

Electronic Supplementary Information

Nonlinear optical limiting properties of polyphthalocyanine porous organic frameworks

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1. Material and Methods

Unless otherwise noted, all chemical reagents from commercial suppliers were received and used without further purification. Chemicals for synthesis were obtained from Shanghai Aladdin Bio-Chem Technology Co., LTD and National Medicines Corporation Ltd. of China. It includes, phthalocyanine, lead(II) phthalocyanine, tin(IV) phthalocyanine dichloride, aluminium chloride (AlCl_3) dichloromethane (DCM), hydrochloric acid(HCl), ethanol and anhydrous methanol. All of which were of analytical grade.

Fourier transform infrared spectroscopy (FT-IR) was collected on a Nicolet iS50 spectrometer. Powder X-ray diffraction patterns were performed from 5 to 40° using a Bruker D8 ADVANCE diffractometer. Scanning Electron Microscope (SEM) images were acquired by a MAIA3 LMH Field Emission Scanning Electron Microscope. Thermogravimetric Analysis (TGA) was provided on a NETZSCH STA 449F5 thermogravimetric analyzer. Samples were heated from 30 °C to 800 °C at a rate of 10 °C/min under air. The UV-vis absorption spectra were performed with a PerkinElmer Lambda 950 spectrophotometer. Gas adsorption isotherms were measured using a Micromeritics ASAP 2020-accelerated surface area analyzer after the samples had been degassed at 120 °C for 12 h under vacuum. The obtained adsorption-desorption isotherms were evaluated to give the pore parameters, including Brunauer-Emmett-Teller (BET) and Langmuir specific surface area, pore size, and pore volume. The pore size distribution was calculated from the adsorption branch with the nonlocal density function theory (NLDFT) approach. The laser was operated at 532 nm with a pulse repetition rate of 1 kHz excitation wavelength from frequency doubled Nd: YAG laser (repetition rate: 10 Hz, pulse width 10 ns). The laser source was focused with an $f=10$ cm lens. An open-aperture (OA) and closed-

aperture (CA) Z-scan system is used to measure the OL behavior of the dispersions. All the DMF dispersions were filled in a 2 mm thick quartz cells, by changing the Pc-POFs concentrations, the linear transmittances of all the samples were adjusted to 60%. On the grounds of NLO theory, the propagation depth as a function of the intensity can be expressed as:

$$\frac{dI}{dz'} = -\alpha(I)I \quad (1)$$

where I is the incident intensity and z' denotes the propagation distance. The Z-scan curves can be fitted using the following equation for quantitative analysis:

$$\alpha(I) = \frac{\alpha_0}{1 + I/I_s} + \beta_{\text{eff}}I \quad (2)$$

where $\alpha(I)$ is the total absorption coefficient, I_s represents the saturation intensity, and α_0 and β_{eff} are the linear absorption coefficient and effective nonlinear absorption coefficient, respectively.

2. Experimental Section

2.1. Synthesis of Pc-POF.

In a typical synthesis, phthalocyanine (0.29 g, 0.56 mmol) was first dispersed into 30 ml dichloromethane (DCM) by stirring adequately under a N_2 atmospheric environment. To the solution was added $AlCl_3$ (1.20 g, 9 mmol) as the catalyst. After that, the mixture was continuous stirring and kept at 0 °C for 6 hours, at 40 °C for 12 hours, at 60 °C for 12 hours and at 80 °C for 24 hours. The polymer was slowly cooled to room temperature and quenched using HCl- H_2O [1:1 (v/v)]. The precipitated solid was filtered and washed fully with water and ethanol., then adequately washed with anhydrous ethanol by Soxhlet

extractions for 48 hours. POF was finally dried in a vacuum oven for 48 hours at 70°C.

2.2. Synthesis of Sn-Pc-POF.

Similarly for the experimental section of Pc-POF, Sn-Pc-POF was synthesized by treating tin(IV) phthalocyanine dichloride (0.40 g, 0.56 mmol) with AlCl₃ (1.20 g, 9 mmol) as the catalyst into 30 ml dichloromethane (DCM).

2.3. Synthesis of Pb-Pc-POF.

Similarly for the experimental section of Pc-POF, Pb-Pc-POF was synthesized by treating lead(II) phthalocyanine (0.41 g, 0.56 mmol) with AlCl₃ (1.20 g, 9 mmol) as the catalyst into 30ml dichloromethane (DCM).

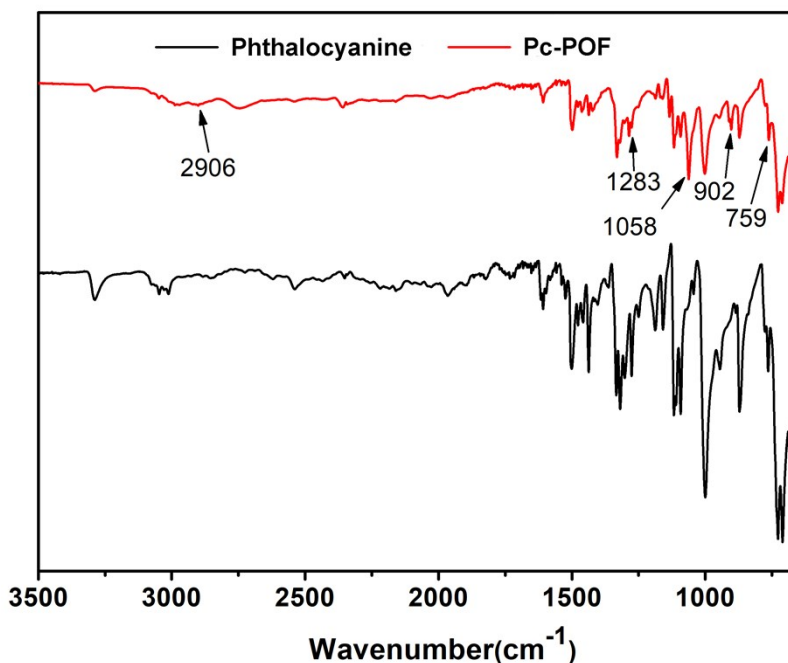


Fig. S1. FT-IR spectra of monomer and Pc-POF

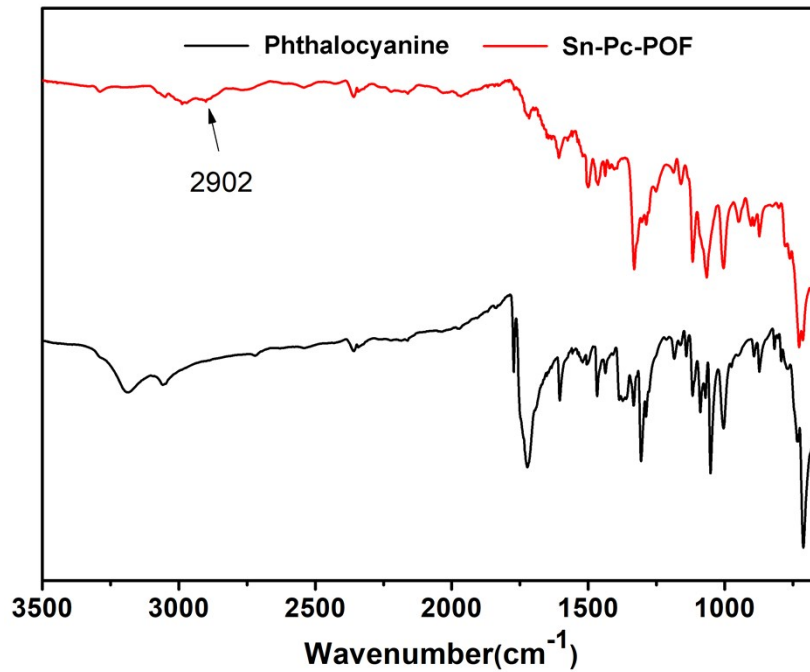


Fig. S2. FT-IR spectra of monomer and Sn-Pc-POF

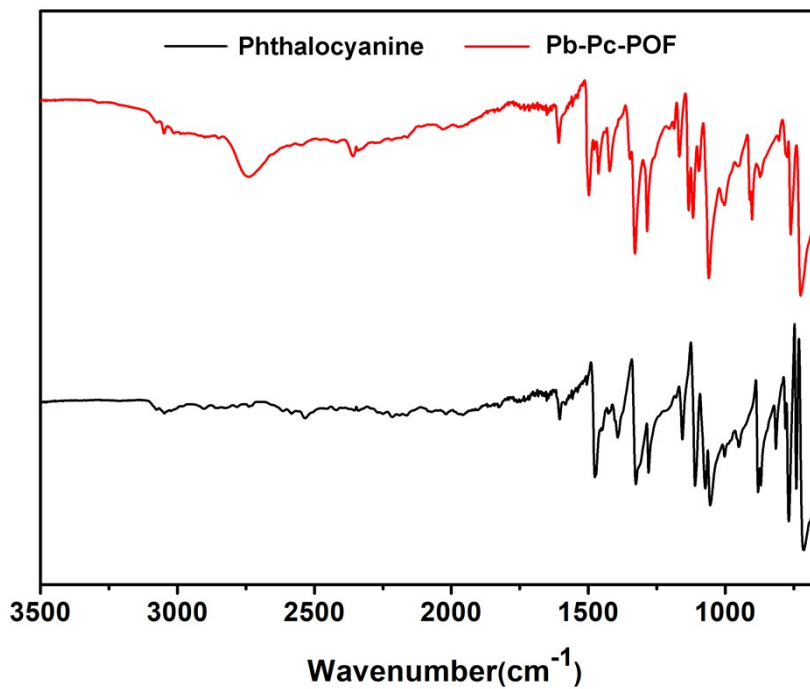


Fig. S3. FT-IR spectra of monomer and Pb-Pc-POF

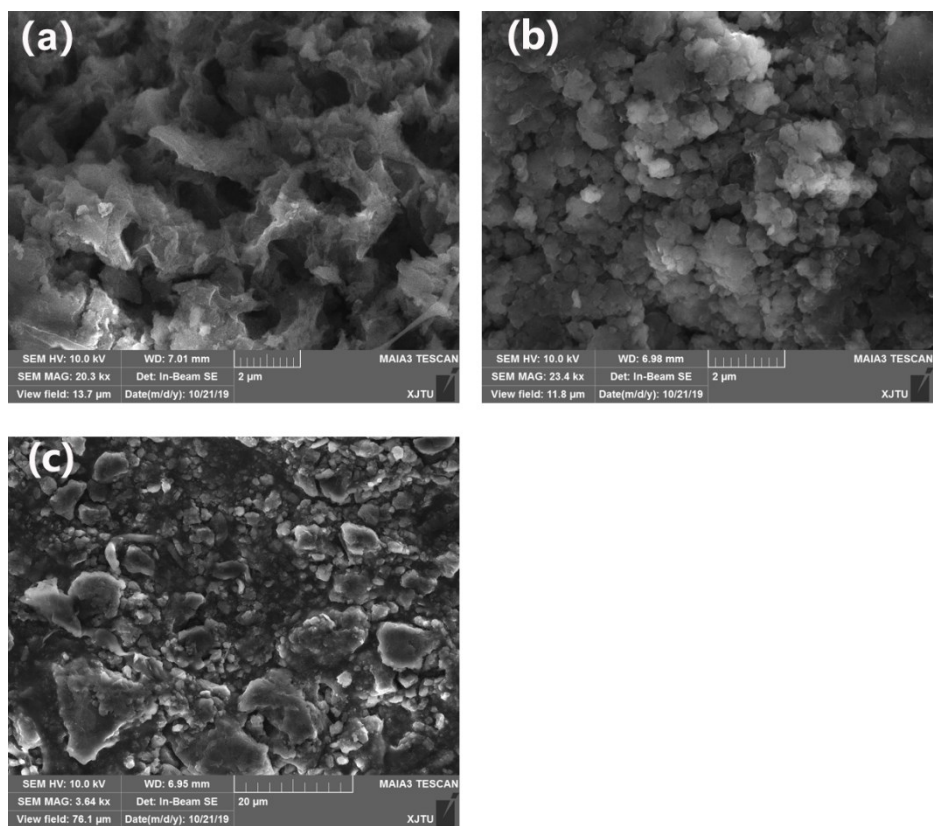


Fig. S4. The SEM images of Pc-POFs (a) Pc-POF, (b)Sn-Pc-POF and (c) Pb-Pc-POF.

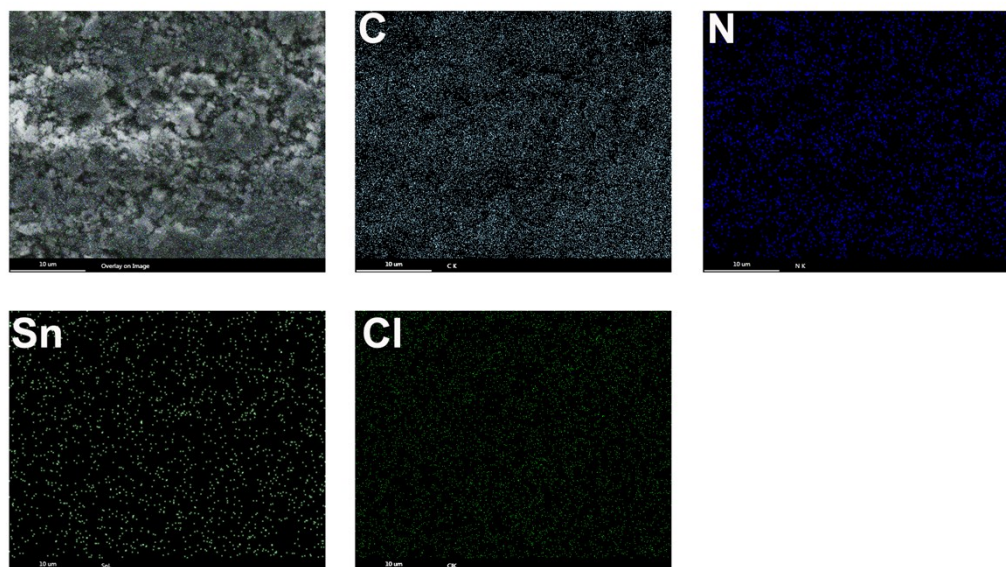


Fig. S5. The EDS elemental mapping of Sn-Pc-POF

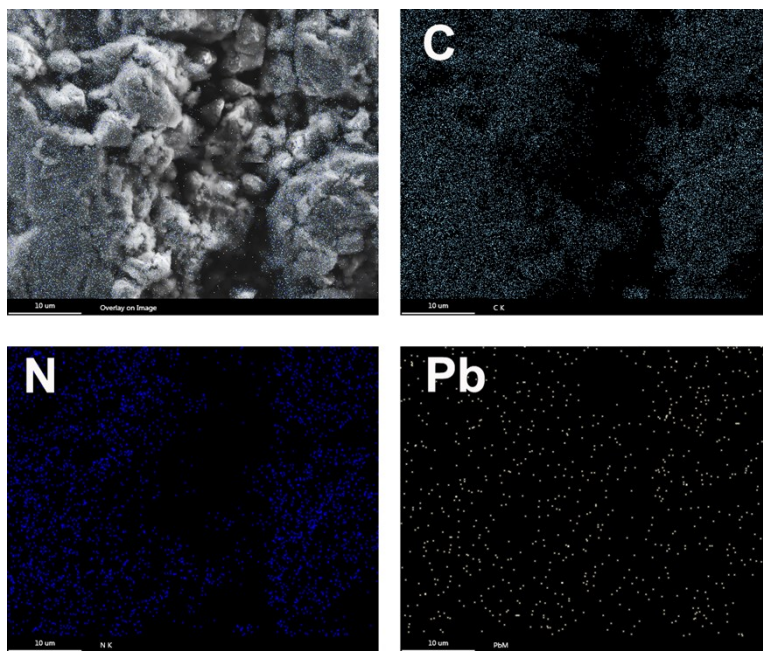


Fig. S6. The EDS elemental mapping of Pd-Pc-POF

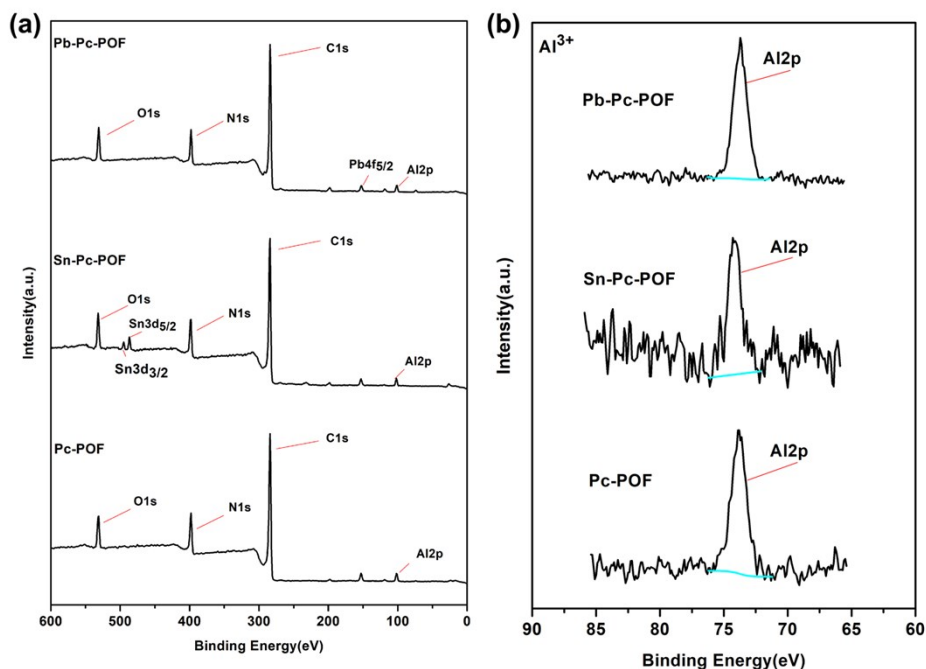


Figure S7. (a) XPS survey spectra of Pb-Pc-POF, Sn-Pc-POF and Pc-POF; (b) The high-resolution XPS spectra of Al 2p for Pb-Pc-POF, Sn-Pc-POF and Pc-POF. **The low signals from Al in enlarged views of XPS spectra indicate that trace residues of catalysts existing in the final Pc-POFs sample.**

Table S1. The C, N, Sn and Pb content calculated by XPS analysis.

	C (wt%)	N (wt%)	Sn (wt%)	Pb (wt%)	Others (wt%)
Pc-POF	82.2	15.7			2.1
Sn-Pc-POF	74.8	10.9	10.6		3.7
Pb-Pc-POF	77.8	14.8		2.4	5

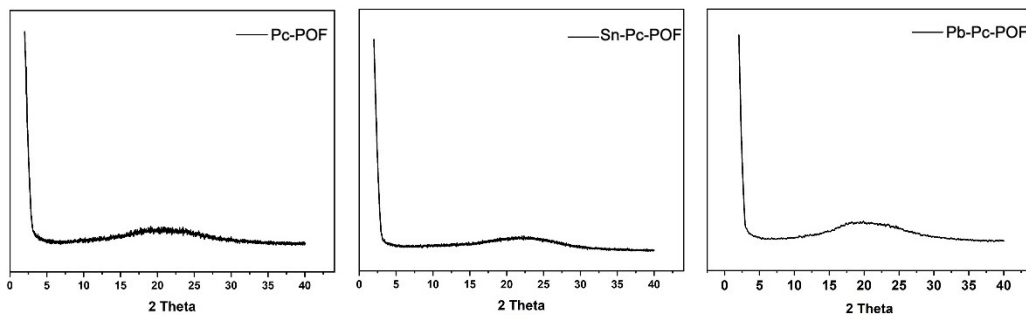


Fig. S8. Powder X-ray diffraction patterns of Pc-POFs

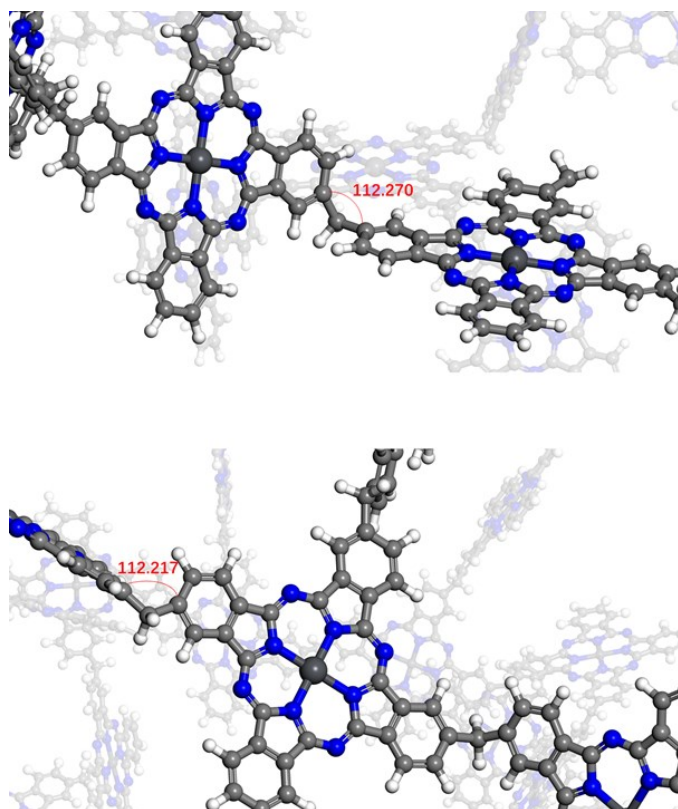


Fig. S9. The simulated network fragments for Pb-Pc-POF, measured the angle between phthalocyanine planes range imposed by alkyl carbon bridge.

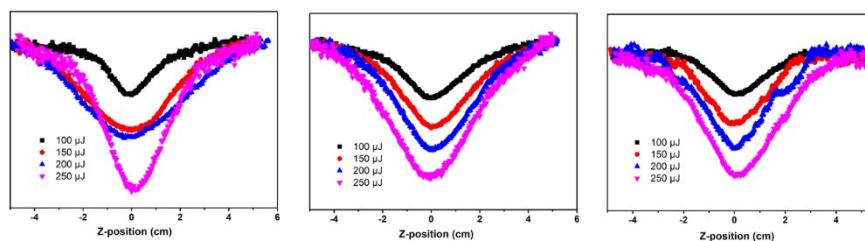


Fig. S10. The open-aperture Z-scan data with normalized transmittance as a function of the sample position Z for phthalocyanine, Sn-phthalocyanine and Pb-phthalocyanine monomers.