Design of high efficiency for two-photon polymerization initiator: combination of radical stabilization and large two-photon cross-section achieved by *N*-benzyl 3,6-bis(phenylethynyl)carbazole derivatives

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Novel A–π–D–π–A V-shaped 3,6-bis(phenylethynyl)carbazole based chromophores were designed and synthesized as two-photon polymerization (TPP) initiators combining a large two-photon absorption cross-section with facilitated radical formation. 9-Benzyl-3,6-bis(4-nitrophenylethynyl)carbazole (**4d**) shows a strong two-photon absorption around 800 nm and exhibits very high two-photon polymerization initiating sensitivity with a threshold power of 0.8 mW at the concentration of 0.18 mol%, which is much lower than the threshold power of 6.37 mW found for benzil. The corresponding threshold of laser exposure intensity for TPP is 3.0×10^7 mJ cm^{-2}. The lowest loading of **4d** is up to 0.012 mol% with a threshold power of 3.2 mW.

1. Introduction

In the past decade, three dimensional (3D) micro-fabrication based on two-photon photopolymerization (TPP), as one of the most important applications of two-photon absorption (TPA), has been attracting great interest for its various applications to micro-electromechanical systems (MEMS), 3D optical integrated circuits and so on.[1–6] Most work in this field has involved commercial photoresist resins using conventional ultraviolet (UV) active initiators. However, the conventional initiators typically have low TPA cross-sections (δ_{TPA}), which result in low two-photon sensitivity.[7] Thus, high excitation power and long exposure time are needed to cure the resin, which often result in damage to the structure.[7,8] The disadvantages of the conventional photoinitiator limit the versatility of three dimensional lithographic micro-fabrication (3DLM) and its scope for widespread application. Developing high-sensitivity initiators is necessary to make the process more reliable and allow structures to be patterned rapidly.[9,10]

There are three ways to improve the sensitivity of two-photon initiator (TPI) systems. The first one is to improve the δ_{TPA} of initiators by extending the conjugate system (Type I),[9–14] which is the common way to improve TPI sensitivity. Some principles for designing TPA materials have been established. Prasad *et al.*[15–17] have pointed out that one dimensional (1D) D–π–A type molecules containing fluorene or dithienothiophene as the rigid π-conjugated backbone have large δ_{TPA}. Marder *et al.*[18,19] have demonstrated that symmetric stilbenes containing donor (D) or acceptor (A) groups linked by a π-conjugate bridge (D–π–D or A–π–A) exhibit large δ_{TPA}. The molecules with D–π–A–π–D and A–π–D–π–A structures are also characterized by large δ_{TPA}. The second one is to optimize two component systems by changing coinitiators with known two-photon initiators (Type II).[12,20] The third one is to fix a coinitiator unit, such as a sulfonium salt, into a large TPA cross-section chromophore (Type III).[9,10] The last one would become the promising route for novel TPI since this kind of photoinitiator are strong two-photon absorbers and efficient initiators.

N,*N*-Disubstituted aniline moieties are widely used in TPA chromphores, and *N*,*N*-dimethylaniline derivatives can act as highly efficient coinitiators for one-photon and two-photon photopolymerization.[20] So the substituents play a key role in radical formation at the initiating stage, and a more stable amine may contribute to higher initiating sensitivity. Meanwhile, the charge-transfer (CT) state of a D–π–A molecule can be directly produced by TPA[21] and radicals can be produced in A-π–D–π–A C_{2v} organic salts for intramolecular change transfer (ICT),[22] which may contribute to highly efficient radical production. Here, by introducing i) a carbon–carbon triple bond to improve the TPA cross-section,[23,24] ii) a carbazole moiety as a coinitiator unit, iii) an alkyl or benzyl group for radical stabilization into an A–π–D–π–A V-shaped molecule, we designed a series of novel Type III initiators, rigid A–π–D–π–A V-shaped 3,6-bis(4-nitro/carbonyl-phenylethynyl)carbazole derivatives (**4a–d**), in which the carbazole moiety acts as a donor, phenylacetylenyl as a conjugate linker and the nitro/carbonyl group as an acceptor. Furthermore, we investigated one-photon/two-photon properties of the chromophores, and evaluated the threshold power and the polymerization rate for TPP. High two-photon polymerization initiating sensitivity was characterized for these novel photoinitiators by TPP experiments, owing to their large δ_{TPA} and

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low fluorescence yield. The proposed concept of molecular design here should provide a new direction for developing TPP initiators with high initiating efficiency.

2. Experimental

2.1 Materials

1,1-Dimethyl-2-butyn-1-ol and 4-bromobenzaldehyde were commercially available from Acros Organics. Dimethylformamide (DMF), sodium hydride (60% in mineral oil, NaH), 9*H*-carbazole, triethylamine, sodium hydroxide (NaOH), copper iodine (CuI), triethylamine, triphenylphosphine, palladium chloride ($PdCl_2$), lithium chloride (LiCl), sodium, benzophenone and 4-bromonitrobenzene were purchased from Beijing Chemical Reagent Company. $Pd(PPh_3)_2Cl_2$[25] and 3,6-dibromo-9-pentyl(benzyl)carbazole[26] were synthesized using literature procedures. Toluene and THF were dried over Na and freshly distilled before use. Triethylamine was dried over calcium hydride and freshly distilled before use. Other solvents were used as received without further purification. Dipentaerythritol hexaacrylate (DEP-6A, trade name: Light Acrylate DEP-6A) was obtained from Kyoeisha Chemical Co., Ltd., Japan.

2.2 Physical measurements

^1H NMR and ^{13}C NMR spectra were recorded on a Varian Jemini-300/Bruker-400 spectrometer and all shifts are referenced to TMS. Mass spectra were measured on a ZAB-HS (Micromass, UK). UV-Visible spectra were recorded at the concentration of 1×10^{-5} M on a UV 3100PC Scanning Spectrophotometer (Shimadzu, Japan). Infrared spectra were recorded on a FT/IR-410 spectrophotometer (JASCO Corp.) Fluorescence spectra were recorded at the concentrations of 1×10^{-6} M on a RF5300PC spectrofluorophotometer (Shimadzu, Japan) with coumarin 307 in acetonitrile as a reference standard ($\Phi_f = 0.58$).[27,28] TPA spectra were obtained by the two-photon-induced excited fluorescence (TPEF) method reported by Xu and Webb,[29] TPEF spectra were recorded on a SD2000 spectrometer (Ocean Optical) with the excitation by a mode-locked Ti-sapphire femtosecond laser (Tsunami, Spectra-Physics) for which the oscillating wavelength, pulse width and repetition rate were 780 nm, 80 fs and 82 MHz, respectively. It is assumed that the fluorescence quantum yield after two-photon excitation is the same as that after one-photon excitation. Then TPA cross-sections were obtained by calibration against fluoroscein in aqueous NaOH solution (pH 11) for the femtosecond measurements.[29]

2.3 Two-photon photopolymerization

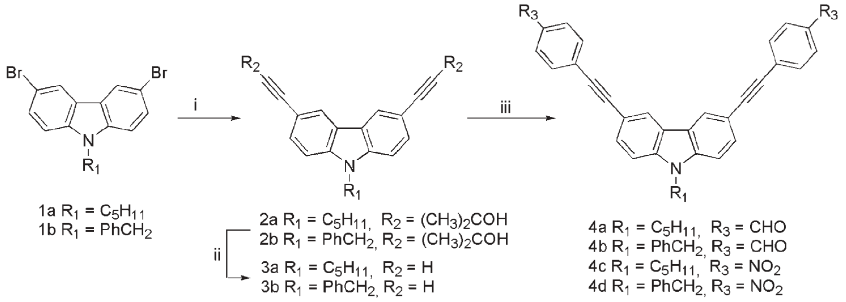
TPP experiments were performed with the irradiation of 80 fs pulses from a mode-locked Ti-sapphire femtosecond laser (Tsunami, Spectra-Physics) with a repetition rate of 80 MHz and wavelength at 800 nm. The photoresist resins were prepared by mixing methylacrylic acid (MAA) as monomer, DEP-6A as cross-linker and dyes **4a–d** as photoinitiators. In the control experiment, commercially available benzil was used as initiator. The lasing source was tightly focused by a 60 × oil-immersion objective lens with a high numerical aperture (N.A. = 1.42, Olympus). The focal point was focused on the liquid photopolymerizable resin which was placed on a cover glass above the *xyz*-step motorized stage controlled by a computer. After laser fabrication, the unpolymerized resins were washed out with ethanol. The images of fabricated lines were observed using a field-emission scanning electron microscope (FE-SEM, JOEL, JSM-6330F).

2.4 Synthesis

Chromophores **4a–d** were synthesized in a facile way by Sonogashira coupling reactions[30] starting from 3,6-dibromocarbazole and 4-bromobenzaldehyde/4-bromonitrobenzene, as shown in Scheme 1.

Synthesis of 1a–b. To a flask containing NaH (60% in mineral oil, 2.00 g, 50 mmol) in DMF (20 mL), a solution of 3,6-dibromo-9-H-carbazole (13.00 g, 40 mmol) in DMF (80 mL) was added dropwise; after one hour, 1-bromopentane (5.4 mL, 40 mmol) was added slowly. The resulting suspension was stirred for another 6 h and carefully poured into water. After filtration and washing with 95% ethanol (2×30 mL), 3,6-dibromo-9-pentyl-carbazole (**1a**) was obtained as a grey solid, yield: 94%. Mp 75–76 °C. ^1H NMR (300 MHz, $CDCl_3$, δ (ppm)): 0.87 (t, 3 H, $J = 6.9$ Hz), 1.33 (m, 4 H), 1.84 (m, 2 H), 4.25 (t, 2 H, $J = 6.9$ Hz), 7.28 (d, 2 H, $J = 8.3$ Hz), 7.55 (d, 2 H, $J = 8.3$ Hz), 8.15 (s, 2 H).

3,6-Dibromo-9-benzyl-carbazole (**1b**): the same procedure as **1a**, yield: 91%. Mp 162–163 °C. ^1H NMR (300 MHz,



Reagents and conditions: i) $Pd(PPh_3)_2Cl_2$, CuI / Et_3N, 1,1-dimethyl-2-butyn-1-ol;
ii) NaOH / toluene; iii) $Pd(PPh_3)_2Cl_2$, CuI / Et_3N, p-substituted bromobenzene.

Scheme 1 Synthetic route of **4a–d**.

$CDCl_3$, δ (ppm)): 5.47 (s, 2 H), 7.07 (m, 2 H), 7.25 (m, 5 H), 7.53 (m, 2 H), 8.18 (s, 2 H).

Synthesis of 2a–b. To a 250 mL three-necked flask, 3,6-dibromo-9-pentyl-carbazole (**1a**) (3.120 g, 8.0 mmol), CuI (76 mg, 0.4 mmol), $PdCl_2(PPh_3)_2$ (140 mg, 0.2 mmol), PPh_3 (104 mg, 0.4 mol), 1,1-dimethyl-2-butyn-1-ol (2.50 mL, 30 mmol) and triethyl amine (100 mL) were added and bubbled with N_2 for 10 min. The resulting mixture was allowed to reflux for 24 h. After cooling, the solvent was removed. The residue was poured into water and extracted with ethyl acetate (3 × 50 mL). Organic layers were combined, dried over $MgSO_4$, concentrated and purified by flash column chromatography using ethyl acetate–petroleum ether (1 : 3 v/v) as eluent to give a pale yellow oil.

3,6-Bis(3,3-dimethyl-3-hydroxy-1-butynyl)-9-pentyl-carbazole (**2a**), yield: 82%. ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 0.86 (t, 3 H, J = 6.6 Hz), 1.30 (m, 4 H), 1.68 (s, 12H), 1.81 (m, 2 H), 2.37 (bs, 2 H), 4.21 (t, 2 H, J = 6.9 Hz), 7.28 (d, 2 H, J = 8.4 Hz), 7.52 (d, 2 H, J = 8.4 Hz), 8.11 (s, 2 H).

3,6-Bis(3,3-dimethyl-3-hydroxy-1-butynyl)-9-benzyl-carbazole (**2b**), yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 1.87 (s, 12 H), 2.13 (s, 2 H), 5.47 (s, 2 H), 7.07 (m, 2 H), 7.25 (m, 5 H), 7.48 (d, 2 H, J = 8.4 Hz), 8.16 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, δ (ppm)): 31.7, 46.7, 65.8, 83.0, 92.3, 109.1, 110.0,113.8, 122.5, 124.2, 126.3, 127.7, 128.9, 129.9, 136.3, 140.6.

Synthesis of 3a–b. To a solution of 3,6-bis(3-methyl-3-hydroxy-1-butynyl)-9-pentyl-carbazole (**2a**) (2.58 g, 6.4 mmol) in toluene (60 mL), was added sodium hydroxide (3.10 g, 77.5 mmol). Then the resulting mixture was refluxed overnight. After filtration and concentration, the dark brown residue was purified by flash column chromatography using ethyl acetate–petroleum ether (1 : 9–1 : 20 v/v) to give a light yellow oil.

3,6-Diethynyl-9-pentyl-carbazole (**3a**), yield: 62%, ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 0.88 (t, 3 H, J = 6.6 Hz), 1.34 (m, 4 H), 1.84 (m, 2 H), 3.1 (s, 2 H), 4.24 (t, 2 H, J = 7.2 Hz), 7.32 (d, 2 H, J = 8.4 Hz), 7.62 (d, 2 H, J = 8.4 Hz), 8.22 (s, 2 H).

3,6-Diethynyl-9-benzyl-carbazole (**3b**), yield: 81%, ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 3.09 (s, 2 H), 5.50 (s, 2 H), 7.10 (m, 2 H), 7.28 (m, 3 H), 7.30 (d, 2 H, J = 8.4 Hz), 7.58 (d, 2 H, J = 8.4 Hz), 8.25 (s, 2 H).

Synthesis of 4a–d. To a 50 mL three-necked flask, 3,6-diethynyl-9-pentyl-carbazole (**3a**) (577 mg, 2.0 mmol), CuI (19 mg, 0.1 mmol), $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol), PPh_3 (26 mg, 0.1 mol), 4-bromobenzaldehyde (1.11 g, 6.0 mmol) and triethyl amine (30 mL) were added and bubbled with N_2 for 10 min. The resulting mixture was allowed to reflux for 20 h. After cooling, the solvent was removed. The residue was poured into water and extracted with chloroform (3 × 30 mL). Organic layers were combined, dried over $MgSO_4$, concentrated and purified by flash column chromatography using chloroform–petroleum ether (1 : 3 v/v) as eluent to give **4a** as a yellow powder (653 mg, 65% yield).

3,6-Bis[2-(4-carbonylphenyl)ethynyl]-9-pentyl-carbazole (**4a**), yield: 65%. Mp 197–198 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 0.90 (t, J = 6.3 Hz, 3 H), 1.38 (m, 4 H), 1.91 (m, 2 H), 4.33 (t, J = 7.2 Hz, 2 H), 7.43 (d, J = 8.4 Hz, 2 H), 7.69 (d, J = 8.4 Hz, 2 H), 7.72 (d, J = 7.8 Hz, 4 H), 7.90 (d, J = 7.8 Hz, 4 H), 8.33 (s, 2 H), 10.04 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, δ (ppm)): 13.9, 22.4, 28.7, 29.4, 43.4, 87.5, 95, 109.2, 109.5, 113.3, 122.5, 124.5, 129.6, 130.0, 130.2, 131.0, 131.9, 132.7, 135.1, 140.8, 191.4; IR (KBr, cm^{-1}): 2965, 2927, 2202, 1694, 1592,1482, 1205, 826; HRMS ($C_{35}H_{27}NO_2$): Calcd.: 493.20418; Obsd.: 493.20491 (1.5 ppm).

3,6-Bis[2-(4-carbonylphenyl)ethynyl]-9-benzyl-carbazole (**4b**), yield: 53%. Mp 244–245 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 5.55 (s, 2H), 7.15 (m, 2H), 7.29 (m, 3H), 7.39 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.1 Hz, 4H), 7.88 (d, J = 8.1 Hz, 4H), 8.36 (s, 2H), 10.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ (ppm)): 46.9, 87.5, 94.7, 109.4, 113.7, 122.6, 124.4, 126.2, 127.8, 128.9, 129.5, 130.0, 130.1, 135.0, 135.9, 140.9, 191.2; IR (KBr, cm^{-1}): 2834, 2738, 2201, 1695, 1592, 1479, 1208, 830, 728; HRMS ($C_{37}H_{23}NO_2$): Calcd.: 513.17288; Obsd.: 513.17344 (1.1 ppm).

3,6-Bis[2-(4-nitrophenyl)ethynyl]-9-pentyl-carbazole (**4c**), yield: 68%. Mp 202–204 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 0.90 (t, J = 6.6 Hz, 3 H), 1.38 (m, 4 H), 1.90 (m, 2 H), 4.32 (t, 2 H, J = 7.1 Hz), 7.41 (d, J = 8.7 Hz, 2 H), 7.67 (d, J = 9.0 Hz, 6 H), 8.22 (d, J = 9.0 Hz, 4 H), 8.32 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm)): 13.9, 22.4, 28.7, 29.4, 46.0, 86.7, 96.3, 109.4, 112.9, 122.5, 123.7, 124.7, 130.1, 130.8, 132.0, 141.0, 146.7; IR (KBr, cm^{-1}): 2962, 2922, 2201, 1585, 1512, 1339, 1105, 854, 749; HRMS ($C_{27}H_{25}N_3O_4$): Calcd.: 527.18451; Obsd.: 527.18474 (0.4 ppm).

3,6-Bis[2-(4-nitrophenyl)ethynyl]-9-benzyl-carbazole (**4d**), yield: 77%. Mp 258–261 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 5.57 (s, 2H), 7.15 (m, 2H), 7.32 (m, 3H), 7.41 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.9 Hz, 4H), 7.88 (d, J = 8.9 Hz, 4H), 8.36 (s, 2H); 46.9, 86.7, 96.1, 109.5, 113.4, 122.6, 123.6, 124.6, 126.2, 127.8, 128.9, 130.2, 130.6, 131.9, 135.2, 141.1, 146.5; IR (KBr, cm^{-1}): 2921, 2201, 1586, 1508, 1338, 1105, 854, 748; HRMS ($C_{35}H_{21}N_3O_4$): Calcd.: 547.15321; Obsd.: 547.15208 (−2.1 ppm).

3. Results and discussion

3.1 One-photon absorption and fluorescence

The normalized one-photon absorption and fluorescence spectra for **4a–d** are presented in Fig. 1, these two pairs of compounds showed very similar absorption and emission spectra. In the same conjugated system, *N*-benzyl derivatives showed a blue shift compared to the *N*-pentyl ones. The absorption maximum in chloroform for **4a** appeared at 383 nm, for **4b** at 378 nm with a 5 nm blueshift. The same phenomenon was observed for **4c** and **4d**: the absorption maximum for **4d** appears at 385 nm with a 11 nm blueshift compared to that of **4c** at 396 nm. **4c** and **4d** showed a dual fluorescence in chloroform, the emission at 450 nm corresponding to a typical π–π* transition, delocalized over the whole conjugated π-electronic system; and the emission at 560 nm representing a typical charge transfer fluorescence.[31]

However, **4a** and **4b** exhibited only one emission peak at about 460 nm. The Stokes shifts of **4c** and **4d** are larger than those of **4a** and **4b**, the Stokes shift of **4d** is 8053 cm^{-1} larger than that of **4c** (7522 cm^{-1}). These results indicated that strong

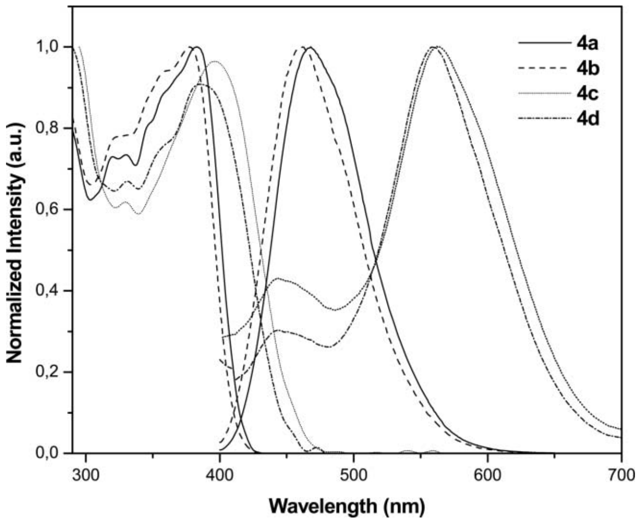


Fig. 1 Normalized UV-Vis and fluorescence spectra of **4a** (solid line), **4b** (dashed line), **4c** (dotted line) and **4d** (dot-dashed line) in chloroform.

intramolecular charge transfer existed in **4c** and **4d** compared to **4a** and **4b**, which might contribute to a larger δ_{TPA}. At the same time, **4c** and **4d** exhibited low fluorescence quantum yields (Φ_f) compared to **4a** and **4b**, which might contribute to improvement of non-irradiative decay and higher initiating efficiency. The fluorescence quantum yields of **4c** and **4d** are much lower in chloroform than in THF, which probably results from the difference in contact charge transfer to the solvent. Photophysical data of UV-Vis absorption and fluorescence of **4a–d** are presented in Table 1.

3.2 Two-photon absorption and fluorescence

TPA cross-sections, δ_{TPA}, were measured to understand their TPA behaviour using the two-photon fluorescence method and the TPA spectra of **4a–d** are presented in Fig. 2. The δ_{TPA} values of **4a–d** are also listed in Table 1. Chromophores **4a** and **4b** had TPA cross-section maxima around 300 GM at the wavelength of 730 nm, and **4c** and **4d** exhibited δ_{TPA} more than 500 GM in the wavelength range 780–820 nm, a range in which laser light is widely used for two-photon microfabrication. This is preferred for two-photon polymerization together with low Φ_f, which might contribute to high triplet quantum yield and usually leads to high initiating sensitivity.[32–35] Therefore, **4c** and **4d** should be promising candidates as photoinitiators.

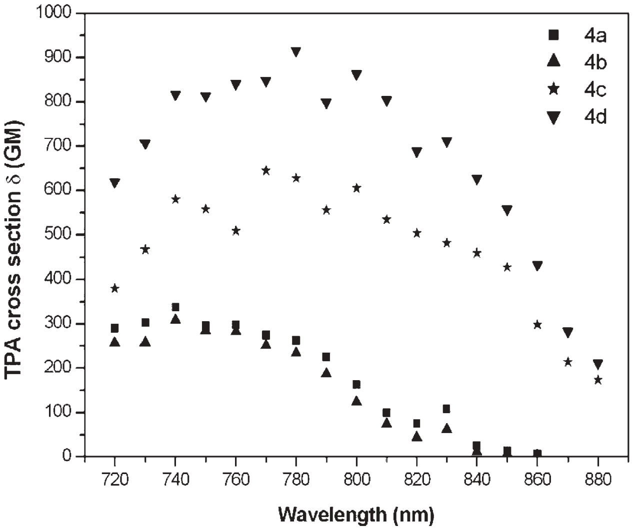


Fig. 2 TPA cross-sections of **4a–d** in range 720–880 nm: **4a–b** measured in chloroform and **4c–d** measured in THF.

3.3 Two-photon photopolymerization

In order to understand the TPP behavior of chromophores **4a–d**, two-photon polymerization experiments were performed. Usually, the threshold energy of polymerization is evaluated as the lowest average laser power with which the polymer lines are produced by the translating resin.[14] Here, the polymerization threshold is defined as the average power before being induced into the objective lens, below which the polymer line can not be fabricated using a linear scan speed of 10 μm s^{-1}. The resin components and polymerization threshold powers of the resins are summarized in Table 2.

At first, **4a–d** were used as initiators in resins with a molar ratio of 0.18%. When **4b** was used as initiator, the threshold power (P_{th}) of **R2** is found to be 1.6 mW which is much lower than that of **R1**, P_{th} = 10.11 mW. Similarly, when **4d** was used as initiator in **R4**, P_{th} = 0.80 mW, which is lower than that of **R3**, P_{th} = 2.02 mW. In the same conditions, when benzil was used, P_{th} increased to 6.37 mW for **R9**. Selected SEM images of **R4** and **R9** after polymerization are shown in Fig. 3. From Fig. 3a, the line width in **R4** declined to 250 nm from 710 nm with the laser power decreasing to 0.80 mW from 2.53 mW. The results indicated that **4b–d** exhibited much higher sensitivity than benzil. The low threshold powers of **R2** and **R4** are due to the benzyl groups in **4b** and **4d** that may stabilize the formed radical in the initiator stage. The thresholds of **R1**

Table 1 Photophysical data of **4a–d** at room temperature

Compd.	Solvent	λ_{abs}^{max}/nm (ε_{max}/$M^{-1}cm^{-1}$)[a]	λ_{em}^{max}/nm[b]	ST[c]/cm^{-1}	Φ_f[d]	δ_{TPA}^{max}[e]/GM
4a	$CHCl_3$	383 (54800)	468	4742	0.63	337 (730)
4b	$CHCl_3$	378 (55700)	460	4715	0.66	308 (730)
4c	$CHCl_3$	396 (42700)	564	7522	0.005	—
	THF	390 (49400)	546	7326	0.065	645 (770)
4d	$CHCl_3$	385 (38700)	558	8053	0.007	—
	THF	384 (42100)	544	7659	0.065	916 (780)

[a] Peak wavelength of one-photon absorption and molar extinction coefficient. [b] Peak wavelength of one-photon fluorescence. [c] ST stands for Stokes shift, which is equal to ($1/\lambda_{abs} - 1/\lambda_{em}$). [d] Fluorescence quantum yield determined relative to coumarin 307 (Φ = 0.58 in acetonitrile). [e] The maximum of two-photon absorption cross-section. 1 GM = 10^{-50} cm^4 s $photon^{-1}$. The numbers in parentheses are the wavelengths of maximum TPA.

Table 2 Components and polymerization thresholds of resins

No.	Initiator	Resin component (wt%) MAA	Initiator	DEP-6A	M.R. (%)[a]	P_{th}/mW[b]
R1	**4a**	66.62	0.72	32.66	0.18	10.11
R2	**4b**	66.60	0.75	32.65	0.18	1.60
R3	**4c**	66.59	0.77	32.64	0.18	2.02
R4	**4d**	66.57	0.80	32.63	0.18	0.80
R5	**4d**	66.84	0.40	32.76	0.09	1.01
R6	**4d**	66.97	0.20	32.83	0.045	1.60
R7	**4d**	67.04	0.10	32.86	0.023	2.53
R8	**4d**	67.07	0.05	32.88	0.012	3.20
R9	benzil	66.90	0.31	32.79	0.18	6.37

[a] Molar ratio of dyes in resin. [b] Threshold power of dye in resin.

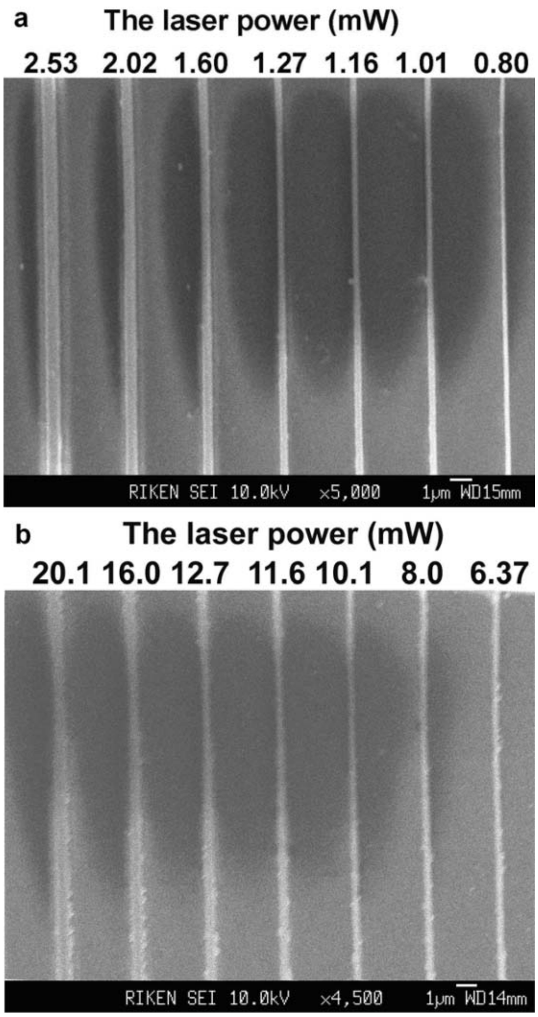


Fig. 3 SEM images of **R4** (a) and **R9** (b) after polymerization. The laser powers used to fabricate lines are shown on the SEM images. The scan speed is 10 µm s^{-1}.

and **R2** were higher than those of **R3** and **R4**, respectively, due to larger δ_{TPA} of **4c–d** compared with those of **4a–b**.

Furthermore, we investigated the substituent effect by calculating the quasi-polymerization rate (R_p) using the equation $R_p = \pi(d/2)^2 v_s$, where d is the width of the line fabricated and v_s is the linear scan speed.[14] The plots of polymerization rate *vs.* laser power for **R2–4** and **R9** are presented in Fig. 4. The polymerization rates of **R2–4** are larger than that of **R9** when the same laser power is used. For example, when the laser power is 8.0 mW, the R_p of **R2** and **R3** are 11.5 and 12.9 µm^3 s^{-1}, respectively, which are one order larger than that of **R9**, R_p = 0.65 µm^3 s^{-1}. This demonstrates that the TPP initiating sensitivities of **4b–d** are higher than that of benzil. The R_p of **R2** is smaller than that of **R3**, although **R2** exhibited a lower threshold power than **R3**. One reason for the lower polymerization rate of **4b** is its high fluorescence quantum yield (Φ_f = 0.66), which results in fast radiative deactivation and leads to a low intersystem crossing yield. The R_p of **R4** is larger than those of **R2** and **R3** at the same laser power. These results showed the rank for higher initiating efficiency is **4d** > **4c** > **4b**. Therefore, low Φ_f, large TPA cross-section and the presence of a benzyl group contributed to the high initiating efficiency for compound **4d**.

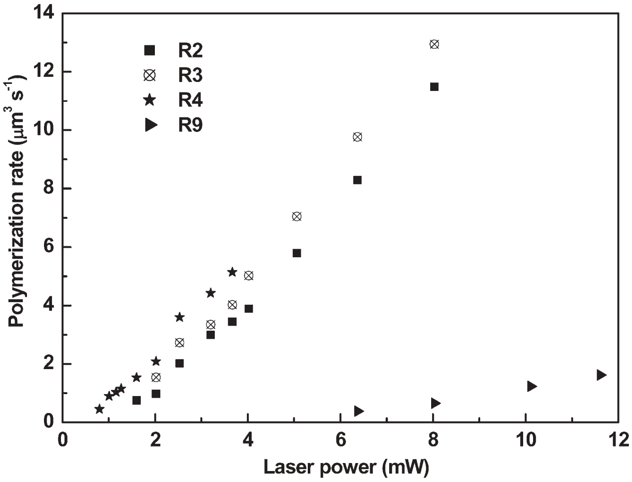


Fig. 4 The dependence of polymerization rate upon laser power for **R2**, **R3**, **R4** and **R9**.

This result encouraged us to further investigate lower loadings of **4d** in the resin. As listed in Table 2, when the molar ratio of **4d** in the resin was reduced from 0.18% (**R5**) to 0.09% (**R6**), the threshold power of the resin increased slowly to 1.01 mW from 0.8 mW. When 0.012% **4d** was used in the resin its threshold energy increased to 3.2 mW for **R8**. The threshold power of a polymerization system is strongly dependent on many factors, including concentration of dyes, monomer, cross-linker, the width of pulses, the size of the focus point, and so on. Since exposure energy per unit area directly reflected the TPP initiating sensitivity, we calculated the threshold exposure. The thresholds of laser exposure intensity for **4d** at 800 nm at the molar ratios of 0.18% and 0.012% are E_{th} = 3.0 × 10^7 and 1.2 × 10^8 mJ cm^{-2}, respectively, which are comparable with the values reported for a two-component initiator system.[14] The above results show that **4d** exhibited high initiating efficiency even at very low loadings.

Conclusions

We have designed a series of novel two-photon polymerization initiators with high sensitivity combining large δ_{TPA} with facilitated radical formation, and successfully synthesized novel 3,6-bis(ethynyl)carbazole derivatives (**4a–d**) in a facile way by a Sonogashira coupling reaction. **4c** and **4d** exhibit large δ_{TPA} from 780–820 nm and low fluorescence quantum yields. Two-photon polymerization experiments verified that the low quantum yield, large δ_{TPA} and benzyl group contributed the high efficiency of **4d** in acrylate resins. The threshold power of **4d** at 0.18 mol% in **R4** is 0.8 mW, which is much lower than the value of 6.37 mW for benzil, and the lowest loading of **4d** is up to 0.012 mol% with a threshold power of 3.2 mW. When **4d** was used as TPP initiator, the corresponding thresholds of laser exposure intensity for **R4** and **R8** are 3.0×10^7 and 1.2×10^8 mJ cm^{-2}, respectively. It showed extremely high sensitivity as a TPP initiator. The concept of combination of radical stabilization and large two-photon cross-section within a molecular structure is significant for developing highly efficient two-photon polymerization initiators.

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