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# Syntheses, structures of *N*-(substituted)-2-aza-[3]-ferrocenophanes and their application as redox sensor for $\text{Cu}^{2+}$ ion

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Rigid *N*-(substituted)-2-aza-[3]-ferrocenophanes **L1** and **L2** were easily synthesized from 1,1-dicarboxyaldehydeferrocene and the corresponding amines. Ligands **L1** and **L2** were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and single-crystal X-ray crystallography. The coordination abilities of **L1** and **L2** with metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  were evaluated by cyclic voltammetry. The electrochemical shift ( $\Delta E_{1/2}$ ) of 125 mV was observed in the presence of  $\text{Cu}^{2+}$  ion, while no significant shift of the  $\text{Fc}/\text{Fc}^+$  couple was observed when  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  metal ions were added to the solution of **L1** in the mixture of MeOH and  $\text{H}_2\text{O}$ . Moreover, the extent of the anodic shift of redox potentials was approximately equal to that induced by  $\text{Cu}^{2+}$  alone when a mixture of  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  was added to a solution of **L1**. Ligand **L1** was proved to selectively sense  $\text{Cu}^{2+}$  in the presence of large, excessive first-row transition and late-transition metal cations. The coordination model was proposed from the results of controlled experiments and quantum calculations. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

**Keywords:** redox sensor; ferrocenophane;  $\text{Cu}^{2+}$

## Introduction

Owing to potential applications in the analytical and environmental areas, recent attention has been focused on the molecular sensor, which is a rapidly growing research field of supramolecular science.<sup>[1]</sup> The development of molecular sensors for metal ions, especially for cations with biological interest, has always been of particular interest.<sup>[2]</sup> The  $\text{Cu}^{2+}$  ion is third in abundance (after  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$ ) amongst the essential heavy metal ions in the human body and plays a pivotal role in a variety of fundamental physiological processes in organisms ranging from bacteria to mammals.<sup>[3]</sup> On the other hand,  $\text{Cu}^{2+}$  can be toxic to biological systems. Alterations in its cellular homeostasis are connected to serious neurodegenerative diseases, including Menkes and Wilson diseases,<sup>[4]</sup> familial amyotrophic lateral sclerosis,<sup>[5]</sup> Alzheimer's disease<sup>[6]</sup> and prion diseases.<sup>[7]</sup> Thus copper, on one hand, is important for life but, on the other hand, is highly toxic to organisms. For these reasons, the past few years have witnessed a number of reports on the design and synthesis of chemical sensors<sup>[8]</sup> for the detection of copper ion. However, the low sensitivity and high order of interference by chemical closely related metal ions have necessitated the development of a new, highly selective and sensitive  $\text{Cu}^{2+}$  sensor.

Electrochemical sensors based on optical signal measurement represent advanced techniques in analytical chemistry because they can be miniaturized and manufactured to monitor our environmental samples quickly and economically, especially heavy metal ions *in situ*.<sup>[9]</sup> The cyclopentadienyl (Cp) complex of ferrocene is easily modified and the electrochemical properties of the  $\text{Fe(II)Cp}_2$  fragment can be tuned by selecting the substituents introduced to the Cp ligand.<sup>[10]</sup> Ferrocene-containing

cryptands have attracted considerable attention in the last decades because of their potential applications in the field of redox sensors. Among these, ferrocenophane, with a rigid bridge containing nitrogen atom, showed remarkably selective cation-sensing properties.<sup>[11]</sup> However, compared to those macromolecules functionalized by ferrocene,<sup>[12–15]</sup> the number of known examples of nitrogen-containing rigid macrocycles with bridged ferrocene units is limited, partly because of the lack of general preparation methods of the compounds and low yields.<sup>[11,16–19]</sup> Here we report a feasible method to synthesize compounds **L1** and **L2** (Scheme 1), and investigate their coordination behaviour with transition metal ions and alkaline earth metal ions, such as  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , by cyclic voltammetry. The coordination model of  $\text{Cu}^{2+}$  with **L1** was proposed with the aid of controlled experiments and quantum calculations.

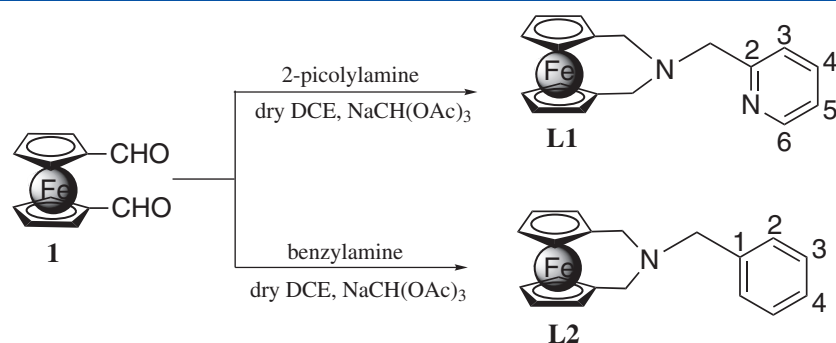
## Experimental

Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX-400

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**Scheme 1.** Synthesis of Ligands **L1** and **L2**.

spectrometer. Mass spectra were obtained on a Waters Q-ToF MicroTM spectrometer. IR spectra were recorded on a Bruker VECTOR 22 spectrometer. Element analyses were obtained on a Carlo Erba 1160 element spectrometer. Melting points (uncorrected) were measured on an XT5 micro-melting point apparatus.

All reactions were carried out under nitrogen atmosphere. Solvents were dried and freshly distilled prior to use. All the chemicals were used as supplied, without further purification, except for 1,1-dicarboxyaldehydeferrocene, which was prepared from ferrocene according to the literature, slightly modified.<sup>[20]</sup>

### Synthesis of **L1** and **L2**

1,1-Dicarboxyaldehydeferrocene (242 mg, 1.0 mmol) and 2-picolylamine (109 mg, 1.01 mmol for **L1**; benzylamine, 108 mg, 1.01 mmol for **L2**) in 250 ml DCE (dichloroethane) were added simultaneously over 8 h to one four-necked 1-liter flask charged with a solution of NaBH(OAc)<sub>3</sub> (1.06 g, 5.0 mmol) in DCE (50 ml). The mixture was stirred under N<sub>2</sub> atmosphere overnight at room temperature. The reaction was monitored by thin-layer chromatography until 1,1-dicarboxyaldehydeferrocene disappeared and quenched by saturated NaHCO<sub>3</sub> solution. The solvent was concentrated under vacuum to approximately 50 ml. The mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 ml). The organic extracts were combined, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The oily residue was purified by column chromatography on silica gel under reduced pressure using hexane–acetic ether (3:1) as eluent to give the pure compounds **L1** and **L2** (128.2 mg for **L1**, 40.3% yield and 125.1 mg for **L2**, 39.5% yield) as a yellow solid.

**L1** IR (KBr pellet): 3085, 3005, 2925, 2861, 2813, 1589, 1469, 1358, 1116, 1040, 756 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) ppm: δ 4.10 (s, 4H, Cp&bondH), 4.14 (s, 4H, Cp&bondH), 2.96 (s, 4H, CH<sub>2</sub>Cp), 4.02 (s, 2H, CH<sub>2</sub>py), 7.20 (like td, *J* = 7.3 Hz, 4.8 Hz, 1.5 Hz, 1H, Py&bondH5), 7.66 (like dd, *J* = 7.9 Hz, 1.5 Hz, 1H, Py&bondH3), 7.74 (like td, *J* = 7.9 Hz, 7.3 Hz, 0.9 Hz, 1H, Py&bondH4), 8.57 (like dd, *J* = 4.8 Hz, 0.9 Hz, 1H, Py&bondH6). <sup>13</sup>C NMR (CDCl<sub>3</sub>) ppm: <sup>13</sup>C NMR (CDCl<sub>3</sub>) ppm: 160.8 (Py&bondC1), 149.1 (Py&bondC5), 136.4 (Py&bondC3), 123.4 (Py&bondC2), 121.8 (Py&bondC4), 83.6, 69.8, 69.1 (Cp&bondC), 63.6 (CH<sub>2</sub>Py), 52.8 (CH<sub>2</sub>Cp). Anal. Found: C, 67.95%; H, 5.70%; N, 8.80%. Calcd. for C<sub>18</sub>H<sub>18</sub>FeN<sub>2</sub>: C, 67.66%; H, 5.59%; N, 8.62%. HRMS (ESI). Calcd for C<sub>18</sub>H<sub>18</sub>FeN<sub>2</sub> ([M + H]<sup>+</sup>): 319.0898. Found: 319.0951.

**L2** IR(KBr): 3085, 3005, 2925, 2861, 2813, 1589, 1469, 1428, 1358, 1116, 1040, 756 cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>) ppm: δ 4.08

(s, 4H, Cp&bondH), 4.12 (s, 4H, Cp&bondH), 2.90 (s, 4H, CH<sub>2</sub>Cp), 3.87 (s, 2H, CH<sub>2</sub>ph), 7.35 (dd, *J* = 7.3 Hz, 7.4 Hz, 2H, phenyl-H3), 7.44 (d, *J* = 7.4 Hz, 2H, phenyl-H2), 7.28 (t, *J* = 7.3 Hz, 1H, phenyl-H4). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 139.5 (phenyl-C1), 129.2 (phenyl-C2), 128.7 (phenyl-C3), 126.6 (phenyl-C4), 84.2, 69.9, 68.5 (Cp-C), 61.6 (CH<sub>2</sub>ph), 51.3 (CH<sub>2</sub>Cp). Anal. Found: C, 72.11%; H, 6.12%; N, 4.50%. Calcd. for C<sub>19</sub>H<sub>19</sub>FeN ([M + H]<sup>+</sup>): 318.0946. Found: 318.0942.

### Electrochemistry

Electrochemical experiments were carried out with a CHI 650A electrochemical analyzer connected to the data acquisition software used for the electrochemical measurements. Cyclic voltammetry experiments were performed in a glass cell enclosed in a Faraday cage, at room temperature under argon. The reference electrode was a 232 model saturated calomel electrode (SCE). The auxiliary electrode was a 7.5 cm platinum wire with a gold-plated connector. The working electrode was a glassy carbon electrode for **L1** and platinum electrode for **L2**. The supporting electrolyte was CH<sub>3</sub>OH and H<sub>2</sub>O containing 0.1 M KNO<sub>3</sub> for **L1** and CH<sub>3</sub>OH containing 0.1 M tetrabutylammonium nitrate (<sup>n</sup>Bu<sub>4</sub>NO<sub>3</sub>) for **L2**. Between each CV scan the working electrode was electro-cleaned by multicycle scanning in the supporting electrolyte solution, polished on alumina 0.3 μm, cleaned with water–methanol and sonicated before use, according to standard procedures. Solutions of **L1** (concentration: 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; KNO<sub>3</sub>: 0.1 mol dm<sup>-3</sup>) and **L2** (concentration: 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, <sup>n</sup>Bu<sub>4</sub>NNO<sub>3</sub>: 0.1 mol dm<sup>-3</sup>) were prepared. All the transition metal ions and alkaline earth metal ions (Cu<sup>2+</sup>, Mg<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>) were from their corresponding nitrate, and their concentration in 0.1 mol dm<sup>-3</sup> KNO<sub>3</sub> for **L1** and 0.1 mol dm<sup>-3</sup> <sup>n</sup>Bu<sub>4</sub>NNO<sub>3</sub> for **L2** were confirmed exactly by titration experiment. All the CV experiments for the metal complexes were performed immediately after solution preparation. The scan rate was 50 mV s<sup>-1</sup>.

### Crystal Structure Determination

All the measurements were made on a RAXIS-IV imaging plate area detector with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and expanded using Fourier techniques and refined by full-matrix least-squares methods. All calculations were performed using the Shelxl-97 crystallographic software package.<sup>[21]</sup>

Yellow single crystals of **L1** and **L2** were developed from the mixture of dichloromethane and hexane. **L1**: C<sub>18</sub>H<sub>18</sub>FeN<sub>2</sub>, *M<sub>r</sub>* = 318.19, triclinic, space group. *a* = 6.4670(13) Å, *b* = 10.267(2) Å, *c* = 11.232(2) Å, α = 94.64(3)°, β = 98.91(3)°, γ = 93.80(3)°.

$V = 732.0(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $D = 1.444 \text{ g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 1.024 \text{ mm}^{-1}$ ,  $F(000) = 332$ . **L2**:  $\text{C}_{19}\text{H}_{19}\text{FeN}$ ,  $M_r = 317.20$ , triclinic, space group.  $a = 6.1380(12) \text{ \AA}$ ,  $b = 11.262(2) \text{ \AA}$ ,  $c = 11.564(2) \text{ \AA}$ ,  $\alpha = 94.94(3)^\circ$ ,  $\beta = 101.86(3)^\circ$ ,  $\gamma = 104.38(3)^\circ$ ,  $V = 749.8(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $D = 1.405 \text{ g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 0.998 \text{ mm}^{-1}$ ,  $F(000) = 332$ .

### Computational Details

The structures of ligand **L1** coordinated with different metal ions ( $[\text{ML1}]^{2+}$  ( $\text{M} = \text{Mg}, \text{Ni}, \text{Pb}, \text{Cd}, \text{Zn}, \text{Cu}$ )) were fully optimized at the B3LYP/Genecp level of theory.<sup>[22]</sup> The 6-31G (d, p) basis set was employed for C, H, O, N atom, while the LanL2DZ basis set with relativistic effective core potentials was used for the remaining metal atoms. The model systems chosen for the computational studies were  $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-(CH}_2)_2\text{N-R}]$  [ $\text{R} = \text{pyridine}$  and  $\text{phenyl}$ ]. All the calculations were performed using Gaussian 03 suite of programs.<sup>[23]</sup>

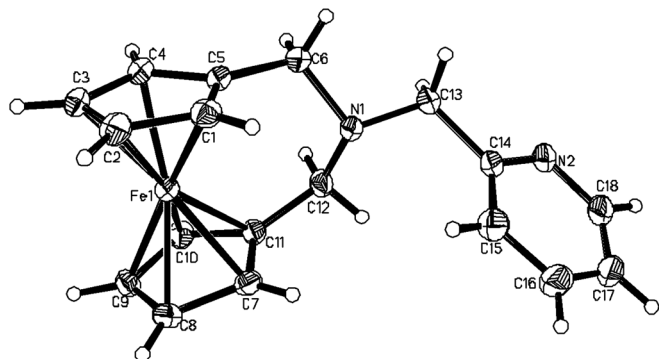
## Results and Discussion

### Synthesis of L1 and L2

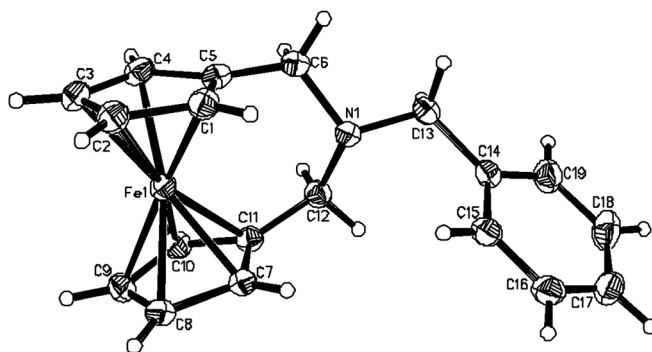
The ligands **L1** and **L2** were prepared by the condensation reaction of 1,1 -dicarbaldehydeferrocene with 2-picolyamine and benzylamine, respectively, in DCE under highly dilute conditions and sequent reduction by  $\text{NaBH}(\text{OAc})_3$ . The reaction was monitored by thin-layer chromatography until no 1,1 -dicarbaldehydeferrocene was detected. The pure desired compounds were obtained in 40.3% yield for **L1** and 39.5% yield for **L2** as a light-yellow solid. **L1** and **L2** were characterized by NMR, IR, MS, HRMS (ESI) and X-crystal diffraction analysis. Both ligands were stable in the air and soluble in common solvents, such as DCM (dichloromethane), acetone and ethyl acetate, and less soluble in methanol and ethanol.

### X-Ray Crystal Structure Analyses of L1 and L2

The molecular structures of **L1** and **L2** were determined by single-crystal X-ray diffraction. Suitable single crystals for X-ray diffraction analysis were obtained by slow evaporation from dichloromethane/hexane at room temperature. Perspective views of their molecular structures are shown in Figs 1 and 2, respectively.



**Figure 1.** Crystal structure of compound **L1**. Selected bond lengths ( $\text{\AA}$ ) for **L1**:  $\text{N}(1)\text{--C}(12)$  1.468(4);  $\text{N}(1)\text{--C}(13)$  1.471(4);  $\text{N}(1)\text{--C}(6)$  1.475(4);  $\text{C}(11)\text{--C}(12)$  1.499(5);  $\text{C}(13)\text{--C}(14)$  1.525(5);  $\text{C}(5)\text{--C}(6)$  1.510(5); selected bond angle ( $^\circ$ ) for **L1**  $\text{C}(12)\text{--N}(1)\text{--C}(13)$  109.2(3);  $\text{C}(12)\text{--N}(1)\text{--C}(6)$  112.0(3);  $\text{C}(13)\text{--N}(1)\text{--C}(6)$  109.4(3);  $\text{N}(1)\text{--C}(12)\text{--C}(11)$  113.6(3);  $\text{N}(1)\text{--C}(13)\text{--C}(14)$  112.6(3);  $\text{N}(2)\text{--C}(14)\text{--C}(15)$  123.1(4);  $\text{N}(2)\text{--C}(14)\text{--C}(13)$  114.9(4).



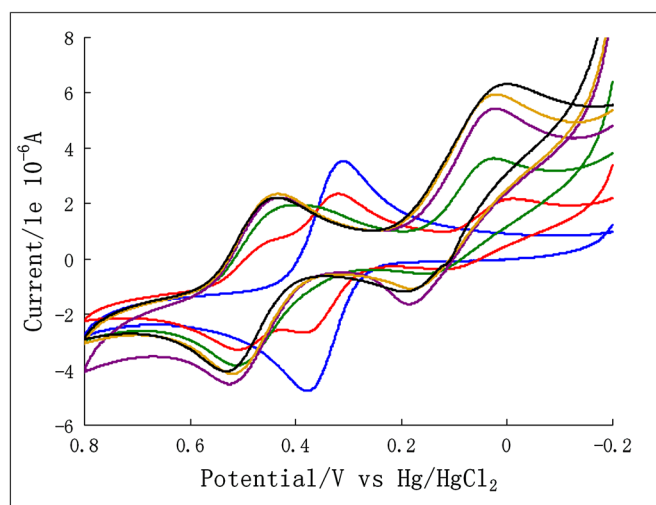
**Figure 2.** Crystal structure of compound **L2**. Selected bond lengths ( $\text{\AA}$ ) for **L2**:  $\text{N}(1)\text{--C}(12)$  1.471(3);  $\text{N}(1)\text{--C}(13)$  1.471(3);  $\text{N}(1)\text{--C}(6)$  1.477(3);  $\text{C}(11)\text{--C}(12)$  1.503(3);  $\text{C}(13)\text{--C}(14)$  1.517;  $\text{C}(5)\text{--C}(6)$  1.504(3); selected bond angle ( $^\circ$ ) for **L2**:  $\text{C}(5)\text{--Fe}(1)\text{--C}(2)$  69.54(10);  $\text{C}(11)\text{--Fe}(1)\text{--C}(2)$  154.39(10);  $\text{C}(1)\text{--Fe}(1)\text{--C}(2)$  40.73(10);  $\text{C}(12)\text{--N}(1)\text{--C}(13)$  109.95(18);  $\text{C}(12)\text{--N}(1)\text{--C}(6)$  112.30(18);  $\text{C}(13)\text{--N}(1)\text{--C}(6)$  110.04(18);  $\text{N}(1)\text{--C}(12)\text{--C}(11)$  113.30(18);  $\text{N}(1)\text{--C}(13)\text{--C}(14)$  113.19(19).

The cyclopentadienyl rings in both ligands were in the eclipsed conformation similar to the structure of the previously reported [3]ferrocenophanes.<sup>[24–27]</sup> Two cyclopentadienyl rings (Cp) of ferrocene were not parallel and formed dihedral angles of  $12.9^\circ$  and  $12.1^\circ$  for **L1** and **L2**, respectively. Moreover, the two Cp rings in both **L1** and **L2** were arranged in nearly eclipsed form. The chelate cycle  $\text{C5--C6--C11--C12--Fe1}$  in molecule **L1** is nearly planar, with the largest distance deviation 0.7598  $\text{\AA}$  of N1 and C5, C6, C11, C12 and Fe1 atoms forming a chelate cycle with the largest distance deviation 0.7289  $\text{\AA}$  of N1 in **L2**. The distances of  $\text{N1--C12}$ ,  $\text{N1--C13}$ ,  $\text{N1--C6}$  were 1.468(4), 1.471(4), 1.475(4)  $\text{\AA}$  in **L1** and 1.471(3), 1.471(3), 1.477(3)  $\text{\AA}$  in **L2**, respectively. These are normal, as the C–N distances of neutral compounds. The bond angles are 109.2(3)–112.0(3) in **L1** and the corresponding angles of C–N1–C in **L2** are 109.95(18)–112.30(18), which is slightly larger than those of *N*-methylated *N*-hexyl-aza[3]ferrocenophanes (103 (1)–114(1)) [24b,24c].

### Electrochemical Studies

Electrochemical experiments are necessary to test new redox-responsive molecules. Therefore, cyclic voltammetry experiments of **L1** alone and in the presence of several cations were performed in a mixture of  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$ . The ligand **L1** exhibited a reversible one-electron redox wave with a half potential ( $\Delta E_{1/2}$ ) of +343 mV vs.  $\text{Hg}/\text{HgCl}_2$  corresponding to the ferrocene–ferrocenium couple. Addition of 0.5 equiv. of  $\text{Cu}^{2+}$  resulted in two reversible one-electron redox waves, which were assigned as redox wave of parent ligand **L1** and complex of copper with ligand in the anodic region ( $\Delta E_{1/2}$  +468 mV). The  $\text{Fc}/\text{Fc}^+$  couple of the parent ligand disappeared when 1.0 equiv. of  $\text{Cu}^{2+}$  was added (Fig. 3). Increasing amounts of  $\text{Cu}^{2+}$  up to 3.0 equiv. and prolonging the reaction time (3 days) did not cause an obvious shift, which implied that **L1** formed a stable mononuclear complex with  $\text{Cu}^{2+}$  ( $\text{L}:\text{M} = 1:1$ ).

Upon addition of metal ions  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  to the solution of **L1**, no significant shift of the redox potential of the  $\text{Fc}/\text{Fc}^+$  couple was observed (supporting information, Figs SI 1–5), which suggested that **L1** did not have any interaction with these metal ions. When a mixture of 1 equiv.  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  was added to the solution of **L1**, the



**Figure 3.** Cyclic voltammograms of **L1** and its complexes with different amounts of  $\text{Cu}^{2+}$  ions in 0.1 M  $\text{KNO}_3$  solution. Scan rate  $50 \text{ mV s}^{-1}$ . Blue line, **L1** only; red line, 0.5 equiv.  $\text{Cu}^{2+}$  with **L1**; green line, 1.0 equiv  $\text{Cu}^{2+}$ ; violet line, 1.5 equiv.  $\text{Cu}^{2+}$ ; orange line, 2.0 equiv.  $\text{Cu}^{2+}$ ; black line, 3.0 equiv.  $\text{Cu}^{2+}$ .

extent of the anodic shift of redox potentials were approximately equal to that induced by  $\text{Cu}^{2+}$  alone. These results indicated that ligand **L1** selectively sense  $\text{Cu}^{2+}$  ion and preferentially coordinated with  $\text{Cu}^{2+}$  without interference by chemically closely related metal ions. Therefore, **L1** could be a good candidate for a molecular sensor to detect copper electrochemically in the presence of large excesses of these first-row transition and post-transition metal cations. The results were unexpected, because the coordination behaviour of aza-ligand with  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  is normally similar to that of  $\text{Cu}^{2+}$ . We suspected that the  $\text{Cu}^{2+}$  may be located in the ferrocenophane cage and only coordinated with one nitrogen atom in the ferrocenophane chain (Fig. 4, Model 1). Perhaps the size of the cage and radius of  $\text{Cu}^{2+}$  ion match each other very well.

To compare with **L1** and test our hypothesis, ferrocenophane **L2** was synthesized by the same procedure. The electrochemical properties were studied by cycle voltammetry. No significant shift of the redox potential of the  $\text{Fc}/\text{Fc}^+$  couple was observed when  $\text{Cu}^{2+}$  ion was added. The results indicate that **L1** did not take the coordination Model 1 with  $\text{Cu}^{2+}$  ion, but Model 2, which means that Cu atom was coordinated by two nitrogen atoms in **L1**.

### Calculation Binding Energies

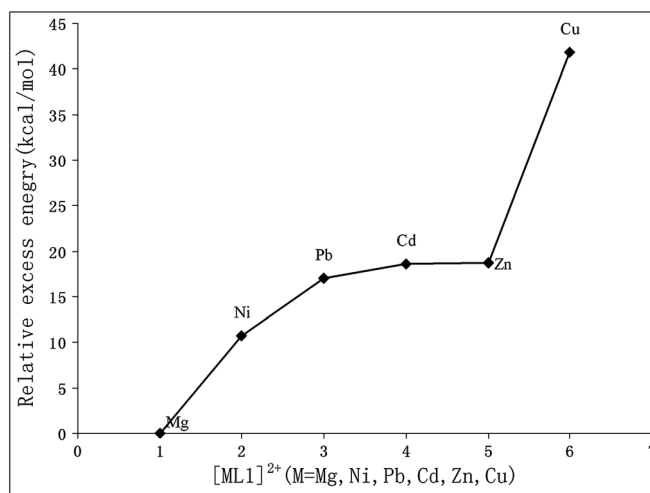
Unfortunately, we failed to obtain a single crystal of Cu complex with **L1**. To clarify why ligand **L1** selectively sensed Cu ion in the presence of other chemically closely related metal ions, we applied computational studies. Quantum calculations based on



**Figure 4.** Proposed coordination model of ligand **L1** with  $\text{Cu}^{2+}$ .

**Table 1.** Energy and relative excess energy ( $\text{kcal mol}^{-1}$ ) of  $[\text{ML1}]^{2+}$  ( $\text{M} = \text{Mg}, \text{Ni}, \text{Pb}, \text{Cd}, \text{Zn}, \text{Cu}$ ) at B3LYP/genecp level (unit: a.u.)

Species	Energy	Excess energy	Relative excess energy
$\text{Cu}(\text{NO}_3)_2$	-756.7656629		
$[\text{Cu L1}]^{2+}$	-1125.3490819	-368.583419	41.84
$\text{Zn}(\text{NO}_3)_2$	-626.2378383		
$[\text{Zn L1}]^{2+}$	-994.7843391	-368.5465008	18.76
$\text{Cd}(\text{NO}_3)_2$	-608.6898887		
$[\text{Cd L1}]^{2+}$	-977.2361029	-368.5462142	18.58
$\text{Pb}(\text{NO}_3)_2$	-564.12656315		
$[\text{Pb L1}]^{2+}$	-932.6703495	-368.54378635	17.06
$\text{Ni}(\text{NO}_3)_2$	-729.9404376		
$[\text{Ni L1}]^{2+}$	-1098.4740958	-368.5336582	10.73
$\text{Mg}(\text{NO}_3)_2$	-561.5600378		
$[\text{Mg L1}]^{2+}$	-930.0765333	-368.5164955	0.00



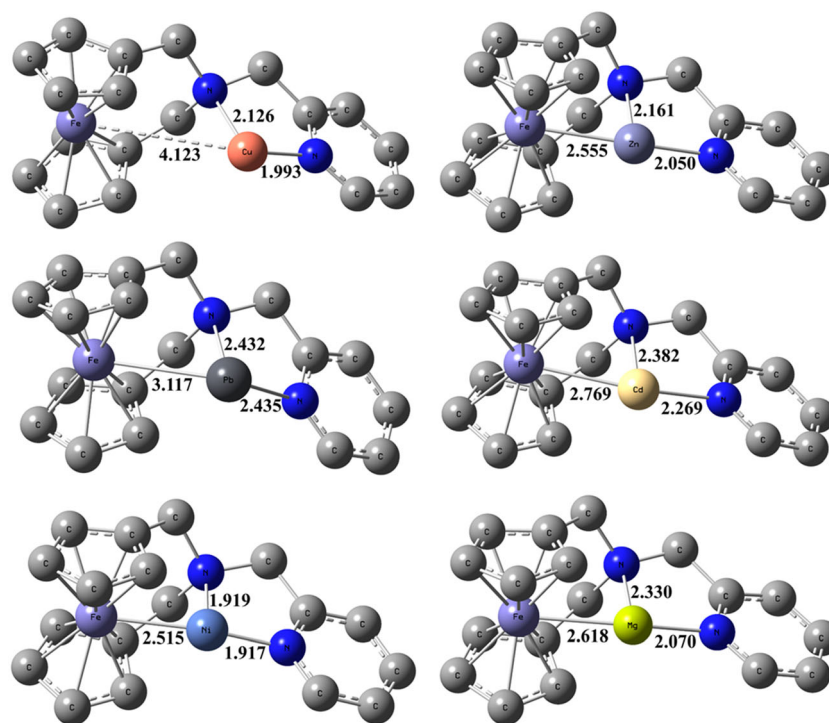
**Figure 5.** Relative excess energy profile of  $[\text{ML1}]^{2+}$  ( $\text{M} = \text{Mg}, \text{Ni}, \text{Pb}, \text{Cd}, \text{Zn}, \text{Cu}$ ) at B3LYP/genecp level.

the stabilization constants have been performed at the B3LYP/6-31G (d, p)/LanL2DZ level of theory using the Gaussian 03 program. The calculation formula of binding energy is  $E = E_{[\text{M}^{2+} + \text{L1}]} - (E_{\text{M}(\text{NO}_3)_2} - 2E_{(\text{NO}_3)^-})$ . The calculated results are summarized in Table 1 and Fig. 5, which show that the largest binding energy was  $41.84 \text{ kcal mol}^{-1}$  for Cu complex with **L1**, followed by  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  complexes. The results indicate that complex **L1**· $\text{Cu}^{2+}$  was the most stable. Moreover, the distance between Cu and Fe is  $4.123 \text{ \AA}$  (Fig. 6), longer than the sum of their radii. The distances of  $\text{Zn-Fe}$  ( $2.555 \text{ \AA}$ ),  $\text{Cd-Fe}$  ( $2.0769 \text{ \AA}$ ),  $\text{Pd-Fe}$  ( $3.117 \text{ \AA}$ ),  $\text{Ni-Fe}$  ( $2.515 \text{ \AA}$ ) and  $\text{Mg-Fe}$  ( $2.0618 \text{ \AA}$ ) are shorter than the sum of their radii, which may lead these complexes to be unstable because of charge repulsion between the metal cations tested and the Fe atom.

### Conclusion

We have developed an easy methodology to synthesize ligands **L1** and **L2**. Ligand **L1** was proved to be a stable and electrochemically selective sensor for  $\text{Cu}^{2+}$  in environments containing





**Figure 6.** Representation of the optimized geometries of the  $[ML_1]^{2+}$  ( $M = \text{Mg, Ni, Pb, Cd, Zn, Cu}$ ) at B3LYP/genecp level (units in Å for bond lengths).

alkaline earth metals, transition and post-transition metal ions, such as  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ions, without interference. The coordination model of **L1** with  $\text{Cu}^{2+}$  was proposed from the results of controlled experiments and quantum calculations.

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The crystal structures of **L1** and **L2** have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers are CCDC 845017 and CCDC 845016, respectively.

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