

Supramolecular Triplet Photosensitizer. Effects of the Cation Binding Mode on *E–Z* Isomerization of 1,2-Dichloroethylene

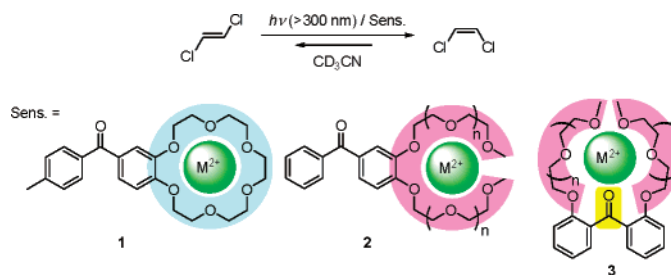
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ABSTRACT



Effects of metal cation recognition on photosensitized *E–Z* isomerization of 1,2-dichloroethylene have been investigated with two types of *m,p*- and *o,o'*-podand (oligo-oxyethylene unit) benzophenones 2 and 3. With increasing cation size, the %*Z* ratio at the photostationary state was changed from 67 to 91% for 2 but remained almost unchanged (86–88%) for 3. These results were interpreted in terms of the variation of excited triplet energy, E_T , associated with the cation complexation of these photosensitizers 2 and 3.

Control of organic reactions by nonbonding interactions, such as an ion dipole interaction, hydrogen bonding, van der Waals attraction, donor–acceptor complexation, and so on, is one of the most attractive subjects in supramolecular chemistry.^{1,2} In recent years, organic photoreactions of crown ether or podand-possessing substrates have been extensively investigated in the application to photochromic materials, electroluminescence and chemiluminescence materials, and phosphorescence ion sensors.^{3,4} Among the photoreactions, photosensitization⁵ is one of the most promising techniques

for promoting the reactions with high efficiency and enhanced selectivity; e.g., photosensitized isomerization of *E*-alkene to thermodynamically less stable *Z*-alkene is a useful synthetic method for the preparation of *Z*-alkene.⁶

Recently, we have found that the triplet photosensitization of 1,2-dichloroethylene (DCE) with crowned benzophenones

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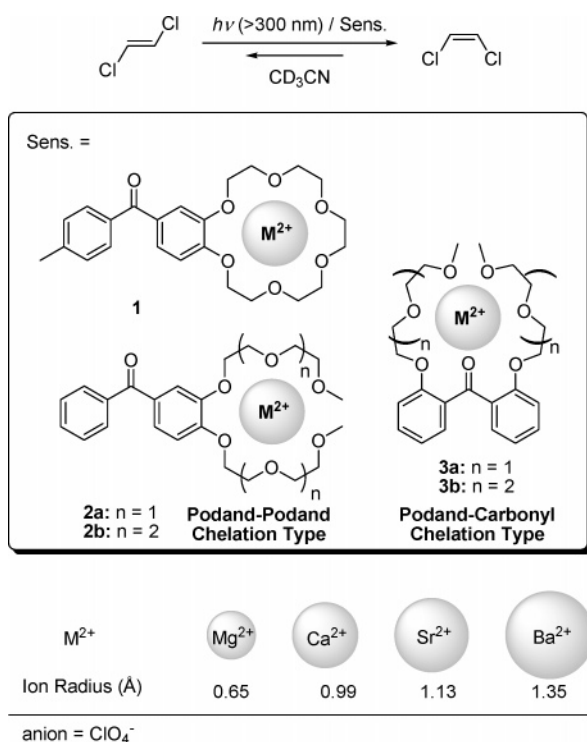
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1 resulted in the cation-dependent increase of the *Z/E* isomer ratios; the addition of alkali and alkaline earth metal ions raised the photostationary state %*Z* values up to ca. 91% compared with the metal-free values of 60%.⁷ To develop this new concept of supramolecular photosensitization, it is desired to know the structural factors which govern the excited triplet energies (E_T) of the cation-bound photosensitizers.

In this paper, we report the cation-recognized photosensitization by two types of novel podand-incorporated benzophenones **2** and **3** with *m,p*- and *o,o'*-disubstituted oligo-oxyethylene chains, respectively. Consequently, we elucidated the effects of the cation recognition mode (podand–podand chelation vs crown ether complexation) on photosensitized *E–Z* isomerization of diagnostic DCE (Scheme 1).

Scheme 1. *E–Z* Photoisomerization of 1,2-Dichloroethylene by Using Photosensitizers **1–3** in the Absence or Presence of Various Alkaline Earth Metal Perchlorates in Acetonitrile



monoiodides instead of tosylates.⁹ The flash silica gel column chromatography gave essentially the pure products as a colorless oil in good to moderate yields (51–66%).

The binding constants of **2a,b** and **3a,b** with various alkaline earth metal ions (Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺) were estimated by the UV titration method; thus, the plots of absorbance change of benzophenones vs added cation concentration were curve fitted to obtain the binding constants *K* by the least-squares method.¹⁰ The log *K* values were summarized along with those of the crowned **1** in Table 1. The binding constants proved to be sufficiently large (>3.5

Table 1. Binding Constants *K* for Complexation of Crowned Benzophenone **1** and Podand Benzophenones **2** and **3** with Alkaline Earth Metals in Acetonitrile^a

cations	log <i>K</i>				
	1	2a	2b	3a	3b
Mg ²⁺	<i>b</i>	<i>b</i>	<i>b</i>	2.5	2.9
Ca ²⁺	6.5	3.7	5.4	3.7	4.5
Sr ²⁺	6.9	4.8	7.4	3.5	5.7
Ba ²⁺	6.3	5.5	6.3	3.7	5.5

^a Determined by UV titration in acetonitrile using metal perchlorate.
^b Could not be obtained because of the too small UV spectral changes.

in log *K* except for Mg²⁺) for the 1:1 complexation of benzophenones with alkaline earth metals in the present photochemical conditions.¹¹ For all sensitizers, the Mg²⁺ cation seemed to be too small (0.65 Å) to show an effective complexation.

As expected, the longer oligo-oxyethylene chain (*n* = 2) of **3b** raised the binding constant *K* ca. 6–160 times as compared with **3a** (*n* = 1) for all cations. This tendency is also the case for the sensitizers **2a,b** for the efficiently bound Ca²⁺–Ba²⁺. However, the straightforward application of the ion-in-the-hole concept¹² seems to be meaningless because of the far more increased flexibility of the podand units.

To examine the applicability as triplet photosensitizers, the photosensitized *E–Z* isomerization of DCE was tested by using the podand benzophenones **2** and **3**. A 1:1 mixture of *E*- and *Z*-DCE (10 mM) and photosensitizers **1–3** (10 mM) in the absence or presence of alkaline earth metal perchlorates (50 mM) in deuterated acetonitrile was irradiated in an NMR tube with Pyrex-filtered light (>300 nm) by using a high-pressure mercury lamp at room temperature under an argon atmosphere (Scheme 1). The *E/Z* isomer ratio of DCE was monitored by ¹H NMR until reaching the photostationary state %*Z*_{PSS} (3~9 h). During the photoirradiation,

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(10) (a) Leggett, D. J. *Computational Methods for the Determination of Formation Constants*; Plenum: New York, 1985. (b) Connors, K. A. *Binding Constants*; Wiley: New York, 1987.

(11) Five equivalent of metal cations induces 1:1 complexation of **1** (10 mM) in 80.8% at log *K* = 2, in 97.6% at log *K* = 3, in 99.8% at log *K* = 4, and in 100.0% at log *K* = 5.

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The podand benzophenones **2a,b** and **3a,b** were synthesized from the corresponding dihydroxy benzophenones by the reaction with monotosylated oligo-ethylene glycols.⁸ However, the direct etherification by tosylates resulted in the low yield formation and the residual tosylates were difficult to separate from the products on silica gel column chromatography. Therefore, we employed the corresponding

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even on long-time irradiation (24 h), no detectable photo-products of these sensitizers were observed by NMR except for **3a** and **3b** which photodegraded in the absence of metal cations or in the presence of less-bound Mg^{2+} cations.¹³

Figure 1 shows the plots of $\%Z_{\text{PSS}}$ thus obtained in the absence or presence of alkaline earth metal cations for the

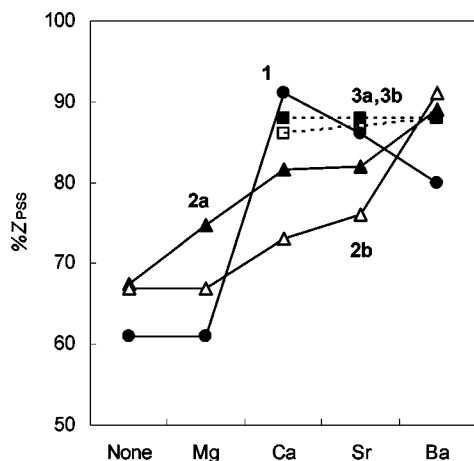


Figure 1. Plots of $\%Z_{\text{PSS}}$ of DCE (10 mM) vs alkaline earth metal ions added (50 mM) in the presence of photosensitizers **1**, **2a,b**, and **3a,b** (10 mM). The plots for **3a,b** in the metal-free conditions and in the presence of Mg^{2+} are missing because of the possible photodegradation.

podand sensitizers **2** and **3** (solid lines) in comparison with the crowned sensitizer **1** (dotted line). The *m,p*-dipodand-substituted sensitizers **2a,b** as well as **1** showed a noticeable variation of the $\%Z_{\text{PSS}}$ ratio from 60 to 70% in the absence of metal ions up to 90% by addition of ions. On the other hand, the *o,o'*-dipodand-substituted sensitizers **3a,b** did not show the appreciable change in the photostationary values of $\%Z_{\text{PSS}}$ ($\sim 90\%$) by changing cations (Ca^{2+} – Ba^{2+}). Unfortunately, as mentioned above, the photolability of **3a,b** did not allow the metal-free photosensitization nor did the presence of too small Mg^{2+} . Incidentally, no change of the starting $\%Z$ value ($=50\%$) was observed for all the combinations of sensitizers and metal ions in the dark conditions.

It is noteworthy that the former crowned benzophenone **1** showed a peak top at Ca^{2+} , whereas the podand benzophenones **2a,b** exhibited the gradual increase of $\%Z_{\text{PSS}}$ with increasing metal ion radius. As we have previously reported,⁷ the crucial factor which performs the high $\%Z_{\text{PSS}}$ is the appropriate energy difference between the triplet energy E_{T} of the photosensitizer and that of the relevant isomeric alkene. Such a situation leads to the highly discriminating energy transfer on each isomer as reported by Hammond and Saltiel.¹⁴ This indicates that $\%Z_{\text{PSS}}$ is determined not by the ion-size fitting concept¹² but by the relative efficiency of the energy transfer to each isomer.

(13) The photoreaction of **3a** and **3b** in the absence of metal cations resulted in expected intramolecular photochemical hydrogen abstraction (Norrish Type II). Current efforts are directed toward the isolation and characterization of these photodegradation products.

To determine the cation recognition effects on the triplet energy E_{T} of each photosensitizer, we have measured the phosphorescence spectra of **2** and **3** at 77 K in frozen acetonitrile. The lowest E_{T} for **2** and **3** was estimated from the onset wavelength of the phosphorescence spectra by a previously reported method.⁷ The compound **2b** exhibited the increasing variation of E_{T} ($\sim 11 \text{ kJ mol}^{-1}$) with increasing metal ion radius (Figure 2a, left), and **3b** also followed the increasing tendency of E_{T} ($\sim 11 \text{ kJ mol}^{-1}$) with the ion radius (Figure 2b, right).

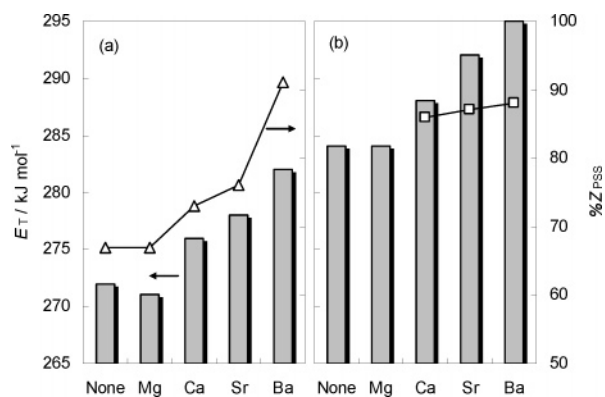


Figure 2. $\%Z_{\text{PSS}}$ (line) and the estimated triplet energy E_{T} (bar) of podand benzophenone **2b** (a; left) and **3b** (b; right) in the absence or presence of alkaline earth metal ions. The points for **3b** in the metal-free conditions and in the presence of Mg^{2+} are missing because of the possible photodegradation.

We have already revealed that the Saltiel plots for various triplet sensitizers in the photoisomerization of DCE provide the $\%Z_{\text{PSS}}$ peak maximum at around $E_{\text{T}} = 290 \text{ kJ mol}^{-1}$ (Figure 3).^{7,15} Thus, the relatively high $\%Z_{\text{PSS}}$ values ($\sim 90\%$) were obtained in the presence of Ba^{2+} for sensitizer **2b** and in the presence of Ca^{2+} – Ba^{2+} for sensitizer **3b** ($285 < E_{\text{T}} < 295 \text{ kJ mol}^{-1}$), whereas the lower $\%Z_{\text{PSS}}$ values ($\sim 70\%$) were attained in the presence of Mg^{2+} , Ca^{2+} , and Sr^{2+} for **2b** ($< 280 \text{ kJ mol}^{-1}$) as well as for metal-free **2b** (272 kJ mol^{-1}). The similar tendency was also observed for the shorter length **2a** and **3a**. On the whole, the cation-recognized sensitizers **2** are scattered on the left-side slope of Saltiel plots, with **3** around the top of the peak.

Such a variation of the E_{T} value by an added metal ion for the *m,p*-dipodand **2a,b** may be explained by the electronic and steric effects caused by cation complexation. The bound cation obviously diminishes the electron densities on the

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(15) We previously reported (in ref 7) that the Saltiel plots for DCE with 13 common sensitizers showed the most pronounced differential isomerization around $E_{\text{T}} = 290 \text{ kJ mol}^{-1}$. Thus, the triplet energy of sensitizer **1**– Ca^{2+} and **2**– Ba^{2+} as well as **3** may be located around 290 kJ mol^{-1} .

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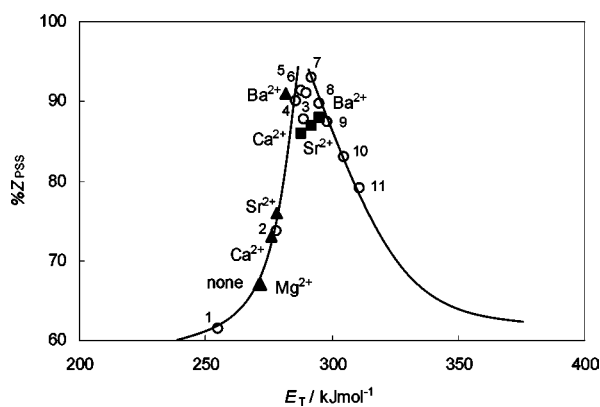


Figure 3. Saltiel plot of the %Z_{PSS} ratio of 1,2-DCE vs various triplet energies of sensitizers **2b**·M²⁺ (▲), **3b**·M²⁺ (■), and common sensitizers¹⁶ (○); Michler's ketone (1), 4-aminoacetophenone (2), benzophenone (3), 4,4'-dichlorobenzophenone (4), 4-chlorobenzophenone (5), 4-methylbenzophenone (6), 4,4'-dimethoxybenzophenone (7), 4-methoxybenzaldehyde (8), 4-methylbenzaldehyde (9), 4-methylacetophenone (10), and acetophenone (11).

oxyethylene units. This would reduce the π -electron-donating ability of *p*-oxyethylene lone-pair electrons and therefore lower the energy of highly conjugated LUMO, leading to a smaller E_T . However, the bound cation necessarily restricts the conformational freedom of cation-chelating podand chains so that the favorable π -resonance effects through the oxyethylene unit are considerably inhibited. Conversely, this stereoelectronic effect may raise the LUMO, bringing about a larger E_T . Furthermore, it can be expected that the binding of **2** with a metal cation results in enhancement of the excited-state energy by state switching on account of the possible partial charge-transfer character (because of the contribution of the two alkoxy substituents) of the excited **2**. The present results imply that the conformational inhibition of π -resonance effects and/or the intramolecular charge-transfer destabilization exceed the former electron-withdrawing effects of the metal cation.¹⁷

On the other hand, the *o,o'*-dipodand sensitizers **3a,b** are expected to equally bind the metal ions with two oligo-

oxyethylene units on the basis of the ¹H and ¹³C NMR measurements for **3a** in the presence of Ba²⁺ (5 equiv, CD₃CN). The obtained spectra revealed the magnetic equivalence of two podand protons as well as the aromatics even at -40 °C (Supporting Information). Interestingly, the Ba²⁺ complexation brought the 2.9 ppm downfield shift for the carbonyl carbon of **3a**. This value is larger than the downfield shift (1.1 ppm) of the corresponding carbonyl carbon for the Ba²⁺ complex of di-2-(2-methoxyethoxy)ethyl phthalate.¹⁸ This indicates the relevant carbonyl group also plays an important role in the chelating complexation of metal ions.¹⁹ Considering the stable twisted conformation of the two aromatics as well as the flexibility of the oligo-oxyethylene chains, the compound **3** can envelop the guest cation.

In conclusion, we found that the easily functionalized oligo-oxyethylene podand benzophenones **2** and **3** exerted the different affection on the *E*-*Z* photoisomerization of DCE as cation-recognized triplet sensitizers. For *m,p*-dipodand **2**, the *Z/E* isomer ratios at the photostationary state were appreciably increased with increasing triplet energies (E_T) because of the scattering on the left-side slope of Saltiel plots in a manner similar to that for crowned **1**. However, *o,o'*-dipodand **3** brought about no noticeable change of %Z_{PSS} because of the peak-top scattering.

Acknowledgment. We are grateful to Dr. K. Nozaki (Osaka University) for the measurement of phosphorescence spectra.

Supporting Information Available: Experimental details, ¹H and ¹³C NMR spectra of complex of **3a** with Ba²⁺, as well as characterization data of new compounds **2a**, **2b**, **3a**, and **3b** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) Indeed, UV spectra of **2b** in acetonitrile showed the blue shift (~10 nm) of the longest wavelength peak ($\lambda_{\max} = 310$ nm) by addition of 50 equiv of Ba²⁺ ions, in accordance with the above argument.

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(19) It is also well-known that the complexation of ketones with Lewis acids resulted in the similar downfield shift of the carbonyl ¹³C chemical shift: Santelli, M.; Pons, J.-M. *Lewis acids and selectivity in organic synthesis*; CRC Press: Boca Raton, 1996; pp 8–11.