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# Nonlinear optical properties of polyphthalocyanine porous organic frameworks<sup>†</sup>

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Phthalocyanines with an 18  $\pi$ -electron conjugated structure have intrinsic nonlinear optical response, but their agglomeration in solution and films is a bottleneck toward their optical limiting device processing. Herein, we develop three sp<sup>3</sup>-hybridized carbon bridge polyphthalocyanine porous organic frameworks (Pc-POFs) with an enhanced nonlinear absorption effect and optical limiting properties. The strong covalent bond linked porous structures in Pc-POFs could improve their optical limiting properties by inhibiting the relaxation of the molecule and increasing their excited state absorption. Moreover, the Sn-Pc-POF which introduces a Sn metal ion in the phthalocyanine center, exhibited an optical limiting threshold of 0.37 J cm<sup>-2</sup> at 532 nm nanosecond laser, which is highly competitive in comparison with the state-of-the-art 2D optical limiting materials such as graphene and layered transition metal dichalcogenides.

The development of high performance nonlinear optical (NLO) and optical limiting materials is very important for optical communication, optical signal processing and ultrafast laser protection.<sup>1-4</sup> The general nonlinear optical limiting materials include organic small molecules, carbon materials, organic metal complexes, liquid crystal materials and inorganic metal

clusters.<sup>5</sup> The structural prerequisite in organic compounds with NLO property is the presence of delocalized  $\pi$ -conjugated electrons, which can suffer fast charge redistribution when they are interacting with rapidly varying electromagnetic fields like laser pulses.<sup>6</sup> The phthalocyanine with an 18  $\pi$ -electron conjugated structure, has intrinsic nonlinear optical response, and good thermal stability. Moreover, the central cavity in a phthalocyanine ring can act as a host to combine with different metal ions, which effectively adjust their nonlinear optical and optical limiting performance. However, the strong  $\pi$ - $\pi$  interaction between phthalocyanine molecules often leads to the formation of phthalocyanine agglomerations, which appears to be the barrier toward its optical limiting device processing.

Porous organic frameworks (POFs) constructed from organic building units via strong covalent bonds have attracted much attention in the field of materials science because of their high porosity, tunable skeleton function and high stability.<sup>7-10</sup> By virtue of their designable structure, most of the POF material research is focused on their adsorption, catalysis and energy storage properties.<sup>11-15</sup> Recently, Loh et al. developed 2D triphenylamine POFs and Biswal et al. reported porphyrin POFs named Por-COF-HH and its metalated congeners (Por-COF-ZnCu and Por-COF-ZnNi) with outstanding NLO activity.16-18 Their pioneering studies inspired us to investigate the phthalocyanine porous materials for advanced NLO applications. Phthalocyanine porous materials have an intrinsic high-density  $\pi$ -conjugated structure in their framework and the strong covalent bond linked porous structure maybe could improve their optical limiting properties by inhibiting the relaxation of molecules and increasing the excited state lifetime. In addition, by choosing suitable polymerization, we can not only reduce their aggregation effect, but also change the spatial electron distribution of phthalocyanine molecules.

Herein, we designed three phthalocyanine POFs with a methylene carbon bridge structure (Fig. 1). Using sp<sup>3</sup>-hybridized carbon as a linker can effectively avoid the aggregation of phthalocyanine molecules. Furthermore, we chose Sn and Pb ions as the

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Fig. 1 Synthesis reaction scheme of the polyphthalocyanine porous organic frameworks (Pc-POF, Sn-Pc-POF and Pb-Pc-POF).

coordination metals in the phthalocyanine center. Sn and Pb have large atomic nucleus and multilayer outer electron arrangement, which can produce strong polarization toward high-energy lasers to increase their optical limiting performance. The phthalocyanine and metallophthalocyanine POFs named Pc-POF, Sn-Pc-POF and Pb-Pc-POF exhibit high nonlinear absorption coefficients and optical limiting threshold, which are highly competitive in comparison with the state-of-the-art NLO materials.

The synthesis of Pc-POF, Sn-Pc-POF and Pb-Pc-POF was achieved by using Friedel-Crafts reactions and dichloromethane was used as both solvent and linker in the presence of AlCl<sub>3</sub> catalyst.19 Pc-POFs feature two key structure components: phthalocyanine rings and sp<sup>3</sup>-hybridized bridge alkyl carbon (Fig. 1). The Fourier transform infrared (FTIR) spectroscopy confirms the co-existence of phthalocyanine and alkyl groups in Pc-POFs (Fig. S1-S3, ESI<sup>†</sup>). Take Pc-POF for example (Fig. S1, ESI<sup>†</sup>); the 2906 cm<sup>-1</sup> C–H vibration absorption peaks in –CH<sub>2</sub> group and the vibration peaks at 759 cm<sup>-1</sup>, 902 cm<sup>-1</sup>, 1054 cm<sup>-1</sup> and 1283 cm<sup>-1</sup> assigned to the phthalocyanine ring can be identified. The morphology of Pc-POFs was observed in scanning electron microscopy (SEM), wherein block particles of Pc-POFs can be clearly visualized (Fig. S4, ESI<sup>†</sup>). Moreover, energy dispersive X-ray analysis (EDX) confirms the presence of Sn and Pb metals within Sn-Pc-POF and Pb-Pc-POF (Fig. S5 and S6, ESI<sup>+</sup>).

The electronic states of C, N, Sn and Pb in Pc-POFs were probed by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 2 and Fig. S7 (ESI†), the XPS survey spectra confirmed the presence of carbon, nitrogen and the corresponding metals in Pc-POFs. The high-resolution spectra of C 1s could be deconvoluted into C—C/C–C, C–N and C—N (at 283.5, 284.8 and 287.4 eV) in Fig. 2a. In the case of N 1s XPS, N–C and metal–N peaks at 397.5 and 398.7 eV are observed, confirming the presence of phthalocyanine macrocycles and central metal ions in the Pc-POFs (Fig. 2b). Moreover, the high-resolution XPS spectra of Sn  $3d_{3/2}$  for Sn-Pc-POF and Pb  $4f_{5/2}$  for Pb-Pc-POF also proved that the Sn and Pb are in their coordination state in the phthalocyanine centers. We verified the individual metal content in the Sn-Pc-POF and Pb-Pc-POF also by using XPS analysis. The XPS results showed that there is 10.6 wt% Sn in Sn-Pc-POF and



**Fig. 2** The high-resolution XPS spectra of C 1s for (a) Pc-POF, Sn-Pc-POF and Pb-Pc-POF; (b) the high-resolution XPS spectra of N 1s for Pc-POF, Sn-Pc-POF and Pb-Pc-POF; and the high-resolution XPS spectra of Sn  $3d_{3/2}$  for Sn-Pc-POF (c) and Pb  $4f_{5/2}$  for Pb-Pc-POF (d).

2.4 wt% Pb in Pb-Pc-POF (Table S1, ESI<sup>†</sup>). Moreover, high-resolution XPS spectra of Al 2p for Pb-Pc-POF, Sn-Pc-POF and Pc-POF indicate that trace residues of AlCl<sub>3</sub> catalysts are present in the Pc-POF samples (Fig. S7b, ESI<sup>†</sup>). Powder X-ray diffraction (Fig. S8, ESI<sup>†</sup>) of Pc-POFs showed a broad diffraction peak at  $23^{\circ}$  to  $27^{\circ}$ , confirming that they are amorphous in nature.

For better clarity that the  $sp^3$  carbon bridge could reduce aggregation of phthalocyanines, structural models for the Pc-POFs fragments were generated using the Materials Studio package. A seed molecule was constructed for each system by fully substituting the phthalocyanine node monomer. Any terminal halogen atoms on the periphery of the fragments were replaced with hydrogen atoms for clarity. The most energetically favorable models that we found were disordered three-dimensional nets. The three-dimensional structure of the Pc-POF networks arises from bending of the plane from the  $sp^3$  carbon between two phthalocyanine planes. The angle between phthalocyanine planes is around 112° imposed by an alkyl carbon bridge (Fig. S9, ESI†).

The permanent porosities of Pc-POFs were evaluated *via* nitrogen sorption experiments at 77 K. All three Pc-POFs show similar isotherm shapes with obvious hysteresis in desorption, characteristic of mesoporous materials (Fig. 4a–c). The Langmuir surface areas of the Pc-POFs derived from  $N_2$  adsorption



Fig. 3 The simulated porous network structure for Pb-Pc-POF.



Fig. 4 Nitrogen adsorption and desorption isotherms at 77.3 K for Pc-POF (a), Sn-Pc-POF (b) and Pb-Pc-POF (c); pore volumes and pore size distribution calculated using density functional theory (DFT) methods for Pc-POF (d), Sn-Pc-POF (e) and Pb-Pc-POF (f).

isotherms exhibit 17 m<sup>2</sup> g<sup>-1</sup>, 36 m<sup>2</sup> g<sup>-1</sup> and 81 m<sup>2</sup> g<sup>-1</sup> for Pc-POF, Sn-Pc-POF and Pb-Pc-POF respectively. The pore size distribution of Pc-POF, Sn-Pc-POF and Pb-Pc-POF (Fig. 4d–f) also proved that the Pc-POFs have abundant mesopores.

To understand the photophysical properties of Pc-POFs after carbon bridge polymerization, we performed UV-Vis absorption of phthalocyanine, metallophthalocyanine and its homologous POFs in their solid powders. As shown in Fig. 5, both the Q-band occurring at about 697 nm and the B-band occurring at about 300 nm originating from the typical phthalocyanine absorption are observed in metal-phthalocyanine monomers. The broad shoulder in the B-band of phthalocyanine may be caused by effects of aggregation of phthalocyanine in the solid powder. The Q-band absorption peaks of phthalocyanine and Sn phthalocyanine are also broadened and those of Pb phthalocyanine are red shifted due to the aggregation of phthalocyanines. When the phthalocyanine monomers are in the solid powder, the plane molecules may be in an association or aggregation state, causing the absorption peaks to be more broadened compared



Fig. 5 UV-Vis spectra of phthalocyanine, metallophthalocyanine and its homologous POFs.

with the reported absorption bands in the solutions.<sup>20</sup> After sp<sup>3</sup>-hybridized carbon bridge polymerization, both the Q-band and B-band of the Pc-POFs are narrowed with respect to those of the monomer, which indicates that the sp<sup>3</sup> carbon covalent bond linked porous structure could prevent the aggregation of phthalocyanines. Combined with the simulated structure results in Fig. 3, we speculate that the methylene carbon bridges would allow a three-dimensional structure to form between the phthalocyanines and reduce their aggregation.

In order to investigate the NLO properties of Pc-POFs, the open aperture Z-scan technique was employed by using 532 nm excitation wavelength from a frequency doubled Nd:YAG laser (repetition rate: 10 Hz, pulse width 10 ns) with different input pulse energies. It is well known that the NLO mechanism of phthalocyanines involves reverse saturation absorption caused by two or multi photon absorption of excited states. In Pc-POFs materials, the B band absorption occurring at about 260-320 nm and the two-photon absorption of excited states are around 520-640 nm. So we chose 532 nm as the excitation wavelength. The laser pulses were focused with a lens of 200 mm focal length, and by changing the distance between the sample and beam focus, the nonlinear transmittances of the samples were recorded. The linear transmittances of the samples were adjusted to 60% in DMF solution. Fig. 6a-c show the excitation pulse energy dependent open-aperture Z-scan results of three Pc-POFs and the Z-scan results of the corresponding phthalocyanine monomers are shown in Fig. S10 (ESI<sup>†</sup>). The transmittance curves showed symmetrical peaks with respect to the focus, indicating that the Pc-POFs have typical optical limiting properties, as the samples exhibited a decreased transmittance when they were brought closer to focus. Along with the input pulse energy increasing, the value of the valley transmittance at focus decreases gradually in the three Pc-POFs. The effective nonlinear saturation absorption coefficients of the Pc-POFs (2.26–2.61  $\times$  10<sup>-10</sup> m W<sup>-1</sup>) are increased after polymerization compared with that of the Pc monomers (1.59–1.97  $\times$  10<sup>-10</sup> m W<sup>-1</sup>) (Table 1), which means that

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Fig. 6 The open-aperture Z-scan data with normalized transmittance as a function of the sample position Z for Pc-POF (a), Sn-Pc-POF (b) and Pb-Pc-POF (c) in DMF solution; transmittance as a function of the incident pulse energy density for phthalocyanine (d), Sn-phthalocyanine (e) and Pb-phthalocyanine (f) monomers and Pc-POF (g), Sn-Pc-POF (h) and Pb-Pc-POF (i).

the sp<sup>3</sup>-hybridized carbon bridge can provide efficient energy absorption involving the population of excited states between phthalocyanines units. Sn-Pc-POF exhibits the highest nonlinear absorption coefficient (2.61  $\times$  10<sup>-10</sup> m W<sup>-1</sup>) in the three Pc-POFs, which means the introduction of high valence metal ion in the phthalocyanine centre can enhance their polarization ability to high-energy laser and increase their excited state absorption. The optical limiting performances of the Pc monomers and Pc-POFs were also measured at 532 nm. The normalized transmittance of the phthalocyanine monomers and Pc-POFs were plotted as functions of input laser energy density (J cm<sup>-2</sup>) in Fig. 6d-i. It

Table 1	NLO coefficients and optical limiting thresholds of phthalocya	a-
nine mor	omers and Pc-POFs at 532 nm	

Samples	The effective nonlinear absorption coefficient $\beta_{\rm eff} (\times 10^{-10} \text{ m W}^{-1})$	Optical limiting threshold (J cm <sup>-2</sup> )
Phthalocyanine	1.59	0.56
Sn–Phthalocyanine	1.97	0.46
Pb-phthalocyanine	1.84	0.68
Pc-POF	2.26	0.48
Sn-Pc-POF	2.61	0.37
Pb-Pc-POF	2.36	0.49

can be observed that the transmittance decreased more sharply in Pc-POFs compared with the phthalocyanine monomers as the incident fluence increased. At the same level of linear transmittance at 532 nm, Sn-Pc-POF showed the best optical limiting performance in three Pc-POFs, which was in agreement with their open Z-scan results. The optical limiting threshold (incident fluence at which the transmittance falls to 50% of the linear transmittance) for Sn-Pc-POF is  $0.37 \text{ J cm}^{-2}$  (in Table 1). This value is lower than some multi-nuclear, double and quintuple-decker phthalocyanine chelates (0.11-0.9 J cm<sup>-2</sup>),<sup>21-24</sup> but surpassed 2D materials such as COF, graphene and layered transition metal dichalcogenides with limiting threshold about 1.2-17 J cm<sup>-2</sup>.<sup>25,26</sup>

In conclusion, three POFs with phthalocyanine units are synthesized through sp<sup>3</sup>-hybridized carbon bridge polymerization. The structural simulation and photophysical properties investigation in the Pc-POFs indicated that the methylene carbon bridge can prevent the aggregation of planar phthalocyanine. Moreover, the NLO properties of these Pc-POFs were studied by using Z-scan technique. The Pc-POFs exhibit stronger nonlinear absorption responses compared with Pc monomers, while the metalated Sn-Pc-POF displays the highest nonlinear absorption coefficient and best optical limiting performance with a limiting threshold of  $0.37 \text{ J} \text{ cm}^{-2}$ . The simple and efficient preparation process and excellent NLO performances make alkyl carbon bridge phthalocyanine POFs promising NLO materials with potential applications in laser protection.

### Conflicts of interest

The authors have no conflicts to declare.

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