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Dual-signaling fluorescent chemosensor based on bisthiazole derivatives

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ABSTRACT

A new bisthiazole chemosensor (**3**) with phenolic substituents at the position 2 of the thiazole rings was prepared. The chemosensor **3** acts as a potential dual-function fluorescence chemosensor with Cu^{2+} and Zn^{2+} ions causing complete quenching and ratiometric change of fluorescence, respectively. The mechanism of fluorescence was based on the cation-induced inhibition of excited-state intramolecular proton transfer (ESIPT).

Fluorescent chemosensors provide a powerful optical method for spying on molecular recognition events. As a result, they have found practical application in cellular imaging, environmental monitoring, and biological assays.[1] Chemosensors that allow the measurement of two different emission bands have the important feature of permitting signal rationing, which can increase the dynamic range and provide built-in correction for environmental effects.[2] Copper plays an important role in various biological processes. It is a vital trace element, the third most abundant in humans, and is present at low levels in a variety of cells and tissues, with its highest concentration in the liver. The average concentration of blood copper in the normal group is 100–150 μg/dL (15.7–23.6 μM).[3] Its high concentration in the neuronal cytoplasm may contribute to the etiology of Alzheimer's or Parkinson's disease.[4,5] Due to industrial applications as a pollutant and an essential trace element in biological systems, much attention has been drawn to the chemosensors for copper(II) based on the chromogenic and fluorogenic probes which are expected to detect copper ions quickly, nondestructively, and sensitively.[6] Zinc(II) is the second most abundant transition metal cation in the biological system.[7] Approximately 300 enzymes contain zinc(II) as an essential component, either for a structural purpose or as a part of a catalytic site. For example, zinc is essential for the regulation of DNA synthesis during the proliferation and differentiation of cells.[8] Zinc is also known to have a role in neurological disorders, such as Parkinson's disease, Alzheimer's disease, amyotrophic lateral sclerosis, and epileptic seizures.[9] Therefore, the design and development of a fluorescent chemosensor selective to zinc is of considerable interest.[10]

Excited-state intramolecular proton transfer (ESIPT) is one of the most common photophysical processes that occur in benzazoles and used to develop ratiometric probes. Inhibition of the ESIPT process by cation binding yields a significant hypsochromic shift of the fluorescence emission maximum.[11,12] In chemosensors a selective binding motif is attached to a fluorophore for signal transduction. However intrinsic fluorescent probes whose fluorescent unit is directly involved in the interaction with metal ions help in quick, sensitive, and selective detection.[13]

It is known that chelating groups such as C=N and C=O exhibit a high affinity to transition and post-transition metal cations but a less binding affinity toward alkali metal and alkaline earth metal cations.[14] Recently we have reported thiazole-based chemosensors **1** and **2** for use as anions and ratiometric fluorescence sensing of zinc[15,16] as illustrated in Figure 1. In both compounds the thiazole ring is substituted by a phenol at the position 2 and phenyl (**1**) or pyridine (**2**) at the position 4. Both exhibit the same mechanism for fluorescence based on the anion or cation-induced inhibition of the ESIPT. Thus a heteroaromatic ring system such as a bisthiazole with phenolic groups at the position 2 can act as a –ONNO– donor receptor with functionality highly selective to transitional metal cations.[17]

Crown ethers that contain thiazole moieties have been reported to exhibit high ammonium,[18] silver,[19] and mercury ion selectivity.[20] Introduction of soft heteroatoms such as N and S, as an electron donor to metal cations can improve the binding selectivity and along with a hydrogen-bonding donar (O–H) can produce some photophysical properties. Our choice of bisthiazole with

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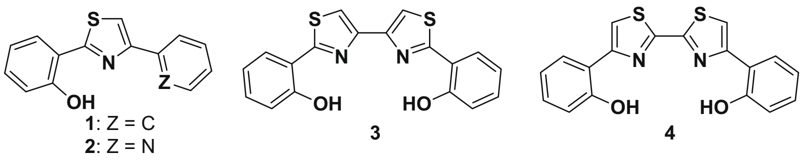


Figure 1. Structures of chemosensors.

the phenolic group at the position 2 is based on the fact that it would not only produce a thiazole-based heterocyclic podand but the phenol and the thiazole rings together can act as a binding as well as a fluorophore resulting in an intrinsic chemosensor.

Although a number of chemosensors for different transition metal ions have been described, dual-function chemosensors[21] which can be used to detect two analytes remain rare. In this paper, we describe the design and the development of a novel bisthiazole-based dual-function fluorescent chemosensor in aq DMSO (1/9, v/v), buffered at pH 7.4, with phenolic substituents at the position 2 of the thiazole rings for copper and zinc ions detection based on ESIPT. It exhibits a complete quenching on the addition of a copper ion and a ratiometric fluorescent response upon addition of a zinc ion. Due to the low solubility of sensors **3** and **4** in water or any other organic solvents we used 100% DMSO and 10% water in DMSO system.

In order to understand the crucial role of phenol at the position 2 of the thiazole rings we prepared 4,4'-bisthiazole (**3**) and its isomeric form 2,2'-bisthiazole (**4**). The chemosensor **3** was obtained in a good yield by Hantzsch condensation reaction of 2-hydroxythiobenzamide with 1,4-dibromo-2,3-butanedione in refluxing ethanol and the chemosensor **4** was synthesized in a good yield by a reaction between dithioxamide and 2-bromo-2'-methoxyacetophenone in ethanol followed by deprotection of the methoxy group with boron tribromide as shown in Scheme 1. The structures of **3** and **4** were confirmed by ^{1}H NMR, ^{13}C NMR and elemental analysis (SI).

The initial UV–vis study of **3** was carried out in DMSO (Figs. S-1 and S-2), and the sensing property of **3** confirmed in a more physiologically acceptable condition of 10% water in DMSO (1:9, v/v) buffered by 10 mM HEPES at pH 7.4. Chemosensor **3** displayed an obvious absorption band at 325 nm (log ε = 4.1). This can be attributed to a π–π^* transition; this is favored by the planar orientation enforced by the intramolecular hydrogen-bonding.[15,22] New absorption bands at 380 nm (log ε = 3.0) and 373 nm (log ε = 2.7) for Cu^{2+} and Zn^{2+}, respectively, increase gradually in intensity

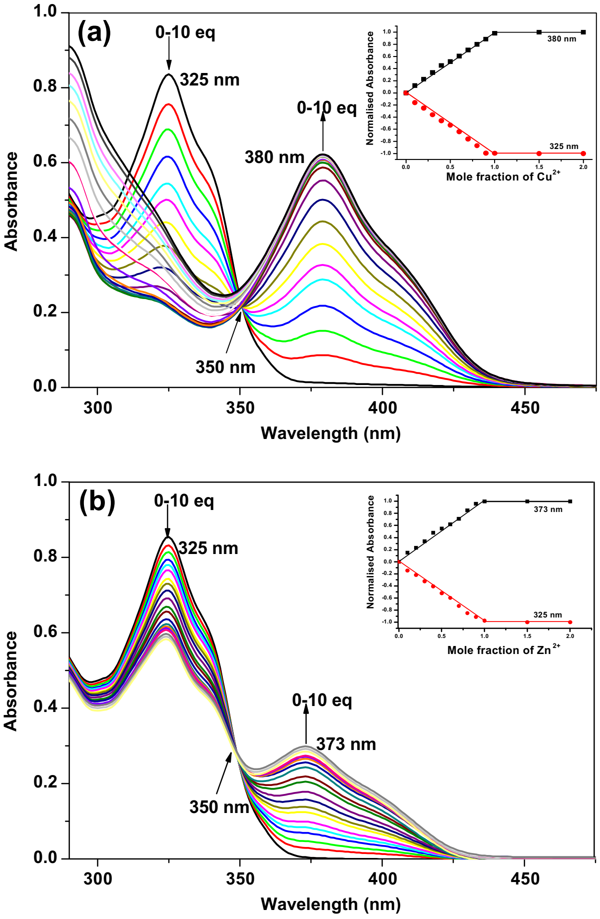
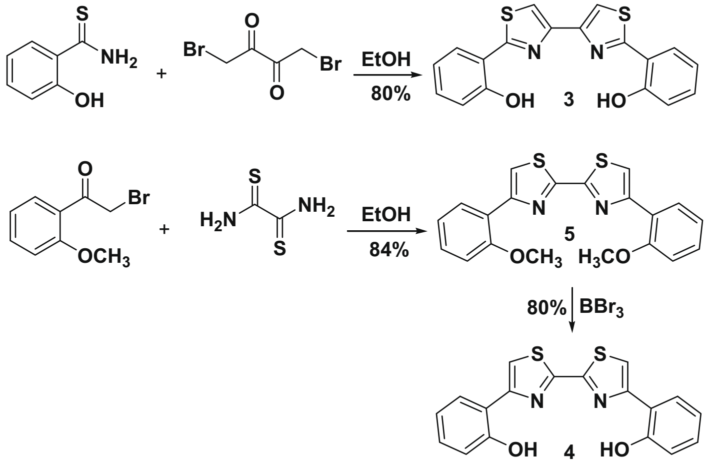


Figure 2. Changes in UV–vis spectra of **3** (30 μM) upon addition of (a) $Cu(ClO_4)_2$ and (b) $Zn(ClO_4)_2$ in aq DMSO (1/9, v/v) containing HEPES buffer (10 mM, pH 7.4). Inset: mol ratio plots of absorbance at (a) 325 and 380 nm, (b) 325 and 373 nm.



Scheme 1. Synthesis of chemosensors **3** and **4**.

Table 1
Photophysical properties of **3** and **4** in aq DMSO (1/9, v/v)

Sensor	Absorption max. nm (log ε)	Emission Max (nm)	Quantum yield[a] (Φ)
3	325 (4.1)	382, 509	0.07
3 + Cu^{2+}	380 (3.0)	0	0
3 + Zn^{2+}	373 (2.7)	462	0.10
4	365 (3.8)	435	0.03
4 + Cu^{2+}	354 (3.9)	435	0.08
4 + Zn^{2+}	365 (3.8)	435	0.03

[a] Quantum yields were obtained using quinine sulfate in 0.5 M H_2SO_4 as a standard.

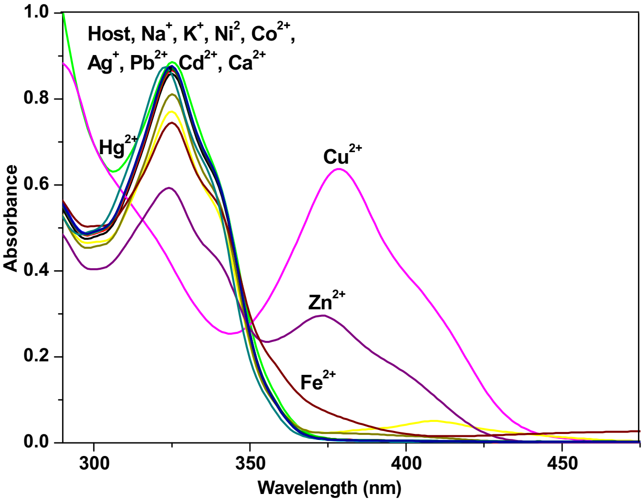


Figure 3. UV–vis spectra of **3** (30 μM) with various cations (10 equiv) in aq DMSO (1/9, v/v) containing HEPES buffer (10 mM, pH 7.4).

while one at 325 nm decreases synchronously with an isosbestic point at 350 nm as shown in Figure 2a and b (also see Table 1). The ratios of increase and decrease in absorption at 325 nm and 380 nm (or 373 nm) are linear up to 1 equiv of metal ion as demonstrated by Figure 2a and b (insets). These observations confirm the formation of an 1:1 complex in both cases.

The absorption spectrum of **3** was also measured in the presence of transition metal ions and other ions such as Fe^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Ag^{+}, Na^{+} and K^{+}. Large red shifts in absorption spectra were observed after addition of Cu^{2+} and Zn^{2+} ions (Fig. 3) with the development of a very faint yellow color with Cu^{2+}.

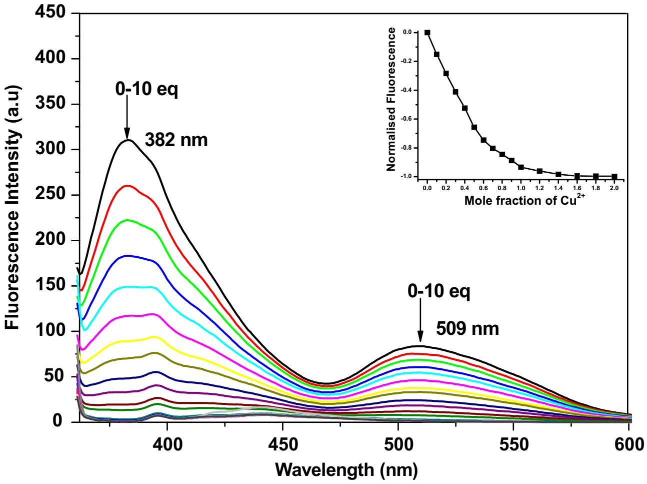


Figure 4. Changes in fluorescence spectra of **3** (30 μM) upon addition of $Cu(ClO_4)_2$ in aq DMSO (1/9, v/v) containing HEPES buffer (10 mM, pH 7.4) (λ_{ex} = 350 nm). Inset: mol ratio plot of emission at 382 nm.

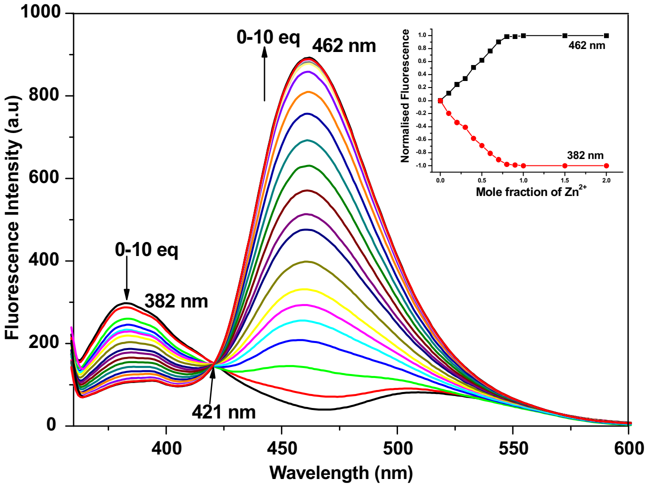
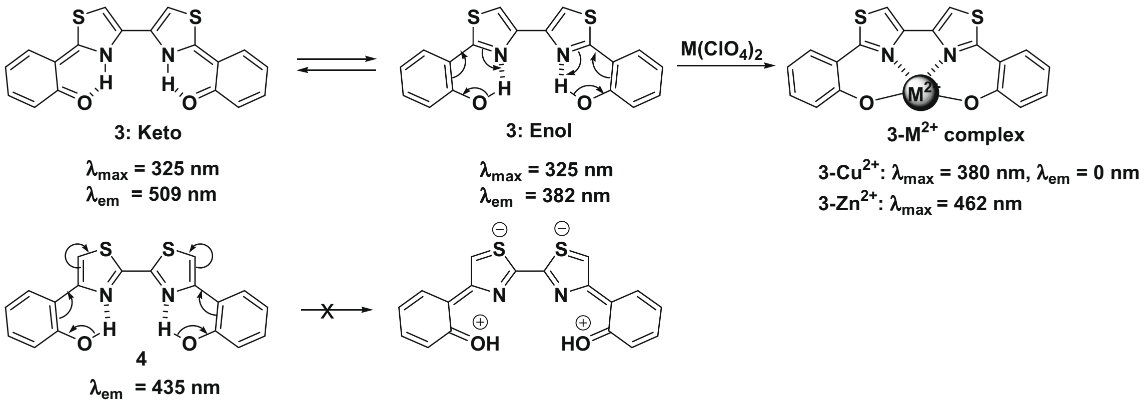


Figure 5. Changes in fluorescence spectra of **3** (30 μM) upon addition of $Zn(ClO_4)_2$ in aq DMSO (1/9, v/v) containing HEPES buffer (10 mM, pH 7.4) (λ_{ex} = 350 nm). Inset: mol ratio plots of emission at 382 nm and 462 nm (λ_{ex} = 350 nm).

Like other benzothiazole derivatives,[11,12] **3** contains an intramolecular hydrogen bond between the phenolic O–H and the nitrogen of the thiazole ring that undergoes ESIPT and yields a normal emis-



Scheme 2. Inhibition of ESIPT of **3** on coordination with metal ion and absence of ESIPT in **4**.

sion at 382 nm and a tautomer emission at 509 nm from the proton transfer tautomer (Scheme 2).[23–25] Coordination **3** to the paramagnetic Cu^{2+} disrupts the ESIPT and completely quenches the fluorescence emission (Fig. 4). The quenching as a result of the addition of Cu^{2+} suggests that an excitation energy or charge transfer may have occurred from **3** to the open-shell *d*-orbitals of Cu^{2+} exhibiting a very fast and efficient nonradiative decay of the excited states of the sensor **3**.[6e,26] Fluorescence titration of **3** with Cu^{2+} was carried out in aq DMSO (1:9, v/v) buffered by 10 mM HEPES at pH 7.4 at a concentration level of 30 μM. Addition of Cu^{2+} to the solution of **3** caused a complete quenching of fluorescent emissions when excited at 350 nm (Fig. 4). The binding mode of **3** with Cu^{2+} was demonstrated to be 1:1 with a binding constant $5.3 \times 10^4\ M^{-1}$ (error limit ⩽ 10%), as evidenced by the fluorescence titration spectra (Fig. 4, inset) and Job's plot (Fig. S-3)

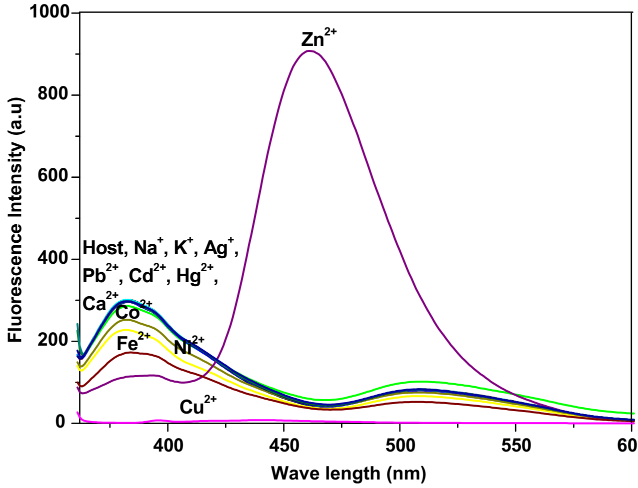


Figure 6. Fluorescence spectra of **3** (30 μM) with various cations (10 equiv) in aq DMSO (1:9, v/v) containing HEPES buffer (10 mM, pH 7.4) (λ_{ex} = 350 nm).

Similarly, Zn^{2+} has closed-shell *d*-orbitals so that energy or charge transfer processes cannot take place. Thus, coordination of Zn^{2+} removes the phenolic proton and disrupts the ESIPT causing emission with a normal Stokes' shift (Scheme 2).[11,12] Fluorescence titration of **3** with Zn^{2+} was carried out in aq DMSO (1:9, v/v) buffered by 10 mM HEPES at pH 7.4 at a concentration level of 30 μM. Addition of Zn^{2+} to the solution of **3** caused development of a new peak at 462 nm, while the peak at 382 nm gradually diminished with an isoemission point at 421 nm (Fig. 5). The fluorescence titration spectra (Fig. 5, inset) and the Job's plot of **3** with Zn^{2+} indicated the formation of an 1:1 complex (Fig. S-4). From fluorescence titration the binding constant of **3** with Zn^{2+} was calculated to be $1.8 \times 10^4\ M^{-1}$ (error limit ⩽ 10%).

The fluorescence selectivity and tolerance of **3** for Cu^{2+} and Zn^{2+} over other metal cations were investigated by adding 10 equiv of different metal cations to the 30 μM solutions of **3**. In the case of Cu^{2+}, the molecular fluorescence was completely quenched to a minimum level. No other metal ions produced such a complete quenching though some paramagnetic ions such as Fe^{2+}, Co^{2+} and Ni^{2+} produced little to partial quenching. The binding constants of Fe^{2+}, Co^{2+} and Ni^{2+} are 7.5×10^2, 1.1×10^2 and $1.3 \times 10^2\ M^{-1}$, respectively, as obtained from fluorescence titration curves in Figures S-5, S-6, and S-7. In the case of Zn^{2+}, there occurred a ratiometric change, and a new peak arose at 462 nm. Such a ratiometric change was absent in other metal ions (Fig. 6).

In addition, as illustrated in Figure S-8, no metal ions show any interference to the sensing of Cu^{2+} by **3**, while the ratiometric sens-

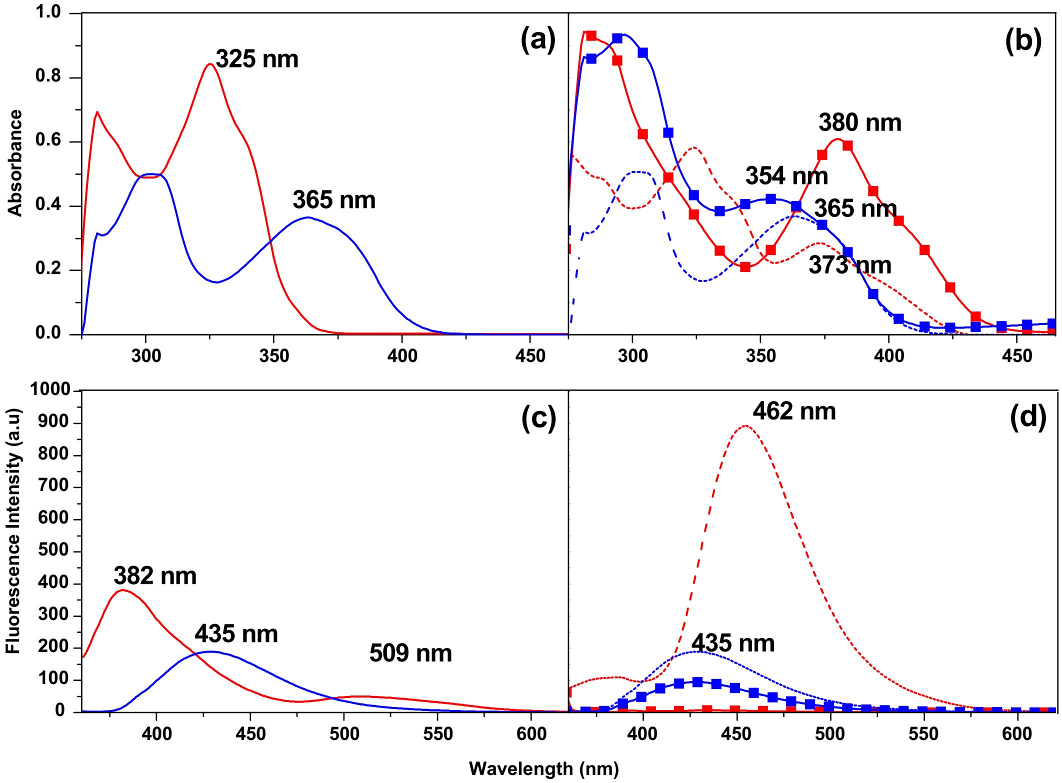


Figure 7. UV–vis spectra of **3**(—) and **4**(—) (a) itself, (b) in presence of 10 equiv of $Cu(ClO_4)_2$ (–■–) and $Zn(ClO_4)_2$ (– –) in aq DMSO (1/9, v/v) containing HEPES buffer (10 mM, pH 7.4). Fluorescence spectra of **3**(—) and **4**(—) (c) itself, (d) in presence of 10 equiv of $Cu(ClO_4)_2$ (–■–) and $Zn(ClO_4)_2$ (– –) in aq DMSO (1/9, v/v) containing HEPES buffer (10 mM, pH 7.4) (λ_{ex} = 350 nm).

ing of Zn^{2+} is not interfered by other cations except Cu^{2+} (Fig. S-9). The quantum yield (Φ) calculated for **3** was 0.07 while that of **3**-Zn^{2+} complex was 0.1. We found that the detection limit of **3** for Cu^{2+} and Zn^{2+} were 40 and 60 μM, respectively. The photophysical properties of sensors **3** and **4** are summarized in Table 1.

Due to magnetic-silent nature,[27] originating from the d^{10} electronic configuration of Zn^{2+} and paramagnetic property of Cu^{2+}, the NMR study for complexation with **3** was not possible. In order to study the binding mode we prepared the complex of **3** with Cu^{2+} and Zn^{2+} in DMSO and characterized by HR-FAB Mass (Figs. S-10 and S-11). The HR mass spectra of both **3**-Cu^{2+} and **3**-Zn^{2+} show an 1:1 stoichiometry with the molecular ion peaks at m/z 413.9554 and 415.0321, respectively.

To understand the crucial role of the position of phenol on the thiazole ring in **3** we also prepared **4**. As shown in Figure 7a and b, unlike **3**, in the case of **4** there is a little blue shift of 11 nm in absorbance on the addition of Cu^{2+} while there are no absorption spectral changes upon addition of Zn^{2+}. In the case of fluorescence spectrum there is an emission peak at 435 nm (Fig. 7c) due to intramolecular charge transfer (ICT) between the phenol and thiazole moiety (Table 1).[28] But ESIPT is not possible due to the absence of conjugation between the nitrogen of the thiazole and O–H of the phenolic ring as shown in Scheme 2. Thus the binding of **4** with Cu^{2+} is very weak ($K_a = 4.2 \times 10^2$ M^{-1}, Fig. S-12) which results in partial quenching of the emission peak of **4** (Fig. 7d). But there is no ratiometric change (Fig. 7d) on addition of Zn^{2+} as ESIPT is absent in **4**.

In conclusion, we have prepared bisthiazole-based dual-function fluorescence chemosensors for Cu^{2+} and Zn^{2+} ions based on ESIPT. The binding of paramagnetic open-shell d-orbital of Cu^{2+} produces a complete quenching of fluorescence due to the inhibition of ESIPT and charge or energy transfers between the Cu^{2+} and **3**. While the closed-shell d-orbital of Zn^{2+} causes inhibition of the ESIPT producing a ratiometric change in emission. We also studied that the dual-function behavior is destroyed in the isomeric form **4** due to absence of the ESIPT.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.04.126.

References and notes

1. (a) de Silva, A. P.; Fox, D. B.; Huxley, A. J. M.; Moody, T. S. *Coord. Chem. Rev.* **2000**, *205*, 41; (b) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. *Coord. Chem. Rev.* **2000**, *205*, 59; (c) Amendola, V.; Fabbrizzi, L.; Licchelli, M.; Mangano, C.; Pallavicini, P.; Parodi, L.; Poggi, A. *Coord. Chem. Rev.* **2000**, *192*, 649; (d) de Silva, A. P.; Fox, D. B.; Huxley, A. J. M.; McClenaghan, N. D.; Roiron, J. *Coord. Chem. Rev.* **1999**, *186*, 297.
2. (a) Kawanishi, Y.; Kikuchi, K.; Takakusa, H.; Mizukami, S.; Urano, Y.; Higuchi, T.; Nagano, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 3438; (b) Deo, S.; Godwin, H. A. *J. Am. Chem. Soc.* **2000**, *122*, 174; (c) de Silva, A. P.; Eilers, J.; Zlokarnik, G. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 8336.
3. Tak, W. T.; Yoon, S. C. *KSN* **2001**, *20*, 863.
4. (a) Barceloux, D. G. *J. Toxicol. Clin. Toxicol.* **1999**, *37*, 217; (b) Mathie, A.; Sutton, G. L.; Clarke, C. E.; Veale, E. L. *Pharmacol. Ther.* **2006**, *111*, 567; (c) Kim, B.-E.; Nevitt, T.; Thiele, D. J. *Nat. Chem. Biol.* **2008**, *4*, 176.
5. (a) Mare, S.; Penugonda, S.; Robinson, S. M.; Dohgu, S.; Banks, W. A.; Ercal, N. *Peptides* **2007**, *28*, 1424; (b) Deraeve, C.; Boldron, C.; Maraval, A.; Mazarguil, H.; Gornitzka, H.; Vendier, L.; Pitie, M.; Meunier, B. *Chem. Eur. J.* **2008**, *14*, 682; (c) Lee, J. C.; Gray, H. B.; Winkler, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 6898.
6. (a) Kim, H. J.; Hong, J.; Hong, A.; Ham, S.; Lee, J. H.; Kim, J. S. *Org. Lett.* **2008**, *10*, 1963; (b) Zheng, Y.; Cao, X.; Orbulescu, J.; Konka, V.; Andreopoulos, F. M.; Pham, S. M.; Leblanc, R. M. *Anal. Chem.* **2003**, *75*, 1706; (c) Gunnlaugsson, T.; Leonard, J. P.; Murray, N. S. *Org. Lett.* **2004**, *6*, 1557; (d) Kumar, S.; Kaur, N. *Supramol. Chem.* **2006**, *18*, 137; (e) Jung, H. S.; Kwon, P. S.; Lee, J. W.; Kim, J.; Hong, C. S.; Kim, J. W.; Yan, S.; Lee, J. Y.; Lee, J. H.; Joo, T.; Kim, J. S. *J. Am. Chem. Soc.* **2009**, *131*, 2008; (f) Dhir, A.; Bhalla, V.; Kumar, M. *Tetrahedron Lett.* **2008**, *49*, 4227; (g) Kim, H. J.; Park, S. Y.; Yoon, S.; Kim, J. S. *Tetrahedron* **2008**, *64*, 1294; (h) Kim, H. J.; Bok, J. H.; Vicens, J.; Suh, I.-H.; Ko, J.; Kim, J. S. *Tetrahedron Lett.* **2005**, *46*, 8765; (i) Sheng, R.; Wang, P.; Gao, Y.; Wu, Y.; Liu, W.; Ma, J.; Li, H.; Wu, S. *Org. Lett.* **2008**, *10*, 5015.
7. de Silva, J. J. R. F.; Williams, R. J. P. *Zinc: Lewis acid catalysis and regulation. In The Biological Chemistry of Elements: The Inorganic Chemistry of Life*, 2nd ed.; Oxford UP: New York, 2001.
8. Beyersmann, D.; Haase, H. *Biometals* **2001**, *14*, 331.
9. (a) Cuajungco, M. P.; Lees, G. J. *Brain Res.* **1997**, *23*, 219; (b) Takeda, A. *Biometals* **2001**, *14*, 343.
10. (a) Mikata, Y.; Yamanaka, A.; Yamashita, A.; Yano, S. *Inorg. Chem.* **2008**, *47*, 7295; (b) Hirano, T.; Kikuchi, K.; Urano, Y.; Nagano, T. *J. Am. Chem. Soc.* **2002**, *124*, 6555; (c) Gee, K. R.; Zhou, Z. L.; Qian, W. J.; Kennedy, R. *J. Am. Chem. Soc.* **2002**, *124*, 776; (d) Lim, N. C.; Bruckner, C. *Chem. Commun.* **2004**, 1094; (e) Komatsu, K.; Urano, Y.; Kojima, H.; Nagano, T. *J. Am. Chem. Soc.* **2007**, *129*, 13447; (f) Hanaoka, K.; Kikuchi, K.; Kojima, H.; Urano, Y.; Nagano, T. *J. Am. Chem. Soc.* **2004**, *126*, 12470; (g) Taki, M.; Watanabe, Y.; Yukio, Y. *Tetrahedron Lett.* **2009**, *50*, 1345; (h) Van Dongen, E.; Dekkers, L. M.; Spijker, K.; Meijer, E. W.; Klomp, L. W. J.; Merk, M. *J. Am. Chem. Soc.* **2006**, *128*, 10754; (i) Bozym, R. A.; Thompson, R. B.; Stoddard, A. K.; Fierke, C. A. *ACS Chem. Biol.* **2006**, *1*, 103; (j) Evers, T. H.; Appelhof, M. A. M.; de Graaf-Heuvelmans, P.; Meijer, E. W.; Merk, M. *J. Mol. Biol.* **2007**, *374*, 411; (k) Evers, T. H.; Appelhof, M. A. M.; Meijer, E. W.; Merk, M. *Protein Eng. Des. Sel.* **2008**, *21*, 529.
11. Henary, M. M.; Fahrni, C. J. *J. Phys. Chem. A* **2002**, *106*, 5210.
12. (a) Taki, M.; Wolford, J. L.; O'Halloran, T. V. *J. Am. Chem. Soc.* **2004**, *126*, 712; (b) Henary, M. M.; Wu, Y. G.; Fahrni, C. J. *Chem. Eur. J.* **2004**, *10*, 3015.
13. (a) Zheng, Y.; Gattás-Asfura, K. M.; Konka, V.; Leblanc, R. M. *Chem. Commun.* **2002**, 2350; (b) Yao, J.; Dou, W.; Qin, W.; Liu, W. *Inorg. Chem. Commun.* **2009**, *12*, 116; (c) Sheng, R.; Wang, P.; Liu, W.; Wu, X.; Wu, S. *Sens. Actuator, B* **2008**, *128*, 507.
14. Yoon, S.; Albers, A. E.; Wong, A. P.; Chang, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 16030.
15. Helal, A.; Thao, N. T. T.; Lee, S.; Kim, H.-S. *J. Inclusion Phenom. Macrocycl. Chem.* **2010**, *66*, 87.
16. Helal, A.; Kim, H.-S. *Tetrahedron Lett.* **2009**, *50*, 5510.
17. (a) Krämer, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 772; (b) Xiang, Y.; Tong, A.; Jin, P.; Ju, Y. *Org. Lett.* **2006**, *8*, 2863; (c) Chen, X.; Li, Z.; Xiang, Y.; Tong, A. *Tetrahedron Lett.* **2008**, *49*, 4697.
18. (a) Kim, H.-S.; Koh, Y. K.; Choi, J. H. *J. Heterocycl. Chem.* **1998**, *35*, 177; (b) Kim, H.-S.; Park, H. J.; Oh, H. J.; Koh, Y. K.; Choi, J. H.; Lee, D. H.; Cha, G. S.; Nam, H. *Anal. Chem.* **2000**, *72*, 4683; (c) Kariuki, B. M.; Lee, S.-O.; Harris, K. D. M.; Kim, H.-S.; Do, K.-S.; Kim, K.-I. *Cryst. Growth. Des.* **2002**, *2*, 309; (d) Kim, H.-S.; Do, K. S.; Kim, K. S.; Shim, J. H.; Cha, G. S.; Nam, H. *Bull. Korean Chem. Soc.* **2004**, *25*, 1465.
19. Kwon, O. S.; Kim, H.-S. *Supramol. Chem.* **2007**, *19*, 277.
20. Lee, S. H.; Helal, A.; Kim, H.-S. *Bull. Korean Chem. Soc.* **2010**, *31*, 615.
21. (a) Collado, D.; Perez-Inestrosa, E.; Suau, R.; Desvergne, J.-P.; Bouas-Laurent, H. *Org. Lett.* **2002**, *4*, 855; (b) Mello, J. V.; Finney, N. S. *Angew. Chem., Int. Ed.* **2001**, *40*, 1536; (c) El-Safty, S. A.; Ismail, A. A.; Matsunaga, H.; Hanaoka, T.; Mizukami, F. *Adv. Funct. Mater.* **2008**, *18*, 1485.
22. Keck, J.; Kramer, H. E. A.; Port, H.; Hirsch, T.; Fischer, P.; Rytz, G. *J. Phys. Chem.* **1996**, *100*, 14468.
23. (a) Tsai, H.-H. G.; Sun, H.-L. S.; Tan, C.-J. *J. Phys. Chem. A.* **2010**, *114*, 4065; (b) Das, K.; Sarkar, N.; Majumdar, D.; Bhattacharyya, K. *Chem. Phys. Lett.* **1992**, *198*, 443.
24. Mosquera, M.; Penedo, J. C.; Rios Rodriguez, M. C.; Rodriguez-Prieto, F. *J. Phys. Chem.* **1996**, *100*, 5398.
25. (a) Han, D. Y.; Kim, J. M.; Kim, J.; Jung, H. S.; Lee, Y. H.; Zhang, J. F.; Kim, J. S. *Tetrahedron Lett.* **2010**, *51*, 1947; (b) Santra, S.; Krishnamoorthy, G.; Dogra, S. K. *J. Phys. Chem. A.* **2000**, *104*, 476.
26. (a) Ressalan, S.; Iyer, C. S. P. *J. Lumin.* **2005**, *111*, 121; (b) Choi, M.-Y.; Chan, M. C.-W.; Zhang, S.; Cheung, K.-K.; Che, C.-M.; Wong, K.-Y. *Organometallics* **1999**, *18*, 2074; (c) Villata, L. S.; Wolcan, E.; Feliz, M. R.; Capparelli, A. L. *J. Phys. Chem. A* **1999**, *103*, 5661.
27. (a) Xue, L.; Wang, H. –H.; Wang, X. –J.; Jiang, H. *Inorg. Chem.* **2008**, *47*, 4310; (b) Lim, N. C.; Freake, H. C.; Bruckner, C. *Chem. Eur. J.* **2005**, *11*, 38.
28. (a) Wong, W.-Y.; Choi, K.-H.; Lu, G.-L. *Organometallics* **2002**, *21*, 4475; (b) Politis, J. K.; Curtis, M. D.; Gonzalez, L.; Martin, D. C.; He, Y.; Kanicki, J. *Chem. Mater.* **1998**, *10*, 1713; (c) Park, J.-W.; Lee, J.-H.; Ko, S.; Kim, T.-W.; Uemura, T.; Chujo, Y. *Synth. Met.* **2001**, *121*, 1689.