Mg^{2+}-Selective Fluorescence Enhancement of Benzo-15-crown-5 Derivative Bearing Vinylanthracene Fluorophore

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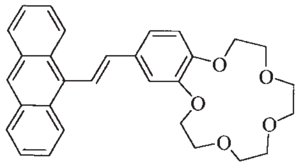
A fluoroionophore, 1-(anthryl)-2-(benzo-15-crown-5)ethene, was synthesized. This crown ether derivative showed remarkably high cation-induced fluorescence enhancement for magnesium ion.

Development of fluoroionophore combining the fluorophore and ionophore is one of the attractive subjects in the studies of chemosensor with selective binding of species and fluorescence as an optimal monitor.[1–6] Ionophore acts as the ion-sensitive receptor and fluorophore as the signal-generator. The sensitivity of fluorophore may be associated with the ionic recognition ability of the ionophore, if the fluorophore may be perturbed by the coordination of cation. According to the nature of the ionophore-fluorophore interaction, the fluorescence signal is modified in intensity or/and in energy.[1–7] In particular, crown ether ionophore is an electron-rich donor as well as a ligand of the ion. The electron pair on the heteroatom in crown ether takes part in the modification of the first electronic transition state of the fluorophore through the charge transfer interaction between ionophore (electron rich donor D) and fluorophore (electron acceptor A) in a π–conjugated D-A arrangement.[8–13] Upon recognition of an ion, the heteroatom electronic pair is stabilized and the original electronic configuration of the unsubstituted compound is recovered. Many such systems including crown ether derivatives containing a styryl moiety as a fluorophore have been investigated.[9–13] However, the main disadvantage of these fluoroionophore is the relatively small changes in fluorescence intensity upon ion binding.

We prepared 1-(9-anthryl)-2-(benzo-15-crown-5)ethene (**1**),[14] a crown ether derivative containing 1-(9-anthryl)-2-phenylethene (9-APE) moiety, by Wittig coupling between 4′-formylbenzo-15-crown-5 and 9-bromomethylanthracene.



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Trans-9-APE[15] is known to show moderate Φ_f of 0.45 in acetonitrile and its fluorescence ($\lambda_f^{max} = 476$ nm) comes from the locally excited state which the excitation energy is localized on anthracene ring. However, for a methoxy derivative of 9-APE, 1-(9-anthryl)-2-(4-methoxyphenyl)ethene (MeO-APE),[15] fluorescence is weak and red-shifted ($\Phi_f = 0.028$, $\lambda_f^{max} = 494$ nm) in acetonitrile due to the contribution of the intramolecular charge transfer state to the lowest excited state. Thus, Φ_f of the crown ether derivative of 9-APE is also expected to be small. In fact, fluorescence of **1** was extremely weak in acetonitrile ($\Phi_f = 0.007$, $\lambda_f^{max} = 501$ nm) in the uncomplexed state, similar to MeO-APE (see Table 1). If intramolecular charge transfer from crown ether moiety to anthrylethene moiety is inhibited by the complexation of cation on the crown cavity of **1**, fluorescence intensity will be restored up to that of unsubstituted compound, 9-APE.

Table 1. Spectroscopic data and association constants for **1** with metal perchlorates in acetonitrile

Salt	λ_a^{max}/nm	λ_f^{max}/nm	I_f/I_f^o	K_f
none	392	501	1	—
$LiClO_4$	388	486	3.8	1200
$NaClO_4$	389	486	4.1	480
$KClO_4$	392	500	1	~0
$CsClO_4$	392	498	1	~0
$Mg(ClO_4)_2$	388	481	17	1400
$Ca(ClO_4)_2$	388	482	6.1	760

Spectroscopic data and association constants of **1** in the presence of various cations were presented in Table 1 and Figure 1. The concentrations of **1** and metal perchlorate were 1×10^{-5} M and 3.3×10^{-3} M, respectively. Fluorescence excitation wavelength of 360 nm was employed. On the addition of cations except K^+ or Cs^+, the absorption maximum of **1** was nearly unchanged, but the fluorescence maximum was blue-shifted and its intensity was enhanced. In the presence of K^+ or Cs^+, both absorption and fluorescence spectra remain unchanged. With magnesium cation, fluorescence intensity was drastically increased up to 17 fold.

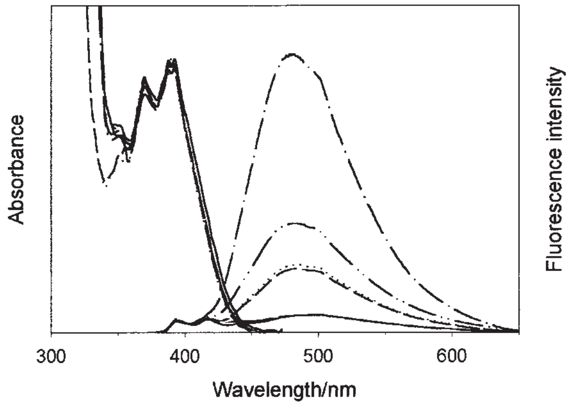

Figure 1. The absorption (left) and fluorescence (right) spectra of 1 in acetronitile with various metal perchlorates (none: solid, $LiClO_4$: short-dashed, $NaClO_4$: dotted, $KClO_4$: medium-dashed $CsClO_4$: long-dashed, $Mg(ClO_4)_2$: dash-dotted line, $Ca(ClO_4)_2$: dash-dot-dotted line).

The complexation of cation on a fluoroionophore can cause the change in fluorescence yield, critically depending on the change of the relative position of the excited state energy levels involved such as emissive locally excited state and the weakly emissive intramolecular charge transfer state. Upon cation addition, the intramolecular charge transfer state is turned into the locally excited state, judging from the fact that **1** displayed not only a blue shift of the fluorescence spectrum, but also high fluorescence enhancement. These analytically desirable effects are attributable to a charge transfer from the lone pair on the oxygen atom of the crown ether to the cation. The subsequent reduction of the electron-donating character of the crown ether group toward the APE moiety leads to a decrease of the charge transfer to the entire conjugated system. The greater the charge of the cation and its adaption to the cavity of the crown, the stronger will be this reduction. Cation complexation to **1** increases the formation of emissive locally excited state and leads to the enhanced fluorescence. Fluorescence enhancement was in the order of $Mg^+ > Ca^{2+} > Na^+$ or Li^+.

In summary, we have shown that efficient cation-induced ‘switching on’ of the fluorescence can be achieved for a simple fluoroionophore **1** and this fluorescence enhancement was remarkably high for Mg^+ ion to allow the use of **1** as a chemosensor for Mg^+ cation.

References and Notes

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14 Spectral data for **1**: ^{1}H NMR($CDCl_3$, 300 MHz) δ 3.8–4.2(m, 16H, OCH_2), 6.9–8.5(m, 14H, ArCH and = CH); IR (KBr, cm^{-1}) 3401, 3052, 2937, 1688, 1595, 1439, 1345, 1271, 1167; MS(FAB) m/z: 470 (M^+).

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