

A selective colorimetric chemosensor based on calixarene framework for lanthanide ions-Dy³⁺ and Er³⁺

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Abstract—A novel photochromic Schiff base derivative, 5,17-*N,N'*-(5,5'-di-methoxy-benzaldehyde)diimine-25,27-dipropoxy-calix[4]arene has been synthesized through incorporation of two imine groups into the upper rims of calix[4]arene. The experiments showed that the addition of Dy³⁺ or Er³⁺ ions to compound **4** results in the solution color change, but other metal ions caused less change. It indicated that the synthetic receptor can selectively recognize Dy³⁺ and Er³⁺ ion by naked eye over other lanthanide cations. Thus, these systems can be applied as chemosensor for Dy³⁺ and Er³⁺ ion in analytical chemistry.
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Chemosensors that convert molecular recognition into highly sensitive and easily detected signals have been actively investigated in recent years. A colorimetric fluorescent chemosensor combines the sensitivity of fluorescence and easy detection of a colorimetric assay.¹

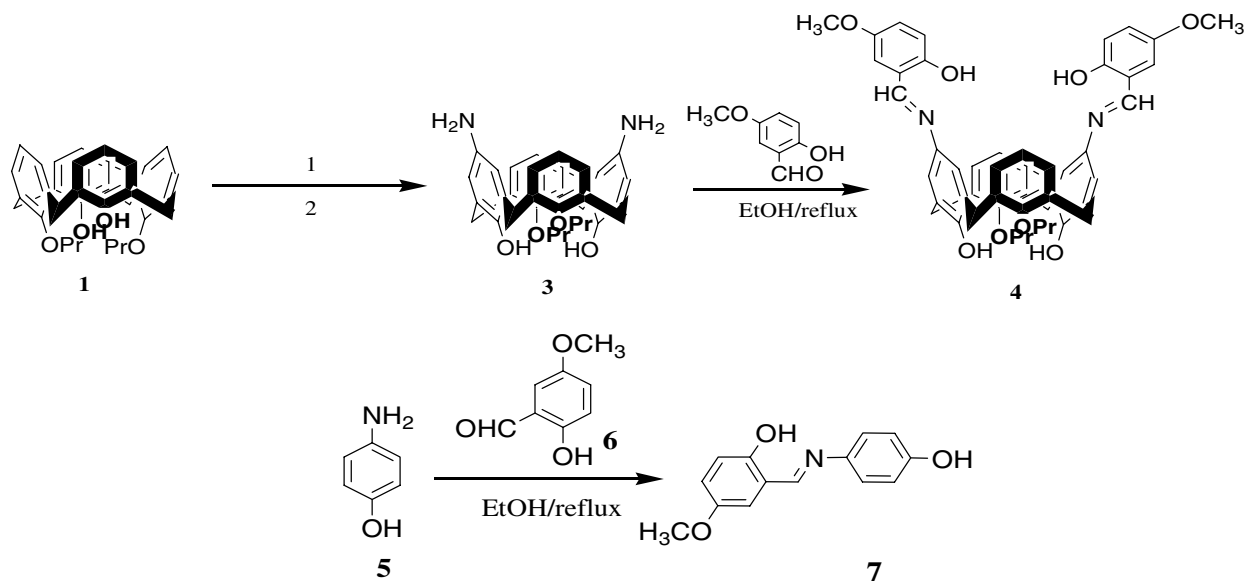
Calixarenes are popular building blocks in supramolecular chemistry, especially in molecular recognition. Recently, many authors have laid particular stress on the sensitized luminescence of lanthanide ions complexes with calixarene derivatives² because these functional complexes show potential applications, such as probes and labels for chemical and biological applications.³ Because of the special structures of Salicylideneanilines derivatives, lanthanide Schiff base complexes have some advantages for luminescence research.⁴ However, there are few reports about selective chemosensors for lanthanide ions,⁵ while a number of reports regarding their application have appeared.^{3,4,6} Previous work from our laboratories showed that novel calix[4]arene derivatives, bearing two spirobenzopyran moieties in the lower rim, can recognize lanthanide ions. Unfortunately, the compound did not show specific selectivity in sensing

single lanthanide ions.^{5a} Thus, we incorporated imine groups into the upper rim of calix[4]arene so as to synthesize the Schiff base-calix[4]arene, **4**. Host **4** can selectively recognize lanthanide ions-Dy³⁺ and Er³⁺ with the solution color changed from colorless to pink for Dy³⁺ and to pale yellow for Er³⁺. Whereas, addition of alkali metal ions, alkali earth metal ions, transition metal ions or other lanthanide ions (such as La³⁺, Pr³⁺, Eu³⁺, Gd³⁺, Yb³⁺) resulted in no visible changes. To the best of our knowledge, the selective colorimetric chemosensors for Dy³⁺ and Er³⁺ have not been reported before. We first find that host compound **4** can be used as chemosensor for Dy³⁺ and Er³⁺ with the naked eye.

The starting compounds **1–3** and host compound **4** were synthesized in several steps as shown in Scheme 1. Compounds **1**, **2** were obtained in accordance with the literature,⁷ the nitro-derivative was reduced to the corresponding amino derivative, **3**,⁸ and compound **3** was then used for the preparation of compound **4**. The overall yield of **4** synthesized from **1** is about 32%. The structure of **4** was identified by IR, ¹H NMR, ¹³C NMR, MALDI-TOF MS, and Element analysis.⁹ Two doublets of the CH₂ bridging groups (at 3.44 and 4.36 ppm) in the ¹H NMR data revealed that **4** is in the cone conformation. The imine group (CH=N) protons for **4** was seen at 8.59 ppm in the ¹H NMR and carbon atom of the imine group was observed at 158.9 ppm in the ¹³C NMR spectra, respectively.

Keywords: Logic switch; Photoswitch; Calix[4]arene; Schiff bases; Molecular recognition.

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Scheme 1. Synthesis routes of compound 4. Reagents and conditions: (1) concd HNO₃/CH₃COOH/CH₂Cl₂ rt; (2) SnCl₄/EtOH/reflux.

5-Methoxysalicylaldehyde-4-phenolamine (7) (Scheme 1), the model molecule, was synthesized following the literature procedures¹⁰ and the structure was identified by IR, ¹H NMR, ¹³C NMR, and MS.¹¹

Preliminary complexation studies were carried out with UV–vis spectra and Fluorescence spectra in dichloromethane. Figure 1 shows the variation of absorption of ligand 4 at constant concentration after adding La³⁺, Pr³⁺, Eu³⁺, Gd³⁺, Dy³⁺, Er³⁺ and Yb³⁺, respectively. Upon addition of La³⁺, Pr³⁺, Eu³⁺, Gd³⁺, and Yb³⁺, such absorption band did not show any noticeable variation, except that the maximum intensity of absorption band at 375 nm is different to that of host compound 4. However, Dy³⁺ and Er³⁺ are different from others, namely, when ligand 4 is complexed with Dy³⁺ or Er³⁺, the original peak at 375 nm is decreased, and a new broad absorption band appeared at 450–550 nm. It is interesting that the colorless compound 4 solution changed to pink immediately when the lanthanide ions-Dy³⁺ was added, and changed to yellow for Er³⁺ after standing in the dark for 24 h (Fig. 2). The

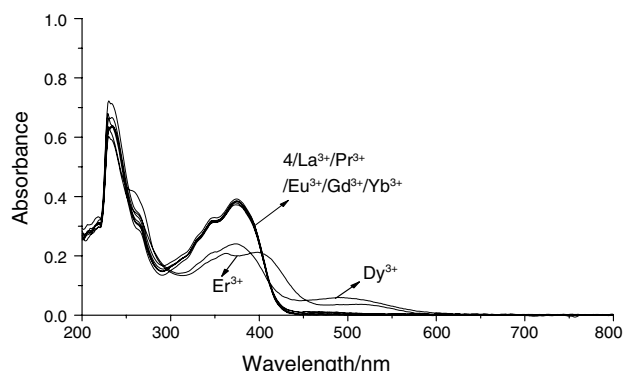


Figure 1. Absorption spectra of ligand 4 (1×10^{-5} M) and its complexes in CH₂Cl₂.

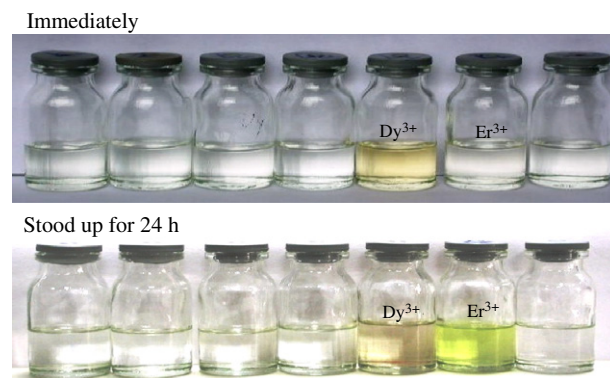


Figure 2. Color changes immediately of compound 4 in dichloromethane induced by addition of Dy³⁺ (top); color changes of compound 4 in dichloromethane induced by addition of Er³⁺ (bottom) stood up for 24 h in the dark condition (from left to right: addition of La³⁺, Pr³⁺, Eu³⁺, Gd³⁺, Dy³⁺, Er³⁺ and Yb³⁺).

changes in the absorption band may be due to expansion of π -conjugated system caused by Dy³⁺ or Er³⁺ and occurrence of donor–acceptor charge transfer (CT) in the large π conjugate system. The new absorption band appeared at longer wavelengths indicating that Dy³⁺ or Er³⁺ accept more charge from the Schiff base.¹²

The fluorescence emission of free ligand 4 and the changes of the compound 4 fluorescence emission in the presence of the lanthanide ions are shown in Figure 3. The very weak fluorescent emission of host compound 4 in visible region was observed at 550 nm. To the best of our knowledge, the imine group, as a spacer, makes the system rigid and the lone pair of electrons on nitrogen is delocalized on to the π -cloud of the methoxyl-phenol. Such rigidity results in photo-induced electron transfer (PET) from imine group to methoxyl-phenol which quenches the fluorescence emission of host 4.¹³ It can be seen clearly that upon addition of lanthanide ions (La³⁺, Pr³⁺, Eu³⁺, Gd³⁺ and Yb³⁺) to the ligand

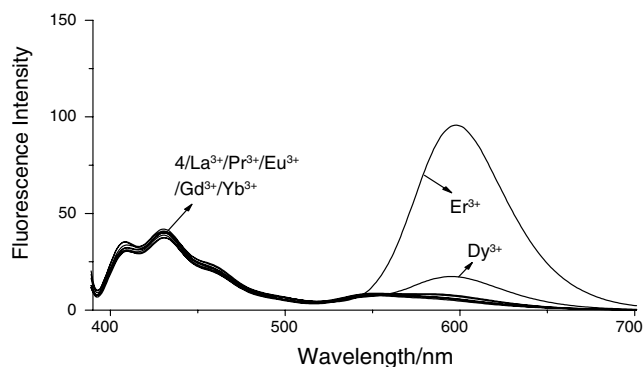


Figure 3. Fluorescence spectra of ligand **4** (1×10^{-5} M) and its complexes in CH_2Cl_2 ; $\lambda_{\text{ex}} = 375$ nm.

solution did not cause any noticeable variation. However, for solution mixtures of Dy^{3+} or Er^{3+} the maximum fluorescent emission peak was observed at 598 nm at excitation of 375 nm, namely, the wavelength took place red shifted by about 48 nm. Upon complexation with Dy^{3+} or Er^{3+} , the nitrogen atom of imine group donates its lone pair electrons to the empty orbital of the cations Dy^{3+} or Er^{3+} , and a large chelation-enhanced fluorescence (CHEF) is observed because the chelation abrogates the PET process. And as mentioned for absorption spectra, the formation of large π conjugate system is beneficial to increasing the plane structure of the molecule which could make the fluorescence emission easy. The broad emission band at 598 nm may originate from the large π conjugate system.

The reason of host compound **4** can selectively recognize Dy^{3+} or Er^{3+} ion may be the size-fit effect of the calix[4]-arene cavity in addition to strengthened π -cation-interaction driven by the electron-donating methoxyl group on the phenylimine unit to result in a region-selectivity in metal ion complexation based on the red shift in this study.¹⁴ Thus, in order to investigate the contribution of the calix[4]arene cavity to the selectivity, we designed model molecules **7** (Scheme 1). In these experiments, the concentration of model **7** (20 μM) is double of that of host **4** so that the concentration of the imine groups is consistent. As shown in Figure 4, adding the lantha-

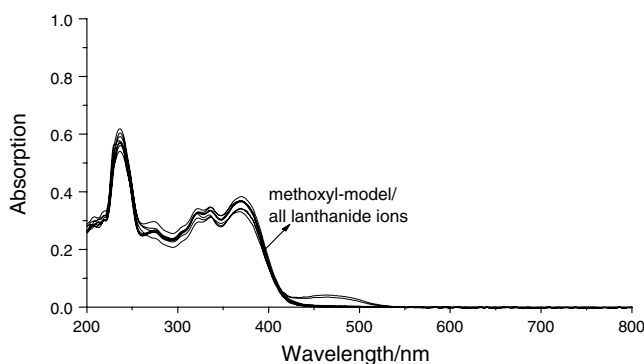


Figure 4. Absorption spectra of 2×10^{-5} M model compound 5-methoxysalicylaldehyde-4-phenolaniline (**7**) and its complexes (La^{3+} , Pr^{3+} , Eu^{3+} , Gd^{3+} , Dy^{3+} , Er^{3+} and Yb^{3+}) in CH_2Cl_2 .

nide ions to the solutions of **7** caused less visible color change than that of the corresponding host, and free ligand and metal complexes of lanthanide ions exhibit similar absorption bands and the similar values of extinction coefficient. It suggests that model **7** shows poor selectivity for the lanthanide ions and host compound **4** can selectively recognize Dy^{3+} and Er^{3+} due to the size-fit effect between the host with Dy^{3+} and Er^{3+} . And the color change of Er^{3+} mixed solution may result from the slow binding of host for Er^{3+} . In order to explain this result, we did time-dependent absorption spectra. As shown in Figure 5, the complex equilibrium for Dy^{3+} or Er^{3+} is reached after about 5 and 20 h, respectively.

The changes in the fluorescence spectra of host compound **4** upon successive addition of Dy^{3+} and Er^{3+} ion are shown in Figures 6 and 7. These fluorescence data were analyzed by using nonlinear least-square method for the stability constant and the stoichiometry of complex.¹⁵ The analysis provided the stoichiometry of the complex formed from host **4** and $\text{Dy}(\text{NO}_3)_3$ was 1:1 (**4**: Dy^{3+}) and the stability constant

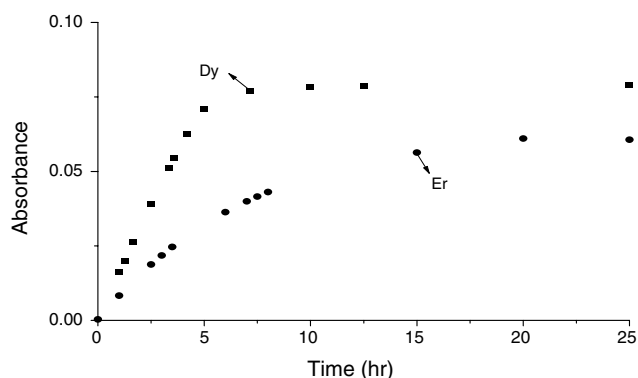


Figure 5. Time-dependent absorption spectra of the mixed solution of host compound (1×10^{-5} M) and Dy^{3+} or Er^{3+} (1×10^{-5} M) in CH_2Cl_2 . Time of detection: 0, 1.0, 1.2, 1.6, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, 7.0, 10.0, 12.0, 15.0, 20.0, 24.0.

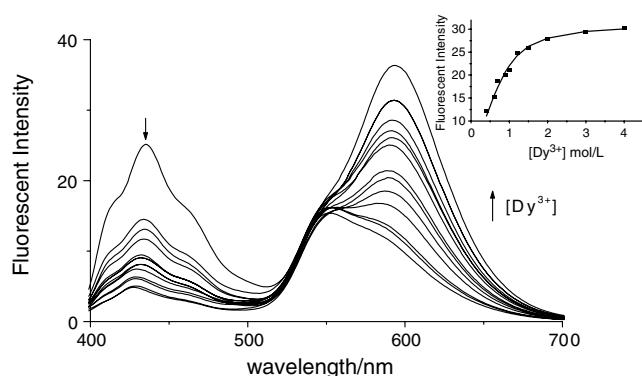


Figure 6. Fluorescence emission spectra of **4** (1×10^{-5} M) in the presence of Dy^{3+} in CH_2Cl_2 . The concentration of Dy^{3+} : 0, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.2, 1.4, 1.5, 1.6, 1.8, 2, 3, 4, 5×10^{-5} M; $\lambda_{\text{ex}} = 375$ nm. Inset: The variations in fluorescent intensity ($I_{598 \text{ nm}}$) of a solution **4** (1×10^{-5} M) in dichloromethane as a function of the concentration of Dy^{3+} .

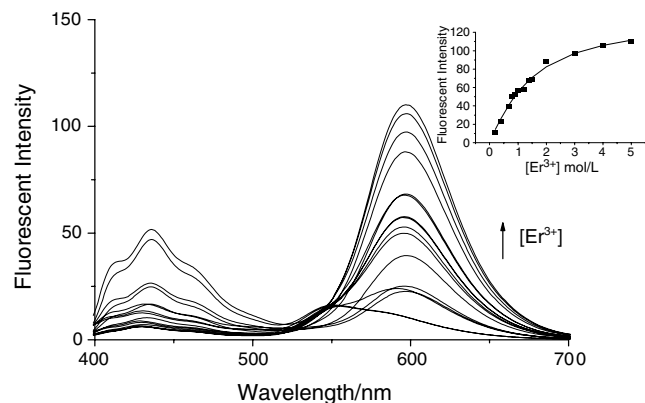


Figure 7. Fluorescence emission spectra of **4** (1×10^{-5} M) in the presence of Er^{3+} in CH_2Cl_2 . The concentration of Er^{3+} : 0, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.2, 1.4, 1.5, 1.6, 1.8, 2, 3, 4, 5×10^{-5} M; $\lambda_{\text{ex}} = 375$ nm. Inset: The variations in fluorescent intensity ($I_{598 \text{ nm}}$) of a solution **4** (1×10^{-5} M) in dichloromethane as a function of the concentration of Er^{3+} .

$\log K = 5.41 \pm 0.14$ with correlation coefficient 0.9899 (Fig. 6); the stability constant $\log K = 5.77 \pm 0.06$ with correlation coefficient 0.9804 whose stoichiometry with 1:1 (**4**: Er^{3+}) for **4** and $\text{Er}(\text{NO}_3)_3$.

In summary, we have synthesized a novel compound containing two photochromic imine groups based on calix[4]arene framework, which can be used to effectively recognize the lanthanide ions- Dy^{3+} and Er^{3+} with the size-fit effect between the Schiff base-calix[4]arene and the two cations. Thus, compound **4** may be applied as chemosensor for Dy^{3+} and Er^{3+} by naked eye visible color change of the mixed solution in analytical chemistry.

Acknowledgement

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- Yields: 80%. Mp > 300 °C; ^1H NMR: δ ppm (CDCl_3) 1.33 (t, $J = 15$ Hz, 6H, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-}$), 2.11 (q, $J = 15$ Hz, 4H, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-}$), 3.75 (s, 6H, CH_3O), 4.02 (t, $J = 12$ Hz, 4H, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-}$), 3.44, 4.36 (2d, $J = 15$ Hz, 4H, Ar- CH_2 -Ar), 6.84 (t, $J = 9$ Hz, 2H, Ar-H), 6.93 (d, $J = 6$ Hz, 4H, Ar-H sal), 6.98 (d, $J = 3$ Hz, 2H, Ar-H sal), 7.00 (d, $J = 9$ Hz, 4H, Ar-H), 7.11 (d, $J = 6$ Hz, 4H, Ar-H), 8.59 (s, 2H, C=N), 10.67 (s, 2H, OH), 13.10 (s, 2H, OH sal); ^{13}C NMR: δ (CDCl_3) 158.9 (C=N), 155.2, 153.0, 152.2, 152.0, 139.6, 133.1, 129.2, 128.9, 125.5, 121.2, 119.5, 117.9, 115.0, 78.5, 56.0 (CH_3O), 31.5, 23.5, 10.9; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1623 (C=N), 1053, 1239 (OCH_3); MALDI-TOF MS: m/z 806 (M^+); Anal. Calcd for $\text{C}_{50}\text{H}_{50}\text{N}_2\text{O}_8$: C, 74.44; H, 6.26; N, 3.47; Found: C, 74.42; H, 6.28; N, 3.52.
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- Yields: 90%. ^1H NMR: δ ppm (DMSO) 3.73 (s, 3H, CH_3O), 6.81 (d, $J = 9$ Hz, 2H, Ar-H), 6.87 (s, 1H, Ar-H sal), 6.96 (d, $J = 12$ Hz, 1H, Ar-H sal), 7.176 (d, $J = 3$ Hz, 1H, Ar-H sal), 7.27 (d, $J = 9$ Hz, Ar-H), 8.86 (s, 1H, C=N), 9.67 (s, 1H, OH), 12.76 (s, 1H, OH sal); ^{13}C NMR: δ (DMSO) 160.3 (C=N), 157.4, 154.6, 152.3, 139.9, 123.1, 120.0, 117.7, 115.6, 110.5, 56.0 (CH_3O); IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1623 (C=N), 1053, 1239 (CH_3); MS: m/z 243 (M^+).
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