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Synthesis and Photophysical Properties of Two-Photon Absorbing Spirofluorene Derivatives

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New spirofluorene-based quadrupolar two-photon absorbing dyes having triphenylamine and N,Ndibutylaniline as electron donors at the end of molcules were designed and synthesized. The thirdorder nonlinear optical properties of these compounds were studied using a two-photon excited fluorescence method. They were found to have high two-photon absorption cross-section owing to extended conjugation of the spirofluorene moiety. The effect of varying the donor strength could be discerned by comparing the two compounds. They were successfully used as a photosensitizers for two-photon initiated polymerization of three-dimensional micro-objects.

Keywords: Spirofluorene, Two-Photon Absorption, Stereolithography.

The study of nonlinear optical (NLO) phenomena in materials has generated enormous interest in recent years because of their application in optical communication systems, medicine and defense.¹⁻⁷ Studies in the past couple of decades have focused on evolving design parameters for second- and third-order NLO materials. Twophoton absorption (TPA) is a third-order NLO property which finds applications in three-dimensional optical data storage, two-photon confocal microscopy, optical power limiting, etc.^{4,7,8} Effective applicability of TPA materials depends on achieving high TPA cross-sections. Several systematic studies have been carried out to find structure-property relationships in TPA chromophores. These have involved approaches like extension of conjugation, substitution of powerful donors (D) or acceptors (A) facilitating effective charge transfer, and increasing the dimension of the molecule.9-14 In the current work, we have designed and synthesized new spirofluorene-based quadrupolar TPA chromophores with a $D-\pi$ -D architecture. The compounds Z1 and Z2 constitute triphenylamine and N,N-dibutylaniline as electron donors, respectively. The fluorene moiety has figured in several highly active TPA molecules. Its rigidity and the resulting extended conjugation make them an ideal choice as a π -center in materials for organic electronics and NLO materials.11, 14, 15

1. INTRODUCTION ivered by Publishing Technology to Spiron linkage ivrefers to the glinkage of two extended $\cup \pi$ -systems with similar or different functions in order to improve their morphological stability while keeping the same electronic properties.¹⁶ The spirofluorene group can be thought of as two fluorene moieties conjoined at their 9,10-positions. The two interconnected fluorene moieties would align perpendicular to each other suppressing interactions between their respective π -systems. This structure assists in preventing intermolecular fluorescence quenching which is common in case of dyes. As a result, these compounds possess high TPA efficiency. They also present an added dimension in NLO materials and are expected to give rise to molecules with superior optical properties.^{16, 17} The compounds were utilized as photosensitizers in twophoton lithography for the fabrication of 3D micro-objects.

2. EXPERIMENTAL DETAILS

2.1. Materials

All materials except SCR 500 were purchased from Aldrich and used without any further purification. The urethane-acrylate resin SCR 500 used for microfabircation was kindly provided by JSR Japan.

2.1.1. Synthesis of 2,7-Dibromofluorenone (2,7-BFO)

Tetrabutylammonium hydroxide (0.39 mL, 0.36 mol) in methanol solution was added to a solution of 2,7dibromofluorene in 15 mL of pyridine. The mixture was

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J. Nanosci. Nanotechnol. 2012. Vol. 12. No. 5

then stirred for 12 h at the room temperature. The resulting mixture was added drop wise to acetic acid. The solution was then washed with water. The product was purified by recrystallization (solvent: chloroform and methanol). 2,7-DFO was obtained as a yellow solid of 4 g (yield: 58%). ¹H NMR (CDCl₃, ppm): 7.39–7.42 (*d*, 2 H), 7.62–7.69 (*d*, 2 H), 7.78 (*s*, 2 H).

2.1.2. Synthesis of 9,9-Bis(4-diphenyl-aminopenyl)-2, 7-Dibromofluorene(2,7-BTPF)

A mixture of 2,7-DFO (3.8 g, 0.011 mol) and triphenylamine (38.8 g, 0.16 mol) in trifluoromethane sulfonic acid (1 mL) was heated for 18 h at 140 °C with stirring under an inert atmosphere. The cooled mixture was extracted with dichloromethane, and the extract was washed with sodium carbonate solution. The organic layer was dried over anhydrous magnesium sulfate and concentrated. The product was purified by column chromatography on silica gel, followed by recrystallization from acetone. 2,7-BTPF was obtained as a white powder of 2.2 g (yield: 23.7%). ¹H NMR (CDCl₃, ppm): 6.85–7.12 (m, 20 H), 7.15–7.29 (m, 8 H), 7.43–7.49 (d, 2 H), 7.49–7.52 (d, 2 H), 7.52–7.60 (d, 2 H).

2.1.3. Synthesis of 4-(Diphenylamino)-Benzaldehyde (F2)ered by Publishing Technology

6.2 mL (0.08 mol) of DMF was cooled to $0_{\triangle}^{\circ}C_{\triangle}$ and treated dropwise with 3.8 mL (0.043 mol) of phosphorus oxychloride. The solution was stirred at 0 °C for an hour, and at room temperature for another hour. To the stirred solution 10 g (0.042 mol) of triphenylamine in dichloromethane was added drop wise. The mixture was refluxed at 90 °C for 5 h and then cooled to 0 °C. Then a solution of 2 N NaOH in 500 mL of cold water was added slowly with stirring. The reaction mixture was stirred for an additional hour and the resulting solution was extracted with dichloromethane. The combined extract was washed with saturated sodium bicarbonate, followed by washing with water. The organic layer was dried over anhydrous magnesium sulfate and concentrated. The product was purified by column chromatography on silica gel. The compound F2 was obtained as a yellow solid of 4.5 g (yield: 40.3%). ¹H NMR (CDCl₃, ppm): 9.97 (s, 1 H), 7.67 (d, 2 H), 7.32 (t, 4 H), 7.14 (d, 6 H) 6.98 (d, 4 H).

2.1.4. Synthesis of N,N-Diphenyl-4-Vinylbenzenamine (F3)

A mixture of sodium hydride (3 g, 0.13 mol) and methyltriphenyl phosphenium bromide (10 g, 0.028 mol) in dry THF solution was added to the solution of F2 (3 g, 0.011 mol) in dry THF. The mixture was refluxed at 60 °C for 12 h and then cooled to room temperature. The solution was added drop wise to MeOH. The resultant mixture was extracted and, washed with saturated sodium bicarbonate. The organic layer was dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel. The compound F3 was obtained as a white solid of 2.2 g (yield: 73.8%). ¹H NMR (CDCl₃, ppm): 7.33–6.93 (*m*, 14 H), 6.65 (*d*, 1 H), 5.63 (*d*, 1 H), 5.09 (*d*, 1 H).

2.1.5. Synthesis of 4-(Dibutylamino)Benzaldehyde (G2)

40 mL of DMF was cooled to 0 °C and 5 mL (0.053 mol) of phosphorus oxychloride was added slowly to it. The solution was stirred at 0 °C for an hour and at room temperature for another hour. To the stirred solution 11 mL (0.048 mol) N.N-dibutyaniline was added. The mixture was refluxed at 110 °C for 5 h and then cooled to 0 °C. A solution of 2 N NaOH in 500 mL of cold water was added slowly with stirring. The stirring was continued for an hour and the resulting solution was extracted with dichloromethane. The combined extract was washed with saturated sodium bicarbonate, and with water. The organic layer was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the product was purified by column chromatography on silica gel. The compound G2 was obtained as a yellow liquid of 5.5 g (yield: 48.4%). ¹H NMR (CDCl₃, ppm): 9.67 (s, 1 H), 7.7 (d, 2 H), 6.6 (d, 2 H), 3.35 (t, 4 H), 1.56 (m, 4 H), 1.37 (*m*, 4 H), 0.95 (*t*, 6 H).

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2.1.6. Synthesis of N,N-Dibutyl-4-Vinylbenzenamine (G3)

A mixture of sodium hydride (6.2 g, 0.28 mol) and methyltriphenyl phosphonium bromide (27.6 g, 0.077 mol) in dry THF solution was added to the solution of G2 (6.0 g, 0.026 mol) in dry THF. The mixture was refluxed at 60 °C for 12 h, cooled to room temperature and added to MeOH. The combined extract was washed with saturated sodium bicarbonate followed by water. The organic layer was dried over anhydrous magnesium sulfate. The product was purified by column chromatography on silica gel. The compound G3 was obtained as a yellow liquid of 3.2 g (yield: 53.7%). ¹H NMR (CDCl₃, ppm): 7.25 (*d*, 2 H), 6.6 (*m*, 2 H), 3.2 (*t*, 4 H), 1.56 (*m*, 4 H), 1.37 (*m*, 4 H), 0.95 (*t*, 6 H).

2.1.7. Synthesis of TPA Dye Z1

The mixture of 2,7-BTPF (0.1 g, 0.12 mmol), F3 (0.08 g, 0.29 mmol), bis(triphenylphosphine) palladium (II) chloride (0.1 g, 0.15 mmol), and tri-*o*-tolyphosphine (0.1 g, 0.33 mmol) were added along with 5 mL of triethylamine to 10 mL of DMF at 60 °C/under argon. The solution was then refluxed at 110 °C for 48 h and cooled to room temperature. The solution was extracted with dichloromethane. The extract was washed with sodium

J. Nanosci. Nanotechnol. 12, 4403-4408, 2012

Lim et al.

carbonate solution, and dried over anhydrous magnesium sulfate and concentrated. The product was purified by column chromatography on silica gel. The compound Z1 was obtained as a yellow powder of 0.03 g (yield: 20.4%). ¹H NMR (CDCl₃, ppm): 7.7 (d, 2 H), 7.5 (t, 4 H), 7.39 (d, 4 H), 7.29–7.19 (m, 20 H), 7.12–6.9 (m, 40 H).

2.1.8. Synthesis of TPA Dye Z2

The mixture of 2,7-BTPF (0.1 g, 0.12 mmol), G3 (0.06 g, 0.29 mmol) and bis(triphenylphosphine)palladium (II) chloride (0.1 g, 0.15 mmol), tri-o-tolyphosphine (0.1 g, 0.33 mmol) were dissolved in 5 mL of triethylamine and 10 mL of DMF at 60 °C under argon. The mixture was then refluxed at 110 °C for 48 h and cooled to room temperature. The solution was extracted with dichloromethane, and the extract was washed with sodium carbonate solution. The organic layer was dried over anhydrous magnesium sulfate and concentrated. The product was purified by column chromatography on silica gel. The compound Z2 was obtained as a yellow powder of 0.07 g (yield: 51.0%). ¹H NMR (CDCl₃, ppm): 7.7 (*d*, 2 H), 7.49 (t, 4 H), 7.37 (d, 4H), 7.29-7.19 (m, 8 H), 7.19-7.02 (*m*, 12 H), 7.0–6.82 (*m*, 12 H), 6.6 (*d*, 4 H), 3.26 (*t*, 8 H), 1.56 (m, 8 H), 1.37 (m, 8 H), 0.95 (t, 12 H). (NMR data of Z1 and Z2 are available as supplementary data).

2.2. Spectroscopic Measurements 178.77.139.235 On:

UV-vis absorption and fluorescence spectra were recorded on a Shimadzu 310 pc spectrophotometer and a Horiba/Jobin-Yvon spectrofluorometer (SPEX 270 M) in toluene, THF and DMF solution $(1 \times 10^{-5}$ M for all compounds). The TPA cross-sections were measured with two-photon excited fluorescence method employing a Ti-Sapphire femtosecond laser with a pulse width of 85 fs. Fluorescein (in 0.1 N NaOH) was used as a reference dye for the TPA measurements.

2.3. Two-Photon Microfabrication Setup

A titanium sapphire laser mode-locked at 80 MHz and a 780 nm wavelength with pulses of less than 100 fs were utilized as the light source for two-photon based micro-fabrication. A set of two galvano mirrors was used to move the focused laser beam in the horizontal plane, and a piezoelectric stage was used for the vertical alignment of the beam. The femtosecond laser source is focused on the volume of the resin through a microscope with a high numerical aperture lens.^{18–20}

3. RESULTS AND DISCUSSION

3.1. Synthesis of TPA Dyes

As shown in Scheme 1, the two-photon absorbing dyes (Z1 and Z2), in which spirofluorene π -centers are

J. Nanosci. Nanotechnol. 12, 4403-4408, 2012



- (i) Tetrabutyl Ammonium Hydroxide/Pyridine
- (ii) Triphenyl amine/ Trifluotomethane sulfonic acid

(iii) POCl₃/DMF, (iv) CH₃P(CH₆H₅)₃Br,NaH/THF

(v) Pd(PPh₃)Cl₂,Tri-o-tolyphosphine/Et₃N, DMF

Scheme 1. Synthetic routes for Z1 and Z2.

coupled with triphenylamine or N,N-dibutylaniline at the end of molecules, were synthesized by the reaction of 9,9-bis(4-diphenylaminopenyl)-2,7-dibromofluorene (2,7-BTPF) with N,N-diphenyl-4-vinylbenzenamine (F3) or N,N-dibutyl-4-vinylbenz-enamine (G3). After purification of final products, the yields of TPA dyes Z1 and Z2 were 20.4 and 51.0%, respectively. The structures of all intermediates and the final compounds were confirmed by spectral analysis. Both compounds are well soluble in common organic solvents like DMF, and O-chlorobenzene.

3.2. One-Photon Absorption and Fluorescence Emission

The one-photon absorption and emission studies of Z1 and Z2 were carried in toluene, THF and DMF (Fig. 1). The one-photon absorption maxima for the Z1 and Z2 in the solutions do not vary much. The maxima was found to be slightly red-shifted with the increasing solvent polarity (toluene < THF < DMF). However, the fluorescent spectra showed greater variations depending on the nature of the solvent. This trend in fluorescent emission is well known in literature and is associated with the rearrangement of



Fig. 1. UV/vis absorption and emission spectra of (a) Z1 and (b) Z2 in toluene, THF and DMF. "Three traces with dense symbols to the left represent the absorption, and three traces with spaced symbols to the right represent emission."

solvent shell around the excited state molecules.^{21–23} The excited state leads to a greater charge separated state which is stabilized by the polar solvent causing a red-shift in the fluorescent emission. The absorption and fluorescence properties of Z1 and Z2 are summarized in Table I. No one-photon absorption was found for these compounds above 530 nm, which makes them potential candidates for two-photon studies in the NIR region.

Table I. One and two-photon photophysical properties of Z1 and Z2 chromophores in toluene.

Compound	$\boldsymbol{\varepsilon}^{a}$	λ_{abs} (nm)	$\lambda_{\rm flu}~({\rm nm})$	Φ^b	$\sigma_2 (GM)^{\alpha}$
Z1	5.1	414	457	0.59	1140
Z2	4.1	417	461	0.55	2596

Notes: ^{*a*}molar extinction coefficient ($10^{-5} \text{ M}^{-1} \text{ cm}^{-1}$); ^{*b*} fluorescent quantum yield; ^{*c*}TPA cross-section ($1 \text{ GM} = 1 \times 10^{-50} \text{ cm}^4$ /photon·molecule); experimental uncertainty ±15%.

3.3. Two-Photon Absorption

TPA cross-section (σ_2) of the spirofluorene derivatives were measured using the two-photon induced fluorescence method.¹⁰ The graphs for two-photon induced fluorescence excitation (TPEF) spectra of Z1 and Z2 are given in Figure 2. And the TPA values are summarized in Table I. The compound Z2 was found to have a greater σ_2 than Z1 in 10⁻⁵ M of toluene solution. This can again be attributed to the greater charge separation in the Z2 substituted with a butylamine moiety when compared to the Z1 which contains with a triphenylamine moiety. It is well known that an increase in charge transfer would lead to an increase in the σ_2 value for centrosymmetric quadrupolar molecules.^{10, 14} For the compound Z1, the interaction of a lone pair in the amine units with surrounding aromatic rings decreases its electron donating ability. This effect is absent in the case of dibutylamine. The lone pair electrons in the butylsubstituted amino group in Z2 interact to greater extent to the core of the molecule than the lone pair electrons on the triphenyl amine moiety in Z1. This would result in the increase of charge transfer in Z2.

3.4. Two-Photon Lithography with Z1 and Z2

In contrast to conventional lithography involving a series of masking, exposing and developing stages; two-photon lithography offers a simpler procedure which involves the direct writing of the required structures in a photoactive medium. The TPA behavior has an inverse dependence on the intensity of the incident radiation. Because of this dependence it has an inherent spatial selectivity in inducing chemical changes in a very small region around the focus of the radiation used.^{24–28} The TPA dyes are used as photosensitizers in two-photon lithography. Achieving high resolution structures by this technique depends on carrying out fabrication at very low powers of the incident radiation. Chromophores with high TPA activities give



Fig. 2. Two-photon-induced fluorescent excitation (TPEF) spectra of Z1 and Z2.

J. Nanosci. Nanotechnol. 12, 4403-4408, 2012

Lim et al.

flexibility over the laser powers that can be used for fabrication. Ideally the TPA sensitizer having a large σ_2 value should be easily dispersible in photopatternable resins. The femtosecond laser source is focused on points inside the photopolymerizable resin to induce very specific polymerization reactions. Complex structures can be directly written using the technique simply by manipulating the position of the focus. We tested both Z1 and Z2 as photosensitizers in two-photon lithography. Both chromophores were mixed well (0.1 wt%) into SCR 500 resin used for fabricating microstructures. Scanning electron microscope (SEM) images of three-dimensional structures fabricated at the same power by two-photon lithography of resins containing Z1 and Z2 are shown in Figure 3. It is obvious from the SEM images that Z2 shows greater TPA sensitization than Z1 for a given power. This can be discerned from the greater line thickness of the structures fabricated



Fig. 3. SEM images of fabricated microstructures, (a), (b) fabricated by resins sensitized with Z1 at 100 mW and 80 mW respectively; (c), (d) fabricated with resins containing with Z2 at the same powers. (f) Shows the structure fabricated at 30 mW with resins containing Z2, (f-1 to f-3) various views of the structure fabricated at 30 mW with Z2 containing resin.

J. Nanosci. Nanotechnol. 12, 4403–4408, 2012

in case of Z2 because of its greater TPA cross-section. At a fabrication power of 100 mW the respective line widths of structures fabricated by Z1 and Z2 were 450 nm and 525 nm, respectively. The higher TPA sensitivity of Z2 allows us to lower fabrication power to achieve smaller dimensions. Microstructures fabricated from resins sensitized with Z2 at 30 mW are showed in the figures(f) and (f-1 to f-3). The fabrication was not possible with resins sensitized with Z1 at the same power.

4. CONCLUSION

We have designed and synthesized highly active spirofluorene based chromophores Z1 and Z2. N,N-dibutyl-4-vinylbenzenamine was found to be a better electron donating moiety compared N,N-diphenyl-4-vinylbenzenamine resulting in a higher TPA cross-sections. Both compounds were found to be useful as sensitizers in twophoton lithography. Because of the higher TPA crosssection of Z2 it could be used at very low powers for fabrication of microstructures.

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