

A photoelectronically active, metal organic framework film by self-directed assembly of silanized porphyrin cobalt monomer

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Experiment Details

I. Materials.

(3-Aminopropyl)triethoxysilane (APTES), 5,10,15,20-tetra(4-carboxylphenyl)porphyrin (TCPP) and pyrrole were purchased from J&K Scientific Ltd. 4-Carboxybenzaldehyde was purchased from Accela Chem Bio. Co. Ltd. All other chemicals were obtained from Sinopharm Chemical Co. Ltd. (A. R.). All commercial chemicals were used without further purification except pyrrole.

II. Synthesis.

Synthesis of 5,10,15,20-tetra(4-carboxylphenyl) porphyrin cobalt (CoTCPP). CoTCPP was synthesized according to the following procedure. Purified pyrrole (0.1342 g, 2 mmol), CoCl₂·6H₂O (0.238 g, 1 mmol) and 4-carboxybenzaldehyde (0.3001 g, 2 mmol) were dissolved in 100 mL of propionic acid and stirred for 2 h at 140 °C. After the mixture was cooled to room temperature, 150 mL of de-ionized water was introduced. The resultant precipitate was washed twice with de-ionized water. Then the precipitate was dispersed into a certain amount of methanol. After being settled down overnight, the mixture was filtered. The filtrate was continued to cool in an ice-bath with stirring. A deep-purple solid can be obtained after being filtered and washed using methanol and hot water, respectively. The resulting solid was dispersed into a mixed solvent of methanol and H₂O (volume ratio = 1:

1, containing 0.959 mol L⁻¹ of KOH solution). The mixture was stirred and refluxed for 1 h. After it was cooled to room temperature, methanol was evaporated. Then the solid was acidified with 1 mol L⁻¹ of hydrochloric acid until no further precipitate was produced. The red solid (CoTCPP) was collected by filtration, washed with water, and dried under a vacuum drying oven. Color of the CoTCPP: purple. ¹H NMR (500 MHz, CD₃OD): δ(ppm), 11.65 (s, 4H, COOH), 8.15 (s, 8H, -pyrrole), 7.8-7.9 (d, 8H, 2,6-phenyl), 7.2-7.3 (d, 8H, 3,5-phenyl). IR (KBr, cm⁻¹): 3438, 1691, 1607, 1509, 1407, 1103, 1007, 792 cm⁻¹. MS (MALDI) m/z calculated for C₄₈H₂₈CoN₄O₈ (M⁺): 847.12, Found: 847.13.

Preparation of SPCM. SPCM was synthesized referencing to the previous reports.^{1,2} Synthesis process of the silanized porphyrin cobalt monomer (SPCM) was summarized in Fig. S1. The typical procedure can be described in the followed. CoTCPP (0.1027 g, 0.1162 mmol) was dissolved in 10.0 mL of THF, and then 1 mL of thionyl chloride (13.76 mmol) was added into the solution. The solution was stirred and heated at 70 °C for 2 h. Therefore, the acyl chloride groups were formed via interaction of thionyl chloride with the carboxyl groups bonded on the peripheries of CoTCPP. After removing excess thionyl chloride, 0.1095 mL of APTES (0.4647 mmol) was introduced. The mixture was stirred and refluxed for 8 h, and then SPCM was obtained.

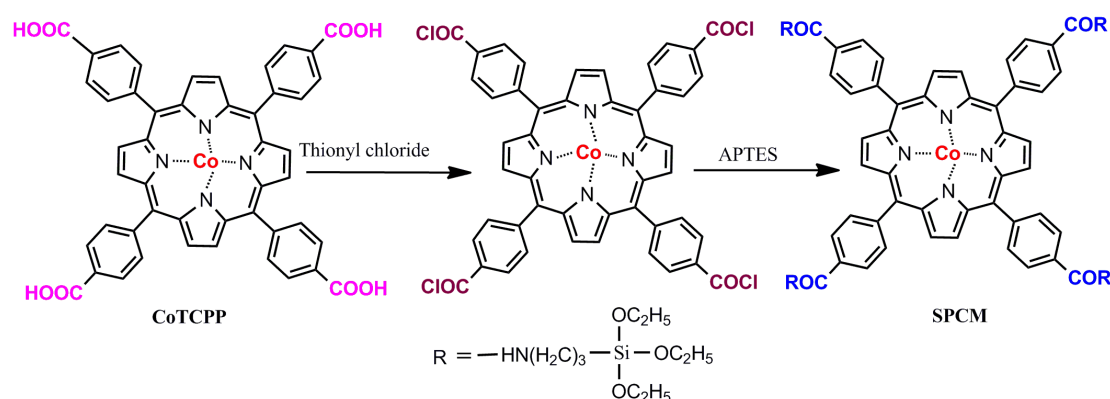


Fig. S1 Synthesis process of SPCM.

Assembly of the porphyrin MOF film. SPCM (0.0784 g, 0.047 mmol) and 4,4'-bipyridine (0.029 g, 0.188 mmol) were added into 10 mL of THF. The mixture was stirred for 30 min under room temperature. Then hydrochloric acid solution (0.1 mol L⁻¹, 1.0 mL) was added and the mixture was heated at 60 °C for 5 h. Finally, the resulting solution (RS1) was casted onto a substrate followed by THF evaporation.

Preparation of sample 2. SPCM (0.0784 g, 0.047 mmol) and hydrochloric acid solution (0.1 mol L⁻¹, 1.0 mL) were added into 10 mL of THF. The mixture was stirred and heated at 60 °C for 5 h. Then the resulting solution (RS2) was casted onto a substrate followed by THF evaporation.

Preparation of sample 3. Thionyl chloride (1 mL, 13.76 mmol) was added into TCPP (0.1162 mol L⁻¹, 10.0 mL) THF solution. The mixture was stirred and heated at 70 °C for 2 h. After removing excess thionyl chloride, ATPES (0.1095 mL, 0.4647 mmol) was introduced. The mixture was stirred and refluxed for 10 h. Finally, the silanized porphyrin base monomer (SPBM) was obtained. SPBM (0.0759 g, 0.047 mmol) was added into 4,4'-bipyridine (0.029 g, 0.188 mmol) THF solution, and was stirred for 30 min under room temperature. Then hydrochloric acid solution (0.1 mol L⁻¹, 1.0 mL) was added and heated at 60 °C for 5 h. Finally, the resulting solution (RS3) was casted onto a substrate followed by THF evaporation.

III. Characterization.

UV-visible absorption spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer (Japan). Atomic force microscopy (AFM) image was obtained by Agilent Technologies N9605A atomic force microscopy with tapping mode (USA). High resolution transmission electron microscope images were taken with a JEOL JEM-2100 transmission electron microscope (Japan). The X-ray diffraction patterns (XRD) was collected on a PANalytical Xpert Pro MRD X-ray diffractometer operated at 40 kV voltage and 40 mA current with Cu-K α radiation ($\lambda = 0.154$ nm) (Netherlands). Scanning was performed under ambient conditions over the 2θ region of 0.3–5° at the rate of 0.1° min⁻¹. Nitrogen adsorption-desorption isotherm was obtained at 77 K by using Micrometrics Model ASAP 2020 volumetric adsorption analyzer (USA). The sample was previously outgassed at 373 K under vacuum. The pore size distribution was obtained from the adsorption branches of the isotherms using a BJH method. Fourier transform infrared spectra (FTIR) were recorded at room temperature on a Nicolet 6700 FTIR spectrometer (USA). Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer TGA-7 thermal analyzer (USA). All samples were heated in N₂ atmosphere from room temperature to 800 °C at a scanning rate of 20 °C min⁻¹. Electrochemical measurements were performed on a CH Instrument CHI 660E electrochemical workstation (China).

Preparation of working electrodes. Fluorine-doped tin oxide (FTO) glass was cleaned by sonication in ethanol, acetone, chloroform, and deionized water for 10 min, respectively, and then dried in the air. The working electrodes were prepared by immersing the cleaned and dried FTO glasses into RS1, RS2 and RS3, respectively. After 30 min, the electrodes were washed with ultrapure water, and then dried.

Photoelectrochemical behavior measurement. The photocurrent measurements were carried out in a phosphate buffer solution (PBS, pH = 7.4) by using a three-electrode system. The FTO glasses assembled with the porphyrin MOF film or other samples was as the working electrode. A Pt wire was as the counter electrode, and a saturated

calomel electrode was as the reference electrode. The light source was a 150 W xenon lamp ($\lambda = 200\text{--}1800\text{ nm}$). The area of light irradiation was 1 cm^2 . The bias voltage was controlled at 0.30 V . All experiments were carried out at about $25\text{ }^\circ\text{C}$.

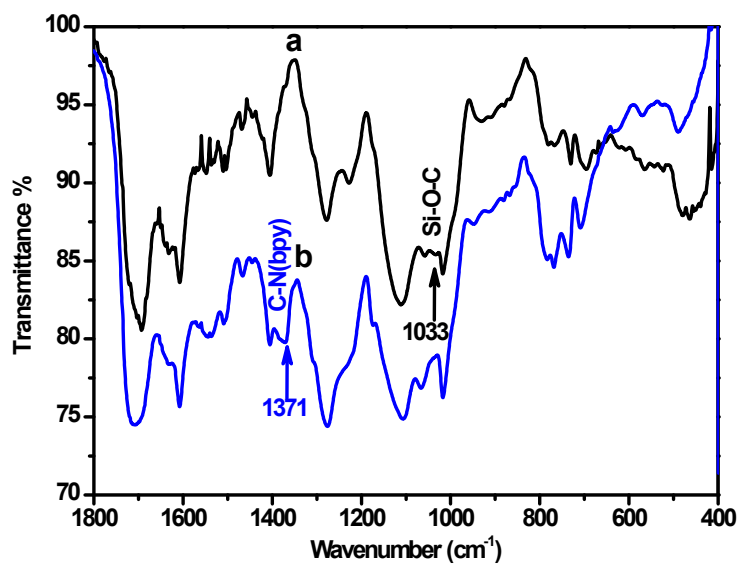


Fig. S2 FTIR of SPCM (a) and the porphyrin MOF film (b).

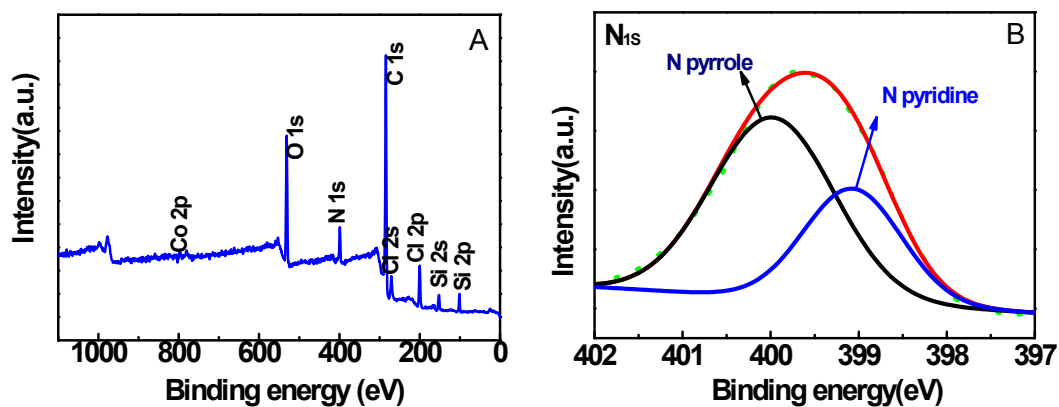


Fig. S3 (A) XPS spectrum of the porphyrin MOF film and (B) high resolution XPS spectrum of the N1s.

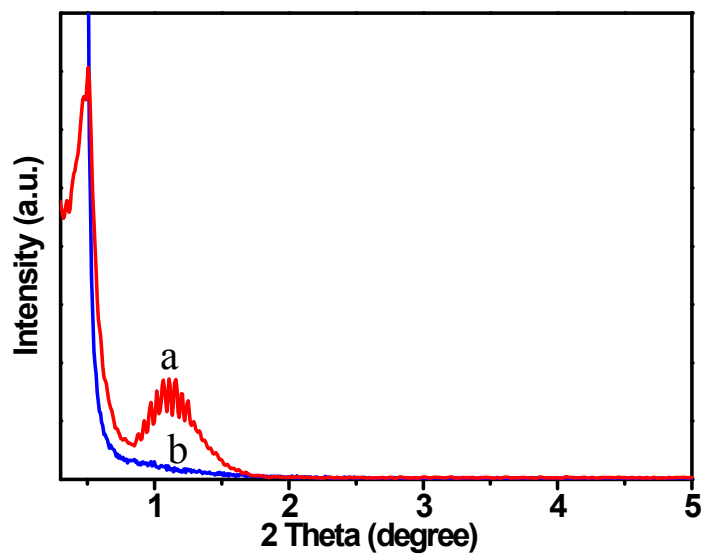


Fig. S4 Small-angle XRD patterns of the porphyrin MOF films (a) and sample 2(b).

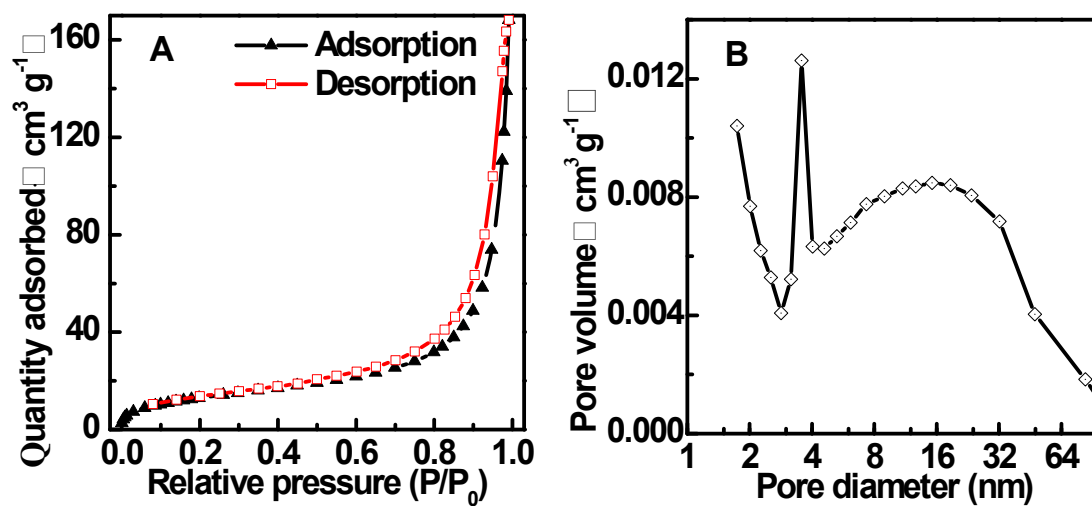


Fig. S5 N₂ adsorption isotherm (A) and pore size distribution (B) of the porphyrin MOF films.

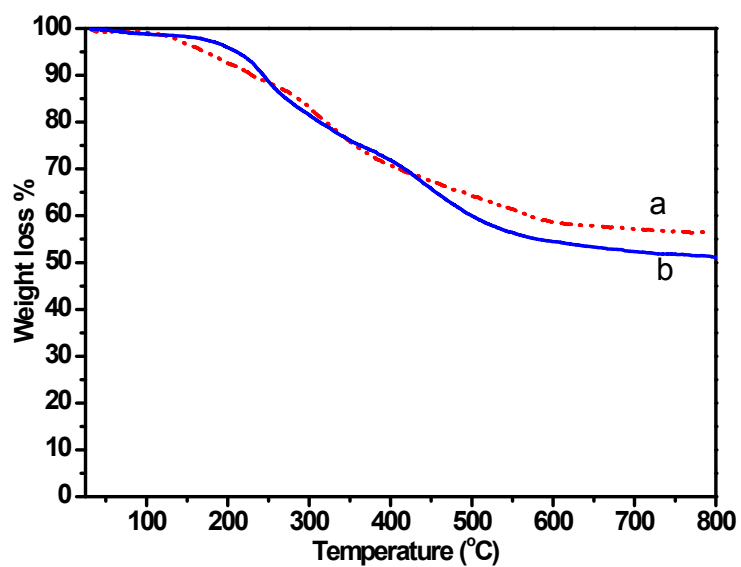


Fig. S6 TGA curves of sample 3 (a) and the porphyrin MOF film (b).

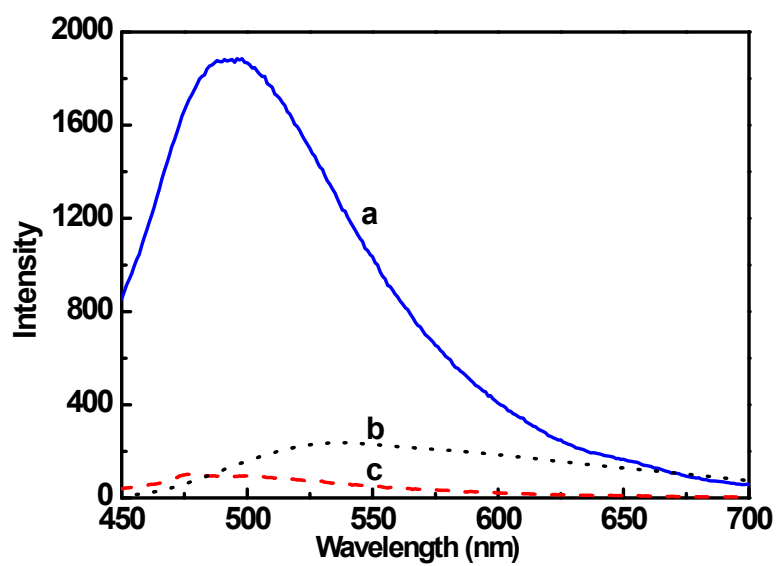


Fig. S7 Fluorescence spectra of the porphyrin MOF film (a), sample 2 (b) and sample 3 (c). $\lambda_{ex} = 415$ nm.

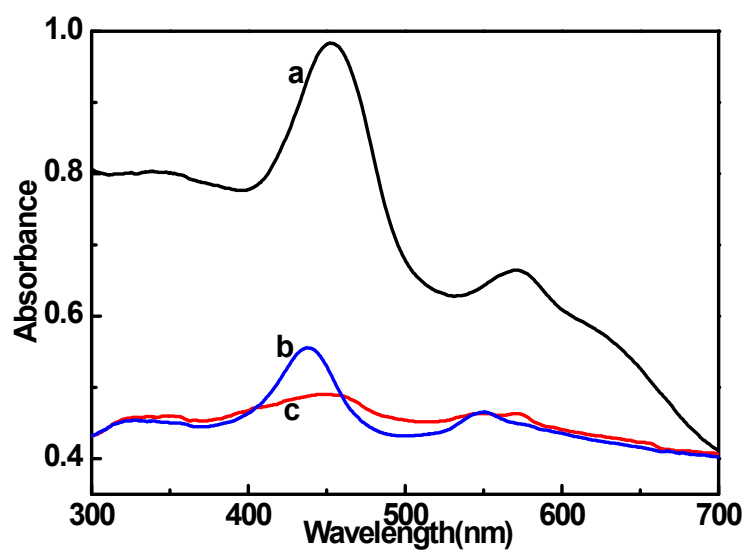


Fig. S8 Solid UV-vis diffuse reflection spectra of the porphyrin MOF film (a), sample 2 (b) and sample 3 (c).

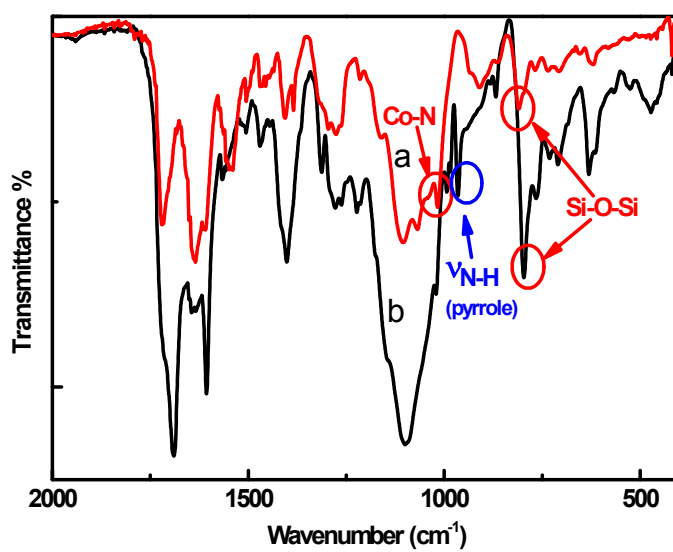


Fig. S9 FTIR of the sample 2 (a) and sample 3 (b).

Table S1 The comparison of our results with the references

	Photoelectric stability	Photocurrent response	Test time	Trend	Light source
Ref. 3	Unstable	Slow	320 S	Decreasing	A 150 W Xe lamp
Ref. 4	Unstable	Slow	800 S	Increasing	A 500 W Xe lamp
Ref. 5	Unstable	Fast	50 S	Increasing	A 500 W Xe lamp
Ref. 6	Unstable	Fast	60 S	Increasing	A 150 W Xe lamp
Ref. 7	Unstable	Fast	200 S	Increasing	A 150 W Xe lamp
Ref. 8	Stable	Fast	25 S	Changeless	A 500W Xe lamp
Ref. 9	stable	Fast	210 S	Changeless	A 150 W Xe lamp
Our result	Stable	Fast	600 S	Changeless	A 150 W Xe lamp

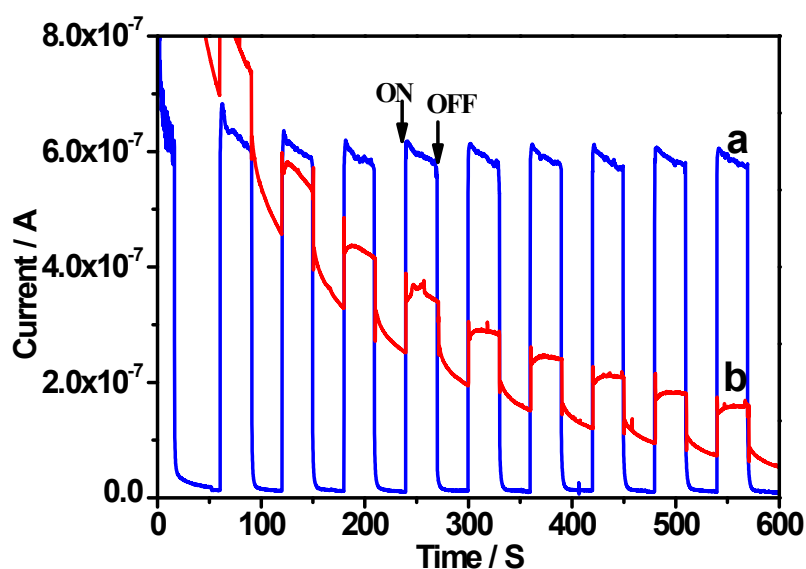


Fig. S10 The photocurrent response of the porphyrin MOF films with bpy (a) and 1,2-bis(4-pyridyl)acetylene (b) as the axial ligand, respectively.

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