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Electronic Supplementary information

Unique photoswitch: Intrinsic photothermal heating induced reversible proton conductivity of HKUST-1 membrane

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1. Experimental details

1.1 Regents and materials

Copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$), Zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), 2-aminoethanol ($NH_2CH_2CH_2OH$) were purchased from Acros Chemicals, 1,3,5-Benzenetricarboxylic acid (H_3BTC, $C_9H_6O_6$), 1-4 terephthalic acid (H_2BDC, $C_8H_6O_4$), N,N-dimethylformamide (DMF, $HCON(CH_3)_2$) were purchased from Sigma-Aldrich. Methanol, Ethanol was purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water of 18.2 MΩ used in all experiments was produced by a Millipore direct-Q system. The membrane to filter was polycarbonate (PC) membranes (Whatman) with a pore diameter of 200 nm and an effective diameter of 20 mm.

1.2 Synthesis of HKUST-1 and MOF-2-DMF membranes

1.2.1 HKSUT-1 membranes

Firstly, copper hydroxide nanostrands (CHNs) were prepared by mixing equal volume 4 mM copper nitrate aqueous solution with 1.4 mM aminoethanol aqueous solution at room temperature and aging for at least 12 h.[1] Then 30 mL CHNs solution was filtered onto PC membrane to form CHNs film, followed by transferring CHNs film from the PC substrate to a clean glass substrate. Noting that there should be enough ethanol on the surface of glass before putting the CHNs film on so that the PC membranes can be successfully removed. Finally, the HKUST-1 membrane was successfully synthesized by immersing the dried CHNs film into 5 mM H_3BTC water-ethanol (water/ethanol volume ratio, 1:1) solution at room temperature for 3 hours. Before testing, the membrane was washed with water-ethanol (water/ethanol volume ratio, 1:1) solution three times.

1.2.2 MOF-2-DMF membranes

MOF-2-DMF membrane was synthesized via similar process like HKSUT-1 membranes.[2] Zinc hydroxide nanostrands (ZHNs) solution was obtained by mixing 4 mM zinc nitrate water-ethanol solution (water/ethanol volume ratio, 3:2) with equal volume 1.6 mM 2-aminoethanol water-ethanol solution (water/ethanol volume ratio, 3:2) at room temperature and aging for 30 min. Then 30 mL ZHNs solution was filtered onto PC membrane and transferred to a clean glass substrate. Finally, the dried ZHNs film was immersed into 10 mM H_2BDC DMF solution at 95 °C for 24 h to synthesize MOF-2-DMF membrane. After reacting, the membrane was washed by DMF and ethanol three times respectively. As-synthesized membrane was immersed into methanol for 24 hours to exchange solvent (DMF) and dried at 100 °C under vacuum for activation.

1.3 Characterization

The morphologies of samples were characterized by scanning electron microscopy (SEM) (Hitachi S-4800/ SU70). The X-ray diffraction (XRD) pattern of the phase of membranes was characterized by an X'Pert PRO (PANalytical, The Netherlands) instrument with Cu K α radiation and 0.02 ° step at room temperature. The UV-vis absorption spectroscopy was measured by UV-visible spectrophotometer (Shimadzu UV-3600). Fourier transform infrared spectroscopy (FT-IR) was recorded on FT-IR TENSOR 27 equipment using a KBr pellet in the range of 400-4000 cm^{-1}. Thermogravimetric analysis (TGA) was carried out by TA Q500 thermogravimetric analyzer.

1.4 Proton conductivity measurement

The proton conductivity of as-synthesized membranes was measured by the alternating current (AC) impedance method which carried out by CHI 660D electrochemical workstation in a frequency range of 1 MHz to 100 Hz at AC amplitude of 10 mV.

At first, pairs of Ag electrodes were evaporated onto the surface of the membranes by ZHN-300S film preparation system (BEIJING TECHNOL CO. LTD). Then the membranes with Ag electrodes plated were placed at BC1300 programmable temperature and humidity controller (Shanghai YIHENG) for more than 2h to stabilize. The light source (PLS-SXE300D/UV, PerfectLight, the visible light range covered) was placed outside the transparent window of the temperature and humidity controller for the AC impedance test under illumination. The intensity of light reaching the surface of samples was 50 mW/cm^2 measured by PLS-MW2000 (PerfectLight). The proton conductivity was calculated according to the following equation:

$$\sigma = \frac{L}{R \times S}$$

Where σ is the proton conductivity, L is the channel length (here is 300 μm), R is the resistance calculated from electrochemical impedance spectra (fitted by R_s (CPE-R_p) model), and S is the cross-section of the flow transportation surface (here is 3 mm (width) × 1.5 μm /4 μm (thickness) for HKUST-1/MOF-2-DMF membranes.

1.5 Water vapor sorption ability of HKSUT-1 and MOF-2-DMF membrane.

Both HKSUT-1 and MOF-2-DMF have good hydrophilicity. TGA curve (Fig. 1i and Fig. S1) indicates that HKSUT-1 membrane absorbs more than 10% of water molecules in the pores, which is consistent with the literature reported.[3] As reported in this literature, water loading of HKSUT-1 at 25°C/90%RH, 40°C/40%RH and 40°C/90%RH are respectively 32mmol·g^{-1} (38%), 13mmol·g^{-1} (19%), 16mmol·g^{-1} (22%). And TGA curve shows that the initial weight loss due to water is ~ 20% higher than that predicted from the water isotherm at 313 K, which is due to the water sorption from air.[3] The literature reported also displays that MOF-2-DMF can absorbs 5.1% water molecules from air[4]. Nice water vapor sorption of both membranes contributes to good intrinsic proton conductivity, which is consistent with the experiment results.

2. Additional figures

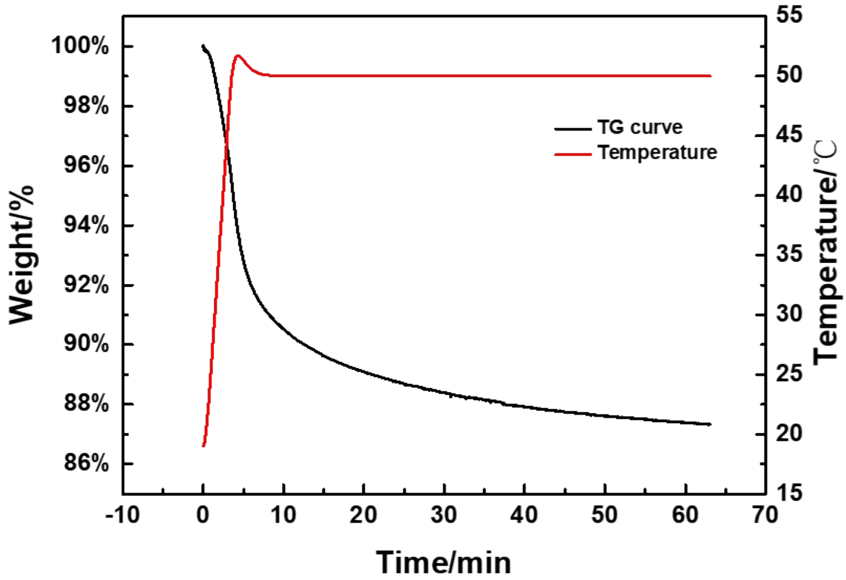

Fig. S1 TG analysis curve of HKUST-1 power (heated to 50 °C and keep for 1 hour).

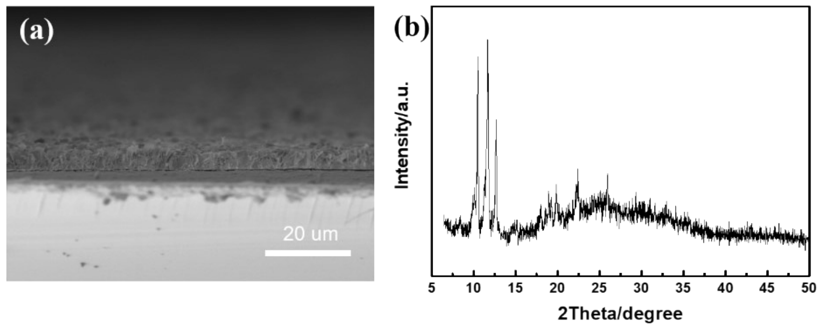

Fig. S2 (a) cross-section SEM image of MOF-2-DMF membrane. (b) XRD pattern of MOF-2-DMF membrane.[5]

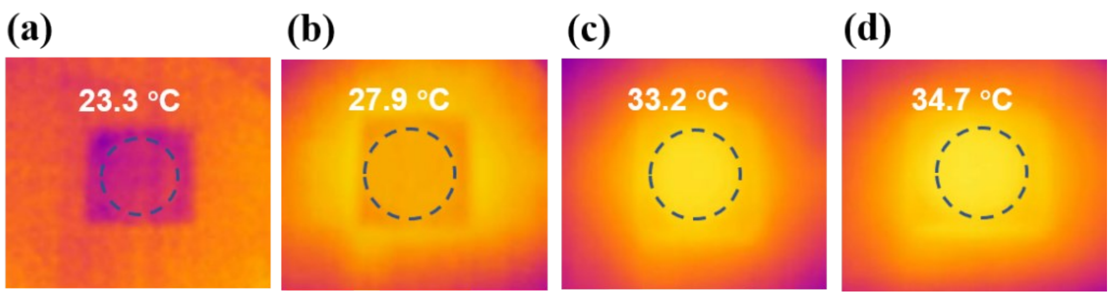

Fig. S3 Infrared camera photos of MOF-2-DMF with different time irradiated by xenon lamp. The time from (a) to (d) is 0min, 1 min, 5 min and 10 min respectively.

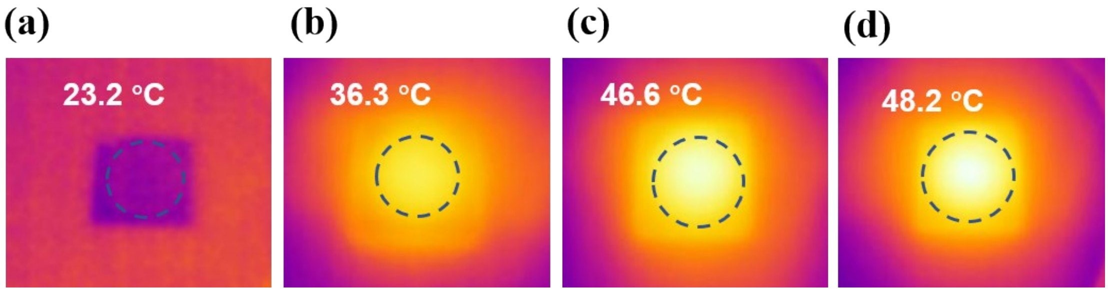

Fig. S4 Infrared camera photos of HKUST-1 with different time irradiated by xenon lamp. The time from (a) to (d) is 0 min, 1 min, 5 min and 10 min respectively.

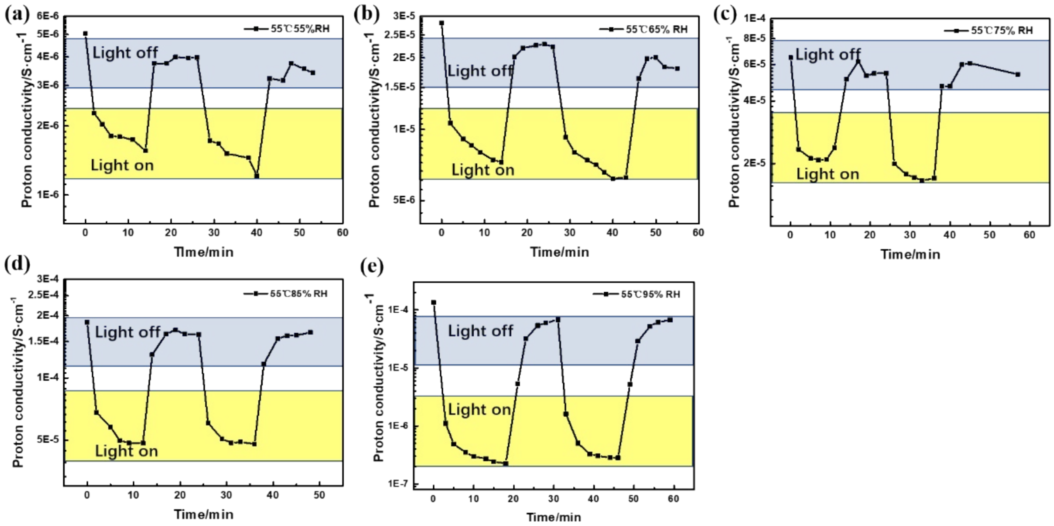

Fig. S5 Proton conductivity changes of HKUST-1 with and without light under different conditions: (a) 55°C55%RH; (b) 55°C65% RH; (c) 55°C75%RH; (d) 55°C85%RH; (e) 55°C95%RH.

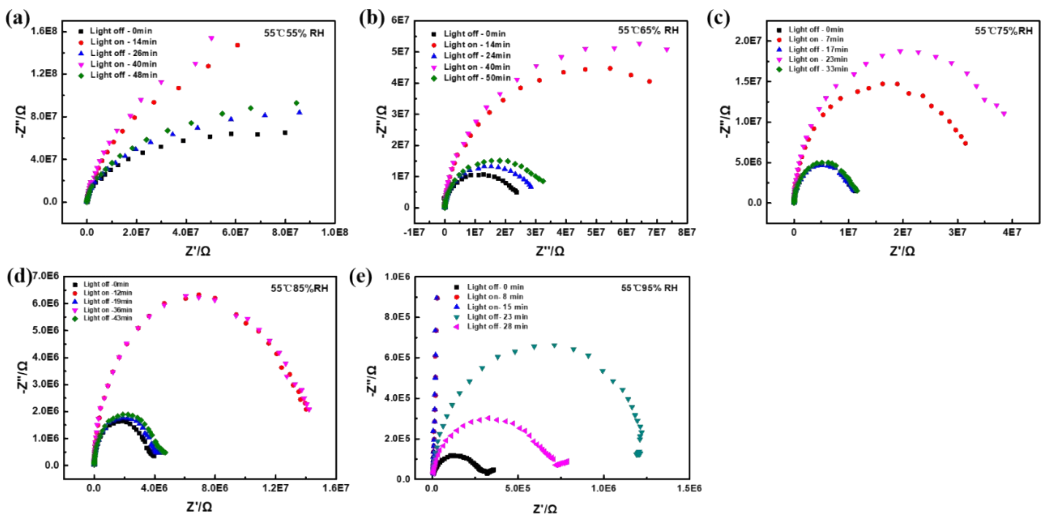

Fig. S6 Nyquist plots of HKUST-1 membrane at different conditions corresponding to Fig. S5.

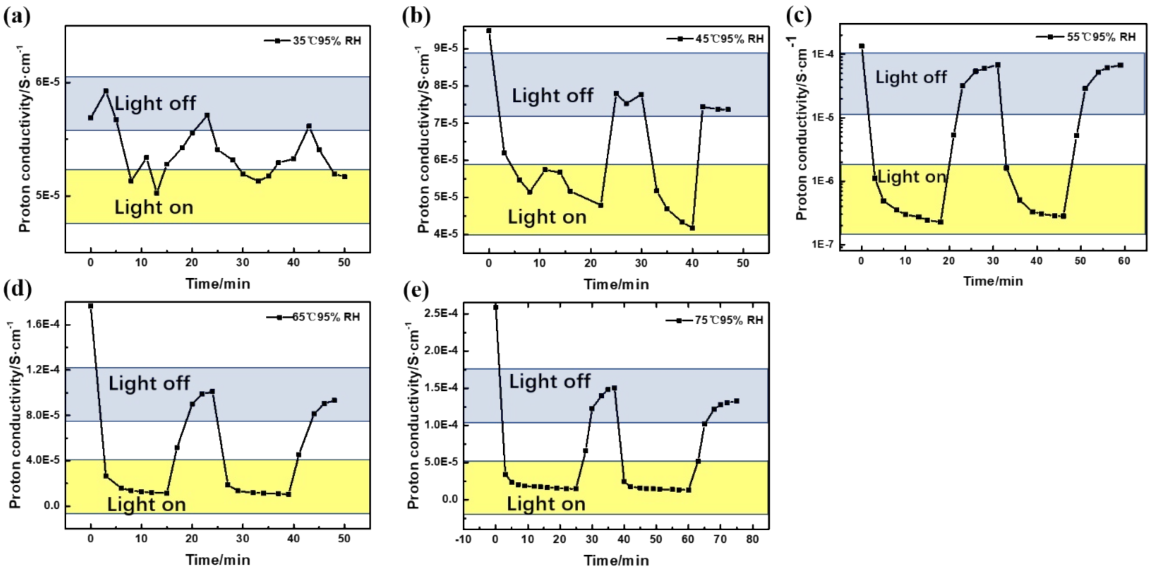

Fig. S7 Proton conductivity changes of HKUST-1 with and without light under different conditions: (a) 35°C95%RH; (b) 45°C95% RH; (c)55°C95%RH; (d) 65°C95%RH; (e) 75°C95%RH.

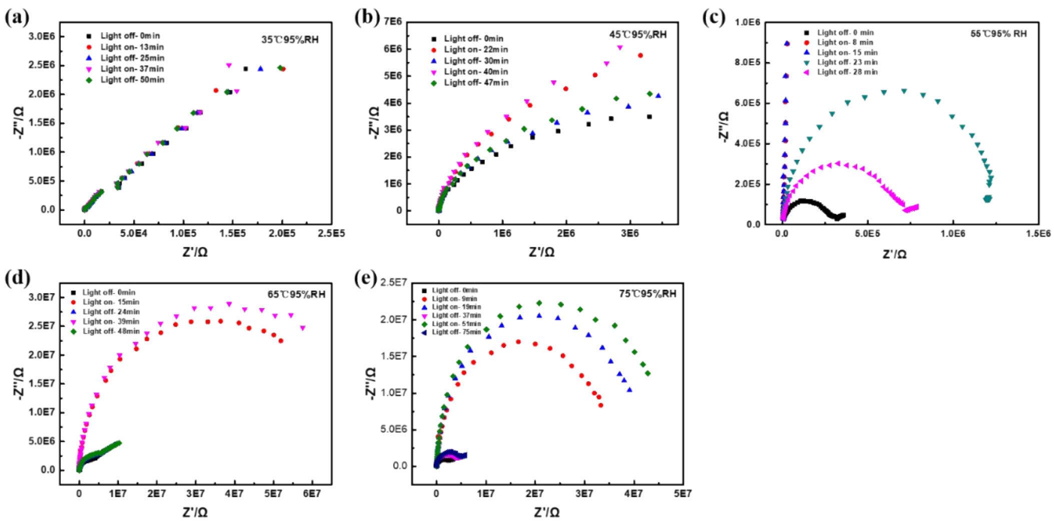

Fig. S8 Nyquist plots of HKUST-1 membrane at different conditions corresponding to Fig. S7

References:

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