Inorganic Chemistry
Article

Inorg. Chem. **2009**, *48*, 11677–11684 **11677**
DOI: 10.1021/ic9016933

Terphenyl Derivatives as “Turn On” Fluorescent Sensors for Mercury

Vandana Bhalla,* Ruchi Tejpal, Manoj Kumar, and Amandeep Sethi

Department of Chemistry, UGC Sponsored-Centre for Advance Studies-I, Guru Nanak Dev University, Amritsar-143005, Punjab, India

Received August 26, 2009

New terphenyl-based reversible receptors **1**−**4** with pyrene and quinoline as the fluorophores have been designed, synthesized, and examined for their cation recognition abilities toward various cations (Sm^{3+}, Nd^{3+}, Pb^{2+}, Hg^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Mg^{2+}, Na^{+}, and Li^{+}) by UV−vis, fluorescence, and NMR spectroscopy. The prepared receptors showed the highly selective and sensitive “Off−On” fluorescence signaling behavior for Hg^{2+} ions in THF and mixed aqueous media (THF:H_2O, 9.5:0.5).

Introduction

Cations play an important role in a wide range of chemical reactions, including biological metabolism as well as many other processes.[1] Much attention has been focused on the development of chemosensors for the selective and efficient detection of these biologically and chemically important species. Among heavy and soft metal ions, mercury is considered highly toxic as elemental and ionic mercury can be converted into methyl mercury by bacteria in the environment, which enters the food chain and accumulates in higher organisms.[2] Mercury contamination also occurs through a variety of natural and soft metal anthropogenic sources[3], including oceanic and volcanic emission,[3,4] gold mining,[5] solid waste incineration, and combustion of fossil fuels.[6] The U.S. Environmental Protection Agency (EPA) standard for the maximum allowable level of inorganic mercury in drinking water is 2 ppb.[6] Thus, considering the ill effects of mercury in day-to-day life, there is the need to develop an approach for simple and rapid tracking of mercury ions in biological, toxicological, and environmental monitoring. Sensors based on the metal ion-induced changes in fluorescence appear to be particularly attractive and are one of the first choices because of the simplicity and high detection limit of fluorescence.[7] Thus, designing fluorescent sensors for mercury[8] has drawn worldwide attention. Generally, mercury is known to cause fluorescence quenching of fluorophores via the spin−orbit coupling[9] effect. Fluorescence quenching is not only disadvantageous for a high signal output upon recognition but also hampers temporal separation of spectrally similar complexes with time-resolved fluorometry.[10] However, the sensors that show fluorescence enhancement on binding to the cation of interest are preferred because these allow a lower detection limit and high-speed spatial resolution via microscope imaging.[11,12] However, designing of fluorescence “Turn On” type sensors upon mercury binding is a challenging issue, and only a few fluorescence “Turn On” sensors for mercury have been reported.[13] One of the approaches to this phenomenon would be design of a receptor having an “Off” state of the fluorophore,

---

*To whom correspondence should be addressed. E-mail: vanmanan@yahoo.co.in.

(1) (a) Valeur, B.; Leray, I. *Coord. Chem. Rev*. **2000**, *205*, 3. (b) Vazquez, M.; Fabbrizzi, L.; Taglietti, A.; Pedriodo, R. M.; Gonzalez-Noya, A. M.; Bermazo, M. R. *Angew. Chem., Int. Ed*. **2004**, *43*, 1962. (c) He, Q.; Miller, E. W.; Wong, A. P.; Chang, C. J. *J. Am. Chem. Soc*. **2006**, *128*, 9316.

(2) (a) Renzoni, A.; Zino, F.; Franchi, E. *Environ. Res*. **1998**, *77*, 68. (b) Boening, D. W. *Chemosphere* **2000**, *40*, 1335. (c) Harris, H. H.; Pickering, I. J.; George, G. N. *Science* **2003**, *301*, 1203.

(3) Benoit, J. M.; Fitzgerald, W. F.; Damman, A. W. *Environ. Res*. **1998**, *78*, 118.

(4) Benzoni, A.; Zino, F.; Franchi, E. *Environ. Res*. **1998**, *77*, 68.

(5) Malm, O. *Environ. Res*. **1998**, *77*, 73.

(6) *Mercury Update: Impact on Fish Advisories*; EPA Fact Sheet EPA-823-F-01−001; Environmental Protection Agency, Office of Water: Washington, DC, 2001.

(7) (a) Callan, J. F.; de Silva, A. P.; Magri, D. C. *Tetrahedron* **2005**, *61*, 8551. (b) Martķnez-Máñez, R.; Sancenón, F. *Chem. Rev*. **2003**, *103*, 4419. (c) 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. (d) Czarnik, A. W. *Acc. Chem. Res*. **1994**, *27*, 302. (e) Kim, J. S.; Quang, D. T. *Chem. Rev*. **2007**, *107*, 3780.

(8) Valeur, B.; Leray, I. *Coord. Chem. Rev*. **2000**, *205*, 3.

(9) McClure, D. S. *J. Chem. Phys*. **1952**, *20*, 682.

(10) Rurack, K.; Resch-Genger, U.; Rettig, W. *J. Photochem. Photobiol., A*. **1998**, *118*, 143.

(11) (a) Yoon, S.; Albers, A. E.; Wong, A. P.; Chang, C. J. *J. Am. Chem. Soc*. **2005**, *127*, 16030. (b) Yoon, S.; Miller, E. W.; He, Q.; Do, P. K.; Chang, C. J. *Angew. Chem., Int. Ed*. **2007**, *46*, 6658.

(12) (a) Zhang, M.; Yu, M. X.; Li, F. Y.; Zhu, M. W.; Li, M. Y.; Gao, Y. H.; Li, L.; Liu, Z. Q.; Zhang, J. P.; Zhang, D. Q.; Yi, T.; Huang, C. H. *J. Am. Chem. Soc*. **2007**, *129*, 10322. (b) Sasaki, E.; Kojima, H.; Nishimatsu, H.; Urano, Y.; Kikuchi, K.; Hirata, Y.; Nagano, T. *J. Am. Chem. Soc*. **2005**, *127*, 3684. (c) Yang, D.; Wang, H. L.; Sun, Z. N.; Chung, N. W.; Shen, J. G. *J. Am. Chem. Soc*. **2006**, *128*, 6004. (d) Lim, N. C.; Freake, H. C.; Bruckner, C. *Chem.—Eur. J*. **2005**, *11*, 38. (e) Zhang, G.; Zhang, D.; Yin, S.; Yang, X.; Shuai, Z.; Zhu, D. *Chem. Comm*. **2005**, 2161. (f) Liu, L; Zhang, G; Xiang, J; Zhang, D; Zhu, D. *Org. Lett*. **2008**, *10*, 4581. (g) Wang, C.; Zhang, D.; Zhang, G.; Xiang, J.; Zhu, D. *Chem.—Eur. J*. **2008**, *14*, 5680.

which upon addition of an external analyte causes fluorescence enhancement by turning "On" the fluorescence.

Our research involves the design, synthesis, and evaluation of thia(calix)[4]arene-based receptors for selective sensing of soft metal ions[14] and anions[15] of biological and environmental interest. We recently reported a ratiometric fluorescent sensor for mercury based on a partial cone conformation of the calix[4]arene, which behaves as a NOR logic gate with a YES logic function[16], and we also reported a "Turn On" fluorescent sensor based on terphenyl appended with pyrene moieties, which exhibits a high binding affinity for mercury.[17] Terphenyls have attracted attention because of a wide range of significant biological activities, e.g., potent immunosuppressant, neuroprotective, antithrombotic, anticoagulant, specific 5- lipoxygenase inhibitory, and cytotoxic activities.[18] These are also being used as key intermediates for the synthesis of symmetrically and unsymmetrically substituted triphenylenes, which have great potential for supramolecular and material chemistry as their liquid crystalline behavior can be modified by changing electronic properties of their substituents. Besides, terphenyls can also be used as building blocks for kinked polyphenylenes.[19] Oligo and polyphenylenes are known to play an important role in academic research as well as industrial applications because of their useful mechanical and optoelectronic properties.[20] Lehmann and co-workers reported crown-5 appended terphenyl, which shows mesomorphic properties in the presence of Na^+ ions.[21] Thus, in continuation of our work, we have now designed and synthesized three new mercury selective fluorescent sensors based on terphenyls, which have pyrene and quinoline moieties as fluorophores. We have chosen pyrene and quinoline as the fluorophores because of their high detection sensitivity.[22] The framework of receptor **2** comprises a quinoline unit as a fluorophore, which is introduced to increase the soft metal binding sites in comparison to the receptor reported earlier.[17] We also synthesized receptors **3** and **4**, having the crown-5 ring in addition to imine moieties to have "On−Off" switchable binuclear chemosensors. Moreover, the electrons on the oxygen atoms of this crown ring are expected to enhance the photoinduced electron transfer (PET)[23] to the fluorophore moiety, which will make the receptor very weakly fluorescent, and the percentage enhancement of fluorescence will be more on coordinating with the specific metal ion. In fact, the results show that the percentage enhancement of fluorescence on binding Hg^{2+} is more in case of those receptors that have a crown ring. All of these receptors are easy to prepare in high yield and are selective for Hg^{2+} over a wide range of metal ions like Sm^{3+}, Nd^{3+}, Pb^{2+}, Hg^{2+}, Ba^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, K^+, Mg^{2+}, Na^+, and Li^+ in comparison to the mercury sensors reported in the literature.[13i−k] Mercury ion selective electrodes[24] have also been formed with one of these receptors, which show excellent selectivity over all other metal ions tested. The results of these studies will be published elsewhere.

Results and Discussion

Terphenyl-based receptors **1−4** were prepared from precursors **7**[17] (Figures S10, S11, and S19 of the Supporting Information) and **9**, respectively (Scheme 1). Suzuki−Miyaura cross coupling of boronic ester **6** (Figures S9 and S18 of the Supporting Information) with **8**[21] catalyzed by Pd (II) furnished compound **9** in 55% yield. The ^{1}H NMR spectrum of compound **9** showed one singlet and two triplets (8H, 4H, 4H) for crown protons, one broad signal for amino (NH_2) protons, and two multiplets and one singlet (4H, 4H, 2H) for aromatic protons of terphenyl moiety (Figures S13 and S14 of the Supporting Information). The FAB mass spectrum showed a parent ion peak at 450 (M^+) corresponding to coupled product **9** (Figure S20 of the Supporting Information).

Condensation of diamine **7**[17] with 2-pyrene carboxaldehyde and 2-quinoline carboxaldehyde in ethanol at room temperature for 2 h gave compound **1** and **2** in 75% and 85% yields, respectively. Products **1** and **2** were separated as pure solids, which gave a satisfactory elemental analysis. The structures of compounds **1** and **2** were confirmed from their spectroscopic and analytical data. In the ^{1}H NMR spectrum, compound **2** showed two singlets (18H, 12H) for the *tert*-butyldimethylsilyl (TBS) group, one singlet and two doublets (2H, 4H, 4H) for aromatic protons of terphenyl moiety, four doublets (2H, 2H, 2H, 2H) and two triplets (2H, 2H) for quinoline protons, and one singlet (2H) for imine protons (N═CH) (Figures S3 and S4 of the Supporting Information). In the IR absorption spectrum, an absorption band appeared at 1632 cm^{-1} due to the C═N group, and there was no band corresponding to the free aldehyde and amino group, which indicates that condensation has taken place. This was confirmed by the FAB mass spectrum, which showed a parent ion peak at 799 (M^+) corresponding to the condensation product (Figure S15 of the Supporting Information). Using the same procedure, we prepared terphenyl receptors **3** and **4** by condensing diamine **9** with 1-pyrene carboxaldehyde

---

(13) (a) Nolan, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **2007**, *129*, 5910. (b) He, G.; Zhao, Y.; He, C.; Liu, Y.; Duan, C. *Inorg. Chem.* **2008**, *47*, 5169. (c) Liu, B.; Tian, H. *Chem. Commun.* **2005**, 3156. (d) Coskun, A.; Akkaya, E. U. *J. Am. Chem. Soc.* **2006**, *128*, 14474. (e) Lu, Z. J.; Wang, P. N.; Zhang, Y.; Chen, J. Y.; Zhen, S.; Leng, B.; Tian, H. *Anal. Chim. Acta* **2007**, *597*, 306. (f) Zhang, H.; Wang, Q. L.; Jiang, Y. B. *Tetrahedron. Lett.* **2007**, *48*, 3959. (g) Wang, J. B.; Qian, X. H. *Chem. Commun.* **2006**, 109. (h) Guo, X. F.; Qian, X. H.; Jia, L. H. *J. Am. Chem. Soc.* **2004**, *126*, 2272. (i) Ábalos, T.; Jiménez, D.; Martķnez-Máñez, R.; Ros-Lis, J. V.; Royo, S.; Sancenón, F.; Soto, J.; Costero, A. M.; Gil, S.; Parra, M. *Tetrahedron. Lett.* **2009**, *50*, 3885. (j) Wang, J.; Qian, X.; Cui, J. *J. Org. Chem.* **2006**, *71*, 4308. (k) Zhang, H.; Han, L. F.; Zachariasse, K.; Jiang, Y. B. *Org. Lett.* **2005**, *7*(19), 4217.

(14) (a) Kumar, R.; Bhalla, V.; Kumar, M. *Tetrahedron* **2008**, *64*, 8095. (b) Bhalla, V.; Kumar, R.; Dhir, A. *Tetrahedron* **2007**, *63*, 11153. (c) Bhalla, V.; Babu, J. N.; Kumar, M.; Hattori, T.; Miyano, S. *Tetrahedron Lett.* **2007**, *48*, 1581. (d) Bhalla, V.; Kumar, M.; Katagiri, H.; Hattori, T.; Miyano, S. *Tetrahedron Lett.* **2005**, *46*, 121. (e) Dhir, A.; Bhalla, V.; Kumar, M. *Org. Lett.* **2008**, *10*, 4891. (f) Dhir, A.; Bhalla, V.; Kumar, M. *Tetrahedron Lett.* **2008**, *49*, 4227.

(15) (a) Babu, J. N.; Bhalla, V.; Kumar, M.; Mahajan, R. K.; Puri, R. K. *Tetrahedron Lett.* **2008**, *49*, 2772. (b) Babu, J. N.; Bhalla, V.; Kumar, M.; Singh, H. *Lett. Org. Chem.* **2006**, *3*, 787.

(16) Dhir, A; Bhalla, V.; Kumar, M. *Org. Lett.* **2008**, *10*, 4891.

(17) Bhalla, V.; Tejpal, R.; Kumar, M.; Puri, R. K.; Mahajan, R. K. *Tetrahedron Lett.* **2009**, *50*(22), 2649.

(18) Liu, J. K. *Chem. Rev.* **2006**, *106*, 2209.

(19) Kissel, P.; Breitler, S.; Reinmuller, V.; Lanz, P.; Federer, L.; Schluter, A. D.; Sakamoto, J. *Eur. J. Org. Chem.* **2009**, *18*, 2953.

(20) See the following reviews for example: (a) List, E.; Jachim, W.; Scherf, U. In *Handbook of Conducting Polymers*, 3rd ed.; CRC Press LLC: Boca Raton, FL, 2007; vol. *1*, pp 5/1−5/35.(b) Grimsdale, A. C.; Müllen, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5592. (c) Wegner, G. *Macromol. Chem. Phys.* **2003**, *204*, 347. (d) Schluter, A. C. *J. Polym. Sci.* **2001**, *39*, 1533.

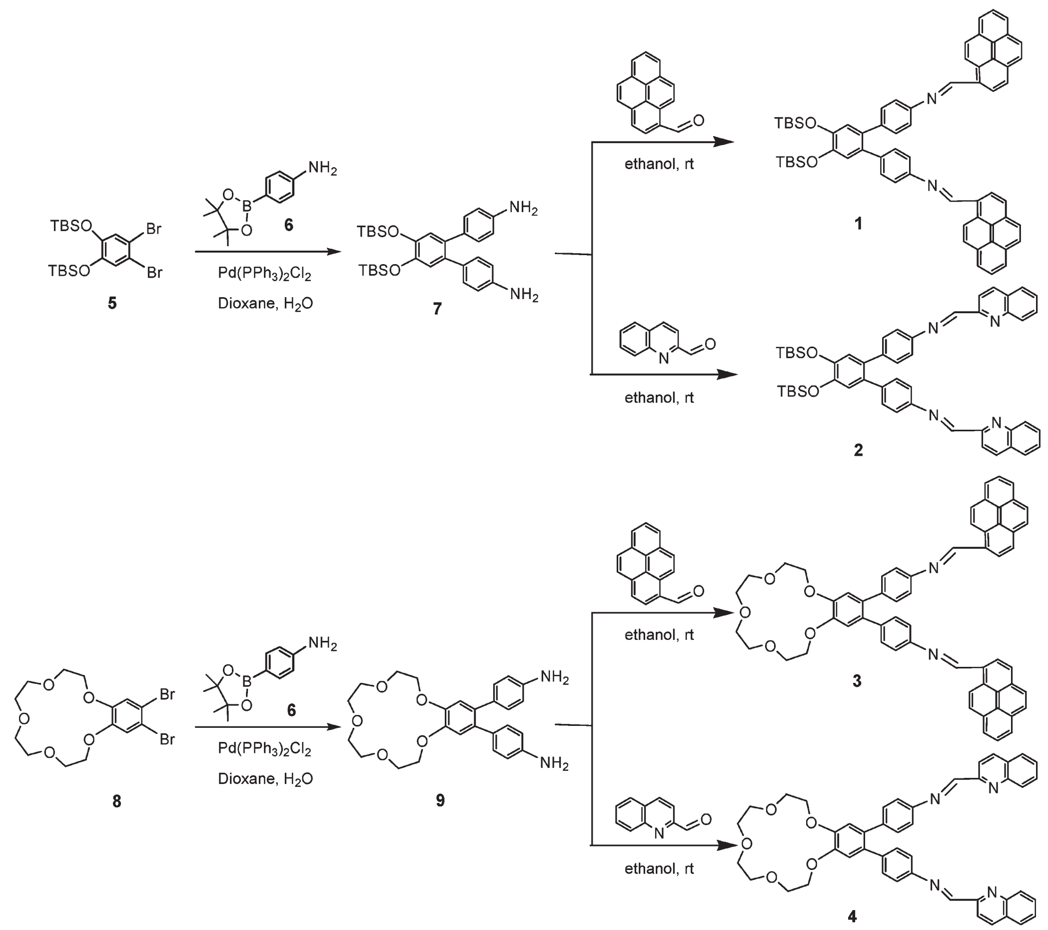
(21) Steinke, N.; Jahr, M.; Lehmann, M.; Baro, A.; Frey, W.; Tussetschlager, S.; Sauer, S.; Laschat, S. *J. Mater. Chem.* **2009**, *19*, 645.

(22) Winnik, F. M. *Chem. Rev.* **1993**, *93*, 587.

(23) (a) Aoki, I.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1992**, 730. (b) Bu, J. H.; Zheng, Q. Y.; Chen, C. F.; Huang, Z. T. *Org. Lett.* **2004**, *6*, 3301.

(24) The results will be published elsewhere.

Scheme 1. Synthesis of Receptors **1**, **2**, **3**, and **4**



and 2-quinoline carboxaldehyde in 74% and 77% yields, respectively. Receptors **3** and **4** contain the crown-5 ring and imine moieties as metal ion binding sites, whereas receptors **1** and **2** contain only imine moieties as metal ion binding sites. The ^{1}H NMR spectra of receptors **3** and **4** showed one singlet and two triplets (8H, 4H, 4H) for crown protons, one singlet and two doublets (2H, 4H, 4H) for aromatic protons of terphenyl moiety, and one singlet (2H) for the imine proton (N=CH). Also there were one multiplet and two doublets (14H, 2H, 2H) for the pyrene group in **3** and four doublets (2H, 2H, 2H, 2H) and two triplets (2H, 2H) for quinoline protons in **4** (Figures S5−S8 of the Supporting Information). This was confirmed by the FAB mass spectra, which showed a parent ion peak at 875 (M^+) and 729 (M^+) corresponding to condensation products **3** and **4**, respectively (Figures S16 and S17 of the Supporting Information). These spectroscopic data corroborate with structures **2**, **3**, and **4** for these compounds.

To evaluate the binding abilities of terphenyl receptors **1**−**4** toward different cations, we carried out UV−vis, fluorescence, and NMR experiments and prepared solid-state ion electrodes in two cases.[24] The titration experiments were carried out in THF and mixed aqueous media (THF:H_2O, 9.5:0.5) by adding aliquots of different metal ions.

Binding Studies. The UV−vis titration experiments were carried by adding aliquots of different metal ions (Sm^{3+}, Nd^{3+}, Pb^{2+}, Hg^{2+}, Ba^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, K^+, Mg^{2+}, Na^+, and Li^+) as their perchlorate/nitrate salts (Figures S22−S32 of the Supporting Information). The absorption spectrum of compound **2** (1×10^{-5} M) in THF exhibited a strong band at 354 nm (Figure 1). Upon addition of Hg^{2+} ions (0−3.0 equiv) to the solution of receptor **2**, the absorption band at 354 nm decreases and a new redshifted band (63 nm) is formed at 417 nm.

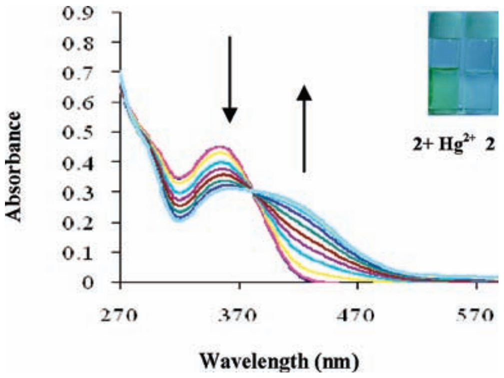


Figure 1. UV−vis spectra of receptor **2** (10 μM) in the presence of Hg^{2+} ions (0.1−3.0 μM) in THF. Inset shows the change in color of receptor **2** (1×10^{-5} M) upon addition of Hg^{2+} ions (3.0 μM).

The formation of new band at 417 nm is attributed to the interaction of these ions with the imino nitrogens leading to the intramolecular charge transfer (ICT)[25]

---

[25] (a) Valeur, B. *Molecular Fluorescence: Principles and Applications*; Wiley-VCH: Weinheim, Germany, 2001; pp 337−350. (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.

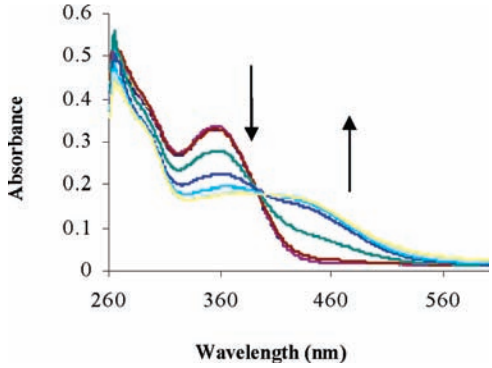


Figure 2. UV−vis spectra of receptor **4** (10 μM) in the presence of Hg^{2+} ions (0.1−3.0 μM) in THF.

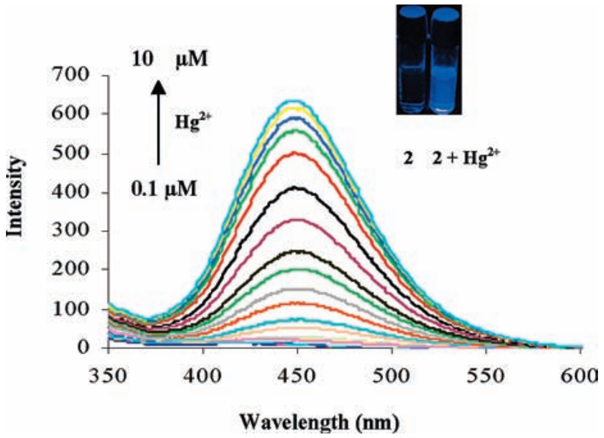


Figure 3. Fluorescence response of receptor **2** (1 μM) on addition of Hg^{2+} (0.1−10 μM) in THF, λ_{ex} = 310 nm. Inset shows the emission intensity of **2** (1×10^{-5} M) at 365 nm as a function of Hg^{2+} ions.

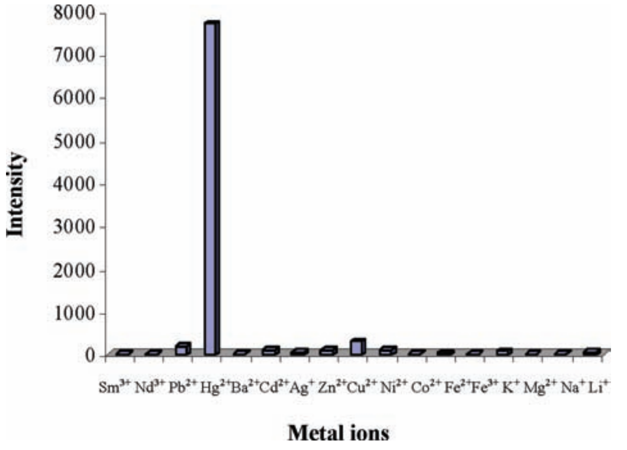


Figure 4. Fluorescence enhancement ratio (I−Io/Io) × 100 of receptor **2** (1 μM) at 310 nm upon addition of different metal ions (10 equiv, 10 μM) in THF.

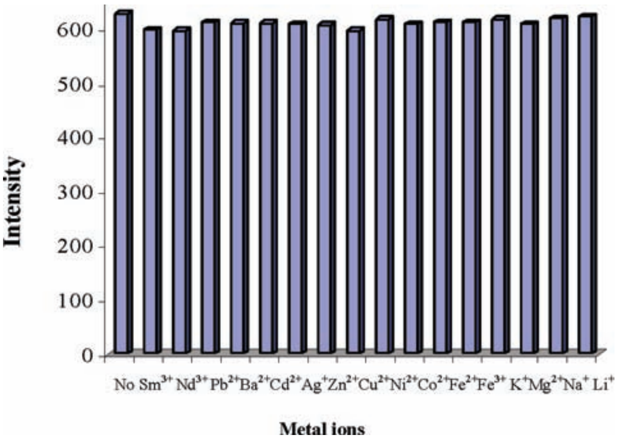


Figure 5. Competitive selectivity of receptor **2** (1.0 μM) toward Hg^{2+} ions (10 μM) in the presence of other metal ions (100 μM).

from the quinoline moiety to the imino group. An obvious color change from colorless to pale yellow was observed by the naked eye. A clear isosbestic point at 393 nm is observed in absorption spectra, indicating the formation of a well-defined **2**−Hg^{2+} complex (Figure 1). Similarly UV−vis experiments were carried out for compound **4** with different metal ions (Sm^{3+}, Nd^{3+}, Pb^{2+}, Hg^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Mg^{2+}, Na^{+}, and Li^{+}) (Figures S38−S48 of the Supporting Information). A more pronounced redshift of 80 nm was observed on addition of Hg^{2+} ions (0−3.0 equiv) to a solution of compound **4**, which contains a crown-5 ring in addition to a quinoline unit (Figure 2). However, no change is observed in the UV−vis spectrum of compound **3** on addition of various metal ions, which exhibited an absorption band at 397 nm. In the fluorescence spectrum, compound **2** exhibited very weak fluorescence emission at 415 nm in THF. The weak fluorescence emission is due to photoinduced electron transfer (PET) from imino nitrogen atoms to the photoexcited quinoline moiety (non-radiative channel from the nπ* state of the emission of the quinoline groups by the lone pair of electrons of the imine nitrogen atoms). Upon addition of increasing amounts of Hg^{2+} ions (0.1−10 μM) to the solution of compound **2** in THF, a remarkable 5000% enhancement with a redshift (38 nm) in the emission maximum from 415 to 453 nm was observed (Figure 3). While in the case of compound **1**, 375% fluorescence enhancement was observed upon adding Hg^{2+} ions to the solution of compound **1**.[17]

Fluorescence enhancement observed for compound **2** is attributed to the formation of the **2**−Hg^{2+} complex as a result of which the PET from imino nitrogen to the photoexcited quinoline moiety is suppressed (the energy of the nπ* state of the emission is increased and that of $\pi\pi$* state of the emission of the quinoline group become the lowest excited state), resulting in the fluorescent enhancement. Under the same condition as used above for Hg^{2+}, we also tested the fluorescence response of compound **2** to other metal ions (Sm^{3+}, Nd^{3+}, Pb^{2+}, Hg^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Mg^{2+}, Na^{+}, and Li^{+}), and as shown in Figure 4, a negligible change in fluorescence occurred in the presence of these metal ions (Figures S33−S37 of the Supporting Information). Further, to check the practical applicability of compound **2** as a Hg^{2+} selective fluorescent sensor, we carried out competitive experiments in the presence of Hg^{2+} at 10 μM mixed with Sm^{3+}, Nd^{3+}, Pb^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Mg^{2+}, Na^{+}, and Li^{+} at 100 μM. As shown in Figure 5, no significant variation in the fluorescence intensity change was found by comparison with or without the other metal ions. The detection limit of compound

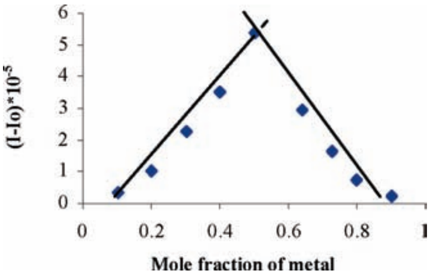


Figure 6. Job's plot for determining the stoichiometry of receptor **2** and Hg^{2+} ion in THF.

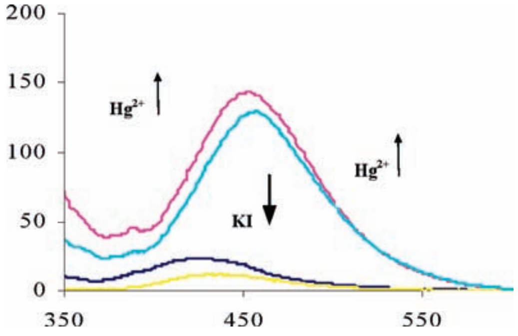


Figure 7. Reversibility of Hg^{2+} coordination to **2** by KI: yellow line, free **2** (1 M); pink line, **2** + 5 equiv Hg^{2+}; blue line, **2** + 5 equiv Hg^{2+} + 100 equiv KI; and sky blue line, **2** + 5 equiv Hg^{2+} + 100 equiv KI + 20 equiv Hg^{2+}.

2 as a fluorescent sensor for the analysis of Hg^{2+} ions was found to be 1×10^{-7} M, which is sufficiently low for the detection of submillimolar concentrations of Hg^{2+} ions as found in many chemical systems.

Fitting the changes in fluorescence spectra of compound **2** with Hg^{2+} ions, using the nonlinear regression analysis program SPECFIT[26] gave a good fit and demonstrated that 1:1 stoichiometry (host:guest) was the most stable species in the solution with the binding constant $(\log \beta) = 4.71$. The method of continuous variation (Job's plot) was also used to prove the 1:1 stoichiometry (host: guest) (Figure 6).

The fluorescence quantum yield[27] (Φ_F) of compound **2** in the free and Hg^{2+}-bound state was found to be 0.001 and 0.45, respectively. The substantial increase in the quantum yield of compound **2** in the presence of 10 μM of Hg^{2+} ions and its high Hg^{2+} selectivity showed its credibility as a good Hg^{2+} sensor. We also carried out a reversibility experiment that proved that Hg^{2+} binding to compound **2** is reversible. In the presence of 100 equiv of KI, the iodide ion, because of its strong affinity for the Hg^{2+}ion, forms a complex with it, which results in decomplexation of the receptor Hg^{2+} complex, i.e., Hg^{2+} ions are not available to bind with the imino nitrogen atoms of the receptors as a result of which the PET phenomena from imino nitrogen will be operative, which will quench the fluorescence emission (Figure 7). The binding of Hg^{2+} ions with compound **2** has also been confirmed by NMR spectroscopy as there is a considerable downfield shift of imino protons by δ 1.2 ppm (Figure 8). The corroborative evidence for the **2**$-Hg^{2+}$ complex is observed in the mass spectrum of their solid complex, which showed mass peak at *m*/*e* 998 corresponding to [2$-Hg^{2+}$] (Figure S21 of the Supporting Information).

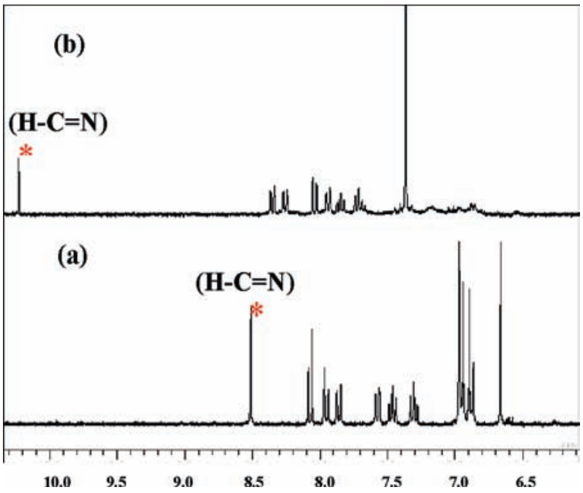


Figure 8. Partial ^{1}H NMR spectrum ($CDCl_3-CD_3CN$, 8:2) of receptor **2** (a) before and (b) after addition of Hg^{2+} ions.

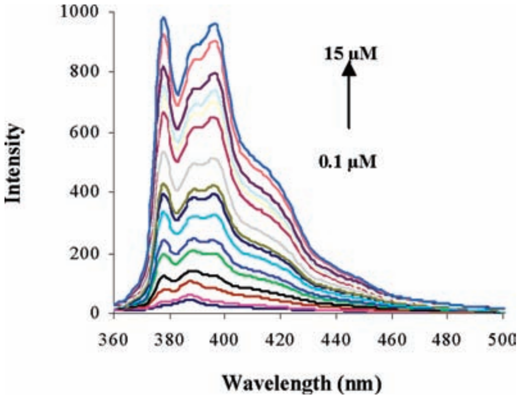


Figure 9. Fluorescence response of receptor **3** (1 μM) on addition of Hg^{2+} (0.1−15 μM) in THF/H_2O (9.5:0.5), $\lambda_{ex} = 345$ nm.

The fluorescence spectrum of compound **3**, which contains two binding sites, a crown-5 ring, and imine units, exhibited a weak monomer emission at 388 nm in THF/H_2O (9.5:0.5) as the solvent. The weak emission might be due to PET from crown oxygen to pyrene moiety. Upon addition of increasing amounts of Hg^{2+} ions (0.1−15 μM) to the solution of compound **3** in THF/H_2O (9.5:0.5), a significant increase of 1900% in the emission band attributed to the compound **3**$-Hg^{2+}$ complex was observed (Figure 9). Under the same conditions as used above for Hg^{2+}, we also tested the fluorescence response of compound **3** to other metal ions (Sm^{3+}, Nd^{3+}, Pb^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Mg^{2+}, Na^{+}, and Li^{+}) besides Hg^{2+} (Figures S49−S54 of the Supporting Information), and as shown in Figure 10, no significant fluorescence change occurred in the presence of these metal ions. The fluorescence quantum yield (Φ_F) of compound **3** in the free and Hg^{2+}-bound state was found to be 0.03 and 0.58, respectively. The practical applicability of compound **3** as a Hg^{2+} selective fluorescence sensor was tested by carrying out competitive experiments in the presence of Hg^{2+} ions

---

[26] Gampp, H.; Maeder, M.; Meyer, C. J.; Zuberbulher, A. D. *Talanta* **1985**, *32*, 95.

[27] Demas, J. N.; Grosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

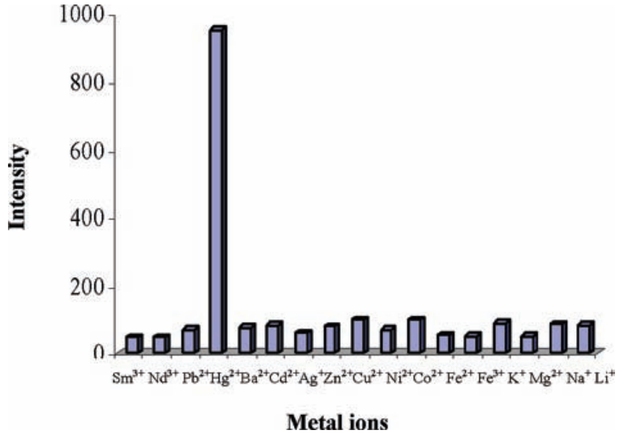


Figure 10. Fluorescence enhancement of receptor **3** (1 μM) at 345 nm upon addition of different metal ions (15equiv, 15 μM) in THF/H_2O (9.5:0.5).

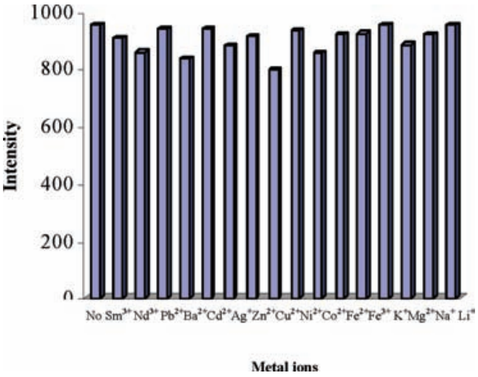


Figure 11. Competitive selectivity of receptor **3** (1.0 μM) toward Hg^{2+} ions (15 μM) in the presence of other metal ions (150 μM).

at 15 μM mixed with Sm^{3+}, Nd^{3+}, Pb^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Mg^{2+}, Na^{+}, and Li^{+} at 150 μM, and as shown in Figure 11, no significant variation in fluorescence intensity change was found by comparison with or without the other metal ions besides Hg^{2+} ions. From the titration results, the detection limit of compound **3** for the analysis of Hg^{2+} ions was estimated to be 4×10^{-8} M, which is sufficiently low for detecting Hg^{2+}. To test if the proposed complex could be reversed, we added a KI solution. The addition of 50 μM of KI could restore the fluorescent signal of compound **3** to its original level and that could be revived again on addition of Hg^{2+} (Figure 12). Further, we calculated the binding constant for the complex by a nonlinear regression analysis program SPECFIT, and the value of the binding constant (log β) was found to be 5.98. The 1:1 stoichiometry (host:guest) was confirmed by the method of continuous variation (Job's plot) (Figure 13).

Compound **4** consisting of crown-5 and quinoline also showed high binding affinity for mercury. On adding 8 μM of Hg^{2+} ions to the solution of compound **4** in THF, a 5700% increase in the emission band was observed. Besides, a considerable redshift of 26 nm in the emission band was observed (Figure 14). The fluorescence quantum yield (Φ_F) of compound **4** in the free and Hg^{2+}-bound state was found to be 0.001 and 0.58, respectively. Under the same conditions as used above for Hg^{2+}, the fluorescence enhancement effects of various metal ions (Sm^{3+}, Nd^{3+}, Pb^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Mg^{2+}, Na^{+}, and Li^{+}) on compound **4** in THF were also investigated (Figures S55−S60 of the Supporting Information).

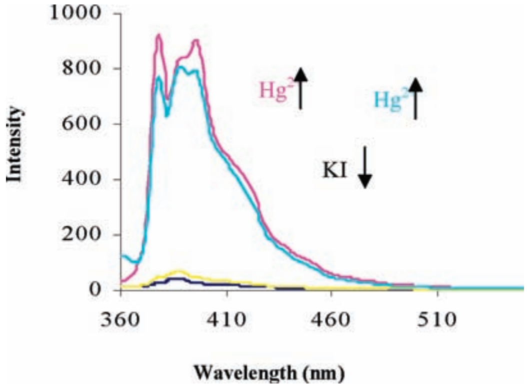


Figure 12. Reversibility of Hg^{2+} coordination to receptor **3** by KI: yellow line, free **3** (1 μM); pink line, **3** + 15 equiv Hg^{2+}; black line, **3** + 15 equiv Hg^{2+} + 100 equiv KI; and blue line, **3** + 15 equiv Hg^{2+} + 100 equiv KI + 30 equiv Hg^{2+}.

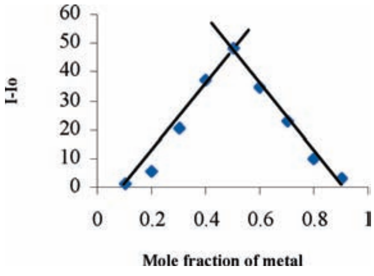


Figure 13. Job's plot for determining the stoichiometry of **3** and Hg^{2+} ion in THF/H_2O (9.5:0.5).

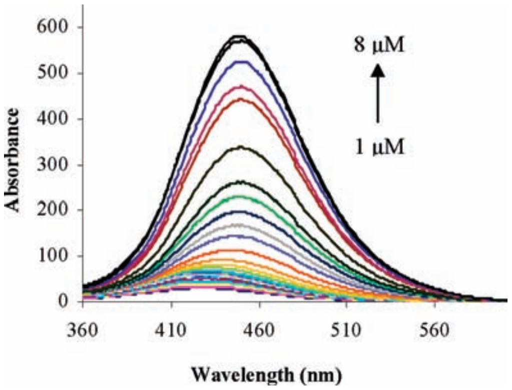


Figure 14. Fluorescence response of receptor **4** (1 μM) on addition of Hg^{2+} (0.1−8.0 μM) in THF, $\lambda_{ex} = 310$ nm.

As shown in Figure 15, no significant spectral changes of compound **4** occurred in the presence of these metal ions. The competitive experiments revealed that the Hg^{2+}-induced fluorescence responses were unaffected in the background of 100 μM of other metal ions (Figure 16). The possible interferences by other metal ions were assessed by measuring Hg^{2+}-induced fluorescence changes of compound **4** in the presence of background metal ions (Sm^{3+}, Nd^{3+}, Pb^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Mg^{2+}, Na^{+}, and Li^{+}) (Figure 16). Compound **4** was found to have a detection limit of 1×10^{-7} M for Hg^{2+} ions, which was sufficiently

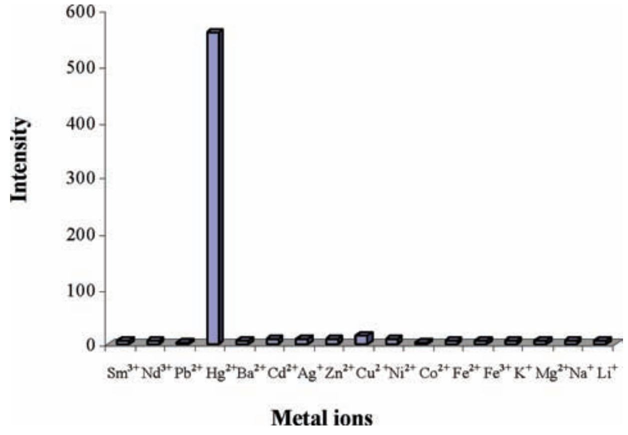


Figure 15. Fluorescence enhancement of receptor **4** (1 μM) at 310 nm upon addition of different metal ions (8 μM) in THF.

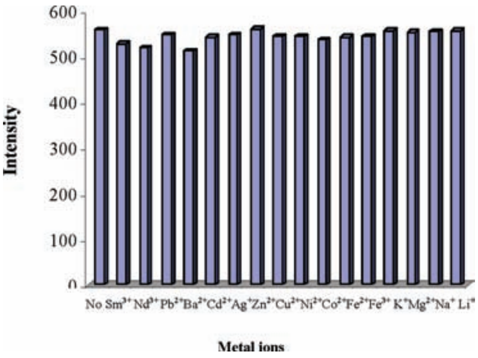


Figure 16. Competitive selectivity of receptor **4** (1.0 μM) toward Hg^{2+} ions (8 μM) in the presence of other metal ions (100 μM).

low for the detection of Hg^{2+} ions in many chemical and biological systems. Moreover, the reversibility of the Hg^{2+} binding to compound **4** was confirmed by using a KI solution (Figure 17). The method of continuous variation (Job's plot) was also used to prove the 1:1 stoichiometry (host:guest) (Figure 18). The value of the binding constant (log β) was found to be 4.57.

In conclusion, we have designed, synthesized, and evaluated three new terphenyl based "Turn On" fluorescent sensors **2**, **3**, and **4**, which showed a remarkably enhanced fluorescence intensity in the presence of Hg^{2+} ions and a high selectivity toward Hg^{2+} ions over a wide range of metal ions in THF and a mixed aqueous solvent. The background metal ions showed small or no interference with the detection of Hg^{2+} ions, indicating that the receptors could be used as an efficient Hg^{2+} selective "Turn On" fluorescent sensors, and subsequently can find practical applications in chemical and biological systems. Among these receptors, chemosensor **3** has better lower limits of detection (4×10^{-8} M) in comparison to chemosensors **1**, **2**, and **4**, which have detection limits of 2×10^{-6} M, 1×10^{-7} M, and 1×10^{-7} M, respectively. The receptors with crown moiety (**3** and **4**) further increase the fluorescence enhancement by involvement of crown oxygens in PET phenomenon, whereas in noncrown receptors (**1** and **2**), only imine units are involved in PET phenomenon. We believe that crown moiety in chemosensors **3** and **4** plays a role in the percentage enhancement of fluorescence but does not participate in the formation of a 1:1 complex as mercury ions prefer to bind with soft donor atoms present in all receptors.

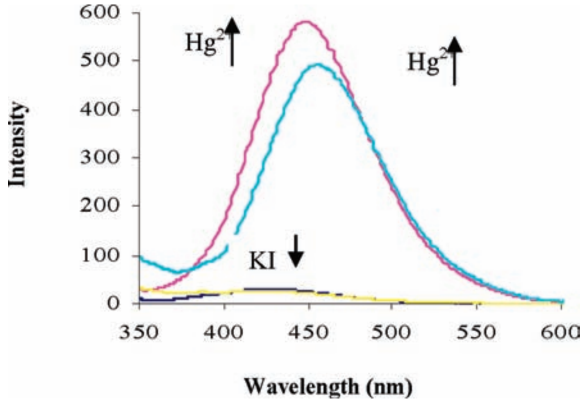


Figure 17. Reversibility of Hg^{2+} coordination to receptor **4** by KI: yellow line, free **4** (1 μM); pink line, **4** + 10 equiv Hg^{2+}; black line, **4** + 15 equiv Hg^{2+} + 50 equiv KI, and blue line; **4** + 10 equiv Hg^{2+} + 50 equiv KI + 30 equiv Hg^{2+}.

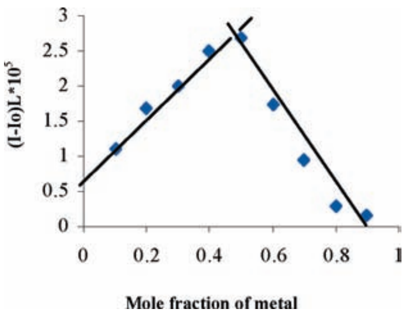


Figure 18. Job's plot for determining the stoichiometry of receptor **4** and Hg^{2+} ions in THF.

Experimental Section

General. All reagents were purchased from Aldrich and were used without further purification. THF was dried over sodium and benzophenone and kept over molecular sieves overnight before use. UV−vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length, 1 cm). The cell holder was thermostatted at 25 °C. The fluorescence spectra were recorded with a SHIMADZU 5301 PC spectrofluorimeter. ^1H and ^{13}C NMR spectra were recorded on a JEOL-FT NMR-AL 300 MHz spectrophotometer using $CDCl_3$/DMSO-d_6 as solvent and tetramethylsilane $SiMe_4$ as internal standards. UV−vis studies were performed in THF AR grade. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad singlet, m = multiplet), coupling constants J (Hz), integration, and interpretation. Silica gel 60 (60−120 mesh) was used for column chromatography. Solutions of compounds **2**, **3**, and **4** and perchlorate salts were prepared in THF.

Syntheses. Synthesis of Compounds 5, 6, and 7. Compounds **5**, **6**, and **7** were synthesized according to the literature procedure.[17]

Synthesis of Compound 2. To synthesize compound **2**, 2-quinoline carboxaldehyde (0.063 g, 0.40 mmol) was added portion-wise to a stirred solution of diamine **7** (0.10 g, 0.19 mmol) in ethanol (15 mL). The resulting reaction mixture was stirred at room temperature for 2 h, during which an off-white solid was obtained. The solid compound was filtered and then washed with ethanol (10 mL) to give 0.13 g of **2** (85%). Mp: 380 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.27 [s, 12H, $Si(CH_3)_2$], 1.14 [s, 18H, $C(CH_3)_3$)], 6.96 (s, 2H, ArH), 7.06 (d, 4H, J = 1.95 Hz, ArH), 7.22 (d, 4H, J = 1.95 Hz, ArH), 7.27 (t, 2H, J = 1.95 Hz, QuinH$_b$), 7.79 (t, 2H, J = 1.95 Hz, QuinH$_c$), 7.88 (d, 2H, J = 8.1 Hz, QuinH$_e$), 8.16 (d, 2H, $J = 8.1$ Hz, QuinH$_b$), 8.25 (d, 2H, $J = 8.1$ Hz, QuinH$_f$), 8.37 (d, 2H, $J = 8.4$ Hz, QuinH$_a$), 8.81 (s, 2H, N=CH). ^{13}C NMR: 3.94, 18.48, 25.98, 118.69, 121.04, 123.07, 127.62, 127.74, 128.87, 129.73, 129.85, 130.78, 133.13, 136.55, 140.29, 140.29, 146.29, 148.00, 148.72, 154.98, 160.31. IR ν_{max} (KBr, cm^{-1}): 1632 (C=N). MS (FAB): 799 (M$^+$), 800 (M$^+$ + 1). Anal. Calcd for $C_{50}H_{54}N_4O_2Si_2$: C, 75.15; H, 6.81; N, 7.01. Found: C, 74.91; H, 6.49; N, 6.91.

Synthesis of Coupled Product 9. To a solution of **8** (1.00 g, 2.34 mmol) and **6** (1.29 g, 5.86 mmol) in dioxane were added K_2CO_3 (0.85 g, 9.36 mmol), distilled H_2O (8 mL), and $[Pd(Cl)_2(PPh_3)_2]$ (0.36 g, 0.51 mmol) under argon, and the reaction mixture was refluxed overnight. The dioxane was then removed under vacuum, and the residue so obtained was treated with water, extracted with dichloromethane, and dried over anhydrous Na_2SO_4. The organic layer was evaporated, and the compound was purified by column chromatography using ethyl acetate as an eluent to give 0.58 g (55%) of compound **9** as white solid. Mp: 220 °C. ^{1}H NMR: δ 3.78 (s, 8H, crownH), 3.92 (t, 4H, $J = 4.5$ Hz, crownH), 4.18 (t, 4H, $J = 4.5$ Hz, crownH), 6.54 (m, 4H, ArH), 6.86 (s, 2H, ArH), 6.90 (m, 4H, ArH). ^{13}C NMR: 68.63, 68.91, 69.76, 70.25, 113.68, 115.89, 129.61, 129.88, 129.88, 133.03, 145.69, 146.99. MS (FAB): 450 (M$^+$). Anal. Calcd for $C_{26}H_{30}N_2O_5$: C, 69.31; H, 6.71; N, 6.22. Found: C, 68.95; H, 7.06; N, 5.90.

Synthesis of Compound 3. Compound **3** was synthesized by portion-wise addition of 1-pyrenecarbaldehyde (0.064 g, 0.28 mmol) to the stirred solution of diamine **9** (0.06 g, 0.13 mmol) in ethanol (10 mL). The resulting reaction mixture was stirred at room temperature for 1 h, during which a yellow solid was obtained. The solid compound was filtered and washed with ethanol to give 0.085 g of **3** (74%). Mp: 190 °C. ^{1}H NMR: δ 3.82 (s, 8H, crownH), 3.98 (t, 4H, $J = 4.5$ Hz, crownH), 4.27 (t, 4H, $J = 4.5$ Hz, crownH), 7.05 (s, 2H, ArH), 7.26 (m, 8H, ArH), 8.01-8.25 (m, 14H, pyreneH), 8.75 (d, 2H, $J = 7.8$ Hz, pyreneH), 9.03 (d, 2H, $J = 9.3$ Hz, pyreneH), 9.53 (s, 2H, imineH). ^{13}C NMR: 69.29, 69.60, 70.51, 71.10, 116.41, 120.92, 122.38, 124.53, 124.82, 124.99, 125.85, 126.08, 126.15, 126.61, 127.42, 128.44, 128.95, 130.50, 130.88, 131.18, 133.22, 133.34, 139.36, 148.42, 150.79, 158.39. IR ν_{max} (CHCl$_3$, cm^{-1}): 1632 (C=N). MS (FAB): 875 (M$^+$). Anal. Calcd for $C_{60}H_{50}N_2O_7$: C, 79.03; H, 5.48; N, 3.07. Found: C, 79.34; H, 5.38; N, 2.97.

Synthesis of Compound 4. Compound **4** was synthesized by portion-wise addition of 2-quinoline carbaldehyde (0.073 g, 0.47 mmol) to the stirred solution of diamine **9** (0.1 g, 0.22 mmol) in ethanol (10 mL). The resulting reaction mixture was stirred at room temperature for 1 h, during which an off-white solid was obtained. The solid compound was filtered and washed with ethanol to give 0.125 g of **4** (77%). Mp: 250 °C. ^{1}H NMR: δ 3.81 (s, 8H, crownH), 3.91 (t, 4H, $J = 4.2$ Hz, crownH), 4.25 (t, 4H, $J = 4.3$ Hz, crownH), 6.87(s, 2H, ArH), 7.23−7.57 (m, 8H, ArH), 7.69 (t, 2H, $J = 8.7$ Hz, QuinH), 7.78 (t, 2H, $J = 8.7$ Hz, QuinH), 7.87 (d, 2H, $J = 7.2$ Hz, QuinH), 8.15 (d, 2H, $J = 8.1$ Hz, QuinH), 8.25 (d, 2H, $J = 8.7$ Hz, QuinH), 8.36 (d, 2H, $J = 8.4$ Hz, QuinH), 8.80 (s, 2H, imineH). ^{13}C NMR: 69.27, 69.61, 70.55, 71.12, 116.23, 118.63, 121.04, 127.61, 127.69, 128.82, 129.66, 129.83, 130.83, 133.01, 136.54, 140.24, 147.94, 148.51, 148.86, 154.87, 160.42. IR ν_{max} (CHCl$_3$, cm^{-1}): 1632 (C=N). MS (FAB): 729 (M$^+$), 730 (M$^+$ + 1). Anal. Calcd for $C_{26}H_{30}N_2O_5$: C, 69.31; H, 6.71; N, 6.22. Found: C, 68.85; H, 7.06; N, 5.90.

Acknowledgment. V.B. is thankful to DST (New Delhi) for financial support (SR/FT/CS/10-2006). The authors are also thankful to the Central Drug Research Institute (CDRI), Lucknow, for the FAB mass spectra and UGC for the SAP program.

Note Added after ASAP Publication. This paper was published ASAP on October 30, 2009, with errors in the contribution line and Scheme 1. The corrected paper was posted on November 12, 2009.

Supporting Information Available: Additional spectroscopic data (absorption and fluorescence spectra with different metal ions, NMR, and mass spectra). This material is available free of charge via the Internet at http://pubs.acs.org.