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Importance of Properties of the Lowest and Higher Singlet Excited States on the Resonant Two-Photon Ionization of Stilbene and Substituted Stilbenes Using Two-Color Two-Lasers

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Radical cations of *trans*-stilbene and substituted *trans*-stilbenes (stilbenes and the radical cations denote **S** and $\mathbf{S}^{\bullet+}$, respectively) were generated from the resonant two-photon ionization (TPI) in acetonitrile with irradiation of one-laser (266- or 355-nm laser) and with simultaneous irradiation of two-color two-lasers (266- and 532-nm or 355- and 532-nm lasers) with the pulse width of 5 ns each. The formation yields of $\mathbf{S}^{\bullet+}$, the TPI efficiency, depended on the properties of **S** in the lowest and higher singlet excited state (**S**(S_1) and **S**(S_n)), generated from one-photon excitation with 266- or 355-nm laser and from two-photon excitation with simultaneous irradiation of 266- and 532-nm or 355- and 532-nm lasers, respectively. The TPI efficiency using two-color two-lasers increased compared with that using one-laser. It is confirmed that the TPI proceeds through two-step two-photon excitation with the $S_0 \rightarrow S_1 \rightarrow S_n$ transition. In addition to the electronic character of **S**(S_0) which depends on the substituent of **S**, oxidation potential, and molar absorption coefficient of the $S_0 \rightarrow S_1$ absorption as well-known important factors for the TPI efficiency, it is shown that properties of **S**(S_1) and **S**(S_n) such as lifetimes, electronic characters of **S**(S_1) and **S**(S_n), molar absorption coefficient of the $S_1 \rightarrow S_n$ absorption, and ionization rate from **S**(S_n) are also important.

Introduction

Two-color two-laser[1−4] and the three-color three-laser flash photolysis techniques have been successfully applied to open new photochemical reactions,[5,6] where the transient intermediates, such as various aromatic molecules in the lowest singlet and triplet excited states, radicals, cations, and radical cations generated from the first or second laser flash photolysis, are selectively excited with the second or third laser irradiation to give those intermediates in the excited states, leading to new reactions such as unimolecular decompositions[4−19] and isomerization,[20−22] bimolecular energy,[23−30] and electron transfer.[22,23,31−34] We have also reported that the enhancement of the yield of di(4-methoxyphenyl)methyl cation was achieved by the second 355-nm laser irradiation at an appropriate timing, through the resonant two-photon ionization (TPI) of di(4-methoxyphenyl)methyl radical generated from the first 308-nm laser irradiation, during the 308-, 355-, and 532-nm three-color three-laser flash photolysis of di(4-methoxyphenyl)methyl chloride.[5]

The TPI of organic compounds proceeds through two-step excitation from the S_0 to S_1 states and from the S_1 to S_n states.[35] The photoionization probability of the TPI depends on the electronic character of the S_1 and S_n states, which depends on the substituent of **S** and has influence on the properties of **S**(S_1) and **S**(S_n), and the electronic conformation of the radical cations.[36] Several groups involving our group have studied the TPI of a series of organic molecules from which an electron is removed and attached to the nearest solvent molecule.[37−46] The dependences of the concentration of the radical cation generated from the TPI on the solvent, fluorescence lifetime, oxidation potential of molecules, and laser wavelength and intensity have been elucidated.[44,45] Since the absorption of the $S_0 \rightarrow S_1$ transition is different from that of the $S_1 \rightarrow S_n$ transition, it is obvious that the $S_0 \rightarrow S_1 \rightarrow S_n$ transition can be selectivity performed by excitation using two-color two-lasers tuned to the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_n$ transitions compared with that using one laser tuned to the $S_0 \rightarrow S_1$ transition which is generally used for the TPI method.

We report here on the TPI of *trans*-stilbene and substituted *trans*-stilbenes (**S**, Scheme 1) in acetonitrile using the two-color two-laser flash photolysis technique (266- and 532-nm lasers and 355- and 532-nm lasers, where the second 532-nm laser irradiation corresponds to the $S_1 \rightarrow S_n$ transition). This is the first example of the two-color two-laser flash photolysis applied to the TPI in solution, where wavelengths of two lasers are tuned to the S_0-S_1 and S_1-S_n absorptions. Effects of substituents of **S** and excitation laser wavelengths (266- or 355-nm) on the concentration of **S** radical cation ($\mathbf{S}^{\bullet+}$) generated from the TPI were examined. The transient singlet−singlet absorption ($S_1 \rightarrow S_n$ absorption) measurements were carried out in order to obtain exact information of the S_1-S_n absorption.

Experimental Section

Materials. *trans*-4-Bromo-4′-methoxystilbene (**MB**), *trans*-4-chloro-4′-methoxystilbene (**MC**), *trans*-4-methoxy-4′-trifluoromethylstilbene (**MF**), *trans*-2,4-dimethoxystilbene (**24MM**), *trans*-3,4-dimethoxystilbene (**34MM**), *trans*-3,5-dimethoxystilbene (**35MM**), and *trans*-4,4′-dimethoxystilbene (**44′**MM) were prepared according to the procedures previously described in the literature.[47−53] Quarterthiophene (**4T**) was also prepared according to the procedures previously.[54,55] Benzophenone was purchased from Wako and purified by recrystallization from ethanol before use. C_{60} (Tokyo Kasei) and acetonitrile (Wako spectroscopic grade) were used without further purification.

Apparatus. Picosecond laser flash photolysis was carried out using a third harmonic generation (THG, 355 nm) of a

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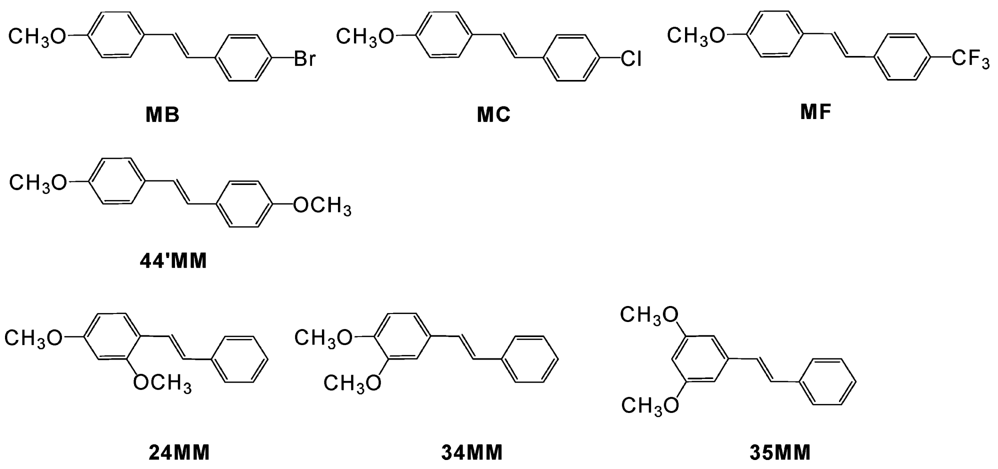
SCHEME 1



picosecond Nd:YAG laser (Continuum, RGA69-10LD, fwhm 30 ps) as an excitation source. A white continuum pulse generated by focusing the fundamental of the ps Nd:YAG laser on a D_2O/H_2O (1:1 volume) cell was used as the monitoring light and detected with a MOS linear imaging head (Hamamatsu Photonics, M2493-40) equipped with a polychromator (Hamamatsu Photonics, C5094). The nanosecond−nanosecond two-color two-laser flash photolysis was carried out using a fourth harmonic generation (FHG, 266 nm) or THG (355 nm) of a Nd:YAG laser (Quantel, Brilliant, fwhm 5 ns) and a second harmonic generation (SHG, 532 nm) of a Nd:YAG laser (Continuum, Surelite, fwhm 5 ns) as the first and second lasers, respectively, which were irradiated to the sample solution at the same time. The monitoring light from a pulsed Xe lamp (Osram, XBO-450, 450 W) was detected with a Si-avalanche photodiode (Hamamatsu Photonics, S5343) equipped with a monochromator (Nikon, G250). The signal from the detector was digitized with an oscilloscope and transmitted to a personal computer via the GPIB interface. Transient absorption spectra were measured by a multichannel analyzer with an image intensifier having a 30-ns gate width. The air-saturated or Ar-saturated sample solutions were prepared to have absorbance of 1.0 at the excitation wavelength of the first 266- or 355-nm laser in a quartz cell. Such high concentrations of **S** were used for the determination of the concentration of $\mathbf{S}^{\bullet +}$ under the present experimental conditions because of the low formation quantum yield of $\mathbf{S}^{\bullet +}$. Consequently, the absorbed photons by **S** during the first 266- or 355-nm laser irradiation were equivalent for all **S**.

TABLE 1: Properties of S^a and Formation Quantum Yields of $S^{\bullet +}$ during the 266- and 355-nm TPI of S in AN (Φ_{ion}^{266} and Φ_{ion}^{355}, Respectively)

S	$S_1 \rightarrow S_n$ absorption peak (λ_{max})/nm	ϵ_{max}/ 10^4 M^{-1} cm^{-1}	IP^b/ eV	$E_{S1}{}^c$/ eV	$\Phi_{ion}^{266\,d}$/ 10^{-2}	$\Phi_{ion}^{355\,d}$/ 10^{-2}
MB	545	1.7	5.30	3.22	2.8	2.1
MC	550	1.8	5.31	3.26	2.6	2.3
MF	500	1.3	5.41	3.27	1.5	1.3
44′MM	600	5.5	5.05	3.33	6.7	2.4
24MM	490	0.85	5.02	3.17	1.8	0.89
34MM	527	2.5	5.12	3.23	3.6	2.5
35MM	507	2.7	5.74	3.17	11.0	9.3

[a] Wavelength (λ_{max}) and molar absorption coefficients (ϵ_{max}) of the $S_1 \rightarrow S_n$ absorption peak, ionization potentials (IP), and energy of the lowest singlet excited state (E_{S1}). [b] IP = (1.473 ± 0.027)E^{ox} + (5.821 ± 0.009).[57] [c] Estimated from the wavelength of the maximum absorption peak. [d] Φ_{ion}^{266} and Φ_{ion}^{355} are the formation quantum yield of $\mathbf{S}^{\bullet +}$ during the 266-nm (20 mJ $pulse^{-1}$, fwhm 5 ns) or 355-nm (60 mJ $pulse^{-1}$, fwhm 5 ns) laser flash photolyses of **S** in AN, respectively. Φ_{ion}^{266} and Φ_{ion}^{355} values were obtained from eq 1.

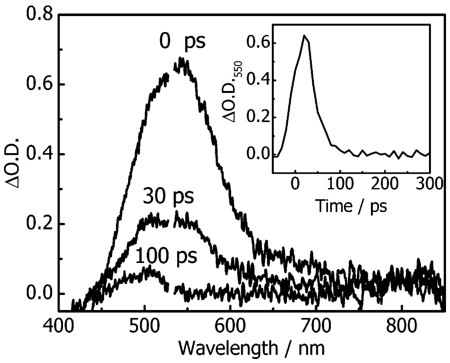


Figure 1. Transient absorption spectra observed at 0, 30, and 100 ps after a 355-nm 30-ps laser pulse during the TPI of **MB** in AN. Inset: time profile of the transient absorption at 550 nm for **MB**. The absorption peaks at 550 nm at 0 ps and at 500 nm at 100 ps are assigned to the $S_1 \rightarrow S_n$ of **MB**(S_1) and $\mathbf{MB}^{\bullet +}$, respectively. The signals around 532 nm were removed because of the stray light from the laser scattering.

Determination of Molar Absorption Coefficient of the $S_1 \rightarrow S_n$ Absorption. The molar absorption coefficient (ϵ) of the $S_1 \rightarrow S_n$ absorption of **S** was determined by the chemical actinometry using **4T** as standard. For **4T**, the transient absorption spectral change corresponding to the intersystem crossing from **4T**(S_1) to **4T**(T_1) was observed by the picosecond laser irradiation. Therefore, the concentration of **4T**(S_1) can be calculated from the optical density at 570 nm (ΔOD_{570}) to be 2.6×10^{-5} M using the reported intersystem crossing yield of 0.71 and molar absorption coefficient of the $T_1 \rightarrow T_n$ absorption ($\epsilon_{T-T} = 1.5 \times 10^4$ M^{-1} cm^{-1} at 570 nm). When an acetonitrile (AN) solution of **MB** was prepared to have equivalent absorbance with that of **4T** at the excitation wavelength, the laser flash photolyses of **MB** and **4T** were performed under the same conditions. The initial concentration of **MB**(S_1) generated during the laser flash photolysis can be assumed to be equivalent with that of **4T**(S_1). Therefore, ϵ_{S-S} of **MB**(S_1) at 545 nm was estimated to be 1.7×10^4 M^{-1} cm^{-1}. Similarly, ϵ values for other **S**(S_1) at the absorption maxima were determined as listed in Table 1.

Results and Discussion

A. Properties of S in the S_1 State (S(S_1)). Figure 1 shows the transient absorption spectra obtained during the laser flash photolysis of **MB** in AN with the 355-nm laser excitation (fwhm 30 ps). Immediately after the laser excitation, a broad absorption band centered around 545 nm was observed. The transient absorption band decayed with the rate constant of 3.6×10^{10} s^{-1}, which agreed well with the fluorescence lifetime of **MB** (28 ps). Therefore, the observed band is assigned to **MB**(S_1) which is similar to that for *trans*-stilbene reported by Oberle et al.[56] At 100 ps after a laser excitation, a long-lived band around 500 nm was observed to be assigned to the **MB** radical cation (**MB**$^{\bullet+}$). The formation of **MB**$^{\bullet+}$ is explained by the TPI using the 30-ps laser because of the high photon density.

The $S_1 \rightarrow S_n$ absorption was also observed for other **S**. **44′MM** showed the intense $S_1 \rightarrow S_n$ absorption band at the longest wavelength among **S**, probably due to the conjugation of the π-π^* orbital with *n*-electrons of oxygen atoms at the *p*-positions in **44′MM**(S_1) having two methoxyl groups at the *p*-positions.

Ionization potentials (IP) in the liquid phase were estimated from the oxidation potentials of **S**.[57] A series of dimethoxystilbenes shows low IP value because of the electron-donating character of *p*-methoxyl substituents. Several properties of **S** are summarized in Table 1.

B. TPI of S with 266- or 355-nm Laser. When an AN solution of **MB** was irradiated with a 266-nm laser (20 mJ $pulse^{-1}$, fwhm 5 ns) or a 355-nm laser (60 mJ $pulse^{-1}$, fwhm 5 ns), a transient absorption spectrum with a peak (λ_{max}) at 500 nm, assigned to **MB**$^{\bullet+}$, was observed immediately after the laser flash. This clearly shows that the TPI of **MB** occurs within the 266- or 355-nm laser flash (5 ns) to give **MB**$^{\bullet+}$ and a solvated electron, as previously observed with irradiation of a 308-nm 25-ns laser flash.[44] The TPI was confirmed from the dependence of the laser intensity on $\Delta\Delta OD_{500} = \Delta OD_{500}{}^{266+532} - \Delta OD_{500}{}^{266}$ or $\Delta OD_{500}{}^{355+532} - \Delta OD_{500}{}^{355}$ which is the concentration of **MB**$^{\bullet+}$ increased by the 532-nm irradiation as the second laser. The ionization potential (IP) of **MB** in AN (5.5 eV) is higher than the one-photon energy of 266- and 355-nm light (4.7 and 3.5 eV, respectively) (Table 1).

Similar transient absorption spectra were observed during the TPI of other **S** such as **MC** and **MF** using the 266- (20 mJ $pulse^{-1}$) or 355-nm (60 mJ $pulse^{-1}$) lasers. Table 1 shows the formation quantum yield of **S**$^{\bullet+}$ with the 266- or 355-nm irradiation ($\Phi_{ion}{}^{266}$ and $\Phi_{ion}{}^{355}$, respectively) estimated from

$$\Phi_{ion}{}^{266} \text{ or } \Phi_{ion}{}^{355} = [\mathbf{S}^{\bullet+}]/[^3Bp^*] \qquad (1)$$

where [**S**$^{\bullet+}$] and [^{3}Bp*] are the concentrations of **S**$^{\bullet+}$ and benzophenone (Bp) in the triplet excited state (^{3}Bp*). [^{3}Bp*] is equal to the photon concentration of the laser flash at 266 or 355 nm, determined using chemical actinometry of the $T_1 \rightarrow T_n$ absorption of Bp as the standard according to the method described. The molar absorption coefficients (ϵ) of all **S**$^{\bullet+}$ were estimated from the transient absorption peak intensities of **S**$^{\bullet+}$ generated by the hole transfer from biphenyl radical cation ($\epsilon_{670} = 1.45 \times 10^4$ M^{-1} cm^{-1})[33] during the 355-nm flash photolysis of a mixture of 9,10-dicyanoanthracene (6.1×10^{-5} M), biphenyl (0.2 M), and **S** in AN. For **44′MM**$^{\bullet+}$, **24MM**$^{\bullet+}$, **34MM**$^{\bullet+}$, and **35MM**$^{\bullet+}$, ϵ values at absorption peaks were reported.[44] For **MB**$^{\bullet+}$, **MC**$^{\bullet+}$, and **MF**$^{\bullet+}$, those were estimated to be 2.5×10^4, 2.4×10^4, and 2.2×10^4 M^{-1} cm^{-1}, respectively. The $\Phi_{ion}{}^{266}$ and $\Phi_{ion}{}^{355}$ values for the 266- and 355-nm laser excitation were 0.015−0.11 and 0.009−0.093, respectively, depending on **S**. It has been suggested that [**S**$^{\bullet+}$] depends on the fluorescence lifetime of **S**(S_1) and molar absorption coefficients of the $S_1 \rightarrow S_n$. In particular, the Φ_{ion} for **35MM** is the largest among **S**, which relates to the longest fluorescence lifetime of **35MM**(S_1) among **S**(S_1) because of the intramolecular charge transfer state assumed for **35MM**(S_1).[44]

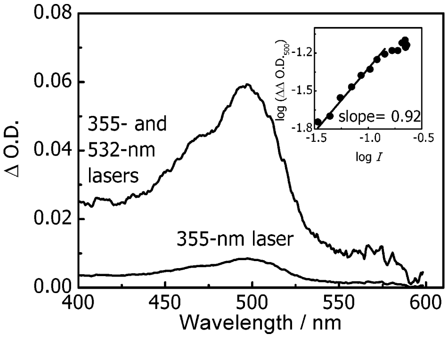


Figure 2. Transient absorption spectra of $MB^{\bullet+}$ observed at 500 ns after the 355-nm 5-ns laser flash and after the 532-nm 5-ns laser flash during the TPI of **MB** using the 355-nm laser and 355- and 532-nm two-lasers, respectively. Inset: plots of log($\Delta\Delta OD_{500}$) vs log *I*, where *I* is the intensity (mJ) of the 532-nm laser flash during the simultaneous irradiation of the 355- and 532-nm lasers.

C. TPI of S with Two-Color Two-Laser Irradiation. Interestingly, **S**$^{\bullet+}$ was generated in a higher yield during the TPI with simultaneous irradiation of the 355- and 532-nm two-laser flashes at the laser intensities of 3 and 150 mJ $pulse^{-1}$, respectively (Figure 2). The concentration of **MB**$^{\bullet+}$ was 2.8×10^{-6} M, which is much higher than 4.7×10^{-7} M obtained during the TPI with irradiation of the 355-nm one laser flash (3 mJ $pulse^{-1}$). No formation of **MB**$^{\bullet+}$ was observed during the laser photolysis with irradiation of the 532-nm laser flash (150 mJ $pulse^{-1}$). Therefore, [**S**$^{\bullet+}$], obtained by ΔOD of the peak absorption of **S**$^{\bullet+}$ divided by the ϵ values of **S**$^{\bullet+}$ during the simultaneous irradiation of the 355- and 532-nm two-laser flashes, increased compared with that during the irradiation of the 355-nm one-laser flash. Similar enhancement of the formation yield of **S**$^{\bullet+}$ was observed during the TPI of other **S** using the 355- and 532-nm two-lasers (Table 2).

The slope of a plot of log *I* against log($\Delta\Delta OD_{500}$) was found to be approximately 1, where *I* is the laser intensity (mJ) of the 532-nm laser flash (Figure 2, inset), suggesting that the TPI occurred from **S** in the higher singlet excited state **S**(S_n) generated from the 532-nm laser excitation of **S**(S_1) (Figure 3). We have reported that a photostationary state of **S**(S_n) can be attained within the 5-ns laser flash duration in the TPI of *trans*-stilbene and methoxy-substituted stilbenes.[58] Similarly, it is suggested that **S**(S_n) exists with a lifetime and undergoes internal conversion to **S**(S_1) or ionization to **S**$^{\bullet+}$. The energy level achieved by the excitation with the 355- and 532-nm two-lasers is estimated to be 5.50 eV from the singlet state energy ($E_{S1} = 3.20$ eV) of **S**(S_1) and the 532-nm laser photon energy (2.30 eV). The excitation energy of 5.50 eV is sufficient to ionize **MB** in AN ($IP_{liq} \sim 5.50$ eV). Thus, the formation of **MB**$^{\bullet+}$ is interpreted by the two-step two-photon resonant excitation of the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_n$ transitions using the 355-nm and 532-nm two-lasers, respectively. In the case of the excitation with the 266- and 532-nm two lasers, the excitation energy is also sufficient to ionize **MB**. The 532-nm laser irradiation of **MB**(S_1) gives **MB**(S_n), from which the ionization occurs subsequently to give **MB**$^{\bullet+}$ and an electron (Figure 3). Similar transient phenomena were observed during the TPI using two-color two-lasers (266 and 532 nm or 355 and 532 nm) of other **S** (Table 2).

The formation quantum yields of **S**$^{\bullet+}$ during the TPI using the 266- and 532-nm two-lasers and 355- and 532-nm two-

TABLE 2: Formation $\mathbf{S}^{\bullet+}$ during the TPI of S in AN using 266- and 355-nm Laser, 266- and 532-nm Two-Lasers, and 355- and 532-nm Two-Lasers, and ΔOD_{S-S}^{532} at 532 nm[a]

S	266[b]	266+532[c]			355[d]	355+532[e]			
	ΔOD	ΔOD	ΔOD/ ΔOD^{266}	Φ_{ion}/ 10^{-2}	ΔOD	ΔOD	ΔOD/ ΔOD^{355}	Φ_{ion}/ 10^{-2}	ΔOD_{S-S}^{532}
MB	0.006	0.045	7.5	0.47	0.012	0.07	5.8	0.71	0.13
MC	0.004	0.032	8.0	0.49	0.008	0.058	7.3	0.84	0.09
MF	0.001	0.016	16.0	0.63	0.005	0.024	4.8	0.88	0.03
44′MM	0.040	0.33	8.3	1.5	0.13	0.59	4.5	2.6	0.11
24MM	0.004	0.044	11.0	1.1	0.03	0.054	1.8	1.3	0.03
34MM	0.01	0.14	14.0	1.4	0.06	0.15	2.5	1.5	0.092
35MM	0.042	0.052	1.2	1.4	0.016	0.070	4.4	1.7	0.044

[a] ΔOD is the optical density of the transient absorption of $\mathbf{S}^{\bullet+}$ at the peak wavelength observed at 100 ns after laser flash photolysis. ΔOD_{S-S}^{532} is the optical density of the $S_1 \rightarrow S_n$ absorption at 532 nm, during the 355-nm (30 ps, 3 mJ pulse^{-1}) laser flash photolysis. [b] 266-nm laser flash photolysis (3 mJ pulse^{-1}). [c] 266- (3 mJ pulse^{-1}) and 532-nm (150 mJ pulse^{-1}) laser flash photolyses. [d] 355-nm laser flash photolysis (3 mJ pulse^{-1}). [e] 355- (3 mJ pulse^{-1}) and 532-nm (150 mJ pulse^{-1}) laser flash photolyses.

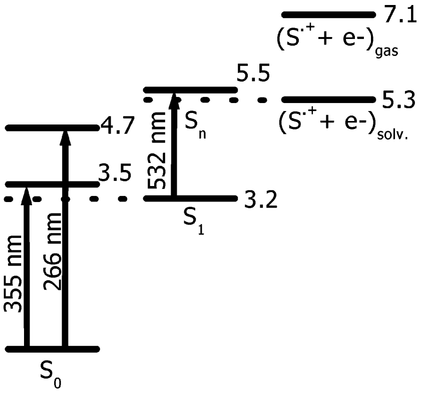


Figure 3. A schematic energy diagram of the TPI for the generation of $ST^{\bullet+}$ using two-color two-laser photolysis. Numbers are energy levels in eV for the electronic states. One-photon energies of 266- and 355-nm light were 4.7 and 3.5 eV, respectively. IP of **S** is estimated to be approximately 5.3 eV. The energy level achieved by the excitation with the 266- or 355- and 532-nm two-lasers is estimated to be 5.50 eV from E_{S1} (3.2 eV) and the 532-nm laser photon energy (2.30 eV).

lasers ($\Phi_{ion}^{266+532}$ and $\Phi_{ion}^{355+532}$, respectively) were calculated from eq 2

$$\Phi_{ion}^{266+532} \text{ or } \Phi_{ion}^{355+532} = 2[\mathbf{S}^{\bullet+}]/([I^{first}] \times \mathrm{Abs}_{266 \text{ or } 355} + [I^{second}] \times (1-10^{-\Delta OD_{S-S}^{532}})) \quad (2)$$

where $[I^{first}]$ and $[I^{second}]$ are the photon concentrations of the first laser flash at 266 or 355 nm and the second laser flash at 532 nm, respectively, determined using chemical actinometry of the $T_1 \rightarrow T_n$ absorption of benzophenone and C_{60} as standard, respectively, according to the method described. The $[I^{first}]$ values were determined to be 4.0×10^{-4} and 6.2×10^{-4} for the 266- and 355-nm irradiations, respectively, while $[I^{second}]$ depended on the experimental conditions. $\mathrm{Abs}_{266or355}$ is the absorbance of the sample solution at 266 or 355 nm. ΔOD_{S-S}^{532}, the optical density of the $S_1 \rightarrow S_n$ absorption of **S** at 532 nm, was determined from the 30-ps laser flash photolysis as described in the Experimental Section. We used the equivalent intensity of 3 mJ pulse^{-1} for the determination of ΔOD_{S-S}^{532} using a 30-ps 355-nm laser flash and for the TPI using the two 5-ns lasers (355 and 532 nm). It is assumed that the equivalent concentration of the S_1 state can be generated by the 30-ps and 5-ns 355-nm laser excitation. Table 2 shows $\Phi_{ion}^{266+532}$, $\Phi_{ion}^{355+532}$, and ΔOD_{S-S}^{532}.

It is interesting to discuss the effects of substituents on Φ_{ion}. **MC**, **MB**, **MF**, and **44′MM** have *para*-methoxyl and *para′*-substituents such as Cl, Br, CF_3, and methoxyl. According to the Hammett analysis, the parameter which denotes the strength of electron-withdrawing and -donating characters of substituents is expressed as σ_p. σ_p values of Cl, Br, CF_3, and methoxyl are 0.23, 0.23, 0.06, and −0.24, respectively. $\Phi_{ion}^{266+532}$ and $\Phi_{ion}^{355+532}$ decreased linearly with the increasing of σ_p.[59] The linear relation indicates that $\Phi_{ion}^{266+532}$ and $\Phi_{ion}^{355+532}$ decreases with the increasing of the intramolecular charge-transfer character of $\mathbf{S}(S_n)$. Since concentrations of all **S** were used to be same for the $S_1 \rightarrow S_n$ transition, properties of $\mathbf{S}(S_n)$ must influence Φ_{ion}. In other words, Φ_{ion} is influenced by the substituent of $\mathbf{S}(S_n)$.

The values of $\Phi_{ion}^{266+532}$ were similar to those of $\Phi_{ion}^{355+532}$ for each **S**. It is obvious that the $S_0 \rightarrow S_1 \rightarrow S_n$ transition is performed by the resonant excitation using the two-color two-lasers. A little formation of $\mathbf{S}^{\bullet+}$ occurs using the 266- or 355-nm one laser, while the efficient formation of $\mathbf{S}^{\bullet+}$ occurs through the $S_0 \rightarrow S_1 \rightarrow S_n$ transition using 266- and 532-nm or 355- and 532-nm two lasers. In contrary to the similar values of $\Phi_{ion}^{266+532}$ and $\Phi_{ion}^{355+532}$ for each **S**, there were large differences between Φ_{ion}^{266} and Φ_{ion}^{355} during the TPI using one laser (266- or 355-nm) because of the large difference between the molar absorption coefficients of the $S_1 \rightarrow S_n$ transition at 266 and 355 nm.

D. Important Factors for TPI. During the one-laser TPI, $[\mathbf{S}^{\bullet+}]$ depends on the fluorescence lifetime of $\mathbf{S}(S_1)$ and the molar absorption coefficients of the $S_1 \rightarrow S_n$. In particular, the Φ_{ion} for **35DM** is the largest among **S** because of the intramolecular charge-transfer character of $\mathbf{35DM}(S_1)$. Differences of Φ_{ion}^{266} (1.5−11.0%) and Φ_{ion}^{355} (0.9−9.3%) were almost 10 times depending on **S** (Table 1) and much larger than those of $\Phi_{ion}^{266+532}$ (0.47−1.4%) and $\Phi_{ion}^{355+532}$ (0.71−2.6%) (Table 2). One reason for the difference is the extremely high Φ_{ion}^{266} and Φ_{ion}^{355} values (11.0% and 9.3%, respectively) for the TPI of **35DM**. Because the molar absorption coefficients of the $S_1 \rightarrow S_n$ transition is considered for the calculation of all Φ_{ion}, the differences of $\Phi_{ion}^{266+532}$ and $\Phi_{ion}^{355+532}$ depending on **S** are much smaller than that of Φ_{ion}^{266} and Φ_{ion}^{355}. The maximum difference of $\Phi_{ion}^{266+532}$ and $\Phi_{ion}^{355+532}$ among the TPI of **S** was approximately three times for **MB** and **44′MM**. It is suggested that $\mathbf{S}(S_n)$ is involved during the TPI of **S** in AN and that properties of $\mathbf{S}(S_n)$, such as the lifetime, electronic character of $\mathbf{S}(S_n)$, and ionization rate, influence the TPI of **S** in AN. Although little is known for the S_n state in solution, the existence of the S_n state is suggested by studies on the $S_1 \rightarrow S_n$ absorption of dyes[60−62] and the $S_n \rightarrow T_n$ transition of texaphyrin[63] and dendrimer[64] during the two-photon excitation.

Conclusions

$\mathbf{S}^{\bullet+}$ was generated during the TPI of **S** in AN using one laser (266- and 355-nm, 5 ns) and two-color two-lasers (266 and 532 nm or 355 and 532 nm, 5 ns). [$\mathbf{S}^{\bullet+}$] generated by the TPI using two-color two-lasers (266 and 355 nm: 3 mJ pulse^{-1}; 532 nm: 150 mJ pulse^{-1}) was larger than that using one-laser (266 and 355 nm: 3 mJ pulse^{-1}), suggesting the importance of the second-step one-photon resonant excitation from $\mathbf{S}(S_1)$ to $\mathbf{S}(S_n)$ for the formation yield of $\mathbf{S}^{\bullet+}$. There were large differences between $\Phi_{ion}{}^{266}$ (at 20 mJ pulse^{-1}) and $\Phi_{ion}{}^{355}$ (at 60 mJ pulse$-$1) for **44′**MM and **24MM** during the TPI using one laser because of the large difference between the molar absorption coefficients of the $S_1 \rightarrow S_n$ transition at 266 and 355 nm. On the other hand, $\Phi_{ion}{}^{266+532}$ was similar to $\Phi_{ion}{}^{355+532}$ for **24MM**, **34MM**, and **35MM**, because the $S_0 \rightarrow S_1 \rightarrow S_n$ transition is performed by the resonant excitation using the two-color two-lasers. The maximum difference of $\Phi_{ion}{}^{266+532}$ and $\Phi_{ion}{}^{355+532}$ was approximately three times for the comparison between **MB** and **44′**MM. The linear relation between $\Phi_{ion}{}^{266+532}$ or $\Phi_{ion}{}^{355+532}$ and σ_p indicates that $\Phi_{ion}{}^{266+532}$ and $\Phi_{ion}{}^{355+532}$ decrease with the increasing of the intramolecular charge-transfer character of $\mathbf{S}(S_n)$. Consequently, it is suggested that $\mathbf{S}(S_n)$ is involved during the TPI of **S** in AN and that properties of $\mathbf{S}(S_n)$, such as the lifetime, electronic character of $\mathbf{S}(S_n)$, and ionization rate, influence the TPI of **S** in AN.

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Supporting Information Available: Properties of **S**: ground-state absorption and fluorescence spectral data in acetonitrile (AN). This material is available free of charge via the Internet at http://pubs.acs.org.

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