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# Two novel two-photon polymerization initiators with extensive application prospects

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## Abstract

Two novel two-photon polymerization initiators, 10-ethyl-3-E-(4-(N,N'-di-n-butylamino)styryl)phenothiazine **5** and 10-ethyl-3,7-E,E-bis(4-(N,N'-di-n-butylamino)styryl)phenothiazine **6**, have been efficiently synthesized with room temperature solid phase Wittig reaction. Two initiators were found to exhibit good single-photon fluorescence emission and their quantum yields, lifetimes and solvent effects have been studied in detail. Two-photon fluorescence spectra were investigated under 800 nm fs laser pulse and two-photon absorption (TPA) cross-sections of the initiators have been evaluated by theoretical calculation. Two-photon initiating polymerization microfabrication experiments have been carried out and artificial defects were made and polymerization mechanism was also discussed.

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## 1. Introduction

In the last century, the rapid development of semiconductor materials and devices made human obtain gigantic benefits from controlling and manipulating electrons. Compared with electrons, photons exhibit some special advantages. So many pioneers have proposed whether photons could be controlled like electrons? Until 1987, the concept of photonic band gap (BPG) was provided by John and Yablonovitch [1,2], which made people believe photons could be manipulated with some special materials, often referred to as photonic crystal (PC). That is a non-light-absorbing material with refractive index modulation at periodicities comparable to the optical wavelength, which influence the behavior of photons in an analogous manner to the influence of the crystal lattice on the behavior of electrons in semiconductors. In the past decades, PCs

have attracted considerable attention both in fundamental research and practical applications, such as light waveguides with low-losses [3], thresholdless lasers [4], high quality reflective lens at all directions [5], photonic switching, calculating and storing [6].

To our knowledge, numerous fabrication techniques, such as lithography [7], holography [8], self-assembly [9], lay-by-lay chemical vapor deposition [10], colloidal crystal growth [11], modulated photoeletrochemical etching [12] and two-photon microfabrication (TPMF) [13], have been utilized to make inorganic and organic PCs. In all these methods, TPMF specially attracted researchers eyes because of perfect spatial resolution and facile fabricating procedures. That two-photon absorption (TPA) probability depends quadratically on the excitation intensity makes photon-induced chemical reaction only happen in the focus with a volume of the order of the cube of the excitation wavelength ( $\lambda^3$ ) with tightly focusing an excitation beam. In addition, the longer wavelength excitation light (Vis-NIR) can easily permeate most of media without any damage. At

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present, Two-photon initiation polymerization (TPIP) is the most important approach of TPMF [14]. Two forms of TPIP have emerged: one approach involved traditional UV polymerization initiators and high power laser pulses to realize TPIP [15], another approach utilized high efficient initiators and common laser pulses to do that [13,16-18]. Considering of practical applying prospects, the latter should be advocated. However, the presently reported new efficient TPIP initiators are very limited and rather intricate synthesis steps were involved generally. It is very significant work to explore new structures and facile synthesis methods for TPIP initiators. In this study, we have described two novel TPIP initiators that were synthesized with simple operations and high yields, which possessed potentials in massive industrial manufacture in future.

## 2. Experimental

## 2.1. Materials and synthesis

All chemicals were available commercially and every solvent was purified as conventional methods before use. All synthesis processes and characterizations were described in detail in supporting information.

#### 2.2. Instruments and measurements

Microanalyses (C,H,N) were performed using a Perkin Elmer 240B elemental analyzer. IR spectra were obtained on a Nicolet NEXUS 870 spectrometer (KBr pellets). <sup>1</sup>HNMR spectra were obtained on a Bruker Advance/DMX 500 NMR spectrometer in CDCl<sub>3</sub> (TMS as internal standard). Mass spectrum was determined with a Micromass GCT-MS (EI source). Absorption spectra were recorded on a UV-265 spectrophotometer. The photoluminescence spectra were collected on a Perkin Elmer LS55 spectrofluorimeter. Two-photon fluorescence (TPF) spectra were measured using streak camera (C5680-01, Hamamatsu) and imaging spectrograph (C5094, Hamamatsu). The pump laser beam came from a mode-locked Ti:sapphire laser system operating at 800 nm, pulse duration 200 fs, repetition rate of 76 MHz (Coherent Mira900-D). The TPIP experiments were carried out on the same laser system. Cyclic voltammetry were carried out on EG & GPAR mode 283 electrochemical system. A platinum-disk working electrode, a platinum-wire auxiliary electrode, and an Ag/ AgCl reference electrode were used in a three-electrode configuration. The concentration of the samples in acetonitrile was 1.0 mmol/L and tetrabutylammonium perchlorate (0.1 mol/L) was used as supporting electrolyte with 50 mV/s scan speed.

#### 3. Results and discussion

### 3.1. Molecular designing and synthesis

The phenothiazine and its derivatives were studied extensively for their excellent photoelectric functions [19]. Based on molecular designing consideration, the phenothiazinyl was introduced to our target molecules according to our synthesis route (Scheme 1). Due to relatively high chemical sensitivity of hydrogen on 10-position N atom of phenothiazine, ethylation reaction assured success of the following derivative steps and, meanwhile, increased charge intensity of the target molecules. Then Vilsmeier reaction was used to introduce active functional groups, formyls, at 3- or/and 6-position of 10-ethylphenothiazine. Molecular  $\pi$ -electron conjugated system was enlarged by forming -CH=CH- with Wittig reaction. [4-(N,N-di-n-butylamino)benzyl]triphenylphosphonium iodide was selected as phosphonium salt because of strong electron-donating ability and good solubility in most organic solvents of 4-(N,N-di-n-butylamino)benzyl moiety.

Similar *N*-alkylation reaction could be carried out under many conditions [20]. In our experiment, common reagents and facile operations were involved, meanwhile, high yield (92%) of **1** was acquired. We have done many experiments of Vilsmeier single- and doubleformylation reactions in different conditions and, at last, the 10-ethylphenothiazine can be quantificationally



Scheme 1. Strategy of synthesis of the target compounds.

translated to 2 or 3. In CHCl<sub>3</sub> reaction solvent, the yield of 10-ethyl-3-formylphenothiazine 2 is as high as 97%, and the yield of 10-ethyl-3,7-biformylphenothiazine 3 is 91% in N,N-dimethyl formamide (DMF). Compared with analogous literatures [21], our synthesis approach is high efficient and facile, no rigorous experimental conditions, no expensive reaction reagents and no separation with column chromatography. [4-(N,N-di-nbutylamino)benzyl]triphenylphosphonium iodide 4 was prepared by one pot reaction [22], which is di-n-butylaniline, formaldehyde, potassium iodide, triphenyl phosphine and reaction solvents placed together in a sealed reaction container and stirred at room temperature for a few days.

The Wittig reactions were carried out under a few reaction systems, such as NaOH/CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>ONa/ C<sub>2</sub>H<sub>5</sub>OH, (CH<sub>3</sub>)<sub>3</sub>COK/THF, (CH<sub>3</sub>)<sub>3</sub>COK/(CH<sub>3</sub>)<sub>3</sub>COH, (CH<sub>3</sub>)<sub>3</sub>COK/DMF, NaH/THF, NaOH/solvent-free. Synthetically considering reaction conditions, reagents, purification processes and yields, the room temperature solid phase reaction was selected as the optimal synthesis route. As we known, room temperature solid phase Wittig reaction was utilized at the first time [23], which agrees with the principles of 'green chemistry' [24]. Aldehyde 2 or 3, phosphonium salt 4 and NaOH were placed in a dry mortar and manually milled for several minutes. Obvious change of reaction mixture exhibited occurrence of the reaction and the reaction process was investigated with TLC. The resulting mixture was added into water and effectively extracted by petroleum ether, in which the products (10-ethyl-3-E-(4-(N,N'-di-n-butylamino)styryl) phenothiazine 5 and 10-ethyl-3,7-E,E-bis (4-(N,N'-di-n-butylamino)styryl) pheno thiazine 6) possess good solubility.

## 3.2. Single-photon and two-photon fluorescence

During synthesis and dealing process, our target compounds were found to emit strong fluorescence in nature light although all starting materials have not. The acetone solution and solid phase of 5 and 6 were irradiated with 365.0 nm ultraviolet light and bright green yellow fluorescence was observed from both solid and solution (Fig. 1). The data of their single-photon fluo-



Fig. 1. Solution (a) and solid (b) luminescent photographs of target compounds **5** and **6** under 365.0 nm ultraviolet irradiance.

rescent (SPF) and absorption spectra in eight different solvents were collected (Table 1) and the influence of solvent on fluorophore was discussed with Lippert equation [25]. The results indicated that the fluorescence of the compounds were tightly related to solvent polarity and another fact was proved, which is the compounds possessed highly delocalized conjugated system. Quantum yields ( $\Phi$ ) of **5** and **6** were determined with reference method [26] and experimental results revealed that all quantum yields were bigger than 60% (Table 1). Meanwhile, SPF lifetimes ( $\tau$ ) in five solvents were measured on the Edinburgh FLS920 fluorometer with a Hydrogen flash lamp (pulse duration <1 ns) and radiative kinetic constants ( $K_r$ ) and nonradiative kinetic constants ( $K_{nr}$ ) were calculated.

Two-photon fluorescence (TPF) spectra of 5 and 6 in three solvents with  $5.0 \times 10^{-3}$  moL/L concentrations were recorded on Ti: sapphire laser at 800 nm with 200 fs pulse width and 76 MHz frequency (Table 1 and Fig. 2). The squared dependence of induced fluorescence power and incident laser intensity was observed and the log-log plot of the fluorescence signal vs. excited light power provided direct evidence for two-photon excited process (the inset of Fig. 2) [27]. However, with the increasing of incident irradiances, the power of emitting fluorescence deviated from the second-order power law and decreased gradually. This deviation may be attributed to some other nonlinear optical processes, such as stimulated emission [28], excited-state absorption [29] and ground-state depletion [30]. TPA cross-sections ( $\sigma$ ) of 5 and 6 were evaluated based on the two-state model [31]. The state dipoles and transition dipole moments were obtained with ZINDO programme and were directly used in the calculations. Assuming 800 nm linear polarized light was used, the calculated  $\sigma$  values of 5 and 6 are 646.74 and  $418.09 \times 10^{-50}$  cm<sup>4</sup> s photon<sup>-1</sup>, respectively, which indicated both compounds exhibited strong TPA at 800 nm laser pulses.

## 3.3. Two-photon initiating polymerization microfabrication

In our TPIP experiments, three-dimensional crosslinked woodpile periodic microstructures were fabricated with negative resins system, which contained oligomer (bisphenyl A epoxide dimethylacrylate) and 0.5% compound **5** or **6** as initiator and a little 1,2-dichloroethane (increasing the compatibility and controlling the viscosity). The same mode-locked Ti: sapphire laser that was used in the TPF measurements was utilized for TPMF at 800 nm. The laser was tightly focused via an objective lens ( $50 \times$ , NA = 0.45), and the focal point was modulated in the gel resin that is on a *xyz*-step monitorized stage controlled by computer. The pulse energy after being focused by the objective lens was ~20 mW. The polymerization results were observed

Table 1						
The date of absorption spectra,	SPF	and	TPF	with	solvent	effects

Solvent	$\lambda_{abs-max}$ (nm)	$\lambda_{\text{em-max}}$ (nm)	$\Phi$	$\tau$ (ns)	$K_{\rm r}  imes 10^8 ~({ m s}^{-1})$	$K_{\rm nr}  imes 10^8 ~({ m s}^{-1})$	$\lambda_{em}$ of TPF
Benzene	382 <sup>a</sup>	463	0.68	0.97	7.01	3.30	
	402	491	0.70	1.35	5.19	2.22	
Toluene	381	460	0.65				
	401	488	0.67				
Benzyl alcohol	382	468	0.61	2.15	2.84	1.81	489
2	402	494	0.63	1.73	3.64	2.14	503
CH <sub>2</sub> Cl <sub>2</sub>	383	472	0.69	1.20	5.75	2.58	480
	402	496	0.70	1.42	4.93	2.11	498
DMF	386	477	0.72	1.68	4.29	1.67	488
	403	499	0.74	1.65	4.48	1.58	502
Acetone	388	479	0.67				
	398	493	0.67				
Ethanol	378	467	0.68	1.44	4.72	2.22	
	399	496	0.69	1.54	4.48	2.01	
Methanol	379	471	0.66				
	400	498	0.65				

<sup>a</sup> In every grid, the up is the data of **5** and the down is the data of **6**.



Fig. 2. TPF spectra of **5** and **6** in DMF; the inset is Log–Log linear of squared dependence of induced fluorescence signal and incident irradiance intensity.

with a polarization microscope (Opton, Germany) and the photographs of microstructures were shown in Fig. 3.

Fig. 3a show a  $1.0 \times 1.0$  mm polymerization region with three layers stereo structure. The distance of every two neighboring polymerization streaks is 10.0 µm. The polymerization reaction did not take place in the part out of the laser focus, where could be easily washed out by tetrahydrofuran. The polymerization solid skeletons are uniform and orderly and the width is about 3 µm (the inset of Fig. 3a). The microstructures could keep stability for a long time under normal condition and no volume shrinkage and distortion happened. The possible reason was that polymerization reaction in the skeletons was very complete and the inner structure was compact and rigid. To investigate the influence of oligomer on



Fig. 3. Micrographs of microstructures fabricated via TPIP with the novel initiators. The size of every grid is  $10.0 \times 10.0 \ \mu$ m.

TPIP reaction, methyl methylacrylate was selected as monomer. Experimental results revealed our novel initiators also could effectively realize TPIP in this resin (Fig. 3b). In order to further explore the fabrication of practical devices, we designed and introduced defects for the functional microstructures. Fig. 3c showed that a simple defect was introduced successfully, which contented the microfabrication requirements of applied devices.

The TPIP mechanisms of these novel initiators are still unclear. According to Cumpston et al. [13], the strong donor substituents on molecular conjugated system make the electron very rich in the molecule, and after one- or two-photon photoexcitation these chromophores would be able to transfer an electron even to relatively weak acceptors, and this process could be used to activate various chemical reactions, such as polymerization. In 5 and 6, heterocycle phenothiazine moiety possessed relative high electron density, and the conjugation systems were enlarged with Wittig reactions, furthermore, one and two strong donor group (N,N'-di-*n*-butylamino) were connected to conjugated system, respectively. So, the initiators possessed very rich electron, which was verified by cyclic voltammetry. The experimental results indicated that the ground-state oxidation potentials of 5 and 6 are -63.62 and -156.24mV (relative to phenothiazinium/phenothiazine). As the initiators possessed big TPA cross-sections, which were evaluated in the front, the two-photon-induced electron transfer should be efficient. So, it is possible that the microstructures were fabricated by free radical type polymerization reaction. The systematic study of the 3D microfabrication with the novel initiators was in progress.

In conclusion, two novel TPIP initiators were designed and prepared with facile operations and high yields. The whole synthesis process, including the use of room temperature solid phase Wittig reaction, agreed with the green chemistry requirements and possessed extensively practical value. The single-photon fluorescence quantum yields, lifetimes, solvent effects of the initiators were studied in detail and both compounds exhibited big delocalized  $\pi$ -electron conjugated system. Theoretical calculation has indicated that the initiators had large TPA cross-section. The primary microfabrication experiments have been carried out and artificial defects were introduced effectively. Our results provided a valuable reference for further study in designing and synthesis of new TPIP initiators or strong TPA chromophores.

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#### References

- [1] E. Yablonovitch, Phys. Rev. Lett. 58 (1987) 2059.
- [2] S. John, Phys. Rev. Lett. 58 (1987) 2486.
- [3] J.D. Joannopoulos, P.R. Villeneuve, S. Fan, Nature 386 (1997) 143.
- [4] S. Noda, M. Yokoyama, M. Imada, A. Chutinan, M. Mochizuki, Science 293 (2001) 1123.
- [5] Y. Fink, J.N. Winn, S. Fan, C. Chen, J. Michel, J.D. Joannopoulos, E.L. Thomas, Science 282 (1998) 1679.
- [6] J.Y. Cheng, C.A. Ross, V.Z.H. Chan, E.L. Thomas, R.G.H. Lammertink, G.J. Vancso, Adv. Mater. 13 (2001) 1174.
- [7] Y. Wang, Y.C. Chang, Adv. Mater. 15 (2003) 290.
- [8] M. Campbell, D.N. Sharp, M.T. Harrison, R.G. Denning, A.J. Turberfield, Nature 404 (2000) 53.
- [9] Y.A. Vlasov, X.Z. Bo, J.C. Sturm, D.J. Norris, Nature 414 (2001) 289.
- [10] E. Yablonovitch, Science 289 (2000) 557.
- [11] D. Wang, F. Caruso, Adv. Mater. 15 (2003) 205.
- [12] J. Schilling, S. Matthias, F. Müller, R.B. Wehrspohn, K. Busch, Appl. Phys. Lett. 78 (2001) 1180.
- [13] B.H. Cumpston, S.P. Ananthavel, S. Barlow, D.L. Dyer, J.E. Ehrlieh, L.L. Erskine, A.A. Helkal, S.M. Kuebler, I.Y.S. Lee, D. McCord-Maughon, J.Q. Qin, H. Röckel, M. Rumi, X.L. Wu, S.R. Marder, J.W. Perry, Nature 398 (1999) 51.
- [14] S. Kawata, H.B. Sun, T. Tanaka, K. Takada, Nature 412 (2001) 697.
- [15] K.D. Belfield, X.B. Ren, E.W.V. Stryland, D.J. Hagan, V. Dubikovsky, E. Miesak, J. Am. Chem. Soc. 122 (2000) 1217.
- [16] C. Martineau, R. Anmian, C. Andraud, I. Wang, M. Bouriau, P.L. Baldeck, Chem. Phys. Lett. 362 (2002) 291.
- [17] T. Watanabe, M. Akiyama, K. Totani, S.M. Kuebler, F. Stellacci, W. Wenseleers, K. Braun, S.R. Marder, J.W. Perry, Adv. Funct. Mater. 12 (2002) 611.
- [18] Y. Ren, X.Q. Yu, D.J. Zhang, D. Wang, M.L. Zhang, G.B. Xu, X. Zhao, Y.P. Tian, Z.S. Shao, M.H. Jiang, J. Mater. Chem. 12 (2002) 3431.
- [19] A. Stockmann, J. Kurzawa, N. Fritz, N. Acar, S. Schneider, J. Daub, R. Engl, T. Clark, J. Phys. Chem. A 106 (2002) 7958.
- [20] A. Bombrun, G. Casi, Tetrahedron Lett. 43 (2002) 2187.
- [21] S. Maruyama, X.T. Tao, H. Hokari, T. Noh, Y.D. Zhang, T. Wada, H. Sasabe, H. Suzuki, T. Watanabe, S. Miyata, J. Mater. Chem. 9 (1999) 893.
- [22] H. Bredereck, G. Simchen, W. Griebenow, Chem. Ber. 106 (1973) 3732.
- [23] V.P. Balema, J.W. Wiench, M. Pruski, V.K. Pecharsky, J. Am. Chem. Soc. 124 (2002) 6244.
- [24] P.T. Anastas, J.C. Warner, Green Chemistry, Theory and Practice, Oxford University Press, Oxford, 1998.
- [25] V.E.Z. Lippert, Electrochem. 61 (1957) 962.
- [26] J.N. Demas, G.A. Crosby, J. Phys. Chem. 75 (1971) 991.
- [27] C. Xu, W.W. Webb, J. Opt. Soc. Am. B 13 (1996) 481.
- [28] J. Kusba, V. Bogdanov, I. Grycznski, J.R. Lakowicz, Biophys. J. 67 (1994) 2024.
- [29] D.J. Bradley, M.H.R. Hutchinson, H. Koetser, T. Morrow, G.H.C. New, M.S. Petty, Proc. R. Soc. London A 328 (1972) 97.
- [30] C. Xu, W. Zipfel, J.B. Shear, R.M. Williams, W.W. Webb, Proc. Natl. Acad. Sci. USA 93 (1996) 10763.
- [31] P. Macak, Y. Luo, H. Ågren, J. Chem. Phys. 114 (2001) 9813.