



## Modulation of internal conversion rate and nonlinear absorption in *meso*-tetraphenylporphyrins by donor/acceptor substitutes



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### ABSTRACT

*Meso*-tetraphenylporphyrin (TPP), (*meso*-tetrakis(4-cyanophenyl)porphyrin [TPP(CN)<sub>4</sub>]) and (*meso*-tetrakis(4-methoxyphenyl)porphyrin [TPP(OMe)<sub>4</sub>]) are synthesized. The donor methoxy substitute (OMe) and acceptor cyano substitute (CN) are introduced into TPP in order to examine their influence on the photophysical properties of TPP. The nonlinear absorption properties of these three porphyrins are studied using open-aperture Z-scan and time-resolved pump-probe techniques in picosecond and nanosecond regimes, and the results are elucidated successfully by a five-level model. As compared to TPP, TPP(OMe)<sub>4</sub> exhibits an accelerated internal conversion from S<sub>1</sub> to S<sub>0</sub> state (0.02 ns), and S<sub>1</sub> to T<sub>1</sub> state (0.03 ns). Moreover, a changeover from saturable absorption to reverse saturable absorption is observed in TPP(OMe)<sub>4</sub> in the ps regime. Whereas the nonlinear absorption behavior of TPP(CN)<sub>4</sub> is similar to that of TPP. The results imply that these two substituents, especially the OMe group, could modulate the photophysical properties of TPP, which may provide a useful option for porphyrin-related applications.

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## 1. Introduction

Porphyrin and its derivatives are attractive nonlinear optical materials due to their fast response time, large nonlinear susceptibilities and also comparatively low fabrication costs [1–9]. In addition, the macrocyclic structure and chemical reactivity in porphyrins can offer architectural flexibility and facilitate the tailoring of chemical, physical and optoelectronic parameters [10,11]. Hence porphyrins are important in the development of photonic and optoelectronic technologies [5,12,13].

Simple symmetric porphyrin *meso*-tetraphenylporphyrin (TPP) and its derivatives are one category of the whole porphyrins system. TPP was first studied in 1985 [14], and shows a typical reverse saturable absorption (RSA). The photophysical response of TPP could be improved or tuned by insertion of different metals in the porphyrin core or by addition of suitable substituents (both at *meso*- and  $\beta$ -positions), or by proper structural modification [15–25]. For grafting peripheral substituents, when new Zn(II) tetraphenylporphyrin (ZnTPP) derivatives was functionalized with electron-rich d<sup>6</sup>-transition metal alkynyl complexes at their periphery, a remarkably large effective two-photon absorption (TPA) cross-sections in the visible range for these compounds can

be observed [16]. The second-order molecular hyperpolarizabilities of heteroleptic phthalocyanine (Pc) and TPP triple decker compounds bridged by samarium are found to be an enhancement of about three orders of magnitude as compared to metal-free Pc and TPP [26]. By structural modification, an analogue of TPP with one pyrrole ring inverted named N-confused tetraphenylporphyrin (NCTPP) is designed and studied by a series of spectroscopic measurements [18–20]. The S<sub>1</sub> state lifetime of NCTPP is extracted to be 1.75 ns, which is much shorter than that of TPP (12.2 ns) [27]. The inverted pyrrole endowed NCTPP an accelerated rate of internal conversion.

It can be seen that many studies has focused on the synthesis and photophysical characterization of TPP compounds. Understanding the basic optical nonlinearities of these tetrapyrrolic derivatives is of considerable interest due to their widespread application potential [28–30]. The most investigated photophysical property is RSA due to its potential use in pulse sensors or in optical limiting devices for protecting sensitive optical components or human eyes from laser-induced damage [7,10,16]. RSA in porphyrin materials is usually induced by two photon absorption or excited-state absorption [31–34]. Saturable absorption (SA) as well as switch between SA and RSA are also observed in porphyrins [35,36], which is useful for mode locking, laser pulse compression, and laser amplification [37]. In this article, cyano (CN) and methoxy (OMe) substitutes as the typical acceptor and donor groups

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are introduced into TPP to synthesize the *meso*-tetrakis(4-cyano phenyl)porphyrin [TPP(CN)<sub>4</sub>], and *meso*-tetrakis(4-methoxyphenyl)porphyrin [TPP(OMe)<sub>4</sub>], respectively. The nonlinear absorption properties of these three porphyrins are investigated using Z-scan techniques with 532 nm, 21 ps and 532 nm, 6 ns laser pulses, respectively. Moreover, their excited-state dynamics are measured using time-resolved pump–probe technique at 532 nm with 21 ps pulses. In addition, density functional theory (DFT) calculations are carried out to further examine the molecular orbital configurations of these molecules. The results could afford advantages for further exploitation of TPP derivatives for particular applications.

## 2. Experimental

### 2.1. Sample preparation

Following the synthesis method of Capitosti et al. [38], *meso*-tetraphenylporphyrin (TPP) and its two derivatives (*meso*-tetrakis(4-cyanophenyl)porphyrin [TPP(CN)<sub>4</sub>], and *meso*-tetrakis(4-methoxyphenyl)porphyrin [TPP(OMe)<sub>4</sub>]) are synthesized. The structures of these three molecules are presented in Fig. 1.

### 2.2. Nonlinear measurements

TPP, TPP(CN)<sub>4</sub> and TPP(OMe)<sub>4</sub> were measured by open aperture Z-scan technique with a nearly top-hat beam of 532 nm in both picosecond (21 ps, full width at half maximum, FWHM) and nanosecond (6 ns FWHM) regime. The excited state dynamics of these compounds are also measured using pump–probe technique with a Gaussian beam at 532 nm with the pulse duration of 21 ps. The laser system of 21 ps pulses was a Q-switched Nd:YAG laser (EKSPLA, PL2143A) with a wavelength of 532 nm. The laser system for nanosecond Z-scan was a Continuum Surelite Q-switched Nd:YAG 532 nm laser with a pulse width of 6 ns. The Z-scan technique was arranged with a 5 mm-radius aperture before a convex lens with a 400-mm focal length for the ps Z-scan, and a lens with a 300-mm focal length for the ns Z-scan [39], respectively. The repetition rate of the laser pulses is 10 Hz for both ps and ns Z-scan experiments. The sample solution placed in a 2 mm-thickness quartz cell was moved along Z-axis with respect to the focal lens by the translation stage, which was controlled by a computer. In our Z-scan experimental arrangements, a small part of the input beam was split by a glass plate for pulse to pulse energy fluctuation monitoring, which probed together with the transmitted beam of the sample by the same type energy detectors (Laser Probe Inc., RjP-765a). Both energy detectors were linked to an energy meter (Laser Probe Inc., Rj-7620 ENERGY RATIONETER) and transmit the data to a computer for processing. The picosecond pump–probe arrangement and conditions in our experiment are the same with

that described by Yang et al. [40]. The molecular orbital configurations are provided for these porphyrins using DFT (B3LYP) method.

## 3. Results and discussion

### 3.1. UV–visible spectra

Fig. 2 shows the UV–visible spectra of TPP, TPP(CN)<sub>4</sub>, and TPP(OMe)<sub>4</sub> in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). The linear absorption spectra of these molecules all exhibit a strong Soret absorption band near ultraviolet region, and a series of weak Q-bands in the visible spectral region, which are typical characters of porphyrins [7,20,32]. The Soret absorption bands of TPP, TPP(CN)<sub>4</sub>, and TPP(OMe)<sub>4</sub> all center around 420 nm, and the Q-bands are located at 500–700 nm, respectively.

### 3.2. Open-aperture Z-scan measurements

The nonlinear absorption of the three samples measured by the Z-scan technique with 21 ps pulses are shown in Fig. 3(a) and (b). Fig. 3(a) gives the normalized transmittance of the open-aperture (OA) Z-scan results of TPP and TPP(CN)<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> at a concentration of  $8.14 \times 10^{-5}$  M with an input peak intensity 1.1 GW/cm<sup>2</sup>. As the sample is brought closer to the focus ( $Z = 0$ ), the transmittance of the sample decreases and reaches the minimum value at the focus, which displays a typical reverse saturable absorption (RSA). Due to the effect of the RSA, the transmittance of TPP and TPP(CN)<sub>4</sub> at the focus drops down to 84.6% and 79.3%, respectively. Whereas the TPP(OMe)<sub>4</sub> shows an entire different nonlinear absorption behavior, which is displayed in Fig. 3(b). When the input intensity is 0.2 GW/cm<sup>2</sup>, the Z-scan curve shows an enhanced

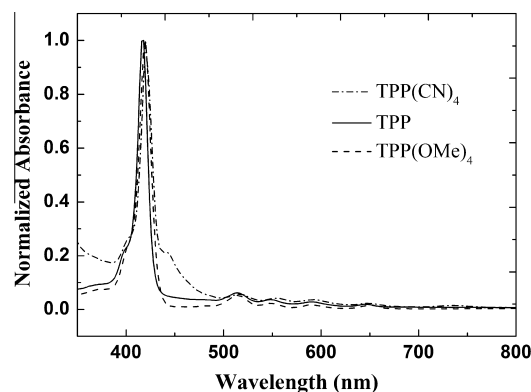


Fig. 2. The UV–visible spectra of TPP, TPP(CN)<sub>4</sub>, and TPP(OMe)<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>.

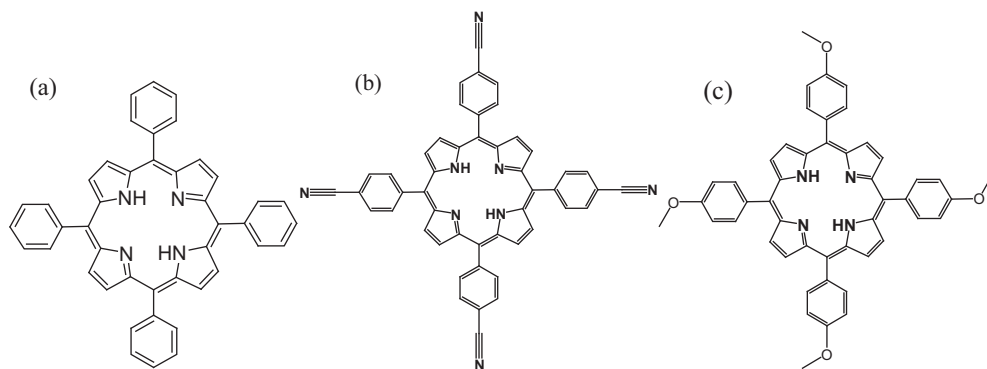


Fig. 1. The molecular structures of (a) TPP, (b) TPP(CN)<sub>4</sub>, and (c) TPP(OMe)<sub>4</sub>.

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