Pump-probe experiments with sub-100 femtosecond pulses for characterizing the excited state dynamics of phthalocyanine thin films.

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ABSTRACT

We present our results on the characterization of ultrafast excited state dynamics of two phthalocyanines in thin film form studied using femtosecond pump-probe technique. One was a symmetric Zinc phthalocyanine (SPc) while the other was an unsymmetrical Zinc phthalocyanine (USPc). The femtosecond (fs) pulses at 800 nm were characterized using a single shot autocorrelator. The pump probe measurements were carried out with 590/610 nm pulses emanating from an optical parametric amplifier. SPc demonstrated an excited lifetime of ~30 ps while the ASPc exhibited ~60 ps lifetime. The potential applications of these molecules are discussed briefly.

Key words: Femtosecond, pump-probe, Phthalocyanines, thin films.

1. INTRODUCTION

Phthalocyanines, Porphyrins, and their derivatives are macromolecules with large number of delocalized π electrons possessing attractive third-order nonlinear optical (NLO) properties with outstanding applications in the areas of optical limiting and ultrafast all-optical switching [1-19]. The advantage with these classes of molecules is the versatility with which one can modify their optical properties. We have recently been evaluating the magnitude of nonlinearities for a new class of phthalocyanines [7-15]. Our studies clearly suggest that these are potential molecules possessing strong nonlinearities (non-resonant) in both solution and thin films. Our endeavor is also to comprehend the time-response of the nonlinearity in these molecules. A combination of huge nonlinearity and an ultrafast response time is required for translating the potential of these materials into devices. The relaxation mechanisms of photo-induced excitation are one of the significant issues that determine the performance of devices in photonic applications. Here, we present results on the studies of ultrafast dynamics of excited states in phthalocyanine thin films achieved using the pump-probe technique.

2. EXPERIMENTS

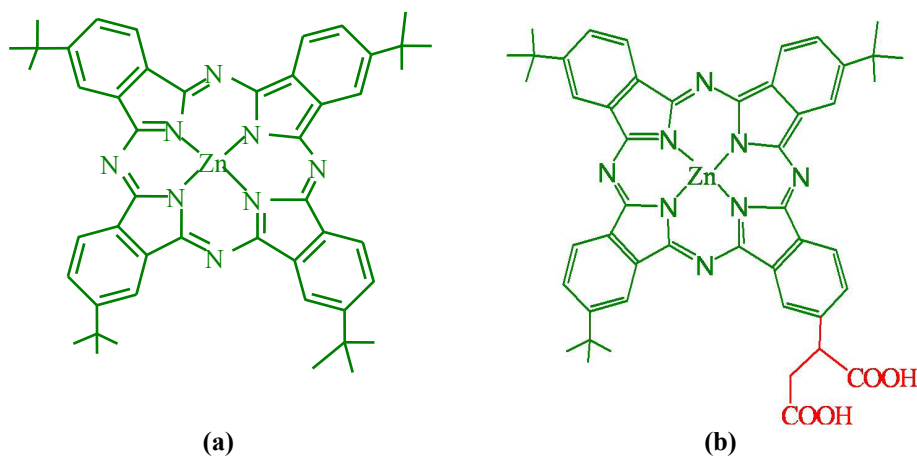(a)   (b)
Figure 1 Structures of symmetric and unsymmetrical phthalocyanines used in the present study.

Figure 1(a) and (b) shows structures of the two samples studied [7, 8] viz. Zinc tetra tert-butyl Phthalocyanine (hereon denoted as SPc) and 2-(3-(Butane-1,4-dioic acid)-9(10),16,(17),23(24)-tri *tert*-butyl Phthalocyanine Zinc(II) (hereon denoted as USPc). Details of the absorption spectra and other spectroscopic information can be found elsewhere [7, 8]. The laser pulses used for pump-probe experiments were obtained from an OPA (TOPAS) pumped by an ultrafast amplifier (Legend, Coherent) with following specifications: ~50 fs duration, 1 kHz repetition rate, and tunable in the whole visible spectral region with typical energies in the 50-120 μJ range. The amplifier was seeded with pulses from an oscillator (MICRA, ~15 fs pulse duration, 80 MHz repetition rate, 1.0 W average power, near 800 nm). Details of the experimental setup utilized for pump-probe technique is depicted in figure 2. The overlap of pump and probe pulses was ensured through pin holes placement/alignment at strategic points in the setup and was confirmed through recording of the probe transmission at all delays (~200 ps). The delay stage had a resolution of 0.5 μm (1.6 fs). The probe transmission was detected using a sensitive power meter (Coherent). The pump beam diameter was larger (~5 mm) than the probe beam diameter (~2 mm) and both the beams were not focused. Typically 15-50 μJ energies were used for the pump beam while the probe beam power was a fraction of that. The pulses at 800 nm from the ultrafast amplifier were characterized using a single shot autocorrelator providing pulse duration of ~50 fs. The pulses emanating from TOPAS were estimated to be of ~60 fs duration while the pulse duration at the sample after traversing different optical components was estimated to be, typically, ~70 fs. Cross-correlation studies are essential to identify the exact pulse duration. Both the phthalocyanines were doped in PMMA and spin coated on to a glass substrate. Typical thickness of the uniform films obtained was ~15-20 μm.

Pump probe technique can be executed in different configurations (a) Degenerate case with 800 nm pump and 800 nm probe (b) 400 nm pump and 800 nm probe (c) 400 nm pump and a white light probe [20]. We had tried working with the configuration mentioned in (a) but were not successful probably due to poor signal-to-noise ratio. Later we had generated 400 nm pulses through second harmonic generation (SHG) of 800 nm but the pulse broadening was high, as demonstrated later in this paper, and was not utilized. We had better results with 590/610 nm as pump and probe since these molecules absorb strongly in that spectral region. Figure 3 shows the typical emission spectrum of SPc indicating an emission peak near 700 nm and absorption peak near 650 nm.
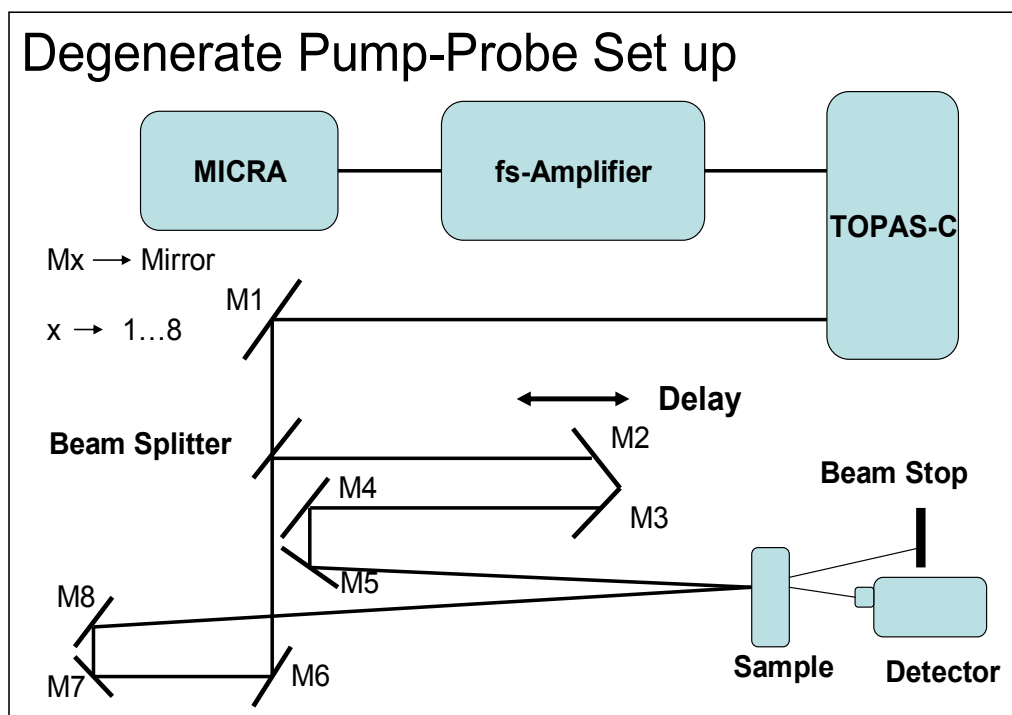

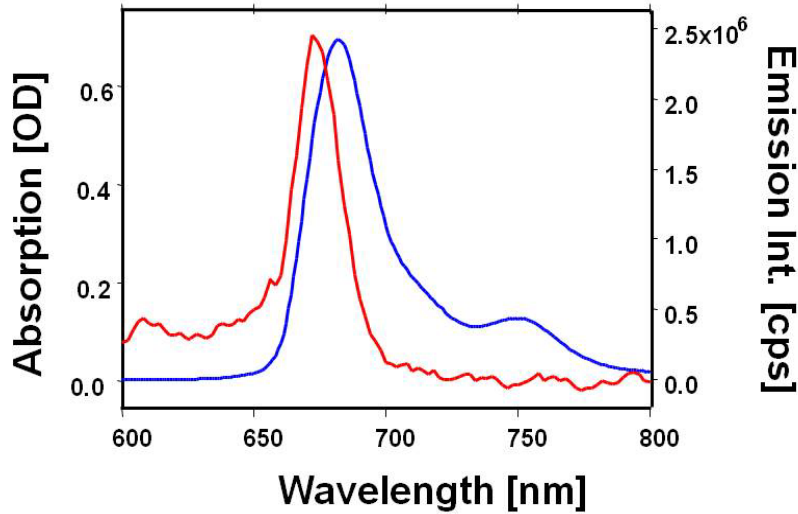**Figure 2.** Schematic of the pump probe experimental technique used in this study.

Figure 3 Emission spectrum (blue, right) and absorption spectrum (red, left) of the symmetric Zn-phthalocyanine study

3. RESULTS & DISCUSSION

To generate 400 nm fs pulses we used the second harmonic generation technique. BBO or beta-BaB$_2$O$_4$ is a nonlinear optical crystal which combines a number of unique features including wide transparency and phase matching ranges, large nonlinear coefficient, high damage threshold and excellent optical homogeneity. Frequency-doubling and -tripling of ultrashort-pulse lasers are the applications in which BBO shows superior properties to KDP and ADP crystals **(d$_{11}$ = 2.3 pm/V)**. An ultrashort laser pulse of even 10 fs can be efficiently frequency-doubled with a thin BBO, in terms of both phase-velocity and group-velocity matching. BBO's relatively narrow angular acceptance bandwidth (especially in the UV) may limit its usefulness in certain applications involving lasers with less than diffraction limited beam quality. BBO has a relatively large d$_{eff}$, **2.01 pm/V** @ 1060 nm and **1.99 pm/V** @ 780 nm, but also a large walk-off which reduces the conversion efficiency.

Sellmeier equation for BBO:

$n_o^2(\lambda) = 2.7359 + 0.01878/(\lambda^2 - 0.01822) - 0.01354\,\lambda^2$; n_0 (800) = 1.6606; n_0 (400) = 1.6930
$n_e^2(\lambda) = 2.3753 + 0.01224/(\lambda^2 - 0.01667) - 0.01516\,\lambda^2$; At λ_0 = 800 nm $v_g(\lambda_0/2)$ = 1.6830 × 10^8 m/s $v_g(\lambda_0)$ = 1.7810 × 10^8 m/s & Group Velocity Mismatch (GVM) @ 800 nm = 192 fs/mm.
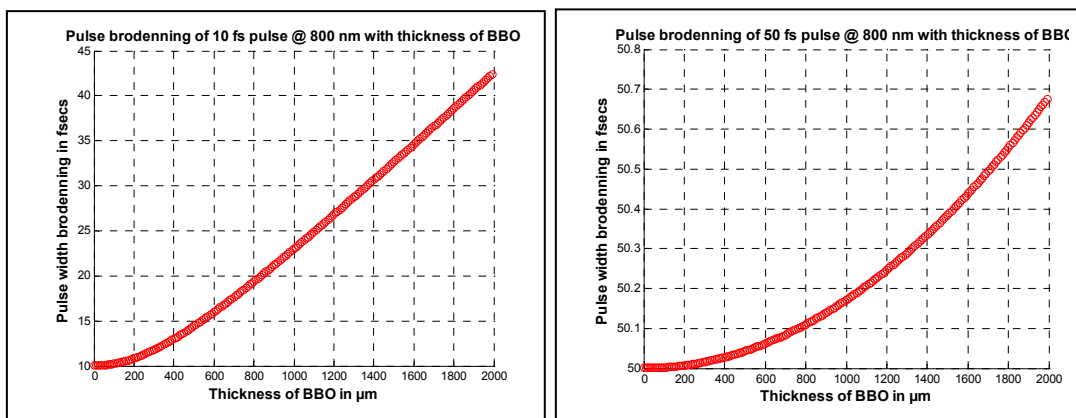

Figure 4 Pulse broadening as a function of BBO crystal length for (a) 10 fs pulse (b) 50 fs pulse.

Figure 4 shows the effects of group velocity dispersion (GVD) on pulse broadening for (a) 10 fs and (b) 50 fs pulses simulated using Matlab software. Figure 5 depicts the GVD as a function of wavelength. GVD value estimated for BBO crystal at 800 nm was 74.73 fs^2/mm.
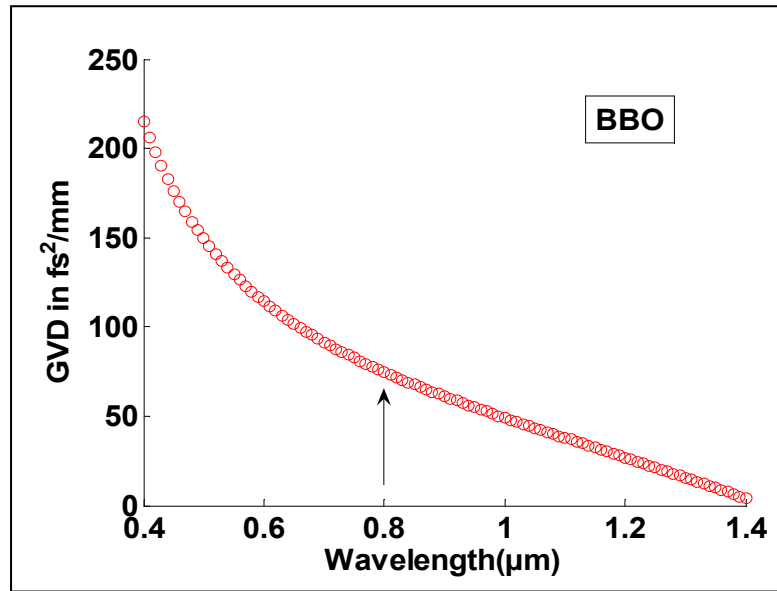

Figure 5 GVD in BBO crystal as a function of wavelength. Inset shows the variation of GVM with wavelength for SHG.
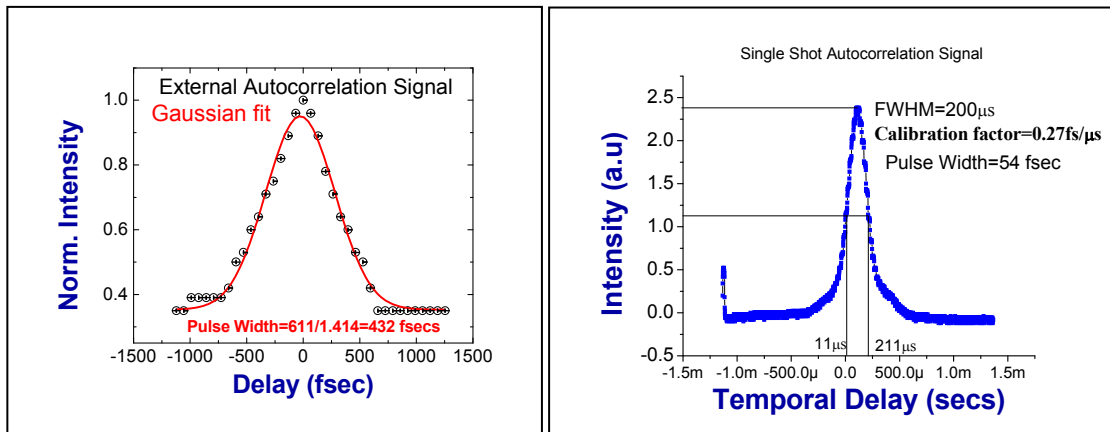

Figure 6 Pulse duration measurements of a 54 fs pulse using (a) External autocorrelation using 2-mm thick BBO crystal (b) Using a commercially available single shot autocorrelator (Coherent).

We had performed autocorrelation studies on ~**50 fs** pulses from an amplifier at 800 nm using a single shot autocorrelator (figure 6b) and an external autocorrelation set up (figure 6a) using 2-mm thick BBO crystal. From the simulations, and using equation given below, we have extracted the actual pulse duration of 400 nm pulses after travelling the BBO crystal (2 mm) to be ~**426 fs**. Experimental value observed in our case was ~**432 fs**. These values (GVM) match very well with those reported in literature [21-23]. Since the blue pulses were broadened quite a bit and the average power associated with them was poor we had switched to tunable radiation available from TOPAS-C (Light Conversion) for pump-probe experiments.

$$\delta t = \frac{L}{V_g(\lambda_0/2)} - \frac{L}{V_g(\lambda_0)} = L \ GVM$$

Figure 7(a) shows a typical pump-probe data for a thin film of USPc doped in PMMA with a pump power (unfocused) of 45 mW. A clear decay was observed post the coherence spike (zero delay) and was reproducible. The lifetime achieved using the single exponential fit was ~60 ps. Figure 7(b) depicts the pump probe data obtained with lower average powers and the lifetime obtained from the best fit to the experimental data was ~50 ps. We expect the small difference arising from the experimental errors (delays, calibration of power meter, fitting errors etc.)
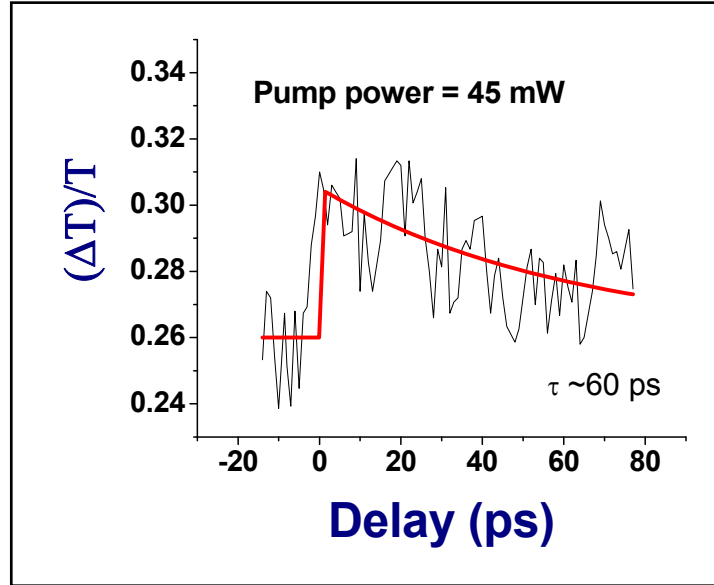
(a)
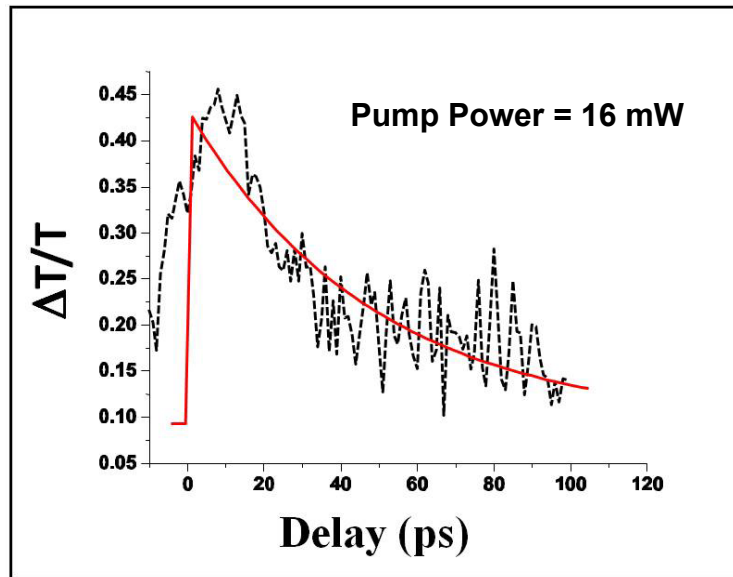
(b)

Figure 7 (a) Pump probe data for unsymmetrical ZnPc (USPc) with an input pump power (unfocused) of ~45 mW. The lifetime obtained from the best fit was ~60 ps. (b) Pump probe data for the same sample with an input pump power of ~16 mW. The lifetime was ~50 ps. Both the data were recorded at 590 nm.

Figure 8 shows the pump-probe data for SPc recorded at 610 nm. The lifetime achieved from the best fit was ~30 ps indicating faster response compare to USPc. We can draw the following conclusions from our data: (a) Signal to noise ratio (SNR) is poor with lots of scattering in the data. Though the data is noisy, the lifetimes were reproducible within an experimental error of ±20%. We are in the process of improving it through a better detection system of sensitive photo-diode and lock-in amplifier combination, (b) These data provide us with order of magnitude for the excited state relaxation mechanism, (c) The data was achieved without focusing the laser pulses so as to achieve better overlap of the pulses and at the same time interrogate larger area of the samples.

In the solid state, phthalocyanine molecules tend to aggregate making the Q-band broader than that of the monomer in solution form [24–28]. In addition, due to the interaction between molecules in the films or because of molecular distortion, the two-fold degeneracy of the lowest unoccupied molecular orbital (LUMO) band is lifted into two bands with finite oscillator strength [29]. Several other phthalocyanines in thin film form were studied [30-33] for their excited state dynamics and lifetimes of few ps to few tens of ps were observed. Ma et al. [30] observed three lifetimes from their ultrafast studies and attributed the shortest (<1 ps) to electron-phonon interaction, the 130 ps lifetime to the intersystem crossing, and the ns lifetime to the radiative transition from S_1 to S_0. Mi et al. [31] found strong wavelength dependence of the Q-band excited state dynamics. They too observed three different timescales in magnesium phthalocyanine thin film and attributed the 1 ps component to exciton-exciton annihilation, 16.5 ps component to the intersystem crossing rate and the longest component of 300 ps to the non-radiative relaxation process.

The origin of lifetimes in our molecules is being thoroughly scrutinized using a while light continuum probe. Our future studies will focus on (a) Improving the SNR, (b) Focusing the beams for achieving higher peak intensities and use lower pulse energies, (c) Check the intensity and polarization dependence of the lifetimes, (d) Investigate the spectral dependence of the excited state dynamics.
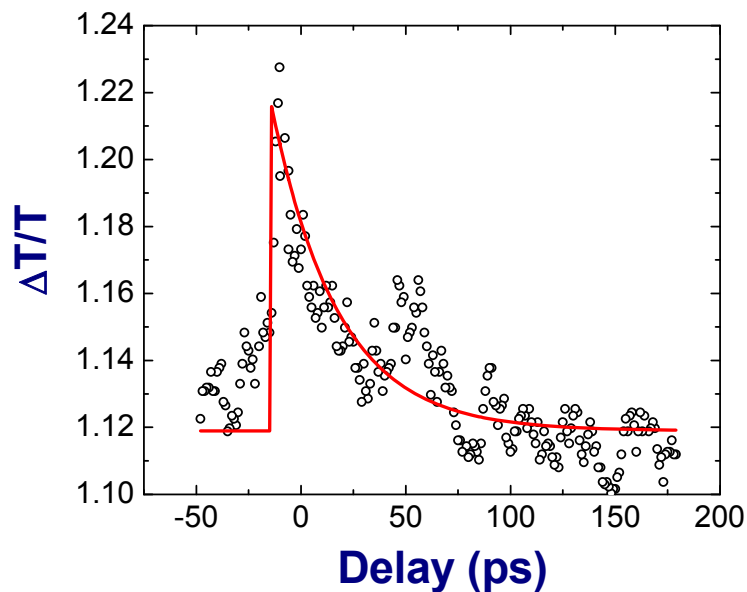

Figure 8 Pump probe data for symmetric ZnPc (SPc) with an input pump power (unfocused) of ~20 mW recorded at 610 nm.

4. CONCLUSIONS

In conclusion the relaxation dynamics of the excited states of SPc and USPc films has been studied using femtosecond pump probe technique. The dynamics of SPc indicated a lifetime of ~30 ps while that of USPc indicated a lifetime of ~60 ps. Further nonlinear optical studies are in progress to identify the magnitude of nonlinearity in these films.

ACKNOWLEDGEMENTS

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