Tetrahedron Letters 50 (2009) 671–675

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

A highly selective fluorescent chemosensor for silver(I) in water/ethanol mixture

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ARTICLE INFO

Article history:
Received 15 October 2008
Revised 19 November 2008
Accepted 25 November 2008
Available online 28 November 2008

ABSTRACT

Synthesis, photophysical, and complexation properties of fluorescent chemosensors, $\mathbf{L^1}$ and $\mathbf{L^2}$, with 'receptor-spacer-fluorophore' motif ($\mathbf{L^1}$: NS_2O_2-cyclic receptor, $\mathbf{L^2}$: acyclic analogue receptor) are described. Maximum chelation-enhanced fluorescence effect (TURN-ON type) was observed in the presence of Ag^+ for both fluoroionophores in a 1:1 (v/v) aqueous ethanol solution: remarkably superior selectivity of $\mathbf{L^1}$ (150-fold) with cyclic receptor than that of the $\mathbf{L^2}$ (50-fold) with acyclic analogue was found. According to the fluorescence and NMR titrations, the excellent selectivity of $\mathbf{L^1}$ is attributed to its topology-based higher affinity in complexation.

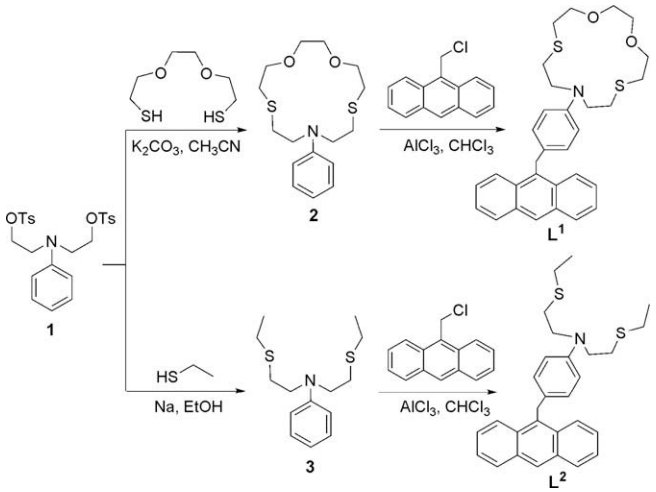
Chemosensor exhibiting high selectivity toward a target analyte is in great demand due to its low cost, high throughput capability, and point-of-care monitoring.[1] Thus, many efforts have been devoted to design and construction of photophysical chemosensors such as colorimetric and/or fluorescent ones. Owing to their selective metal ion recognition and sensitive signaling capacity, macrocycle-receptor-based fluoroionophores make them good candidates for the chemosensors for the metal ions.[2]

On the other hand, a range of mono- and multinuclear complexes of thiaoxa- or thiaoxaaza-macrocycles with discrete and continuous types were reported by us[3] and other workers.[4] We are interested in extending these results in the macrocycle-based approach to develop chemosensors for thiaphilic d^{10} metal ion species such as Ag^+ and Hg^{2+}. In particular, Ag^+ has received considerable attention because of its bioaccumulation and toxicity.[5] Furthermore, the mechanism of antimicrobial activities of Ag^+ has not been well established because of a lack of suitable detection and imaging methodologies.[6]

Recently, several research groups reported NS_2-macrocyle-based donor-acceptor type chemosensors for Ag^+ and/or Hg^{2+}.[7] We also developed an azo-attached dibenzo-NS_2O_2 donor-macrocylce as a chromogenic chemosensor for heavy metal ion in acetonitrile.[8] More recently, we employed the same macrocycle to modify the nanotube as solid matrix for the detection of heavy metal ion.[9]

The fluoroionophore system showing high selectivity for Ag^+ in aqueous solution associated with fluorescence OFF–ON changes (TURN-ON type) has important implications for use as chemosensors; however, the number of reported examples of these types is quite limited.[10] The fluoroionophore based on 'receptor-spacer-fluorophore' motif[2c,d] has been demonstrated to be an effective way of developing both anion[11] and cation[2] chemosensors. In brief, the Ag^+ detection can be tuned by both the choice of receptor and fluorophore. These two subunits also control the water-solubility of a sensor molecule. Therefore, the need for developing efficient fluorescent sensor toward Ag^+ that satisfies the TURN-ON type high selectivity in aqueous media has attractive growing attention.

In this regard, we herein describe the synthesis of an NS_2O_2-macrocycle-based fluoroionophore, $\mathbf{L^1}$, with the 'receptor-spacer-fluorophore' motif and its photophysical properties as a highly selective TURN-ON type fluorescence chemosensor for Ag^+ in aqueous ethanol solution (Scheme 1). At the same time, its acyclic ana-



Scheme 1. Synthesis of $\mathbf{L^1}$ and $\mathbf{L^2}$.

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0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.11.090

logue **L²** as a reference counterpart has also been prepared and included for comparison because these two compounds are expected to have discriminated photophysical properties due to the different topologies in the receptor units.

In the synthesis of the fluoroionophores, N-phenylated macrocyclic precursors **2** and **3** were prepared based on reported coupling reactions between ditosylate **1** and corresponding dithiols (Scheme 1).[12,13] The incorporation of 9-methylanthracene moiety on the spacer unit was achieved by aluminum chloride induced Friedel–Crafts alkylation of with 9-chloromethylanthracene in good yields.[14] The target compounds were purified by silica-gel flash column chromatography. Their ^{1}H and ^{13}C spectra exhibit characteristic singlets at 4.90 (**L¹**), 4.87 (**L²**), and 51.85 (**L¹**), 51.58 (**L²**) ppm, respectively, arising from the each methylene proton between two aromatic units.

The structure of **L¹** was also characterized in the solid state by single-crystal X-ray crystallography (Fig. 1a). Single-crystals of **L¹** were obtained by slow evaporation from the solution of CH_2Cl_2/CH_3CN. Since two S donors show exocyclic fashion to the ring cavity, the S···S distance is as large as 6.286(1) Å. The S1–C–C–N1 [167.5(4)°] and S2–C–C–N1 [−168.6(4)°] are arranged anti-conformation. The pale yellow single crystals of **L¹** exhibit a broad band with blue-green emission maxima at 485 nm (λ_{ex} = 365 nm) arising from the intermolecular charge transfer (ICT) states between the N-phenylated macrocylic unit and excited anthracene terminal group (Fig. 1b).[7a,f]

To probe the optimum condition for the photophysical properties of the fluoroionophores prepared, the pH responses were examined in the 1:1 (v/v) aqueous ethanol solution (Figs. S3 and S4). In the basic condition (pH 3.5–12), virtually no fluorescent emission was observed (OFF state) due to the photo-induced electron transfer (PET) quenching by the lone pair of electrons on the tertiary N donor atom in each molecule (Table 1).[2b] However, in the pH range of 1.0–3.0, the typical anthracene emission was observed. This result makes these compounds very attractive for use in both physiological and environmental criteria. Lippard[17] and Gunnlaugsson[18] also reported similar results for Zn^{2+} and Cd^{2+} sensor systems. Based on above results, we employed the pH 7.2 condition buffered with 20 mM HEPES in EtOH/H_2O (1:1 v/v) for the measurements of the photophysical properties

Table 1
Spectroscopic and complexation data for **L¹**, **L²** and their complexes

Species	λ_{em} (nm)	Quantum yield[a]			log K[b]
		Φ_0	Φ	Φ/Φ_0	
L¹	414	0.001	—	260	—
[Ag·**L¹**]⁺	414	—	0.26		10.2
L²	415	0.006	—	13.7	—
[Ag·**L²**]⁺	414	—	0.082		8.9

[a] Quantum yields are based on anthracene, Φ = 0.27 in ethanol.[15]
[b] Stability constants for a 1:1 (metal to ligand) complexation with Ag^+ were obtained from the fluorescence titrations shown in Figure 4.[16]

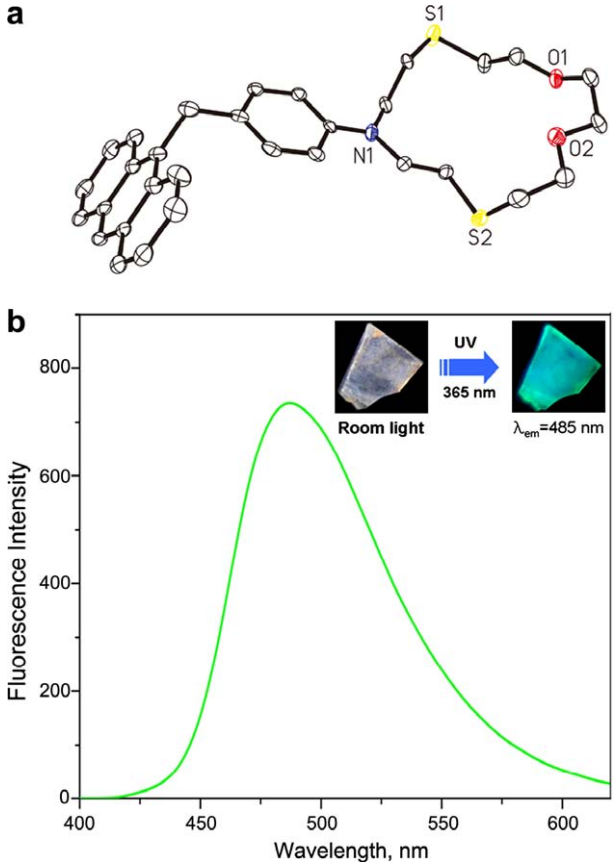

Figure 1. (a) Crystal structure and (b) solid state photoluminescence spectrum of **L¹**.

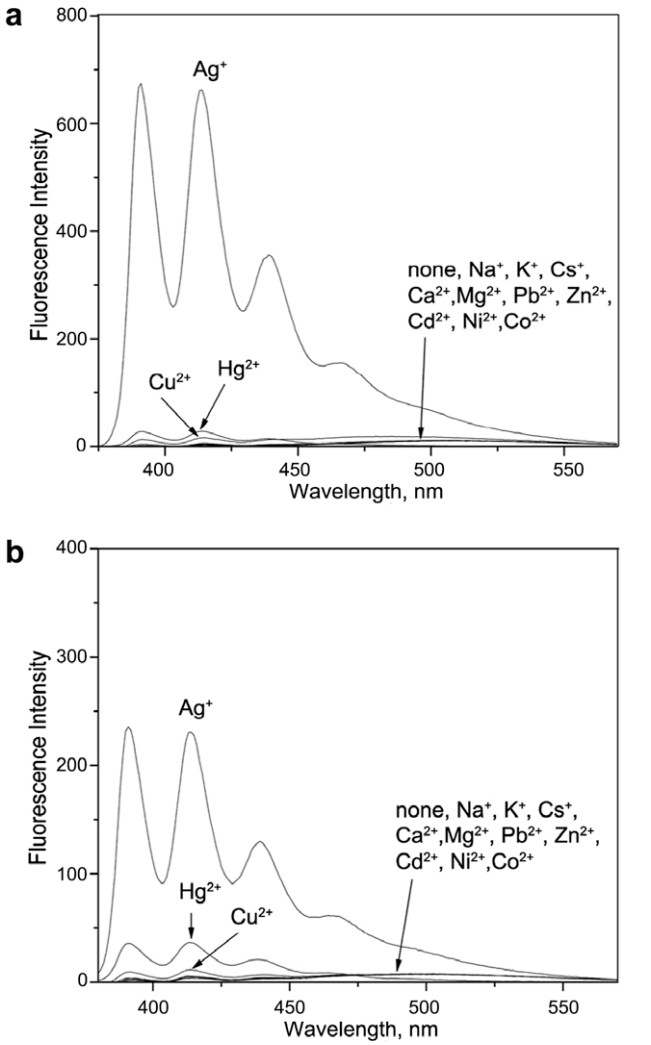

Figure 2. Fluorescence spectra of (a) **L¹** and (b) **L²** in the presence of metal ions in EtOH/H_2O (1:1, v/v, pH = 7.2, HEPES buffer). Cs^+, Ag^+, Pb^{2+}, Zn^{2+}, Cd^{2+},Hg^{2+}, Cu^{2+} Ni^{2+}, and Co^{2+} (10 equiv) and Na^+, K^+, Ca^{2+}, and Mg^{2+} (1000 equiv) were added to each ligand solution (5.0 μM).

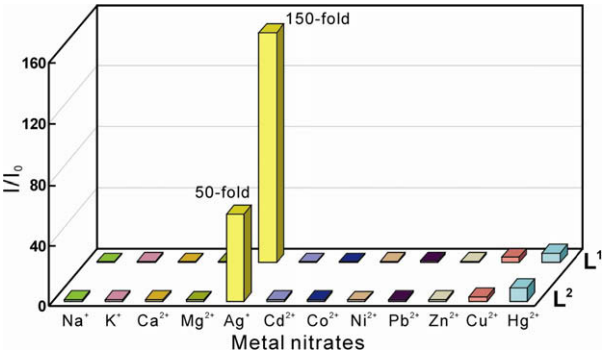

Figure 3. Normalized fluorescence intensities (I/I_0) of $\mathbf{L^1}$ and $\mathbf{L^2}$ in the presence of metal ions.

throughout this study. Under this physiological condition, as expected, $\mathbf{L^1}$ and $\mathbf{L^2}$ exhibit negligible fluorescence quantum yields $\Phi_0 = 0.001$ and 0.006 in the absence of Ag^+, respectively (Table 1).

To examine the selectivity of $\mathbf{L^1}$ and $\mathbf{L^2}$ as fluorescent sensors, responses to diverse metal ions are compared (excitation at 368 nm). It is worth noting that Figure 2 shows the maximum chelation enhanced fluorescence (CHEF) effect (ON state) for each fluoroionophore upon addition of Ag^+. In both cases, the typical pattern of the anthracene appears very strongly without change in the emission maxima. This can be explained that the coordination to such tertiary N donor atom prevents the PET quenching effectively.[2b] More significantly, upon addition of Ag^+ the normalized fluorescence intensity (I/I_0) of $\mathbf{L^1}$ (150-fold increase) shows much higher selectivity compare to $\mathbf{L^2}$ (50-fold increase) (Fig. 3). The group IA, IIA, and d-block transition metal ions, however, show no or less influences on the fluorescence intensity especially for $\mathbf{L^1}$ which suggests the higher selectivity than that of $\mathbf{L^2}$. Furthermore, the competition experiments by a range of the interfering ions revealed that Ag^+-induced fluorescence enhancement for $\mathbf{L^1}$ is unaffected in the presence of physiologically (1000 equiv) and environmentally (10 equiv) relevant metal ions (Fig. S5). As we understand, the proposed system with cyclic receptor ($\mathbf{L^1}$) affords the largest CHEF reported to date that results from Ag^+ complexation in aqueous media.

On the other hand, the fluorescence titrations of $\mathbf{L^1}$ and $\mathbf{L^2}$ with $AgNO_3$ in the same solvent media resulted in the intensity gradually increasing between 0 and 1.0 equiv of Ag^+, and then achieves a plateaus with the quantum yields $\Phi = 0.26$ and 0.082, respectively, suggesting a 1:1 complexation (Fig. 4 and Table 1). In addition, the 1:1 (metal to ligand) stoichiometry for the complexations was also demonstrated by Job plots (Fig. S6). On the basis of the nonlinear fitting analysis of the fluorescence titration data, the stability constants ($\log K$) for the 1:1 complexes of $\mathbf{L^1}$ and $\mathbf{L^2}$ were determined to be 10.2 and 8.9 for Ag^+, respectively (Table 1). It should be noted that the preorganized fluoroionophore $\mathbf{L^1}$ showed improved binding (~20 times) with Ag^+ compared to its acyclic analogue $\mathbf{L^2}$ probably due to the additional stabilization of the macrocyclic effect. The detection limits[19] were also estimated from the titration results ($\mathbf{L^1}$; 2.2×10^{-7} M and $\mathbf{L^2}$; 5.8×10^{-7} M).

Unfortunately, we were not able to obtain the single crystals of the related Ag^+ complexes. Instead, NMR titrations were carried out in DMSO-d_6 to understand further structural characteristics of the Ag^+ complexes in solution (Fig. 5 for $\mathbf{L^1}$ and Fig. S7 for $\mathbf{L^2}$). Upon stepwise addition of Ag^+, in both cases, every proton in each ligand shifted, suggesting the stable complexation for the fast exchanging system. Here again, the NMR titration curves clearly show an inflection point at mole ratio (Ag^+/**L**) of 1.0, indicating that the stoichiometry for the formation of the complex is also 1:1 ratio (metal to ligand).

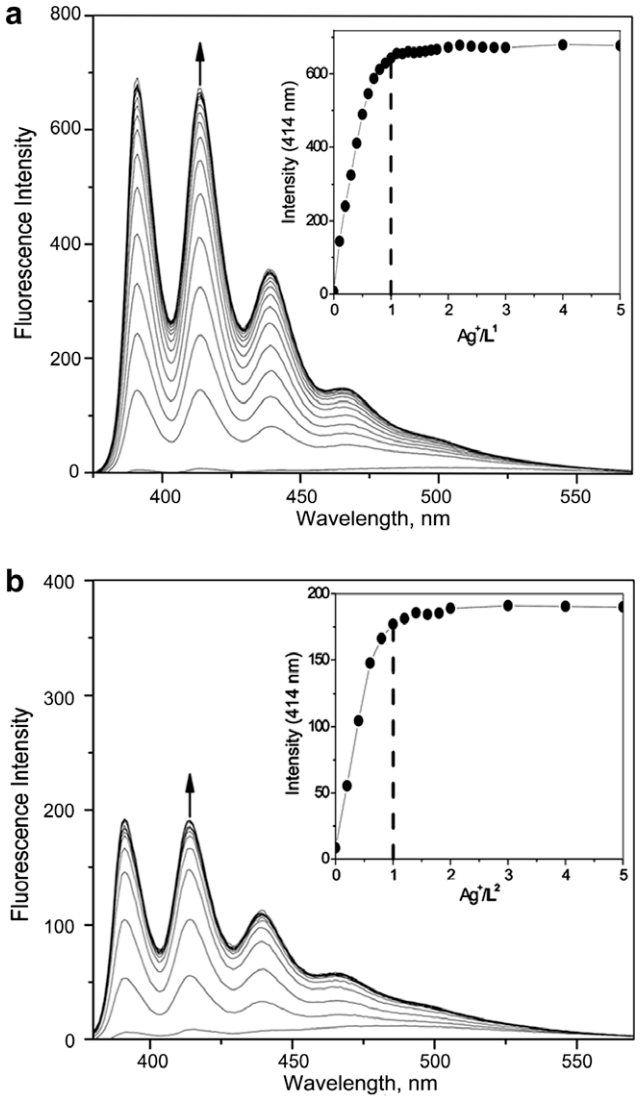

Figure 4. Fluorescence titrations of (a) $\mathbf{L^1}$ and (b) $\mathbf{L^2}$ with $AgNO_3$ in EtOH/H_2O (1:1, v/v, pH 7.2, HEPES buffer).

The magnitude of the Ag^+-induced chemical shifts for the protons varies with their positions. Very notably, the aromatic proton H_a which is closest to the tertiary N donor shows largest chemical shift change than others in both cases: $\Delta\delta = 0.59$ and 0.39 ppm for $\mathbf{L^1}$ and $\mathbf{L^2}$, respectively, suggesting the nitrogen-affinity of Ag^+ is important. This change seems to be caused by synergic effect of the metal-donor and metal–π interactions.[20] For the aliphatic region, the order of magnitude of the chemical shift variation is H_2 ($\Delta\delta$: −0.3 ppm), H_4 (0.3 ppm) >> H_1 (0.1 ppm) > H_3,H_5 (0.07 ppm): Ag^+ causes a much larger shift for the H_2 and H_4 peaks than for those of others. Thus, Ag^+ appears to be more strongly coordinated by potential tridentate NS_2 donor-set, while the O donors interact with the Ag^+ relatively weakly. Similar results were observed for both $\mathbf{L^1}$ and $\mathbf{L^2}$ but the $\mathbf{L^1}$ shows relatively larger chemical shift changes than $\mathbf{L^2}$, indicating the stronger receptor toward Ag^+ in solution. The unexpected Ag^+-induced upfield shift for H_2 and H_3 appears to be caused by a ring current effect.[21] The observed 1:1 stoichiometry for the Ag**L** type complexation is further confirmed by the ESI-MS of the complex solutions, which correspond to the species $[\mathbf{L^1}\cdot Ag]^+$ (m/z 624.9) and $[\mathbf{L^2}\cdot Ag]^+$ (m/z 568.8), respectively (Figs. S8 and S9).

In conclusion, two fluoroionophores with 'receptor-spacer-fluorophore' motif were synthesized and their photophysical and com-

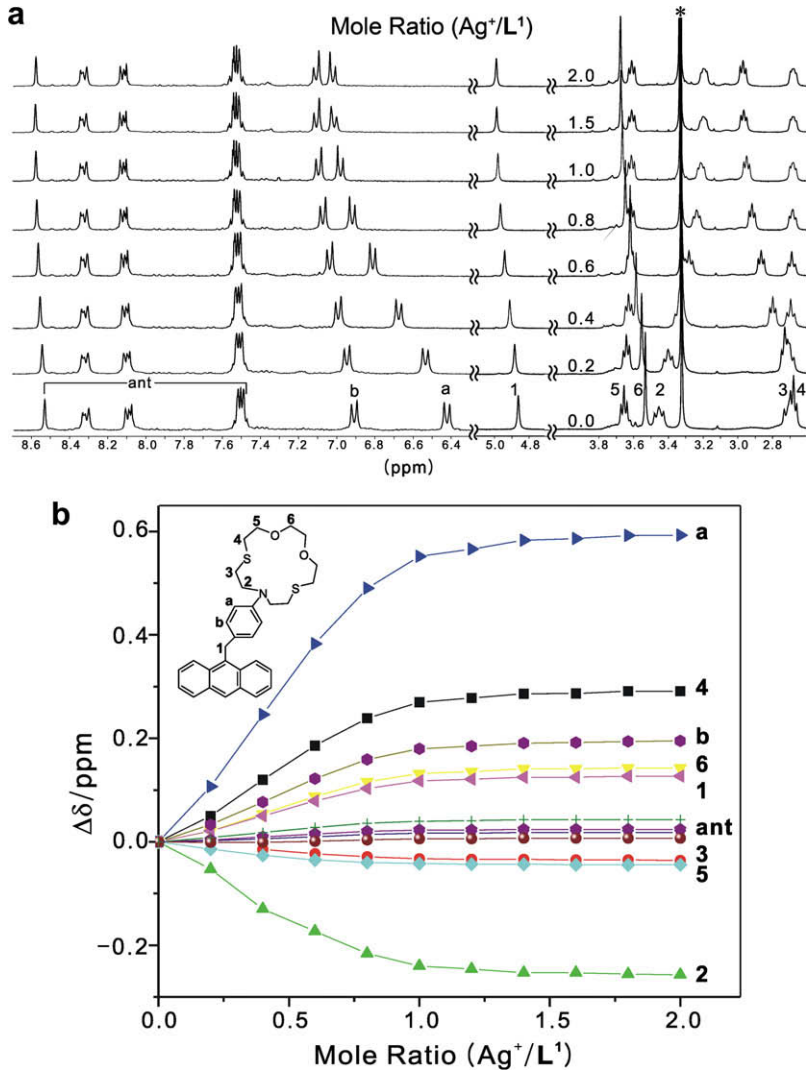

Figure 5. (a) ^{1}H NMR spectra of $\mathbf{L^1}$ by stepwise addition of $AgNO_3$ and (b) ^{1}H NMR titration curves for $\mathbf{L^1}$ with $AgNO_3$ in DMSO-d_6.

plexation properties were investigated. The proposed sensor molecule with cyclic receptor unit exhibited excellent turn-on type fluorescence selectivity toward Ag^+ in aqueous ethanol solution. From the results, it is concluded that the unique selectivity for Ag^+ based on the complexation-induced inhibition of the PET process is due to the several cooperative factors, such as transduction capacity of anthracene fluorophore, the spacer group contribution and synergic effect of the NS_2O_2 donors with well-preorganized coordination environment of the cyclic receptor.

Acknowledgment

This work was supported by a Korea Science and Engineering Foundation (R01-2007-000-20245-0).

Supplementary data

Supplementary crystallographic data associated to L^1 have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 704607. Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: http://www.deposit@ccdc.cam.ac.uk), or electronically via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.11.090.

References and notes

1. (a) Czarnik, A. W. *Fluorescent Chemosensors for Ion and Molecule Recognition*; American Chemical Society: Washington, DC, 1993; (b) Desvergne, J. P.; Czarnik, A. W. *Chemosensors of Ion and Molecular Recognition*; NATO ASI Series; Kluwer: Dordrecht, The Netherlands, 1997; (c) Valeur, B. *Molecular Fluorescence*; Wiley-VCH: New York, 2001.
2. (a) Czarnik, A. W. *Acc. Chem. Res.* **1994**, *27*, 302; (b) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515; (c) de silva, A. P.; Fox, D. B.; Huxley, A. J. M.; Moody, T. S. *Coord. Chem. Rev.* **2000**, *205*, 41; (d) Amendola, V.; Fabbrizzi, L.; Lincchelli, M.; Mangano, C.; Pallavicini, P.; Parodi, L.; Poggi, A. *Coord. Chem. Rev.* **1999**, *190*(192), 649.
3. (a) Seo, J.; Song, M. R.; Lee, J.-E.; Lee, S. Y.; Yoon, I.; Park, K.-M.; Kim, J.; Jung, J. H.; Park, S. B.; Lee, S. S. *Inorg. Chem.* **2006**, *45*, 952; (b) Habata, Y.; Seo, J.; Otawa, S.; Osaka, F.; Noto, K.; Lee, S. S. *Dalton Trans.* **2006**, 2202; (c) Song, M. R.; Lee, J.-E.; Lee, S. Y.; Seo, J.; Park, K.-M.; Lee, S. S. *Inorg. Chem. Commun.* **2006**, *9*, 75; (d) Yoon, I.; Seo, J.; Lee, J.-E.; Song, M. R.; Lee, S. Y.; Choi, K. S.; Jung, O.-S.; Park, K.-M.; Lee, S. S. *Dalton Trans.* **2005**, 2352; (e) Seo, J.; Yoon, I.; Lee, J.-E.; Song, M. R.; Lee, S. Y.; Park, S. H.; Kim, T. H.; Park, K.-M.; Kim, B. G.; Lee, S. S. *Inorg. Chem. Commun.* **2005**, *8*, 916; (f) Kim, H. J.; Yoon, I.; Lee, S. Y.; Seo, J.; Lee, S. S. *Tetrahedron Lett.* **2007**, *48*, 8464; (g) Kim, H. J.; Yoon, I.; Lee, S. Y.; Choi, K. S.; Lee, S. S. *New J. Chem.* **2008**, *32*, 258.
4. (a) Janzen, D. E.; Mahne, L. F.; VanDerveer, D. G.; Grant, G. J. *Inorg. Chem.* **2005**, *44*, 8182; (b) Vetrichelvan, M.; Lai, Y.-H.; Mok, K. F. *Eur. J. Inorg. Chem.* **2004**, 2086; (c) Contu, F.; Dermartin, F.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lippolis, V.; Salis, A.; Verani, G. *J. Chem. Soc., Dalton Trans.* **1997**, 4401; (d) Watzky, M. A.;

Waknine, D.; Heeg, M. J.; Endicott, J. F.; Ochrymowyzc, L. A. *Inorg. Chem.* **1993**, *32*, 4882; (e) Blake, A. J.; Halcrow, M. A.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1992**, 2803.

5. (a) Ratte, H. T. *Environ. Toxicol. Chem.* **1999**, *18*, 89; (b) Ganjali, M. R.; Norouzi, P.; Alizadeh, T.; Adib, M. *J. Braz. Chem. Soc.* **2006**, *17*(7), 1217; (c) Zhang, X. B.; Han, Z. X.; Fang, Z. H.; Shen, G. L.; Yu, R. Q. *Anal. Chim. Acta* **2006**, *562*, 210; (d) Peng, H. Q.; Brooks, B. W.; Chan, R.; Chyan, O.; Point, T. W. L. *Chemosphere* **2002**, *46*, 1141; (e) Kazuyuki, M.; Nobuo, H.; Takatoshi, K.; Yuriko, K.; Osamu, H.; Yashihisa, I.; Kiyoko, S. *Clin. Chem.* **2001**, *47*, 763; (f) Wan, A. T.; Conyers, R. A.; Coombs, C. J.; Masterton, J. P. *Clin. Chem.* **1991**, *37*, 1683.
6. (a) Rurack, K.; Kollmannsberger, M.; Resch-Genger, U.; Daub, J. *J. Am. Chem. Soc.* **2000**, *122*, 968; (b) Yang, R. H.; Chan, W. H.; Lee, A. W. M.; Xia, P. F.; Zhang, H. K.; Li, K. A. *J. Am. Chem. Soc.* **2003**, *125*, 2884; (c) Coskun, A.; Akkaya, E. U. *J. Am. Chem. Soc.* **2005**, *127*, 10464; (d) Kang, J.; Choi, M.; Kwon, J. Y.; Lee, E. Y.; Yoon, J. *J. Org. Chem.* **2002**, *67*, 4384.
7. (a) Cheung, S.-M.; Chan, W.-H. *Tetrahedron* **2006**, *62*, 8379; (b) Ishikawa, J.; Sakamoto, H.; Nakao, S.; Wada, H. *J. Org. Chem.* **1999**, *64*, 1913; (c) Liu, L.; Zhang, G.; Xiang, J.; Zhang, D.; Zhu, D. *Org. Lett.* **2008**, *10*, 4581; (d) Liu, L.; Zhang, D.; Zhang, G.; Xiang, J.; Zhu, D. *Org. Lett.* **2008**, *10*, 2271; (e) Yuan, M.; Li, Y.; Li, J.; Li, C.; Liu, X.; Lv, J.; Xu, J.; Liu, H.; Wang, S.; Zhu, D. *Org. Lett.* **2007**, *9*, 2313; (f) Yang, J.-S.; Lin, Y.-D.; Chang, Y.-H.; Wang, S.-S. *J. Org. Chem.* **2005**, *70*, 6066.
8. Lee, S. J.; Jung, H. J.; Seo, J.; Yoon, I.; Park, K.-M.; Lindoy, L. F.; Lee, S. S. *Org. Lett.* **2006**, *8*, 1641.
9. (a) Lee, S. J.; Lee, J.-E.; Seo, J.; Jeong, I. Y.; Lee, S. S.; Jung, J. H. *Adv. Funct. Mater.* **2007**, *17*, 3441; (b) Lee, S. J.; Lee, S. S.; Jeong, I. Y.; Lee, J. Y.; Jung, J. H. *Tetrahedron Lett.* **2007**, *48*, 393; (c) Lee, S. J.; Bae, D. R.; Han, W. S.; Lee, S. S.; Jung, J. H. *Eur. J. Inorg. Chem.* **2008**, 1559.
10. (a) Raker, J.; Glass, T. E. *J. Org. Chem.* **2001**, *66*, 6505; (b) Tong, H.; Wang, L. X.; Jing, X. B.; Wang, F. S. *Macromolecules* **2002**, *35*, 7169; (c) Singh, P.; Kumar, S. *Tetrahedron* **2006**, *62*, 6379; (d) Schmittel, M.; Lin, H. W. *Inorg. Chem.* **2007**, *46*, 9139; (e) Xu, S.; Li, W.; Chen, K. C. *Chin. J. Chem.* **2007**, *25*, 778; (f) Zhu, X.; Fu, S.; Wong, W.-K.; Wong, W.-Y. *Tetrahedron Lett.* **2008**, *49*, 1843.
11. (a) Gale, P. A. *Acc. Chem. Res.* **2006**, *39*, 465; (b) Yoon, J.; Kim, S. K.; Singh, N. J.; Kim, K. S. *Chem. Soc. Rev.* **2006**, *35*, 355; (c) Gunnlaugsson, T.; Glynn, M.; Tocci, G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094; (d) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486; (e) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609; (f) Ojida, A.; Miyahara, Y.; Wongkongkatep, J.; Tamaru, S.-I.; Sada, K.; Hamachi, I. *Chem. -Asian. J.* **2006**, *1*, 555; (g) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419; (h) Gong, W.-T.; Harigae, J.; Seo, J.; Lee, S. S.; Hiratani, K. *Tetrahedron Lett.* **2008**, *49*, 2268.
12. (a) Sancenón, F.; Descalzo, A. B.; Martínez-Máñez, R.; Miranda, M. A.; Soto, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2640; (b) Sancenón, F.; Martínez-Máñez, R.; Soto, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1416; (c) Descalzo, A. B.; Martínez-Máñez, R.; Radeglia, R.; Rurack, K.; Soto, J. *J. Am. Chem. Soc.* **2003**, *125*, 3418; (d) Jiménez, D.; Martínez-Máñez, R.; Sancenón, F.; Ros-Lis, J. V.; Soto, J.; Benito, Á.; García-Breijo, E. *Eur. J. Inorg. Chem.* **2005**, 2393.
13. Ishikawa, J.; Sakamoto, H.; Wada, H. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1273.
14. *Synthesis of* $\mathbf{L^1}$. 9-Chloromethylanthracene (0.71 g, 3.1 mol), compound **2** (1.0 g, 3.1 mmol), and $AlCl_3$ (0.41 g, 3.1 mmol) were dissolved in dry $CHCl_3$ (50 mL) at 0 °C. The solution was refluxed under stirring overnight. After the reaction was completed (monitoring by TLC) the solution was cooled and washed with three 80 mL portions of water. The organic portion was dried over Na_2SO_4. After evaporation of the solvent, crude product was subjected to column chromatography (SiO_2; 5% ethyl acetate/*n*-hexane) and yielded pure $\mathbf{L^1}$ as light yellow solid (0.65 g, 41%). Mp 154–155 °C. $C_{31}H_{35}NO_2S_2$ (517.8): Anal. Calcd: C, 71.91; H, 6.81; N, 2.71; S, 12.39. Found: C, 72.02; H, 6.63; N, 2.75; S, 12.08. IR (KBr) 3053, 2920, 2854, 1609, 1515, 1444, 1349, 1281, 1130, 1099, 734, 661 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.23–8.26 (m, 2H), 7.99–8.03 (m, 2H), 7.42–7.46 (m, 4H), 6.96 (d, 2H, J = 8.6 Hz), 6.46 (d, 2H, J = 8.6 Hz), 4.89 (s, 2H), 3.74 (t, 4H, J = 5.1 Hz), 3.60 (s, 4H), 3.50 (t, 4H, J = 7.7 Hz), 2.79 (t, 4H, J = 7.7 Hz), 2.69 (t, 4H, J = 5.1 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.1, 132.8, 131.7, 130.5, 129.1, 129.1, 128.4, 126.2, 125.7, 125.0, 124.9, 111.9, 74.3, 29.5, 70.7, 51.9, 32.4, 31.1 ppm. ESI-MS m/z (MH^+) 518.7 (calcd 518.2). *Synthesis of* $\mathbf{L^2}$. The synthetic procedure was almost the same as for $\mathbf{L^1}$ except for the use of compound **3**. Column chromatography (SiO_2; 20% dichloromethane/*n*-hexane) afforded the product as a pale yellow solid (0.84 g, 49%). Mp 90–91 °C. $C_{29}H_{33}NS_2$ (459.7): Anal. Calcd: C, 75.77; H, 7.24; N, 3.05; S, 13.95. Found: C, 75.85; H, 7.54; N, 3.17; S, 13.72. IR (KBr) 3046, 2960, 2918, 1609, 1515, 1443, 1391, 1344, 1281, 1176, 1140, 724, 687 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.20–8.24 (m, 2H), 7.97–8.00 (m, 2H), 7.40–7.43 (m, 4H), 6.95 (d, 2H, J = 8.6 Hz), 6.46 (d, 2H, J = 8.6 Hz), 4.89 (s, 2H), 3.38 (t, 4H, J = 7.5 Hz), 2.59 (t, 4H, J = 7.5 Hz), 2.47(q, 4H, J = 7.4 Hz), 1.18 (t, 6H, J = 7.4 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ 145.1, 132.7, 131.8, 130.5, 129.2, 129.2, 128.9, 126.4, 125.8, 125.06, 124.9, 111.9, 51.6, 32.5, 28.9, 26.3, 15.1 ppm. ESI-MS m/z (MH^+) 460.8 (calcd 460.2).
15. Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229.
16. a Stability constants were obtained using the computer program ENZFITTER, available from Elsevier-BIOSOFT, 68 Hills Road, Cambridge CB2 1LA, United Kingdom.; (b) Connors, K. A. *Binding Constants*; Wiley: New York, 1987.
17. (a) Nolan, E. M.; Lippard, S. J. *Chem. Rev.* **2008**, *108*, 3443; (b) Goldsmith, C. R.; Lippard, S. J. *Inorg. Chem.* **2006**, *45*, 6474; (c) Nolan, E. M.; Jaworski, J.; Racine, M. E.; Sheng, M.; Lippard, S. J. *Inorg. Chem.* **2006**, *45*, 9748; (d) Nolan, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 14270; (e) Nolan, E. M.; Lippard, S. J. *J. Mater. Chem.* **2005**, *7*, 4943.
18. (a) Gunnlaugsson, T.; Lee, T. C.; Parkesh, R. *Org. Lett.* **2003**, *5*, 4065; (b) Gunnlaugsson, T.; Lee, T. C.; Parkesh, R. *Tetrahedron* **2004**, *60*, 11239.
19. (a) Shortreed, M.; Kopelman, R.; Kuhn, M.; Hoyland, B. *Anal. Chem.* **1996**, *68*, 1414; (b) Song, K.-C.; Kim, M. H.; Kim, H. J.; Chang, S.-K. *Tetrahedron Lett.* **2007**, *48*, 7464.
20. (a) Ungaro, R.; Casnati, A.; Ugozzoli, F.; Pochini, A.; Dozol, J.-F.; Hill, C.; Rouquette, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1506; (b) Ikeda, A.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 3102; (c) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303.
21. Ishikawa, J.; Sakamoto, H.; Nakamura, M.; Doi, K.; Wada, H. *J. Chem. Soc., Dalton Trans.* **1999**, 191.