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A selective colorimetric chemosensor for lanthanide ions

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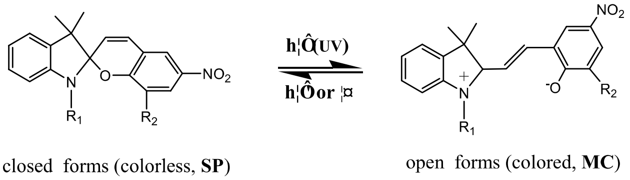
Abstract—The synthesis and complexing properties of a calix[4]arene derivate (**6**) carrying two spirobenzopyran moieties are described. The addition of lanthanide ions resulted in significant UV–vis spectral shifts (68–84 nm) in visible region. It indicates that the synthetic receptor can recognize lanthanide ions by naked eyes over other cations including Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+}. The mechanism of recognition was studied with ^1H NMR, UV–vis spectra and emission spectra. The receptor may be applied to sense lanthanide ions.

1. Introduction

Lanthanide ions have been widely applied in many fields, for example, as probes and labels in chemical and biological applications.[1] In order to overcome the weak absorption coefficients of the lanthanide ions and sensitize their luminescence, many lanthanide (III) chelates have been designed containing 'antenna effect'.[2] The macrocyclic chelating agents including cryptands,[3] calixarene,[4] cyclodextrins[5] and crown-ether derivatives,[6] are commonly used to sensitize luminescence of Eu (III) and Tb (III) ion.

Spirobenzopyran derivatives have been extensively investigated for their photochromism[7] and applications in photoswitchable molecular devices.[8] Under the irradiation of ultraviolet light (or in dark conditions), the colorless, neutral spiropyran (**SP**) forms are isomerized to the colored, zwitterionic merocyanine forms (**MC**) while the s–p hybridization of a single C atom becomes p-conjugation over the whole molecule (Scheme 1). The zwitter-ionic merocyanine forms may have stronger affinity for lanthanide ions than the neutral host for their electrostatic interaction.[9]



Scheme 1. Photochromic reactions of spirobenzopyran derivatives.

In the present work, we report the synthesis of receptor **6** by incorporating two 1′,3′,3′-trimethyl-6-nitro-8-hydromethyl-spiro-(2-*H*-1-benzopyran-2,2′-indoline) (**5**) groups to a 5,11,17,23-tetra-*tert*-butyl-25,27-bis(chloroformylmethoxy)-26,28-dihydroxycalix[4]arene (**4**) (Scheme 2). The structure of compound **6** was identified by IR, ^1H, ^{13}C NMR, elemental analysis and MALDI-TOF MS. Two doublets of the CH_2 bridging groups (at 3.26 and 4.35 ppm) in the ^1H NMR data revealed that **6** is in the cone conformation. The host compound **6** can selectively recognize lanthanide ions with significant hypsochromic shifts and enhancement of maximum absorption intensity in visible region. Meanwhile, the color of the solution changed from purple to yellow. Whereas, addition of alkali metal cations (such as Na^+, K^+), alkali earth metal cations (such as Mg^{2+}, Ca^{2+}) or transition metal cations (such as Fe^{3+}, Cu^{2+}, Zn^{2+}) resulted in no visible changes in the UV–vis absorption spectra. Thus, compound **6** may be applied as a lanthanide sensor with naked eye. The model compound **8** (Scheme 2) without calix[4]arene cavity had poorer selective ability for lanthanide ions than compound **6**. Compound **5** (Scheme 2) is of the least selectivity for the investigated ions among these three receptors. In this paper, we studied the mechanism of recognition by means of ^1H NMR, UV–vis spectra and emission spectra of the **6**-Eu^{3+} complexes.

2. Results and discussion

2.1. Metal cations recognition

We investigated the recognition ability of receptor **6** for metal ions such as alkali metal cations (Na^+, K^+), alkali earth metal cations (Mg^{2+}, Ca^{2+}), transition metal cations (Fe^{3+}, Cu^{2+}, Zn^{2+}) and lanthanide cations (La^{3+}, Pr^{3+}, Eu^{3+}, Gd^{3+},

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Keywords: Calix[4]arene derivatives; Spirobenzopyrans; Recognition; Lanthanide ions; Sensors.

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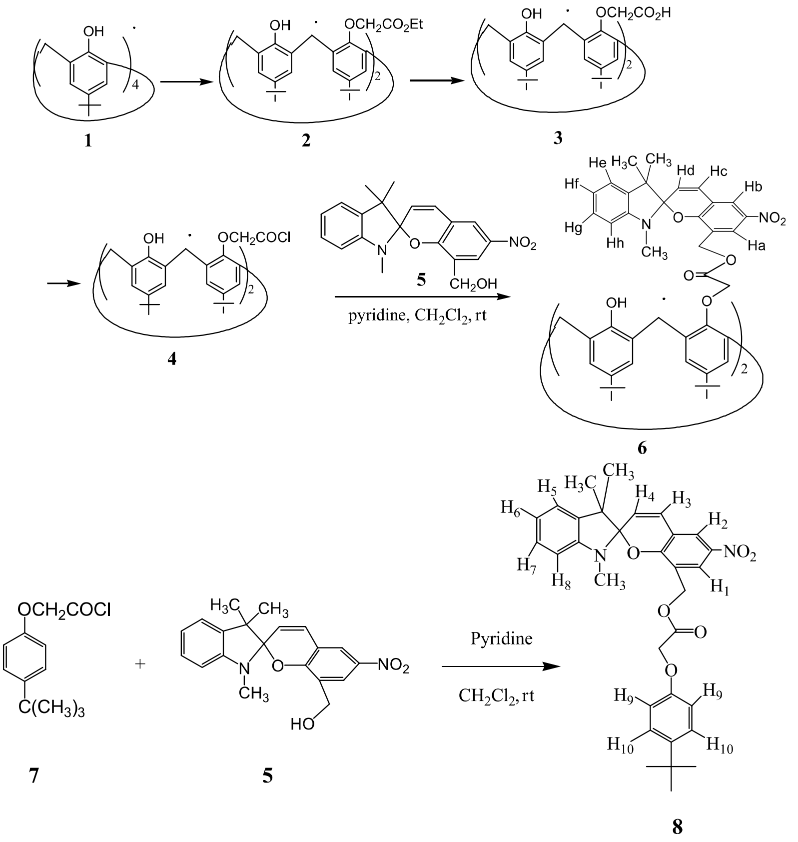

Scheme 2. Synthesis of receptor **6** and model compound **8**.

Dy^{3+}, Er^{3+}, Yb^{3+}). When the colorless lanthanide solutions in acetonitrile were added to the purple solution of receptor **6** in acetonitrile, the color changed to yellow immediately. However, there was no remarkable color change upon the addition of Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+}. As shown in Figure 1, the color change of **6** upon the addition of lanthanide ions is visible to the naked eye. Figure 2 shows the absorbance at the maximum absorption wavelength of the mixed solution of receptor **6** with equally molar metal cations, which were allowed to stand for 48 h under dark conditions for complete complexation. The addition of lanthanide ions caused significant hypsochromic shifts (68–84 nm) and enhancement of maximum absorption intensity (5.5–9.0 folds, Table 1) in visible region. The hypsochromic shifts can be explained by the location of electron cloud of the open merocyanine forms (**Calix-2MC**) attributed to electrostatic interaction between the phenolate anions of merocyanine groups (**MC**) and trivalent lanthanide ions under dark conditions. These changes suggest **6** coordinated with lanthanide ions. The complexing process was described in Scheme 3 (**Calix-2SP** and **Calix-2MC** denote the closed forms and the open forms of receptor **6**, respectively. **Calix-2MC·Ln^{3+}** means the complexes of the open **6** and lanthanide ions). According to hard soft acid base principle, lanthanide ions belong to hard acid, which have strong affinity for hard alkali (such as oxygen). In the lower rim of the receptor **6**, there are 10 oxygen atoms, which are not only able to coordinate with lanthanide ions but also meet their large coordination number. What is interesting is that the trend of spectral changes is $Yb^{3+} > Er^{3+} > Gd^{3+} > Dy^{3+} > Eu^{3+} > Pr^{3+} > La^{3+}$ opposite to that of the lanthanide ions' radii. This implies that the recognition process is relative to the size-fit effect. Hence upon the addition of lanthanide ions, the receptor changes color due to strong electrostatic interaction, hard acid–hard alkali interaction and size-fit effect between **Calix-2MC** and lanthanide ions.

Figure 1. Color change of compound **6** (50 μM) in acetonitrile induced by addition of 2 equiv of metal nitrate (from left to right: compound **6** without metal ion; addition of Na^+; Ca^{2+}; Zn^{2+}; La^{3+}; Pr^{3+}; Eu^{3+}; Gd^{3+}; Er^{3+}).

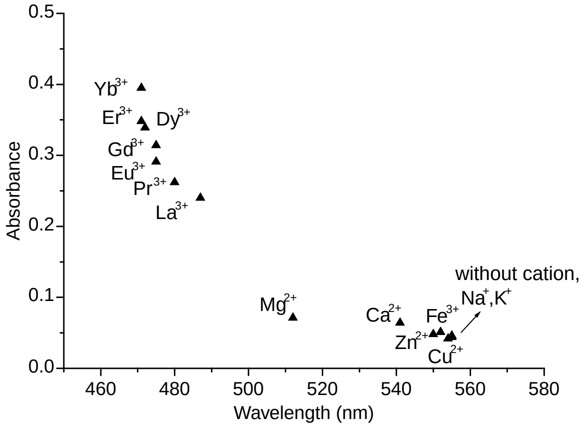

Figure 2. UV–vis spectra of compound **6** (20 μM) in the presence of and without metal ions (20 μM) in acetonitrile under dark conditions for 48 h.