Third-order nonlinear optical properties in $[(C_4H_9)_4N]_2[Cu(C_3S_5)_2]$-doped PMMA thin film using Z-scan technique in picosecond pulse

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Abstract An organometallic complex, $[(C_4H_9)_4N]_2[Cu(C_3S_5)_2]$, abbreviated as BuCu, was synthesized. Then the BuCu-doped polymethylmethacrylate (PMMA) thin film with a doping concentration 1% by weight (1 wt.%) was fabricated using a spin-coating method and its third-order nonlinear optical properties were characterized using the Z-scan technique with 20 ps pulse duration at 532 and 1064 nm, respectively. The Z-scan curves have revealed that the material exhibits a self-defocusing effect at both wavelengths. Saturable absorption at 532 nm and two-photon absorption at 1064 nm were also found, respectively. Additionally, the calculated results of the material in film were compared with that of acetone solution, which indicated that the values in film were larger than that of acetone solution for about two orders in magnitude. The origins were analyzed of the difference between the two wavelengths. Our results suggest that considerable nonlinear optical properties were confirmed in BuCu-doped PMMA film. The material can easily be doped into PMMA film and forms a waveguide mode. So this material should be considered to be manufactured into devices and applied in all-optical switching, laser locking-mode, optical limiting fields etc.

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1 Introduction

In recent years, materials with large third-order nonlinear optical (NLO) properties and ultrafast response time have given rise to great interest for its widespread applications in optical switching, signal processing, ultrafast optical communications and optical limiting [1–4]. Organic materials with delocalized electrons have attracted basic and applied research because of their large nonlinear optical susceptibilities, architectural flexibility, and ease of fabrication. The delocalization of an electron in the molecular frame enhances the optical nonlinearity and this has been one of the most successful strategies for improving nonlinearity. Organometallic complexes with large two-dimensional π-conjugated systems have exhibited an excellent ultrafast non-resonant nonlinear response due to the combinations of central metals and ligands as well as the charge-transfer nature of the metal-ligand bonds [5]. Materials such as metal-alkene, metallophthalocyanine and metalloporphyrin etc. have been widely investigated recently because of their π-electron conjugated delocalization properties [6, 7]. Metal-dmit (dmit = 4, 5-dithiolato-1,3-dithiole-2-thione) complex showed its particular advantages as one of these materials.

The synthesis and characterization of dmit complexes and related selenium- and oxygen-substituted isologues have been reported in the literature [8, 9]. As a special π-electron delocalization conjugated system, dmit^{2-} and related ligand complexes have been used in the assembly of highly electrically conducting radical anion salts and charge-transfer complexes. They are generally used as important building blocks for organic, organometallic and co-ordination complex electrical conductors and superconductors [10, 11]. Recently, organometallic structures have become an interesting class of potentially highly nonlinear molecular blocks. These structures, which contain transition

metal ions, may exhibit new properties due to the richness of various excited states present in these systems in addition to the tailorability of metal-organic ligand interactions. Also the transfer of electron densities between metal atom and the ligands makes this kind of compounds exhibit a large molecular hyperpolarizability. So, much attention has been paid to the third-order NLO properties of some dmit organometallic compounds [12, 13].

The Z-scan technique is based on the self-focusing or defocusing of a converging beam of known spatial structure induced by moving a nonlinear sample along the light-propagation direction (Z-axis). The technique permits a rapid evaluation of the magnitude and sign of both the real (nonlinear refraction, NLR) and imaginary (nonlinear absorption, NLA) parts of the nonlinearity of transparent solids and liquids. As far as NLR is concerned, the transmission across the aperture in the far field is registered as a function of the sample position along Z-axis (closed aperture (CA) Z-scan), while NLA can be inferred either by CA Z-scan or, more accurately, by independently measuring the overall sample transmission versus its position along the Z-axis (open aperture (OA) Z-scan) [14]. In this paper, the NLO properties of BuCu-doped PMMA thin film were investigated using a picosecond laser by the Z-scan technique at the visible and near-infrared regimes, respectively. The origins were also analyzed for the differences between both conditions.

2 Experimental

The molecular structure of BuCu is illustrated in Fig. 1. The synthesis of the sample is a modification of a method from the literature [15, 16]. To degassed dimethyl formamide (DMF, 48 ml), CS_2 (24 ml) was added and the mixture was cooled to 273 K. Sodium (1.45 g) was added

to the solution and the mixture was vigorously stirred with cooling until the reaction was completed. Several ml methanol was slowly added. To this solution, separate solutions of (i) $CuCl_2 \cdot 2H_2O$ (2.66 g) dissolved in 25–28% NH_3 (40 ml), and (ii) Bu_4NBr (10.12 g) in water (30 ml) were added consecutively with stirring at room temperature. The mixture was stirred overnight, and then the product was isolated by filtration and washed with water and methanol, to afford dark-violet long bar crystals of BuCu. Its spectroscopic, X-ray powder diffraction and thermal analysis properties had been reported in the literature [17]. To prepare the BuCu-doped PMMA thin film, BuCu and PMMA were first separately dissolved in a quantity of 1,2-dichloroethane. Subsequently, the solutions of both materials were thoroughly mixed ultrasonically and filtrated by a micro-aperture filter. Then the mixed solution was spin-coated onto the cleaned quartz substrate at a rotating speed of 3000 r/min for 20 s and dried at room temperature for 72 h. The doping concentration of thin film by weight was 1%. The thickness of the film is about 1.23 μm and the film sample has good purity and uniform thickness.

The linear absorption spectra of BuCu-doped PMMA film as well as pure PMMA film were recorded using a UV–Vis–NIR scanning spectrophotometer (Hitachi U-4100, Japan) with the wavelength region of 200–1400 nm at room temperature, which was shown in Fig. 2. There are two peaks one at 220 nm and the other at 377 nm, which is due to the $\pi-\pi^*$ transition of the dmit ligand and the Cu ← S
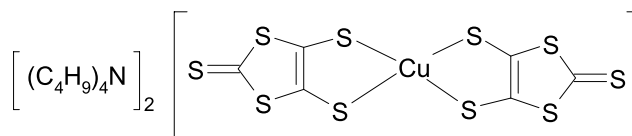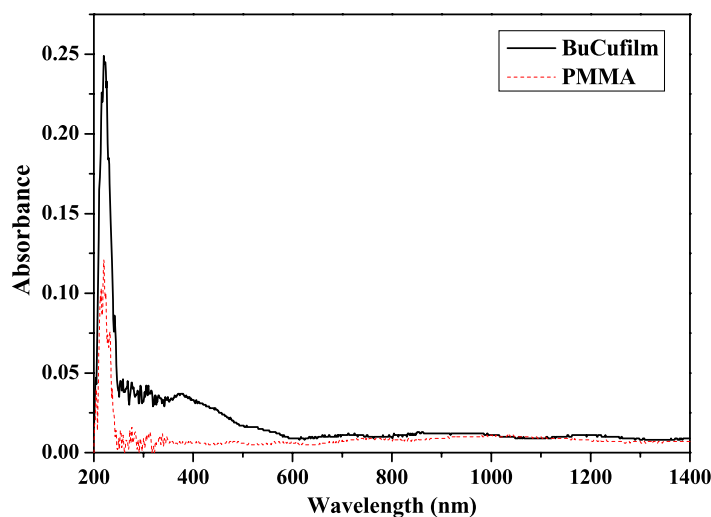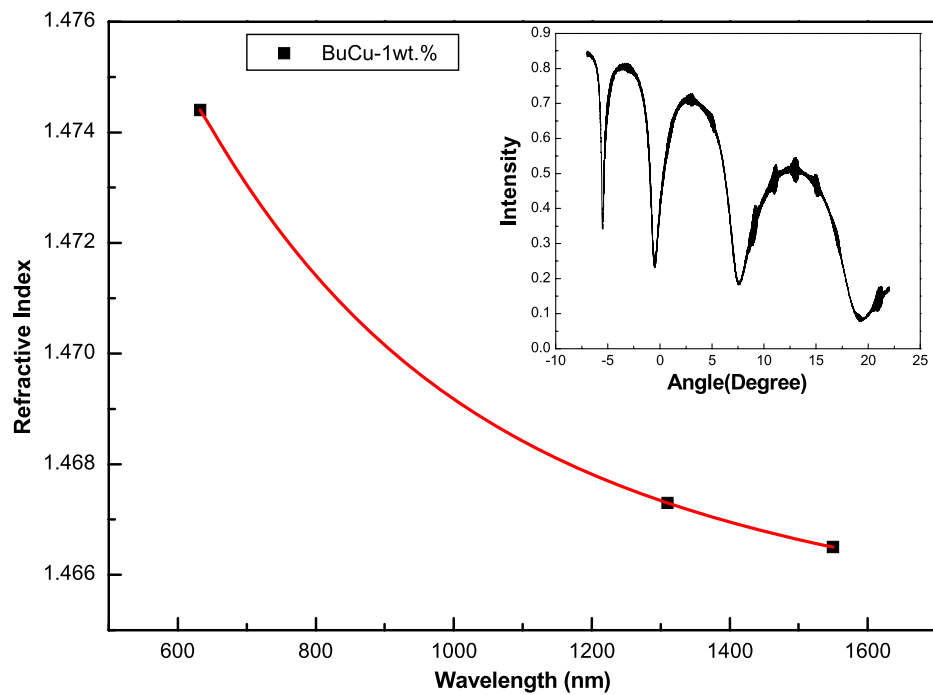

Fig. 1 Molecular structure of BuCu crystal

Fig. 2 UV–Vis–NIR absorption spectra of BuCu-doped PMMA film and pure PMMA film at room temperature

Fig. 3 The linear refractive-index curve of the BuCu-doped PMMA thin film and the relationship between waveguide mode profile and laser incident angle (*upper-right corner*)

charge-transfer transition, respectively. The Cu ← S charge-transfer band existing in the BuCu compound can form a highly delocalized electronic state and thus may induce larger third-order optical responses [18].

A prism coupling measuring system (SPA-4000, Korea) was used to investigate the refractive index and the thickness of the polymeric thin film [19]. The refractive index of the prism used in the measurement was 1.965, the index resolution was ±0.0005 and the index accuracy was less than 0.001. The polarization state of the laser light was transverse electric (TE) mode. The refractive-index curve of the BuCu-doped PMMA thin film is illustrated in Fig. 3. The wavelengths of three measurement laser beams were 632.8, 1310 and 1550 nm, respectively. The measured waveguide mode profile as a function of incident angle is shown in the upper-right corner of the figure. The thickness of the film was calculated to be 1.23 µm at the above three wavelengths. Variations of refractive index n with the wavelength λ were theoretically fitted by the Sellmeier dispersion formula: $n = A + B/\lambda^2 + C/\lambda^4$, where A, B and C are the Sellmeier coefficients. Using this theoretically fitted curve, we can obtain the refractive indices of 532 nm (1.477) and 1064 nm (1.469).

In the experiment, the third-order NLO properties of BuCu-doped PMMA thin film with doping concentration 1 wt.% were determined by Z-scan technique at 532 and 1064 nm, respectively. A mode-locked Nd:YAG laser (PY61C-10, Continuum) was used as the light source with a repetition rate of 10 Hz and pulse width of 20 ps (full width at half-maximum, FWHM). The sample was moved along the Z-axis through the focus of the lens, which has a focal

length of 150 mm. The radius of the beam waist (ω_0) was 21.4 µm at 532 nm and 27.7 µm at 1064 nm. $z_0 = \pi\omega_0/\lambda$ is the Rayleigh length. The values of z_0 of the beam were calculated to be 2.70 mm at 532 nm and 2.27 nm respectively, both much longer than the thickness of either the film or the 0.5 mm thick quartz substrate. The reference beam and the on-axis transmitted beam energy through a CA or an OA were measured by a dual-channel energy meter simultaneously. The distance between the detector and the focus of the lens was high enough to satisfy the far-field approximation. Before measuring this sample, the system was calibrated using CS₂ in a quartz cell as reference. The value was measured to be 3.31×10^{-18} m²/W, which is well accorded with the literature [14]. We performed the Z-scan measurement both on the BuCu-doped PMMA film and pure PMMA film, validating that the measured NLO phenomena originate from BuCu only.

3 Results and discussion

3.1 Z-scan at 532 nm

Z-scan measurements were performed at 532 nm as shown in Fig. 4, which exhibits the OA and division of the CA by OA (CA/OA) data Z-scan curves. The irradiance at focus of the laser beam (I_0) was adopted as 3.61 GW/cm². The peak-to-valley configuration of the CA/OA curve suggests that the refractive-index change is negative, exhibiting a self-defocusing effect. In addition, the OA curve demonstrates a negative nonlinear absorption, which was regarded
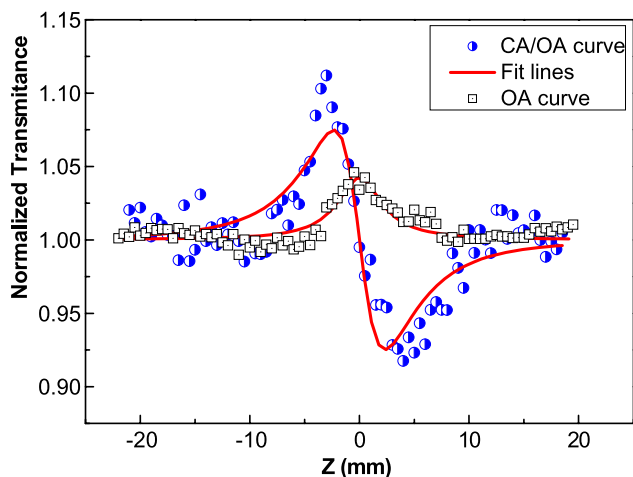
Fig. 4 Normalized Z-scan transmittance curves of BuCu-doped PMMA thin film at 532 nm wavelength

as the saturable absorption (SA) for the near-resonant band at 532 nm. In the vicinity of this wavelength the linear absorption coefficient is larger than that of off-resonant bands and strong pumping leads to SA rather than to reverse saturable absorption (RSA) [20]. This is a very attractive feature for applications such as laser locking-mode and optical bistability etc.

The nonlinear absorption coefficient β(m/W) can be obtained from a best fitting performed on the experimental data of the OA measurement with the equation [14]

$$T_{\text{OA}} = \sum_{m=0}^{\infty} \frac{[-\beta I_0 L_{\text{eff}}/(1 + z^2/z_0^2)]^m}{(m+1)^{3/2}} \quad (1)$$

where T_{OA} is the normalized transmittance for the OA, $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0$ is the effective thickness of the film (L denotes its thickness), and α_0 is the linear absorption coefficient of the sample.

To obtain the nonlinear refractive coefficient n_2, we fit the transmission curves by the well-established formula. In general, the normalized transmittance dependence can be presented as follows:

$$T_{\text{CA/OA}} = 1 + \frac{4\Delta\Phi_0 x}{(x^2+9)(x^2+1)} \quad (2)$$

where $T_{\text{CA/OA}}$ is the normalized transmittance for the CA/OA, $x = z/z_0$, $\Delta\Phi_0$ is the on-axis nonlinear phase shift at the focus.

Then the nonlinear refractive coefficient n_2 can be easily obtained through the equation $\Delta\Phi_0 = k n_2 I_0 L_{\text{eff}}$. Here $k = 2\pi/\lambda$ is the wave vector.

Accordingly, the real and imaginary parts of the third-order nonlinear susceptibility $\chi^{(3)}$ of the material can be calculated by the following equations [21]:

$$\chi^{(3)} = \chi_R^{(3)} + i\chi_I^{(3)} \quad (3)$$
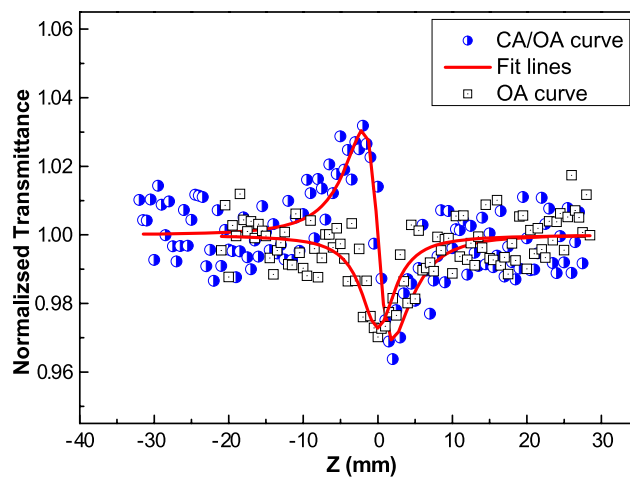
Fig. 5 Normalized Z-scan transmittance curves of BuCu-doped PMMA thin film at 1064 nm wavelength

$$\chi_R^{(3)} \text{ (esu)} = \frac{cn_0^2}{120\pi^2} n_2 \ (\text{m}^2/\text{W}) \quad (4)$$

$$\chi_I^{(3)} \text{ (esu)} = \frac{c^2 n_0^2}{240\pi^2\omega}\beta \ (\text{m/W}) \quad (5)$$

where n_0 is the linear refractive index of the sample, ω is the angular frequency of the light field and c is the velocity of light in vacuum.

Forwards, the second-order hyperpolarizability γ of the sample molecule may be estimated through the equation [13]

$$\gamma = \frac{\chi^{(3)}}{N_c L} \quad (6)$$

where N_c is the concentration of the solution and L is the local field correction factor which equals $[(n_0^2 + 2)/3]^4$.

3.2 Z-scan at 1064 nm

The measurements at 532 nm were considered to be a performance by near-resonant absorption, so the measurement wavelength was shifted to 1064 nm to obtain fully off-resonant values. The irradiance at focus of the laser beam (I_0) was set up as 3.14 GW/cm². The CA/OA and OA Z-scan curves of the sample are illustrated in Fig. 5. The peak-to-valley configuration of the CA curve also reveals a self-defocusing effect at 1064 nm. Additionally, the OA curve indicates a positive nonlinear absorption, which was regarded as two-photon absorption (TPA) but not reverse saturable absorption (RSA) which generally occurs in the valley region of the linear spectrum lying in between Q and S bands [22]. A five-level system model, which is shown in Fig. 6, is usually used to analyze the relationship of various NLA responses [23, 24]. Depending on the input pulse duration, TPA in the materials normally occurs through transitions

from $S_0 \rightarrow S_n$ by instantaneous TPA or from $S_0 \rightarrow S_1 \rightarrow S_n$ by a two-step resonant TPA, while for another, excited state absorption normally occurs through transitions from $S_0 \rightarrow S_{1v} \rightarrow S_1 \rightarrow S_n$ by SA (S_{1v} is the vibrational state of S_1) or from $T_1 \rightarrow T_n$ by RSA. For organometallic complexes the intersystem crossing time τ_{isc}, which is of the order of few nanoseconds, is of minor consequence because of the picosecond regime of pulse duration in our measurement. Therefore, we can neglect intersystem crossing and the five-level model is simplified as an effective three-level system with S_0, S_1 and S_n states. The NLA excited at 1064 nm in our measurement can be attributed to TPA induced by singlet-singlet state transition but not RSA. Using the same procedure and equations as at 532 nm, the nonlinear refraction coefficient n_2, the nonlinear absorption coefficient β and the second-order hyperpolarizability γ at 1064 nm wavelength can also be obtained.

The values of NLO properties and relevant parameters are listed in Table 1. It is indicated that the values of both
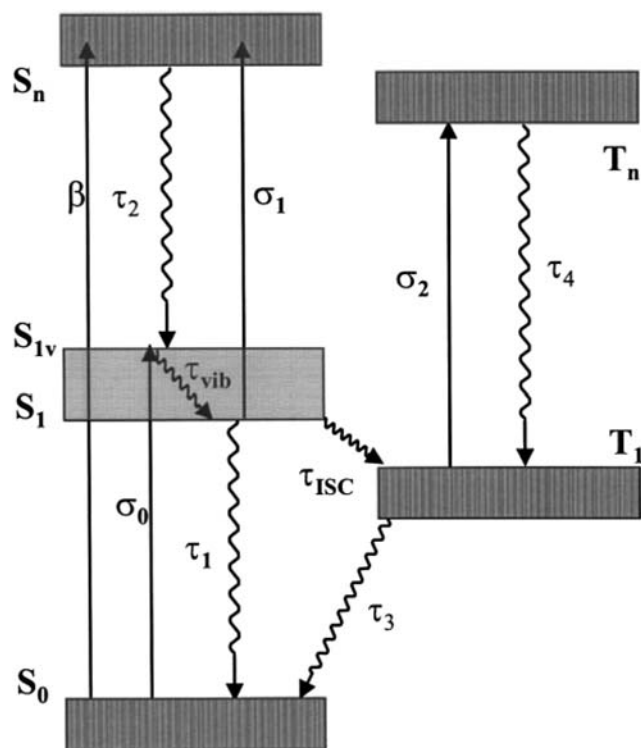
Fig. 6 The five-level system model diagram

$\chi_R^{(3)}$ and $\chi_I^{(3)}$ lie in the same magnitudes at both 532 and 1064 nm. Thus the imaginary part $\chi_I^{(3)}$, which stands for the nonlinear absorption, cannot be neglected comparing to the real part $\chi_R^{(3)}$, which stands for nonlinear refraction. So the material is not an eligible candidate for all-optical switching application. Additionally, the results revealed that the values at 532 nm were slightly larger than those at 1064 nm, which confirms that the NLO effect depends on wavelength. The wavelength of 532 nm is located in the near-resonant domain of the sample, a large SA occurs and this strongly enhances the molecular hyperpolarizability [25, 26]. However, the measured OA curve at 1064 nm demonstrates a positive nonlinear absorption, which is regarded as TPA but not RSA, which is attributed to not only the off-resonant domain but also TPA region of the sample at 1064 nm. All the results were compared with the homologous material in organic solvent and it was found that the values of the doped PMMA thin film were about two orders of magnitude larger than that of organic solutions [27]. The reason was deduced: that the doping concentration in PMMA film was much larger than that of solution. The concentration 1 wt.% of BuCu-doped PMMA was equal to about 1.26×10^{-2} mol/L, which was much larger than that mentioned in [27]. The better results of NLO properties in the PMMA thin film greatly enhanced the application possibility of the material, which can be considered to be used in laser locking-mode (SA), optical limiting fields (TPA), and so on. The thermal lens behavior can also be neglected because of the laser light source of the picosecond regime, the weaker incident irradiance and the insignificant influence of linear absorption at both 532 and 1064 nm.

All the above-mentioned results have revealed that BuCu possesses large third-order NLO properties originating with its structure characteristics. The extended electronically delocalized core comprising the central Cu^{2+} ion, four S atoms and the adjacent C=C units is the striking physical characteristic of BuCu. Cu^{2+} takes the place of group 12 metal ions (Zn^{2+}, Cd^{2+} and Hg^{2+}); the electron delocalization is enhanced due to the unfilled d electron shell of Cu^{2+}, which allows for the possibility of low-energy charge-transfer transitions. In addition, the 3p orbital of S and 3d orbital of Cu^{2+} can overlap to form a highly delocalized system. The delocalization will strongly enhance the hyperpolarizability and the nonlinear susceptibility and will lead to large third-order NLO properties.

Table 1 Nonlinear optical properties at 532 and 1064 nm of the sample

Sample	λ (nm)	n_0	I_0 (GW/cm²)	$n_2 \times 10^{-16}$ (m²/W)	$\beta \times 10^{-9}$ (m/W)	$\chi_R^{(3)} \times 10^{-11}$ (esu)	$\chi_I^{(3)} \times 10^{-11}$ (esu)	$\chi^{(3)} \times 10^{-11}$ (esu)	$\gamma \times 10^{-28}$ (esu)
BuCu/PMMA	532	1.477	3.61	−4.15	−3.00	−22.95	−7.19	23.98	7.906
(1 wt.%)	1064	1.469	3.14	−1.71	1.07	−9.35	4.95	10.58	3.456

4 Conclusions

In summary, an organometallic complex BuCu was prepared and doped in the PMMA thin film with a doping concentration of 1% by weight. Its third-order nonlinear optical properties were investigated utilizing a short pulse Z-scan technique at 532 and 1064 nm wavelength with 20 ps pulse width and 10 Hz repetition rate. The negative nonlinear refraction was found both at 532 and 1064 nm, and therefore the material represents a self-defocusing effect. Additionally, it was found that the material shows a noticeable saturable absorption at 532 nm as well as two-photon absorption at 1064 nm, which were located in the near-resonant and off-resonant area of the linear absorption spectrum of the sample, respectively. The origins of the NLO properties were interpreted by the molecular structure of the material. Both nonlinear refraction and nonlinear absorption of the film were stronger than the homologous material of organic solution for about two orders of magnitude. The remarkable values of our measurements make the material feasible for practical requirements. The measurements on linear refractive index and thickness validate the uniformity and purity of the polymeric film, so it may be easily fabricated into devices and the application possibility of the material was greatly enhanced. Overall, we can conclude that the material may be a promising candidate for the optical device applications because of its stronger nonlinear absorption, high transmittance and the characteristic of ease in doping into a polymeric film.

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