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Two-photon absorption property and photopolymerization sensitizing efficiency of asymmetrical benzylidene cyclopentanone dyes

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Abstract

Five, asymmetrical benzylidene cyclopentanone dyes were synthesized and their one- and two-photon photophysical properties were investigated. Measurements revealed that the two-photon absorption cross-sections (TPACS) of these compounds in chloroform were of the order of 10^{-48} cm^4 s $molecule^{-1}$ $photon^{-1}$ in the wavelength range 700–880 nm. The sensitizing efficiencies of the dyes in photopolymerization systems were also considerable and matching those of the commercial initiator *o*-Cl-hexaarylbisimidazoles (HABI). The two-photon polymerization results proved that these photosensitizers possess large potential for two-photon absorption induced polymerization.

Keywords: Two-photon absorption; Benzylidene cyclopentanone; Photosensitizer

1. Introduction

Research into two-photon absorbing compounds is of considerable interest for their potential application in two-photon excited fluorescence microscopy [1], high-density optical data storage [2–4], three-dimensional microfabrication [4,5], two-photon up-converted lasing [6,7] two-photon optical power limiting [8] and photodynamic therapy [9]. These applications take advantage of the fact that the transition probability of two-photon absorption (TPA) depends quadratically on the intensity of the incident laser and, therefore, under tightfocusing conditions, any initiated photochemical or photophysical processes are confined to a volume of the order λ^3 (where λ is the laser wavelength). Furthermore, the wavelength used for two-photon excitation is roughly twice that for one-photon excitation, so the excitation light can easily permeate most media without damage. Based on these characteristics, two-photon absorption induced polymerization (TPP) provides a convenient and powerful approach to fabricate micro-size and even nano-size, three-dimensional functional devices [5,10,11] and to realize high-density optical data storage [4]. Exploiting efficient photoinitiators and photosensitizers in TPP is important in terms of bringing TPA application to reality. For a photoinitiator or a photosensitizer used in TPP, both a large two-photon absorption cross-sections (TPACS) value and a high initiating or sensitizing efficiency are required at one time. Some leading research groups in microfabrication and high-density optical data storage using TPP prefer commercially available UV photocurable materials despite their small TPACS [5,11–13]. Other groups have begun the design and synthesis of new initiators with large TPACS or the improvement of traditional UV initiators recently [4,14]. However, the structure–property relationships of these initiators or sensitizers are not clear.

A series of sensitizers with large TPACS and high sensitizing efficiency have been synthesized by our group and their structure–property relationships investigated [15,16]. Benzylidene cyclopentanone dyes have been extensively investigated as highly efficient photosensitizers in common UV photopolymerization [17–19]. These compounds are generally

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combined with commercially available photoinitiators such as 4,4′-dimethyl diphenyliodinium hexafluorophosphate (Omnicat 820) or *o*-Cl-hexaarylbisimidazoles (HABI) as highly efficient photoinitiating composites [17–19]. In this paper, we describe the synthesis of five, asymmetrical benzylidene cyclopentanone dyes with a variety of substituents (Fig. 1) and the study of their one-photon photophysical properties, TPA properties, photosensitizing efficiencies and two-photon polymerization potentiality.

2. Experimental

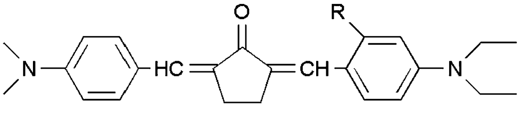
2.1. Synthesis

Cyclopentanone and 3-ethyl aniline were from Acros Organics; 4-dimethylaminobenzaldehyde, 4-diethylaminobenzaldehyde, 3-methyl aniline, 3-chlorin aniline, 3-isopropyl aniline, iodoethane, phosphorus oxychloride and *N*,*N*-dimethyl formamide (DMF) were purchased from Beijing Chemical Co. Ltd., *o*-Cl-hexaarylbisimidazoles (HABI) was from Tokyo Kasei Kogyo Co. Ltd., 2-phenoxyethyl acrylate (SR339), pentaerythritol triacrylate (SR444) and epoxy acrylate (CN124A80) were products of Sartomer Co. Ltd. DMF and other organic solvents were purified with common methods before use.

2-[4-(Dimethylamino)-benzylidene]-cyclopentanone (DMA) was prepared according to the literature [20]. The synthetic routes for compounds **1–5** are shown in Scheme 1 and the details are given below.

2.1.1. 2-(4-(Diethylamino)benzylidene)-5-(4-(dimethylamino)benzylidene)cyclopentanone (*1*)

In a 100 ml flask, 0.43 g (2 mmol) DMA and 0.35 g (2 mmol) 4-diethylaminobenzaldehyde were dissolved in ethanol (10 ml) and heated to reflux. After sodium hydroxide (0.015 g) was added as catalyst, the colour of the mixture turned to red immediately and a precipitate separated out. Reaction was continued for 6 h, after which the mixture was cooled, the precipitate filtered, washed with a small amount of ethanol and recrystallized from toluene to afford **1** (0.32 g). Yield: 53%. Anal. calcd for $C_{25}H_{30}N_2O$: C, 80.17; H, 8.07; N, 7.48. Found: C, 80.31; H, 8.35; N, 7.35%. ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ_H: 7.53 (m, 6H), 6.72 (m, 4H), 3.42 (q, $J = 6.9$ Hz, 4H), 3.07 (s, 4H), 3.04 (s, 6H), 1.21 (t, $J = 6.9$ Hz, 6H). TOF-MS: *m/z* 375.3 [M + H], 397.3 [M + Na].



R=H(**1**), Cl(**2**), CH_3(**3**), C_2H_5(**4**), i-C_3H_7(**5**)

Fig. 1. Chemical structure of compounds **1–5**.

2.1.2. 2-(2-Chloro-4-(diethylamino)benzylidene)-5-(4-(dimethylamino)benzylidene)cyclopentanone (**2**)

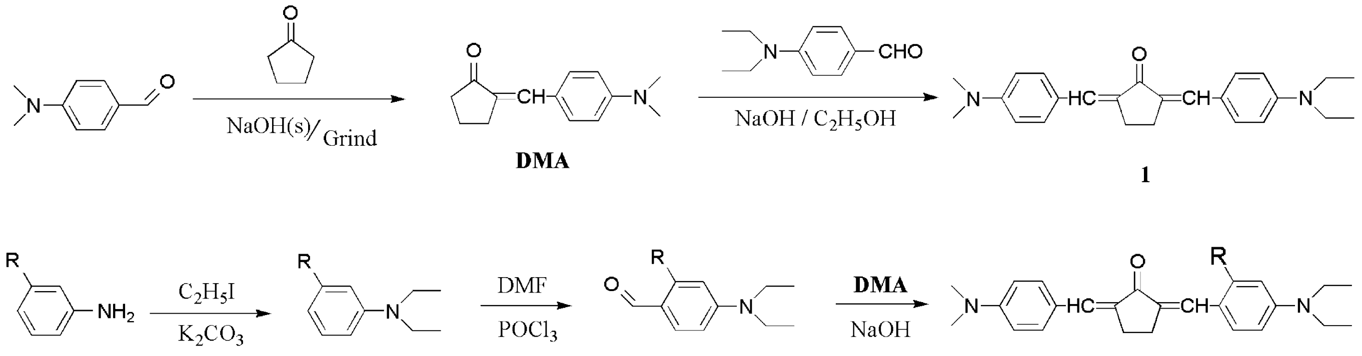
Compound **2** was synthesized based on the following steps.

2.1.2.1. 3-Chloro-N,N-diethylbenzenamine. 3-Chlorine aniline 6.38 g (0.05 mol) and 50 ml acetone were added to a three-necked flask equipped with magnetic stirrer and were heated to reflux. Anhydrous potassium carbonate 13.8 g (0.10 mol) was added to the flask and reflux continued for 20 min. Iodoethane 15.6 g (0.10 mol) was added dropwise to the flask and reaction was continued for 10 h. After cooling, anhydrous potassium carbonate was added and the solvent removed by rotary evaporation. The residual liquid mixture was purified by chromatography using a silica gel column employing chloroform as eluent to afford the pure liquid product. Yield: 71%. ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ_H: 7.12 (m, 1H), 6.57 (m, 3H), 3.35 (q, $J = 7.1$ Hz, 4H), 1.18 (t, $J = 7.1$ Hz, 6H).

2.1.2.2. 2-Chloro-4-(diethylamino)benzaldehyde. Phosphorus oxychloride 3.07 g (0.02 mol) was added dropwise to stirred 2.92 g (0.04 mol) of *N*,*N*-dimethyl formamide (DMF) at 0 °C. The mixture was stirred at this temperature for 1 h and at room temperature for another 1 h. After the addition of 3.67 g (0.02 mol) of 3-chloro-*N*,*N*-diethylbenzenamine dissolved in 13 ml dichloroethane, the mixture was stirred and heated to reflux for 2 h. After cooling, the solution was poured into cold water. The resulting mixture was neutralized to pH 7 with aqueous 2 N NaOH solution and extracted with dichloromethane. The extract was washed with brine and the solvent removed by rotary evaporation. The residue was purified by chromatography on a silica gel column using chloroform as eluent and 2-chloro-4-(diethylamino)benzaldehyde was obtained as a yellow liquid. Yield: 57%. ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ_H: 10.24 (s, 1H), 7.57 (m, 1H), 6.70 (m, 2H), 3.39 (q, $J = 7.1$ Hz, 4H), 1.19 (t, $J = 7.1$ Hz, 6H).

*2.1.2.3. 2-(2-Chloro-4-(diethylamino)benzylidene)-5-(4-(dimethylamino)benzylidene)cyclopentanone (**2**).* DMA 0.65 g (3 mmol) and 0.64 g (3 mmol) 2-chloro-4-(diethylamino)benzaldehyde were dissolved in ethanol (15 ml) and heated to reflux. After sodium hydroxide (0.03 g) was added as catalyst, the colour of the mixture turned to red immediately and a precipitate formed after several minutes. Reaction was continued for 10 h, after which the mixture was cooled, the precipitate was filtered and purified by chromatography on a silica gel column using chloroform as eluent to afford **2**. Yield: 47%. Anal. calcd for $C_{25}H_{29}ClN_2O$: C, 73.42; H, 7.15; Cl, 8.67; N, 6.85. Found: C, 73.15; H, 7.32; Cl, 8.43; N, 7.09%. ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ_H: 7.90 (s, 1H), 7.53 (m, 4H), 6.76 (m, 3H), 6.62 (s, 1H), 3.38 (q, $J = 7.1$ Hz, 4H), 3.05 (s, 4H), 3.03 (s, 6H), 1.21 (t, $J = 7.1$ Hz, 6H). TOF-MS: *m/z* 409.2 [M + H], 431.2 [M + Na].

Compounds **3**, **4**, and **5** were prepared according to the same method as compound **2**.



R=Cl(**2**), CH_3(**3**), C_2H_5(**4**), i-C_3H_7(**5**)

Scheme 1. Synthetic routes to compounds **1**–**5**.

2.1.3. 2-(4-(Diethylamino)-2-methylbenzylidene)-5-(4-(dimethylamino)benzylidene)cyclopentanone (*3*)

Yield: 45%. Anal. calcd for $C_{26}H_{32}N_2O$: C, 80.37; H, 8.30; N, 7.21. Found: C, 80.55; H, 8.49; N, 6.97%. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ_H: 7.81 (s, 1H), 7.54 (m, 4H), 6.74 (d, $J = 8.8$ Hz, 2H), 6.56 (d, $J = 10.7$ Hz, 2H), 3.42 (q, $J = 6.9$ Hz, 4H), 3.05 (s, 4H), 3.04 (s, 6H), 2.49 (s, 3H), 1.21 (t, $J = 6.9$ Hz, 6H). TOF-MS: *m*/*z* 389.3 [M + H], 411.3 [M + Na].

2.1.4. 2-(4-(Diethylamino)-2-ethylbenzylidene)-5-(4-(dimethylamino)benzylidene)cyclopentanone (*4*)

Yield: 40%. Anal. calcd for $C_{27}H_{34}N_2O$: C, 80.55; H, 8.51; N, 6.96. Found: C, 80.68; H, 8.39; N, 7.17%. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ_H: 7.83 (s, 1H), 7.54 (m, 4H), 6.73 (d, $J = 8.8$ Hz, 2H), 6.56 (d, $J = 11.0$ Hz, 2H), 3.42 (q, $J = 6.9$ Hz, 4H), 3.05 (s, 4H), 3.04 (s, 6H), 2.84 (q, $J = 7.0$ Hz, 2H), 1.26 (t, $J = 7.0$ Hz, 3H), 1.21 (t, $J = 6.9$ Hz, 6H). TOF-MS: *m*/*z* 403.3 [M + H], 425.3 [M + Na].

2.1.5. 2-(4-(Diethylamino)-2-isopropylbenzylidene)-5-(4-(dimethylamino)benzylidene)cyclopentanone (*5*)

Yield: 47%. Anal. calcd for $C_{28}H_{36}N_2O$: C, 80.72; H, 8.71; N, 6.72. Found: C, 80.51; H, 8.89; N, 6.55%. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ_H: 7.91 (s, 1H), 7.52 (m, 4H), 6.74 (d, $J = 8.7$ Hz, 2H), 6.62 (s, 1H), 6.56 (d, $J = 8.5$ Hz, 1H), 3.53 (m, $J = 7.1$ Hz, 1H), 3.42 (q, $J = 6.9$ Hz, 4H), 3.05 (s, 4H), 3.04 (s, 6H), 1.26 (t, $J = 6.9$ Hz, 6H), 1.22 (d, $J = 7.1$ Hz, 6H). TOF-MS: *m*/*z* 417.3 [M + H], 439.2 [M + Na].

2.2. Experimental methods

UV–visible absorption spectra were measured on a Jasco V-530 spectrophotometer. One-photon fluorescence measurements were determined using 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.

TPA cross-section (δ) values of all compounds in chloroform solution (10^{-3} M) were determined using two-photon-excited fluorescence (TPEF) with femtosecond laser pulses (from a mode-locked Tsunami Ti:sapphire laser, 700–880 nm, 80 MHz, <130 fs) following the experimental protocol described by Xu and Webb [21]. Fluorescein in 0.1 N NaOH solution (10^{-4} M) was used as a reference in the absorption and two-photon-excited fluorescence experiments. The experimental uncertainty amounted to ±10%. The TPACS (δ) of compounds **1**–**5** were calculated according to Eq. (1) by comparing their TPEF intensities with that of fluorescein under the same measurement conditions [22].

$$\delta = \frac{S_s \Phi_r \varphi_r c_r}{S_r \Phi_s \varphi_s c_s} \delta r \tag{1}$$

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. *c* is the number density of the molecules in solution.

One-photon photopolymerization experiments were also carried out. The monomers were a mixture of SR339, SR444 and CN124A80 (m_{SR339}:m_{SR444}:$m_{CN124A80} = 1:3:5$); the co-initiator was HABI. Compounds **1**–**5** were used as sensitizer, respectively. The light source was an EFOS Lite 50 W miniature arc lamp, with a 5 mm crystal optical fiber and intensity of irradiation of 20 mW cm^{-2}. A band-pass filter was inserted to select visible light above 470 nm. A Nicolet 5700 infrared spectrophotometer was used to monitor the change of the double bond absorption peak at 6164 cm^{-1} in near-IR region.

The same Ti:sapphire laser used in TPEF measurement was used for two-photon photopolymerization experiments. The formulation of the photocurable resin was the same as that used in the one-photon experiments. The laser was tightly focused by a 100× oil-immersion objective lens of high numerical aperture (NA = 1.4, Olympus) into the photocurable resin which was fixed on an *xyz*-step motorized stage controlled by a computer. The average power of laser beam was 12 mW. Polymerization patterns were recorded with scanning electron microscope (SEM; Hitachi S-4300FEGd).

3. Results and discussions

3.1. One-photon optical properties

The linear absorption and normalized one-photon excited fluorescence spectra of the compounds in chloroform are shown in Fig. 2. Their photophysical characteristics are listed in Table 1. The absorption bands around 260 nm and 350 nm are due to localized $\pi \rightarrow \pi^*$ transition of the phenyl and stilbene moieties, respectively. The absorptions at longer wavelength (460–490 nm) are intramolecular charge-transfer absorption bands [23,24]. There was no linear absorption from above 600 nm for all compounds. The obvious blue-shift of the linear absorption peak of compound **2** is due to the weaker electron donor property of the chlorine substituent. Although methyl, ethyl, isopropyl groups have different electron donor ability, compounds **3**, **4**, and **5** do not show obvious differences in their linear absorption peak. At the same time the fluorescence emission peaks are little different for all the compounds. Comparing compound **1** with the other compounds, the lower Φ of **1** may be due to their increasing excited state charge transfer caused by the substituents.

Table 1
One- and two-photon optical properties of compounds **1**–**5** in chloroform

Compound	$\lambda_{max}^{(1)}$ (nm)	ε_{max} (10^5 M^{-1} cm^{-1})	λ_{max}^{ft} (nm)	$\Delta\nu$ (cm^{-1})	Φ	δ_{max} (GM)	δ_{avg} (GM)
1	475	0.75	538.0	2465	0.119	506	284
2	469.5	0.61	533.4	2552	0.063	510	300
3	476.5	0.67	544.8	2631	0.076	386	230
4	475	0.56	542.8	2630	0.066	466	267
5	474.5	0.56	544.6	2713	0.068	403	248

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

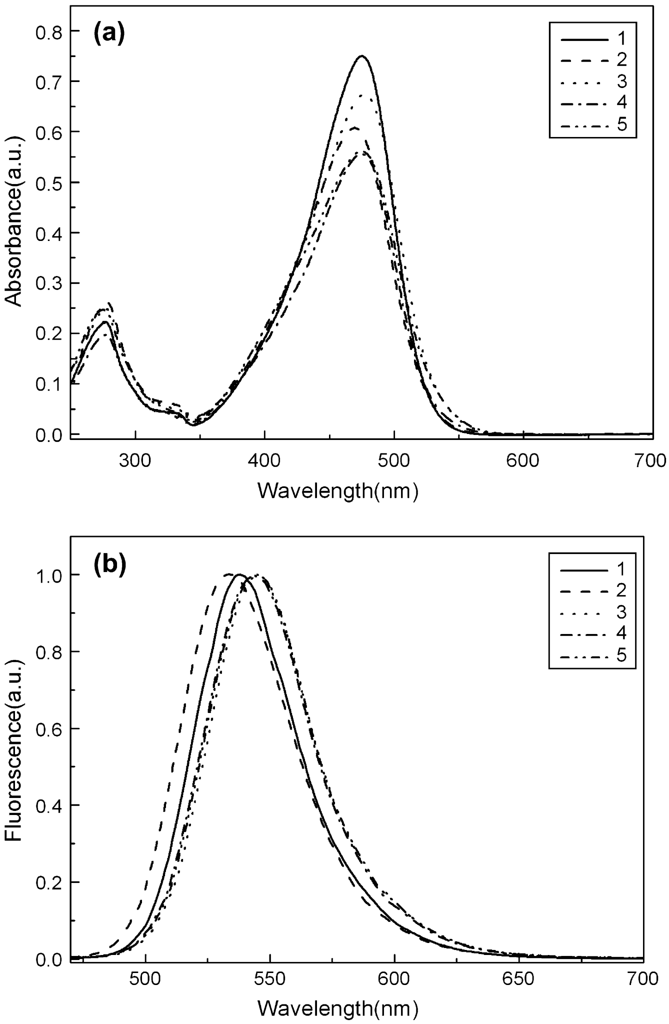


Fig. 2. One-photon absorption (a) and normalized fluorescence spectra excited at 460 nm (b) of compounds **1**–**5** in chloroform solution, [dye] = 1×10^{-5} mol L^{-1}.

3.2. Two-photon absorption

Using the TPEF method, we measured the two-photon-excited spectra of compounds **1**–**5** at 700–880 nm. To eliminate disturbance from other photophysical or photochemical processes and to ensure that the two-photon excited fluorescence intensity was quadratically dependent on excitation intensity, the intensity of the input pulses was confined within a certain range. As an example, the results for compound **3** are shown in Fig. 3(b) and a slope of 1.9 was obtained in the logarithmic plot of the fluorescence intensities induced by TPA versus excitation intensity at 800 nm. From Fig. 3(a), it is evident that the maximum TPA cross-sections (δ_{max}) of compounds **1**–**5** were 506, 510, 386, 466, 403 GM, respectively. The two-photon absorption cross-sections of the compounds in chloroform were of the order 10^{-48} cm^4 s $molecule^{-1}$ $photon^{-1}$ in the wavelength range 700–880 nm. These values are among the largest values obtained for molecules of a similar size by use of femtosecond pulses [16,25].

3.3. Photopolymerization sensitizing efficiency

By one-photon photopolymerization experiments, we investigated the sensitizing efficiencies of dyes **1**–**5** with respect to the initiator HABI. When the dye/HABI bimolecular combination was exposed to visible light of wavelength >470 nm, active aryl radicals were generated due to electron transfer between the excited dyes and HABI. These radicals would 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

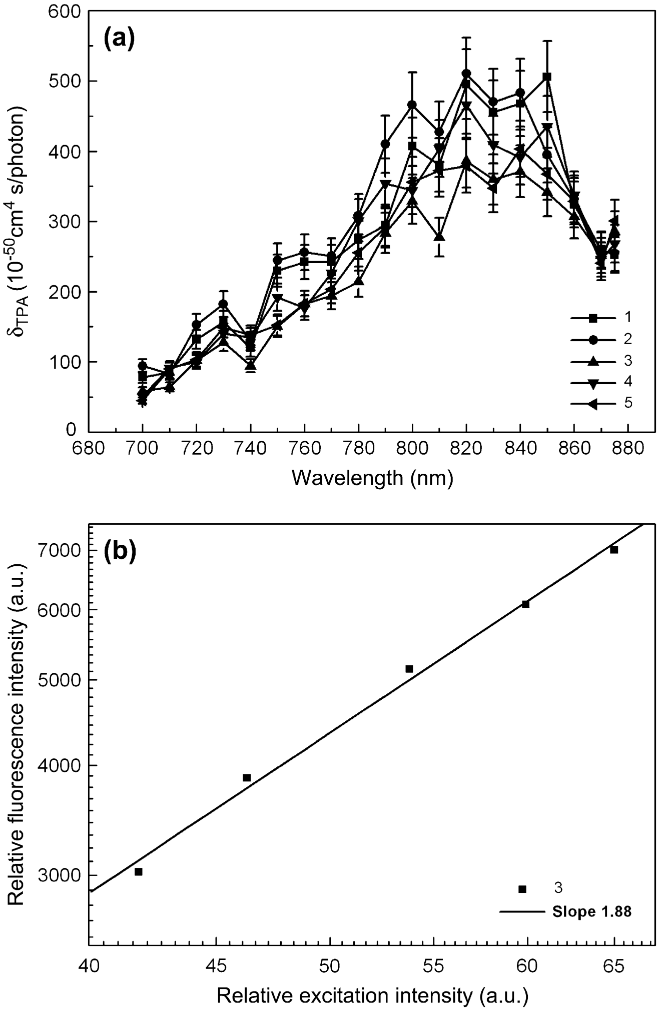


Fig. 3. (a) Two-photon excited spectra of compounds **1**–**5** in chloroform. (b) Logarithmic plots of TPA induced fluorescence versus excitation power for compound **3** at 800 nm.

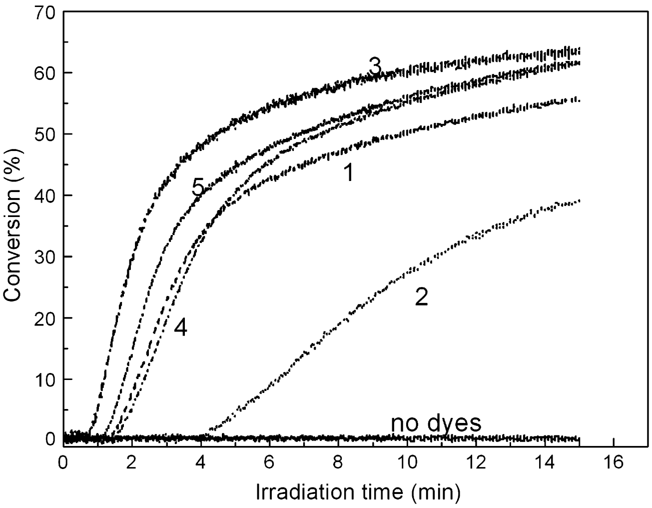


Fig. 4. One-photon polymerization conversion of photocurable resins containing dye/HABI bimolecular combination, $[\text{dye}] = 1.1 \times 10^{-4}\ \text{mol kg}^{-1}$, $[\text{HABI}] = 2.3 \times 10^{-2}\ \text{mol kg}^{-1}$.

photopolymerization sensitizing efficiencies of different dyes could be determined. The double bond conversion as a function of time curves of photocurable resin films containing different dyes at the same molar concentration as the sensitizer are shown in Fig. 4. For contrast, a resin film with only HABI and no dyes was also investigated under the same experimental conditions. The results show that the efficiency of the polymerization reaction benefited from each of the photosensitizers. The resin film with no dyes underwent virtually no change during lengthy irradiation, whereas the addition of compounds **1**–**5** greatly enhanced both the conversion rate and reaction speed. It is apparent that although these dyes were of similar structure, there were major differences in their polymerization induction periods and polymerization reaction speeds. This phenomenon highlights the importance of substituent effects on electron transfer. Dye **2** displayed relatively lower photosensitizing efficiency owing to the weak electron-donating property of its chlorine substituent. Dyes **3**, **4** and **5** exhibited more efficient sensitizing due to their stronger electron-donating groups. It can be seen that all the dyes are efficient photosensitizers to the initiator HABI.

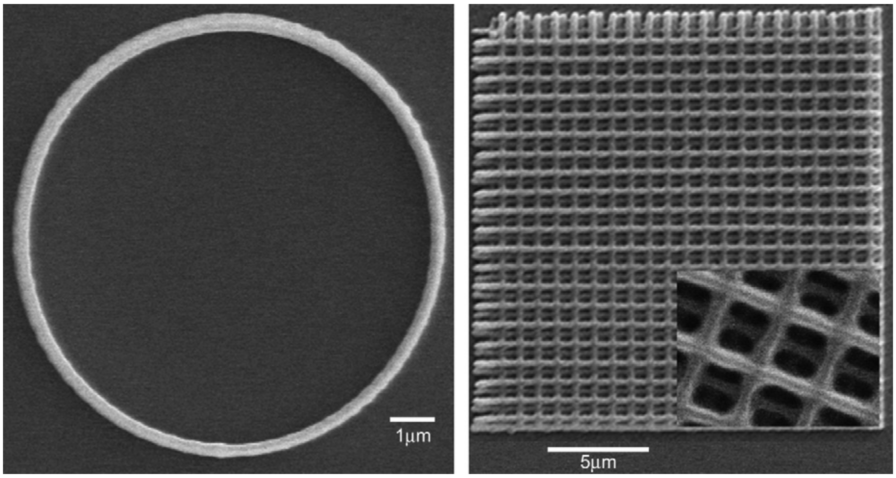


Fig. 5. Micrographs of microstructures fabricated via TPP with dye **3** and Omnicat 820 as the initiating system.

3.4. Two-photon photopolymerization

In two-photon photopolymerization experiments, three-dimensional periodic microstructures were fabricated in a mixed resins system containing dye **3** and HABI as the bimolecular initiating system. The polymerization reaction did not take place in areas out of the laser focus, where could be easily washed out with proper solvents. Fig. 5 shows the optical micrographs of the polymerization patterns. A circle (Fig. 5a) and a four-layer cross-linked woodpile microstructure (Fig. 5b) are observed very clear. The experimental results proved our novel dyes would have large potentialities in TPP.

4. Conclusions

Each of the synthesized five, asymmetrical benzylidene cyclopentanone dyes displayed large, two-photon absorption cross-sections in the wavelength range 700−880 nm in chloroform. The sensitizing efficiencies of the dyes in photopolymerization systems matched those of the commercial initiator *o*-Cl-hexaarylbisimidazoles (HABI). Two-photon polymerization experiments revealed that these photosensitizers possess large potential for application in three-dimensional microfabrication and high-density optical data storage.

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