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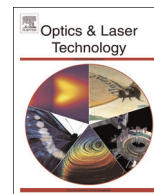


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Ultrafast dynamics of excited state of phenoxy-phthalocyanines in solution

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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 π -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 4.53×10^{-4} mol/L. The linear absorption spectra

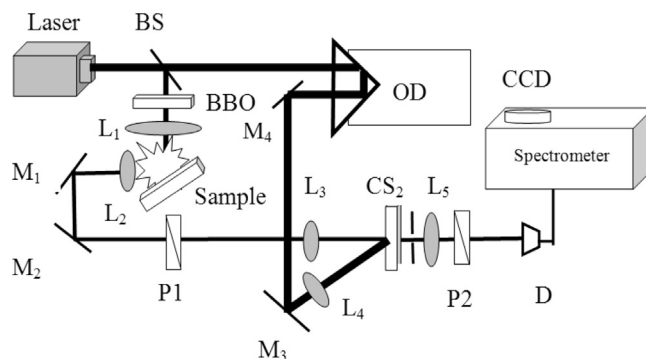


Fig. 2. Schematic diagram of the time-resolved fluorescence measurement system. BS, beam splitter; M1–4, mirrors; L1–5, lens; OD, optical delay; and D, detector.

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 $S_0(a_{1u}) \rightarrow S_1(e_g)$ transition in the Q-band. The pumping at 400 nm excites the transition $S_0(a_{2u}) \rightarrow S_1(e_g)$ 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

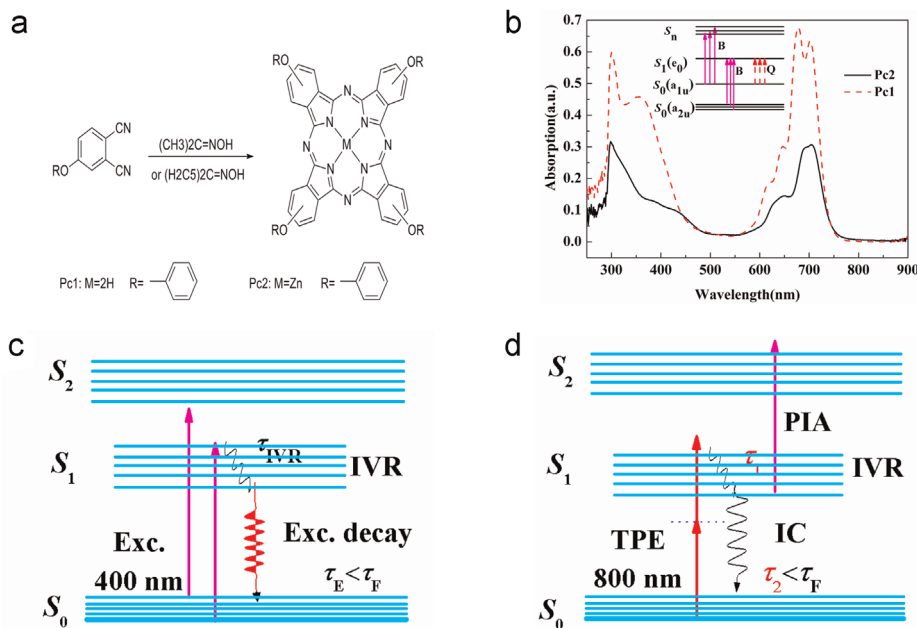


Fig. 1. (a) Synthesis of phthalocyanine compounds; (b) the linear absorption spectra of samples in solution; (c) excitation of the excited electronic states pumped with the pulses at 400 nm; (d) energy level diagram of Pcs depicting the various relaxation times from different excited states: femtosecond pulses, focused pump 800 nm and probe data 400 nm. IVR: Intramolecular Vibrational Relaxation (τ_{IVR} or τ_1); PIA: Photo-Induced Absorption; IC: Internal Conversion (τ_2); TPE: Two Photon Excitation; τ_E : Exc. Decay time; τ_F : Fluorescence lifetime (7.5–18.5 ns) [21], respectively.

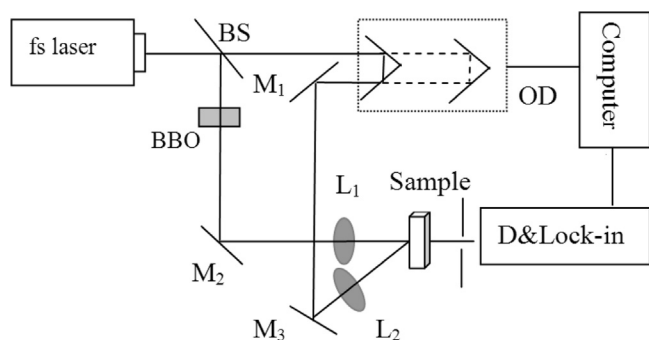


Fig. 3. Schematic diagram of two-color pump-probe experiment. BS, beam splitter; M1–3, mirrors; L1–2, lens; and D, detector.

beam by a polarizer (P1). Another polarizer (P2) with orthogonal polarization to P1 was placed behind the sample to study the polarization effect. The fluorescence signals were collected in the direction perpendicular to the incident excitation beam by a spectrum analyzer.

The two color femtosecond pump-probe experiments were also carried out using a Ti:sapphire laser system centered at 800 nm. This experimental technique has been reported in some papers [24,25]. Briefly, a Ti:sapphire laser system, supplied by Thales Optronique SA, Elancourt, France, provides the pulses of about 100 fs. The experiment was performed at peak intensity of $7.27 \times 10^{13} \text{ W/m}^2$. The fundamental output was split into pump and probe beams by a beam splitter. The pump pulses of 400 nm were generated for exciting of the samples by frequency-doubling of one part of the amplifier output at 800 nm in a 0.5 mm thick BBO crystal, as shown in Fig. 3. The other part of the amplifier output was used to generate the white light continuum (470–1000 nm) probe through a sapphire plate with the thickness of 2 mm. By using the OD line to adjust the optical path of pump light, two beams can be focused on the same point on samples. After absorbing the pump photon, the molecules on the ground state will jump to excited states. Moreover, the particles on each energy state will absorb the probe light and jump. The sample absorption for the probe light is not only related to the absorption cross section and particles numbers of ground state, but also related to those of the excited states. Once the optical path of pump light arrives the sample before the probe light with a time difference of Δt , the particles excited by pump light will relax to the other excited states (the vibration levels). In this way, both the ground and the excited states contribute to the probe light absorption. Therefore, for the three cases mentioned above, the light intensity through the sample undergoes different rules, which also reflects the relaxation process of the particle number on the excited states and the dynamic information of the sample. The time-

resolved transient absorption spectra were recorded using a femtosecond pump-probe spectrometer, as described in other works [26,27]. All experiments were performed at room temperature.

3. Results and discussion

Fig. 4 shows the TRFL dynamics excited by 400 nm femtosecond pulses and detected at the peak wavelength of fluorescence emission of Pc in DMF. The measured TRFL results of two Pc can be well fitted with a biexponential decay function. Fig. 4 shows the normalized TRFL results for two Pcs in DMF. The biexponential expression fit $I(t) = \alpha_1 \exp(-(t-t_0)/\tau_1) + \alpha_2 \exp(-(t-t_0)/\tau_2)$ are in good agreement with the experimental results. Again, two decay processes can be clearly seen from Fig. 4, where a fast decay process shows a time constant of 12 ps and 16 ps, and a slow component with a time constant of 116 ps and 124 ps. There are two kinds of samples, in which a fast process was resulted from the exciton migration and the long decay time reflects the slow recombination process of the relaxed excitons with a pair of wider separated charges. Yan et al. [28] reported similar data in modified phthalocyanines, where the p-HPcZn and p-HPcCo were excited by femtosecond pulses at 400 nm. In their case, these molecules experienced vibrational relaxation to the bottom of the first excited state, which then rapidly converted to the low-lying charge-transfer state. By analyzing the lifetimes of the two processes, we proposed a three-level system to explain the biexponential decay in Pc solution. Singlet excited state S_1 was populated initially upon photon excitation at 400 nm. Photo-excited electrons can decay by radiative (S_1 to ground state transition). The fast component is attributed to the intramolecular vibrational relaxation (IVR) in the S_1 states of these molecules, while the slow component constant can be assigned to the radiative decay (or internal conversion IC) from S_1 to ground state, as shows in the Fig. 1(c). Jarota et al. [29] reported similar excitation of the excited electronic states pumped with the pulses at 360 and 677 nm in metal complexes of tetrasulphonated phthalocyanines.

To better understand the dynamics of the excited state, we performed ultrafast two-color pump-probe experiment to investigate the dynamics of singlet state S_1 in monomer Pc1 and Pc2 solution. The fs laser wavelength was tuned to 800 nm, nearly in resonant with the Q-band absorption of both Pc1 and Pc2. In pump-probe experiment, the molecules in S_1 state have a larger absorption at 800 nm than in the ground state, which induce a transient absorption signal. The excitation-transfer processes, including the nonradiative process from S_1 state directly to the ground state and the energy transfer between S_1 state and internal conversion transition happens in few ps scale, leading to the fast decay component in pump-probe dynamics. The slow decay component corresponds to the evolution of the excitation within

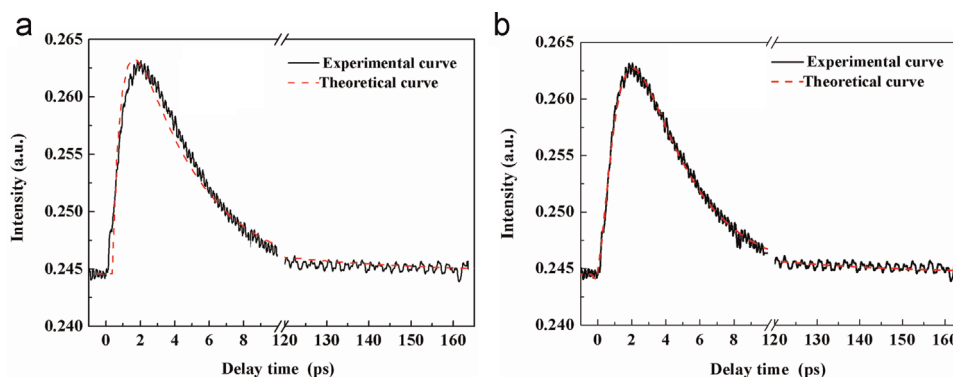


Fig. 4. Results of TRFL experiments for Pc1 (a) and Pc2 (b) solutions in DMF, respectively.

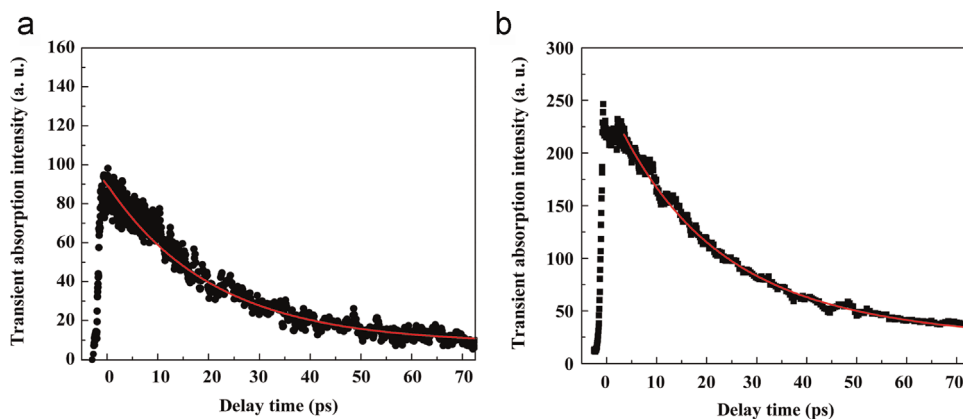


Fig. 5. Result of two-color pump-probe for Pc1 (a) and Pc2 (b) solutions in DMF, respectively.

internal conversion transition state. Fig. 5 shows the results obtained from the two-color pump-probe experiment. The pump beam at 800 nm could effectively excite the molecules via linear absorption, while the probe beam was at 400 nm. By using the biexponentially decay processes in combination with the deconvolution of the instrumental response function to fit the experimental traces, we obtain the values of decay times τ_1 and τ_2 for polymer solutions. The transmitted probe data was fitted using the equation $\alpha_1 \exp(-(t-t_0)/\tau_1) + \alpha_2 \exp(-(t-t_0)/\tau_2)$. In DMF solution, the τ_1 and τ_2 for Pc1 are determined to be 17 and 147 ps, respectively, while for Pc2 in DMF solution, the short decay time is 8.6 ps and the long decay time is about 136.5 ps. The time constants are of the same order as those obtained by Howe and Zhang [30]. Comparing with the results obtained from the TRFL experiment, we attribute the fast decay process to the exciton migration and the slow decay to the recombination process of the relaxed excitons. Photo-excited electrons can decay by radiative (S_1 to ground state transition). The fast component is attributed to the IVR in these molecules, while the slow component constant can be assigned to the IC from S_1 to ground state, as shows in the Fig. 1(d). The longest time constants in the range of 150–500 ps have been assigned to the decay from S_1 to the ground state, as suggested by Howe and Zhang, because we have found dynamics occurring on a similar time scale as that in Ref. [30].

Fig. 6 shows the time-resolved differential TA spectra recorded following photoexcitation of Pc1 and Pc2 in DMF using 400 nm laser pulses, which excite the molecules to the S_2 state. The TA spectrum recorded at 0.2 ps delay time consists of two excited state absorption (ESA) bands, one in the 500–680 nm region and another in the 720–1000 nm region, as well as a negative absorption band (bleaching) in the 680–720 nm. The near

coincidence of the maximum between the negative absorption band and the Q-band absorption of Pc2 at 690 nm in this solvent suggests that the former band can be assigned to the bleaching due to depletion of population in the ground electronic state following photoexcitation, but not to the stimulated emission (SE).

4. Conclusions

In summary, we have measured the ultrafast dynamics of newly synthesized Pcs by using the fs laser spectroscopic techniques. Two phthalocyanines exhibit intense two-photon induced FL under the excitation of fs pulses at wavelength of 800 nm. The observed dynamics from the transient absorption and TRFL experiments are similar for the two decay components, and reflected the intrinsic properties of the excitation and the relaxation processes in these Pcs. Rate constants corresponding to different transitions happening via relaxation processes were determined. The fast decay process in two experimental dynamics can be attributed to the exciton migration and the slow decay component to the recombination process of the relaxed excitons. It is demonstrated that the fast decay component in the pump-probe experiment is caused by the relaxation process from the excited-state to the internal conversion transition state. The Pc and MPc based switches would be potentially useful in optical signal processing and photodynamic therapy.

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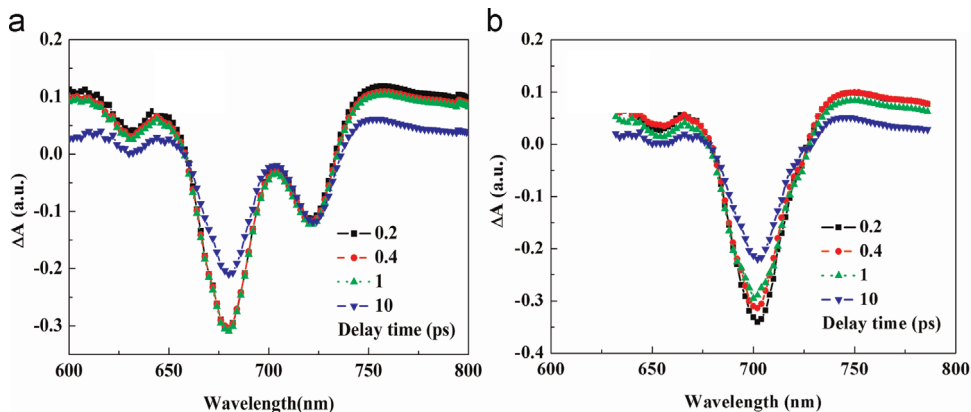


Fig. 6. Time-resolved TA spectra of Pc1 (a) and Pc2 (b) solutions in DMF, respectively.

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