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Selective transportation of metal ions by photo-induced crown ether compounds

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Abstract

A novel photoresponsive system that we call a photo-induced crown ether (PIC) is described, in which excimers are used to fix the conformation of a molecule for relatively long periods. 1,*n*-bis(3-(1-pyrenyl)propylcarboxy)-oxaalkanes (DP3*n*: $n = 3$–6), linear oligooxyethylenes with pyrenyl groups at both ends, were prepared and investigated to determine whether they might work as PICs. DP35 molecules were found to capture and transport calcium ions more effectively when they were irradiated. This result is consistent with the finding that five-unit crown ether transported the greatest amount of calcium ions. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Most photoresponsive systems that have been described so far employ photochemical reactions, such as photochromism [1]. Here we describe a novel reversible photoresponsive system that employs a photophysical process. We introduced pyrenyl groups onto both ends of linear oligooxyethylenes (Fig. 1). When irradiated with UV light, the pyrenyl groups link together to form an excimer with a lifetime in the sub-microsecond range. This structure is analogous to that of crown ethers, which are cyclic ethylene glycols capable of transporting ionic compounds into an organic phase. Here we show that one of these compounds indeed has the properties of a crown ether: when irradiated, it can capture calcium ions and transport them through a CCl_4 phase. Accordingly, we refer to them as photo-induced crown ether compounds (PICs).

Several studies have investigated oligooxyethylenes having aromatic compounds at both ends. These studies can be classified into three types: (1) studies on the expansion or cyclization of an oligomer or polymer in fluid solution [2,3]; (2) attempts to develop a fluorescent reagent to monitor metal ions captured by them [4–7]; and (3) attempts to develop a compound to capture metal ions by irradiation [8]. In the first two types of study, excimers formed between aromatic end groups were used as probes to get the information on 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 is the first attempt to use excimers to fix the conformation of a molecule for relatively long periods. Since the concentration of metal ions in a PIC solution can be changed by

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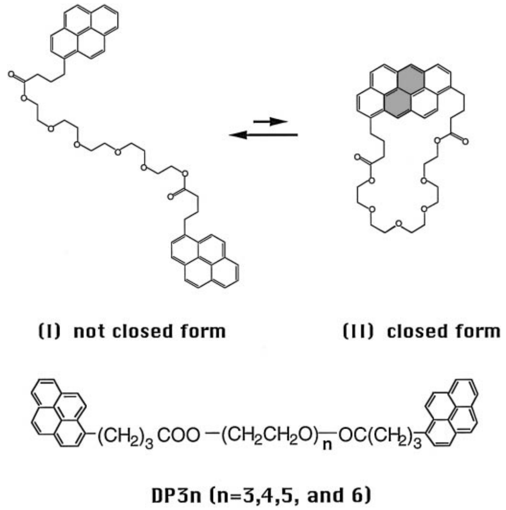

Fig. 1. A schematic drawing of a photo-induced crown ether compound together with the chemical structure of DP3*n*. The probability that a compound will be in the closed form, which is similar to a crown ether, is usually very small in the absence of light. However, if one of the pyrenyl groups of DP3*n* is irradiated, it links to the other pyrenyl group to form an excimer that stabilizes this conformation.

irradiation, such solutions might have applications as photo-switches.

2. Experimental

The structure of the 1,*n*-bis(3-(1-pyrenyl)propylcarboxy)-oxaalkanes (DP3*n*) studied in the present work is shown in Fig. 1. To prepare the DP3*n*s, 1-pyrenebutanoic acid was first converted to the acid-chloride by using thionyl chloride in benzene. Each acid-chloride was then reacted in benzene including a small amount of pyridine under N_2 flux 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. The products were separated with a Sephadex L-20 chromatographic column using THF as the eluent.

Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi F-4500 spectrofluorometer. Fluorescence decay curves were obtained by using a Horiba NAES550 single-photon counting machine and were analyzed by the deconvolution method after O'Connor and Phillips [9], using the Durbin–Watson factor [10] to assess the validity of the trial fitting function. The concentration of calcium ion was determined with a Hitachi Z-8270 polarized Zeeman atomic absorption spectrophotometer. NMR signals of DP3*n* in CD_3CN were measured on a JEOL GX 400 FT-NMR spectrometer.

3. Results

Information on the conformation of DP3*n* in fluid solution can be obtained by measuring its photostationary and transient fluorescence. Fig. 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 [11]. In fact, the excitation spectra for the fluorescence between 380 and 550 nm of all samples were almost identical. They were also identical with their absorption spectra. No concentration dependence was observed for the fluorescence spectra of the DP3*n*s below 10 μM, meaning that all the excimers shown in Fig. 2 are formed intramolecularly. The fluorescence spectra of DP3*n* in THF, water, chloroform and dichloromethane all

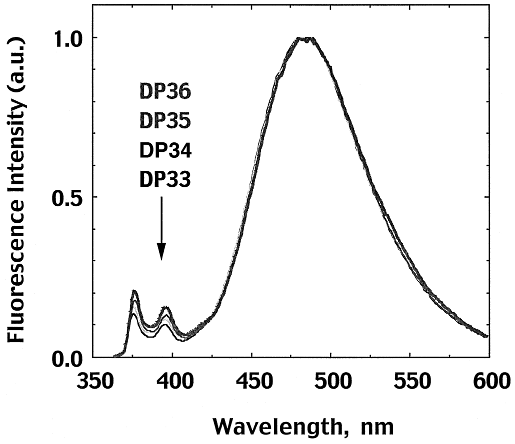

Fig. 2. Fluorescence spectra of DP3*n* in aerated acetonitrile. All the spectra are normalized to the peak. The excitation wavelength is 342 nm.

showed strong excimer fluorescence and weak monomeric fluorescence, meaning that DP3*n* readily takes a closed form similar to a crown ether.

The ratio of excimer fluorescence intensity, I_E, to monomer fluorescence intensity, I_M, was inversely related to the number of oxyethylene units: the order of I_E/I_M was DP33 > DP34 > DP35 > DP36.

Transient measurements of the pyrenyl monomer and excimer fluorescence give the time constant for excimer formation from the excited monomers, τ_{em}. The values of τ_{em} for DP33, DP34, DP35 and DP36 in degassed THF were 5.2, 5.6, 6.8 and 7.9 ns, respectively. All the lifetimes of excimer fluorescence, τ_e, were 50 ± 2 ns. The decay component of 50 ns was not detectable in the monomer fluorescence. Thus the excimer dissociation of DP3*n* can be neglected at room temperature. In this case, I_E/I_M is proportional to the rate of excimer formation, i.e., to the rate of the cyclization process. The order of I_E/I_M among the DP3*n*s was identical to the order of the τ_{em} values, and indicates that the rate of the cyclization process is dependent on the average distance between the two pyrenyl end groups.

The fluorescence results show that: (1) DP3n normally (i.e., in the dark) exists in the open form (I in Fig. 1); (2) it requires a few nanoseconds to form a closed form (II in Fig. 1); (3) τ_{em} becomes longer with longer chains; and (4) roughly 40% (1/e) of DP3*n* would remain in the closed conformation even 50 ns after the irradiation.

Next, we examined whether the addition of calcium ions influences the excimer formation of DP3*n*. We measured the dependence of DP3*n* fluorescence on calcium concentration using 3 μM DP3*n* and [Ca(SCN)$_2$] ranging from 10^{-5} to 10^{-2} M. Since DP3*n* is more stable in acetonitrile than in water, the

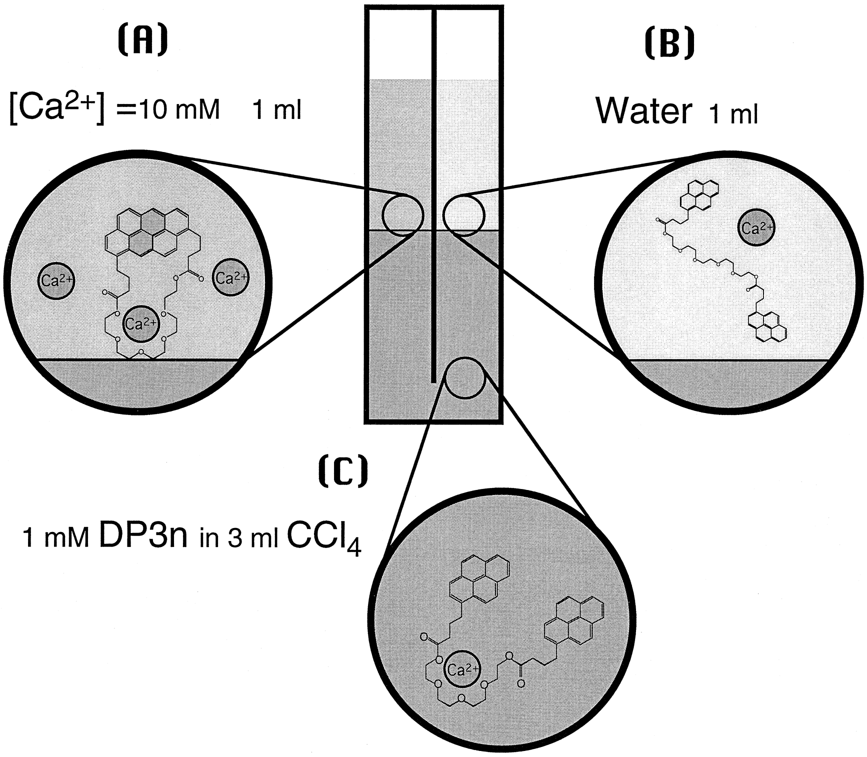

Fig. 3. A quartz cell for determining whether irradiated PICs of different sizes are capable of transporting calcium ions. Only part (A) is irradiated.

measurements were made in acetonitrile. Addition of Ca^{2+} did not change the shapes of the spectra of any of the DP3*n*s. Thus, even if there is some interaction between DP3*n* and calcium ions, it did not have any effect on the intramolecular excimer formation process.

Moreover, we examined the ability of the DP3*n*s to form a complex with Ca^{2+} by ^{1}H-NMR measurements using CD_3CN as a solvent. In the case of oligooxyethylenes (OE*n*; $n = 3$–6), the addition of Ca^{2+} increased the chemical shifts of methylene protons by at most 0.23 ppm, but the strength of the interaction was not significantly different among the different OEns. However, in the case of DP3*n*, the chemical shifts of DP35 changed most by the addition of Ca^{2+}, while those of the other DP3*n*s changed by smaller amounts. The signal assigned to the hydrogen atoms of the oxyethylene part was shifted as follows: (unit, ppm) 0.015 (DP33), 0.11 (DP34), 0.33 (DP35) and 0.19 (DP36) in mid-chain (–O–CH–C–), 0.019 (DP33), 0.12 (DP34), 0.18 (DP35) and 0.079 (DP36) in end-chain (–CO–O–CH–C–O–), and 0.017 (DP33), 0.10 (DP34), 0.32 (DP35) and 0.11 (DP36) in the end-chain (–CO–O–C–CH–O–). Thus, the NMR results show that DP35 has the strongest interaction with Ca^{2+} among the DP3*n*s studied in this work.

There is no effective direct way to measure the ability of DP3*n* to capture metal ions when it is irradiated. Therefore, we employed a quartz cell (1 cm × 1 cm × 6 cm high) with a partition (Fig. 3) to determine the amount of Ca^{2+} transported by a PIC in the presence and absence of UV light, after a method for measuring transportation yield of metal ions [12]. A solution of 1 mM DP3*n* in CCl_4 was placed in part (C). An aqueous solution of 10 mM $Ca(NO_3)_2$ and 10 μM DP3*n*, and pure water were simultaneously layered on top of (C) in (A) and (B), respectively. The transportation yield of Ca^{2+} in (B) was measured by atomic absorption spectroscopy. In the case of Ca^{2+}, the limit of detection is 5×10^{-9} M.

Calcium ions are normally insoluble in CCl_4. Thus, when we did not dissolve any DP3*n* in (A) and (C), no Ca^{2+} was observed in (B) even after 1 h either with and without UV irradiation. To measure transportation yields of Ca^{2+} by DP3*n*, part (A) was either kept in the dark for 10 min, or irradiated at 6.4×10^{18} photons/s for 10 min, and then an additional 10 min was allowed to pass to provide time for the diffusion of Ca^{2+}-bearing PIC molecules to (B). When part (A) was not irradiated, Ca^{2+} was not observed in (B), regardless of which DP3*n* was dissolved in (C). However, when part (A) was irradiated, Ca^{2+} was detected in the water cell (B) (Fig. 4).

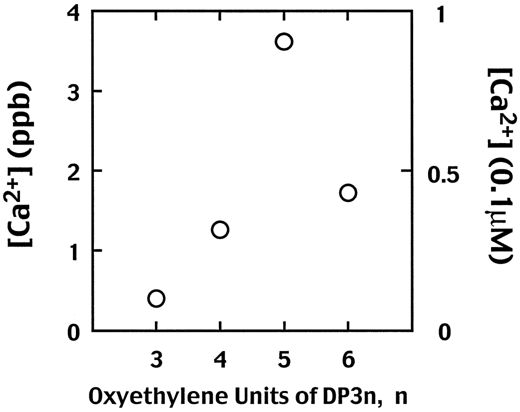

Fig. 4. Transport of calcium ions by DP3*n*, where *n* is the number of oxyethylene units.

The values shown in Fig. 4 are averaged over several measurements. Since (C) was not stirred, we estimate that the errors in these averages are 20–30%. In any case, the PIC with 5 oxyethylene units transported the greatest amount of Ca^{2+}: the Ca^{2+} concentration in (B) reached 0.1 μM after irradiation for 10 min.

4. Discussion

The data in Fig. 4 clearly show that some DP3*n*s can work as photo-induced crown ether compounds and transport Ca^{2+} only when the DP3*n*s are irradiated with light, because Ca^{2+} was detected in (B) only when DP3*n*s were irradiated. The Ca^{2+} is assumed to be transported to (B) by the following mechanism. When irradiated, PICs in (A) capture Ca^{2+}. Some of those near (C) would diffuse into (C). Although (C) is not irradiated, the Ca^{2+} ion cannot be released from the PIC because it is not soluble in CCl_4. Some of the Ca^{2+}-bearing PIC molecules would diffuse into (B), where they could then release the Ca^{2+} ion. Thus, some of the Ca^{2+} would end up in (B).

The greater transport of Ca^{2+} by DP35, which has five units of oxyethylene, is consistent with its size: the diameter of the hole in 5-unit-crown ether (15C5) is 170–220 pm [13] while that of Ca^{2+} is 200 pm.

We assume that DP35 molecules do not start with capturing Ca^{2+} after forming an excimer, but rather they have some interaction with Ca^{2+} before being excited. This is because (1) the NMR results indicate that DP3*n* interacts with Ca^{2+} to some extent, (2) DP35 has the strongest interaction among the DP3*n* studied, and (3) it is considered to take microseconds for a crown ether to capture metal ions. The intramolecular excimer formation between the pyrenyl end groups is considered to make DP35 bind Ca^{2+} very tightly. In this sense, excimer formation plays an important role in making the strong interaction between DP3*n* and Ca^{2+}. Because it is somewhat difficult for the crown ether conformation bearing Ca^{2+} to be solvated by water molecules, the Ca^{2+}-bearing DP35 molecules are assumed to be more stable in CCl_4.

The present study is the first to use an excimer to fix the conformation of a molecule, and shows that these photo-induced-crown-ether compounds effectively capture and transport Ca^{2+} only when they are irradiated by light.

Acknowledgements

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