Spectrochimica Acta Part A 71 (2008) 1224–1227

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

A highly selective and colorimetric naked-eye chemosensor for Cu^{2+}

Zhijun Wang[a], Xiaojun Fan[b], Donghong Li[c], Liheng Feng[c,*]

[a] Department of Chemistry, Changzhi University,
Changzhi 046011, PR China
[b] Key Laboratory of Chemical Biology and Molecular Engineering of
Ministry of Education, Institute of Biotechnology,
Shanxi University, Taiyuan 030006, PR China
[c] School of Chemistry and Chemical Engineering,
Shanxi University, Taiyuan 030006, PR China

ARTICLE INFO

Article history:
Received 11 January 2008
Accepted 19 March 2008

Keywords:
Chemosensor
Colorimetric naked-eye
Copper ion (Cu^{2+})
Selectivity

ABSTRACT

A sample and practical colorimetric naked-eye chemosensor 3-nitro-4-ethylenediamido-nitrobenzene (**2**) for metal cations was designed and synthesized. It displays high selectivity and sensitivity for Cu^{2+} by the UV absorption which appeared a new peak at 525 nm and color change from yellow to red by naked-eye in CH_3OH/H_2O pH 7.6.

1. Introduction

Design and synthesis of new chemosensors for transition and heavy metal ions have been of interest to chemists for many years because these ions play important roles in the areas of biological, environmental and chemical systems [1,2]. Especially important in this regard is sensors that monitor toxic heavy metal ions [3]. As we know, copper (Cu^{2+}) is the third in abundance (after Fe^{3+} and Zn^{2+}) among the essential heavy transition metals in the human body and plays an important role in various physiologic processes [4,5]. Moreover, Cu^{2+} can be toxic to biological systems when levels of Cu^{2+} ions exceed cellular needs, and it is also able to displace other metal ions which act as cofactor in enzyme-catalyzed reactions [6,7]. Thus, copper, on one hand, is important for life, however, on the other hand, is highly toxic to organisms. For these reasons, a number of the design and synthesis of fluorescent sensors for the detection of Cu^{2+} ions have been reported in the past few years [8–10]. Among these, the UV–vis absorption and fluorescent emission chemosensors have been developed quickly for their simplicity and high sensitivity. Recently, colorimetric sensing of metal ions has been shown to be a less labor-intensive alternative to techniques based on UV–vis absorption and fluorescent emission [11].

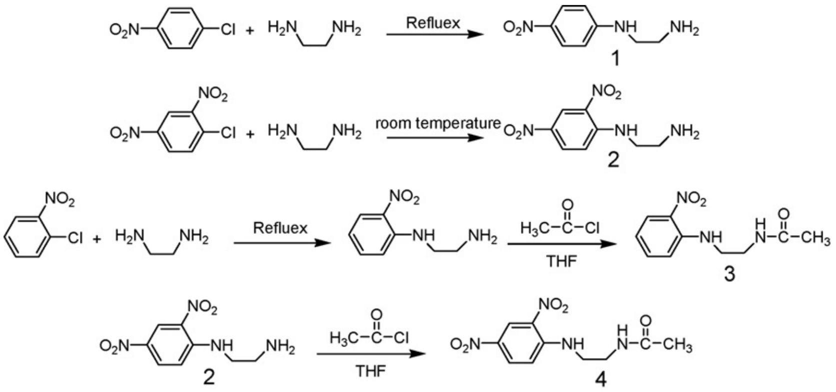
To detect Cu^{2+}, some receptors indicating remarkable colorimetric [12], electrochemical [13] and fluorescent responses [14] have been generally investigated. Since Cu^{2+} is well known to be quenched effectively by fluorescence [15], most of fluorescent sensors for Cu^{2+} were designed by fluorescence quenching strategy [16]. Only a few sensors in which the binding of Cu^{2+} caused an increase in the fluorescence emission have been reported [17]. Sensors with ratiometric fluorescence measurements have scarcely been reported [18]. As a result, the design and synthesis of colorimetric chemosensors for Cu^{2+} has become a very active area of research owing to the demand for more sensitive and selective chemosensors for visible to the naked-eye.

It is well known that during the derivatives of aminobenzene simple ethylenediamine receptors were chosen as the electron donors and nitro moiety as the electron acceptor. Therefore, we designed and synthesized four derivatives of aminobenzene (Scheme 1), The recognition behavior of **1**, **2**, **3** and **4** with several metal cations (Na^+, K^+, Al^{3+}, Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Ag^+, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}) in CH_3OH and H_2O (v:v = 2:1) pH 7.6 (0.1 M HEPES), was investigated by UV–vis measurements, respectively. **2** has high selectivity and sensitivity of this sensor for Cu^{2+} under physiological pH conditions. Here, the Cu^{2+} detection gives rise to large changes in the absorption spectra (form yellow to red), which are clearly visible to the naked-eye. However, for **1**, **3** and **4**, no transition-metal ion sensing was observed. It is can be interpreted that in the case of **2**, the use of *o*-nitro functionality gave rise to an extra chelation site, however, for **1**, no the third chelation site

---

* Corresponding author. Tel.: +86 351 7018731; fax: +86 351 7018731.
E-mail address: zbchen@sxu.edu.cn (L. Feng).

1386-1425/$ – see front matter
doi:10.1016/j.saa.2008.03.021



Scheme 1. The synthesis route of **1–4**.

was offered. Addition, owing to the space-configuration of chelation of **3** and **4**, it would block the effective combine of ligand and metal ion.

2. Experimental

2.1. Materials and instrument

All the solvents were of analytic grade. ^{1}H NMR was measured on a Bruker ARX300 spectrometer with chemical shifts reported as ppm (in $CDCl_3$, TMS as an internal standard). Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). Absorption spectra were recorded on a Varian Cary 300 absorption spectrophotometer. All the experiments were carried out at room temperature. A Metrohm 632 pH-meter with a Metrohm double junction glass electrode was used for pH adjustment. Spectral titrations were carried out by injection of aliquots of metal ion solutions into receptor solutions. The standard stock solutions (1.0×10^{-3} M) inorganic salts were prepared in redistilled water and CH_3OH (v:v = 1:2); working solutions were made by dilution of the stock solutions. The stock solution (1.0×10^{-3} M) of **1**, **2**, **3** and **4** were prepared by dissolving corresponding mass of compounds in 100 mL of CH_3OH and H_2O (v:v = 2:1). Working standard solutions of lower concentrations were prepared by suitable dilution of the stock solution. All of the working solutions were buffered at pH 7.6 ± 0.1 using 0.1 mol/L HEPES.

2.2. Synthesis and characterization of compounds *1–4*

Derivatives of aminobenzene **1** and **2** were synthesized by ethylenediamine and the corresponding chloro-nitrobenzene in THF. **3** and **4** both prepared by two steps: firstly, it was the likely processes with **1** and **2**, then the obtained middle compounds were mixed with acetyl chloride in THF and refluxed for 2 h. The obtained crude products were purified by ethanol recrystallization and fully characterized by ^{1}H NMR, elemental analysis.

1: ^{1}H NMR ($CDCl_3$, δ ppm): 8.12(d, 2H), 6.94(d, 2H), 4.32(t, 1H), 3.41(m, 2H), 3.04(m, 2H), 2.33(t, 2H); elemental analysis: calcd. (%) for $C_8H_{11}N_3O_2$ (108.19) C, 53.03; H, 6.12; N, 23.19; found: C, 52.97; H, 6.14; N, 23.03.

2: ^{1}H NMR ($CDCl_3$, δ ppm): 8.96(s, 1H), 8.33(d, 1H), 7.03(d, 1H), 4.28(t, 1H), 3.36(m, 2H), 3.08(m, 2H), 2.31(t, 2H); elemental analysis: calcd. (%) for $C_8H_{10}N_4O_4$ (226.19) C, 42.48; H, 4.46; N, 24.77; found: C, 42.53; H, 4.48; N, 25.13.

3: ^{1}H NMR ($CDCl_3$, δ ppm): 8.08(t, 1H), 7.82–7.15(m, 4H), 4.21(t, 1H), 3.33(m, 2H), 3.02(m, 2H), 2.40(s, 3H); elemental analysis: calcd. (%) for $C_{10}H_{13}N_3O_3$ (223.23) C, 53.80; H, 5.87; N, 18.82; found: C, 52.97; H, 5.92; N, 18.86.

4: ^{1}H NMR ($CDCl_3$, δ ppm): 8.98(s, 1H), 8.27–8.11(m, 2H), 7.12(d, 1H), 4.26(t, 1H), 3.38(m, 2H), 3.06(m, 2H), 2.38(s, 3H); elemental analysis: calcd. (%) for $C_{10}H_{12}N_4O_5$ (268.23) C, 44.78; H, 4.51; N, 20.89; found: C, 44.71; H, 4.62; N, 20.34.

3. Results and discussion

3.1. The selectivity of *1–4* for metal ions

The UV–vis absorption spectra of **1–4** were investigated in Fig. 1. It can be seen from Fig. 1, the maximum wavelength of **2** and **4** were almost same at around 348 nm, it indicated the acetyl group was hardly effect to the electron conjugation process. However, the maximum wavelength of **1** and **3** were at 380 and 425 nm, respectively, it showed that *o*-nitro group was more intense drawing electron action that *o*-nitro group.

Firstly, we investigated derivatives of aminobenzene **1–4** chemosensor selectivity for metal cations (K^+, Ca^{2+}, Al^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+} and Hg^{2+}, respectively). The results showed that K^+, Ca^{2+}, Al^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Cd^{2+} and Pb^{2+} nearly had no significant effect on absorption spectra of compounds **1–4**, only slightly intensity reduction of absorption spectra. Surprisingly, the absorption response of **1–4** had obviously different change in the presence of Cu^{2+} (Figs. 2 and 3). Here, during the derivatives of aminobenzene **1–4** selectivity, the absorption peaks of **2** at 348 and 416 nm gradually reduced in intensity with the formation of two new absorption bands at ca. 376 and 525 nm and with

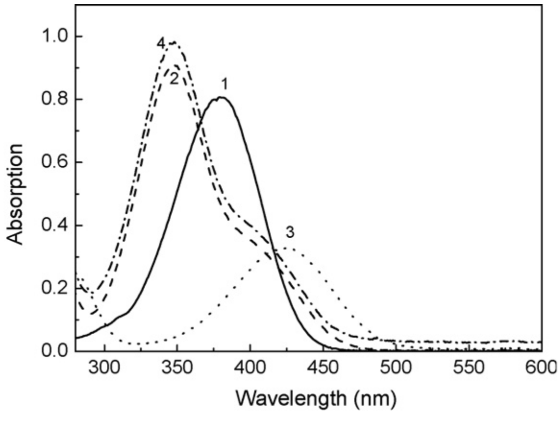


Fig. 1. The absorption spectra of **1**, **2**, **3**, **4** in CH_3OH/H_2O (1:1, v:v) pH 7.6. Concentration: **1**, 5.28×10^{-5} M; **2**, 5.53×10^{-5} M; **3**, 5.67×10^{-5} M; **4**, 5.39×10^{-5} M.

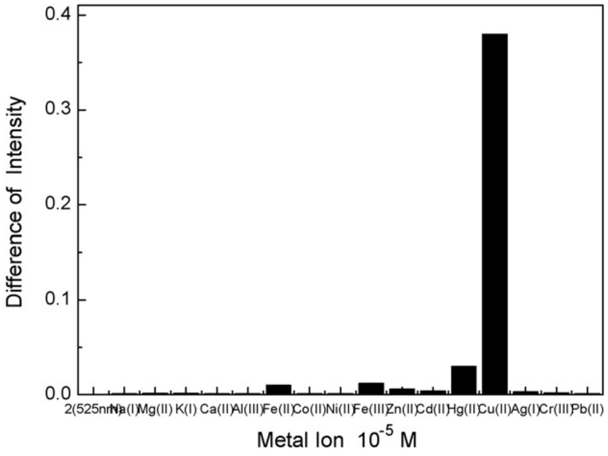


Fig. 2. The different intensity change profile of **2** (1.2×10^{-4} M) at 525 nm in CH_3OH/H_2O (1:1, v:v) in the presence of Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, and Pb^{2+} ions (6.0×10^{-5} M, for all).

the formation of isosbestic points at 364 and 392 nm, respectively (Fig. 3). The appearance of 525 nm absorption peak was due to the d–d transition of Cu^{2+} and indicated the form of complex of Cu^{2+} and **2**. More importantly, the Cu (II) sensing and the concomitant absorption changes were clearly visible to the naked-eye that the yellow solution of **2** became red upon titration with Cu (II). Moreover, these changes are also fully reversible as the addition of EDTA reversed the color changes. The above results showed that **2** was highly selective and colorimetric naked-eye chemosensor for Cu^{2+}.

3.2. *The pH effect of **2** to recognize Cu^{2+}*

Photoionophores are usually disturbed by a proton in the detection of metal ions, so their low sensitivities to the operative pH are extremely important [19,20]. The absorption spectra change of **2** in the different pH was investigated (Fig. 4). The results showed that the absorption maxima (340 nm) gradually decreased in intensity at pH < 5.5. These changes correspond to the protonation of the amino moiety, reducing the binding character of the molecule. By plotting the changes at 340 nm as a function of pH a sigmoidal curve was observed where the major changes occurred at pH < 5.0. These changes were fully reversible, as the addition of strong base to this acidic solution reversed these effects. It was also obtained that only minor changes occurred above ca. pH 5.5. From the facts, it can be clearly indicated that **2** can be used in physiological environment where the pH > 6.

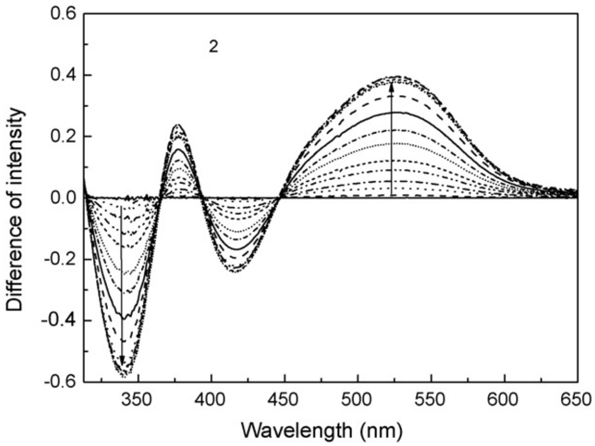


Fig. 3. The difference spectra of **2** (3.0×10^{-5} M) in CH_3OH/H_2O (1:1, v:v) pH 7.6 with the addition of Cu^{2+}.

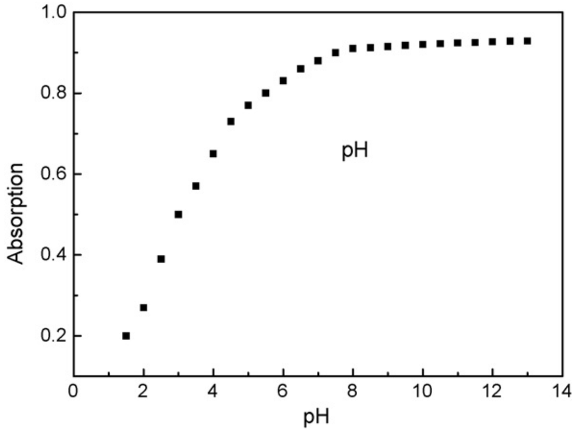


Fig. 4. Absorption of **2** (1.2×10^{-4} M) at 348 nm vs. pH in a mixed solution of CH_3OH/H_2O (1:1, v:v). Absorption spectra were recorded on a Varian Cary 300 absorption spectrophotometer.

3.3. *The stoichiometry and sensitivity of **2** with the metal ions*

A titration experiment was conducted to determine the binding ratio between Cu^{2+} and the **2** molecule (Fig. 5). The titration curve of

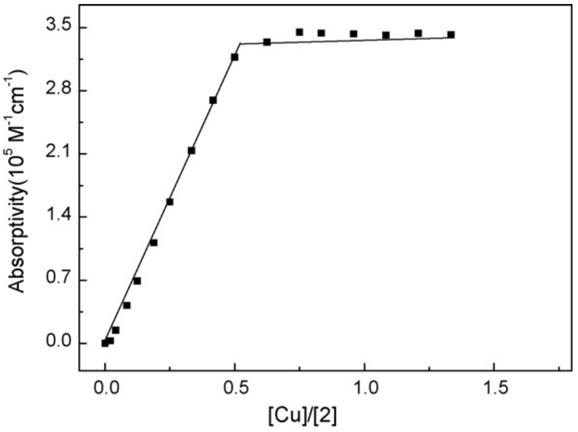


Fig. 5. The titration curve of Cu^{2+} to **2** in CH_3OH/H_2O (1:1, v:v) pH 7.6.

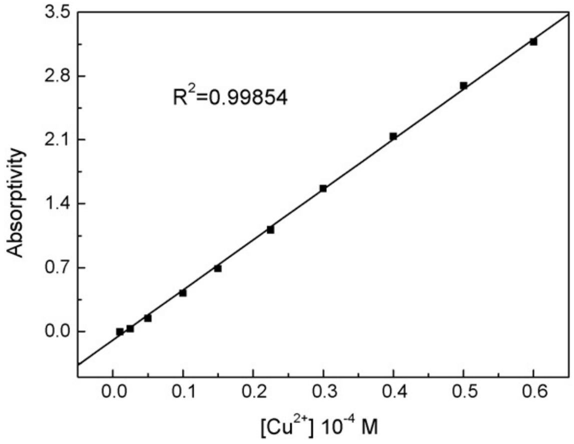


Fig. 6. The absorption ratio of **2** (1.2×10^{-4} M) to Cu^{2+} in CH_3OH/H_2O (1:1, v:v) pH 7.6.

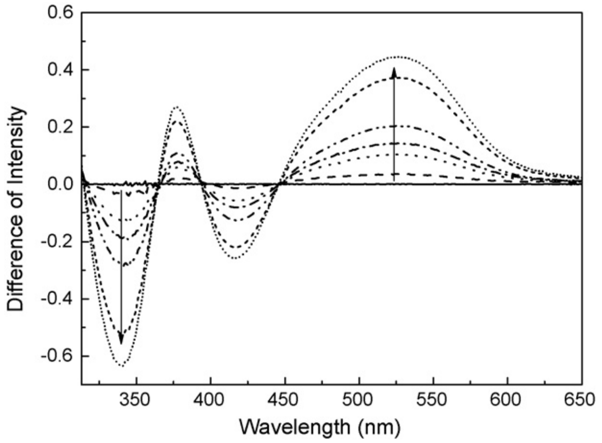


Fig. 7. Absorption spectra of **2** (1.2×10^{-4} M) in a mixture (1:1, v:v) of CH_3OH/H_2O (1:1, v:v) with increasing of Cu^{2+} in the presence of Na^+, K^+, Ca^{2+}, Mg^{2+} and Al^{3+} (6.0×10^{-5} M, respectively).

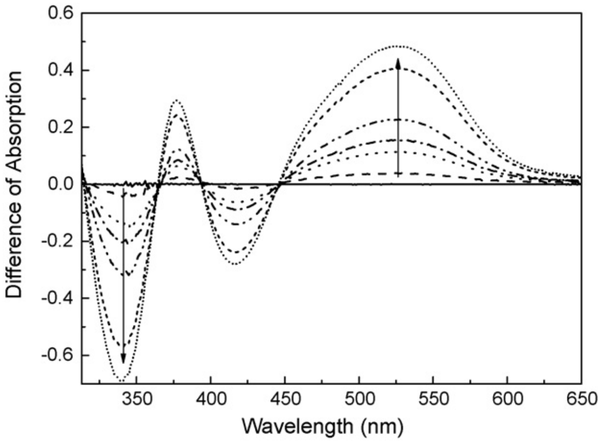


Fig. 8. Difference UV spectra of **2** (1.2×10^{-4} M) in a mixture (1:1, v:v) of CH_3OH/H_2O (1:1, v:v) with increasing of Cu^{2+} in the presence of Fe^{3+}, Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, and Pb^{2+} (6.0×10^{-5} M, respectively).

Cu^{2+} to CH_3OH/H_2O **2** suggests a 2:1 binding mode. This 2:1 binding stoichiometry was also accordant with hypothesis binding model of **2** and Cu^{2+}.

The sensitive signal response of **2** toward Cu^{2+} was preserved in $CH_3OH–H_2O$ (v/v = 1/1, pH 7.6) by absorption spectra. The complexation resulted in a strong change of **2** in its absorption intensity and appeared a new length wave peak upon the addition of increasing amounts of Cu^{2+}, which might be caused by the interaction of Cu^{2+} with the lone electron pair of N, O atoms and formed stable complex. Its new absorption increased linearly with the concentration of Cu^{2+} ($(0.01–0.6) \times 10^{-4}$ M, $R^2 = 0.99854$) up to a ratio (**2**/Cu^{2+}) of 2:1, and there it remained (Fig. 6). Furthermore, Cu^{2+} could be detected at least down to 1.0×10^{-6} M when **2** was employed at 1.00×10^{-5} M in $CH_3OH–H_2O$ (v/v = 1/1, pH 7.6), and its absorbance intensity also increased linearly with the concentration of Cu^{2+}.

To explore further the practical utility of **2** as an ion-selective chemosensor for Cu^{2+}, the interference in the selective responses of **2** in the presence Cu^{2+}, from the other metal cations tested, was also studied by using cross-selectivity experiments (Figs. 7 and 8). No significant variation in its spectrum and solution color was found by comparison with that without the other metal ions besides Cu^{2+}. Moreover, no obvious interference was observed in its spectrum while performing the titrations with Cu^{2+} in the different mixtures of metal ions. The above results indicated that its selectivity for Cu^{2+} was remarkable.

4. Conclusion

In summary, we have developed a simple colorimetric chemosensor **2** for recognition of metal cations, and it displays high selectivity and sensitivity for Cu^{2+} by the UV–vis absorption (appearing a new peak at 525 nm) and color change. The recognition of Cu^{2+} gave rise to major color changes from yellow to red that was clearly visible to the naked-eye. Such Cu^{2+} selective colorimetric chemosensors could be of great importance and practicability in widely field, such as serum detection of medical diagnostics. The practical application of chemosensor **2** to recognition Cu^{2+} in some samples will be investigated in the future.

Acknowledgements

This work was supported by the National Natural Science Foundation of PR China (No. 30700534) and the Natural Science Foundation of Shanxi Province (No. 20031017).

References

[1] Z.C. Xu, X.H. Qian, J.N. Cui, Org. Lett. 7 (2005) 3029.
[2] L.H. Feng, Z.B. Chen, Sens. Actuators B: Chem. 120 (2007) 665.
[3] R. Sundari, M. Ahmad, L.Y. Heng, Sens. Actuators B: Chem. 113 (2006) 201.
[4] T. Mayr, I. Klimant, O.S. Wolfbeis, T. Werner, Anal. Chim. Acta 462 (2002) 1.
[5] V.K. Gupta, A.K. Jain, G. Maheshwari, H. Langb, Z. Ishtaiwi, Sens. Actuators B: Chem. 117 (2006) 99.
[6] N. Mahendra, P. Gangaiya, S. Subramaniam, R. Narayanaswamy, Sens. Actuators B: Chem. 90 (2003) 118.
[7] Y. Xiang, A.J. Tong, P.Y. Jin, Y. Ju, Org. Lett. 8 (2006) 2863.
[8] K. Rurack, M. Kollmannsberger, U.R. Genger, J. Daub, J. Am. Chem. Soc. 122 (2000) 968.
[9] Q. Wu, E.V. Anslyn, J. Am. Chem. Soc. 126 (2004) 14682.
[10] J.S. Yang, C.S. Lin, C.Y. Hwang, Org. Lett. 3 (2001) 889.
[11] R. Martinez, F. Zapata, A. Caballero, A. Espinosa, A. Tárraga, P. Molina, Org. Lett. 8 (2006) 3235.
[12] T. Gunnlaugsson, J.P. Leonard, N.S. Murray, Org. Lett. 6 (2004) 1557.
[13] M.L. Jose, M.M. Ramon, P. Teresa, S. Juan, E.P.T. Miguel, Chem. Commun. (1998) 837.
[14] Y. Xiao, X. Qian, Tetrahedron Lett. 44 (2003) 2087.
[15] H. Yang, Z.Q. Liu, Z.G. Zhou, E.X. Shi, F.Y. Li, Y.K. Du, T. Yia, C.H. Huang, Tetrahedron Lett. 47 (2006) 2911.
[16] Y. Zheng, J. Orbulescu, X. Ji, F.M. Andreopoulos, S.M. Pham, R.M. Leblanc, J. Am. Chem. Soc. 125 (2003) 2680.
[17] S. Banthia, A. Samanta, J. Phys. Chem. B 106 (2002) 5572.
[18] Z. Xu, Y. Xiao, X. Qian, J. Cui, D. Cui, Org. Lett. 7 (2005) 889.
[19] H. Stephan, H. Spies, B. Johannsen, C. Kauffmann, F. Vogtle, Org. Lett. 2 (2000) 2343.
[20] D.A. Loy, B. Mather, A.R. Straumanis, C. Baugher, D.A. Schneider, A. Sanchez, K.J. Shea, Chem. Mater. 16 (2004) 2041.