Photoisomerization Mechanism of All-Z-Oligo(phenylenevinylene)s

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Photoisomerization mechanism of *para*-substituted oligo(phenylenevinylene)s (**OPVs**) was dependent on the number of olefin units. While mono-olefin **OPV1** underwent two-way photoisomerization, other **OPVs** (**OPV2**, **OPV3**, and **OPV4**) underwent photochemical one-way *Z*-to-*E* isomerization. As the number of olefin units increased, contribution of the triplet excited state to the *Z*-to-*E* isomerization becomes larger.

Oligo(phenylenevinylene)s (**OPVs**) are well known, highly fluorescent compounds, which are desirable for applications as fluorescent polymers and organic electroluminescent materials.[1–11] Extension of π-conjugation of aromatic compounds can be synthetically achieved by combining of aromatic rings with carbon–carbon double bond or triple bond. In many cases, π-conjugated compounds with C=C double bonds undergo *Z*–*E* isomerization without exhibiting fluorescence emission. However, all-*E* isomers of **OPVs** often exhibit fluorescence emission with a high quantum yield. Thus, the understanding of the potential energy surface of photoisomerization of **OPVs** is also important to develop photofunctional materials utilizing **OPVs**.

Mechanisms of *Z*–*E* isomerization of aromatic compounds, such as stilbene, 1,4-diphenylbutadiene, and 1,6-diphenylhexatriene, have been extensively studied.[12–16] As for *p*-distyrylbenzene derivatives, it has been reported that all-*Z* isomers undergo isomerization to all-*E* isomers upon triplet sensitization.[13,17–20] Since **OPVs** have long alkyl chains on the phenyl ring of the olefin units, we became interested in studying the effect of the alkyl group and the number of olefin units on the isomerization mechanism and the excited state properties of **OPVs**.

Usually, **OPVs** are synthesized as all-*E* isomers, which exhibit fluorescence with a high quantum yield. Recently, the synthetic procedure of pure all-*Z* isomer has been reported (Fig. 1).[21,22] We report here the effect of the number of olefin units on the photoisomerization mechanism of **OPVs**. These **OPVs**, i.e., **OPV2**, **OPV3**, and **OPV4**, showed one-way *Z*-to-*E* photoisomerization, during which the major deactivation process, involving the spin state (the singlet excited state or the triplet excited state), depended on the number of olefin units. From the results of determination of the quantum yield of isomerization and intersystem crossing, and observation of the transient absorption spectra by laser flash photolysis, it is proposed that contribution of the triplet excited state of **OPVs** to the *Z*-to-*E* isomerization process becomes larger with a larger number of olefin units.

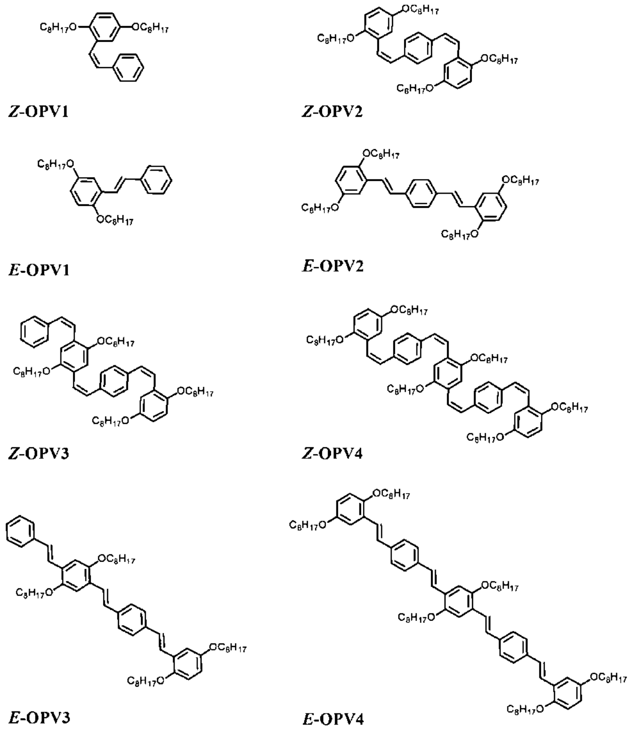

Fig. 1. Structures for the *p*-oligo(phenylenevinylene)s (**OPVs**).

OPV1 underwent photoisomerization mutually between *E* and *Z* isomers as usual stilbene derivatives, and the quantum yield of isomerization were determined to be 0.44 and 0.21 for *Z*-to-*E* and *E*-to-*Z* isomerization, respectively, in benzene. On the other hand, *Z*-**OPV2**, *Z*-**OPV3**, and *Z*-**OPV4** exhibited almost one-way photoisomerization to the all-*E* isomers. Upon irradiation at 365 nm light in benzene, the absorption spectra of all-*Z* isomers changed to those of the all-*E*-isomers. The spectral changes were consistent with the ^{1}H NMR analysis in benzene-d_6, which indicated photoisomerization solely from the all-*Z* to all-*E* isomers.[22] The quantum yields of *Z*–*E* isomerization of **OPVs** were determined by the absorbance change at the maximum wavelength of the all-*E* isomer upon laser excitation at 308 nm with a XeCl excimer laser and by using the triplet–triplet absorption spectra of benzophenone as a standard for actinometory. The quantum yield of isomerization decreased with an increase in the number of olefin units, and that of *Z*-**OPV2**, *Z*-**OPV3**, and *Z*-**OPV4** was 0.21, 0.13, and 0.07, respectively.

The quantum yield of one-way *Z*-to-*E* isomerization of aromatic olefins increased with an increase in the *Z*-isomer concentration, exceeding unity.[13,23] The quantum yields of *Z*-to-*E* isomerization of **OPV2**, **OPV3**, and **OPV4** were independent of the concentration, indicating that triplet energy transfer from all-*E* isomer to all-*Z* isomer did not occur. This

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means that the one-way isomerization occurs in the singlet excited state, or the triplet energy of all-*E* isomer is much lower than that of all-*Z* isomer. Otherwise, the concentration is too low to induce energy transfer from the excited triplet state to the ground state *Z* isomer.

In order to elucidate the potential energy surface of photoisomerization, the triplet state of *E*-**OPV2**, *Z*-**OPV2**, *E*-**OPV3**, *Z*-**OPV3**, *E*-**OPV4**, and *Z*-**OPV4** were observed by laser flash photolysis. In **OPV2**, **OPV3**, and **OPV4**, the transient absorption spectra of all-*E*-isomers were the same as those of the corresponding all-*Z*-isomers, indicating that both the all-*E* and the all-*Z* isomers have the same triplet excited state. The absorption maximum of the triplet state was 530 nm (the triplet lifetime; $\tau_T = 7\,\mu s$), 600 nm ($\tau_T = 15\,\mu s$), and 660 nm ($\tau_T = 15\,\mu s$) for **OPV2**, **OPV3**, and **OPV4**, respectively. The quantum yield of intersystem crossing (Φ_{isc}) of *Z*-**OPV2**, *Z*-**OPV3**, and *Z*-**OPV4** were estimated to be ≈0, 0.03, and 0.09, respectively, based on the results of analysis of the triplet energy transfer from **OPVs** to β-carotene by laser flash photolysis.[24,25] The absorption maximum of the triplet state shifted to longer wavelength with an increase in the number of olefin units. The π-conjugation system in the triplet excited state of **OPVs** should be longer with an increase in the olefin units, and therefore, the observed transient absorption spectra were assigned to the triplet excited state of all-*E* isomer. In addition, isomers, e.g. the (*E*, *E*, *Z*) or (*E*, *Z*, *Z*) conformation in the case of **OPV3**, were not detected by HPLC analysis. UV–vis absorption spectra changes from *Z*-**OPVs** to *E*-**OPVs** also had an isosbestic point,[22] indicating that the phoisomerization occurs between two conformations. These results show that all-*Z* isomers convert solely to all-*E* isomers upon photoirradiation.

From the results of transient absorption spectra and the determination of the quantum yield, we now discuss the photoisomerization mechanism. The transient absorption spectra of *Z*-**OPV2** and time profiles at 410 and 530 nm in laser flash photolysis experiments are shown in Fig. 2. The transient absorption at 530 nm, which was assigned to be the triplet excited state (^3E-**OPV2***) was observed just after laser irradiation at 308 nm, and decayed within 7 µs. ^3Z-**OPV2*** isomerized to ^3E-**OPV2*** during the laser pulse within 50 ns. On the other hand, in the time profile at 410 nm, the absorbance increased to 0.16 just after laser excitation at 308 nm and remained constant for approximately 40 µs. Comparing the absorption spectra of *E*-**OPV2** and *Z*-**OPV2** with the transient absorption spectra, the absorbance change at 410 nm upon laser excitation at 308 nm can be assigned to the absorbance change due to the *Z*-to-*E* isomerization. Since the absorbance change at 410 nm occurred just after laser excitation and was independent of the time profile at 530 nm, the *Z*-to-*E* isomerization in **OPV2** took place mainly in the singlet excited state.

The transient absorption spectra of *Z*-**OPV4** and time profiles at 440 and 660 nm in laser flash photolysis experiment are shown in Fig. 3. The transient absorption at 660 nm, which was assigned to be the triplet excited state (^3E-**OPV4***), was observed just after 308 nm laser excitation and decayed with a lifetime of 15 µs. ^3Z-**OPV4*** isomerized to ^3E-**OPV4*** during the laser pulse within 50 ns. On the other hand, in the time profile at 440 nm, the absorbance changed by 0.05 just after laser excitation, followed by a gradual increase with time. The absorbance change by 0.05 within the laser pulse was due to the *Z*-to-*E* isomerization via the singlet excited state. The rise profile from 0.05 to 0.28 in absorbance during the 40 µs after the laser pulse is in accordance with the lifetime of ^3E-**OPV4***. These results indicate that the *Z*-to-*E* isomerization of **OPV4** takes place both in the singlet and in the triplet excited state. The expected potential energy surfaces of isomerization of **OPV2** and **OPV4** are shown in Fig. S1 (Supporting Information). For **OPV2**, one-way isomerization may occur by a step-wise process via the *ZE*-**OPV2** excited state or by directly producing the *EE*-**OPV2** excited state. Although the mechanism of **OPV4** should be more complicated, the experimental results indicate that all-*Z*-**OPV4** undergoes an one-way isomerization by directly producing the all-*E*-**OPV4** excited state.

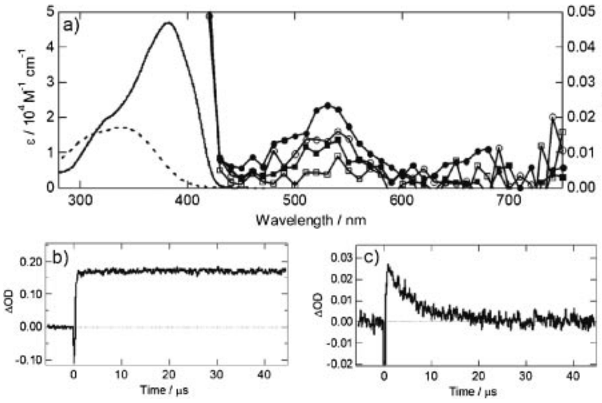

Fig. 2. (a) Absorption spectra of all-*E*-**OPV2** (solid line) and all-*Z*-**OPV2** (dotted line) and transient absorption spectra of all-*Z*-**OPV2** at 1.1 µs (●), 3.5 µs (○), 6.5 µs (■), and 12 µs (□) after laser excitation at 308 nm in benzene. In addition, time profiles of absorbance change at (b) 410 nm and (c) 530 nm upon laser excitation at 308 nm are shown.

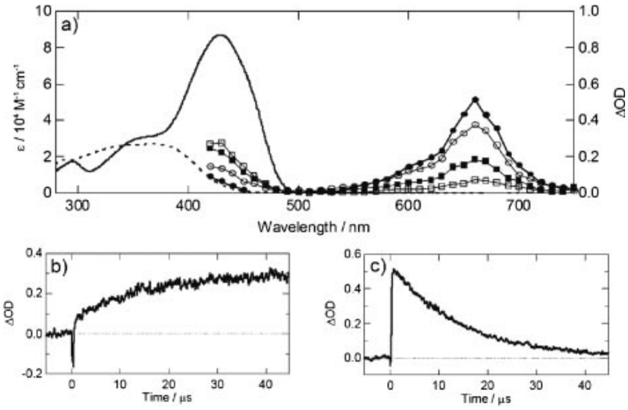

Fig. 3. (a) Absorption spectra of all-*E*-**OPV4** (solid line) and all-*Z*-**OPV4** (dotted line) and transient absorption spectra of all-*Z*-**OPV4** at 0.8 µs (●), 5.0 µs (○), 15 µs (■), and 30 µs (□) after laser excitation at 308 nm in benzene. In addition, time profiles of absorbance change at (b) 440 nm and (c) 660 nm upon laser excitation at 308 nm are shown.

Table 1. Quantum Yields of Isomerization and Intersystem Crossing of *Z*-**OPVs**

	$\Phi_{Z\to E}$ a)	Φ_{isc} b)	Direction of isomerization
Z-**OPV1**	0.44	0	two-way
Z-**OPV2**	0.21	0.03	one-way
Z-**OPV3**	0.13	0.09	one-way
Z-**OPV4**	0.07	0.05	one-way

a) Determined by change of absorbance upon laser irradiation.
b) Determined by triplet–triplet energy transfer to β-carotene.

One can estimate the contribution of the singlet excited state and the triplet excited state to the *Z*-to-*E* isomerization of **OPV4** from the absorbance change at 440 nm in the laser flash photolysis experiments, since the ΔODs of 0.05 and 0.23 (the value of 0.23 was calculated from the final absorbance (0.28)–the initial absorbance change (0.05) in Fig. 3b) are assigned to the absorbance change due to the isomerizaiton in the singlet excited state and triplet excited state, respectively. The quantum yield of isomerization ($\Phi_{Z\to E}$) was 0.07 as discussed above, and the whole change in absorbance ΔOD was 0.28 as shown in Fig 3b. From the results, the quantum yield of isomerization in the singlet excited state was calculated to be $0.05/0.28 \times 0.07 = 0.013$. Therefore, the quantum yield of isomerization in the triplet excited state was calculated to be $0.07 - 0.013 = 0.057$. This value is consistent with the quantum yield of intersystem crossing estimated by energy transfer to β-carotene (0.05) within experimental error. These results indicate that the triplet excited state of the *E* isomer (^{3}all-*E*-**OPVs***) deactivates solely to the ground state *E* isomer (^{1}all-*E*-**OPVs**).

The quantum yield of isomerization ($\Phi_{Z\to E}$) and intersystem crossing (Φ_{isc}) of *Z*-**OPVs** are summarized in Table 1. $\Phi_{Z\to E}$ and Φ_{isc} of *Z*-**OPV2** were 0.21 and 0.03, respectively, which indicate that *Z*-to-*E* isomerization of *Z*-**OPV2** mainly takes place in the singlet excited state. On the other hand, in *Z*-**OPV3** and *Z*-**OPV4**, the values of $\Phi_{Z\to E}$ and Φ_{isc} were almost the same, indicating that *Z*-to-*E* isomerization mainly takes place in the triplet excited state.

Photoisomerization mechanism of *Z*-to-*E* isomerization of **OPVs**, depends on the number of olefin units. The alkyl chain does not seem to affect the excited state properties of **OPVs**. However, the presence of alkyl groups may increase the solubility of **OPVs** in benzene. **OPV1** exhibited photoisomerization behavior similar to that of usual stilbene derivatives. **OPV2** exhibited one-way *Z*-to-*E* isomerization mainly via the singlet excited state. With an increase in the number of olefin units, Φ_{isc} increased and *Z*-to-*E* isomerization mainly occurs via the triplet excited state.

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Supporting Information

Figure S1 shows the expected potential energy surfaces of isomerization of **OPV2** and **OPV4**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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