Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Facet-Dependent Catalytic Activity of ZIF-8 Nanocubes and Rhombic Dodecahedra Based on Tracing Substrate Diffusion in Pores by SERS: A Case Study for Surface Catalysis of MOFs

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Experimental section

Materials and Characterization

All chemical reagents were used as purchased without further purification. Cetyltrimethylammonium bromide (CTAB) and polyvinylpyrrolidone (PVP, M_w= 55000) was purchased from Sigma Aldrich, and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. China. Deionized water (resistance > 18.2 MΩ/cm) was used in all reactions. Copper specimen grids (300 mesh) with carbon film (referred to as TEM grids in the text) were purchased from Beijing XXBR Technology Co.

Transmission electron microscopy (TEM) images were collected on a Tecnai F30 operated at 300 kV. X-ray diffraction (XRD) was preformed with a Rigaku D/Max 2400 automatic powder X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å). Raman spectra were recorded in Horiba Jobin-Yvon LabRAM HR Evolution Raman Spectrometer. X-ray photoelectron spectroscopy (XPS) was conducted with an ESCAlab 250 X-ray photoelectron spectrometer. Thermal analysis was carried out on TA instruments SDT-Q600 simultaneous TGA/DSC. The leaching Zn element was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Optima 2000DV. N_2 sorption isotherm at 77 K was carried out Micromeritics 3Flex Surface Characterization Analyzer after being degassed in vacuum at 200 ^oC for 12 h.

Synthesis of ZIF-8 NPs

Synthesis of ZIF-8 RDs with a mean size of 135 nm. A Hmim solution (50 mL, 25 mM in methanol) was added to $Zn(NO_3)_2$ solution (50 mL, 25 mM in methanol) one shot at room temperature, and the resulting mixture was kept at 50 °C for 2h without disturbing.

Synthesis of ZIF-8 NCs with a mean size of 110 nm. ZIF-8 NCs were prepared by a hydrothermal growth process derived from the previous reports.[1] CTAB aqueous solution (100 μL, 0.1 M) was added to $Zn(NO_3)_2$ aqueous solution (0.0336 M) that was prepared by dissolving $Zn(NO_3)_2$•$6H_2O$ (60 mg) into 6 mL of deionized water, and Hmim aqueous solution (10 mL, 1.096 M) was subsequently added under stirring. The resulting mixture was transferred into 25 mL of Teflon-lined autoclave and kept at 120 °C for 6 h in an oven, and then cooled down to the room temperature naturally.

Both products were collected by centrifugation at 10000 *g* for 5 min, washed twice with methanol, and dried in vacua at 100 °C for subsequent characterization of structures. For ZIF-8 NCs, the sample was dispersed into 100 mL methanol and stirred for 2 d; for both ZIF-8 nanocrystals, these samples were annealed at 300 ^oC for 1 h in a tube furnace in nitrogen atmosphere before performing catalytic reactions.

SERS test

Synthesis of spiky Au@ZIF-8 composites. Spiky Au NPs were firstly synthesized by a modified procedure.[2] HCl (300 μL, 1 M) and fresh Au NPs solution (3 mL, d = 15 nm) were introduced into $HAuCl_4$ aqueous solution (300 mL, 0.25 mM). Under vigorous stirring, $AgNO_3$ (60 μL, 100 mM) and ascorbic acid (1.5 mL, 0.1 M) aqueous solutions were sequentially added. After 10 min, PVP aqueous solution (1 wt%, 3 mL) was added, and stirred for additional 8 h. The

resultant product was collected by centrifugation at 4000 *g* for 5 min and washed with methanol for subsequent incubation.

The spiky Au NPs concentrated from 40 mL of original solution were dispersed into methanol (20 mL), and Hmim (10 mL, 25 mM) and $Zn(NO_3)_2$ methanolic solution (10 mL, 25 mM) were added. After gentle shaking, the resulting mixture was kept at room temperature for 12h without disturbing.

Spiky Au@ZIF-8 as SERS probe to detect 4-nitrobenzaldehyde. The spiky Au@ZIF-8 composites were concentrated by centrifugation and dried in a tube furnace at 300 °C for 1 h under nitrogen atmosphere. Subsequently, the composites were dispersed into 4-nitrobenzaldehyde ethanolic solution (1.9 M) and incubated for different durations. Afterwards, the mixture was separated by centrifugation, and the solid was washed with ethanol before dropped on a slide glass for SERS measurement. The SERS spectra were carried out at 633 nm excitation with a 1800 l/mm grating.

Investigation of facet-dependent catalytic performance of ZIF-8 NPs. Using ZIF-8 RDs and NCs as catalyst for Knoevenagel condensation of aldehyde (benzaldehyde, 4-nitrobenzaldehyde, and 4-methylbenzaldehyde) and malononitrile was carried out in a 20 mL of vial with gently shaking. A uniform suspension was obtained by dispersing ZIF-8 powders (10 mg) into 4 mL of toluene/ethanol (*v*/*v* = 3.5:0.5) solvent under ultrasonication. Aromatic aldehyde (0.95 mmol), malononitrile ethanolic solution (500 μL, 3.8 M), and *n*-dodecane (100 μL) were sequentially placed into a vial containing 3.5 mL of ZIF-8 solution aforementioned. After the resulting mixture shaking for required reaction time at room temperature, the catalytic system was poured into an identical amount of acetone to quench the condensation reaction.

The catalyst was immediately removed by centrifugation at 10000 *g* for 5 min. The conversion efficiency of aldehyde was immediately analyzed by gas chromatography on Agilent 7000B GC/MS system using *n*-dodecane as internal standard.

REFERENCES

1. Z. Li, H. C. Zeng, *Chem. Mater.* 2013, **25**, 1761.
2. A. M. Fales, H. Yuan and T. Vo-Dinh, *Langmuir*, 2011, **27**, 12186.

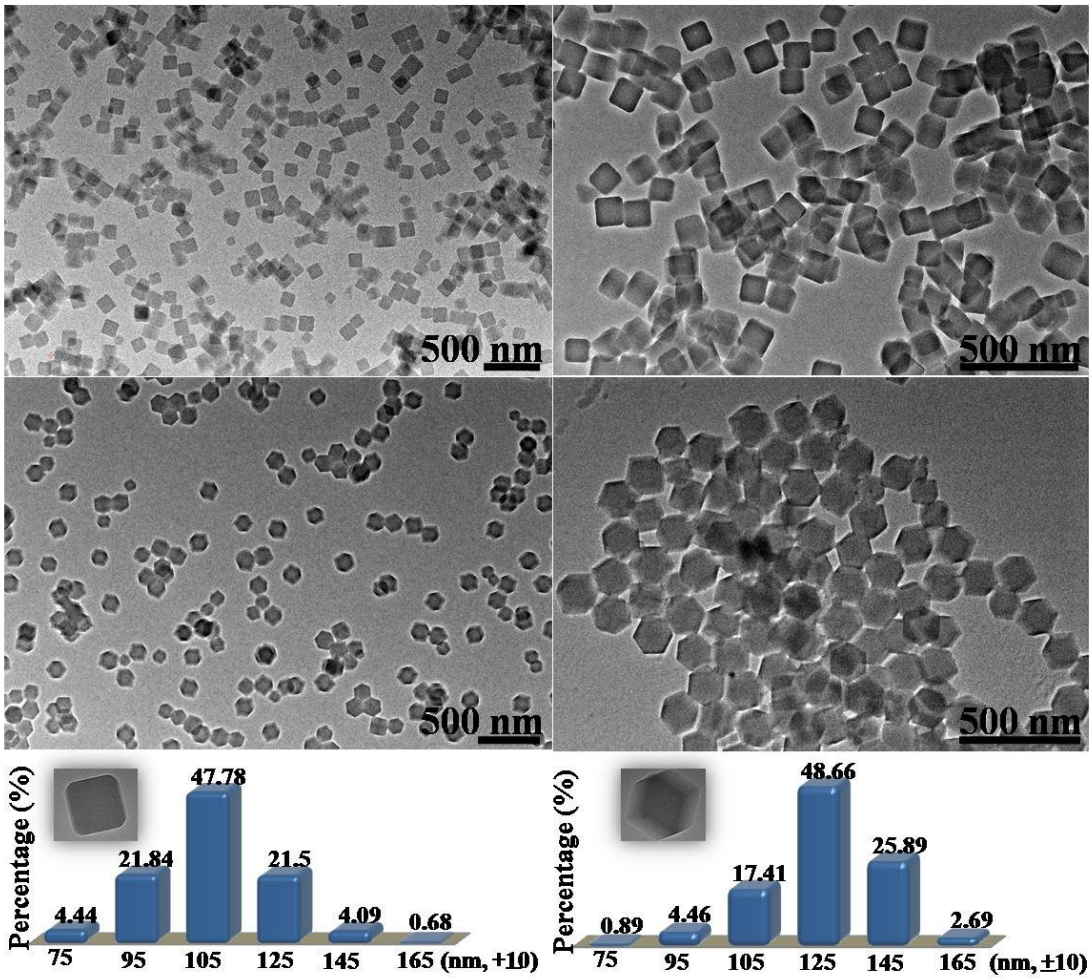

Figure S1. TEM images of as-synthesized ZIF-8 nanocubes and rhombic dodecahedrons; histograms of the size distribution of ZIF-8 nanocubes and rhombic dodecahedra in the TEM images, respectively.

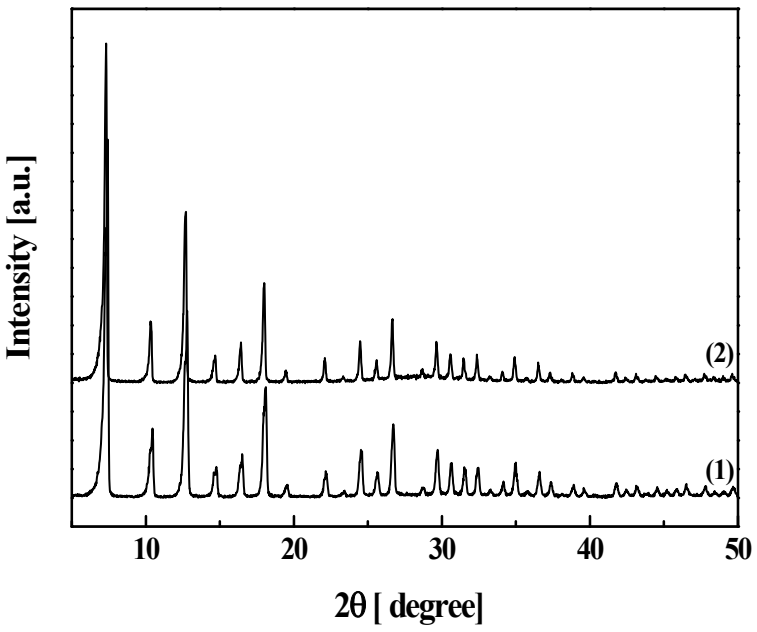

Figure S2. XRD patterns of ZIF-8 (1) rhombic dodecahedra and (2) nanocubes.

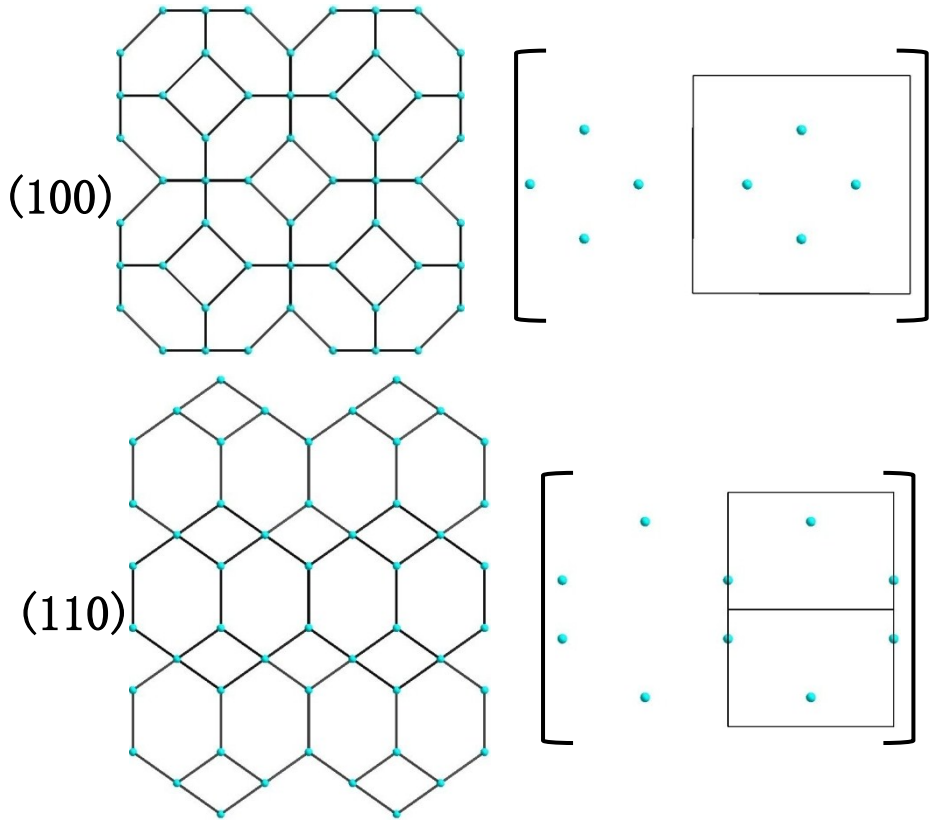

Figure S3. The topological structures of ZIF-8 observed from <100> and <110> direction illustrate the density of Zn^{2+} ion on the external surfaces of ZIF-8 nanocubes and rhombic dodecahedra.

For (100) plane

$D_{Zn^{2+}} = \frac{4}{a^2}$, where *D* represents density, and *a* is the edge length of the unit cell.

For (110) plane

$D_{Zn^{2+}} = \frac{2 + 4/2}{\sqrt{2}a^2} = \frac{2.8}{a^2}$.

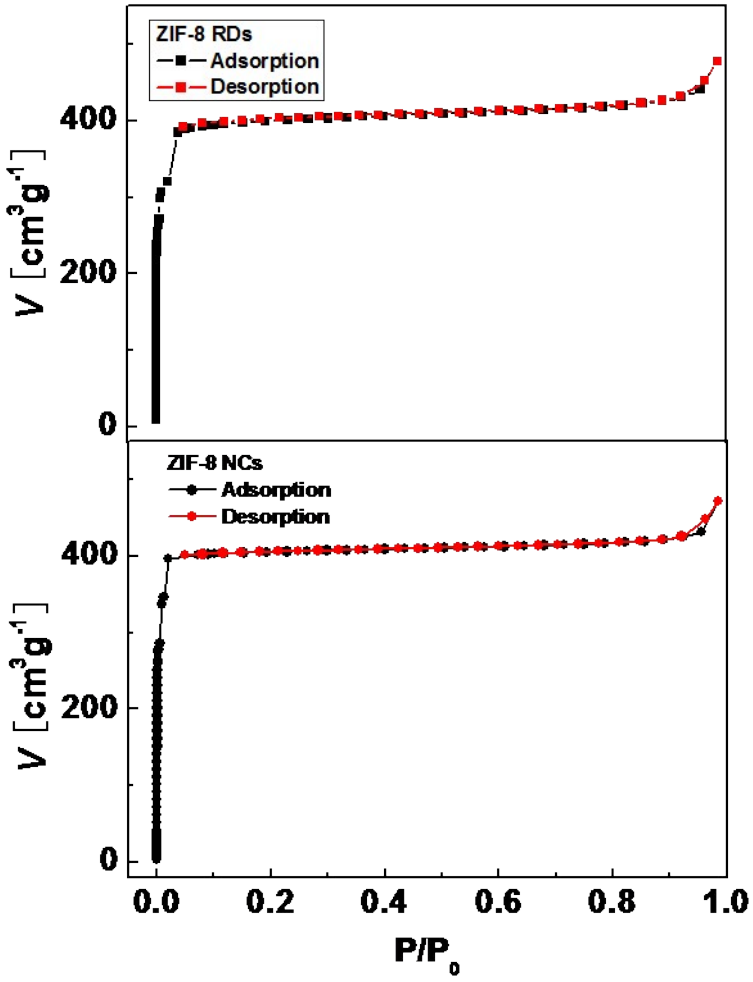

Figure S4. Nitrogen sorption isotherms at 77 K (black, adsorption; red, desorption) of ZIF-8 rhombic dodecahedra and nanocubes.

Both samples exhibited type I isotherm originated from microporous structures, and possessed similar Barrett-Emmett-Teller (BET) surface area of 1578 m^2/g for ZIF-8 rhombic dodecahedra and 1560 m^2/g for ZIF-8 nanocubes.

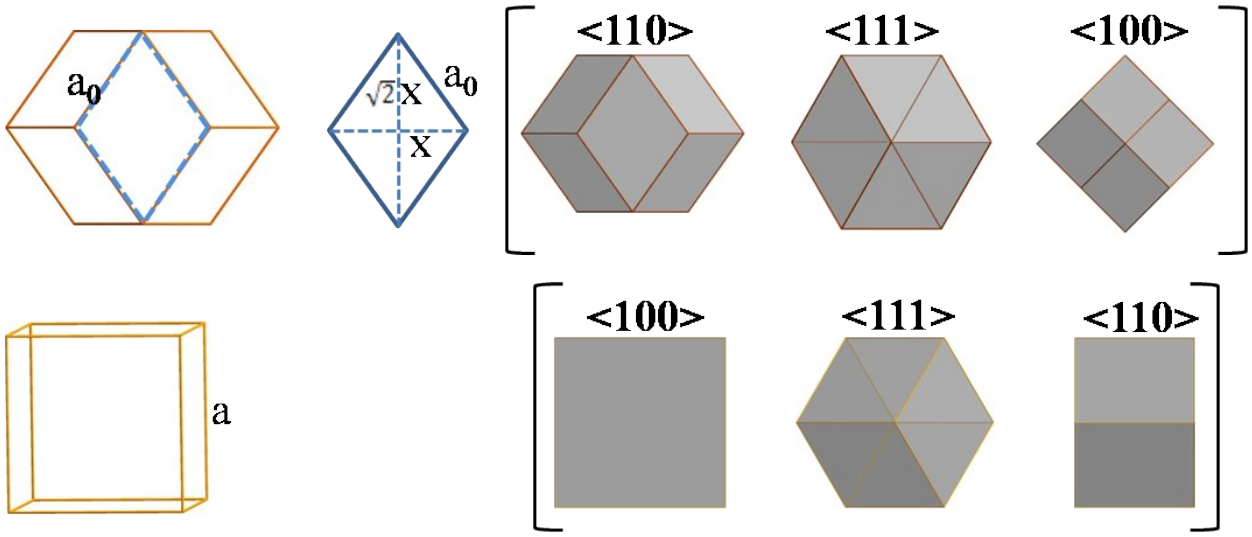

Figure S5. Schematics illustrating the possible "shapes" of ZIF-8 rhombic dodecahedron (RD) and nanocube (NC) nanoparticles in TEM images.

Most ZIF-8 RDs lie on the TEM grid using {110} facets due to this "shape" with relatively lower "potential energy" compared to other "shapes" like observing from <111> and <100> directions. Thus, the mean size of RD NPs by statistics from TEM images should be the longer diagonal of the rhombic facet.

$$d_{mean} = \sqrt{2}x = 135\ nm,$$

$$a_0^2 = \left(\frac{\sqrt{2}}{2}x\right)^2 + \left(\frac{1}{2}x\right)^2 = \left(\frac{135}{2}\right)^2 + \left(\frac{135}{2\sqrt{2}}\right)^2,\ a_0 = 83.67\ nm$$

For each ZIF-8 RD volume

$$V_{RD} = \frac{16\sqrt{3}}{9}a_0^3 = \frac{16\sqrt{3}}{9}(82.67)^3$$

For each ZIF-8 RD surface area

$$S_{RD} = 8\sqrt{2}a_0^2 = 8\sqrt{2}(82.67)^2$$

As stated as above, most ZIF-8 NCs using {100} facets lie on the TEM grid, and the mean size of NC NPs by statistics from TEM images is their edge length.

$d_{mean} = 115\ nm$;

For each ZIF-8 NC volume

$V_{NC} = a^3 = (115)^3$

For each ZIF-8 NC surface area

$S_{NC} = 6a^2 = 6(115)^2$

The ratio of the number of ZIF-8 NCs to the number of ZIF-8 RDs for identical amount of both samples

$\frac{N_{NC}}{N_{RD}} = \frac{V_{RD}}{V_{NC}} = 1.144\ ;\ \frac{S_{NC}}{S_{RD}} = 1.026$

The ratio of the population of Zn^{2+} on the external surfaces of ZIF-8 between NCs and RDs for the identical amount of both samples

$\frac{P_{Zn-NC}}{P_{Zn-RD}} = \frac{N_{NC}}{N_{RD}} \times \frac{S_{NC}}{S_{RD}} \times \frac{D_{Zn-NC}}{D_{Zn-RD}} = 1.68$

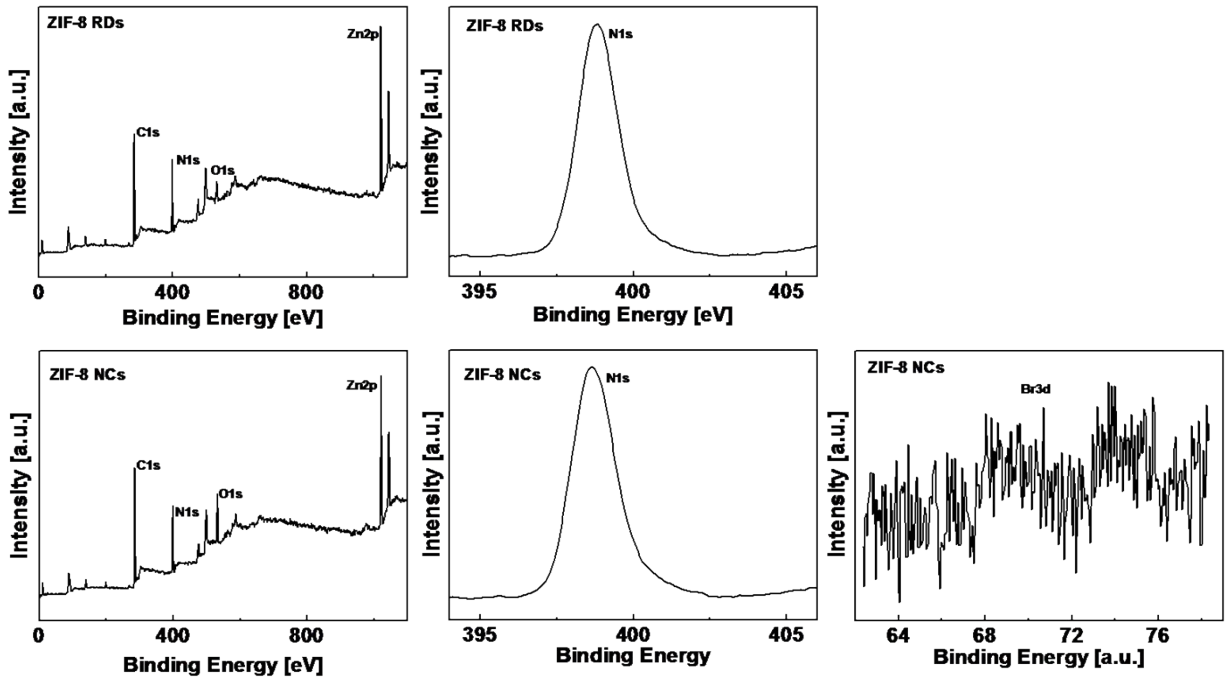

Figure S6. XPS spectra of as-synthesized ZIF-8 rhombic dodecahedra and ZIF-8 nanocubes that were stirred in methanol for 2 d: survey and high-resolution N1s and Br3d binding energy spectra.

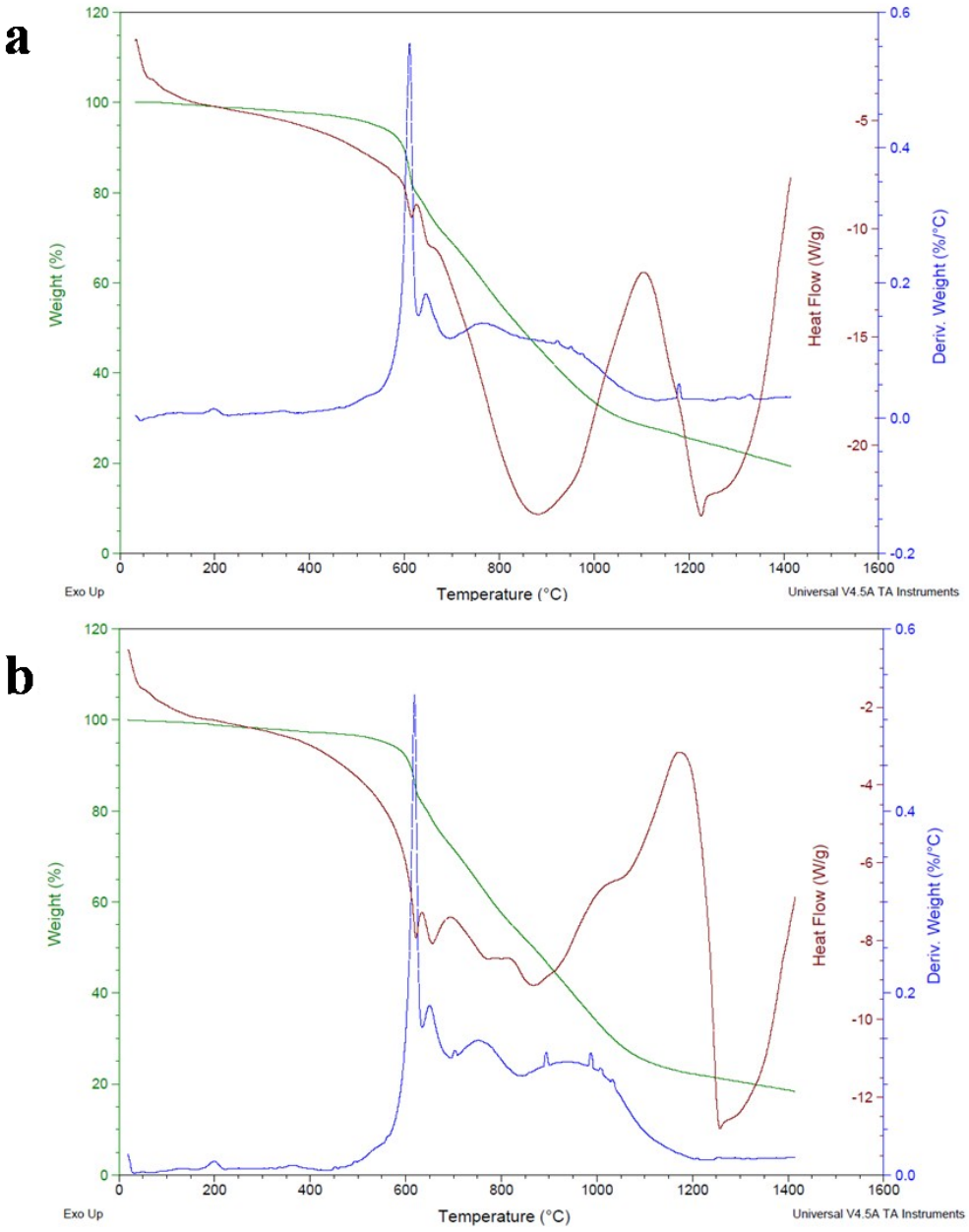

Figure S7. Thermal analysis of ZIF-8 (a) rhombic dodecahedra and (b) nanocubes.

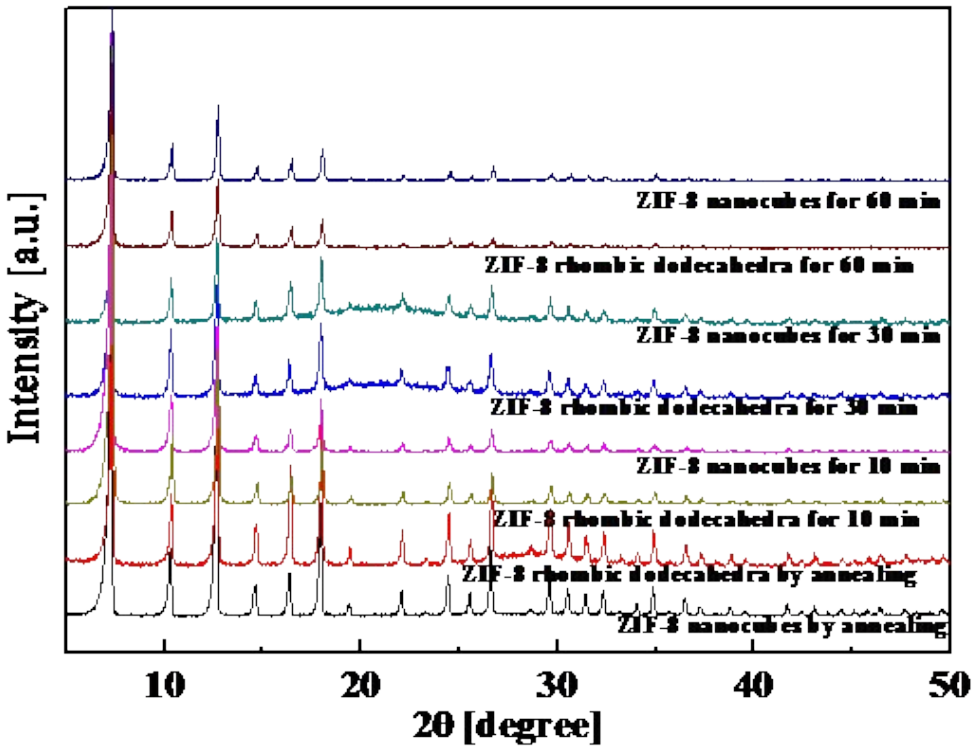

Figure S8. XRD patterns of ZIF-8 rhombic dodecahedra and nanocubes by annealing at 300 °C and as catalyst for subsequent Knoevenagel condensation of benzaldehyde and Malononitrile with different periods of time.

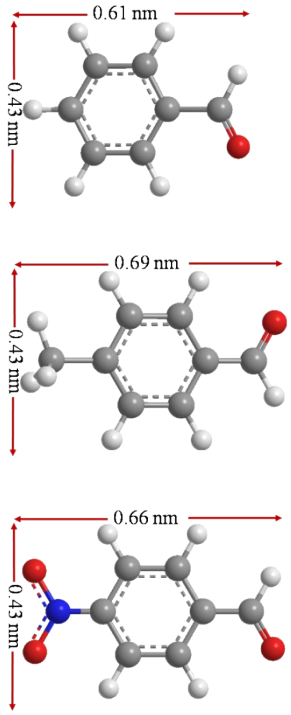

Figure S9. The sizes of aromatic aldehyde molecules measured in ChemBio 3D.

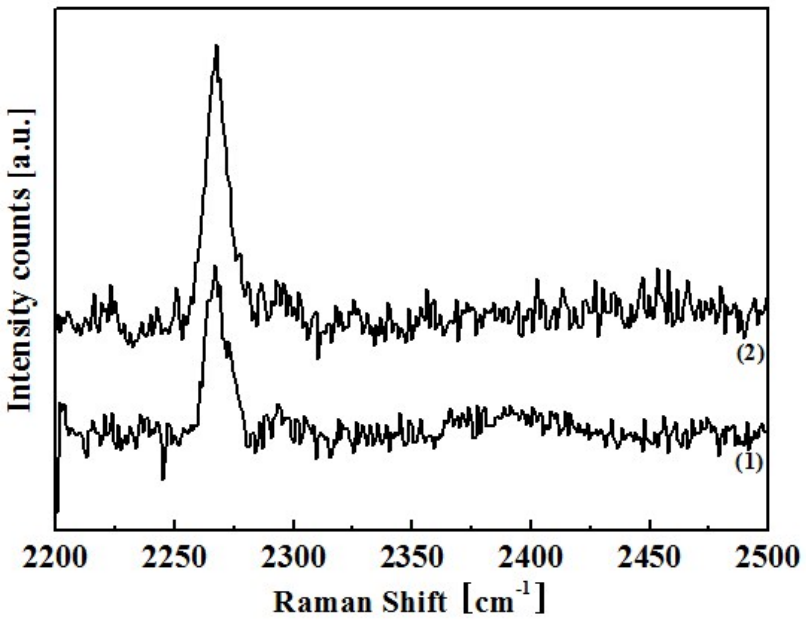

Figure S10. Raman spectra of ZIF-8 (1) nanocubes and (2) rhombic dodecahedra incubated in malononitrile ethanolic solution. Excitation wavelength is 633 nm. The symmetric vibration of cyano group is assigned at about 2268 cm^{-1}.