Dyes and Pigments 97 (2013) 324-329

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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



Zhengping Dong*, Xin Tian, Yuanzhe Chen, Jingran Hou, Yueping Guo, Jian Sun, Jiantai Ma*

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, South Tianshui Road, Lanzhou 730000, China

ARTICLE INFO

Article history: Received 14 September 2012 Received in revised form 27 November 2012 Accepted 2 January 2013 Available online 16 January 2013

Keywords: Chemosensor Mercury Rhodamine B Logic gate Selective detection Reversibility

1. Introduction

Mercury, one of the most prevalent toxic heavy metals in the environment, can easily pass through biological membranes and through respiratory and gastrointestinal tissues [1-3]. When absorbed in the human body, it will produce damage to the brain, kidneys and endocrine system [4]. As a result, there has been considerable interest in the development of effective tools for detecting Hg²⁺ ions in the environment. As fluorescence measurement provides a powerful way for detecting metal ions because of its low detection limit and simple instrumentation, considerable efforts have been devoted to design fluorescent chemical sensors for detecting Hg^{2+} [5–10]. Many Hg^{2+} sensors based on pyrene [11–13], naphthalimide [14–16], bispyrenyl [17], terphenyl [18,19], naphthylthiourea [20], dansyl [21-23] have been reported. However, most of these sensors are irreversible, and cannot be used to monitor both the increase and the decrease of Hg^{2+} concentration in the environment or some biological metabolite. Therefore, the development of reversibly fluorescent chemosensors for Hg²⁺ determination with light "off-on" and high selectivity is still highly desirable [24].

Rhodamine is a dye used extensively as a fluorescent signal transducer due to its excellent photophysical properties [25]. In

ABSTRACT

A novel and simple fluorescent chemosensor based on rhodamine (R-2) is designed and synthesized to detect Hg^{2+} . Probe R-2 exhibits high selectivity and sensitivity for sensing Hg^{2+} with a detection limit at 10^{-8} M level, and displays a significant color change from colorless to pink color in the presence of Hg^{2+} . About a 400-fold increase in fluorescence emission intensity is observed upon binding excess Hg^{2+} in 50% H_2O/CH_3CN HEPES buffer at pH 7.00. The titration results show a 1:1 complex formation between R-2 and Hg^{2+} . The reversibility of chemosensor R-2 is verified through its spectral response toward Hg^{2+} and I^- titration experiments. Using Hg^{2+} and I^- as chemical inputs and the fluorescence intensity signal as outputs, R-2 can be utilized as an INHIBIT logic gate at molecular level.

© 2013 Elsevier Ltd. All rights reserved.

PIĞMĔNTS

recent years, many Hg^{2+} sensors based on rhodamine derivatives have been developed [14,19,26–30]. Most of the developments have shown that rhodamine derivatives are promising structural scaffold for the design of reversible and selective chemosensors. The cation-sensing mechanism of most of the rhodamine probes is based on a change from the spirolactam to an open-ring amide, resulting in a color change, highly fluorescent compound. When some ligands which exhibit stronger coordination ability with Hg^{2+} are added to the Hg^{2+} -rhodamine sensing system, the open-ring amide will change to spirolactam, and the reversibility is realizable.

On the other hand, since the pioneering work by de Silva [31], using fluorescent signal as outputs and chemically encoded information (such as pH, temperature, light, anions and metal ions) as inputs to design molecular logic gates is an area of intense research activity [32–37]. And molecular systems showing functions such as AND, NAND, OR, XOR, and INHIBIT have been widely explored [37–40]. In all the molecular logic gates systems, the molecule demonstrates "on" or "off" switching of the fluorescence signal meaning "1" or "0" output, in response to the addition "1" or no addition "0" of the input chemicals. Thus, they have the potential for computation on a molecular level that silicon based devices cannot address.

Bearing the above statement in mind, we herein report the design, synthesis and spectral characteristics of a mercuric probe R-2 based on rhodamine B. It shows highly fluorescent selective for Hg^{2+} over other metal ions. Adding I⁻ to the mixture of Hg^{2+} and



^{*} Corresponding authors. Tel.: +86 0931 8912577; fax: +86 0931 8912582. E-mail addresses: dongzhp@lzu.edu.cn (Z. Dong), majiantai@lzu.edu.cn (J. Ma).

^{0143-7208/\$ –} see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.dyepig.2013.01.002

R-2 solution, the fluorescence is turned off and the pink color of the $Hg^{2+}/R-2$ system also turned colorless, indicating that I⁻ sequesters Hg^{2+} of the mixture, liberates the free R-2 [19,24,41]. And the reversibility of R-2 is realizable. Using Hg^{2+} and I⁻ as chemical inputs and the fluorescence intensity signal as outputs, R-2 can be utilized as an INHIBIT logic gate at molecular level. We hope such rhodamine-based fluorescent sensors and molecular logic devices will find application in the development of cations sensing probes and digital devices.

2. Experimental

2.1. Regents

Rhodamine B and hydrazine hydrate were purchased from Aladdin Chemistry Co. Ltd. Cationic compounds such as NaClO₄, KClO₄, Mg(ClO₄)₂, Ca(ClO₄)₂, Fe(ClO₄)₃, Co(ClO₄)₂, Ni(ClO₄)₂, Cu(ClO₄)₂, Zn(ClO₄)₂, Cd(ClO₄)₂, Al(ClO₄)₃, Pb(ClO₄)₂, AgClO₄ and Hg(ClO₄)₂ were purchased from Aldrich and used as received. All other chemicals were of the reagent-grade purchased from Tianjing Guangfu Chemical Companies and used as supplied. All solvents used for synthesis and measurements were redistilled before use.

2.2. Synthesis of compound R-1

Rrhodamine hydrazide was synthesized following the reported procedure [42]. To rhodamine B hydrochloride (0.96 g, 2 mmol) dissolved in 30 mL methanol, excess amount of hydrazine hydrate (1 mL, 6.98 mmol) was added and the reaction mixture was refluxed till the pink color disappeared. After that, the reaction mixture was cooled to room temperature, poured into distilled water and extracted with ethyl acetate (6×25 mL). The combined extract was washed with brine, dried with anhydrous sodium sulfate, filtered, and then concentrated under reduced pressure to yield 0.64 g (70%) of compound R-1. ¹H NMR (CDCl₃, 400 MHz): δ 1.168 (t, J = 7.2 Hz, 12H), 3.36 (q, J = 7.0 Hz, 8H), 3.63 (s, 2H), 6.30 (d, J = 2.4 Hz, 2H), 6.42 (d, J = 2.4 Hz, 2H), 6.48 (s, 1H), 6.52 (s, 1H), 7.11 (m, 1H), 7.46 (m, 2H), 7.94 (m, 1H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ 11.9, 43.7, 65.3, 96.4, 103.6, 107.5, 122.7, 123.2, 127.6, 128.4, 131.8, 147.4, 150.9, 153.6, 165.3 ppm; ESI: (m/z) 457.4 $[M + H]^+$.

2.3. Synthesis of compound R-2

4-Methyl-2, 6-Diformyl Phenol was synthesized as reported [43]. ¹H NMR (CDCl₃, 400 MHz): δ 2.39 (s, 3H), 7.77 (s, 2H), 10.22 (s, 2H), 11.46 (s, 1H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ 20.06, 120.1, 129.1, 132.6, 136.9, 196.7 ppm; EI: (*m*/*z*) 164.

A stirred solution of R-1 (1.0 g, 2.2 mmol), 4-Methyl-2, 6-Diformyl Phenol (0.164 g, 1.0 mmol) in ethanol (50 mL) was heated under reflux for 5 h under N₂ in the dark. After the ethanol had been evaporated under reduced pressure, the residue was purified by silica gel column chromatography (CH₂Cl₂/MeOH/Et₃N = 200:1:1) to

give R-2 (0.77 g, yield: 74%). ¹H NMR (d⁶-DMSO, 400 MHz): δ 0.97 (m, 24H), 1.93 (s, 3H), 3.19 (m, 16H), 6.25 (m, 4H), 6.40 (m, 8H), 7.02 (m, 4H), 7.53 (s, 4H), 7.90 (s, 2H), 8.88 (s, 2H), 11.14 (s, 1H) ppm; ¹³C NMR (d⁶-DMSO, 100 MHz): δ 12.20, 18.46, 19.53, 43.55, 55.98, 65.31, 97.38, 104.83, 108.02, 119.93, 122.94, 123.60, 127.40, 127. 87, 128.31, 128.66, 130.18, 133.8, 146.78, 148.42, 151.15, 152.58, 154.18, 163.45 ppm; ESI: (*m*/*z*) 1041.9 [M + H]⁺.

2.4. General methodology adopted for spectroscopic studies

¹H NMR and ¹³C NMR spectra were recorded using 400 MHz and 100 MHz. Chemical shifts were expressed in ppm and coupling constants (*J*) in Hz. Absorption spectra were determined on a Varian UV-Cary100 spectrophotometer. Fluorescence spectra measurements were performed on a Hitachi F-4500 spectrofluorimeter. HEPES buffer solutions (20 mM, pH = 7.0) were prepared in deionized water.

UV–vis titrations were performed on 1×10^{-5} M solution of ligand R-2 in HEPES buffer (20 mM, pH = 7.0) containing 50% (v/v) H₂O/CH₃CN. Typical aliquots of freshly prepared Hg(ClO₄)₂ solutions (1×10^{-2} M to 1×10^{-5} M solutions in CH₃CN) were added and the UV–vis spectra of samples were recorded.

Fluorescence titrations were performed on 1×10^{-5} M solution of ligand R-2 in HEPES buffer (20 mM, pH = 7.0) containing 50% (v/ v) H₂O/CH₃CN. Typical aliquots of freshly prepared metal perchlorates (Hg²⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺, Cd²⁺, Zn²⁺, Ni²⁺, Co²⁺, Pb²⁺, Fe³⁺ and Ag⁺) standard solutions (1 \times 10⁻² M to 1 \times 10⁻⁵ M solutions in CH₃CN) were added and the fluorescence spectra of samples were recorded.

3. Results and discussion

In this paper, compound R-1 was synthesized by the reaction of rhodamine B and hydrazine hydrate, the new probe R-2 was synthesized by the condensation reaction between R-1 and 4-Methyl-2, 6-Diformyl Phenol (Scheme 1). Its structure was confirmed by ESI data, ¹H NMR and ¹³C NMR spectrum, and it was designed to chelate with metal ions via its carbonyl O and amine N atoms. Similar to other rhodamine spirolactam derivatives [25,44], compound R-2 forms a fluorescence inactive solution in either aqueous buffer solution or pure organic solvent, indicating that the spirolactam form exists predominantly.

3.1. Fluorescence and UV-vis spectral responses of R-2

The fluorescence intensity changes of R-2 were monitored upon adding metal ions to determine the cations binding abilities. Fig. 1a showed fluorescence spectra of R-2 in the presence and absence of 500 μ M of cations. R-2 showed only a very weak fluorescence in the absence of metal ions. A high-intensity fluorescence band at 595 nm was observed upon addition of Hg²⁺ into the solution of R-2. Fluorescence almost did not change in Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺, Cd²⁺, Zn²⁺, Ni²⁺, Co²⁺, Pb²⁺, Fe³⁺ and Ag⁺ solutions. Like some



Scheme 1. Synthetic procedure of chemosensor R-2.



Fig. 1. (a) Fluorescence spectra of R-2 (10 μ M) upon addition of 50 eq. of Hg²⁺ and 50 eq. other metal ions in CH₃CN-HEPES buffer solution (20 mM HEPES, 50:50, v/v, pH 7.0). (b) Fluorescence response of R-2 (10 μ M) to 50 eq. Hg²⁺ in CH₃CN-HEPES buffer solution (20 mM HEPES, 50:50, v/v, pH 7.0) containing 50 eq. various metal ions. The black bars represent the addition 50 eq. of the competing metal ion to a 10 μ M solution of R-2. The gray bars represent the change of the emission that occurs upon the subsequent addition of 50 eq. Hg²⁺ to the above solution. $\lambda_{ex} = 500 \text{ nm}, \lambda_{em} = 595 \text{ nm}.$

other reported rhodamine-based mercury sensors [25,27,45], the fluorescence intensity of R-2 was affected to some extent in Cu^{2+} solutions. High concentration of Cu^{2+} contamination is likely to mislead the fluorescent selectivity of Hg^{2+} . So, when R-2 is used as the probe for Hg^{2+} , high concentration of Cu^{2+} interference must be eliminated by using quinoline derivative based adsorbent [46]. On the other hand, an important feature of the chemosensor is its high selectivity toward the analyte over the other competitive species. Herein, a competition experiment was also carried out by adding Hg^{2+} to the solution of R-2 in the presence of other metal ions. Fig. 1b showed the comparison between the fluorescence response of R-2 with each metal ion and the emission that occurred after the addition of Hg^{2+} . The results indicated that the sensing of Hg^{2+} by R-2 was hardly affected by the commonly co-existent ions. In other words, the selectivity of R-2 for the Hg^{2+} over other competitive cations was remarkably high.

In order to gain an insight into the signaling properties of R-2 toward Hg²⁺, fluorescence titration experiments were carried out in CH₃CN-HEPES buffer solution (20 mM, pH = 7.0 50% (v/v) H₂O/CH₃CN). A new emission band at 595 nm gradually appeared



Fig. 2. Fluorescence spectra of R-2 (10 μ M) in CH₃CN-HEPES buffer solution (20 mM HEPES, 50:50, v/v, pH 7.0) upon addition of different amounts of Hg²⁺ ion. Inset: fluorescence intensity at 595 nm of R-2 (10 μ M) as a function of Hg²⁺ concentration (0–500 μ M). $\lambda_{ex} = 500$ nm.



Fig. 3. (a) Absorption spectra of R-2 (10 μ M) with addition increasing concentration (0– 2 eq.) of Hg²⁺ in CH₃CN-HEPES buffer solution (20 mM HEPES, 50:50, v/v, pH 7.0). Inset: The color changes of R-2 (10 μ M) to Hg²⁺ in CH₃CN-HEPES buffer solution (20 mM HEPES, 50:50, v/v, pH 7.0). (b) Absorbance at 600 nm of R-2 (10 μ M) as a function of Hg²⁺ concentration (0–20 μ M). Inset: The nonlinear fitting (absorbance at 600 nm) of R-2.

upon the addition of Hg^{2+} (Fig. 2). In the presence of 50 eq. of Hg^{2+} , the mixture showed an intense orange fluorescence and a >400-fold enhancement in the fluorescence intensity at 595 nm. Furthermore, for the UV-vis titration spectra of R-2, in the addition of Hg^{2+} (0–2 eq.), there was also a new absorption peak at 600 nm. which was consistent with the result of fluorescence spectra (Fig. 3a). After the addition of various concentration of Hg^{2+} (from 0 to 2 eq.) to R-2 solution (1*10⁻⁵ M), it was found that, when the concentration of Hg^{2+} reached 10^{-8} M, the absorption intensity at 600 nm of R-2 enhanced in the visible range at room temperature. And the absorption intensity gradually enhanced when increasing Hg²⁺. For practical application, the detection limit of this new chemosensor was also evaluated by fluorescence and UV-vis titration, and the titration results demonstrated that the detection limit of Hg^{2+} was at $10^{-8}~\mathrm{M}$ level.

The unique and highly selective of rhodamine based fluorescent sensors for Hg^{2+} can also be easily observed by even naked eye detection [4,47,48]. The color change of R-2 in CH₃CN-HEPES buffer solution with Hg²⁺ was shown in Fig. 3a *inset*. From Fig. 3a *inset*, it can be seen that, Hg²⁺ caused visible detectable color change of R-2 solution, from colorless to pink.

3.2. Determination of binding constant

In this work, the spirolactam moiety of the rhodamine group acts as a signal switcher, which is envisioned to turn on when the cation is binded (Scheme 2). When sensor R-2 meets Hg²⁺, the spirolactam form (fluorescence-off) of R-2 converts to the Hg²⁺-promoted ring-opened amide form (fluorescence-on), the $R-2 + Hg^{2+}$ system forms a large conjugated system, which serves as the foundation for a novel chemosensor for Hg^{2+} [49]. Moreover, the sensor is most likely to chelate metal ions via the imide N and phenol O atoms like other reported sensors [7,30,50-52].

As a highly selective fluorescent chemosensor, the binding constant of R-2 for Hg^{2+} was also investigated. By assuming a 1:*n* stoichiometry for interaction between R-2 and metal ions, the association constant of R-2 for Hg²⁺ determined from the following equation [53,54] to be $K_{Hg}^{2+} = 9.21 \times 10^5 \text{ M}^{-1}$.



Fig. 4. Job's plot of Hg^{2+} versus R-2 ([Hg^{2+}] + [R-2] = 20 μ M) at 600 nm.

$$lg \frac{A - A_{\min}}{A_{\max} - A} = lgK + nlg[M^{n+}]$$

In the equation, K is the association constant, A_{max} is the absorbance of R-2 in the presence of excess amount of Hg^{2+} , A is the absorbance of R-2 obtained with various concentration of Hg²⁺, A_{\min} is the absorbance of R-2 without any cation. The nonlinear fitting of the titration curve showed a 1:1 stoichiometry between R-2 and Hg²⁺ (Fig. 3b). This result was further confirmed by the Job's plot (Fig. 4). From Fig. 4, it can be observed that the absorbance went through a maximum at a molar fraction of about 1/2, indicating that a 1:1 stoichiometry was most possible for the binding mode of Hg²⁺ and R-2. Thus, in accordance with the 1:1 stoichiometry, the possible binding mode between R-2 toward Hg²⁺ was proposed in Scheme 2.

3.3. Logic gate

Due to the reversibility is an important aspect for a chemical sensor to be widely employed in the detection of specific analyses,



R-2 ESI(+): [M+H]⁺=1041.9

ESI(+): [M+Hg²⁺+H]⁺=1241.4 R-2+Hg²⁺

327

Scheme 2. Proposed binding mode of R-2 with Hg²⁺.



Fig. 5. Fluorescence spectrum ($\lambda_{ex} = 500 \text{ nm}$) of R-2 (10 μ M) in the presence of Hg²⁺ (500 μ M) and I⁻ (1 mM) in CH₃CN-HEPES buffer solution (20 mM HEPES, 50:50, v/v, pH 7.0), truth table, and logic scheme (Inset, A: R-2+ Hg²⁺, B: R-2+ Hg²⁺+I⁻).

the reversibility experiment has been carried out. In light of the strong binding ability of the I⁻ toward Hg²⁺, the reversibility of the system was investigated by introduction of iodide anion [26] (Fig. 5). When I⁻ was added to the system, the fluorescence emission did not change. The addition of Hg²⁺ to the solution of R-2 caused fluorescence enhancement. Upon addition of excess amount of I⁻ to the mixture of R-2 and Hg²⁺, the color of the mixture changed from pink to colorless (Fig. 5, inset), and fluorescent emission intensity of the system was quenched, indicating that I⁻ replaced the receptor R-2 to coordinate Hg²⁺.

These behaviors can be analyzed with the combinational logic circuit. The two input signals are Input 1 (Hg^{2+}) and input 2 (I^-). Input 1 leads to fluorescence enhancement in its occupied state, equivalent to a YES operation. The interaction of input 2 with its corresponding receptor leads to fluorescence quenching, thereby implementing the necessary NOT gate. The receptor acts in parallel on the fluorescence output signals, which implements the required AND function. In the presence of both inputs, the quenching (by input 2) overrides the fluorescence enhancement by input 1, in accordance with the truth table shown in Fig. 5. Therefore, monitoring the fluorescence at 595 nm, upon addition of Hg^{2+} , I^- and their reacting dose mixture lead to an INHIBIT logic gate.

4. Conclusion

In summary, a simple and easy-to-prepare rhodamine-based optical chemosensor R-2 for the detection of Hg^{2+} ions has been synthesized. The sensor R-2 displayed highly selective and sensitive fluorescent enhancement and colorimetric change upon the addition of Hg^{2+} . The fluorescent selectivity of R-2 for Hg^{2+} may be slightly affected when coexisted with Cu^{2+} . The reversibility of the sensor was realizable by introduction of iodide anion. Moreover, the fluorescent changes of R-2 upon the addition of Hg^{2+} and I^- can be utilized as an INHIBIT logic gate. Therefore, this simple sensor could be potential candidate for the development of a new generation of digital devices.

Acknowledgments

This work was supported by the Fundamental Research Funds for the Central Universities (lzujbky-2012-68).

References

 Lu H, Xiong L, Liu H, Yu M, Shen Z, Li F, et al. A highly selective and sensitive fluorescent turn-on sensor for Hg²⁺ and its application in live cell imaging. Org Biomol Chem 2009;7:2554–8.

- [2] Chen C, Wang R, Guo L, Fu N, Dong H, Yuan Y. A squaraine-based colorimetric and "turn on" fluorescent sensor for selective detection of Hg²⁺ in an aqueous medium. Org Lett 2011;13:1162–5.
- [3] Liu W, Chen J, Xu L, Wu J, Xu H, Zhang H, et al. Reversible "off-on" fluorescent chemosensor for Hg²⁺ based on rhodamine derivative. Spectrochim Acta A 2012;85:38–42.
- [4] Wang F, Nam SW, Guo Z, Park S, Yoon J. A new rhodamine derivative bearing benzothiazole and thiocarbonyl moieties as a highly selective fluorescent and colorimetric chemodosimeter for Hg²⁺. Sens Actuators B 2012;161:948–53.
- [5] Cheng X, Li Q, Qin J, Li Z. A new approach to design ratiometric fluorescent probe for mercury(II) based on the Hg²⁺-promoted deprotection of thioacetals. ACS Appl Mater Interf 2010;2:1066–72.
- [6] Yoon S, Miller EW, He Q, Do PH, Chang CJ. A bright and specific fluorescent sensor for mercury in water, cells, and tissue. Angew Chem Int Edit 2007;46: 6658–61.
- [7] Zhao Y, Zheng BZ, Du J, Xiao D, Yang L. A fluorescent "turn-on" probe for the dual-channel detection of Hg(II) and Mg(II) and its application of imaging in living cells. Talanta 2011;85:2194–201.
- [8] Xie ZJ, Wang K, Zhang CL, Yang ZH, Chen YC, Guo ZJ, et al. A fluorometric/ colorimetric dual-channel Hg²⁺ sensor derived from a 4-amino-7-nitro-benzoxadiazole (ANBD) fluorophore. New J Chem 2011;35:607–13.
- [9] Wu YZ, Dong Y, Li JF, Huang XB, Cheng YX, Zhu CJ. A highly selective and sensitive polymer-based fluorescence sensor for Hg²⁺-ion detection via click reaction. Chem Asian J 2011;6:2725–9.
- [10] Jiang X-J, Wong C-L, Lo P-C, Ng DKP. A highly selective and sensitive BODIPYbased colourimetric and turn-on fluorescent sensor for Hg²⁺ ions. Dalton Trans 2012;41:1801-7.
- [11] Weng JN, Mei QB, Ling QD, Fan QL, Huang W. A new colorimetric and fluorescent ratiometric sensor for Hg²⁺ based on 4-pyren-1-yl-pyrimidine. Tetrahedron 2012;68:3129–34.
- [12] Zhou Y, Zhu C-Y, Gao X-S, You X-Y, Yao C. Hg²⁺-selective ratiometric and "offon" chemosensor based on the azadiene-pyrene derivative. Org Lett 2010;12: 2566–9.
- [13] Lin W-C, Wu C-Y, Liu Z-H, Lin C-Y, Yen Y-P. A new selective colorimetric and fluorescent sensor for Hg²⁺ and Cu²⁺ based on a thiourea featuring a pyrene unit. Talanta 2010;81:1209–15.
- [14] Liu YL, Lv X, Zhao Y, Chen ML, Liu J, Wang P, et al. A naphthalimide-rhodamine ratiometric fluorescent probe for Hg²⁺ based on fluorescence resonance energy transfer. Dyes Pigm 2012;92:909–15.
- [15] Chen T, Zhu W, Xu Y, Zhang S, Zhang X, Qian X. A thioether-rich crown-based highly selective fluorescent sensor for Hg²⁺ and Ag⁺ in aqueous solution. Dalton Trans 2010;39:1316–20.
- [16] He C, Zhu W, Xu Y, Chen T, Qian X. Trace mercury (II) detection and separation in serum and water samples using a reusable bifunctional fluorescent sensor. Anal Chim Acta 2009;651:227–33.
- [17] Kumar M, Dhir A, Bhalla V, Sharma R, Puri RK, Mahajan RK. Highly effective chemosensor for mercury ions based on bispyrenyl derivative. Analyst 2010; 135:1600–5.
- [18] Bhalia V, Tejpal R, Kumar M, Sethi A. Terphenyl derivatives as "turn on" fluorescent sensors for mercury. Inorg Chem 2009;48:11677–84.
- [19] Bhalla V, Tejpal R, Kumar M. Rhodamine appended terphenyl: a reversible "off-on" fluorescent chemosensor for mercury ions. Sens Actuators B 2010; 151:180–5.
- [20] Chen Y, Sun Z-H, Song B-E, Liu Y. Naphthylthiourea-modified permethylcyclodextrin as a highly sensitive and selective "turn-on" fluorescent chemosensor for Hg²⁺ in water and living cells. Org Biomol Chem 2011;9: 5530-4.
- [21] Li H-W, Wang B, Dang Y-Q, Li L, Wu Y. A highly selective fluorescent sensor for mercury ions in aqueous solution: detection based on target-induced aggregation. Sens Actuators B 2010;148:49–53.
- [22] Wang X, Wang P, Dong Z, Dong Z, Ma Z, Jiang J, et al. Highly sensitive fluorescence probe based on functional SBA-15 for selective detection of Hg²⁺. Nanoscale Res Lett 2010;5:1468–73.

- [23] Dhir A, Bhalla V, Kumar M. Ratiometric sensing of Hg²⁺ based on the calix[4] arene of partial cone conformation possessing a dansyl moiety. Org Lett 2008; 10:4891–4.
- [24] Lin W, Cao X, Ding Y, Yuan L, Yu Q. A reversible fluorescent Hg²⁺ chemosensor based on a receptor composed of a thiol atom and an alkene moiety for living cell fluorescence imaging. Org Biomol Chem 2010;8:3618–20.
- [25] Kaewtong C, Wanno B, Uppa Y, Morakot N, Pulpoka B, Tuntulani T. Facile synthesis of rhodamine-based highly sensitive and fast responsive colorimetric and off-on fluorescent reversible chemosensors for Hg²⁺: preparation of a fluorescent thin film sensor. Dalton Trans 2011;40:12578–83.
 [26] Zhao Y, Sun Y Ly X Lin Y, Chen M, Cur W P, Standard M, Sun Y Ly X Lin Y, Chen M, Cur W P, Standard M, Standard M, Standard M, Standard M, Standard M, Sun Y Ly X Lin Y, Chen M, Cur W P, Standard M, St
- [26] Zhao Y, Sun Y, Lv X, Liu Y, Chen M, Guo W. Rhodamine-based chemosensor for Hg²⁺ in aqueous solution with a broad pH range and its application in live cell imaging. Org Biomol Chem 2010;8:4143–7.
- [27] Wang Y, Huang Y, Li B, Zhang L, Song H, Jiang H, et al. A cell compatible fluorescent chemosensor for Hg²⁺ based on a novel rhodamine derivative that works as a molecular keypad lock. RSC Adv 2011;1:1294–300.
- [28] Hu Z-Q, Lin C-S, Wang X-M, Ding L, Cui C-L, Liu S-F, et al. Highly sensitive and selective turn-on fluorescent chemosensor for Pb²⁺ and Hg²⁺ based on a rhodamine-phenylurea conjugate. Chem Commun 2010;46:3765–7.
- [29] Saha S, Mahato P, Reddy UG, Suresh E, Chakrabarty A, Baidya M, et al. Recognition of Hg²⁺ and Cr³⁺ in physiological conditions by a rhodamine derivative and its application as a reagent for cell-imaging studies. Inorg Chem 2012;51:336–45.
- [30] Jiang L, Wang L, Zhang B, Yin G, Wang R-Y. Cell compatible fluorescent chemosensor for Hg²⁺ with high sensitivity and selectivity based on the rhodamine fluorophore. Eur J Inorg Chem 2010:4438–43.
- [31] de Silva AP, McClenaghan ND. Molecular-scale logic gates. Chem Eur J 2004; 10:574-86.
- [32] Amir RJ, Popkov M, Lerner RA, Barbas CF, Shabat D. Prodrug activation gated by a molecular "OR" logic trigger. Angew Chem Int Edit 2005;44:4378–81.
- [33] Andréasson J, Terazono Y, Albinsson B, Moore TA, Moore AL, Gust D. Molecular AND logic gate based on electric dichroism of a photochromic dihydroindolizine. Angew Chem Int Edit 2005;44:7591–4.
- [34] Bhalla V, Vij V, Dhir A, Kumar M. Hetero-oligophenylene-based AIEE material as a multiple probe for biomolecules and metal ions to construct logic circuits: application in bioelectronics and chemionics. Chem Eur J 2012;18:3765–72.
- [35] Szacilowski K. Molecular logic gates based on pentacyanoferrate complexes: from simple gates to three-dimensional logic systems. Chem Eur J 2004;10:2520_8.
- [36] Mishra RK, Upadhyay KK. Coumarin-based chromogenic receptor for Ni²⁺ in aqueous medium exhibiting a reconfigurable logic gate pattern. Eur J Org Chem 2011:4799–805.
- [37] Maligaspe E, D'Souza F. NOR and AND logic gates based on supramolecular porphyrin-fullerene conjugates. Org Lett 2009;12:624–7.
- [38] Li A-F, Ruan Y-B, Jiang Q-Q, He W-B, Jiang Y-B. Molecular logic gates and switches based on 1,3,4-oxadiazoles triggered by metal ions. Chem Eur J 2010; 16:5794-802.

- [39] Kluciar M, Ferreira R, de Castro B, Pischel U. Modular functional integration of a two-input INH logic gate with a fluorophore-spacer-receptor1-spacer-receptor2 conjugate. J Org Chem 2008;73:6079–85.
- [40] Zhou J, Arugula MA, Halamek J, Pita M, Katz E. Enzyme-based NAND and NOR logic gates with modular design. J Phys Chem B 2009;113:16065–70.
- [41] Wu D, Huang W, Lin Z, Duan C, He C, Wu S, et al. Highly sensitive multiresponsive chemosensor for selective detection of Hg²⁺ in natural water and different monitoring environments. Inorg Chem 2008;47:7190–201.
- [42] Chereddy NR, Thennarasu S. Synthesis of a highly selective bis-rhodamine chemosensor for naked-eye detection of Cu²⁺ ions and its application in bio-imaging. Dyes Pigm 2011;91:378–82.
- [43] Wu JC, Tang N, Liu WS, Tan MY, Chan ASC. Intramolecular hydrogen bond selftemplate synthesis of some new Robson-type macrocyclic ligands. Chin Chem Lett 2001;12:757–60.
- [44] Ma Q-J, Zhang X-B, Zhao X-H, Jin Z, Mao G-J, Shen G-L, et al. A highly selective fluorescent probe for Hg²⁺ based on a rhodamine-coumarin conjugate. Anal Chim Acta 2010;663:85–90.
- [45] Zeng X, Dong L, Wu C, Mu L, Xue S-F, Tao Z. Highly sensitive chemosensor for Cu(II) and Hg(II) based on the tripodal rhodamine receptor. Sens Actuators B 2009;141:506–10.
- [46] Mu Shi, Chang JC, Lee S-T. Silicon nanowires-based fluorescence sensor for Cu(II). Nano Lett 2008;8:104–9.
- [47] Wang H, Li Y, Xu S, Li Y, Zhou C, Fei X, et al. Rhodamine-based highly sensitive colorimetric off-on fluorescent chemosensor for Hg²⁺ in aqueous solution and for live cell imaging. Org Biomol Chem 2011;9:2850–5.
 [48] Huang J, Xu Y, Qian X. A rhodamine-based Hg²⁺ sensor with high selectivity
- [48] Huang J, Xu Y, Qian X. A rhodamine-based Hg²⁺ sensor with high selectivity and sensitivity in aqueous solution: a NS2-containing receptor. J Org Chem 2009;74:2167–70.
- [49] Zhang XL, Xiao Y, Qian XH. A ratiometric fluorescent probe based on FRET for imaging Hg²⁺ ions in living cells. Angew Chem Int Edit 2008;47:8025–9.
- [50] Mahato P, Saha S, Suresh E, Di Liddo R, Parnigotto PP, Conconi MT, et al. Ratiometric detection of Cr³⁺ and Hg²⁺ by a naphthalimide-rhodamine based fluorescent probe. Inorg Chem 2012;51:1769–77.
- [51] Lee PF, Yang C-T, Fan D, Vittal JJ, Ranford JD. Synthesis, characterization and physicochemical properties of copper(II) complexes containing salicylaldehyde semicarbazone. Polyhedron 2003;22:2781–6.
- [52] Wang LN, Yan JX, Qin WW, Liu WS, Wang R. A new rhodamine-based single molecule multianalyte (Cu²⁺, Hg²⁺) sensor and its application in the biological system. Dyes Pigm 2012;92:1083–90.
- [53] Dong M, Ma T, Zhang A, Dong Y, Wang Y, Peng Y. A series of highly sensitive and selective fluorescent and colorimetric "off-on" chemosensors for Cu (II) based on rhodamine derivatives. Dyes Pigm 2010;87:164–72.
- [54] Jana A, Kim JS, Jung HS, Bharadwaj PK. A cryptand based chemodosimetric probe for naked-eye detection of mercury(II) ion in aqueous medium and its application in live cell imaging. Chem Commun 2009:4417–9.