Supporting Information

2D Hydrogen-Bonded Organic Frameworks: In-Site Generation and Subsequent Exfoliation

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Methods

Materials

The syntheses of 2D HOFs were performed under solvent-thermal conditions; the preparation of 2D HOFs nanosheets were performed under ambient conditions; all of the chemicals were of analytical grade and used without further purification. The raw materials for the syntheses of 2D were commercially available from Sigma-Aldrich, all of the used solvents were purchased from Sinopharm Chemical Reagent Co. Ltd (China).

Preparations of 2D HOFs

SEU-1 (TCPP.[HCO₂]⁻.[(NH₂(CH₃)₂)]⁺) was prepared as follows: To a 10 mL DMF solution, 158 mg TCPP (C₄₈H₃₀N₄O₈, 0.200 mmol) were added under continuously stirring. After stirred for 20 min, the obtained purple mixtures were transferred into Teflon-lined suto clave (25 mL) and kept at 160 °C for 8h. After that, the mixtures were cooled to room temperature slowly. The resulted purple solution was then filtered and allowed to evaporate under ambient conditions. The cubic-like purple coloured crystals of SEU-1 were obtained within two weeks, which were separated from the solution via vacuum filtration IR (KBr pellet, cm⁻¹): 2962, 2919, 2851, 1660, 1607, 1404, 1382, 1308, 1260, 1096, 1024, 802, 668. Anal. Calcd for C₅₄H₄₈N₆O₁₀: C 68.92, N 8.93, H 5.14; found: C 67.95, N 8.11, H 5.66.

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SEU-2 (TCPP.[HCO₂]⁻.[(NH₂(CH₃)₂)]⁺.2(H₂O)) were prepared as follows: To a 5 mL formic acid solution, 5 mL DMF solution containing 158 mg TCPP (C₄₈H₃₀N₄O₈, 0.200 mmol) were added dropwise under continuously stirring. After stirred for 30 min, the obtained purple mixtures were transferred into Teflon-lined suto clave (25 mL) and kept at 160 °C for 8h. After that, the mixtures were cooled to room temperature slowly. The resulted purple solution was then filtered and allowed to evaporate under ambient conditions. The cubic-like purple coloured crystals of SEU-2 were obtained within two weeks, and were separated from the solution via vacuum filtration. IR (KBr pellet, cm⁻¹): 2963, 2919, 2850, 1712, 1662, 1607, 1382, 1260, 1096, 1022, 964, 866, 799, 732, 668. Anal. Calcd for C₅₄H₅₂N₆O₁₂: C 66.38, N 8.60, H 5.36; found: C 67.05, N 8.24, H 5.91.

Preparations of 2D HOFs nanosheets

In a typical experiment, 15 mg of bulk HOFs precursors was firstly ground into loose powder, and then dispersed in 30 mL of aqueous solution. The mixture was sonicated in an ultrasonic bath (Brandson, CPX2800H-E, 110 W, 40 KHz) for 90 min. The obtained purple-coloured suspension was then kept vigorous stirring for 24 h under ambient condition. After that, the colloidal suspension was let standing for one week. The colloidal suspension of the exfoliated 2D HOFs nanosheets was collected by centrifugation to remove the sedimentation of bulked samples. The powdered samples of 2D HOFs nanosheets were obtained by freezing drying of the aqueous colloidal suspension.

Photocatalytic activities

9,10-Diphenylanthracene (DPA) was used as the label for the detection of singlet oxygen generation. In a typical procedure, to the aqueous colloidal suspension with 2D nanosheets of SEU-1 (0.5 mg mL⁻¹), 5 mL CH₃CN solution containing DPA (1.6 mg/mL) were added. The obtained mixtures were then bubbled with oxygen for 20 min and irradiated with an LED light (λ = 660 nm,12 mW/cm²). The generation of singlet oxygen was measured by UV-vis spectroscopy at interval of 10 min.

Physical Measurements

Elemental analyses of crystals were performed by a Vario-EL III elemental analyzer for carbon, hydrogen, and nitrogen. IR spectra were recorded on a Shimadzu IR prestige-21 FTIR-8400S spectrometer in the spectral range 4000-400 cm⁻¹, with the samples in the form of potassium bromide pellets. TGA measurements were performed using a Mettler-Toledo TGA/DSC STARe System at a heating rate of 10 K min⁻¹ under an atmosphere of dry N₂ flowing at 20 cm³min⁻¹ over a range from 50 to 800 °C. The SEM images were recorded by using a Field emission scanning electron microscope (FE-SEM, HITACHI S-4800 20 kV), TEM images were recorded by using a Tecnai-G220 transmission electron microscope (E-TWIN 200 kV), with the aqueous suspensions were added

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dropwise onto the holey carbon-coated carbon support Si/SiO₂ and then naturally dried. AFM images were recorded by using a Cypher microscope (Asylum Research). PXRD measurements were performed on an Ultima IV diffractometer equipped with Cu K α radiation (λ = 1.5418 Å) in the range 5-50°at room temperature. Nitrogen sorption isotherms of were measured on a Micromeritics ASAP 2020 surface area analyser.

Calculations

Molecular Hirshfeld surface calculations (3D d_{norm} Hirshfeld surfaces, 2D fingerprint plots) were performed by using the CrystalExplorer17 program.

Single Crystal X-ray Diffractions

The single-crystal X-ray diffraction data for 2D HOFs were collected with a Bruker-AXS SMART APEXII diffractometer equipped with a CCD type area detector and Mo-K α radiation ($\lambda = 0.71073$ Å) in ω -2 θ scan mode. The diffraction data were corrected for Lorentz and polarization effects and for absorption by using the SADABS program. The structures were solved by direct methods, and the structure solution and refinement based on $|F|^2$ were performed with the SHELX software. All geometrical calculations were performed with the SHELXL-2014 software. CCDC numbers 1940052 and 1940053 contain the supplementary crystallographic data of 2D HOFs SEU-1 and SEU-2. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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Fig. S1 Interpenetrated 3D structure of TCPP monomer.



Fig. S2 2D square-like grid skeleton of SEU-1 with dimethylamine presented.



Fig. S3 3D porous diagram of SEU-1.



Fig. S4 Illustrating of the connecting style on the both ends of formate.



Fig. S5 The different orientation of the H_2TCPP molecules distribution in the two ends of formate, the spacing between them has been presented.



Fig. S6 The 2D connecting style of TCPP-based 2D MOFs.¹⁶



Fig. S7 2D square-like grid skeleton of SEU-2.



Fig. S8 3D porous diagram of SEU-2.



Fig. S9 The packing style of 2D sheets in SEU-1 with inter-layer spacing has been presented.



Fig. S10 Height of the single-layered 2D square-like grid sheet.



Fig. S11 Comparison between the PXRD patterns of 2D nanosheets of SEU-1 and TCPP monomer.



Fig. S12 Comparison between the IR spectra of as-prepared SEU-1 and its related 2D nanosheets.