# **Temporary Crown Ether Compounds Induced by UV Irradiation**

## Hideyuki Itagaki,\* Wakako Masuda, Yukiko Hirayanagi, and Kazuya Sugimoto

Department of Chemistry, School of Education and Graduate School of Electronic Science and Technology, Shizuoka University, 836 Ohya, Shizuoka 422-8529, Japan

Received: August 20, 2001; In Final Form: November 29, 2001

A new reversible photoresponsive system using a photophysical process is presented and proved in detail. 1,*n*-bis(3-(1-pyrenyl)propylcarboxy)oxaalkanes (DP3*n*: n = 3 to 6), linear oligooxyethylenes with pyrenyl groups at both ends, were shown to form a relatively stable cyclic structure analogous to a crown ether in fluid solution during their photoexcited states, occurring due to the formation of an intramolecular excimer between two terminal pyrenyl groups. Moreover, DP34 molecules were found to capture and transport cadmium ions more effectively when they were irradiated. Accordingly, these compounds are referred to as photoinduced crown ether compounds (PICs) because they work as a crown ether when irradiated and they can select metal ions to capture according to their diameters. Our study is the first to attempt to use excimers to fix the conformation of a molecule for relatively long periods and to put this photophysical process to practical use.

#### Introduction

In a short communication, we have described a novel reversible photoresponsive system that employs a photophysical process.<sup>1</sup> We introduced pyrenyl groups onto both ends of linear oligooxyethylenes (Figure 1). When irradiated with UV light, the pyrenyl groups link together to form an excimer with a lifetime in the sub-microsecond range.<sup>2</sup> This structure is analogous to that of crown ethers, which are cyclic ethylene glycols capable of transporting ionic compounds into an organic phase. We showed that one of these compounds indeed had the properties of a crown ether: when irradiated, it could capture calcium ions and transport them through a  $CCl_4$  phase. Accordingly, we have referred to them as photoinduced crown ether compounds (PICs).

Here we report that a PIC is a general phenomenon. To prove that a PIC can select a metal ion whose size fits the cavity of its closed form, we examine a case in which cadmium ions are added into a PIC system: water is easily polluted by calcium because it is present everywhere, but water has no chance of being spontaneously contaminated by cadmium.

On the other hand, several studies have investigated oligooxyethylenes having aromatic compounds at both ends. These studies can be classified into three types: (i) studies on the expansion or cyclization of an oligomer or polymer in fluid solution,<sup>3,4</sup> (ii) attempts to develop a fluorescent reagent to monitor metal ions captured by oligooxyethylenes,<sup>5-8</sup> and (iii) attempts to develop a compound to capture metal ions by irradiation.<sup>9,10</sup> In the first two types of studies, excimers formed between aromatic end groups were used as probes to obtain the information regarding the physical properties or the amounts of metal ions present. The third type of study used photodimerization, which is a photochemical reaction, to permanently link the aromatic end groups. Accordingly, our work was the first attempt to use excimers to fix the conformation of a molecule for relatively long periods. Needless to say, it is reversible because a compound capturing metal ions dissociates its excimer in the dark and would release them in water. Since the





## (I) open form (II) closed form

**Figure 1.** A schematic drawing of a photoinduced crown ether compound. The probability that a compound will be in the closed form, which is similar to a crown ether, is usually very small in the absence of light. However, if one of the terminal pyrenyl groups of oligooxy-ethylene compounds is irradiated, it links to the other pyrenyl group to form an excimer that stabilizes this conformation. Here shows an extended conformation as an example of open form (I), but a longer oxyethylene chain prefers helical conformations.

concentration of metal ions in a PIC solution can be changed by irradiation, such solutions might have applications as photoswitches.

### **Experimental Section**

**Materials.** The structure of the 1,*n*-bis(3-(1-pyrenyl)propylcarboxy)oxaalkanes (DP3*n*; n = 3, 4, 5, 6) studied in the present work is shown in Scheme 1. To prepare the DP3*n*'s, 1-pyrenebutyric acid (PB) was first converted to the acid-chloride, 3-(1pyrenyl)propylcarbonyl chloride (PPCC), and then reacted with triethylene glycol (OE3; n = 3), tetraethylene glycol (OE4; n = 4), pentaethylene glycol (OE5; n = 5), and hexaethylene glycol (OE6; n = 6) to produce DP33, DP34, DP35, and DP36, respectively.



To a solution of 2.0 g of PB in 190 mL of benzene, 4.3 g of thionyl chloride was added dropwise with stirring. The solution was refluxed at 80 °C for 4 h. A 2.2 g quantity of PPCC was obtained by evaporating the solvent and dried under vacuum. PPCC (1.0 g) was then reacted in 100 mL of benzene including 1 mL of pyridine (PPCC/pyridine = 1 g/1 mL) under  $N_2$  flux with OE3, OE4, OE5, and OE6, respectively. The mole ratio of PPCC and OEn (n = 3-6) was 4. The solution was refluxed at 80 °C for 7 h. After evaporating the solvent, 150 mL of 1% aqueous HCl was added and the organic products were extracted into diethyl ether. The combined extracts were washed with 1% aqueous HCl (three times), 1% aqueous NaOH (three times), and distilled water (two times), and saturated NaCl solution, and then were evaporated and dried under vacuum. The products were separated with a Sephadex L-20 (Pharmacia) chromatographic column using THF as the eluent. Since impurities having a pyrenyl group at only one end do not show excimer fluorescence, the fractions whose fluorescence spectra consisting of monomer and excimer fluorescence were identical with one another were collected all together. Because an impurity having only one terminal pyrenyl group shows strong fluorescence of monomeric pyrenyl group about 100 times as much as DP3n does, note that the fluorescence measurements are quite effective to show the purity: for example, we can detect the existence of the impurity with only one terminal pyrenyl group even if its fraction is 0.1%.

DP33. <sup>1</sup>H NMR (CD<sub>3</sub>CN)( $\delta$  in ppm, J in Hz): 2.03 (qui, 4H, J = 7.5), 2.36 (t, 4H, J = 7.2), 3.28 (t, 4H, J = 8.0), 3.50 (s, 4H), 3.54 (t, 4H, J = 4.8), 4.09 (t, 4H, J = 4.8), 7.82–8.30 (m, 18H). <sup>13</sup>C NMR (CD<sub>3</sub>CN)( $\delta$  in ppm): 26.5, 31.9, 33.1, 63.0, 68.5, 69.9, 123.2, 124.5, 124.6, 125.8, 126.3, 126.9, 127.2, 127.3. IR (neat): 3040, 2950, 1730, 1600, 1510, 1460, 1250, 1180, 1130, 960, 850, 760, 720. HRFAB-MS: (M + H)<sup>+</sup> calcd. 691.3060 for C<sub>46</sub>H<sub>43</sub>O<sub>6</sub>. Found: 691.2965.

DP34. <sup>1</sup>H NMR (CD<sub>3</sub>CN)( $\delta$  in ppm, J in Hz): 2.06 (qui, 4H, J = 7.5), 2.40 (t, 4H, J = 7.1), 3.31 (t, 4H, J = 7.7), 3.40– 3.45 (m, 8H), 3.52 (t, 4H, J = 4.8), 4.10 (t, 4H, J = 4.8), 7.84– 8.31 (m, 18H). <sup>13</sup>C NMR (CD<sub>3</sub>CN)( $\delta$  in ppm): 26.6, 31.9, 33.2, 63.1, 68.5, 69.9, 69.9, 123.3, 124.5, 124.7, 125.8, 126.3, 127.0, 127.2, 127.3. IR (neat): 3040, 2880, 1730, 1600, 1460, 1250, 1110, 960, 850, 760, 720. HRFAB-MS: (M + H)<sup>+</sup> calcd. 735.3322 for C<sub>48</sub>H<sub>47</sub>O<sub>7</sub>. Found: 735.3265. DP35. <sup>1</sup>H NMR (CD<sub>3</sub>CN)( $\delta$  in ppm, J in Hz): 2.06 (qui, 4H, J = 7.5), 2.41 (t, 4H, J = 7.3), 3.32 (t, 4H, J = 7.7), 3.36– 3.47 (m, 12H), 3.55 (t, 4H, J = 4.8), 4.12 (t, 4H, J = 4.8), 7.84–8.32 (m, 18H). <sup>13</sup>C NMR (CD<sub>3</sub>CN)( $\delta$  in ppm): 26.3, 31.8, 33.3, 62.9, 69.0, 69.3, 70.0, 70.4, 123.3, 124.5, 124.6, 125.8, 126.3, 127.0, 127.2, 127.3. IR (neat): 3040, 2880, 1730, 1600, 1590, 1460, 1420, 1350, 1250, 1180, 1130, 960, 850, 760, 720. HRFAB-MS: (M + H)<sup>+</sup> calcd. 778.3506 for C<sub>50</sub>H<sub>51</sub>O<sub>8</sub>. Found: 778.3491.

DP36. <sup>1</sup>H NMR (CD<sub>3</sub>CN)( $\delta$  in ppm, J in Hz): 2.07 (qui, 4H, J = 7.6), 2.42 (t, 4H, J = 7.2), 3.33 (t, 4H, J = 7.7), 3.35– 3.49 (m, 16H), 3.57 (t, 4H, J = 4.8), 4.13 (t, 4H, J = 4.8), 7.85–8.33 (m, 18H). <sup>13</sup>C NMR (CD<sub>3</sub>CN)( $\delta$  in ppm): 26.5, 31.9, 33.2, 63.1, 68.5, 69.8, 69.9, 69.9, 123.2, 124.5, 124.7, 125.8, 126.3, 127.0, 127.2, 127.3. IR (neat): 3040, 2880, 1730, 1600, 1460, 1420, 1350, 1250, 1180, 1110, 960, 850, 760, 720. HRFAB-MS: (M + H)<sup>+</sup> calcd. 823.3846 for C<sub>52</sub>H<sub>54</sub>O<sub>9</sub>. Found: 823.3828.

The solvents used for photophysical measurements were THF, which was freshly distilled, and acetonitrile (Wako, luminasol grade) without purification. Cadmium perchlorate hexahydrate and calcium thiocyanate tetrahydrate were purchased from Kishida Chemical Ltd. and Wako Ltd., respectively.

Measurements. Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi F-4500 spectrofluorometer. The sample temperature was controlled by an Oxford DN1704 cryostat with an ITC-4 digital temperature controller, which can regulate to better than  $\pm 0.1$  K. Independent temperature measurement was carried out by means of a second thermocouple and a potentiometer. All samples were kept at each set temperature and spectra were run repeatedly for more than 30 min even after perfect duplication was obtained to make sure that the equilibrium state was attained. Fluorescence decay curves were obtained by using a Horiba NAES550 single photon counting machine with a nanosecond flash lamp. The excitation wavelength was separated to be 340 nm through an interference filter. The emission decay was measured at 25 °C through an interference filter of 383- (monomeric singlet), or 479-nm (excimer). We analyzed fluorescence decay curves by the deconvolution method after O'Connor and Phillips<sup>11</sup> using the Durbin-Watson factor (DW)<sup>12,13</sup> to assess the validity of the trial fitting function. DW is calculated from

$$DW = \sum_{i=2}^{N} (R_i - R_{i-1})^2 / (\sum_{i=1}^{N} R_i^2)$$

where the weighted residual  $R_i = (Y_i - F_i)/Y_i^{1/2}$ ,  $Y_i$  and  $F_i$  are the values of the experimental data and trial calculation value corresponding to the time channel *i*, and *N* is the number of experimental points. For the best fit, the value of DW approaches 2.0.

All NMR experiments of DP3*n* in CD<sub>3</sub>CN were performed using a JEOL GX400 FT-NMR spectrometer with a static field strength of 399.65 MHz for <sup>1</sup>H and 100.4 MHz for <sup>13</sup>C. The concentration of cadmium ion transferred was determined with a Hitachi Z-8270 polarized Zeeman atomic absorption spectrophotometer.

## **Results and Discussion**

**Photophysical Processes of DP3***n***.** Figure 2 shows the fluorescence spectra of DP3*n* in aerated acetonitrile at 25 °C. The peaks near 378 and 480 nm were assigned to the pyrenyl monomer singlet and excimer emission, respectively.<sup>14</sup> In fact, the excitation spectra for the fluorescence between 380 and 550



**Figure 2.** Fluorescence spectra of DP3*n* in aerated THF (concentration of pyrenyl groups is less than 1  $\mu$ M). All the spectra are normalized to the peak of excimer fluorescence. The excitation wavelength is 342 nm.

nm of all samples were almost identical. They were also identical to their absorption spectra. No concentration dependence was observed for the fluorescence spectra of the DP3*n*'s below 10  $\mu$ M, meaning that all the excimers shown in Figure 2 are formed intramolecularly. The fluorescence spectra of DP3*n* in THF, water, chloroform, and dichloromethane all showed strong excimer fluorescence and weak monomeric fluorescence, indicating that DP3*n* readily takes a closed form similar to a crown ether as shown in Figure 1.

The ratio of excimer fluorescence peak intensity,  $I_{\rm E}$ , to monomer fluorescence peak intensity,  $I_{\rm M}$ , was inversely related to the number of oxyethylene units: the order of  $I_{\rm E}/I_{\rm M}$  was DP33 > DP34 > DP35 > DP36. The intramolecular excimers are formed after excitation of one of the pyrenyl moieties in a diffusional encounter with the other pyrenyl moiety. The  $I_{\rm E}/I_{\rm M}$ of two terminal aromatic groups attached to a chain is already known to have such a similar dependence on a chain length as the dependence of the yields of organic ring closure reactions on ring size.<sup>15,16</sup> Thus, the order of  $I_{\rm E}/I_{\rm M}$  shown above is quite reasonable because the average distance between two terminal pyrenyl groups must be in the order of DP33 < DP34 < DP35 < DP36.

To examine the dynamic process of the excimer formation in the DP3*n* system, we measured the time profile of monomer and excimer fluorescence of DP3*n* (n = 3-6) in degassed THF and acetonitrile by means of the nanosecond single photon counting technique. The monomer fluorescence of DP3*n* in both solvents was determined to decay dual-exponentially (eq 1) with the reciprocal of decay constants of 2 to 8 ns and 200 ns.<sup>17</sup>

$$I_{\rm M}(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t), A_1 + A_2 = 1$$
 (1)

The decay curve of excimer fluorescence was fitted well to

$$I_{\rm E}(t) = A_3 \exp(-\lambda_{\rm e} t) - A_4 \exp(-\lambda_3 t)$$
(2)

Roughly speaking,  $\lambda_1$  and  $\lambda_3$  almost agree with each other and  $A_3$  is a little larger than  $A_4$ . The calculated decay parameters are summarized in Table 1. In the case in which  $\lambda_3$  is short, the error is large, so we present only  $\lambda_e$  values in Table 1.

The first conclusion deduced from the transient measurements is that the excimer dissociation of DP3*n* can be neglected even at room temperature, because the decay component with  $\tau_e$  is not detectable in the monomer fluorescence. Therefore the kinetics of excimer formation in the DP3*n* system is considered to conform to the conventional model shown in Scheme 2.<sup>23</sup> Here the correspondence between  $\lambda_1$  and  $\lambda_3$  is explicable.

 TABLE 1: Fluorescence Decay Profiles of DP3n in Degassed
 Solutions of THF and Acetonitrile

samples	$A_1$	$1/\lambda_1$ (ns)	$A_2$	$1/\lambda_2$ (ns)	$1/\lambda_e$ (ns)	$k_{\rm EM} \ (10^{-8}  {\rm s}^{-1})$	$\tau_{\rm EM}$ (ns)		
In THF									
1-pyrenebutyric acid	1.0	210							
DP33	0.93	5.2	0.069	200	52	1.9	5.3		
DP34	0.93	5.6	0.069	200	51	1.7	5.8		
DP35	0.92	6.8	0.078	200	50	1.4	7.0		
DP36		7.9			52	1.2	8.2		
		In Ace	tonitrile						
1-pyreneacetic acid	1.0	267							
DP33	0.91	1.8	0.090	200	54	5.5	1.8		
DP34	0.89	2.1	0.11	200	53	4.7	2.1		
$DP34 + Cd^{2+b}$	0.96	2.0	0.039	200	51	5.0	2.0		
DP35	0.89	2.2	0.11	200	49	4.5	2.2		
DP36	0.94	2.9	0.057	200	53	3.4	2.9		

<sup>*a*</sup> [DP3*n*]  $\sim 1 \ \mu$ M. <sup>*b*</sup> [Cd<sup>2+</sup>]  $\sim 30 \ \mu$ M.

SCHEME 2<sup>*a*</sup>



<sup>*a*</sup> M\* and E\* are monomer singlet and excimer, respectively.  $k_{\text{FM}}$  and  $k_{\text{FE}}$  are the rate constants for the radiative deactivation from excited monomer and excimer state, respectively.  $k_{\text{IM}}$  and  $k_{\text{IE}}$  are those for the nonradiative deactivation, and  $k_{\text{EM}}$  is the rate constant for excimer formation, respectively.

However, the problem is that there is a smaller decay constant,  $\lambda_2$ , which is the same as the monomer singlet lifetime (~200 ns) of pyrenyl moiety, although Scheme 2 never predicts its existence. The decay component with a time constant of 200 ns means that some DP3n's cannot form excimers and that this fraction is more than 6%.<sup>24</sup>

Two explanations for this are possible: one is because there are some conformations that can never change to the conformation possible to form excimers within the excited lifetime of the pyrenyl group, and another is because some pyrenyl groups are photodegraded during the measurements of fluorescence decay curves, and eventually a DP3*n* with a degraded pyrenyl group at one end cannot form an excimer intramolecularly.

The photodegradation of pyrenyl groups was assured because the excimer fluorescence of DP3*n* decreased after the irradiation of UV light. Thus, when we repeatedly measured the fluorescence decay curves of one sample, the fraction of component with 200 ns  $(1/\lambda_2)$  was found to increase. However, the decay curves of each DP3*n* were ascertained to agree with one another in the case where we measured each new degassed solution with irradiating them for a short time period. Thus, we think that some conformations of DP3*n* could be impossible to form an intramolecular excimer within the excited lifetime of the pyrenyl group (200 ns), but the information on their fraction was contaminated by the photodegradation of a terminal pyrenyl group. In the present paper, we would like to consider only the larger decay constant,  $\lambda_1$ .

Under the assumption that Scheme 2 where excimer dissociation can be neglected as described above is valid, eqs 3 and 4 hold.

$$\lambda_1 = k_{\rm FM} + k_{\rm IM} + k_{\rm EM} \tag{3}$$

$$I_{\rm E}/I_{\rm M} = k_{\rm FE} k_{\rm EM} / (k_{\rm FM} (k_{\rm FE} + k_{\rm IE}))$$
 (4)

Because  $k_{\text{FM}} + k_{\text{IM}}$  can be substituted by the experimental value



**Figure 3.** Temperature dependence of  $I_E/I_M$  for 1.0  $\mu$ M DP35 in degassed THF. All the  $I_E/I_M$  values are equilibrium values.

 TABLE 2: Values of Activation Energies of DP3n in THF (kJ/mol)

	DP33	DP34	DP35	DP36
$\Delta E_{\rm EM}$	20	19	19	13

of PB, each  $k_{\rm EM}$  of DP3*n* can be calculated as shown in Table 1. As a reference, the reciprocal of  $k_{\rm EM}$  is defined as  $\tau_{\rm EM}$ , which indicates the time required for two terminal pyrenyl groups to encounter each other, i.e., the average time required for taking a closed conformation as II in Figure 1. The transient results are found to agree well with the photostationary results. As shown in eq 4,  $I_{\rm E}/I_{\rm M}$  is proportional to the rate of excimer formation, i.e., to the rate of the cyclization process. The order of  $I_{\rm E}/I_{\rm M}$  among the DP3*n*'s was identical to the order of the  $\tau_{\rm EM}$  values, and indicates that the rate of the cyclization process is dependent on the average distance between the two pyrenyl end groups. In conclusion, the DP3*n* with a shorter oxyethylene chain readily takes a closed conformation, i.e., DP33 > DP34 > DP35 > DP36.

Next we measured the temperature dependence of DP3*n* fluorescence in THF. The peak wavelength of the excimer emission is not changed at low temperatures, although a slight blue-shift is observed above 260 K. Figure 3 demonstrates the temperature dependence of  $I_E/I_M$  of DP35 in THF. A plot of  $\ln(I_E/I_M)$  versus 1/T was found to give a straight line below 240 K, where the isoemissive point was observed, and to yield a value of 19 kJ/mol as an activation energy of excimer formation,  $\Delta E_{\rm EM}$  k<sub>EM</sub> =  $A \exp(-\Delta E_{\rm EM}/RT)$ . Table 2 summarizes the values of  $\Delta E_{\rm EM}$  of DP3*n* obtained by using the same method. Because the formation process of these intramolecular excimers is diffusion-controlled and the  $k_{\rm EM}$  should be dependent on the average distance between the two pyrenyl end groups, it is quite reasonable that the values of  $\Delta E_{\rm EM}$  are identical with one another.

It is needless to say that the excimer formation between two terminal pyrenyl groups of DP3*n* is influenced by the viscosity of solvent, which is dependent on temperature. Thus, the values of  $\Delta E_{\rm EM}$  in Table 2 are not the net values for the molecular motion of only DP3*n*'s own but rather include the temperature dependence of solvent viscosity. Here, viscosity,  $\eta$ , follows a relationship of  $\eta = A \exp(\Delta E_{\rm vis}/RT)$  where  $\Delta E_{\rm vis}$  is the activation energy for solvent molecules to flow. By using the reference values between 248 and 323 K,<sup>26</sup>  $\Delta E_{\rm vis}$  of THF is calculated to be 4.4 kJ/mol. Because  $\Delta E_{\rm EM}$  is five times as large as  $\Delta E_{\rm vis}$ , the results show that the activation energy is not dependent on the unit number of the oxyethylene chain (*n*) among *n* = 3 to 5. It means that  $\Delta E_{\rm EM}$  is determined only by the local motion of the pyrenyl group.

 $\Delta E_{\rm EM}$  of only DP36 was found to be lower than those of other DP3*n*'s. It could be due to the fact that polyoxyethylene chains prefer helical conformations instead of extended ones shown in Figure 1. Six units of oxyethylene cannot have a linear



**Figure 4.**  $Cd^{2+}$  concentration dependence of  $I_E/I_M$  of DP3*n* in aerated acetonitrile: DP33 ( $\bigcirc$ ), DP34 ( $\blacktriangle$ ), DP35 ( $\bigtriangledown$ ), and DP36 ( $\blacksquare$ ).  $(I_E/I_M)_{[Cd^{2+}]=0}$  and  $(I_E/I_M)_{[Cd^{2+}]}$  are the values of  $I_E/I_M$  in the absence and presence of Cd<sup>2+</sup> ions. All the concentrations of DP3*n*'s are 0.50  $\mu$ M.

extended form but could have a helical conformation where an excimer conformation is formed differently from the case of DP3*n* with  $n \leq 5$ .

Thus far, we have clarified the information regarding the process of intramolecular excimer formation in the DP3*n* system. The fluorescence results show that (i) DP3*n* normally (i.e., in the dark) exists in the open form (for example, I in Figure 1), (ii) it requires a few nanoseconds to form a closed form (II in Figure 1), (iii)  $\tau_{\rm EM}$  becomes longer with longer chains, and (iv) roughly 40% (1/e) of DP3*n* would remain in the closed conformation at even 50 ns after irradiation.

Photophysical Processes of DP3n when Cadmium Ions are Added. We examined whether the addition of cadmium ions influences the excimer formation of DP3n. We measured the dependence of DP3n fluorescence on Cd2+ concentration using  $3 \,\mu\text{M}$  DP3*n* (absorbance ~ 0.05) and [Cd(ClO<sub>4</sub>)<sub>2</sub>] ranging from  $10^{-5}$  to  $10^{-2}$  M. Since DP3*n* is more stable in acetonitrile than in water, the measurements were made in acetonitrile. The fluorescence of the pyrenyl group of DP3n and its monomeric model, PB, was found to be not quenched at all by the addition of Cd<sup>2+</sup>. Figure 4 shows the Cd<sup>2+</sup> concentration dependence of  $I_{\rm E}/I_{\rm M}$  of DP3*n*: if there is no change,  $(I_{\rm E}/I_{\rm M})_{\rm [Cd^{2+}]}/(I_{\rm E}/I_{\rm M})_{\rm [Cd^{2+}]=0}$ should be 1. Addition of Cd<sup>2+</sup> up to 3 mM did not significantly change the  $I_{\rm E}/I_{\rm M}$  values of DP33, 35, and 36. The change of  $I_{\rm E}/I_{\rm M}$  observed when Cd<sup>2+</sup> was added into DP3*n* is by far smaller than that when  $Ca^{2+}$  was added into DP3*n*. Thus, the interaction between DP3n and  $Cd^{2+}$  ions is assumed to be weaker than that between DP3n and  $Ca^{2+}$  ions. Accordingly, we have to comment that the fluorescence of any DP3n is useless for monitoring Cd<sup>2+</sup>. However it should be noted that the excimer formation efficiency of DP34 increased by 10% when Cd<sup>2+</sup> was added. The increase in  $I_{\rm E}/I_{\rm M}$  is not so noticeably large, but it is reproducible. Then, we measured the fluorescence decay curves of degassed acetonitrile solutions of DP34 when Cd2+ was added into them. However, the decay patterns of DP34 with Cd2+ were found to be almost identical with those of DP34 without  $Cd^{2+}$ : the values of three decay constants were perfectly the same. The difference is only the fraction of two components observed in monomer fluorescence. The results might suggest that the addition of Cd<sup>2+</sup> decreases the fraction of the conformations unable to form an intramolecular excimer within the excited lifetime of the pyrenyl group (200 ns).

We do not think that this is a strong evidence for the association of DP34 with  $Cd^{2+}$ . However, we may safely say that the unique change was observed for DP34 with  $Cd^{2+}$ .

**Interaction between DP3***n* **and Cadmium Ions Monitored by NMR Measurements.** We used <sup>1</sup>H NMR and <sup>13</sup>C NMR measurements employing CD<sub>3</sub>CN as a solvent to examine the ability of the DP3*n*'s to form a complex with Cd<sup>2+</sup>. First, we measured the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of oligooxyeth-



**Figure 5.** The averaged difference values,  $\Delta\delta$ , of the <sup>1</sup>H NMR chemical shifts of OE*n* (*n* = 3–6) in CD<sub>3</sub>CN when the Cd<sup>2+</sup> ions ([Cd<sup>2+</sup>]/[OE*n*] ~ 50) were added ( $\delta_{[Cd^{2+}]}$ ) and absent ( $\delta_{[Cd^{2+}]=0}$ ):  $\Delta\delta = \delta_{[Cd^{2+}]} - \delta_{[Cd^{2+}]=0}$ .



**Figure 6.** The averaged increased values,  $\Delta \delta$ , of some <sup>1</sup>H NMR chemical shifts of DP3*n* (*n* = 3–6) in CD<sub>3</sub>CN when the Cd<sup>2+</sup> ions ([Cd<sup>2+</sup>]/[DP3*n*] ~ 50) were added ( $\delta_{[Cd^{2+}]}$ ) and absent ( $\delta_{[Cd^{2+}]=0}$ ):  $\Delta \delta = \delta_{[Cd^{2+}]} - \delta_{[Cd^{2+}]=0}$ .

ylenes (OE*n*; n = 3 to 6) with and without Cd<sup>2+</sup>. In the case of <sup>13</sup>C NMR spectra of OE*n*, the addition of Cd<sup>2+</sup> did not induce any meaningful shifts of any signals: the largest change was 72.1 ppm to 68.7 ppm observed for OE3, and the other shifts were found to be around 1 ppm. However, the addition of Cd<sup>2+</sup> increased the <sup>1</sup>H NMR chemical shifts of methylene protons by 0.25–0.27 ppm (for example, in the case of OE5, 3.57 to 3.84 ppm (0.27), 3.50 to 3.77 ppm (0.27), and 3.49 to 3.76 ppm (0.27)). Figure 5 shows the average shifts of <sup>1</sup>H NMR signals of OE*n* when Cd<sup>2+</sup> was added. Although there exists an interaction between OE*n* and Cd<sup>2+</sup>, its strength was not significantly different among the different OE*n*'s.

The <sup>1</sup>H NMR and <sup>13</sup>C NMR chemical shifts of DP3n's did not change significantly even by the addition of  $Cd^{2+}$  (see Figure 6), while those of OEn's changed very much: in particular, no remarkable changes were observed for <sup>13</sup>C NMR spectra. These results are completely different from those for DP3n and Ca<sup>2+</sup> (Figure 7). For example, the <sup>1</sup>H NMR signals assigned to the hydrogen atoms of the oxyethylene part of DP3n with  $Ca^{2+}$ shifted as follows: (unit, ppm) 0.015 (DP33), 0.11 (DP34), 0.33 (DP35), and 0.19 (DP36) in midchain (-O-CH-), 0.019 (DP33), 0.12 (DP34), 0.18 (DP35), and 0.079 (DP36) in endchain (-COO-CH). Thus, the NMR results show that DP35 has the strongest interaction with  $Ca^{2+}$  among the DP3*n*'s (*n* = 3-6). Compared with these changes, the changes shown in Figure 6 can be neglected. If we dare to find any small differences in Figure 6, the <sup>1</sup>H NMR signals of only DP34 shifted to a direction different from those of the other DP3n's, although the shifts were not so remarkable.

**Transportation of Cadmium Ions by DP3***n* with and without Irradiation of Light. There is no effectively direct way to measure the ability of DP3*n* to capture metal ions when it is irradiated. Therefore, we employed a quartz cell with a partition as shown in Figure  $8^{27}$  to determine the amount of



**Figure 7.** The averaged increased values,  $\Delta \delta$ , of some <sup>1</sup>H NMR chemical shifts of DP3*n* (*n* = 3–6) in CD<sub>3</sub>CN when the Ca<sup>2+</sup> ions ([Ca<sup>2+</sup>]/[DP3*n*] ~ 50) were added ( $\delta_{[Ca^{2+}]}$ ) and absent ( $\delta_{[Ca^{2+}]=0}$ ):  $\Delta \delta = \delta_{[Ca^{2+}]} - \delta_{[Ca^{2+}]=0}$ .



Figure 8. A quartz cell for determining whether irradiated PICs of different sizes are capable of transporting cadmium ions.

 $Cd^{2+}$  transported by a DP3*n* in the presence and absence of UV light, after a method for measuring the transportation yield of metal ions.<sup>28</sup> A solution of 1 mM DP3n in CCl<sub>4</sub> was placed in part (C). An aqueous solution of 10 mM Cd(ClO<sub>4</sub>)<sub>2</sub> and 10  $\mu$ M DP3*n*, and pure water were simultaneously layered on top of (C) in (A) and (B), respectively. The transportation yield of Cd<sup>2+</sup> in (B) was measured using atomic absorption spectroscopy. In the case of Cd<sup>2+</sup>, the limit of detection is 2.2 nM. Cadmium ions are normally insoluble in CCl<sub>4</sub>. Thus, when we did not dissolve any DP3n in (A) and (C), no  $Cd^{2+}$  was observed in (B) even after 10 min either with and without UV irradiation. To measure transportation yields of Cd<sup>2+</sup> by DP3n, part (A) was either kept in the dark for 3 min, or irradiated at 6.4  $\times$ 10<sup>18</sup> photons/s for 3 min.<sup>29</sup> Figure 9 shows that these experiments have a relatively large error. We did not stir the solution because we were afraid that the splash drop might directly go into (B) from (A). Nevertheless, Figure 9 clearly shows that a greater amount of Cd<sup>2+</sup> was transported to (B) by way of (C) when (A) was irradiated. These experiments provided that DP34 worked effectively as a PIC and that it transported  $4 \times 10^{-7}$ M after irradiation for 3 min.

Using the same method as described above, we measured the amount of  $Cd^{2+}$  transported by DP3*n* when part (A) was irradiated and not irradiated. More than five experiments were performed to obtain the values of  $Cd^{2+}$  transported. Figure 10 shows the average values of  $Cd^{2+}$  transported by DP3*n*. In the case of DP33 and DP36, the values were almost the same in



Figure 9. Transport of cadmium ions by DP34 in the presence and absence of UV light.



**Figure 10.** Transport of cadmium ions by DP3*n* where *n* is the number of oxyethylene units in the presence ( $\bigcirc$ ) and absence ( $\bigcirc$ ) of UV light irradiation.

the presence and absence of UV light, meaning that they do not work as a PIC at all. On the contrary, DP34 and DP35 transported  $Cd^{2+}$  when they were irradiated, and in particular DP34 showed the greatest amount of  $Cd^{2+}$  transported.

As we have shown in a short communication,<sup>1</sup> DP35 transported the greatest amount of  $Ca^{2+}$ , whereas it is DP34 that transported the greatest amount of  $Cd^{2+}$ . This difference suggests that the size of oligooxyethylene is strongly related to the capture of metal ions.

What Occurs in This PIC system? Here we describe a probable mechanism governing the process taking place during the experiments using a cell shown in Figure 8, and also describe some possible weaknesses regarding our experiments.

The  $Cd^{2+}$  is assumed to be transported to (B) by the following mechanism, which is shown as an illustration in Figure 11. When irradiated, PICs in (A) capture  $Cd^{2+}$ . Some of those near (C) would diffuse into (C). Although (C) is not irradiated, the  $Cd^{2+}$  ion cannot be released from the PIC because it is not soluble in  $CCl_4$ . Some of the  $Cd^{2+}$ -bearing PIC molecules would diffuse into (B), where they could then release the  $Cd^{2+}$  ion. Thus, some of the  $Cd^{2+}$  would end up in (B).

One problem here is that only diffusion for 3 min at room temperature would result in not so many  $Cd^{2+}$ -bearing PICs being transported between the two aqueous solutions (A) and (B). For example, if the diffusion coefficient,  $\Lambda$ , of a PIC molecule is  $10^{-5}$  cm<sup>2</sup>/s, the rms distance, L, of a molecule diffused for 3 min is calculated to be 1 mm since  $L = (6\Lambda t)^{1/2}$ for t seconds. Thus, we have to consider that the convection plays a role in the migration of  $Cd^{2+}$  between compartments under our experimental conditions because infrared photons were not filtered out during UV irradiation. However, no  $Cd^{2+}$  was observed in (B) without any DP3n's after the UV irradiation for even 10 min. Thus, it is obvious that the increased degree of  $Cd^{2+}$  transportation is not due to the heating effect when the solution is irradiated.



**Figure 11.** Schematic drawing of the behavior of DP3*n* during measurements using a cell shown in Figure 8 as a photoinduced crown ether compound. Only part (A) is irradiated.

In the case of DP35 and Ca<sup>2+</sup>, some strong evidence indicates that they form a sort of complex even in the dark: by the addition of Ca<sup>2+</sup>, (i) <sup>1</sup>H NMR chemical shifts of DP35 changed to a great degree (nearly 0.4 ppm), and (ii) the efficiency of the excimer formation decreased very much.1 The greater transport of Ca<sup>2+</sup> by DP35, which has five units of oxyethylene, is consistent with its size: the diameter of the hole in 5-unit-crown ether, 15-crown-5 (15-C-5), is 170 to 220 pm<sup>31</sup> while that of Ca<sup>2+</sup> is 200 pm. Thus, we assume that DP35 molecules do not start with capturing Ca<sup>2+</sup> after forming an excimer, but rather they have some interaction with Ca<sup>2+</sup> before being excited. The intramolecular excimer formation between the pyrenyl end groups is considered to make DP35 bind with  $Ca^{2+}$  very tightly. Eventually, excimer formation plays an important role in creating the strong interaction between DP3*n* and  $Ca^{2+}$ . Because it is somewhat difficult for the crown ether conformation bearing Ca<sup>2+</sup> to be solvated by water molecules, the Ca<sup>2+</sup>-bearing DP35 molecules are assumed to be more stable in CCl<sub>4</sub>.

In the case of Cd<sup>2+</sup> ions, we obtained no strong evidence that they are captured by DP3n's in the dark, compared with the change of DP35 with Ca<sup>2+</sup>. If DP34 has no interaction with  $Cd^{2+}$  in the dark and starts with binding  $Cd^{2+}$  after the UV irradiation, this is the ideal system of the photoinduced temporary crown ethers that we hope to develop. However, we do not have clear evidence so far about whether DP34 starts with capturing Cd<sup>2+</sup> just after the irradiation or it only strengthens the binding of Cd<sup>2+</sup> when irradiated. In the latter case, the following results could support the existence of some interaction between DP34 and Cd<sup>2+</sup>, although they are not strong evidences: (i) the NMR results of DP34 with  $Cd^{2+}$  are a bit different from those of DP3n with  $Cd^{2+}$ , and (ii) the excimer formation efficiency of DP34 increased by the addition of Cd<sup>2+</sup>. In any rate, it is clear that intramolecular excimer formation between two terminal pyrenyl groups plays an important role in making the strong interaction of DP3*n* with  $Cd^{2+}$  and in the transportation of  $Cd^{2+}$  shown in Figures 9 and 10.

As a matter of fact, the diameter of  $Cd^{2+}$ , which is 190 pm, is slightly smaller than that of  $Ca^{2+}$  but larger than the cavity size of 12-crown-4 (12-C-4), which is around 144 pm.<sup>32</sup> This means that  $Cd^{2+}$  cannot be captured as tightly by a 12-C-4 molecule. However, some reports have shown that  $Cd^{2+}$  is stabilized by the formation of a sandwich dication such as [(12-

C-4)<sub>2</sub>Cd]<sup>2+</sup>. Colton et al. used electrospray mass spectrometry to investigate the interactions in solutions between some crown ethers and 17 metal ions.<sup>33</sup> Upon mixing with 12-C-4, only cadmium, zinc, and lead were found to give ions containing the metal and 12-C-4. As expected from their radii, they all gave species with two crown ether ligands coordinated to the metal ion. Bobrowski et al. examined the complexation of essentially nonsolvated cations including Cd<sup>2+</sup> with some crown ethers.<sup>34</sup> They found that a strong complex of Cd<sup>2+</sup> was formed in dichloromethane with 12-C-4 and that the ratio of the ligand to cadmium ion in the complex is larger than 1:1. Zhang et al. showed that the  $[(12-C-4)_2Cd]^{2+}$  dications in  $[(12-C-4)_2Cd][Cd_2-$ (SCN)<sub>6</sub>] and [(12-C-4)<sub>2</sub>Cd] [Cd<sub>2</sub>(SCN)<sub>8</sub>] serve not only as the spacer of the crystal packing, but also as a template for the formation of the two-dimensional layers.35,36 This also constitutes evidence that  $[(12-C-4)_2Cd]^{2+}$  dication has a sort of stable structure.

The present study is the first to use an excimer to fix the conformation of a molecule, and shows that these photoinducedcrown-ether compounds effectively capture and transport  $Cd^{2+}$  only when they are irradiated by light. In this paper, we have presented evidence proving our concept of a photoinduced crown ether.

Acknowledgment. This work was supported by a Grantin-aid for Scientific Research (B) (09450348) from the Ministry of Education, Science, Sports and Culture of Japan, and by the Iwatani Naoji Foundation. The authors are grateful to A. Yagi for operating FAB-MS to determine molecular weights of DP3*n*'s.

#### **References and Notes**

(1) Itagaki, H.; Masuda, W.; Hirayanagi, Y. Chem. Phys. Lett. 1999, 30, 402.

(2) Itagaki, H. In *Experimental Methods in Polymer Science: Modern Methods in Polymer Research and Technology*; Tanaka, T., Ed.; Academic Press: New York. 2000: Chapter 3.

(3) Horie, K. *Kobunshi* **1983**, *32*, 196.

(4) Mita, I.; Horie, K. J. Macromol. Sci. Rev. Macromol. Chem. Phys. 1987, C27, 91.

(5) Tung, C.-H.; Wang, Y.-M. J. Am. Chem. Soc. 1990, 112, 6322.

(6) Kakizawa, Y.; Akita, T.; Nakamura, H. Chem. Lett. 1993, 1671.

(7) Suzuki, Y.; Morozumi, T.; Kakizawa, Y.; Bartsch, R. A.; Hayashita, T.; Nakamura, H. *Chem. Lett.* **1996**, 547.

(8) Kawakami, J.; Komai, Y.; Ito, S. Chem. Lett. 1996, 617.

(9) Desvergne, J.-P.; Bouas-Laurent, H. J. Chem. Soc. Chem. Commun. 1978, 403.

(10) Desvergne, J.-P.; Fages, F.; Bouas-Laurent, H.; Marsau, P. Pure Appl. Chem. 1992, 64, 1231, and references therein.

(11) O'Connor, D. V.; Phillips, D. *Time-correlated Single-photon Counting*; Academic Press: London, 1985.

(12) Durbin, J.; Watson, G. S. Biometrika 1950, 37, 409.

(13) Durbin, J.; Watson, G. S. Biometrika 1951, 38, 159.

(14) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970; p 302.

(15) Hirayama, F. J. Chem. Phys. 1965, 42, 3163.

(16) Zachariasse, K. A.; Kühnle, W. Z. Phys. Chem. (Wiesbaden) 1976, 101, 267.

(17) Some compounds were reported to show fluorescence from an intramolecular excimer having two pyrenyl groups overlapped partially with each other.<sup>18,19</sup> The kinetic scheme including the formation of two excimers was discussed by some authors.<sup>19–22</sup> However, our DP3*n* systems can be best fitted to the conventional kinetic scheme shown in Scheme 2 with DW factors being near 2.0.

(18) Collart, P.; Demeyer, K.; Toppet, S.; De Schryver, F. C. Macromolecules 1983, 16, 1390.

(19) Zachariasse, K. A.; Duveneck, G.; Busse, R. J. Am. Chem. Soc. 1984, 106, 1045.

(20) Itagaki, H.; Obukata, N.; Okamoto, A.; Horie, K.; Mita, I. J. Am. Chem. Soc. 1982, 104, 4469.

(21) Itagaki, H.; Horie, K.; Mita, I. *Macromolecules* 1983, *16*, 1395.(22) De Schryver, P.; Collart, J.; Vandendriessche, R.; Goedeweeck,

A. M.; Swinnen, M.; Van der Auweraer, Acc. Chem. Res. 1987, 20, 159. (23) Klöpffer, W. In Organic Molecular Photophysics; Birks, J. B., Ed.;

Wiley: New York, 1974; p 371.

(24) The existence of a fluorescence component having the same lifetime as the isolated monomeric fluorescence was observed for oxyethylene compounds with pyrenyl groups at both ends.<sup>25</sup>

(25) Nakamura, H. (Hokkaido University), Private communication.

(26) CRC Handbook of Chemistry and Physics, 76th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, 1995.

(27) The cell is different from that employed in ref 1.

(28) Rosano, H. L.; Schulman, J. H.; Weisbuch, J. B. Ann. N.Y. Acad. Sci. 1961, 92, 457.

(29) The intensity of the irradiation light for pyrenyl moieties was determined by using the potassium ferrioxalate actiometry method.  $^{30}$ 

(30) Murov, S. L. Handbook of Photochemistry; Marcel Dekker: New York, 1973; p 119.

(31) Vögtle, F. Supramolecular Chemistry: An Introduction; Wiley: Chichester, 1989; Chapter 2.

(32) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. Chem. Rev. 1974, 74, 351.

(33) Colton, R.; Mitchell, S.; Traeger, J. C. Inorg. Chim. Acta 1995, 231, 87.

(34) Bobrowski, A.; Bond, A. M.; Ellis, S. R. Inorg. Chim. Acta 1999, 293, 223.

(35) Zhang, H.; Wang, X.; Zhu, H.; Teo, B. K. J. Am. Chem. Soc. 1997, 119, 5463.

(36) Zhang, H.; Wang, X.; Zhu, H.; Xiao, W.; Zhang, K.; Teo, B. K. Inorg. Chem. 1999, 38, 886.