

Supporting Information

Visible-light-induced controlled radical polymerization of methacrylates mediated by zirconium-porphryinic metal-organic framework

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Characterization

Gel permeation chromatography (GPC) was performed on a Waters 1525, The column was Agilent PLgel 5 μm MIXED-C (made in GB) and separation module with a Waters 2414 refractive index detector. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at $35 \text{ }^\circ\text{C}$. Powder X-ray diffraction (PXRD) data was recorded on a Rigaku D-MAX 2550 diffractometer using Cu K_α radiation, $\lambda = 0.15417 \text{ nm}$) with 2θ ranging from 3° to 40° and a scanning rate of 5° min^{-1} at room temperature. N_2 sorption measurements were measured at the liquid nitrogen temperature, using a Micromeritics ASAP 2020 system. The samples were immersed in methanol for guest-exchange and further degassed at $100 \text{ }^\circ\text{C}$ for 10 h before the measurements. ICP spectroscopy was conducted on a Spectro Ciros Vision ICP-OES spectrometer that is equipped with vacuum optics covering the spectral range from 175 to 777 nm, plasma power, 1300 w; coolant flow, 15.00 L/min; auxiliary flow, 0.80 L/min; nebulizer 0.70 L/min. UV-vis absorption spectra of liquid sample were recorded on a SHIMADZU UV-2550 spectrophotometer. UV-vis spectra of solid-state samples were recorded on a HITACHI U-4100 spectrophotometer. The morphologies of samples were characterized by a field emission scanning electron microscopy (XL30ESEM-FEG, USA). The photoluminescence (PL) spectra were measured on FLSP920 fluorescence spectrometers. Photocurrent measurements were performed in a standard three-electrode system with the MOF-coated indium tin oxide as the working electrode, Pt and Ag/AgCl electrodes as the counter electrode and reference electrode, respectively. Aqueous solution of Na_2SO_4 (0.2 M) was used as electrolyte.

ICP spectrometric evaluation of Zn content

10 mg dried MOF-545(Zn) $\{\text{Zr}_6(\mu_3\text{-OH})_8(\text{OH})_8(\text{Zn-TCPP})_2\}$ was treated with aqua regia (4 mL) and aqueous hydrogen peroxide (30 wt%, 1 mL). The whole mixture was allowed to stay at room temperature for 2 h and heated at $150 \text{ }^\circ\text{C}$ to reduce the total volume to about 0.5 mL (If possible, the digestion procedure might be repeated twice). The resulted solution was diluted volumetrically with an aqueous solution of nitric acid (2%) to 25 mL, which was then evaluated by inductively coupled plasma optical emission spectrometer (ICP-OES) for Zn contents. The Zn content was measured in ppm (mg L^{-1}) based on calibration curves obtained with a series of calibration standard solutions doped with different amount of Zn.

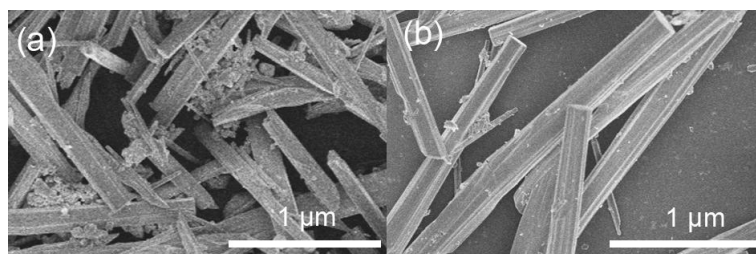


Fig. S1 The SEM of as-prepared (a) MOF-545(H₂), (b) MOF-545(Zn).

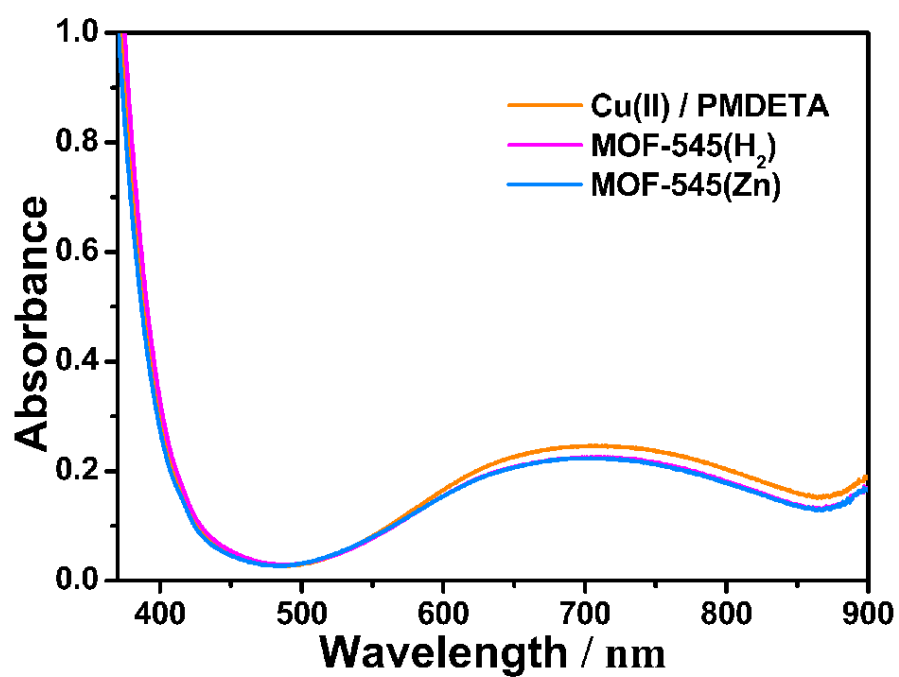


Fig. S2 The UV-vis spectrum of the adsorption test.

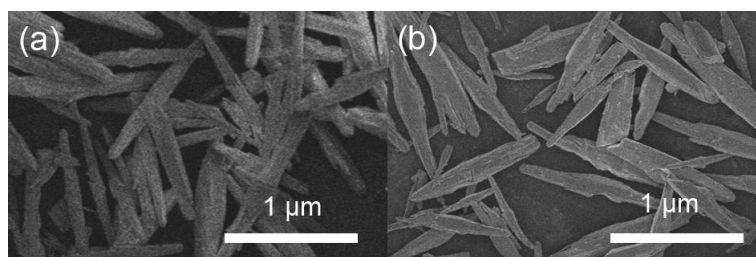


Fig.S3 The SEM of (a) MOF-545(H₂), (b) MOF-545(Zn) after photopolymerization.

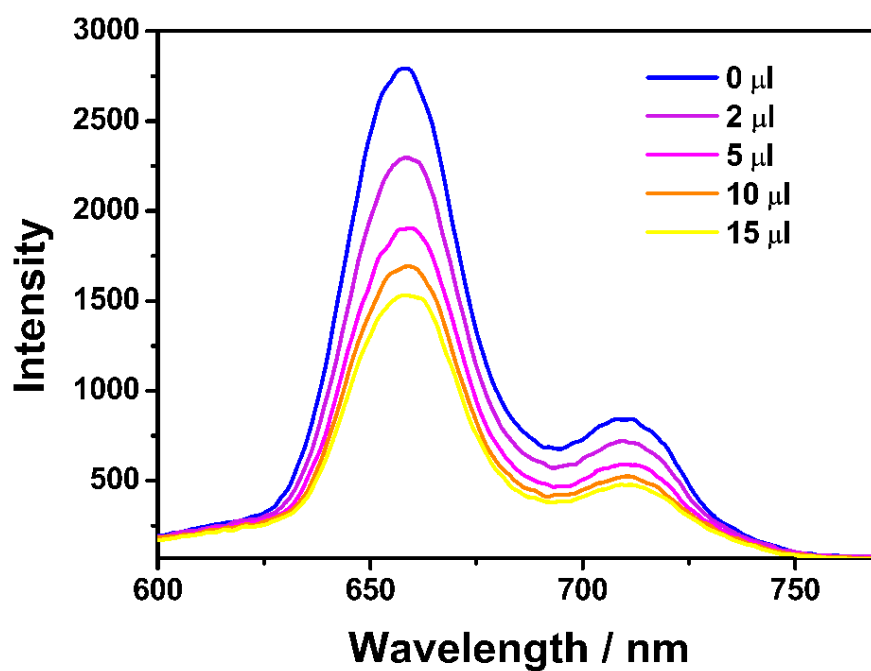


Fig. S4 The fluorescence of MOF-545(H₂) dispersed in acetonitrile (excited at 500 nm) quenched by Cu(II)/PMDETA complex. (The concentration of copper complex is 0.004 mmol/mL.)

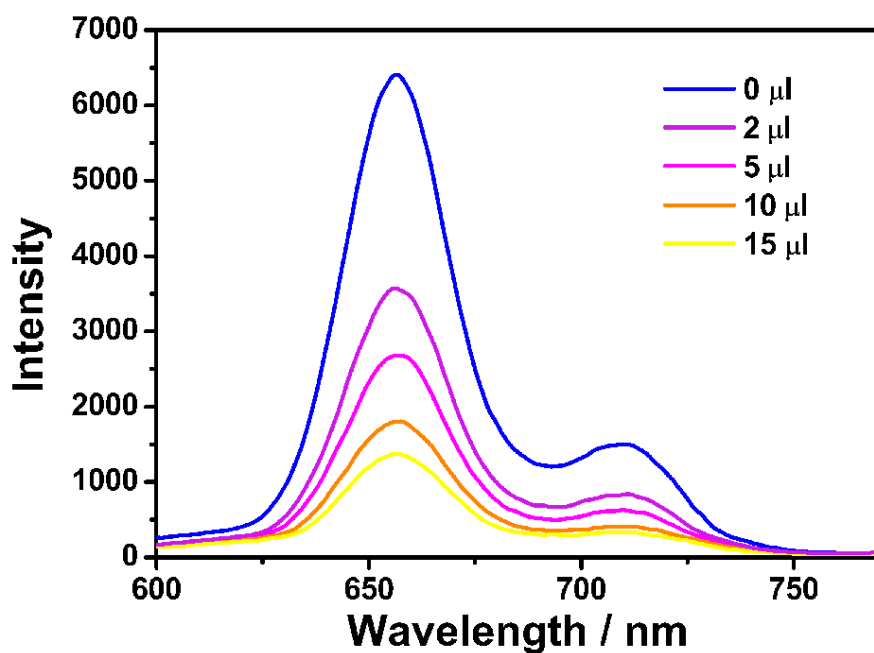


Fig. S5 The fluorescence of MOF-545(Zn) dispersed in acetonitrile (excited at 500 nm) quenched by Cu(II)/PMDETA complex. (The concentration of copper complex is 0.004 mmol/mL.)

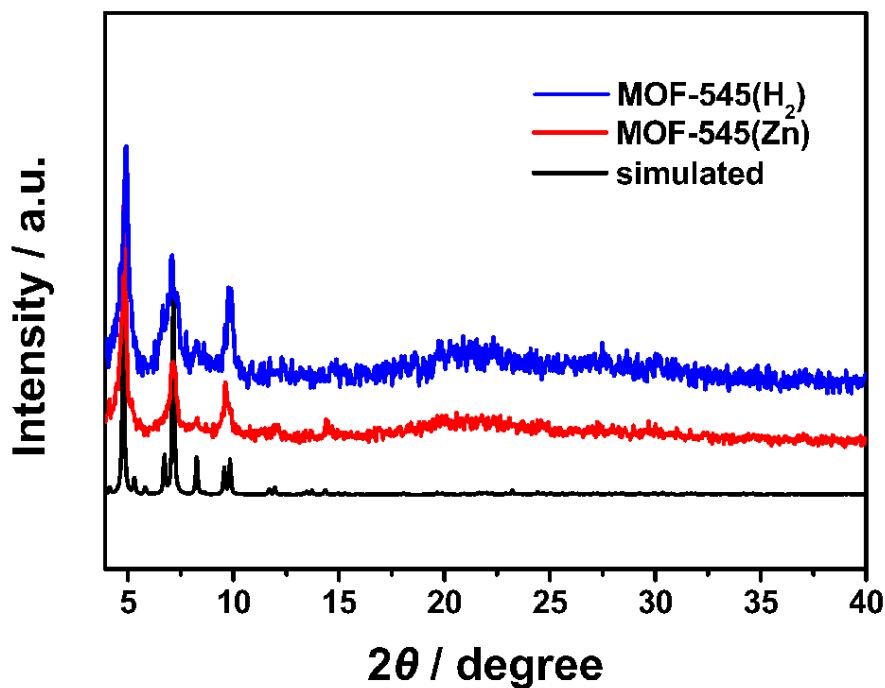


Fig. S6 PXRD patterns of MOF-545(H₂) and MOF-545(Zn) after 12 hours reaction and simulated MOF-545(H₂/Zn).

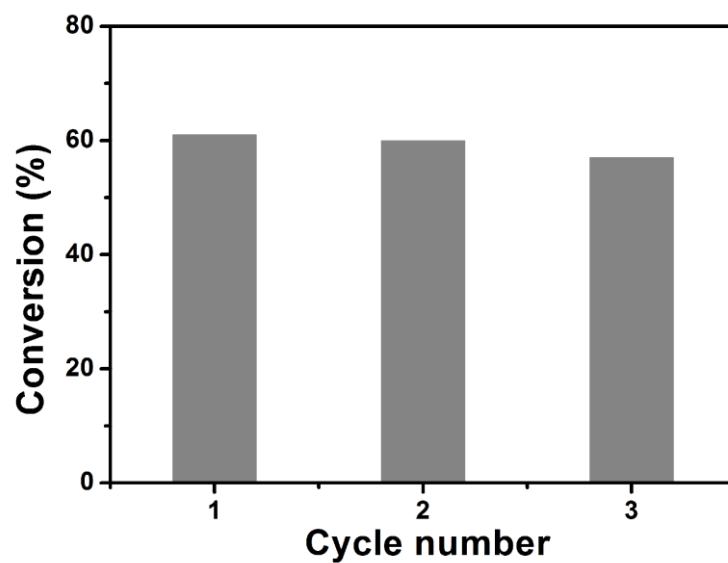


Fig. S7 The cyclic tests of MOF-545(H₂) to initiate the photoinduced polymerization, irradiation time = 9 h.

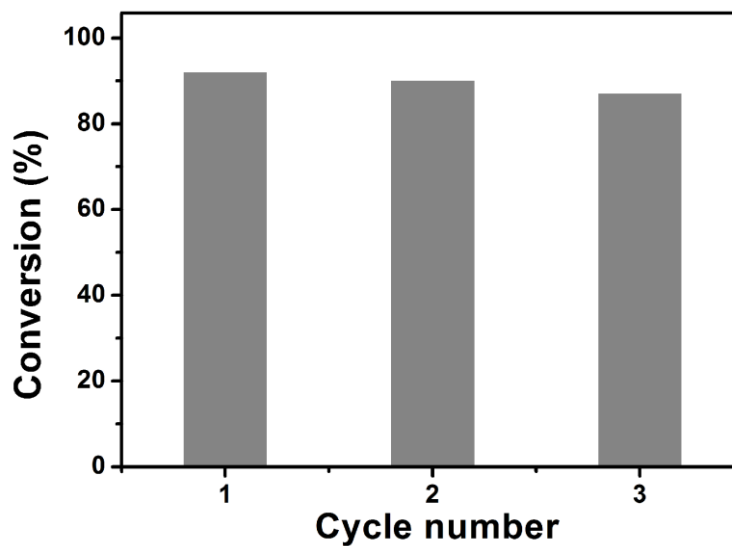


Fig. S8 The cyclic tests of MOF-545(Zn) to initiate the photoinduced polymerization, irradiation time = 9 h.