Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2012, 22, 5291

www.rsc.org/materials

COMMUNICATION

A new strategy for highly selective fluorescent sensing of F^- and Zn^{2+} with dual output modes⁺

Yinyin Bao, Bin Liu, Fanfan Du, Jiao Tian, Hu Wang and Ruke Bai*

Received 5th December 2011, Accepted 30th January 2012 DOI: 10.1039/c2jm16364k

A new strategy for highly selective and sensitive detection of both $F^$ and Zn^{2+} with dual output modes was developed, which is based on a combination of F^- induced desilylation reaction and chelationenhanced fluorescence effect caused by Zn^{2+} .

Numerous chemosensors and receptors for anions1 as well as metal ions² have been reported in recent years due to their biological importance. Among the anions, fluoride is the smallest and has unique chemical properties because of the high electronegativity and strong basicity. Fluoride exists in toothpaste and pharmaceutical agents and plays an important role in preventing dental caries and in the treatment of osteoporosis.3 However, excessive ingestion of F- may result in fluorosis, cause nephrotoxic changes in both humans and animals, and lead to urolithiasis.⁴ On the other hand, zinc, as the second most abundant transition-metal ion in the human body, plays vital roles in biological processes. The quantity variance of zinc would affect the function of the proteins and enzymes concerning neural signal transmission, DNA reproduction, and other processes.5 Therefore, the accurate determination of the concentration of fluoride and zinc is very important for human health and environment protection.

The fluorescent sensing method has been developed as a useful tool for detecting anions and metal ions due to the simplicity, high sensitivity, high selectivity, and real-time detection.^{1d,e} Although a number of F⁻ (ref. 6–8) and Zn²⁺ (ref. 9 and 10) fluorescent chemosensors have been reported, the probes which can exhibit obvious fluorescence response to both F⁻ and Zn²⁺ are rather rare,¹¹ and the sensing properties especially selectivity of the probes remain unsatisfied. In addition, most of the dual functional fluorescent sensors for anions and cations are based on the displacement approach,^{11a,d} which means the sensing output mode is single and the selectivity may be limited. In order to develop new multifunctional fluorescent sensors and improve the sensing properties, the design of the sensors for F⁻ and Zn²⁺ with a new sensing mechanism is still a quite important and intriguing theme.

This journal is © The Royal Society of Chemistry 2012

8-Hydroxy-2-methylquinoline (Oxn) is a well-known building block for chelation enhanced fluorescent (CHEF) sensors for transition metals.¹² In our previous papers, the sensors based on 8-hydroxyquinoline were prepared and used to detect F- (ref. 13) and Cd²⁺ (ref. 14) ions, respectively. Herein we report a new strategy for highly selective and sensitive detection of both F⁻ and Zn²⁺ utilizing fluorescent chemosensor 1, by a combination of F- induced desilylation reaction¹⁵ and chelation-enhanced fluorescence (CHEF) effect caused by Zn²⁺. The sensor 1 was synthesized through Suzuki coupling reaction and the synthetic routes are illustrated in Scheme 1. The commercial 8-hydroxy-2-methylquinoline was reacted with tertbutyldimethylsilyl chloride (TBDMSCl) in CH₂Cl₂ (ref. 16) and brominated with N-bromosuccinimide (NBS) at room temperature to form 3. Then 3 was borylated by pinacolborane to afford 2 with a yield of 79%. Finally, 2 was reacted with 4-bromobenzaldehyde through Suzuki coupling, resulting in the sensor molecule 1 in 70% yield. The product was characterized by ¹H NMR, ¹³C NMR, and mass spectra analysis (see ESI[†]).

The emission spectrum of sensor **1** in CH₃CN shows a bright blue fluorescence with a peak at 458 nm and upon addition of fluoride ions, a strong quenching phenomenon was observed. As shown in Fig. 1, the emission peak at 458 nm gradually decreases with increasing the amount of F^- ions, and the intensity exhibits linear changes with the concentration of F^- from 0 to 20 µM. It was found that more than 95% of the fluorescence can be quenched after interaction with 1.0 equiv. F^- ions, and the emission color changes under UV lamp can be distinctly observed by the naked eye (Fig. 7). The quantum yields of the chemosensor **1** before and after interaction with F^- ions are calculated to be 0.12 and 0.008, respectively (see ESI[†]). The detection limit of F^- was determined at least down to



Scheme 1 Synthesis of the sensor 1.

CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, P. R. China 230026. E-mail: bairk@ustc.edu.cn; Fax: +86-551-3631760; Tel: +86-551-3600722

[†] Electronic supplementary information (ESI) available: Synthetic procedures, experimental details, additional spectroscopic data. See DOI: 10.1039/c2jm16364k



Fig. 1 (a) Fluorescence spectra of sensor 1 + TBAF in CH₃CN in the presence of increasing F⁻ concentrations. (b) Emission intensity at 458 nm as a function of F⁻ concentrations. [1] = 20 μ M. λ_{ex} = 340 nm.

1.0 μ M by fluorimetric assay (Fig. S4, ESI[†]). This indicates that compound 1 is an efficient ON–OFF fluorescent sensor.

To examine the selectivity of **1** toward various anions, the fluorescence responses upon the addition of Cl^- , Br^- , l^- , ClO_4^- , HSO_4^- , AcO^- , $H_2PO_4^-$, and CN^- were examined. As shown in Fig. 2, upon addition of 5.0 equiv. of various anions, only F^- ion induced a dramatic emission quenching effect, and all the other anions did not cause any obvious intensity decreases. This result indicates that the new fluorescent chemosensor exhibits a high selectivity for fluoride anions in CH₃CN.

The obvious fluorescence changes of 1 upon interaction with F^- ions can be attributed to the F^- induced desilylation reaction. Upon addition of fluoride ions, the sensor 1 is deprotected to give 5-(4-aldehyde)-8-hydroxy-2-methylquinoline, which is non-fluorescent owing to the efficient radiationless relaxation to the ground state by intra and intermolecular excited-state proton transfer (ESPT).¹⁷ The detection process was studied by ¹H NMR spectroscopy (Fig. S3, ESI†). It could be observed that the Si–CH₃ signal upfield shifted from 0.34 to 0.17 ppm, and exhibited a doublet as a result of coupling with the fluoride, and the C(CH₃)₃ signal upfield shifted from 1.09 to 0.92 ppm. The evidence above is consistent with the deprotection reaction and formation of a C–F chemical bond. The desilylation reaction was also confirmed by the UV-vis titration experiment (Fig. S1, ESI†).

The effect of the reaction time on the fluorescence emission of the sensor with various amounts of F^- was examined from 0 to 15 min. The result shown in Fig. 3 and S7† implicates that the fluorescence quenching rate depends on F^- concentration, this is because the fact that the higher the F^- concentration, the faster the desilylation reaction is. The emission intensity of sensor 1 reaches its saturation value in about half an hour upon interaction with 1.0 equiv. F^- ions (Fig. S5 and S6, ESI†).



Fig. 3 Time course of the fluorescence response of 1 in CH₃CN upon addition of various concentrations of F^- (1–6 equiv.).

The cation-binding properties of sensor 1 after addition of F- ions were studied in CH₃CN. It was found that the sensor exhibits high sensitivity and selectivity for detection of Zn²⁺. The fluorescence spectrum of 1 exhibits a weak blue emission band at 458 nm in CH₃CN ($\Phi = 0.008$, $\lambda_{ex} = 340$ nm) upon interaction with F⁻ ions. However, after addition of Zn²⁺ ions it immediately exhibited strong yellowish-green fluorescence. As shown in Fig. 4a, the emission intensity at 458 nm gradually decreased and a new peak with a large red shift and enhanced intensity appeared at 540 nm with increasing the concentration of Zn²⁺, which is due to the ESPT process being well blocked by the interaction with Zn²⁺. The complex shows large Stokes shift of 200 nm, which is much bigger than that of most traditional dyes such as fluorescein, rhodamine, and polymethine cyanine.9,10 The fluorescence intensity and the ratio of emission intensities $(F_{540 \text{ nm}}/F_{458 \text{ nm}})$ change linearly with the concentration of Zn^{2+} (Fig. 4b and S8, ESI⁺). The quantum yield of the Zn^{2+} complex was calculated to be 0.05, and the detection limit of Zn2+ was determined at least down to 120 nM by fluorimetric assay. By direct fluorimetric titration,¹⁸ the association constants (log K_a) of the complex were calculated to be 10.22. In addition, the fluorescence detection did not exhibit any appreciable time-dependent effects. These indicate that the system is an excellent ratiometric fluorescent sensor as well as a chelation-enhanced fluorescence (CHEF) sensor for Zn²⁺ with high sensitivity. Meanwhile, the absorption titration also showed obvious changes in the spectrum, indicative of the formation of the Zn²⁺ complex (Fig. S2, ESI[†]).

Upon interaction with 1.0 molar equivalent of various metal ions of alkali (Na⁺, K⁺), alkaline earth (Mg²⁺, Ca²⁺), and transition-metal



Fig. 2 (a) Fluorescence spectra of **1** in the presence of various anions (5 equivalents of F⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻, ClO₄⁻(TBA⁺ salts), AcO⁻, H₂PO₄⁻, CN⁻(Na⁺ salt)) in CH₃CN. (b) F_0/F of the sensor system at 458 nm in the presence of various anions. [**1**] = 20 μ M. λ_{ex} = 340 nm.



Fig. 4 (a) Fluorescence spectra of the system $[1 + F^-] + Zn^{2+}$ in CH₃CN in the presence of increasing Zn^{2+} concentrations. (b) Ratiometric calibration curves F_{540nm}/F_{458nm} as a function of Zn^{2+} concentrations. [1] = $[F^-] = 20 \ \mu M. \ \lambda_{ex} = 340 \ nm.$

ions (Ag⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺), the system shows excellent selectivity to Zn²⁺. As shown in Fig. 5, only Zn²⁺ induces a dramatic fluorescence enhancement of 32-fold at 540 nm. Upon addition of 3.0 equivalent Cd2+ ions, a new peak at 525 nm was observed. However, the intensity is obviously much lower than that of the Zn²⁺ complex. And no increase of fluorescence was identified in the presence of other metal ions. It should be pointed out that Zn²⁺ metal ions can be distinguished from others by naked eve because of the bright yellowish-green emission. Thus, the molecule 1 after addition of F- ions can be used as a highly selective fluorescent sensor for distinguishing Zn^{2+} from other metal ions, especially from Cd^{2+} .

The solvent effect of the novel fluorescent sensor 1 was also examined. With decreasing solvent polarity from CH₃CN, acetone, to THF, the λ_{em} values of sensor 1 shifted significantly to the shorter wavelength region by 48 nm (from 458 nm in CH₃CN, 440 nm in acetone, to 418 nm in THF) along with decreasing the fluorescence intensity (Fig. 6). The fluorescent quantum yields of sensor 1 in acetone and THF were calculated to be 0.023 and 0.006, respectively. The sensing properties of sensor 1 toward F⁻ in acetone and THF were studied. In acetone, the emission peak at 440 nm gradually decreases upon addition of F- ions, and the fluorescence quenching is similar to that in CH₃CN (Fig. S9 and S10, ESI[†]). However, the sensor 1 in THF exhibits quite different changes when interacting with F⁻ ions. As shown in Fig. S20,† after addition of fluoride ions, sensor 1 immediately changes from blue-violet fluorescence to yellowish-green fluorescence. The emission intensity at 418 nm gradually decreases and a new peak at 520 nm appears upon interaction with the fluoride anion (Fig. S12 and S13, ESI⁺). This phenomenon has been observed in our previous report,13 which can also be attributed to the combination of desilvlation reaction and excited state proton transfer from the desilylation product to fluoride. The ratiometric fluorescence can only be observed in THF, which may be due to the fact that F⁻ ions have much stronger binding abilities to the OH group of the desilvlation product in THF compared with that in CH₃CN and acetone.

The Zn²⁺ sensing properties of sensor 1 after addition of F⁻ ions were also examined in acetone and THF. We observed that the system exhibits a dramatic fluorescence enhancement upon addition of Zn²⁺ ions both in acetone and THF. The quantum yields of the complex system in acetone and THF were calculated to be 0.091 and 0.092, respectively, and the values are bigger than the quantum yield of the complex system in CH₃CN ($\phi = 0.05$). And the detection limits of Zn2+ in acetone and THF were determined to be about 20 nM and 28 nM by fluorimetric assay, respectively (Fig. S14-S17, ESI⁺), which



Fig. 5 (a) Fluorescence spectra of the system $[1 + F^{-}]$ in the presence of various metal ions (30 equiv. of Na+, K+; 3 equiv. of Mg2+, Ca2+, Ag+, Zn²⁺, Cd²⁺, Ni²⁺, Cu²⁺, Co²⁺, Fe³⁺) in CH₃CN. (b) Intensity ratios F_{540nm}/F_{458nm} of the sensor system in the presence of various metal ions. $[1] = [F^{-}] = 20 \ \mu M. \ \lambda_{ex} = 340 \ nm.$



Fig. 6 Fluorescence spectra of 1 in CH₃CN, acetone, and THF. $[1] = 20 \ \mu M. \ \lambda_{ex} = 340 \ nm.$

are much lower than that in CH₃CN. In addition, the system also exhibits different responses to Cd2+ in different solvents (Fig. S18 and S19, ESI[†]). Therefore, the sensing properties of sensor 1 and its desilvlation compound for detection of F⁻, Zn²⁺, and Cd²⁺ can be efficiently tuned by changing the solvents. It is necessary to point out that the sensor 1 and its desilvlation compound can be used as a small sensor array, the naked eye sensing array was shown in Fig. 7.

In conclusion, we have developed a new strategy for highly selective and sensitive detection of both F⁻ and Zn²⁺ utilizing fluorescent chemosensor 1, which is based on a combination of F- induced desilvlation reaction and chelation-enhanced fluorescence effect (CHEF) caused by Zn²⁺. The sensor 1 shows excellent selectivity for F- over other anions, and the deprotection product in situ exhibits high selectivity to Zn²⁺ with a nanomolar range detection limit. The fluorescent sensing process can be obviously observed by the naked eve under UV illumination, and the sensing properties to F⁻ and Zn²⁺ can be efficiently tuned by varying the solvents. Thus, the novel "naked eyes" fluorescent sensor is indeed an excellent candidate probe for the detection of fluoride and zinc ions, which provides a new idea for the development of multifunctional sensors for both cations and anions with dual output modes.

The financial support from National Natural Science Foundation of China (no. 20974104 and no. 21074120) and Ministry of Science and Technology of China (no. 2007CB936401) is gratefully acknowledged.



Fig. 7 Naked eye under UV lamp fluorescent color changes observed for 1 upon addition of F-, Zn2+ and Cd2+ in CH3CN, acetone, and THF. $[1] = [F^{-}] = 20 \ \mu M. \ [Zn^{2+}] = [Cd^{2+}] = 60 \ \mu M. \ \lambda_{ex} = 340 \ nm.$ (Full photography can be seen in Fig. S20, ESI[†].)

Wavelength (nm)

Notes and references

- (a) P. A. Gale, Coord. Chem. Rev., 2001, 213, 79; (b) J. L. Sessler and J. M. Davis, Acc. Chem. Res., 2001, 34, 989; (c) P. D. Beer and P. A. Gale, Angew. Chem., Int. Ed., 2001, 40, 486; (d) R. Martinez-Máñez and F. Sancenón, Chem. Rev., 2003, 103, 4419; (e) T. Gunnlaugsson, M. Glynn, G. M. Tocci, P. E. Kruger and F. M. Pfeffer, Coord. Chem. Rev., 2006, 250, 3094.
- (a) B. Valeur and I. Leray, Coord. Chem. Rev., 2000, 205, 3; (b)
 L. Prodi, F. Bolletta, M. Montalti and N. Zaccheroni, Coord. Chem. Rev., 2000, 205, 59; (c) K. Rurack, Spectrochim. Acta, Part A, 2001, 57, 2161; (d) V. Amendola, L. Fabbrizzi, F. Forti, M. Licchelli, C. Mangano, P. Pallavicini, A. Poggi, D. Sacchi and A. Taglieti, Coord. Chem. Rev., 2006, 250, 273.
- 3 (a) H. S. Horowitz, J. Public Health Dent., 2003, 63, 3; (b) J. R. Farley,
 J. E. Wergedal and D. J. Baylink, Science, 1983, 222, 330; (c)
 M. Kleerekoper, Endocrinol. Metab. Clin. North Am., 1998, 27, 441.
- 4 (a) J. A. Weatherall, Pharmacology of Fluorides, in *Handbook of Experimental Pharmacology XX/1*, Springer-Verlag, Berlin, Part 1, 1969, pp. 141–172; (b) M. L. Cittanova, B. Lelongt and M. C. Verpont, *Anesthesiology*, 1996, 84, 428; (c) P. P. Singh, M. K. Barjatiya, S. Dhing, R. Bhatnagar, S. Kothari and V. Dhar, Urol. Res., 2001, 29, 238.
- 5 (a) B. L. Vallee and K. H. Falchuk, *Psychol. Rep.*, 1993, 73, 79; (b)
 J. M. Berg and Y. Shi, *Science*, 1996, 271, 1081.
- 6 (a) M. Cametti and K. Rissanen, *Chem. Commun.*, 2009, 2809; (b)
 R. Martinez-Máñez and F. Sancenón, *J. Fluoresc.*, 2005, 15, 267.
- 7 (a) C. R. Wade, A. E. J. Broomsgrove, S. Aldridge and F. P. Gabbaï, Chem. Rev., 2010, 110, 3958; (b) E. Galbraith and T. D. James, Chem. Soc. Rev., 2010, 39, 3831; (c) S. Yamaguchi, S. Akiyama and K. Tamao, J. Am. Chem. Soc., 2001, 123, 11372; (d) X. Liu, D. Bai and S. Wang, Angew. Chem., Int. Ed., 2006, 45, 5475; (e) W. Tan, D. Zhang, Z. Wang, C. Liu and D. Zhu, J. Mater. Chem., 2007, 17, 1964; (f) Z. Liu, M. Shi, F. Li, Q. Fang, Z. Chen, T. Yi and C. Huang, Org. Lett., 2005, 7, 5481; (g) Y. You and S. Y. Park, Adv. Mater., 2008, 20, 3820; (h) H. Sun, X. Dong, S. Liu, Q. Zhao, X. Mou, H. Y. Yang and W. Huang, J. Phys. Chem. C, 2011, 115, 19947.
- 8 (a) E. J. Cho, J. W. Moon, S. W. Ko, J. Y. Lee, S. K. Kim, J. Yoon and K. C. Nam, J. Am. Chem. Soc., 2003, 125, 12376; (b) M. Boiocchi, L. D. Boca, D. E. Gómez, L. Fabbrizzi, M. Licchelli and E. Monzani, J. Am. Chem. Soc., 2004, 126, 16507; (c) D. A. Jose, D. K. Kumar, B. Ganguly and A. Das, Org. Lett., 2004, 6, 3445; (d) G. Xu and M. A. Tarr, Chem. Commun., 2004, 1050; (e) B. Liu and H. Tian, J. Mater. Chem., 2005, 15, 2681; (f) P. Anzenbacher, Jr, K. Jursíková and J. L. Sessler, J. Am. Chem. Soc., 2000, 122, 9350; (g) H. Maeda, Y. Haketa and T. Nakanishi, J. Am. Chem. Soc., 2007, 129, 13661.
- Recent reviews: (a) Z. Xu, J. Yoon and D. R. Spring, Chem. Soc. Rev., 2010, **39**, 1996; (b) E. M. Nolan and S. J. Lippard, Acc. Chem. Res., 2009, **42**, 193; (c) E. L. Que, D. W. Domaille and C. J. Chang, Chem. Rev., 2008, **108**, 1517; (d) Z. Dai and J. W. Canary, New J. Chem., 2007, **31**, 1708; (e) N. C. Lim, H. C. Freake and

C. Brückner, *Chem.-Eur. J.*, 2005, **11**, 38; (*f*) K. Kikuchi, K. Komatsu and T. Nagano, *Curr. Opin. Chem. Biol.*, 2004, **8**, 182; (*g*) P. Carol, S. Sreejith and A. Ajayaghosh, *Chem.-Asian J.*, 2007, **2**, 338; (*h*) P. Jiang and Z. Guo, *Coord. Chem. Rev.*, 2004, **248**, 205; (C. F. W. 2014), *Chem. Rev.*, 2004, **248**, 205; (C. F. W. 2014), *Chem. Rev.*, 2004, **248**, 205; (C. F. W. 2014), *Chem. Rev.*, 2004, **248**, 205; (C. F. W. 2014), *Chem. Rev.*, 2004, **248**, 205; (C. F. W. 2014), *Chem. Rev.*, 2004, **248**, 205; (C. F. W. 2014), *Chem. Rev.*, 2004, **248**, 205; (C. F. W. 2014), *Chem. Rev.*, 2004, *Chem. Rev.*, 2005, *Chem. Rev.*, 2004, *Chem. Rev.*, 2004, *Chem. Rev.*, 2004, *Chem. Rev.*, 2004, *Chem. Rev.*, 2005, *Chem. Rev.*, 2004, *Chem. Rev.*, 2005, *Chem. Rev.*, 2004, *Chem. Rev.*, 2004, *Chem. Rev.*, 2004, *Chem. Rev.*, 2004, *Chem. Rev.*, 2005, *Chem. Rev.*, 2004, *Chem. Rev.*, 2005, *Chem. Rev.*, 2004, *Chem. Rev.*, 2004, *Chem. Rev.*, 2004, *Chem. Rev.*, 2005, *Chem. Rev.*, 2004, *Chem. Rev.*, 2

- (i) E. Kimura and T. Koike, *Chem. Soc. Rev.*, 1998, **27**, 179.
- 10 (a) Z. Xu, K.-H. Baek, H. N. Kim, J. Cui, X. Qian, D. R. Spring, I. Shin and J. Yoon, J. Am. Chem. Soc., 2010, 132, 601; (b) F. Qian, C. Zhang, Y. Zhang, W. He, X. Gao, P. Hu and Z. Guo, J. Am. Chem. Soc., 2009, 131, 1460; (c) J. Wang, Y. Xiao, Z. Zhang, X. Qian, Y. Yang and Q. Xu, J. Mater. Chem., 2005, 15, 2836; (d) L. Xue, C. Liu and H. Jiang, Chem. Commun., 2009, 1061; (e) C. He, W. Zhu, Y. Xu, Y. Zhong, J. Zhou and X. Qian, J. Mater. Chem., 2010, 20, 10755; (f) X. Lu, W. Zhu, Y. Xie, X. Li, Y. Gao, F. Li and H. Tian, Chem.-Eur. J., 2010, 16, 8355; (g) Y. Mei, C. J. Frederickson, L. J. Giblin, J. H. Weiss, Y. Medvedevac and P. A. Bentley, Chem. Commun., 2011, 47, 7107.
- 11 (a) S. He, S. T. Iacono, S. M. Budy, A. E. Dennis, D. W. Smith, Jr and R. C. Smith, J. Mater. Chem., 2008, 18, 1970; (b) R. M. F. Batista, E. Oliveira, S. P. G. Costa, C. Lodeiro and M. M. M. Raposo, Org. Lett., 2007, 9, 3201; (c) A. M. Costero, J. Sanchis, S. Gil, V. Sanza and J. A. G. Williams, J. Mater. Chem., 2005, 15, 2848; (d) Y. Sun and S. Wang, Inorg. Chem., 2010, 49, 4394.
- 12 (a) D. A. Pearce, N. Jotterand, I. S. Carrico and B. Imperiali, J. Am. Chem. Soc., 2001, 123, 5160; (b) G. Farruggia, S. Iotti, L. Prodi, M. Montalti, N. Zaccheroni, P. B. Savage, V. Trapani, P. Sale and F. I. Wolf, J. Am. Chem. Soc., 2006, 128, 344; (c) L. Xue, Q. Liu and H. Jiang, Org. Lett., 2009, 11, 3454.
- 13 Y. Bao, B. Liu, H. Wang, J. Tian and R. Bai, *Chem. Commun.*, 2011, 47, 3957.
- 14 Y. Bao, B. Liu, H. Wang, F. Du and R. Bai, Anal. Methods, 2011, 3, 1274.
- 15 (a) S. Yamaguchi, S. Akiyama and K. Tamao, J. Am. Chem. Soc., 2000, 122, 6793; (b) A. B. Descalzo, D. Jiménez, J. E. Haskouri, D. Beltrán, P. Amorós, M. D. Marcos, R. Martínez-Máñez and J. Sotoa, Chem. Commun., 2002, 562; (c) T. H. Kim and T. M. Swager, Angew. Chem., Int. Ed., 2003, 42, 4803; (d) S. Y. Kim and J. I. Hong, Org. Lett., 2007, 9, 3109; (e) X. Yang, Spectrochim. Acta, Part A, 2007, 67, 321; (f) S. Y. Kim, J. Park, M. Koh, S. B. Park and J. I. Hong, Chem. Commun., 2009, 4735; (g) X. Yang, H. Qi, L. Wang, Z. Su and G. Wang, Talanta, 2009, 80, 92; (h) O. A. Bozdemir, F. Sozmen, O. Buyukcakir, R. Guliyev, Y. Cakmak and E. U. Akkaya, Org. Lett., 2010, 12, 1400; (i) R. Hu, J. Feng, D. Hu, S. Wang, S. Li, Y. Li and G. Yang, Angew. Chem., Int. Ed., 2010, 49, 4915; (j) B. Zhu, F. Yuan, R. Li, Y. Li, Q. Wei, Z. Ma, B. Du and X. Zhang, Chem. Commun., 2011, 47, 7098.
- 16 N. Jotterand, D. A. Pearce and B. Imperiali, J. Org. Chem., 2001, 66, 3224.
- (a) M. Goldman and E. L. Wehry, *Anal. Chem.*, 1970, 42, 1178; (b)
 E. Bardez, I. Devol, B. Larrey and B. Valeur, *J. Phys. Chem. B*, 1997, 101, 7786.
- 18 E. Cielen, A. Stobiecka, A. Tahri, G. J. Hoornaert, F. C. De Schryver, J. Gallay, M. Vincent and N. Boens, J. Chem. Soc., Perkin Trans. 2, 2002, 2, 1197.