Electronic Supplementary Information (ESI)

Metal-Porphyrinic Framework Film as Efficient Optical Limiting layer in Electro-Optical Switchable Device

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Table of Contents

Experimental section

Materials and instrumentations

All of the chemicals were used after purchasing without further purification. The ITO coated PE (ITO-PE) film was first cleaned using distilled water in an ultrasonic bath and dried before activation. And then they was treated with a mixture of 0.2 mM NaOH aqueous solution and hydrogen peroxide (30%) with a volume ratio 3:1 at 80 °C for 30 min and then cleaned with deionized water and dried under nitrogen flux for the next preparation. The powder X-ray diffraction (PXRD) analysis were performed on a MiniFlex2 X-ray diffractometer using Cu−Kα radiation (λ = 0.1542 nm). IR spectra were recorded using a Bruker Vertex 70 FTIR spectrometer. Scanning electron microscope (SEM) images for the morphology of thin films were measured by JSM6700. The UV-vis spectra for the samples were measured by Lambda 365. The electro-optical switching property of the obtained devices were measured by applied voltage in a range of 0-50 V.

Fabrication of CuTCPP thin film prepared on conducitve ITO-PE substrate

The CuTCPP thin film used in the present work were grown using the layer-by-layer autoarm immersion method and were fabricated using the following diluted ethanolic solutions of copper acetate (1.0 mM) and TCPP (5,10,15,20-(4-carboxyphenyl) porphyrin (0.1 mM). The detail was shown as follow: fristly, the functionalizd substrate was immersed in the solution of copper acetate for 10 min and then was immersed in solution of TCPP for 15 min. Each step was washed with ethanol to remove residual reactants. The above process was regarded as one cycle. A total of 30 growth cycles were used for CuTCPP thin film grown on the substrate (CuTCPP SURMOF).

Fabrication of CuTCPP SURMOF/PDLC device

PDLC/CuTCPP SURMOF device was prepared using a polymerization induced phase separation with heating. Briefly, a mixture of 65 wt% E7 liquid crystal molecule, 23.3 wt% bisphenol-A epoxy resin E51, and 11.7 wt% polyamide 650 were well mixed at 65℃. Note that the ratio of the compoents was referred from the reported PDLC film in the literature.[1] The obtained mixture were sandwiched between two Cu-TCPP SURMOF modified PET-ITO substrates, then dried in a vacuum oven at 65℃ for 6 hours. After cooling to room temperature, the CuTCPP SURMOF/PDLC device was obtained.

Z-scan measurements

The nonlinear optical limiting of the sample was evaluated using the Z-scan technique. The excitation light source was an Nd:YAG laser with a repetition rate of 10 Hz. The laser pulses (period, 5 ns; wavelength, 532 nm) were split into two beams with a mirror. The pulse energies at the front and back of the samples were monitored using energy detectors 1 and 2. All of the measurements were conducted at room temperature. The sample was mounted on a computer-controlled translation stage that shifted each sample along the z-axis.

The measured Z-scan curves were fitted by the following expression:

$$T(Z,S=1)=\frac{1}{\sqrt{\pi}(Z,0)}\int_{-\infty}^{\infty}Ln\left[1+q_0(Z,0)e^{-r^2}\right]dr \qquad \textit{eq. (1)}$$

$$q_0(Z,0)=\beta I_0 L_{eff} \qquad \textit{eq. (2)}$$

$$L_{eff}=\frac{1-e^{-\alpha l}}{\alpha} \qquad \textit{eq. (3)}$$

$$T(Z,\Delta\Phi)=1+\frac{4\Delta\Phi x}{(x^2+9)(x^2+1)} \qquad \textit{eq. (4)}$$

$$\Delta\Phi=2\pi\gamma I_0 L_{eff}/\lambda \qquad \textit{eq. (5)}$$

$$\chi_I^{(3)}=\frac{\varepsilon_0 c^2 n_0^2}{\omega}\beta \qquad \textit{eq. (6)}$$

$$\chi_R^{(3)}=2c\gamma n_0^2\varepsilon_0 \qquad \textit{eq. (7)}$$

$$|\chi^{(3)}|=\sqrt{(\chi_R^{(3)})^2+(\chi_I^{(3)})^2} \qquad \textit{eq. (8)}$$

In these equations, I_0 is the on-axis peak intensity at the focus (Z = 0), L_{eff} is the effective thickness of the sample, α_0 is the linear absorption coefficient, and l is the sample thickness, x = z/z_0, z is the Z-scan displacement, $\Delta\Phi$ is the phase change, ε_0 is the permittivity of vacuum, c is the speed of light, n_0 is the refractive index of the medium, $\omega=2\pi c/\lambda$. By fitting the curves, the nonlinear absorption coefficient β were obtained.

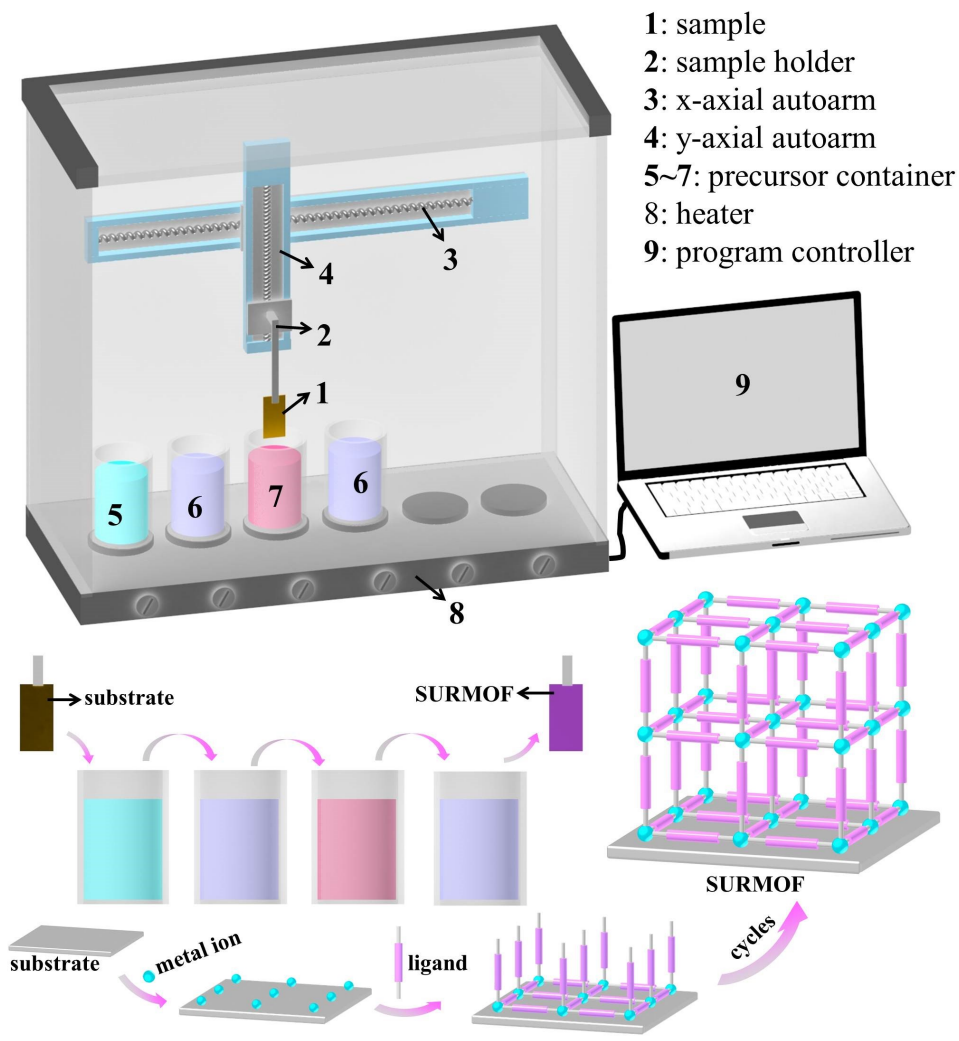

Figure S1. Schematic illustration for *van der Waals* epitaxial growth of CuTCPP SURMOF prepared by layer by layer immersion setup.

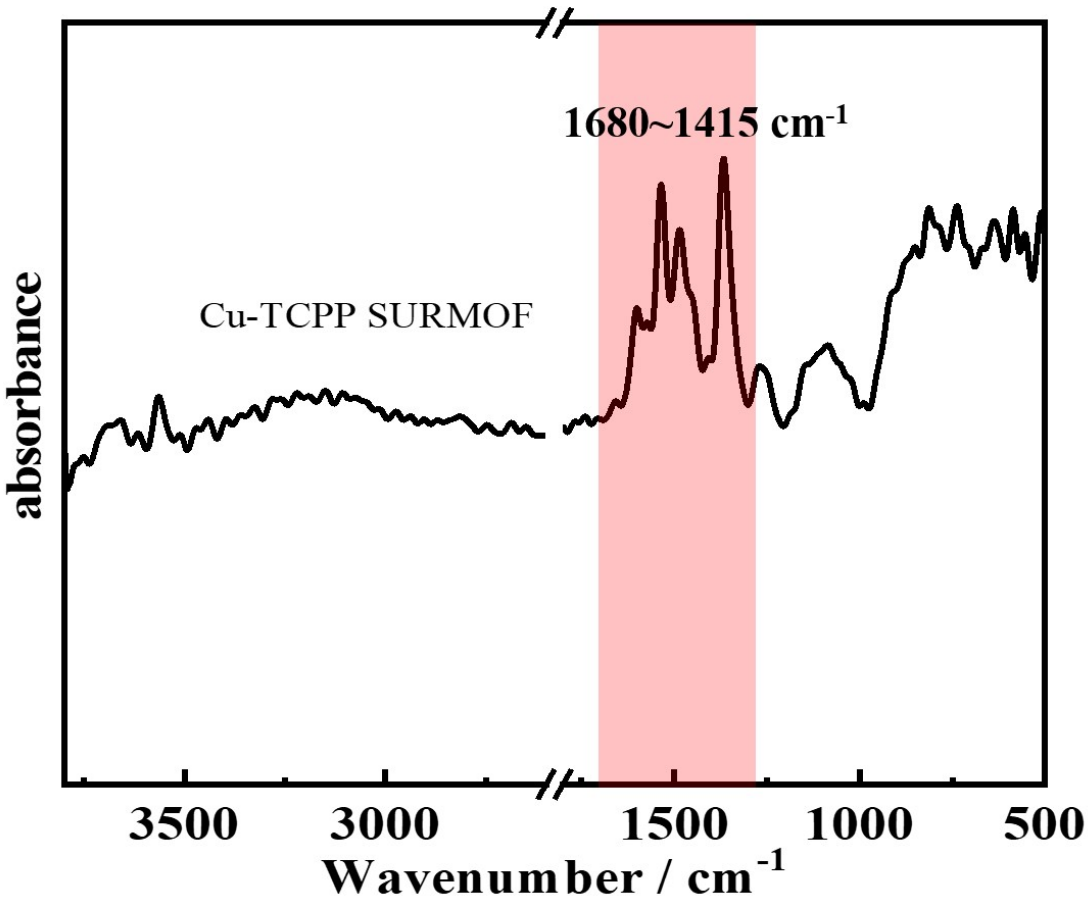

Figure S2. The IR spectra of CuTCPP SURMOF.

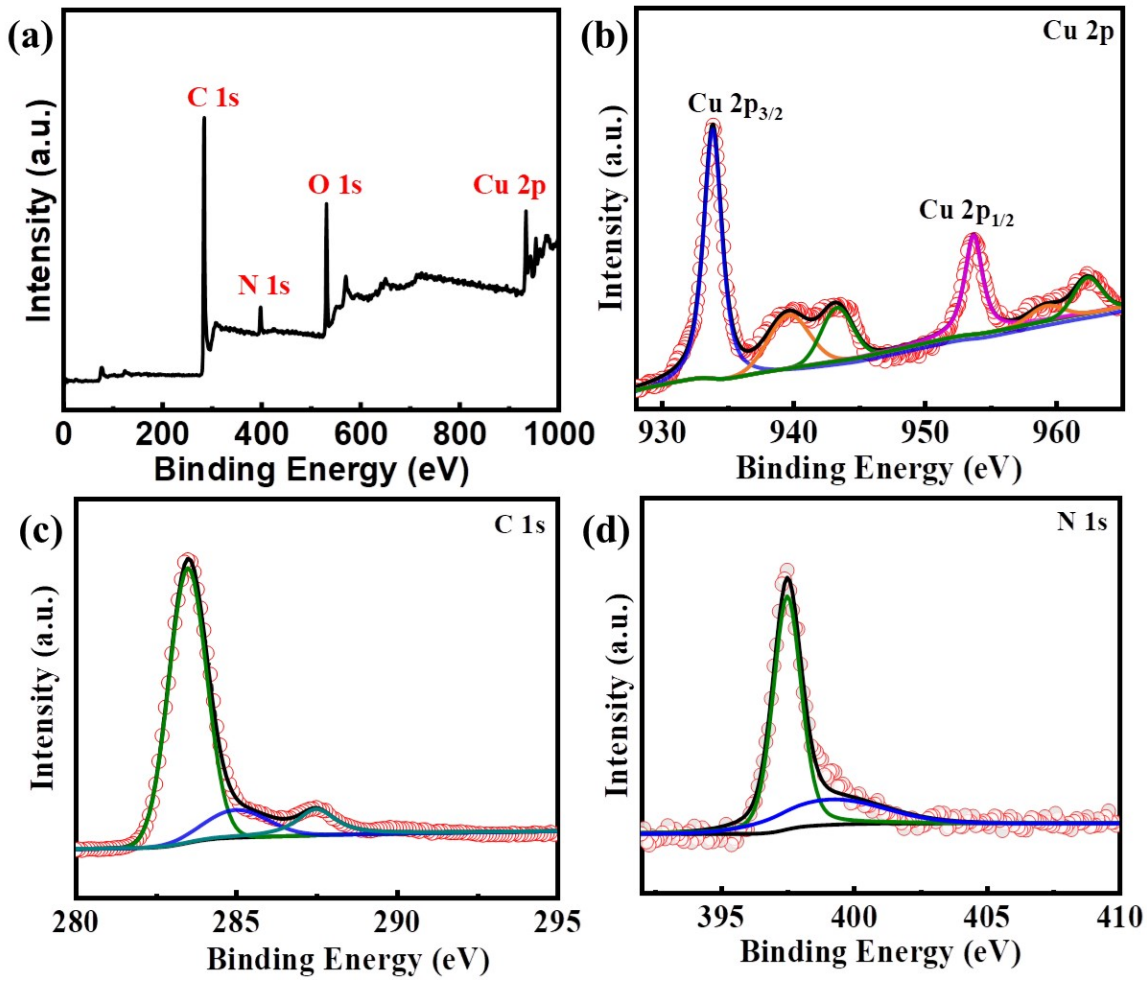

Figure S3. The XPS spectra of CuTCPP SURMOF: (a) Survey spectra; High resolution spectra of (b) Cu 2p, (c) C 1s, and (d) N 1s.

Figure S4. The behavior of electro-optical switching turn-off and turn-on states of is our PDLC module with ITO substrate on CuTCPP SURMOF/PDLC device that connecting with two electrodes system with applying different voltages (0~50 V).

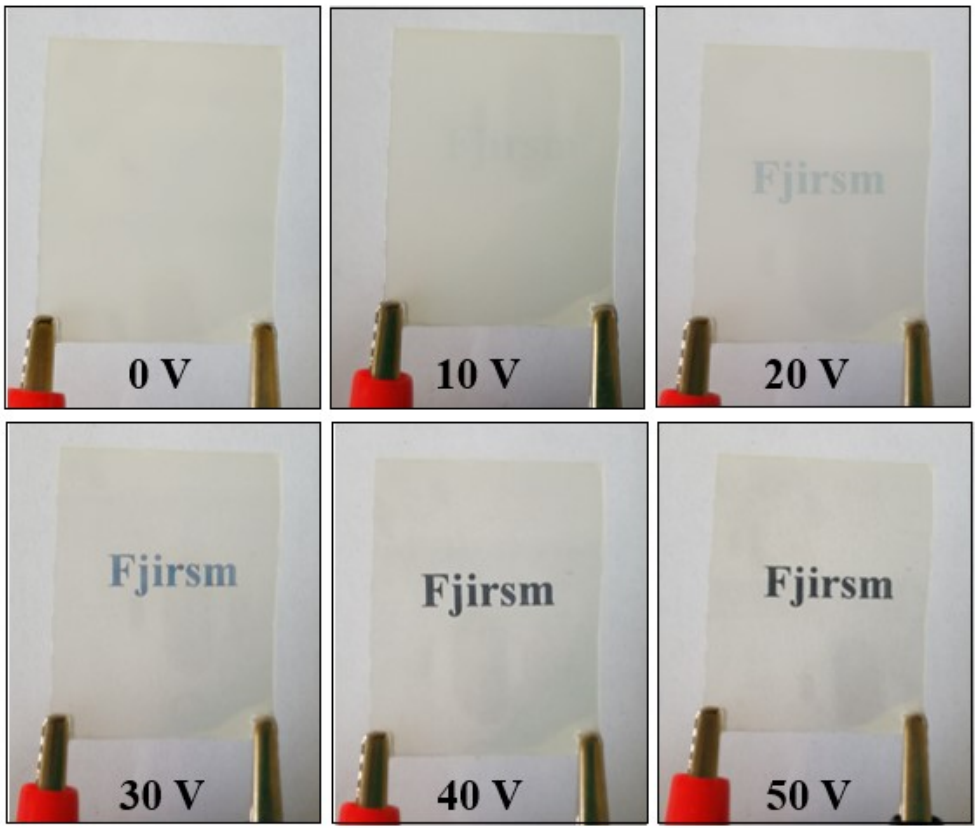

Figure S5. The behavior of electro-optical switching turn-off and turn-on states of is our PDLC module with ITO-PE substrate on PDLC device that connecting with two electrodes system with applying different voltages (0~50 V).

Reference

1 An, Y.; Guo, X.; Zhang, S.; Du, Z., *Adv. Mater. Res.*, 2014, **1015**, 89-92.