Femtosecond nonlinear optical response of metallophthalocyanine films

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Abstract

The third-order nonlinear optical properties of copper phthalocyanine (CuPc) and magnesium phthalocyanine (MgPc) films were investigated by femtosecond optical Kerr effect (OKE) and pump-probe techniques. For both CuPc and MgPc, the third-order nonlinear optical susceptibility was enhanced at least by one order of magnitude in comparison with that of the metal-free Pc, and the enhancement effect arises from different mechanisms for both films. From pump-probe measurement, quite different transmittance and decay behavior between CuPc and MgPc films were observed. The CuPc films show an ultrafast decay, while the decay behavior of MgPc film is complicated with several temporal components, which could be explained by the relaxation of singlet excited state. © 2001 Published by Elsevier Science Ltd.

1. Introduction

Phthalocyanine (Pc) family is one of the most attractive macrocycle systems for third-order nonlinear optical (NLO) response due to its unusual chemical and optical properties, and its potential application in photonic devices, such as optical switching and optical limiting [1–5]. Pc material is a two-dimensional conjugated π-electrons system. There are many factors affecting the magnitude and response of the third-order nonlinear optical susceptibility ($\chi^{(3)}$) of metallophthalocyanine (MPc) materials, such as central metal [6,7], peripheral [8] and dimer or higher aggregates [8,9]. Many researchers have investigated the influence of the central atom on the magnitude of $\chi^{(3)}$ for MPc and reported the value of $\chi^{(3)}$ by several orders of variation with different central atom substitutions [6,7,10]. Some explanations have been proposed to explain the influence of central metal on the $\chi^{(3)}$ for MPc. One is the d valence

orbital contribution from transition metal, for example, the magnitude of $\chi^{(3)}$ for platina Pc (PtPc) was measured to be 45 times larger than that for the metal-free Pc reported by Janes et al. [6]. Another study stated that the central metal may locate out of the ring plane by matrix or light field [7,11], this would produce a dipole moment perpendicular to the ring plane, and the alignment of the permanent dipole moment would contribute to the magnitude of $\chi^{(3)}$ of MPc [7]. Central metal substitutions have the influence on molecular aggregations, and the conditions of film deposition also affect the molecular structure and energy level structure. Shaoli Fang et al. reported that the value of $\chi^{(3)}$ for vanadium-oxide Pc (VOPc) film grown on KBr was of about seven times larger than that of film grown on fused silica [12]. It is expected that the response of various mechanisms of $\chi^{(3)}$ should have their characteristic time, which can be resolved by time-resolved measurement. Novel femtosecond technique provides an excellent time-resolved tool for studying various contributions to the $\chi^{(3)}$ by analyzing the temporal evolution of nonlinear optical signal of MPc materials.

In this paper, we reported the fabrication of CuPc and

M=Cu, Mg
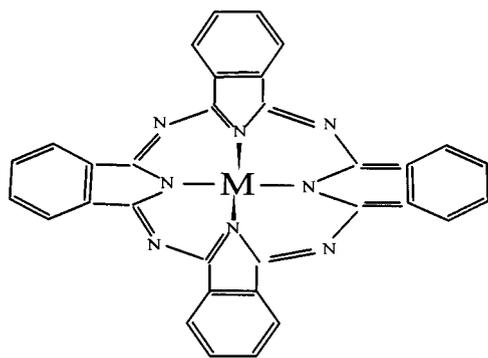
Fig. 1. The molecular structure of copper and magnesium phthalocyanine.

MgPc films by Physical jet deposition technique and the study of their nonlinear optical response by using femtosecond (fs) OKE and one color pump-probe technique both at 800 nm. The result shows that the magnitude of $\chi^{(3)}$ for CuPc and MgPc is at least one order of magnitude larger than that for the metal-free Pc. For CuPc film, both OKE and pump-probe response show an ultrafast response. However, for MgPc film, the results of OKE and pump-probe response show an ultrafast response followed by two slow decay components extending to hundreds of picosecond.

2. Experimental

2.1. Metallophthalocyanine synthesis and films fabrication

The molecular structure of CuPc and MgPc is shown in Fig. 1. The synthesis procedure was as follows: a mixture of
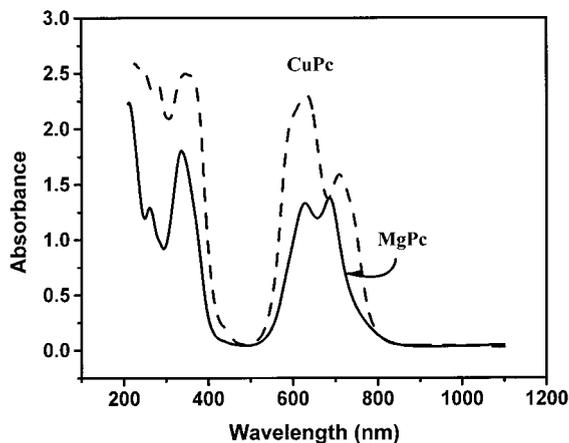
Fig. 2. The absorption spectra of CuPc and MgPc films.

1,2-dicyanlobenzene (*o*-phthalodinitrile) and quinoline (1 g, 8 ml) was heated to 140°C under nitrogen atmosphere with stirring. After dissolving entirely, a stoichiometric amount of metal chlorides was added to the solution; then the temperature was raised to 160–190°C and the reaction processed with stirring for about 3–5 h. After the reaction was complete, the product was filtered and then washed several times with DMF, and afterwards the Pcs were purified by train sublimation. The purity of the target materials was 99.9%. The detailed procedure has been described in Ref. [13]. The CuPc and MgPc films were fabricated by physical jet deposition (PJD) method described in details in our previous paper [14]. Briefly, the MPc powder was heated to 450°C in vacuum chamber, the vapor of MPc was carried by Ar-gas and deposited on the fused silica substrate. The thickness of films was measured on ZYO MPM-Z profile-meter, and the absorption spectra were obtained using UV3101-PC spectrophotometer.

2.2. Arrangement of nonlinearity measurement

NLO properties of CuPc and MgPc films were examined via a time-resolved optical Kerr effect and pump-probe experiment. The femtosecond laser pulse was generated from a Ti/sapphire laser system (Coherent Mira 900 B) operating at 76 MHz. The full width at half maximum (FWHM) of the pulse was about 120 fs, the central wavelength of the laser beam was 800 nm and was nearly resonant with the Q band of the samples. The pump and probe beams were split from the laser output, the pump beam was chopped at 1620 Hz and it went through an optical delay line controlled by a computer. A polarizer P1 was put into the probe beam path to set its polarization to be 45° with respect to that of pump beam. Two beams were focused on the same spot of the sample with a spot size of about 50 μm by a lens with $f = 5$ cm. The transmitted probe beam passed through an analyzer P2 with crossed polarization to P1. The signal was detected by a photodiode connected with a lock-in amplifier and the data were stored into a computer. For pump-probe measurement, the polarization of both pump and probe beams was set to be parallel.

3. Results and discussion

3.1. Absorption measurement

The absorption spectra of the CuPc and MgPc PJD films are shown in Fig. 2. There are two bands in the absorption spectra, a broad Q band in visible and a soret or B band in the ultraviolet region are attributed to the $\pi-\pi^*$ transition in MPc. The broad Q band was split into two bands with their peaks at 628, 708 and 625, 684 nm for CuPc and MgPc, respectively, it arises from the aggregations of the molecules or molecular distortion [8,15–17]. In the stack formation of Pc films, the transition moments in the excited states can be coupled between two adjacent phthalocyanine molecules.
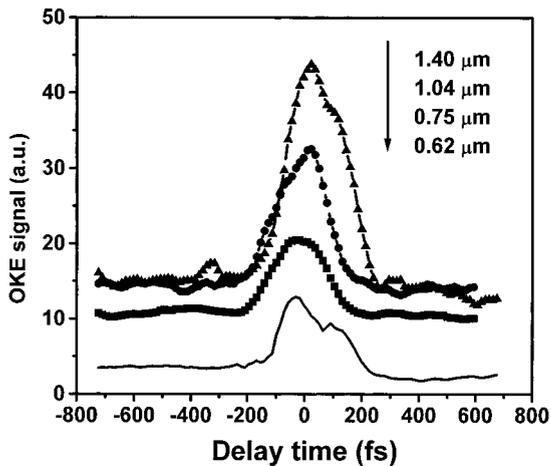
Fig. 3. The OKE response of CuPc films with different thickness.

With D_{4h} symmetry, the exciton coupling will result in a higher- and a lower-energy excited states. In the case of fully parallel, cofacial exciton coupling, transition only to the higher excited state is allowed, which yields blue-shifted absorption [8,15]. This can explain the much stronger blue-shifted absorption at 628 nm of CuPc. The red-shifted absorption peak at 708 nm may result from the partially cofacial exciton coupling and/or the molecular distortion. The molecular distortion was reported by Mizuguchi et al. [16,17], which was used to explain the red-shifted absorption in TiOPc films. Molecular distortion would reduce molecular symmetry and remove the two-fold lowest unoccupied molecular orbit (LUMO), giving rise two optical absorption bands. Both absorption bands are transition allowed. They also expected that the extent of molecular distortion would be significantly large if the central metal atom of MPc was out of the molecular plane [16]. For VOPc, PbPc, ClAlPc and TiOPc whose central metal
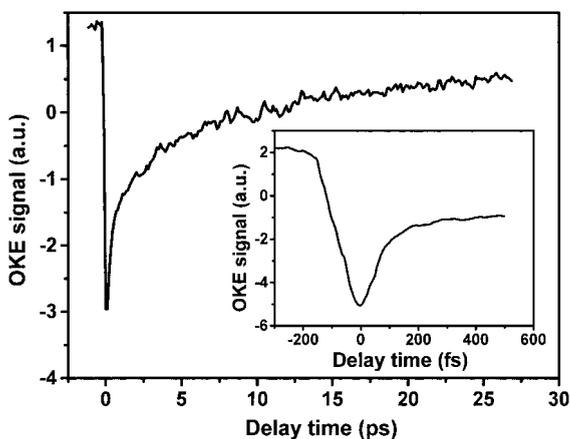
Fig. 4. The OKE response of MgPc film, extended scale is given in the inset.

atom is out of the molecular plane, MPc molecule is greatly deformed due to intermolecular interaction. CuPc is entirely planar in solution but is slightly deformed in the solid state. In the absorption spectrum of MgPc, two peaks in Q band have nearly equal absorbance, which can also be assigned to the effect of molecular distortion. MgPc is very sensitive to the environment and may form pyramidal structure because the Mg atom could easily ligate with other molecules. It was reported that the ligand complex could be formed between MgPc and water, or MgPc and pyridine [13]. In addition to this, MPc in the film would be in the form of the dimer or even higher aggregate, which would shift the absorption to the blue side. Some paper reported that the monomer MPc has the absorption peak around 800 nm, so we think that there would be aggregate MPc state in our PJD film.

3.2. OKE measurement

The temporal evolutions of the transient optical anisotropy of CuPc films with different thickness are shown in Fig. 3. The OKE signal is nearly symmetric with a peak centered at zero delay point, and the FWHM of the peak is almost as same as that of the pulse duration, which indicates that the OKE response of CuPc film is very fast. We measured several CuPc films which all show an ultrafast response as shown in Fig. 3. It is widely accepted that the delocalized electrons will show ultrafast optical response. Phthalocyanine molecule has 18 delocalized π-electrons, the unfilled d orbit of Cu atom will couple with the conjugated electrons of Pc ring leading to the extension of the conjugated systems. As a result, the CuPc film with larger conjugated electron system will show larger optical nonlinearity than the metal-free Pc. The ultrafast and strong response of the CuPc film should arise from the contribution of the extended π-conjugated electrons.

The OKE response of MgPc film is shown in Fig. 4, consisting of several different processes, a very fast decay, and a slow decay process followed by an even slower decay, which is quite different from that of CuPc. The ultrafast component with decaying time less than 200 fs dominates the curve, which can be assigned to the contribution of delocalized electrons. The slow and the very slow components come from the contribution of the relaxation of the population of the singlet and triplet excited state of MgPc, respectively. These results have an indication that the photo-induced anisotropy can maintain to hundreds of picoseconds (ps).

By taking CS_2 ($\chi_{CS2}^{(3)} = 1 \times 10^{-13}$ esu in 100 fs scale) as a reference, the magnitude of $\chi^{(3)}$ for CuPc and MgPc films can be calculated with the following formula [10]:

$$\chi_s^{(3)} = (I_s/I_r)^{1/2}(n_s/n_r)^2(L_r/L_s) \, \chi_r^{(3)} \alpha L / \{\exp(-\alpha L_s/2)[1 - \exp(-\alpha L_s)]\}$$

where I is the intensity of OKE signal at zero delay time, n the refractive index, α absorption coefficient of the films.
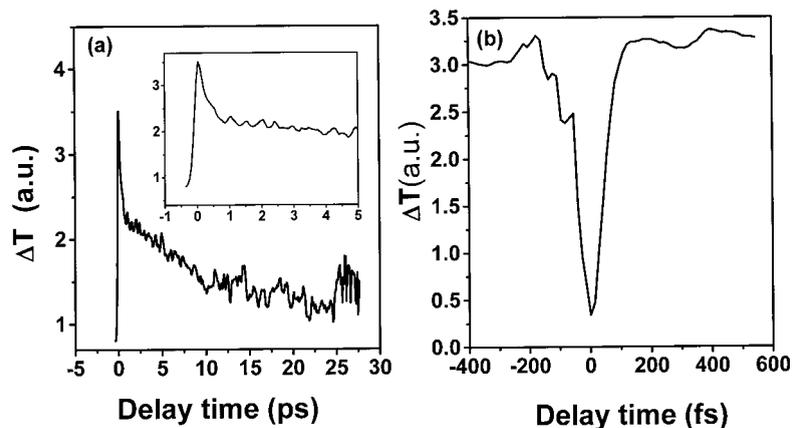
Fig. 5. The transient transmittance change of (a) MgPc and (b) CuPc films. The extended scale of MgPc is shown in the inset.

The subscript s and r stands for MPc films and CS_2, respectively. L_s is the thickness of the samples and L_r the interaction length of pump beam and probe beam over the CS_2 cell. The magnitudes of $\chi^{(3)}$ for CuPc and MgPc films were calculated to be 1.3×10^{-10} and 5.6×10^{-11} esu, respectively.

For comparison, we measured the $\chi^{(3)}$ of metal-free Pc suspended in chloroform, but no detectable OKE signal was observed for the metal-free Pc due to its low concentration in our experiment. If we take the value of about 4×10^{-12} esu for metal-free Pc reported by others [6], the measured value of $\chi^{(3)}$ for the CuPc and MgPc films shows that there are about 32 and 14 times of magnitude enhancement compared with the metal-free Pc. In past years, there were many papers that reported the value of $\chi^{(3)}$ for CuPc, but the measured value scattered a lot. For example, in Ref. [7], the authors reported that the $\chi^{(3)}$ for CuPc solution and amorphous films were 7.1×10^{-13} and 2.7×10^{-12} esu by third-harmonic generation measurement, respectively, which was smaller than that of other nonplanar MPc materials. By using nonlinear self-refraction method, Ramos et al. got a very large $\chi^{(3)}$ value of 2.3×10^{-4} esu for the CuPc doped silica film [18]. These results show that even for same MPc material, its NLO property would be affected greatly by the state and the fabrication condition of the film, which will result in the different configuration or stacking of the Pc molecules in the film. The value of $\chi^{(3)}$ obtained in our measurement for PJD CuPc films imply that the film structure is different from that reported in other papers. To our knowledge, there is no NLO data about the MgPc published, so we could not make any comparison with our data.

The enhancement of $\chi^{(3)}$ of CuPc in comparison to the metal-free Pc comes from the d valence orbital contribution of central atom, copper. The unfilled d valence orbital will be split into serials level due to the interaction between the d electrons and π-conjugation electrons of Pc ring, this result will lower the transition energy in low-lying d orbital–

ligand or d–d transition [3,6]. In addition, the strong cofacial coupling will enlarge the delocalized π-electrons in the vapor deposited film of CuPc. According to the nonlinear optical theory, the existence of excited state with low transition energy will enhance the nonlinear optical susceptibilities of the material. The Mg atom is a main group element without the d valence orbit, therefore, we suggest that the enhancement of $\chi^{(3)}$ of the MgPc film should originate from a different mechanism. As mentioned in Section 3.1, Mg atom may locate out of the Pc ring plane, which could induce a permanent dipole moment [19]. The alignment of the dipole moment along the direction of electric field of strong pump beam will contribute to the magnitude of the nonlinear optical susceptibility of the molecule. Thus, the enhancement of nonlinear optical susceptibility of MgPc may arise from the pyramidal structure of MgPc. From the absorption spectrum shown in Fig. 2, the smaller split in Q-band is an indication of weaker molecular distortion in the MgPc film, implying a small displacement of the Mg atom out of the Pc ring plane. Therefore, the contribution of the induced dipole moment to the third order nonlinear optical susceptibility is limited; as a result, the magnitude of $\chi^{(3)}$ for MgPc is smaller than that of PtPc reported in Ref. [6], smaller even than that for CuPc with planar structure.

3.3. Pump-probe measurement

From the above-mentioned OKE measurement, it was found that the photo-induced anisotropy of MgPc could keep up to hundreds of picosecond, we suggest that it comes from the contributions of excited state. In order to investigate the mechanisms of the optical nonlinearlity, we performed one-color pump-probe experiment at 800 nm. The temporal evolution of transmittance change of MgPc is shown in Fig. 5a. An ultrafast bleaching or saturated absorption followed by slow recovery process was observed, this behavior is quite similar to that of the OKE

response for a MgPc film. The bleaching recovery processes consist of three components, an ultrafast process with time constant less than 200 fs, a slow process of 6 ps time scale and a very slow process with recovery time about hundreds of ps to even ns scale.

The transient bleaching of the MgPc film could come from the saturable absorption (SA) or the stimulated emission (SE). Under photoexcitation, the singlet excited state would be populated, and the SA will take place if the absorption cross section of the excited state is smaller than that of ground state. As we did not observe detectable photoluminescence (PL) emission from the MgPc films, SE process could be excluded. The ground state bleaching should arise from the SA effect.

In general, the recovery of ground state bleaching involves several decay mechanisms: (a) exciton–phonon coupling (internal conversion) [20]; (b) exciton–exciton annihilation [15,21]; (c) fluorescence[22]; (d) inter-system crossing (ISC) transfer from singlet state to triplet state [10,15] and (e) nonradiative recovery through triplet states[8,10];

The ultrafast component may be assigned to the internal conversion due to a strong interaction between exciton and phonon [9,20]. The exciton–exciton annihilation can also dominate the ultrafast process under strong excitation density [15,21]. But in our experiment, the excitation density is about 0.1 GW/cm^2, and the absorbance of MgPc at 800 nm is very small. In this case, we consider that the contribution to the ultrafast component is not a bimolecular process but the electron–phonon interaction. Yuan et al. found that for an HDVPC LB film, the ultrafast component of OKE signal increased dramatically with the temperature of the sample, and it was also reported that for polydiacetylene, phonon emission process could be as fast as 50–180 fs. The phonon emission is actually a process in which energy redistributes between the phonons and excitons, and so it can be considered as a kind of exciton–phonon coupling.

The recovery process of photo-induced bleaching also reflects the relaxation of the population in the singlet excited state S_1, other relaxation processes should include the process of $S_1 \rightarrow T_1$(triplet state) by ISC, $S_1 \rightarrow S_0$ via radiative transition or the nonradiative transition. As mentioned earlier, there is nearly no PL emission observed from the MgPc film, the radiative process is really ineffective in the MgPc film. Some papers pointed out that ISC process in MPc materials could be ranged in ps domain [22], even in fs scale [23], which would dominate the lifetime of the singlet excited state. Usually, the ISC rate in a solid material is larger than that in a solution. A very effective crossing transfer rate ($\Phi \sim 1$) and long lifetime of triplet state (~ns) were reported in various Pc films [15,20,22,24]. Therefore, the slow component with recovery time about 6 ps can be assigned to the decay of singlet excited state via ISC process, and the very slow component is due to the nonradiative relaxation from triplet state to the ground state.

Fig. 5b shows the temporal transmittance change at 800 nm of the CuPc films, a reverse saturable absorption (RSA) with ultrafast response was observed. If the material has a larger cross section of excited state (σ_{ex}) than that of ground state (σ_g), and the incident light is sufficiently intense, there will be a significant population in the excited state, resulting in RSA. It was reported that the σ_{ex} and σ_g of the CuPc monomolecule were about 5.2×10^{-18} and 2.0×10^{-18} cm^2 at 590 nm, respectively [25]. Although both the σ_{ex} and σ_g of CuPc depends on the wavelength as observed from the photoinduced absorption spectrum, the low absorbance at 800 nm would result in RSA process as well. The ultrafast decay of the photo-induced absorption in the CuPc film is much faster than that of bleaching recovery in MgPc film. As the decay of the photo-induced absorption should also strongly relate to the relaxation of the singlet excited state, it means that the relaxation process in the CuPc film should be much faster than that in the MgPc film. In film of CuPc, due to electron coupling between the unfilled d orbit of central Cu ion and PC^{2-} ligand, the ground state of CuPc is singdoublet state ($^2\Gamma$), the first excited state also become singdoublet (^2Q), and the triplet state is split into tripdoublet (^2T) and tripquartet (^4T) which states lie between $^2\Gamma$ and ^2Q [8,15]. As a result, the inter-system crossing process from $^2S \rightarrow {}^2T/{}^4T$ becomes very fast, which results in very short lifetime of the singlet excited state, so the ultrafast relaxation process could result from fast ISC process in the CuPc film.

4. Conclusions

In summary, we have investigated experimentally the NLO response of the CuPc and MgPc films by femtosecond OKE and pump-probe technique. These results indicate that the central metal atom affects greatly the magnitude of the nonlinear optical susceptibility of MPc films. In CuPc with planar structure, the unfilled d valance orbit probably couple with π-electrons of the Pc rings and enlarge the conjugation system, as a result, the CuPc films show large third-order nonlinear optical property, while the enhanced third-order optical nonlinearity of the MgPc film arises mainly from its pyramidal structure. From the pump-probe experiment, the RSA and SA process was found in the CuPc and MgPc film, respectively. The ultrafast OKE response and decay of photo-induced RSA of the CuPc film is assigned to fast intersystem crossing from singlet to triplet state. For MgPc film, long decay of both OKE signal and photo-induced bleaching would arise from the ISC process from the singlet state to triplet state and relaxation process from the triplet state to ground state.

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