = 2) and (c) NaOH (pH = 12) treatment.



Fig. S7 The pore size distribution of a) 1, b) 2 and c) 3.



Fig. S8 Isosteric heats of CO_2 adsorption (Qst) for 1.



Fig. S9 Isosteric heats of CO₂ adsorption (Qst) for 2.



Fig. S10 Isosteric heats of CO_2 adsorption (Qst) for 3.



Fig. S11 Isosteric heats of CO_2 adsorption (Qst) for 4.



Fig. S12 Isosteric heats of CO_2 adsorption (Qst) for 5.



Fig. S13 (a) Photoinduced solid state emission spectra of 1, its I₂-loaded samples luminescence change at 0~30 min ($\lambda_{ex} = 311$ nm and $\lambda_{em} = 405$ nm). (b) After immersed in ethanol for 25 min, the luminescence intensity of 1 was gradually recovered.



Fig. S14 The photographs for 1 of adsorption (hexane) and releasing I_2 (ethanol) in two cycles.



Fig. S15 X-ray powder diffraction patterns of **1** after releasing I_2 in second (dark yellow) and first cycle (green), **1** soaked in a hexane solution (0.03 mol·L⁻¹) of I_2 at room temperature for 60 minutes (blue), as-synthesized (red) and simulated **1** (black).



Fig. S16 Photographs and UV/Vis spectra of aqueous solutions of mixture of MO and MB dyes with (a) **2**, (b) **4** and (c) **5** (UV/Vis spectra of dye releasing in MeOH are showed at the top).

5					
	1	2	3	4	5
Formula	$C_{13}H_{19}N_7O_6Zn_2$	$C_{17}H_{22}N_8O_6Zn_2$	$C_{17}H_{20}N_7O_6BrZn_2$	$C_{21}H_{23}N_7O_6Zn_2$	$C_{26}H_{30}N_8O_7Zn_2$
Formula weight	500.09	565.17	629.05	600.20	697.32
Crystal system	tetragonal	tetragonal	tetragonal	tetragonal	triclinic
Space group	P4/ncc	P4/ncc	P 4/n	<i>I</i> /4 <i>m</i>	P -1
<i>a</i> (Å)	13.673(5)	13.530(5)	13.635(5)	13.794(5)	13.628(5)
<i>b</i> (Å)	13.673(5)	13.530(5)	13.635(5)	13.794(5)	13.644(5)
<i>c</i> (Å)	22.794(5)	27.172(5)	27.026(5)	27.262(5)	19.080(5)
α (°)	90.000(5)	90.00	90.000(5)	90.00	109.41
β (°)	90.000(5)	90.00	90.000(5)	90.00	91.28
γ (°)	90.000(5)	90.00	90.000(5)	90.00	90.88
$V(Å^3)$	4261(2)	4974(4)	5024(3)	5187(3)	3344.3(19)
Ζ	8	8	8	8	4
$D_{calcd.}[gcm^{-3}]$	1.559	1.509	1.663	1.537	1.385
F(000)	2032	2304	2512	2448	1432
Reflections collected	21664/2064	23555/2200	25720/4428	11277/1854	16642/10891
<i>R</i> (int)	0.0418	0.0393	0.0576	0.0594	0.0298
Goodness-of-fit on F^2	1.032	1.011	1.119	1.005	0.924
$R_1^a \left[I > 2\sigma(I)\right]$	0.0320	0.0410	0.0870	0.0794	0.0612
wR_2^b	0.0912	0.1471	0.2734	0.1924	0.1586

 Table S1 Crystal data and structure refinements for 1-5.

	Experimental pore volume (cm ³ g ⁻¹)	Theoretical pore volume (cm ³ g ⁻¹)
1a	0.212	0.434
2a	0.320	0.381
3 a	0.245	0.299

 Table S2 The comparison of experimental pore volume and theoretical value.

 Table S3 The comparison of adsorption amount and surface area.

Treatment	Original	H ₂ O	HCl	NaOH
			(pH=2)	(pH=12)
N ₂ adsorption	118	94	84	97
amount (cm ³ /g)				
$\frac{S_{BET}}{(m^2 g^{-1})}$	363	165	162	150

Matariala	V(C)	O_2	$Q_{st}(CO_2)$	Reference
waterials	(cm ² g ²)			
	273K 298K		J	
1	103.7	70.2	33	This work
bio-MOF-11		92	45	[1]
$[Co_3(ndc)(HCOO)_3(\mu_3-OH)(H_2O)]_n$	127	70	41	[2]
SNU-50'	120	80	25.8	[3]
HKUST-1 (295K)		72.6	23.3	[4]
MOF-177		23.6	15.7	[4]
IRMOF-3		30.4	17.4	[4]
Tbo-MOF-2	109	62	35.2	[5]
$Zn_2(BME-bdc)_2(bpee) \cdot 2DMF$	52	33		[6]

Table S4 CO₂-uptakes and enthalpy of adsorption for selected MOFs and 1.

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Table S5 The Q_{st} at zero coverage of CO_2 for 1-5.

	1	2	3	4	5
Qst at zero	33.06	32.22	23.50	25.84	26.24
(KJ mol ⁻¹)					