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Linear and nonlinear optical properties of covalently bound C.I. Disperse Red 1 chromophore/silica hybrid film

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Abstract

The third-order nonlinearity of an organic–inorganic hybrid silica film covalently doped and dispersed with C.I. Disperse Red 1 was studied using the Z-scan technique. The micropores in the sol–gel derived silica matrix were smaller than the dye ligand which led to dye aggregation. A nonlinear refractive index of -3.4×10^{-9} esu and a nonlinear susceptibility of 5.9×10^{-10} esu were recorded at 1064 nm. The large blue shift of the absorption band due to dye aggregation resulted in an enhanced two-photon absorption. The observed nonlinearity is attributable to both two-photon absorption resonance and the refraction change induced by the enlarged π-delocalization conjugation between the dye and the silica matrix.

Keywords: C.I. Disperse Red 1; Chromophore aggregation; Hybrid film; Nonlinear optics; Two-photon absorption; Nonlinear absorption

1. Introduction

Nonlinear optics (NLO) has been expected to play an essential role in emerging technologies of photoelectronics and photonics [1,2]. Organic molecules with high π-electron delocalization are considered as promising nonlinear optical materials [3,4] because of their large nonlinearities, ultrafast responses and potential applications in such optical devices as data processor, high-speed optical switchers, and optical limiters, etc. [5–8].

Among various NLO chromophores, azobenzene has good optical and thermal stabilities, dissolvability and easy preparation virtues [4,9], and has been a well-known nonlinear optically active chromophore due to its unique optical properties [10–12]. The second- and third-order nonlinear optical properties of azobenzene chromophores have been widely studied in solution and/or in polymer matrices [13–17], such as widely used polymethyl methacrylate (PMMA) and polyphenylene vinylene (PPV) matrices. However, the polymer matrices always suffer from poor optical and thermal stabilities, and the solution does not fit for practical applications.

Recently, sol–gel derived organic–inorganic hybrid materials that combine the advantages of both organic chromophores and inorganic matrix have received significant attention for optical and photonic applications because of the inherent properties of the silica matrix [18–20]. Optical chromophore molecules can be incorporated into sol–gel matrices in two ways: by guest–host chemistry or by covalently linking them into matrices as main-chains or side-chains [21]. In a guest–host system, separations of chromophore from matrix always occur at high concentrations; while in the latter case, the chromophores were covalently grafted into the silica networks, allowing an easy tailoring of the chromophore concentration and better control of the chemical and processing parameters [18].

So far no reports can be found on the third-order NLO of azobenzene chromophore covalently incorporated inorganic systems. In fact, the optical properties sensitively depend on the linkage between the chromophore and matrix. Moreover, the laser wavelengths used in the past studies always stand in the resonant and/or near resonant wavelength region of

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around 500 nm, using the strong resonant effect during the *trans–cis* photoisomerization of azo dyes. However, the resonant excitation would lead to significant light losses and thermal effect. So it is necessary to find a system having large third-order nonlinearity outside the resonance region together with thermal and optical stabilities.

In this paper, the third-order nonlinearity of hybrid silica films covalently doped with azobenzene dye, Disperse Red 1 (DR1), was studied by Z-scan technique at 1064 nm. DR1 contains disparate electron affinities on the opposite sites of benzene rings, exhibiting an extended π-electron delocalization. The schematic synthesis procedure of hybrid films is shown in Scheme 1. DR1 was pre-modified by the siloxane with an isocyanate group (product named DR1ASD) [10,12,22], and then co-hydrolyzed and co-condensed with tetraethoxysilane (TEOS) in acidic condition to form hybrid film.

2. Experimental

2.1. Chemicals

C.I. Disperse Red 1 (DR1, purity >95%) and 3-isocyanatopropyl triethoxysilane (ICPTES, purity >96%) were purchased from Aldrich Chem. Co. and Diamond Chem. Co. (China), respectively, and were used as received. Tetrahydrofuran (THF) was distilled over Na/benzophenone before use.

2.2. Preparation of hybrid films

Typically, 0.386 g DR1ASD and 1.7 ml of tetraethoxysilane (TEOS, AR) were dissolved in 3 ml of tetrahydrofuran (THF), and 0.93 g HCl (pH = 2) was introduced as catalyst. The mixture was stirred for 2 h and aged for 1 d to get the precursor sol. The hybrid films were finally obtained by spin coating (3000 rpm, 30 s) from the hydrolyzed sol with a component molar ratio of TEOS:DR1ASD:H_2O:HCl:THF = 0.92:0.08:6:0.004:3.75, and dried at 80 °C overnight.

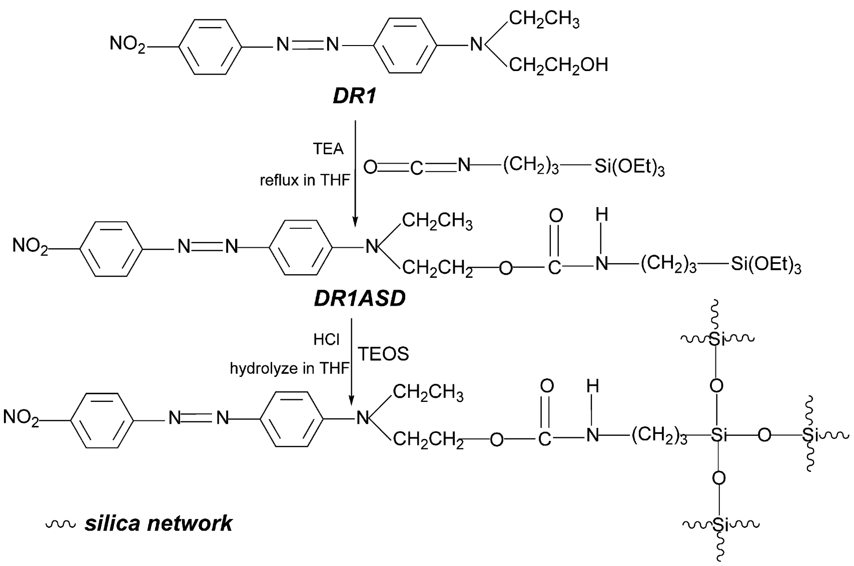
2.3. Z-scan measurements

The third-order nonlinear optical properties were measured using a Z-scan technique [23,24]. The Z-scan technique is based on the principles of spatial beam distortion, and offers simplicity as well as very high sensitivity for measuring both the nonlinear refractive index and nonlinear absorption coefficient. In our experiment we used an Nd:YAG laser operating at 1064 nm with a pulse duration of 40 ps and a repetition of 10 Hz to eliminate the accumulative thermal effect. The light intensities, transmitted across the samples, were measured as a function of the sample position in the *Z*-direction with respect to the focal plane either through a small aperture (closed aperture) or without an aperture (open aperture), in order to resolve the nonlinear refraction and absorption coefficients. The laser beam was focused to a beam waist (ω_0) of 35 μm and the corresponding Rayleigh length z_0 can be found to be 3.6 mm, calculated by the formula $z_0 = \pi\omega_0^2/\lambda$, much thicker than the hybrid film thickness ($L = 1078$ nm measured with an ellipsometer for the film). The NLO property of DR1 solution in THF was also measured with a 1 mm sample cell using the same conditions as used in the measurement of the film. Before measuring, CS_2 was used as a standard reference to calibrate the Z-scan system.

3. Results

3.1. Linear optical properties

Fourier transformation infrared (FT-IR) spectra were recorded on a Nicolet 7000-C spectrometer with 4 cm^{-1} resolutions using KBr pellets. The film was scratched from the glass substrate for the measurement. Fig. 1 shows the FT-IR spectra



Scheme 1. Synthesis of DR1ASD and preparation of hybrid films.

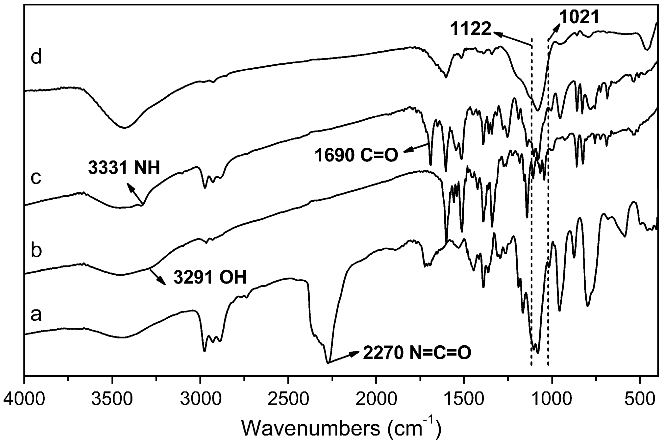


Fig. 1. FT-IR spectra of (a) ICPTES, (b) DR1, (c) DR1ASD and (d) the as-synthesized hybrid films.

of DR1, ICPTES, DR1ASD and the as-synthesized hybrid films. DR1ASD was prepared through the reaction of hydroxyl groups (3291 cm^{-1}) in DR1 with the isocyanate groups (2270 cm^{-1}) in ICPTES. In DR1ASD (Fig. 1c), the bands of both OH and N=C=O disappeared, and instead new sharp absorption bands at 3331 and 1690 cm^{-1} appear, corresponding to the NH and C=O stretching, respectively, indicating the complete reaction between N=C=O and OH. The bands at about 1122 and 1021 cm^{-1}, attributed to the Si–O–Et groups of the silane in ICPTES, remained in DR1ASD, indicating that no condensation has occurred at this point [25]. However, in the as-synthesized film (Fig. 1d), Si–O–Et group bands disappeared, only the Si–O–Si and O–Si–C bands at about 1100 cm^{-1} remained. All the results lead to a conclusion that DR1 chromophore has been covalently linked onto the isocyanate siloxane successfully, and consequently been covalently linked into the silica matrix framework.

UV–vis diffusing reflectance spectra were measured on a Shimadzu UV-3101. Fig. 2a shows the UV–vis spectra of DR1 in THF solution (dashed line, 10^{-5} M) and hybrid film (solid line), respectively. DR1 in solution presents a symmetric absorption band at about 490 nm, a fundamental absorption of monomeric azobenzene chromophore due to π–π* electronic transition. However, a strongly asymmetric absorption band and a large blue shift of main absorption band by more than 50 nm were observed in hybrid film, which noticeably differs from the usual spectra obtained with DR1 in various environments [11]. Two absorption bands at 425 and 485 nm were determined for the film using Gaussian multi-peak fitting model, shown as dotted lines in Fig. 2b, which are assigned to π–π* electronic transitions occurring in aggregated and free azobenzene chromophores, respectively [12].

3.2. Nonlinear optical properties

Fig. 3 shows the normalized transmittances with an open aperture ($S = 1$) as a function of the sample position Z for DR1 solution (10^{-2} M in THF) and hybrid film, respectively. Both transmittances are symmetric with respect to the focus

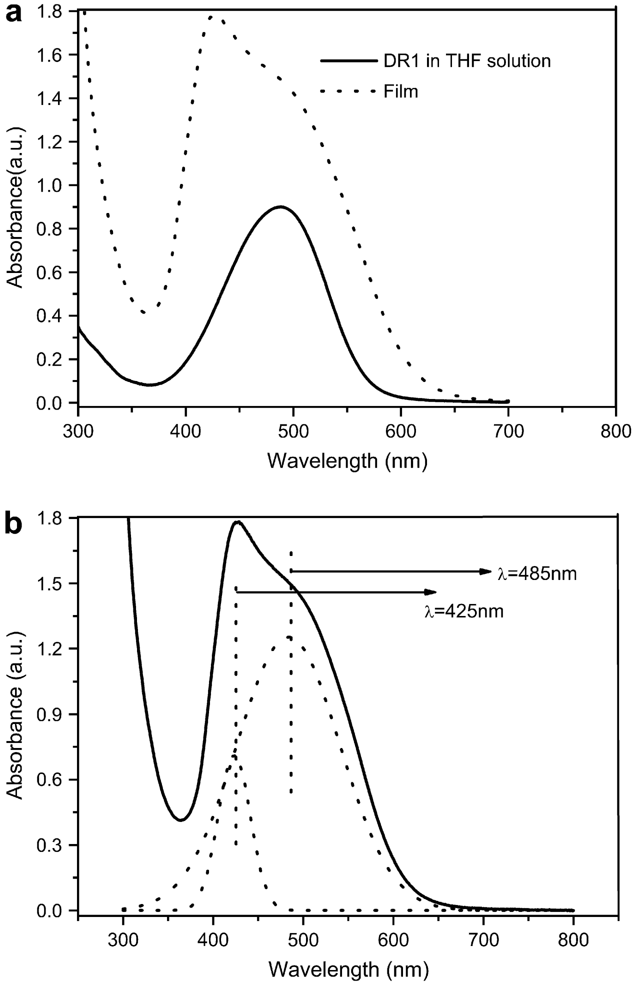


Fig. 2. (a) UV–vis spectra of DR1 solution in THF (10^{-2} M) and hybrid films; (b) two absorption bands (dotted lines) for hybrid film fitted with Gaussian model.

($Z = 0$) where they have minimum transmittances, indicating an induced absorption, i.e. reverse saturated absorption.

The nonlinear absorption coefficient β can be estimated from the open-aperture Z-scan data by the formula,

$$\beta = 2\sqrt{2}(1 - T)\big/ I_0 L_{\text{eff}}$$

where I_0 is the peak on-axis irradiance with the sample at focus, and $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$ the effective thickness of the sample, α the linear absorption coefficient and L is the thickness of the sample.

Due to the presence of nonlinear absorption, the pure nonlinear refractive property should be assessed from the division of the normalized closed-aperture (CA) data by the open-aperture data. Fig. 4 shows the divided CA curves for DR1 solution and hybrid film, respectively. We can see a valley–peak shape (Fig. 4a), representative of a positive nonlinear refractive index ($n_2 > 0$) and a self-focusing effect, in DR1 solution. However, the hybrid film exhibits a peak followed by a valley (Fig. 4b), indicating a negative nonlinear refractive index

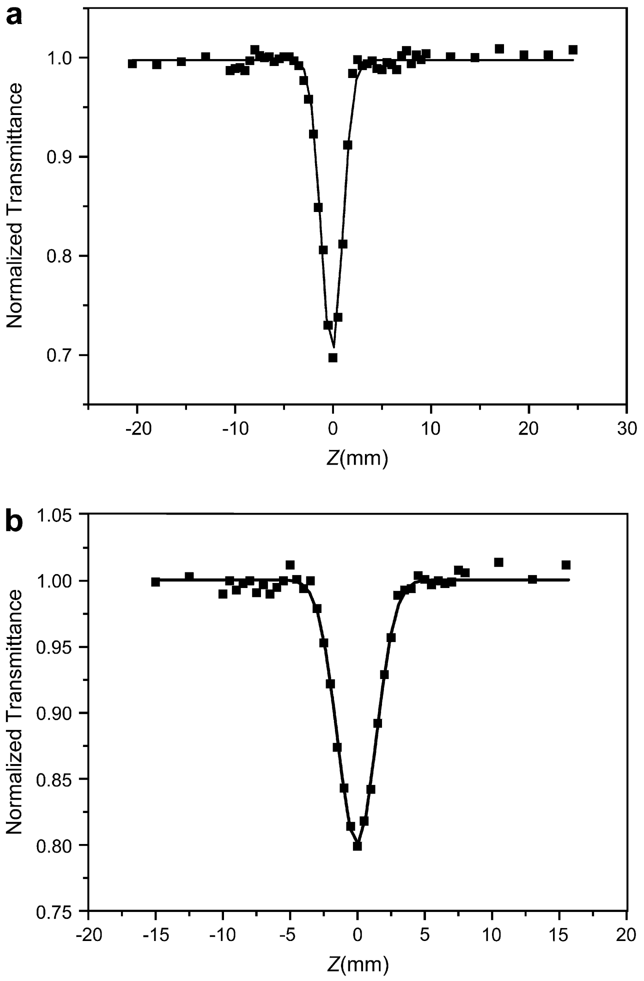


Fig. 3. Open-aperture Z-scan experiment results for (a) DR1 solution (10^{-2} M) and (b) hybrid film.

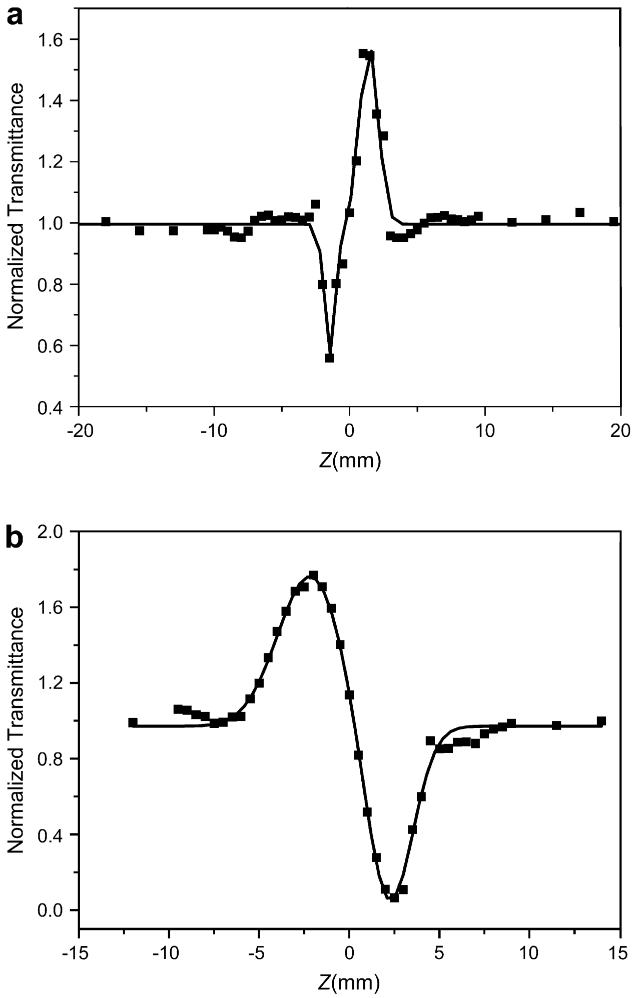


Fig. 4. Corrected closed-aperture Z-scan experiment results for (a) DR1 solution (10^{-2} M) and (b) hybrid film.

($n_2 < 0$) and a self-defocusing effect. We define the change in normalized transmittance between the peak and valley in a CA curve as $\Delta T_{\mathrm{pv}} = T_{\mathrm{p}} - T_{\mathrm{v}}$, where T_{p} and T_{v} are the normalized transmittances at the peak and valley, respectively.

$$\Delta T_{\mathrm{pv}} \cong 0.406(1 - S)^{0.25} |\Delta \Phi_0|,$$

with $\Delta \Phi_0 = 2\pi n_2 I_0 L_{\mathrm{eff}} / \lambda$, where S is the transmittance of the aperture in the absence of a sample. $\Delta \Phi_0$ is the on-axis peak nonlinear phase shift with the sample at focus, and n_2 is the nonlinear refractive index.

$$n_2\ (\mathrm{esu}) = (c n_0 / 40\pi) n_2\ (\mathrm{m}^2/\mathrm{W})$$

where c is the light speed in vacuum and n_0 is the linear refractive index. The n_0 of hybrid film was determined to be 1.55 by an ellipsometer, and we approximate that of DR1 solution to the n_0 value of the solvent (1.41 for THF).

The real ($\mathrm{Re}\chi^{(3)}$) and imaginary ($\mathrm{Im}\chi^{(3)}$) parts of the third-order nonlinear optical susceptibility $\chi^{(3)}$ can be determined by the experimental measurements of n_2 and β according to the following relations [26],

$$\mathrm{Re}\chi^{(3)}\ (\mathrm{esu}) = \varepsilon_0 c^2 n_0^2 n_2 / \pi\ (\mathrm{m}^2/\mathrm{W})$$

$$\mathrm{Im}\chi^{(3)}\ (\mathrm{esu}) = \varepsilon_0 c^2 n_0^2 \lambda \beta / 4\pi^2\ (\mathrm{m}/\mathrm{W})$$

where ε_0 is the vacuum permittivity. All NLO properties of DR1 solution and hybrid film are summarized in Table 1 according to the formula above.

4. Discussions

After the hydrolysis and co-condensation of DR1ASD with TEOS, some micropores would exist in silica matrix of the as-deposited films, and the dyes were always thought to dissolve in the pore liquids [11,27–29]. Considering that the real concentration of the dyes in the pore liquids should be much higher than that in the starting sol, the aggregation is thought to result from the increase in dye concentration caused by the solvent evaporation [27]. Furthermore, the sol–gel substrate pore is commonly regarded to be smaller than the size of DR1ASD ligands when in the *trans* fundamental configuration [1], so we can no longer expect that the dyes are present as

Table 1
The third-order NLO parameters of the hybrid film and DR1 solution at 1064 nm

Samples	n_2		β	$\mathrm{Re}\chi^{(3)}$	$\mathrm{Im}\chi^{(3)}$	$\chi^{(3)}$
	$\mathrm{m^2/W}$	esu	m/W	esu	esu	esu
Film	-9.18×10^{-16}	-3.40×10^{-9}	3.66×10^{-9}	-5.59×10^{-10}	1.89×10^{-10}	5.9×10^{-10}
Solution	2.53×10^{-19}	8.51×10^{-13}	4.66×10^{-13}	1.27×10^{-13}	1.99×10^{-14}	1.29×10^{-13}

monomers. As a result, the disperse red chromophores were randomly incorporated into the microporous silica network during the coating and aging processes, leading to partial aggregation of DR1 chromophore and a strong absorption band at 425 nm, as shown in Fig. 2.

The NLA coefficient of hybrid film is calculated to be 3.66×10^{-9} m/W and is nearly four orders larger than that of DR1 solution, indicating a strong reverse saturated absorption. In the case of excluding the thermal effect, both excited state absorption (ESA) and two-photon absorption (TPA) may be responsible for these measured nonlinear absorption (NLA) effects. According to a two-level model, a positive n_2 due to electronic nonlinearity should be obtained after the TPA wavelength [17], while a negative n_2 can be obtained if the nonlinearity of the sample is mainly due to TPA [13]. From Fig. 4, the film case is consistent with the two-level model for two-photon absorption nonlinear response, while the DR1 solution has a reverse expression, i.e. electronic nonlinearity. This may be explained with the help of an energy diagram, as shown in Fig. 5. Because the intersystem crossing and triplet–triplet transitions occur on the nanosecond scale [8], a three-level energy diagram in singlet states was referred in the present case. A large blue shift for hybrid film due to partial aggregations of molecules leads to an energy increase (ΔE) from the ground state to the excited state. Although the irradiation wavelength (1064 nm) used in this experiment lies far from the one-photon resonant transition, both film and solution still have absorptions at 532 nm, as shown in the linear absorption spectra. When the molecule absorbs two photons, electrons transit from the ground state (S_0) to the excited state (S_1) in film, denoted as TPA, while in solution, ESA from excited state (S_1) to higher excited state (S_2) may occur due to the smaller energy gap, resulting in a decrease of population in S_1 and consequently a low TPA coefficient. So we attribute the NLA to TPA in hybrid film and combination of TPA and ESA in solution.

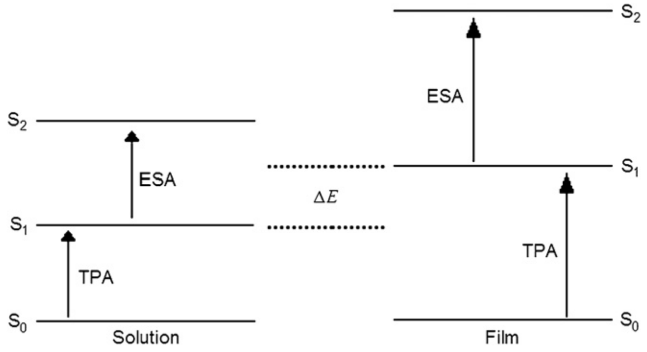


Fig. 5. Schematic three-level energy diagram for DR1 in solution and film.

The nonlinear refractive index of the hybrid film was calculated to be -9.18×10^{-16} $\mathrm{m^2/W}$, three magnitudes higher than that of DR1 solution, which can be attributed to the interaction between the matrix and chromophores. Similar results have been found in azo dye-doped PMMA film [15] and sol–gel system [1]. In solution, photoisomerization and reorientation of molecules should be the dominant mechanisms of excitation due to the high mobility of molecules. However, when the chromophores were caged and restricted in the rigid silica network, the above mechanisms in solution could hardly occur in film. Literature, where the nonlinear refractive indexes of DR1 in PMMA [13] and poly(maleic anhydride-*co*-octadecence) [30] were measured to be at the magnitude of 10^{-17} and 10^{-19} $\mathrm{m^2/W}$ at 1064 nm, emphasized the TPA resonance enhancement on the nonlinearity. In the present hybrid film, TPA resonance also exists. Except for the effect of chromophore concentration, however, as we believe, the TPA resonance should not be the main reason for the measured large nonlinearity in this experiment. Furthermore, as the energy level in the excited state becomes higher due to the molecular aggregations, the contribution from the excited state would be less important because the expression for third-order nonlinearity contains their transition energy term in its denominator [31–33]. All results imply that a strong interaction between chromophore and silica matrix exists. The silane grafting and covalent linkage into silica matrix enhance the π conjugation of the azobenzene chromophore, and thus increase the π–π^* transition band gap [34], in agreement with the blue shift in linear absorption spectrum. So we attribute the large nonlinearity of the present hybrid films to the two-photon absorption resonance and the enlarged delocalization of π-electron caused by the interactions between chromophore and silica matrix.

For the present film, $\mathrm{Im}\chi^{(3)}$ and $\mathrm{Re}\chi^{(3)}$ have the same magnitude, indicating that both the real and imaginary parts contribute to the nonlinearity. However, as $\mathrm{Re}\chi^{(3)} > \mathrm{Im}\chi^{(3)}$, so $\mathrm{Re}\chi^{(3)}$, which gives rise to the refraction change, is dominant.

5. Conclusions

In conclusion, we have measured the third-order nonlinearity of the DR1 azobenzene dye covalently doped organic–inorganic hybrid films using Z-scan technique. A nonlinear absorption (NLA) was detected and was mainly associated with two-photon absorption (TPA) effect that originated from the electronic transition from the ground state (S_0) to the first excited state (S_1) due to the partial aggregations of molecules. A large and negative off-resonance third-order nonlinear refractive index as high as 10^{-9} esu was observed at 1064 nm, induced by an enlarged π-electron conjugation and TPA resonance.

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