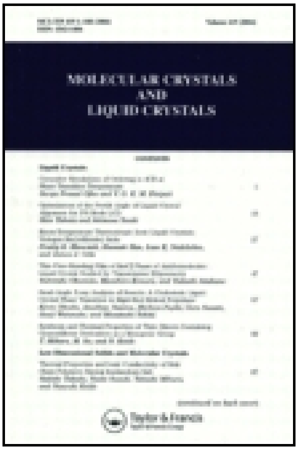

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# Efficient Two-Photon Absorbing Photosensitizers Based on Diazafluorene Moiety for 3-D TPP Fabrication

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*Efficient diazaflourene-based two-photon absorbing dyes for two-photon induced photopolymerization (TPP) have been synthesized. Their linear optical properties display a slight bathochromic shift with increasing branches. The chromophores give rise to a blue emission which is useful for two-photon lithographic microfabrication. Their TPA cross-section ($\sigma_2$) values evaluated by 100 femtosecond pulsed laser are found to be increased with the number of branches; 570 GM (760 nm) for dibranched diazafluorene (**1**) and 820 GM (760 nm) for tribranched diazafluorene (**2**). By using the resulting TPA chromophores we have succeeded to fabricate three-dimensional pattern with lattice structure.*

**Keywords:** diazafluorene; 3-D microfabrication; two-photon

## INTRODUCTION

Organic molecules with large two-photon absorption (TPA) activity are of great interest in the field of material science due to their applicability in various fields such as microfabrication [1–2], optical power limiting [3–5], three-dimensional (3-D) optical data storage [6–7] and photodynamic therapy [8–10]. The development of tailor-made TPA materials have been strongly pursued to meet the material demands of different applications; the desired properties being a large value of TPA cross-section ($\sigma_2$), tunability of wavelength of TPA or fluorescence,

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high fluorescence quantum yield and high thermal/optical stability, etc. Large TPA activity is commonly required for most of the application purposes. The $\pi$-electron donor-acceptor-donor (D-A-D), donor-$\pi$-donor (D-$\pi$-D) and acceptor-$\pi$-acceptor (A-$\pi$-A) quadrupolar molecular types are known to give rise to quite large $\sigma_2$ values due to the highly extended $\pi$-conjugation and the appropriate intramolecular charge transfer (ICT) between a donating groups and an accepting groups mediated through a $\pi$-bridge.

In this article we report the synthesis of two diazaflourene derivatives and investigation of their one- and two-photon optical properties. We have used diazafluorene as $\pi$-center and *N,N*-diphenyl-4-styrylbenzenamine groups are attached at both ends. We have also prepared three branched chromophore. The dependence of TPA activities on the number of branches has been discussed. The additive enhancement of TPA in multi-branched structures is detected, which may provide a way to develop novel TPA chromophores exhibiting large two-photon activities without the change of the maximum emission wavelength. In addition we demonstrate the dependence of TPP fabrication resolution on the TPA cross-sections of photosensitizers.

## EXPERIMENTAL PART

## Synthesis

### *4,5-Diaza-2′,7′-bis(N,N-diphenyl-4-styrylbenzenamine)-9,9′-spirobifluorene (1)*

A mixture of 4,5-diaza-2′,7′-dibromo-9,9′-spirobifluorene(SPN-2Br) [11] (0.5 g, 1.05 mmol), (*E*)-4-(4-(diphenylamino)styryl)phenylboronic acid (TP-B) (0.9 g, 2.31 mmol) and $Pd(PPh_3)_4$ (97 mg, 0.084 mmol) in a 25 mL flask were added to a mixture of toluene (20 mL) and 2 M $Na_2CO_3$(aq) (5.2 mL, 10.5 mmol). The reaction mixture was stirred at 90°C for 24 hrs. After cooling, the product was extracted with $CHCl_3$, washed with water and dried over $MgSO_4$. The solvent was evaporated, affording the crude mixture. After column chromatography on silica gel ($CHCl_3$/EtOAc = 5/1), pure compound (1.44 g, 61%) was obtained as a yellow solid.

$^1$H NMR ($CDCl_3$): $\delta$ (ppm, from TMS), 6.98–7.18(m, 20 H), 7.22–7.28(m, 16 H), 7.36–7.48(m, 12 H), 7.70–7.73(dd, 2 H, $J = 1.65$ Hz), 7.93–7.96(d, 2 H, $J = 7.97$ Hz), 8.76–8.78(dd, 2 H, $J = 1.67$ Hz); MALDI-TOF: $m/z$: 1009.42 ($M^+$, 100%). Anal. Calcd. For $C_{75}H_{52}N_4$: C, 89.26; H, 5.19; N, 5.55. Found: C, 84.66; H, 5.10; N, 5.06.

### *4,5-diaza-2′,7′,10′-tri(N,N-diphenyl-4-styrylbenzenamine)-9,9′-spirobifluorene (2)*

A mixture of 4,5-diaza-2′,7′,10′-tribromo-9,9′-spirobifluorene(SPN-3Br) (0.5 g, 0.9 mmol), (*E*)-4-(4-(diphenylamino)styryl)phenylboronic acid(TP-B) (1.16 g, 2.99 mmol) and $Pd(PPh_3)_4$ (84 mg, 0.072 mmol) in a 25 mL flask were added to a mixture of toluene (20 mL) and 2 M $Na_2CO_3$(aq) (4.5 mL, 9 mmol). The reaction mixture was stirred at 90°C for 24 hrs. After cooling, the product was extracted with $CHCl_3$, washed with water and dried over $MgSO_4$. The solvent was evaporated, affording the crude mixture. After column chromatography on silica gel ($CHCl_3$/EtOAc = 5/1), pure compound (1.6 g, 39%) was obtained as a yellowish solid.

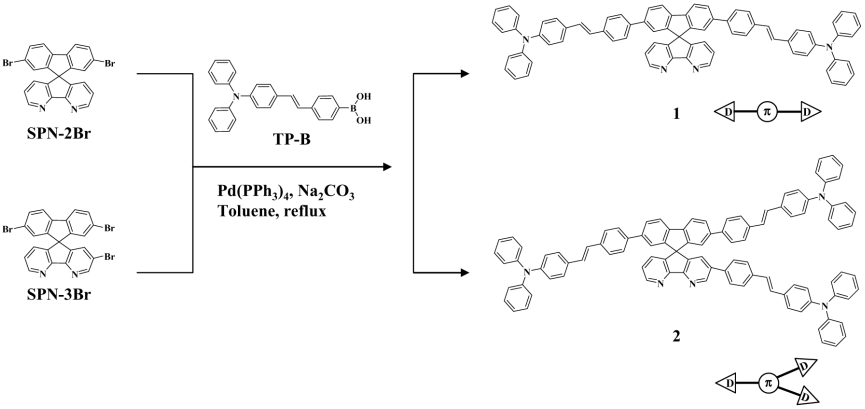
$^1$H NMR (CDCl3): $\delta$ (ppm, from TMS),6.96–7.48(m, 65 H), 7.56–7.57(d, 2 H, $J = 1.65$ Hz), 7.65–7.76(m, 5 H), 8.78–8.80(dd, 2 H, $J = 1.37$ Hz); MALDI-TOF: $m/z$: 1354.42 ($M^+$, 100%); Anal. Calcd. For $C_{101}H_{71}N_5$: C, 89.55; H, 5.28; N, 5.17. Found: C, 87.77; H, 5.39; N, 4.95.

## Measurements

Linear absorption spectra were recorded on a spectrophotometer (Perkin Elmer, Lambda 14) in diluted solutions, $1.0 \times 10^{-6}$ M in THF. The fluorescence measurement was conducted with $1 \times 10^{-6}$ M in THF using a Jobin-Ynon Fluorog FL-311 spectrofluorimeter. Mass spectroscopic data were obtained with a MALDI-TOF of Voyager-DETM STR Biospectrometry Workstation model. The TPA cross-section was obtained by induced fluorescence (TPIF) method according to the method described in the literature [12]. Fluorescence intensities obtained from two-photon excitation of unknown samples were compared with that of reference molecules at the same conditions. Mode-locked Ti-sapphire 100 femtosecond pulse laser was employed with a repetition rate of 90 MHz. The study was carried out in the range of 720 nm to 940 nm regime using fluorescein as a reference fluorophore.

## RESULTS AND DISCUSSION

The synthetic routes for di- and tri-branched TPA chromophores are displayed in Scheme 1. The TPA chromophores were synthesized by Suzuki coupling reaction between 4,5-diaza-9,9′-spirobifluorene and (*E*)-4-(4-(diphenylamino)styryl)phenylboronic acid. The chemical structures of two chromophores were confirmed by $^1$H NMR spectroscopy, MALDI-TOF mass spectroscopy and elemental analysis.



**SCHEME 1** Synthetic route of TPA chromophores **1** and **2**.

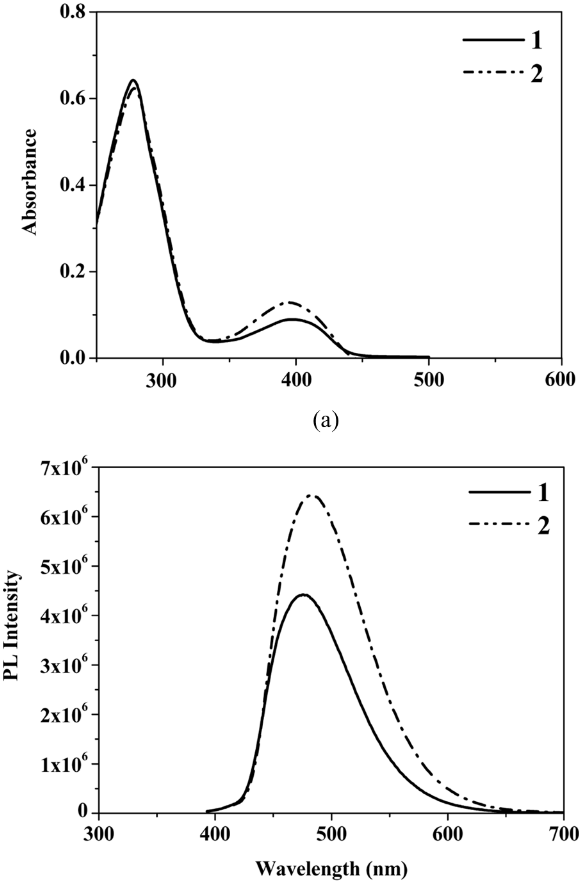
The one-photon photophysical characteristics of di-branched (**1**) and tri-branched chromophores (**2**) are summarized in Table 1. There is only a slight red shift (less than 2 nm) in the linear absorption and fluorescence spectra of the tribranched molecule (**2**) as compared to the dibranched molecule (**1**), which implies that there is a little delocalization between branches and $\pi$-core. This can be explained that geometrical distortion might be exist between $\pi$-core and a branch. We have also observed that a small increase in the fluorescent quantum yield with the number of branches. Presumably it can be related with a little larger transition dipole moment [13].

As shown in Figure 1, both of the chromophores show two characteristic absorption bands: one is the higher energy band at 280 nm and the other is lower energy band at 395 nm which can be attributed

**TABLE 1** Photophysical Data of Diazafluorene-Based TPA Chromophores

| cpd | $\lambda_{\text{abs}}^{(1)}$ (nm) | $\varepsilon$ ($M^{-1}\,cm^{-1}$)$^a$ | $E_{\text{ge}}^b$ | $\lambda_{\text{flu}}$ (nm) | $\Phi^c$ | $\lambda_{\text{max}}^{(2)}$ (nm)$^d$ | Detuning energy (eV)$^e$ | $\sigma_2$(GM)$^f$ | $\sigma_2$(GM)/$N^g$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 396.5 | 104,000 | 3.16 | 486.5 | 0.38 | 760 | 1.52 | 569 | 76 |
| 2 | 395 | 144.800 | 3.16 | 488 | 0.41 | 760 | 1.52 | 818 | 78 |

$^a$molar extinction coefficient; $^b$energy of the transitions between the ground state and the one-photon allowed excited state; $^c$fluorescence quantum yield; $^d$maximum of the two-photon fluorescence excitation spectrum; $^e$detuning energy $\Delta E = E_{ge} - 1/2E_{ge'}$; $^f$two-photon absorption cross section ($1 \times 10^{-50}$ cm$^4$photon$^{-1}$ molecule$^{-1}$) experimental uncertainty: ±15%; $^g$$N$ is the number of double bonds in the conjugated molecules; all the data in this table were measured in THF.



(a)

(b)

**FIGURE 1** Absorption spectra (a) and fluorescence spectra (b) of chromophores **1** and **2** in THF.

to $\pi$-$\pi^*$ and n-$\pi^*$ transition, respectively. The n-$\pi^*$ transition of compound **2** is increased with respect to that for **1**, which originates from the addition of one more branch to the $\pi$-center. The molar extinction coefficient of the compound is found to increase with the number of branches which mainly comes from the lower absorption band around 395 nm. The electron-donating triphenylamine end groups in chromophores **1** and **2** also would endow good solubility in organic solvents.

The wavelength-dependent TPA spectra for molecules, **1** and **2** are shown in Figure 2. In this system, triphenylamine is acts as an

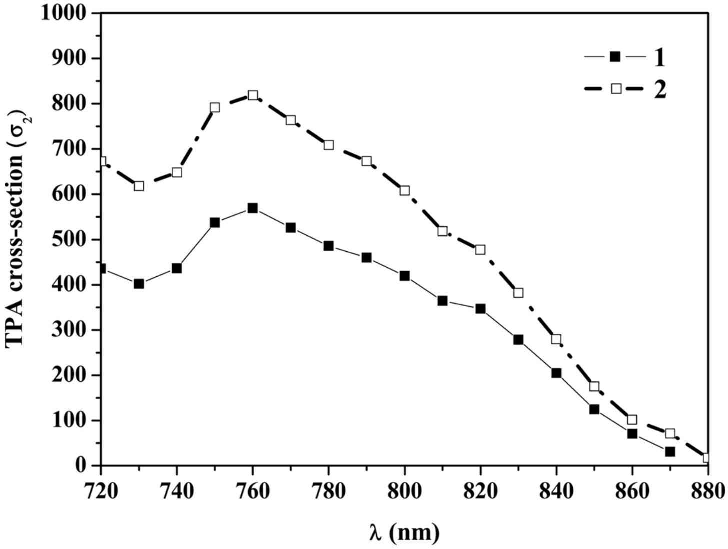


**FIGURE 2** Two-photon excitation spectra ($\sigma_2$) of chromophores **1** and **2** in THF.

electron-donor and the $\pi$-core behaves like a weak acceptor. It is noted that tri-branched chromophore **2** shows larger TPA activity than the di-branched chromophore **1**. As a result of increasing number of branches TPA cross-section values are increased. It also can be mentioned that this enhancement of TPA cross-section is attributed to the increased number of triphenylamine moieties present in the molecule, which contributes to increase the extent of intermolecular charge trasfer. In the recent work for triphenylamine-based multi-branched system, a strong cooperative TPA enhancement has been originated from the interbranch electronic coupling by comparing TPA properties for single-armed and tri-armed triphenylamine chromophores [14]. In contrast, when the core nitrogen atom was replaced with benzene ring, only a simple additive enhancement was observed [15]. The latter shows the breakage of $\pi$-conjugation between a core and a branch and as a consequence the coherent interaction between them is negligible due to the delocalization of the excited-state through strong inter-arm interactions. The nature of connection between the $\pi$-core and a branch changes not only the geometry of the molecule but also their electronic interaction. It should be noted that $\sigma_{2(\max)}/N$ for both chromophores (Table 1) exhibit nearly same value, 76 and 78 for 1 and 2, respectively, where $N$ is the number of

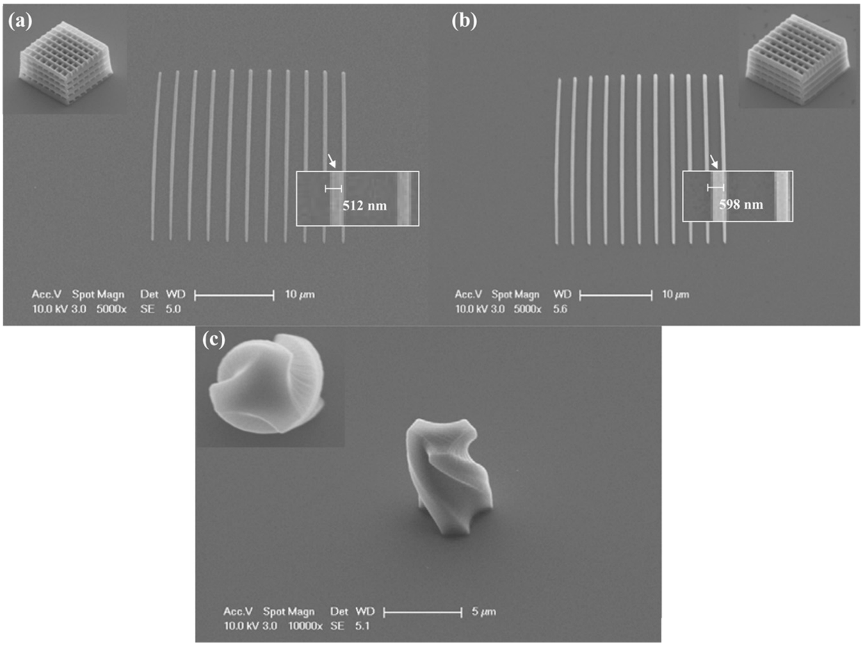


**FIGURE 3** (a) SEM images of the line pattern TPP fabricated using the dye **1** and (b) using the dye **2** under the same condition like a power of 80 mW with an exposure time of 2 ms, and (c) 3-D screw micro-structure using dye **1** as a two photosensitizer.

double bonds and the phenyl rings were counted equivalent to 1.5 double bonds. Thus the contribution of double bonds to the TPA activity is identical, which means $\sigma_{2(\max)}/N$ increases linearly with the number of double bonds or number of branches in this conjugated molecular system. This indicates that interbranch electronic coupling does not take place. Consequently, there is almost no ICT between branches and the $\pi$-center. Assume that the TPA scale to the number of branches, and the magnitude of TPA cross-section of **2** divided by the half of that of **1**, their values are given to be 2 and 2.9 respectively, which are consistent with the above results and the one-photon optical characteristics. The TPA cross-section depends on the transition dipole moments for one-photon and two-photon absorption, and detuning energy, $\Delta E = E_{ge} - 1/2E_{ge'}$ where $g$ is the ground state, $e$ the lowest one-photon allowed state, $e'$ the first two-photon allowed state and $E$ transition energy [16]. If we consider the detuning energies for **1** and **2** are identical, the major origin of TPA enhancement of **2** can be attributed to the larger transition dipole moments (Table 1).

This observation gives the way to improve the TPA activity without the change of the emission wavelength and loss of quantum yields.

To investigate the dependence of the resolution of TPP microfabrication on the TPA cross-section values of **1** and **2**, line patterns have been fabricated on the glass substrate using them as photosensitizers in 0.1 wt% mixed with a urethane acrylate resin, SCR500 supplied by JCR. A mode-locked Ti:Sapphire laser has been employed as a light source and the central wavelength 780 nm with a pulse width 100 fs and a repetition rate of 80 MHz. The laser power was 80 mW and the exposure time was 2 ms. Scanning proceeded in on-and-off method and the speed was 30 nm/1 ms. The laser setup for TPP micropatterning is shown in our earlier article [17].

Fine line patterns could be obtained by TPP microfabrication using both dyes as shown in Figures 3(a) and (b). There are many factors to influence the line width of TPP fabricated nano patterns such as laser power, exposure time, radical quenchers, numerical aperture of lens and other optical profiles. When the other conditions were kept identical, the resulting line width was measured to be 512 nm with dye **1** and to be 598 nm with dye **2**. This result suggests that the magnitude of two photon cross-section is associated with the line width. However, it requires further study to clearly determine the relationship between TPA cross-section and the line width of patterns. The optical efficiency of TPA dyes is not determined by $\sigma_2$ alone. Actual optical efficiency of a photosensitizer is represented by TPA cross-section multiplied by quantum yield, $\sigma_2 \cdot \Phi$, of which dye **2** is also larger than that of dye **1**, leading to a better TPP patterning resolution and better suited to this application. Following the line patterning, we were able to fabricate a 3-D structure using dye **1** as displayed in Figure 3(c). The diameter of and the height of the 3-D screw structure using the photosensitizer **1** were 4 and 10 µm, respectively. The fabrication of finer patterns will enable us to make complex 3-D structures with widespread applications in a number field like nanophotonic circuits.

## CONCLUSION

This article presented the investigation of one- and two-photon absorption spectra for di- and tri-branched molecules based on diazaflourene with *N,N*-diphenyl-4-styrylbenzenamine branch units. The two-photon absorption cross section increases almost linearly with the number of branches, indicating that each branch barely couples with $\pi$-core and subsequently with one another. Their one-photon spectral data also support their additive characteristics. Their TPA cross-section ($\sigma_2$) values were moderate and found to be 570 GM (760 nm) for di-branched molecules and 820 GM (760 nm) for tri-branched molecules, respectively. We demonstrate the dependence of TPP fabrication resolution on the TPA cross-section values of photosensitizers. New chromophores turned out to be good candidates for two photon sensitizers in two photon photopolymerization.

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