

Excited state dynamics in phthalocyanines studied using degenerate four wave mixing with incoherent light

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ABSTRACT: We present our experimental results on the measurements of excited state dynamics in phthalocyanines (Pc, CuPc, FePc, and ZnPc) using degenerate four wave mixing with incoherent light (DFWM-IL). Three different timescales were observed, for all samples, in the phase conjugate signal recorded as a function of delay in probe beam in the standard backward geometry. The fastest component (< 170 fs) is associated to the phase relaxation in the S_n states and the slowest components (~ 3 -5 ps and 35-55 ps) to the vibration and population relaxation times from the S_1 state. The present results are compared with those obtained with shorter pulses and various techniques for similar molecules. The consequences of such short lifetimes are also discussed in view of the strong optical limiting properties of these molecules. Copyright © 2002 Society of Porphyrins & Phthalocyanines.

KEYWORDS: degenerate four wave mixing, incoherent light, excited state dynamics, population relaxation.

INTRODUCTION

Metallophthalocyanines and related compounds hold considerable promise for the development of nonlinear optical devices because of their large third-order nonlinearity, fast response times, unique electronic absorption characteristics, and high thermal and environmental stability [1-3]. The large nonlinearity originates from their extensively delocalized π -electron distribution. They are highly stable and versatile compounds, capable of including more than 70 different metallic and non-metallic ions in the ring cavity. It is also possible to incorporate a variety of peripheral substituents around the phthalocyanine core as well as replace some of the isoindole units by other heterocyclic moieties, giving rise to different phthalocyanine analogues. Another peculiar and useful feature of these compounds is their

ability to form different kinds of condensed phases. It is possible to make thin films by several techniques such as spin coating, molecular beam epitaxy, and Langmuir Blodgett technology that allow fabrication of practical devices. Phthalocyanine-based thin films have been successfully applied to a wide range of technological areas such as photodynamic therapy, gas sensors, electro-chromic devices, field effect transistors, and photovoltaic cells [4]. Harmonic generation [5], wave mixing [6], optical limiting and switching [7] have been extensively studied in these molecules for a wide range of wavelengths. There have been several reports on the measurement of third-order nonlinearity [8, 9] in phthalocyanine, related compounds and their derivatives. The effects of central metal atom [10], peripheral substituents [11], and additional conjugations [12] on the third-order nonlinearity have also been widely investigated. In such scenario, the excited-state dynamics of phthalocyanines are expected to play an important role in various applications. Our particular interest in the excited-state dynamics of phthalocyanines was driven by the fact that these

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materials are potential candidates for optical limiting. Moreover, one of our recent works [13] also suggests that CuPc is a broadband optical limiter in the visible region (440-700 nm). To get an insight into the mechanism(s) responsible for optical limiting one has to gain complete information on lifetimes of the excited states involved. In this paper we report our experimental results on the measurement of excited states dynamics in the solutions of a few metallophthalocyanines. We used the technique of degenerate four wave mixing with incoherent light (DFWM-IL). The use of incoherent light for the measurement of ultrafast relaxation times is well established [14-20]. For example, our previous experiments in metalloporphyrins and C_{60} using incoherent light yielded picosecond (ps) resolution using nanosecond (ns) input pulses, and lifetimes of high lying excited states in these molecules could be easily estimated [17-20].

EXPERIMENTAL

Two intense bands characterize the linear absorption spectra of these compounds, the Q-band (centered around 670 nm) and the B-band in the near UV region (centered around 340 nm) and both are correlated to π - π^* transitions. We performed the DFWM-IL measurements on Pc, CuPc, FePc and ZnPc. Figure 1 shows the linear absorption spectra of the samples, ZnPc and CuPc, used in DFWM-IL studies. The obtained spectra match well with spectra reported in literature. All of the samples were dissolved in spectroscopic grade, highly purified solvents. CuPc was dissolved in 16% concentrated H_2SO_4 , FePc in DMSO, Pc and ZnPc were dissolved in toluene. CuPc and FePc gave clear solutions whereas the samples dissolved in toluene were placed in a sonicator for about half an hour to achieve better

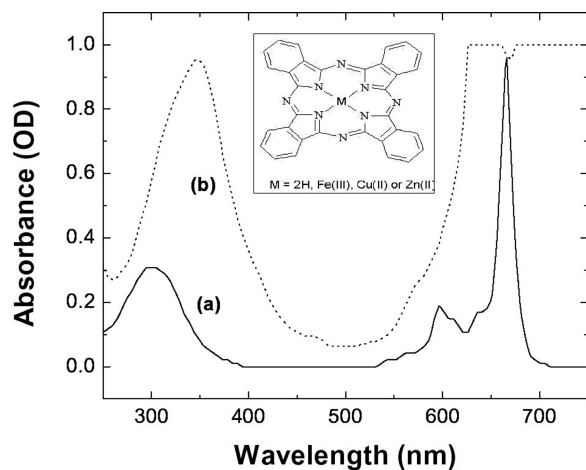


Fig. 1. Absorption spectra of (a) ZnPc (DMSO) and (b) CuPc (Conc. H_2SO_4). Inset shows the structure of the compounds

solubility. Essential details of our experimental setup [17, 18] used for the DFWM - IL are as follows. An Nd: YAG laser (6 ns, 100 mJ in 532 nm, 10 Hz) was used for pumping a home built Rhodamine B dye laser. The dye laser output peaked at 594 nm and had a line width (FWHM) of approximately 7.5 nm corresponding to a correlation time (τ_c) of ~ 170 fs. Three beams of equal intensity were derived from this beam. Beam 1 (k_1) and beam 2 (k_2) are designated as pumps and beam 3 (k_3) is the probe. The forward pump and probe beams made an angle of 10° with each other. All three beams were focused down to a beam width of about 100 μm and intersect in the sample kept in a 1 mm cuvette. The peak intensities reached were about 300-500 MW/cm². Beam 1 was fixed, whereas beams 2 and 3 pass through variable optical delays. The resolution of each delay line is 5 μm , which corresponds to a temporal resolution of 33 fs (with a retro-reflector). The phase conjugate (PC) signal (in $-k_3$ direction) was recorded as a function of τ (delay between beams 1 and 3) for different values of δ (delay between beams 1 and 2). An optional half wave plate (HWP) was used to rotate the state of polarization of any given beam as desired. Data acquisition hardware consisted of a fast photodiode, lock-in amplifier, an ADC card and a PC.

RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the DFWM-IL signals in the samples CuPc and FePc for $\delta = 8$ ps and $\delta = 9$ ps, respectively. The solid line represents the PC signal in the Rhodamine B (RhB) and open circles are the experimental data in samples. Since the phase relaxation time in RhB is much smaller than 170 fs, the signal acted as an autocorrelation trace. The signal structure remained the same as observed in our earlier studies involving porphyrins and C_{60} [17-20]. A double-peak structure (viz. a sharp, intense peak and a broad, weak hump) has been observed for all the samples used in the present study. It had already been shown by Okamoto et al. [15] that the ratio of these peaks leads to the population relaxation time ($T_1 = \text{ratio of the intensity of two peaks} \cdot \tau_c$) and we had shown earlier [17-20] that the widths of the peaks give information on (a) the vibrational relaxation time (T_2) of the higher excited singlet states S_n , (b) the vibrational relaxation time (τ_{vib}) of the Franck-Condon states of the first excited singlet ($S_{1V}-S_{10}$). The different lifetimes calculated, from the widths and ratio of two peaks, for various samples are summarized in Table 1. The population relaxation times measured from the PC signal were found to be ~ 35 -55 ps and the vibrational relaxation times within the S_1 state to be ~ 3 -4.5 ps. There have been several other experimental results on the dynamics

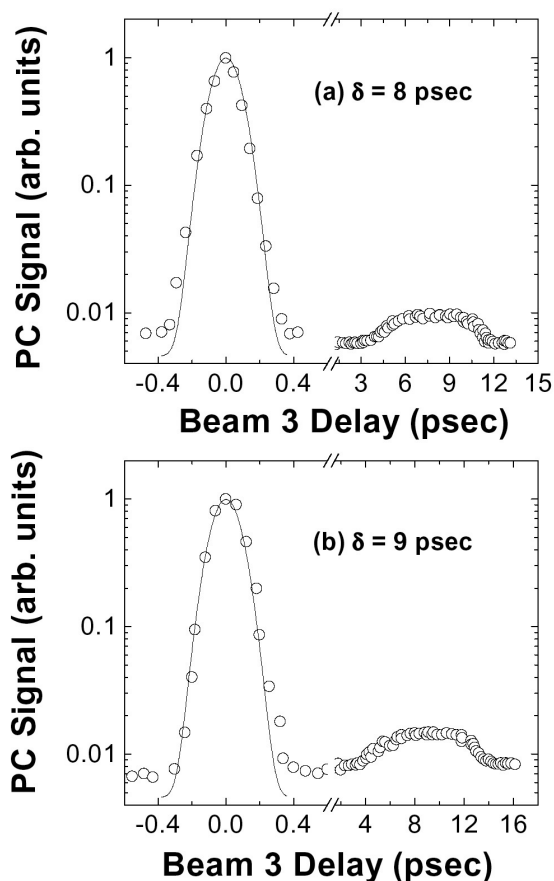


Fig. 2. (a) PC Signal as a function of τ for a fixed value of $\delta = 8$ ps in copper phthalocyanine, CuPc (H_2SO_4) (b) PC signal in the sample iron phthalocyanine (DMSO) for $\delta = 9$ ps

of various phthalocyanines using different pulse widths and with various techniques [21-31]. Several of the metallophthalocyanines have been reported as non-fluorescent, indicating excited-state lifetimes of few tens of ps [21]. Comparing the values obtained using our technique with those reported in literature, for similar compounds, Asahi et al. [22] working with copper phthalocyanine performed femtosecond transient grating spectroscopy and obtains a 100 ps component in their excited state dynamics measurements which they attribute to the intrinsic lifetime of the exciton. Zhenrong et al. [8] also reports a 100 ps component in their time-resolved Z-scan measurements on a copper phthalocyanine

thin film. Howe et al. [23] investigated the excited-state dynamics of PcS_4 and ZnPcS_4 in both aqueous and organic solutions using femtosecond laser spectroscopy. Their studies suggest that the dynamics in aqueous solution are dominated by aggregates, which have short lifetimes (< 80 ps). In the organic solvent DMSO, these phthalocyanines exist primarily in the monomeric form, and the excited-states are much longer lived. The observed lifetimes in their studies (~ 10 ps and ~ 300 ps) were attributed to the S_n to S_1 state relaxation and S_1 to S_0 state, respectively. The results of their kinetic model yield lifetimes of ~ 130 ps and ~ 160 ps for the S_1 state in PcS_4 and ZnPcS_4 , respectively. For our samples Pc and ZnPc, we observe lifetimes of 55 ps and 35 ps, respectively, through DFWM-IL studies, which are in good agreement with the values reported by them. From their direct ps time-resolved absorption measurements Millard et al. [24] measured the excited singlet state lifetimes for NiPc and CoPc in 1-chloronaphthalene solution to be ~ 3 and 2 ps, respectively. Similar measurements on FePc in DMSO solution yielded a lifetime of 3.5 ps. However, in their case they had strong evidence for dimerization of FePc in DMSO. Our studies suggest a lifetime of ~ 40 ps for FePc/DMSO solution.

Using femtosecond pulses Ho et al. [25] reports exciton-phonon coupling decay time of 4 ps in their thin film sample of fluoro-aluminium phthalocyanine. They also report a 550 fs exciton-exciton annihilation decay time, which is intensity dependent. Terasaki et al. [26] studied the relaxation kinetics of excited electronic states of vanadyl phthalocyanines in various molecular configurations by femtosecond time-resolved spectroscopy and found that the dominant relaxation processes were formation of the tripdoublet and tripquartet states with lifetimes much longer than the lifetimes of hundreds of ps in the isolated molecules. Brannon et al. [27] obtained ns fluorescence lifetimes for group 3A phthalocyanines in solutions using ps pulses. From their experimental data Williams et al. [28] reported time- and wavelength-resolved the sub-ps and few ps relaxation mechanisms in fluoro- and chloroaluminum phthalocyanine thin films and deduced few-ps lifetime for the exciton decay from

Table 1. The transverse and longitudinal lifetimes calculated for different samples using DFWM-IL

Sample	Dephasing of the S_n state (T_2) in fs	Vibrational relaxation in S_1 state (τ_{vib}) in ps	Population relaxation time (T_1) in ps
Phthalocyanine (toluene)	< 170	3.80 ± 0.76	55.0 ± 11.0
Copper phthalocyanine (conc. H_2SO_4)	< 170	4.30 ± 0.86	46.0 ± 9.20
Iron phthalocyanine (DMSO)	< 170	4.00 ± 0.20	40.0 ± 8.00
Zinc phthalocyanine (toluene)	< 170	3.50 ± 0.70	35.0 ± 7.00

the S_1 state. Reports do indicate lifetimes of 24 ps [31] for the excited state for other phthalocyanines, though in the dimeric state.

The small values of the lifetimes obtained with our present set up could also be attributed to various reasons. The population relaxation time is related to the ratios of the peaks and the correlation time, and we used pulses with very short correlation times, which effectively implies a very large ratio (~3000-6000) for T_1 values greater than 50-100 ps. For such large values of the ratio, the SNR for the second peak is very low thereby rendering the present setup inadequate for measurements of lifetimes greater than 100 ps. Addressing the question of aggregation, we chose the concentration of the samples so as to inhibit the formation of dimers. The lifetimes of the excited states depend critically on the excitation wavelength, intensity of the input pulses, central metal ion, peripheral substituents, etc. A systematic and careful study is essential to completely evaluate the excited state dynamics in these materials. We are in the process of such studies and the results will be a subject of a future publication.

The ramification of such a short lifetime for the S_1 state will be obvious, especially in the optical limiting performance of these materials. Optical limiting in solutions of organic materials with ns pulses requires a large excited state absorption cross-section and long lifetime for the triplet state along with a short lifetime for the singlet state. If the lifetime of the singlet state is long enough, it inhibits the population crossing over to the triplet state and thereby reduces the reverse saturable absorption (RSA) effect. This was clearly evident in our Z-scan results of C_{60} (which has similar RSA properties compared to phthalocyanines) obtained with ns pulses from an OPO [32]. We are at present analyzing the Z-scan data obtained for a CuPc over the entire visible range (440-700 nm) and expect that the above results on excited state dynamics will help in easily understanding the RSA behavior.

CONCLUSION

In summary, we have studied the solution excited state dynamics of a few phthalocyanines using DFWM-IL. Our studies indicate that these compounds possess three different relaxation times, each related to different excited states. The fastest component is due to the phase relaxation from the S_n states; the slower components are due to vibrational and population relaxations from the S_1 state. These versatile compounds with fast relaxation times, combined with their large nonlinearity, would be appropriate candidates for nonlinear optical device applications.

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