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A new dinuclear ferrocene with amide–thiourea binding sites for dual electrochemical sensing to Hg(II) and anions

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ABSTRACT

A new dinuclear ferrocene-base receptor bearing amide and thiourea binding sites, **1**, was prepared and characterized by X-ray crystal structure analysis. This receptor shows a dual electrochemical sensing to Hg(II) and anions. Upon the addition of Hg(II), its redox potential shows a positive shift for the mercury-promoted intramolecular cyclic guanylation mechanism. In addition, **1** also shows distinctive electrochemical sensing to $H_2PO_4^-$ over other anions with a large negative shift of its redox potential for N–H…anion hydrogen bond interaction between anion and **1**.

1. Introduction

The design of sensors capable of recognizing both metal ions and anions is one of the most challenging topics because they play an important role in biological industry and environmental processes [1]. Among various metal ions, the selective and sensitive detection of mercuric ion is very important for its high toxicity and widespread distribution in the environment [2–7]. On the contrary, phosphates ions are known to be important in biology through signaling, energy transduction and information storage and expression, and to be highly toxic via eutrophication when present in excess in waterways [8–13]. Therefore, development chemosensors for rapid and convenient detection of mercuric ion and phosphates ions is highly important.

To obtain receptors capable of recognizing anions and cations, a common way is through the integrating cationic and anionic guest binding sites in a single molecule [14–16]. This design criterion makes thiourea group attractive. Thiourea is a well known anions donor for its strong hydrogen bonding and multiple binding sites. A variety of anions recognition receptors containing thiourea have been designed over the past years [17,18]. In addition, the thiourea is also a valuable ligand in coordination and organometallic chemistry [19,20]. Especially, the sulfur atom of the thiourea is a good donor for Hg(II). Some sophisticated Hg^{2+} selective chemosensors based on desulfurization of thiourea have been developed [21–23]. Furthermore, mercury-promoted intramolecular cyclic guanylation mechanism is also reported when amide exists at the γ position of the thiourea group [24–26]. However, to the best of our knowledge, examples dealing with the use of amide and thiourea derivatives as chemosensors for sensing to mercuric ion and phosphates ions are still rare [27].

In this context, we describe here the synthesis and electrochemical sensing properties of a new receptor **1** (Scheme 1), in which the two ferrocenyl moieties are used as the antenna units, and the amide and thiourea groups as heteroditopic binding sites. Its electrochemical, UV–Vis and ^1H NMR spectral behavior toward various metal ions and anions are investigated.

2. Experimental

2.1. General instrumentations and reagents

All the starting materials for synthesis were commercially available and used as received. All the solvents used for titration measurements were purified by standard procedures. [((2-Aminoethyl)amino)carbonyl]ferrocene (**2**) and ferrocenoyl isothiocyanate (**3**) were prepared according to the literature method [24,28]. UV–Vis spectra were recorded on a S-3100 spectrophotometer. Electrochemical measurements were performed with a CHI 624C instrument. NMR

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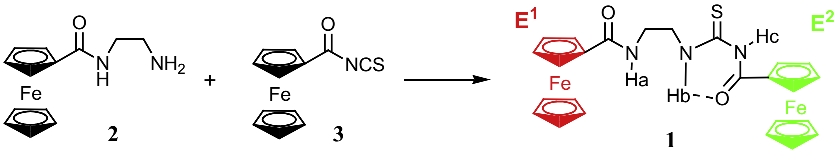

Scheme 1. Synthesis route of compound **1**.

spectra were recorded using a Varian instrument (300 MHz). The metal ions are perchlorate salts, and the anions are tetrabutylammonium (TBA) salts.

2.2. Preparation of UV–Vis and electrochemical titration solutions

Stock solutions of metal ions (0.01 M) and anions (0.01 M) were prepared in CH_3CN solution. The concentration of **1** in the UV–Vis titrations was 0.03 mM in CH_3CN solution. During the titration, metal ion solution was added into a solution of **1** (2 mL) using a micro injector and the whole volume of the final system can be considered constant because the volume of metal ion solution added is negligible compared to that of **1**'s solution.

The electrochemical measurements were carried out in a one-compartment cell under a nitrogen atmosphere at 25 °C, equipped with a Pt disk working electrode, a platinum wire counter electrode, and a Ag/$AgNO_3$ (0.1 M in CH_3CN solution) reference electrode. The working electrode surface was carefully polished with a basic Al_2O_3-water slurry, washed with MeOH and sonicated in a H_2O–MeOH–CH_3CN 1:1:1 mixture at 40 °C for 15 min prior to use. All potentials in this paper were recorded in CH_3CN and are quoted relative to Ag/$AgNO_3$, and were calibrated using decamethylferrocene ($E_{1/2} = 0.46$ V versus Ag/Ag^+). The supported electrolyte was a 0.10 M CH_3CN solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$). Differential pulse voltammetry (DPV) measurements were also carried out with a 50 ms pulse width. The concentration of **1** for CV/DPV titration is 0.3 mM in CH_3CN solution.

2.3. X-ray crystallographic analysis

Single crystals of **1** were obtained by direct diffusion of hexane into its CH_2Cl_2/MeOH (95:5, v/v) solution. A suitable single crystal was mounted in a glass fiber, and diffraction measurements were taken with a Bruker Smart APEX CCD-based diffractometer with Mo Kα graphite monochromated radiation. The structure was solved by direct methods using the program SHELXL-97 [29]. The refinement and all further calculations were carried out using SHELXL-97 [30]. The non-H atoms were refined anisotropically, using weighted full matrix least-squares on F^2. One of the cyclopentadiene ring (C1–C5) in **1** was disordered. The site occupation factor 0.4:0.6 of these disordered atoms was adjusted to give reasonable thermal parameters.

2.4. Synthesis of 1

Under nitrogen, 136 mg (0.5 mmol) **2**, 136 mg (0.5 mmol) **3** and 0.5 mL triethylamine were dissolved in 30 mL dry CH_2Cl_2 solvent, and then stirred for 24 h at room temperature. After removal of the solvent, the crude product was purified over silica gel using CH_2Cl_2/MeOH (98:2, v/v) as the eluent to yield **1** as an orange solid (230 mg, 85.2% yield). IR (KBr): 1633, 1528, 1455, 1273, 1171, 822, 730 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 10.96 (s, 1H), 8.53 (s, 1H), 6.54 (s, 1H), 4.76 (t, 2H, $J = 2.0$ Hz), 4.72 (t, 2H, $J = 2.0$ Hz), 4.53 (t, 2H, $J = 2.0$ Hz), 4.34 (t, 2H, $J = 2.0$ Hz), 4.25 (s, 5H), 4.21 (s, 5H), 4.04 (m, 2H), 3.72 (m, 2H). FAB-MS m/z (M^-) Calc. 543.2. Found 542.1, [M+1], 578.1 [M+Cl^-].

3. Results and discussion

3.1. Synthesis and characterization

The synthesis route of **1** is shown in Scheme 1. With commercial available ferrocenecarboxylic acid as starting material, we firstly prepared the key precursors [((2-aminoethyl)amino)carbonyl]ferrocene (**2**) and ferrocenoyl isothiocyanate (**3**) according to the literature method [24,28]. Then the target compound **1** was easily obtained (in 88% yield, dark orange) by condensation of **2** and **3** in the presence of triethylamine in CH_2Cl_2 solution. Its molecular structure was confirmed by IR, ^1H NMR, ESI-MS spectra and X-ray crystal analysis.

The three N–H protons (Scheme 1) in **1** are assigned since they are important for anions binding. In $CDCl_3$ solution, the protons Ha and Hc locate at 6.54 and 8.53 ppm, respectively, while proton Hb is in downfield of 10.96 ppm, which is attributed to the intramolecular hydrogen bond formation between N–H moiety and the amidic O donor atom in **1** [31,32]. Strong intramolecular hydrogen bond is often observed in acylthiourea ligands [33,34].

The strong intramolecular hydrogen bond in **1** is also confirmed by the X-ray crystal analysis (Fig. 1). Single crystal of **1** was obtained by slow diffusion of hexane to its CH_2Cl_2/MeOH (95:5, v/v) solution, and the detailed crystallographic data are shown in Table 1. The X-ray structure of **1** shows that the two ferrocenyl units are in a *cis*-conformation, while the three N–H donors adopt a *trans*-conformation. In addition, The atoms O1–C11–N1–C12–N2–H2a form strong intramolecular hydrogen bond (N2–H2A···O1, 1.93 Å, 2.609(3) Å 135°) to give a planar six-membered ring, which is almost parallel to the appended cyclopentadienyl ring of the ferrocene moiety (dihedron angle 18.6°).

3.2. Cations sensing properties

The recognition of **1** toward various of metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}) was first investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in 0.2 mM CH_3CN solution containing 0.1 M [n-Bu_4N]ClO_4 as a supporting electrolyte. The CV and DPV of **1** show two closely spaced reversible one-electron redox

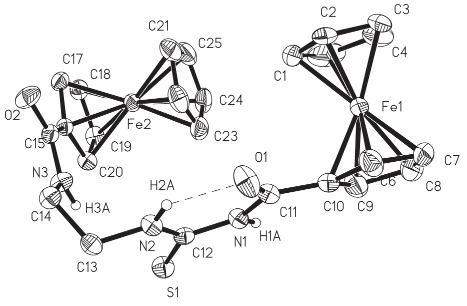

Fig. 1. X-ray structure of **1**, the hydrogen atoms except N–H protons were omitted for clarity. Selected bond lengths (Å) and angles (°): O1–C11, 1.225(4); S1–C12, 1.674(3); O2–C15, 1.224(3); O1–C11–N1, 122.0(3); O1–C11–C10, 120.7(3); N1–C11–C10, 117.2(3); N2–C12–N1, 116.6(2); N2–C12–S1, 124.7(2); N1–C12–S1, 118.8(2).