Ionic self-assembly of surface functionalized metal-organic polyhedra nanocages and their ordered honeycomb architecture at the air/water interface

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Supporting Information

Experiment Section

Materials

Cu(NO₃)₂·3H₂O was purchased from Sinopharm Chemical Reagent Co., Ltd. 5-Sulfoisophthalic acid monosodium salt and 2,6-Dimethylpyridine were purchased from Alfa Aesar. Dimethyldistearyl ammonium Chloride (DODAC) were purchased from Tokyo chemical industry Co., Ltd. Methanol was purchased from Tiantai Fine Chemical Co., Ltd. Of Tianjin. Trichloromethane, toluene and N,N-Dimethyl acrylamide (DMA) were purchased from Beijing Chemical works. All materials were used without further purification.

Preparations

MOP-SO₃ crystals

Slightly modified according to reference 5, a MeOH (3 mL) solution of Cu(NO₃)₂·3H₂O (0.119 g) was mixed with a MeOH solution (3 mL) of NaH₂(5-SO₃-1,3-BDC) (0.135 mg) in a glass vial and stirred for 10 min at room temperature. After that, 2,6-Dimethylpyridine (0.175 mL) and DMA (4 mL) were added to this solution and then sealed the vial standing at room temperature. After about a week, homogeneous blue block crystals were collected for further using.

The data of C, H, N and S analysis are C 42.6 wt%, H 4.8 wt%, N 6.0 wt% and S 5.7 wt%. The content of Cu is 11.2 wt% measured by ICP.

{MOP-SO₃}-DODA powder

In a typical synthesis reaction, after the dried MOPs-SO₃ crystals (0.08 g) dissolved in aqueous solution (2 mL), the chloroform solution (2 mL) of DODAC (0.13 g) was added into the water solution drop by drop as soon as possible. The mixed solution was stirred for 10 min and then sealed the solution standing at room temperature overnight. The organic phase was separated, and {MOP-SO₃}-DODA was obtained by evaporating the chloroform to dryness. Then the product was washed with deionized water and MeOH and placed in a vacuum desiccator until the weight remained constant.

The data of C, H, N and S analysis are C 68.7 wt%, H 11.6 wt%, N 2.6 wt% and S
1.7 wt%.

{MOP-SO₃}-DODA ordered honeycomb film

In a typical synthesis, the {MOP-SO₃}-DODA powder was re-dissolved in chloroform solution (1.7mg·mL⁻¹). Subsequently, the solution was stirred for 20 min and equilibrated at 25°C for 2 days. Then several drops of the solution were spread on the pure water surface and the honeycomb architectures of {MOP-SO₃}-DODA film was formed after the chloroform solution was totally evaporated. This film can be transferred to any solid surface for further study.

Measurements

Powder X-ray diffraction (XRD) data were collected on a Rigaku 2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). The step size was 0.02° and the count time was 2s.

Small angle X-ray scattering (SAXS) were done with a high-flux SAXS instrument (SAXSess, Anton Paar) equipped with a Kratky camera system and an imaging plate (IP) as the detector. The IP with a pixel size of 42.3µm² extends into the wide-angle range (the q range covered by the IP is up to 28 nm⁻¹, q=(4πsinθ)/λ, where the λ is the wavelength of 0.1542 nm and 2θ is the scattering angle). The liquid samples for SAXS measurement were carefully loaded into a quartz capillary with a diameter of 1 mm. The exposure time was 30 min for each one. The pair-distance distribution functions (PDDF) were calculated from the scattering curves using the generalized indirect Fourier transform (GIFT) program included in the SAXSess software package. MOP-SO₃ crystals were dissolved in MeOH at a concentration of 20 g/L; {MOP-SO₃}-DODA was dissolved in mixed solution (VMeOH:Vtoluene=3:2) at a concentration of 20 g/L. The solutions were directly filtered into capillaries using 20 nm pore-size filters.

Transmission electron microscope (TEM) was carried out by using a FEI Tecnai G2 F20 s-twin D573 transmission electron microscope operated at 200 kV, respectively. The sample for TEM was mounted on a carbon polymer supported on a copper grid.

The infrared (IR) spectra were recorded within the 400-4000cm⁻¹ region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets.

The elemental analyses were performed on a Perkin-Elmer 2400 LSII CHN analyzer.

The thermal gravimetric analyses (TGA) were performed on a TGA Q500 V20.10 Build 36 thermogravimetric analyzer in air atmospheric environment with a heating rate of 10 °C·min⁻¹.

UV/vis spectra were recorded using a Shimadzu UV2450 spectrometer. MOP-SO₃ crystals were dispersed in MeOH and {MOP-SO₃}-DODA was dissolved in mixed solution (VMeOH:Vtrichloromethane=3:2). Then both the solutions were filtered using a membrane filter with 0.45 µm pore size for UV/vis measurement.
Experimental results Figures

Fig. S1 X-ray diffraction (XRD) patterns of MOP-SO₃ crystals: pattern simulated from single-crystal structure in black, experimental pattern for the as-synthesized sample in red

Fig. S2 A) Thermogravimetric analysis of \{MOP-SO₃\}-DODA, Weight loss of product is about 95.6%. B) The XRD patterns of \{MOP-SO₃\}-DODA residue (black line) coinciding with that of CuO (red line)

Based on above-mentioned data with elemental C, H, N and S analysis and ICP test of MOP-SO₃ crystals, we can calculate the molar ratio of Cu : N : S in the \{[Cu₂(5-SO₃-bdc)₂L₂]₁₂\}^{24⁻} unit was about 1:2.4:1. As shown in Fig. S2, because the residue of \{MOP-SO₃\}-DODA is mainly CuO with the content at 4.4 wt%, so we can obtain the content of Cu at about 3.5 wt%. Combined with the C, H, N and S analysis data of \{MOP-SO₃\}-DODA, the molar ratio of Cu : N : S is about 1:3.4:1. Compared with the molar ratio of Cu : N : S in MOP-SO₃ crystals and our product, the redundant nitrogen atoms mainly derive from the surfactant DODAC (C₃₈H₈₀ClN) with the molar ratio of Cu : DODA⁺ : S at about 1:1:1. Then, the the molar ratio of \{[Cu₂(5-SO₃-bdc)₂L₂]₁₂\}^{24⁺} unit to DODA⁺ is calculated at 1:24, which is consistent with the value expected from the electric charge balance between them. The molecular formula could be briefly written as (DODA)₂₄[Cu₂(5-SO₃-bdc)₂L₂]₁₂.
**Figure S3** Characterizations of the ordered honeycomb film (A) IR spectrum (B) UV/vis absorption spectrum. Compared with the \{MOP-SO₃\}-DODA, it can be clearly seen that the bond binding of MOP nanocages remained intact in the film.