Active tuning of nonlinear absorption in a supramolecular zinc diphenylporphyrin-pyridine system

Zhi-Bo Liu¹, Jian-Guo Tian¹*, Jian-Yu Zheng², Zhi-Yun Li², Shu-Qi Chen¹, and Yan Zhu²

¹ The Key Laboratory of Advanced Technique and Fabrication for Weak-Light Nonlinear Photonics Materials, Ministry of Education, and TEDA Applied Physical School, Nankai University, Tianjin 300457, China
² State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, China
jjtian@nankai.edu.cn

Abstract: We report on an active tuning of nonlinear absorption from reverse saturable absorption to saturable absorption in supramolecular zinc diphenylporphyrins by the combination of molecular and supramolecular levels at 532, 542 and 552 nm. Firstly, the modifications of molecular structures with bromination result in a discrete but regular change in magnitude and sign of nonlinear absorption (NLA). Furthermore, a fine tuning of NLA was obtained by the intermolecular weak interaction of pyridine and zinc porphyrins. Using an association model, we theoretically simulate the change of NLA. Compared with modifying molecular structures of conventional organic materials, the weak intermolecular interaction of supramolecular porphyrins has another advantage that it can be realized more easily and flexibly to change NLA.

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OCIS codes: (190.4710) Optical nonlinearities in organic materials; Reverse saturable absorption; Saturable absorption; (160.4330) Nonlinear optical materials; (300.1030) Absorption.

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Porphyrins are well known to exhibit excited state absorption (ESA), including reverse saturable absorption (RSA) and saturable absorption (SA), in the visible wavelength range \( \sigma \) and triplet excited state cross-section \( \sigma_T \). As a type of nonlinear absorption (NLA), ESA is usually described by a five-level model \([17]\). It is caused by the further promotion of the excited electron from the first excited state \( S_1 \) or \( T_1 \) to a higher-lying state \( S_0 \) or \( T_0 \) after the electrons in ground state were excited. The singlet excited state cross-section \( \sigma_S \) and triplet excited state cross-section \( \sigma_T \) are larger or smaller than that of ground state \( \sigma_0 \) for RSA or SA, respectively.

In this paper, we report an active tuning of NLA from RSA to SA by supramolecular incorporation of pyridine into zinc diphenylporphyrins at 532, 542, and 552 nm. This method can provide a simple and convenient route to change NLA of supramolecular porphyrins materials in practical applications, such as optical limiting \([18, 19]\), optical switching \([20]\), and spatial light modulation \([21]\), etc.

### 1. Introduction

Organic nonlinear optical (NLO) materials have been thought of as one of prospective materials because of their potential flexibility and variability \([1-3]\). To enhance and control optical nonlinearities, the structure-nonlinearity relationship has been investigated in large numbers of organic materials \([4-9]\). However, it is difficult to realize a fine-tuning and large enhancement of optical nonlinear coefficients, if only depending on the modifications of molecular structures. The emergence of supramolecular chemistry, the chemistry beyond the molecule, brought a new chance to the development of organic NLO materials due to the introduction of a weak intermolecular interaction called non-covalent bond \([10]\). For example, optical nonlinearities have been enhanced about 2-3 orders of magnitude in supramolecular porphyrins \([11-13]\).

Porphyrins are well known to exhibit excited state absorption (ESA), including reverse saturable absorption (RSA) and saturable absorption (SA), in the visible wavelength range \([14, 15]\) and even near-infrared wavelength range \([16]\). As a type of nonlinear absorption (NLA), ESA is usually described by a five-level model \([17]\). It is caused by the further promotion of the excited electron from the first excited state \( S_1 \) or \( T_1 \) to a higher-lying state \( S_0 \) or \( T_0 \) after the electrons in ground state were excited. The singlet excited state cross-section \( \sigma_S \) and triplet excited state cross-section \( \sigma_T \) are larger or smaller than that of ground state \( \sigma_0 \) for RSA or SA, respectively. In this paper, we report an active tuning of NLA from RSA to SA by supramolecular incorporation of pyridine into zinc diphenylporphyrins at 532, 542, and 552 nm. This method can provide a simple and convenient route to change NLA of porphyrins materials in practical applications, such as optical limiting \([18, 19]\), optical switching \([20]\), and spatial light modulation \([21]\), etc.
2. Experiment section

A series of diphenylporphyrins we synthesized have been characterized by $^1$H NMR recorded on a Bruker Av300 spectrometer and MALDI-TOF-MS spectra using a Thermo Finnigh LCQ Advantage mass spectrometer. UV absorption spectra and titration spectra were recorded at 25°C on a Cary 300 UV spectrophotometer, using a quartz cell of 1cm path length. The concentrations of all porphyrins are 1.0×10⁻⁶ M for UV spectra in chloroform. In titration measurements, a aliquot of a solution of pyridine (5.0×10⁻³ M in chloroform) was added to a solution of zinc porphyrins (2.0×10⁻⁵ M in chloroform), and the resulting solutions were subjected to linear absorption spectroscopy at 25°C. Each spectrum was corrected with a dilution factor and background subtraction. In measurements of nonlinear absorption using Z-scan technique, a Q-switched Nd:YAG laser (Continuum Surelite-II) and a mode-locked Nd:YAG laser (Continuum Model PY61) were used to generate 5-ns pulses and 30-ps pulses at the wavelength of 532 nm. The lasers at 512 nm, 542 nm, and 552 nm are from a commercial optical parametric oscillator (Continuum Panther OPO) pumped by the third harmonic (355 nm) from Continuum Surelite-II with a repetition rate of 10 Hz and tunable in the range of 420-2500 nm, and the pulse duration is about 4-5 ns. The beam waist was 18-24 μm for different wavelengths and different pulse duration. The incident and transmitted pulse energies were measured simultaneously with two energy detectors (Molectron J3S-10). All of solutions of porphyrins used in Z-scan measurements had a concentration of 2.0×10⁻⁴ M and were poured in a 1-mm quartz cuvette.

3. Results and discussion

The spectra and structures of diphenylporphyrins used in our experiments are shown in Fig. 1(a). There are about 10nm red-shift in both Soret and Q bands as bromination increases. Nonlinear absorption measurements were carried out by the open-aperture Z-scan technique [22]. Figure 1(b) gives the open-aperture Z-scan curves of three porphyrins with 5-ns pulse duration at 532 nm, and the solid lines are theoretical fitting curves. The change of open-aperture Z-scan curves from peak to valley indicated that a transition from SA to RSA happens with bromination. Since the ESA is dominated by absorption of triplet excited states (T₁→Tₙ) in the case of nanosecond pulsed laser incidence, and by absorption of singlet excited states (S₁→Sₙ) in the case of picosecond pulsed laser incidence [23], to exactly obtain the value of $\sigma_S$, we have also performed Z-scan experiments of picosecond pulsed laser. The photophysical parameters of ZnDPP, ZnDPPBr, and ZnDPPBr₂ obtained are shown in Tab. 1, where $\tau_0$ and $\tau_{ISC}$ are the lifetime of S₁ and the intersystem crossing time of S₁→T₁, respectively.

![Fig. 1. The linear and nonlinear absorption data of ZnDPP, ZnDPPBr, and ZnDPPBr₂. (a) Molecular structures and Linear absorption spectra. (b) Open-aperture Z-scan curves with 5-ns pulse duration at 532nm. Symbols represent experimental data; solid lines are theoretical fittings using a five-level model.](image-url)
Table 1. Photophysical parameters of ZnDPP, ZnDPPBr, and ZnDPPBr$_2$

| Material    | Soret-bands $\lambda_{\text{max}}$ (nm) | Q-bands $\lambda_{\text{max}}$ (nm) | $\sigma_0$ (10$^{-17}$cm$^2$) | $\sigma_S$ (10$^{-17}$cm$^2$) | $\sigma_T$ (10$^{-17}$cm$^2$) | $\tau_0$ (ns) | $\tau_{\text{ISC}}$ (ns) |
|-------------|--------------------------------------|-------------------------------------|------------------------------|-------------------------------|-------------------------------|---------------|-----------------|
| ZnDPP       | 409                                  | 536                                 | 8.72                         | 2.5                           | 2.7                           | 5.0           | 3.0             |
| ZnDPPBr     | 419                                  | 545                                 | 4.25                         | 3.4                           | 3.6                           | 3.0           | 7.0             |
| ZnDPPBr$_2$ | 430                                  | 554                                 | 1.26                         | 4.6                           | 4.8                           | 0.7           | 5.0             |

The modifications of molecular structures by bromination result in a discrete but regular change in magnitude and sign of NLA. However, in practical application of NLA, such as optical limiting, all optical switching, and spatial light modulation, it may be necessary to continuously tune NLA. Using solvent effect, we have obtained flexible alteration of optical nonlinearities in the solutions of iodine [24], but the nature of solvent effect remains unclear.

Since weak interactions in supramolecular porphyrins can provide a sufficient thermodynamic driving force to influence optical properties of system, here we utilize the binding model of the pyridine group coordinated to zinc porphyrins, which has been intensively investigated [25], to manipulate the fine-tuning process. Pyridine is chosen as a ligand in our study because it has almost no nonlinear response in visible-wavelength region, and simple 1:1 prophyrin-pyridine (Por·Py) complexes can be obtained.

![Equation 1](image)

Fig. 2. Change of nonlinear absorption for ZnDPP with various concentration of pyridine. (a) Open-aperture Z-scan curves of at 532nm. (b) Absorption cross-sections of ground and excited states vs $[\text{Py}]_0 : [\text{Por}]_0$. The solid lines are fittings with $K=0.48 \times 10^4$ M$^{-1}$ using association model. Inset gives the equilibrium equation between zinc porphyrins and pyridine.

Figure 2 shows the open-aperture Z-scan curves in the case of nanosecond pulsed laser incidence and absorption cross-sections of ground and excited states of ZnDPP with the change of concentration of pyridine at 532 nm. In our measurements, the concentration of zinc porphyrins was kept unchanged. It should be noted that the transmittances in Fig. 2(a) are not normalized by linear transmittance, not like that in Fig. 1(b). As the concentration of pyridine increased, more Por·Py was formed, which led to a drastic decrease of linear absorption (see the transmittance change at both sides of Z-scan curves), but a small change of ESA in nonlinear region (see the transmittance change at the focus). Under the co-effect of linear absorption and ESA, a transition from SA to RSA with gradual change is shown in Fig. 2(a). From Fig. 2(b), we can see the changes of linear absorption and ESA more clearly.

The equilibrium equation between porphyrin and pyridine due to zinc-pyridine interaction is given in the inset of Fig. 2(b), where

$$K = \frac{[\text{Por} \cdot \text{Py}]}{[\text{Por}][\text{Py}]} = \frac{[\text{Por} \cdot \text{Py}]}{([\text{Por}]_0 - [\text{Por} \cdot \text{Py}]) ([\text{Py}]_0 - [\text{Por} \cdot \text{Py}])}$$  (1)
is the association constant [26], and [Por·Py], [Por], and [Py] are the equilibrium concentrations of zinc Por·Py complex, zinc porphyrin, and pyridine, while [Por]₀ and [Py]₀ are the total concentrations of zinc porphyrin and pyridine, respectively. Because the [Por]₀ (2.0×10⁻⁴ M) was kept unchanged in our experiments, when pyridine was added in excess amounts, [Por·Py]→[Por]₀ and optical properties of system tended to saturate gradually. When the ratio of [Py]₀ to [Por]₀ is about larger than 20, the changes of Z-scan curves and σ₀ became very slow, as shown in Fig. 2.

![Spectrophotometric titrations of (a) ZnDPP, (b) ZnDPPBr, and (c) ZnDPPBr₂ with pyridine. The cross section difference (σ_T−σ₀) of (d) ZnDPP, (e) ZnDPPBr, and (f) ZnDPPBr₂ vs the concentration of pyridine [Py]₀:[Por]₀. The dotted lines represent σ_T−σ₀=0. If σ_T−σ₀<0, RSA will occur, and if σ_T−σ₀>0, SA will occur. The solid fitting curves are obtained directly from the association model.](image)

To obtain the value of K, titrations of ZnDPP, ZnDPPBr, and ZnDPPBr₂ with pyridine were performed, and such absorption spectral changes are illustrated in Figs. 3(a)-3(c). Upon the addition of pyridine, the Q bands at 536 nm, 546 nm, and 555 nm corresponding to the unbound zinc porphyrins gradually disappeared and new bands appeared at 550 nm, 560 nm, and 570 nm for ZnDPP, ZnDPPBr, and ZnDPPBr₂. The new bands are characteristics of Por·Py complexes. Clear isosbestic points are observed at 542 nm, 552 nm, and 563 nm for ZnDPP, ZnDPPBr, and ZnDPPBr₂, respectively, and this is indicative of sequential two-state equilibria. The black lines are the absorption spectra with extreme excessive pyridine, which can be thought that the coordination interaction between pyridine and zinc porphyrins is sufficient. The calculated K for pyridine ligation to the zinc are 0.48×10⁴ M⁻¹, 1.03×10⁴ M⁻¹, and 1.55×10⁴ M⁻¹ for ZnDPP, ZnDPPBr, and ZnDPPBr₂, respectively. If [Py]₀, [Por]₀ and K are given, [Por·Py] can be derived from Eq. (1). And then, we can easily predict the change of nonlinear absorption of system according to the ratio of porphyrins to Poy-Py complexes. The
theoretical fittings using the model above, called association model, agree well with the experimental data, as shown in Fig. 2(b). The similar results can be also observed for ZnDPPBr at 542 nm and ZnDPPBr$_2$ at 552 nm due to about 10 nm red-shift of absorption band.

For ZnDPP, as pyridine is added, absorption spectral changes at 512 nm, 542 nm, and 552 nm are different from that at 532 nm in Fig. 3(a). We now consider the tuning of NLA at other three wavelengths (512 nm, 542 nm, and 552 nm), and Z-scan experiments with nanosecond pulsed laser incidence were performed to obtain values of $\sigma_T$ at different wavelengths. It should be noted that $\sigma_T$ has also a dependence on [Por-Py], but it is much weaker than $\sigma_0$ as shown in Fig. 2(b). Here, the cross section difference ($\sigma_T-\sigma_0$) is introduced as a useful indicator of NLA. Because the weak interaction between porphyrin and pyridine has a larger effect on $\sigma_0$ than on $\sigma_T$, it can be predicted how the nonlinear absorption of ZnDPP changes at these wavelengths. As the ratio of [Py]$_0$ to [Por]$_0$ increases, there is an opposite change of NLA at 552 nm compared with that at 532 nm, as shown in Fig. 3(d), but RSA at 512 nm and SA at 542 nm almost remain unchanged. In the same way, Figs. 3(e) and 3(f) give the regularity of changes of $\sigma_T-\sigma_0$ for ZnDPPBr and ZnDPPBr$_2$ at different wavelengths. For ZnDPPBr and ZnDPPBr$_2$, faster tendency to saturation of $\sigma_T-\sigma_0$ can be caused by a larger $K$ compared with ZnDPP, which indicates that they have a stronger association with pyridine than ZnDPP. The agreement between the experimental data and the fitting curves seems to support the association model. The red-shift of linear absorption band can arise from a destabilization of the highest occupied molecular orbital (HOMO) with little effect on the lowest unoccupied molecular orbital (LUMO) due to a flow of charge from the axial ligand to the porphyrin ring through the zinc ion [27]. Therefore, the addition of pyridine to zinc porphyrin can cause a destabilization of ground state, but has little effect on excited states. We believe that this is why there is a major drop in linear absorption whereas $\sigma_T$ almost remains unchanged when the complex Py:Por is formed.

4. Conclusion

In summary, it is feasible for a fine-tuning of NLA in a large range shown in Fig. 3, and we can easily realize a flexible alteration from a positive NLA (RSA) to a negative NLA (SA) or a reverse alteration at 532, 542 and 552 nm, based on the bromination of zinc diphenylporphyrins and the weak interaction between zinc porphyrins and pyridine. Compared with modifying molecular structures of conventional organic materials, the weak intermolecular interaction of supramolecular porphyrins or other supramolecular materials has another advantage that it can be realized more easily and flexibly. In applications of NLO materials, such as optical limiting, optical switching, etc, a fine-tunable nonlinear response should be more useful, and it makes designs of NLO devices more convenient.

With the rapid development of supramolecular chemistry, more means using weak interaction will be utilized to control and tune optical nonlinearities of materials, which may be not easy or even impossible for traditional molecular chemistry. Besides absorption bands, tuning of polarization, polarizability, and extent of charge transfer in supramolecular system will be expected to lead to a change of other optical nonlinearities, such as nonlinear refraction and two-photon absorption. Even we expect to use optical nonlinearities to characterize supramolecular system. Supramolecular materials have demonstrated better tailorable optical nonlinearities than conventional organic NLO materials. Therefore, we think that supramolecular porphyrins are strong candidates for future NLO materials.

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