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Synthesis, nonlinear optical properties and the possible mechanism of photopolymerization of two new two-photon absorption chromophores

Yunxing Yan,[a,*] Xutang Tao,[a] Yuanhong Sun,[b] Guibao Xu,[a] Chuankui Wang,[b] Jiaxiang Yang,[a] Xian Zhao,[a] and Minhua Jiang[a]

[a] *Institute of Crystal Materials, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China*
[b] *Department of Physics, Shandong Normal University, Jinan 250014, PR China*

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Abstract

Efficient Witting and Pd-catalyzed Heck coupling methodologies are employed to synthesize two new two-photon free-radical photopolymerization initiators 9-ethyl-3-{2-[4-(2-pyridin-4-yl-vinyl)-phenyl]-vinyl}-9H-carbazole (abbreviated to EPVPC) and 9-octadecyl-3-{2-[4-(2-pyridin-4-yl-vinyl)-phenyl]-vinyl}-9H-carbazole (abbreviated to OPVPC). The experimental results confirm that the two compounds are good two-photon absorbing chromophores and operative two-photon photopolymerization initiators. The calculated two-photon absorption cross-sections of EPVPC and OPVPC are 56.6 and $62.0 \times 10^{-50}\,\mathrm{cm}^4\,\mathrm{s\,photon}^{-1}$, respectively. A microstructure by using EPVPC as initiator has been fabricated under irradiation of 200 fs, 76 MHz Ti:sapphire femtosecond laser at 780 nm. The possible mechanism of photopolymerization is discussed.

Keywords: Synthesis; Two-photon absorption; Nonlinear optical properties; Microstructure; Photonpolymerization; Initiator; EPVPC; OPVPC

1. Introduction

Two-photon absorption (TPA) laser microfabrication has paved a way to direct laser writing of three-dimensional (3D) microstructures [1–4] to satisfy the requirements of modern applications such as photonic devices, micromachines, zero-threshold lasers and integrated optical waveguides [5–8]. These applications take advantage of the fact that the TPA depends quadratically on intensity of incident laser, so under tight-focusing conditions, the absorption at the focus is confined to a volume of order λ^3 (where λ is the laser wavelength). Although 3D microfabrication has been illustrated by using two-photon-initiated polymerization of resins incorporating conventional ultraviolet-absorbing initiators, the TPA cross-sections δ of these initiators are typically very small ($\delta \leqslant 10 \times 10^{-50}\,\mathrm{cm}^4\,\mathrm{s}$ per photon), and as a result they exhibit low two-photon sensitivity. Resins containing these initiators can be patterned only by means of long exposure times and high excitation intensities that frequently result in damage to the structure. Although some approaches to improve the photosensitivity of photointiator molecules have been reported such as improving the two-photon cross-section δ and the photochemical quantum yield Φ of the molecule [9–12], effective two-photon photopolymerization initiators are still rare because the photopolymerization mechanism and relationships of structure/property for the initiator remain unclear. Therefore, the search for effective and high photosensitive two-photon photopolymerization initiators is urgently required. Here we report two new initiators of EPVPC and OPVPC by use of efficient Witting and Pd-catalyzed Heck coupling methodologies. The experimental results confirm that the two compounds are all good two-photon absorbing chromophores and operative two-photon photopolymerization initiators. The

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*Corresponding author. Fax: +86-531-8565403.
E-mail address: yxyan@icm.sdu.edu.cn (Y. Yan).

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TPA cross-sections of the two compounds are calculated by the program Dalton [13]. A microstructure has been fabricated by using EPVPC as initiator excited with 780 nm, 200 fs, 76 MHz Ti:sapphire laser source. The possible mechanism of photopolymerization is discussed.

2. Experimental section

2.1. Chemicals

Photoluminescence and absorption measurements are conducted in various solvents including DMF, dichloromethane, benzyl alcohol, THF and chloroform. All of the above solvents are anhydrous grade after further purification. Moreover, each of the solutions used for the single-photon fluorescence measurements is freshly prepared and kept in the dark before the measurements. The solution concentration is $1 \times 10^{-5}\,\text{mol}\,\text{L}^{-1}$.

2.2. Instruments

The 600 MHz ^{1}H NMR and ^{13}C NMR spectra are obtained on a Bruker av600 spectrometer. Elemental analysis is performed using PE 2400 elemental analyzer. UV-Vis-near-IR spectra are measured on a Hitachi U-3500 recording spectrophotometer. Melting point is measured on DSC822^{e} Mettler-Toledo instruments. The steady-state fluorescence spectra measurement is performed using an Edinburgh FLs920 spectrofluorimeter. A 450 W Xe arc lamp provides the ~400 nm excitation source. Spectra are record between 420 and 700 nm using a photomultiplier tube as detector, which is operated in the single-photon counting mode. The spectral resolution is 0.1 nm. The quartz cuvettes used are of 1 cm path length.

2.3. Computation

The hybrid density functional theory (B3LYP) coded in GAUSSIAN package [14] is applied to optimize the geometry of the molecules. The basis set is taken as 6-31G. The excited energies of the two molecules are computed at the time-dependent density functional theory level. The program Dalton is used to study the TPA cross-sections.

2.4. Synthesis and characterizations

The synthetic sequence for the preparation of the two compounds is shown in Scheme 1.

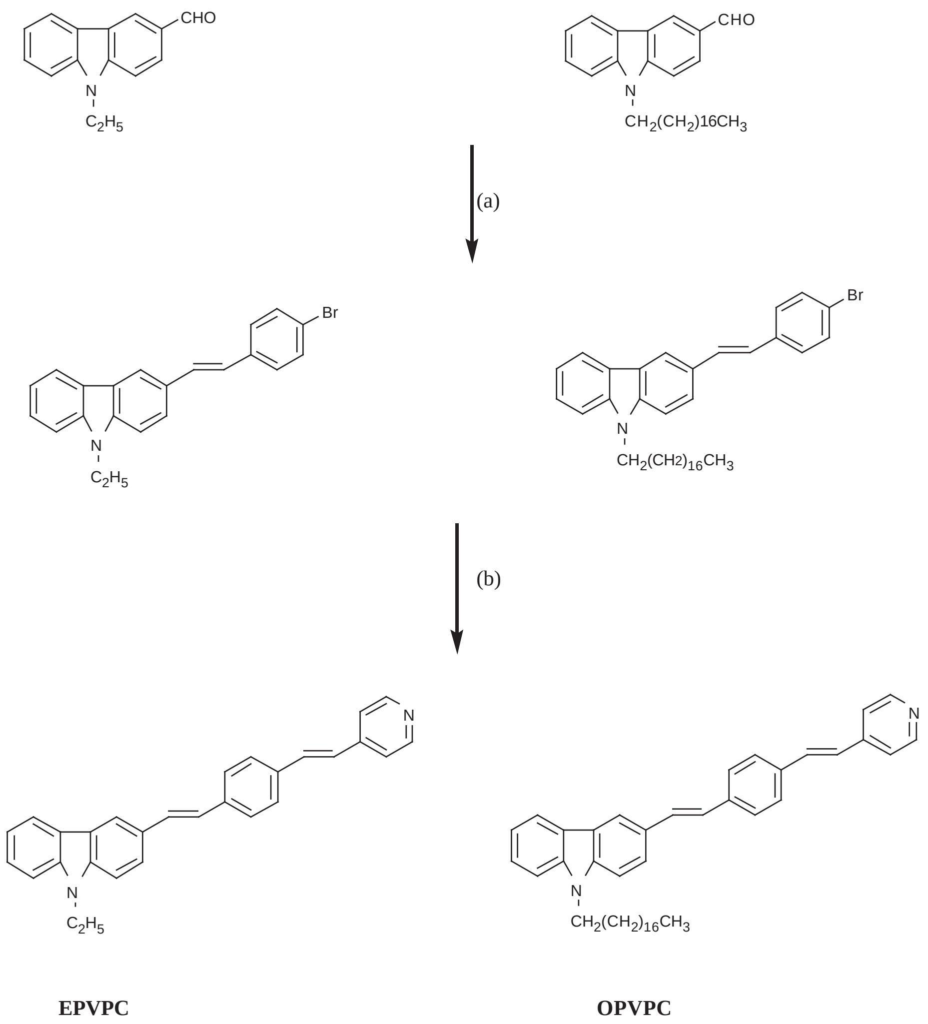
4-Bromobenzyl(triphenyl)phosphonium bromide, 9-ethyl-9H-carbazole-3-carbaldehyde and 9-octadecyl-9H-carbazole-3-carbaldehyde are synthesized according to the reported methods [15,16].

2.4.1. 9-Ethyl-3-{2-[4-(2-pyridin-4-yl-vinyl)-phenyl]-vinyl}-9H-carbazole (abbreviated to EPVPC)

At room temperature, 2.23 g (0.01 mol) 9-ethyl-9H-carbazole-3-carbaldehyde, 7.68 g (0.015 mol) 4-bromobenzyl(triphenyl)phosphonium bromide, 8.00 g (0.2 mol) NaOH and 2 mL THF are added into a mortar. Then the mixture is grounded and poured into 200 mL distilled water, neutralized with dilute hydrochloric acid, and extracted with dichloromethane. The organic layer obtained is dried over anhydrous magnesium sulfate. After filtration, the solvent is removed from the solution at reduced pressure and the residue is dissolved in dichloromethane. Then the solution is chromatographed on silica gel using petroleum ether as eluent. The obtained green compound is added to a mixture of 0.98 g (3.22 mmol) tri-*o*-tolylphosphine, 1.74 mL (16.12 mmol) vinylpyridine, 0.09 g palladium (II) acetate (0.4 mmol) and 100 mL redistilled triethylamine. The reaction mixture is refluxed in an oil bath under nitrogen. An orange product is obtained after heating and stirring for 24 h. Then the solvent is removed under reduced pressure and the residue is dissolved in methylene chloride, washed three times with distilled water, and dried with anhydrous magnesium sulfate. The yellow product is chromatographed on silica gel using ethyl acetate/petroleum ether (1:2) as eluent and crystallized using ethyl acetate with a yield of 52% and mp 262.5°C. Anal. calcd for $C_{29}H_{24}N_2$: C 87.00%; H 6.00%; and N 7.00%. Found: C 87.98%; H 6.19%; and N 7.23%. ^{1}H NMR, δ ($CDCl_3$, 600 MHz): 8.59 (d, $J = 4.0$ Hz, 2H); 8.27 (s, 1H); 8.15 (d, $J = 7.7$ Hz, 1H); 7.71 (d, $J = 8.4$ Hz, 1H); 7.59 (q, $J = 9.9$ Hz, 4H); 7.50 (t, $J = 7.2$ Hz, 1H); 7.42 (q, $J = 4.6$ Hz, 4H); 7.37 (d, $J = 12.4$ Hz, 2H); 7.33 (s, 1H); 7.17 (d, $J = 16.2$ Hz, 1H); 7.05 (d, $J = 16.2$ Hz, 1H), 4.40 (q, $J = 7.2$ Hz, 2H); 1.48 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR, δ (600 MHz, $CDCl_3$): 149.68, 145.30, 140.43, 139.93, 138.79, 134.69, 133.36, 130.54, 128.35, 127.52, 126.64, 125.94, 125.27, 125.16, 124.56, 123.41, 122.98, 120.91, 120.52, 119.15, 118.94, 108.73, 108.71, 37.71, 13.87.

2.4.2. 9-Octadecyl-3-{2-[4-(2-pyridin-4-yl-vinyl)-phenyl]-vinyl}-9H-carbazole (abbreviated to OPVPC)

It is obtained by similar synthetic method. The yellow-green compound is chromatographed on silica gel using ethyl acetate/petroleum ether (1:2) as eluent and crystallized using ethyl acetate with a yield of 46% and mp 181.7°C. Anal. calcd for $C_{45}H_{56}N_2$: C 86.54%; H 8.97%; and N 4.49%. Found: C 87.17%; H 9.11%; and N 4.56%. ^{1}H NMR, δ ($CDCl_3$, 600 MHz): 8.60 (d, $J = 4.9$ Hz, 2H); 8.26 (s, 1H); 8.14 (d, $J = 7.7$ Hz, 1H); 7.70 (d, $J = 8.4$ Hz, 1H); 7.58 (q, $J = 8.2$ Hz, 4H); 7.49 (t, $J = 7.7$ Hz, 1H); 7.40 (m, 6H); 7.33 (d, $J = 16.2$ Hz, 1H); 7.17 (d, $J = 16.2$ Hz, 1H); 7.04 (d, $J = 16.2$ Hz, 1H); 4.31 (t, $J = 7.2$ Hz, 2H); 1.89 (q, $J = 7.2$ Hz, 2H); 1.31 (m, 32H); 0.89 (t, $J = 6.7$ Hz, 3H). ^{13}C NMR, δ



Scheme 1. Synthesis of two compounds: (a) THF/4-bromobenzyl(triphenyl)phosphonium bromide, grind, room temperature. (b) Vinylpyridine/tri-*o*-tolylphosphine/palladium (II) acetate/triethylamine, reflux.

($CDCl_3$, 600 MHz): 149.87, 145.07, 140.90, 140.41, 138.74, 134.71, 133.17, 130.50, 128.28, 127.46, 126.61, 125.87, 125.24, 125.21, 124.48, 123.27, 122.85, 120.83, 120.40, 119.21, 118.83, 108.94, 108.91, 43.23, 31.91, 30.87, 29.68, 29.64, 29.62, 29.58, 29.54, 29.47, 29.37, 29.34, 29.30, 29.22, 29.12, 28.97, 27.28, 22.67, 14.08.

3. Results and discussion

3.1. Linear absorption and fluorescence spectra

The photophysical properties of the two compounds are summarized in Table 1. The linear absorption spectra of two compounds are measured in solvents of different polarity at a concentration of $c = 1 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$, in which the solvent influence is not included. The one-photon fluorescence spectra are measured with the same concentration as that of the linear absorption spectra. The maximum excited wavelengths of EPVPC and OPVPC are 387 and 392 nm, respectively. Figs. 1 and 2 are linear absorption and one-photon fluorescence spectra of the two compounds in chloroform. From Table 1, one can see that the maximum absorption peaks show slightly a blue-shift, the maximum fluorescence peaks clearly show a red-shift and the fluorescent lifetime are lengthened except for benzyl alcohol with the increase of the polarity of the solvent for each compound. This can be explained by the fact that the excited state of two compounds may possess higher polarity than that of the ground state, for solvatochromism is associated with the energy level lowering. Increased dipole–dipole interaction between the solute and solvent leads to lowering the energy level greatly [17,18]. For the case of the benzyl alcohol, we can easily realize the possibility of forming the hydrogen bonding between the solvent and solute molecules that will push the excitation energy lower [20]. It should be noted that both the largest one-photon oscillator strength and the maximum TPA cross-section are taken

Table 1
Data of absorption, one- and two-photon fluorescence spectra with solvent effects

Compds	Solvent	ε	$\lambda_{max}^{(1a)}$ (nm)	ε_{res} (10^4)	$\lambda_{max}^{(1f)}$ (nm)	τ (ns)	Φ	$\lambda_{max}^{(2)}$ (nm)
EPVPC	DMF	37.6	382	3.05	532	2.07	0.78	536
	CH_2Cl_2	9.1	384	3.18	510	1.78	0.71	514
	Benzyl alcohol	13.1	396	3.22	538	1.55	0.93	542
	THF	7.58	383	3.23	500	1.62	0.68	506
	$CHCl_3$	4.806	387	3.29	490	1.57	0.71	496
OPVPC	DMF	37.6	383	4.12	532	1.88	0.78	Insolvable
	CH_2Cl_2	9.1	385	4.23	510	1.53	0.71	514
	Benzyl alcohol	13.1	397	4.37	538	1.39	0.94	Insolvable
	THF	7.58	384	4.35	500	1.47	0.67	503
	$CHCl_3$	4.806	388	4.50	490	1.41	0.73	495

$\lambda_{max}^{(1a)}$, $\lambda_{max}^{(1f)}$ and $\lambda_{max}^{(2)}$ are one-photon absorption, one-photon fluorescence and two-photon fluorescence maxima peak, respectively. Φ is one-photo quantum yield determined using coumarin 307 as the standard [19]. τ is one-photon fluorescence lifetime. ε is the relative permittivity that was measured at 20°C [23]. ε_{res} is the corresponding molar absorption coefficient.

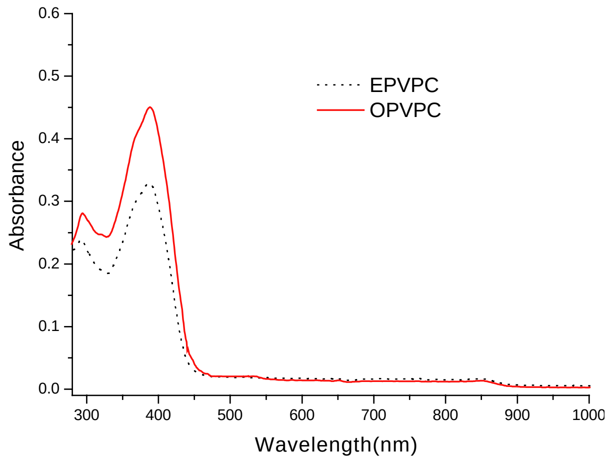


Fig. 1. Linear absorption spectra of two compounds in chloroform with concentration of 1×10^{-5} mol L^{-1}.

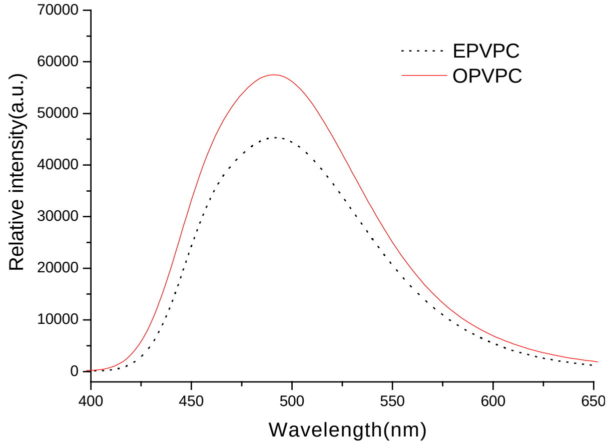


Fig. 2. One-photon fluorescence spectra of two compounds in chloroform with a concentration of 1×10^{-5} mol L^{-1}.

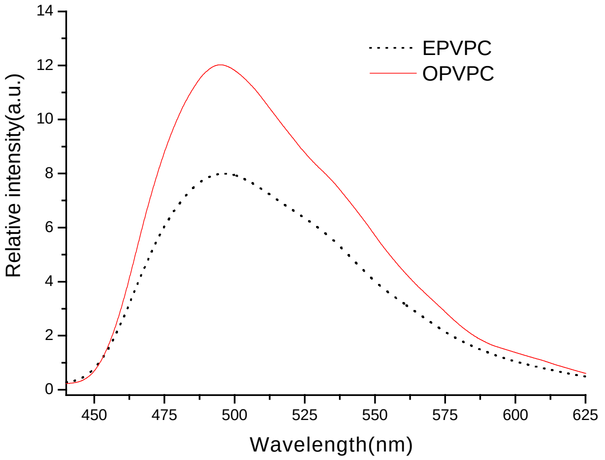


Fig. 3. Two-photon fluorescence spectra of two compounds in chloroform with a concentration of 0.01 mol L^{-1}.

place on the same excited state, the charge-transfer (CT) state, in the lower energy region because of the asymmetrical characteristics of the present molecules. Therefore, when we study the two-photon fluorescence spectra as described in the following section, the excited wavelength at 780 nm is applied [21].

3.2. Two-photon fluorescence spectra

Fig. 3 is the two-photon fluorescence of the two compounds in chloroform with the concentration of $c = 0.01$ mol L^{-1}. The two-photon-induced fluorescence spectra can be observed with a mode-locked Ti:sapphire laser (Coherent Mira 900F) as the pump source with a pulse duration of 200 fs, a repetition rate of 76 MHz and a single-scan streak camera (Hamamatsu Model C5680-01) together with a monochromator as the recorder. The excitation wavelengths of EPVPC and OPVPC are all at 780 nm. From Fig. 3 and Table 1, one can see that the maximum peaks of the two-photon fluorescence show a slight red-shift compared to that of one-photon fluorescence in the same solvent for each compound. This can be explained by the effect of reabsorption because the linear absorption band has a slight overlap with the

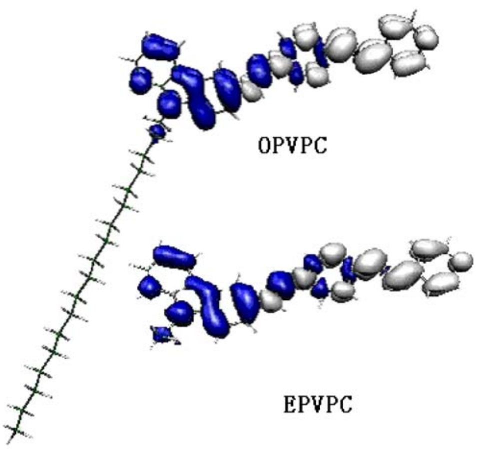


Fig. 4. Density difference between the CT and ground states of two compounds in gas phase. Areas with chickenwire and dots represent the electron lose and gain, respectively, upon excitation.

emission band and our two-photon fluorescence experiments are carried out on concentrated solutions that made reabsorption significant. Although, from Figs. 1–3, one can see that the intensity of the absorption and fluorescence of OPVPC is stronger than that of EPVPC due to the difference of donor with linkage to N atom, the maximum peak position has little change. Fig. 4 is the charge density difference between the ground and the CT states for EPVPC and OPVPC in gas phase, which is visualized by the use of MOLEKEL program [22]. From Fig. 4, one can see that the C atoms that are far from N atom have scarcely taken part in the CT process. This is the reason that the substitutes on N atom have a little influence on the maximum peak position of the absorption and fluorescence for the two compounds.

In addition to the similarities between one-photon fluorescence and two-photon fluorescence, the two-photon fluorescence peak positions are also independent of the laser wavelength used. Thus although the electrons can be pumped to the different excited states by linear absorption or TPA due to the different selection rules, they would finally relax to the same lowest excited state via internal conversion and/or vibrational relaxation.

3.3. TPA cross-section

In terms of sum-over-state formula, the two-photon matrix element for the two-photon resonant absorption of identical energy is written as

$$S_{\alpha\beta} = \sum_j \left[\frac{\langle 0|\mu_\alpha|j\rangle\langle j|\mu_\beta|f\rangle}{\omega_j - \omega_f/2} + \frac{\langle 0|\mu_\beta|j\rangle\langle j|\mu_\alpha|f\rangle}{\omega_j - \omega_f/2} \right], \qquad (1)$$

where $|0\rangle$ and $|f\rangle$ denote the ground state and the final state, respectively. $|j\rangle$ means all the intermediate states, including the ground state. ω_j is the excitation energy of the excited state $|j\rangle$.The TPA cross-section is given by orientational averaging over the TPA probability

$$\delta_{\mathrm{tpa}} = \sum_{\alpha\beta} [F \times S_{\alpha\alpha} S^*_{\beta\beta} + G \times S_{\alpha\beta} S^*_{\alpha\beta} + H \times S_{\alpha\beta} S^*_{\beta\alpha}], \qquad (2)$$

where the coefficients F, G and H are related to the incident radiation. For the linearly polarized light, F, G and H are 2, 2 and 2, but for the circular case, they are -2, 3, and 3, respectively. In the present work, we only consider the results with the linearly polarized laser beam. The summation goes over the molecular axes α, $\beta = \{x, y, z\}$.

The TPA cross-section directly comparable with experimental measurements is defined as

$$\sigma_{\mathrm{tpa}} = \frac{4\pi^2 a_0^5 \alpha}{15 c_0} \frac{\omega^2 g(\omega)}{\Gamma_{\mathrm{f}}} \delta_{\mathrm{tpa}}, \qquad (3)$$

where a_0 is the Bohr radius, c_0 is the speed of light, α is the fine structure constant, $\hbar\omega$ is the photon energy of the incident light, $g(\grave{u})$ denotes the spectral line profile, which is assumed to be a δ function. $\tilde{A}_{\mathrm{f}}$ is the lifetime broadening of the final state, which is assumed to be 0.1 eV [10].

We utilize the GAUSSIAN-98 program package to optimize the molecular geometrical structure with the hybrid density functional theory (DFT/B3LYP) and a basis set 6-31G. The excited energies for two molecules are then calculated by the time-dependent density functional theory. The first excited energies for molecules EPVPC and OPVPC are 426 and 428 nm, respectively.

The program, Dalton, is used to study the TPA cross-sections of the two molecules. For the first excited state, the TPA cross-sections σ ($10^{-50}\,\mathrm{cm}^4\,\mathrm{s\,photon}^{-1}$) for molecules EPVPC and OPVPC lighted by the linearly polarized laser are, respectively, 56.6 and 62.0, which indicate that the two molecules have a relatively large TPA cross-section under the experimental circumstance. Therefore, these two molecules can be used as two-photon polymerization initiators.

3.4. Two-photon photopolymerization

A three-dimensional lattice is created by two-photon polymerization of an acrylic eater oligomer where EPVPC is used as an initiator. A film of the mixture of initiator and oligomer with a weight ratio of ~4% to ~5% (a little dichloroethane is added to make a solution of initiator and oligomer) is prepared by spin-coating onto glass plates. The same mode-locked Ti:sapphire, laser as that used in the two-photon fluorescence measurements, is used for two-photon microfabrication. The 780 nm lasing source is tightly focused via an objective lens (×40, NA = 0.65), and the focal point is focused on the sample film on the xy-step monitorized stage controlled by computer. The pulse energy before being focused by the objective lens is ~1.2 W. The polymerized solid skeleton is obtained after the unreacted liquid mixture had been washed out. The lattice fabricated is observed through a microscope (Olympus BX-51). Its photograph is illustrated in Fig. 5.

The photopolymerization mechanisms of these new initiators are still unknown. According to Cumpston et al. [4], strong donor substituents would make the conjugated system electron rich, and after one- or two-photon photoexcitation, these chromophores would be able to transfer an electron even to relatively weak acceptors, and this process could be used to activate the polymerization reaction. In order to demonstrate this process, we try to make a theoretical investigation. Our ab initio calculation at time-dependent hybrid density functional theory B3LYP level coded in GAUSSIAN package for the EPVPC molecule shows that the first excited state is the CT state with the excited energy $\lambda = 426\,\text{nm}$ ($\Delta E = 2.9089\,\text{eV}$, $f = 1.4878$). When the molecule is irradiated by 780 nm laser, it can be expected that the molecule will simultaneously absorb two photons and is excited to the first excited state (the CT state). From Fig. 4, one can see that upon excitation, charges are mainly transferred from the acceptor side to the donor side of the molecule. It can be seen that upon excitation, charges are mainly transferred from the acceptor side to the donor side of the molecule. In the CT state, there are more electrons at the donor side, indicating that the molecule could give away its electron to its surrounding. This picture seems to support Cumpston's discussion. However, whether the photo-induced electron-transfer reaction can be energetically feasible needs to be further investigated theoretically. The systematic study of the microstructure created by two-photon free-radical photopolymerization using EPVPC as the initiator will be reported in detail elsewhere.

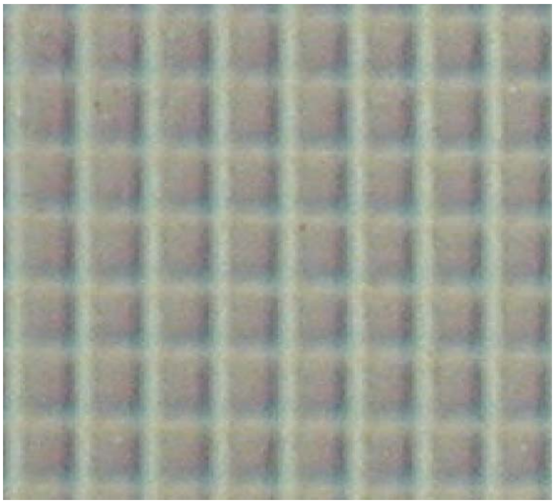


Fig. 5. Optical micrograph of the lattice fabricated via two-photon polymerization of an acrylic eater oligomer by using EPVPC as initiator.

4. Conclusion

Two new two-photon photopolymerization initiators of EPVPC and OPVPC have been synthesized and characterized by ^{1}H NMR spectra, ^{13}C NMR spectra, and elemental analyses. Linear absorption, single-photon-induced and two-photon-induced fluorescence in different solvents have been studied. The experimental results confirm that the two compounds are good two-photon-absorbing chromophores and operative two-photon photopolymerization initiators. The calculated TPA cross-sections of EPVPC and OPVPC are 56.6 and $62.0 \times 10^{-50}\,\text{cm}^4\,\text{s}\,\text{photon}^{-1}$, respectively. EPVPC and OPVPC can initiate two-photon photopolymerization excited with 780 nm laser beam. A microstructure has been fabricated by using EPVPC as two-photon photopolymerization initiator and the possible mechanism of photopolymerization is discussed.

Acknowledgments

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