Synthesis and Complexing Behavior of a New Fluorescent Ligand Using Interaction between Two Substituents

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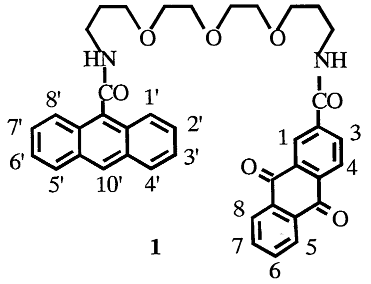
A fluorescent reagent (**1**) which has an electron donor and an acceptor at each terminal of linear polyether chain was synthesized, and the complexation behavior of **1** with alkaline earth metal ions was investigated. Quenching of the fluorescence spectrum and changes of ^{1}H–NMR spectrum at the complexation with the metal ions showed the interaction between two moieties in both excited state and ground state.

Many kinds of macrocyclic compounds analogous to crown ethers have been applied to analytical uses.[1] Especially, chromogenic crown ether reagents have been reported for spectrophotometric determination of alkali or alkaline earth metal ions. Previously, we have reported a complexing behavior of a linear polyether carrying symmetrically pendant anthracene units with alkaline earth metal ions.[2] However, detailed structural information from NMR was not observed, because symmetrical structure of the complex only gave averaged peak positions in ^{1}H–NMR. In this study, we synthesized an asymmetric polyether compound **1**, and will report complexing behavior with alkaline earth metal ions and structural information of the complexes.



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The compound **1** was prepared in the same manner as reported previously,[2] except that stepwise reaction was carried out. The reaction anthracene–9–carbonyl chloride with equimolar amount of 1,13–diamino–4,7,10–trioxatridecane afforded mono amide compound. The desired compound **1** was obtained by the reaction of this mono amide compound with anthraquinone–2–carbonyl chloride, and was purified with a silica gel column chromatography.[3]

Fluorescence and absorption spectra were measured in purified acetonitrile at 25 °C. The concentration of **1** for these experiments was 1.8×10^{-5} mM or 1×10^{-5} mM (1 M = 1 mol dm^{-3}) otherwise noted, and to prevent a non–linearity of the fluorescence intensity, isosbestic points (368, 372, 372, and 371 nm for Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, respectively) of the absorption spectrum were chosen for an excitation wavelength. For the measurement of complex formation, metal ions were added into the solution of **1** as perchlorate salts.

When the compound **1** formed complexes with alkaline earth metal ions, the fluorescence of the anthracene moiety was quenched (Figure 1). The degree of quenching depended on the concentration of the metal ions, and the complex formation constants (K) and the fluorescence intensities of the complexes (I_{ML}) were evaluated from these intensities, using non–linear least square curve fitting method. The fluorescence intensities at 409 nm were used for the calculation. In the case of Ca^{2+}, the fluorescence intensity decreased until equimolar amount of Ca^{2+} was added, and reached an asymptotic intensity. This shows that **1** formed a 1 : 1 complex with Ca^{2+}. In the case of other alkaline earth metal ions, similar behaviors were observed. These complex formation constants of **1** were determined for several alkaline earth metal ions, and listed in Table 1. The order of the formation constants of **1** is Ca^{2+} > Sr^{2+} > Ba^{2+} > Mg^{2+}. This order was the same as that of previous reagent having two anthracene units (**2**).[2] However, the selectivity of **1** for alkaline earth metal ions was less than that of **2**. This may be caused by the less rigid of crown–ether like ring of the complex of **1** due to more weak interaction between anthracene and anthraquinone than that between two anthracenes. These

Table 1. The complex formation constants (K) and fluorescence quenching efficiency (Φ_Q) of **1**

Metal ion	log K	Φ_Q
Mg^{2+}	5.53	0.78
Ca^{2+}	6.43	0.89
Sr^{2+}	6.10	0.84
Ba^{2+}	5.71	0.83

[**1**] = 1×10^{-4} M for Mg^{2+}, Ba^{2+}, 1.8×10^{-5} M for Ca^{2+}, Sr^{2+}

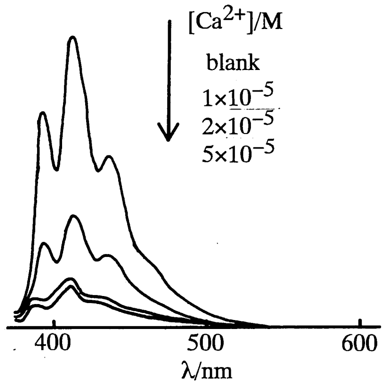

Figure 1. Fluorescence spectra of **1** and its Ca^{2+} complex. Excitation Wavelength: 372 nm. [**1**] = 1.8×10^{-5} M in acetonitrile.

Table 2. Chemical shifts of aromatic protons before and after complexation in acetonitrile-d_3[a]

	Anthracene unit					Anthraquinone unit[b]				
	H-1',8'	H-2',7'	H-3',6'	H-4',5'	H-10'	H-1	H-3	H-4	H-5,8	H-6,7
1	7.93	7.43	7.37	7.92	8.35	8.35	7.97	8.07	8.25,8.19	7.95,7.93
1·Mg^{2+}	–[c]	7.40	7.25	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]
1·Ca^{2+}	7.84	7.43	7.28	7.57	7.99	7.91	7.27	7.04	8.33,–[c]	7.96,–[c]
1·Sr^{2+}	7.90	7.42	7.33	7.75	8.19	8.09	7.44	7.00	8.30,7.99	7.96,–[c]
1·Ba^{2+}	7.88	7.40	7.31	7.69	8.12	8.12	7.54	7.20	8.31,–[c]	7.98,7.93

[a] These assignments were determined by H-H COSY and NOESY spectra. [b] The peaks of anthraquinone protons in **1**·Mg^{2+} were not observed below 7.5 ppm. [c] These could not be assigned because of too complicated spectra.

show that the complexing ability was mostly determined by the polyether moiety, not by the pendant aromatic moieties.

Fluorescence intensity of the complexes were much smaller than that of **1**. This is attributed to the fluorescence quenching by the anthraquinone units. Since the quenching efficiency $(\Phi_Q)^4$ was independent of the concentration of the reagent, the quenching was static one, and occurred by intramolecular process. The quenching efficiencies were not unity, and depended on the cation in the complex. The most effective quenching was observed in Ca^{2+} complex. The order of Φ_Q was $Ca^{2+} > Sr^{2+} \approx Ba^{2+} > Mg^{2+}$, and was almost the same as the order of the complex formation constants. There was no spectral overlap between fluorescence spectrum of anthracene and the absorption spectrum of anthraquinone, and redox potential of anthracene (*ca.* –1.75 V in excited S_1 state) is more negative than that of anthraquinone (–0.70 V). Therefore, the quenching mechanism should be an electron transfer from the excited anthracene to the anthraquinone. In this case, the quenching efficiency should be correlated with the distance and conformation between the two moieties.

^{1}H-NMR spectra in acetonitrile-d_3 gave good information to structures of the complexes. The chemical shifts of aromatic region of **1** and its Ca^{2+} complex are shown in Table 2. When **1** complexed with Ca^{2+}, almost all peaks of the aromatic protons shifted to higher magnetic field. Etherial proton of crown ethers usually shifts to downfield, since the electron density of the oxygen atoms is reduced by the coordinated cation. On the other hand, these high magnetic field shifts of the aromatic protons should be attributed to diamagnetic effect from the ring current of the each aromatic unit. Especially, H-1, H-3, and H-4 protons showed large high magnetic field shifts. These shifts were also observed in the Sr^{2+} and Ba^{2+} complexes. However, in many cases, the magnitude of the shifts was smaller than that of Ca^{2+}, and tends to be small with the increase of ionic diameter. As shown in Table 2, H-4', H-5' and H-10' protons also showed large high magnetic field shifts, and other protons showed small. Furthermore, one of H-5 or H-8 proton showed a down field shift. From these consideration, the possible conformation of the complex is suggested in Figure 2. When the cation with larger ionic diameter complexed with **1**, the distance between the two moieties would become long, and consequently the magnitude of the shifts is reduced. This is also consistent with the trend of quenching efficiencies.

It will be concluded in the case of Ca^{2+}, the five oxygen atoms in polyether and carbonyl groups enclose Ca^{2+} suitably, and the two aromatic units properly approach to each other. Therefore, Ca^{2+} can make a complex with **1** most strongly. On the other hand, Mg^{2+} complexed with **1** most weakly. The diameter of Mg^{2+} is too small for **1** to enclose the surface of Mg^{2+} properly. This was also suggested from that the large upfield shift of H-3 was not observed in the case of Mg^{2+} complex, and from relatively small quenching efficiency.

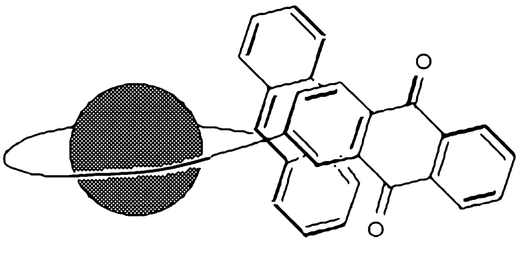

Figure 2. Proposed structure of **1** complexed with Ca^{2+}.

References and Notes

1 R. D. Tsingrelli, L. K. Shpigun, V. V. Samoshin, O. A. Zelyonkina, M. E. Zapolsky, N. S. Zefirov, and Y. A. Zolotov, *Analyst*, **117**, 853 (1992); T. Hayashita, J. H. Lee, M. G. Hankins, J. C. Lee, J. S. Kim, J. M. Knobelock, and R. A. Bartsch, *Anal. Chem.*, **64**, 815 (1992); M. Shiga, H. Nishida, H. Nakamura, M. Takagi, and K. Ueno, *Bunseki Kagaku*, **32**, E293 (1983); M. Takagi and H. Nakamura, *J. Coord. Chem.*, **15**, 53 (1983), and literatures therein.

2 Y. Kakizawa, T. Akita, and H. Nakamura. *Chem. Lett.*, **1993**, 1671; because of impurity in the solvent (CH_3CN), log K_1 values in this paper should be corrected as follows; Mg^{2+}, 4.67; Ca^{2+}, 6.41; Sr^{2+}, 5.25; Ba^{2+}, 4.81. K_2 values were too small to be determined.

3 Compound **1**: amorphous; ^{1}H-NMR ($CDCl_3$) δ 1.84 and 2.05 (m, 4 H, C-CH_2-C), 3.22–3.88 (m, 16 H, O-CH_2- and N-CH_2-), 6.97 and 7.53 (m, 2 H, -NH), 7.32–7.43 and 7.70–8.38 (m, 16 H, aromatic). Anal. Calcd for $C_{40}H_{38}N_2O_7$: C, 72.93; H, 5.81; N, 4.25. Found: C, 72.72; H, 5.94; N, 4.13.

4 The quenching efficiencies were calculated by the equation: $\Phi_Q = (I_L - I_{ML}) / I_L$, where I_L and I_{ML} are the fluorescence intensities of **1** and its metal complex, respectively.