Protonation effect on the nonlinear absorption, nonlinear refraction and optical limiting properties of tetraphenylporphyrin*

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Nonlinear optical properties of tetraphenylporphyrin (H_2TPP) and protonated tetraphenylporphyrin (H_4TPP^{2+}) in toluene were investigated by Z-scan technique using a nanosecond laser with 5 ns pulse at 532 nm. Results show that H_4TPP^{2+} exhibits weaker nonlinear refraction but enhanced reverse saturable absorption (RSA) and optical limiting performance in comparison with pristine H_2TPP. Since no nonlinear scattering is observed in H_4TPP^{2+} under low input fluence, and H_4TPP^{2+} exhibits weaker nonlinear scattering signals than H_2TPP under high input fluence, the enhancement of RSA and optical limiting performance can be attributed to the larger ratio of excited state absorption cross-section to that of the ground state of H_4TPP^{2+}. H_4TPP^{2+} also exhibits superior optical limiting performance, even better than the benchmark RSA material C_{60}.
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The development of laser science and technology has motivated an extensive research for designs of optical limiting systems for eye and sensor protection. Among widely investigated materials for optical limiting, organic compounds with extended π-conjugated systems have exhibited strong optical limiting properties due to reverse saturable absorption (RSA), such as phthalocyanines and porphyrins[1-3]. In the past decades, people have paid much attention on the modification of porphyrin structures to get a larger ratio of excited state absorption cross-section to that of ground, which usually lead to enhanced RSA and optical limiting properties[1]. Compared with various complicated modification approaches for porphyrin, the core of porphyrin can be modified simply by adding acid into the solution, meanwhile, the photophysics and RSA properties of porphyrins are also changed[4-8].

Free base tetraphenylporphyrin (H_2TPP) is a common porphyrin which has been used as benchmark for various functional porphyrin[9]. Blau et al[10] reported that H_2TPP can be protonated in chloroform during sonication, Liu et al[7] reported the nonlinear absorption of H_2TPP and protonated H_2TPP (H_4TPP^{2+}) in chloroform, however, the reports about the RSA, optical limiting properties of H_2TPP and H_4TPP^{2+} in other solvents, such as toluene, were few. What' more, most reports on porphyrins were concentrated on studies of RSA, but their nonlinear refraction properties are seldom reported so far.

In this paper, we study and compare the nonlinear refraction, nonlinear absorption, optical limiting properties of H_2TPP and H_4TPP^{2+} in toluene. Results show that H_2TPP in toluene can be protonated by adding acid into the solution, while H_2TPP cannot be protonated in N:N-dimethylformamide (DMF). The H_4TPP^{2+} in toluene shows decreased nonlinear refraction response but enhanced RSA properties due to the larger ratio of excited state absorption cross-section to that of the ground state of H_4TPP^{2+}. Although H_4TPP^{2+} shows the weakest nonlinear scattering signals, it exhibits the strongest optical limiting performance compared with H_2TPP in toluene, H_2TPP in DMF and C_{60} in toluene, due to the enhanced RSA properties.

H_2TPP was bought from Sigma-Aldrich Co., LLC. H_2TPP was prepared with the concentration of 2×10^{-4} mol/L in toluene. H_4TPP^{2+} was prepared by adding excess amounts of trifluoroacetic acid into H_2TPP solutions. In H_4TPP^{2+}, two more protons were added to the central nitrogens of the porphyrin macrocycle, and this process is reversible.

The Z-scan method was utilized to determine simultaneously the magnitude and sign of nonlinear refraction and nonlinear absorption [11,12]. The Z-scan experiments

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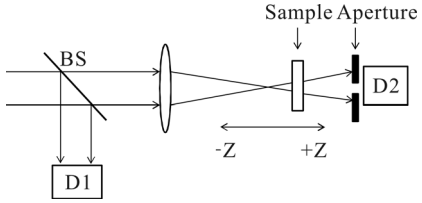
were performed by 5 ns pulsed laser with a 10 Hz repetition rate at 532 nm, generated from a frequency doubled Q-switched Nd:YAG laser (Continuum Surelite-II). A TEM00 Gaussian beam was focused to produce a beam waist radius of 23 μm.

Fig.1 shows the closed-aperture *Z*-scan experimental apparatus. For the open-aperture *Z*-scan apparatus, the aperture is removed, and a lens is placed behind the sample to ensure all laser transmitted from the sample can be collected by the detector D_2.



BS: beam splitter; D1: Detector 1; D2: Detector 2

Fig.1 The closed-aperture Z-scan experimental apparatus

For Z-scan experiments, all the solutions were poured in a 1 mm quartz cuvette. All samples were poured in a 5 mm quartz cuvette for optical limiting and nonlinear scattering measurements. For the measurements of optical limiting, the single pulse mode was used, the experimental configuration is the same as those in Refs.[13] and [14]. For nonlinear scattering measurements, a small area lens was placed at 38° with respect to the *Z* axis to collect the scattered signals. All the samples were adjusted to have the same linear transmittance of 75% at 532 nm for optical limiting and nonlinear scattering measurements. No nonlinear response and damage of the quartz cuvette were observed at the fluence used in our experiments.

The absorption spectra shown in Fig.2 present the characteristic bands of porphyrins. The Soret band of H_2TPP in toluene is located around 419 nm, and four Q bands are around 514 nm, 548 nm, 591 nm and 648 nm, respectively. Compared with H_2TPP, the Soret band of H_4TPP^{2+} is located around 438 nm, and there is a red shift of 19 nm. Upon protonation of H_2TPP, the absorption spectrum of H_4TPP^{2+} in the visible region is characterized by two strong Q bands at 601 nm and 652 nm. Since the protonation process is reversible, the deprotonation can be obtained by adding solvent of DMF. As shown in Tab.1, after adding DMF to the H_4TPP^{2+} toluene solution, Soret band of the products shifts back to 418 nm, and four Q bands emerge at around 514 nm, 549 nm, 591 nm and 648 nm, respectively, which are the same to those of H_2TPP. This indicates that the deprotonation of H_4TPP^{2+} by the addition of DMF. Our further experiments show that H_2TPP cannot be protonated in DMF. The absorption spectra data of these three samples are summarized in Tab.1.

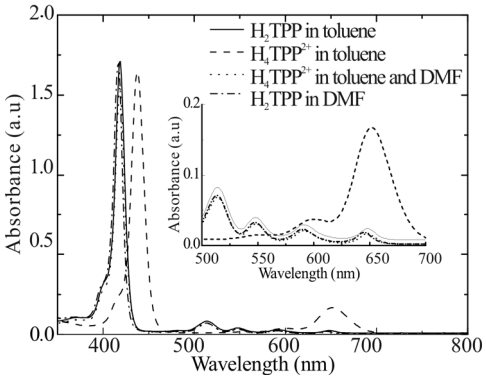


Fig.2 Absorption spectra of H_2TPP (in toluene), H_4TPP^{2+} (in toluene), H_2TPP^{2+} (in toluene and followed by adding DMF) and H_2TPP (in DMF) (Inset shows the Q bands of the samples.)

Tab.1 Absorption data of H_2TPP (in toluene), H_4TPP^{2+} (in toluene), H_2TPP^{2+} (in toluene and followed by adding DMF) and H_2TPP (in DMF)

Samples	Soret band, λ_{max} (nm)	Q-band, λ_{max} (nm)			
H_2TPP	419	514	548	591	648
H_4TPP^{2+}	438	–	–	601	652
$^{*}H_4TPP^{2+}$	418	514	549	591	648
$^{**}H_2TPP$	417	514	548	590	645

"*" means the solvent is toluene and followed by adding DMF, and "**" means the solvent is DMF.

Fig.3 shows the Z-scan curves of H_2TPP and H_4TPP^{2+}. As shown in Fig.3(a), the open-aperture curves of H_4TPP^{2+} shows the larger dip, indicating the enhanced RSA by protonation. However, as shown in Fig.3(b), H_4TPP^{2+}exhibits the weaker nonlinear refraction compared with H_2TPP. Since the dominant mechanism of TPP is RSA arising from excited state absorption, the enhanced nonlinear absorption of H_4TPP^{2+} can be attributed to the change of absorption cross-sections of ground and excited states. In general, the RSA process of organic molecules can be depicted by a five-level mode[7], and the exact calculation of absorption cross-sections of excited states requires rate equation analysis considering all the states in the energy level, but due to unavailability of parameters, such as relaxation times of different states, a simplified three-level model can be used for the estimation of RSA and optical limiting performance[8,15-17]. Rate equations of the three-level model can be written as

$$\frac{\mathrm{d}N_0}{\mathrm{d}t} = -\frac{\sigma_0 I N_0}{\hbar\omega} + \frac{N_{\mathrm{ex}}}{\tau_{\mathrm{ex}}}, \tag{1}$$

$$\frac{\mathrm{d}N_{\mathrm{ex}}}{\mathrm{d}t} = \frac{\sigma_0 I N_0}{\hbar\omega} - \frac{N_{\mathrm{ex}}}{\tau_{\mathrm{ex}}}, \tag{2}$$

$$\frac{\mathrm{d}I}{\mathrm{d}z} = -\alpha I = -\left(\sigma_0 N_0 + \sigma_{\mathrm{eff}}^{\mathrm{ex}} N_{\mathrm{ex}}\right) I, \tag{3}$$

$$\frac{\mathrm{d}\phi}{\mathrm{d}z} = k\Delta n = \sigma_{\mathrm{r}}^{\mathrm{ex}} N_{\mathrm{ex}}, \tag{4}$$

where N_0 and N_{ex} are the population of the ground state and excited states, respectively, σ_0 is the ground state

absorption cross-section, and $\sigma_{\text{eff}}^{\text{ex}}$ is the effective excited state absorption cross-section (it includes the absorption of the first excited singlet state and the first excited triplet state). I is input laser intensity, $\hbar\omega$ is the photon energy, τ_{ex} is the effective decay time of the excited states, α is the total absorption coefficient, Δn is the change of the refraction index of the sample, k is the wave vector, and $\sigma_{\text{r}}^{\text{ex}}$ is the effective refraction cross-section. The ground-state absorption cross-sections σ_0 of the samples were calculated from the formula $\sigma_0=\alpha_0/N$, where α_0 is the linear absorption coefficient, and N is the number of molecules per cubic centimeter. By theoretically simulating the open-aperture and nonlinear refraction Z-scan experimental data, we can obtain the values of σ_0, $\sigma_{\text{eff}}^{\text{ex}}$, $\sigma_{\text{r}}^{\text{ex}}$ and τ_{ex} in the case of 5 ns pulses, and the values are listed in Tab.2.

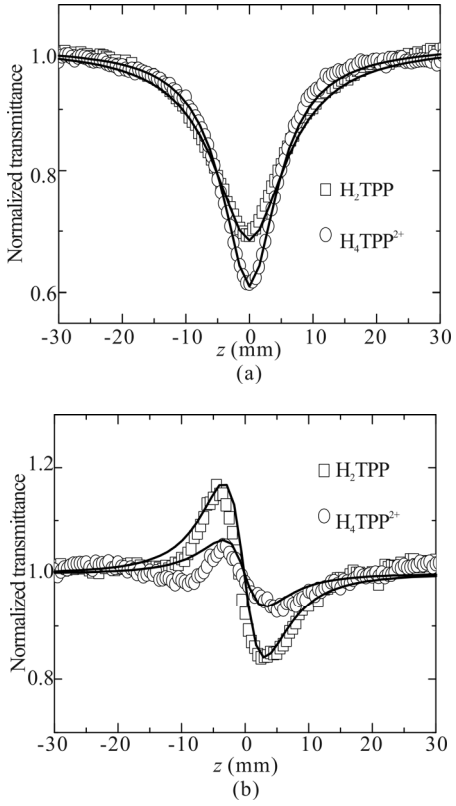


Fig.3 (a) Open-aperture Z-scan curves and (b) nonlinear refraction curves of H_2TPP (in toluene), H_4TPP^{2+} (in toluene)

Tab.2 Photophysics parameters of the samples at 532 nm

Samples	σ_0 ($\times10^{-17}$, cm^2)	$\sigma_{\text{eff}}^{\text{ex}}$ ($\times10^{-17}$, cm^2)	$\sigma_{\text{r}}^{\text{ex}}$ ($\times10^{-17}$, cm^2)	τ_{ex} (ns)	$\sigma_{\text{eff}}^{\text{ex}}/\sigma_0$
H_2TPP in toluene	1.96	6.90	-3.40	4.0	3.52
H_4TPP^{2+} in toluene	0.63	13.5	-2.80	2.5	21.4
H_2TPP in DMF	0.97	4.20	-	5.0	4.43

It can be seen that H_4TPP^{2+} shows smaller σ_0, larger $\sigma_{\text{eff}}^{\text{ex}}$ and $\sigma_{\text{eff}}^{\text{ex}}/\sigma_0$ than those of H_2TPP, which leads to the enhanced RSA. Fig.3(b) shows the nonlinear refraction Z-scan curves of H_2TPP and H_4TPP^{2+} obtained by dividing closed-aperture Z-scan data by corresponding open-aperture Z-scan data. It can be seen that H_2TPP shows negative nonlinear refraction, and $\sigma_{\text{eff}}^{\text{ex}}$ is -3.4×10^{-17} cm^2 by fitting experimental data. However, H_4TPP^{2+} shows a decreased nonlinear refraction with $\sigma_{\text{r}}^{\text{ex}}$ of -2.8×10^{-17} cm^2, the nonlinear refraction Z-scan curves is not well due to the strong RSA properties for H_4TPP^{2+}, since strong nonlinear absorption always affects nonlinear refraction Z-scan curves[18].

The optical limiting performances of the samples are measured as shown in Fig.4. As shown in Fig.4, H_4TPP^{2+} shows the strongest optical limiting performance, even stronger than C_{60}. For example, at the input fluence of 21.5 J/cm^2, the output fluence values are 1.57 J/cm^2, 4.06 J/cm^2, 5.19 J/cm^2 and 7.30 J/cm^2 for H_4TPP^{2+} in toluene, C_{60} in toluene, H_2TPP in DMF and H_2TPP in toluene, respectively. Nonlinear absorption and nonlinear scattering are two main mechanisms leading to optical limiting effect. To investigate the optical limiting mechanisms in the samples, nonlinear scattering versus input fluence was measured.

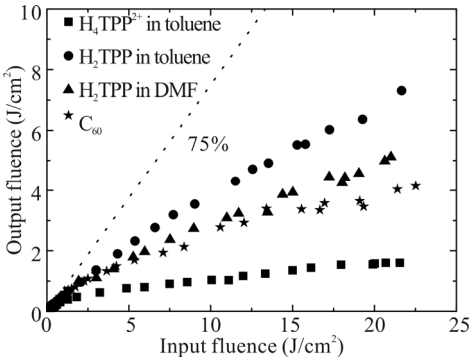


Fig.4 The optical limiting of H_2TPP (in toluene), H_4TPP^{2+} (in toluene), H_2TPP (in DMF) and C_{60} (in toluene) with the same linear transmittance of 75%

As shown in Fig.5, all sample shows the decreasing transmittance as the increase of input fluence, and no obvious nonlinear scattering signals occur for the input fluence lower than 2.0 J/cm^2. For input fluence higher than 2.0 J/cm^2, all samples exhibit obvious nonlinear scattering signal. Although H_4TPP^{2+} shows the weakest nonlinear scattering signal, it exhibits the strongest optical limiting performance, indicating the dominant RSA mechanism. Nonlinear refraction arising from excited refraction also contributes to the optical limiting performance of H_4TPP^{2+}, what's more, since H_4TPP^{2+} has a smaller σ_0 than that of H_2TPP for the same linear transmittance, H_4TPP^{2+} has the higher concentration, the higher concentration also leads to large RSA and nonlinear refraction response. So H_4TPP^{2+} shows the best

RSA and optical limiting performance due to the combination of its high concentration and a large value of $\sigma_{eff}^{ex}/\sigma_0$.

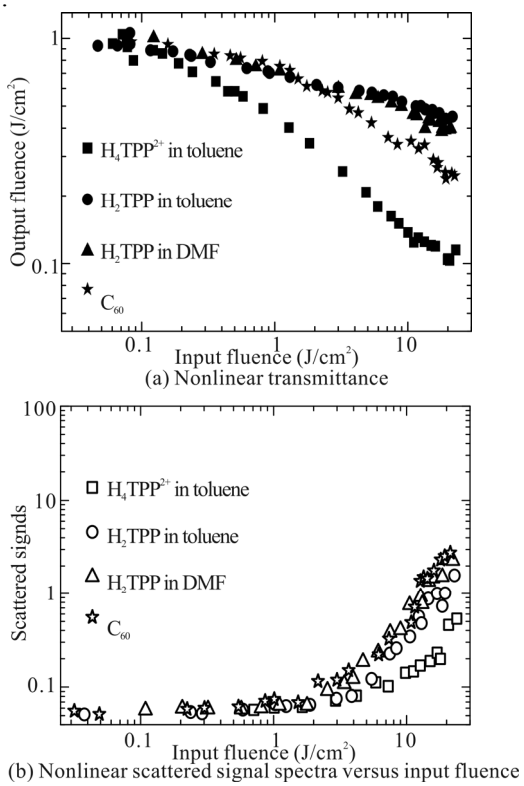


Fig.5 The optical limiting of H_2TPP (in toluene), H_4TPP^{2+} (in toluene), H_2TPP (in DMF) and C_{60} (in toluene) with the same linear transmittance of 75%

In conclusion, nonlinear optics and optical limiting properties of H_2TPP and H_4TPP^{2+} were investigated. Although H_4TPP^{2+} exhibits weaker nonlinear refraction, it still shows the best RSA, and optical limiting performance due to its large value of $\sigma_{eff}^{ex}/\sigma_0$, even better than C_{60}. The protonation can change the properties of ground and excited states of porphyrins, giving us an approach to conveniently modify and improve the optical limiting performance for porphyrin materials.

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