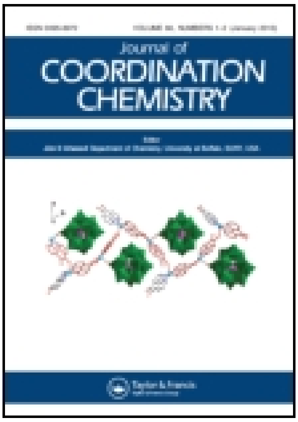
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:50
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

8-hydroxyquinoline-5-carbaldehyde-(benzotriazol-1′-acetyl)hydrazone as a potential Mg^{2+} fluorescent chemosensor

XIULONG JIN [a] , ZHENGYIN YANG [a] , TIANRONG LI [a] , BAODUI WANG [a] , YONG LI [a] , MIHUI YAN [a] , CHUNJIAO LIU [a] & JUNMEI AN [a]

[a] State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering , Lanzhou University , Lanzhou , P.R. China

Accepted author version posted online: 05 Dec 2012.Published online: 21 Jan 2013.

To cite this article: XIULONG JIN , ZHENGYIN YANG , TIANRONG LI , BAODUI WANG , YONG LI , MIHUI YAN , CHUNJIAO LIU & JUNMEI AN (2013) 8-hydroxyquinoline-5-carbaldehyde-(benzotriazol-1′-acetyl)hydrazone as a potential Mg^{2+} fluorescent chemosensor, Journal of Coordination Chemistry, 66:2, 300-305, DOI: 10.1080/00958972.2012.756102

To link to this article: http://dx.doi.org/10.1080/00958972.2012.756102

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Coordination Chemistry
Vol. 66, No. 2, 20 January 2013, 300–305

8-hydroxyquinoline-5-carbaldehyde-(benzotriazol-1′-acetyl) hydrazone as a potential Mg^{2+} fluorescent chemosensor

XIULONG JIN, ZHENGYIN YANG*, TIANRONG LI, BAODUI WANG, YONG LI, MIHUI YAN, CHUNJIAO LIU and JUNMEI AN

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, P.R. China

(*Received 15 August 2012; in final form 11 October 2012*)

8-hydroxyquinoline-5-carbaldehyde-(benzotriazol-1′-acetyl)hydrazone **1** was synthesized and found to show sensitivity and selectivity to Mg^{2+}. Compared to other metal ions, the fluorescence intensity of **1** increased 65-fold upon addition of Mg^{2+} with a low detection limit of 2.4 ppb in acetonitrile.

Keywords: 8-hydroxyquinoline-5-carbaldehyde-(benzotriazol-1′-acetyl)hydrazone; Fluorescent chemosensor; Mg(II); Selectivity

1. Introduction

Mg^{2+} plays vital roles in most cellular and pathological processes [1, 2], such as enzyme cofactors in DNA synthesis, proliferation of cells and the photosynthesis of green plants [3]. Moreover, lack or overdose of Mg^{2+} can cause physiological diseases, such as cardiovascular disease and migraines, and it is important to monitor Mg^{2+} concentration in physiological environment and its distribution throughout living system. Detection and determination techniques of Mg^{2+} have attracted interest in biology, pharmaceutical studies, medicines, and chemistry [4]. Methods, such as atomic absorption, Mg^{2+}-selective electrodes, NMR, and fluorescent chemosensors, have been developed for detection of Mg^{2+} [5]. Fluorescent sensors have drawn increasing attention for simplicity, selectivity, sensitivity, potential application in biological systems, and real-time response in contrast to the traditional methods [6–8] resulting in design and synthesis of high selectivity and sensitivity fluorescent sensors for Mg^{2+} [9–13]. Many Mg^{2+}-selective chemosensors are based on crown ethers [14–17], polyethers [18], hydroxyquinoline derivatives [19–21], fluorescein [22], coumarin derivatives [23–26], and nanomaterial-based ionophores [27, 28]; many suffer from Ca^{2+} interference due to similar chemical properties and stronger binding affinity of Ca^{2+} compared to Mg^{2+}, reducing or even quenching the sensitivity of Mg^{2+} sensors [29, 30]. Only a few sensors can distinguish Ca^{2+} and Mg^{2+}, and display good competitive abilities against most transition metals [31, 32].

The compound, 8-hydroxyquinoline, is an excellent fluorophore with good coordination ability and superior optical properties, and is widely used in chemical and biological

---

*Corresponding author. Email: yangzy@lzu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2012.756102

sensors. In this article, we report 8-hydroxyquinoline-5-carbaldehyde-(benzotriazol-1′-acetyl)hydrazone **1** as a selective and sensitive sensor for Mg^{2+}; **1** could discriminate Ca^{2+} from Mg^{2+}, displaying great selectivity over alkali, alkaline earth, and transition metal ions, with a low determination limit of 2.4 ppb in CH_3CN. The results show that **1** can be used as a potential chemosensor for Mg^{2+} detection.

2. Experimental

2.1. *Materials and instrumentation*

All chemicals were obtained from commercial suppliers and used without purification. ^1H NMR spectra were measured on Bruker 400 MHz instruments using TMS as an internal standard. The ESI-MS was determined on a Bruker esquire 6000 spectrometer. The UV-vis absorption spectra were determined on a Shimadzu UV-240 spectrophotometer. Fluorescence spectra were recorded on a Hitachi RF-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length. The IR spectra were obtained in KBr disks on a Thermo Mattson FTIR spectrometer from 4000–400 cm^{-1}.

Quantum yield was determined by an absolute method using an integrating sphere based upon that originally developed by de Mello *et al.* [33]. The experiment was conducted on an FLS920 from Edinburgh Instruments. The quantum yield was determined according to the equation: $\Phi_u = \Phi_s\ (F_uA_sn_u^2/F_sA_un_s^2)$, where Φ_u is the quantum yield, F is the integrated area under the corrected emission spectra, A is the absorbance at the excitation wavelength, n is the refractive index of the solution, and the subscripts *u* and *s* refer to the unknown and standard, respectively. Acridine orange ($\lambda_{ex} = 400$ nm, $\Phi_f = 0.20$) was used as the fluorescence standard.

2.2. *Synthesis of 1*

As seen in Scheme S1, **1** was obtained by refluxing 8-hydroxyquinoline-5-carbaldehyde **2** (0.346 g, 2 mmol) [34] and benzotriazol-1-acetic hydrazide **3** (0.402 g, 2 mmol) [35] in ethanol (20 mL) in a 50 mL round bottom bottle for 10 h, during which a light yellow precipitate appeared. The resulting precipitate was filtered and washed three times with hot ethanol, recrystallized from dimethyl sulfoxide (DMSO) to give **1** (0.512 g, 72%); m.p. $>300\,°C$. ^1H-NMR(400 MHz, DMSO-d_6): δ (ppm) 11.76 (s, 1H), 9.49 (d, J = 2.0 Hz, 1H), 8.93–8.94 (m, 1H), 8.62 (s, 1H), 8.07 (d, J = 11.2 Hz, 1H), 7.85–7.89 (m, 2H), 7.68–7.74 (m, 1H), 7.55–7.58 (m, 1H), 7.39–7.46 (m, 1H), 7.16–7.19 (m, 1H), and 6.13 (s, 2H); IR: 3433, 3007–3210, 2978, 2894, 1692, 1617, 1599, 1574, 1511, 1457, 1418, 1293, 1238, 1006, 786, and 745. EI-MS *m/z*: 357.1 ($[M+H]^+$).

3. Results and discussion

The optical responses of **1** towards Mg^{2+} were investigated by absorption and fluorescence emission spectra in CH_3CN. As shown in figure S1, the absorption spectra of chemosensor **1** in CH_3CN exhibited two bands at 280 and 354 nm with respective molar absorption coefficients of 2.62×10^4 and $1.56 \times 10^4\ M^{-1}\,cm^{-1}$, which correspond to π, π^* transition of **1**. Upon addition of Mg^{2+}, the absorbance bands at 280 and 354 nm gradually decreased, while a new peak at 318 nm and a broad band from 390 to 450 nm appeared.

The clear isosbestic points at 249, 291, and 368 nm indicate formation of a stable **1**–Mg^{2+} complex.

Fluorescence properties of the probe were also investigated. The fluorescence response behavior of **1** towards increasing concentration of Mg^{2+} is shown in figure 1. Chemosensor **1** shows a weak emission at 450 nm with increasing Mg^{2+} from 0.1 to 1 equiv; a new emission peak appeared at 525 nm and the fluorescence intensity gradually reached 65-fold with a fluorescence quantum yield (Φ) of 0.149. The emission wavelength of **1** red-shifts from 450 to 525 nm in CH_3CN, as shown in scheme 1.

To investigate the selectivity of **1** towards Mg^{2+}, the related alkali, alkaline earth, and other metal ions, such as Li^+, Na^+, K^+, Ca^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}, Ag^+, and Fe^{3+} were introduced to observe the changes of fluorescence intensity of **1** (figure 2).

The metal ions display very weak fluorescence enhancement and **1** can distinguish Ca^{2+} from Mg^{2+}, exhibiting excellent selectivity towards Mg^{2+} compared to other cations. To confirm **1** as an ion-selective fluorescence chemosensor, competitive experiments were also taken into consideration. Compound **1** was treated with 2 equiv of Mg^{2+} in the presence of 2 equiv of other metal ions, and the changes of fluorescence emission intensity are shown in figure S2.

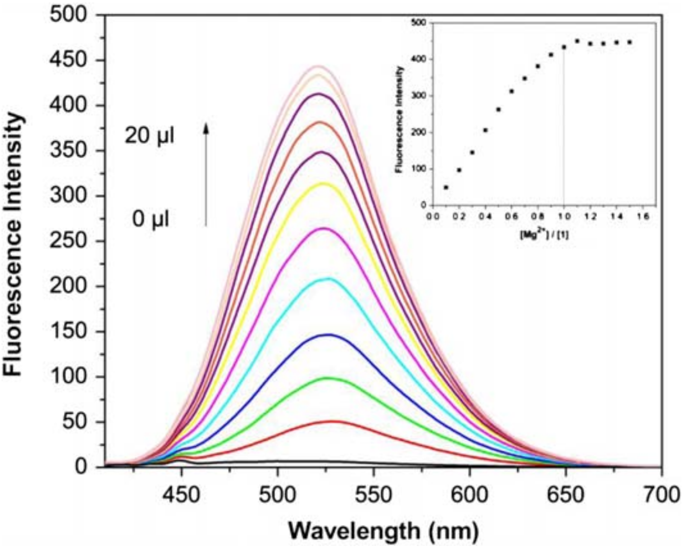
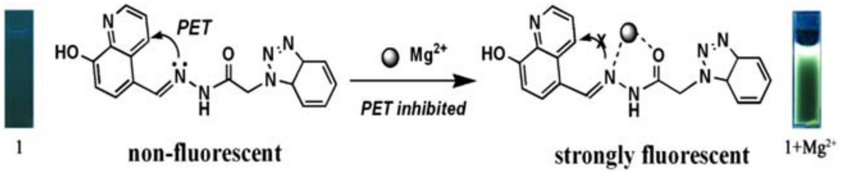


Figure 1. Fluorescence emission response upon titration of 1.0 mM Mg(II) into a 10.0 μM solution of **1** at 25 °C in CH_3CN, $\lambda_{ex} = 395$ nm and $\lambda_{em} = 525$ nm. Inset: the increase in fluorescence emission intensity related to the amounts of Mg(II) added.



Scheme 1. Proposed binding mode of chemosensor **1** with Mg^{2+}.

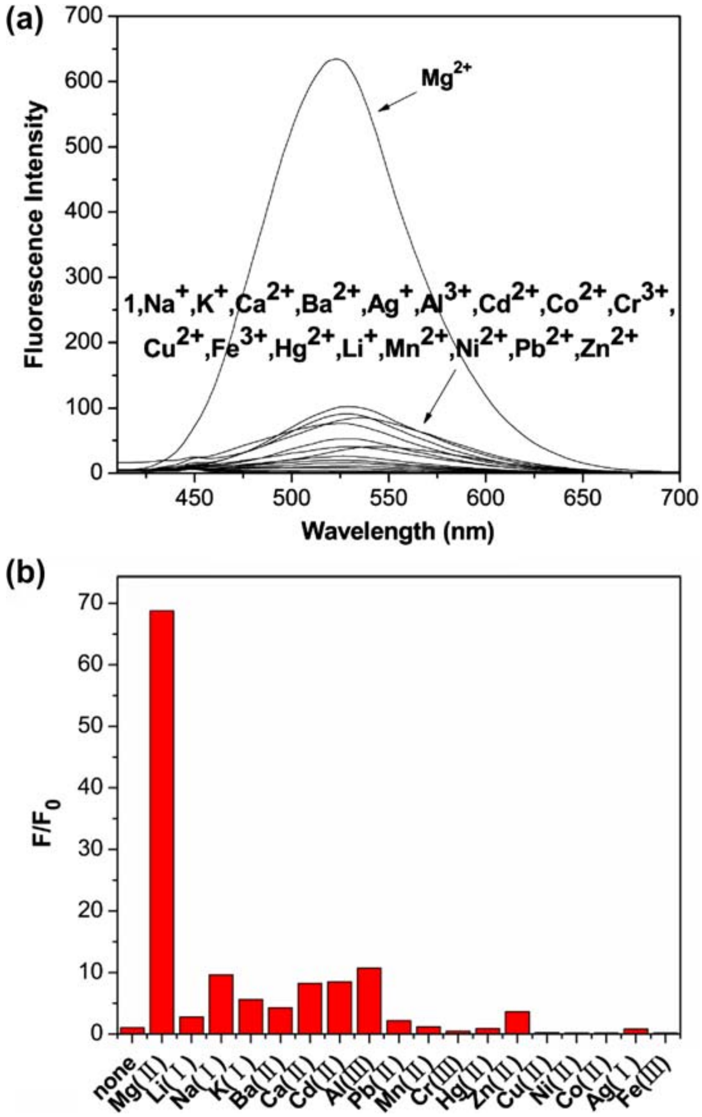


Figure 2. (a) Fluorescence spectra of **1** (1.0×10^{-5} M) upon addition of 1 equiv of different metal ions in CH_3CN when excited at 395 nm. (b) Bar diagram showing the relative emission intensity.

Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, and Fe^{3+} quenches the fluorescence of chemosensor **1** because of stronger binding abilities than Mg^{2+}. But Hg^{2+} and Pb^{2+} display little influence on fluorescence intensity attributed to the configuration of **1** when binding with metals. The influence of alkali and alkaline earth metal ions can be ignored. Thus, chemosensor **1** can be used as a Mg^{2+} selective fluorescent sensor in the presence of many common metal ions. Reversibility of target ion binding is important in the design of a chemosensor; reversibility of Mg^{2+} binding to **1** was investigated by ethylene diamine tetraacetic acid (EDTA) titration. As seen in figure S3, with increasing concentration of EDTA-2Na, the fluorescence intensity of **1**–Mg^{2+} decreased gradually. Figure S4 shows the detection limit of chemosensor **1** was 2.4 ppb, which indicates that **1** was highly sensitive to Mg^{2+}.

The binding mode between **1** and Mg^{2+} was investigated by fluorescence titration and Job's plot. The inset of figure 1 is the binding isotherm from the fluorescence titration, fitted to a 1 : 1 stoichiometry of **1**–Mg^{2+} complex. Figure S5 shows the plot of $F_0/(F - F_0)$ versus $[Mg^{2+}]^{-1}$, the good linear relation further confirmed that Mg^{2+} and **1** form **1**-Mg^{2+} with 1 : 1 binding, and the binding constant of **1**-Mg^{2+} is $6.37 \times 10^6\,M^{-1}$. The 1 : 1 stoichiometry of Mg^{2+} binding to **1** was also proved by Job's plot (figure S6).

From ^1H NMR titrations in DMSO-d_6 (DMSO-d_6 was chosen as solvent because of poor solubility for **1** in CD_3CN), as shown in figure S7, the –NH (H_a) resonance of **1** was at 11.77 ppm, –N=C–H (H_b) at 8.51 ppm and –CH_2– ($H_{c,\ d}$) at 6.14 ppm. In the presence of Mg^{2+} up to 1.0 equiv, H_a and $H_{c,d}$ experience a slight upfield shift to 11.76 and 6.13 ppm, respectively. The proton H_b suffered a slight downfield shift to 8.52 ppm, possibly due to deshielding effects of the metal ion interacting with **1**, indicating involvement of the carbonyl O and N (–N=C–H) binding with Mg^{2+}. The fluorescence signaling mechanisms of chemosensor **1** were mainly based on photoinduced electron transfer (PET) and intramolecular charge transfer [36, 37]. Before addition of Mg^{2+}, the lone pair electrons from the Schiff-base nitrogen contributed to the PET phenomenon, which quenched fluorescence emission of **1**. As seen in scheme 1, accompanied by increasing amounts of Mg^{2+}, the PET was gradually inhibited and fluorescence intensity increased quickly. The fluorescence was turned from "off" to "on" and displays bright yellow fluorescence.

4. Conclusion

We have prepared a Mg^{2+}-fluorescent chemosensor **1**, which displays excellent sensitivity towards Mg^{2+} with a low detection limit of 2.4 ppb in CH_3CN. Compound **1** also shows selectivity against other metal ions, especially Ca^{2+}, which can seriously influence the selectivity of a probe. Results from this work demonstrate that **1** can be used as a potential fluorescent chemosensor for Mg^{2+} detection. Compared to previous work by Liu, Chattopadhyay and Phaniband [38–40], Schiff-base compounds which have more than two chelating points display potential in recognition of traditional and alkaline metal ions. It also gives a good idea to design a simple chemosensor.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (20975046, 81171337).

References

[1] H. Komatsu, N. Lwasawa, D. Citterio, Y. Suzuki, T. Kubota, K. Tokuno, Y. Kitamura, K. Oka, K. Suzuki. *J. Am. Chem. Soc.*, **126**, 16353 (2004).

[2] H. Hama, T. Morozumi, H. Nakamura. *Tetrahedron Lett.*, **48**, 1859 (2007).

[3] Y. Liu, Z.Y. Duan, H.Y. Zhang, X.L. Jiang, J.R. Han. *J. Org. Chem.*, **70**, 1450 (2005).

[4] Y. Dong, J.F. Li, X.X. Jiang, F.Y. Song, Y.X. Cheng, C.J. Zhu. *Org. Lett.*, **9**, 2252 (2011).

[5] M.Q. Tian, H. Ihmels, S. Ye. *Org. Biomol. Chem.*, **10**, 3010 (2012).

[6] L.N. Wang, W.W. Qin, X.L. Tang, W. Dou, W.S. Liu. *J. Phys. Chem. A*, **115**, 1609 (2011).

[7] K. Liu, Y. Zhou, C. Yao. *Inorg. Chem. Commun.*, **14**, 1798 (2011).

[8] M. Lu, X. Ma, Y.J. Fan, C.J. Fang, X.F. Fu, M. Zhao, C.H. Yan. *Inorg. Chem. Commun.*, **14**, 1864 (2011).

[9] H.M. Kim, P.R. Yang, M.S. Seo, J.S. Yi, J.H. Hong, S.J. Jeon, Y.G. Ko, B.R. Cho. *J. Org. Chem.*, **72**, 2088 (2007).
[10] V. Chandrasekhar, M.D. Pandey, P. Bag, S. Pandey. *Tetrahedron*, **65**, 4540 (2009).
[11] S. Abada, A. Lecointre, M. Elhabiri, D. Esteban-Gómez, C. Platas-Iglesias, L.J. Charbonnière. *Chem. Commun.*, **48**, 4085 (2012).
[12] K. Tanaka, T. Kumagai, H. Aoki, M. Deguchi, S. Iwata. *J. Org. Chem.*, **66**, 7328 (2001).
[13] P. Saluja, H. Sharma, N. Kaur, N. Singh, D.O. Jang. *Tetrahedron*, **68**, 2289 (2012).
[14] Q.Z. Yang, L.Z. Wu, H. Zhang, B. Chen, Z.X. Wu, C.H. Tung. *Inorg. Chem.*, **43**, 5195 (2005).
[15] A. Hamdi, S.H. Kim, R. Abidi, P. Thuèry, J.S. Kim. *Tetrahedron*, **65**, 2818 (2009).
[16] J. Brandel, M. Sairenji, K. Ichikawa, T. Nabeshima. *Chem. Commun.*, **46**, 3958 (2010).
[17] A.J. Pearson, J.J. Hwang, M.E. Ignatov. *Tetrahedron Lett.*, **42**, 3537 (2001).
[18] J. Kim, T. Morozumi, H. Nakamura. *Org. Lett.*, **22**, 4419 (2007).
[19] G. Farruggia, S. Iotti, L. Prodi, M. Montalti, N. Zaccheroni, P.B. Savage, V. Trapani, F.I. Wolf. *J. Am. Chem. Soc.*, **128**, 344 (2006).
[20] R.T. Bronson, M. Montalti, L. Prodi, N. Zaccheroni, R.D. Lamb, N.K. Dalley, R.M. Izatt, J.S. Bradshawa, P.B. Savagea. *Tetrahedron*, **42**, 3537 (2001).
[21] L. Prodi, F. Bolletta, M. Montalti, N. Zaccheorni. *Tetrahedron Lett.*, **39**, 5451 (1998).
[22] T. Shoda, K. Kikuchi, H. Kojima, Y. Urano, H. Komatsu, T. Nagano. *Analyst*, **128**, 719 (2003).
[23] Y. Dong, X.R. Mao, X.X. Jiang, J.L. Hou, Y.X. Cheng, C.J. Zhu. *Chem. Commun.*, **47**, 9450 (2011).
[24] M. Suresh, A. Das. *Tetrahedron Lett.*, **50**, 5808 (2009).
[25] H. Komatsu, T. Miki, D. Citterio, T. Kubota, Y. Shindo, Y. Kitamura, K. Suzuki. *J. Am. Chem. Soc.*, **127**, 10798 (2005).
[26] D. Ray, P.K. Bharadwaj. *Inorg. Chem.*, **47**, 2252 (2008).
[27] R. Velu, V.T. Ramakrishnan, P. Ramamurthy. *Tetrahedron Lett.*, **51**, 4331 (2010).
[28] B.I. Ipe, K. Yoosaf, K.G. Thomas. *J. Am. Chem. Soc.*, **128**, 1907 (2006).
[29] A. Momotake, T. Arai. *Tetrahedron Lett.*, **43**, 7277 (2003).
[30] X.Q. Wang, Z.P. Liu, F. Qian, W.J. He. *Inorg. Chem. Commun.*, **15**, 176 (2012).
[31] S. Watanabe, S. Ikishima, T. Matsuo, K. Yoshida. *J. Am. Chem. Soc.*, **123**, 8402 (2001).
[32] K.C. Song, M.G. Choi, D.H. Ryu, K.N. Kim, S.K. Chang. *Tetrahedron Lett.*, **48**, 5397 (2007).
[33] J.C. de Mello, H.F. Wittmann, R.H. Friend. *Adv. Mater.*, **9**, 230 (1997).
[34] R.N. Sen, S.K. Ray. *J. Indian Chem. Soc.*, **9**, 173 (1932).
[35] S.M. El-Khawass, N.S. Habib. *J. Heterocycl. Chem.*, **1**, 177 (1989).
[36] Y. Liu, M. Han, H.Y. Zhang, L.X. Yang, W. Jiang. *Org. Lett.*, **13**, 2873 (2008).
[37] Y.Y. Ma, H. Liu, S.P. Liu, R. Yang. *Analyst*, **137**, 2313 (2012).
[38] C.J. Liu, Z.Y. Yang, M.H. Yan. *J. Coord. Chem.*, **21**, 3845 (2012).
[39] T. Chattopadhyay, M. Mukherjee, K.S. Banu, A. Banerjee, E. Suresh, E. Zangrando, D. Das. *J. Coord. Chem.*, **6**, 967 (2009).
[40] M.A. Phaniband, S.D. Dhumwad. *J. Coord. Chem.*, **14**, 2399 (2009).