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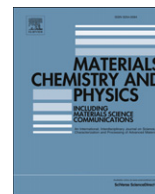274 PUBLICATIONS   3,656 CITATIONS

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The effect of aggregation on the nonlinear optical absorption performance of indium and gallium phthalocyanines in a solution and co-polymer host

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HIGHLIGHTS

► The effect of aggregation on the nonlinear absorption and the excited state lifetimes were studied.
► UV−Vis absorption spectra revealed that organization of investigated molecules in PMMA films show H-aggregation.
► Fast transitions (intermolecular energy transfers) in PMMA films were observed.
► Intermolecular energy transfer due to aggregation reduces transition to triplet levels.
► Aggregation reduces RSA signal observed in OA Z-scan experiments for the samples in a host PMMA polymer matrix.

GRAPHICAL ABSTRACT
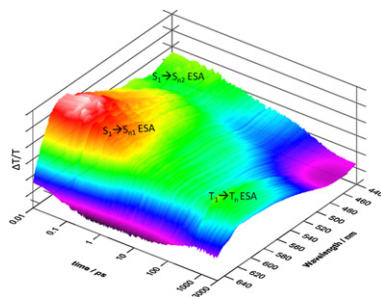
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ABSTRACT

The nonlinear optical properties (NLO) of Pcs can be modified by substituting different metal atoms into the ring or altering peripheral and axial functionalities. In this study, nonlinear optical absorption properties of tetra-substituted gallium and indium phthalocyanine complexes both in solution and polymeric film have been investigated by open aperture Z-scan measurements with nanosecond pulses at 532 nm. All investigated compounds exhibited reverse saturable absorption for both solution and film experiments. The investigated compounds in the solution showed better nonlinear optical absorption properties than polymeric films. The observed nonlinear optical absorption differences depending on the aggregation are discussed using the ultrafast dynamics and decay processes of excited states found from femtosecond pump-probe spectroscopy with white light continuum experiments.

1. Introduction

Metallophthalocyanines (MPcs) show fast, large and reversible nonlinear optical absorption which is based on reverse saturable absorption (RSA) [1,2]. Chemical modifications of Pcs like axial substitution at the central metal atom or peripheral substitution on the Pc macrocycle make it possible to reduce the intermolecular

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interactions, tailor the nonlinear response and control the opto-electronic properties of these molecules [3,4]. A device application requires the casting of the optically active compounds in the solid state. However, the effect of aggregation on the RSA properties becomes very important in the solid state. Although RSA properties of MPcs are mostly studied in the literature, systematic studies for the effect of aggregation on nonlinear optical properties of MPcs are not sufficient.

It was demonstrated that insertion of heavy metal atoms into the phthalocyanine ring as central metal, such as indium [2,5–7] causes a significant improvement in RSA behavior, owing to an increased rate of inter-system crossing from the lowest excited singlet state to the strongly absorbing triplet state. In this study, Ga (III) and In(III) metals have been chosen as central atoms due to their heavy diamagnetic nature and axially substituted capacity. It is known that axial substitution can introduce a dipole moment perpendicular to macrocycle, and via steric effect it can alter the spatial relationship between neighboring molecules [8]. Therefore, axial substitution affects the molecular packing properties in the solid state. It is also known that intermolecular interactions are stronger for chloro substituted compounds than aryl compounds [8]. Thus, chlorine atom has been chosen as an axial ligand for indium (ClInPcs) and gallium (ClGaPcs) phthalocyanines. Peripheral substitution and its position also effect the aggregation and nonlinear absorption properties of MPcs. The aggregation for 4-benzyloxyphenoxy substituted ClGaPcs and ClInPcs in the solid state was observed in our earlier work [9]. More recently, we have shown that long chain octacis (hexylthio) substituted ZnPc molecules in peptide nanofibers and in the film form show strong aggregation [10]. In another work long chain tetra(13,17-dioxanonacosane-15-hydroxy)-substitution resulted in aggregation of ZnPc complexes in toluene and other less polar solvents [11]. Therefore, triethyleneoxythia groups have been used as peripheral and non-peripheral substituents for this work. Different substituted ZnPC molecules in various solution and thin film form have been also worked in the literature [12,13].

In this paper, we studied the effect of aggregation on the nonlinear optical absorption properties of peripherally and non-peripherally triethyleneoxythia substituted indium (ClInPcs) and gallium (ClGaPcs) phthalocyanines in the form of both solution and PMMA polymer film. The linear optical absorption spectra of the investigated compounds were recorded to see whether there is aggregation. Open aperture (OA) Z-scan technique was used to investigate the nonlinear absorption properties of the samples. In an attempt to explain the experimental results obtained from OA Z-scan experiments, ultrafast dynamics and decay processes of excited states both in solution and films were measured by using femtosecond white light continuum pump-probe technique.

2. Experimental

The molecular structures of the compounds are shown in Fig. 1 and their synthetic procedures have been described in details in literature [14]. For the fabrication of the solid-state MPc/polymer film, a 100 g L^{-1} solution of PMMA in cyclohexanone was placed in a low power sonic bath for 48 h until completely dissolved. The indium (1 and 3) and gallium (2 and 4) phthalocyanines were added (%10wt) and sonically agitated until it is completely dissolved. The homogeneous solution was formed. Solid-state films were formed on quartz glass substrates by using multi-layer conventional spin casting technique (SCS-Spin Coat G3P). Between each layer MPc/polymer films were baked approximately 1 h at 100 °C to facilitate the removal of residual solvent. Thicknesses of the MPc/polymer films were determined using spectroscopic ellipsometer (SE) M2000V (J.A. Woollam Co.). SE experiments were performed in the
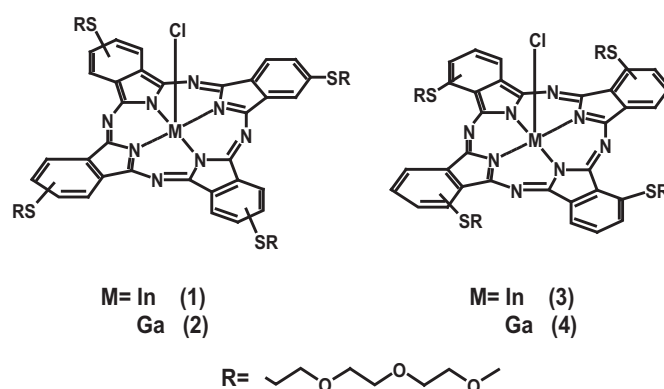
Fig. 1. Chemical structures of investigated indium (III) and gallium (III) phthalocyanine compounds.

photon energy range from 1.24 to 3.34 eV (from 370 to 999 nm). All of the spectra were recorded at three angles of incidence (60°, 65° and 70°) to increase the fitting accuracy. The best fits were obtained by using multilayer analysis with Cauchy model [15].

The UV−Vis absorption spectra were recorded using a scanning spectrophotometer (Shimadzu UV-1800).

A Q-switched Nd:YAG laser (Quantel Brillant) was used as a light source with repetition rate of 10 Hz, pulse duration of 4 ns and wavelength of 532 nm. The experimental technique used in these measurements was the OA Z-scan technique [16]. In OA Z-scan experiments while sample was moved through the focus, transmitted open aperture signals were detected with a silicon detector (Thorlabs-DET36A). A lens with 20 cm focal length was used to focus the beam. The solution based OA Z-scan experiments were undertaken in quartz cuvettes with 1 mm path length. The absorption spectrum of each solution was measured before and after numerous scans at varying laser intensity to determine any possible degradation [7].

The laser source for the ultrafast pump-probe experiments was Ti:sapphire laser amplifier-optical parametric amplifier system (Spectra Physics, Spitfire Pro XP, TOPAS). Pulse durations were measured as 110 and 80 fs for the experiments in solutions and films, respectively. Pump beam wavelengths was 750 nm was for the pump-probe experimental setup with white light continuum (Spectra Physics, Helios). Pump-probe experiments of the compounds 3 and 4 were performed in solution and solid forms to determine the influence of heavy-metal effect on the ultrafast dynamics and decay processes of excited states. Absorption spectrum of each solution was measured before and after every pump-probe experiments to investigate whether there is any degradation.

3. Results and discussion

3.1. The effect of aggregation on the UV−Vis absorption spectra

The ground state electronic absorption spectra of ClInPcs (1 and 3) and ClGaPcs (2 and 4) in chloroform solutions (Fig. 2a) show monomeric behavior, typical of metalated phthalocyanine compounds [17] evidenced by a single (narrow) Q band due to the D_{4h} symmetry of molecules. In chloroform, the Q bands are observed at: 716 nm for 1, 715 nm for 2, 739 nm for 3 and 741 nm for 4. The Q bands of the non-peripheral tetra substituted complexes (3 and 4) are red-shifted by 23 and 26 nm when compared to the corresponding peripheral tetra substituted (1 and 2) complexes in chloroform. The observed red spectral shift is typical for phthalocyanine compounds with substituents at the non-peripheral positions and has been explained to be due to linear
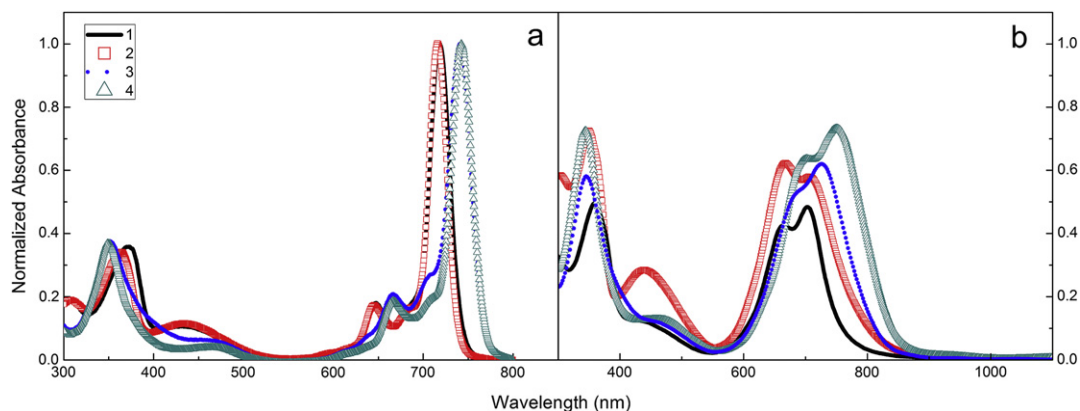
Fig. 2. Normalized absorption spectra of : (a) All materials in chloroform (b)**1**, **2**, **3** and **4** MPcs-PMMA films.

combination of the atomic orbitals (LCAO) coefficients at the non-peripheral positions of the highest occupied molecular orbital (HOMO) which is greater than those at the peripheral positions [18]. As a result, the HOMO level is destabilized more at the non-peripheral position than that at the peripheral position. Essentially, the energy gap (ΔE) between the HOMO and lowest unoccupied molecular orbital (LUMO) becomes smaller, resulting in a bathochromic shift. The shoulder between 400 and 500 nm may be due to charge transfer from the electron-rich ring to the electron-poor central metal atom. The B-bands are broad due to the superimposition of the B_1 and B_2 bands at $\sim$350 nm for peripherally tetra substituted phthalocyanine compounds and $\sim$365 nm for non-peripherally tetra substituted phthalocyanine compounds in chloroform [19].

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It depends on the concentration, nature of the solvent, nature of the substituents, central metal ions and temperature. When more than one Pc macrocycles are close to each other, the transition dipole moments can couple (exciton coupling) to cause drastic spectral changes particularly in the Q band region. In general aggregates of Pc monomers are not chemically bonded but exist as loosely associated species which can be dissociated by an organic solvent. Thus aggregation in MPc complexes is due to a coplanar association of rings, resulting in splitting with a blue shifted peak (630−640 nm) and broadening of the spectra. The lower energy band is due to the monomer and higher energy band is due to the aggregates. The aggregates which are blue shifted are so called "H-aggregates". The aggregation is more severe for MPcs-PMMA thin films (Fig. 2b) which is expected in the solid state. Red-shifts of the Q band have mostly been observed in the solid-state where the Pcs are aligned in a slipped co-facial manner (the so called "J-aggregates") [20]. However, Fig. 2b shows only H-aggregates due to the blue shifted Q band.

3.2. The effect of aggregation on the nonlinear absorption

The UV−Vis absorption spectra for all compounds in solution were recorded before and after OA Z-scan experiments to observe any degradation. UV−Vis absorption spectra did not reveal any changes and sample degradation [7]. Open-aperture Z-scan spectra with normalized transmittance plotted as a function of sample position (z) are given in Fig. 3 for both solutions and MPc/PMMA films. In order to compare the nonlinear response figures are plotted at the same scale. All of the OA Z-scan experiments exhibited a transmittance decrease around the focus which is a typical behavior of induced nonlinear absorption (intensity dependent absorption) of the incident light. Effective nonlinear absorption coefficient β_{eff} was calculated using theory previously reported in literature [16]. The normalized transmittance $T_{Norm}(z)$ as a function of position z is given by

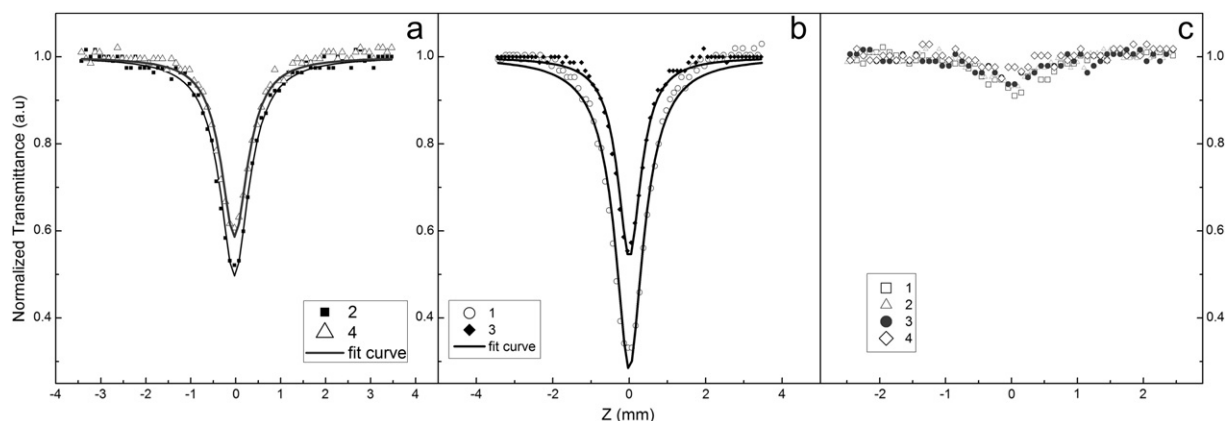$$T_{Norm}(Z) = \frac{\log_e[1 + q_0(Z)]}{q_0(Z)} \tag{1}$$

Fig. 3. Open-aperture Z-scan spectra with normalized transmittance plotted as a function of sample position z for (a) **2,4** in chloroform (b) **1,3** in chloroform (c) MPcs-PMMA films.

where $q_0(z)$ is given by

$$q_0(Z) = \frac{q_{00}}{1 + (Z/Z_0)^2}, \quad q_{00} \sim \beta_{eff} I_0 L_{eff} \qquad (2)$$

where z_0 is the diffraction length of the beam, β_{eff} is the effective nonlinear absorption coefficient and I_0 is the intensity of the light at focus. $L_{eff} \sim [1 - \exp(-\alpha_0 L)]/\alpha_0$ is known as the effective length of the sample and defined in terms of the linear absorption coefficient α_0, and the true optical path length through the sample L. All open aperture Z-scan data sets were fitted using the method of least-squares regression with equations (1) and (2). The beam waist radius w_o, and the effective nonlinear absorption coefficient β_{eff} were treated as free parameters in the fit.

Very recently, it was found that β_{eff} was largely dependent on the linear absorption coefficient [9]. Therefore, all samples were prepared in chloroform at the same linear absorption coefficient α_0 (1.4 cm^{-1}). As seen from Table 1, all compounds have almost the same β_{eff} values. The results showed that the substitution position and nature of coordination metal have no considerable effect on the nonlinear absorption of the investigated compounds.

The thickness and linear absorption coefficient of MPc/PMMA films were given in Table 2. The density of Pcs molecules in the film can be increased dramatically in comparison with the solution. Since the concentration of absorbing molecules in the MPc/PMMA is significantly higher than that of in solution, it is expected that the MPc/PMMA system shows higher nonlinear absorption than MPc/solution system. As it can be seen from Fig. 3, the investigated compounds in the solution show better nonlinear optical absorption performance than MPc/PMMA films. However, our previous work [9] showed that 4-benzyloxyphenoxy- substituted ClGaPc and ClInPc/PMMA composite films have better nonlinear absorption properties than MPc/solution system. These results may be due to aggregation. It is known that aggregation changes the excited state dynamics of the compounds [8,21–24]. In an attempt to investigate whether these findings are due to aggregation or not we have performed femtosecond white light continuum pump probe experiments on the investigated samples.

3.3. The effect of aggregation on the excited state lifetimes

Ultrafast pump-probe experiments were utilized to investigate the ultrafast optical dynamics and decay processes of excited states of ClGaPc and ClInPc both in solution and PMMA composite films. The Q band in the absorption spectra (Fig. 2) has an intense maximum at approximately 750 nm for non-peripherally tetra-substituted Pcs (3 and 4). Therefore, this wavelength was used for the pump beam to populate S_1 state.

Pump-probe data as a function of time and wavelength for sample 3 and 4 in chloroform are provided in Fig. 4. Pump-probe data in solutions reveal broad positive excited state absorption (ESA) bands superimposed with a deep negative signal, due to the ground state bleach and stimulated emission (SE). Similar results were also obtained for ZnPc in DMSO and these signals were identified as Bleach + SE, $S_1 \rightarrow S_{n1}$ ESA, $S_1 \rightarrow S_{n2}$ ESA, and $T_1 \rightarrow T_n$

ESA [7]. The time evolutions of these signals are provided in Fig. 5a and b. $S_1 \rightarrow S_{n1}$ ESA (C), $T_1 \rightarrow T_n$ ESA (B), and $S_1 \rightarrow S_{n2}$ ESA (A) signals can be seen clearly around 605 nm, 560 nm, and 440 nm respectively. As shown in Fig. 4, ESA signal around 560 nm day until 100 ps, then it increases gradually. Therefore, it is attributed to $T_1 \rightarrow T_n$ transition (B). Transient absorption data versus wavelength for various time delays is shown in Fig. 5c. The 3D-image of these signals is given in graphical abstract.

Pump-probe data as a function of time and wavelength for samples 3 and 4 in PMMA composite films are given in Fig. 6. $T_1 \rightarrow T_n$ (B) ESA signal seen in ClGaPc and ClInPc in solution does not appear in none of ClGaPc and ClInPc in PMMA composite films. There is a broad ESA signal between 500 nm and 620 nm for all film samples. Pump-probe absorption data versus wavelength for various time delays for samples 3 and 4 in PMMA composite films are shown at Fig. 7a and b.

The decay of the nonlinear absorption signals were fitted to four exponentials with better convergence (Fig. 7c). The time constants are given in Table 3. As is seen in Table 3, due to the heavy atom effect, the solution form of compound 3 has faster processes than that of compound 4 as observed in the literature [25]. On the other hand, these decay processes of excited states are faster in solid phase than in solution phase as observed in the literature [26,27]. The lifetime of the first triplet state was reported as a few ns for MPcs films [28,29] whereas it was about 20–300 μs for solutions [26,27]. Observed fast transitions in PMMA films reveal that the contribution of triplet levels to the measured nonlinear absorption signals (OA Z-scan) is less in films than in solution forms. That is because fast transitions are indication of the efficient nonradiative energy relaxation due to intermolecular aggregation [30]. The faster decay times for the film samples are on the order of ps time scales. These fast temporal behaviors for film samples can be observed upon significant aggregation. The singlet–singlet anni-hilation [30,31] or exciton–exciton annihilation [32] might represent the energy migration processes. It is known that annihilation decay times critically depend on the number of electronically connected chromophores which in turn depends on the aggregation level [31,33] and the orientation of the dipole moments [31]. The UV–Vis absorption spectra also revealed that organization of investigated molecules in PMMA films results in H-aggregation.

We have recently reported nonlinear optical absorption of 4-benzyloxyphenoxy substituted ClGaPcs and ClInPcs in solution and the solid state. We have seen that although these molecules showed aggregation, samples in PMMA films exhibited better RSA properties than in solution [9]. The only differences between the molecules previously studied and the current ones are the periph-eral substitution groups. Very recently, we have shown that long chain octacis (hexylthio) substituted ZnPc molecules in peptide nanofibers and in the form of film showed very strong aggregation [10]. In another work, long chain tetra(13,17-dioxanonacosane-15-hydroxy)-substitution resulted in aggregation of ZnPc complexes in toluene and other less polar solvents [11]. Therefore, observed aggregation and its effect on the RSA properties may be attributed to long chain triethyleneoxythia peripheral substitution for ClInPcs and ClGaPcs in PMMA host matrix. We leave this point open to discussion.

Table 1
Linear and nonlinear coefficients for 1, 2, 3 and 4 at the same linear absorption coefficient in chloroform solution (at focal intensity 0.15 GW cm^{-2}).
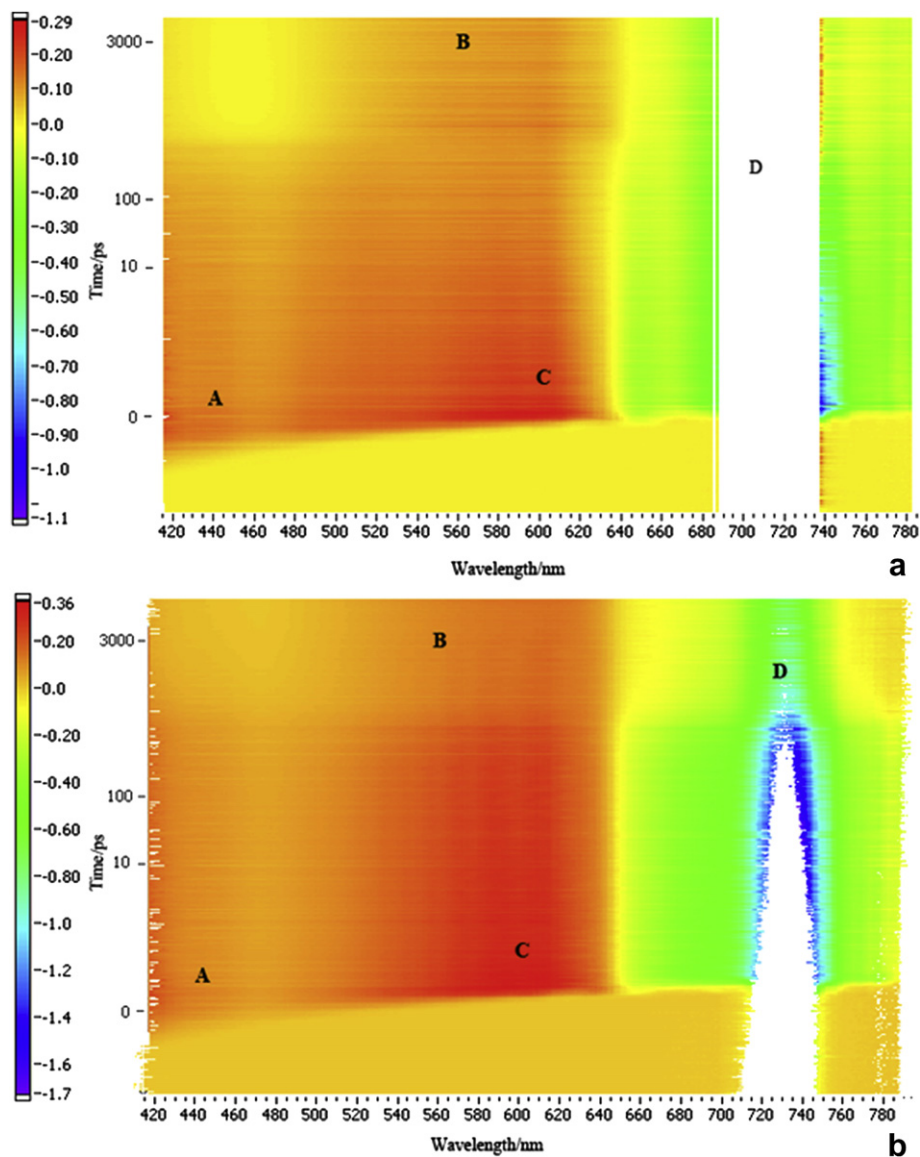
Materials	α_0 [cm^{-1}]	β [cm W^{-1}]
1	1.4	3.89×10^{-7}
2	1.4	2.93×10^{-7}
3	1.4	2.37×10^{-7}
4	1.4	1.93×10^{-7}

Table 2
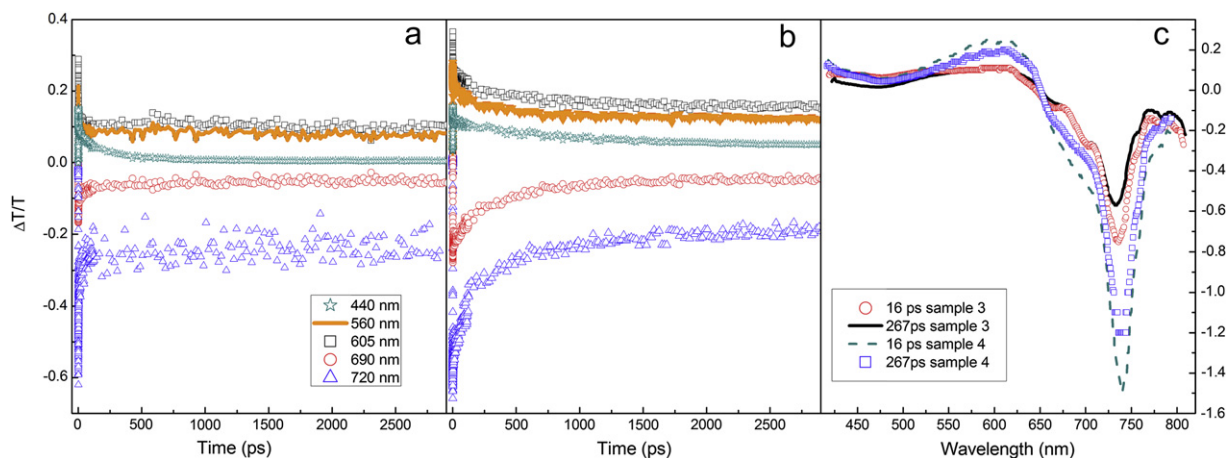The thickness and linear absorption coefficients for 1, 2, 3 and 4 in PMMA.

Materials	Thickn. [μm]	Layer	α_0 [cm^{-1}]
1	4.18	3	115
2	1.62	1	387
3	2.94	2	265
4	1.71	1	286

Fig. 4. Pump-probe data as a function of time (y) and wavelength (x) for (a) **3** and (b) **4** in chloroform. The characteristic features of singlet ESA (A and C), triplet ESA (B) and bleach (D) are indicated.

Fig. 5. Time evolution of the nonlinear absorption of (a) **3** and (b) **4** in chloroform. Transient absorption data versus wavelength for various time delays for (c) **3** and **4** in chloroform.
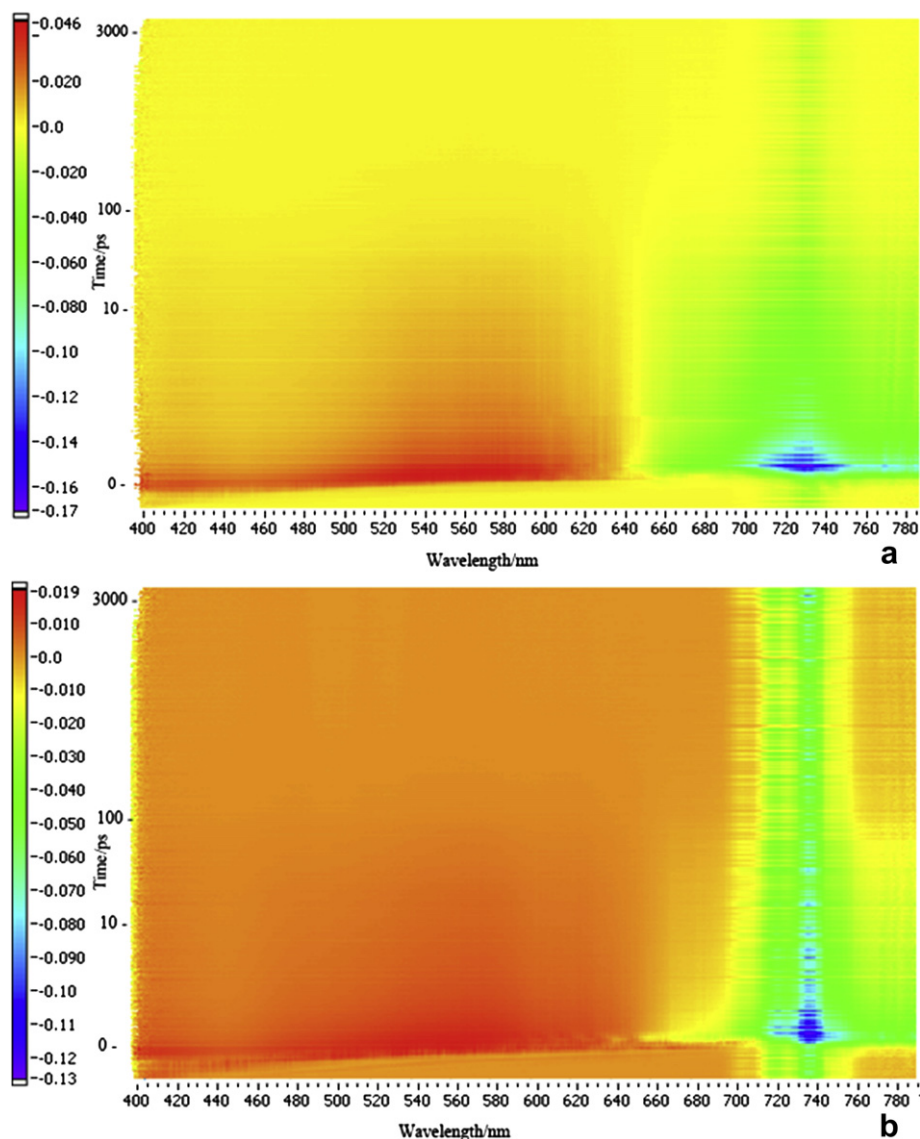
Fig. 6. Pump-probe data as a function of time (*y*) and wavelength (*x*) for (a) **3** and (b) **4** MPcs-PMMA films.
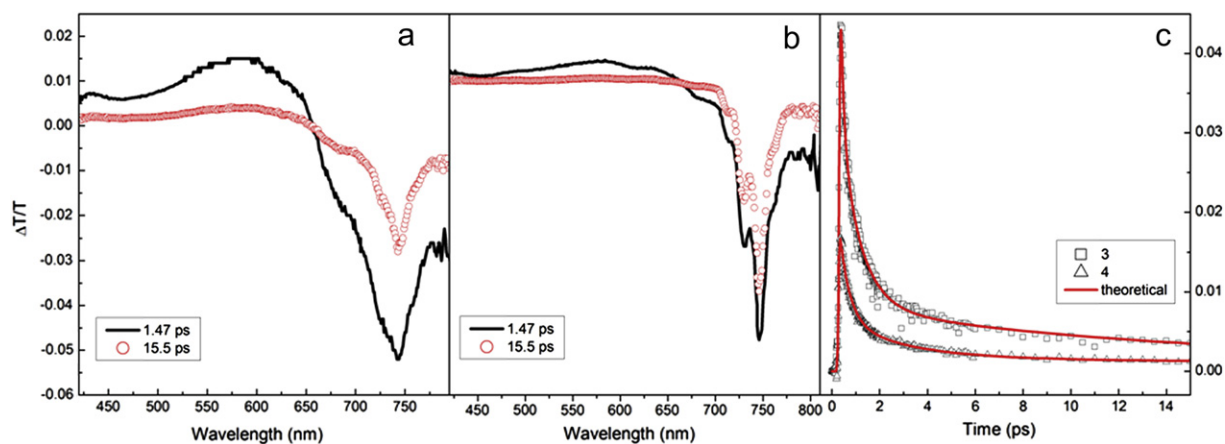

Fig. 7. Transient absorption data versus wavelength for various time delays for (a) **3** and (b) **4** MPcs-PMMA films. Time evolution of the nonlinear absorption of (c) **3** and **4** MPcs-PMMA films at 560 nm.

Table 3
Fitting parameters of 750 nm pump − 560 nm probe data for **3** and **4** in chloroform solutions and solid phase (PMMA).

Materials	Phase	t_1 (ps)	t_2 (ps)	t_3 (ns)	t_4
3	Solution	0.89	32.3	3.05	Inf.
4	Solution	1.28	256.7	4.02	Inf.
Materials	Phase	t_1(ps)	t_2(ps)	t_3(ps)	t_4(ns)
3	Solid	0.14	0.83	11.85	2.15
4	Solid	0.40	2.56	34.40	2.52

4. Conclusion

The nonlinear optical absorption properties of peripherally and non-peripherally tetra-triethyleneoxythia substituted indium (ClInPcs) and gallium (ClGaPcs) phthalocyanines has been investigated both in chloroform and a host PMMA polymer matrix by using the open aperture nanosecond Z-scan technique. The nonlinear response demonstrated that samples in chloroform exhibit better nonlinear absorption (RSA) properties than samples in a host PMMA polymer matrix. The ultrafast pump-probe experiments were used to investigate role of aggregation and the role of decay processes of excited states of investigated MPcs both in solution and solid phase. The results showed that nonradiative energy relaxation due to intermolecular aggregation reduced transition to triplet levels and therefore reduced RSA signal observed in OA Z-scan experiments for the samples in a host PMMA polymer matrix. On the other hand pump probe experiments revealed that due to the heavy metal atom effect, ClInPc has faster processes than ClGaPc both in solution and PMMA polymer matrix. Triethyleneoxythia substitution may be responsible for the observed aggregation and its effect on the RSA properties for ClInPcs and ClGaPcs in PMMA host matrix.

Acknowledgments

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