Supporting Information

Top-down fabrication of crystalline metal-organic framework nanosheets

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Experimental section

General

All the reagents and solvents employed were commercially available and used without further purification. All the experiment were carried out in the laboratory atmosphere at room temperature (20 – 30 °C). FT-IR spectra were recorded on a BIORAD FTS-6000e spectrometer. Thermogravimetric analyses (TGA) were carried out at a ramp rate of 5 °C/min from room temperature to 600 °C under helium atmosphere on a Shimadzu DTG-50 instrument. Powder X-ray diffraction (XRD) measurements were performed on a Rigaku 2000 diffractometer at 40 kV and 40 mA with Cu Kα radiation (λ = 1.5406 Å). Scanning electron microscopy (SEM) measurements were performed on a Hitachi S-5000 SEM instrument. Atom force microscope (AFM) measurements were performed on a SPA-300 (SII Nanotechnology) AFM instrument.

Preparation of the bulk crystals of MOF-2

$Zn(NO_3)_2 \cdot 4H_2O$ (0.262 g, 1.0 mmol) and terephthalic acid (TPA, 0.166 g, 1.0 mmol) were dissolved in N,N-dimethylformamide (DMF, 10 mL). After solvo-thermal reaction at 105 °C for 24 hours in a Teflon-Steel autoclave, the most part of the mother-liquid was discarded and the mother-liquid soaked crystals were moved into a petri dish and diffused by distilled water at 45 ^oC for 4 hours. Then the colorless crystals of MOF-2 were obtained and washed by fresh DMF and H_2O and dried naturally (yield: about 86% based on TPA).

The synthesized crystals of MOF-2 were characterized by X-ray single crystal diffraction and powder XRD measurements. The refined cell parameters (monoclinic $P2_1/n$ space group, a = 6.729(1) Å, b = 15.513(3) Å, c = 12.454(3) Å, β = 102.77(3)°, V = 1267.9(4) Å^3, Z = 4) were in good agreement with the reported data. The structural information of MOF-2 is shown in Fig. S1. The powder XRD data of the polycrystalline powder of MOF-2 also agreed well with the simulated data from the single crystal (see Fig. S2).

Preparation of MOF-2 nanosheets

The TGA result of as-synthesized MOF-2 (see Fig. S3) showed the framework was stable below 380 ^{o}C, and part of water and all discrete DMF molecules can be removed below 160 ^{o}C. Samples for preparing the MOF-2 nanosheets were pretreated by evacuating the as-synthesized MOF-2 at 160 ^{o}C for 4 hours.

Delamination in various solvents (methanol, ethanol, isopropanol, hexane, toluene, DMF, acetone) was tried with various methods (shaking, reflux, ultrasonication). Ultrasonication with acetone as the solvent was found to be the best.

Delamination was done by ultrasonicating the dried powder of MOF-2 (10 mg) in acetone (10 mL) for about 1 hour at room temperature. Then the milky colloidal suspension was kept quietly for 12 hours for sedimentation to get the upper-layer MOF-2 nanosheets/acetone colloidal suspension, of which the concentration is about 0.1 mg/mL, corresponding to the yield of about 10% (It should be noted that the yield might be dependent on the ratio of the dried MOF-2 and acetone used).

Tyndall light scattering was observed for the as-prepared MOF-2 nanosheet acetone colloidal suspension. The colloidal MOF-2 nanosheets underwent restacking upon volatilizing the dispersant (acetone) slowly. The powder XRD data of the restacked MOF-2 showed that the main peaks agreed well with the peaks of dried MOF-2 (see Fig. S2). No peaks of ZnO were observed. The FT-IR result also showed that the product is consistent with dried MOF-2 (see Fig. S6). The delaminated product in the acetone should be MOF-2 nanosheets.

SEM measurements for the MOF-2 nanosheets

The samples were prepared by depositing few droplets of the MOF-2 nanosheet acetone suspension onto the amorphous carbon coated copper grids, which were dried under argon atmosphere. A Hitachi S-5000 scanning electron microscopy (SEM) was employed for the detailed investigation of the size and morphology of the prepared MOF-2 nanosheets (see Fig. S7).

AFM measurements for the MOF-2 nanosheets

An atom force microscope (AFM, SPA-300, SII Nanotechnology) was employed to obtain morphological images of the delaminated MOF-2 nanosheets. Samples were prepared by dropping few droplets of the MOF-2 nanosheet acetone suspension (5 μL) onto a freshly cleaved mica substrate. Measurements were carried out at room temperature in tapping mode with a Si cantilever with a 10 nm radius and a spring constant of 15 N/m. All AFM images were taken with feedback amplitude of about 70% of the free-oscillation amplitude. Analyses of the images were done using the off-line software SPIWin and WSxM (see Fig. S8).

Amine intercalated MOF-2 nanosheets

Amine (0.200 mL) was added into MOF-2 nanosheet colloidal suspension (0.1 mg/mL acetone solution, 10 mL) and aggregation was observed after shaking for several minutes and keeping quietly for about 30 min at room temperature.

The samples for the powder XRD measurements were collected by centrifugation at 3000 rpm, washed by fresh acetone, and then dried naturally. The powder XRD results showed that the amine intercalation occurred. Intercalation of MOF-2 nanosheets with the attendance of the amines exhibited powder XRD patterns different from those of the amine-TPA salts as shown in Fig. S9.

Samples of amine intercalated MOF-2 nanosheets for AFM and SEM measurements were prepared and measured in the same methods as those for MOF-2 nanosheets (see Fig. S10, S11).

Amine exchange

The powders of as-prepared BA-MOF-2 nanosheets (or MBA-MOF-2 nanosheets) were collected by centrifugation at 3000 rpm in a 2 mL centrifugal tube, and then washed by fresh acetone. After removing acetone, 4-methylbenzylamine (or benzylamine, 0.200 mL with 1.0 mL of fresh acetone) was added, which was shaken vigorously for several minutes, and kept quietly for exchange for about 1 hour. After repeating this process for two times, the sample of 4-methyl-benzylamine (or benzylamine) exchanged MOF-2 nanosheets was collected, washed by fresh acetone, and dried naturally for the powder XRD measurement.

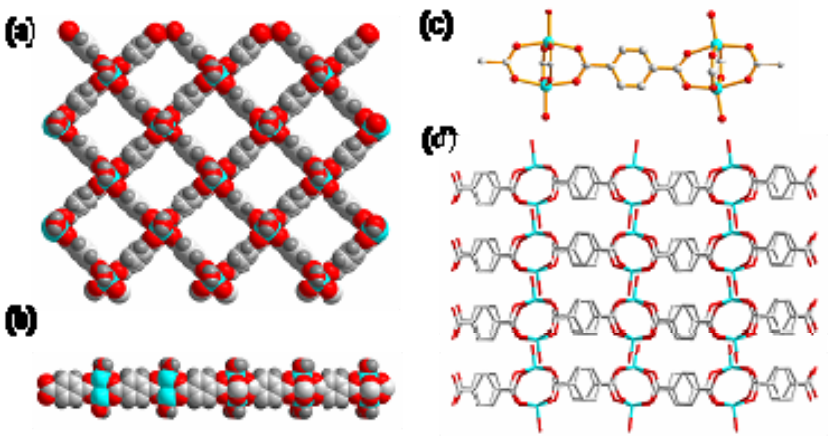

Fig. S1 The neutral, two-dimensional layered framework of MOF-2; (a) view along the vertical direction, (b) view along the horizontal direction, (c) the paddle-wheel clusters and terephthalate fragment, (d) the layer-by-layer stacking model in the crystals of MOF-2, showing hydrogen-bonding interactions between two neighboring layers.

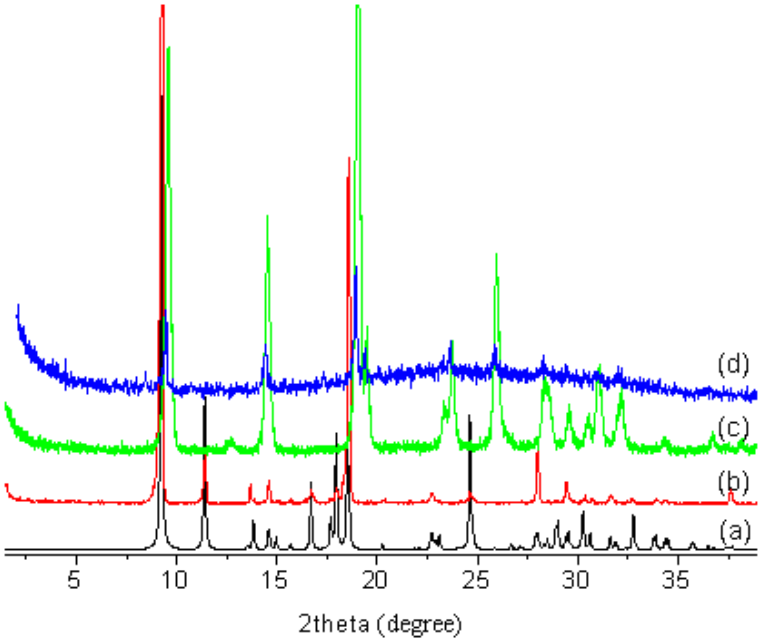

Fig. S2 Powder XRD patterns (a) simulated from the single crystal data of MOF-2, (b) of the as-synthesized polycrystalline powder of MOF-2, (c) the dried powder of MOF-2 and (d) the restacked MOF-2 by volatilizing the acetone from the MOF-2 nanosheet colloidal suspension.

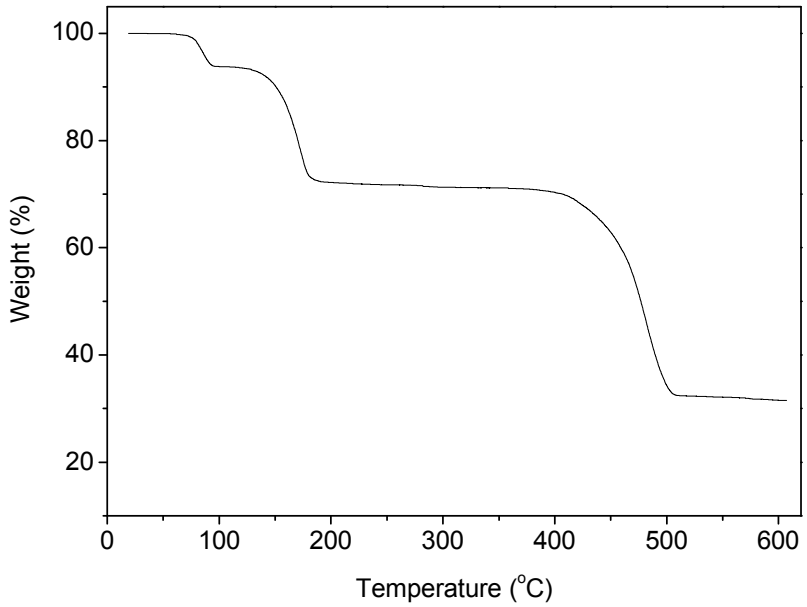

Fig. S3 TGA data of MOF-2. Three steps of weight losses were observed. The first step weight loss is observed below 100 °C, corresponding the loss of water molecules. The second step is around 160 °C, corresponding to the volatilization of the discrete DMF molecules in the framework. The third step is above 380 °C, corresponding to the decomposition of the MOF-2 framework.

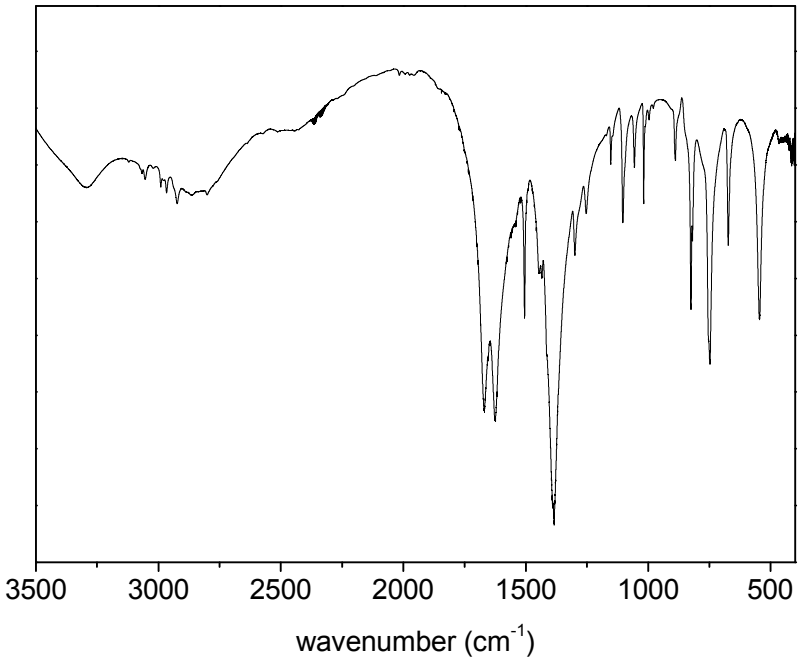

Fig. S4 FT-IR spectrum of the synthesized MOF-2.

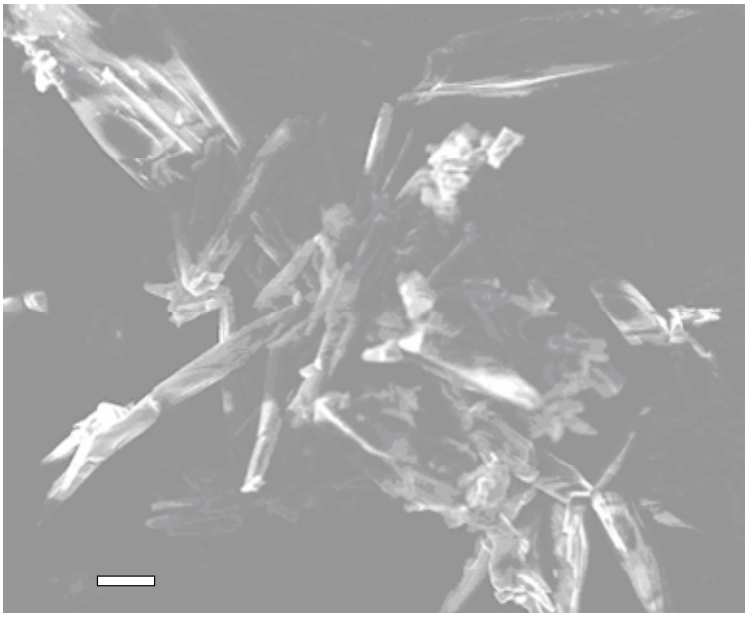

Fig. S5 SEM image of the crystals of as-prepared MOF-2. The scale bar represents 15 μm.

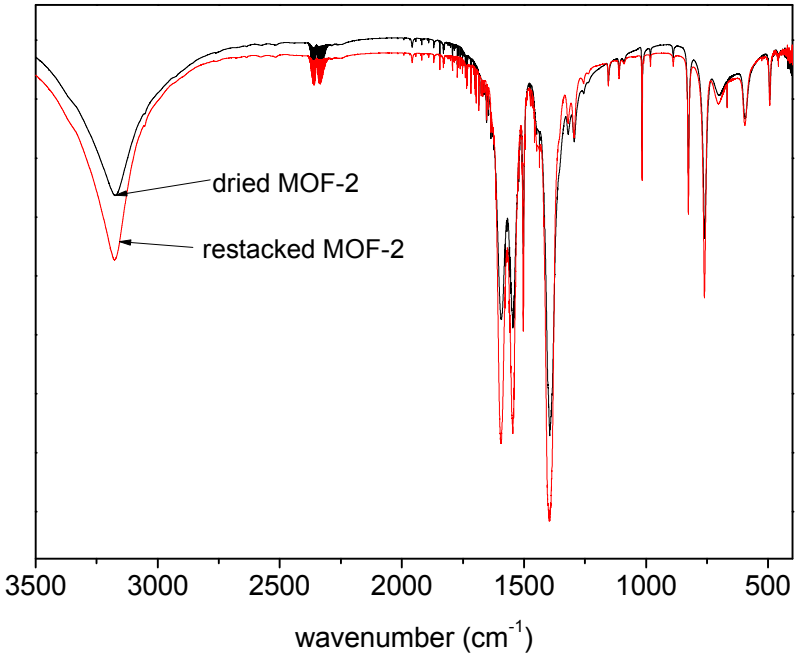

Fig. S6 FT-IR spectra of dried MOF-2 and restacked MOF-2, showing that they were the same as each other and no ZnO was generated on the process of delamination.

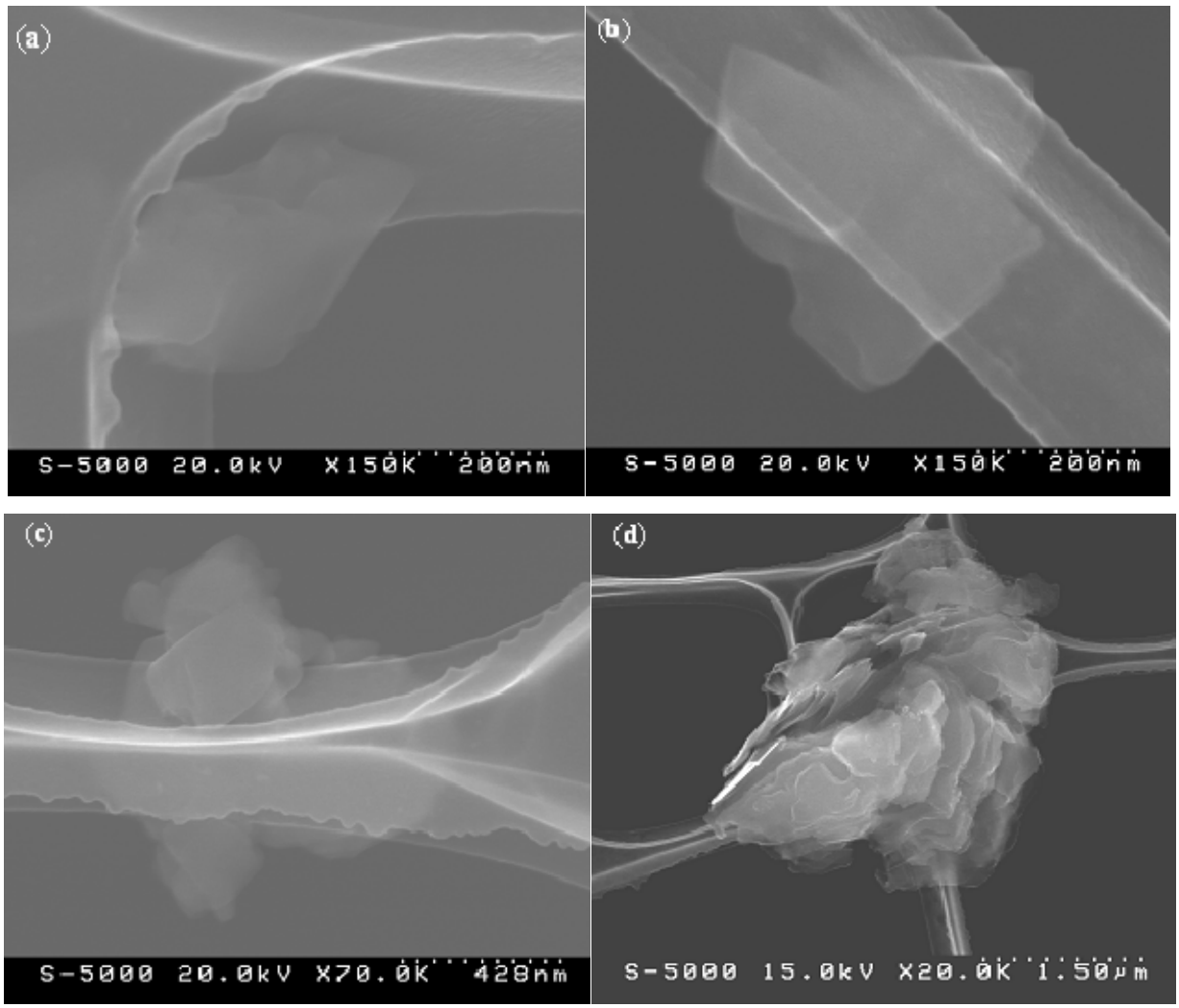

Fig. S7 SEM images of delaminated MOF-2 nanosheets deposited on copper grids, (a) - (c) showing the 2D profiles of the lateral dimensions in 100 nm – 1 micrometer; (d) showing an aggregated large particle, which is also composed of MOF nanosheets.

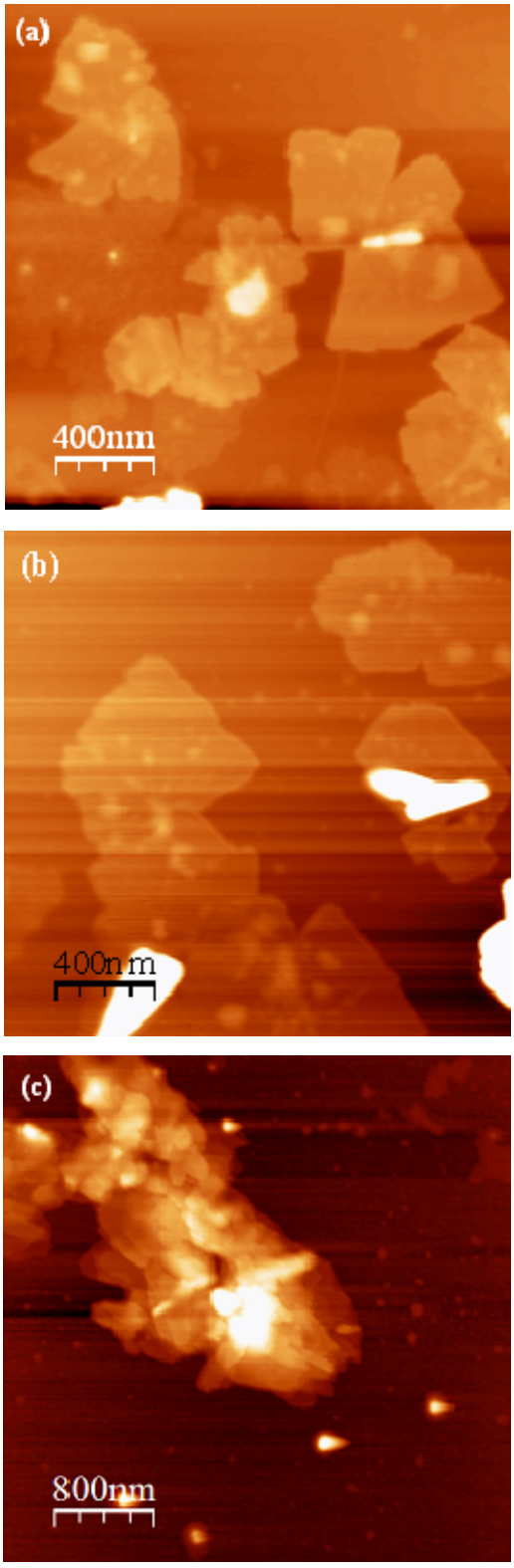

Fig. S8 Tapping-mode AFM images of the delaminated MOF-2 nanosheets deposited on Mica substrates, (a) - (b) showing the 2D profiles with thickness of 1.5 – 6.0 nm and the lateral dimensions of 100 nm – 1 micrometer; (c) showing an aggregated large particle, which is also composed of MOF nanosheets.

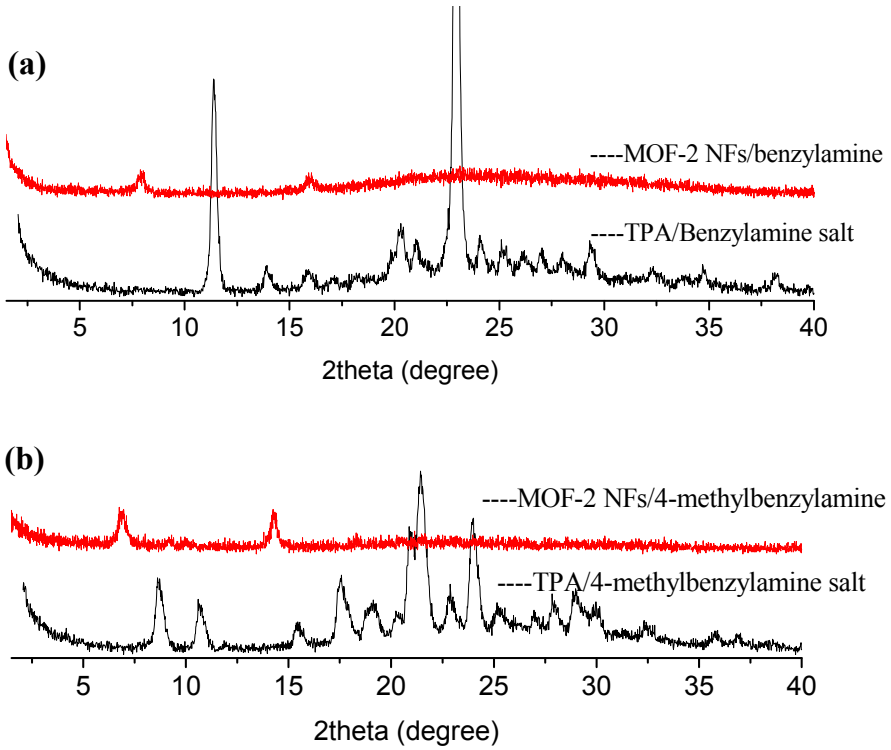

Fig. S9 Powder XRD data of (a) benzylamine intercalated MOF-2 nanosheets and benzylamine-TPA salt; (b) 4-methylbenzylamine intercalated MOF-2 nanosheets and 4-methylbenzylamine-TPA salt.

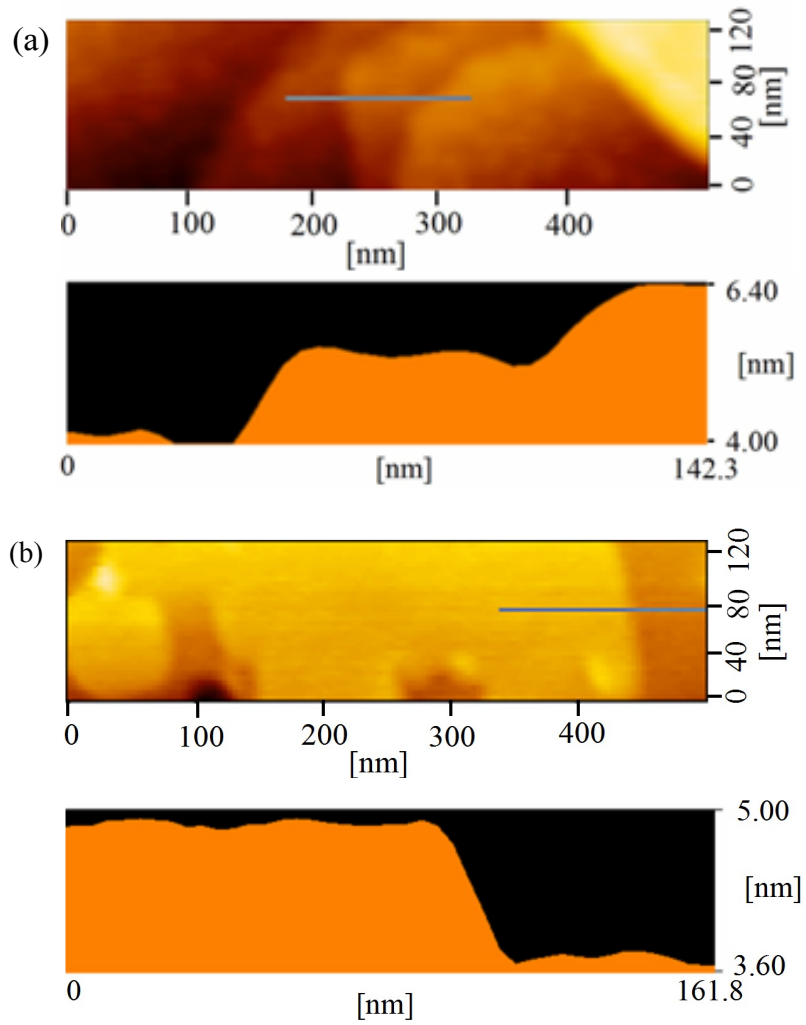

Fig. S10 The AFM images of (a) BA-MOF-2 nanosheets and (b) MBA-MOF-2 nanosheets, showing a distance of ~ 1.1 and ~ 1.3 nm between two neighboring intercalated MOF-2 nanosheets, respectively.

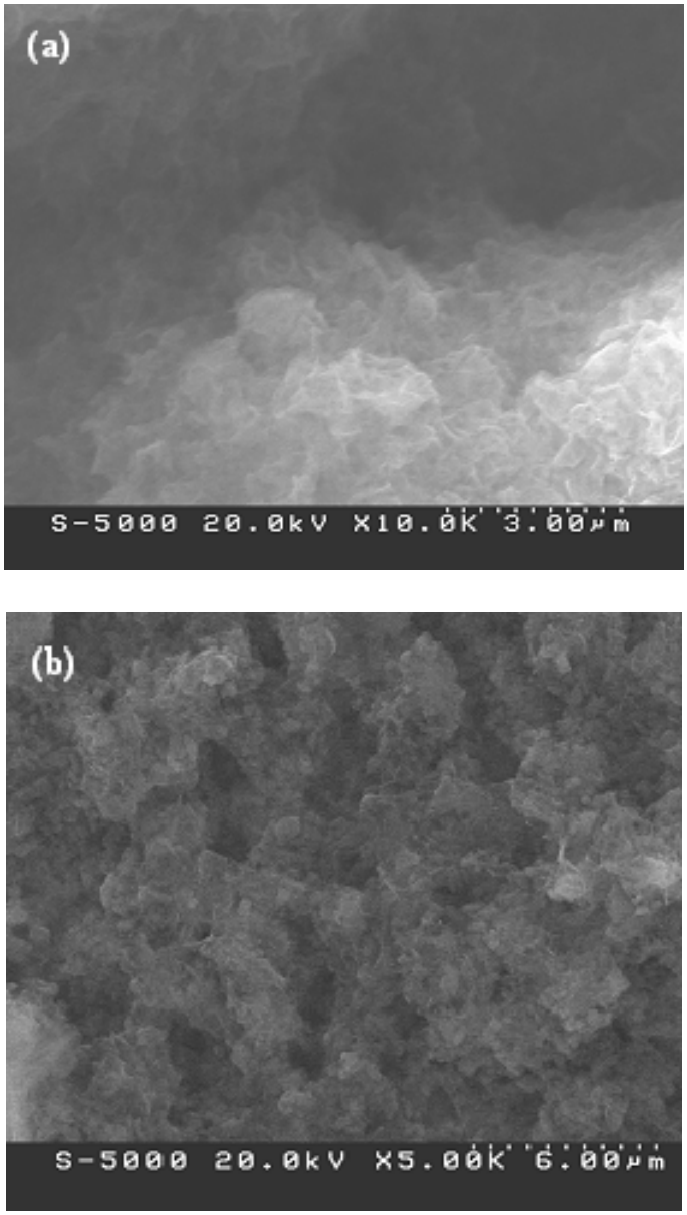

Fig. S11 Scanning electric micrographs for (a) BA-MOF-2 and (b) MBA-MOF-2.