Multibranched benzylidene cyclopentanone dyes with large two-photon absorption cross-sections

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Multibranched benzylidene cyclopentanone dyes with a triphenylamine core were synthesized. Their two-photon optical properties were characterized using a Ti:sapphire femtosecond laser. The results showed that the two-photon absorption cross-sections (δ) of these compounds were increased with increasing numbers of branches. The largest δ value of the three-branched compound **3** was 3298 GM which was almost six times larger than that of a model compound, 2,5-bis-[4-(dimethylamino)benzylidene]cyclopentanone (**BDMA**). The sensitizing efficiencies of three new dyes in photopolymerization systems were all higher than that of **BDMA** matching with the commercial initiator 4,4′-dimethyldiphenyliodinium hexafluorophosphate (Omnicat 820). The two-photon polymerization initiated by the bimolecular system composed of compound **3** and Omnicat 820 was investigated under femtosecond laser pulses.

1 Introduction

Two-photon absorption (TPA) is a process in which a molecule absorbs two photons simultaneously under intense laser pulses when the sum of energies of the two absorbed photons matches well with the energy gap between an allowed excited state and the ground state. Compared with one-photon absorption (OPA) process, the wavelength of absorbed photons in TPA is longer and the transition probability of TPA depends quadratically on the excitation intensity, which provide high penetration depth and spatial resolution of the excitation beam. Due to these characteristics, research on organic compounds with large two-photon absorption cross-sections (δ) is one of the hot topics in the field of functional materials for their potential applications, such as three-dimensional microfabrication,[1,2] high-density optical data storage,[3] optical power limitation,[4,5] localized photodynamic therapy,[6] and two-photon laser scanning fluorescence imaging.[7,8]

In recent years, a variety of TPA compounds including dipoles,[9] quadrupoles,[10–12] multibranched compounds,[13–15] and dendrimers[16] have been synthesized and their structure–property relationships have been investigated.[10–20] The results of these studies reveal that the δ value of a compound will be increased by elongating the molecular conjugated system for charge transfer or incorporating multi-dipole or quadrupole TPA chromophores into one molecular structure. Though many compounds with large TPA properties have been reported few are available for two-photon photopolymerization (TPP). For a photoinitiator or a photosensitizer used in photopolymerization, both a large δ value and a high initiating or sensitizing efficiency are simultaneously required. Most reported TPA compounds can not be used as photoinitiators directly because their large molecular conjugated structures supply a good stabilizing system for generated free radicals, cations or anions. In addition, most of them also can not be matched very well with commercially available highly efficient photoinitiators as photosensitizers. Hence leading research groups in microfabrication and high-density optical data storage using the TPP technique always use commercially available UV photocurable materials.[2,21,22]

Benzylidene cyclopentanone dyes have been extensively investigated as highly efficient photosensitizers in common UV photopolymerization.[23–25] They are generally combined with the commercially available photoinitiators 4,4′-dimethyldiphenyliodinium hexafluorophosphate (Omnicat 820) or *o*-chlorohexaarylbisimidazoles (HABI) as highly efficient photoinitiating composites.[23–25] In this paper, we incorporated a 2-[4-(dimethylamino)benzylidene]cyclopentanone chromophore (**DMA**) with a triphenylamine moiety, synthesized multibranched compounds, and investigated their TPA properties, photosensitizing efficiencies and suitability in TPP.

2 Experimental

2,5-Bis[4-(dimethylamino)benzylidene]cyclopentanone (**BDMA**) and 2-[4-(dimethylamino)benzylidene]cyclopentanone (**DMA**) were prepared according to the literature procedures.[23,26,27] Benzaldehyde derivatives **a**–**c** were synthesized following the literature.[19] 4,4′-Dimethyldiphenyliodinium hexafluorophosphate (Omnicat 820, from TH-UNIS Insight Co. Ltd), 2-phenoxyethyl acrylate (SR339, from Sartomer Co. Ltd), pentaerythritol triacrylate (SR444, from Sartomer Co. Ltd) and epoxy acrylate (CN124A80, from Sartomer Co. Ltd) were used as received. Other A.R. grade solvents were used after

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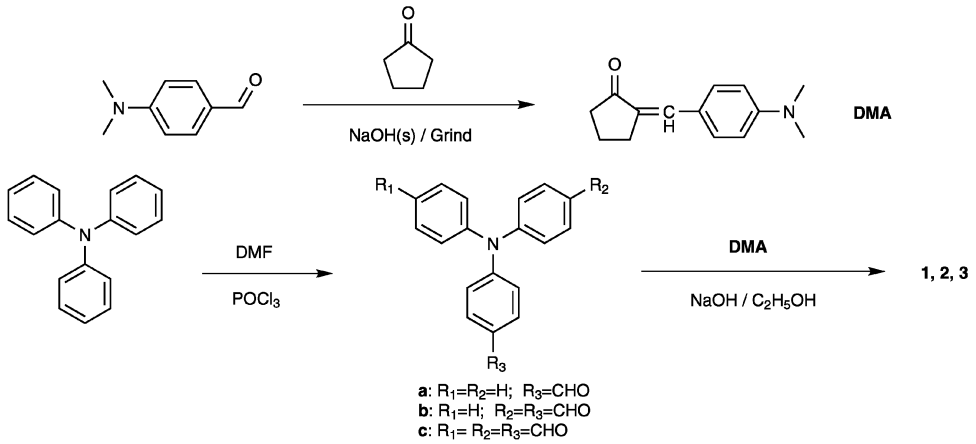

Scheme 1 Synthetic routes to compounds **1–3**.

purification and dried with common methods. Optical characterizations were characterized by using solutions of the compounds in chloroform. UV-visible absorption spectra were measured on a Jasco V-530 spectrophotometer. One-photon fluorescence measurements were carried out on a Hitachi F-4500 fluorescence spectrophotometer. ^{1}H NMR spectra were obtained on a Bruker DPX 400 spectrometer. Elemental analyses were preformed using a FLASH EA1112 elemental analyzer. Mass spectra were recorded using a BIFLEXIII MALDI-TOF mass spectrometer.

The synthetic routes for compounds **1–3** are shown in Scheme 1 and details are given below. The chemical structures of compounds **1–3** and **BDMA** are shown in Fig. 1.

2-[4-(Dimethylamino)benzylidene]-5-[4-(diphenylamino) benzylidene]cyclopentanone (1)

4-(*N*,*N*-Diphenylamino)benzaldehyde (**a**) (0.24 g, 0.88 mmol) and **DMA** (0.19 g, 0.88 mmol) were dissolved in ethanol (7 ml) and heated to reflux. After sodium hydroxide (0.02 g) dissolved in ethanol (2 ml) was added as catalyst, the colour of the mixture turned to red immediately and a precipitate separated out. The reaction was continued for 1 h. After cooling, the precipitate was filtered off, washed with a small amount of ethanol and purified by chromatography over a silica gel column using chloroform as the eluent to afford **1**. Yield: 62%. Anal. Calc. for $C_{33}H_{30}N_2O$: C, 84.22; H, 6.42; N, 5.95. Found: C, 84.35; H, 6.71; N, 5.69%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) δ_H: 7.57 (s, 1H), 7.56 (d, *J* 8.4, 2H), 7.52 (s, 1H), 7.49 (d, *J* 8.7, 2H), 7.31 (t, *J* 7.8, 4H), 7.16 (d, *J* 7.8, 4H), 7.12 (t, *J* 7.4 2H), 7.07 (d, *J* 8.7, 2H), 6.80 (d, *J* 8.4 2H), 3.09 (s, 4H), 3.07 (s, 6H). TOF-MS: *m*/*z* 470.4 [M + H], 493.4 [M + Na].

Compound 2

Benzaldehyde derivative **b** (0.3 g, 1.0 mmol) and **DMA** (0.5 g, 2.3 mmol) were dissolved in ethanol (14 ml) and heated to reflux. After sodium hydroxide (0.04 g) dissolved in ethanol (4 ml) was added as catalyst, the colour of the mixture turned to red immediately and a precipitate separated out. The reaction was continued for 1.5 h. After cooling, the precipitate was filtered off, washed with a small amount of ethanol and purified by chromatography over a silica gel column using chloroform as the eluent to afford **2**. Yield: 43%. Anal. Calc. for $C_{48}H_{45}N_3O_2$: C, 82.85; H, 6.52; N, 6.04. Found: C, 83.09; H, 6.80; N, 5.85%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) δ_H: 7.58 (s, 2H), 7.57 (d, *J* 8.7, 4H), 7.54 (s, 2H), 7.53 (d, *J* 8.2, 4H), 7.36 (t, *J* 7.8, 2H), 7.17 (m, 7H), 6.85 (d, *J* 8.7, 4H), 3.10 (s, 8H), 3.08 (s, 12H). TOF-MS: *m*/*z* 695.3 [M + H], 718.3 [M + Na].

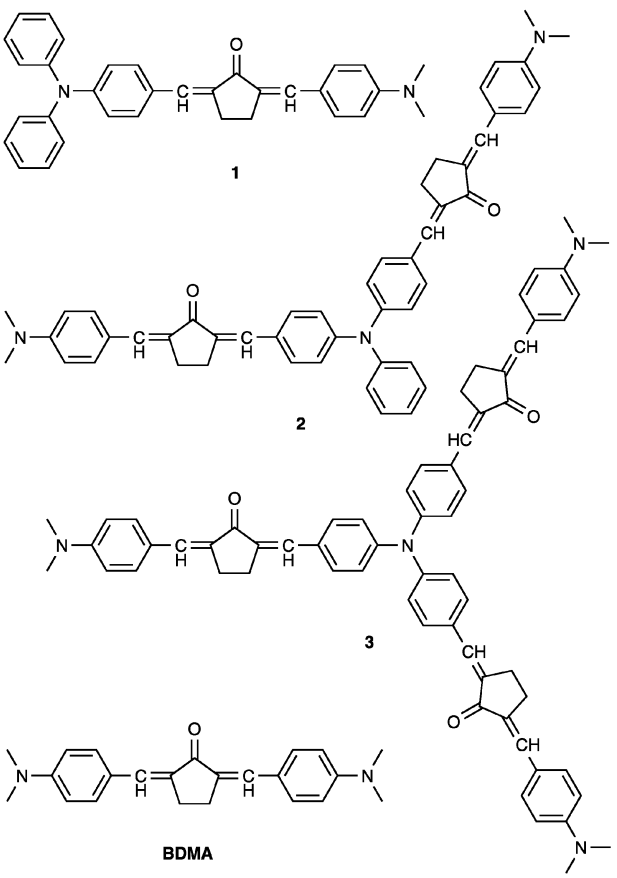

Fig. 1 Chemical structure of compounds **1–3** and **BDMA**.

Compound 3

Benzaldehyde derivative **c** (0.16 g, 0.48 mmol) and **DMA** (0.48 g, 2.23 mmol) were dissolved in ethanol (20 ml) and heated to reflux. After sodium hydroxide (0.03 g) dissolved in ethanol (2 ml) was added as catalyst, the colour of the mixture turned to red immediately and a precipitate separated out. The reaction was continued for 5 h. After cooling, the precipitate was filtered off, washed with a small amount of ethanol and purified by chromatography over a silica gel column using chloroform as the eluent to afford **3**. Yield: 47%. Anal. Calc. for $C_{63}H_{60}N_4O_3$: C, 82.14; H, 6.57; N, 6.08. Found: C, 82.35; H, 6.85; N 6.35%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) δ_H: 7.56 (m, 18H), 7.20 (d, *J* 8.6, 6H), 6.76 (d, *J* 8.8, 6H), 3.11 (s, 12H), 3.07 (s, 18H). TOF-MS: *m*/*z* 920.4 [M + H], 943.4 [M + Na].

TPA cross-section (δ) values of all compounds in chloroform solution (10^{-4}–10^{-3} M) were determined by using the two-photon-excited fluorescence (TPEF) technique with femtosecond laser pulses following the experimental protocol described in detail by Xu and Webb.[28] The excitation light source was a mode-locked Tsunami Ti:sapphire laser (690–880 nm, 80 MHz, <130 fs). Fluorescein in 0.1 M NaOH solution (10^{-4} M) was used as a reference in our experiment since its absorption and two-photon-excited fluorescence were in a similar region to the tested samples. The δ values of fluorescein in 0.1 M NaOH solution in the range 690–880 nm has been reported by Xu and Webb.[28] The δ of compounds **1–3** and **BDMA** were calculated according to eqn (1) by comparing their TPEF intensities with that of fluorescein under the same measurement conditions.[29]

$$\delta = \frac{S_s \Phi_r \varphi_r c_r}{S_r \Phi_s \varphi_s c_s} \delta_r \qquad (1)$$

Here, the subscripts r and s stand for the reference and sample, respectively; S is the integral area of the two-photon-excited fluorescence; Φ is the fluorescence quantum yield; φ is the overall fluorescence collection efficiency of the experimental apparatus, and c is the number density of the molecules in solution.

In one-photon photopolymerization experiments, the monomers were a mixture of SR339, SR444 and CN124A80 ($m_{SR339} : m_{SR444} : m_{CN124A80} = 1 : 3 : 5$). The initiator was Omnicat 820 while compounds **1–3** and **BDMA** were used as sensitizers. A dichloromethane–methanol (9 : 1) mixed solvent was used. The mixed photocurable solutions containing all the components were poured onto a glass substrate and dried in a vacuum oven overnight to evaporate off all solvent. The film thickness was controlled to be about 0.5 mm. The light source was an EFOS Lite 50 W miniature arc lamp with a 5 mm crystal optical fiber and an intensity of irradiation of 20 mW cm^{-2}. A band-pass filter was inserted to choose light of 400–500 nm for our experiments. A Nicolet 5700 infrared spectrophotometer was used to monitor the change of the double bond absorption peak at 6164 cm^{-1} in the near-IR region. The polymerization conversion efficiency of the double bond was calculated by the data processing software series 7-1.

The same Ti:sapphire laser used in TPEF measurement was used for two-photon photopolymerization experiments. The photocurable resin films were prepared by spin-coating the mixed resin solution containing SR 339, SR 444 and CN 124A80 as monomers, dye **3** as sensitizer, Omnicat 820 as initiator and chloroform as solvent onto glass substrates and dried in a vacuum oven overnight to evaporate off the chloroform. The film thickness was controlled to be about 50 μm. The laser was tightly focused *via* an objective lens (40×, NA = 0.45) into the sample. The average power of the laser beam was 20 mW. The sample was fixed on an *xyz*-step motorized stage (P-762.3L nanopositioner) controlled by a computer. Polymerization patterns were recorded with an Olympus IX-70 microscope.

3 Results and discussion

3.1 One-photon optical properties

One-photon absorption and fluorescence spectra of **1–3** in chloroform solution are depicted in Fig. 2 and photophysical characteristics are listed in Table 1. The absorptions around 300 nm should be due to localized $\pi \rightarrow \pi^*$ transitions of phenylene moieties. The absorptions at longer wavelength region (around 480 nm) are considered as intramolecular

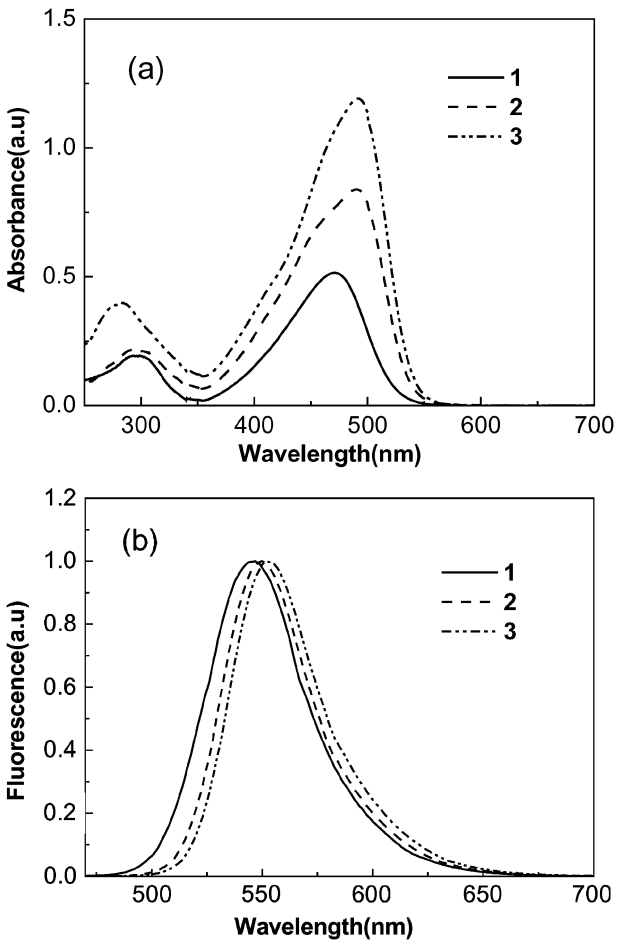

Fig. 2 One-photon absorption (a) and normalized fluorescence spectra excited at 460 nm (b) of compounds **1–3** in chloroform solution.

Table 1 One- and two-photon optical properties of compounds **1–3** and **BDMA** in chloroform

Compound	$\lambda_{max}^{(1)}$ [a]/nm	$10^{-5}\varepsilon_{max}$ [b]/M^{-1} cm^{-1}	λ_{max}^{fl} [a]/nm	$\Delta\nu$ [c]/cm^{-1}	Φ [d]	δ_{max} [e]/GM	δ_{avg} [e]/GM
1	470.5	0.51	546.4	2952	0.11	781	374
2	490.5	0.84	550.0	2205	0.15	2475	1052
3	492	1.19	552.6	2229	0.16	3299	1375
BDMA	466.5	0.65	535.4	2759	0.13	526	247

[a] $\lambda_{max}^{(1)}$, λ_{max}^{fl} are the one-photon absorption, one-photon fluorescence maxima peak, respectively. [b] ε_{max} is the corresponding molar absorption coefficient. [c] $\Delta\nu$ is the Stokes shift. [d] Φ is the one-photon fluorescence quantum yield determined using fluorescein in 0.1 M NaOH as the standard. [e] δ_{max}, δ_{avg} are the maximum and average two-photon absorption cross-section, respectively, in the range 700–880 nm.

charge-transfer absorption bands.[30,31] The absorption peaks ($\lambda_{max}^{(1)}$) of the three compounds occur at 470.5, 490.5 and 492 nm, respectively. The red-shift of $\lambda_{max}^{(1)}$ with increasing numbers of branches shows that the central triphenylamine moiety participates in the conjugation. However, the only 2 nm increase from **2** to **3** indicates that the cross-conjugation effect becomes relatively unimportant when adding more branches.[32] The fluorescence spectra of three compounds are very similar and their emission peaks (λ_{max}^{fl}) also show a red-shift from **1** to **3**. The decrease of the Stokes shift from **1** to **2** and **3** may be due to a decreased excited-state charge transfer in multibranched structures induced by the cross-conjugation effect. The fluorescence quantum yield (Φ) of **1–3** was measured in chloroform solutions and fluorescein in 0.1 M NaOH was used as a standard (Φ = 0.90).[33] The increase of Φ from **1** to **2** and **3** could be also due to their decreasing excited state charge transfer.

3.2 Two-photon absorption

Using the TPEF method, we measured the two-photon-excited spectra of compounds **1–3** and **BDMA** in the range 700–880 nm (shown in Fig. 3(a)). All of them present a clear TPA band around 780–880 nm. In the range 700–780 nm, the δ values of **1** and **BDMA** are very similar to each other. However, from 800 to 880 nm, δ of **1** are almost one order of magnitude larger than those of **BDMA**, which should be due to the larger contribution of two phenyls to the intramolecular charge transfer compared to two methyls. The TPA abilities of compounds **2** and **3** are somewhat larger than that of **1**. The maximum TPA cross-sections (δ_{max}) of **1–3** are 781, 2474 and 3298 GM, respectively. These values are comparable with the data of other strong two-photon absorption compounds measured by the same method.[34–36] The ratio of δ_{max} for the three compounds is 1 : 3.2 : 4.2 (for each branch chromophore in **1–3**, the ratio is 1 : 1.6 : 1.4). To avoid the possible error induced by one-wavelength data, we calculated the average TPA cross-sections (δ_{avg}) of **1–3** in the range 700–880 nm, which were 374, 1052 and 1375 GM, respectively, with a ratio of 1 : 2.8 : 3.7 (for each branch chromophore in **1–3**, the ratio is 1 : 1.4 : 1.2). Obviously, both **2** and **3** present a significant enhancement for their TPA compared to **1**. Previous research results attributed such enhancements in multibranched compounds to interbranch vibronic coupling and electronic coupling. Chung *et al.* considered that the electronic coupling between the branches was a main reason.[13] However, Macak *et al.* revealed by theoretical study that the enhancement was mainly caused by interbranch vibronic coupling.[18] In our data (1 : 1.6 : 1.4 maximum, 1 : 1.4 : 1.2 average), it was noted that

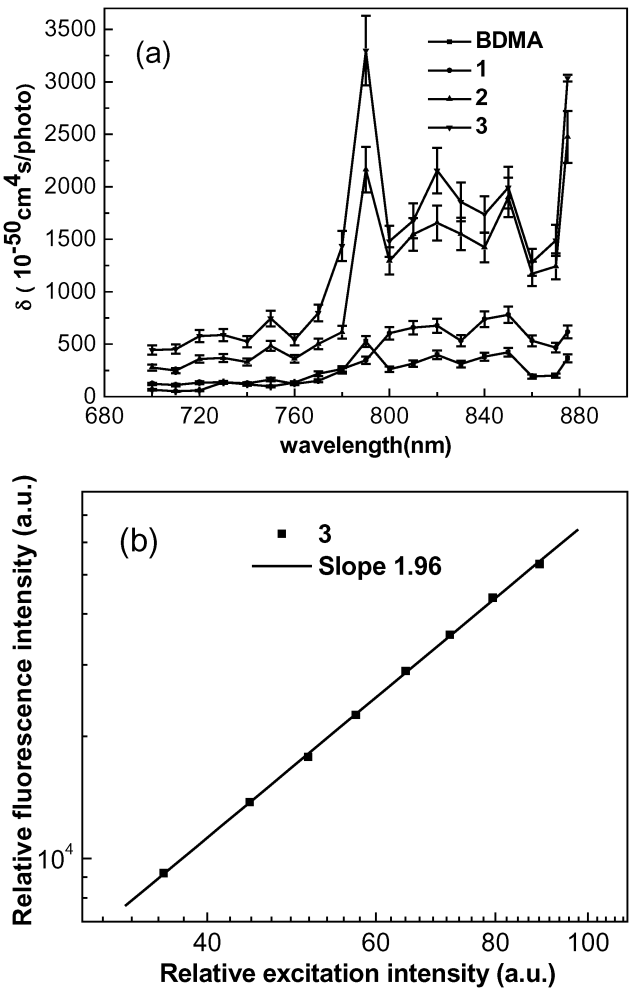

Fig. 3 (a) Two-photon excited fluorescence spectra of compounds **1–3** and **BDMA** in chloroform. (b) Logarithmic plots of TPA induced fluorescence *vs.* excitation power for compound **3** at 800 nm.

the enhancement of δ values decreased with increasing numbers of branches, which coincided with the trend of the cross-conjugation effect. We suppose that the contribution of electronic coupling is a main reason for the enhancement of TPA in compound **2**. In addition, such contribution decreases with increasing numbers of branches. It is difficult to evaluate the extent of vibronic coupling from our results.

Theoretically, the TPA induced fluorescence intensity of compounds is proportional to the square of the excitation intensity. This relationship was examined and confirmed in our measurement for all compounds. As an example, we

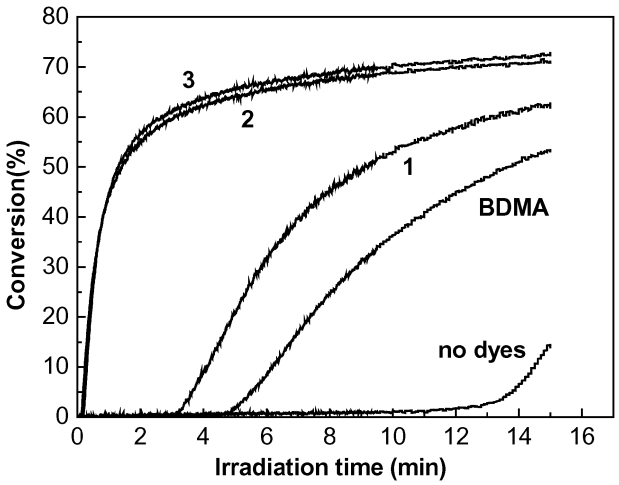

Fig. 4 One-photon polymerization conversion of photocurable resins containing dye/Omnicat 820 bimolecular combinations: [dye] = 1×10^{-4} mol kg^{-1}, [Omnicat 820] = 4×10^{-2} mol kg^{-1}.

present the result of compound **3** in Fig. 3(b) and a slope of 1.96 was obtained in the logarithmic plots of the fluorescence intensities induced by TPA *vs.* excitation intensities at 800 nm.

3.3 Photopolymerization sensitizing efficiency

In one-photon photopolymerization experiments, we investigated the sensitizing efficiencies of dyes **1–3** and **BDMA** to the initiator Omnicat 820. When the dye/Omnicat 820 bimolecular combination was exposed to 400–500 nm light, active aryl radicals were generated due to the electron transfer between excited dyes and Omnicat 820. These radicals start a chain process in acrylate monomers. Through monitoring the relative change of the double bond absorption of acrylate monomers at 6164 cm^{-1} in the near-IR region, the photopolymerization sensitizing efficiencies of different dyes could be determined. The double bond conversion *vs.* time curves of photocurable resin films containing different dyes with the same molar concentration as sensitizer are displayed in Fig. 4. For comparison, a resin film with only Omnicat 820 and no dyes was also investigated under the same experimental conditions. The results show that all photosensitizers have a significant benefit on the efficiency of the polymerization reaction. Though the chain process for the resin film in the absence of dye also occurs after a long time of irradiation, the reaction is very slow, especially in the first 10 min. The addition of **1–3** or **BDMA** can greatly enhance the conversion rate and speed of reaction. Because the absorbance of **1** is lower than that of **BDMA** in the range 400–500 nm (see data in Table 1), its faster reaction speed indicates it has a higher photosensitizing quantum yield compared to **BDMA**. For **2** and **3**, though they have higher absorbance, their reaction speeds are somewhat even larger than that of **BDMA**, which also show they have higher photosensitizing efficiency. The similar conversion curves of **2** and **3** may due to reaction saturation considering their high extinction coefficient and photosensitizing efficiency.

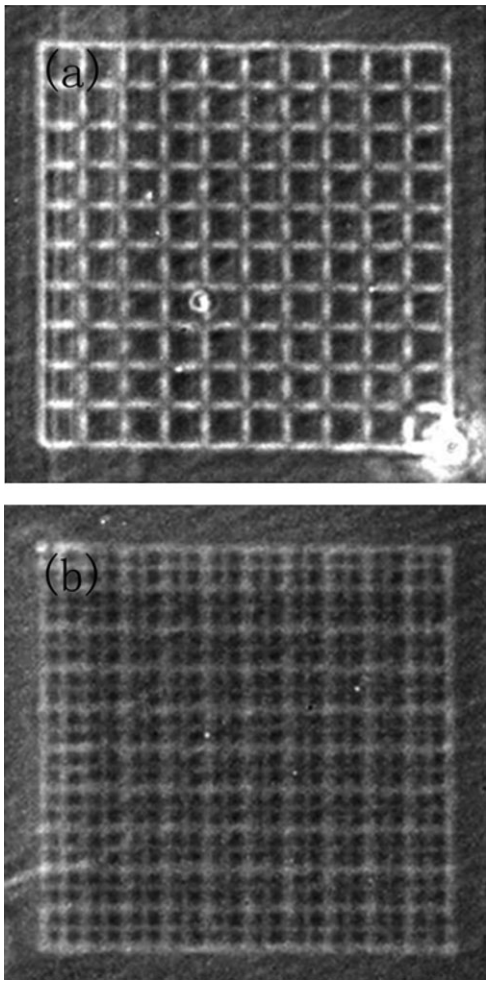

Fig. 5 Micrographs of microstructures fabricated *via* TPP with dye **3** and Omnicat 820 as the initiating system.

3.4 Two-photon photopolymerization

To explore the application of compounds **1–3** in two-photon polymerization, three-dimensional cross-linked woodpile periodic microstructures were fabricated in a mixed resin system containing **3** and Omnicat 820 as the bimolecular initiating system. Fig. 5 shows the optical micrographs of two polymerization patterns. Due to the different refractive indices of exposed and unexposed materials, both two-layer (Fig. 5(a)) and four-layer (Fig. 5(b)) cross-linked woodpile microstructures are very clearly observed. In each layer, the distance between two proximate streaks is 10 μm. The polymerization reaction did not take place in areas out of the laser focus, which could be easily washed out with suitable solvents. The experimental results showed our novel dyes can have large potential applications in TPP.

4 Conclusions

In this work we have synthesized novel multibranched benzylidene cyclopentanone dyes with a triphenylamine core using a very convenient method and studied their linear and nonlinear optical properties systemically. The maximum TPA cross-

sections obtained with femtosecond laser pulses was as high as 3298 GM, which was comparable with the data of other strong two-photon absorption compounds measured by the same method. In addition, we observed a cooperative enhancement effect of TPA in two- and three-branched dyes **2** and **3**. Compared with the well-known dye **BDMA**, all three compounds presented larger TPA cross-sections and higher sensitizing efficiency matching with the commercial UV initiator Omnicat 820. Primary microfabrication experiments have been carried out and revealed our dyes/co-initiator system could effectively realize TPP. Owing to their large TPA cross-section and high sensitizing efficiency, these dyes would have extensive application prospects in microfabrication and high-density optical data storage.

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