Supporting information

Toluene-assisted synthesis of RHO-type zeolitic imidazolate frameworks: Synthesis and formation mechanism of ZIF-11 and ZIF-12

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Figures

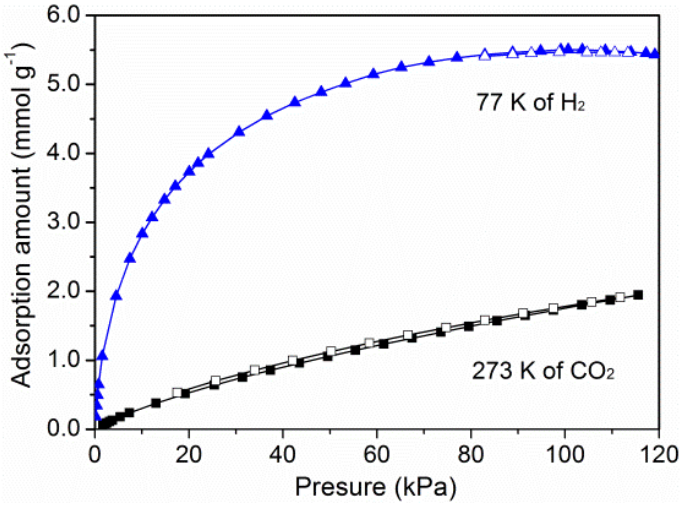

Figure S1. H_2 and CO_2 adsorption isotherms for as-synthesized ZIF-11 prepared with a Zn: bIm: NH_3: C_2H_5OH: toluene molar composition of 1:2:2:300:100. Plain symbols: adsorption; open symbols: desorption. ZIF-11 was impermeable to nitrogen because its aperture size (3.0 Å) was smaller than the kinetic diameter of N_2 (3.6 Å). However, it was able to absorb H_2 and CO_2. The profiles showed H_2 uptake of 5.5 mmol g^{-1} at 77 K and 1 atm, and CO_2 uptake of 2.0 mmol g^{-1} at 273 K and 1 atm.

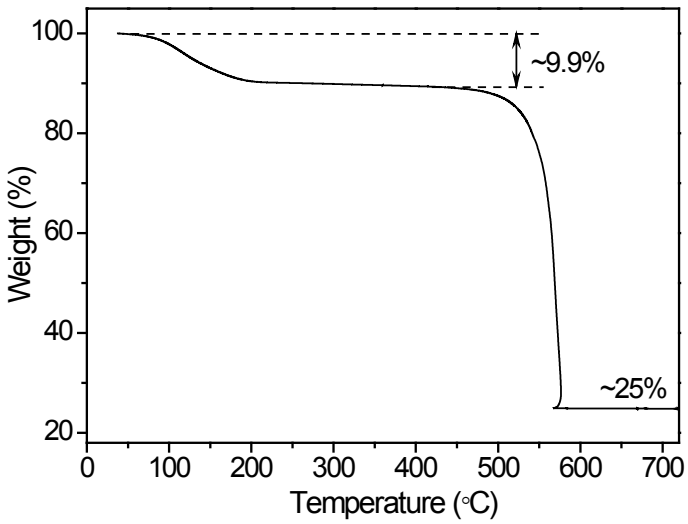

Figure S2. TGA curves of as-synthesized ZIF-11 sample under air flow. The first weight loss of about 9.9% from the starting temperature to 200 °C corresponds to the desorption of guest toluene and the molecular formula is calculated to be $Zn(C_7H_5N_2)_2 \cdot 0.36C_7H_8$. A long gradual plateau in the TGA up to 450 ºC indicates the high thermal stability of ZIF-11 in the absence of guest molecules. The second sharp weight loss takes place after 450 °C that corresponds to the framework structural decomposition. The residue of the heated sample was ZnO and the residue weight of 25% perfectly consistent with the calculated value from the above mentioned molecular formula.

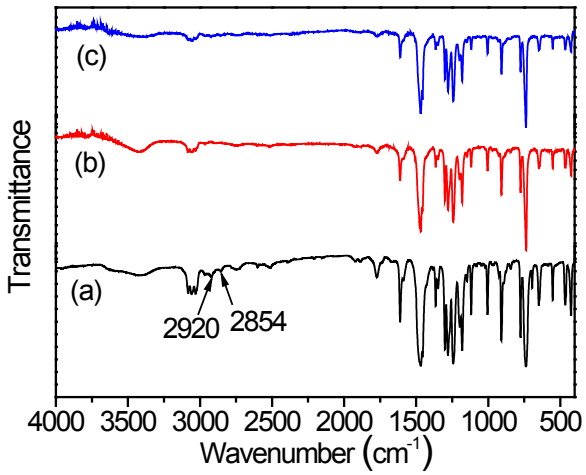

Figure S3. FT-IR spectra of the as-synthesized ZIF-11 (a), after washed three times (b) and thermally treated at 300 ºC for 2 h (c). the =C–H stretches of aromatics (3099, 3068, 3032 cm^{-1}), the C–C stretches in the aromatic ring (1611, 1465 cm^{-1}) and the –C–H stretches of methyl (2920, 2854 cm^{-1}). Since both toluene and bIm have phenyl groups, the toluene content is determined by the change of the absorbance of methyl group. As the bands at 2920

and 2854 cm^{-1} disappear completely in (b) and (c), it indicates the totally removal of the toluene from the cavities upon heating or washing with solvent.

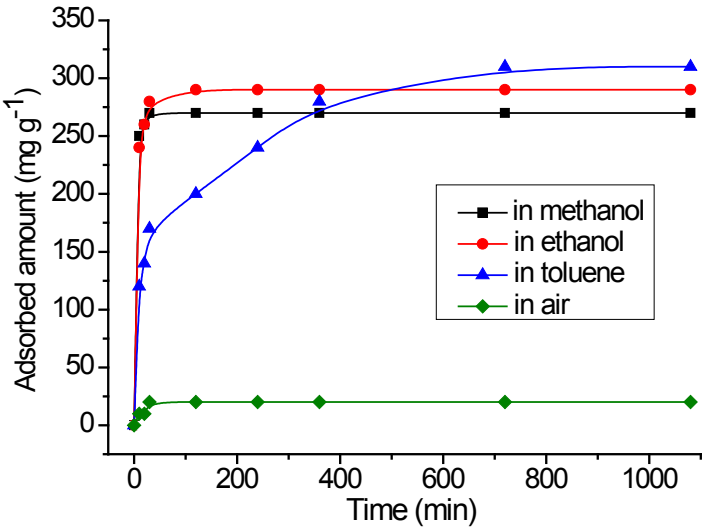

Figure S4. Volatile organic vapors adsorption at room temperature on 300 °C heat-treated ZIF-11 as a function of adsorption time.

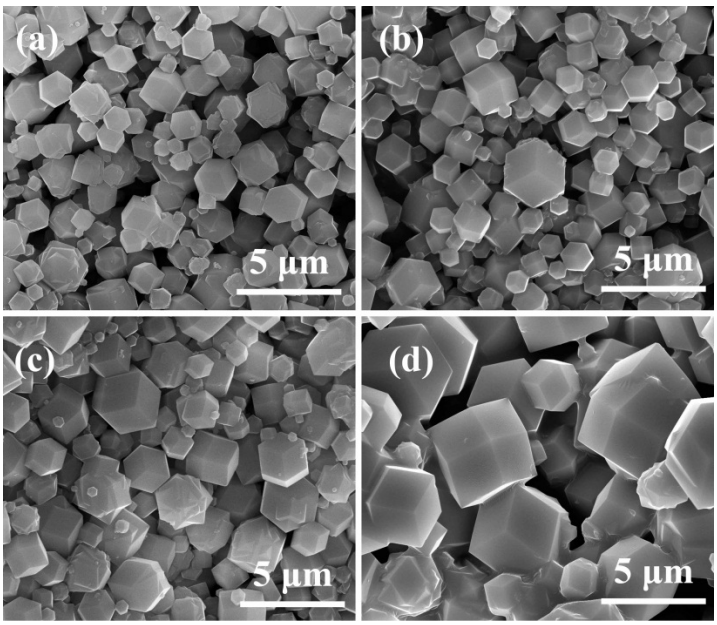

Figure S5. SEM images of ZIF-11 prepared with different Zn/NH_3 molar ratios of 1:2 (a), 1:4 (b), 1:10 (c) and 1:40 (d) in methanol-toluene mixed solution. With the increase of the ammonia hydroxide usage, larger grains with well-defined crystals can be observed. The increase of solution basicity shifts the reaction equilibrium and thereby drives the deprotonation of organic ligands, resulting in crystal growth in all directions and yielding larger,

well-intergrown crystals.[1]

[1] M. C. McCarthy, V. Varela-Guerrero, G. V. Barnett and H.-K. Jeong, *Langmuir* **2010**, *26*, 14636-14641.

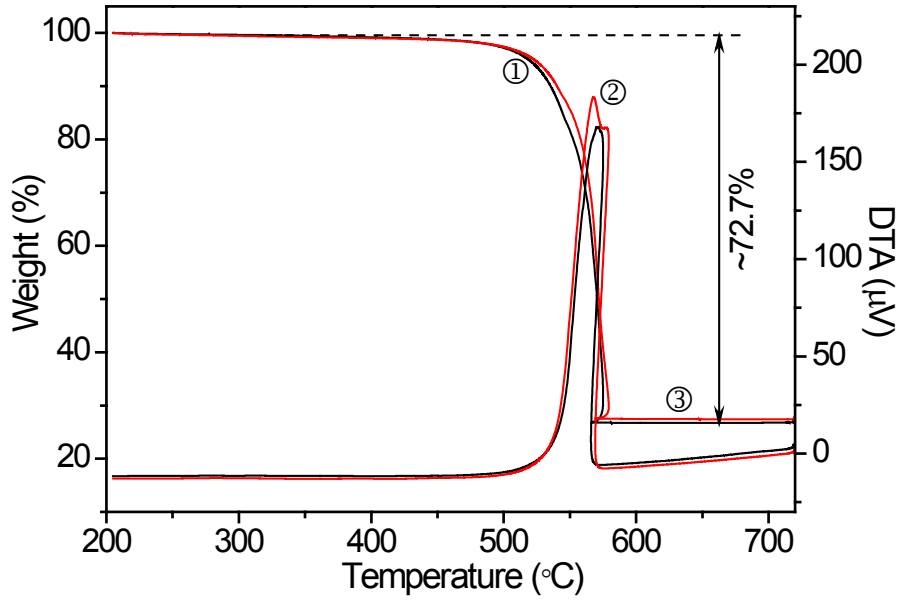

Figure S6. TG-DSC curves of the as-synthesized ZIF-11 prepared with the molar ratios of Zn: bIm: NH_3: methanol: toluene at 1: 2: 2: 300: 20 (black line) and 1: 2: 2: 300: 100 (red line) respectively under air flow. All TG curves show a sharp drop in mass of ~72% corresponding to the structural degradation and release of organic ligand, which was in good agreement with that ZIF-11 ($Zn(C_7H_5N_2)_2$, Mw: 299) is completely converted into zinc oxide (Mw: 81). However for the samples prepared with the higher toluene usage (red line), it is noteworthy that there are slight differences in TG-DSC curves in the following three aspects: 1) the higher initial decomposition temperature, 2) larger area underneath the exothermic peak, 3) more residuals after 600 ^{o}C. Thus it is possible to conclude that more toluene in the precursor solution prefers to form a higher crystalline ZIF-11.