



## 八核茂铁-钌金属大环对钙离子的电化学和荧光识别

蔡 苹<sup>1</sup> 李明雪<sup>1,2</sup> 段春迎<sup>\*,1</sup> 赵永刚<sup>1</sup> 孟庆金<sup>1</sup>

(<sup>1</sup> 南京大学配位化学研究所, 配位化学国家重点实验室, 南京 210093)

(<sup>2</sup> 河南大学药学院, 开封 475004)

关键词: 茂铁; 金属大环; 电化学; 荧光; 识别

中图分类号: O614.81<sup>+</sup>1; O614.82<sup>+</sup>1; O614.23<sup>+</sup>1

文章标识码: A

文章编号: 1001-4861(2005)01-0141-04

### A New Calcium Selective Electrochemical and Fluorescent Chemosensor Based on Ferrocenyl-containing Octanuclear Metallocyclic Ru<sub>4</sub>Fc<sub>4</sub>

CAI Ping<sup>1</sup> LI Ming-Xue<sup>1,2</sup> DUAN Chun-Ying<sup>\*,1</sup> ZHAO Yong-Guang<sup>1</sup> MENG Qing-Jin<sup>1</sup>

(<sup>1</sup> Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093)

(<sup>2</sup> College of Pharmacy, Henan University, Kaifeng 475004)

**Abstract:** The ruthenium unit was introduced into the redox-active molecular polygon to assembly new Ru-Fc metallocycles (Compound **1**), in which the redox active (ferrocene) and fluoresecent (ruthenium) signaling subunits are directly attached by the putative cation-binding sites. The compound **1** displayed high selectivity for Ca<sup>2+</sup> by electrochemical tests. The measurements of the fluorescence spectra on titration of **1** with Ca<sup>2+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> or Ba<sup>2+</sup> ion indicate the unique ability of **1** to detect Ca<sup>2+</sup> ions selectively.

**Key words:** ferrocene; metallocyclic; electrochemistry; fluorescence; reorganization

## 0 Introduction

Molecular squares and rectangles with metal corners and unsaturated ligand sides have become a representative class of “supramolecular” species<sup>[1]</sup>. In addition to the remarkable self-assembly formation reactions and the unusual structures, these systems have been receiving increasing attention due to their potential for the molecular recognition of substrates, for the interactions with light (antenna function), and for the intramolecular magnetic exchange coupling<sup>[2,3]</sup>. The desired functionality in metallosupra-molecular squares may be introduced by employing functional ligands or properly functionalized metal corners with appropriate

size and shape. Considerable efforts have been devoted to the design and preparation of metal corners, containing crown ether, calixarene and ferrocene<sup>[4]</sup>, however, only few functional bridging ligands have been reported so far<sup>[5]</sup>. In our precedent publication<sup>[6]</sup>, we reported the self-assembly of an octanuclear metallocyclic complex Ni<sub>4</sub>Fc<sub>4</sub> by incorporating the redox-active unit, ferrocene, into a bis-carbazone ligand (Scheme I), and studied the potential application as an electrochemical sensor for Mg<sup>2+</sup> both in solution and in the solid state. As a continuance of our research work in the assemblies and properties of ferrocene-containing polynuclear complexes<sup>[7]</sup>, here we report the ruthenium unit into the redox-active molec-

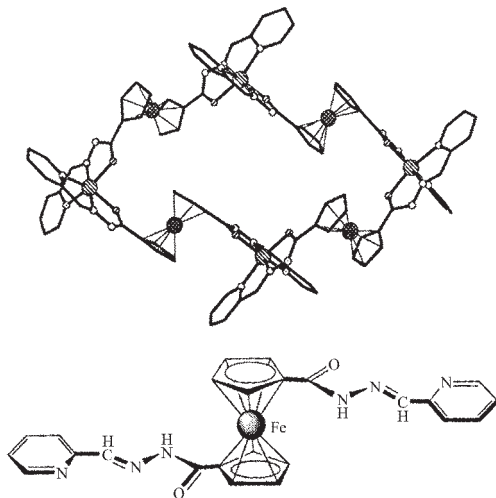
收稿日期: 2004-10-23. 收修改稿日期: 2004-12-02.

国家自然科学基金资助项目(No.20131020).

\*通讯联系人。E-mail: duancy@nju.edu.cn

第一作者: 蔡 苹, 女, 28 岁, 博士; 研究方向: 功能配位化学。

ular polygon to assembly new Ru-Fc metallocycles, in which the redox active (ferrocene) and fluorescent (ruthenium) signaling subunits are directly attached by the putative cation-binding sites. The modulation or control of the photophysical properties of a fluorescent  $\text{Ru}^{\text{II}}$  moiety incorporated in such a molecular square is a fascinating challenge for modern chemistry and would thus yield a combined fluorescence and redox-sensor in a single molecule<sup>[8]</sup>.



Scheme I

## 1 Experimental

### 1.1 Physical measurements

The elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240 analyzer. The infrared spectra were recorded on a Vector 22 Bruker spectrophotometer with KBr pellets in the 4 000~400  $\text{cm}^{-1}$  regions. UV/Vis spectra were obtained at room temperature on a Shimadzu 3100 spectrophotometer in methanol solution. Fluorescence emission spectra were recorded on an Aminco Bowman Series 2 spectrofluorimeter equipped with a R928 photomultiplier working at 850 V and pass width is 4 nm. Electrospray mass spectra on a LCQ system (Finnigan MAT) using methanol as the mobile phase. Differential pulse voltammetry results were recorded with an EG&G PAR model 273 instrument. The solution-state measurement were performed in  $\text{CH}_2\text{Cl}_2$  with  $n\text{-Bu}_4\text{NClO}_4$  ( $0.1 \text{ mol} \cdot \text{L}^{-1}$ ) for **1** and  $\text{CH}_3\text{CN}$  with  $n\text{-Bu}_4\text{NClO}_4$  ( $0.1 \text{ mol} \cdot \text{L}^{-1}$ ) for **2** as supporting electrolyte, in a three-electrode cell which has a 50 ms pulse width with current samples 40 ms after the pulse was applied.

The cell comprises a platinum wire working electrode, a platinum auxiliary electrode and SCE as reference electrode.

### 1.2 Preparation

**Ru<sub>4</sub>Fc<sub>4</sub> 1:** After the 45 mL mixture methanol solution of  $\text{AgNO}_3$  (0.34 g, 2.0 mmol) and  $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$  (0.49 g, 1.0 mmol) was refluxed for 30 min and filtrated to remove the deposited  $\text{AgCl}$ , the ligand  $\text{H}_2\text{L}$  (0.48 g, 1 mmol) was added and the solution was refluxed for 8 h under  $\text{N}_2$ . The solid obtained after the solvent was removed. Calcd (%) for  $\text{C}_{114}\text{H}_{132}\text{N}_{30}\text{O}_{35}\text{S}_9\text{Fe}_4\text{Ru}_4$ : C 40.3, H 4.0, N 12.4; Found: C 40.2, H 4.1 N 12.4.

## 2 Results and discussion

Since the rigid pre-organized bridged bis-tridentate Ru-corner made the construction of molecular polygon more general and predictable, the title compound  $[\text{Ru}_4(\text{HL})_2(\text{H}_2\text{L})_2](\text{NO}_3)_6$  was synthesized by simple reaction of  $\text{Ru}(\text{DMSO})_4\text{Cl}_2$  and the ferrocene-containing ligand  $\text{H}_2\text{L}$  in a 1:1 molar ratio in methanol solution in high yield. The ESI-MS spectra (Fig.1) in  $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$  solution exhibited three teams of peaks at  $m/z$  502.6, 622.6, 742.5. Three peaks corresponding to  $[\text{Ru}_4(\text{H}_2\text{L})_4(\text{NO}_3)_3]^{5+}$  (502.6),  $[\text{Ru}_4(\text{H}_2\text{L})_3(\text{HL})(\text{NO}_3)_2(\text{H}_2\text{O})_2]^{5+}$  (497.6) and  $[\text{Ru}_4(\text{H}_2\text{L})_2(\text{HL})_2(\text{NO}_3)(\text{CH}_3\text{CN})(\text{H}_2\text{O})_2]^{5+}$  (492.7) were found at about  $m/z$  502.6. Four peaks corresponding to  $[\text{Ru}_4(\text{H}_2\text{L})_2(\text{HL})_2(\text{NO}_3)_2(\text{CH}_3\text{CN})]^{4+}$  (622.6),  $[\text{Ru}_4(\text{H}_2\text{L})_2(\text{HL})_2(\text{NO}_3)_2(\text{H}_2\text{O})]^{4+}$  (617.5),  $[\text{Ru}_4(\text{H}_2\text{L})_2(\text{HL})_2(\text{NO}_3)_2]^{4+}$  (612.5) and  $[\text{Ru}_4(\text{H}_2\text{L})(\text{HL})_3(\text{NO}_3)(\text{CH}_3\text{CN})]^{4+}$  (607.5) were found at about  $m/z$  622.6, respectively. Four peaks corresponding to  $[\text{Ru}_4(\text{H}_2\text{L})_3(\text{HL})_2(\text{NO}_3)_2(\text{CH}_3\text{CN})]^{4+}$  (742.5),  $[\text{Ru}_4(\text{H}_2\text{L})_3(\text{HL})_2(\text{NO}_3)_2]^{4+}$  (737.4),  $[\text{Ru}_4(\text{H}_2\text{L})_3(\text{HL})_2(\text{NO}_3)_2]^{4+}$  (732.4) and  $[\text{Ru}_4(\text{H}_2\text{L})_2(\text{HL})_3(\text{NO}_3)(\text{CH}_3\text{CN})]^{4+}$  (727.4) were found for peaks centered at about 742.5, respectively. The  $[\text{Ru}_4$

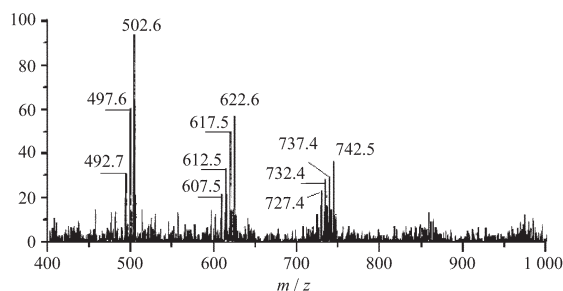


Fig.1 Electrospray mass spectrum of complex **1** in acetonitrile/methanol solution

(H<sub>2</sub>L)<sub>3</sub>(HL)<sub>2</sub>] species was formed from the Ru<sub>4</sub>Fc<sub>4</sub> species attached with one of the neutral ligand through  $\pi$ - $\pi$  interaction of the ferrocenyl and the pyridine rings. No species corresponding to the fragments resulted from the loss of metal ions and ligands was observed, indicating that the octanuclear fragment of the complex **1** was the most stable conformation in solution. Considering the similar coordination geometry of the Ni<sup>II</sup> and Ru<sup>II</sup> with two rigid N<sub>2</sub>O tridentate ligand, it is assumed that ruthenium compound **1** has the similar square fragment with the nickel analogue.

Electrochemical tests were preformed with **1** (10<sup>-3</sup> mol·L<sup>-1</sup>) in acetonitrile, in the presence of alkali and alkaline earth cations. The compound **1** displayed a single reversible Fe<sup>II</sup>/Fe<sup>III</sup> redox couple centered on 0.84 V vs SCE. The electrochemical response of compound **1** to various cations and its selectivity for Ca<sup>2+</sup> are illustrated in Fig.2. Compound **1** was not sensitive to LiNO<sub>3</sub>, NaNO<sub>3</sub>, KNO<sub>3</sub>, Ba(NO<sub>3</sub>)<sub>2</sub> and poorly sensitive to Mg(NO<sub>3</sub>)<sub>2</sub>. However, stepwise addition of up to 2 equiv. of Ca(NO<sub>3</sub>)<sub>2</sub> to a solution of compound **1** resulted in a clear cathodic shift of  $\Delta E_{1/2}$  = -90 mV. Further addition of Ca(NO<sub>3</sub>)<sub>2</sub> (until 5 equivalents) had no significant effect, indicative of the formation of the stable 1:2 molar ratio [**1** C 2Ca<sup>2+</sup>) interior.

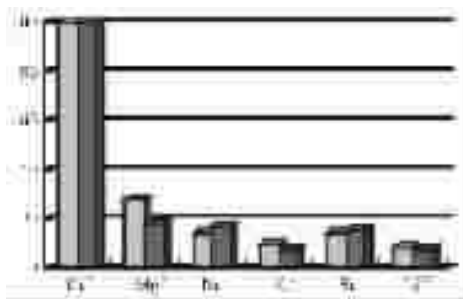


Fig.2 Multiresponse of **1** to various cations in acetonitrile

The response is normalized with respect to the response of the 2 equivalents of Ca<sup>2+</sup>. The gray bars represent the percent of cathodic shift in the  $E_{1/2}$  of cations to that of Ca<sup>2+</sup>. The black bars represent to percent of emission intensities of cations to that of Ca<sup>2+</sup>.

Generally, the addition of a metal cation into the sensor compounds will induce a classical anodic shift of the iron potential. In compound **1**, the opposite is observed. Few examples about the cathodic redox-potential shift have been reported upon cation addition and were assigned to the important electronic reorga-

nization of molecules<sup>[9]</sup>. Interestingly, the nickel complex Ni<sub>4</sub>Fc<sub>4</sub> can highly selectively recognize the Mg<sup>2+</sup> through the oxygen atoms attached to the nickel atoms, however, the title complex can only be coordinated to the Ca<sup>2+</sup>. The poor coordination ability to Mg<sup>2+</sup> for compound **1** might be due to that the protonation of ligand weakens the coordination ability of the oxygen atoms attached to the ruthenium atoms. The high selectivity of the Ca<sup>2+</sup> strongly suggests a different binding pattern that has not been found in the nickel complex. Theoretical calculations and experiments are underway to validate this explanation of the intriguing electrochemical behaviour involving Ca<sup>2+</sup> cation. The design of chemosensors specific for the detection of biologically relevant cations, such as Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, is a topic of considerable interest<sup>[10]</sup>. In particular selective detection of one of these cations in the presence of others, such as the sensing of Ca<sup>2+</sup> ions in the presence of Na<sup>+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup> ions is a challenging task. There are large number of excellent Ca<sup>2+</sup> fluorescence sensors and redox sensors available commercially<sup>[11]</sup>, but relatively less effort has been devoted to the design of multi-responsive cation sensors<sup>[8]</sup>.

UV-Vis and emission spectra of the complex **1** were measured. The free ferrocene-containing ligand H<sub>2</sub>L exhibits a strong absorption at  $\lambda_{\max}$  300 nm with a shoulder at 350 nm, and a tail band at about 460 nm. The ruthenium complex exhibits a peak at about 310 nm with shoulder at ca. 400 nm, which is assigned to the Ru-center MLCT band. While the free ligand does not exhibit obvious emission, emission spectrum of the ruthenium complex exhibits a band with  $\lambda_{\max}$  at 435 nm by exciting the acetonitrile solution of compound **1** ( $\lambda_{\text{ex}}$ , 396 nm). On titration of **1** with Ca(NO<sub>3</sub>)<sub>2</sub> from 0 to 5 equiv., dramatic increase of the emission intensity was observed as shown in Fig.3. Unlike many fluorescent chemosensors for calcium, the fluorescence is "switch on" rather than "switch off" upon recognition. This fact could be of interest because in sensing processes, fluorescence enhancement, rather than quenching, is usually preferred in order to observe a high signal output. In a separate experiment, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> or Ba<sup>2+</sup> ion was added to a solution of **1** in acetonitrile, which changed its absorption or emission properties poorly, indicating the unique ability of **1** to detect Ca<sup>2+</sup> ions selectively.

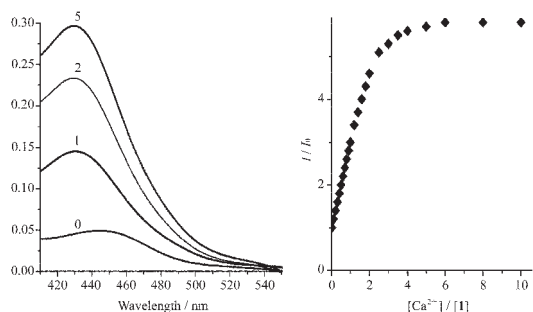


Fig.3 Fluorescence response of compound **1** to addition of Ca<sup>2+</sup> in acetonitrile  
Excitation was at 350 nm. (Left) The right showing the fluorescent titration curves for compound **1** with Ca<sup>2+</sup>.  
0 represents, fluorescence response of compound **1**; 1, 2, 5 represent the fluorescence response of 1:1, 1:2 and 1:5 mixture of compound **1** and Ca<sup>2+</sup>, respectively.

In summary, molecules that contain two or more distinct signaling units will be the keystones of new families of ion chemosensors potentially usable by two or more different and complementary techniques. The modulation of redox and fluorescent units incorporated in metallocyclic and the high selective Ca<sup>2+</sup> sensing observed both by electrochemistry and fluorescence spectroscopy indicated that high selective multi-response metallomacrocyclic receptor should be desired. The fabrication of these types of systems and their integration into different supports will probably lead to novel prototype molecular sensing devices of commercial usage.

## References:

- [1] (a)Stang P J, Olenyuk B. *Acc. Chem. Res.*, **1997**,**30**:502~518  
(b)Leininger S, Olenyuk B, Stang P. *J. Chem. Rev.*, **2000**, **100**:853~908  
(c)Moulton B, Zaworotko M J. *Chem. Rev.*, **2001**, **101**:1629~1628  
(d)Cotton F A, Lin C, Murillo C. *Acc. Chem. Res.*, **2001**,**34**: 759~771  
(e)Fujita M, Kwon Y J, Washizu S, et al. *J. Am. Chem. Soc.*, **1994**,**116**:1151~1152
- [2] (a)Belanger S, Keefe M H, Welch J L. *Coord. Chem. Rev.*, **1999**,**192**:29~45  
(b)Whiteford J A, Stang P J, Huang S D. *Inorg. Chem.*, **1998**, **37**:5595~5601  
(c)Beer P D, Gale P A. *Angew. Chem. Int. Ed.*, **2001**,**40**:487~516  
(d)Johnson D W, Raymond K N. *Supramol. Chem.*, **2001**,**13**: 639~659
- [3] (a)Slone R V, Benkstein K D, Be'langer S, et al. *Coord. Chem. Rev.*, **1998**,**171**:221~243  
(b)Sun S S, Lees A J. *Inorg. Chem.*, **1999**,**38**:4181~4182  
(c)Campo-Fernandez C S, Cle'rac R, Dunbar K R. *Angew. Chem. Int. Ed.*, **1999**,**38**:3477~3479
- [4] (a)Stang P J, Cao D H, Chen K, et al. *J. Am. Chem. Soc.*, **1997**,**119**:5163~5168  
(b)Stang P J, Olenyuk B, Fan J, et al. *Organometallics.*, **1996**, **15**:904~905  
(c)Sun S S, Anspach J A, Lees A J. *Inorg. Chem.*, **2002**,**41**: 1862~1869
- [5] (a)Slone R V, Hupp J T. *Inorg. Chem.*, **1997**,**36**:5422~5423  
(b)Jengo E, Milani B, Zangrando E, et al. *Angew. Chem. Int. Ed.*, **2000**,**39**:1096~1097  
(c)Marquis A, Kintzinger J P, Graff R, et al. *Angew. Chem. Int. Ed.*, **2002**,**41**:2760~2761  
(d)Gabai R, Shipway A N, Willner I. *Chem. Commun.*, **1999**: 1937~1938  
(e)You C C, Wurthner F J. *Am. Chem. Soc.*, **2003**,**125**:9716~9725
- [6] Li M X, Cai P, Duan C Y, et al. *Inorg. Chem.*, **2004**,**43**:5174~5175
- [7] (a)Guo D, Han G, Duan C Y, et al. *Chem. Commun.*, **2002**: 1096~1097  
(b)Fang C J, Duan C Y, Guo D, et al. *Chem Commun.*, **2001**: 2540~2541  
(c)Fang C J, Duan C Y, He C, et al. *Chem. Commun.*, **2000**: 1187~1188
- [8] (a)Beer P D, Szemes F, Balzani V, et al. *J. Am. Chem. Soc.*, **1997**,**119**:11864~11875  
(b)Maynadie J, Nicot B D, Forgue S F, et al. *Inorg. Chem.*, **2002**,**41**:5002~5004  
(c)Wiskur S L, Floriano P N, Anslyn E V, et al. *Angew. Chem. Int. Ed.*, **2003**,**42**:2070~2072
- [9] (a)Beer P D, Danks J P, Hesek D, et al. *Chem. Commun.*, **1993**:1735~1736  
(b)Maynadie' J, Delavaux-Nicot B, Lavabre D, et al. *Inorg. Chem.*, **2004**,**43**:2064~2077
- [10](a)de Silva A P, Gunaratne H Q N, Gunnlaugsson T, et al. *Chem. Rev.*, **1997**,**97**:1515~1566  
(b)McQuade D T, Pullen A E, Swager T M. *Chem. Rev.*, **2000**,**100**:2537~2574  
(c)He H, Mortellaro M A, Leiner M J P, et al. *J. Am. Chem. Soc.*, **2003**,**125**:1468~1469
- [11]Ajayaghosh A, Arunkumar E, Daub J. *Angew. Chem. Int. Ed.*, **2002**,**41**:1766~1767