Two-Photon Absorption Cross-Sections of Fluorene Derivatives with Cationic Substituents

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Two novel fluorene derivatives having cationic substituents were synthesized. Two-photon absorption (TPA) properties of the derivatives were evaluated using the fluorescence-based technique with a femtosecond pulse emitted from a Ti:sapphire laser. Maximum TPA cross-sections of the compounds were estimated from the TPA spectra. TPA cross-sections of compounds with cationic substituents were found to be significantly larger than those of the compounds without cationic substituents.

Rapid growth in the interest in molecular two-photon absorption (TPA) in recent years[1] has brought a new reality to the variety of photonic and biological applications such as 3D-microfabrication,[2] optical power limiting,[3,4] optical data storage,[5] two-photon-excited fluorescence imaging,[6] and two-photon photodynamic therapy.[7] However, the TPA characteristics of organic materials developed up until now still need to be improved in order to fulfill the requirements of practical applications. The design principle for a molecule with a large TPA cross-section ($\sigma^{(2)}$) at a required wavelength remains to be fully developed. The complete understanding of the structure-property relationship of organic TPA materials is of great importance.

It is noteworthy that a simple D-π-A molecule with a large molecular hyperpolarizability (β) tends to exhibits a large $\sigma^{(2)}$.[8,9] Furthermore, large β values have been reported in ionic molecules.[10,11] This finding suggests that an ionic molecule is capable of exhibiting a large $\sigma^{(2)}$. Several ionic molecules exhibiting large $\sigma^{(2)}$'s have been reported.[3,12,13] In this study, fluorene derivatives with ionic substituent, 1-ethyl-4-[2-(7-diphenylamino-9,9-diethyl-9H-fluorene-2-yl)-2,1-ethenediyl]-pyridinium inium perchlorate (**2**) and 1,1′-diethyl-4,4′-(9,9-diethyl-2,7-fluorenediyl-2,1-ethenediyl)dipyridinium perchlorate (**4**) were prepared by methyl iodide methylation of the parent compounds *N*,*N*-diphenyl-7-[2-(4-pyridinyl)ethenyl]-9,9-diethyl-9*H*-fluorene-2-amine (**1**) and 4,4′-(9,9-diethyl-2,7-fluorenediyl-2,1-ethenediyl)bis-pyridine (**3**), respectively (Figure 1). We observed a significant enhancement of the $\sigma^{(2)}$ values of the ionic molecules.

The TPA cross-sections of **1–4** were estimated by fluorescence-based technique.[14] This technique is known to provide an accurate value of TPA cross-section with simple analysis.[14] One can estimate a TPA cross-section by comparing the linear and two-photon induced fluorescence spectra with those of a reference compound. Rhodamine B is commonly used as a reference compound, though two different values of TPA cross-sections at the same wavelength region between 800–850 nm were reported.[14] We adopted the lower values among them as the references because of avoiding overestimations of TPA cross-sections. A pulsed beam from a Ti:sapphire laser was used for excitation. The typical pulse duration, maximum pulse energy and repetitive rate were 125 fs, 10 nJ and 82 MHz, respectively. Quadratic dependencies of the fluorescence intensities on the incident laser power were determined for all the measurements. In addition, we confirmed that the results estimated by our experimental setup are consistent with those obtained by Z-Scan technique making use of the identical light source.

TPA induced fluorescence spectra, which were taken for **1–3** in 10^{-3} M chloroform solution and for **4** in 10^{-3} M methanol solution, are shown in Figure 2. The maximum values for the $\sigma^{(2)}$'s and the two-photon absorption spectra ($\lambda^{(2)}{}_{\max}$) are summarized in Table 1 together with the maximum values for the molar ab-

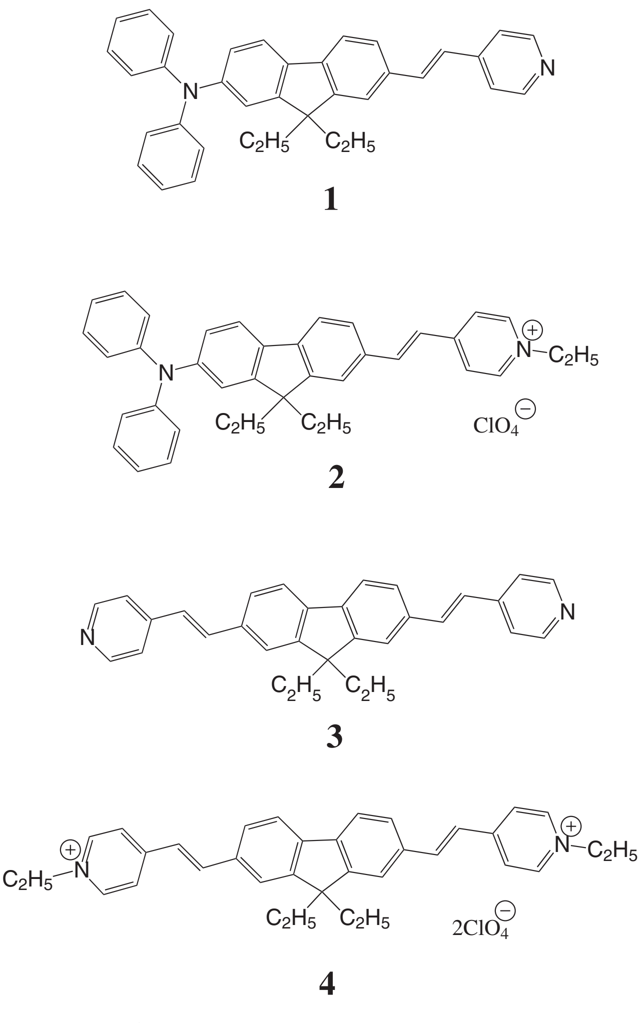

Figure 1. Fluorene derivatives studied.

Table 1. The TPA cross-sections and the related characteristics of **1–4**

Compound	ε_{max} /dm^3 mol^{-1} cm^{-1}	$\lambda^{(1)}{}_{max}$ /nm	$\lambda_{emission}$ /nm	$\sigma^{(2)}$ /GM	$\lambda^{(2)}{}_{max}$ /nm	Detuning Energy /eV
1	4.3×10^4	396	501	124	820	1.62
2	3.4×10^4	453	669	438	980	1.47
3	7.1×10^4	378	418	6	760	1.71
4	7.8×10^4	432	529	400	740	1.19

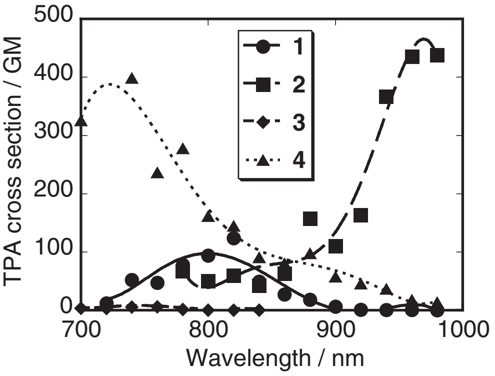

Figure 2. The TPA spectra of **1–4**. 1 GM = 1×10^{-50} cm^4 s/photon.

sorption coefficient (ε_{max}), the maximum wavelengths of the linear absorption spectra ($\lambda^{(1)}{}_{max}$), and the fluorescence spectra ($\lambda_{emission}$) in 10^{-5}–10^{-6} M solution. It is well known that the use of a high concentration solution causes concentration quenching of the fluorescence intensity, however, we can obtain more accurate TPA cross-section values in concentrated solution rather than dilute one. A large error is often included in the measurement of TPA cross-section in dilute solution owing to the quite low signal intensity of TPA induced fluorescence. In fact, a high concentration solution was widely used for estimation of TPA cross-section. Therefore, we employed the solution with a high concentration, i.e. 10^{-3} M.

As shown in Table 1, the $\sigma^{(2)}$ value of **2**, which was derived from **1**, was only about three times that of **1**, while the $\sigma^{(2)}$ value of **4** was more than sixty times that of **3**. The experimental setup used in this study enabled us to measure the TPA spectra over a wavelength range of 700 to 980 nm. In view of the relationship between the $\lambda^{(1)}{}_{max}$ and $\lambda^{(2)}{}_{max}$ values (Table 1), it seems improbable that compound **3** exhibits a much larger $\sigma^{(2)}$ value at wavelengths shorter than 700 nm. As for **3**, ε_{max} and $\lambda^{(1)}{}_{max}$ were taken also in methanol. The values of 6.9×10^4 dm^3 mol^{-1} cm^{-1} for ε_{max} and 376 nm for $\lambda^{(1)}{}_{max}$ indicate less contribution of solvent dependency to the electronic state of compound **3**. Therefore, the $\sigma^{(2)}$ value of **3** in chloroform should be quite similar to that in methanol.

The three-state model of two-photon absorption teaches us that $\sigma^{(2)}$ is proportional to the square of the transition moment, and the reciprocal of the transition energy of the linear absorption[9] and detuning energy.[15] For each of **2** and **4** in Table 1, the decrease in transition energy was observed as a bathochromic shift of the $\lambda^{(1)}{}_{max}$ on introducing a cationic substituent. This change is in accordance with large $\sigma^{(2)}$ of **2** and **4**. In addition, ε_{max}, which is proportional to a transition moment, increased on introduction of a cationic substituent on **3** leading to **4**, while ε_{max}'s of **2** is rather smaller than that of **1**. More importantly, the reduction of detuning energy is more significant when cationic substituents are introduced on **3** leading to **4** than that on **1** to **2**. Those differences coincide with the much larger increase in $\sigma^{(2)}$ observed on going from **3** to **4** than that from **1** to **2**. Although it is still difficult to predict the detuning energy of a given compound precisely, it might be possible to design a prominent TPA material by reducing the detuning energy.

In summary, significant enhancement of $\sigma^{(2)}$ was observed when a cationic substituent was introduced into the fluorene derivatives. In order to confirm the effectiveness of ionic substituents towards enhancing the molecular $\sigma^{(2)}$'s, further measurements of $\sigma^{(2)}$'s for a variety of organic ionic molecules, derived from a number of different molecular backbones is currently underway.

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