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Development of Photochromic Two-Photon Absorption Dyes

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We synthesized three photochromic two-photon absorptive diarylethene derivatives with styrylbenzene unit and measured two-photon absorption cross-sections at 800 nm by using an open aperture Z-scan method with 120 femtosecond pulses. It was found that two of the dyes have large values ($\delta = 52$ GM) equivalent to AF-50.

Keywords: diarylethenes; photochromism; styrylbenzene; two-photon absorption

INTRODUCTION

Organic photochromic compounds have increasingly attracted attentions for optical data storage. Among them, diarylethene derivatives are very promising compounds due to their excellent properties of fatigue resistance and thermal stability [1–3]. On the other hand, various new approaches have been proposed to increase the recording density. One of the potential candidates is the three dimensional recording by use of two-photon absorption (TPA) [3–5]. In order to take both advantages together, we synthesized three diarylethene derivatives with

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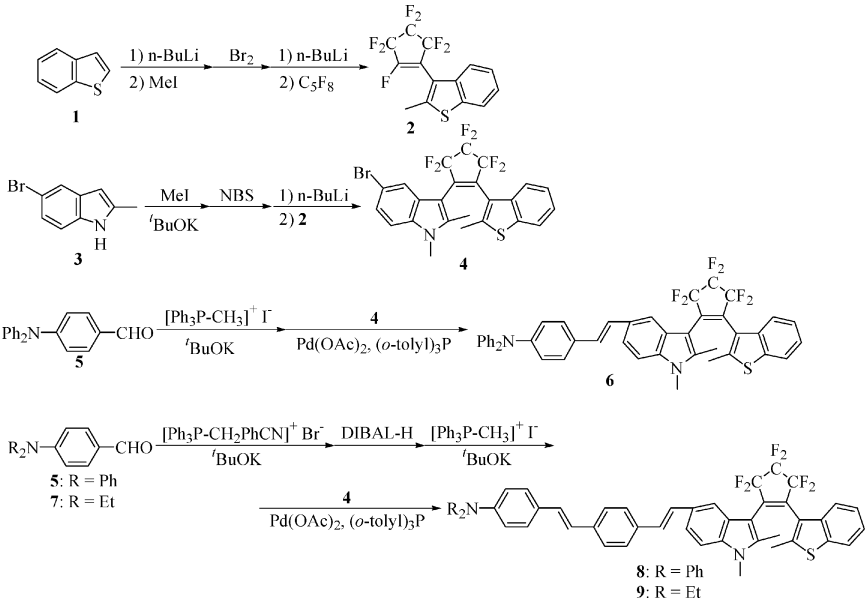
styrylbenzene unit, which is known to have large TPA cross-section [4–5], and measured TPA cross-sections at 800 nm using femtosecond laser.

EXPERIMENTAL

1-(2-Methyl-benzo[b]thiophene-3-yl)-2-(1,2-dimethyl-1H-indol-3-yl)-hexafluoro-cyclopentene derivatives with styryl substituent at 5 position of indole ring, **6**, **8**, and **9** were prepared according to the reaction route shown in Scheme 1. Diarylethenes **6**, **8**, and **9** were purified carefully by GPC. The molecular structures were confirmed by NMR and Mass spectra.

Linear (one-photon) absorption spectra were measured in THF solution. 1 mg samples of open forms were dissolved in 100 ml THF and closed forms were produced by ultraviolet light irradiation of open forms.

TPA cross-sections were measured at 800 nm by using an open aperture Z-scan method with femtosecond pulses [6] which were generated from an 1 kHz repetition Ti:sapphire regenerative amplifier system (Quantronix Integra). The pulse width was 120 fs and the spatial profiles were characterized by knife-edge method and confirmed to be



SCHEME 1 Synthetic routes of the molecules studied in this work.

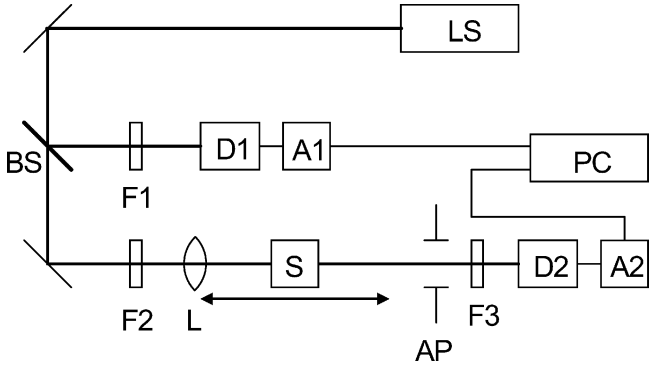


FIGURE 1 Experimental setup for two-photon absorption cross-section measurement: LS, light source; BS, beam splitter; F1, F2, F3, ND filters and color filters; L, lens; S, sample cell; D1, D2, detector; AP, open aperture; A1, A2, amplifier; PC, personal computer.

Gaussian. The experimental setup for open aperture Z-scan measurements is schematically shown in Figure 1. An incident laser power level was controlled at about 10 mW by ND filters and the power density was changed from 0.5 to 30 GW/cm^2 at sample position. A power-density dependent transmittance was acquired by dividing the solution-transmitted intensity by the solvent-transmitted intensity. The measured data were analyzed by the method described in the literature [7,8]. After some approximations and calculations, the derived final formula is written as

$$T_i = \frac{\ln(1 + I_o L\beta)}{I_0 L\beta}, \tag{1}$$

where T_i is the nonlinear transmittance, I(0) is the initial intensity, L is the sample thickness, β is the nonlinear absorption coefficient that is due to two-photon absorption. By fitting the experimental nonlinear transmittance data T_i with Eq. (1), one can determine the nonlinear absorption coefficient β. The TPA cross-section δ of one solute molecule (in units of cm^4·s/photon) can be determined by using the following relationship:

$$\beta = \frac{\delta N_A d \times 10^{-3}}{h\nu}, \tag{2}$$

where N_A is the Avogadro constant, d is the concentration of the TPA compound in the solution (in units of M/L), h is the Planck constant, and ν is the frequency of incident laser.

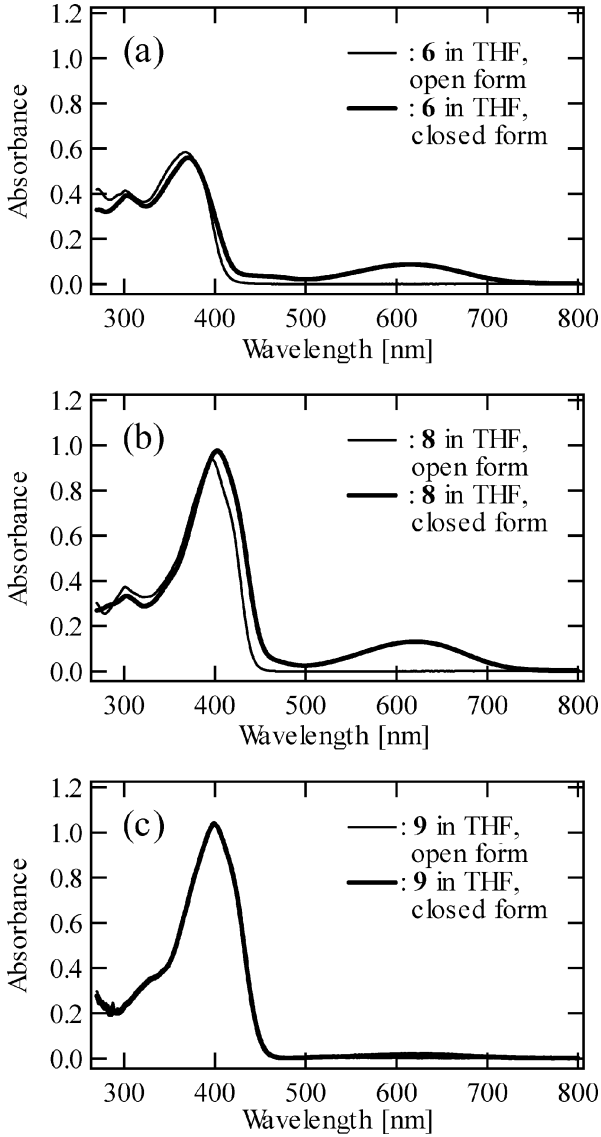


FIGURE 2 Linear (one-photon) absorption spectra of **6** (a), **8** (b), and **9** (c) in the open form (thin lines), and in the closed form (thick lines), respectively. The solvent is tetrahydrofuran and closed forms are produced by UV light irradiation.

RESULTS AND DISCUSSION

Linear absorption spectra of three compounds with both forms are shown in Figure 2. Absorption maximum wavelengths and molar absorption coefficients are summarized in Table 1, including TPA data. One can see that although total amounts of UV light irradiation were same, closed form of compound **9** has less absorption around 600 nm. Another feature is that both forms, open and closed, of all three compounds have almost same absorbance at 400 nm.

Nonlinear transmittances versus power density of incident laser light for toluene solutions of three compounds **6**, **8**, **9** are displayed in Figure 3. Best fit results by Eq. (1) are also shown with solid lines. Concentrations were 2.5 mM and thickness of the quartz cell was 1 cm. An AF-50 (N,N-Diphenyl-7-[2-(4-pyridinyl)ethenyl]-9,9-di-n-decyl-9H-fluoren-2-amine) 3.3 mM benzene solution was also measured as a reference using the same experimental conditions because it is well known to have a relatively large TPA cross-section [9].

It is noteworthy that open forms of compounds **6**, **8**, and **9** absorb two photons with the wavelength 800 nm simultaneously and rise to excited states corresponding to the energy of one photon with the wavelength 400 nm. Then excited molecules undergo ring closing reaction at a certain percentage. So we tried to take minimum time to measure TPA cross-sections in order to avoid ring closing reactions and decrease of open forms. We took linear absorption spectra of the samples before and after TPA cross-section measurements and confirmed that absorption at 600 nm, which is attributed to closed form, hardly changed during TPA cross-section measurements.

All TPA cross-section data are also summarized in Table 1. Against our expectations, a TPA value of a compound **6** is only 1.6 GM.

TABLE 1 Summary of Linear and Two-photon Absorption Data for Three Photochromic Diarylethene Compounds and AF-50

Compound	Mw	Open form abs max [nm][a]	Closed form abs max [nm][a]	Open form δ [GM][b]
6	734.79	368 (3.63)	371 (3.61), 616 (2.80)	1.6
8	836.93	396 (3.89)	403 (3.91), 620 (3.04)	52.4
9	740.84	398 (3.89)	400 (3.88), 616 (2.09)	51.8
AF-50	717.09	394 (4.72)	NA	50.1

[a] $\log \varepsilon$ is given in parenthesis, ε is molar absorption coefficient (expressed in $M^{-1}cm^{-1}$).
[b] δ is the two-photon absorption coefficient (expressed in GM and $1\,GM = 10^{-50}\,cm^4s$/photon-molecule). A laser wavelength is 800 nm and the pulse width is 120 fs.

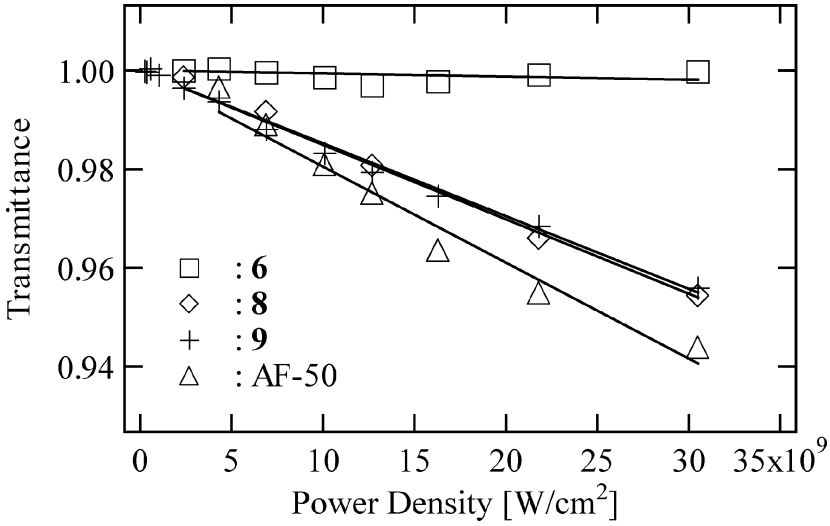


FIGURE 3 Laser power dependence of the transmittance of compound **6** (squares), **8** (diamonds), **9** (crosses), and AF-50 (triangles) in 1 cm quartz cell. The solvent is toluene for **6**, **8**, and **9** and benzene for AF-50. The concentrations of **6**, **8**, **9**, and AF-50 were 2.5 mM, 2.5 mM, 2.5 mM, and 3.3 mM, respectively. Best fit results by Eq. (1) are also shown (solid lines).

Generally speaking, π-electron delocalization enhances transition dipole moment and shifts two-photon allowed states to longer wavelength. These two factors work to increase TPA cross-sections [4,5]. Concerning about our compounds, it seems to be insufficient for a compound **6** to get a large TPA cross-section because of a relatively short π-conjugation length.

On the contrary, TPA values of compounds **8** and **9** are about 52 GM which is comparable to AF-50 (50.1 GM). These two compounds have longer π-conjugation length than a compound **6**, which should be favorable to enhance TPA cross-sections. Additionally, it is found that the difference of donor substituents between compound **8** (-diphenyl) and **9** (-diethyl) did not affect the TPA values.

In conclusion, we synthesized three photochromic diarylethene derivatives and confirmed that two of them have large TPA cross-sections which are equivalent to AF-50 in hundred femtosecond regime. To further increase TPA cross-sections of photochromic diarylethene compounds, research for novel substituents and continuous analyses of TPA process should be needed.

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