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Degenerate Multi-Photon Properties of Spirofluorene Derivatives

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Two- and three-photon absorption properties of the fluorene-based chromophores have been investigated. The two- and three-photon absorption cross-section are found to be increased with the strength of the electron donor groups in the order of *N*-ethylcarbazoyl (**1**), triphenylamino (**2**), and *N*,*N*-dibutylanilino (**3**) groups. This nonlinear absorption enhancement can be interpreted by the increase of intramolecular charge transfer facilitated by strong electron donors and the decreased detuning energy (ΔE). Furthermore, direct laser microfabrication by two-photon photopolymerization with compound **2** as a two-photon sensitizer was carried out. Laser exposure time-dependent lateral voxel size has also been studied.

Keywords: Two-Photon Absorption, Three-Photon Absorption, Fluorene Derivatives, 3D Microfabrication.

1. INTRODUCTION

Over the past decade, two- and three-photon absorption (2PA and 3PA) behaviors from organic molecules have generated tremendous interest because of their potential applications in a 3D microfabrication, fluorescence imaging, photodynamic therapy, and optical power limiting.[1–4] For the practical applications, efficient chromophores having a large 2PA and 3PA cross-section are required. Therefore, numerous efforts have been made to study the structure–property relationships of multi-photon absorbing chromophores. It has been found that 2PA and 3PA properties are related to the strength of substituted electron donor and acceptor and the efficiency of charge transfer through the entire molecular backbone. In our previous studies, we have investigated the 2PA properties of fluorene-based chromophores and have demonstrated the 3D microfabrication using these chromophores as two-photon sensitizers.[4–6] The rigid planar structure of the fluorene group allows efficient symmetric intramolecular charge transfer from the electron donor to the fluorene center in the donor-π-donor (D-π-D) structure and, consequently, enhances the multiphoton properties of the molecules.

With the development of high repetition rate lasers operating at longer wavelengths, it is feasible to study 2PA and 3PA properties of a wide range of chromophores. While 2PA has been well studied the latter have not been as deeply explored. There have been few studies involving application of three-photon absorbing chromophores as gain media in stimulated emissions, and also as a medium for optical power limiting.[2,7,8] More recently its has been proposed that a greater understanding of three-photon absorption phenomenon would go a long way towards developing high resolution imaging techniques utilizing IR and NIR wavelengths.[9] In the presented work we investigate 2PA and 3PA properties of chromophores consisting of the fluorene as a π-center with symmetrically substituted electron donors. We measured 2PA and 3PA cross section (σ_2 and σ_3, respectively) by direct nonlinear transmission method. It was found that the donor strength and the detuning energy play an important role in the two- and three-photon transition. We have also successfully demonstrated the use of the chromophores as two-photon photosensitizers in two-photon stereolithography.

2. EXPERIMENTAL DETAILS

2.1. Materials

All materials are purchased from Aldrich and used without any further purification. Vinyl-substituted *N*-ethylcarbazole, triphenylamine, and *N*,*N*-dibutylaniline

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were synthesized according to previously reported methods.

2.1.1. Synthetic Procedure for Compound 1, 2 and 3

9,9-Bis(4-octyloxyphenyl)-2,7-dibromofluorene (12 mmol), vinyl-substituted compound (30 mmol), palladium acetate (0.08 mmol), tri-*o*-tolylphosphine (0.08 mmol), and tributylamine (20 mL) in 100 mL of dimethylforamide were refluxed for 24 h. After completion of the reaction, the solution was concentrated and poured into methanol to give a yellowish crude product. The precipitate was purified by a column chromatography using *n*-hexane/methylene chloride (4:1 in vol.) as an eluent. The pure compound was then obtained by recrystallization with methanol and methylene chloride.

2.1.1.1. Compound 1. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.13$ (2H, s), 8.08 (2H, d), 7.81 (2H, d), 7.55–6.93 (24H, m), 6.73 (4H, s), 4.35 (4H, q), 4.11 (4H, t), 1.89 (4H, m), 1.78–1.11 (20H, m), 0.99 (6H, t), 0.89 (6H, t); MS (EI): m/z 1012.6 $(M^{+1})^+$.

2.1.1.2. Compound 2. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.68$ (2H, d), 7.47 (4H, d), 7.34 (4H, d), 7.29–6.96 (32H, m), 6.76 (4H, d), 3.88 (4H, t), 1.73 (4H, m), 1.46–1.18 (20H, m), 0.86 (6H, t); MS (EI): m/z 1113.6 $(M^{+1})^+$.

2.1.1.3. Compound 3. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.67$ (2H, d), 7.46 (4H, d), 7.36 (4H, d), 7.21–7.00 (6H, m), 6.87–6.75 (6H, m), 6.62 (4H, d), 3.91 (4H, t), 3.29 (8H, t), 1.75 (4H, m), 1.59 (8H, m), 1.49–1.21 (28H, m), 0.98 (12H, t), 0.89 (6H, t); MS (EI): m/z 1032.7 $(M^{+1})^+$.

2.2. Spectroscopic Measurements

UV/Vis absorption and fluorescence spectra were recorded on a Shimadzu 310pc spectrophotometer and a Horiba/Jobin-Yvon spectrofluorometer (SPEX 270M) in a THF solution (1×10^{-5} M for all compounds). Coumarin 102 (Aldrich, 99%, $\Phi_f = 0.93$ in ethanol) was used as a reference for the fluorescence quantum yields. 2PA and 3PA cross-section were measured by direct nonlinear transmission method (775 nm and 160 fs laser pulses for 2PA and 1310 nm and 160 fs laser pulses for 3PA) in THF solution.

2.3. Two-Photon Microfabrication

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 microfabrication. 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. 0.1 wt% of compound **2** was mixed with a photo-curable acrylic resin (SCR-500). The laser beam was closely focused on the volume of the resin through a microscope with a high numerical aperture lens.

3. RESULTS AND DISCUSSION

Scheme 1 shows a synthetic route of fluorene-based chromophores (Compound **1**, **2**, and **3**) for comparing multi-photon properties. Synthesized vinyl compounds were coupled with 9,9-bis(4-octyloxyphenyl)-2,7-dibromofluorene by Heck reaction. The fluorene unit at the 9-position possesses bulky alkoxyphenyl substituents which can increase solubility, and restrict aggregation of molecules. All compounds were adequately characterized by ^{1}H NMR, MALDI-TOF MS, UV/vis absorption, and fluorescence data.

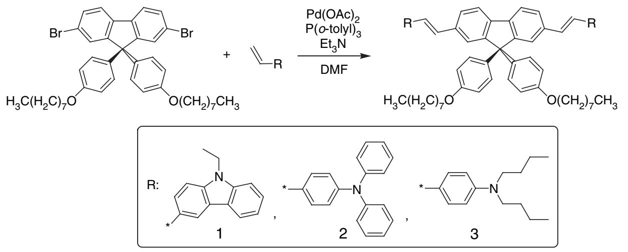
Figure 1 shows the one-photon absorption and fluorescence spectra for compound **1**, **2**, and **3**. Their absorption and emission are clearly red-shifted from 399 nm to 417 nm and from 440 nm to 494 nm with the increase of the strength of electron donors; *N*-ethylcarbazole < triphenylamine < *N*,*N*-dibutylaniline. This red-shift results from the stabilization of the one-photon-allowed $1B_u$ state by the type of amino groups. The fluorescence quantum yields (Φ_f) for **1**, **2**, and **3** decrease with increasing donor strength, which might be originated from nonradiative decay rate (k_{nrad}) (Table I). We have also observed these phenomena in similarly substituted spirofluorene compounds.[9]

The 2PA and the 3PA properties were measured by direct nonlinear transmission method in THF solution with concentration of 7.8 mM/L at 775 and 1310 nm as the probing wavelengths for the 2PA and the 3PA, respectively. AF 350 was used as a reference solution.[10] According to the nonlinear absorption theory, the intensity change of the incident laser beam along the optical propagation path z can be described as:[5]

$$\frac{dI(z)}{dz} = -\alpha I(z) - \beta I^2(z) - \gamma I^2(z) - \cdots \tag{1}$$

Here $I(z)$ is the beam intensity through the absorbing medium, and α, β, and γ are the one-, two- and three-photon absorption coefficients of the absorbing medium. If the linear absorption is negligible at the excitation frequency (v) and a degenerate 2PA or 3PA are the major mechanism for the nonlinear absorption, the solutions of Eq. (1) for the degenerate 2PA process is:

$$I(z, v) = \frac{I(0, v)}{1 + \beta(v) z I(0, v)} \tag{2}$$



Scheme 1. Synthetic route for compound **1**, **2**, and **3**.

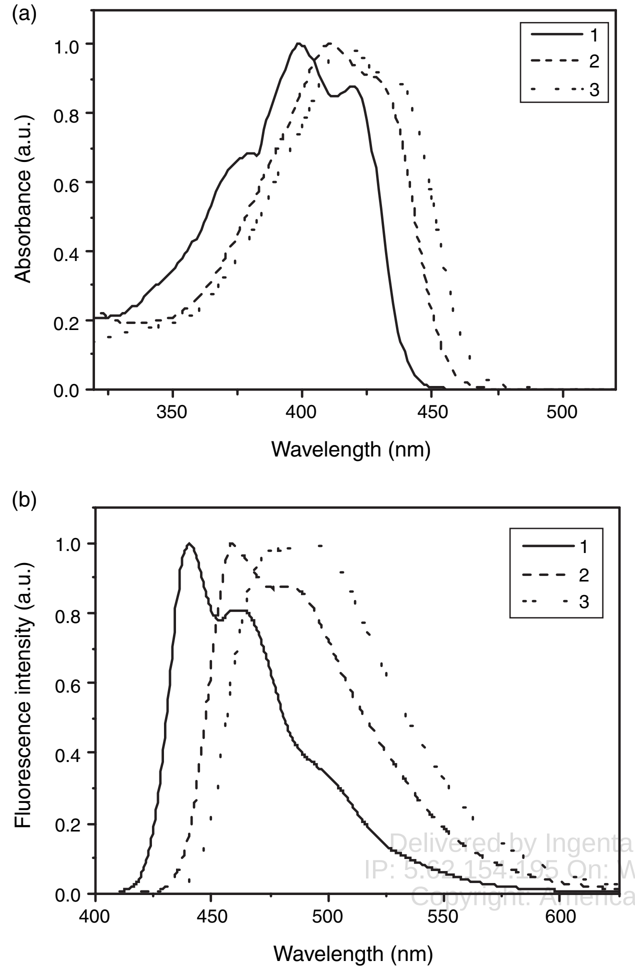


Fig. 1. (a) One-photon absorption and (b) fluorescence spectra for compound **1**, **2**, and **3**.

and for the degenerate 3PA process is:

$$I(z, v) = \frac{I(0, v)}{\sqrt{1 + 2\gamma(v) z I^2(0, v)}} \tag{3}$$

Table I. One- and two-photon photophysical properties.

Compd	λ^a_{abs} (nm)	ε^b	Λ^a_{flu} (nm)	$\Delta\nu^c$	Φ^d_{f}	E^e_{ge} (eV)	$E^f_{\text{ee}'}$ (eV)	ΔE^g (eV)
1	399	12.8	440	2335	0.86	3.11	—	—
2	411	11.7	459	2544	0.71	3.02	3.3	1.36
3	417	10.1	494	3738	0.60	2.97	3.3	1.32

[a] Absorption and emission maxima measured in THF; [b] Molar extinction coefficient (10^4 M^{-1} cm^{-1}); [c] Stokes shift; [d] Fluorescence quantum yield; [e] Energy of the transitions between the ground state and the one-photon allowed excited state; [f] Energy of the transitions between the ground state and the two-photon allowed excited state obtained from the two-photon induced fluorescence excitation experiment; [g] Detuning energy $\Delta E = E_{\text{ge}} - 1/2E_{\text{ge}'}$.

Table II. Two- and three-photon photophysical properties.

Compd	σ_2 (10^{-20}cm^4/GW)	σ_2 (GM)^a	σ_3 (10^{-25}cm^6/GW^2)
AF350	0.530	132	2.64
1	0.167	42	1.45
2	0.500	124	1.84
3	0.602	150	1.84

2PA and 3PA cross section were measured by direct nonlinear transmission method (775 nm and 160 fs laser pulses for 2PA and 1310 nm and 160 fs laser pulses for 3PA) in THF solution. Molar concentration is 5 mM/L for AF350 and 7.8 mM/L for 1–3. [a] 2PA cross section (1 GM ≡ 10^{-50} cm^{4}s photon^{-1} molecule^{-1}). Experimental uncertainty: ±15%.

where $I(0, v)$ is the incident intensity of the excitation light, and $\beta(v)$ and $\gamma(v)$ are the 2PA and 3PA coefficients respectively. From the value of the input intensity $I(0, v)$ and the value of the corresponding nonlinear transmissivity T_i, β and γ can be experimentally determined. Using these values and molar concentration, the 2PA and 3PA cross-section (σ_2 and σ_3) can be determined from the following two equations:

$$\sigma_2 = \frac{\beta}{10^{-3} N_{\text{A}} d_0} \tag{4}$$

and

$$\sigma_2 = \frac{\gamma}{10^{-3} N_{\text{A}} d_0} \tag{5}$$

where N_{A} is the Avogadro constant and d_0 is the molar concentration of the molecules. 2PA and 3PA cross-section values for **1**, **2**, and **3** are shown in Table II. The σ_2 value for **3** is 150 GM, which is 3.6 times larger than that for **1** (42 GM).

It is well known that strong electron donor facilitates the intramolecular charge transfer over the entire molecule and decreases the detuning energy (**ΔE**) (see Table I) and, consequently enhances the 2PA as well as the 3PA activity.[11] Therefore enhanced σ_2 value of **3** results from the increase of the strength of electron donor and the decrease of the ΔE. Furthermore, this nonlinear enhancement was also observed in the 3PA process. The σ_3 value for **1** was 1.45×10^{-25} cm^6/GW^2, and the values for **2** and **3** were 1.84×10^{-25} cm^6/GW^2. Due to their strong multiphoton absorption properties the flourene

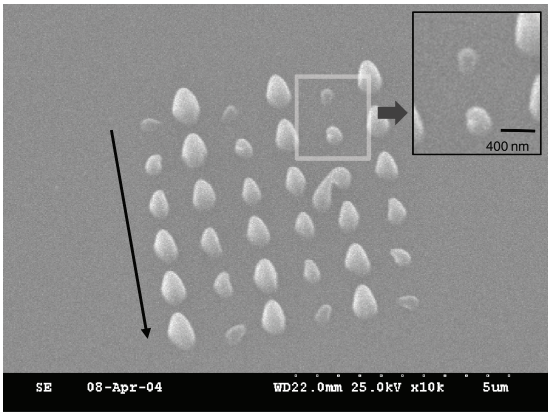


Fig. 2. SEM image of fabricated voxels by two-photon initiated photopolymerization. The size of voxel was varied by changing exposure time in the arrow direction (2, 4, 8, 16, 32, and 64 ms). The inset shows the magnified image of voxels, which reaches 200 nm for lateral dimension.

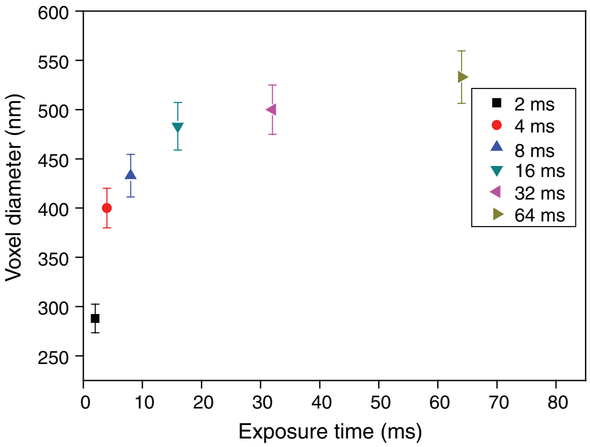


Fig. 3. Variation of voxel size by changing exposure time.

based ‘D-π-D’ molecules studied here has potential in practical applications.

We used compound **3** to study the exposure time dependent voxel size for two-photon initiated microfabrication (or photopolymerization). A voxel is a volume pixel that forms the basic building unit of a microstructure which can be three dimensionally repeated to fabricate complex structures.[12] In the two-photon microfabrication, a deep understanding of the single voxel is crucial to achieve 2D and 3D microfabrication with high resolution. Generally, the voxel size can be controlled by adjusting the laser power or by changing the laser exposure time. An efficient two-photon dye can facilitate the fabrication of structures at lower powers due to its high photo sensitization capability. This enables creation of fine structures at low energies. The interaction between the sensitizer and light is dependent on the square of light intensity, which enables sub-micron spatial resolution because two-photon initiated photopolymerization occurs mainly at a focal point of incident laser beam in the resin. Figure 2 shows a scanning electron microscope image (SEM) of fabricated voxels with **3** in a urethane-acrylate photopolymerizable resin (SCR 500, JSR Co). The size of voxel was varied by changing exposure time at constant power of 15 mW in the arrow direction (2, 4, 8, 16, 32, and 64 ms). The reproducibility of the voxel dimensions were tested by zigzag repetition of the microfabrication. The inset in Figure 2 shows the magnified image of voxels. As shown in the inset, we successfully fabricated high resolution of microstructures to below 250 nm using short exposure time and weak laser power. This resolution is better than that achieved in our previous results using a long exposure technique.[4]

In Figure 3, lateral voxel diameters versus exposure time are plotted as observed from SEM images. The voxel size increases steeply up to 16 ms, and then increases gently until 64 ms. It should be concluded, from what has been said above, that **3** can be used effectively as an efficient two-photon sensitizer because of its large σ_2 value, which is comparable with the best reported spirofluorene derivatives.[4]

4. CONCLUSION

In conclusion, we have synthesized D-π-D type spirofluorene derivatives, and investigated its structure–property relationship. 2PA and 3PA cross-sections for the compound **1**, **2**, and **3** increased with the strength of electron donors, which result from increased intramolecular charge transfer and decreased detuning energy (ΔE). We have also studied the two photon polymerization process in order to make a 3D microfabrication. Fabricated voxel size was successfully controlled by exposure time. The resolution of voxel reaches 250 nm, which is difficult to obtain using conventional one-photon based laser rapid prototyping. These results are important not only for 3D optical data storage application in the view of basic physical knowledge but also a basis of structure–property relationship on 2PA and 3PA study.

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