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Water-soluble benzylidene cyclopentanone dye for two-photon photopolymerization

Xiaojun Wan[a,b], Yuxia Zhao[a,*], Jianqiang Xue[a,b], Feipeng Wu[a,*], Xiangyun Fang[a]

[a] Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China

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ABSTRACT

A novel water-soluble benzylidene cyclopentanone dye was synthesized by introducing four sodium carboxylate groups into 2,5-Bis-[4-(diethylamino)-benzylidene]-cyclopentanone (BDEA). Its two-photon absorption (TPA) cross-section in water solution was determined by nonlinear transmission method with Ti:sapphire femtosecond laser as exciting light source. 287 GM at 800 nm was obtained, which was quite larger than TPA cross-section of water-soluble xanthene dyes. Using this new dye as initiator, two-photon polymerization (TPP) of water-soluble acrylate could be induced directly. Low threshold energy of 0.51 mW and a high resolution of 400 nm were achieved, indicating this dye would have extensive application prospects in TPP under aqueous environments.

1. Introduction

Compared to common UV photopolymerization, two-photon polymerization (TPP) has two outstanding advantages: (i) using near-infrared photons enables the light penetrating into photocurable media deeply and initiates photopolymerization only at focused point [1], which can realize true three dimensional (3D) fabrication with a simple and fast procedure; (ii) a quadratic dependence of polymerization rate on excitation intensity allows to generate structures with a high degree of spatial selectivity using a tightly focused laser beam. Though Webb et al. had verified experimentally the possibility of 3D fabrication with TPP in 1992 [2], this technology did not get enough attention and development till Kawata et al. reported a real 3D structure by TPP in 1997 [3]. Hereafter, large amount of research efforts on realizing high resolution 3D micro-fabrication by TPP and exploring new TPP materials have been done. Actually, 20–30 nm lateral spatial resolution has been achieved [4], many novel high-efficiency photoinitiators and sensitizers have been applied [5–7], TPP has been recognized as a very powerful technology in 3D micro-fabrication. However, till now most of reported TPP materials are hydrophobic, which prevents them from being used in biological applications.

For 3D biological fabrication applications involving a variety of biomaterials, biosensors, and biomolecule spatial positioning, the ability of fabrication under an aqueous environment is a fundamental requirement. Campagnola et al. studied TPP of acrylamide in aqueous solution using water-soluble commercial xanthene dyes [8]. Their results showed that rose bengal, eosin and erythrosine could successfully initiate TPP. However, because the two-photon absorption (TPA) cross-sections of these dyes were very small (only 10 GM at 800 nm), a high laser intensity (100 mW) and long exposure time (300–400 μs) were required in their experiments. Recently, Bazan et al. developed a series of water-soluble TPA compounds based on 3D [2.2] paracyclophane as the core [9], which exhibited quite large TPA cross-sections values, up to 700 GM in water. For their high fluorescence quantum yield (0.4–0.5), these compounds are good candidates for biological imaging as water-soluble fluorophores in two-photon fluorescence microscopy (TPM). However, their application potentiality in water-soluble TPP is limited. As we know, till now, seldom research on novel dyes for TPP under aqueous environments has been reported.

Benzylidene cyclopentanone dyes have been extensively investigated as high-efficient triplet photosensitizers in common photopolymerization. In our previous study [10–12], we reported that several series of benzylidene cyclopentanone dyes had extensive application prospects in TPP for their large TPA cross-sections and high photosensitizing efficiencies. However, these compounds are all hydrophobic. In this letter, we synthesized a water-soluble benzylidene cyclopentanone dye, 2,5-Bis-{4-[bis-(2-sodiumcarboxylate-ethyl)-amino]-benzylidene}-cyclopentanone

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* Corresponding authors. Tel.: +86 10 82543571; fax: +86 10 82543491.
E-mail addresses: yuxia.zhao@mail.ipc.ac.cn (Y. Zhao), fpwu@mail.ipc.ac.cn (F. Wu).

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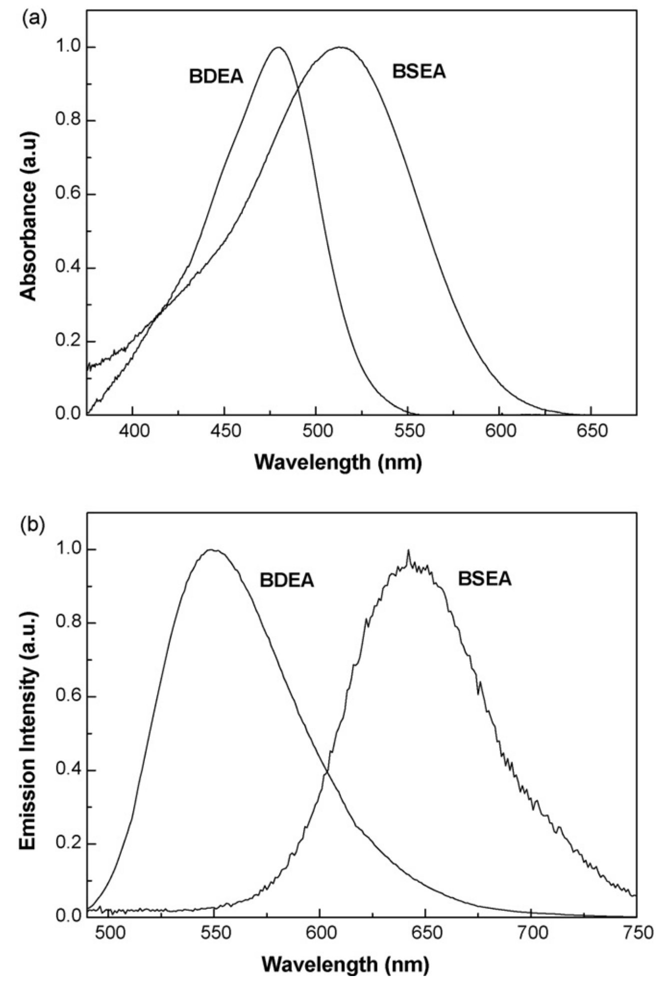


Fig. 1. Normalized one photon absorption (a) and fluorescence spectra (b) of BDEA in DMF and BSEA in water.

(BSEA), by introducing hydrophilic sodium carboxylate groups into 2,5-Bis-[4-(diethylamino)-benzylidene]-cyclopentanone (BDEA), studied its TPA property and TPP potentiality under aqueous environments.

2. Experimental

2.1. Materials

Cyclopentanone was from Arcos Organics; acrylic acid, 4-aminobenzaldehyde, triethanolamine (TEOA), ethanol, N, N-dimethylformamide (DMF), eosin and NaOH were purchased from Beijing Chemical Co. Ltd.; SR610 [polyethylene glycol (600) diacrylate] was from Sartomer Co. Ltd. All materials were used directly without further purification. BDEA was prepared according to the literature procedures [13]. BSEA was synthesized through the routes shown in Scheme 1.

2.1.1. 4-[(2-Sodiumcarboxylate-ethyl)-amino]-benzaldehyde (*1*)

4-Aminobenzaldehyde (0.605 g, 5 mmol) and acrylic acid (10 ml) were mixed and heated under stirring at 80 °C for 5 h, then cooled to room temperature. 10 ml water was added and the mixture was kept at 5 °C for 2 h. Some precipitate appeared and was collected by filtration, washed with water (5 × 10 ml) several times, then mixed with 10 ml water again. A saturation NaOH solution was added dropwise under stirring till all precipitate was dissolved. By evaporating off water, 0.59 g of light yellow solid (yield 44.5%) was obtained. ^{1}H NMR (400 MHz, D_2O) δ: 9.41 (s, 1H), 7.66 (d, J = 8.7, 2H), 6.70 (d, J = 8.7, 2H), 3.41 (t, J = 7.0, 2H), 2.48 (t, J = 7.0, 2H). HRMS-ESI theoretical m/z $[M{-}Na{+}2H]^+$ = 194.0812, found 194.0817.

2.1.2. 2, 5-Bis-{4-[(2-sodiumcarboxylate-ethyl)-amino]-benzylidene}-cyclopentanone
(*2*)

Cyclopentanone (0.19 g, 2.26 mmol), **1** (0.97 g, 4.52 mmol) and 10 ml water were mixed together and heated to 80 °C. 0.01 g NaOH was added as catalyst. The reaction solution was kept at 80 °C under stirring for 4 h, then cooled to room temperature. 50 ml ethanol was added. The solution was kept at 5 °C for 5 h. Some precipitate appeared and was collected, washed with ethanol (3 × 50 ml), and dried under vacuum to afford 0.29 g of dark red solid (yield 26.8%). ^{1}H NMR (400 MHz, D_2O) δ: 7.27 (d, J = 8.4, 4H), 7.12 (s, 2H), 6.57 (d, J = 8.4, 4 H), 3.18 (t, J = 7.0, 4 H), 2.50 (s, 4H), 2.38 (t, J = 7.0, 4 H). HRMS-ESI theoretical m/z $[M{-}2Na{+}3H]^+$ = 435.1925, found 435.1915.

2.1.3. 2, 5-Bis-{4-[bis-(2-sodiumcarboxylate-ethyl)-amino]-benzylidene}-cyclopentanone
(BSEA)

2 (0.55 g, 1.15 mmol) was dissolved in 5 ml water. Hydrochloric acid (1 mol/L, 10 ml) was added dropwise till the pH was modified to 6–7. After stirring for 1 h, precipitate appeared. 50 ml acrylic acid was added to the mixture and kept at 80 °C for 5 h. After cooled to room temperature, 100 ml water was added and the solution kept at 5 °C for 3 h. Some precipitate appeared and was collected, washed with water (3 × 50 ml), then mixed with 5 ml water. A saturation NaOH solution was added dropwise under stirring till all precipitate was dissolved. 20 ml ethanol was added. The solution was kept at 5 °C for 3 h. Some precipitate appeared and was collected, washed with ethanol (40 ml), and dried under vacuum to afford 0.60 g of dark red solid (yield 78.4%). ^{1}H NMR (400 MHz, D_2O) δ: 7.46 (d, J = 8.8, 4H), 7.18 (s, 2H), 6.74 (d, J = 8.8, 4H), 3.54 (t, J = 7.4, 8H), 2.76 (s, 4H), 2.43 (t, J = 7.4, 8H); HRMS-ESI theoretical m/z $[M{-}4Na{+}5H]^+$ = 579.2347, found 579.2337.

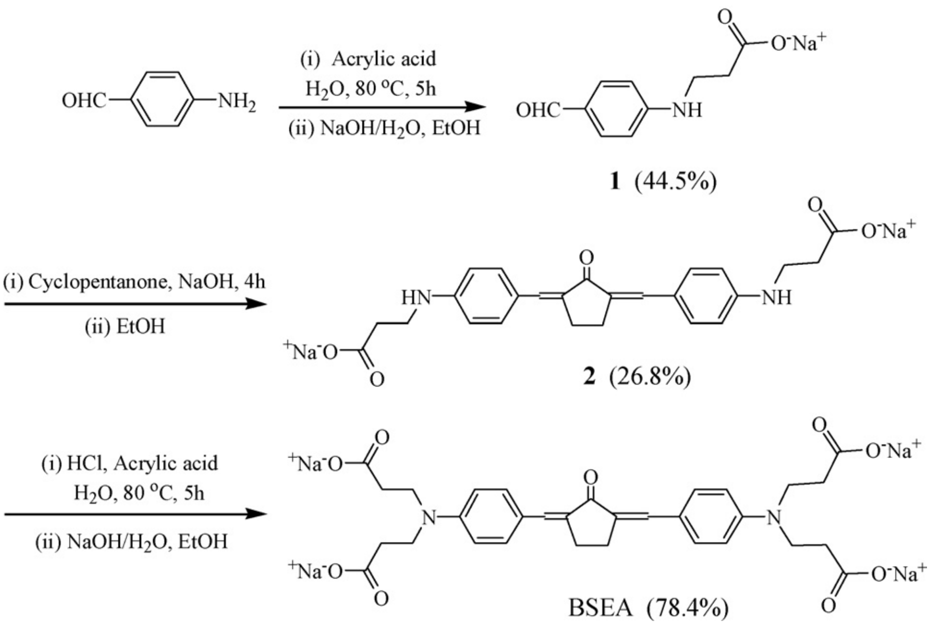
2.2. Methods

UV–vis spectra were recorded on a Jasco V-530 spectrophotometer. Steady-state fluorescence was performed at room temperature using Hitachi F-4500 spectrometer. Fluorescence quantum yields (Φ) were measured in diluted solutions (6×10^{-7} mol/L) using Rhodamine B in methanol as a standard ($\Phi = 0.7$) [14]. ^{1}H NMR spectra were obtained on a Bruker DPX 400 spectrometer. The HRMS analyses were carried out on a Bruker apex_IV_FT mass spectrometer. FTIR spectra were monitored on an Excalibur 3100 infrared spectrophotometer.

TPA cross-section (σ) values of compounds were determined using nonlinear transmission (NLT) method [15] and two-photon excited fluorescence (TPEF) method [16] with femtosecond laser. In NLT measurement, the light source is a regeneratively amplified Ti:sapphire system (Spitfire F-1K, 800 nm, 1 kHz, ~130 fs). Samples were dissolved in solvents with a concentration of 1×10^{-2} mol/L and filtered by 0.1 μm syringe filters. Pure solvent was used as reference to eliminate the attenuation influences from the cell windows and the solvent itself to transparent beam. The TPA coefficient β of the sample solution could be determined by Eq. (1). Furthermore, the TPA cross-section σ (in unite of cm^4 s/photon) of the sample was calculated by Eq. (2).

$$T = \frac{I(L)}{I_0} = \frac{\left[\ln(1 + I_0 L\beta)\right]}{I_0 L\beta} \qquad (1)$$

$$\beta = \frac{\sigma N_0}{h\nu} = \frac{\sigma N_A d \times 10^{-3}}{h\nu} \qquad (2)$$



Scheme 1. Synthetic routines of BSEA.

Here, I_0 is the incident intensity, $I(L)$ is the transparent intensity, L is the thickness of the sample cell, $h\nu$ is the energy of an incident photon, N_0 is the molecular density of sample, N_A is the Avogadro constant, d is the concentration of the sample solution. In TPEF measurement, the light source is a Tsunami mode-locked Ti: sapphire system (800 nm, 80 MHz, <130 fs). Up-converted fluorescence spectra are recorded by a fiber spectrometer (Ocean Optics USB2000 CCD). The concentration of sample is 5×10^{-5} mol/L. Rhodamine B in methanol solution (10^{-4} M) was used as reference. The TPA cross-section σ of sample is calculated by equation reported previously [10].

In TPP experiments, BSEA and eosin were used as photoinitiators, triethanolamine was used as coinitiator, monomer was water-soluble acrylate SR610, solvent was pure water (m_{SR610}:m_{H2O} = 4:1). The mixed photo-curable resins were poured onto glass substrate. The laser (Tsunami Ti: sapphire, 780 nm, 80 MHz, 80 fs) was tightly focused via an oil-immersion objective lens (100×, NA = 1.45, Olympus) into the sample which was fixed on a xyz-step motorized stage controlled by a computer. After laser fabrication, the unpolymerized resin was washed out by solvent. The obtained microstructures were characterized by SEM (Hitachi S-4300FEGd).

The same resins were used in one-photon polymerization experiments. A 532 nm laser was used as light source. Its intensity of irradiation was 40 mW/cm^2. The polymerization conversion efficiency was calculated by the change of the double bond absorption peak area at 6164 cm^{-1} in near-IR region.

The one-photon or two-photon polymerization process of these samples can be expressed as follows:

$$\text{Dye(BSEA or Eosin)} \xrightarrow{h\nu \text{ or } 2h\nu} \text{Dye}^*,$$

$$\text{Dye}^* + \text{TEOA} \rightarrow [\text{Dye}\ldots\text{TEOA}]^* \xrightarrow[(2)\text{–H}^+]{(1)\text{electron transfer}} \text{TEOA}^\bullet$$

$$\text{TEOA}^\bullet + \text{monomer} \rightarrow \text{polymer}$$

or

$$\text{Dye}^* + \text{RH (hydrogen donor)} \rightarrow [\text{Dye}\ldots\text{RH}]^* \xrightarrow{\text{hydrogen abstraction}} \text{R}^\bullet$$

$$\text{R}^\bullet + \text{monomer} \rightarrow \text{polymer}$$

Here, RH could be dye itself or monomer when no coinitiator.

3. Results and discussions

3.1. Synthesis and characterization

Scheme 1 provides the synthesis route of BSEA. Using a modified literature method, the reaction of 4-aminobenzaldehyde with acrylic acid afforded **1** in 44.5% yield. Due to the strong electron-withdrawing ability of aldehyde group at para-position, the nucleophilic addition reaction of amino group with acrylic

Table 1
One- and two-photon optical properties of BSEA in water and BDEA in DMF.

Compound	λ_{max}^{abs} (nm)	ε_{max}[a] (10^4 M^{-1} cm^{-1})	λ_{max}^{fl} (nm)	Φ[b]	$\Delta\nu$[c] (cm^{-1})	$\sigma_{800\,nm}$[d] (GM[f])	$\sigma_{800\,nm}$[e] (GM)
BSEA	513	5.4	642	0.0023	3916	287	–
BDEA	479.5	6.9	549	0.15	2640	604	1032
Eosin	516	8.8	537	0.205	758	–	13

[a] ε_{max} is molar absorption coefficient at λ_{max}^{abs}.
[b] Φ is fluorescence quantum yield.
[c] $\Delta\nu$ is stoke's shift.
[d] The TPA cross-section is determined by NLT method.
[e] The TPA cross-section is determined by TPEF technique.
[f] 1 GM = 10^{-50} cm^4 s/photon.

acid only happened one equivalent. When the aldol condensation reaction of **1** with cyclopentanone finished, the nucleophilicity of nitrogen increased. Thus, further addition reaction of **2** with acrylic acid provided target compound BSEA.

3.2. One photon optical properties

The UV–vis absorption spectra and steady-state fluorescence spectra of BSEA in water and BDEA in DMF are shown in Fig. 1. Their comprehensive photophysical characteristics are listed in Table 1. It is showed that both of two compounds present a strong intramolecular charge transfer (ICT) absorption band within 400–600 nm. Compared to BDEA, the absorption peak of BSEA exhibits a red-shift of 33 nm. It is interesting to notice that this phenomenon is contrary to another one reported by Bazan et al. In their experiment, a slight blue-shift was observed after water-soluble groups were introduced into distyrylbenzene chromophores [17]. They supposed this blue-shift was due to hydrophobic nature of conjugated backbone which might induce aggregation of optical unites in water and hydrogen bonding to the donor groups which could perturb the donor strength of nitrogen atom. We think their first viewpoint is reasonable. For a long hydrophobic backbone and centrosymmetric structure of their chromophores, the aggregation of optical unites is inevitable. However, for BSEA, its hycrophobic backbone is shorter and its structure is dissymmetric, so it is possible to avoid aggregation and dissolve in water homogeneously, exhibiting a positive solvatochromic effect.

The emission peak of BSEA also has a large red-shift of 93 nm compared to BDEA, together with a sharp decrease of fluorescence quantum yield from 0.15 for BDEA to only 0.0023 for BSEA. Obviously, the high polarity of water strengthens the ICT character of the D-π-A-π-D conjugated backbone in BSEA and relaxes its emission state.

3.3. TPA cross-sections

Fig. 2 shows the transmissivity of BSEA in water and BDEA in DMF versus the input laser beam intensity, respectively. The solid curves are given by fitting the corresponding experimental data with Eq. (1). The β value of BDEA is obtained as 0.14 cm/GW and then its σ is calculated as 604 GM. For BSEA, β and σ are determined as 0.07 cm/GM and 287 GM, respectively. Here the TPA cross-section of BSEA is lower compared to that of BDEA. The similar results had been reported by Bazan and co-workers [9,17]. A substantial decrease of σ in water was observed after water-soluble groups were introduced into chromophores. Bazan et al. suggested this decrease was due to aggregation or structure distortion of optical unites and hydrogen bonding to the donor groups based on their blue-shift spectra. However, in our experiment, the red-shift spectrum is incompatible with their viewpoint. It indicates that the exact mechanism is much more complicated than what we can deduce from obtained experimental data. Though the characters of the ground state and first exited state of molecules can be investigated clearly by linear optical properties, the characters of second and higher exited state are not clear at present stage, which may have crucial effects on TPA of most compounds. Thus, more efforts, including theoretic calculation, experimental method and equipment, are required on this field to disclose the exact mechanism.

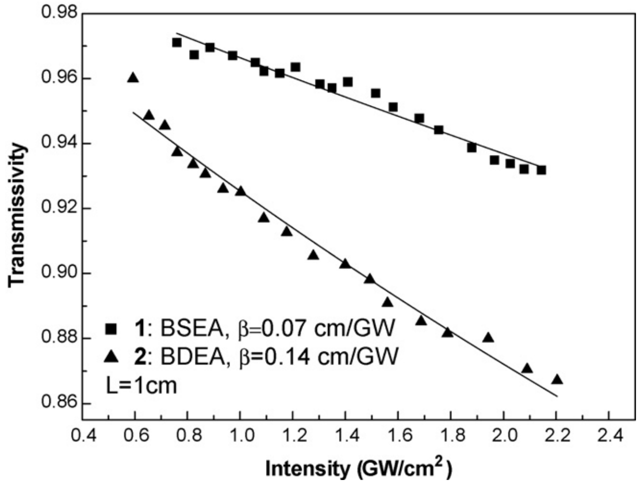


Fig. 2. Transmissivity of compounds' solutions *vs* the input laser beam intensity, the solid curves are given by fitting with Eq. (1).

For compare, we measured the TPA cross-section of eosin in water by NLT method. However, its NLT signal was very weak and almost covered by background noise signal. No exact datum can be fitted. Using TPEF method, the σ value of eosin was obtained as 13 GM, which was comparable to 10 GM reported by Campagnola et al. [8]. It is a pity that the TPA cross-section of BSEA cannot be measured by TPEF method for its very low fluorescence quantum yield. To ensure the comparability of σ values of compounds obtained by different methods, the TPA properties of BDEA was investigated by two methods. 1032 GM was measured by TPEF, while 604 GM was obtained by NLT. Considering the frequency of excitation resource in TPEF is 80 MHz, much higher than 1 KHz in NLT, the contribution from excitation state absorption to TPA cannot be eliminated in TPEF measurement. Thus, the discrepancy between the two data is reasonable and acceptable. Compared to eosin, the TPA cross-section of BSEA is quite larger.

3.4. Two-photon polymerization

BSEA and eosin were used as initiators to carry out TPP experiments. For comparison, five resins (R1-R5) with different components (listed in Table 2) were investigated. R1 and R2 contained 0.16% BSEA and eosin as initiators, respectively. R3 and R4 were added 1.6% TEOA as coinitiator based on R1 and R2. R5 was pure monomer and water. Using line scanning method [18], the TPP threshold energy (E_{th}) and the laser-induced breakdown threshold energy (E_{break}) of R1-R5 were determined. Here, E_{th} was defined by the lowest laser power at focus point that can fabricate a solid line with a line scan speed of 10 μm/s and E_{break} was defined by the

Table 2
Components of photo-curable resins used in TPP.

Resin	SR610 (wt%)	Water (wt%)	BSEA (wt%)	Eosin (wt%)	TEOA (wt%)	E_{th}[a] (mW)	E_{break}[b] (mW)	DPR[c]
R1	79.87	19.97	0.16	0	0	0.51	4.73	9.27
R2	79.87	19.97	0	0.16	0	2.15	4.73	2.2
R3	78.6	19.6	0.16	0	1.6	0.46	4.3	9.35
R4	78.6	19.6	0	0.16	1.6	1.51	–	–
R5	80	20	0	0	0	4.73	4.73	1

[a] TPP threshold energy.
[b] Laser-induced breakdown threshold energy.
[c] Dynamic power range of resins.

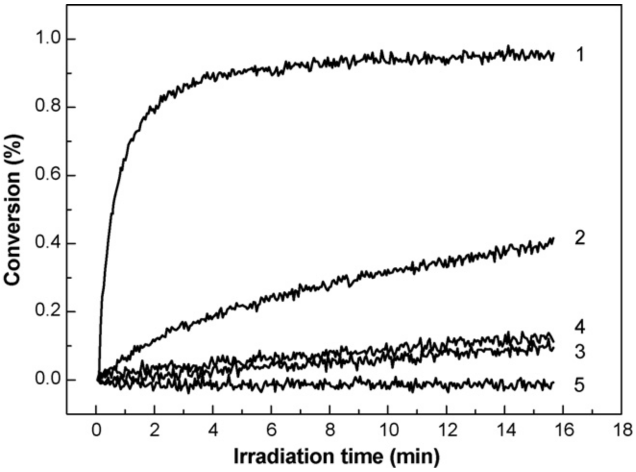


Fig. 3. Double-bond conversion rate *vs* irradiation time in one-photon polymerization. **1**: Eosin (0.016%) + TEOA (1.6 %); **2**: BSEA (0.016%) + TEOA (1.6 %); **3**: Eosin (0.08%); **4**: BSEA (0.08%); **5**: TEOA (1.6%).

lowest laser power at focus point that can induce intense damage to materials under the same scan speed. Both of E_{th} and E_{break} could be observed by CCD on live.

The experimental results are listed in Table 2. It is shown that the E_{th} of R1 is only 0.51 mW compared to 4.73 of R5, which indicates BSEA is a high efficient photoinitiator for TPP. In addition, the effect of BSEA is much better than that of eosin, whose E_{th} is 2.15 mW. After added TEOA as a coinitiator, the E_{th} of R3 only decreases 10%, while the E_{th} of R4 decreases 30%. Obviously, the matching between BSEA and TEOA is not as good as matching between eosin and TEOA. Even so, the E_{th} of R3 is still quite lower than that of R4. The E_{break} of R1, R2 and R5 are same, which means that the small amount of initiator has no visible effect on resins' anti-damage properties. The E_{break} of R3 decreases 9%. This may be due to the effect of TEOA. An interesting phenomenon is noticed that the E_{break} of R4 cannot be observed. The whole material of R4 would be solidified gradually during line scanning process, including exposed and unexposed areas. After careful analysis, we find it is due to the effect of the light resource of Olympus microscope. For observation by CCD on live, this light is always on during experiments. Its spectrum covers 400–700 nm. When exposed under this light for 5 min, R4 was solidified totally, while other resins had no visible change. This showed that the initiating efficiency of eosin plus TEOA under visible light is very high. To prove it, one-photon polymerization experiments were carried out. The results showed (Fig. 3) that the polymerization reaction of resin containing 0.016% eosin as initiator and 1.6% TEOA as coinitiator was certainly much faster than other four resins.

In our previous work [12], we reported that the polymerization of pure acrylate monomers could happen under irradiation of a focused 780 nm femtosecond laser beam and supposed it was due to avalanche ionization and thermal accumulation. However, here R5 (consisting of 80% SR610 and 20% water) did not polymerize under irradiation, only E_{break} was observed. It may be due to the high dielectric constant of water, which decreases the electron transfer within resins generated by avalanche ionization.

2D nanopatterns were fabricated in resins by changing the incident energy with a fixed line scan speed (10 μm/s). The polymerized lines were easily obtained by developing in water. It is shown (Fig. 4a) that incident energy have significant effects on the line width. A 3D woodpile (Fig. 4b) was fabricated using R1 with 0.8 mW and 110 μm/s scan speed. It indicates that BSEA can be used as a high sensitive photoinitiator directly in TPP.

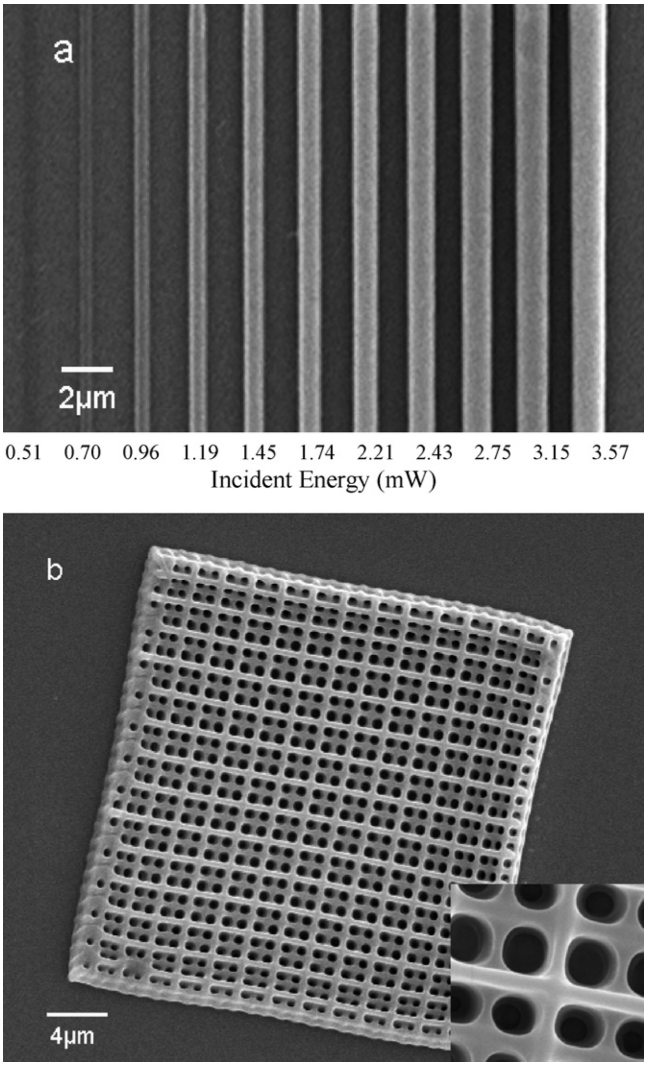


Fig. 4. 2D micropattern fabricated in R1 (a) by changing the incident energy with a fixed line scan speed of 10 μm/s; (b) 3D wood pile structure fabricated in R1 with 0.8 mW power and 110 μm/s scan speed.

4. Conclusion

A novel water-soluble benzylidene cyclopentanone dye BSEA was synthesized by a simple route. The linear optical spectra of BSEA showed a positive solvatochromic effect, indicating that its molecule could avoid aggregation and dissolve in water homogeneously. Compared to its prototype compound BDEA, the TPA cross-section of BSEA in water solution decreased more than 50%. However, it was still quite larger than TPA cross-section of water-soluble xanthene dyes. Using this new dye as initiator, two-photon polymerization of water-soluble acrylate could be induced directly. Low threshold energy of 0.51 mW and a high resolution of 400 nm were achieved, indicating this dye would have extensive application prospects in TPP under aqueous environments.

Acknowledgement

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