

Ultrafast Excited State Dynamics of Modified Phthalocyanines: p-HPcZn and p-HPcCo

Yongli Yan,^{†,‡} Shan Lu,[§] Bo Li,^{†,‡} Rongyi Zhu,^{†,‡} Jiahong Zhou,[§] Shaohua Wei,[§] and Shixiong Qian^{*,†}*Physics Department and Surface Science Lab (National Key Lab), Fudan University, Shanghai 200433, P. R. China, and Jiangsu Engineering Research Center for Bio-medical Function Material, Nanjing Normal University, Nanjing, 210097, P. R. China**Received: March 27, 2006; In Final Form: July 11, 2006*

Two modified metallophthalocyanines (MPcs) containing sulfonic naphthoxy substituents were synthesized. The measurements of transient absorption and time-resolved photoluminescence were used to study the ultrafast response and excited state dynamics of two MPcs in dimethyl sulfoxide (DMSO) solution, which were predominantly in the monomeric form. Under excitation at 400 nm, these molecules experience vibrational relaxation to the bottom of the first excited state and then the excitation rapidly converts to the low-lying charge-transfer (CT) state and finally reaches the triplet states. Under excitation at 800 nm, they show a two-photon absorption character, and their excited state dynamics exhibit strong dependence on the probe wavelength. The main results with 400 nm pumping are similar to the results with 800 nm pumping. For p-HPcZn, weak two-photon photoluminescence was also observed with a lifetime of 52 ± 2 ps. A four-level model was used to illustrate the excited state dynamics of p-HPcZn, while a five-level model was suggested for p-HPcCo molecule.

Introduction

Phthalocyanines (Pcs) and metallophthalocyanines (MPcs) have received considerable attention over the past 2 decades since their first synthesis in 1907.¹ Owing to their unique 18 π -electron delocalization system and intense metal–phthalocyanine interaction, these compounds exhibit large nonlinear susceptibilities and fast response, which lead to potential applications in photonic,^{2–4} data processing,⁵ optical switching,⁶ optical limiting,⁷ and so on. Their structural stability and intense absorption in the near-IR region make phthalocyanines ideal candidates for photodynamic therapy (PDT).^{8–10} However, their large π -conjugation also leads to a strong stacking tendency in solution, which usually decreases their luminescence quantum yields, shortens their triplet state lifetime, and reduces their photosensitizing efficiencies. Because of their low fabrication costs, different kinds of modifications with improved optical properties can be easily performed via rational design, for example, adding different peripheral substitutions^{11,12} or binding different metal ions at the ring center.^{13,14} It has been shown that zinc helicenocyanine (ZnHc), where four helicense groups are fused with a phthalocyanine core through all-carbon linkages, exhibits a strong optical absorption covering most of the visible region. The electronic coupling of the groups to the Pc core via expansion of the π -conjugation is attenuated by the “lock washer” conformation, which prevents π -conjugation throughout the entire macrocycle.¹⁵

The excited state dynamics of phthalocyanines is known to be sensitive to their host environments.¹⁶ For example, exciton–exciton annihilation is dominant in film,¹⁷ while energy relaxation is important in water solution and stimulated emission

happens in DMSO.¹⁴ Even in solutions, the lifetime of excited state differs significantly among MPcs with different central metal ions, especially for transition metals. Millard et al. showed that the lifetimes of the excited singlet state for nickel Pc and cobalt Pc in 1-chloronaphthalene solution are 2.8 ± 0.2 and 2.1 ± 0.2 ps, respectively.¹⁸ Theoretical research also demonstrated that the valence electron structures of FePc and CoPc differ significantly from those of other MPcs, such as CuPc, ZnPc, and MgPc. Nikolaitchik found that when Co is presented as the central metal ion in π -macrocycles of Pcs, the orbitals couple with π -orbital systems and provide additional channels for π^* -deactivation.¹⁹ Liao et al. found that the HOMO in CoPc is metal 3d-like, whereas in ZnPc, the HOMO is localized on the Pc ring by using a density functional method.²⁰ So far, a lot of time-resolved studies on Pc molecules have been reported; however, the decay rates were quite scattered, dependent on experiment conditions and processes of preparation, and only little work has been carried out to investigate the dynamics of the photoluminescence emission because the quantum yield is so low that many MPcs were reported as nonfluorescent.²¹

In the present paper, we report the study on the excited state dynamics of two novel soluble MPc derivatives (p-HPcCo and p-HPcZn) containing four sulfonic naphthoxy substituents, as shown in Figure 1, in dimethyl sulfoxide (DMSO) solution using femtosecond transient absorption spectroscopy and time-resolved photoluminescence (TRPL) spectroscopy. The four peripheral substituents could prevent molecular aggregation in solution by providing steric hindrance. The observed dynamics shows a photoabsorption (PA) feature for both samples under excitation at 400 nm, but the relaxation behavior of p-HPcCo is more complex than that of p-HPcZn. With excitation at 800 nm, the dynamics shows two-photon absorption character, and two-color pump-probe dynamics depends greatly on the probe wavelength. In addition to transient absorption and bleaching, the decay of PL emission of p-HPcZn in DMSO was also measured for the first time, which behaves as a monoexponential decay

* Corresponding author. Tel: 86-21-65642084. Fax: 86-21-65104949. E-mail: sxqian@fudan.ac.cn.

[†] Physics Department, Fudan University.

[‡] Surface Science Lab (National Key Lab), Fudan University.

[§] Nanjing Normal University.

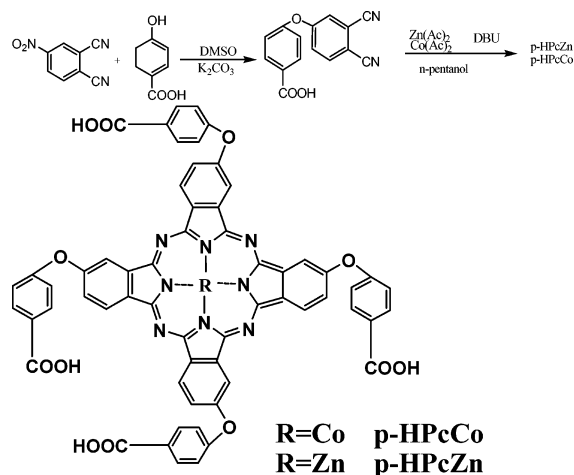


Figure 1. The molecular structures of p-HPcCo and p-HPcZn.

process. Different energy level models were used to explain the observed dynamic features.

Experimental Methods

Materials. Dimethyl sulfoxide (DMSO) and other agents of analytical grades were obtained from Beijing Chemical Plant. 4-Nitrophthalonitrile was prepared and purified according to the methods described in the literature.²² All reaction solvents were dried over 4-Å molecular sieves and further distilled before use.

Equipments. IR spectra were recorded on a PARAGN1000 FT-IR spectrometer using KBr pellets. ¹H NMR spectra were obtained in deuterated DMSO on a Gemini-2000 analyzer (300 MHz, Varian Ltd.).

Synthesis of 4-(4-Carboxyphenoxy)phthalonitrile.²³ A suspension of K₂CO₃ (3.50 g, 25 mmol) in dry DMSO (30 mL) was added to 4-nitrophthalonitrile (2.00 g, 11.5 mmol) and *p*-hydroxybenzoic acid (2.36 g, 17.1 mmol). Further K₂CO₃ (3.50 g, 25 mmol) was added after 3 h and after 24 h. The suspension which had been stirred at 25 °C for 5 days was added to water (600 mL) and the pH was adjusted to 1 with concentrated HCl. The resulting precipitate was recrystallized from methanol (50 mL) to give pure 4-(4-carboxyphenoxy)phthalonitrile (2.59 g, 85%) as a white solid. IR (cm⁻¹): 3088–3038 (Ar, H), 2231 (Ar–C≡N), 1256 (Ar–O–Ar), 1676 (–C=O). ¹H NMR (DMSO): δ 13.05 (s, 1H), 8.15 (d, 1H), 8.05 (d, 2H), 7.95 (d, 1H), 7.55 (m, 1H), 7.25 (d, 2H). MS: 264.1 (M⁺).

Preparation of p-HPcZn/p-HpcCo. 4-(4-Carboxyphenoxy)phthalonitrile (0.528 g, 2 mmol), dry 1-pentanol (15 mL), and 0.092 g (0.5 mmol) of anhydrous zinc carboxylic were mixed. The mixture was heated to 50 °C in a nitrogen atmosphere during stirring and then DBU (0.6 mL) was added into. The suspension was slowly brought to boiling and refluxed for 5 h. Upon cooling the reaction mixture to 60 °C, 15 mL of methanol was added to the mixture, which was stirred for 10 min and then filtered. Dilute HCl was added to filter liquor, and the resulting precipitate was washed with double distilled water. The crude product was extracted with dichloroethane and acetone in a Soxhelt extractor and purified by column chromatography (silica gel, THF–toluene, 8:2). The blue fraction was collected, evaporated under vacuum, and dried in vacuo at 100 °C. Yield: 0.214 g (38.6%), deep blue powder. IR (cm⁻¹): 1597, 1503, 1468 (C=C, C=N), 1232 (Ar–O–Ar). ¹H NMR (DMSO): δ 9.0–8.85 (d, 4H), 8.55–8.45 (d, 4H), 8.2–8.05 (m, 8H), 7.9–7.75 (m, 4H), 7.6–7.45 (m, 8H). Anal. Calcd for (C₆₀H₃₂N₈O₁₂Zn): C, 64.21; H, 2.87; N, 9.98. Found: C, 64.01; H, 3.01; N, 9.57.

The preparation of p-HPcCo is similar to that of p-HPcZn.

Steady-State Absorption and Photoluminescence. Steady-state absorption spectra and one-photon and two-photon excited photoluminescence emission spectra for monomeric molecules in DMSO solution were recorded with a spectrometer. The PL signal was detected in the perpendicular direction to the incident excitation beam and was corrected for a reference. The concentrations we used in the measurements were both 6×10^{-6} M. In addition to the observed one-photon excited PL emission, two-photon PL emission was also detected from p-HPcZn solution, but nearly no two-photon PL emission was detected from p-HPcCo solution, indicating that there is a difference between the two molecules.

Pump-Probe Experiment. The transient absorption spectra of MPc solutions were obtained using a pump-probe technique based on a regeneratively amplified, mode-locked femtosecond Ti:sapphire laser system (SPECTRA PHYSICS). The output pulses have duration of 140 fs, pulse energy of 0.2 mJ, and repetition rate of 1 kHz. For one-color pump-probe measurement, the beam was frequency-doubled in a BBO crystal to generate a 400 nm beam with pulse energy of 20 μJ, which was divided into two beams (pump and probe) by a beam splitter. After passing through an optical delay line, the pump beam was overlapped with the probe beam and was focused in the MPc solution in a 1-mm cuvette. Behind the solution, the pump beam was blocked and the transmitted probe beam was detected by a silicon photodiode connected to a lock-in amplifier (SR830, Stanford Research Systems). For two-color pump-probe measurement, a portion of the 800 nm beam was used to generate a supercontinuum through a 5-mm-thick flow cell with flowing water, while the residual 800 nm beam or the 400 nm SHG beam served as the pump beam. Both pump beam and probe beam were focused on a 0.3 mm diameter spot in the sample. A monochromator behind the sample cell was used to select the probe wavelength.

TRPL Experiment. The details of the time-resolved photoluminescence experiment based on the optical Kerr-gate technique²⁴ were described elsewhere.²⁵ Briefly, laser pulses at 800 nm of 140 fs duration were divided into two beams. The intense beam was used as the gate beam to open the Kerr-gate through birefringence of Kerr material, while the other beam was frequency-doubled to 400 nm and was used to effectively excite samples. We collected the PL emission in the direction perpendicular to that of the incident 400 nm beam to avoid the interference of the excited beam. The polarization of the collected PL emission was set at 45° with respect to that of the gate beam by a polarizer (P1). Then two beams, gate beam and PL signal, were focused to overlap on a 5-mm-thick cell filled with Kerr material (CS₂). An analyzer with orthogonal polarization to P1 was placed in front of a monochromator, and a photomultiplier (Hamamatsu R1104) connected to a lock-in amplifier (SR830, Stanford Research Systems) was used to detect the transmitted PL signal. All experiments were performed at room temperature.

Results and Discussion

Steady-State Absorption Spectra. The static electronic absorption spectra of p-HPcCo and p-HPcZn in DMSO are shown in Figure 2. For both MPc solutions, there are two strong absorption bands: the characteristic Q-band, corresponding to the $n \rightarrow \pi^*$ transition near 700 nm ($\lambda_{\text{max}} = 673$ and 680 nm for p-HPcCo and p-HPcZn, respectively) with a typical sharp profile for the Pc monomers,²⁶ and the Soret band, corresponding to the $\pi \rightarrow \pi^*$ transition in near-UV region. It is reported that Pcs

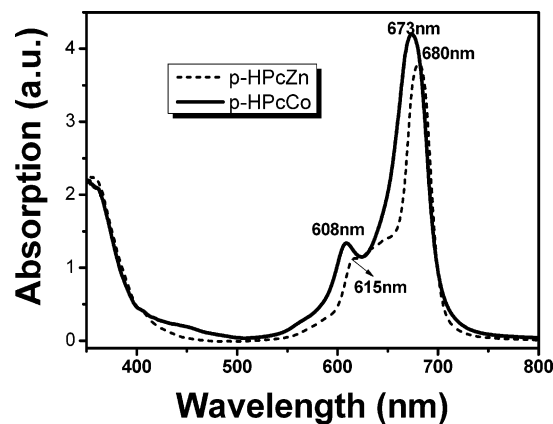


Figure 2. Absorption spectra of p-HPcCo and p-HPcZn in DMSO (6×10^{-6} M).

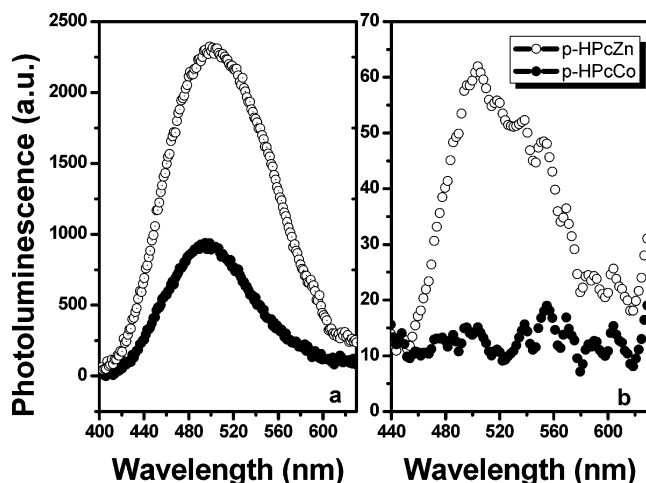


Figure 3. One-photon (a) and two-photon (b) photoluminescence spectra of p-HPcCo and p-HPcZn in DMSO (6×10^{-6} M). Excitation wavelengths were 400 and 800 nm, respectively.

tend to form aggregates in water, while in DMSO they exist predominantly in the monomeric form and exhibit very different dynamics from that of aggregates.¹⁴

Photoluminescence Spectra. Figure 3 shows one-photon PL emission spectra (a) and two-photon PL emission spectra (b) of p-HPcZn and p-HPcCo. Under excitation at 400 nm, they showed weak PL emissions centered at 495 nm. The PL intensity of p-HPcCo is about 40% of that of p-HPcZn. Under excitation at 800 nm, an even weaker emission centered at 495 nm with a full width at half-maximum of about 100 nm was observed for p-HPcZn, while the PL emission of p-HPcCo is too weak to be detected. Because of the facts that there is nearly no one-photon absorption at 800 nm and the sum of two incident photon energy is within the absorption band, the observed PL emission should be reasonably generated from two-photon excitation. It is known that porphyrins with open-shell metal atoms generally have short excited state lifetimes, due to rapid charge transfer from the excited porphyrin to the metal atoms.²⁷ In Co ion, there is an unpaired electron in a d_z^2 orbital. According to the research of Ake and Goutherman,²⁸ interaction of the electron with the singlet and triplet states induces the formation of doublet and quadruplet states; the ground state is a doublet, whereas the low ($\pi-\pi^*$) excited states are singdoublet, $^2Q(\pi,\pi^*)$; a tripdoublet, $^2T(\pi,\pi^*)$; and a tripquadruplet, $^4T(\pi,\pi^*)$, from the highest to the lowest. The deactivation pathway suggested by Antipas et al. was in a two-step $^2Q \rightarrow ^2T \rightarrow$ charge transfer (CT) state.²⁹ Cobalt ion could accelerate the transition from CT states to

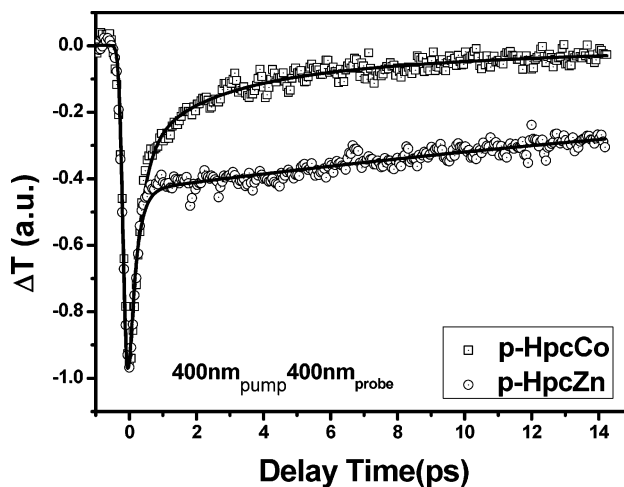


Figure 4. The experimental transient response (symbol) and fitted data (line) for p-HPcCo and p-HPcZn at 400 nm.

triplet state, which dramatically quenches the excited state population. For p-HPcZn, there is still weak emission observed due to the lack of this acceleration. The two-photon absorption (TPA) may be enhanced by the four peripheral substituents, serving as electron donor along with central metal atom to form the $D-\pi-A$ structure, which can significantly increase the two-photon absorption cross section.^{30,31} Similar results were reported by Michel Fournier et al. in their studying of the two-photon photodynamics of copper and nickel Pc tetrasulfonates.¹⁰

Pump-Probe Dynamics Study. The pump-probe technique allows us to measure the lifetimes of excited states. Figure 4 shows the one-color pump-probe dynamics of two samples carried out at a wavelength of 400 nm, where the fitting curves are also shown in the figure together with the normalized experimental data. The molecules can be efficiently excited by pump beam via linear absorption. The transient profiles of two sample solutions in DMSO at three different concentrations (12, 6, and 3 μ M, data not shown) were also acquired, which showed no distinct dependence on the concentration, strongly indicating that they were in the monomeric form in DMSO, not molecular aggregates.¹⁴

The signals of two MPc molecules show similar transient behavior with a very fast decay component and some slow components. From the multiexponential functions fitting (biexponential for p-HPcZn and three-exponential for p-HPcCo, respectively) with deconvolution of the instrumental response, the lifetimes for decay processes are determined to be 0.21 and 32 ps for p-HPcZn while 0.29, 1.9, and 9 ps for p-HPcCo, as shown in Table 1. The ultrafast decay process, less than 300 fs, may be ascribed to the intraband energy relaxation of the first excited state via vibrational cooling. The second decay process, corresponding to the formation of CT state of p-HPcCo (about 1.9 ps), is certainly much faster than that of p-HPcZn (about 32 ps), because the coupling between the d-electron and π -orbital can provide additional channels for deactivation^{31,32} and can also accelerate the intersystem crossing. The third process in p-HPcCo dynamics with lifetime of 9.0 ps represents the evolution of the CT state, including transfer to the triplet state or return to the ground state.

To gain more information about the excited state dynamics of two MPc molecules, we also carried out two-color pump-probe experiments. Figure 5 shows the excited state dynamics of both samples in DMSO at three representative probe wavelengths under 800 nm excitation (Figure 5a for p-HPcCo and Figure 5b for p-HPcZn, respectively). Very different features

TABLE 1: Summary of the Lifetime Data of p-HPcZn and p-HPcCo in DMSO

compd	$\lambda_{\text{pump/probe}}/\text{nm}$	decay/ps (%)		
		τ_1	τ_2	τ_3
p-HPcCo	400/400	0.29 (76)	1.9 (14)	9 (10)
p-HPcZn	400/400	0.21 (73)	32 (27)	—
p-HPcCo	800/510	0.65 (63)	20 (37)	—
	800/621	0.51 (47)	5.8 (53)	—
p-HPcZn	800/661	0.52 (57)	10 (42)	—
	800/510	37	—	—
	800/621	82	—	—
p-HPcCo	800/661	53	—	—
	400/561	no signal		
p-HPcZn	400/621	0.98 (91)	>100 (9)	—
	400/661	0.89 (57)	10(43)	—
p-HPcCo	400/561	313	—	—
	400/621	89	—	—
	400/661	700	—	—

were observed at the three probe wavelengths. Notice that these molecules have very weak absorption at 800 nm (shown in Figure 1) and the observed up-conversion photoluminescence emission of p-HPcZn centers at 495 nm, so we conclude that both molecules show two-photon absorption character.

At a probe wavelength of 510 nm, where both molecules seem to be transparent, the dynamics is dominated by the transient absorption signal, which means that the excited state has a larger absorption cross section than the ground state, $\sigma_{\text{ex}} > \sigma_{\text{g}}$. An interesting phenomenon is that there is a sharp PA peak observed in p-HPcCo within the time scale of pulse duration. We ascribe this ultrafast peak to the TPA process, absorbing one photon from the pump pulse and another photon from the probe pulse simultaneously.³³ This special TPA process can only happen within the cross-correlation time between the pump beam and the probe beam. The subsequent decay dynamics of the PA signal just reveals the relaxation of the population in the excited state. For p-HPcZn, there is a more effective population excitation in the excited state, which generates a more intense PA signal, leading to the ultrafast peak being hidden. The recovery times of PA signal for p-HPcCo and p-HPcZn are found to be 0.7 and 37 ps, which reflects the formation of the CT state. The subsequent process of p-HPcCo with a lifetime of 9 ps suggested relaxation from the CT state to the 2T_1 state.

At 621 nm, the dynamics appears quite different from that at 510 nm. Because there is an absorption shoulder around 620 nm, the absorption cross section at this wavelength, which is larger than that at 510 nm, would be comparable or even larger than that of the excited state. From Figure 5, we can see that the main dynamics of both samples turns to a weak photobleaching (PB) feature, demonstrating that the absorption cross section of the ground state surpasses that of the excited state. Of course, the ultrafast PA peak, which is very clear for both samples, can still be ascribed to the special TPA process.

When the probe wavelength was tuned to 661 nm (near at the absorption peak of the Q-band), both samples show intense PB behavior at this wavelength. The PB signal for p-HPcZn solution is more intense than that of p-HPcCo, reflecting the fact that there is more population in the excited state of p-HPcZn than in p-HPcCo. In addition to the intense signal, the slow decay of the PB signal of p-HPcZn is again observed, showing the long lifetime of the excited state in p-HPcZn. At all three probe wavelengths, the decay dynamics of the transient signal in p-HPcZn are always slower than those in p-HPcCo, demonstrating the longer lifetime of the excited state in p-HPcZn, which is in agreement with the measured PL emission spectra.

In fact, we did two-color pump-probe measurements at many different probe wavelengths, but these traces for the three probe wavelengths given in Figure 5 are representative. Usually, the long lifetime and the resulting large population of the excited state would lead to high intensity of PL emission; it is true for p-HPcZn. The calculated rate constants (the influence of TPA process has been eliminated) of the excited states are also listed in Table 1.

All curves for p-HPcCo showed two-process character while only one-process character showed for p-HPcZn, which should be caused by energy splitting induced by the unpaired electron in the Co atom. For p-HPcCo, the fast process with lifetime about 0.5–0.6 ps is attributed to formation of the CT state, and the second process is attributed to transition from the CT state to the split triplet state. For p-HPcZn, the only process relating to the transition from the CT state to the normal triplet state has a lifetime of tens of picoseconds.

Two-color pump-probe measurement was also carried out with a pump wavelength of 400 nm (shown in Figure 6). The main results of the observed dynamics are similar to those with 800 nm pumping. By tuning the probe wavelength from 700 to 500 nm, the dynamic behavior gradually changes from PB to PA, depending on the relation of the absorption cross sections between the ground state and the excited state. Because there is weak absorption at the blue side of the Q-band, at probe wavelength shorter than 600 nm, the dynamics is dominated by the PA feature.

The main difference of the dynamics between two pump wavelengths is that there is no ultrafast component under excitation at 400 nm. We concluded that the sum of two-photon (800 and 500–600 nm) energy just locates in the Soret band (see Figure 2), so molecules could simultaneously absorb two photons, one from the 800 nm pump beam and the other from the probe beam, and induce a sharp cross-correlation signal in the dynamic curve. When excited at 400 nm, the sum of the two-photon energy is beyond the Soret band, so we did not see the TPA process. To obtain an accurate value of the decay time of the PA and PB processes, the experimental data were fit to a convolution of the multiexponential (biexponential for p-HPcCo and monoexponential for p-HPcZn) function and a Gaussian function (listed in Table 1). It can be seen that the relaxation of the excited state in p-HPcCo is certainly much faster than that of p-HPcZn.

Time-Resolved Photoluminescence Study. Figure 7 shows the TRPL dynamics excited by 400 nm femtosecond pulses and detected at the peak wavelength of PL emission of p-HPcZn in DMSO. Because the PL emission band covers more than 100 nm in the visible range, as shown in Figure 3, the states relating to PL emission contain different energy levels.²⁵ One decay constant is acquired after fitting experimental data with a monoexponential function. The lifetime of PL emission band (~ 52 ps) is on the same order as that determined from two-color pump-probe results. The excited state lifetime of p-HPcZn is relatively long comparing to that of p-HPcCo, resulting in much more intense PL emission.

For illustrating the processes happening in two MPC solutions, we propose energy level diagrams, which are shown in Figure 8. These models are extended from a four-level model proposed by Ake and Couerman for Cu-centered porphyrins.²⁴ The excitation of the 400 nm beam excites the molecules to the high-lying levels of the first excited state, from which the energy relaxes rapidly to the lowest vibrational level and then transfers to the CT state, from which they finally relax to the triplet state via intersystem crossing.

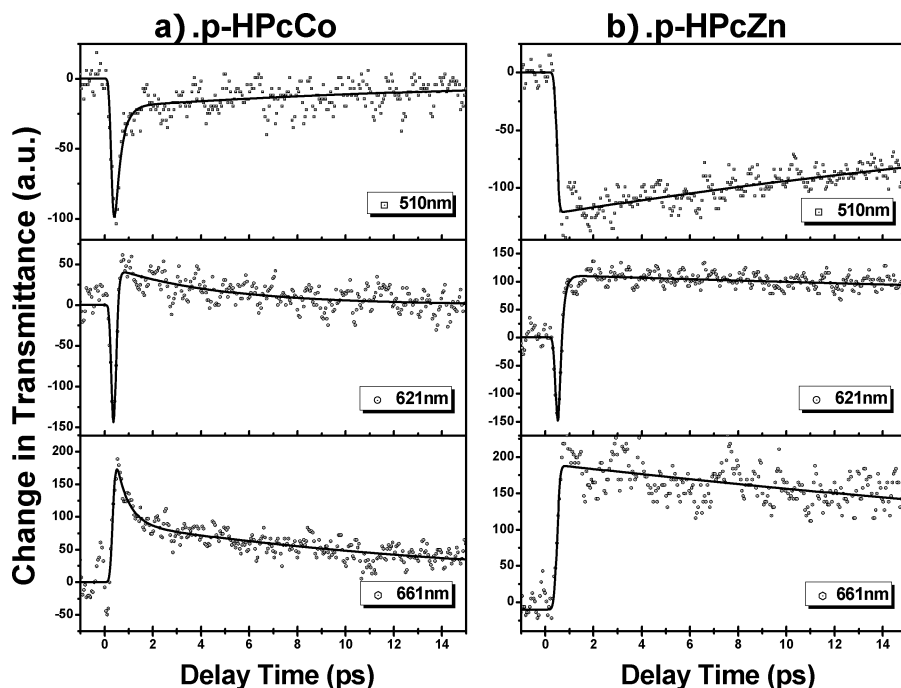


Figure 5. Two-color pump-probe traces of p-HPcCo and p-HPcZn (as labeled in each panel) in DMSO (6×10^{-6} M) at three probe wavelengths with 800 nm pumping: (a) the dynamics of p-HPcCo, (b) the dynamics of p-HPcZn.

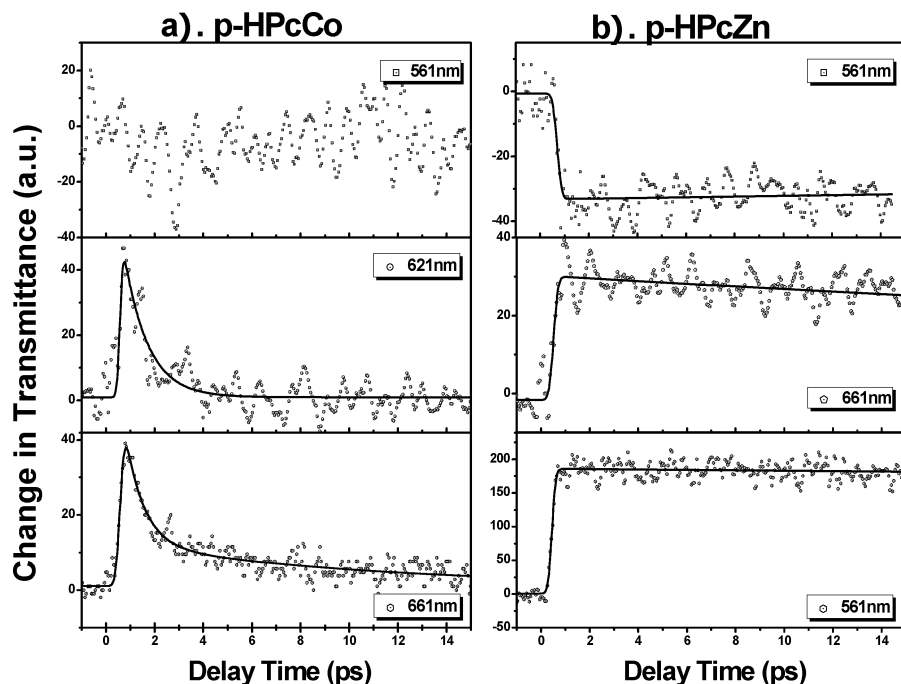


Figure 6. Two-color pump-probe traces of p-HPcCo and p-HPcZn (as labeled in each panel) in DMSO (6×10^{-6} M) at three probe wavelengths with 400 nm pumping: (a) the dynamics of p-HPcCo, (b) the dynamics of p-HPcZn.

For p-HPcZn, only four energy levels exist in our model, due to a lack of energy-level splitting induced by the unpaired electron (shown in Figure 8A). The pathways to depopulate the excited state are nonradiative relaxation to the triplet state and the spontaneous radiation to the ground state. The decay times are close as the probe wavelength was tuned under excitation at 800 nm, indicating that the decay times reflect the lifetime of the same CT states, and different probe wavelength refers to different involved energy levels in CT states. But under 400 nm excitation, the lifetimes of the excited states at different probe wavelengths scatter a lot, which may show different behaviors of the different excited levels.

For p-HPcCo, the unpaired electron in the d-orbital couples with the π -orbital system and splits singlet into doublets ($S_0 \rightarrow {}^2S_0$, $S_1 \rightarrow {}^2S_1$, and $S_2 \rightarrow {}^2S_2$), while the normal triplet state splits into a doublet (tripdoublet 2T_1) and a quadruplet (4T_1).¹⁰ Therefore, the model for p-HPcCo contains five energy levels. Because the population in the S_1 state exhibits a larger absorption at 510 nm than that in the ground state, this induces a transient absorption signal in two-color pump-probe experimental dynamics. At 621 nm, the dynamics is a mixture of the sharp TPA peak and PB signal, while at 661 nm there is pure PB signal because of the large absorption cross section of the ground state. We suggest that it is the unpaired electron dramati-

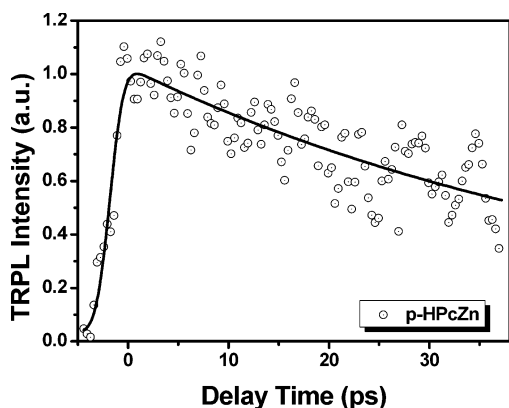


Figure 7. TRPL dynamics of p-HPcZn in DMSO detected at 490 nm.

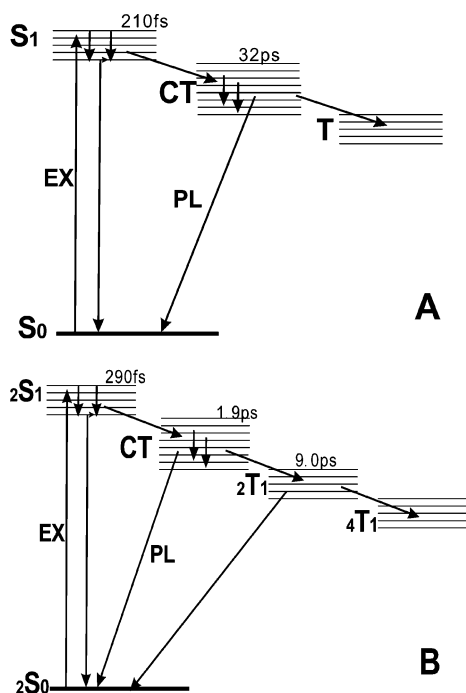


Figure 8. Energy level diagrams for p-HPcZn (A) and p-HPcCo (B).

ically quenching the PL emission in p-HPcCo that results in the great difference between the two samples.

In the TRPL experiment, the transient signal directly reflects the relaxation of the population relating to PL emission. In that case, the signal appears when the excitation transfers to CT states and the population begins to increase. The decay of TRPL is caused by the energy transfer from the CT state to the triplet state. For p-HPcCo, the excitation energy can efficiently transfer to the split energy levels, resulting in very weak PL emission and short decay time.

Conclusion

The excited state dynamics of p-HPcZn and p-HPcCo in DMSO solution was investigated by using femtosecond laser spectroscopic techniques. Rate constants corresponding to different transitions happening via relaxation processes were determined. It is shown that the excited state absorption can be increased by the modification of central metal ions and peripheral substituents. The dynamics of the transient absorption and TRPL show dramatic differences between p-HPcCo and p-HPcZn due to the different electronic structure. Inserting close-

shell metal ion (Zn) into Pc cores can lead to the slower relaxation of the excited state than MPc with an open-shell metal ion. In addition to this, binding an electron donor or acceptor to form a D- π -A (A- π -A) structure in MPcs can greatly improve two-photon absorption, just as for sulfonic naphthoxy substituents in our experiment.

Acknowledgment. The authors from Fudan University thank the National Science Foundation of China for support under Grants No. 10274013 and 10374020.

References and Notes

- (1) Moser, F. H.; Thomas, A. L., Eds. *The Phthalocyanines*; CRC Press: Boca Raton, FL, 1983; Vol I-II.
- (2) Hanack, M.; Schneider, T.; Barthel, M.; Shrik, J. S.; Flom, S. R.; Pong, R. G. S. *Coord. Chem. Rev.* **2001**, 219-221, 235.
- (3) Nagamura, T. *Springer Ser. Photonics* **1999**, 2, 376.
- (4) Manas, E. S.; Spano, F. C.; Chen, L. X. *J. Chem. Phys.* **1997**, 107, 707.
- (5) Gregory, P. J. *Porphyryns Phthalocyanines* **2000**, 4, 432.
- (6) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991.
- (7) O'Flaherty, S. M.; Hold, S. V.; Cook, M. J.; Torres, T.; Chen, Y.; Hanack, M.; Blau, W. J. *Adv. Mater.* **2003**, 1, 19.
- (8) Pandey, R. K. *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed; CRC Press: Boca Raton, FL, 2004; pp 1, 144.
- (9) Allen, C. M.; Sharman, W. M.; Van Lier, J. E. *J. Porphyryns Phthalocyanines* **2001**, 5, 161.
- (10) Fournier, M.; Pépin, C. *Photochem. Photobiol. Sci.* **2004**, 3, 120.
- (11) Prasad, D. R.; Ferraudi, G. *Inorg. Chem.* **1982**, 21, 2967.
- (12) Dini, D.; Hanack, M.; Meneghetti, M. *J. Phys. Chem. B* **2005**, 109, 12691.
- (13) Zhu, R.-Y.; Chen, Y.; Zhou, J.; Li, B.; Liu, W.-M.; Qian, S.-X.; Hanack, M.; Araki, Y.; It, O. *Chem. Phys. Lett.* **2004**, 398, 308.
- (14) Howe, L.; Zhang, J. Z. *J. Phys. Chem. A* **1997**, 101, 3207.
- (15) Chen, L. X.; Shaw, G. B.; Tiede, D. M.; Zuo, X.; Zapol, P.; Redfern, P. C.; Cuiertiss, L. A.; Sooksimuang, T.; Mandal, B. K. *J. Phys. Chem. B* **2005**, 109, 16598.
- (16) Terasaki, A.; Hosoda, M.; Wada, T.; Tada, H.; Koma, A.; Yamada, A.; Sasabe, H.; Garito, A. F.; Kobayashi, T. *J. Phys. Chem.* **1992**, 96, 1034.
- (17) Sakakibara, Y.; Bera, R. N.; Mizutani, T.; Ishida, K.; Tokumoto, M.; Tani, T. *J. Phys. Chem. B* **2001**, 105, 1547.
- (18) Millard, R. R.; Greene, B. I. *J. Phys. Chem.* **1985**, 89, 2976.
- (19) Nikolaitchik, A. V.; Rodgers, M. A. J. *J. Phys. Chem. A* **1999**, 103, 7597.
- (20) Liao, M.-S.; Scheine, S. *J. Chem. Phys.* **2001**, 114, 9780.
- (21) Vincett, P. S.; Voigt, E. M.; Rieckhoff, K. E. *J. Chem. Phys.* **1971**, 55, 4131.
- (22) Young, J. G.; Onyebuagu, W. *J. Org. Chem.* **1990**, 55, 2155.
- (23) Danuta, F.; Alfons, P.; Aneta, W.; et al. *J. Photochem. Photobiol. A* **2001**, 141, 101.
- (24) Takeda, J.; Nakajima, K.; Kurita, S.; Tomimoto, S.; Saito, S.; Suemoto, T. *Phys. Rev. B* **2000**, 62, 10083.
- (25) Li, B.; Tong, R.; Zhu, R.; Meng, F.; Tian, H.; Qian, S. *J. Phys. Chem. B* **2005**, 109, 1070.
- (26) Leznoff, C. C.; Lever, A. B. P., Eds. In *Phthalocyanines: Properties and Applications*; VCH: New York, 1989.
- (27) Irvine, M. P.; Harrison, R. J.; Strahand, M. A.; Beddard, G. S. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, 89, 226.
- (28) Ake, R. L.; Gouterman, M. *Theor. Chim. Acta* **1969**, 15, 20.
- (29) Gouterman, A. M. *J. Am. Chem. Soc.* **1983**, 105, 4896.
- (30) Liu, Z. Q.; Fang, Q.; Wang, Q.; Xue, G.; Yu, W. T.; Shao, Z. S.; Jiang, M. H. *Chem. Commun.* **2002**, 2900.
- (31) Chung, S. J.; Lin, T. C.; Kim, K. S.; Swiatkiewicz, J.; Prasad, P. N.; Baker, G. A.; Bright, F. V. *Chem. Mater.* **2001**, 13, 4071.
- (32) Tait, C. D.; Holten, D. *Chem. Phys. Lett.* **1983**, 100, 268.
- (33) Mi, J.; Li, B.; Zhu, R.; Liu, W.; Qian, S.; Meng, F.; Tian, H. *Appl. Phys. B* **2005**, 80 (4-5), 541.