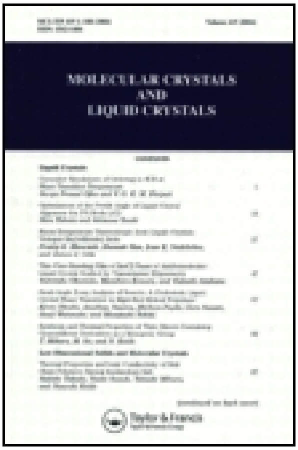

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Efficiently Site-Isolated Two-Photon Absorbing Dendrimer with Stilbazolium Chromophore

Moon-Soo Kim [a], Hyun-Kwan Yang [a], Jin Sun Park [a], Bong-Keun So [a] & Kwang-Sup Lee [a]

[a] Department of Advanced Materials, Hannam University, Yuseong-Gu, Daejeon, South Korea

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Moon-Soo Kim, Hyun-Kwan Yang, Jin Sun Park,
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[1]Department of Advanced Materials, Hannam University,
Yuseong-Gu, Daejeon, South Korea

To prevent the chromophore aggregation, a dendritic stilbazolium salt-type chromophore was synthesized via base-catalyzed coupling reaction of trihydroxy-functionalized tetraphenylborate stilbazolium salt core with appropriate peripheral Fréchet-type dendrons G3-benzyl bromide. The casted solid film of the resulting two-photon absorbing dendrimer showed high fluorescence efficiency and optical power limiting activity which were not observed from the bare chromophore without dendrons. This result is attributed to the site isolation effect of its dendritic structure. By introducing this chromophore we have successfully fabricated micropatterns with high resolution by two-photon polymerization.

Keywords: dendrimer; micropatterns; optical power limiting; photopolymerization; stilbazolium salt; two-photon absorption

INTRODUCTION

Two-photon absorption (TPA) has been a well-known phenomenon in nonlinear optics since Göppert-Mayer's theoretical work in 1931 [1] and the experimental confirmation reported by Kaiser and Garrett in 1961 [2]. TPA is one of the important nonlinear features in which a molecule can absorb simultaneously two photons, when irradiated by intense laser pulses, and make an electronic transition from the

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Address correspondence to Prof. Kwang-Sup Lee, Department of Advanced Materials, Hannam University, 461-6 Jeonmin-Dong, Yuseong-Gu, Daejeon 305–811, South Korea. E-mail: kslee@hnu.kr

ground state to an excited state by the sum of the energies of the two absorbed photons. Its practical importance has been recognized by various pioneering efforts in the field of photonics and biological applications [3]. However, this field remained inactive largely because of the lack of TPA-active materials with sufficiently large TPA cross-sections. Since late 1990s, several new classes of chromophores showing large effective TPA cross-section values were reported by the authors [4] and other groups [5]. In the conjunction with the use of femtosecond laser in the 1990s, not only has the interest stimulated much activities in the preparation of novel dye molecules with enhanced σ values, but also in various applications such as three-dimensional (3-D) lithographic microfabrication, 3-D optical data storage, optical power limiting, two-photon pumped up-converted lasing, TPA f1uorescence microscopy, photodynamic therapy, etc. [6].

Recent reports disclosed the molecular design strategies for efficient TPA systems with various electron-donor (D) and electron-acceptor (A) moieties, which are attached symmetrically or asymmetrically to a conjugated π-center; D-π-D, A-π-A or D-π-A [4,5,7]. However, most TPA compounds based on π-conjugated structures present a problem of reduction in TPA activities due to the quenching of fluorescences resulting from the formation of π-complex through the chromophore-chromophore interactions. Enhancement of TPA activity by increasing the local concentration of the chromophore is prerequisite to widening the utility of TPA materials. To achieve this goal we have prepared TPA stilbazolium salt chromophore with bulky dendrons so as to prevent the chromophore aggregation by the induction of steric hindrance. We inferred that dendritic architecture might be very effective in site isolation of the chromophores since they would serve to reduce electrostatic interaction between the dyes. The preliminary results have been appeared in elsewhere [8]. In this paper, we describe the detailed synthetic method of TPA chromophore-based dendrimer and its optical properties including optical power limiting activities. Lithograpic microfabrication was also performed by TPA-induced photopolymerization with TPA-dendrimer.

EXPERIMENTAL

Chemicals and Characterizations

Methylene chloride (MC) and dimethylformamide (DMF) were distilled from calcium hydride under nitrogen atmosphere. Other solvents were purified by standard procedures. Unless otherwise specified, all reactions were performed under nitrogen atmosphere.

All chromatographic separations were carried out on silica gel (60 M, 230–400 mesh). ^1H NMR spectra were recorded on a Varian 300 MHz spectrometer. Mass spectra were recorded on a Hewlett-Packard gas chromatograph/mass spectrometer (GC/MS) 5995. The ultraviolet (UV)-visible spectra were obtained by using a Perkin-Elmer Lambda 14 spectrophotometer. The photoluminescence (PL) spectrum was obtained using a Flouro Max-2 fluorescence spectrophotometer.

Synthesis of TPA Chromophore

p-[N,N-Bis(2-acetoxyethyl)amino]benzaldehyde (1)

Following reference [9], compound **1** was obtained as a light gray liquid having yield of 83%. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 9.80 (s, 1H), 7.80 (d, 2H), 6.90 (d, 2H), 4.30 (t, 4H), 3.70 (t, 4H), 2.00 (s, 6H).

4-Methyl-N-(3-hydroxyethyl)pyridinium chloride (2)

Following reference [10], compound **2** was obtained as a yellow solid. The yield was 92%. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 7.20 (d, 2H), 6.70 (t, 3H), 4.20 (t, 4H), 3.50 (t, 4H), 2.00 (s, 6H).

Trans-4-[p-(N,N-bis(hydroxyethyl)amino)styryl]-N′-(3-hydroxypropyl)pyridinium tetraphenylborate (SS)

The TPA chromophore SS was prepared by the following reference method [10]. 5.19 g (1.77 mmol) of *p*-[*N*,*N*-bis(2-acetoxyethyl)amino]-benzaldehyde (**1**), 3.32 g (1.77 mmol) of compound **2**, and 50 mL of anhydrous ethanol were mixed. 0.01 mL (0.12 mmol) of piperidine was added into the mixture. Then the solution was heated to reflux for 60 h. After cooling, 0.605 g (1.77 mmol) of sodium tetraphenylborate was added into the solution. The solution again was heated to reflux for 20 min. A red solid formed after cooling. The solution was filtered and the solid was washed with methanol followed by water three times each. The yield was 78%. ^1H NMR (300 MHz, DMSO-d_6, ppm) δ 8.90 (d, 2H), 8.40 (d, 2H), 7.90 (d, 1H), 7.60 (d, 2H), 7.30–6.70 (m, 23H), 4.90 (t, 2H), 4.80 (t, 1H), 4.50 (t, 1H), 3.60–3.40 (m, 8H).

Synthesis of TPA Active Dendrimer

Synthesis of Dendron G3-Br

Following reference [11], dendron **G3-Br** was obtained as a white solid. The yield was 80%. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 7.27–7.40 (m, 40H), 6.65 (d, 8H, $J = 2$ Hz), 6.63 (d, 4H, $J = 2$ Hz), 6.60 (d, 2H, $J = 2$ Hz), 6.55 (t, 4H, $J = 2$ Hz), 6.52 (m, 3H), 5.00 (s, 16H), 4.95 (s, 8H), 4.93 (s, 4H), 4.36 (s, 2H).

Synthesis of G3-SS Dendrimer

G3-Br (5 eq.) and **SS** (1 eq.) was dissolved in acetone (30 mL). To the solution were added K_2CO_3 (3 eq.) and 18-crown-6 (0.3 eq.). Then the mixture was heated to reflux for 48 h. After cooling, the reaction mixture was poured into water/MC mixture and extracted. The organic layer was separated, dried with $MgSO_4$, concentrated by rotary evaporator, and purified by column chromatography and recrystallization from hexane/MC (1:3) solvents to give a reddish-yellow solid with 67% yield. FAB MS: m/z 5389 (M^+). IR (KBr): 1595, 1470, 1360, 1170, 1065. ^1H NMR (300 MHz, DMSO-d_6, ppm) δ 7.50–7.71 (d, 4H), 7.40 (d, 1H), 7.27–7.41 (m, 40H), 7.10 (d, 2H), 6.41–6.80 (m, 21H), 6.65 (d, 8H), 6.63 (d, 4H), 6.60 (d, 2H), 6.55 (t, 4H), 6.52 (m, 3H), 5.00 (s, 16H), 4.95 (s, 8H), 4.93 (s, 4H), 4.90 (t, 2H), 4.36 (s, 2H), 3.60–3.41 (m, 2H), 2.80 (m, 2H), 2.30 (m, 2H), 1.70 (m, 2H), 1.30 (m, 2H).

Measurements

The TPA absorption cross-section value (σ_2) was determined by using a 8-ns pulsed Nd:YAG laser and a mode-locked Ti-sapphire 80 fs pulse laser with a repetition rate of 90 MHz. The light source for optical power limiting measurement was a Q-switched Nd:YAG laser pumped β-barium borate (BBO) crystal-based optical parametric oscillator (OPO) producing a signal tunable from 430 to 700 nm (idler:720–2000 nm). The repetition rate, typical pulse duration, and spectral width of the signal were 10 Hz, 7 ns, and less than 2 nm, respectively. Optical power limiting (OPL) behavior was estimated by measuring the transmitted pulse energy by varying the input nanosecond pulse energy. The input and transmitted pulse energies were measured with a calibrated pyroelectric detector and silicon photodiode. Also for the microfabrication we have employed a laser system (Fig. 1) of mode-locked Ti-sapphire laser of 780-nm wavelength, 80-fs pluse width and 82-MHz repetition rate, which was focused by a high numerical aperture (NA ≈ 1.4) objective lens into the resin [11].

RESULTS AND DISCUSSION

Materials Synthesis

As shown in Scheme 1, two-photon absorbing stilbazolium salt-type chromophore **SS** was synthesized by the same procedure as described in reference 10. The **G3-Br** dendron was also obtained by the literature method [12]. Dendritic TPA material **G3-SS** was prepared by

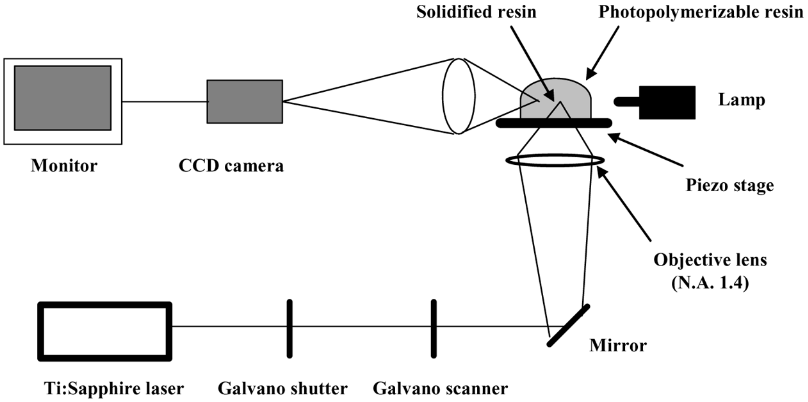
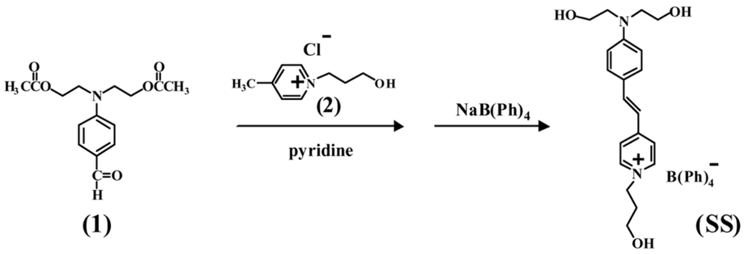


FIGURE 1 Femtosecond laser system for 3-D microfabrication.

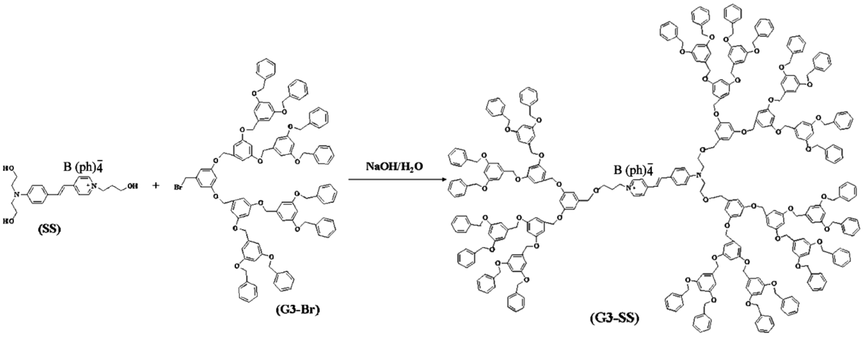
the reaction of TPA core molecule **SS** and dendron **G3-Br** as presented in Scheme 2. All intermediates and the final product were confirmed by ^{1}H NMR, infrared spectroscopy (IR), and/or mass spectroscopic analysis. Due to the introduction of benzyl ether type dendron **G3-Br** onto stilbazolium salt type chromophore (**SS**), the solubility of **G3-SS** dendrimer was much improved compared with the bare chromophore **SS**. As a result, the TPA dendrimer could easily be spin-casted onto the substrate like a glass and quartz plate.

UV Absorption and PL Emission

The UV-visible absorption and PL emission spectra of the bare chromophore **SS** and dendritic TPA material **G3-SS** measured in tetrahydrofuran solvent are shown in Figure 2. The absorption/emission maxima of **SS** and **G3-SS** were observed at 497/603 and 521/604 nm,

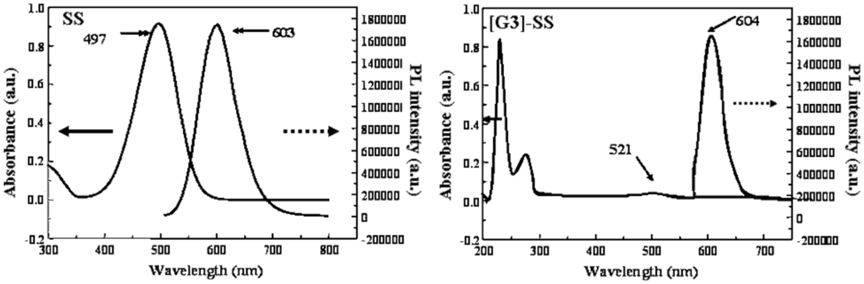


SCHEME 1 Synthetic route for TPA core chromophore **SS** of stilbazolium salt type.



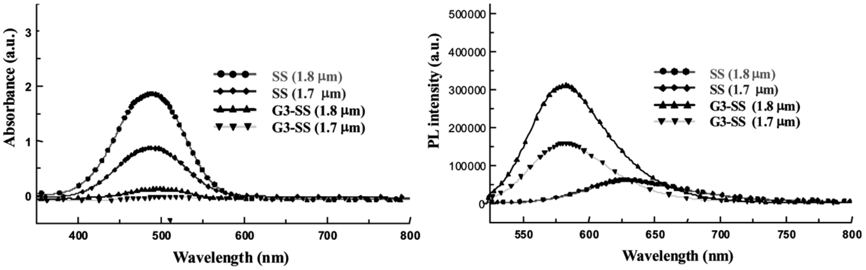
SCHEME 2 Synthetic route of two-photon absorbing dendrimer **G3-SS**.

respectively. Figure 3 shows UV and PL spectra of bare chromophore **SS** and dendrimer **G3-SS** in the solid state. The absorption intensity of both compounds increase with increasing film thickness. The lower UV absorbance of dendritic compound compared with bare chromophore is due to the low number density of chromophores. In contrast, PL emission of the dendrimer shows opposite optical behavior. A large enhanced PL emission of the dendrimer **G3-SS** was detected and their emissions increase with increasing film thickness. This result indicate that the core chromophore unit (**SS** component) is effectively site-isolated from each other by bulky dendrons as described by Frechet *et al.* [13]. However, we have observed nearly no PL emission peaks except a broad emission band at around 630 nm from bare chromophore. Here, the broad band represents the excimer formation owing to π-π interaction of molecules in the neighborhood of bare chromophore **SS**



(a) (b)

FIGURE 2 UV-vis and fluorescence spectra for (a) SS and (b) G3-SS in THF solution.



(a) (b)

FIGURE 3 (a) UV and (b) fluorescence spectra of SS and G3-SS in solid film.

in solid state. As a visual evidence of site isolation effect in solid state of dendrimer, we have observed strong PL emission from the **G3-SS** film coated onto quartz plate (Fig. 4). The utility of TPA materials suffers from the dilemma that high photoluminescence output is critically dependent on chromophore concentration. Simply increasing the amount of chromophore is not a viable option since chromophore aggregation can lead to excimer formation, thus resulting in less efficient photoluminescence. Therefore, an approach attaching the PL-active chromophore within dendrons can greatly contribute to overcome the excimer formation problem causing the PL quenching of TPA chromophores based on π-conjugated structure.

TPA-Related Properties and Microfabrication

Figure 5 shows the TPA dispersion curves of bare chromophore **SS** and dendrimer **G3-SS** measured in THF solution by 80 fs excitation in the

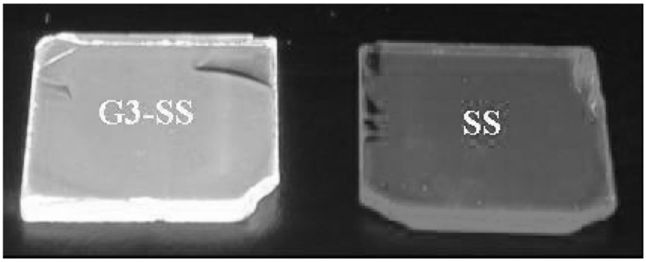


FIGURE 4 Photoluminescence activity for SS, G3-SS films coated onto quartz plate.

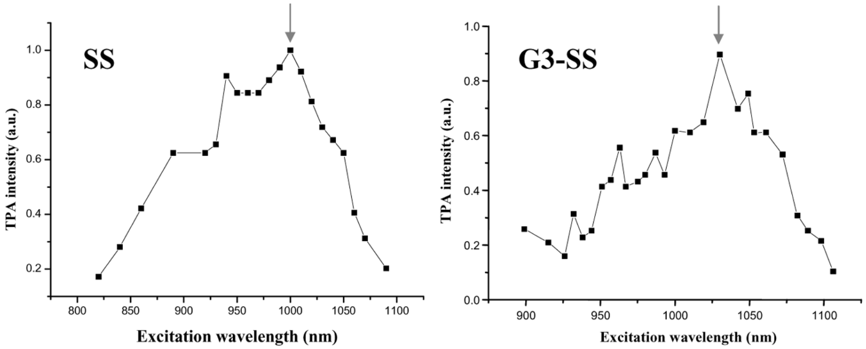


FIGURE 5 TPA dispersion spectra of bare chromophore **SS** and dendrimer **G3-SS** (80 fs laser).

spectral range of 820 ~ 1120 nm. The maximum TPA peaks of bare chromophore **SS** and dendrimer **G3-SS** appeared at 1000 and 1030 nm, respectively. The experimental TPA cross-section σ_2 values of these compounds were evaluated to be 240 GM ($1\,GM = 1 \times 10^{-50}\,cm^{-4}$ sec/photon) at 1000 nm for **SS** and 110 GM at 1030 nm for **G3-SS**. The σ_2 value of **SS** obtained by using a 8-ns pulsed Nd:YAG laser was 3,100 GM at 1000 nm wavelength. The TPA value of **SS** detected by ns laser system might be over-estimated due to the excited state absorption of chromophore.

Based on TPA activity of **SS** and **G3-SS** compounds we have evaluated the optical power limiting properties in the solid state (sample film obtained by spin casting) by using a Q-switched Nd:YAG laser with pulse duration of 8 ns. Among the application fields of TPA materials, optical power limiting (OPL) activity of TPA materials against intense laser beam can play an important role in several viewpoints including protection of the human eye or sensitive sensors [14]. To evaluate the optical power limiting activity of **SS** and **G3-SS** at ns pulse duration regime, we fixed the pumped wavelength at 1000 and 1030 nm, respectively and measured the transmitted pulse energy in a 1 cm path solution. The pumping beam of ns-OPO was loosely focused to the sample cell, making a full-width half-maximum (FWHM) diameter of 0.1 mm. The pulse energy of the input and the transmitted beams were measured simultaneously. As shown in Figure 6, TPA dendrimer (**G3-SS**) exhibits much higher OPL efficiency than stilbazolium salt by itself, even when the number density of chromophore in dendrimer is much lower. As we discussed in previous part, this result is a consequence of the site isolation effect

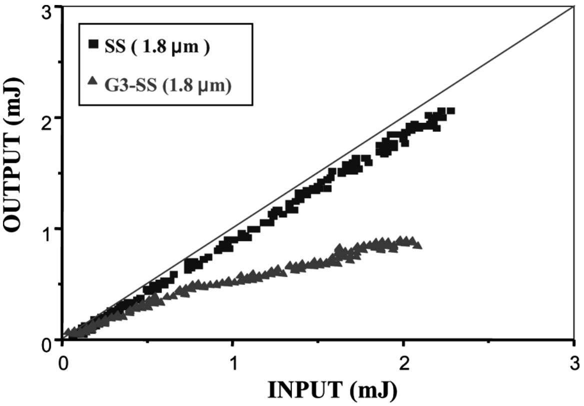
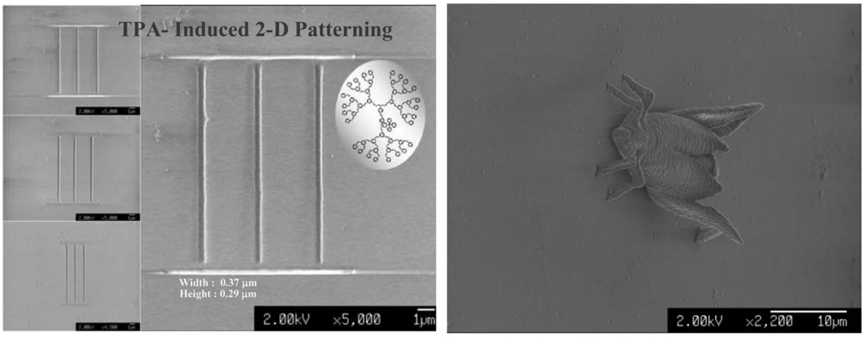


FIGURE 6 Optical power limiting properties of **SS** and **G3-SS** (film thickness: 1.8 µm) with 7 ns laser pulse and 10 Hz repetition rate.

between chromophores by the steric hindrance of dendrons attached in chromophore.

TPA photopolymerization has been well known as a useful tool for 3-D stereolithography because of its capability of deep penetration into medium and sub-diffraction-limited spatial resolution which are advantages over the conventional lithography [15]. To improve resolution of micro-patterns, efficient TPA chromophores are in great demand at the moment. We have performed microfabrication using **G3-SS** as a photosensitizer for TPA-induced polymerization. A 80 fs mode-locked Ti:sapphire laser was employed and the control of three dimensional directions were performed by using a Galvano shutter to polymerize



(a) (b)

FIGURE 7 SEM images of (a) 2-D and (b) 3-D micropatterns fabricated by using dendritic TPA-acitve material (**G3-SS**).

desired part of the photo-active resin, which is a mixture of SCR-500 resin (99.9%) and TPA dendritic chromophore, **G3-SS** (0.1%). After the photopolymerization (solidification process) of SCR-resin by TPA-induced polymerization, the unpolymerized resin was washed away with ethanol. By employing this technique, we have successfully fabricated several micro-patterns with high spatial resolution at 4.0 mW incident laser power and 1 ms laser exposure time. Figure 7 shows SEM images of the resulting micro-patterns (shown as Roman numeral III) in which the size of the pattern was 0.37 (width) × 0.29 μm (hight). We have also achieved the microfabrication of 3-D insect shaped object of 20 (width)×20 (length)×10 μm (hight) size.

CONCLUSIONS

A TPA active dendritic molecule (**G3-SS**) was prepared by the coupling reaction of trihydroxy functionalized stilbazolium salt (**SS**) and third generation dendron of benzyl ether type **G3-Br**. The linear absorption maxima of **SS** and **G3-SS** were observed at 497 and 521 nm, and the photoluminescence spectral maxima were at 603 and 604 nm, respectively. In solid state, the **G3-SS** film reveals highly efficient fluorescence emission with respect to the **SS** film, indicating the spatially isolated and structurally restricted stilbazolium dye within the dendrons. We also observed a distinct nonlinearity on input as function of output laser power from G3-SS film demonstrating that this is a potential material for optical power limiting. We have successfully applied the dendritic chromophore as two photon sensitizer in the fabrication of 2-D and 3-D micropatterns with high resolution by TPA-induced photopolymerization.

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