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Solvent-conjugation-induced ultrafast dynamics of enhanced reverse saturable absorption in lead phthalocyanine derivatives solutions

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Abstract

With the continued development of high-power laser technology, research on laser protection has become extremely important. In this study, an analysis of Z-scan and femtosecond transient absorption spectra data for lead (II) tetrakis (4-cumylphenoxy) phthalocyanine (4-PbPc) solutions prepared using different concentrations and solvents established that charge transfer plays an important role in the optical limiting dynamics of this molecule. Based on the correlation of decay-associated difference spectra (DADS) for different decay channels, it was confirmed that greater charge transfer efficiency was associated with more highly conjugated solvent molecules. In a dilute solution, the polarity of the solvent molecules will influence the optical limiting performance of the solution to an extent, whereas in a highly concentrated solution, the degree of conjugation of the solvent molecules is the main influence. Therefore, the more highly conjugated the solvent and the higher the solution concentration, the higher the excited state absorption cross-section and effective two-photon absorption coefficient, and the longer the triplet lifetime. These results should provide theoretical guidance and experimental clues for the design of materials with better optical limiting performance and promote the further development of laser protection.

1. Introduction

High-power laser technology has been continuously developing since its emergence [1], and it has been widely used in various fields. Accordingly, to prevent high-power laser damage to eyes and devices, research on laser protection has also received a great deal of attention. Within this field, there are many ways to achieve optical limiting, among which nonlinear absorption (NLA) is the most common mechanism [2]. In recent years, NLA dynamics research of materials has played an important role not only in optical limiting but also in the fields of molecular design [3] and photocatalysis [4]. Such nonlinear materials include carbon nanotubes [5], graphene [6], transition metal sulfides [7], porphyrins [8], and phthalocyanines [9–13]. The study of charge transfer kinetics of nonlinear materials is a necessary means to promote the nonlinear properties of materials.

At present, the most studied nonlinear absorption mechanism is reverse saturable absorption (RSA), which provides the best optical limiting performance [14, 15]. Among the current RSA materials, phthalocyanine (Pc) has a highly conjugated π-electron covalent bond system [16], which offers the benefits of a wide limiting window, fast corresponding speed, long excited state life, and the possibility of easy structural tailoring [17]. In 1992, Li *et al* studied the steady-state and dynamic characteristics of reverse saturable absorption in phthalocyanine organometallic compounds. The research showed that singlet absorption was dominant at 300–400 nm, while triplet absorption was dominant at 400–600 nm [18]. Phthalocyanines have two absorption bands in the spectroscopic region spanning the near UV, visible (600–800 nm), namely the Q band and the B band, whose precise characters vary with the choice of central metal atom [19]. It has been observed that the absorption wavelength of the triplet state gradually redshifts as the atomic number of the metal is increased [20], and this is accompanied by accelerated intersystem crossing rates, shortened triplet state lifetimes, and a gradual increase in the fluorescence quantum yield.

In addition, the optical properties of Pc are typically affected by their solubility and aggregation properties [21]. On the one hand, in dilute solution, phthalocyanine exists as a single molecule surrounded by solvent molecules, but as the solution concentration is increased, aggregation occurs [22]. In the aggregated state, the electronic structure of the complex phthalocyanine ring, including its ground state and excited state, is perturbed [23, 24], and this results in changes in the absorption cross-section. On the other hand, the macrocyclic nature of Pc itself is conducive to binding with various substituents, in its peripheral or nonperipheral regions, to improve solubility [25]. Compared with solid samples, liquid samples are very fluid and have uniform particle number density distributions; hence, they play an important role in basic research. In recent years, Zhu *et al* reported the optical limiting performance and ground-state absorption spectrum of different concentrations of CuPc in toluene. Their results showed that the concentration of the solution had an effect on its RSA characteristics: the higher the concentration, the better the RSA characteristics [26]. Swain *et al* compared the emission spectra of thio-ZnPc in toluene (TOL), dichloromethane (DCM), tetrahydrofuran (THF), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) solvents and concluded that the triplet quantum yield decreased with increased solvent polarity, but this trend was not discussed in depth [27]. Bhattacharya *et al* studied the femtosecond transient absorption spectra of ZnPc in different solvents with different concentrations. The results show that the polarity of the solvent governs the excited-state lifetime of the compound [28]. However, few studies on the specific physical processes, and related mechanisms involving solvent molecules, affecting the optical limiting properties of metal Pc materials have been reported. In this study, the ultrafast dynamic mechanism of solvent molecules affecting the optical limiting behavior of lead (II) tetrakis (4-cumylphenoxy) phthalocyanine material was analyzed by means of the Z-scan technique, steady-state spectroscopy, and transient absorption spectroscopy. The results should provide new approaches for the design of improved molecular structures as well as theoretical guidance and experimental hints to facilitate the exploration of materials with better optical limiting performance [29, 30], promoting the further development of the field of laser protection.

2. Experiment

2.1. A. Sample preparation

The experiment was carried out at room temperature. Firstly, an appropriate amount of lead (II) tetrakis (4-cumylphenoxy) phthalocyanine (4-PbPc) was weighed using an electronic balance (SHIMADZU AUW220D), and then dissolved in DMF, THF, and TOL to prepare sample solutions with different concentrations (1, 0.8, 0.6, 0.4, and 0.2 mM). Finally, the mixture was stirred with a magnetic stirrer for 5 min to ensure that the 4-PbPc was completely and evenly dissolved in the solvent. The three solvents and 4-PbPc used in this experiment were purchased from the Aldrich company. The purity of the 4-PbPc molecule is 90%. The purity of the solvents are: TOL 99.8%, DMF 99.8%, and THF 99.9%.

2.2. B. Z-scan experiment

The Z-scan technique was used to study the nonlinear absorption properties of 4-PbPc/THF, 4-PbPc/DMF, and 4-PbPc/TOL solutions of different concentrations. In this experiment, an Nd:YAG laser with a central wavelength of 532 nm was used as the light source. The laser pulse duration and repetition frequencies were 8 ns and 10 Hz, respectively, and the pulse energy was 0.22 mJ. A 2-mm quartz cuvette was used to hold the sample solutions. The laser beam was focused on the sample using a lens with a focal length of 300 mm, and the sample was moved back and forth in the vicinity of the focus. The experimental device is described in detail elsewhere [31]. After passing through the sample, the transmitted portion of beam was collected and measured using a lens (focal length, 75 mm) and an energy meter. The nonlinear optical coefficients of the sample solution were obtained by fitting the experimental data.

2.3. C. Steady-state absorption spectroscopy

UV–Vis absorption spectra of three sample solutions with different concentrations (0.2 and 1 mM) were recorded in the wavelength range of 200–1160 nm using an optical fiber spectrometer (AvaSpec-ULS2048x64-EVO)

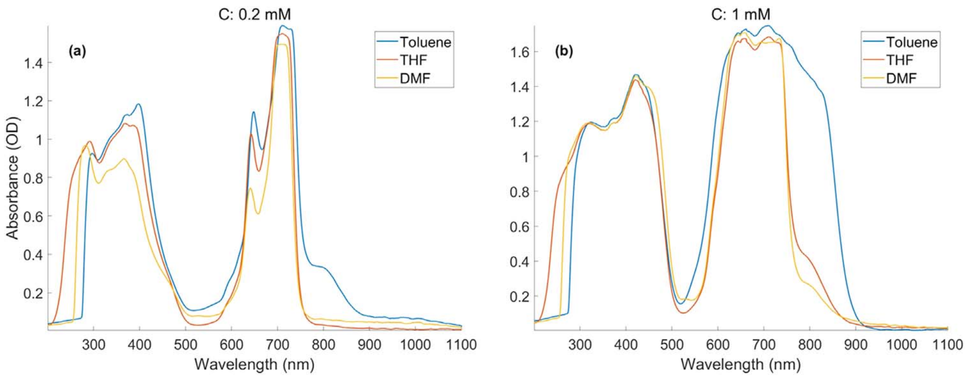

Figure 1. UV–Vis absorption spectra of different concentrations of 4-PbPc in three solvents: (a) 0.2 mM and (b) 1 mM.

at room temperature, as shown in figure 1. The absorption coefficient of each sample was subsequently determined by analyzing the corresponding obtained steady-state absorption spectrum.

2.4. D. Transient absorption spectroscopy

Transient absorption spectra were acquired at room temperature. The basic light source for the experimental setup was provided by a Ti:sapphire regenerative-amplifier laser system (Spectra-Physics; center wavelength, 800 nm; maximum pulse energy, 30 mJ; pulse duration, 50 fs; pulse repetition rate, 1 kHz). A part of the output light beam from this system was focused onto a BBO crystal to produce a frequency-doubled pump pulse (400 nm). A broadband detection pulse (white-light continuum) was generated by focusing another part of the 800-nm beam onto a sapphire crystal. The pump and detection beam were spatially and approximately temporally overlapped in the sample. After passing through the sample, the detection pulse was focused on an optical fiber and directed into a spectrometer (Ava-Spec-1650F). The laser pulse energy was adjusted using the combination of a half-wave plate and a Glan prism [32]. The energy of the probe pulse was much lower than that of the pump pulse. In this experiment, a neutral density filter was used to ensure that the 400-nm excitation pulse energy was 0.001 mJ. The light intensity of the spot on the sample was $2.5\ \mathrm{GW/cm^2}$. A chopper was used to generate 500-Hz pump and detection pulses [33] and hence to finally obtain the difference between the optical density (OD) of the ground state and the excited state, that is, the transient absorption spectrum (ΔOD). Pump-probe delay scan measurements were repeated five times for each sample solution and averaged.

3. Results and discussion

3.1. A. UV–Vis absorption spectra

As shown in figure 1, the UV–Vis absorption spectra of 4-PbPc at concentrations of 0.2 and 1 mM in three different solvents were obtained. It can be seen from the figure that when the solution concentration is 0.2 mM, the characteristic absorption peak of the B band occurs at about 400 nm and the maximum absorption peak of the Q band is at 710 nm. When the solution concentration is 1 mM, the characteristic absorption peak of the B band is at 421 nm and the maximum absorption peak of the Q band at 710 nm. We observed that the higher the concentration corresponded to a redshift of the B-band absorption peak and increases in the B-band and Q-band bandwidths.

At 532 nm, the absorption of 4-PbPc is higher in TOL than in THF or DMF, whether in dilute or concentrated solution. In TOL, the absorption of 4-PbPc in concentrated solution is higher than that in dilute solution, especially at longer wavelengths. This is because TOL itself is highly conjugated, and hence collisions between solute and solution molecules mean that the delocalized electrons are prone to electron transfer, increasing the polarizability of the sample.

When the solution concentration is lower, the number density of solute particles in the solution is less, and there are more solvent molecules on the surface of the solute molecules. The conjugacy of solvent molecules has a great impact on the absorption (B-band) of the system in the near-ultraviolet band, while the conjugacy of THF and DMF solvents is weak relative to TOL, so the charge transfer between the solvent molecules and 4-PbPc molecules is weak. The charge transfer process reduces the barrier of LUMO electron transiting to HOMO, the energy required for electron transition in the case of 4-PbPc/TOL is lower, so the B-band absorption peak of 4-PbPc/THF and 4-PbPc/DMF solutions moves to a shorter wavelength comparing to 4-PbPc/TOL. When the

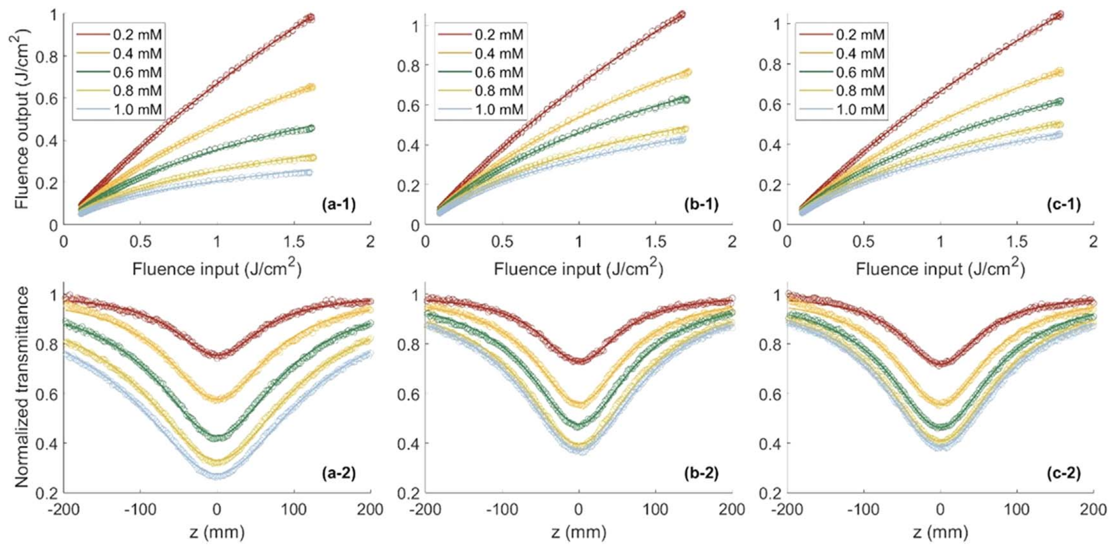

Figure 2. Optical limiting curve (1) and open-aperture Z-scan curve (2) for different concentrations of 4-PbPc in three solvents: (a) TOL (b) THF, and (c) DMF (circles, experimental data; solid lines, fits).

Table 1. Nonlinear optical parameters of different concentrations of phthalocyanine in three solvents.

Nonlinear optical parameters	Excited-state absorption cross-section σ_e (10^{-17} cm^2)					Effective two-photon absorption coefficient β (cm/GW)				
Concentration (mM)	0.2	0.4	0.6	0.8	1.0	0.2	0.4	0.6	0.8	1.0
TOL	1.0145	1.2890	1.4037	1.7345	1.7791	0.32336	0.94840	1.61168	2.87592	3.71736
THF	1.2771	1.5687	1.4357	1.7776	1.6970	0.30624	0.78232	1.05728	1.80808	2.14264
DMF	1.2862	1.5602	1.5328	1.6214	1.5263	0.30480	0.76656	1.12624	1.60320	1.86784

solution concentration is high, there are few solvent molecules on the surface of the solute molecules, which may lead to an unobvious solvent effect, so the B-band peaks in terms of all solutions are at 421 nm.

3.2. B. Z-scan experiment

An open-aperture Z-scan setup was used to obtain the nonlinear absorption of the sample and measure the nonlinear Z-scan transmittance [34]:

$$T_{\mathrm{N}} = \frac{1}{\sqrt{\pi}\,q(x)}\int_{-\infty}^{+\infty} \ln[1 + q(x)e^{-\tau^2}]d\tau, \tag{1}$$

where $x = z/z_0$, $q(z, t) = \beta I_0(t)L_{\mathrm{eff}}/(1 + z^2/{z_0}^2)$, and $L_{\mathrm{eff}} = (1 - e^{-\alpha L})/\alpha$; L_{eff} is the effective thickness of the sample, α is the linear absorption coefficient, I_0 is the axial intensity at the focus, z_0 is the diffraction length of the beam, and z is the position of the sample, which is varied during the scan acquisition.

According to [34], the effective two-photon absorption coefficient β is given by

$$\beta = \frac{\sigma_{\mathrm{g}} N(\sigma_{\mathrm{e}} - \sigma_{\mathrm{g}})}{2\hbar\omega\tau_{\mathrm{p}}}, \tag{2}$$

where σ_g is the ground state absorption cross-section, σ_e is the excited state absorption cross-section, N represents the number density (particles per unit volume), τ_p is the pulse width of incident pulses, and $\hbar\omega$ is the photon energy.

The optical limiting curves and Z-scan curves of 4-PbPc in three solvents at various concentrations are shown in figure 2. It can be seen from the figure that the trend for the variation of the optical limiting curves and Z-scan curves with concentration is consistent. When TOL was used as the solvent, the valleys of the Z-scan curve of the more highly concentrated solutions are deeper, which indicates that the effect of concentration on the optical limiting performance of 4-PbPc in TOL solvent is more significant than that for 4-PbPc in the other two solvents. The nonlinear optical parameters of the phthalocyanine solutions of different concentrations and in different solvents were fitted, and the resultant fit parameters are listed in table 1.

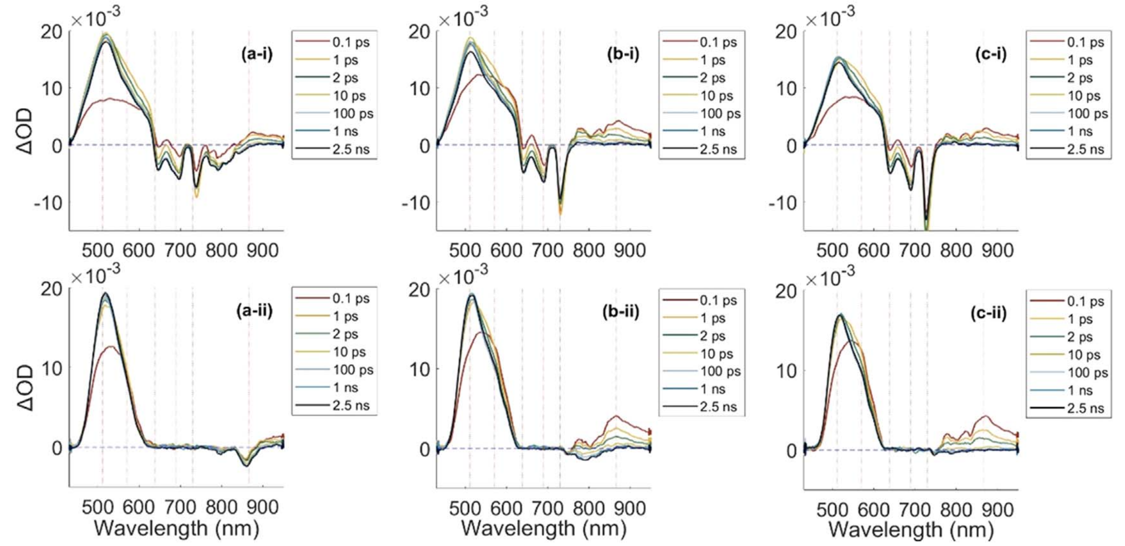

Figure 3. Femtosecond transient absorption spectra of different concentrations (i, 0.2 mM; ii, 1 mM) of 4-PbPc in (a) TOL, (b) THF, and (c) DMF. In each plot, the horizontal blue dashed line highlights the baseline and the vertical red dotted lines highlight specific wavelengths.

It can be seen from the above table that the effective two-photon absorption coefficients of the 4-PbPc/THF, 4-PbPc/DMF, and 4-PbPc/TOL solutions increase with concentration, with the variation for the 4-PbPc/THF and 4-PbPc/DMF solutions being almost the same. However, the effective two-photon absorption coefficient of the 4-PbPc/TOL solution is higher than those of the other two solutions.

Moreover, with the increase of solution concentration, the excited-state absorption cross-section also increases due to the enhanced interaction between the solvent molecules and the phthalocyanine molecules, the effective nonlinear absorption coefficient also increases. The variation of excited-state absorption cross-section with a concentration in 4-PbPc/TOL is similar to the effective two-photon absorption coefficient, while the variation trend of two parameters in 4-PbPc/THF and 4-PbPc/DMF are different.

The reason is that, among the three solvents, TOL has relatively stronger conjugation and solvent effects. 4-PbPc molecules are difficult to aggregate due to the steric hindrance effect caused by adherent toluene molecules, so the excited-state absorption cross-section increases monotonically with the increase of the number of particles. However, THF and DMF have relatively weaker conjugation and weaker steric hindrance effect, and 4-PbPc molecules tend to aggregate in these two solutions, so their excited-state absorption cross-section changes are relatively irregular. The effect of ClGaPc and ClInPc aggregation in chloroform solution on excited-state dynamics was investigated in [22], in which the polarity of chloroform is similar to that of THF and DMF in this paper. Hence, it is presumed that the aggregation effect in 4-PbPc/THF and 4-PbPc/DMF solutions has a similar effect on the excited-state absorption cross-section.

However, it is worth noting that the excited-state absorption cross-section of 4-PbPc/TOL is lower than those of 4-PbPc/THF and 4-PbPc/DMF in the dilute solutions, whereas the excited-state absorption cross-section of 4-PbPc/TOL is higher than those of 4-PbPc/THF and 4-PbPc/DMF in the concentrated solutions. This is because toluene is a relatively strong linear absorber compared to the other two solutions (shown in figure 1), and this influences the effective two-photon absorption coefficient.

3.3. Femtosecond transient absorption spectra

Femtosecond transient absorption (TA) spectroscopy technology based on the use of femtosecond pulses to produce supercontinuum white light allows measurement of the absorption of excited molecules over the entire visible wavelength range. TA studies can reveal the transient dynamic behavior of a material, which can be used to understand the effects of energy transfer, charge transfer, and other factors on the nonlinear optical properties of the material.

$$\Delta \mathrm{OD} = \lg \frac{I_{\mathrm{nopump}}}{I_{\mathrm{pump}}}, \tag{3}$$

where I_{nopump} is the supercontinuum white light intensity transmitted through the sample in the absence of pump light and I_{pump} is the supercontinuum white light intensity transmitted through the sample in the presence of the pump light.

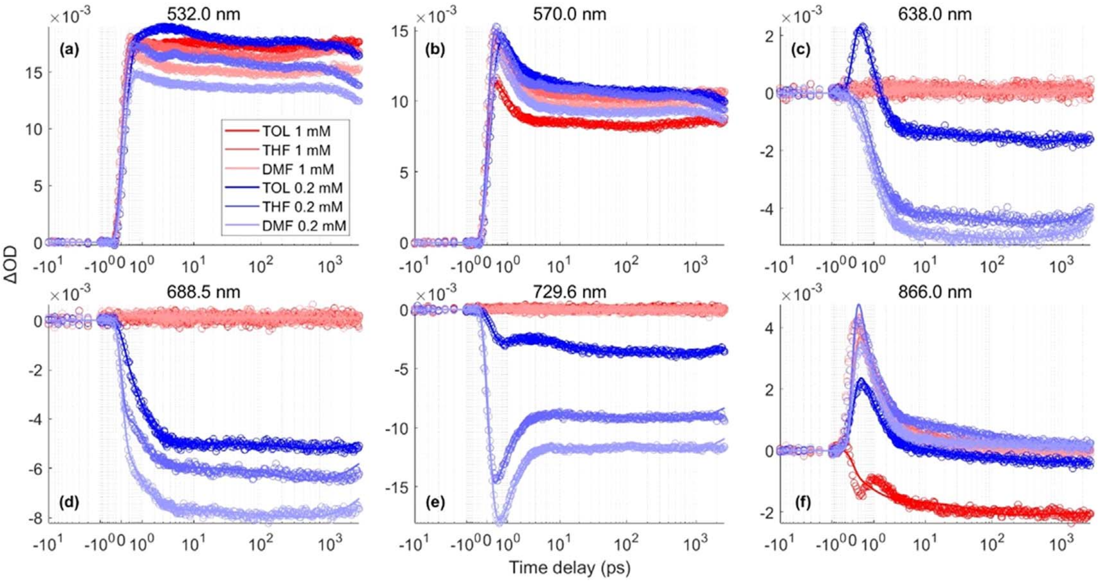

Figure 4. TA kinetic traces with fit results overlaid (circles, experimental data; solid line, fit) for two different concentrations of 4-PbPc in TOL, THF, and DMF (red lines, 1 mM; blue lines, 0.2 mM) at six wavelengths corresponding to the red dotted lines in figure 3: (a) 532.0 nm, (b) 570.0 nm, (c) 638.0 nm, (d) 688.5 nm, (e) 729.6 nm, and (f) 866.0 nm. Note that the abscissa is a logarithmic axis.

Table 2. Decay channel lifetimes of 4-PbPc in three different solvents at concentrations of 0.2 and 1.0 mM.

Lifetime (ps)	τ_1	τ_2	τ_3	τ_4
Toluene (0.2 mM)	1.13	17.92	310.60	$\approx 3.19 \times 10^4$
THF (0.2 mM)	1.03	49.77	240.84	$\approx 1.63 \times 10^4$
DMF (0.2 mM)	1.18	43.95	354.28	$\approx 1.80 \times 10^4$
Toluene (1.0 mM)	1.21	70.83	308.69	$\approx 1.2 \times 10^5$
THF (1.0 mM)	1.69	58.03	359.07	$\approx 1.0 \times 10^5$
DMF (1.0 mM)	1.41	61.87	502.36	$\approx 1.2 \times 10^5$

As can be seen in figure 3, in the 430–630 nm band, each concretion of the three solutions showed excited state absorption. For each solution, when the concentration was higher, the ground-state bleaching spectral band was redshifted and narrowed with respect to the lower-concentration result, and this band can even be neglected when considering the photophysics of the system. A reasonable interpretation is that the proportion of the ground-state molecules being pumped in the low-concentration solution is relatively high, and most of the ground-state molecules are pumped to the excited state, resulting in strong ground-state bleaching; while in the high-concentration solution, only part of the ground-state molecules are pumped to the lower energy levels of excited state S_1, so the bleaching signal is relatively weak. However, it is particularly noteworthy that there are significant differences between the TA spectral profiles of 4-PbPc/THF and 4-PbPc/DMF and 4-PbPc/TOL, regardless of the concentration. The ground-state bleaching bands of the first two are narrower than that of 4-PbPc/TOL and concentrated at shorter wavelengths; at the same time, the excited-state absorption is stronger at 760–950 nm.

Because the solutes of the three samples are the same, considering the steady-state absorption spectra of the three samples, it can be suggested that the stronger interaction between TOL and the solute increases the probability of electron wavefunction overlap for the solute and solvent molecules. This shifts the ground-state absorption to lower-energy (longer-wavelength) light, making the 4-PbPc/TOL sample more prone to ground-state bleaching. In addition, the transient absorption peak positions (540 nm) of 4-PbPc/THF and 4-PbPc/DMF shifted to the longer wavelength direction compared to 4-PbPc/TOL at a time delay of 0.1 ps. This phenomenon might be caused by the stronger interaction between the toluene molecules and 4-PbPc molecules in 4-PbPc/TOL, which makes the solute molecules in the ground state occupy lower energy levels (compared to THF/DMF) since toluene has stronger conjugacy than the other two solvents. Therefore, in this case, higher photon energy is required to transit to the higher level. To further illustrate this difference and the specific mechanism of the above interaction, we performed global fitting [35] on the TA spectra of the three solutions

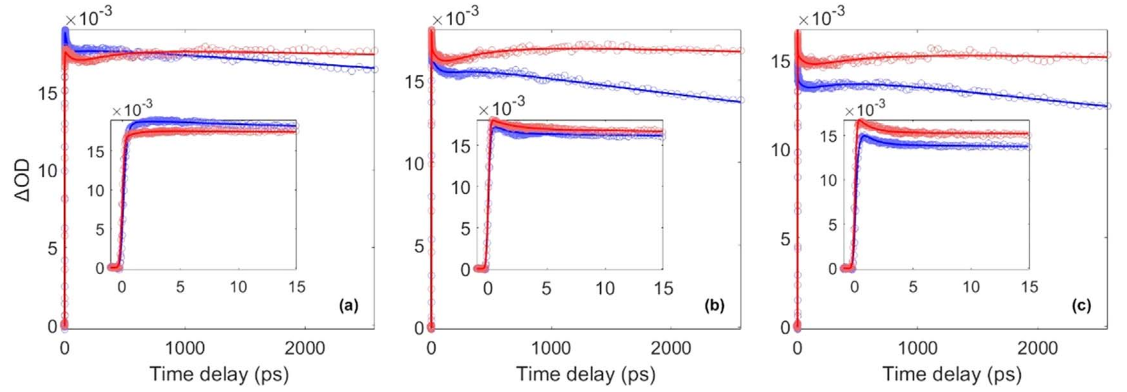

Figure 5. TA kinetic traces at 532 nm (circles, experimental data; solid lines, fits) for different concentrations of 4PbPC (red lines, 1 mM; blue lines, 0.2 mM) in (a) TOL, (b) THF, and (c) DMF.

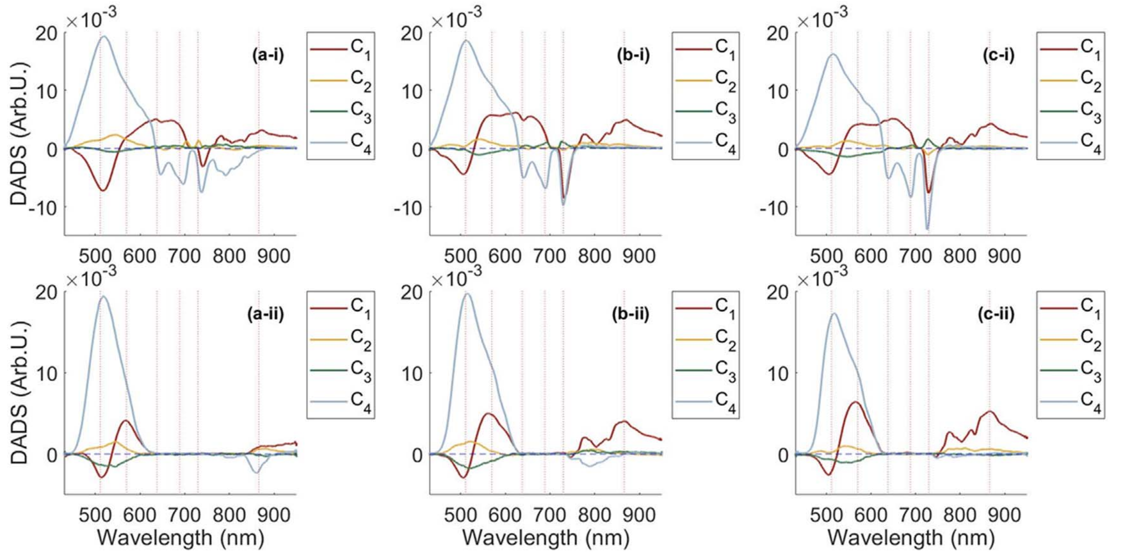

Figure 6. DADS for four different channels C_1, C_2, C_3, and C_4 of 4-PbPc in (a) TOL, (b) THF, and (c) DMF at different concentrations (i, 0.2 mM; ii, 1 mM). In each plot, the horizontal blue dashed line highlights the baseline and the vertical red dotted lines highlight specific wavelengths.

and obtained the lifetimes of the four channels (see table 2). The fitted curves of the global fitting are shown in figure 4.

From the global fitting curves, we selected several representative wavelengths, 532.0, 570.0, 638.0, 688.5, 729.6, and 866.0 nm, for closer examination; these are plotted in figure 4. It can be seen from the figure that the fits are, in general, in good agreement with the experimental data. However, we found that in dilute solution, the fit for the 660–740 nm band deviated greatly from the data; in other words, the corresponding triplet lifetime of the molecule is long. This is because the number of triplet-state molecules resonating with photons of this band is negligible, resulting in strong ground-state bleaching of the TA spectral body in the corresponding band, so it will not affect the corresponding decay channel lifetime.

The data in table 2 are the lifetimes of different decay channels for 4-PbPc solutions in three different solvents at two different concentrations (0.2 mM, 1 mM). It is apparent that τ_4 (the triplet lifetime) of the 4-PbPc/TOL solution is higher than that of 4-PbPc/DMF and 4-PbPc/THF solutions. With the increase in concentration, the lifetime of each channel of the three solutions increased. Additionally, when the concentration is 0.2 mM, it is apparent that τ_2 of the 4-PbPc/TOL solution is shorter than the other two solutions.

This is due to fact that when the concentration is lower, there are more solvent molecules on the surface of solute molecules. In this case, since toluene has a strong solvent effect compared with the other two solvents, the

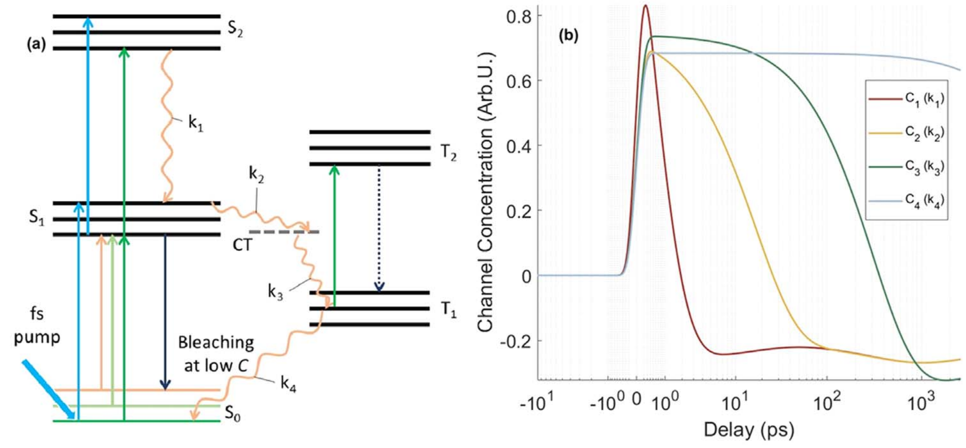

Figure 7. (a) Five-level model. S_0, S_1, and S_2 represent the ground state, first excited singlet state, and second excited singlet state, respectively; T_1 and T_2 represent the first and second excited triplet states, respectively. *CT* indicate the charge transfer state. (b) Channel concentrations versus time delay (the abscissa is a logarithmic axis; C_1, C_2, C_3, are C_4 are four different channels).

charge transfer rate between the solvent molecules and 4-PbPc molecules is faster, and the transition rate from S_1 to T_1 is faster, so the lifetime is reduced.

Next, to further explore the relationship between the TA spectra of the three solutions and the optical limiting performance, we selected the TA kinetic trace at 532 nm (i.e., the central wavelength of the Z-scan) for a more detailed analysis, and plots for each of the solutions are presented separately in figure 5.

To more clearly observe the long-lifetime optical limiting dynamics of the 4-PbPc/TOL, 4-PbPc/THF, and 4-PbPc/DMF solutions, in figure 5, we present the kinetic trace plots using a linear horizontal axis. It is apparent that at 532 nm, the decay traces of 4-PbPc/THF and 4-PbPc/DMF have the same trend with the time delay in 2.5 ps. However, for 4-PbPc/TOL, immediately after interaction with the pump pulse, the absorption coefficient of the triplet state is high, that is, the quantum efficiency is high, and the triplet state is long-lived (see also table 2). We speculate that this is because of the highly conjugated nature of the TOL solvent molecules and the influence of concentration.

In an attempt to test this hypothesis, we obtained decay-associated difference spectra (DADS) for different channels via global fitting, and these are shown in figure 6. It can be seen from the figure that the DADS corresponding to the C_2 and C_3 channels of all of the samples have the same forms in terms of the variations with respect to their baselines. There is a strong correlation between C_2 and C_3 which means that they share the same population and ESA characteristics. Noticing that the interaction between the solute and solvent molecules are relatively weak since there is no covalent bond but only collisions between them, it strongly suggests that one of these channels refers to the *CT* process between the solvent molecules and phthalocyanine molecules since generally, it does not change the nonlinear absorption spectral profile but promote its performance [36]. In the dilute solution, the DADS intensities of the C_2 and C_3 channels of 4-PbPc/TOL were found to be higher than those of the other two solutions, while in the concentrated solution, the DADS intensity of the three solutions were higher than that of the more dilute solution. This is because when the concentration was higher, charge transfer between solvent molecules and phthalocyanine molecules was more likely to occur, but when the concentration of the 4-PbPc/TOL solution was lower, because the π electrons of TOL molecules were strongly conjugated, the charge-transfer efficiency was higher than those of the other two solutions, resulting in higher absorption (see figure 5), which is consistent with the conclusions of Danilov and coworkers [37, 38].

To further analyze the charge transfer mechanism of the 4-PbPc system, we have described its ultrafast dynamics based on a five-level model [39] [figure 7(a)]. In this model, k_1 is the rate at which molecules relaxes back to S_1 (via the C_1 channel) from the S_2 level, k_2 is the rate at which molecules in the S_1 state transit to *CT* via the C_2 channel, k_3 is the rate at which molecules in the *CT* state transit to T_1 via C_3, and k_4 is the rate at which the molecules return to S_0 (via C_4) from the T_1 level. Figure 7(b) shows the evolution of the channel concentration with time delay. It can be seen from the figure that the populations of the C_1, C_2, and C_3 channels are all rapidly reduced, but with different lifetimes, to produce ground state bleaching after being pumped to a certain extent relative to C_4.

Reference to such model, we give the rate equations as well as the corresponding kinetic matrix:

$$\frac{d\boldsymbol{N}}{dt} = \boldsymbol{KN} \tag{4}$$

where

$$\boldsymbol{K} = \begin{bmatrix} -k_1 & 0 & 0 & 0 \\ k_1 & -k_2 & 0 & 0 \\ 0 & \Phi_{\text{isc}} k_2 & -k_3 & 0 \\ 0 & 0 & k_3 & k_4 \end{bmatrix} \tag{5}$$

and Φ_{isc} is the quantum efficiency of the intersystem-crossing.

From the above analysis and our Z-scan, steady-state spectra, and transient absorption spectra analyses, we arrived at two principal conclusions: First, solute concentration has a significant effect on the optical limiting characteristics of a solution. From the dynamic point of view, this effect is mainly observed as increases in the excited state lifetime and absorption cross-section with concentration, because charge transfer between solvent molecules and phthalocyanine molecules increases with concentration. Second, the nature of the solvent molecules in the solution will also affect the optical limiting performance of a phthalocyanine solution. Comparing the three solvents, we can see that the variation of each optical limiting parameter is the almost the same for the DMF and THF solvents, while the optical limiting performance of the TOL solution is significantly different from those of the other two solutions because TOL is highly conjugated. Specifically, in a dilute solution (0.2 mM), the excited state absorption cross-section of 4-PbPc/TOL was found to be smaller than those of the other two solutions, but at a higher concentration (1 mM), the excited-state absorption cross-section of 4-PbPc/TOL was greater than those of 4-PbPc/DMF and 4-PbPc/THF. Considering previous results [27, 28] as well as those described above, we speculate that the higher polarity of solvent molecules at low concentrations may reduce the triplet quantum yield of phthalocyanine molecules, resulting in a slight decrease in the effective excited state absorption cross-section. However, in highly concentrated solutions, the enhanced conjugation of solvent molecules will result in increased charge transfer between solvent and 4-PbPc molecules. Thus, the effective excited state absorption cross-section is increased. As is well known, the permanent dipole moment or higher-order multipole moment of the molecule determines its polarity, and for a conjugated molecule, electron delocalization (an expanded electron cloud) increases its polarizability (which is proportional to the radial integral of the first-order response of the electron density to the electric field). Therefore, we can conclude that in a dilute solution, the effective excited-state absorption cross-section may be strongly influenced by the permanent dipole moment or higher-order multipole moment of solvent molecules, but in more concentrated solutions, the impact of solvent molecule conjugation will dominate the effective excited-state absorption cross-section of the solution, which is reflected by its positive correlation with the polarizability. This suggests a new approach for obtaining liquid samples with strong optical limiting performance characteristics: high concentrations of phthalocyanine materials can be dissolved in highly conjugated solvents such as TOL and measured using a thinner container, to improve the linear transmittance of the sample and enhance the excited-state absorption cross-section.

4. Conclusion

In conclusion, we studied the effects of three solvents with different concentrations on the nonlinear optical limiting characteristics and ultrafast dynamics of 4-PbPc materials by Z-scan and transient absorption spectroscopy. The results of the Z-scan experiment revealed that with increasing solution concentration, the excited state absorption cross-section and effective two-photon absorption coefficient both increased, especially in the case of 4-PbPc/TOL. In addition, by analyzing the femtosecond transient absorption spectra, based on the DADS correlation of C_2 and C_3, we proved that the conjugation of solvent molecules affects the efficiency of charge transfer. Thus, in highly concentrated solutions, the conjugation of solvent molecules dominates the optical limiting performance of the solution. However, in dilute solution, the polarity of solvent molecules may have some effect on this behavior. We expect that this work will provide theoretical guidance and experimental clues for the design of optical limiting devices, and that our results will promote the further development of laser protection technology.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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