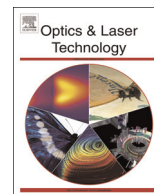




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# Ultrafast dynamics of excited state of phenoxy-phthalocyanines in solution



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## ABSTRACT

Ultrafast dynamics of the excited state of 2,9,16,23-phenoxy-phthalocyanine (Pc1) and 2,9,16,23-phenoxy-phthalocyanine-zinc (Pc2) has been investigated using femtosecond transient absorption (TA) and time-resolved fluorescence (TRFL) techniques. The observed dynamics of femtosecond TA and TRFL experiments are similar, which demonstrated the intrinsic properties of the excitation and the relaxation processes in both kinds of phthalocyanines with two decay components. A multi level model has been proposed to explain the photophysical processes after Soret-band excitation. The results show that the fast decay component dynamics comes from the intramolecular vibrational relaxation, the slower ones from the internal conversion. The samples are expected to be a potential candidate for optical applications and photodynamic therapy.

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## 1. Introduction

Phthalocyanines (Pcs) and metallophthalocyanines (MPcs) have aroused intense research interest since the first synthesis in 1907 [1]. Owing to their high stability under intense heat and light, the properties of diversity, coordinating easily with metal element, and unique 18  $\pi$ -electron delocalization system. These compounds exhibit large nonlinear susceptibilities, which lead to potential applications in a variety of new technology fields, including nonlinear optics [2], electrochromic display devices [3], liquid crystals [4], and so on. Pcs are promising nonlinear optical material with high dielectric constant, fast response time (femtosecond scale), easily integrating into optical components and intense absorption in the near-IR region [5–7], which lead to their potential applications in photonic [8,9], data processing [10], optical switching [11], optical limiting [12,13], photodynamic therapy (PDT) [14,15]. In particular, zinc phthalocyanine complexes have attracted much interest because of their intense absorption in the red region of visible light, appreciably long triplet lifetimes (microsecond scales), enhanced fluorescence and singlet oxygen producing properties, which prompted their roles in the detection and treatment of tumors in PDT [16] and enhanced fluorescence

imaging performance of hydrophobic colloidal ZnO nanoparticles by a facile method [17]. The MPcs can be modulated by changing the peripheral and non-peripheral substituents on the ring in addition to changing the central metal and the axial ligands. Many photochemical and photophysical properties of molecules depend on the kinetics of excited-state processes after the photon absorption. Therefore, it is important to understand how excited states behave as a function of time. The conventional view of this temporal evolution indicates that photoreactivity is largely dictated by the characteristics of the lowest energy excited state of a molecule. Thus, higher energy excited states are presumed to convert to this lowest energy state and remove any functional role from photochemical and photophysical transformations. The nonlinear optical materials modified from phthalocyanine are increasingly being developed and researched.

In a previous report, we studied the synthesized 2,9,16,23-phenoxy-phthalocyanine (Pc1) and 2,9,16,23-phenoxy-phthalocyanine-zinc (Pc2) using the reported methods [18]. Moreover, we have investigated some interesting third-order nonlinear optical (NLO) properties of Pc1 and Pc2 at 800 nm using femtosecond pulses and revealed the singular nonlinear absorption properties and large NLO coefficients [19]. Several other groups have also demonstrated their potential applications, such as two-photon imaging, 3D-optical memory, and ultrafast switches. Two-photon absorption (TPA) was the dominant mechanism in experiment, but one cannot rule out the presence of excited state absorption from first excited singlet state ( $S_1$ ) to second excited singlet state ( $S_2$ )

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[20]. The optical limiting properties of Pc1 and Pc2 solution were studied for different power of incident laser. The laser damage threshold is defined here to be the intensity necessary to cause a permanent measurable change in the sample transmission measurements [21]. However, the relaxation characteristics of molecules between excited state and vibration level caused by the multiphoton absorption has not been reported.

In this paper, we will elucidate processes responsible for fast dynamics of phthalocyanines occurring on the time scale from femtoseconds to nanoseconds monitored by the pump-probe transient absorption spectroscopy when they are induced by femtosecond laser pulses centered at 800 nm and 400 nm, corresponding to the absorption maxima of the Soret band and the Q-band, respectively. Moreover, the relaxation processes of the fluorescence emission state were studied by time-resolved fluorescence (TRFL) experiment. The result shows that the first decay time is about several picoseconds for two polymers, and the slow relaxation process has the lifetime longer than hundred picoseconds. The fast decay process observed in two experiments is assigned to the intramolecular vibrational relaxation and the slow decay time is related to the internal conversion.

## 2. Materials and experiment

The Pc1 and Pc2 are hydrogen or zinc connected with four ligands by nitrogen bridges. Especially Pc1 and Pc2 are two-dimensional (2D) large molecules [21], and their molecular weights are 883u and 946u, respectively. In our experiment, Pc1 and Pc2 are synthesized using mild reaction coordination method. The proton nuclear magnetic resonance of the two synthesized phthalocyanines compounds has been reported in Ref. [18]. The results show that the number and relative intensities of the peaks in spectra, and splittings are identical with the target product (Pc1, Pc2) structure. They have been presented in Fig. 1(a).

All the experiments were performed with samples dissolved in N,N-dimethylformamide (DMF) solutions. The solution has a concentration of  $4.53 \times 10^{-4}$  mol/L. The linear absorption spectra

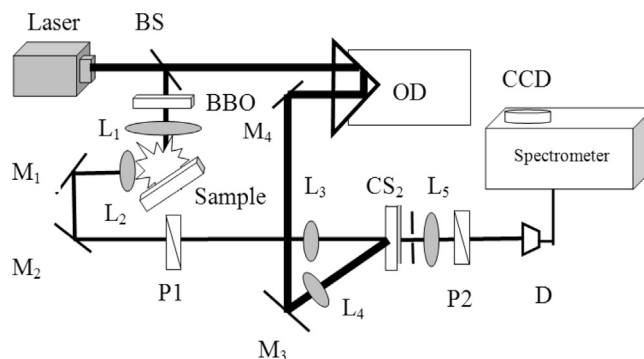


Fig. 2. Schematic diagram of the time-resolved fluorescence measurement system. BS, beam splitter; M1–4, mirrors; L1–5, lens; OD, optical delay; and D, detector.

of Pc1 and Pc2 in ground state ( $S_0$ ) were measured with a UV-visible spectrometer (HITACHI U-3310), and the results are shown in Fig. 1(b). For both Pcs there are two strong broad bands: the B-band ( $\pi \rightarrow \pi^*$ ) in the near-UV ( $\lambda_{\max} = 314$  and 298 nm for Pc1 and Pc2, respectively), and the Q-band ( $n \rightarrow \pi^*$ ) in the red ( $\lambda_{\max} = 712$  nm for Pc1 and 704 nm for Pc2). To get a deep insight into the mechanisms of energy dissipation in phthalocyanines, we have monitored the excited-state dynamics in DMF solvents upon excitation at 800 nm, which promotes the  $S_0(a_{1u}) \rightarrow S_1(e_0)$  transition in the Q-band. The pumping at 400 nm excites the transition  $S_0(a_{2u}) \rightarrow S_1(e_0)$  and/or the  $S_n$  state, as the inset show in Fig. 1(b).

The time-resolved fluorescence experiment is based on the optical Kerr-gate technique [22], which has been described in detail elsewhere [23]. Briefly, the laser pulse of 100 femtoseconds (fs) duration at 800 nm was divided into two beams by a beam splitter (BS). After passing an optical delay (OD) line, the first part of the 800 nm beam was used as a gate beam to open the Kerr gate through photoinduced birefringence of Kerr material, while the second part of the 800 nm beam was used as the excitation pulse of a sample, or being frequency-doubled by a BBO crystal in advance, as shown in Fig. 2. The collected fluorescence beam by the lens was set either parallel or perpendicular to that of the incident

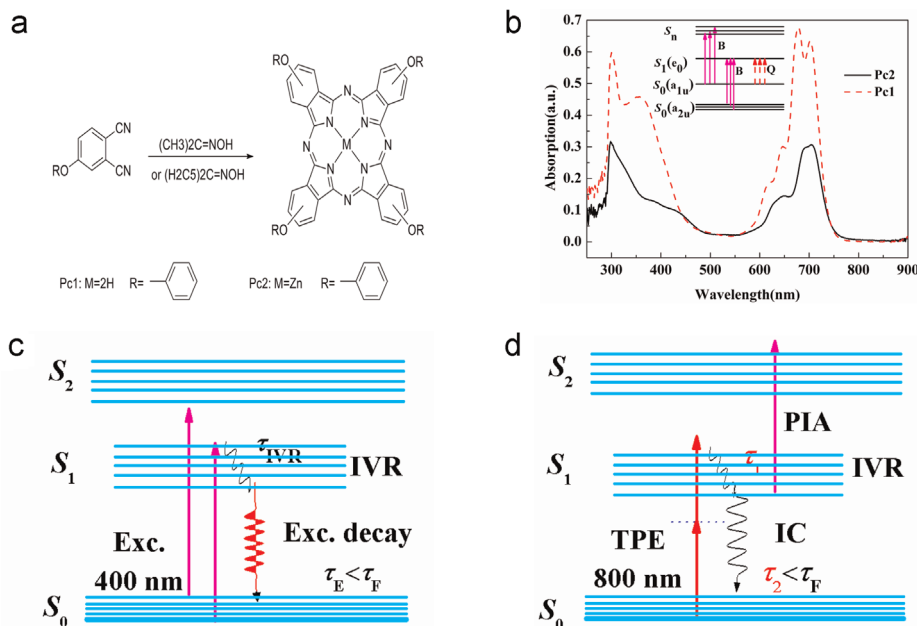


Fig. 1. (a) Synthesis of phthalocyanine compounds; (b) the linear absorption spectra of samples in solution; (c) excitation of the excited electronic states pumped with the pulses at 400 nm; (d) energy level diagram of Pcs depicting the various relaxation times from different excited states: femtosecond pulses, focused pump 800 nm and probe data 400 nm. IVR: Intramolecular Vibrational Relaxation ( $\tau_{\text{IVR}}$  or  $\tau_1$ ); PIA: Photo-Induced Absorption; IC: Internal Conversion ( $\tau_2$ ); TPE: Two Photon Excitation;  $\tau_E$ : Exc. Decay time;  $\tau_F$ : Fluorescence lifetime (7.5–18.5 ns) [21], respectively.

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