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Voltammetric metal cation sensors based on ferrocenylthiosemicarbazone

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Abstract

Electrochemical studies on redox-active ferrocenylthiosemicarbazone $\mathbf{L_{1-4}}$ were carried out in acetonitrile in the presence of various metal cations. Electrochemical investigation have demonstrated that the binding of Cu^{2+}, Hg^{2+} and Ni^{2+} guest cations by $\mathbf{L_{1-4}}$ results in large shifts of respective Fc/Fc^{+} redox couple to more positive potentials. Moreover, for compound $\mathbf{L_4}$, significant fluorescence enhancement was found in the presence of the Cu^{2+}, and this suggests it can act as a biresponsive fluorescent and electrochemical chemosensor for Cu^{2+}.

Keywords: Ferrocene; Electrochemistry; Fluorescence; Cation sensing

Selective sensing of cations, anions even neutral molecules play important roles in the environmental areas, biological and chemistry process, which has attracted much interest in the supramolecular science [1]. It is well documented in literature that a well-defined chemical sensor consists two basic parts: the signal report unit and the binding unit. In the signaling system, redox-active moieties (e.g. ferrocene, other metallocene) have been well employed for signaling unit since the binding information can be readout with the changing of the redox behavior through the host–guest interactions such as ‘through space’ electrostatic perturbation and/or via various conjugated bond linkages [1a,1b,1c,2]. In addition, various chromophores or flurophores have been also successfully engaged in developing normal optical chemosensors which can translate the binding event into a measurable signal such as fluorescence quenching or enhancement, and/or color changing through the variety interactions between the host and guest [3]. On the other hand, various functional groups such as amine, polyamines, imine, amide, thiourea, guanidinium and crown-ether, etc. [1a,1c] are well employed as binding units in developing new cation and/or anion sensors. Generally, sensing for a specific guest can be achieved through carefully designing the binding unit and the signal report unit.

It is known that the shiff base (C=N) and thiourea can form stable complexes with various metal ions and anions, respectively [4]. However, to our surprising there has been limited study about the electrochemical sensing properties of the ferrocenyl-bearing thiosemicarbazone compounds. Taking these into consideration, ferrocenyl-thiosemicarbazone $\mathbf{L_{1-3}}$ were synthesized and investigated. Moreover, to achieve multiresponsive sensing of guest, we report the compound $\mathbf{L_4}$ which consists of a redox-active ferrocene moiety and a photoactive naphthalene group as an electrochemical and fluorescent chemosensor. In our study, it is achieved by electrochemical and fluorescent sensing of Cu^{2+}.

Ferrocenylthiosemicarbazone $\mathbf{L_{1-4}}$ were prepared in high yields by several easy steps (Scheme 1). Their structures were well characterized by ^{1}H NMR, HRMS and IR [5]. To investigate the solid-state structure of compound

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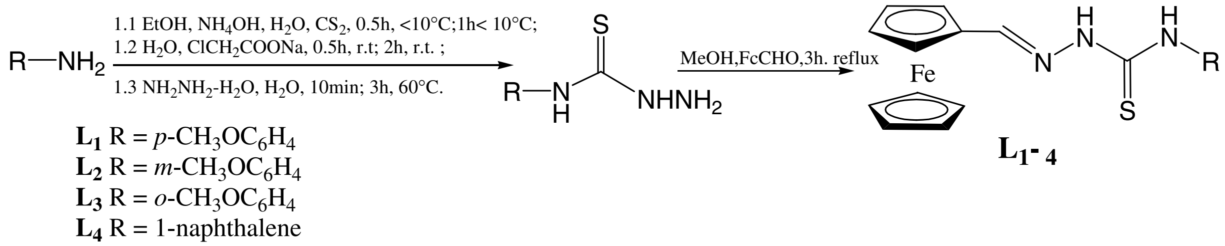

Scheme 1. Synthesis of the ferrocenylthiosemicarbazone $\mathbf{L_{1-4}}$.

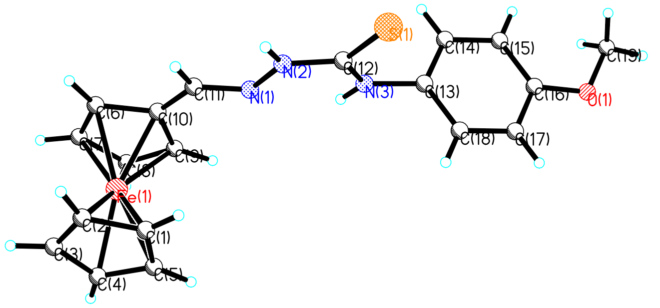

Fig. 1. Molecular structure of $\mathbf{L_1}$. Selected bond lengths (Å): C10–C11 1.442(4), C12–S1 1.686(3), C11–N1 1.276(4), C12–N2 1.340(4), C12–N3 1.334(4), C13–N3 1.438(4), N1–N2 1.386(3),C16–O1 1.367(3), C19–O1 1.439(4); Selected angles (°): C11–N1–N2 116.1(3), C12–N2–N1 120.3(3), C12–N3–C13 124.7(3), C16–O1–C19 117.1(3), N3–C12–N2 116.2(3), N3–C12–S1 123.1(2), N2–C12–S1 120.7(2), C14–C13–N3 120.3(3), C18–C13–N3 119.6(3), O1–C16–C17 116.1(3), O1–C16–C15 124.4(3).

L, the single-crystal structure of $\mathbf{L_1}$ was determined, which is in good agreement with the proposed structures [6]. The crystal structure of compound $\mathbf{L_1}$ is shown in Fig. 1. The bond lengths and angles of the ferrocenyl fragment are unexceptional in contrast with the report in the literature. It is clear from the structure that C11N1N2C12S1N3 is planar (the mean deviation is 0.0227) and almost coplanar to the cyclopentadienyl ring plane to which it is attached, and the dihedral angle is 165.2°. C11N1N2C12S1N3 is vertical (the dihedral angle is 91.2°) to the phenyl ring. The hydrogen bonds linkages are the N–H···S–C which have N···S distances of 3.389(3) Å [N2···S1$^{\#1}$, $\#1 = -x + 1, -y, -z + 1$] and the strong hydrogen bond which have N3–H···N1 distances of 2.628(4) Å [N3···N1]. The vital hydrogen bonds caused the dimer form in the solid state of $\mathbf{L_1}$.

Table 1
Electrochemical parameters of $\mathbf{L_{1-4}}$ (ca 1.0×10^{-3} mol L^{-1})

Compounds	E_{pa} (mV)	E_{pc} (mV)	ΔE_p (mV)	$E_{1/2}$ (mV)	i_{pa}/i_{pc}
$\mathbf{L_1}$	569	493	76	533	1.16
$\mathbf{L_2}$	569	497	72	533	1.13
$\mathbf{L_3}$	581	506	75	543	1.17
$\mathbf{L_4}$	582	510	72	546	1.19

All potentials Data are referred to the saturated calomel electrode (SCE) at a scan rate of 100 mV s^{-1} in acetonitrile solution using TBAP (0.1 mol L^{-1}) as the supporting electrolyte on a GC working electrode, CV recorded from 0.0 to 1.0 V.
$\Delta E_p = (E_{pa} - E_{pc})$, $E_{1/2} = (E_{pa} + E_{pc})/2$.

Table 2
Electrochemical response for $\mathbf{L_{1-4}}$ vs selected metal cations in acetonitrile in 0.1 M tetrabutylammonium perchlorate

Receptor	$\Delta E_{1/2}$(mV)								
	Ca^{2+}	Mg^{2+}	Mn^{2+}	Zn^{2+}	Cu^{2+}	Co^{2+}	Hg^{2+}	Pb^{2+}	Ni^{2+}
$\mathbf{L_1}$	<10	<10	<10	17	155	45	102	40	181
$\mathbf{L_2}$	<10	<10	<10	13	157	40	99	39	182
$\mathbf{L_3}$	<10	<10	<10	<10	155	45	103	38	182
$\mathbf{L_4}$	<10	<10	<10	<10	157	42	103	39	190

$\Delta E_{1/2}$ is define as $E_{1/2}$ (receptor + cation) − $E_{1/2}$ (free receptor). Scan rate: 100 mV s^{-1}. All potentials Data are referred to the saturated calomel electrode (SCE) at a scan rate of 100 mV s^{-1} in acetonitrile solution using TBAP (0.1 mol L^{-1}) as the supporting electrolyte on a GC working electrode, CV recorded from 0.0 to 0.9 V.

The electrochemical properties of $\mathbf{L_{1-4}}$ were investigated using CV in acetonitrile. Each compound exhibited a reversible redox wave typical of a ferrocene derivative (Table 1). For $\mathbf{L_{1-4}}$ the peak current of the Fc oxidation peak are proportional to the square root of the scan rate, indicating a diffusion-controlled process. The addition of Ni^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+} and Co^{2+} (all cations are added as perchlorate salts) to acetonitrile solutions of $\mathbf{L_{1-4}}$ led significant anodic shifts of the redox potential of the Fc/Fc$^+$ couple (Table 2). Two typical CV behavior for the Fc center in $\mathbf{L_{1-4}}$ have been obtained upon addition of increasing amounts of a given metal ions (see support information): (1) the growth at a higher positive potential of a new redox wave at the expense of the original wave, such as Ni^{2+} and Cu^{2+}; (2) a gradual positive shift in the Fc/Fc$^+$ potential, for Hg^{2+}, Pb^{2+} and Co^{2+}. All the complexes presented quasi-reversible behavior. $\Delta E_{1/2}[E_{1/2}$ (receptor + cation) − $E_{1/2}$ (free receptor)] was observed by addition of various metal cations to $\mathbf{L_{1-4}}$ (Table 2), and only in the presence of Cu^{2+}, $Ni^{2+}$and Hg^{2+} large anodic shifts were caused (e.g. for $\mathbf{L_4}$ 157 mV, 190 mV and 103 mV, respectively). Though slightly changes for $\Delta E_{1/2}$ were noticed with the various substituent (Ar) of **L**, the $\Delta E_{1/2}$ tendency of **L** with different metal cations are in the sequence of $Ni^{2+} > Cu^{2+} > Hg^{2+} > Co^{2+} > Pb^{2+}$. No obvious $\Delta E_{1/2}$ shifts were noticed in the measure condition by addition of Ca^{2+}, Mg^{2+} to $\mathbf{L_{1-4}}$. Furthermore, when an equimolar mixture Ni^{2+}, Cu^{2+}, Hg^{2+}, Co^{2+}, Pb^{2+}, Ca^{2+} and Mg^{2+} was added to the solution of $\mathbf{L_{1-4}}$, the extent of the anodic shift of the redox potentials is approximately equal to that induced by

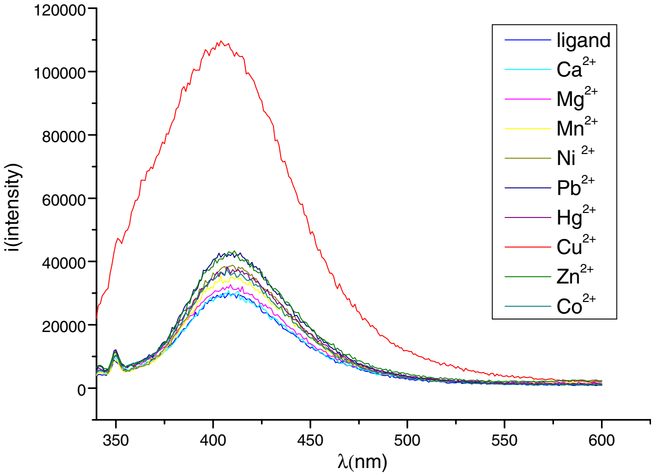

Fig. 2. The changes in the fluorescence emission spectra of $\mathbf{L_4}$ (ca 2.5×10^{-5} mol L^{-1}) upon addition of the perchlorate salt of measured cations (2 equiv.) in acetonitrile.

Hg^{2+} alone. This result suggests that in the presence of all these metal ions $\mathbf{L_{1-4}}$ preferentially coordinates to Hg^{2+}. Therefore $\mathbf{L_{1-4}}$ is a good candidate for a sensor to detect the toxic Hg^{2+}.

Moreover, to make good use of florescent and electrochemical multiresponsive sensing of metal cations, naphthalene group was introduced in $\mathbf{L_4}$. The fluorescent spectrum studies (by excitation at 317 nm in acetonitrile solution) of $\mathbf{L_4}$ with selected metal ions (all cations are added as perchlorate salts) reveal that fluorescence enhancement was noticed by addition of Ni^{2+}, $Cu^{2+}$and Hg^{2+} from titration study, and this is most stinking for Cu^{2+} (Fig. 2). The fluorescent spectrum studies of $\mathbf{L_{1-3}}$ with different metal cations were also investigated for contrast, but only $\mathbf{L_4}$ has the special property. It is assumed that the naphthalene group plays an important role in the MLCT process in resulting large fluorescence emission enhancement. The result is accordant with the reported two urea group substituted **BMPUN** [8]. Up to our known, it is one of the few reported sensors which the binding of Cu^{2+} caused great changes both in fluorescence emission and potential shift of the redox-center.

To investigate the binding modes of **L** with different metal ions, complexes of $\mathbf{L_4}$ with Cu^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} were prepared from methanol and finally recrystallized from dichloromethane. Careful analysis of the IR spectrum of the ligand $\mathbf{L_4}$ and its complexes has helped in identifying the donor points of the ligand involved in coordination to the cation (II) center. The coordination of the ligands in their thione form is indicated by the presence of ν(C=S) band in the 850–810 cm^{-1} region. Shift of the band of the ν(C=S) ligand to the 800–840 cm^{-1} region along with the shift of the ν(C=N), ν(C=C) band at 1599–1543 cm^{-1} by 5–20 cm^{-1} in the complexes indicate that the ligand is attached to the metal ion through the thiocarbonyl sulfur and the azomethine nitrogen atom of the thiosemicarbazone moiety. Additionally, IR spectrum of the complexes exhibit characteristic bonds of the perchlorate ion in the region 1090–1140 cm^{-1}, which is also conformed that the ligand $\mathbf{L_4}$ takes a keto form in chelating metal ions not a thioenol form which loses a proton and results in a deprotonated complex [9]. The evidence described above suggests that coordination mode is similar to those prepared previously using other thiosemicarbazones [4c,4d,9].

In summary, we developed ferrocenylthiosemicarbazone $\mathbf{L_{1-4}}$ as a new set of electrochemical sensors for metal ions such as Cu^{2+} and Hg^{2+}. The compound $\mathbf{L_4}$ presents very interesting properties and shows a highly sensitive response in its emission toward Cu^{2+}, which is rarely reported in the multiresponsive sensors for metal ions. Furthermore, $\mathbf{L_{1-4}}$ presented in this work is a suitable molecular sensor for the toxic Hg^{2+} since it presented a unique $\Delta E_{1/2}$ which is substantially different from that found for other metal ions.

Acknowledgements

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Appendix A. Supplementary material

CCDC 647555 for compound $\mathbf{L_1}$ contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.09.015.

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[5] *Synthesis of* **L:** A mixture of ferrocenecarboxaldehyde (0.428 g, 2.0 mmol) and aromatic thiosemicarbazide (2.0 mmol) was refluxed in MeOH (20 ml) with AcOH (0.1 ml) as catalysis for 3 h. The resulting solution was then cooled at ice-bath. The red precipitate was collected by filtration and washed with MeOH several times. The crude product was purified by recrystallization from $CHCl_3$/MeOH to give **L** as red crystals. Yield 82–95%. For $\mathbf{L_1}$: m.p.: 187–188 °C; HRMS: Calcd for $C_{19}H_{20}FeN_3OS$ $[M+H]^+$ 394.0677, found 394.0680; IR ν_{max}(KBr): 3343, 1606, 1541,1241, 1026, 816 cm^{-1}; ^1H NMR (400 MHz): 3.83(s, 3H, $-OCH_3$), 4.23(s, 5H, cp-H), 4.44(s, 2H, cp-H), 4.61(s, 2H, cp-H), 6.94(d, $J = 8$ Hz, 2H, Ar–H), 7.49(d, $J = 8$ Hz, 2H, Ar–H), 7.77(s, 1H, CH=N), 8.91(s, 1H, CSN–H), 9.63(s, 1H, Ar–NH). For $\mathbf{L_2}$: m.p.: 145–146 °C; HRMS: Calcd for $C_{19}H_{20}FeN_3OS$ $[M+H]^+$ 394.0677, found 394.0680; IR ν_{max} (KBr): 3297, 1597, 1549,1291, 1160, 771 cm^{-1}; ^1H NMR (400 MHz): 3.76(s, 3H, $-OCH_3$), 4.24(s, 5H, cp-H), 4.46(s, 2H, cp-H), 4.84(s, 2H, cp-H), 6.75(d, $J = 8$ Hz, 2H, Ar–H), 7.20–7.27(m, 2H, Ar–H), 7.35(s, 1H, CH=N), 8.00(s, 1H, Ar–H), 9.73(s, 1H, CSN–H), 11.61(s, 1H, Ar–NH). For $\mathbf{L_3}$: m.p.: 198–199 °C; HRMS: Calcd for $C_{19}H_{20}FeN_3OS$ $[M+H]^+$ 394.0677, found 394.0680; IR ν_{max} (KBr): 3269, 1600, 1551,1241, 754 cm^{-1}; ^1H NMR (400 MHz): 3.94(s, 3 H, $-OCH_3$), 4.22(s, 5H, cp-H), 4.44(s, 2H, cp-H), 4.63(s, 2H, cp-H), 6.94(d, $J = 8$ Hz, 1H, Ar–H), 7.02(t, J = 8 Hz, 1H, Ar–H), 7.15(t, $J = 8$ Hz, 1H, Ar–H), 7.77(s, 1H, CH=N), 8.75(d, $J = 8$ Hz, 1H, Ar–H), 9.47(s, 1H, CSN–H), 9.75(s, 1H, Ar–NH). For $\mathbf{L_4}$: m.p.: 139–140 °C; HRMS: Calcd for $C_{22}H_{20}FeN_3S$ $[M+H]^+$ 414.0727, found 414.0730; IR ν_{max} (KBr): 3330, 1600, 1542,1498, 744 cm^{-1}; ^1H NMR (400 MHz): 4.23(s, 5H, cp-H), 4.44(s, 2H, cp-H), 4.61(s, 2H, cp-H), 7.51–7.58(m, 3H, Ar–H), 7.84(s, 1H, CH=N), 7.86–8.00(m, 4H, Ar–H), 9.31(s, 1H, CSN–H), 10.12(s, 1H, Ar–NH).

[6] *Date collection and refinement of* $\mathbf{L_1}$: Red crystals of $\mathbf{L_1}$ suitable for X-ray analysis were obtained by slow evaporation of CH_2Cl_2/CH_3OH solution. It belongs to monoclinic system $P2(1)/n$ space group, $a = 12.763(3)$ Å, $b = 9.0043(18)$ Å, $c = 15.998(3)$ Å, $\beta = 95.12(3)°$. $V = 1831.2(6)$ Å^3, $Z = 4$, $D_c = 1.427$ g cm^{-3}, R_1 $[I > 2\sigma(I)] = 0.0452$, ωR_2 (all data) $= 0.1129$. The crystal structure was determined on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at temperature 291(2) K. Reflections ($I > 2\sigma$) of 3231 were corrected for Lorentz-polarization effects. All calculations were performed using the Shelxl-97 crystallographic software package [7].

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