Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters 48 (2007) 1629–1632
Tetrahedron Letters

A new fluorescent chemosensor for copper(II) and molecular switch controlled by light

Zhi Liang,[a] Zhilian Liu,[b] Lin Jiang[c] and Yunhua Gao[a,*]

[a]Lab of Organic Optoelectronic Functional Materials and Molecular Engineering, Technical Institute of Physics and Chemistry & Graduate University, Chinese Academy of Sciences, Beijing 100080, PR China
[b]The School of Chemistry and Chemical Engineering of Jinan University, Jinan 250022, PR China
[c]Department of Applied Materials, The Central Research Lab of BYD Company Limited, PR China

Received 11 October 2006; revised 21 December 2006; accepted 22 December 2006
Available online 4 January 2007

Abstract—A novel fluorescent chemosensor with two 5-nitro-salicylaldehyde groups at the upper rim of calix[4]arene has been synthesized. The chemosensor can effectively recognize copper(II) ion. This system could be considered as a molecular switch. By alternating the light irradiation of mixed solution formed by the host and Cu^{2+}, off–on–off fluorescent switching is carried out.

Molecular recognition and supramolecular chemistry have attracted considerable interest for the understanding of biological phenomena and development of new materials. The design and synthesis of luminescent signaling systems-fluorescent chemosensors that display large differences between their 'off' (no emissive) and 'on' (emissive) states is an active area of research within the field of supramolecular chemistry.[1] The development of such simple first generation switches has led to the development of more complex arrays or single molecules that can perform complicated tasks such as mimicking the function of simple logic gate operations.[2]

Calixarenes are popular building blocks in supramolecular chemistry, especially in molecular recognition. Salicylideneaniline derivatives show photochromism that is explained by an intramolecular proton transfer from the hydroxyl oxygen to the imine nitrogen through the hydrogen bond.[3] Such behavior suggests the possibility of using these compounds as elements for constructing the optical switches. Thus, we incorporated imine groups into the upper rim of calix[4]arene so as to synthesize the Schiff base-calix[4]arenas, **4**. Although host compound **4** did not show a higher selectivity in recognizing transition metal ion-Cu^{2+} than other host molecules in some reports,[4] the compound indeed effectively recognizes Cu^{2+} over other metal ions in our work. It is more important that the fluorescence of host–Cu^{2+} complex can be switched on and off by light.

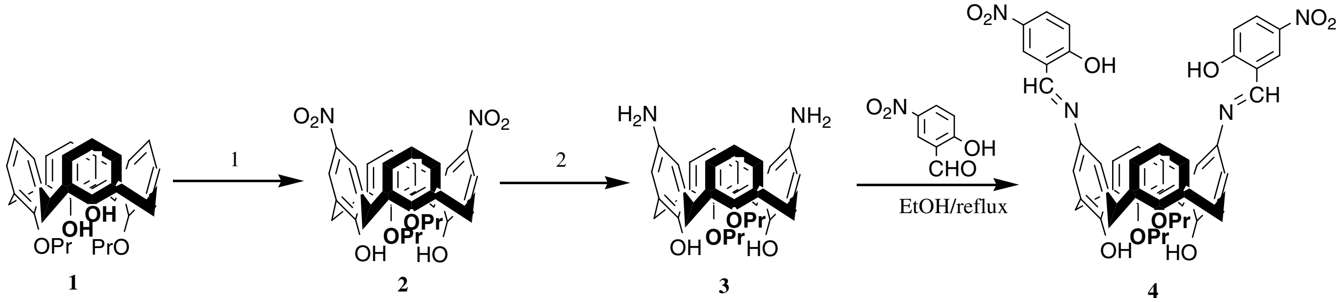
The starting compounds **1**–**3** and host compound **4** were synthesized in several steps as shown in Scheme 1. Compounds **1** and **2** were prepared following the literature procedures,[5,6] and nitro-derivative was reduced to the corresponding amino derivative **3**,[7] which was converted to compound **4**. The structure of **4** was identified by IR, ^1H NMR, ^{13}C NMR, MALDI-TOF MS, and Element analysis.[8] Two doublets of the CH_2 bridging groups (at 3.52 and 4.32 ppm) in the ^1H NMR spectrum revealed that **4** is in the cone conformation. The chemical shift of the imine (CH=N) protons of **4** was at 8.67 ppm in the ^1H NMR spectrum and the chemical shift of the carbon atom of the imine group (CH=N) was observed at 159.2 ppm in the ^{13}C NMR spectrum, respectively.

The maximum absorption wavelength of host compound **4** is 365 nm in the dark condition. The addition of $Cu(NO_3)_2$ resulted in a hypsochromic shift about 17 nm and a decrease of maximum absorption intensity, but other metal ions (such as Ca^{2+}, Mg^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}) cause no visible changes in the absorption spectra. The fluorescent spectra of compound **4** whose fluorescence emission has been previously attributed to excited keto-tautomer species generated by a very fast enol-imine* → *cis*-keto-amine*

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

* Corresponding author. Tel./fax: +86 10 82543581; e-mail: yhgao@mail.ipc.ac.cn

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.12.133



Scheme 1. Synthesis routes of compound **4**. Reagents and conditions: (1) concd $HNO_3/CH_3COOH/CH_2Cl_2$ rt; (2) $SnCl_2$/EtOH/reflux.

excited state intramolecular proton transfer (ESIPT)[9] showed different behaviors in the presence of different metal ions (Fig. 1). In order to avoid signal interference by the phenyl ring, we choose $\lambda = 365$ nm as the excitation wavelength to study the fluorescent properties of **4** toward metal ions.[10] It can be seen clearly that the fluorescent intensity of host **4** can be evidently quenched by Cu^{2+} ion with no significant change in the position of the emission maxima. Since under this condition $Cu(NO_3)_2$ has no absorption at the excitation wavelength, the decrease of fluorescent intensity was not due to the absorption of $Cu(NO_3)_2$. Similar measurements for other metal ions were examined. The changes in the fluorescent spectra could scarcely be detected after the addition of Pb^{2+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, Fe^{3+}, respectively; only the transition metal ion-Co^{2+} decreased the intensity of the fluorescent spectra to a certain degree. This phenomenon is consistent with the rule of Irving–Willians.[11] Copper(II) has a particularly high thermodynamic affinity for typical *N*,*O*-chelate ligands and fast metal-to-ligand binding kinetics. Although the other transition metal ions also have the complex ability as well, which is not as strong as copper ions, they only lead to the decreasing of fluorescence to a certain degree. Evidently, the binding between imine and Cu^{2+} caused this pronounced decrease, which also demonstrated the recognition ability of imine toward Cu^{2+}. The changes in the fluorescence spectra of compound **4** upon successive addition of Cu^{2+} ion are shown in Figure 2. These fluorescence data were analyzed by using nonlinear least-square method for the stability constant and the stoichiometry of complex.[12] The stoichiometry of the complex formed from host **4** and $Cu(NO_3)_2$ was 1:1 (**4**:Cu^{2+}) and the stability constant $\log K = 5.2 \pm 0.2$ with correlation coefficient 0.9957 (Fig. 3). The detection limit is about 6×10^{-7} M by calculation. Herein, host compound **4** is sensitive to Cu(II) fluorescent probe.

The mixed solution of host **4** and equal molar Cu^{2+} in dichloromethane was allowed to stand for 24 h under dark condition for complete metal ion complexation. The maximum fluorescent wavelength was observed at 512 nm (Fig. 4, curve a). Nevertheless, after the irradiation of ultraviolet light, the fluorescent intensity of the mixture was increased remarkably (Fig. 4, curve b) to that of host **4** (Fig. 4, curve c) and the color of the solution changed from colorless to pale yellow. It is interesting that its fluorescent intensity was decreased with the irradiation of visible light (Fig. 4, curve d).

The mechanism of photoswitching fluorescent intensity may involve internal charge transfer (ICT), tautomerization of host compound **4** (between enol-form and keto-form) and coordinate-release of metal ions (Scheme 2). The complex of host **4**–Cu^{2+} showed a weaker fluorescence under a dark condition as expected. Since the host

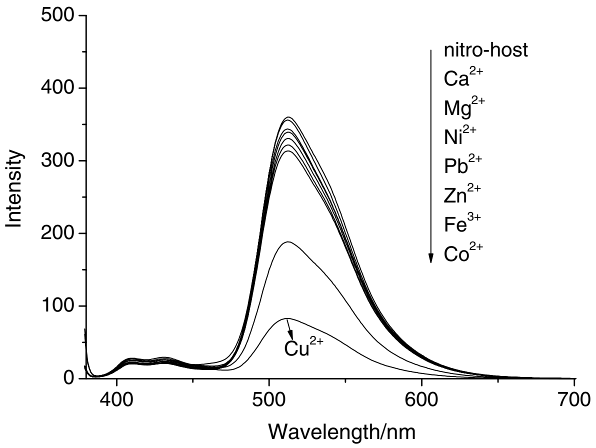


Figure 1. Fluorescence spectra of host **4** (1×10^{-5} M) in the presence of different transition metal ions (1×10^{-5} M) in CH_2Cl_2.

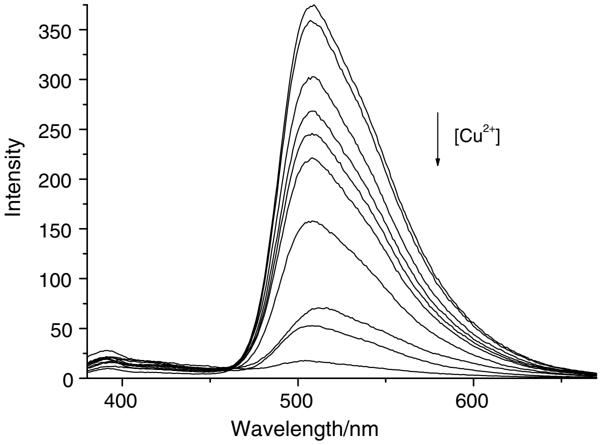


Figure 2. Fluorescence emission spectra of **4** (1×10^{-5} M) in the presence of Cu^{2+} in CH_2Cl_2. The concentration of Cu^{2+}: 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5×10^{-5} M; $\lambda_{ex} = 365$ nm.

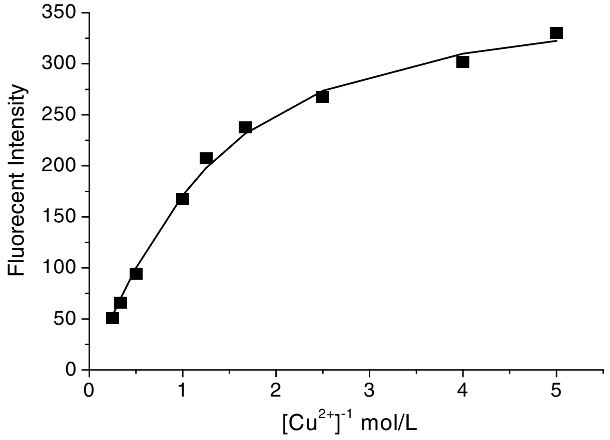


Figure 3. The variations in fluorescent intensity (I_{512} nm) of a solution **4** (1×10^{-5} M) in dichloromethane as a function of the concentration of copper nitrate.

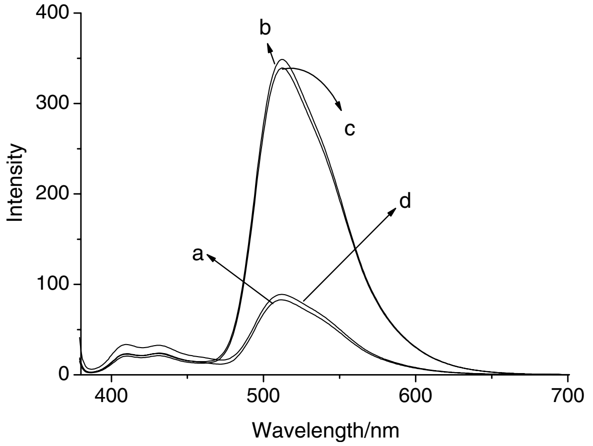


Figure 4. Fluorescence emission spectra: (a) host **4** and equal molar Cu^{2+} (1×10^{-5} M) under dark condition; (b) equal molar **4** and Cu^{2+} (1×10^{-5} M) after the irradiation of ultraviolet light for 120 s; (c) host **4** (1×10^{-5} M); (d) equal molar **4** and Cu^{2+} (1×10^{-5} M) after the irradiation of visible light for 300 s.

compound has 'push–pull' system, excitation could lead to a significant redistribution of electron density, so that a substantial dipole may be created. When Cu^{2+} binds tightly to the host compound, intracomplex quenching could take place via ICT.[13] Thus, ICT may prevent the ESIPT process and quench the luminescence coming from intraligand transitions. And the weaker fluorescence could be attributed to the free ligands ESIPT and the internal charge transfer quenching by Cu^{2+} ion. Upon the irradiation of ultraviolet light, the enol-form may tautomerize to the keto-form which would release the Cu^{2+}. In general, enol-form is photoreactive and not luminescent, keto-form displays a distinct green fluorescence.[9] Hence, the stronger fluorescence emission (Fig. 4, curve b) may be ascribed to the keto-form of the ligand. After the irradiation of visible light for several minutes, the keto-form could tautomerize to the enol-form which could coordinate to the Cu^{2+} ion, and the fluorescent intensity would be quenched (Fig. 4, curve d).

This system could be applied as a molecular logic switch.[1,14] The input signals would be **I1** (ultraviolet light, $\lambda = 365$ nm) and **I2** (visible light, $\lambda > 400$ nm). The output signal would be fluorescence emission at 512 nm (**O1**). Each signal could be either *off* or *on* and can be represented by binary digital (Fig. 5). Thus, signal communicating molecules may transduce a string of two input data (**I1** and **I2**) into an output signal (**O1**). For example, the input signals would be 00 when both of the input signals are *off* or when **I1** is off and **I2** is on, the input signals would be 01. Under these condi-

Input	Input	Output
UV light irradiation **I1**	Visible light irradiation **I2**	Emission at 512 nm **O1**
0	0	0
1	0	1
0	1	0
1	1	0

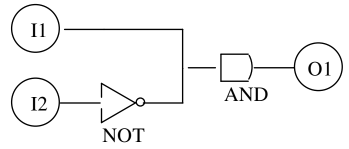
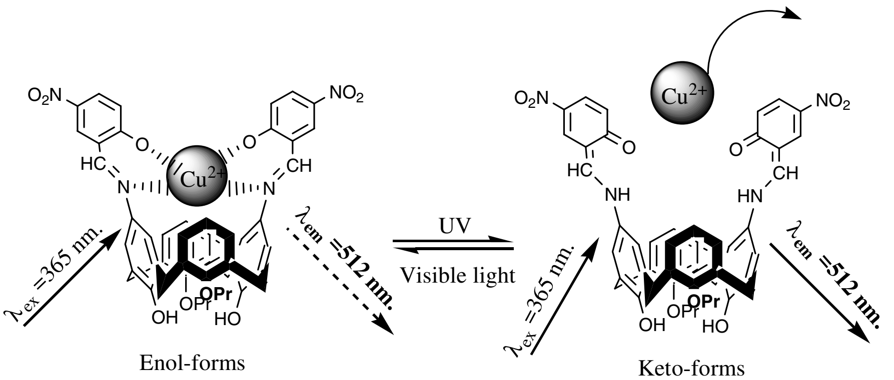


Figure 5. True table and INH logic circuit for the communicating molecular switches.



Scheme 2. The proposed mechanism of photoswitching fluorescence intensity.

tions (dark condition or visible light irradiation), the system is in a state of enol-form $\cdot$Cu^{2+}. As a result, the fluorescent intensity of host **4** is quenched, and the output signal (**O1**) would be *off*. When **I1** is *on* and **I2** is *off*, the input signals would be 10. Under these conditions (ultraviolet light irradiation), the system is in a state of keto-form $\cdot$Cu^{2+} and the output signal (**O1**) would be 1. This logic gate mimics the function of INHIBIT (INH) gate.

In summary, we have developed a novel fluorescent chemosensor with imine as ionophore based on calixarene framework, which can effectively recognize Cu^{2+}. More interestingly this chemosensor could be considered as a molecular logic switch. Off–on–off fluorescent switching is realized by the irradiation of ultraviolet and visible light. Based on these results, the corresponding true table and INH logic gate were suggested, and these results may be useful for further mimicing the function of more complex logic gates.

Acknowledgment

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

References and notes

1. *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH, Weinheim: Germany, 2001.
2. (a) de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. *Nature* **1993**, *364*, 42; (b) de Silva, A. P.; Dixon, I. M.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Maxwell, P. R. S.; Rice, T. E. *J. Am. Chem. Soc.* **1999**, *121*, 1393; (c) Liu, Z. L.; Jiang, L.; Liang, Z.; Gao, Y. H. *Tetrahedron Lett.* **2005**, *46*, 885; (d) Li, F.-y.; Shi, M.; Huang, C.-h.; Jin, L.-p. *J. Mater. Chem.* **2005**, *15*, 3015.
3. (a) Yakoyama, Y. *Chem. Rev.* **2000**, *100*, 1717; (b) Irie, M. *Chem. Rev.* **2000**, *100*, 1685.
4. (a) Cheng, Y. F.; Zhao, D. T.; Zhang, M.; Liu, Z. Q.; Zhou, Y. F.; Shu, T. M.; Li, F. Y.; Yi, T.; Huang, C. H. *Tetrahedron Lett.* **2006**, *47*, 6413; (b) Yang, H.; Liu, Z. Q.; Zhou, Z. G.; Shi, E. X.; Li, F. Y.; Du, Y. K.; Yi, T.; Huang, C. H. *Tetrahedron Lett.* **2006**, *47*, 2911; (c) Jun, E. J.; Kim, J. A.; Swamy, K. M. K.; Park, S.; Yoon, J. *Tetrahedron Lett.* **2006**, *47*, 1051.
5. Zeng, C. C.; Zheng, Q. Y.; Tang, Y. L.; Huang, Z. T. *Tetrahedron* **2003**, *59*, 2539.
6. Gustche, C. D.; Lin, L. G. *Tetrahedron* **1986**, *42*, 1633.
7. Mogck, O.; Böhemr, V.; Ferguson, G.; Vogt, W. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1711.
8. Compound **4**: mp >300 °C; ^{1}H NMR: δ ppm (CDCl$_3$) 1.33 (t, $J = 15$ Hz, 6H, *CH*$_3$–CH$_2$–CH$_2$–O–), 2.12 (q, $J = 15$ Hz, 4H, CH$_3$–*CH*$_2$–CH$_2$–O–), 4.04 (t, $J = 15$ Hz, 4H, CH$_3$–CH$_2$–*CH*$_2$–O–), 3.52 (2d, $J = 15$ Hz, 4H, Ar–*CH*$_2$–Ar), 4.32 (2d, $J = 15$ Hz, 4H, Ar–*CH*$_2$–Ar), 6.86 (t, $J = 15$ Hz, 2H, Ar–H), 7.03 (t, $J = 15$ Hz, 4H, Ar–H), 7.09 (s, 2H, Ar–H sal), 7.16 (s, 4H, Ar–H), 8.23 (2d, $J = 12$ Hz, 2H, Ar–H sal), 8.36 (d, $J = 12$ Hz, 2H, Ar–H sal), 8.67 (s, 2H, C=N), 8.75 (s, 2H, OH), 14.92 (br, 2H, OH sal); ^{13}C NMR: δ (CDCl$_3$) 169.7, 159.2 (C=N), 156.6, 154.5, 142.3, 140.0, 135.4, 131.8, 131.3, 130.4, 130.2, 128.1, 123.9, 120.8, 81.1, 34.0, 26.0, 13.4. IR (KBr) $\nu_{\max}$/cm^{-1}: 1623 (C=N), 1523, 1337 (NO$_2$). MALDI-TOF MS: *m*/*z* 837 ([M$^+$]+H); Anal. Calcd for $C_{48}H_{44}N_4O_{10}$: C, 68.90; H, 5.26; N, 6.69. Found: C, 68.93; H, 5.32; N, 6.63.
9. (a) Alarcon, S. H.; Pagani, D.; Bacigalupo, J.; Olivieri, A. C. *J. Mol. Struct.* **1999**, *475*, 233; (b) Vargas, V. C. *J. Phys. Chem. A.* **2004**, *108*, 281; (c) Joshi, H.; Kamounah, F. S.; Gooijer, C.; Zwan, G.; Antonov, L. *J. Photochem. Photobiol. A: Chem.* **2002**, *152*, 183; (d) Ohshima, A.; Momotake, A.; Arai, T. *J. Photochem. Photobiol. A: Chem* **2004**, *162*, 473; (e) Kunlely, H.; Vogler, A. *J. Photochem. Photobiol. A: Chem.* **2002**, *138*, 51.
10. Cao, Y. D.; Zheng, Q. Y.; Chen, C. F.; Huang, Z. T. *Tetrahedron Lett.* **2003**, *44*, 4751.
11. Ci, Y. X.; Zhou, T. Z. *The Coordinated Complexes in Analytical Chemistry*; Peking University Press: Beijing, 1984.
12. (a) Davies, D. E. J.; Ripmeester, J. A. In *Comprehensive Supramolecular Chemistry*; Pergamon: New York, 1996; Vol. 8, p 442; (b) Valeur, B.; Pouget, J.; Bourson, J.; Kaschke, M.; Ernsting, N. P. *J. Phys. Chem.* **1992**, 6545.
13. (a) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3; (b) Callan, J. F.; de Silva, A. P.; Magri, D. C. *Tetrahedron* **2005**, *61*, 8551; (c) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T. A.; Huxley, T. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515; (d) Fabbrizzi, L.; Licchelli, M.; Pallavicini, P.; Perrotti, P.; Tagletti, A.; Sacchi, D. *Chem. Eur. J.* **1996**, *2*, 75.
14. (a) Raymo, F. M.; Giordani, S. *J. Am. Chem. Soc.* **2001**, *123*, 4651; (b) Raymo, F. M.; Giordani, S. . *Org. Lett.* **2001**, *3*, 1833; (c) Raymo, F. M.; Giordani, S. *Org. Lett.* **2001**, *3*, 3475; (d) Raymo, F. M.; Alvarado, R. J.; Giordani, S.; Cejas, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 2361; (e) Giordani, S.; Raymo, F. M. *Org. Lett.* **2003**, *5*, 3559; (f) Guo, X.-F.; Zhang, D.-Q.; Zhou, Y.-C.; Zhu, D.-B. *Chem. Phys. Lett.* **2003**, *375*, 484; (g) Guo, X.-F.; Zhang, D.-Q.; Zhou, Y.-C.; Zhu, D.-B. *J. Org. Chem.* **2003**, *68*, 5681; (h) Grofcsik, A.; Baranyai, P.; Bitter, I.; Grün, A.; Köszegi, E.; Kubinyi, M.; Pál, K.; Vidóczy, T. *J. Mol. Struct.* **2002**, *614*, 69.