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ORIGINAL PAPER

A Fe^{3+}/Hg^{2+}-Selective Anthracene-Based Fluorescent PET Sensor with Tridentate Ionophore of Amide/β-Amino Alcohol

Kuangsen Sung · Hong-Kai Fu · So-Hong Hong

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Abstract A new anthracene-based fluorescent PET sensor **1** with a tridentate ionophore of amide/β-amino alcohol displays very good selectivity and sensitivity for Fe^{3+} (K_a=1.6×10^3 M^{-1}) and Hg^{2+} (K_a=2.1×10^3 M^{-1}) in CH_3CN–H_2O (3:7, *v*/*v*) with detection limit of 1 μM. More fluorescence enhancement was observed when **1** selectively detected Fe^{3+} or Hg^{2+} in CH_3CN and its detection limit was up to 0.03 μM.

Keywords Fluorescent chemosensor · Photo-induced electron transfer · Fluorophore

Introduction

Detection of cations is of great interest and importance in the fields of chemical, biological, medicinal, and environmental sciences [1–7]. Among several analytic methods for cations, fluorescent chemosensors offer distinct advantages of sensitivity, selectivity, response time, and local observation [1–7]. Fluorescent chemosensors for cations usually consist of two parts: ionophore and fluorophore. The ionophore is responsible for selective recognition of cations, and the fluorophore immediately convert the recognition events into optical signals by means of several types of photophysics mechanisms.

Photo-induced electron transfer (PET), one type of photophysics mechanisms used in fluorescent chemosensors, usually involves promotion of an electron in HOMO of the fluorophore to LUMO upon excitation, followed by PET from HOMO of donor in the ionophore to that of the fluorophore, causing fluorescence quenching of the fluorophore [1–7]. Upon binding with a cation, HOMO energy of the ionophore decreases and PET becomes thermodynamically unfavorable, so that fluorescence quenching is suppressed.

There are some known fluorescent PET sensors for selective recognition of cations, such as **2** for Ag^+ [8, 9], **3** for K^+ [10], **4** for Zn^{2+} [11], **5** for Zn^{2+} and Cu^{2+} [12, 13], **6** for Zn^{2+} and Cu^{2+} [14, 15], **7** for Ni^{2+} and Cu^{2+} [16–18], **8** for Ni^{2+} and Cu^{2+} [19], **9** for Hg^{2+} and Cu^{2+} [20], and **10** for Cu^{2+} and Hg^{2+} [21, 22]. It is clear that development of highly selective fluorescent chemosensors for various metal ions is still a challenge.

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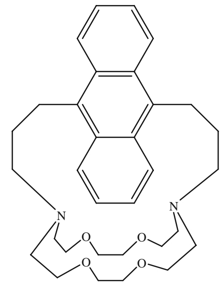
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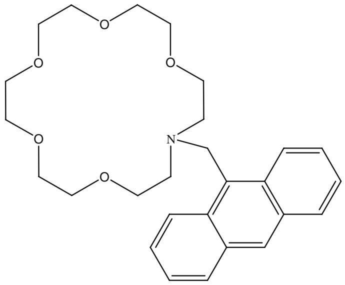
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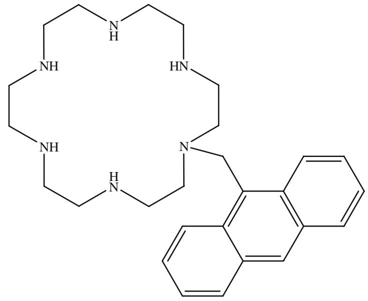
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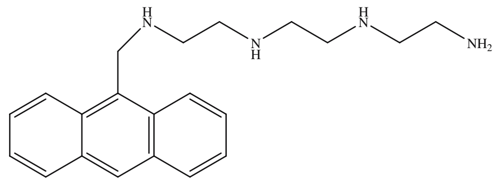
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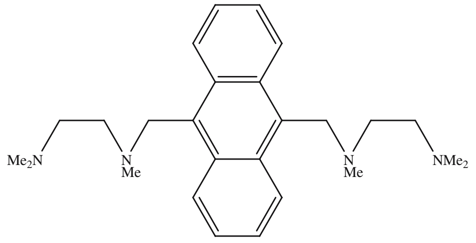
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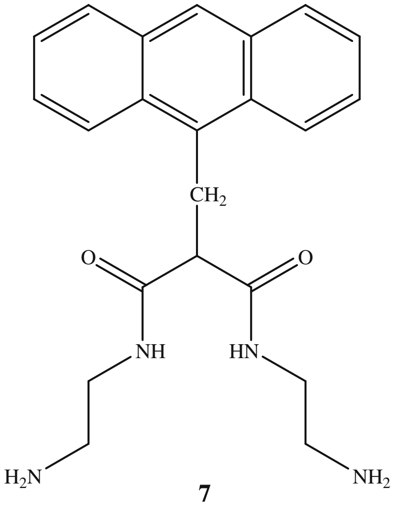
6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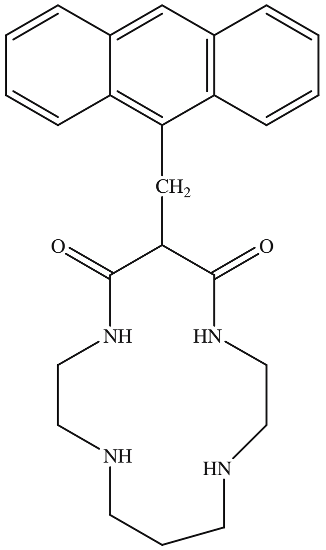
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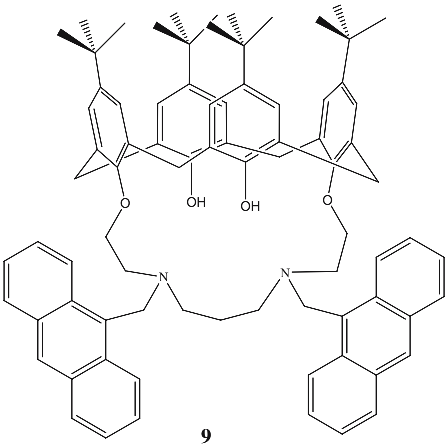
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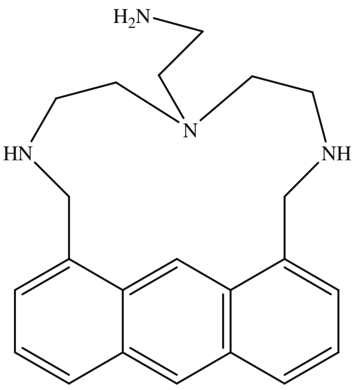
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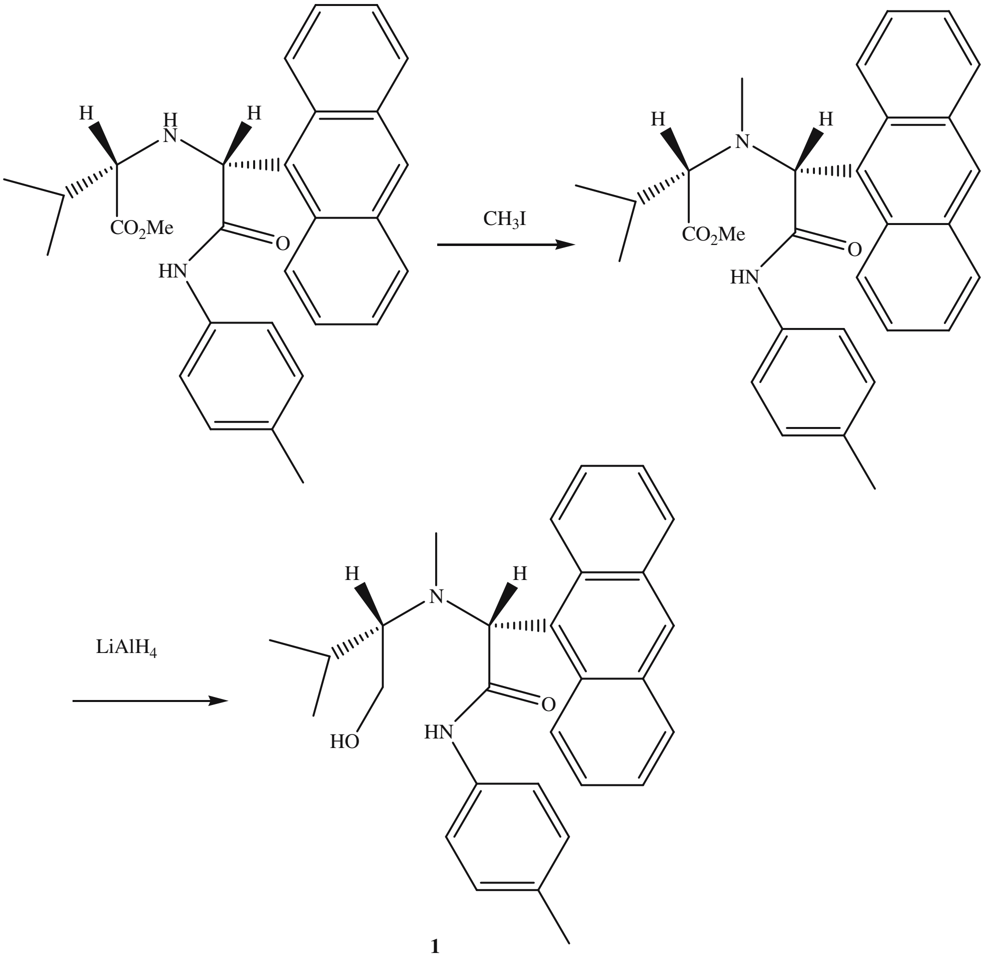
Scheme 1 Synthesis of **1**



1

In this article, we use anthracene as a fluorophore and PET as a photophysics mechanism of the fluorophore. A tridentate ligand of amide/β-amino alcohol was designed as an ionophore for selective recognition of cations. Then we synthesized the fluorescent PET cation sensor **1** by U-4CR followed by *N*-methylation and reduction [23] (Scheme 1). The ionophore and fluorophore of **1** are close enough to communicate with each other, and its performance as a fluorescent PET cation sensor is shown in this article.

Experimental

General All the reagents were obtained from commercial suppliers and used as received. Counter anions for all the metal ions are all chloride. All UV-visible absorption spectra were recorded on a Perkin Elmer Lamda 40 spectrophotometer and all fluorescence emission spectra were recorded on a Perkin Elmer LS45 fluorescence spectrophotometer.

Absorption titration experiments

Absorption spectra of **1** (1.8×10^{-5} M) with addition of 0, 0.6, 1.2, 1.6, 1.8 equiv. of $FeCl_3$ or $HgCl_2$ in CH_3CN–H_2O (3:7, *v*/*v*) were measured on a Perkin Elmer Lamda 40 spectrophotometer. The association constant was calculated from the plot of the absorbance ratio, $A_0/(A-A_0)$, versus 1/[metal cation] according to Eq. 1 [24], where $[C_g]$ is the concentration of the added metal ion, ε_M and ε_c are molar extinction coefficients of the free **1** and a complex of **1**/metal cation at a selected wavelength, and A_0 and A denotes the absorbance of free **1** and the solution after adding a metal cation at a selected wavelength.

Results and discussion

The fluoroionophoric properties of **1** were investigated by fluorescence measurements in the presence of various metal

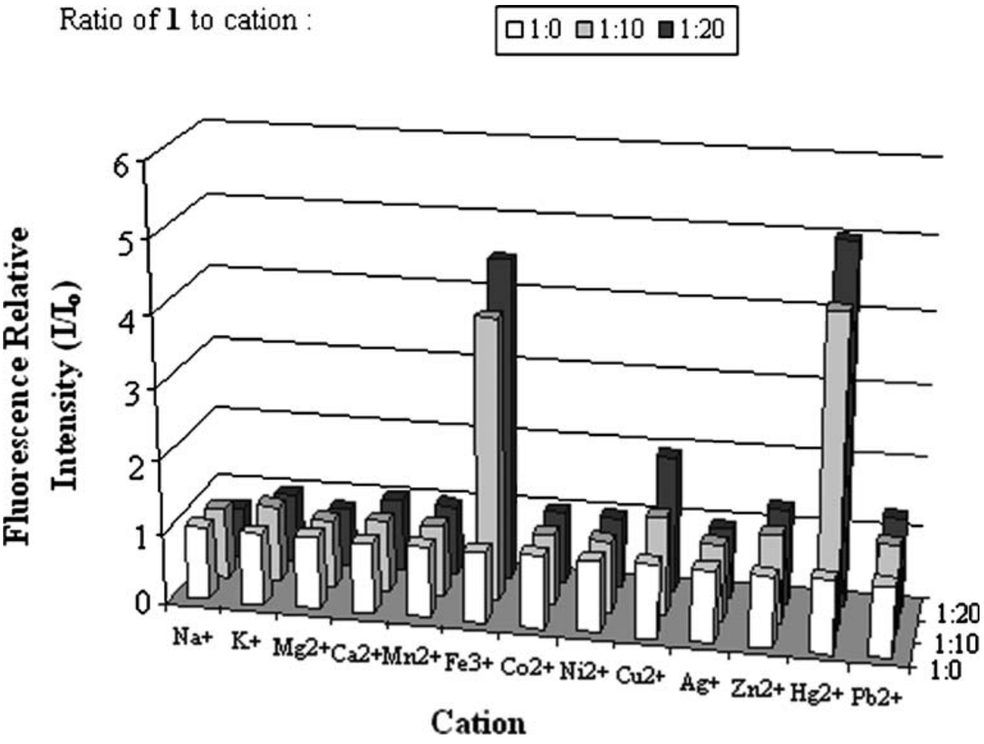


Fig. 1 Fluorescence enhancement ratios (I/I_0) at 420 nm for interaction of **1** with various metal ions in $CH_3CN–H_2O$ (3:7, *v*/*v*). λ_{ex}=368 nm. [**1**]=7.3×10^{-7} M

ions. The fluorescence spectrum of the free host **1** was measured in $CH_3CN–H_2O$ (3:7, *v*/*v*, 7.3×10^{-7} M, λ_{ex}= 368 nm) and it showed very weak fluorescence, indicating that fluorescence of the anthracene group in **1** is quenched by intramolecular photo-induced electron transfer from the lone pair of electrons of the nitrogen to the adjacent anthracene group. Upon interaction of **1** with 20 equiv. of alkali metals (Na^+, K^+), alkaline earth metals (Mg^{2+}, Ca^{2+}), transition metals (Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Ag^+), or Pb^{2+}, the fluorescence was affected very little (Fig. 1). Similarly, fluorescence of **1** was increased a little by addition of 20 equiv. of Cu^{2+}. However, Fe^{3+} or Hg^{2+} made a significant fluorescence enhancement of **1** in $CH_3CN–H_2O$ (3:7, *v*/*v*) and their detection limit can be up to 1 μM.

When the fluoroionophoric properties of **1** were investigated in CH_3CN, the fluorescence enhancement was dramatically increased by 40-fold, and so is the selectivity of **1** for Hg^{2+} and Fe^{3+} (Fig. 2). Its detection limit for Hg^{2+} and Fe^{3+} can be up to 0.03 μM. On the other hand, the fluorescence enhancement of **1** by Cu^{2+} in CH_3CN became insignificant. In comparison with other fluorescent PET sensors **2~10** [8–22], **1** shows outstanding selectivity for Fe^{3+} and Hg^{2+} and excellent sensitivity (up to 0.03 μM in CH_3CN), which is close to that of **2~10**.

Absorption spectrum of **1** was measured in $CH_3CN–H_2O$ (3:7, *v*/*v*) and it showed characteristic absorption of anthracene at around 345~395 nm. The absorption titration spectra of **1** with Fe^{3+} in $CH_3CN–H_2O$ (3:7, *v*/*v*) are shown in Fig. 3. Isosbestic points found in the absorption titration spectra strongly suggest that the solution involves two-

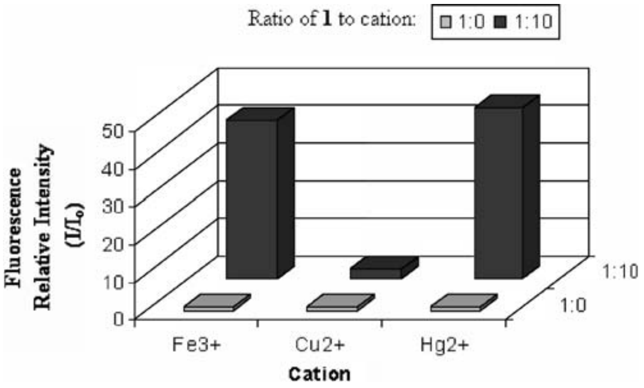
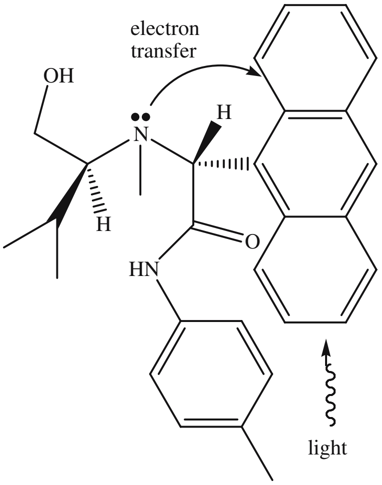
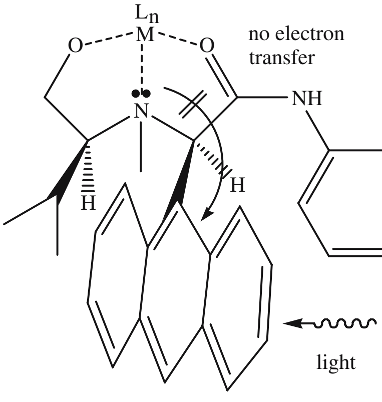


Fig. 2 Fluorescence enhancement ratios (I/I_0) at 420 nm for interaction of **1** with Fe^{3+}, Cu^{2+}, or Hg^{2+} in CH_3CN. λ_{ex}=368 nm. [**1**]=7.3×10^{-7} M



1 (nonfluorescent)



1 (fluorescent)

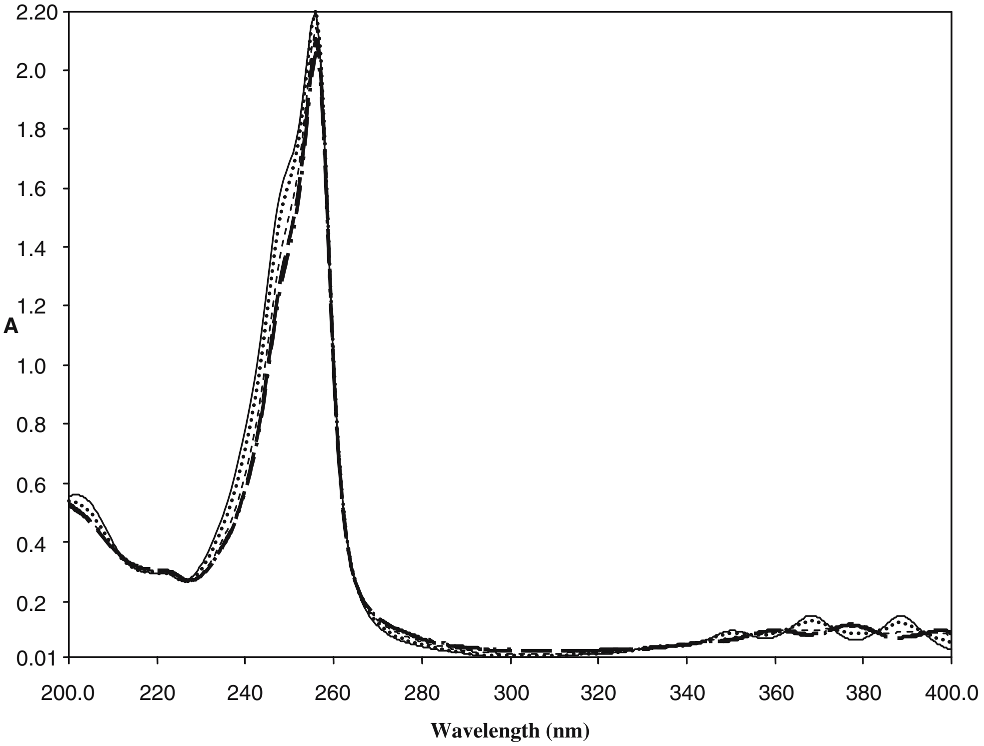
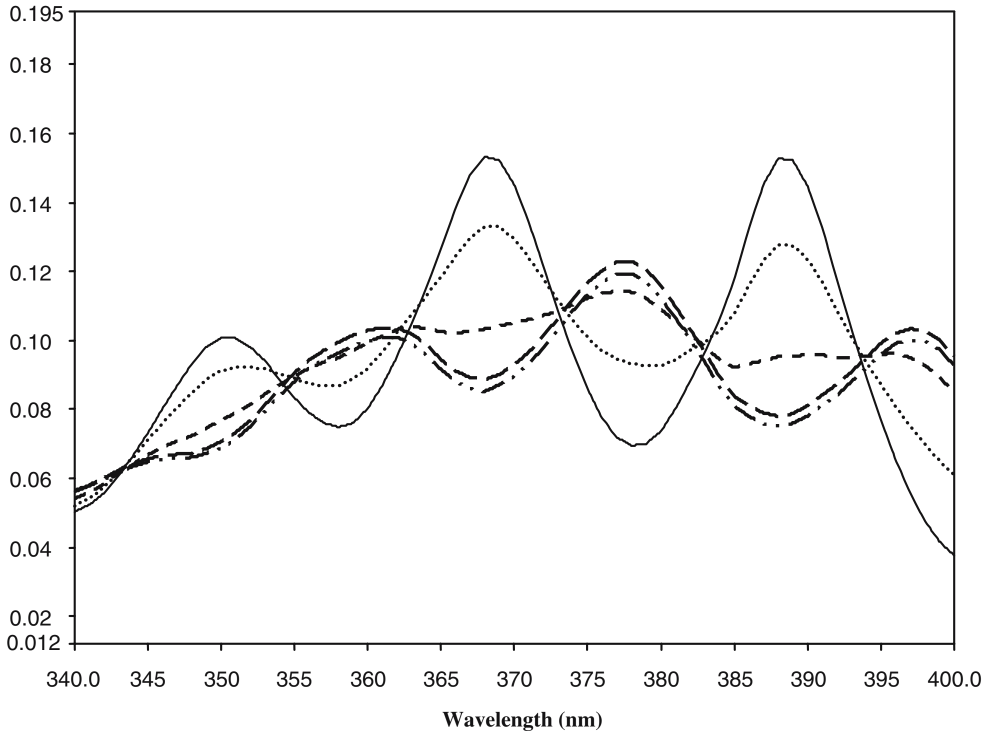


Fig. 3 Absorption titration spectra of **1** (1.8×10^{-5} M) in $CH_3CN–H_2O$ (3:7, *v*/*v*) by Fe^{3+} (0 equiv. ——, 0.6 equiv. ········, 1.2 equiv. - - - - ·, 1.6 equiv.– – –, 1.8 equiv. – ·· – ··)

species equilibrium between free host **1** and one host-guest complex. Absorption changes at 345~395 nm were quite significant in the absorption titration spectra and they were used to calculate the association constant (K_a) between **1** and Fe^{3+}. According to Eq. 1 [24], the plot of the absorbance ratio, $A_0/(A-A_0)$, versus $1/[Fe^{3+}]$ was generated and a straight line was obtained, indicating that the host–guest complex throughout the titration is 1:1 **1**/Fe^{3+} complex and the association constant (K_a) is 1.6×10^3 M^{-1}. Similar results were found with the UV-Vis titration of **1** with Hg^{2+}. The straight line of the absorbance ratio, $A_0/(A-A_0)$, versus $1/[Hg^{2+}]$ indicates that the host–guest

Fig. 3 (continued)



complex throughout the titration is 1:1 **1**/Hg^{2+} complex and the association constant (K_a) is 2.1×10^3 M^{-1}.

$$\frac{A_0}{A-A_0}=\left(\frac{\varepsilon_M}{\varepsilon_c-\varepsilon_M}\right)\left[\frac{1}{K_a\left[C_g\right]}+1\right] \tag{1}$$

According to the fluorescence measurement results for the fluoroionophoric properties of **1**, the tridentate ionophore of **1** selectively binds with Fe^{3+} and Hg^{2+}. Once the host–guest complex is formed, the lone pair of electrons on the nitrogen of **1** is stabilized and it is thermodynamically unfavorable for them to do intramolecular photoinduced electron transfer to the adjacent anthracene group upon photoexcitation of **1**, resulting in the significant fluorescence enhancement. To our knowledge, it is the first time to report that the tridentate ionophore of amide/β-amino alcohol does selective recognition of Fe^{3+} and Hg^{2+}.

Conclusion

The tridentate ionophore of amide/β-amino alcohol in **1** selectively recognizes Fe^{3+} and Hg^{2+}. The fluorophore of anthracene in **1** responses the recognition event of the ionophore by following PET mechanism. The sensitivity of **1** for Fe^{3+} and Hg^{2+} in CH_3CN can be up to 0.03 μM.

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