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A dansyl-rhodamine chemosensor for Fe(III) based on off-on FRET



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- The chemosensor was synthesized relatively in a simple way.
- The skeleton of the chemosensor is composed of a dansyl and rhodamine group.
- Off-on FRET was induced by Fe³⁺ binding to the chemosensor.
- The chemosensor showed high selectivity and sensitivity for Fe³⁺.



A R T I C L E I N F O

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ABSTRACT

A novel fluorescent chemosensor bearing a rhodamine and a dansyl moiety was developed for highly selective detection of Fe³⁺ based on fluorescence resonance energy transfer (FRET) mechanism. Binding of Fe³⁺ to the chemosensor induced spirolactam ring opening in the rhodamine moiety and subsequent off–on FRET from the dansyl energy donor to the rhodamine energy acceptor due to the spectral overlap between the emission of the dansyl moiety and the absorption of the ring opened rhodamine moiety. Job's plot analysis indicated a 1:1 binding stoichiometry between the chemosensor and Fe³⁺. The association constant was estimated to be 2.72×10^3 M⁻¹ according to the Benesi–Hildebrand method. With the feature of easy synthesis, simple structural skeleton and excellent sensing ability, the newly synthesized chemosensor provided the potential for applying as a highly selective fluorescent probe in complex samples containing various competitive metal ions and developing other metal ion chemosensors to fulfill various needs of biological and environmental field.

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Introduction

Highly selective and sensitive detection of heavy metal and transition metal ions, have attracted considerable attention in recent years because of their important roles in environmental and biological systems [1–4]. As one of the most essential trace metals within human body, iron ion plays crucial roles in protein synthesis and structural maintenance, enzymatic reaction, oxygen

transportation and energy metabolism [5,6]. Unbalanced iron content within human body can cause a variety of diseases, such as iron deficiency anemia [7–10]. Some recent researches have even revealed that Fe^{3+} could involve in some neurodegenerative diseases, such as Parkinson's and Alzheimer's disease [11–14]. Researches on developing Fe^{3+} sensing platforms have been of great interest and challenge. To date, most Fe^{3+} sensing assays depend on the fluorescence quenching mechanism because of the paramagnetic nature of ionic iron, which inevitably give high background signals [15,16]. Relatively, there are only a few fluorescent chemosensors reported for detecting Fe^{3+} based on fluorescent

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"turn on" mechanism [17–19]. Thus, there is still an intense demand for developing highly selective and sensitive Fe³⁺ chemosensors to satisfy various needs of environmental and biological fields.

A certain number of rhodamine based fluorescent chemosensors have been developed for monitoring various metal ions of biologically and environmentally importance, due to their excellent photophysical properties such as high absorption coefficient, high fluorescence quantum yield, good photostability and relatively long emission wavelength [20-22]. The equilibrium between the spirolactam (non-fluorescent) and the spirocyclic form (fluorescent) makes the rhodamine framework an ideal off-on fluorescent probe, especially for metal ions, such as Cu²⁺, Hg²⁺, Pb²⁺, Cr³⁺, Cd²⁺, Zn^{2+} . However, the small Stokes shift (~30 nm) of the fluorescent probe tends to induce serious fluorescence quenching and Rayleigh scattering, which leads to severe detection errors. To solve the problem. FRET was chosen and applied in many detection platforms for its convenience to modify the excitation source [23-29]. FRET is defined as a nonradiative energy transfer process in which the excited donor energy is transferred to an acceptor unit without photoemission. Since the pseudo-Stokes shift of FRET based probes are larger than the Stokes shift of either the donor or acceptor dyes, the fluorescence detection errors can be efficiently avoided [30]. Although rhodamine based Fe³⁺ chemosensors have been intensively studied, but off-on FRET based fluorescent sensors containing tren-spaced rhodamine are still rare.

In this research, we have designed and synthesized a new fluorescent probe for Fe^{3^+} based on off–on FRET. The skeleton of the probe was composed of a rhodamine dye and a dansyl group [22,31–33], which displayed significant spectral overlap between the emission spectra of the dansyl energy donor and the absorption spectra of the rhodamine energy acceptor upon binding with Fe^{3^+} . The binding of Fe^{3^+} causes structural change in the rhodamine moiety and induces the spirolactam ring opening, facilitating the intramolecular FRET from donor to acceptor in the probe [23,34]. To the best of our knowledge, this is the first time that a compound containing a rhodamine (energy acceptor) and a dansyl group (energy donor) has been used as a fluorescent probe for Fe^{3^+} based on FRET.

Experimental

Materials and instrumentation

All chemicals were obtained from commercial suppliers and used without further purification unless otherwise mentioned. Absorption spectra were recorded with a Shimadzu UV-2550 spectrophotometer (Shimadzu, Japan). Fluorescence spectra were taken on RF-5301PC spectrofluorophotometer (Shimadzu, Japan). The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV-300 spectrometer (300 MHz for ¹H and 75 MHz for ¹³C) (Bruker, Switzerland). Mass spectra were measured on an Agilent 7500a ICP-MS Mass spectrometer (Agilent, USA). IR spectra were obtained with a Shimadzu FT-IR Prestige-21 instrument (Shimadzu, Japan) (KBr pressed disc method). The silica gel (J&K Scientific Ltd., Beijing, China) used for flash chromatography was 200-300 mesh. Rhodamine B, ethylenediamine, dansyl chloride, TsCl, triethylamine were purchased from Aladdin (Shanghai, China) and used without further purification. All cationic compounds such as perchlorate of Ag⁺, Âl³⁺, Ba²⁺, Ca²⁺, Cu²⁺, Fe²⁺, Cr³⁺, Fe³⁺, Hg²⁺, K⁺, Mg²⁺, Ni²⁺, Pb²⁺ Zn²⁺ were obtained from Strem Chemicals (Newburyport, MA, USA).

Synthesis

Compound 1

Under nitrogen, a solution of rhodamine B (0.5 g, 1.0 mmol), ethanediamine (90 mg, 1.5 mmol) and methanol (40 mL) was heated at 80 °C for 5 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. Then, the resulting mixture was dissolved by adding CH_2Cl_2 (100 mL) and water (200 mL). After removing the organic layer, the residue was dried over anhydrous Na₂SO₄ and filtered. The solvent was evaporated under reduced product was purified by column chromatography (ethyl acetate:ethanol = 1:3) to give 0.43 g of saffron yellow 1 in 85% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.91 (dd, J = 5.6, 3.0 Hz, 1H), 7.45 (dd, J = 5.6, 3.1 Hz, 2H), 7.10



Scheme 1. Synthesis of chemosensor 2.



Fig. 1. Normalized absorption and emission spectra of both donor and acceptor moiety. The spectral overlap between the emission of the donor and the absorption of the acceptor is marked with oblique line.

(dd, *J* = 5.5, 3.0 Hz, 1H), 6.43 (d, *J* = 8.8 Hz, 2H), 6.37 (d, *J* = 2.4 Hz, 2H), 6.27 (dd, *J* = 8.8, 2.5 Hz, 2H), 3.33 (q, *J* = 7.1 Hz, 8H), 3.19 (t, *J* = 6.6 Hz, 2H), 2.39 (t, *J* = 6.6 Hz, 2H), 1.16 (t, *J* = 7.0 Hz, 12H).

Compound 2

In an ice bath, a solution of dansyl chloride (100 mg, 1.0 mmol) in anhydrous dichloromethane (10 mL) was added slowly to a mixture of compound 1 and triethylamine (0.5 mL) in anhydrous dichloromethane (20 mL), and then the resulting mixture was stirred for 0.5 h at room temperature. With the similar workup procedures as described in synthesis of compound 1, a crude product of compound 2 was obtained. And the crude product was purified by column chromatography (ethyl acetate:petroleum ether = 1:1) to give 120 mg of saffron yellow 2 in 82% yield. ¹H NMR (300 MHz, $CDCl_3$) δ 8.48 (d, I = 8.5 Hz, 1H), 8.29 (d, I = 8.7 Hz, 1H), 8.11 (d, *I* = 8.5 Hz, 1H), 7.89 (d, *I* = 6.4 Hz, 1H), 7.45 (ddd, *I* = 24.1, 16.5, 8.7 Hz, 4H), 7.03 (d, *I* = 7.5 Hz, 1H), 6.91 (d, *I* = 7.8 Hz, 1H), 6.28 (d, J = 2.5 Hz, 2H), 5.95 (dd, J = 8.9, 2.5 Hz, 2H), 5.84 (d, J = 8.9 Hz, 2H), 3.29 (q, J = 7.0 Hz, 8H), 3.21-3.16 (t, 2H), 2.78 (s, 6H), 2.63 (t, J = 9.9, 4.6 Hz, 2H), 1.14 (t, J = 7.0 Hz, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 169.80, 153.37, 152.66, 151.19, 148.35, 134.28, 132.31, 129.67, 129.46, 128.53, 123.79, 121.76, 119.05, 114.73, 107.63, 103.76, 97.21, 78.06, 75.91, 76.43, 76.43, 65.18, 45.02, 43.90, 39.47, 12.19. MS: [M⁺] at 718.

Compound 3

In an ice bath, a solution of TsCl (39.3 mg, 1.0 mmol) in anhydrous dichloromethane (10 mL) was added slowly to a mixture of compound 1 and triethylamine (0.5 mL) in anhydrous dichloromethane (20 mL), and then the resulting mixture was stirred for 0.5 h at room temperature. With the similar workup procedures as described in synthesis of compound 1, a crude product of compound 3 was obtained. And the crude product was purified by column chromatography (ethyl acetate:petroleum ether = 1:1) to give saffron yellow 3 in 83% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.89 (dd, *J* = 6.2, 2.5 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.45 (dd, *J* = 5.4, 2.9 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.08-7.00 (m, 1H), 6.35 (d, J = 1.8 Hz, 2H), 6.24 (d, / = 8.8 Hz, 2H), 6.16 (dd, / = 8.9, 1.8 Hz, 2H), 6.03 (t, J = 4.6 Hz, 1H), 3.33 (q, J = 7.0 Hz, 8H), 3.20–3.13 (m, 2H), 2.76 (dd, J = 10.3, 5.0 Hz, 2H), 2.36 (s, 3H), 1.59 (s, 2H), 1.17 (t, I = 7.0 Hz, 13H). ¹³C NMR (75 MHz, CDCl₃) δ 169.28, 153.22, 152.83, 148.50, 142.31, 132.41, 129.91, 129.02, 127.87, 126.74, 123.42, 122.46, 107.80, 104.08, 97.37, 76.84, 76.20, 65.15, 43.96, 43.24, 39.74, 21.05, 12.19. MS: [M⁺] at 638.9.



Fig. 2. Absorption (a) and emission (b) spectra of chemosensor 2 (10 μ M) upon addition of various metal ion (10 equiv) in ethanol solution. $\lambda_{ex} = 420$ nm.

Procedures for metal ion sensing

A stock solution of compound 2 (1.0×10^{-5} M) was prepared in ethanol. Stock solutions of the metal perchlorate salts were prepared in ethanol with a concentration of 2.0×10^{-3} M. Each time a stock solution of compound 2 (2.0 mL) and less than 100 μ L of a metal ion stock solution were filled in a quartz cell of 1 cm optical path length using a micro-pipette for spectral measurements. For all measurements of fluorescence spectra, excitation wavelength was 420 nm unless otherwise mentioned and the temperature is 20 °C.

Results and discussion

As shown in Scheme 1, compound 2 (chemosensor 2) was facilely prepared by a simple condensation reaction between compound 1 and dansyl chloride at room temperature in 82% yield. The structure of chemosensor 2 was confirmed by NMR (¹H and ¹³C) spectra, ESI mass spectrometry and IR spectroscopy (supporting information). The ¹H NMR spectrum of chemosensor 2 displayed a triplet (12H) at 1.14 ppm corresponding to the methyl protons, a singlet (6H) at 2.78 ppm corresponding to the methyl protons, two triplet (2H each) at 2.60-2.65 and 3.18-3.21 corresponding to CH_2 of ethanediamine moiety, a guarlet (8H) at 3.25–3.32 ppm corresponding to the methylene protons, three mutiplets (2H each) at 5.83-5.93, 5.94-5.97 and 6.27-6.28 ppm corresponding to aromatic protons, seven multiplets (1H, 1H, 5H, 1H, 1H, 1H and 1H respectively) at 6.90-6.92, 7.02-7.04, 7.38-7.51, 7.88-7.90, 8.09-8.12, 8.28-8.31 and 8.47-8.50 ppm corresponding to aromatic and NH protons (Fig. S2). Mass spectrum of chemosensor 2 showed a parent ion peak at m/z 718 (Fig. S4). A



Fig. 3. Color (top) and fluorescence (bottom) images of chemosensor 2 (10 μ M) upon addition of various metal ion in ethanol solution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Scheme 2. Proposed mechanism for chemosensor 2 + Fe³⁺ complex.

stretching band at 1678 cm⁻¹ corresponding to the C=O group was observed in the IR spectrum of chemosensor 2 (Fig. S5). There was no absorption band of free hydroxyl group in the IR spectrum, which confirmed that the condensation reaction has been successfully occurred. Free chemosensor 2 solution is colorless and nonfluorescent, which indicated the rhodamine moiety exist in its ring-closed spirolactam form.

The absorption and emission spectra of individual components of chemosensor 2 are shown in Fig. 1. The dansyl moiety has strong and broad emission in the visible range (450–650 nm) which covers a part of the absorption of the ring-opened rhodamine moiety, providing the favorable condition for FRET. The ethanediamine moiety acts as both a linking ligand to connect the rhodamine and dansyl moiety in close proximity and a chelating ligand to provide crucial chelating sites for Fe³⁺ by coordination with the dansyl moiety [35,36].

The binding behavior of chemosensor 2 towards various metal ions (Ag⁺, Al³⁺, Ba²⁺, Ca²⁺, Cu²⁺, Fe³⁺, Hg²⁺, K⁺, Mg²⁺, Ni²⁺, Pb²⁺, Zn²⁺, Fe²⁺, Cr³⁺) was studied by fluorescence and UV–vis spectroscopy. As shown in Fig. 2a, a characteristic absorption peak of the ring-opened rhodamine moiety was appeared at 555 nm upon forming 2-Fe³⁺ complex. While, other metal ions did not induce any distinct spectral changes in the visible region, implying that chemosensor 2 has no special binding ability for these metal ions. Upon excitation at 420 nm, a strong emission peak at 578 nm was observed in addition to the relatively weak emission at about 507 nm in the fluorescence spectrum of the $2-Fe^{3+}$ complex (Fig. 2b), indicating the FRET occurring from the dansyl energy donor to the rhodamine energy acceptor. However, for other metal ions, there was no other emission peak observed except the relatively weak emission peak at 507 nm which were produced from the dansyl moiety. More than 10-fold fluorescence enhancement was estimated in the 2-Fe³⁺ complex, according to the ratio of the fluorescence intensity of the energy acceptor at 578 nm to that of the energy donor at 507 nm. Moreover, upon irradiation at 555 nm, strong fluorescence emission at around 578 nm in the spectrum of the 2-Fe³⁺ complex was observed, confirming the spirolactam ring opening in the rhodamine moiety (data not shown). Color and fluorescence images of the corresponding metal ion testing solutions showed that Fe³⁺ was the only ion that changed the color of chemosensor 2 solution from colorless to pink and fluorescence from green to brown as shown in Fig. 3, which implied that the rhodamine moiety is in its ring-opened spirocyclic form.



Fig. 4. Absorption (a) and fluorescence (b) change of chemosensor 2 (10 μ M) upon addition of Fe³⁺ (10 equiv) in the presence and absence of other metal ions (10 equiv) in ethanol solution. $\lambda_{ex} = 420$ nm. Red bars and black bars represent the 2-Fe³⁺ complex without and with other metal ions, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

To further confirm the fluorescence from the rhodamine moiety was actually due to FRET from the dansyl energy donor to the rhodamine energy acceptor, we replaced the dansyl group with a tosyl one in chemosensor 2 to obtain compound 3 through the similar condensation way as shown in Scheme 1. Interestingly, compound 3 (chemosensor 3) also exhibited good sensing ability towards Fe³⁺ as that shown by chemosensor 2 (Figs. S10 and S11). However, extremely different sensing mechanism between the two chemosensors



Fig. 5. Absorption (a) and fluorescence (b) titration spectra of chemosensor 2 (10 μ M) upon addition of Fe³⁺ (0–15 equiv) in ethanol solution. λ_{ex} = 420 nm. (a) Inset: Job's plot for determining the stoichiometry of chemosensor 2 and Fe³⁺. (b) Inset: plot of fluorescence intensity at 578 nm as a function of Fe³⁺ concentration. The detection limit (DL) of Fe³⁺ using chemosensor 2 was determined from the following equation: DL = $K \times SD/S$, where K = 3; SD is the standard deviation of the blank solution; S is the slope of the calibration curve. DL = 1.05 × 10⁻⁶ M.

seems exist. In the case of 3-Fe^{3+} complex, the fluorescence from the rhodamine moiety could only be observed when excited at 555 nm (absorption of the rhodamine moiety with spirocyclic form) other than other wavelength which implied that there was no FRET between the tosyl moiety and the rhodamine one since the tosyl moiety has no characteristic absorption in the visible region at all. Thus, we can confirm that the fluorescence of the 2-Fe³⁺complex was due to FRET from the dansyl energy donor to the rhodamine energy acceptor. Although the FRET efficiency in the system was relatively low (around 50%, see supporting information), but the fluorescence dual-switch (two different excitation wavelengths of 420 and 555 nm) feature may find its superiority in complex sample solution, such as living cell imaging [37,38], by providing double evidences in one time.

According to the sensing performance of chemosensor 2 for Fe³⁺, the possible binding mechanism was proposed as shown in Scheme 2. The IR spectra showed that the amide carbonyl peak (1678 cm⁻¹) disappeared after Fe³⁺ was added (Fig. S12), which provide evidence that the amide carbonyl O of chemosensor 2 is actually involved in coordination with metal ions. The binding process of chemosensor 3 with Fe³⁺ is expected to be in the similar way as that shown by chemosensor 2.

The selectivity of chemosensor 2 for Fe³⁺ over other metal ions was further evaluated by performing interference experiments in ethanol solution. Chemosensor 2 was mixed with a mixture of

10 equiv of Fe^{3+} and 10 equiv of other metal ions $(Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cu^{2+}, Hg^{2+}, K^+, Mg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Fe^{2+}, Cr^{3+})$ separately, and the resulting individual test solution was analyzed by UV–Vis and fluorescence spectrophotometer. As displayed in Fig. 4, there was no significant spectral change for the 2-Fe³⁺ complex with and without other metal ions, which confirmed that chemosensor 2 can be used as a selective probe for Fe³⁺ in the presence of other metal ions in both colorimetric and fluorescent way.

Absorption and fluorescence titrations of chemosensor 2 were conducted to monitor the spectral changes in accordance with the amount of Fe³⁺. The UV-vis spectra (Fig. 5a) exhibited that the absorption at 555 nm was gradually increased with the addition of Fe³⁺ (0–15 equiv), accompanied with visible color change in corresponding test solution. Job's plot analysis showed that the binding stoichiometry between chemosensor 2 and Fe³⁺ was 1:1 (Fig. 5a, inset). The emission band centered at 578 nm was also gradually increased with the increasing amounts of Fe³⁺ and reached a plateau after the addition of 15 equiv of Fe^{3+} (Fig. 5b). And the association constant of $2.72 \times 10^3 \text{ M}^{-1}$ was obtained using the Benesi-Hildebrand method by plotting $1/\Delta F$ against $1/[Fe^{3+}]$ for chemosensor 2 and Fe³⁺ (Fig. S13). Moreover, nearly linear relationship between the fluorescence change and Fe³⁺ concentration in the range of $10-150 \mu$ M was achieved (Fig. 5b, inset), with a detection limit of 1.05 µM, which is comparable with that mentioned in the literatures [39–41].

Conclusions

In summary, a new fluorescent probe containing a rhodamine energy acceptor and a dansyl energy donor was synthesized and applied for selective detection of Fe^{3+} based on FRET off–on mechanism. The success of off–on FRET from the dansyl energy donor to the rhodamine energy acceptor not only drastically reduced background signal by enlarging the pseudo-Stokes shift but also provided a good structural skeleton for designing Fe^{3+} chemosensor for more widely use. In addition, the relatively high selectivity and sensitivity for Fe^{3+} over other metal ions showed the possibility for potential use in complex samples containing various competitive metal ions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.03.002.

References

- [1] M. Dutta, D. Das, Trac-Trend. Anal. Chem. 32 (2012) 113–132.
- [2] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515–1566.
- [3] D.W. Domaille, E.L. Que, C.J. Chang, Nat. Chem. Biol. 4 (2008) 168-175.
- [4] X.G. Li, Y.W. Liu, M.R. Huang, S. Peng, L.-Z. Gong, M.G. Moloney, Chem.-Eur. J. 16 (2010) 4803–4813.
- [5] B. D'Autreaux, N.P. Tucker, R. Dixon, S. Spiro, Nature 437 (2005) 769-772.
- [6] J.F. Collins, J.R. Prohaska, M.D. Knutson, Nutr. Rev. 68 (2010) 133-147.
- [7] D. Galaris, V. Skiada, A. Barbouti, Cancer Lett. 266 (2008) 21–29.
- [8] T. Thum, S.D. Anker, Lancet 370 (2007) 1906.
- [9] R.S. Ajioka, J.P. Kushner, Blood 101 (2003) 3351-3354.
- [10] J.D. Haas, T. Brownlie, J. Nutr. 131 (2001) 676s-688s.
- [11] J.R. Burdo, J.R. Connor, Biometals 16 (2003) 63-75.
- [12] J.R. Burdo, D.A. Antonetti, E.B. Wolpert, J.R. Connor, Neuroscience 121 (2003) 883–890.

- [13] D.J. Bonda, H.G. Lee, J.A. Blair, X.W. Zhu, G. Perry, M.A. Smith, Metallomics 3 (2011) 267–270.
- [14] A.S. Pithadia, M.H. Lim, Curr. Opin. Chem. Biol. 16 (2012) 67-73.
- [15] J.L. Bricks, A. Kovalchuk, C. Trieflinger, M. Nofz, M. Buschel, A.I. Tolmachev, J. Daub, K. Rurack, J. Am. Chem. Soc. 127 (2005) 13522–13529.
- [16] J.P. Sumner, R. Kopelman, Analyst 130 (2005) 528–533.
 [17] M.Y. She, Z. Yang, B. Yin, J. Zhang, J. Gu, W.T. Yin, J.L. Li, G.F. Zhao, Z. Shi, Dyes
- Pigments 92 (2012) 1337–1343.
- [18] S.R. Liu, S.P. Wu, Sensor. Actuat. B-Chem. 171 (2012) 1110–1116.
- M.-R. Huang, S.-J. Huang, X.-G. Li, J. Phys. Chem. C 115 (2011) 5301–5315.
 M.H. Lee, T. Van Giap, S.H. Kim, Y.H. Lee, C. Kang, J.S. Kim, Chem. Commun. 46 (2010) 1407–1409.
- [21] Z. Yang, M.Y. She, B. Yin, J.H. Cuo, Y.Z. Zhang, W. Sun, J.L. Li, Z. Shi, J. Org. Chem. 77 (2012) 1143–1147.
- [22] M.H. Lee, H.J. Kim, S. Yoon, N. Park, J.S. Kim, Org. Lett. 10 (2008) 213-216.
- [23] H.B. Yu, Y. Xiao, H.Y. Guo, X.H. Qian, Chem.-Eur. J. 17 (2011) 3179-3191.
- [24] Y.L. Liu, X. Lv, Y. Zhao, M.L. Chen, J. Liu, P. Wang, W. Guo, Dyes Pigments 92 (2012) 909–915.
- [25] D. Maity, D. Karthigeyan, T.K. Kundu, T. Govindaraju, Sensor. Actuat. B-Chem. 176 (2013) 831–837.
- [26] A. Coskun, E.U. Akkaya, J. Am. Chem. Soc. 127 (2005) 10464–10465.
- [27] W.Y. Lin, L. Yuan, L.L. Long, C.C. Guo, J.B. Feng, Adv. Funct. Mater. 18 (2008) 2366–2372.
- [28] Z.P. Liu, C.L. Zhang, W.J. He, Z.H. Yang, X.A. Gao, Z.J. Guo, Chem. Commun. 46 (2010) 6138–6140.
- [29] Z.X. Han, X.B. Zhang, L. Zhuo, Y.J. Gong, X.Y. Wu, J. Zhen, C.M. He, L.X. Jian, Z. Jing, G.L. Shen, R.Q. Yu, Anal. Chem. 82 (2010) 3108–3113.
- [30] S.R. Adams, A.T. Harootunian, Y.J. Buechler, S.S. Taylor, R.Y. Tsien, Nature 349 (1991) 694–697.
- [31] M.W. Piepkorn, D. Lagunoff, G. Schmer, Arch. Biochem. Biophys. 205 (1980) 315–322.
- [32] J. Fan, M. Hu, P. Zhan, X. Peng, Chem. Soc. Rev. 42 (2013) 29-43.
- [33] B.E. Leonard, N.N. Osborne, in: N. Marks, R. Rodnight (Eds.), Research Methods in Neurochemistry, Springer, US, 1975, pp. 443–462.
- [34] A. Ben Othman, J.W. Lee, J.S. Wu, J.S. Kim, R. Abidi, P. Thuery, J.M. Strub, A. Van Dorsselaer, J. Vicens, J. Org. Chem. 72 (2007) 7634–7640.
- [35] L. Dong, C. Wu, X. Zeng, L. Mu, S.F. Xue, Z. Tao, J.X. Zhang, Sensor. Actuat. B-Chem. 145 (2010) 433–437.
- [36] L.Z. Zhang, J.Y. Wang, J.L. Fan, K.X. Guo, X.J. Peng, Bioorg. Med. Chem. Lett. 21 (2011) 5413–5416.
- [37] N.R. Chereddy, K. Suman, P.S. Korrapati, S. Thennarasu, A.B. Mandal, Dyes Pigments 95 (2012) 606–613.
- [38] B. Bag, B. Biswal, Org. Biomol. Chem. 10 (2012) 2733-2738.
- [39] Y. Wei, Z. Aydin, Y. Zhang, Z. Liu, M. Guo, ChemBioChem 13 (2012) 1569–1573.
 [40] S. Sen, S. Sarkar, B. Chattopadhyay, A. Moirangthem, A. Basu, K. Dhara, P.
- Chattopadhyay, Analyst 137 (2012) 3335–3342.
- [41] X.-G. Li, Y. Liao, M.-R. Huang, V. Strong, R.B. Kaner, Chem. Sci. 4 (2013) 1970– 1978.