

Photo-switchable molecular devices based on metal-ionic recognition

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Received 1 September 2004; revised 12 November 2004; accepted 16 November 2004

Available online 15 December 2004

Abstract—A novel calix[4]arene derivative, bearing two spirobenzopyran moieties in the lower rim, can recognize lanthanide ions. Alternating irradiation with ultraviolet and visible light controls the ligand-to-metal charge transfer (LMCT) and energy transfer of the host–Eu³⁺ complexes. Thus, fluorescence of Eu³⁺ can be switched on and off through light. The system may be applied as molecular logic switches.

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Signal transduction and associated process at the molecular level have attracted increasing attention for its potential applications in ultraminiaturized computer processors.¹ A remarkable example of signal transduction in organism is vision process carried out by the isomerization of a simple molecule called retinal. People may achieve signal transduction at molecular level through imitating the vision process. The photoswitch would be simple and effective method due to its simple instrumentation and high selectivity in signal processing.

Calixarenes are popular building blocks in supramolecular chemistry, especially in terms of molecular recognition. Lanthanide ions recognition based on calixarenes has been reported.² Spirobenzopyran derivatives have been extensively investigated for its photochromism.³ Under the irradiation of ultraviolet light (or in dark conditions), the colorless, neutral spiropyran (SP) forms are isomerized to their colored, zwitter-ionic merocyanine forms (MC). Meanwhile, the s–p hybridization of a single C atom changes to p-conjugation over the whole molecule. The characteristics indicate potential usefulness of controlling intermolecular interaction under light stimulus. Compound **4** was prepared by incorporation of two spiropyran groups to *p*-tert-butylcalix-

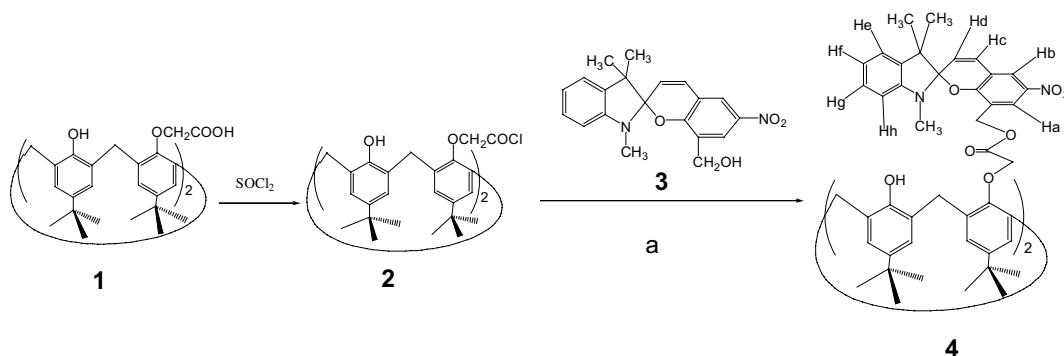
[4]arenes. The host compound **4** can selectively recognize lanthanide ions. It is of interest that the fluorescence of Eu³⁺ in the host solution can be switched on and off by light.

The host compound **4** was synthesized as shown in Scheme 1, from **2** and 2 equiv of **3** in the presence of pyridine. Compound **1**, **2**, and **3** were obtained in accordance with the literature.^{4,5} The structure of **4** was identified by IR, ¹H NMR, ¹³C NMR, elemental analysis, and MALDI-TOF MS.⁶ Two doublets of the CH₂ bridging groups (at 3.26 and 4.35 ppm) in the ¹H NMR data revealed that **4** was in the cone conformation.

In the absorption spectra of **4** in dark conditions, the maximum band in the visible region is at 555 nm, typical absorption of merocyanine forms. Under dark conditions, addition of lanthanide ions resulted a significant hypsochromic shift and an increase of maximum absorption intensity in visible region. La³⁺, Pr³⁺, Eu³⁺, Gd³⁺, Dy³⁺, Er³⁺, Yb³⁺ brought a shift of 68, 75, 80, 80, 83, 84, 84 nm and an increase of 5.5, 6.0, 6.6, 7.1, 7.7, 7.9, 9.0 folds, respectively. The solution's color changed from purple to yellow. Whereas, addition of alkali metal cations (such as Na⁺, K⁺), alkali earth metal cations (such as Ca²⁺) or transition metal cations (such as Fe³⁺, Cu²⁺, Zn²⁺) showed no noticeable change in the absorption spectra. The blue shift can be explained by location of electron cloud of the merocyanine forms (Calix-2MC) attributed to electrostatic interaction

Keywords: Molecular devices; Logic switches; Molecular recognition; Photoswitch; Calix[4]arene; Spiropyran; Eu³⁺.

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Scheme 1. Synthesis routes of compound **4**. Reagents: (a) 2.2 equiv pyridine/ CH_2Cl_2 .

between the merocyanine groups and Eu^{3+} . These changes suggest **4** and lanthanide ions can form complexes. It indicates that **4** can recognize lanthanide ions by the naked eye (Fig. 1). It could be a new organic reagent for separation and analysis of lanthanide elements.

It is known that the typical fluorescence emission band of Eu^{3+} is narrow and line-like spectrum at 616 nm (Fig. 2, curve b). The merocyanine forms of spiropyran derivatives show weak fluorescence emission at 637 nm (Fig. 2, curve a).⁷ In the fluorescence spectra of a mixed solution of **4** and equal molar Eu^{3+} in acetonitrile, which was allowed to stand for 48 h under dark conditions for complete metal ion complexation,⁸ maximum emission wavelength was observed at 616 nm too. Nevertheless, its emission intensity increased and its spectrum became broader than that of Eu^{3+} (Fig. 2, curve c). After the irradiation of visible light (>500 nm), fluorescence emission intensity of the mixture decreased remarkably (Fig. 2, curve d).

The mechanism of photoswitching fluorescence intensity may involve the ligand-to-metal charge transfer (LMCT) of the host- Eu^{3+} complexes, which disturbs the f-f transition of Eu^{3+} and causes broader emission spectrum. Under the irradiation of visible light, the zwitter-ionic merocyanine forms (**Calix-2MC**) are isomerized to the neutral spiropyrans (**Calix-2SP**), which interact with Eu^{3+} only through coordinative bonds without electrostatic interaction. Moreover, the coordinative bonds between **Calix-2SP** and Eu^{3+} are weaker than phenolate-interaction with metal ion in **Calix-2MC** and Eu^{3+} mixture. Namely the LMCT is weaker in the system of **Calix-2SP** and Eu^{3+} (**Calix-2SP**· Eu^{3+}) than that of **Calix-2MC** and Eu^{3+} (**Calix-2MC**· Eu^{3+}) system (Scheme 2). Meanwhile, energy transfer occurs from the excited state of **Calix-2MC** to

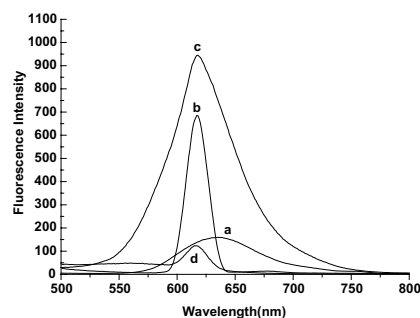
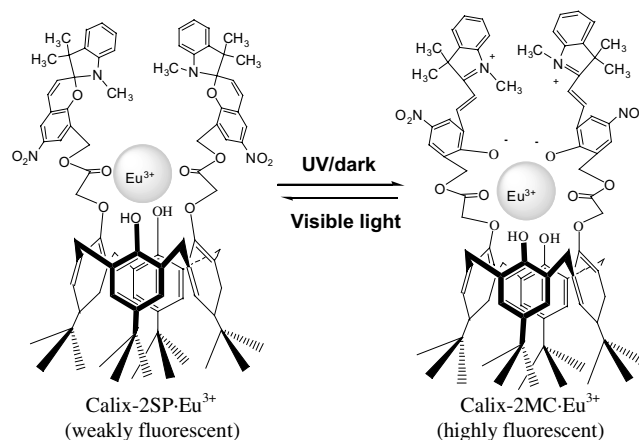


Figure 2. Fluorescence emission spectra of **4** (50 μM) under dark conditions (a); Eu^{3+} (50 μM) (b); equal molar **4** and Eu^{3+} (50 μM) under dark conditions (c); equal molar **4** and Eu^{3+} (50 μM) after the irradiation of visible light (>500 nm) (d) in acetonitrile. λ_{ex} = 310 nm.



Scheme 2. The mechanism of photoswitching fluorescence intensity.



Figure 1. Color change of compound **4** (50 μM) in acetonitrile induced by addition of 2 equiv of metal nitrate (from left to right: compound **4** without metal ion; addition of Na^+ ; Ca^{2+} ; Zn^{2+} ; La^{3+} ; Pr^{3+} ; Eu^{3+} ; Gd^{3+} ; Er^{3+}).

Eu^{3+} for their matchable energy levels. As a result, the fluorescence intensity was enhanced in mixed solution of **Calix-2MC** and Eu^{3+} (Fig. 2, curve c). The maximum emission wavelength of curve c (616 nm) is the same as curve b because curve c may contain emission of uncomplex Eu^{3+} (free Eu^{3+}) and complex Eu^{3+} (**Calix-2MC**· Eu^{3+}) in the mixed solution of **Calix-2MC** and Eu^{3+} . It is different from that of the host (curve a) for no host's emission in **Calix-2MC** and Eu^{3+} mixture due to energy transfer. Curve d is only the emission spectrum of uncomplex free Eu^{3+} for no energy transfer from **Calix-2SP** to Eu^{3+} in the **Calix-2SP**· Eu^{3+} com-

| Input data | | Output data |
|------------------------|--------------------|-------------------------|
| Ultraviolet light (I1) | visible light (I2) | emission at 616 nm (O1) |
| 0 | 0 | 1 |
| 1 | 0 | 1 |
| 0 | 1 | 0 |
| 1 | 1 | 1 |

I1 — NOT — O1

Figure 3. Truth table and logic circuit for the communicating molecular switches.

plexes (lower π^* energy level of **Calix-2SP** than the excited state energy level of Eu^{3+}).

The system could be applied as molecular logic switches.¹ The input signals are **I1** (ultraviolet light, $300 \text{ nm} < \lambda < 400 \text{ nm}$) and **I2** (visible light, $\lambda > 500 \text{ nm}$). The output signal is **O1** (the emission at 616 nm of Eu^{3+}). Each signal can be either *off* or *on* and can be represented by a binary digit (Fig. 3). Thus, signal communicating molecules transduce a string of two input data (**I1** and **I2**) into an output signal (**O1**). For example, the input string is 00 when both of the input signals are *off*. Under these conditions, the system is in state **Calix-2MC**· Eu^{3+} . Energy transfer from **Calix-2MC** to Eu^{3+} occurs and the emission is strong. As a result, the output signal **O1** is *on* and the output digit is 1. When **I1** is *on* and **I2** is *off*, the input string is 10. Under these conditions (ultraviolet light), the system is in state **Calix-2MC**· Eu^{3+} and the output signal is 1. When **I1** is *off* and **I2** is *on*, the input string is 01. Under these conditions (visible light), the system is in state **Calix-2SP**· Eu^{3+} . No energy transfer occurs and the emission is weak. Thus the output signal **O1** is *off* and the output digit is 0 (Fig. 3).

In summary, we have developed a novel molecular switch based on calix[4]arene carrying two spirobenzopyran groups, of which the fluorescent intensity can be regulated through light. Further studies on the mechanism of photoswitching fluorescence intensity is underway by several means in our laboratories.

Acknowledgements

We would like to thank the National Natural Sciences Foundation of China (NSFC, Grant No. 20275042) for their financial support.

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- Compound **4** mp: 143–144 °C; ^1H NMR: δ ppm (CDCl_3) 0.93 (s, 18H, Bu^t), 1.19 (s, 6H, SP-CH_3), 1.28 (s, 18H, Bu^t), 1.31 (s, 6H, SP-CH_3), 2.68 (s, 6H, SP-NCH_3), 3.26 (d, $J = 13.2$, 4H, ArCH_2Ar), 4.35 (d, 4H, $J = 13.2$, ArCH_2Ar), 4.56 (s, 4H, $\text{ArOCH}_2\text{CO}_2-$), 4.96 (d, $J = 12.9$, 2H, $\text{ArCH}_2\text{O}-$), 5.05 (d, $J = 12.9$, 2H, $\text{ArCH}_2\text{O}-$), 5.89 (d, $J = 10.3$, 2H, SP-H_d), 6.49 (d, $J = 7.5$, 2H, SP-H_h), 6.72 (s, 2H, Ar-OH), 6.75 (s, 4H, Ar-H), 6.80 (t, $J = 7.5$, 2H, SP-H_f), 6.92 (d, $J = 10.3$, 2H, SP-H_c), 7.01 (s, 4H, Ar-H), 7.02 (d, $J = 7.5$, 2H, SP-H_e), 7.09 (t, $J = 7.5$, 2H, SP-H_g), 7.97 (s, 2H, H_b), 8.07 (s, 2H, H_a); ^{13}C NMR: δ 168.5, 157.3, 150.6, 150.3, 147.3, 147.1, 141.5, 140.5, 135.8, 132.2, 128.1, 127.9, 126.0, 125.7, 125.6, 125.3, 125.1, 122.6, 122.5, 121.6, 121.4, 120.1, 118.8, 107.1, 107.0, 77.3, 77.0, 76.7, 71.9, 60.8, 52.0, 33.9, 33.8, 32.8, 32.1, 31.7, 31.5, 31.3, 31.0, 28.8, 26.0, 20.0. IR $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3430 and 1762; MALDI-TOF MS: m/z 1432 ($[\text{M}]^+$), 1455 ($[\text{M}+\text{Na}]^+$), 1471 ($[\text{M}+\text{K}]^+$). Anal. Calcd for $\text{C}_{88}\text{H}_{96}\text{N}_4\text{O}_{14}$: C, 73.74; H, 6.69; N, 3.91. Found: C, 73.18; H, 7.20; N, 3.64.
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