Chinese Chemical Letters xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Chinese Chemical Letters

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

Original article

Synthesis, fluorescence properties and selective Cr(III) recognition of tetraaryl imidazole derivatives bearing thiazole group

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ARTICLE INFO

Article history:
Received 28 November 2012
Received in revised form 27 December 2012
Accepted 5 January 2013
Available online xxx

Keywords:
Tetraaryl imidazole
Thiazole
Fluorescent
Selectivity Cr^{3+}

ABSTRACT

Three tetraaryl imidazole derivatives **5a–5c** bearing thiazole groups were synthesized in the presence of [Bmin]Br by one-pot reaction and their structures were fully characterized by the ^1H NMR, IR, MS and elemental analysis. The results of UV–vis spectra and fluorescent spectra upon metal ions complexation show that compound **5a** displays high selectivity and sensitivity for Cr^{3+} ions. The complexation ratio of compound **5a** and Cr^{3+} is 1:1.

1. Introduction

Because of its simplicity and sensitivity, selective fluorimetric detection of heavy and transition metal ions is much better than other detection techniques such as electrochemical [1] and potentiometric ones [2]. In the recent past, much attention has been paid to the design and synthesis of colorimetric/fluorescent chemosensors for the selective and efficient detection of biologically and chemically important cations [3] (*e.g.* Cu^{2+}, Fe^{3+}, Cr^{3+}, Pb^{2+}, Hg^{2+}, *etc.*). Among the transition-metal ions, Cr^{3+} is of great importance and plays an indispensable role in the growth and development of living systems [4]. However, the reported chemosensors for fluorescent detection of Cr^{3+} are still rare due to the lack of a proper selective ionophore for Cr^{3+} [5]. So, it is urgent to synthesize the fluorescence chemosensors and investigate systematically the specific detection of Cr^{3+} especially for aqueous systems.

Imidazole derivatives, as ligands for transition metal ions, have widely employed in coordination chemistry and supra-molecular chemistry [6]. They have displayed significant analytical applications utilizing their fluorescence and chemiluminescence properties [7]. Most imidazole molecules based fluorescent chemosensors have been designed and investigated based on appreciable changes in fluorescence upon binding of metal ion. Some research about the photoluminescent and chemiluminescent properties of tri- or tetra- phenylimidazole derivatives [8] has been reported, which means that multiarylimidazole derivatives can exhibit favorable optical properties and be used to construct highly sensitive fluorescent chemisensors for sensing and imaging of metal ions.

In the present paper we summarized a comprehensive study of the tetraaryl imidazole derivatives bearing thiazole group synthesized by one-pot and their structures were characterized by IR, ^1H-NMR, MS and elemental analyses. The metal-binding properties toward cations show compound **5a** displays a highly selective and sensitive response toward Cr^{3+} in CH_2Cl_2.

2. Experimental

All reagents were purchased from Aladdin and were used without further purification. Thin layer chromatography (TLC) was carried out on alumina backed plates coated with Merck gel F254. IR spectra (KBr) were recorded on a Perkin Elmer FTIR. ^1H NMR spectra were recorded at room temperature on a Bruker Avance-400 NMR spectrometer. Chemical ionization (CI) mass spectrometry was performed using Agilent 1100 LC/MS. Elemental analyses were made with a CHN CODRDER MT-3. The UV–vis spectra were measured using a Lambda-900 spectrometer. The fluorescence emission spectra were measured using a LS-55 spectrometer.

Synthesis of tetraaryl imidazole compounds **5a–5c**: Benzil (1 mmol), aldehyde (1 mmol), 2-aminothiazole (1 mmol), and ammonium acetate (1 mmol) were added to 1-butyl-3-methylimidazolium {[Bmin]Br} (0.5 g) without another solvent. The mixture was heated to 140 °C and stirred at temperature for

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http://dx.doi.org/10.1016/j.cclet.2013.01.031

about 10 h until the reaction was completed (monitored by TLC). After this, the mixture was cooled to room temperature, water (20 mL) was added and stirred magnetically for 30 min. Insoluble products were filtered off and dried. The crude products were purified by silica gel column chromatography (EtOAc-petroleum ether) to afford the pure products **5a–5c**.

2,4,5-Triphenyl-1-(thiazol-2-yl)-1H-imidazole (**5a**)*:* Yield: 71%. mp 268–270 °C; IR (KBr, cm^{-1}): ν 3037, 1601, 1488, 1461, 1320, 1257, 766, and 697. ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, 2H, J = 7.2 Hz), 7.50 (d, 4H, J = 7.2 Hz), 7.44–7.39 (m, 4H), 7.36–7.29 (m, 5H), 7.27–7.26 (m, 2H). MS (m/z): 380.5 ($M+H^+$). Anal. calcd. for $C_{24}H_{17}N_3S$ (%): C, 75.96; H, 4.52; N, 11.07. Found: C, 75.84; H, 4.67; N, 10.99.

2-(4-Chlorophenyl)-4,5-diphenyl-1-(thiazol-2-yl)-1H-imidazole (**5b**): Yield: 68%. mp 134–136 °C; IR (KBr, cm^{-1}): ν 3063, 1603, 1486, 1437, 1317, 830, 765, and 696. ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, 2H, J = 7.2 Hz), 7.44 (d, 4H, J = 7.2 Hz), 7.34 (d, 4H, J = 8.0 Hz), 7.30–7.26 (m, 4H), 7.24–7.21 (m, 4H). MS (m/z): 415.1 ($M+H^+$). Anal. calcd. for $C_{24}H_{16}ClN_3S$ (%): C, 69.64; H, 3.90; N, 10.15. Found: C, 69.81; H, 4.03; N, 10.27.

2-(4-Methoxyphenyl)-4,5-diphenyl-1-(thiazol-2-yl)-1H-imidazole (**5c**): Yield: 67%. mp 205–207 °C; IR (KBr, cm^{-1}): ν 3030, 2922, 2838, 1608, 1497, 1449, 1290, 1176, 1130, 829, and 695. ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 2H, J = 7.2 Hz), 7.55 (d, 4H, J = 7.2 Hz), 7.35 (d, 4H, J = 4.8 Hz), 7.31 (m, 4H), 6.97 (d, 2H, J = 7.2 Hz), 3.85 (s, 3H). MS (m/z): 410.4 ($M+H^+$). Anal. calcd. for $C_{25}H_{19}N_3OS$ (%): C, 73.32; H, 4.68; N, 10.26. Found: C, 73.49; H, 4.49; N, 10.35.

Recovery of ILs: After the reaction was completed, the insoluble solid was isolated and the water in which [Bmin]Br was soluble was evaporated and then washed by ethyl acetate three times (8 mL × 3 mL), and dried under reduced pressure. [Bmin]Br was recovered in yield of 95% and reused in next time.

3. Results and discussion

Tetraaryl imidiazole derivatives bearing thiazole groups were prepared using a conventional one-pot four component reaction as outlined in Scheme 1. Benzil was prepared according to the literature [9]. Benzaldehydes, 2-aminothiazole and ammonium acetate were obtained from commercial resources without purification. The crude products were synthesized by the reaction of benzil (1 mmol), benzaldehydes (1 mmol), 2-aminothiazole (1 mmol) and ammonium acetate (1 mmol) in presence of 1-butyl-3-methylimidazolium {[Bmin]Br} (0.5 g) without another solvent and were purified by silica gel column chromatography (EtOAc-petroleum ether) to form the final compounds **5a–5c** in moderate yields. The structures were characterized by ^1H NMR, IR, elemental analysis and MS. One thing to be mentioned was that ILs, [Bmin]Br, as a solvent could be recovered and reused after the simple workup.

The complexation properties of compound **5a–5c** were studied to various heavy metal and transition metal cations, including Ca^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Fe^{3+}, Na^+, Al^{3+}, Mg^{2+}, Ag^+, Cr^{3+}, by UV–vis and fluorescence spectra and the results show that compound **5a** demonstrates selective recognition of Cr^{3+} (the similar results were obtained for the studies of compound **5b** and **5c**). Preliminary complexation properties of compound **5a** were investigated in CH_2Cl_2 toward various heavy and transition metal cations by UV–vis spectroscope. As shown in Fig. 1, the maximum absorption band at 304 nm showed the formation of metal complexation. An obvious change of absorption intensity was observed on the spectroscopic investigation of addition of Cr^{3+} and the original peak was significantly strengthened. The change of this intensity preliminarily implied that the compound **5a** could selectively recognize Cr^{3+}.

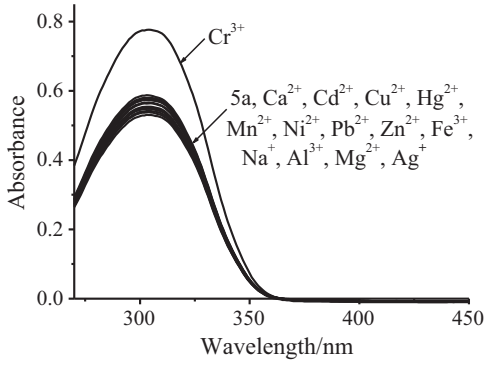


Fig. 1. UV–vis spectra of compound **5a** (10 μmol/L) upon addition of various metal ions (10 μmol/L) in CH_2Cl_2.

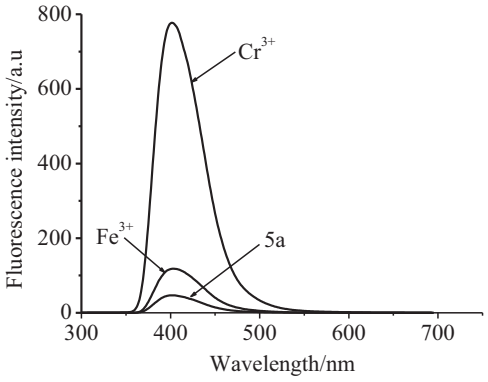
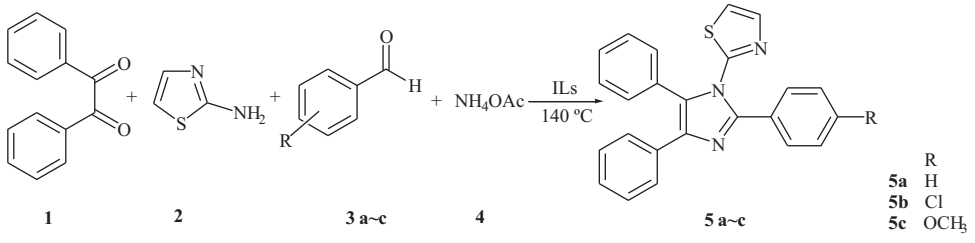


Fig. 2. Fluorescence emission spectra of compound **5a** upon addition of various metal ions (10 μmol/L) in CH_2Cl_2.

Selectivity is a very important parameter for evaluating the performance of a fluorescence sensor. For further clarification of the bonding properties, the fluorescence behavior of the compound **5a** was examined in the presence of various metal cations. Fluorescence emission spectra of **5a** (1.0×10^{-5} mol/L) in CH_2Cl_2 with 2 equiv. metal cations were shown in Fig. 2. Compound **5a** exhibited very low background fluorescence emission at 406 nm. The fluorescence was slightly influenced by the addition of Fe^{3+} with a small enhancement in fluorescence. Addition of Cr^{3+} to compound **5a** gives rise to a significant fluorescence enhancement. The corresponding changes in the fluorescence spectra in the presence of different metal ions were caused by the PET process in



Scheme 1. One-pot synthesis of tetraaryl imidazole derivatives bearing thiazole group.

Please cite this article in press as: B. Zhao, et al., Synthesis, fluorescence properties and selective Cr(III) recognition of tetraaryl imidazole derivatives bearing thiazole group, Chin. Chem. Lett. (2013), http://dx.doi.org/10.1016/j.cclet.2013.01.031

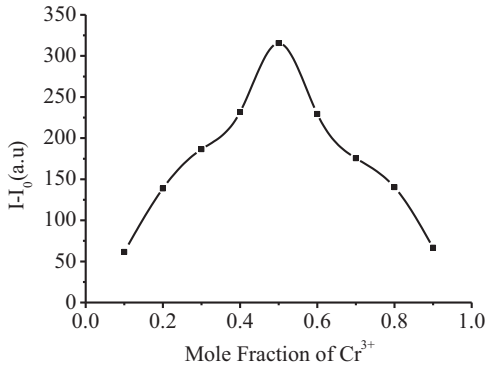


Fig. 3. Job's plot for determining the stoichiometry of receptor **5a** and Cr^{3+} ion in CH_2Cl_2, I and I_0 are the fluorescence intensity of **5a** in the presence and absence of Cr^{3+}, respectively, the total concentration of **5a** and Cr^{3+} ion is 0.1 mmol/L (λ_{ex} = 358 nm).

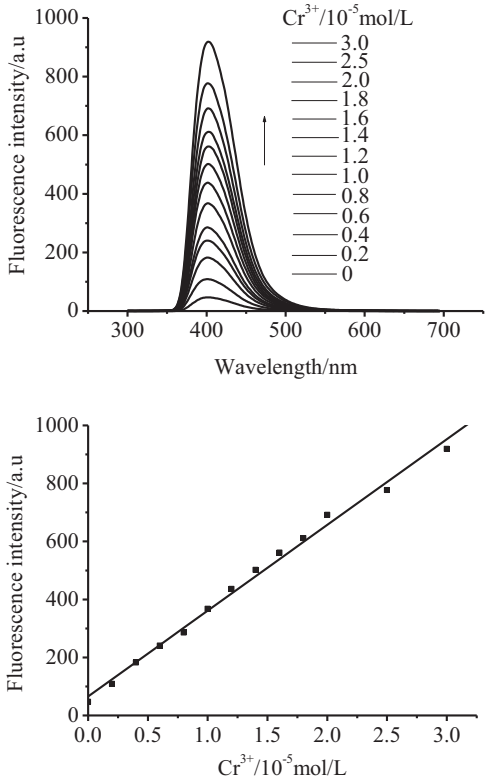


Fig. 4. Fluorescence emission spectra of compound **5a** (10 μmol/L) for Cr^{3+} ion titration in CH_2Cl_2.

which the lone pair electrons of N and S atoms were donated to the empty orbital of metal cations. The distinct exhibitions of compound **5a** to various metal cations depicted the different bonding ability of metal cations with imidazole receptors. These results clearly indicated that the selectivity of compound **5a** for Cr^{3+} is very high.

To determine the complexation ratio between compound **5a** with Cr^{3+}, we carried out the Job's plot experiment by varying the concentrations of both compound **5a** and Cr^{3+}. As shown in Fig. 3, the maximum point at the mole fraction of 0.5 indicated that a 1:1 stoichiometry was reasonable for the binding mode of Cr^{3+} with compound **5a**.

The selective and sensitive signal response of compound **5a** to Cr^{3+} is investigated. Fig. 4 shows the fluorescence spectral changes of compound **5a** with increasing amounts of Cr^{3+}. Its fluorescence intensity increased gradually with concentration of Cr^{3+} [$(0-3)\times10^{-5}$ mol/L]. The strong changes of compound **5a** in its absorption intensity upon the addition of increasing amounts of Cr^{3+} might be ascribed to the interaction of Cr^{3+} with the lone pair electron of the N and S atoms in the imidazole derivative bearing thiazole group.

4. Conclusion

In summary, the tetraaryl imidazole derivatives **5a–5c** bearing thiazole group have been synthesized in presence of [Bmin]Br by one-pot reaction and the results of the complexation properties toward to metal cations show that compound **5a** exhibits high selectivity and sensitivity for Cr^{3+}.

Acknowledgments

This work was supported by the Science Fund for Young Scholars of Heilongjiang Province of China (No. QC2009C61), the Program for Young Teachers' Scientific Research at Qiqihar University (No. 2012K-Z09) and Qiqihar University Graduate Innovation Fund Grants (No. YJSCX2011-026X).

References

[1] A.K. Singh, R. Singh, P. Saxena, Tetraazacyclohexadeca macrocyclic ligand as a neutral carrier in a Cr ion-selective electrode, Sensors 4 (2004) 187–195.
[2] S.S.M. Hassan, M.S. EL-Shahawi, A.M. Othman, M.A. Mosaad, A potentiometric rhodamine-B based membrane sensor for the selective determination of chromium ions in wastewater, Anal. Sci. 21 (2005) 673–678.
[3] (a) V. Balzani, G. Bergamini, P. Ceroni, From the photochemistry of coordination compounds to light-powered nanoscale devices and machines, Coord. Chem. Rev. 252 (2008) 2456–2469;
(b) H.W. Wang, Y.Q. Feng, J.Q. Xue, A novel fluorescent calix[4]arene derivative with benzimidazole units for selective recognition to Fe, Lett. Org. Chem. 6 (2009) 409–411;
(c) L.J. Fan, W.E. Jones Jr., A highly selective and sensitive inorganic/organic hybrid polymer fluorescence "turn-on" chemosensory system for iron cations, J. Am. Chem. Soc. 128 (2006) 6784–6785;
(d) J. Weerasinghe, A.C. Schmiesing, E. Sinn, Highly sensitive and selective reversible sensor for the detection of Cr^{3+}, Tetrahedron Lett. 50 (2009) 6407–6410;
(e) J.Y. Kwon, Y.J. Jang, Y.J. Lee, et al., A highly selective fluorescent chemosensor for Pb^{2+}, J. Am. Chem. Soc. 127 (2005) 10107–10111;
(f) J. Huang, Y. Xu, X. Qian, A rhodamine-based Hg^{2+} sensor with high selectivity and sensitivity in aqueous solution: a NS_2-containing receptor, J. Org. Chem. 74 (2009) 2167–2170.
[4] H. Arakawa, R. Ahmad, M. Naoui, H. Tajmir-Riahi, A comparative study of calf thymus DNA binding to Cr(III) and Cr(VI) ions, J. Biol. Chem. 275 (2000) 10150–10153.
[5] (a) M. Sarkar, S. Banthia, A. Samanta, A highly selective 'off–on' fluorescence chemosensor for Cr(III), Tetrahedron Lett. 47 (2006) 7575–7578;
(b) Z. Zhou, M. Yu, H. Yang, K.W. Huang, F.Y. Li, FRET-based sensor for imaging chromium(III) in living cells, Chem. Commun. 29 (2008) 3387–3389;
(c) K. Huang, H. Yang, Z. Zhou, et al., Multisignal chemosensor for Cr^{3+} and its application in bioimaging, Org. Lett. 10 (2008) 2557–2560.
[6] (a) K. Kamaraj, E. Kim, B. Galliker, et al., Copper(I) and copper(II) complexes possessing cross-linked imidazole-phenol ligands: structures and dioxygen reactivity, J. Am. Chem. Soc. 125 (2003) 6028–6029;
(b) X. Li, X. Weng, R. Tang, et al., Conformational isomerism of 1,2-bis(imidazol-1′-yl)ethane affected by the orientation of functional carboxylate groups in cadmium and cobalt helical coordination polymers, Cryst. Growth Des. 10 (2010) 3228–3236.
[7] (a) N. Fridman, M. Kaftory, Y. Eichen, S. Speiser, Spectroscopy, photophysical and photochemical properties of bisimidazole derivatives, J. Photochem. Photobiol. A: Chem. 188 (2007) 25–33;
(b) F. Dierschke, K. Müllen, Blue emission of a soluble poly(p-phenylene) with a cross-conjugated bisimidazole-based chromophore, Macromol. Chem. Phys. 208 (2007) 37–43;
(c) M. Tsunenaga, H. Iga, M. Kimura, Location effect of an OH group on the chemiluminescence efficiency of 4-hydroperoxy-2-(o-, m-, or p-hydroxyphenyl)-4,5-diphenyl-4H-isoimidazoles, Tetrahedron Lett. 46 (2005) 1877–1880;
(d) H.G. Zhang, X.T. Tao, K.S. Chen, et al., Off–on–off luminescent switching of a dye containing imidazo[4,5-f][1,10]phenanthroline, Chin. Chem. Lett. 22 (2011) 647–650.
[8] (a) H.M. Zhang, W.F. Fu, S.M. Chi, J. Wang, An asymmetric imidazole derivative as potential fluorescent chemosensor for Fe^{3+} in aqueous solution, J. Lumin. 129 (2009) 589–594;
(b) N. Bian, Q. Chen, X.L. Qiu, A.D. Qi, B.H. Han, Imidazole-bearing tetraphenylethylene: fluorescent probe for metal ions based on AIE feature, New J. Chem. 35 (2011) 1667–1671.
[9] Y. Suzuke, A. Bakar, T. Tanoi, N. Nomura, M. Sato, Synthesis of unsymmetrical benzils using N-heterocyclic carbene catalysis, Tetrahedron 67 (2011) 4710–4715.

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