http://dx.doi.org/10.5012/bkcs.2013.34.7.1985

Salicylimine-Based Colorimetric and Fluorescent Chemosensor for Selective Detection of Cyanide in Aqueous Buffer

Jin Young Noh, In Hong Hwang,* Hyun Kim, Eun Joo Song, Kyung Beom Kim, and Cheal Kim*

Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul 139-743, Korea
**E-mail: hwang817@naver.com (I. H. Hwang); chealkim@seoultech.ac.kr (C. Kim)*
Received March 20, 2013, Accepted April 2, 2013

A simple colorimetric and fluorescent anion sensor **1** based on salicylimine showed a high selectivity and sensitivity for detection of cyanide in aqueous solution. The receptor **1** showed high selectivity toward CN^- ions in a 1:1 stoichiometric manner, which induces a fast color change from colorless to orange and a dramatic enhancement in fluorescence intensity selectively for cyanide anions over other anions. Such selectivity resulted from the nucleophilic addition of CN^- to the carbon atom of an electron-deficient imine group. The sensitivity of the fluorescence-based assay (0.06 μM) is below the 1.9 μM suggested by the World Health Organization (WHO) as the maximum allowable cyanide concentration in drinking water, capable of being a practical system for the monitoring of CN^- concentrations in aqueous samples.

Key Words : Cyanide sensing, Colorimetric, Fluorescent, Chemosensor, Schiff base

Introduction

Anion recognition is an area of growing interest in supramolecular chemistry due to its crucial role in a wide range of environmental, chemical and biological applications.[1] Among the various anions, cyanide is one of the most concerned. It is known as one of the most rapidly acting and powerful poisons, and the toxicity results from its propensity to bind to the iron in cytochrome *c* oxidase, interfering with electron transport and resulting in hypoxia.[2] Also, even very small amounts of the cyanide lead to diseases of the vascular, cardiac, visual, endocrine, central nervous and metabolic systems.[3] Despite its extreme toxicity, cyanide is used in many industries such as gold mining, electroplating, metallurgy, polymer production such as nitriles, nylon, and acrylic plastics which produce nearly 140,000 tons of cyanide per year worldwide.[4] It is therefore evident that reliable and efficient ways of detecting the presence of cyanide are needed.

In recent years, many efforts have been devoted to design various chemosensors specific for cyanide detection.[5] The most attractive approach focuses on the research of novel colorimetric cyanide anion sensors, which allow naked eyes detection of the color change without resorting to the use of expensive instruments.[6] Moreover, a fluorescent method is especially attractive mainly because of its high sensitivity, easy operation, rapid response rate, and relative low cost.[7] Thus, a dual colorimetric-fluorescent probe for detection of cyanide is particular attractive.

Many of the cyanide anion receptors reported to date have relied on hydrogen-bonding motifs and, as a consequence, have several limitations such as poor selectivity over F^- or OAc^-.[8] To overcome this limitation, reaction-based receptors, rationally designed cyanide anion indicators, have been developed recently.[9] This reaction based recognition takes advantage of strong nucleophilicity and weak hydrogen-bonding ability of cyanide ion in aqueous media. Reported reaction-based indicators of CN^- include probes based on oxazines,[10] cationic boranes,[11] acridinium salts,[12] benzyl-based systems,[13] β-turn motifs,[14] α,β-unsaturated systems,[15] coumarins,[16] hydrazones,[17] aldehydes, and ketones.[18] However, most of these probes suffer from limitations such as utilization of expensive instruments, complicated synthesis, requirements of high temperature, and lack of visible changes in color. Most importantly, many of these are reported to work only in organic media. Therefore, it is absolutely necessary to develop new reaction-based probes for detecting CN^- in aqueous solution.

With these considerations in mind, we report a simple salicylimine-based colorimetric and fluorescent cyanide selective chemosensor **1**, which can work effectively in aqueous media. Receptor **1** can detect cyanide ion *via* naked-eye discernible color change and exhibits an unique 'turn-on' fluorescence with high selectivity and sensitivity in a water/THF solution.

Experimental Section

General Information. All the solvents and reagents (analytical grade and spectroscopic grade) were obtained from Sigma-Aldrich and used as received. *o*-Phenolsalicylimine (**1**) was synthesized as previously reported.[19] ^{1}H NMR measurements was performed on a Varian 400 MHz spectrometer and chemical shifts are recorded in ppm. Electrospray ionization mass spectra (ESI-MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument. Absorption spectra were recorded at 25 °C using a Perkin Elmer model Lambda 2S UV/Vis spectrometer. Fluorescence measurements were performed on a Perkin Elmer model LS45 fluorescence spectro-

meter.

UV-Vis Measurements. Receptor **1** (53.3 mg, 0.25 mmol) was dissolved in tetrahydrofuran (5 mL) and 3 μL of receptor **1** (50 mM) was diluted to 2.997 mL 10% bis-tris/THF buffer (0.01 M, pH 7.0) to make the final concentration of 50 μM. Tetraethylammonium cyanide (234.4 mg, 1.5 mmol) was dissolved in tetrahydrofuran (5 mL). 5-30 μL of CN^- solution (300 mM) was transferred to each receptor solution (50 μM) prepared above. After mixing them, UV absorption spectra were taken at room temperature.

Fluorescence Measurements. Receptor **1** (53.3 mg, 0.25 mmol) was dissolved in tetrahydrofuran (5 mL) and 3 μL of the receptor **1** (50 mM) was diluted in 2.997 mL 10% Bis-tris/THF buffer (0.01 M, pH 7.0) to make the final concentration of 50 μM. Tetraethylammonium cyanide (234.4 mg, 1.5 mmol) was dissolved in tetrahydrofuran (5 mL). 4-35 μL of CN^- solution (300 mM) was transferred to each receptor solution (50 μM) prepared above. After mixing, fluorescence spectra were obtained at room temperature.

Job Plot Measurement. Receptor **1** (10.7 mg, 0.05 mmol) was dissolved in tetrahydrofuran (2 mL). 12, 10.8, 9.6, 8.4, 7.2, 6.0, 4.8, 3.6, 2.4, and 1.2 μL of receptor **1** solution were taken and transferred to vials. Each vial was diluted with 10% Bis-tris/THF buffer (0.01 M, pH 7.0) to make a total volume of 2.988 mL. Tetraethylammonium cyanide (7.81 mg, 0.05 mmol) was dissolved in tetrahydrofuran (2 mL). 0, 1.2, 2.4, 3.6, 4.8, 6.0, 7.2, 8.4, 9.6, 10.8, and 12 μL of the tetraethylammonium cyanide solution were added to each diluted receptor **1** solution. Each vial had a total volume of 3 mL. After shaking the vials for a few minutes, fluorescence spectra were taken at room temperature.

NMR Titration. For ^{1}H NMR titrations of receptor **1**, five NMR tubes of receptor **1** (2.13 mg, 0.01 mmol) dissolved in a mixture of THF-d_8 (630 μL) and D_2O (70 μL) were prepared and then five different concentrations (0.01, 0.03, 0.05, 0.1 and 0.3 mmol) of tetraethylammonium cyanide dissolved in THF-d_8 were added to each solution of receptor **1**. After shaking them, ^{1}H NMR spectra were taken at room temperature.

Results and Discussion

Colorimetric Anion-Sensing. The chromogenic sensing ability of **1** was examined first with tetraethylammonium (TEA) salts of a series of anions including F^-, Cl^-, Br^-, I^-, CN^-, OAc^- in aqueous THF solutions (Fig. 1(a)). Upon the addition 60 equiv of each anion, only CN^- induced distinct spectra changes while other anions did not induce any spectra changes. As a result, the solution color of **1** changed from colorless to orange only with cyanide with fast response time (Fig. 1(b)), indicating that receptor **1** can serve as a "naked-eye" indicator for CN^- in aqueous media. The high selectivity of **1** for cyanide may be due to the nucleophilicity of cyanide in water. The water decrease the anion's nucleophilicity by hydrogen bonding to the nucleophile. Anions such as F^- and OAc^- interact with water through hydrogen-bonding leading to a large decrease in their nucleophilicity and basicity, thus, resulting in a poor deprotonation reaction. In contrast, cyanide has much weaker hydrogen-bonding ability in comparison with F^- and OAc^- and stronger nucleophilicity toward the imine group, which results in the addition reaction of CN^- to the carbon atom of an electron-deficient imine group and, subsequently, fast proton transfer of the phenol hydrogen to the neighboring nitrogen anion through an intramolecular hydrogen bond (Scheme 1).[20] In an aprotic solvent such MeCN, the selectivity of **1** for CN^- was poor as shown in Fig. S1. All the basic anions such as CN^-, F^- and OAc^- caused the solution color of **1** to change from colorless to orange by a simple deprotonation reaction, because there are no hydrogen bonding between MeCN and the basic anions.[21] A quantitative investigation of the binding affinity of **1** with CN^- was studied by UV-vis titration (Fig. 2). The addition of CN^- ions to a solution of **1** resulted in a decrease of absorption band at 354 nm and the appearance of a new band at 426 nm with a clear isosbestic

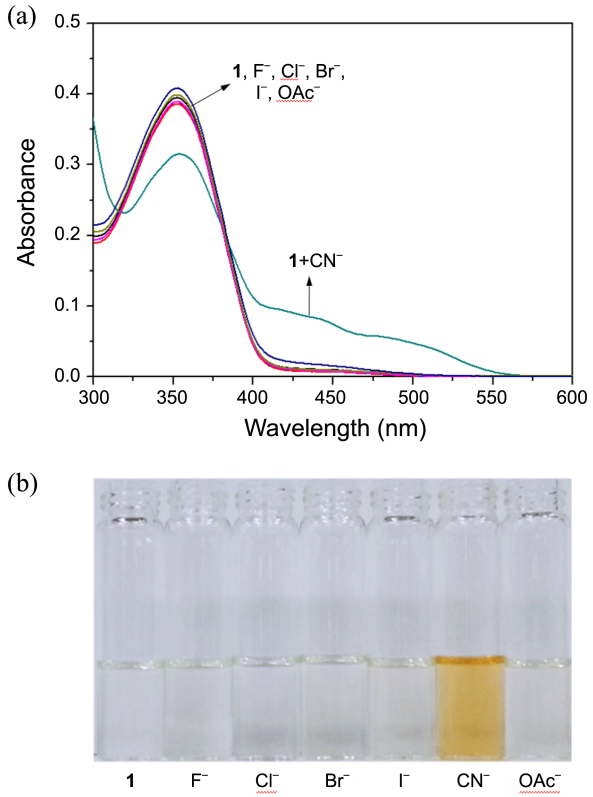
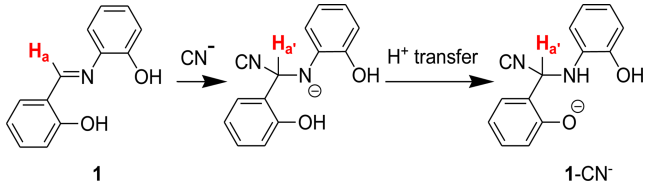


Figure 1. (a) Absorption spectra changes of **1** (30 μM) in the presence of 30 equivalents of different anions. (b) The color changes of **1** (30 μM) upon addition of various anions (30 equiv) in 10% Bis-tris/THF buffer (0.01 M, pH 7.0).



Scheme 1. The proposed sensing mechanism of **1** for cyanide in 10% Bis-tris/THF buffer (0.01 M, pH 7.0).

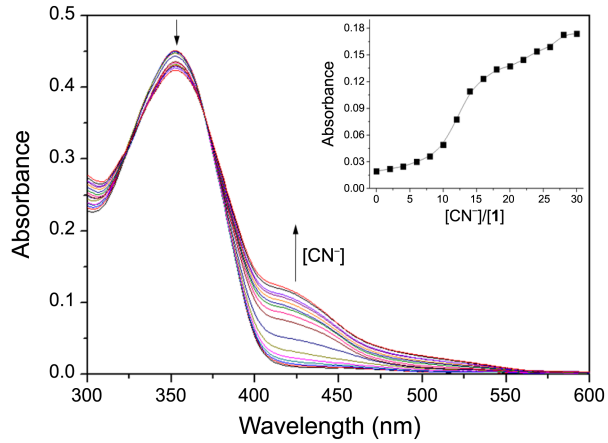


Figure 2. Absorption spectra changes of **1** (30 μM) in the presence of different concentrations of CN^- ions (2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28 and 30 eq) at room temperature. Inset: absorbance at 448 nm versus the number of equivalents of CN^- added.

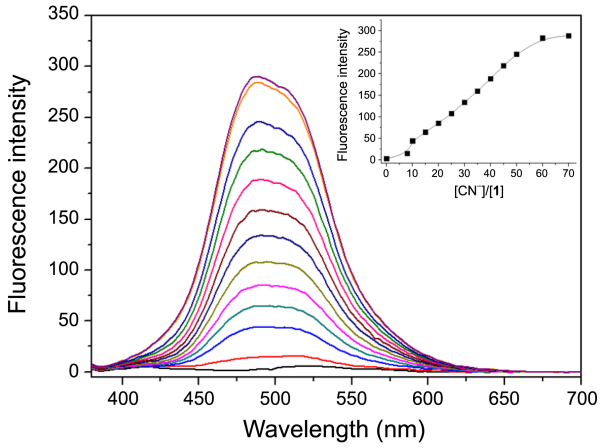


Figure 4. Fluorescence spectra of 50 μM receptor **1** (λ_{ex} = 370 nm) after addition of increasing amounts of CN^- ions (8, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60 and 70 eq) at room temperature. Inset: intensity at 492 nm versus the number of equivalents of CN^- added.

point at 371 nm, indicative of a clean conversion of **1** into the **1**-CN^- complex. From the Benesi-Hildebrand equation,[22] the association constant was found to be $2.0 \pm 0.5 \times 10^3$ M^{-1} for the **1**-CN^- anion complexation (Fig. S3). To check the possible interference of other anions on cyanide complexation with receptor **1**, competition experiments were performed in the presence of CN^- mixed with various anions (Fig. S4). All of these competing anions such as F^-, Cl^-, Br^-, I^- and OAc^- did not interfere with naked-eye detection of CN^- by **1** in aqueous solution, which means that the receptor **1** displays a good selectivity for CN^- over other competing anions. Therefore, absorption studies clearly showed that receptor **1** can act as a specific chromogenic chemodosimeter for cyanide in aqueous solution.

Fluorescent Anion-sensing. To further explore the utility of receptor **1** as an anion-selective fluorescent chemosensor for CN^- ions, the fluorogenic behavior of **1** was investigated with various anions in aqueous THF solution. As shown in Figure 3, receptor **1** alone displayed a very weak fluorescence emission with an excitation of 370 nm. Also, the addition of some anions such as F^-, Cl^-, Br^-, I^- and OAc^- to the solution of **1** showed no significant changes of the fluorescence. In contrast, the addition of CN^- resulted in a drastic enhancement (102-fold) of the emission intensity positioned at 492 nm. In order to study in details the fluorescent sensing behavior of **1**, fluorescence titration experiments were performed (Fig. 4). When the receptor **1** was titrated with CN^-, the fluorescence intensity increased up to 60 equiv and then no further change was observed. The Job plot for the binding between **1** and CN^- exhibited a 1:1 stoichiometry (Fig. S2).[23] The fluorescence quantum yields of receptor **1** without and with CN^- were found to be 0.001 and 0.085, respectively.[24] The detection limit of receptor **1** for the analysis of CN^- ions on the basis of 3σ/K was calculated to be 6.0×10^{-8} M (Fig. S5).[25] As cyanide concentrations lower than 1.9×10^{-6} M are acceptable in drinking water according to the World Health Organization (WHO),[26] the detection limit of **1** is far below the WHO guidelines of drinking water, which means that receptor **1** is a powerful tool for the detection of cyanide in water. To check further the practical applicability of receptor **1** as a CN^--selective fluorescence sensor, we carried out competition experiments (Fig. S6). When **1** was treated with 60 equiv of CN^- in the presence of other anions of the same concentration, the fluorescence enhancement caused by CN^- was retained with F^-, Cl^-, Br^-, I^- and OAc^-. These results indicate that receptor **1** shows an excellent selectivity for cyanide anion in the presence of other anions, making it very useful in practical applications.

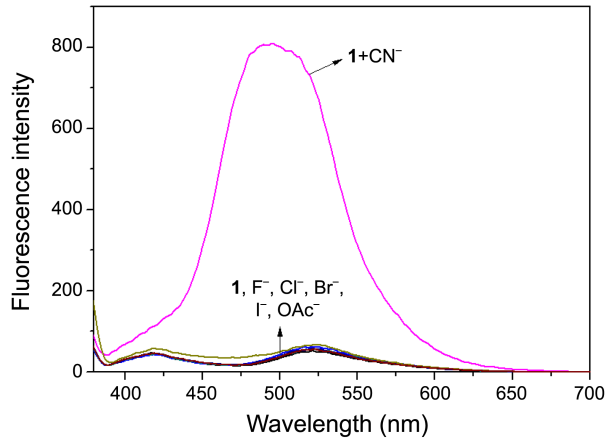


Figure 3. Flourescence spectra of receptor **1** (50 μM) upon addition of tetraethylammonium salts (60 equiv) of F^-, Cl^-, Br^-, I^-, CN^-, OAc^- with an excitation of 370 nm.

^{1}H NMR and ESI-MS Studies. The ^{1}H NMR titration experiments were studied in the mixed solvent (THF-d_8: D_2O = 9:1, v/v) to examine the binding mode between **1** and CN^- ion. ^{1}H NMR spectra of receptor **1** before and after treatment with 30 equiv of CN^- are shown in Figure 5. With the increasing of cyanide concentration, the H_a proton of the imine group at 8.9 ppm disappeared and a new peak ($H_{a'}$) at

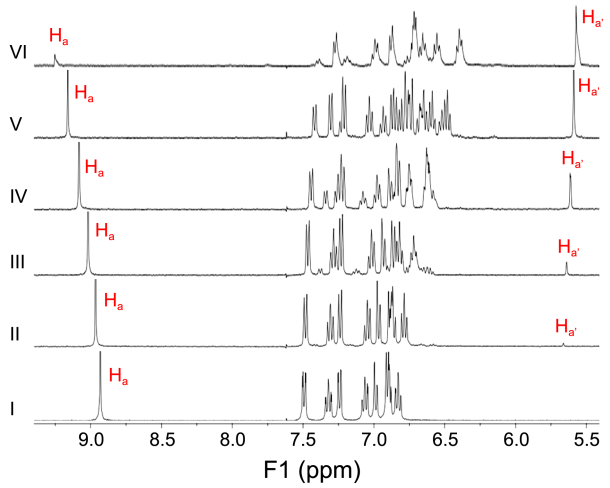


Figure 5. ^{1}H NMR spectra of **1** with TEACN in THF-d_8:D_2O = 9:1 (v/v): (I) **1**; (II) **1** with 1 equiv of CN^-; (III) **1** with 3 equiv of CN^-; (IV) **1** with 5 equiv of CN^-; (V) **1** with 10 equiv of CN^-; (VI) **1** with 30 equiv of CN^-.

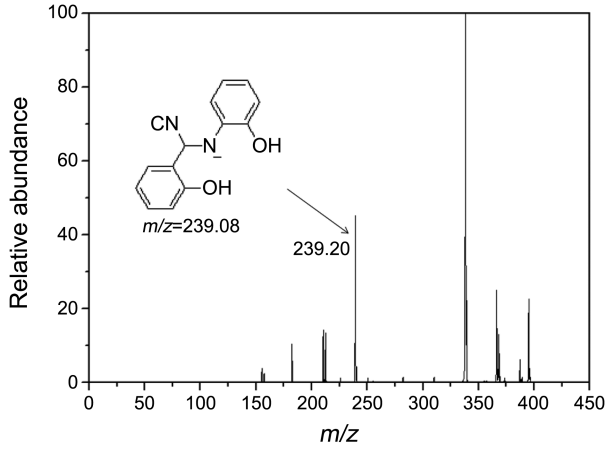


Figure 6. Negative-ion electrospray ionization mass spectrum of **1** upon addition of 30 equiv of CN^- in MeCN.

5.7 ppm started appearing, indicating that the cyanide anion functions as a nucleophile in aqueous solution. All aromatic protons were shifted to upfield, which suggests that the negative charge developed by the attack of CN^- ion delocalized through the whole receptor molecule. The formation of cyanide adduct was further confirmed by mass spectroscopy. The negative-ion mass spectrum of **1** upon addition of 30 equiv of CN^- showed the formation of the **1**+CN^- complex [*m/z*: 239.20; calcd, 239.08] (Fig. 6). Based on the Job plot, ^{1}H NMR titration and ESI-Mass analysis, we propose the structure of an 1:1 complex of **1** and CN^-, as shown in Scheme 1.

Conclusions

In summary, we have reported a simple imine-based turn-on colorimetric and fluorescent chemodosimeter, which displays high selectivity and sensitivity for detection of cyanide in aqueous solution. The receptor **1** showed high selectivity toward CN^- ions in a 1:1 stoichiometric manner, which induces a fast color change from colorless to orange and a dramatic enhancement in fluorescence intensity selectively for cyanide anions over other anions. Such selectivity results from the nucleophilic addition of CN^- to the carbon atom of an electron-deficient imine group and, subsequently, the fast proton transfer of the phenol hydrogen to the neighboring nitrogen anion through an intramolecular hydrogen bonding. Moreover, the detection limit of **1** for CN^- falls below the WHO detection level. Consequently, the chemodosimeter **1** appears to be a practical system for monitoring CN^- concentrations in aqueous solution.

Acknowledgments. Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012001725 and 2012008875) are gratefully acknowledged.

References

1. (a) Miller, C. *Nature* **2006**, *440*, 484. (b) Dutzler, R.; Campbell, E. B.; Mackinnon, R. *Science* **2003**, *300*, 108. (c) Dutzler, R.; Campbell, E. B.; Cadene, M.; Chait, B. T.; Mackinnon, R. *Nature* **2002**, *415*, 287. (d) Beer, P. D.; Gale, P. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 486.
2. (a) Vennesland, B.; Comm, E. E.; Knownles, C. J.; Westly, J.; Wissing, F. *Cyanide in Biology*; Academic Press: London, 1981. (b) Kulig, K. W. *Cyanide Toxicity*; U.S. Department of Health and Human Services: Atlanta, GA, 1991.
3. Baird, C.; Cann, M. *Environmental Chemistry*; New York, Freeman: 2005.
4. (a) Hachiya, H.; Ito, S.; Fushinuki, Y.; Masadome, T.; Asano, Y.; Imato, T. *Talanta* **1999**, *48*, 997. (b) *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: New York, 1999. (c) Koenig, R. *Science* **2000**, *287*, 1737. (d) Young, C.; Tidwell, L.; Anderson, C. *Cyanide: Social, Industrial and Economic Aspects: Minerals*, Metals, and Materials Society, Warrendale, 2001. (e) Sun, H.; Zhang, Y. Y.; Si, S. H.; Zhu, D. R.; Fung, Y. S. *Sens. Actuators B* **2005**, *108*, 925.
5. (a) Odago, M. O.; Colabello, D. M.; Lees, A. J. *Tetrahedron* **2010**, *66*, 7464. (b) Kim, D. S.; Ahn, K. H. *J. Org. Chem.* **2008**, *73*, 6831. (c) Tomasolu, M.; Raymo, F. M. *Org. Lett.* **2005**, *7*, 4633. (d) Xu, Z.; Pan, J.; Spring, D. R.; Cui, J.; Yoon, J. *Tetrahedron* **2010**, *66*, 1678. (e) Niu, H. T.; Jiang, X.; He, J.; Cheng, J. P. *Tetrahedron Lett.* **2009**, *50*, 6668. (f) Chen, X.; Nam, S. W.; Kim, G. H.; Song, N.; Jeong, Y.; Shin, I.; Kim, S. K.; Kim, J.; Park, S.; Yoon, J. *Chem. Commun.* **2010**, *46*, 8953. (g) Tomasulo, M.; Sortino, S.; White, A. J. P.; Raymo, F. M. *J. Org. Chem.* **2006**, *71*, 744. (h) Ajayaghosh, A. *Acc. Chem. Res.* **2005**, *38*, 449. (i) Abalos, T.; Royo, S.; Martinez-Manez, R.; Sancenon, F.; Soto, J.; Costero, A. M.; Gil, S.; Parra, M. *New J. Chem.* **2009**, *33*, 1641. (j) Kim, S. H.; Hong, S. J.; Yoo, J.; Kim, S. K.; Sessler, J. L.; Lee, C. H. *Org. Lett.* **2009**, *11*, 3626. (k) Lee, J. H.; Jeong, A. R.; Shin, I. S.; Kim, H. J.; Hong, J. I. *Org. Lett.* **2010**, *12*, 764.
6. (a) Martinez-Manez, R.; Sancenon, F. *Coord. Chem. Rev.* **2006**, *250*, 3081. (b) Gunnlaugsson, T.; Glynn, M.; Tocci, G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094. (c) Martinez-Manez, R.; Sancenon, F. *Chem. Rev.* **2003**, *103*, 4419. (d) Shao, J.; Lin, H.; Yu, M.; Cai, Z. S.; Lin, H. K. *Talanta* **2008**, *75*, 551.
7. (a) Gentili, P. L. *Chem. Phys.* **2007**, *336*, 64. (b) Zeng, Q.; Cai, P.; Li, Z.; Qin, J.; Tang, B. Z. *Chem. Commun.* **2008**, 1094. (c) Chow, C. F.; Lamand, M. H. W.; Wong, W. Y. *Inorg. Chem.* **2004**, *43*,

8387. (d) Kim, Y. H.; Hong, J. I. *Chem. Commun.* **2002**, 512. (e) Shang, L.; Jin, L. H.; Dong, S. J. *Chem. Commun.* **2009**, 3077.
8. (a) Park, I. S.; Heo, E. J.; Kim, J. M. *Tetrahedron Lett.* **2011**, *52*, 2454. (b) Anzenbacher, P., Jr.; Tyson, D. S.; Jursikova, K.; Castellano, F. N. *J. Am. Chem. Soc.* **2002**, *124*, 6232. (c) Gimeno, N.; Li, X.; Durrant, J. R.; Vilar, R. *Chem. Eur. J.* **2008**, *14*, 3006. (d) Miyaji, H.; Sessler, J. L. *Angew. Chem.* **2001**, *113*, 158.
9. (a) Chen, C.-L.; Chen, Y.-H.; Chen, C.-Y.; Sun, S.-S. *Org. Lett.* **2006**, *8*, 5053. (b) Ros-Lis, J. V.; Martinez-Manez, R.; Soto, J. *Chem. Commun.* **2002**, 2248. (c) Lee, K. S.; Kim, H. J.; Kim, G. H.; Shin, I.; Hong, J. I. *Org. Lett.* **2008**, *10*, 49. (d) Chung, Y.; Lee, H.; Ahn, K. H. *J. Org. Chem.* **2006**, *71*, 9470. (e) Miyaji, H.; Kim, D. S.; Chang, B. Y.; Park, E.; Park, S. M.; Ahn, K. H. *Chem. Commun.* **2008**, 753. (f) Tomasulo, M.; Sortino, S.; White, A. J. P.; Raymo, F. M. *J. Org. Chem.* **2006**, *71*, 744. (g) Garcia, F.; Garcia, J. M.; Garcia-Acosta, B.; Martinez-Manez, R.; Sancenon, F.; Soto, J. *Chem. Commun.* **2005**, 2790.
10. Tomasulo, M.; Sortino, S.; White, A. J. P.; Raymo, F. M. *J. Org. Chem.* **2005**, *70*, 8180.
11. Hudnall, T. W.; Gabbai, F. P. *J. Am. Chem. Soc.* **2007**, *129*, 11978.
12. Yang, Y. K.; Tae, J. *Org. Lett.* **2006**, *8*, 5721.
13. Cho, D. G.; Kim, J. H.; Sessler, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 12163.
14. Jo, J.; Lee, D. *J. Am. Chem. Soc.* **2009**, *131*, 16283.
15. (a) Yuan, L.; Lin, W.; Yang, Y.; Song, J.; Wang, J. *Org. Lett.* **2011**, *13*, 3730. (b) Wu, X.; Xu, B.; Tong, H.; Wang, L. *Macromolecules* **2011**, *44*, 4241. (c) Afkhami, A.; Sarlak, N. *Sens. Actuators B* **2007**, *122*, 437. (d) Hong, S. J.; Lee, C. H. *Tetrahedron Lett.* **2012**, *53*, 3119.
16. Yang, Z.; Liu, Z.; Chen, Y.; Wang, X.; He, W.; Lu, Y. *Org. Biomol. Chem.* **2012**, *10*, 5073.
17. Lv, X.; Liu, J.; Liu, Y.; Zhao, Y.; Chen, M.; Wang, P.; Guo, W. *Org. Biomol. Chem.* **2011**, *9*, 4954.
18. (a) Ding, Y.; Li, T.; Zhu, W.; Xie, Y. *Org. Biomol. Chem.* **2012**, *10*, 4201. (b) Lee, H.; Chung, Y. M.; Ahn, K. H. *Tetrahedron Lett.* **2008**, *49*, 5544. (c) Niu, H. T.; Jiang, X.; He, J.; Cheng, J. P. *Tetrahedron Lett.* **2008**, *49*, 6521.
19. (a) Kim, S.; Noh, J. Y.; Kim, K. Y.; Kim, J. H.; Kang, H. K.; Nam, S.-W.; Kim, S. H.; Park, S.; Kim, C.; Kim, J. *Inorg. Chem.* **2012**, *51*, 3597. (b) Prabhu, S.; Saravanamoorthy, S.; Ashok, M.; Velmathi, S. *J. Luminescence* **2012**, *132*, 979.
20. Sun, Y.; Liu, Y.; Chen, M.; Guo, W. *Talanta* **2009**, *80*, 996.
21. (a) Kim, Y.-J.; Kwak, H.; Lee, S. J.; Lee, J. S.; Kwon, H. J.; Nam, S. H.; Lee, K.; Kim, C. *Tetrahedron* **2006**, *62*, 9635. (b) Kang, J.; Song, E. J.; Kim, H.; Kim, Y.-H.; Kim, Y.; Kim, S.-J.; Kim, C. *Tetradedron Lett.* **2013**, *54*, 1015. (c) Kang, J.; Jang, S. P.; Kim, Y.-H.; Lee, J. H.; Park, E. B.; Lee, H. G.; Kim, J. H.; Kim, Y.; Kim, S.-J.; Kim, C. *Tetrahedron Lett.* **2010**, *51*, 6658. (d) Park, J. J.; Kim, Y.-H.; Kim, C.; Kang, J. *Tetrahedron Lett.* **2011**, *52*, 2759. (e) Kang, J.; Lee, Y. J.; Lee, S. K.; Lee, J. H.; Park, J. J.; Kim, Y.; Kim, S.-J.; Kim, C. *Supramol. Chem.* **2010**, *22*, 267. (f) Hijji, Y. M.; Barare, B.; Kennedy, A. P.; Butcher, R. *Sens. Actuators B* **2009**, *136*, 297.
22. Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.
23. Job, P. *Ann. Chim.* **1928**, *9*, 113.
24. Burdette, S. C.; Walkup, G. K.; Spingler, B.; Tsien, R. Y.; Lippard, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 7831.
25. Tsui, Y.-K.; Devaraj, S.; Yen, Y.-P. *Sens. Actuators B* **2012**, *161*, 510.
26. *Guidelines for Drinking-Water Quality*; World Health Organization: Geneva, 1996.