



Supramolecular Chemistry

ISSN: 1061-0278 (Print) 1029-0478 (Online) Journal homepage: http://www.tandfonline.com/loi/gsch20

# 1,3-Bis(pyren-1-yliminomethyl)calix[4]arene as a selective fluorescent turn-on sensor for mercury(II) ion

Shinya Tanaka, Kengo Hirasawa, Kyohei Watanabe & Tetsutaro Hattori

To cite this article: Shinya Tanaka, Kengo Hirasawa, Kyohei Watanabe & Tetsutaro Hattori (2017): 1,3-Bis(pyren-1-yliminomethyl)calix[4]arene as a selective fluorescent turn-on sensor for mercury(II) ion, Supramolecular Chemistry, DOI: 10.1080/10610278.2017.1388510

To link to this article: http://dx.doi.org/10.1080/10610278.2017.1388510

| 1 |   |
|---|---|
|   | + |

View supplementary material



Published online: 12 Oct 2017.



🖉 Submit your article to this journal 🕑



View related articles 🗹



View Crossmark data 🗹

Full Terms & Conditions of access and use can be found at http://www.tandfonline.com/action/journalInformation?journalCode=gsch20

# 1,3-Bis(pyren-1-yliminomethyl)calix[4]arene as a selective fluorescent turn-on sensor for mercury(II) ion

Shinya Tanaka, Kengo Hirasawa, Kyohei Watanabe and Tetsutaro Hattori

Department of Biomolecular Engineering, Graduate School of Engineering, Tohoku University, Sendai, Japan

#### ABSTRACT

A novel calixarene-based diimine, 1,3-bis(pyren-1-yliminomethyl)calix[4]arene (5), serves as a turnon-type fluorescent sensor, which selectively detects Hg<sup>2+</sup> in THF/H<sub>2</sub>O (99:1, v/v) in the presence of various other metal ions. Such selectivity is not seen with half salen 1 derived from salicylaldehyde and 1-aminopyrene. <sup>1</sup>H NMR analysis reveals that it is a chemodosimetric sensor based on its hydrolysis mediated by Hg<sup>2+</sup> to release 1-aminopyrene molecules as fluorescent chromophores.

> Hg<sup>2</sup> OHC (1 eq.) OH THF-H<sub>2</sub>O (99:1) H<sub>2</sub>N But 300 250 200 ور سور 150 م 100 50 0 none Ag\* Ca\* Cd2\* Co2+ Cs\* Cu2+ Hg2+ K\* Mg2+ Na+ Ni2+ Pb2+ Zn2+

**ARTICLE HISTORY** Received 28 July 2017 Accepted 29 September 2017

**KEYWORDS** Calixarene; turn-on sensor; chemodosimeter

#### Introduction

Mercury is a toxic heavy metal, which causes serious damage to human beings and the natural environment (1). Therefore, much attention has been paid to the development of mercury sensors with high selectivity and sensitivity (2). Among such entities, fluorescent sensors are of particular interest, because fluorescent sensing has advantages of the simplicity of implementation and fast response over other analytical techniques including ICP emission analysis. Chemodosimetric sensors for Hg<sup>2+</sup> have been developed by using irreversible chemical reactions mediated by Hq<sup>2+</sup> (3). Hydrolysis of a Schiff base was applied to the chemodosimetric reaction for the first time by Kim et al., who found that half-salen-type compound **1** serves as a turn-on fluorescent sensor for  $Hg^{2+}$  (4,5). However, the influence of coexistent metal ions on the detection has not been reported.

Calixarenes (e.g. 2) have been extensively utilized as molecular scaffolds for sensing devices, because receptor unit(s) and physicochemical transducer unit(s) can be preorganized on a calix skeleton in a three-dimensional fashion by chemical modifications (6). To date, a number of fluorescent sensors with calix skeletons have been developed for  $Hg^{2+}$  (7,8). Most of them are turn-off sensors using the heavy atom effect of Hg<sup>2+</sup>. This causes a problem in detecting Hg<sup>2+</sup>

CONTACT Shinya Tanaka 🖾 shinya.tanaka.d8@tohoku.ac.jp; Tetsutaro Hattori 🖾 tetsutaro.hattori@tohoku.ac.jp Supplemental data for this article can be accessed https://doi.org/10.1080/10610278.2017.1388510.



in the presence of other metal ions, such as Pb<sup>2+</sup> and Cd<sup>2+</sup>, which also exhibit heavy atom effects. In addition, it remains a challenge to improve the detection sensitivity, as most of existing calixarene-based Hg<sup>2+</sup> sensors require a large excess of Hg<sup>2+</sup> ions in detection. We have been developing novel methods to displace the hydroxy groups of calix[4] arenes with other functional groups (9). We recently prepared 1,3-diphosphonic acid 3 by using one of those methods and showed that this compound precisely discriminates the ionic radii of rare-earth metal ions and exhibits high extraction selectivity toward heavy rare-earth metal ions in solvent extraction (9b). The performance was superior to that of its analogue bearing two phosphono groups on two facing hydroxy oxygens of compound 2 through methylene linkages. This indicates that in order to achieve high recognition ability toward metal ions, it is favorable to introduce metal recognition sites onto the calix skeleton in a way that limits their conformational flexibility. In this study, we have designed and synthesized diimine 5, in which two facing hydroxy groups of compound 2 are replaced with pyrenyliminomethyl groups, and examined its performance as a chemodosimetric turn-on sensor for Hg<sup>2+</sup> by fluorescence spectroscopy.



#### **Results and discussion**

In a previous paper (9e), we reported a synthetic method of dialdehyde **4** from tetraol **2** by using Ullmann-type iodination and formylation of a lithiated intermediate with *N*-formylpiperidine as key steps. Diimine **5** could be readily prepared from dialdehyde **4** by dehydrative condensation with 1-aminopyrene. The <sup>1</sup>H NMR spectrum of diimine **5** in CDCl<sub>3</sub> exhibited two singlets (18H each) for the *tert*-butyl protons, a pair of doublets (4H each) for the bridging methylene protons, one singlet (2H) for the imino protons, and two singlets (4H each) for the aryl protons of the calix skeleton; the magnetic equivalences suggest a  $C_{2v}$ -symmetric structure, that is, cone or 1,3-alternate conformation. In addition, a singlet signal (2H) assigned to the hydroxy protons appeared at a low field (10.97 ppm), suggesting the presence of strong hydrogen bonds between the hydroxy and imino groups. These observations indicate that the diimine adopts a cone conformation in the solution. This was supported by NOESY analysis, which exhibited five cross peaks between the two aryl signals, one of the two methylene signals and the two aryl signals, the other methylene signal and the imino and hydroxy signals.

The fluorescence spectrum of diimine 5 was measured in THF/H<sub>2</sub>O (99:1, v/v) in the presence or absence of a metal perchlorate (1 molar equiv) at an excitation wavelength of 340 nm (Figures 1 and S1); the solvent system was chosen in consideration of the reproducibility of the hydrolysis (vide infra). The diimine itself emitted almost no fluorescence despite bearing pyrene chromophores (Figure 1). This was attributed to quenching by strong hydrogen bonds between the imino and hydroxy groups, as discussed for half salen 1 in the literature (10). Interestingly, only  $Hg(CIO_4)_2$  increased the fluorescence intensity dramatically among the metal perchlorates tested; the ratio of the maximum intensity of the solution containing diimine **5** and  $Hg(ClO_4)_2$  ( $I_{max}$ ) to that of the solution containing only diimine **5**  $(I_0)$  is 271 (Figure 2). The Hg(ClO<sub>4</sub>)<sub>2</sub>-induced spectrum is in good agreement with that of 1-aminopyrene (Figure S2), indicating that this fluorescence was originated from 1-aminopyrene released from diimine 5. In fact, in <sup>1</sup>H NMR analysis of diimine 5 in THF- $d_{o}/D_{2}O$  (99:1), the signals of the diimine completely disappeared upon the addition of 10 molar equiv of  $Hg(ClO_4)_2$  and novel signals assigned to dialdehyde 4 and 1-aminopyrene appeared (Figure 3). Although metal ions other than Hg<sup>2+</sup> did not affect much on the fluorescence intensity of diimine 5, they caused a change in the spectral shape (Figure S1); increasing the amount of the metal ions (100 molar equiv) made this change clearer (Figure S3). This indicates that not only Hg<sup>2+</sup> but also other metal



**Figure 1.** (Colour online) Change in the fluorescence spectrum of diimine **5** (6 × 10<sup>-5</sup> M) in THF/H<sub>2</sub>O (99:1, v/v) upon the addition of various metal ions as metal perchlorates (1 molar equiv) ( $\lambda_{ex}$  = 340 nm).

Note: Each spectrum was recorded 10 min after the addition of a metal ion.



**Figure 2.** (Colour online) Fluorescence intensity ratio  $I_{max}/I_o$  of a solution of diimine **5** ( $6 \times 10^{-5}$  M) in THF/H<sub>2</sub>O (99:1, v/v). Note:  $I_o$  and  $I_{max}$  denote the fluorescence intensity at 432 nm in the absence and presence of a metal ion (1 molar equiv), respectively.



**Figure 3.** Expanded <sup>1</sup>H NMR spectra of diimine **5** in THF- $d_8$ -D<sub>2</sub>O (99:1) before (a) and after the addition of Hg(ClO<sub>4</sub>)<sub>2</sub> (10 molar equiv) (b), as compared to those of dialdehyde **4** (c) and a mixture of 1-aminopyrene and Hg(ClO<sub>4</sub>)<sub>2</sub> (1:5) (d).

ions interact with diimine **5**. However, their influence on the fluorescence spectrum of diimine **5** was much smaller than that of Hg<sup>2+</sup>.

To investigate the influence of coexistent metal ions on the Hg<sup>2+</sup>-mediated hydrolysis of diimine 5, the fluorescence spectrum of diimine 5 was measured in THF/H<sub>2</sub>O (99:1, v/v) in the presence of Hg(ClO<sub>4</sub>)<sub>2</sub> and another metal perchlorate (1 molar equiv each). Figure 4 shows I<sub>max</sub> for the solutions containing various coexistent metal perchlorates as percentage values relative to I<sub>max</sub> for a solution containing only **5** and  $Hg(CIO_4)_2$ . The  $Hg^{2+}$ -mediated hydrolysis was not much affected by coexistent metal ions; the relative intensities are more than 88% except  $Cu(ClO_4)_2$ . The same experiment was performed for half salen 1 (Figure 5). Although the fluorescence spectrum of half salen 1 (i.e. 1-aminopyrene) was selectively induced by  $Hg(CIO_{4})_{2}$  as in the case of diimine 5 (Figure S4a compared to Figure 1), the fluorescence intensity was seriously affected by most of the coexistent metal ions tested (Figure 5). Coexistent metal ions should interact with the imino and/or hydroxy



**Figure 4.** (Colour online) Fluorescent intensity of a solution of diimine **5** ( $6 \times 10^{-5}$  M) in THF/H<sub>2</sub>O (99:1, v/v) at 432 nm in the presence of Hg<sup>2+</sup> and another metal ion as metal perchlorates (1 molar equiv each).

Note: Data are shown as percentage values relative to the intensity of a solution of diimine  ${\bf 5}$  and Hg(ClO\_4)\_2.



**Figure 5.** (Colour online) Fluorescent intensity of a solution of half salen 1 ( $12 \times 10^{-5}$  M) in THF/H<sub>2</sub>O (99:1, v/v) at 432 nm in the presence of Hg<sup>2+</sup> and another metal ion as metal perchlorates (1 molar equiv each).

Note: Data are shown as percentage values relative to the intensity of a solution of half salen **1** and  $Hg(ClO_a)_2$ .

groups of half salen **1**, as suggested by the spectral change of **1** upon the addition of various metal ions (Figure S4b). This inhibits the Hg<sup>2+</sup>-mediated hydrolysis. Diimine **5** does not seem to be susceptible to this inhibition, because the two iminomethyl groups are preorganized in a manner suitable for the nitrogen atoms to coordinate to a Hg<sup>2+</sup> ion in a trans fashion. Therefore, it may be concluded that the selective detection of Hg<sup>2+</sup> in the presence of other metal ions was achieved by fixing the iminomethyl groups on the calix skeleton.

#### Conclusion

We have shown here that diimine **5** bearing pyrenyliminomethyl moieties serves as a turn-on-type fluorescent sensor. It selectively detected Hg<sup>2+</sup> in the presence of various other metal ions. Such selectivity was not seen with half-salen-type compound **1**, suggesting that the selectivity was realized by regulating the dispositions of the receptor units with the calix skeleton.

# **Experimental**

#### General

Dialdehyde **6** (*9e*) and 1-aminopyrene (*11*) were prepared according to the literature procedure. Toluene was distilled from sodium diphenyl ketyl. Metal perchlorates and THF (anhydrous, stabilizer free) were used as purchased.

# 25,26-Bis(pyren-1-yliminomethyl)-tetra-p-tertbutylcalix[4]arene (5)

A solution of dialdehyde 4 (130 mg, 0.193 mmol) and 1-aminopyrene (125 mg, 0.575 mmol) in toluene (5.0 mL) was azeotropically refluxed for 12 h using a Dean-Stark trap; the reaction mixture was gradually concentrated and dried. After cooling, the residue was purified by crystallization from chloroform/methanol to give diimine 2 (169 mg, 82%) as a greenish yellow powder, mp 293-296 °C (uncorrected); IR (KBr) 3499, 3045, 2960, 1621, 1486, 1361, 1305, 1280, 1210, 840 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>2</sub>)  $\delta$  0.96 (s, 18H), 1.44 (s, 18H), 3.65 (d, J = 13.0 Hz, 4H), 5.05 (d, J = 13.0 Hz, 4H), 6.36 (d, J = 8.0 Hz, 2H), 6.43 (d, J = 8.8 Hz, 2H), 6.91 (s, 4H), 7.30 (s, 4H), 7.45 (d, J = 7.2 Hz, 2H) 7.47 (d, J = 8.0 Hz, 2H), 7.96–8.03 (m, 4H), 8.07–8.14 (m, 4H), 8.43 (d, J = 8.8 Hz, 2H), 9.04 (s, 2H), 10.97 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 30.8, 32.1, 34.1, 34.4, 35.4, 117.7, 123.3, 124.17, 124.21, 124.4, 124.5, 124.67, 124.74, 125.7, 125.8, 126.4, 126.6, 127.3, 127.8, 128.0, 128.7, 131.2, 131.5, 140.0, 141.1, 145.1, 152.0, 152.6, 166.4. Anal. Calcd for C<sub>78</sub>H<sub>74</sub>N<sub>2</sub>O<sub>2</sub>·H<sub>2</sub>O: C, 85.99; H, 7.03; N, 2.57. Found: C, 86.06; H, 6.94; N, 2.70.

#### Fluorescence analysis

Stock solutions of diimine **5** (120  $\mu$ M) and metal perchlorates (12 mM) in THF/H<sub>2</sub>O (99:1, v/v) were prepared. The stock solutions of diimine **5** (594  $\mu$ L) and metal perchlorate(s) (6  $\mu$ L) were mixed, and the resulting solution was diluted with THF/H<sub>2</sub>O (99:1, v/v) until the volume reached to 1.2 mL. After stirring for a short time, the mixture was left for 10 min and charged into a 1-cm cell. Fluorescence spectra were routinely recorded on a Hitachi F-7000 spectrometer at an excitation wavelength of 340 nm with an emission slit-width of 5.0 nm.

# **Disclosure statement**

No potential conflict of interest was reported by the authors.

## Funding

This work was supported in part by Japan Society for the Promotion of Science (JSPS) [grant number KAKENHI 15K05466].

# References

- (a) Basu, N.; Scheuhammer, A.; Grochowina, N.; Klenavic, K.; Evans, D.; O'Brien, M.; Chan, M. *Environ. Sci. Technol.* **2005**, *39*, 3585–3591. (b) Zhang, Z.; Wu, D.; Guo, X.; Qian, X.; Lu, Z.; Zu, Q.; Yang, Y.; Duan, L.; He, Y.; Feng, Z. *Chem. Res. Toxicol.* **2005**, *18*, 1814–1820. (c) Tchounwou, P.B.; Ayensu, W.K.; Ninashvili, N.; Sutton, D. *Environ. Toxicol.* **2003**, *18*, 149–175.
- (2) For reviews, see: (a) Nolan, E.M.; Lippard, S.J. Chem. Rev.
  2008, 108, 3443–3480. (b) Kim, H.N.; Ren, W.X.; Kim, J.S.; Yoon, J. Chem. Soc. Rev. 2012, 41, 3210–3244. (c) Chen, G.; Guo, Z.; Zeng, G.; Tang, L. Analyst 2015, 140, 5400–5443.
- (3) (a) Zhang, G.; Zhang, D.; Yin, S.; Yang, X.; Shuai, Z.; Zhu, D. Chem. Commun. 2005, 16, 2161-2163. (b) Liu, B.; Tian, H. Chem. Commun. 2005, 3156–3158. (c) Yang, Y.K.; Yook, K.J.; Tae, J. J. Am. Chem. Soc. 2005, 127, 16760-16761. (d) Song, K.C.; Kim, J.S.; Park, S.M.; Chung, K.; Ahn, S.; Chang, S. Org. Lett. 2006, 8, 3413–3416. (e) Ko, S.K.; Yang, Y.K.; Tae, J.; Shin, I. J. Am. Chem. Soc. 2006, 128, 14150-14155. (f) Wu, J.S.; Hwang, I.C.; Kim, K.S.; Jong, S.K. Org. Lett. 2007, 9, 907–910. (g) Lee, M.H.; Cho, B.-K.; Yoon, J.; Kim, J.S. Org. Lett. 2007, 9, 4515-4518. (h) Zhang, X.; Xiao, Y.; Qian, X. Angew. Chem. Int. Ed. 2008, 47, 8025-8029. (i) Chen, X.; Nam, S.W.; Jou, M.J.; Kim, Y.; Kim, S.J.; Park, S.; Yoon, J. Org. Lett. 2008, 10, 5235-5238. (j) Lee, M.H.; Lee, S.W.; Kim, S.H.; Kang, C.; Kim, J.S. Org. Lett. 2009, 11, 2101-2104. (k) Yang, Y.-K.; Ko, S.-K.; Shin, I.; Tae, J. Org. Biomol. Chem. 2009, 7, 4590-4593. (I) Choi, M.G.; Kim, Y.H.; Namgoong, J.E.; Chang, S.-K. Chem. Commun. 2009, 3560-3562. (m) Ma, W.; Xu, Q.; Du, J.; Song, B.; Peng, X.; Wang, Z.; Li, G.; Wang, X. Spectrochim. Acta, Part A 2010, 76, 248–252. (n) Lin, W.; Cao, X.; Ding, Y.; Yuan, L.; Long, L. Chem. Commun. 2010, 46, 3529-3531. (o) Lee, J.-Y.; Rao, B.A.; Hwang, J.-Y.; Son, Y.-A. Sensors Actuators B Chem. 2015, 220, 1070-1085.
- (4) Kim, J.H.; Kim, H.J.; Bae, C.W.; Park, J.W.; Lee, J.H.; Kim, J.S. Arkivoc 2010, vii, 170–178.
- (5) See also: (a) Bhalla, V.; Kumar, M.; Sharma, P.R.; Kaur, T. *Dalton Trans.* 2013, 15063–15068. (b) Mukhopadhyay, S.; Biswas, A.; Pandey, R.; Gupta, R.K.; Pandey, D.S. *Tetrahedron Lett.* 2014, *55*, 1437–1440. (c) Kumar, A.; Dubey, M.; Pandey, R.; Gupta, R.K.; Kumar, A.; Kalita, A.C.; Pandey, D.S. *Inorg. Chem.* 2014, *53*, 4944–4955. (d) Zhang, X.; Zhu, Y.Y. *Sens. Actuators, B Chem.* 2014, *202*, 609–614. (e) García-Beltrán, O.; Rodríguez, A.; Trujillo, A.; Cañete, A.; Aguirre, P.; Gallego-Quintero, S.; Nuñez, M.T.; Aliaga, M.E. *Tetrahedron Lett.* 2015, *56*, 5761–5766.
- (6) For reviews, see: (a) Kim, J.S.; Quang, D.T. Chem. Rev. 2007, 107, 3780–3799. (b) Leray, I.; Valeur, B. Eur. J. Inorg. Chem. 2009, 3525–3535.
- (7) For turn-off type Hg sensor with calixarenes, see: (a) Talanova, G.G.; Elkarim, N.S.A.; Talanov, V.S.; Bartsch, R.A. Anal. Chem. **1999**, *71*, 3106–3109. (b) Métivier, R.; Leray, I.; Valeur, B. Photochem. Photobiol. Sci. **2004**, *3*, 374–380. (c) Kim, J.H.; Hwang, A.-R.; Chang, S.-K. Tetrahedron Lett. **2004**, *45*, 7557–7561. (d) Chen, Q.-Y.; Chen, C.-F. Tetrahedron Lett.

**2005**, *46*, 165–168. (e) Métivier, R.; Leray, I.; Lebeau, B.; Valeur, B. *J. Mater. Chem.* **2005**, *15*, 2965–2973. (f) Chang, K.-C.; Su, I.-H.; Senthilvelan, A.; Chung, W.-S. *Org. Lett.* **2007**, *9*, 3363–3366. (g) Praveen, L.; Ganga, V.B.; Thirumalai, R.; Sreeja, T.; Reddy, M.L.P.; Varma, R.L. *Inorg. Chem.* **2007**, *46*, 6277–6282. (h) Dinake, P.; Prokhorova, P.E.; Talanov, V.S.; Talanova, R.J.; Talanova, G.G. *Tetrahedron Lett.* **2010**, *51*, 5016–5019.

- (8) For turn-on type Hg sensor with calixarenes, see: (a) Cha, N.R.; Kim, M.Y.; Kim, Y.H.; Choe, J.-I.; Chang, S.-K. J. Chem. Soc. Perkin Trans. 2002, 2, 1193–1196. (b) Kumar, M.; Dhir, A.; Bhalla, V. Dalton Trans. 2010, 39, 10122–10127. (c) Qazi, M.A.; Qureshi, I.; Memon, S. J. Fluoresc. 2011, 21, 1231–1238. (d) Kumar, M.; Kumar, N.; Bhalla, V. Sens. Actuators B Chem. 2012, 161, 311–316. (e) Erdemir, S.; Kocyigit, O.; Karakurt, S. Sens. Actuators B Chem. 2015, 220, 381–388.
- (9) (a) Katagiri, H.; Iki, N.; Hattori, T.; Kabuto, C.; Miyano, S. J. Am. Chem. Soc. 2001, 123, 779–780. (b) Katagiri, H.; Tanaka, S.; Ohkubo, K.; Akahira, Y.; Morohashi, N.; Iki, N.; Hattori, T.; Miyano, S. RSC Adv. 2014, 4, 9608–9616. (c) Nakamura, Y.; Tanaka, S.; Serizawa, R.; Morohashi, N.; Hattori, T. J. Org. Chem. 2011, 76, 2168–2179. (d) Morohashi, N.; Hayashi, T.; Nakamura, Y.; Kobayashi, T.; Tanaka, S.; Umetsu, T.; Nebuya, S.; Morohashi, N.; Hattori, T. J. Org. Chem. 2012, 41, 1520–1522. (e) Tanaka, S.; Umetsu, T.; Nebuya, S.; Morohashi, N.; Hattori, T. J. Org. Chem. 2015, 80, 1070–1081. (f) Hirasawa, K.; Tanaka, S.; Horiuchi, T.; Kobayashi, T.; Sato, T.; Morohashi, N.; Hattori, T. Organometallics 2016, 35, 420–427.
- (10) Kim, H.J.; Bhuniya, S.; Mahajan, R.K.; Puri, R.; Liu, H.; Ko, K.C.; Lee, J.Y.; Kim, J.S. Chem. Commun. 2009, 7128–7130.
- (11) Niamnont, N.; Kimpitak, N.; Wongravee, K.; Rashatasakhon, P.; Baldridge, K.K.; Siegel, J.S.; Sukwattanasinitt, M. Chem. Commun. 2013, 49, 780–782.