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Solvent effects on the fluorescence and effective three-photon absorption of a Zn(II)-[meso-tetrakis(4-octyloxyphenyl)porphyrin]

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ABSTRACT

The fluorescence and effective three-photon absorption (3PA) properties of Zn(II)-[meso-tetrakis(4-octyloxyphenyl)porphyrin] (labeled Zn(II)-porphyrin) dissolved in three different polar solvents were systematically investigated. The electrochemical and photophysical properties of Zn(II)-porphyrin were investigated by ^{1}H NMR spectra, IR spectra, mass spectroscopy, and electronic absorption spectra. The fluorescence emission of Zn(II)-porphyrin in three different solvents excited at the wavelengths of 420 nm (Soret band) and 550 nm (Q-band) were analyzed. By performing Z-scan experiments with femtosecond laser pulses at a wavelength of 800 nm, the effective 3PA process of Zn(II)-porphyrin in three different solvents was observed and the underlying mechanism was discussed in detail. It is found that the fluorescence spectra slightly depend on the polarity of the solvent. Interestingly, the effective 3PA properties of Zn(II)-porphyrin strongly depend on the solvent polarity. The lower the solvent polarity is, the larger effective 3PA cross-section is. Low polar solvents are beneficial to applications of Zn(II)-porphyrin in optical limiting, photodynamic therapy, etc.

1. Introduction

Porphyrin and its derivates widely exist in nature and endow with excellent photophysical properties induced by the 18π-electron conjugated aromatic system. Porphyrins have tunable photophysical properties owing to flexible molecule structures that could be modulated by substituting the peripheral positions, changing the central atom, altering the degree of electronic conjugation of macrocycle, and attaching ligands to the central atom. Blau et al. [1] firstly reported the reverse saturable absorption in tetraphenylporphyrins under the excitation of picosecond laser pulses at 532 nm. Since then, researchers have investigated the nonlinear optical properties of a variety of porphyrin derivates, such as porphyrin arrays, porphyrin dimers, self-assemble porphyrins, and expanded porphyrins [2–5]. Due to outstanding optical nonlinearities, porphyrin and its derivates have the potential applications in optical limiting, fluorescence microscope, 3D microfabrication, photodynamic therapy, and so on [6–9].

As well known, three-photon absorption (3PA) refers to the simultaneous absorption of three identical photons, promoting an electron from the ground state of a system to an excited state by virtual intermediate states. This process is called a one-step 3PA. Under the excitation of intense laser pulses, however, a two-photon absorption (2PA) process may considerably increase molecular populations in the excited state, and subsequently, the cascaded one-photon absorption (1PA) from an excited state may create an equivalent stepwise (2PA:1PA) 3PA process. This two-step 3PA is an effective 3PA process of 2PA-induced excited-state absorption (ESA) [10]. The effective 3PA process has been observed in many materials, including charge-transfer salts [11], nanocomposites [12], and organic molecules [13]. Up to now, many researchers have reported 2PA properties of porphyrin derivates [14]. However, studies on effective 3PA properties of porphyrin derivates are relatively less [15].

The chemical environment plays a significant role in photophysical properties of organic materials. It is found that the solvent effect has a great impact on nonlinear optical properties of organic materials with different molecule structures, such as D-π-A [16], D-π-A-π-D [17], A-π-π-π-A [18], and symmetric charge-transfer molecule [19]. Moreover, strong solvent dependence has also been observed in the 2PA process [20], reverse saturable absorption [21], and 3PA process [18,19]. On the other hand, due to the diverse molecule structures of porphyrin derivates, there are rich

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mechanisms of solvent effects on their optical nonlinearities. For instance, Kimball et al. [22] demonstrated that the 2PA effect of zinc tetrabenzoporphyrin compounds was severely weakened by high polar solvents in nanosecond regime arising from the modified intersystem crossing rate, resulting in the decrease of optical limiting ability. Zawadzka et al. [21] found that optical limiting abilities of two series of 5,10-A_2B_2 porphyrins could be improved by the enhancement of the reverse saturable absorption induced by the nonlinear scattering of solvents. To exploit the 3PA applications of porphyrin derivates, it is desirable to fully understand solvent effects.

Based on above strategies, we synthesized Zn(II)-[meso-tetrakis (4-octyloxyphenyl)porphyrin] (Zn(II)-porphyrin). A series of characterization methods, including ^{1}H NMR spectra, mass spectra, IR spectra, and electronic absorption spectra, were performed to analyze the electrochemical and photophysical properties of the Zn (II)-porphyrin. Three different polar solvents were chosen to dissolve Zn(II)-porphyrin for investigating solvent effects on fluorescence and effective 3PA properties. In particular, the influence of solvent effects on the effective 3PA cross-sections of Zn(II)-porphyrin was systematically studied by the femtosecond-pulsed Z-scan measurements at different levels of laser intensities.

2. Experimental section

2.1. Material synthesis and characterization

In order to obtain Zn(II)-porphyrin, as a precursor, a meso-tetrakis(4-octyloxyphenyl)porphyrin was firstly synthesized according to previously reported methods [23]. Briefly, 4-octyloxybenzaldehyde, pyrrole, and 4-iodobenzaldehyde were added in propyl acid; based on the established Adler-Longo method [24], meso-tetrakis(4-octyloxyphenyl)porphyrin was determined. Then this porphyrin derivate was purified and isolated by silica-gel (Merck, Kieselgel 60, 200–300 mesh) column chromatography. Note that all the reagents and solvents were used as received from commercial suppliers.

The synthetic procedure of Zn(II)-porphyrin is shown in Fig. 1, a solution of $Zn(OAc)_2{\cdot}2H_2O$ (10 mg) in ethanol was added to the solution of meso-tetrakis (4-octyloxyphenyl)porphyrin (20 mg) in $CHCl_3$ and stirred overnight at room temperature under N_2 in the dark. After removing the volatiles in vacuo, the residue was chromatographed on silica-gel column with $CHCl_3$/petroleum ether (3:7) as eluent followed by recrystallization from $CHCl_3$/MeOH, affording the product as a purple solid (18 mg, 85%).

The synthesized Zn(II)-porphyrin was confirmed and investigated by various spectroscopic methods as follows. ^{1}H NMR spectra were recorded on a Bruker AVANCE III 600 MHz in $CDCl_3$. Spectra were referenced internally by using the residual solvent resonance (δ = 7.26 for $CDCl_3$) relative to $SiMe_4$. The IR spectrum was monitored in KBr pellet with 0.09 cm^{-1} resolution using a NEXUS670 spectrometer. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high resolution mass spectrometer with α-cyano-4-hydroxycinnamic acid as matrix. Electronic absorption and linear transmittance spectra were detected with a Shimadzu UV-3600 spectrophotometer. Fluorescence emission spectra were performed with a RF-5301PC spectrofluorophotometer.

It is confirmed that the Zn(II)-porphyrin has been successfully synthesized by ^{1}HNMR and mass spectrometry. ^{1}H NMR (300 Hz, 25 °C, TMS): δ, 0.96 (t, 12H, CH_3), 1.48 (m, 32H, $CH_2CH_2CH_2CH_2$), 1.66 (m, 8H, CH_2), 1.98 (m, 8H, CH_2), 4.26 (t, 8H, OCH_2), 7.31 (AA′BB′, 8H, ArH), 8.18 (AA′BB′, 8H, ArH), 8.91 (m, 8H, β-pyrrole); MS (MALDI-TOF): m/z = 1191 [calcd. for $C_{76}H_{92}N_4O_4Zn$ $[M^{+3}]^+$ 1191].

2.2. Nonlinear optical characterization technique

To investigate the solvent effects on the nonlinear optical properties of the synthesized Zn(II)-porphyrin, we chose dichloromethane (DCM), trichloromethane (TCM), and bromobenzene (BB) as solvents due to the following three facts: (i) the Zn(II)-porphyrin is highly soluble in these three solvents; (ii) the solvent polarity increases in the order of BB < TCM < DCM; and (iii) all three solvents have negligible nonlinear absorption effects under the excitation of femtosecond laser pulses at 800 nm, as we will demonstrate in Fig. 5. The Zn(II)-porphyrin was respectively dissolved in DCM, TCM, and BB with the same concentration of $d_0 = 2.9 \times 10^{-4}$ M. We prepared three organic solutions with relatively diluted concentration because the molecular aggregation effect is very weak and can be neglected. Three Zn(II)-porphyrin solutions, labeled as ZnPor-DCM, ZnPor-TCM, and ZnPor-BB, were contained in 1-mm-thick quartz cell for both the linear and nonlinear optical measurements. The linear transmissions of ZnPor-DCM, ZnPor-TCM, and ZnPor-BB samples at the wavelength of 800 nm were measured to be 90%, 90%, and 89% by optical transmittance measurements, respectively.

The nonlinear optical measurements of three Zn(II)-porphyrin solutions were conducted by the single-beam Z-scan technique at the wavelength of 800 nm with a pulse duration of 170 fs and a repetition rate of 1 kHz. The laser pulses, which have a near-Gaussian temporal and spatial profiles, were generated by a Ti:sapphire regenerative amplifier (Coherent Inc.). The laser beam was focused by an achromatic lens with a focal length of 150 mm, producing the waist radius at the focus $\omega_0 = 15$ μm. To carry out Z-scan measurements, the sample was scanned across the focus along the optical axis using a computer-controlled translation stage, while the transmitted pulse energies were completely monitored by a detector, obtaining the open-aperture Z-scan trace. The optical limiting experiments, which were performed by tuning the input pulse energies and by detecting both the incident and the transmitted pulse energies simultaneously, were carried out with the same measurement system used for the Z-scan experiments except that the sample was fixed at the focal plane. Besides, the Z-scan measurement system was calibrated by measuring 2PA

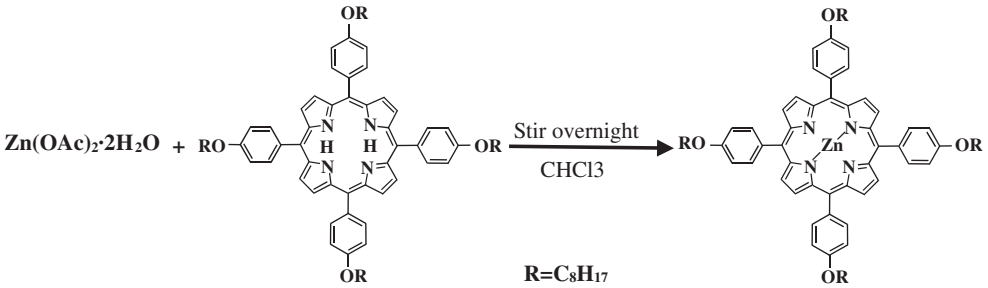

Fig. 1. Synthetic procedure of Zn(II)-porphyrin.