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Highly selective recognition of lead ion in water by a podand fluoroionophore/γ-cyclodextrin complex sensor†

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We report herein a novel podand fluoroionophore/γ-cyclodextrin (γ-CyD) complex sensor that shows markedly high selectivity for lead (Pb^{2+}) ion in water.

Due to the toxicity of Pb^{2+}, the real-time and *in situ* monitoring of Pb^{2+} in the environment as well as in biological systems remains an important issue.[1] Although ICP emission and atomic absorption spectroscopies are efficient tools for Pb^{2+} detection, they generally require a large amount of samples and are not suitable for real-time and *in situ* analysis.[2] Optical sensors involving fluoroionophores are becoming popular because of their ease of use in solution as well as their high sensitivity to and selectivity for trace analytes.[3] Whereas many efficient fluoroionophores have been developed for alkali metals,[4] alkaline earth metals[5] and Zn^{2+},[6] the number of Pb^{2+}-selective fluoroionophores is still limited.[7] The calix[4]arene fluoroionphore recently developed by Métivier *et al*. exhibits high sensitivity (detection limit of 0.02 μM) to and selectivity for Pb^{2+}, but it requires a 60% CH_3CN/40% water (v/v) medium for analysis.[8] The difficulty in designing Pb^{2+}-selective fluoroionophores lies mainly in the lack of a design concept and problems in fluorescence quenching by heavy metal ions based on enhanced spin–orbital coupling[9] and electron or energy transfer.[10]

Recently, we have developed supramolecular benzo-15-crown-5 fluoroionophore/γ-CyD complex sensors for K^+ ion recognition in water.[11] The dimerization of the fluoroionophore inside the γ-CyD was found to be selectively promoted by K^+ ion binding, thereby resulting in a K^+-selective pyrene dimer emission. This supramolecular function can be used in the design of Pb^{2+}-selective fluoroionophores because the recognition site is efficiently separated from the photosignal transduction site by an alkyl chain spacer to avoid fluorescence quenching. For selective Pb^{2+} recognition, we have proposed a design concept based on 1) a hard binding site constructed from O-donor atoms to reduce the interaction with other relatively soft heavy metal ions, and 2) a podand structure possessing a flexible pseudo-crown ether cavity to stabilize chelate complexes with large metal ions such as Pb^{2+} while reducing the interaction with alkali metal cations.[12]

Based on the above design concept, we have designed a podand fluoroionophore (**PD-1**) that possesses a pseudo-18-crown-6 structure as the Pb^{2+} recognition site and a pyrene moiety as the photosignal transducer† and examined its response to heavy metal ions in the presence of γ-CyD in water (Fig. 1).

Fig. 2 shows the fluorescence spectra of **PD-1** (2.0×10^{-6} M) in 98% water/2% methanol (v/v) at pH 4.3. In the absence of γ-CyD, no obvious fluorescence was noted (spectrum a). By contrast, significant fluorescence emission appeared in the presence of 12.0 mM γ-CyD (spectrum b), indicating that **PD-1** is solubilized in water by forming an inclusion complex with γ-CyD, which also enhances the fluorescence quantum yield.[13] The fluorescence spectrum of **PD-1**/γ-CyD complex in the presence of 1.0 mM Pb^{2+} is depicted in spectrum c. It is evident that the broad emission observed in the longer wavelength region (471 nm) is intensified whereas the pyrene monomer emission at 370–410 nm is decreased. In addition, the absorption spectrum of the **PD-1**/γ-CyD complex in the presence of Pb^{2+} shows a reduction in resolution and intensity of the absorption compared with that in the absence of Pb^{2+}. This characteristic feature is attributed to ground-state interactions between two pyrenyl moieties.[14] The results strongly demonstrate that the dimer formation of **PD-1** inside γ-CyD is induced by Pb^{2+} binding, in accordance with our design concept (Fig. 1).

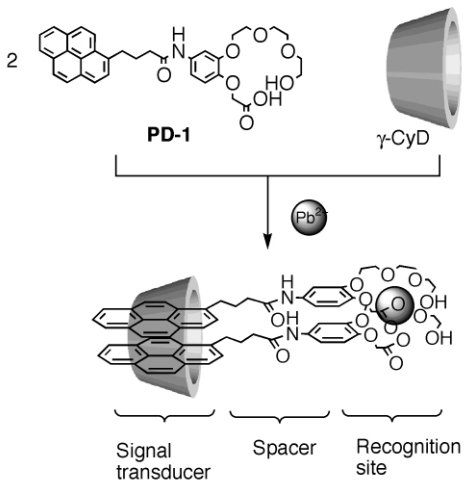

Fig. 1 Design concept of the **PD-1**/γ-CyD complex sensor for Pb^{2+} recognition in water.

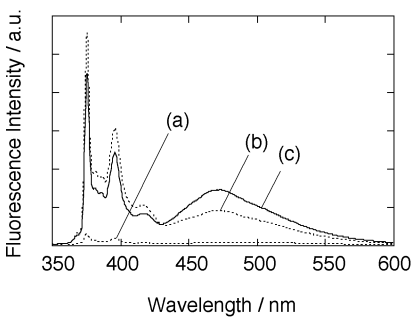

Fig. 2 Fluorescence spectra of **PD-1** ([**PD-1**] = 2.0×10^{-6} M in 98% water/2% MeOH (v/v)) with added species. (a) [γ-CyD] = 0.0 mM, (b) [γ-CyD] = 12.0 mM, and (c) [γ-CyD] = 12.0 mM and [Pb^{2+}] = 1.0 mM. Excitation wavelength, 328 nm. pH = 4.3 adjusted with 0.010 M acetate buffer.

† Electronic supplementary information (ESI) available: synthesis of **PD-1**, effect of γ-CyD concentration, effect of pH, and metal ion selectivity. See http://www.rsc.org/suppdata/cc/b3/b305758e/

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As we have previously reported, the fluorescence response of the **PD-1**/γ-CyD complex must be dependent on γ-CyD concentration.[15] Preliminary experiments revealed that selectivity for Pb^{2+}/Cu^{2+} increased monotonically with an increase in γ-CyD concentration from 2.0 mM to 14.0 mM.† In this study, a γ-CyD concentration of 12.0 mM was selected for subsequent experiments. The pH of the sample solutions was adjusted to 4.3 by 0.010 M acetate buffer with an ionic strength of 0.10 by $NaNO_3$. No significant difference in the selectivity for Pb^{2+}/Cu^{2+} was noted in the pH range from 3.7 to 5.5.†

Fig. 3a shows changes in the fluorescence spectra of the **PD-1**/γ-CyD complex with the addition of Pb^{2+}. As the Pb^{2+} concentration was increased, the intensity of the monomer emission decreased whereas that of the dimer emission increased. Fig. 3b shows plots of the intensity ratio (I_{471}/I_{378}) as a function of Pb^{2+} concentration. When the change in fluorescence is induced only by the 2 : 1 complex formation between **PD-1** and the metal ion (M^{2+}), the fluorescence ratio (I_{471}/I_{378}) can be expressed by the following equations:[11]

$$\frac{I_{471}}{I_{378}} = \frac{4\frac{\phi_{f1}}{\phi_{f2}} + \frac{\phi_{c1}}{\phi_{f2}}\left(-1+\sqrt{1+8K_{21}[M^{2+}][\mathbf{PD-1}]_0}\right)}{4+\frac{\phi_{c2}}{\phi_{f2}}\left(-1+\sqrt{1+8K_{21}[M^{2+}][\mathbf{PD-1}]_0}\right)} \quad (1)$$

$$K_{21} = \frac{[M^{2+}(\mathbf{PD-1})_2]}{[M^{2+}][\mathbf{PD-1}]^2} \quad (2)$$

where $[\mathbf{PD\text{-}1}]_0$ is the initial concentration of the fluoroionophore, and ϕ_{f1} and ϕ_{f2} are the fluorescence quantum yields for **PD-1** at 471 and 378 nm, respectively. Similarly, ϕ_{c1} and ϕ_{c2} are those for the 2 : 1 complex at 471 and 378 nm, respectively. K_{21} is the apparent 2 : 1 binding constant of **PD-1** with M^{2+}. As shown in Fig. 3b, the observed values are well fitted by eqn. (1) (solid line), and the binding constant is calculated as $(1.17 \pm 0.75) \times 10^9\ M^{-2}$. Also shown in Fig. 3b are the fluorescence responses of the **PD-1**/γ-CyD complex in the presence of Zn^{2+} and Cu^{2+}. The **PD-1**/γ-CyD complex did not show any obvious spectral changes upon the addition of Zn^{2+} and Cu^{2+}, indicating that fluorescence quenching by heavy metal ions was negligible. No fluorescence response upon the addition of 1.0 mM K^+, Mg^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, and Cd^{2+} was also confirmed.†

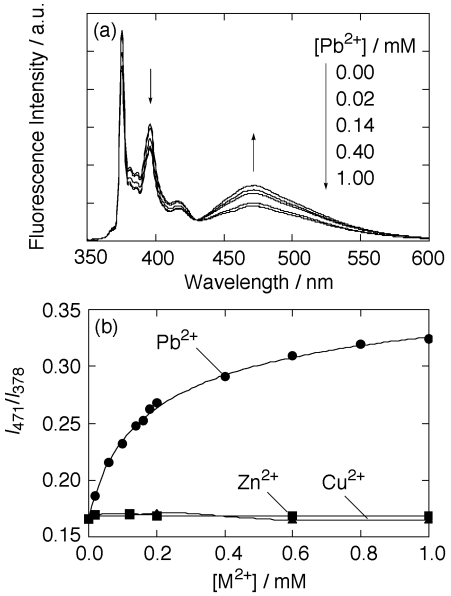

Fig. 3 (a) Fluorescence spectra of **PD-1**. [**PD-1**] = 2.0×10^{-6} M in 98% water/2% MeOH (v/v); [γ-CyD] = 12.0 mM. Excitation wavelength, 328 nm. pH = 4.3 adjusted with 0.010 M acetate buffer (I = 0.10 by $NaNO_3$). (b) Dependence of I_{471}/I_{378} on the concentration of Pb^{2+}, Cu^{2+}, and Zn^{2+}.

Thus, the **PD-1**/γ-CyD complex was found to exhibit high selectivity for Pb^{2+} ion in water.

In summary, a supramolecular **PD-1**/γ-CyD complex sensor that exhibited the monomer/dimer emission ratio response with markedly high selectivity for Pb^{2+} in water was successfully designed. It should be noted that the observed detection limit of 10 μM is evidently insufficient for practical Pb^{2+} ion analysis (0.02–1.0 μM) in water.[1] Although we selected the pseudo-18-crown-6 structure as the Pb^{2+} binding site, the podand structure as well as the alkyl spacer design in the fluoroionophore is an important factor for enhancing the Pb^{2+} recognition efficiency of the γ-CyD complex sensors by several order of magnitude.[15] Such modifications are being actively undertaken in our laboratory in order to develop more advanced fluoroionophore/γ-CyD complex sensors for heavy metal ion recognition in water.

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