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Excited-state dynamics of magnesium phthalocyanine thin film

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Abstract

Ultrafast excitation relaxation dynamics of magnesium phthalocyanine (MgPc) thin film were investigated by femtosecond pump-probe spectroscopy. The excited state dynamics of MgPc's Q-band were found to be strongly dependent on the probe wavelength. Ultrafast exciton–exciton annihilation with a $t^{-1/2}$ time dependence of the excited-state population was observed. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

Phthalocyanines (Pcs) are promising materials for their unique properties such as photoconducting, optical limiting, large optical nonlinearity and ultrafast optical response, due to their macrocycle delocalized 18π -electron systems [1]. Pcs are characterized by two broad strong absorption bands in the UV-vis region, chemical and thermal stability, relative ease of thin-film fabrication, and a high laser damage threshold. Many investigations have indicated Pcs' promising applications such as a photoreceptor in laser print system [2], light emitting devices [3], gas sensor [4], photovoltaic cell [5] and nonlinear optical devices [6]. The relaxation mechanism of the photo-induced excitation is one of the most important factors

determining the performance of such devices. Thus, the fundamental knowledge of photo-excitation dynamics in Pcs is required in view of their application in the photonic field.

Magnesium phthalocyanine (MgPc) is a near-IR-active photoconductor used practically for laser printer. Recently, its special optical properties and crystal structure have attracted much attention. Mizuguchi et al. [7] studied the optical spectra of solid-state MgPc regarding molecular distortions and exciton coupling effects, and suggested that the MgPc molecule is not planar in the solid state, but the central Mg atom is located out of the molecular plane, forming a pyramidal structure. X-ray single crystal diffraction investigated by Janczak et al. [8] and π – π interaction evaluated by energy partition analysis by Mizuguchi [9] demonstrated that intermolecular Mg–N interactions along the molecular stacks stabilize MgPc by the formation of five-coordinate MgPc complexes (dimers).

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Photoluminescence properties studied by Sakakibara et al. [10] showed that fluorescence quantum yields of MgPc films at room temperature were much smaller than that of the monomer in solution, indicating that nonradiative relaxation is dominant in the solid films. These investigations resulted in the understanding of the MgPc's structural properties and absorption spectra, however there was not much knowledge about its excited states dynamics. In our previous work [11], the nonlinearity and its dynamics were investigated by femtosecond (fs) optical Kerr effect and pump-probe spectroscopy. A third order susceptibility $\chi^{(3)} = 5.6 \times 10^{-11}$ esu was reported. The excited states of MgPc decayed through several processes: an ultrafast process with lifetime less than 200 fs, a slow process on a 6 ps time scale and a very slow process with recovery time of hundreds picoseconds. The ultrafast component was explained as the internal conversion due to a strong exciton–phonon interaction, the slow component was assigned to the decay of singlet excited state via inter-system-crossing (ISC), and the very slow component was due to the nonradiative relaxation from the triplet state to the ground state. These results were obtained at relatively low excitation intensity (hundreds of MW/cm²) and with the probe wavelength located near the bottom of Q-band. However, at high excitation intensity, nonlinear bimolecular interactions will play a vital role and excitation saturation will take place, which should lead to quite different excited states dynamics. In that case, by tuning the probe wavelength within the Q-band and using high pump intensities, more information about excited-state dynamics can be explored.

The present study focuses on the excited-state relaxation dynamics and mechanisms of MgPc thin film fabricated by physical jet deposition (PJD) technique in the whole Q-band region after excited with intense excitation. By performing femtosecond pump-probe spectroscopy, strong probe wavelength dependent dynamics and nonlinear exciton–exciton annihilation were observed.

2. Experimental section

2.1. Sample preparation

The synthesis of MgPc was described in our previous work [11]. MgPc films were fabricated by PJD

technique described in detail elsewhere [12]. Simply speaking, the MgPc powder was heated to 410 °C in a vacuum chamber at pressure of 10⁻² Torr, the vapor of MgPc was carried by the high speed flowing Ar-gas and deposited on the fused silica substrates. The thickness of the film was about 1 μm. The absorption spectrum was measured by using UV3101-PC spectrophotometer.

2.2. Femtosecond pump-probe setup

Pulses of 100 fs pulse duration, 5 nJ pulse energy and 82 MHz repetition rate at 800 nm were generated by a mode-locked Ti:Sapphire oscillator (Spectra Physics, Tsunami), which were amplified by a regenerated amplifier (Spectra Physics, Spitfire) pumped by a Q-switched Nd:YLF laser. The amplified pulses beam with 120 fs duration, 500 μJ pulse energy and 1 kHz repetition rate was split into two beams. The intense one with pulse energy about 300 μJ was focused onto a 10 mm-thick quartz plate to generate white-light supercontinuum. The fs supercontinuum pulses covering the 450–1000 nm spectral region was used as the probe beam. Various interference narrow band filters (with FWHM around 10 nm) were used to select the desired probe wavelength from the white-light supercontinuum. The weaker 800 nm beam chopped at 600 Hz was used as the pump beam, which passed through a variable optical delay line. The diameters of the focused laser spots of the pump and probe beams on the sample were 200 and 30 μm, respectively. Two beams with parallel polarization were spatially overlapped inside the sample. After penetrating through the sample, the pump beam was blocked by an aperture, while the transmitted probe beam was collimated to a photodiode, amplified by a lock-in amplifier and monitored as a function of time delay between the pump and the probe beams. For one color dynamics investigation at 800 nm, a weak beam split from the amplified pulses was used as the probe, and the intensity of the pump beam was controlled by a quarter-wave plate and polarizer combination. For pulses beam with 200 μm spot diameter, 1 mW average power, 1 kHz repetition rate and 120 fs duration, the pump intensity in the sample is estimated to be 26 GW/cm².

3. Results and discussion

3.1. Absorption spectrum

The absorption spectrum of the MgPc thin film (Fig. 1) shows two strong bands, attributed to the $\pi-\pi^*$ electronic transitions in MgPc, a broad Q-band in visible and a Soret or B-band in the ultraviolet region. The Q-band is much broader and split into two components with peaks located at 694 and 750 nm, red shifted as compared to the monomer with a peak at 670 nm [13]. The splitting of Q-band was explained by the aggregations of the molecules or molecular distortion [14–20]. In the solid state, Pc's molecules are aggregated and the Q-band becomes much broader than that of the monomer in solution due to strong intermolecular interactions resulting in exciton coupling effects (including the Davydov splitting) of the allowed transitions or the lift of the degeneracy of two LOMO orbits induced by molecular distortion. For adjacent MgPc molecules of D_{4h} symmetry, exciton coupling results in a splitting of the excited state into two energy levels. The relative orientation of the transition dipole moments determines which of these energy levels would give rise to light absorption. In the case of cofacial dimers, transitions to the higher energy levels are allowed, which yields blue shifted absorption. On the contrary, in the case of parallel but not cofacial ('edge to edge') dimers, a red shift is expected. Investigations performed by Janczak et al. [8] and Mizuguchi [7,9] revealed that the magnesium atom is in a position

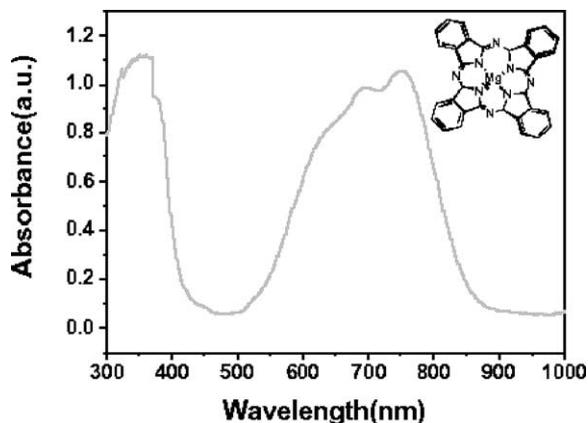


Fig. 1. The absorption spectrum of MgPc PJD thin film.

to accept an electron lone pair of the nitrogen atom forming a five-coordinate complex in the solid state. The magnesium phthalocyanine in the solid state is not planar, the Mg atom is projected upward, out of the plane by about 0.45 Å, thus forming a pyramidal structure (C_1 symmetry). This strong molecular deformation upon crystallization lifts the degeneracy of the excited state and induces a band splitting. The molecular distortion also leads to a change in the direction of the transition dipoles. Molecular distortion is found to increase the band splitting in such a way that the longer wavelength band is displaced toward longer wavelength, while the short-wavelength band is shifted toward shorter wavelength.

3.2. Excited states dynamics

Fig. 2 shows the transient excited states dynamics probed at various wavelengths under excitation intensity of 7.8 GW/cm² at 800 nm. The dynamics parameters summarized in Table 1 were got by fitting the experiment data based on a biexponential model, $\Delta T = \Delta T_1 \times \exp(-t/t_1) + \Delta T_2 \times \exp(-t/t_2) + C$, where ΔT_1 , ΔT_2 and t_1 , t_2 are the contributions and lifetimes of two corresponding components, respectively, C is a constant. At initial time after excitation, the whole Q-band shows an ultrafast increase of the

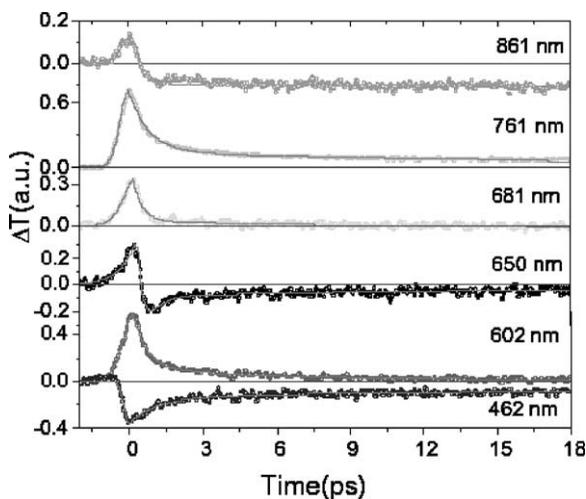


Fig. 2. Dynamics of differential transmission of MgPc PJD thin film probed at different wavelengths, excited by 120 fs, 800 nm pulses with intensity of 7.8 GW/cm².

Table 1
Parameters of the decay process at different probe wavelengths

Wavelength (nm)	ΔT_1	t_1 (fs)	ΔT_2	t_2 (ps)
861	0.25	468	-0.1	> 1000
800 ^a	0.76	1100	0.18	16.5
761	0.59	790	0.14	19.7
681	0.31	380	0.04	3.5
650 ^a	1.37	245	-0.94	0.42
602	0.46	550	0.11	5.2
462	-0.23	1220	-0.13	53.2

^a Decay dynamics at 650 and 800 nm are fitted by a triexponential component: $\Delta T = \Delta T_1 \times \exp(-t/t_1) + \Delta T_2 \times \exp(-t/t_2) + \Delta T_3 \times \exp(-t/t_3) + C$, for 650 nm $\Delta T_3 = -0.1$, $t_3 = 22.5$ ps, for 800 nm, $\Delta T_3 = 0.1$, $t_3 = 397$ ps.

transmission of the probe beam, while it shows an ultrafast decrease with probe beam at 462 nm. When the absorption cross section of the excited state is smaller than that of the ground state, the saturation absorption will take place, and vice versa the excited state absorption will happen, leading to a photoabsorption. Metallophthalocyanines (MPcs) usually show large singlet and triplet excited states absorption in the wavelength region between the Q-band and B-band (Soret band), where the ground state absorption is small [21]. The location of 462 nm is just in this region. Therefore, the transient absorption at 462 nm could be attributed to the absorption from the excited singlet states and/or the triplet states. However, in the Q-band, the ground state absorption is very strong which results in the ground state bleaching. In principle, the stimulated emission will amplify the probe beam and results in an increasing transmission of the probe beam, but it herein could be excluded by the fact that the fluorescence quantum yield of MgPc's film is quite low [10].

The excited state absorption at 462 nm decays through an ultrafast process with a life time of 1.2 ps and a slow one of 53 ps. The evolution of the bleaching in the Q-band region is strongly dependent on the wavelength. The bleaching at 861 and 650 nm changes into excited state absorption in less than 1 ps, the excited state absorption of 650 nm with duration about 22 ps, but over one nanosecond for 861 nm. The quite low fluorescence quantum yield of MgPc's film demonstrates that the nonradiative relaxation is a dominating process, while ISC process is more effective than that of monomer MPcs in solution. It has been reported that the ISC processes is greatly enhanced in Cu(II) porphyrins, the $^2S \rightarrow ^2T/4T$ transition being so

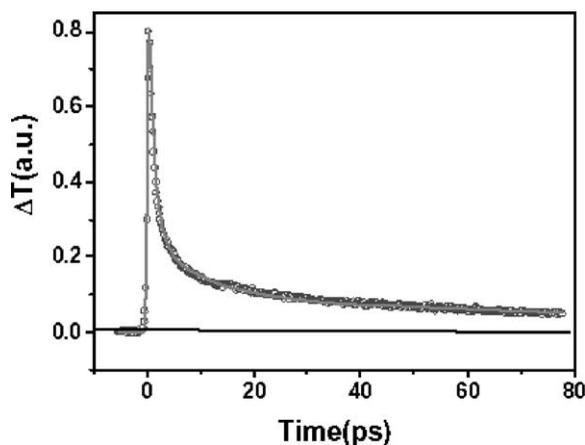


Fig. 3. The bleaching dynamic of MgPc PJD thin film by one color pump-probe measurement at 800 nm with the pump intensity of 7.8 GW/cm^2 .

fast to be resolved with 300 fs time resolution [22]. Much longer lifetime of excited states absorption of 462 and 861 nm might originate from the excitons of the triplet states, which was relaxed from the singlet states by ultrafast ISC process. The bleaching at 681 nm decays rapidly below baseline and shows weak absorption. The strong bleaching at 800, 761 and 602 nm, where strong bleaching was reported in many previous investigations on MPcs [23–27], finally evolves into a long-lived process. Under excitation with 7.8 GW/cm^2 intensity, 1 kHz, 120 fs and 800 nm laser pulses, bleaching decay dynamics at 800 nm (Fig. 3) was investigated in long delay time scale. Decay of bleaching includes an ultrafast component with lifetime of 1.1 ps, a fast component of about 16.5 ps and a slow component lasting longer than 300 ps.

All the transient dynamics show an ultrafast excitation response process. These ultrafast ground state bleachings/excited state absorptions evolve into a fast processes with lifetime about tens of ps and a long-live processes with duration of hundreds of picosecond. The ultrafast component is excitation intensity dependent and can be assigned to bimolecular process, such as exciton–exciton annihilation. We suggest that the fast component could be assigned to the decay of singlet excited state via ISC process or exciton–phonon coupling, and the long-lived component is due to the nonradiative relaxation of the triplet state.

The bleaching in the center of Q-band (~ 650 nm) changes rapidly to absorption in 1 ps. One feasible

mechanism, energy transfer between different phthalocyanine phase forms or molecular species having different spectral properties, suggested by Gulbinas et al. [23,24], may be the probable reason for this rapid changing of the bleaching into absorption in these wavelengths region.

Another suggestion based on the formation of charge-separated pair that MgPc anions and cations have different absorption spectra compared with neutral MgPc is applicable. Both theoretical [28,29] and experimental [30–32] investigations indicated that the absorption spectrum of MgPc⁻ has a strong band in the visible region around 560 and 650 nm [28–30, 32], while MgPc⁺ has two strong absorption bands in 320–505 nm and at 825 nm [28,31], respectively. The 560 and 650 nm bands of MgPc⁻ was assigned to $\pi^*\pi^*$ transition out of degeneracy lifted e_g^* into b_{1u}^* and b_{2u}^* (${}^2E_g \rightarrow {}^2B_{1u}/{}^2B_{2u}$). The 825 nm band of MgPc⁺ originates from $\pi\pi^*$ transition from a_{1u} into e_g (${}^2A_{1u} \rightarrow {}^2E_g$). Pcs are highly efficient in photogeneration of the charge carrier. Neutral excitons with high density created in MgPc thin film by ultrashort intense pulses, are favorable to form MgPc⁺ and MgPc⁻ charge pairs with large separation distance via thermalization of the hot electron created during autoionization of neutral excitons. With the excitation intensity of 7.8 GW/cm², the exciton density is as high as about one third of MgPc molecular density. That is to say, one exciton is created on about three MgPc molecules. Gulbinas [33] studied the dynamics of charge carrier precursor photogeneration in Y-form titanyl phthalocyanine and found that the charge carrier precursors-charge pairs were generated only during the short time interval (within ~ 1 ps) after the excitons were excited. This short time interval is comparable with the time of evolution of bleaching into absorption observed in the center of MgPc's Q-band. Thus, it can be expected that with the generation of the charge pairs by intense femtosecond pump pulse, the bleaching of the Q-band would rapidly change into the absorption of [(MgPc)]⁺ and [(MgPc)]⁻ charge pairs. The transient absorption of 650 nm is from the 650 nm band absorption of [(MgPc)]⁻, and the time interval about 0.6 ps (the time from the peak of the bleaching to the valley of the absorption) reflects the generation time of the [(MgPc)]⁺ and [(MgPc)]⁻ charge pairs after excitation. The transient absorption at 650 nm decreases to baseline after about 20 picoseconds

due to the recombination of [(MgPc)]⁺ and [(MgPc)]⁻ charge pairs.

3.3. Exciton–exciton annihilation

The transient bleaching at 800 nm measured with various excitation intensities is shown in Fig. 4, and the inset shows the dependence of the bleaching on the excitation intensity. The magnitude of the peak bleaching signal is linearly proportional to the excitation intensity at low excitation level. However, with the excitation intensity rising up to tens of GW/cm², an obvious excitation saturation was observed. The strong excitation intensity dependence of the initial ultrafast bleaching decay reveals that nonlinear interaction between excitons is essential. Migration of excitons via the dipole–dipole mechanism and annihilation of the excitons is usually considered to be the consequence of the interaction.

Exciton annihilation is conceived as a composite process, separable into two steps, the migration of the excitons, and the annihilation of two excitons once they are sufficiently close to interact. In the previous studies, the time-dependent annihilation rate was measured, which was determined by the individual microscopic rates of these two steps. In principle, time-dependent energy-transfer rates are expected in the process of the exciton annihilation. This arises from the fact that subsequent to the initial creation of a spatial homogeneous exciton population, proximate pairs

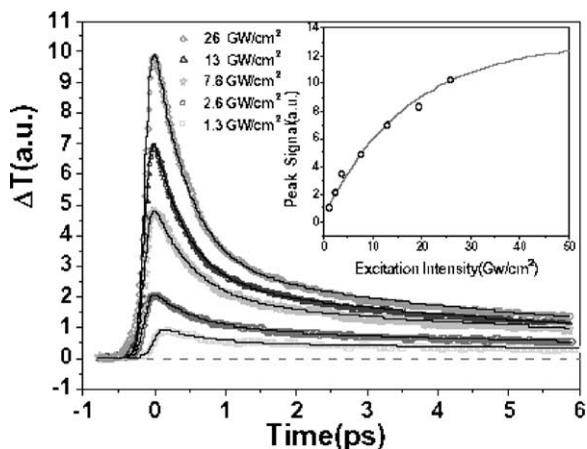


Fig. 4. Excitation intensity dependence of bleaching dynamics of MgPc PJD thin film at 800 nm under excitation by 120 fs, 800 nm pulses.

of excitons will interact first. Progressively greater inter-particle distance would result in the decreasing characteristic interaction rates. Both the motion-limited diffusion theory and annihilation via Förster long range dipole–dipole interactions leads to a time-dependent annihilation constant, which can approximately be expressed as $\gamma = \gamma_0 t^{-h}$ [34,35], where h may take a value between 1/6 and 1/2, and the exact value depends on the dimensionality of the exciton motion. Exciton–exciton annihilation can be described phenomenologically by the follow equation [36]:

$$dN/dt = -\gamma_0 t^{-h} N^2, \quad (1)$$

where N is the exciton density. Integration of Eq. (1) yields:

$$N = (1/N_0 + 2\gamma_0 t^{1-h})^{-1}, \quad (2)$$

where N_0 is the maximum exciton density created by the excitation. Fig. 5 shows the absorption bleaching data plotted in the form of $1/N - 1/N_0$ vs. \sqrt{t} . A well straight line with slope $2\gamma_0$ implies that $h = 1/2$, which corresponds to the case of one-dimensional diffusion-limited annihilation. A low-dimensional diffusion is expected because the phthalocyanines crystals usually have a column-like stacked structure. Between stacked molecular planes, the inter-plane distance is the smallest. Exciton hopping can therefore has preferred directions due to the different distances and/or orientations between neighboring molecules. The excitons may migrate along the columnar direction. One-dimensional diffusion-limited an-

nihilation has been observed in other Pcs [23,24,34, 35]. Single-crystal specific-gravity measurements indicated the exciton density for total saturation to be $1.68 \times 10^{21} \text{ cm}^{-3}$ [37], which is the molecular density. Considering the saturation under high excitation intensity as showed in inset of Fig. 4, a value of $6.3 \times 10^{20} \text{ cm}^{-3}$ is estimated for the exciton density under excitation intensity of 7.8 GW/cm^2 . This excitation density corresponds to the condition in which one exciton is created on about every three molecules. Higher exciton density would easily result in nonlinear exciton–exciton interaction. Line fitting of Fig. 5 gives the $\gamma_0 = 1.5 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1/2}$. One-dimensional diffusion-limited annihilation confirms that MgPc molecules in the PJD thin film are stacked or aggregated, consistent with the splitting of Q-band absorption. It is interesting to note that the fitted line in Fig. 5 does not go through the origin. This effect can be attributed to the discrete nature of the crystal lattice being inadequately described by a model assuming a continuous distribution of the exciton–exciton spacing.

4. Conclusions

In conclusion, ultrafast excitation relaxation dynamics of MgPc PJD thin film has been investigated using femtosecond pump-probe spectroscopy. The Q-band splitting is attributed to the aggregation/stack or molecular distortion of MgPc molecules in the film. The dynamics of the excited states of Q-band are strongly probe wavelength-dependent. The energy transfer between different molecular species and formation of charge pair of $[(\text{MgPc})^n]^+$ and $[(\text{MgPc})^n]^-$, are suggested to be responsible for the evolution from the weak bleaching to absorption in the central region of Q-band. The decay of bleaching at 800 nm evolves by three steps, an ultrafast process within 1.1 ps, a fast process enduring about 16.5 ps and then a long-lived process lasting more than 300 ps, which are attributed to ultrafast exciton–exciton annihilation, decay of singlet excited state via ISC process or exciton–phonon coupling, and nonradiation relaxation process, respectively. Exciton–exciton annihilation was found to have a $t^{-1/2}$ time dependence of the excited-state population, which corresponds to one-dimensional exciton diffusion.

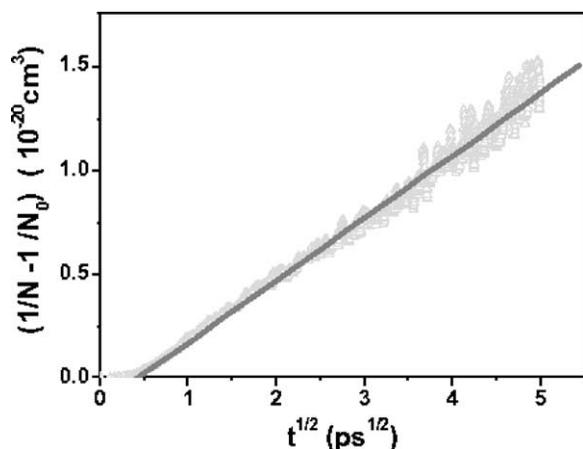


Fig. 5. $t^{-1/2}$ dependence of the exciton–exciton annihilation rate.

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References

- [1] C.C. Leznoff, A.B.P. Lever, *Phthalocyanine: Principles and Properties*, Vol. III, VCH, New York, 1993.
- [2] S. Yamaguchi, S. Sasaki, *J. Phys. Chem. B* 103 (1999) 6835.
- [3] D. Hohnholza, S. Steinbrecherb, M. Hanacka, *J. Mol. Struct.* 521 (2000) 231.
- [4] C.J. Liu, C.H. Peng, Y.H. Ju, J.C. Hsieh, *Sens. Actuators B* 52 (1998) 264.
- [5] E.J. Orti, *Chem. Phys.* 92 (1990) 1228.
- [6] H. Tajalli, J.P. Jiang, J.T. Murray, N.R. Armstrong, A. Schmidt, M. Chandross, S. Mazumdar, N. Peyghambarian, *Appl. Phys. Lett.* 67 (1995) 1639.
- [7] A. Endo, S. Matsumoto, J. Mizuguchi, *J. Phys. Chem. A* 103 (1999) 8193.
- [8] J. Janczak, R. Kubiak, *Polyhedron* 20 (2001) 2901.
- [9] J. Mizuguchi, *J. Phys. Chem. A* 105 (2001) 10719.
- [10] Y. Sakakibara, R.N. Bera, T. Mizutani, K. Ishida, M. Tokumoto, T. Tani, *J. Phys. Chem. B* 105 (2001) 1547.
- [11] G.H. Ma, L.J. Guo, J. Mi, Y. Liu, S.X. Qian, D.H. Pan, Y. Huang, *Solid State Commun.* 118 (2001) 633.
- [12] J. Qian, C. Xu, S.X. Qian, W.J. Peng, *Chem. Phys. Lett.* 257 (1996) 563.
- [13] E. Ough, T. Nyokong, K.A.M. Creber, M.J. Stillman, *Inorg. Chem.* 27 (1988) 2724.
- [14] M. Tian, S. Yanagi, K. Sasaki, T. Wada, H. Sasabe, *J. Opt. Soc. Am. B* 15 (1998) 846.
- [15] A. Terasaki, M. Hosoda, T. Wada, H. Tada, A. Koma, A. Yamada, H. Sasabe, A.F. Garito, T. Kobayashi, *J. Phys. Chem.* 96 (1992) 10534.
- [16] A.S. Davydov, *Theory of Molecular Excitons*, McGraw-Hill, New York, 1962.
- [17] L.K. Chau, C.D. England, S. Chen, N.R. Armstrong, *J. Phys. Chem.* 97 (1993) 2699.
- [18] M. Kasha, in: B. DiBartolo (Ed.), *Spectroscopy of the Excited State*, Plenum Press, New York, 1976, p. 337.
- [19] J. Mizuguchi, G. Ribs, H.R. Karfunkel, *J. Phys. Chem.* 99 (1995) 16217.
- [20] J. Mizuguchi, S. Matsumoto, *J. Phys. Chem. A* 103 (1999) 614.
- [21] Z.Z. Ho, N. Peyghambarian, *Chem. Phys. Lett.* 148 (1988) 107.
- [22] V.S. Williams, S. Mazumdar, N.R. Armstrong, Z.Z. Ho, N. Peyghambarian, *J. Phys. Chem.* 96 (1992) 4500.
- [23] V. Gulbinas, M. Chachiilis, A. Persson, S. Svanberg, V. Sundstrom, *J. Phys. Chem.* 98 (1994) 8118.
- [24] V. Gulbinas, M. Chachiilis, L. Valkunas, V. Sundstrom, *J. Phys. Chem.* 100 (1996) 2213.
- [25] L. Howe, J.Z. Zhang, *J. Phys. Chem. A* 101 (1997) 3207.
- [26] V. Gulbinas, *Chem. Phys.* 261 (2000) 69.
- [27] M. Tsushima, Y. Motojima, N. Ikeda, H. Yonehara, H. Etori, C. Pac, T. Ohno, *J. Phys. Chem. A* 106 (2002) 2256.
- [28] P.C. Minor, M. Gouterman, A.B.P. Lever, *Inorg. Chem.* 24 (1985) 1894.
- [29] M.G. Cory, H. Hirose, M.C. Zerner, *Inorg. Chem.* 34 (1995) 2969.
- [30] D.W. Clack, J.R. Yandle, *Inorg. Chem.* 11 (1972) 1738.
- [31] E. Ough, Z. Gasyna, M.J. Stillman, *Inorg. Chem.* 30 (1991) 2301.
- [32] J. Mack, S. Kirkby, E.A. Ough, *Inorg. Chem.* 31 (1992) 1717.
- [33] V. Gulbinas, R. Jakubenas, S. Pakalnis, A. Undzenas, *J. Chem. Phys.* 107 (1997) 4927.
- [34] R. Kopelmna, S. Parus, J. Prasad, *Phys. Rev. Lett.* 56 (1986) 1742.
- [35] R. Kopelmna, S. Parus, J. Prasad, *Chem. Phys.* 128 (1988) 209.
- [36] B.I. Greene, R.R. Millard, *Phys. Rev. Lett.* 55 (1985) 1331.
- [37] F.H. Moser, A.L. Thomas, *Phthalocyanine Compounds*, Reinhold, New York, 1963, p. 15.