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Ultrafast excited state dynamics and dispersion studies of nonlinear optical properties in dinaphthoporphycenes

Debasis Swain,[1] P. T. Anusha,[1] T. Shuvan Prashant,[1] Surya P. Tewari,[1] Tridib Sarma,[2] Pradeepta K. Panda,[1,2] and S. Venugopal Rao[1,a)]

[1]*Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Gachibowli, Hyderabad 500046, India*
[2]*School of Chemistry, University of Hyderabad, Gachibowli, Hyderabad 500046, India*

Ultrafast excited state dynamics of dinaphthoporphycenes were investigated using femtosecond and picosecond degenerate pump-probe techniques at 600 nm and 800 nm, respectively. Femtosecond pump-probe data indicated photo-induced absorption at 600 nm resulting from two-photon/single photon excitation, whereas picosecond pump-probe data demonstrated photo-bleaching which was a consequence of three-photon absorption. The fastest lifetimes (100–120 fs) observed are attributed to the intramolecular vibrational relaxation, the slower ones (1–3 ps) to internal conversion, and the slowest components (7–10 ps) to non-radiative decay back to ground state. Z-scan studies in the 560–600 nm range were also carried out. © *2012 American Institute of Physics.*
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Porphyrins, phthalocyanines, and porphycenes are large aromatic molecules with huge number of π electrons in conjugation and, consequently, possess interesting optical and nonlinear optical (NLO) properties. Combined with their ultrafast response, numerous studies have demonstrated that these materials find potential applications in a variety of fields such as photodynamic therapy (PDT), biological imaging, dye-sensitized solar cells, and photonics.[1–17] Porphycene is the first constitutional isomer of porphyrin and found to act as better photo-sensitizer than the latter.[18,19] Porphycenes and their derivatives display unique physical and optical properties, including strong absorptions in the red region of the UV-Vis spectrum.[20–24] Recently, we have investigated a set of dinaphthoporphycenes possessing interesting third-order NLO properties.[25,26] NLO studies performed at 800 nm using ps pulses revealed singular nonlinear absorption properties and large NLO coefficients.[25,26] Several other groups have also demonstrated their potential in applications such as two-photon imaging, PDT, 3D-optical memory, and ultra-fast switches.[27–29] The true potential of any molecule is revealed only through extensive studies using different pulses (ns, ps, and fs pulses). Extending our earlier studies,[25,26] further we deliberated the NLO properties with ps pulses at 560 nm, 580 nm, and 600 nm. Importantly, we have also investigated the temporal response of these molecules using ultrashort pulses. A significant progress has been made for studying the photo-physical properties of such molecules.[30–35] Due to lack of dipole moments in these molecules, relaxation from excited states may be conveniently observed without any solvation effects.[30] Detailed pump-probe (p-p) results of dinaphthoporphycenes at 800 nm, obtained using ~2 ps pulses, and at 600 nm, obtained using ~60 fs pulses, are discussed here.

Different porphycenes (Po1-Po5) were synthesized and purified using the methods reported elsewhere.[25] The compounds were dissolved in chloroform to obtain solutions of 0.25 mM concentration corresponding to a linear transmittance of 70%–80% near 800 nm. Z-scan measurements[36] were performed at 560 nm, 580 nm, and 600 nm using ~2 ps (FWHM) pulses with a repetition rate of 1 kHz from TOPAS (Light Conversion) pumped with an amplified Ti:Sapphire system (Legend, Coherent). The amplifier was seeded with pulses of duration ~15 fs (FWHM, ~60 nm bandwidth) from an oscillator (Micra, Coherent). A quartz cuvette (1 mm thick) containing the sample solution was traversed in the focusing geometry enabled by an achromat lens of 200 mm focal length. The beam waist $(2\omega_0)$ at focal plane was estimated to be $60 \pm 4\,\mu m$ (FW1/e^{2}M) with a corresponding Rayleigh range (Z_r) of 3.5 ± 0.4 mm ensuring the validity of thin sample approximation. The solvent used in all the studies was chloroform, and the solvent contribution was found to be insignificant. The fits to the data were performed using standard two photon absorption (2PA) equations.[37]
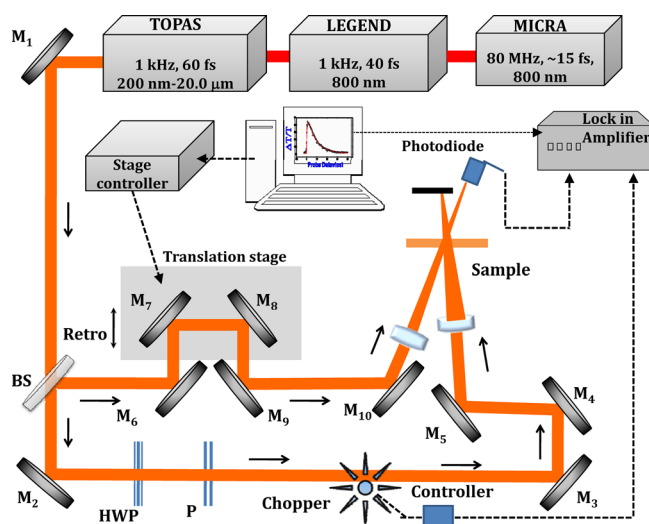

FIG. 1. Schematic diagram of the experimental set up used for pump-probe studies at 600 nm.

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a)Authors to whom correspondence should be addressed. Electronic addresses: svrsp@uohyd.ernet.in and soma_venu@yahoo.com.
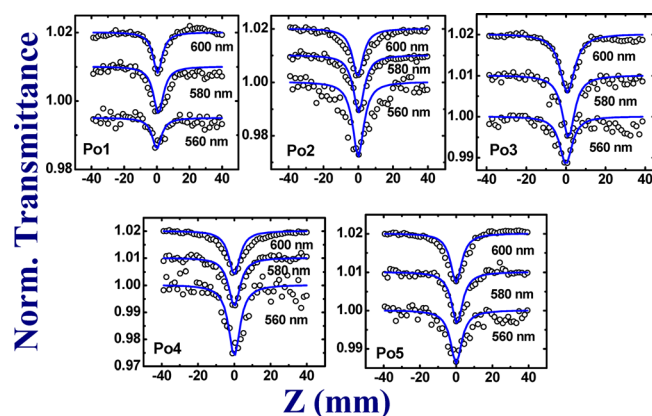
FIG. 2. Open aperture Z-scans of Po1-Po5 at different wavelengths at 560 nm, 580 nm, and 600 nm indicating 2PA behavior. Some of the plots have been shifted vertically for clarity.

FIG. 3. (a)-(e) Excited state dynamics data of Po1-Po5 obtained using ps pulses at 800 nm. Noisy lines (Black lines) represent the experimental data, while the smooth solid lines (red lines) are fits to the data.

The fs degenerate pump-probe experiments were performed at 600 nm, while the ps experiments were performed at 800 nm. A schematic of the set up is shown in Figure 1 for the fs case. In both cases, the liquid sample was taken in a 5 mm thick glass cuvette. In the fs case, molecules were excited by pulses from 1 kHz optical parametric amplifier (TOPAS-C, Light Conversion, Coherent) delivering pulses of ~60 fs duration pumped by a Ti:Sapphire regenerative amplifier. Pump pulses in the energy range of 5–50 μJ were used. The probe beam diameter was ~2 mm, and pump beam diameter was ~4 mm. The pulse-width at the sample in our fs experiments was estimated (taking into account the optics and lenses involved) to be ~70 fs. The pump beam was focused using a 150 mm lens, while the probe beam was focused using a longer focal length lens (500 mm). Typical pump beam intensity was ~0.3–3 TW/cm^2, while the probe beam intensity was ~5 GW/cm^2. The ratio of pump to probe intensities was at least 60. The pump beam was modulated at ~100 Hz with the help of a chopper, and the change in probe transmitted intensity was measured with a combination of a photodiode (SM05R/M, Thorlabs) and a lock-in amplifier (7265, Signal Recovery). In the ps pump-probe set up, the pump and probe beam diameters were ~4 mm and ~2 mm, respectively. The pump and probe beams were focused using 200 mm lenses. Typical peak intensities of pump and probe beams in the ps case were ~150 GW/cm^2 and ~2–4 GW/cm^2, respectively. The ratio of pump to probe intensities was at least 75. The focusing in both the cases was such that the probe beam diameter was ensured to be slightly smaller than the pump beam diameter. The polarization of pump and probe
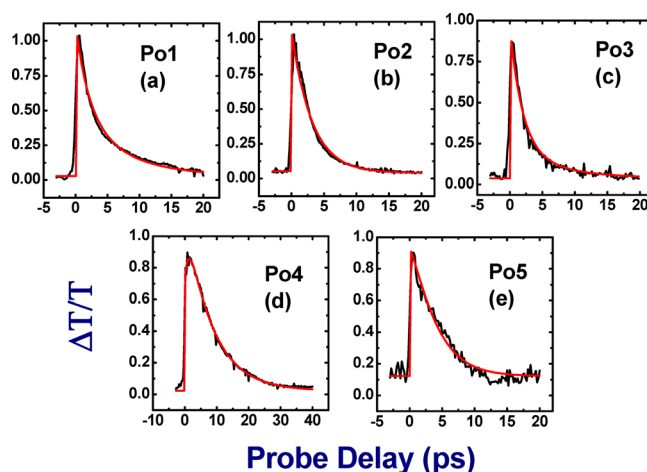
beams was perpendicular in both the cases to avoid diffraction effects leading to coherent artefacts.[38]

The absorption spectra (already reported in Refs. 25 and 26) illustrate red shifted Soret bands and Q-bands compared to β-alkylated porphycenes, owing to the rigidification and extended-π system resulted by the fusion of two naphthalenes onto the porphycene macrocycle. The absorption spectra of free-base porphycene (Po1, Po2, Po3) display relatively intense low energy Q-band (15 625 cm^{-1} to 12 000 cm^{-1}) peaking near 14 000 cm^{-1} and well defined Soret or B-bands peaking near 25 000 cm^{-1}. Figure 2 shows the open aperture Z-scan data obtained for Po1-Po5 at 560 nm, 580 nm, and 600 nm. 2PA was the dominant mechanism observed, but one cannot rule out the presence of excited state absorption from S_1 to S_2 states. The fits to the data provided the values of an *effective* 2PA coefficient (β) in the range of 1.05×10^{-12} cm/W–8.70×10^{-12} cm/W. Evidently, these values are an order of magnitude lower than the values reported at 800 nm, which was a resonant two-photon wavelength for these molecules. The values of n_2 in the ps regime recorded for Po1-Po5 were in the range of 5–35×10^{-17} cm^2/W at 560 nm, 6.5–71×10^{-17} cm^2/W at 580 nm, and 10.8–78×10^{-17} cm^2/W at 600 nm. Interestingly, the n_2 values increased as excitation wavelength changed from 560 nm to 600 nm. This could be attributed to the excited state population as one gets closer to 600 nm where the absorption also increases slightly. The values at 560 nm, possibly, represent the true electronic nonlinearity to a great extent since there is minimal absorption at this

TABLE I. Nonlinear optical properties porphycenes at 560 nm, 580 nm, and 600 nm.

Sample	β (ps) 560 nm (cm/W) $\times 10^{-12}$	β (ps) 580 nm (cm/W) $\times 10^{-12}$	β (ps) 600 nm (cm/W) $\times 10^{-12}$	n_2 (ps) 560 nm (cm^2/W) $\times 10^{-17}$	n_2 (ps) 580 nm (cm^2/W) $\times 10^{-17}$	n_2 (ps) 600 nm (cm^2/W) $\times 10^{-17}$
CHCl$_3$	—	—	—	—	—	—
Po1	2.30	3.50	3.00	8.88	6.58	16.3
Po2	1.10	1.05	8.70	35.3	70.7	78.2
Po3	3.00	4.40	3.75	14.8	7.24	22.7
Po4	7.50	5.00	4.50	7.28	22.4	21.8
Po5	3.50	3.40	3.20	5.12	9.76	10.8

wavelength. Po2 had the largest n_2 values for all the wavelengths investigated in this study. Po4 had the largest 2PA values for both fs and ps excitations (except at 600 nm ps excitation). The values of nonlinear coefficients obtained from closed and open aperture data for all the molecules are tabulated in Table I.

It is well established that depending on the excitation wavelength and intensity, one can observe 2PA, three photon absorption (3PA), excited state absorption, or a combination of more than one process in such molecules owing to the configuration of their electronic states.[12,13,26,39,40] We performed the degenerate pump-probe experiments, and Figure 3 illustrates the data obtained with ps pulses at 800 nm. Depending on the energy levels of these molecules, one would expect multi-exponential decay following different excitation mechanisms. The transmitted probe data was fitted using the equation given below. For the case of single decay, it was observed only τ_1, for double decay, τ_1 and τ_2, and for triple exponential decay, τ_1, τ_2, and τ_3 were used.

$$\frac{\Delta T(t)}{T} = y_0 + A_1 e^{-(t-t_0)/\tau_1} + A_2 e^{-(t-t_0)/\tau_2} + A_3 e^{-(t-t_0)/\tau_3},$$

where $\Delta T(t)$ is the time dependent change in probe transmission, induced by the pump at time "t" after the pump excitation, and T is the probe transmission in the absence of pump. The peak intensities ($\sim$150 GW/cm^2) used in ps experiments were sufficient to access the three-photon states.[26] We observed photo-bleaching for all the porphycenes studied. The data were fitted with a double exponential decay, and two lifetimes were retrieved from the fits. We tried to fit the data for a single exponential, but the overall fit was poor. Fast decay retrieved was in the range of 1.8–3.1 ps, while the slow component varied from 7 ps to 8.5 ps for different samples. The fast component is attributed to the internal conversion (IC) in these molecules (S_2 to S_1 states), whereas the slower one to the non-radiative decay back to the ground state (S_1 to S_0 states). Similar decay times were observed in porphycene reported by Fita *et al.*[32] One needs to keep in mind that the pulse duration used was $\sim$2 ps, and any lifetime less than this would not be resolved. To resolve further the dynamics below 2 ps, we performed the experiments with $\sim$60 fs pulses at 600 nm. Photo-induced absorption was observed in the 600 nm fs pump-probe data for all the porphycenes. The negative transmission observed at 600 nm is depicted in Figure 4 for all the samples Po1-Po5. The data were obtained with focused pump and probe pulses with pump peak intensities sufficient to excite the molecules to S_2 states. Probe is absorbed from these states to higher states (S_n), thereby reducing the transmission. Fits obtained using single/double exponential were not providing perfect match to the experimental data, and therefore, triple exponential equation was utilized and three different lifetimes were retrieved from the fits. The fastest lifetime observed was in the 100–135 fs which is attributed to the intramolecular vibrational relaxation (IVR) within S_2 states, while the slower component of 0.8–1.5 ps could be due to the IC and the slowest one in the 7.3–10.0 ps range again due to non-radiative decay. To ensure that we are indeed exciting the molecules in S_2 states (followed by excitation into S_n states),
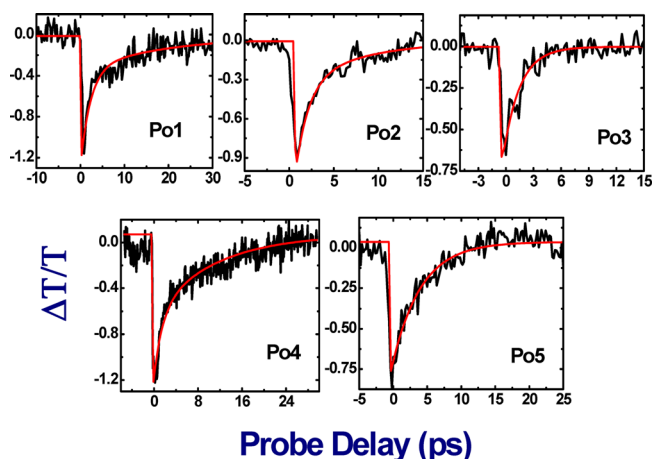

FIG. 4. (a)-(e) Excited state dynamics of Po1-Po5 using $\sim$70 fs pulses at 600 nm. The data were obtained using focused pump/probe beams. Noisy lines (Black lines) represent the experimental data, while the smooth solid lines (red lines) are fits to the data.

we performed the fs pump-probe measurements without focusing the pump and probe pulses, thereby ensuring there was no nonlinear absorption. When the beams are not focused, the excitation is limited to S_1 states only and, therefore, induced absorption from S_1 states to S_2 states suggesting decrease in probe transmission. The representative data obtained with unfocused pulses is shown in Figure 5 for Po1, Po2, and Po4. The data could be fitted with a single exponential, and the lifetimes extracted were 7.5 ps, 7.0 ps, and 10.9 ps for Po1, Po2, and Po4, respectively. Relaxation times extracted for all the samples are enlisted in Table II.

A qualitative explanation for relaxation mechanisms in both ps and fs regimes (focused and unfocused data) using detailed energy level structure is depicted in Figure 6. An unfocused 600 nm photon (16 667 cm^{-1}) will only excite the molecules to S_1 states at the best and, therefore, we observed only a single lifetime (assigned to S_1-S_0 decay). Though the scattering is evident in the data, we could fit a single lifetime and, more importantly, we could see the difference in shape of the probe transmission curve when recorded with high peak intensities. When excited with higher peak intensities at 600 nm, we expect the high lying S_2 states (33 333 cm^{-1}) to be populated through two photon absorption (to just below the S_n states) followed by excited state absorption from S_2 to S_n states and were able to observe three relaxation rates (IVR, IC, and S_1-S_0). When excited with ps pulses at 800 nm, we observed two distinct lifetimes which are
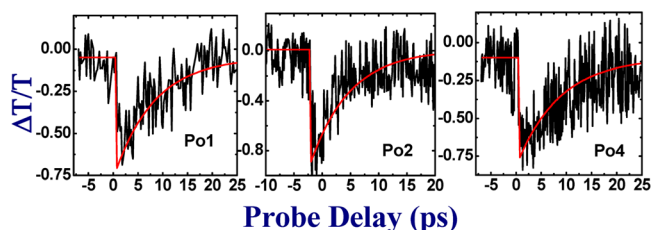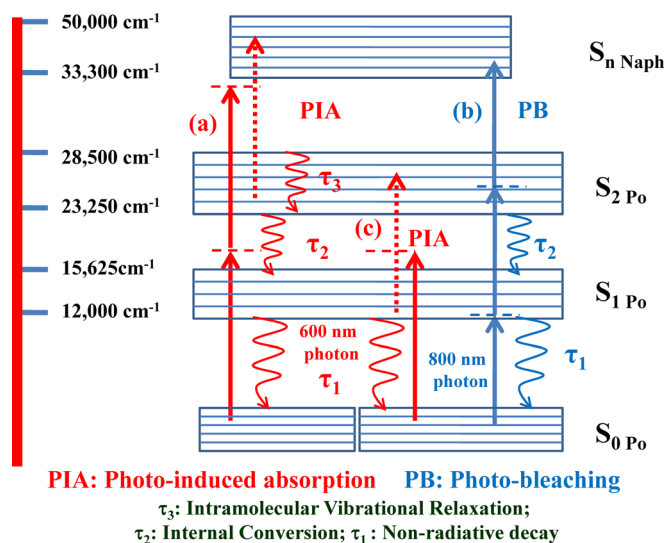

FIG. 5. Excited state dynamics of Po1, Po2, and Po4 using $\sim$60 fs pulses at 600 nm using unfocused pump/probe pulses. Noisy lines (Black lines) represent the experimental data, while the smooth solid lines (red lines) are fits to the data.

TABLE II. Lifetimes of porphycenes obtained using ps and fs pump-probe studies.

Samples	τ_2 800 nm (ps p-p)	τ_1 800 nm (ps p-p)	τ_3 600 nm (fs p-p)	τ_2 600 nm (fs p-p)	τ_1 600 nm (fs p-p)	τ_1 600 nm (fs p-p unfocused)
Po1	2.0 ps	7.2 ps	120 fs	0.8 ps	8.0 ps	7.5 ps
Po2	3.1 ps	7.6 ps	105 fs	1.4 ps	7.3 ps	7.0 ps
Po3	2.0 ps	7.2 ps	102 fs	1.2 ps	8.2 ps	—
Po4	1.8 ps	8.5 ps	100 fs	1.5 ps	10.0 ps	10.9 ps
Po5	1.8 ps	7.0 ps	135 fs	1.2 ps	8.1 ps	—

attributed to the S_2-S_1 transition (IC) and S_1-S_0 transition (slowest component). The values presented in Table II confirm that the fs data and ps data are corroborating each other, within experimental errors, and support our arguments about different excitation schemes. Since these are non-fluorescent molecules, we feel that the lifetimes observed are due to non-radiative transitions (thermalization processes). The errors (from experiments and fitting procedures) in these measurements were estimated to be ∼15% for the focused data and ∼20% for unfocused data.

In summary, we have performed degenerate pump-probe using ∼60 fs at 600 nm and ∼2 ps laser pulses centred at 800 nm of five different dinaphthoporphycenes. Our ps Z-scan results clearly demonstrate 2PA at all wavelengths. Two component carrier relaxation dynamics with the fast time constant in the range of 1.8–3.1 ps and the slower one in 7.0–10.0 ps range were observed with ps excitation. We could observe three decay time constants of 100–120 fs, 0.8–1.5 ps, and 7.3–10.0 ps in the fs pump-probe data. The lifetimes observed were similar in both the ps and fs cases. The fastest lifetime is attributed to IVR in the S_2 states, while the intermediate lifetime to the S_2 to S_1 states de-excitation (IC). The longest life time is characteristic of the S_1 to S_0 non-radiative decay. The present results demonstrating the strong nonlinear absorption properties of dinaphthoporphycenes combined with ultrafast response times may find possible applications in photonics.

FIG. 6. Energy level diagram of Po1-Po5 depicting the various relaxation times from different excited states: (a) fs pulses, focused pump and probe data, 600 nm; (b) ps pulses, focused pup and probe data, 800 nm; (c) fs pulses, unfocused pump and probe data, 600 nm.

[1]M. O. Senge, M. Fazekas, E. G. A. Notaras, W. J. Blau, M. Zawadzka, O. B. Locos, and E. M. N. Mhuircheartaigh, Adv. Mater. **19**, 2737 (2007).
[2]G. de la Torre, P. Vazquez, F. Agullo-Lopez, and T. Torres, Chem. Rev. **104**, 3723 (2004).
[3]J. S. Shirk, R. G. S. Pong, F. J. Bartoli, and A. W. Snow, Appl. Phys. Lett. **63**, 1880 (1993).
[4]M. Pawlicki, H. A. Collins, R. G. Denning, and H. L. Anderson, Angew. Chem., Int. Ed. **48**, 3244 (2009).
[5]F. E. Hernández, S. Yang, E. W. Van Stryland, and D. J. Hagan, Opt. Lett. **25**, 1180 (2000).
[6]T. H. Wei, D. J. Hagan, M. J. Sence, E. W. Van Stryland, J. W. Perry, and D. R. Coulter, Appl. Phys. B **54**, 46 (1992).
[7]R. A. Norwood and J. R. Sounik, Appl. Phys. Lett. **60**, 295 (1992).
[8]S. Venugopal Rao, N. K. M. N. Srinivas, L. Giribabu, B. G. Maiya, D. Narayana Rao, R. Philip, and G. R. Kumar, Opt. Commun. **182**, 255 (2000).
[9]S. Venugopal Rao, N. K. M. N. Srinivas, L. Giribabu, B. G. Maiya, D. Narayana Rao, R. Philip, and G. R. Kumar, Opt. Commun. **192**, 123 (2001).
[10]S. Venugopal Rao and D. Narayana Rao, J. Porphyr. Phthalocyanines **6**(3), 234 (2002).
[11]P. Prem Kiran, D. Raghunath Reddy, B. G. Maiya, A. K. Dharmadhikari, G. Ravindra Kumar, and D. Narayana Rao, Opt. Commun. **252**, 150 (2005).
[12]R. S. S. Kumar, S. Venugopal Rao, L. Giribabu, and D. Narayana Rao, Chem. Phys. Lett. **447**, 274 (2007).
[13]N. Venkatram, D. Narayana Rao, L. Giribabu, and S. Venugopal Rao, Chem. Phys. Lett. **464**(4–6), 211 (2008).
[14]P. T. Anusha, L. Giribabu, S. P. Tewari, and S. Venugopal Rao, Mater. Lett. **64**, 1915 (2010).
[15]S. Venugopal Rao, P. T. Anusha, L. Giribabu, and S. P. Tewari, Pramana **75**(5), 1017 (2010).
[16]S. Venugopal Rao, N. Venkatram, L. Giribabu, and D. N. Rao, J. Appl. Phys. **105**, 053109 (2009).
[17]N. Venkatram, L. Giribabu, D. N. Rao, and S. Venugopal Rao, Appl. Phys. B **91**, 149 (2008).
[18]E. Vogel, M. Kocher, H. Schmickler, and J. Lex, Angew. Chem., Int. Ed. Engl. **25**, 257 (1986).
[19]J. L. Sessler, A. Gebauer, and E. Vogel, "Porphyrin Isomers," in *The Porphyrin Handbook*, edited by K. M. Kadish, K. M. Smith, and R. Guilard (Academic, New York, 2000), Vol. **2**, Chap. 8.
[20]D. Sanchez-Garcia and J. L. Sessler, Chem. Soc. Rev. **37**, 215 (2008).
[21]O. Arad, J. Morros, X. Batllori, S. Teixido, S. Nonell, and J. I. Borrell, Org. Lett. **8**, 847 (2006).
[22]S. Gawinkowski, G. Orzanowska, K. Izdebska, M. O. Senge, and J. Waluk, Chem.-Eur. J. **17**, 10039 (2011).
[23]L. Cuesta, E. Karnas, V. M. Lynch, P. Chen, J. Shen, K. M. Kadish, K. Ohkubo, S. Fukuzumi, and J. L. Sessler, J. Am. Chem. Soc. **131**, 13538 (2009).
[24]V. Roznyatovskiy, V. Lynch, and J. L. Sessler, Org. Lett. **12**, 4424 (2010).
[25]T. Sarma, P. K. Panda, P. T. Anusha, and S. Venugopal Rao, Org. Lett. **13**, 188 (2011).
[26]S. Venugopal Rao, T. Shuvan Prashant, D. Swain, T. Sarma, P. K. Panda, and S. P. Tewari, Chem. Phys. Lett. **514**, 98 (2011).
[27]J. C. Stockert, M. Canete, A. Juarranz, A. Villanueva, R. W. Horobin, J. Borrell, J. Teixidó, and S. Nonell, Curr. Med. Chem. **14**, 997 (2007).
[28]M. K. Abdel-Latif and O. Kuhn, Theor. Chem. Acc. **128**, 307–316 (2011).

[29]J. Arnbjerg, J.-B. Ana, J. P. Martin, S. Nonell, J. I. Borrell, O. Christiansen, and P. R. Ogilby, J. Am. Chem. Soc. **129**, 5188 (2007).

[30]J. Dobkowski, V. Galievsky, A. Starukhin, E. Vogel, and J. Waluk, J. Phys. Chem. A **102**, 4966 (1998).

[31]J. Dobkowski, Y. Lobko, S. Gawinkowski, and J. Waluk, Chem. Phys. Lett. **416**, 128 (2005).

[32]P. Fita, C. Radzewicz, and J. Waluk, J. Phys. Chem. A **112**, 10753 (2008).

[33]J. Waluk, M. Muller, P. Swiderek, M. Kocher, E. Vogel, G. Hohlneicher, and J. Michl, J. Am. Chem. Soc. **113**, 5511 (1991).

[34]J. Dobkowski, V. Galievsky, A. Starukhin, E. Vogel, and J. Waluk, J. Phys. Chem. A **102**, 4966 (1998).

[35]M. Gil, J. A. Organero, J. Waluk, and A. Douhal, Chem. Phys. Lett. **422**, 142–146 (2006).

[36]M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. J. Hagan, and E. W. Van Stryland, IEEE J. Quantum Electron. **26**(4), 760 (1990).

[37]K. V. Saravanan, K. C. James Raju, M. G. Krishna, S. P. Tewari, and S. Venugopal Rao, Appl. Phys. Lett. **96**, 232905 (2010).

[38]H. Liu, H. Zhang, J.-H. Si, L.-H. Yan, F. Chen, and X. Hou, Chin. Phys. Lett. **28**(8), 086602 (2011).

[39]M. Morisue, K. Ogawa, K. Kamada, K. Ohta, and Y. Kobuke, Chem. Commun. **46**(12), 2121 (2010).

[40]R. L. Sutherland, M. C. Brant, J. Heinrichs, J. E. Slagle, D. G. McLean, and P. A. Fleitz, J. Opt. Soc. Am. B **22**, 1939 (2005).