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# **Electronic Supplementary Information (ESI)**

# Green and rapid preparation of hierarchically porous metal–organic zeolites and simulation of their growth

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### **Experimental section**

Chemical reagents: Zinc oxide (ZnO, 99%), zinc acetate dihydrate  $(Zn(CH_3CO_2)_2 \cdot 2H_2O, 99\%)$ , zinc nitrate hexahydrate  $(Zn(NO_3)_2 \cdot 6H_2O, 99\%)$ , imidazole (Im, 99%), 2-methylimidazole (2Im, 99%), imidazole-2-carboxyaldehyde (ICA, 98%), sodium benzene sulfonate ( $C_6H_5NaO_3S$ , 98%), sodium ptoluenesulfonate (C<sub>7</sub>H<sub>8</sub>NaO<sub>3</sub>S, 98%), sodium dodecyl benzene sulphonate  $(C_{18}H_{29}NaO_3S, 95\%)$ , sodium 1-hexadecylsulfonate  $(C_{16}H_{33}NaO_3S, 98\%)$ , N,Ndimethylformamide (DMF, 99.5%), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH, 99.7%), and methanol (CH<sub>3</sub>OH, 99.5%) were purchased from J&K or aladdin Chemical Ltd. All of above chemical reagents were used without further purification.

### Synthesis of conventional ZIF-8 using solvothermal method at 140°C

In a typical synthesis,<sup>1</sup> 0.24 g of Zn (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.06 g of 2Im were dissolved in 18 mL of DMF and stirred for 10 min. Then the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave stewing and heated to 140 °C for 24 h. After cooling down 25 °C, the solid product was filtered and dried at 120 °C for 12 h. The resulting product is denoted as C-ZIF-8.

# Control experiment 1: Synthesis of ZIF-8\_S using solvothermal method at 140°C

In a typical synthesis,<sup>2</sup> 0.24 g of Zn (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), 0.06 g of 2Im, and 0.145 g of sodium benzene sulfonate (SBS) were dissolved in 18 mL of DMF and stirred for 10 min. Then the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave stewing and heated to 140 °C for 24 h. After cooling down 25 °C, the solid product was filtered and washed by ethanol (25 mL, 4 times), and then dried in an oven at 120 °C for 12 h. The resulting product is denotes as ZIF-8 S.

# Control experiment 2: Room-temperature synthesis of ZIF-8 with SBS as template

0.24 g of  $Zn(CH_3CO_2)_2 \cdot 2H_2O$ , 0.06 g of 2Im, and 0.145 g of sodium benzene sulfonate (SBS) were dissolved in 18 mL of DMF and stirred for 1 min.

# Ultrafast room-temperature synthesis of hierarchically porous ZIF-8 using SBS

## as template

In a typical synthesis,<sup>3</sup> 1 mmol of ZnO was dissolved in 2 mL deionized water to get solution A, and 1 mmol of  $Zn(CH_3CO_2)_2 \cdot 2H_2O$  was dissolved in 1 mL of DMF to get solution B. Solution B was added to solution A and stirred for 24 h to get hydroxy double salt (HDS) (denoted as solution C). Then, amount of sodium benzene sulfonate (SBS) and 6 mmol of 2Im were dissolved in 9 mL of DMF to get solution D. After that, solution C was added to the solution D under fast magnetic stirring for 60 s at room temperature and pressure. The white product was subsequently filtered and washed by ethanol (25 mL, 4 times), and then dried in an oven at 120 °C for 12 h. The resulting products were synthesized at SBS/Zn<sup>2+</sup> molar ratios of 0.1 (ZIF-8\_A1), 0.25 (ZIF-8 A2), 0.5 (ZIF-8 A3), 1 (ZIF-8 A4) and 2 (ZIF-8 A5).

# Ultrafast room-temperature synthesis of hierarchically porous ZIF-8 using other anionic surfactants as the templates

In a typical synthesis,<sup>3</sup> 1 mmol of ZnO was dissolved in 2 mL of deionized water to get solution A. 1 mmol of  $Zn(CH_3CO_2)_2 \cdot 2H_2O$  was dissolved in 1 mL of DMF to get solution B. Solution B was added to solution A and stirred for 24 h to get solution C. Then, 6 mmol of 2Im and 2 mmol of anionic surfactant were dissolved in 9 mL of DMF to get solution D. After that, solution C was added to the solution D under fast magnetic stirring for 60 s at room temperature and pressure. White product was subsequently filtered and washed by ethanol (25 mL, 4 times), and then dried in an oven at 120 °C for 12 h. The resulting product is denoted as ZIF-8\_X (X = B, C, D, where X represents the type of surfactants, B: sodium *p*-toluenesulfonate, C: sodium dodecyl benzene sulfonate; D: sodium 1-hexadecylsulfonic; the molar ratio of surfactant/Zn<sup>2+</sup> = 1).

# Ultrafast room-temperature synthesis of hierarchically porous ZIF-61

1mmol of ZnO was dissolved in 2 mL of  $H_2O$  to get solution A. 1 mmol of  $Zn(CH_3CO_2)_2 \cdot 2H_2O$  was dissolved in 1 mL of DMF to get solution B. Solution B was added to solution A and stirred for 24 h to get solution C. Then, 6 mmol of Im, 4

mmol of 2Im and 2 mmol of sodium benzene sulfonate (SBS) were dissolved in 40 mL methanol to get solution D. After that, solution C was added to the solution D under fast magnetic stirring for 60 s at room temperature and pressure. The white product was subsequently filtered and washed by ethanol (25 mL, 4 times), and then dried in an oven at 120 °C for 12 h. The resulting product is denoted as HP-ZIF-61.

# Ultrafast room-temperature synthesis of hierarchically porous ZIF-90

1mmol of ZnO was dissolved in 2 mL of  $H_2O$  to get solution A. 1 mmol of  $Zn(CH_3CO_2)_2 \cdot 2H_2O)$  was dissolved in 1 mL of DMF to get solution B. Solution B was added to solution A and stirred for 24 h to get solution C. Then, 2 mmol of sodium benzene sulfonate (SBS) and 6 of mmol ICA were dissolved in 9 mL DMF to get solution D. After that, solution C was added to the solution D under fast magnetic stirring for 60 s at room temperature and pressure. The white product was subsequently filtered and washed by ethanol (25 mL, 4 times), and then dried in an oven at 120 °C for 12 h. The resulting product is denoted as HP-ZIF-90.

# In Situ Time-Resolved ATR-FTIR for hierarchically porous ZIF-8 growth

The infrared probe was placed in the mixture of surfactant and 2-methylimidazole. Then, the prepared HDS was added into the mixture solution. The chemical information of the crystal growth can be observed through the change of infrared absorption peak. And the infrared absorbing bands of different groups were recorded every 15s.

### **Calculation of STY**

Space-time-yield (STY) is an important parameter for industrial production,<sup>3</sup> which can be calculated by the following Eq. (1)

$$STY = \frac{m_{MOZ}}{V_{solution} \cdot \tau} \times 1.44 \times 10^6$$
(1)

where  $m_{MOZ}$  represents the powder mass (g) of hierarchical porous ZIF-8, *Vsolution* represents the total volume (cm<sup>3</sup>) for mixture, and  $\tau$  represents the stirring time (min).

# **Computational methods**

# Simulation detail

During the mesoscopic dynamic (MesoDyn) simulation, in order to reproduce the chemical properties of the system, a coarse-grained model is needed to represent the Gaussian chain of each repeating unit.<sup>4, 5</sup> Molecules are simplified into one or more beads and all the beads have the same volume and mass. The bond between molecules is expressed by spring with the stretching behavior between beads. Here we choose MOZ precursors and the SDAs ( $C_6H_4NaSO_3$ ) as the objects to study. As shown in Figure S1, the coarse-grained model of  $C_6H_5NaSO_3$  can be treated as a Gaussian chain with  $B_1S_1$  topology, where one B bead represents a benzene segment and one S bead represents the sodium sulfonate segment. Here we construct  $B_1S_1$  for sodium benzene sulfonate. In addition, the chelates composed of  $Zn^{2+}$  and 2-methylimidazole are represented by a T bead while the solvent molecule DMF is represented by a D bead. The volume of B and T bead is 0.06 and the volume of other species of beads is set to 0.02.



Figure S1. Coarse-grained model for the SDA of C<sub>6</sub>H<sub>4</sub>NaSO<sub>3</sub>.

The repulsive parameter  $a_{ij}$  between bead *i* and bead *j* is defined as  $a_{ij} = \alpha_{ii} + 3.27\chi_{ij6}$ (where  $\alpha_{ii}$  is the repulsive parameter among the same beads and  $\chi_{ij}$  is the Flory-Huggins parameter.) In this work,  $\alpha_{ii} = 25$  basing on the compressibility of pure liquid.<sup>7</sup>  $\chi_{ij}$  is calculated by the Blends module of the Materials Studio (7.0) software package. Table S1 lists the  $a_{ij}$  between beads used in this paper. In order to simulate the electrostatic interaction and ionizing environment between the molecules of the system, 1e negative charge is assigned to each S bead (sulfonic) and 2e positive charge is assigned to each T bead, while B and D beads keep electrical neutrality. The charge distribution and electrostatic interaction of the beads are realized by Donnan equilibrium. This method is equivalent to placing the beads in the electrolyte (such as chloride ion) to keep the system neutral and the salt concentration of the system is 0.1 mol/L.

Bead	В	S	D	Т	
В	25.0	33.7	34.13	36.47	
S		25.0	30.42	28	
D			25.0	33.46	
Т				25.0	

**Table S1.** Repulsive parameter  $a_{ij}$  between different beads.

The simulation is carried out by the MesoDyn module of the Materials Studio (7.0) software package. The bond length between beads  $d = ah^{-1} = 1.1543$  (where *a* is Gaussian bond length, *h* is grid size). Diffusion coefficient is set as  $10^{-7}cm^2s^{-1}$  and the system's noise coefficient  $\Omega = V'h^3 = 75.019$  (where V is the volume of bead). The size of the simulated box is set as  $32 nm \times 32 nm \times 32 nm$ . In the simulation system of HP-MOZs formation, the volume fraction of B<sub>1</sub>S<sub>1</sub>, T and D beads are 17%, 17%, and 67%, respectively.

In order to simulate the mixing environment during the synthetic process, a constant shear effect was introduced into the simulation system after 0.25 ms. The X axis is the direction of velocity, and the Y axis is the direction of velocity gradient. The Z axis is the neutral axis.<sup>5</sup> The program achieves stable shear, that is, the velocity gradient is uniform:  $\frac{d!v_x}{d!v_y} = \hat{v}_{\gamma}$  keeps constant and the shear rate  $\gamma = 5 \times 10^5 s^{-1}$ . The simulated time step  $\Delta \tau = 50 ns$ , and the total simulation time is 1.0 ms (20000 steps in total).

Element	N%	С%	Н%	S%
C-ZIF-8	17.35	31.67	3.803	0.000
ZIF-8_A4	24.13	43.59	4.198	0.066

Table S2. The ZIFs products were characterized by elemental microanalysis.

Samula	Moar ratio of	$S_{\rm BET}{}^a$	Vt <sup>b</sup>	$V_{\rm micro} c$	$V_{\rm meso} d$	STY <sup>e</sup>
Sample	surfactant/ $Zn^{2+}$	$[m^2 \cdot g^{-1}]$	$[cm^3 \cdot g^{-1}]$	$[cm^3 \cdot g^{-1}]$	$[cm^{3} \cdot g^{-1}]$	$[kg \cdot m^{-3} \cdot d^{-1}]$
ZIF-8_A4	1:1	1424	1.20	0.59	0.60	$3.20 \times 10^4$
ZIF-8_B	1:1	1322	1.06	0.54	0.52	$2.78  imes 10^4$
ZIF-8_C	1:1	1121	0.96	0.46	0.50	$2.61 \times 10^4$
ZIF-8_D	1:1	1169.4	0.88	0.46	0.42	$1.35 \times 10^4$

**Table S3.** Textural parameters and STYs of ZIF-8\_X(X = A, B, C, D).

<sup>*a*</sup>S<sub>BET</sub>: Brunauer–Emmett–Teller (BET) surface area; <sup>*b*</sup>V<sub>1</sub>: total pore volume; <sup>*c*</sup>V<sub>micro</sub>: micropore volume; <sup>*d*</sup>V<sub>meso</sub>: mesopore volume; <sup>*e*</sup>Space–time yield (STY) is calculated based on the mass of active products.

Material	$STY/kg \cdot m^{-3} \cdot day^{-1}$	References
Al-MIL-53( Basolite A100)	160	8
HKUST-1( Basolite C 300)	225	8
Fe-BTC( Basolite F300)	20	8
ZIF-8(Basolite Z1200)	100	8
[Mg(O <sub>2</sub> CH) <sub>2</sub> ]( Basosiv M050)	300	8
Fe-MIL-100	120~300	9, 10
C-ZIF-8	3875	11
HP-ZIF-8	12900	12

Table S4. Space-time-yield (STY) of other MOF materials.



**Figure S2.** (a) Powder XRD patterns of ZnO and SBS; and FT-IR spectra: (b) ZnO and (c) template of sodium benzene sulfonate (SBS).



**Figure S3.** (a) SEM and (b) TEM images of the C-ZIF-8 prepared with conventional solvothermal method.



**Figure S4.** The thermogravimetric analysis (TGA) of (a) fresh ZIF-8\_A*n* and C-ZIF-8; and (b) treated samples by using water soaking (pH = 6) and alkaline leaching (pH = 11) after three days.



**Figure S5.** Powder XRD patterns of the hierarchically porous ZIF-8\_A4 samples treated with water soaking (pH = 6) and alkaline leaching (pH = 11) after three days.



Figure S6. Powder XRD patterns of ZIF-8\_S and the simulated ZIF-8 pattern.



Figure S7. (a) N<sub>2</sub> adsorption–desorption isotherms and (b) pore size distributions of the ZIF-8\_S.



**Figure S8.** Powder XRD patterns of the ZIF-8\_X (X = B, C, D) and C-ZIF-8, and the simulated ZIF-8 pattern.



Figure S9. Powder XRD pattern of the HP-ZIF-61 and the simulated ZIF-61 pattern.



Figure S10. (a) N<sub>2</sub> adsorption-desorption isotherm and (b) pore size distributions of HP-ZIF-61.



Figure S11. (a) SEM and (b) TEM images of hierarchical porous ZIF-61.



Figure S12. Powder XRD pattern of the HP-ZIF-90 and the simulated ZIF-90 pattern.



Figure S13. The N<sub>2</sub> adsorption–desorption isotherm and pore size distributions of HP-ZIF-90.



Figure S14. (a) SEM and (b) TEM images of hierarchical porous ZIF-90.

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