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# Synthesis and nonlinear optical properties of novel multibranched two-photon polymerization initiators

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Efficient Witting and Pd-catalyzed Heck coupling methodology are employed to synthesize three multibranched two-photon photopolymerization initiators diphenyl-(4-{2-[4-(2-pyridin-4-yl-vinyl)-phenyl]-vinyl}phenyl)-amine (abbreviated to DPVPA), phenyl-bis-(4-{2-[4-(2-pyridin-4-yl-vinyl)-phenyl]-vinyl}-phenyl)-amine (abbreviated to BPVPA) and tris-(4-{2-[4-(2-pyridin-4-yl-vinyl]-vinyl]-vinyl}-phenyl]-vinyl}-amine (abbreviated to TPVPA). The experimental results confirm that all these compounds are good two-photon absorbing chromophores and operative two-photon photopolymerization initiators. The calculated two-photon absorption cross sections of DPVPA, BPVPA and TPVPA for the lowest excited state are 59.3, 30.2 and  $42.4 \times 10^{-50}$  cm<sup>4</sup> s photon<sup>-1</sup>, respectively. A microstructure using BPVPA as initiator has been fabricated under irradiation of 200 fs, from a 76 MHz Ti:sapphire femtosecond laser at 820 nm. The possible photopolymerization mechanism is discussed.

# 1. Introduction

Extensive attention has been paid to the photochemical and photophysical processes induced by two-photon absorption due to their potential use in applications such as optical power limiting,<sup>1–3</sup> two-photon upconversion lasing,<sup>4,5</sup> two-photon fluorescence excitation microscopy,<sup>6–10</sup> and three-dimensional optical data storage and microfabrication.11-16 These applications take advantage of the fact that the two-photon absorption (TPA) probability depends quadratically on intensity, so under tight-focusing conditions, the absorption is confined at the focus to a volume of the order of  $\lambda^3$  (where  $\lambda$  is the laser wavelength). This characteristic of two-photon processes has made TPA-based photopolymerization an effective tool for processing photonic devices, micromachines, zero-threshold lasers and integrated optical waveguides in three dimensions with high spatial resolution.<sup>17-20</sup>

For two-photon free radical photopolymerization, the polymerization rate and photo-initiation threshold is closely related to the absorption behavior of the initiator at the excitation wavelength that is generally twice the corresponding onephoton absorption wavelength. Up until now, effective initiators are still few because the design strategy, or in other words, the relationship of the initiator structures and their properties for initiating two-photon photopolymerization, needs to be investigated in depth.

Some approaches to improve the photosensitivity of photoinitiators are based on the idea of increasing their TPA cross sections.<sup>21</sup> According to Albota *et al.*<sup>22</sup> and Reinhardt *et al.*,<sup>23</sup> the conjugation length, donor and acceptor strength, and planarity of the  $\pi$  center are important parameters for enhancing the TPA cross sections. Based on this design strategy, some one-dimensional two-photon polymerization initiators with charge-transfer conjugated character are synthesized.<sup>24</sup> Recently, ab initio calculations have been carried out for increasing dimensionality of the charge-transfer networks and shown that the TPA cross sections of multi-branched molecules can strongly be enhanced compared with those of their one-branched counterparts.<sup>25,26</sup> Experimental measurements have

also confirmed this conclusion.<sup>27</sup> In this article, we report the synthesis and characterization of three new initiators DPVPA, BPVPA and TPVPA with respective one-, two-, and threebranched structures by use of an efficient Witting and Pdcatalyzed Heck coupling methodology. All these dyes show strong two-photon fluorescence. A microstructure has been fabricated by use of BPVPA as initiator excited with a 820 nm, 200 fs, 76 MHz Ti:sapphire laser source and the possible interpretation is discussed in terms of the charge-transfer process when the laser irradiation is applied.

# 2. Experimental

#### 2.1 Chemicals

4-Vinylpyridine (95%), palladium(II) acetate (47.5% Pd) and triphenylamine are from Acros Organics, and tri-o-tolylphosphine is purchased from Tokyo Kasei Kogyo Co., Ltd. The above chemicals are used without further purification.

Dichloromethane, THF, chloroform, ethyl acetate and petroleum benzene are anhydrous grade after further purification. Moreover, each of the solutions used for the one-photon fluorescence measurements is freshly prepared and kept in the dark before measurement. The solution concentration is  $1 \times 10^{-5} \text{ mol } \text{L}^{-1}$ .

#### 2.2 Instruments

The 600 MHz H<sup>1</sup> NMR spectra and <sup>13</sup>C NMR are obtained on a Bruker av600 spectrometer. Elemental analysis is performed using a PE 2400 elemental analyzer. UV-Vis-near-IR spectra are measured on a Hitachi U-3500 recording spectrophotometer. Melting point is measured on DSC822<sup>e</sup> Mettler-Toledo instruments. The steady-state fluorescence spectra measurement is performed with use of an Edinburgh FLs920 spectrofluorimeter. A 450 W Xe arc lamp provides the  $\sim$ 400 nm excitation source. Spectra are recorded between 420 and 700 nm using a photomultiplier tube as detector, which is operated in

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the single photon counting mode. The spectral resolution is 0.1 nm. The quartz cuvettes are of 1 cm path length.

## 2.3 Synthesis

The synthetic sequence for the preparation of three compounds is shown in scheme 1.

4-Formyltriphenylamine, 4,4'-diformyltriphenylamine, tris-(4-formylphenyl)amine and 4-bromobenzyl(triphenyl)phosphonium bromide are synthesized according to reported methods.<sup>24,28</sup> {4-[2-(4-Bromo-phenyl)-vinyl]-phenyl}-diphenyl-amine(abbreviated to BVDA). At room temperature, 2.73 g (0.01 mol) 4-(N,N-diphenylamino)benzaldehyde, 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 ground. It became orange after 5 min. The mixture is 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



**Scheme 1** Synthesis of three compounds: (a) First step: DMF, 0 °C, second step:  $POCl_3$ , 95–100 °C. (b) THF/4-bromobenzyl(triphenyl)-phosphonium bromide, room temperature. (c) Vinylpyridine/tri-*o*-tolylphosphine/palladium( $\pi$ ) acetate/triethylamine, reflux.

solution at reduced pressure and the residue dissolved in dichloromethane. The solution obtained is chromatographed on silica gel using petroleum ether as eluent. The green compound is crystallized in ethyl acetate with a yield of 75% and m.p. 179.6 °C. The enthalpy is  $-89.8 \text{ mJ mg}^{-1}$ . Anal. Calcd for C<sub>26</sub>H<sub>20</sub>NBr: C, 73.24; H, 4.69; N, 3.29. Found: C, 73.31; H, 4.75; N, 3.34. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) [ppm]  $\delta$ : 7.46 (d, J = 8.3 Hz, 2H), 7.36 (m, 4H), 7.27 (t, J = 7.7 Hz, 4H), 7.12 (d, J = 7.9 Hz, 4H), 7.04 (m, 5H), 6.92 (d, J = 16.2 Hz, 1H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>) [ppm]  $\delta$ : 147.78, 147.61, 136.77, 131.78, 131.18, 129.33,129.09, 127.79, 127.47, 125.81, 124.68, 123.48, 123.21, 120.93.

Diphenyl-(4-{2-[4-(2-pyridin-4-yl-vinyl)-phenyl]-vinyl}-phenyl)amine (DPVPA). 2.13 g (5 mmol) {4-[2-(4-bromo-phenyl)vinyl]-phenyl}-diphenyl-amine, 0.65 (2.15)g mmol) tri-o-tolylphosphine, 1.16 mL (10.75 mmol) vinylpyridine, 0.06 g palladium(II) acetate (0.27 mmol) and 100 mL redistilled triethylamine under nitrogen, are added to a three-necked flask equipped with a magnetic stirrer, a reflux condenser, and a nitrogen input tube. 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. Then it is filtered and concentrated. The resulting solution is chromatographed on silica gel using ethyl acetate/petroleum ether (1:1) as eluent. The orange compound is crystallized using ethyl acetate with a yield of 60% and m.p. 229.0 °C. The enthalpy is  $-93.43 \text{ mJ mg}^{-1}$ Anal. Calcd for C<sub>33</sub>H<sub>26</sub>N<sub>2</sub>: C, 88.00; H, 5.78; N, 6.22%. Found: C, 88.15; H, 5.81; N, 6.26%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) [ppm]  $\delta$ : 8.59 (d, J = 4.0 Hz, 2H), 7.54 (s, 4H), 7.41 (d, J = 8.9Hz, 4H), 7.30 (m, 4H), 7.14 (d, J = 7.7 Hz, 4H), 7.11(s, 1H), 7.07 (t, J = 7.2 Hz, 4H), 7.03(s, 2H), 7.00 (s, 1H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>) [ppm] *b*: 149.55, 147.65, 147.46, 145.25, 138.41, 134.88, 133.33, 131.13, 129.31, 128.9 8, 127.48 (CH), 127.46, 126.72, 126.18, 125.27, 124.62, 123.36, 123.17, 120.90.

Phenyl-bis-(4-{2-[4-(2-pyridin-4-yl-vinyl)-phenyl]-vinyl}-phenyl)amine (abbreviated to BPVPA). It is obtained by a similar method to DPVPA. The red compound was purified by column chromatography on silica gel using ethyl acetate/alcohol (1:1) as eluent with a yield of 47% and m.p. 300.2 °C. The enthalpy is  $-32.61 \text{ mJ mg}^{-1}$ . Anal. Calcd for C<sub>48</sub>H<sub>37</sub>N<sub>3</sub>: C, 87.94; H, 5.65; N, 6.41%. C, 87.57; H, 5.41; N, 6.25%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) [ppm]  $\delta$ : 8.59 (d, J = 4.0 Hz, 4H), 7.53 (t, J = 4.9 Hz, 6H), 7.44 (m, 4H), 7.41(s, 1H), 7.38(d, J = 4.3 Hz, 3H), 7.36 (d, J = 5.0 Hz, 2H), 7.15 (t, J = 6.4 Hz, 2H), 7.10 (m, 5H), 7.04 (m, 3H), 6.99 (m, 1H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>) [ppm]  $\delta$ : 150.17, 147.19, 147.13, 144.69, 138.16, 135.14, 132.78, 129.88, 129.37, 129.29, 127.41, 126.94, 126.74, 125.74, 125.59, 124.98, 123.90, 123.23, 120.79.

**Tris-(4-{2-[4-(2-pyridin-4-yl-vinyl)-phenyl]-vinyl}-phenyl)-amine** (abbreviated to TPVPA). It is obtained by a similar method to DPVPA. The red compound was purified by column chromatography on silica gel using ethyl acetate/alcohol (1:1) as eluent with a yield of 41% and m.p. 358.5 °C. The enthalpy is  $-28.37 \text{ mJ mg}^{-1}$ . Anal. Calcd for C<sub>63</sub>H<sub>48</sub>N<sub>4</sub>: C, 87.91; H, 5.58; N, 6.51%. C, 87.68; H, 5.43; N, 6.33%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) [ppm]  $\delta$ : 8.59 (d, J = 4.0 Hz, 6H), 7.55 (s, 10H), 7.46 (t, J = 8.2 Hz, 6H), 7.33 (m, J = 10 Hz, 10 H), 7.14 (t, J = 8.6Hz, 8H), 7.05 (m, 8H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>) [ppm]  $\delta$ : 151.68, 148.29, 146.16, 139.57, 136.72, 134.25, 130.79, 130.14, 129.10, 128.92, 128.43, 128.27, 127.15, 125.81, 122.30.

 Table 1
 The absorption data, one- and two-photon fluorescence spectra with solvent effects of three compounds

Compounds	Solvents	$\lambda_{\max}^{(1a)}/nm$	$\epsilon/10^4$	$\lambda_{\rm max}^{(1{\rm f})}/{\rm nm}$	τ/ns	$\lambda_{\max}^{(2f)}/nm$
DPVPA	DMF	397	5.76	570	2.44	559
	CH <sub>2</sub> Cl <sub>2</sub>	399	4.80	540	2.19	542
	Benzyl alcohol	409	4.28	558	1.01	574
	THF	398	5.39	536	1.93	538
	CHCl <sub>3</sub>	401	4.66	520	1.74	523
BPVPA	DMF	412	7.13	578	1.43	
	CH <sub>2</sub> Cl <sub>2</sub>	416	6.39	546	1.22	
	Benzyl alcohol	427	4.41	564	1.12	
	THF	415	6.21	542	1.19	
	CHCl <sub>3</sub>	419	5.03	526	1.13	529
TPVPA	DMF	419	8.35	582	1.35	
	CH <sub>2</sub> Cl <sub>2</sub>	423	7.86	550	1.17	
	Benzyl alcohol	434	6.83	568	1.39	
	THF	421	7.69	546	1.17	
	CHCl <sub>3</sub>	425	7.23	528	1.10	534
(1a) $(1f)$	(26)					

 ${}^{a} \lambda_{\text{max}}^{(1a)}, \lambda_{\text{max}}^{(1)}$  and  $\lambda_{\text{max}}^{(21)}$  are one-photon absorption, one-photon fluorescence cence and two-photon fluorescence maxima peaks, respectively.  $\tau$  is the one-photon fluorescence lifetime.

## 3. Results and discussion

#### 3.1 One- and two-photon fluorescence

The photophysical properties of these compounds are summarized in Table 1. The linear absorption spectra of these compounds are measured in solvents of different polarity at a concentration of  $c = 1 \times 10^{-5}$  mol L<sup>-1</sup>, 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. From Table 1, one can see that the maximum absorption peaks show a slightly blue-shift, while 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 these compounds may possess higher polarity than the ground state, since the solvatochromism is associated with the energy level lowering. Increasing dipole-dipole interaction between the solute and solvent leads to lowering the energy level greatly.<sup>29,30</sup> Fig. 1 and Fig. 2 are the linear absorption and one-photon fluorescence in chloroform of these compounds, respectively. The maximum excited wavelengths of DPVPA, BPVPA and TPVPA are 400, 410 and 420 nm, respectively. From Fig. 1 and Fig. 2, one can see that the linear absorption peaks and one-photon fluorescence peaks are all red-shifted in the same solvent with increasing molecular dimensionality.



Fig. 1 Linear absorption spectra of three compounds in chloroform with a concentration of 1  $\times$  10<sup>-5</sup> mol  $L^{-1}.$ 



Fig. 2 One-photon fluorescence spectra of three compounds in chloroform with a concentration of  $1\,\times\,10^{-5}$  mol  $L^{-1}.$ 

Fig. 3 is the one-photon fluorescence spectra of the three solid compounds. The measurement apparatus and the excitation wavelengths are the same as those of one-photon fluorescence in solution. From Fig. 3, one can see that the maximum peaks of the DPVPA, BPVPA and TPVPA are 564, 588 and 596 nm, respectively. One can see that the maximum fluorescence peak in Fig. 3 shows red-shifted compared to the corresponding counterpart in Fig. 2. The maximum fluorescence peak in solid form also shows red-shifted with increasing molecular dimensionality as is the case in solution.

Fig. 4 shows the two-photon fluorescence of three compounds in chloroform with a concentration of c = 0.01 mol  $L^{-1}$ . The two-photon induced fluorescence spectra can be observed with a certain laser beam from a mode-locked Ti:sapphire laser (Coherent Mira 900 F) 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 DPVPA, BPVPA and TPVPA are 800, 820 and 830 nm, respectively. From Fig. 4, one can see that the maximum peaks of the two-photon fluorescence also show redshifted with increasing molecular dimensionality.

From Table 1, one can see that the peak position of the twophoton fluorescence is slightly red-shifted compared to that of the one-photon fluorescence in chloroform for each compound. As an example, we present the absorption and fluorescence spectra of TPVPA in Fig. 5. From Fig. 5, one can clearly see the red-shifted phenomenon for the fluorescence spectra of



Fig. 3 One-photon fluorescence spectra of three compounds in solid form.



Fig. 4 Two-photon induced emission spectrum of three compounds in chloroform with a concentration of  $1 \times 10^{-2}$  mol L<sup>-1</sup>.

one- and two-photon cases. This can be explained by the effect of reabsorption such that the linear absorption band has a slight overlap with the emission band and our two-photon fluorescence experiments were carried out in concentrated solutions that made reabsorption significant.

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

#### 3.2 One- and two-photon absorption

The transition intensity for one-photon absorption (OPA) is described by an oscillator strength

$$\delta_{op} = \frac{2\omega_f}{3} \sum_{\alpha} |\langle 0|\mu_{\alpha}|f\rangle|^2 \tag{1}$$

where  $\mu_{\alpha}$  is the electric dipole moment operator,  $\omega_f$  denotes the excitation energy of the excited state  $|f\rangle$ ,  $|0\rangle$  denotes the ground state, and the summation is performed over the molecular *x*, *y* and *z* axes.

In terms of sum-over-state formula, the two-photon matrix



**Fig. 5** Absorption and fluorescence spectra of TPVPA (a) linear absorption with  $c = 1 \times 10^{-5} \text{ mol } \text{L}^{-1}$  in chloroform, (b) one-photon fluorescence spectra with  $c = 1 \times 10^{-5} \text{ mol } \text{L}^{-1}$  in chloroform, (c) two-photon fluorescence spectra with  $c = 1 \times 10^{-2} \text{ mol } \text{L}^{-1}$  in chloroform.

element for the two-photon resonant absorption of identical energy is written as

$$S_{\alpha\beta} = \sum_{j} \left[ \frac{\langle 0|\mu_{\alpha}|j \rangle \langle j|\mu_{\beta}|f \rangle}{\omega_{j} - \omega_{f}/2} + \frac{\langle 0|\mu_{\beta}|j \rangle \langle j|\mu_{\alpha}|f \rangle}{\omega_{j} - \omega_{f}/2} \right]$$
(2)

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.  $\omega j$  is the excitation energy of the excited state  $|j\rangle$ . The TPA cross section is given by orientational averaging over the two-photon absorption probability<sup>31</sup>

$$\delta_{\text{tpa}} = \sum_{\alpha\beta} \left[ F \times S_{\alpha\alpha} S^*_{\beta\beta} + G \times S_{\alpha\beta} S^*_{\alpha\beta} + H \times S_{\alpha\beta} S^*_{\beta\alpha} \right]$$
(3)

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  $\alpha$ ,  $\beta = \{x, y, z\}$ .

The TPA cross section directly comparable with experimental measurements is defined  $as^{32}$ 

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

where  $a_0$  is the Bohr radius,  $c_0$  is the speed of light,  $\alpha$  is the fine structure constant,  $\hbar \omega$  is the photon energy of the incident light,  $g(\omega)$  denotes the spectral line profile, here it is assumed to be a  $\delta$  function.  $\Gamma_f$  is the lifetime broadening of the final state, which is assumed to be 0.1 eV.<sup>22</sup>

We utilized the GAUSSIAN-98 program package<sup>33</sup> to optimize the molecular geometrical structure with the hybrid density functional theory (DFT/B3LYP) and a basis set 6-31G. The excited energies and the OPA intensities for the three molecules are then calculated by the time-dependent density functional theory. The numerical results show that the OPA spectra are mainly dominated by absorption to the first excited state for all three molecules. The lowest excited states for DPVPA, BPVPA, and TPVPA are situated at 466 nm, 503 nm, and 511 nm, respectively, with the respective oscillator strengths 1.25, 1.76, 2.99. The excited energies show a red-shift as the dimensionality of the molecules is increased. The reason can be ascribed to the electronic coupling becoming stronger with increasing molecular branches. The stronger electronic coupling would push down the lowest excitation energy. It is clearly seen that the simulation for OPA gives a similar trend as the measurement shown by Fig. 1 for the three molecules.

The analytical response theory<sup>34</sup> is used to study the twophoton absorption cross sections of the three molecules. The implementation has been coded as the Dalton<sup>35</sup> program package. The TPA cross sections of the three molecules are calculated in the random phase approximation with a 6-31G basis set. For the first excited state, the TPA cross sections  $\sigma$  $(10^{-50} \text{ cm}^4 \text{ s photon}^{-1})$  for molecules DPVPA, BPVPA, and TPVPA lit by the linearly polarized laser are 59.3, 30.2, and 42.4, respectively, which indicates that all three molecules have relatively large two-photon absorption cross sections under the experimental conditions. Therefore, these three molecules can be used as two-photon polymerization initiators. We should note that our theoretical calculations do not show enhancement of the two-photon absorption cross section with increasing molecular dimensionality. The reason is that here we only consider the electronic contribution to the two-photon absorption process. However, according to the result given by Macak et al.,<sup>26</sup> the vibronic contributions can play an important role for multi-branched molecules, which definitely indicates that a full description of the two-photon absorption properties of multi-branched molecules needs to consider vibronic contributions. The corresponding work is under way. From the theoretical results reported above, it should be noted that both one-photon and two-photon absorptions exist for the first excited state of all molecules, which indicates that the electronic states have mixed symmetry. In measurements, the two-photon excitation wavelengths are simply taken as twice those of the one-absorption maxima and the two-photon fluorescence spectra are observed. In such a point of view, the computational work corresponds highly with the observation.

#### 3.3 Two-photon photopolymerization

The wavelengths for initiating two-photon polymerization reactions of DPVPA, BPVPA and TPVPA are 800, 820 and 830 nm, respectively. A three dimensional lattice is created by a two-photon polymerization of an acrylic ester oligomer using BPVPA as initiator. A film of the initiator and oligomer mixture with a weight ratio of  $\sim 4$  to  $\sim 5\%$  (a little dichloroethane is added to make a solution of the 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 applied for twophoton microfabrication. The 820 nm lasing source is tightly focused via an objective lens ( $\times 40$ , NA = 0.65), and the focal point is focused on the sample film on the xy-step motorized stage controlled by computer. The pulse energy after being focused by the objective lens is  $\sim 20$  mW. The polymerized solid skeleton is obtained after the unreacted liquid mixture has been washed out. The fabricated lattice is observed through a polarization microscope (Olympus, BX-51). Its photograph is illustrated in Fig. 6.

The photopolymerization mechanisms of these new initiators are still unknown. According to Cumpston et al.,11 strong donor substitutes would make the conjugated system electron rich, and after one- or two-photon excitation, 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 attempted to make a theoretical investigation. Our ab initio calculation at time-dependent hybrid density functional theory B3LYP level coded in GAUSSIAN package<sup>33</sup> for the BPVPA molecule shows that the first excited state is the charge-transfer (CT) state with the excited energy  $\lambda = 503$  nm. When the molecule is irradiated by a 820 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). For a better understanding of the charge-transfer process, we have plotted the charge density difference between the ground and the CT states for BPVPA in the gas phase (see Fig. 7), which is visualized by the use of the MOLEKEL program.<sup>36</sup> It can be seen that upon excitation, charges are mainly transferred from



5µm

Fig. 6 Optical micrograph of the lattice fabricated *via* two-photon polymerization of an acrylic ester oligomer using BPVPA as initiator.



**Fig. 7** Density difference between the charge-transfer and ground states of BPVPA in the gas phase. Areas with criss-cross marking and dots represent electron loss and gain, respectively, upon excitation.

the acceptor side to the donor side of the molecule. In the CT state, there are more electrons on average at the donor side, indicating that the molecule could be ready to give away its electron to its surroundings. This picture seems to support the Cumpston discussion. However, whether the photoinduced 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 BPVPA as initiator will be reported in detail elsewhere.

## 4. Conclusion

In summary, three new two-photon photopolymerization initiators have been synthesized using Witting and Heck reactions. These dyes produce strong one-photon fluorescence both in the solid state and in solution. The experimental results confirm that all these compounds are good two-photon absorbing chromophores and effective two-photon photopolymerization initiators. The wavelengths for initiating twophoton polymerization reactions of DPVPA, BPVPA and TPVPA are 800, 820 and 830 nm, respectively. A microstructure has been fabricated of BPVPA as a two-photon photopolymerization initiator and a possible mechanism *via* the charge-transfer process when laser irradiation is applied is discussed.

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