Electronic Supplementary Information

Enhanced nonlinear optical response from dihydroxy(5,10,15,20-tetraphenyl porphyrinato)tin(IV) or SnTPP in a fully plastic photonic crystal microcavity

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Experimental Section

Preparation of SnTPP sample

The SnTPP sample was synthesized using a protocol reported elsewhere.^{1,2} Appropriate amount of SnTPP (Structure of SnTPP is shown in Fig.S1, ¹H NMR and ¹³C NMR spectra of SnTPP are given in Fig.S2 & Fig.S3 respectively) was dissolved in spectroscopic grade of Diacetone alcohol under ultra soniccation for 1 hour and was diluted to have linear transmittance of about 65% at 532nm for Z-scan measurements.

Fabrication of 1 D PC microcavity

An organic 1D PC microcavity was built by introducing a defect layer of SnTPP doped CA between two symmetric DBRs comprising alternate quarter wave stacks of CA and PVK. Polymer Solutions with an initial concentration of 4wt% for the fabrication process were prepared by making PVK and CA soluble in chlorobenzene and diacetone alcohol respectively. An orthogonal solvent system was followed by choosing chlorobenzene and diacetone alcohol for the selected polymers, in order to prevent intermixing of different polymeric layers during multilayer preparation.^{3,4} To fabricate a PC cavity with cavity resonance at a wavelength of 532nm, individual layers of DBRs were made with an optical thickness of $\lambda/4$ whereas the defect layer thickness was set as $\lambda/2$ thus providing efficient coupling of light to the cavity. Optical thickness of single layer films can be monitored using a spectrometer due to the fact that reflectance for a single layer will be maximum or minimum at the quarter wavelength multiplied by odd numbers.⁵

The spin coater used for the deposition process was Laurell WS-650MZ-23NPPB. By changing the concentration of solutions and by varying the spin coating parameters such as spin speed, spinning time and acceleration, the PVK and CA single layer films of desired thickness were finally achieved with 1.5wt% of PVK solution coated at a spin rate of 2300 rpm, and 2wt% of CA solution at a spin speed of 2000 rpm. The spinning time was set as 50 seconds in both cases. DBR containing 10 unit cells of CA/PVK was then grown on a

thoroughly cleaned glass substrate followed by heating at 110°C for 15 minutes after each spin coating process. For the defect layer, 200µl of SnTPP solution in diacetone alcohol (0.5mg/ml) was added to 5ml of the pre-calibrated CA solution and mixed well under soniccation. The final structure of PPCC was realized by the deposition of the defect layer SnTPP:CA over the first DBR and then placing another DBR consisting 10 periods. It was then calcined at 110°C for five hours in order to remove any residual solvent and thus to improve the optical quality of the fabricated PPCC.

Characterization Techniques

The absorbance spectrum was measured on a UV/Vis double beam Spectrophotometer (UV-2450 Schimadzu) and reflectance spectra were recorded using a reflectance accessory attached to the spectrophotometer. Perkin Elmer LS 55 luminescence spectrophotometer was used to collect the emission spectrum of the sample. In order to investigate the nonlinear optical absorption properties, open Z-scan technique was used in which the transmittance of the sample is monitored as a function of sample position by moving it along the axis of a focused Gaussian beam. Fig.S4 shows the schematic diagram of the Z-scan experimental set up. A Q-switched Nd:YAG laser (Quanta-Ray, Spectra Physics) operating at 532nm, with a pulse width of 7ns and repetition rate of 10Hz was used as the source of excitation. A convex lens having focal length of 15cm was used to focus the Gaussian laser beam and the beam spot size was estimated as 16.94µm. This configuration resulted a Rayleigh range of 1.69mm which was greater than the sample length and thus satisfying the thin sample approximation condition, a prerequisite in Z-scan measurements. The incident and transmitted beam energies were collected and monitored by means of two pyroelectric detectors (RiP-735) and an energy ratio meter (Rj-7620). For closed Z-scan set up where the dispersive properties of the nonlinear samples are analyzed, an aperture of 4mm in diameter was introduced in front of the detector measuring the transmitted signal.

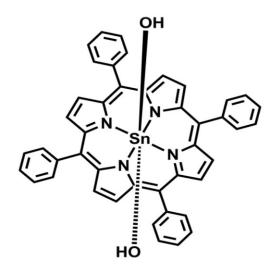


Fig.S1: Structure of SnTPP

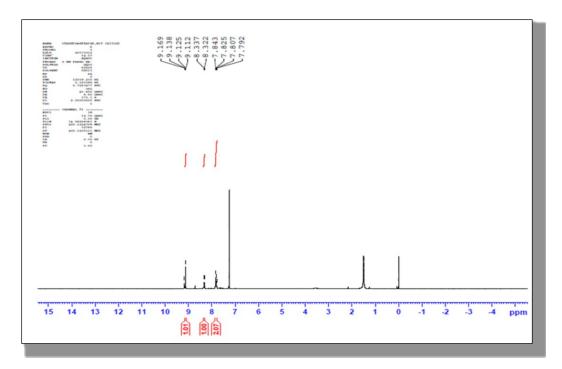


Fig.S2: ¹H NMR spectra of SnTPP

 $[^{1}H NMR (400 MHz CDCl_{3}): \delta 7.79-7.84 (m, 5H), 8.33 (d, 2H, j = 6Hz), 9.14 (S, 2H)]$

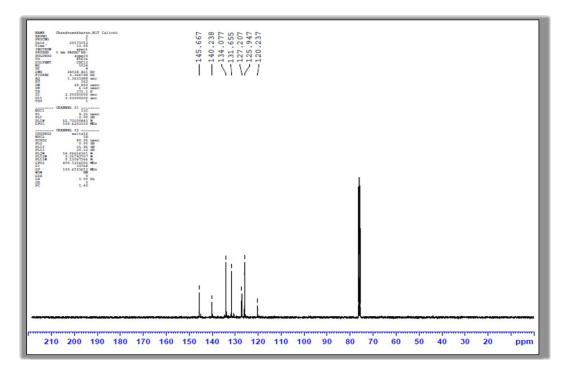
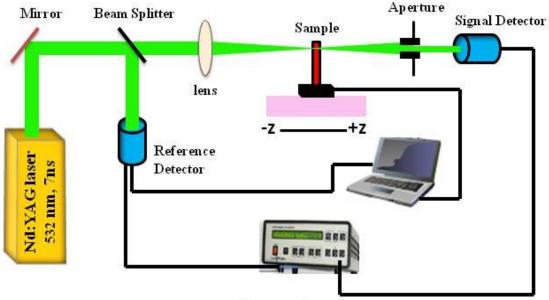


Fig.S3: ¹³C NMR spectra of SnTPP

[¹³C NMR (100 MHz, CDCl₃) : δ 120.24, 125.95, 127.21, 131.66, 134.08, 140.24, 145.67]



Energy ratio meter

Fig.S4: Schematic diagram of Z-scan experimental set up

References

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