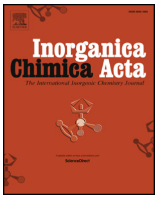
Inorganica Chimica Acta 483 (2018) 425–430

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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



Research paper

New ferrocene-pyrene dyads bearing amide/thiourea hybrid donors for anion recognition

Hongwei Huang[a,*], Zhaohui Xin[b], Lin Yuan[a], Bin-Yong Wang[c], Qian-Yong Cao[c,*]

[a] College of Chemistry and Bio-Engineering, Yichun University, Yichun 336000, PR China
[b] School of Foreign Language, Yichun University, Yichun 336000, PR China
[c] Department of Chemistry, Nanchang University, Nanchang 330031, PR China

ARTICLE INFO

Keywords:
Ferrocene
Pyrene
Anions
Fluorescent sensing
Electrochemical sensing

ABSTRACT

Two new ferrocene-pyrene dyads (**1** and **2**) bearing amide and thiourea donors were designed and prepared for anion recognition. The structure of **1** was also characterized by X-ray single crystal analysis. The anion recognition ability of **1** and **2** was fully investigated by elecotrochemical and fluorescent techniques. In CH_3CN solution, both **1** and **2** showed a good electrochemical sensing toward F^-, AcO^- and $H_2PO_4{}^-$, with the ferrocene-based redox potential showing a large negative shift. Interestingly, both **1** and **2** exhibited an exclusive fluorescence sensing of F^- over other anions, with the fluorescence of the receptors showing a turn-off response. Further, the binding mechanism between receptors and anions was confirmed by ^1H NMR titrations, which reveal that the two thiourea NH donors, cooperative with the amide donor, play a key role for binding the anions.

1. Introduction

Anions play an important role in the environment and biosystem. For example, fluoride shows beneficial effects on human physiology for the prevention of dental caries and osteoporosis [1–6], while the phosphate anion is known to be important in biology for signaling, energy transduction and information storage and expression [7–12]. Thus, many man-made anion receptors incorporating different signaling subunits (electrochemical active units or chromogenic units) and binding sites have been developed for sensitive and selective sensing and detection of anions [13–21].

In the field of electrochemical detection, ferrocene has a promising application for its stable one-electron ferrocene/ferrocenium redox potential [22]. Thus, a series of ferrocene-based receptors containing various anions binding sites, such as amide [23–25], urea [26–28], thiourea [29,30], triazole [31,32], triazolium [33,34] and imidazolium [35], have been reported. These receptors show a good electrochemical response toward anions, especially basic anions such as F^-, AcO^- and $H_2PO_4{}^-$, with a large cathodic potential shift upon binding with the target anion guest.

Regarding the simplicity and the high sensitivity of a fluorescence assay, researchers tentatively incorporated an organic fluorophore into the ferrocene-based receptors. These organic fluorophore appended ferrocene chemosensors may exhibit fluorescence and electrochemistry dual signaling response upon binding a target guest [36]. Some organic fluorophore (naphthalene, pyrene and anthracene) appended ferrocenes with different linker (urea, triazole/triazolium and imidazolium) for anion recognition have been reported by us and other groups [37–42], which allow anion detection via fluorescence and redox potential dual signal read-out. These multiple signaling systems, could lower the likelihood of false positives [43].

In this context, herein we describe two new pyrene-ferrocene dyads (**1** and **2**, Scheme 1) bearing amide and thiourea binding sites for anion recognition. The pyrene unit was chosen for its high quantum yield of the monomer and excimer emission in the ultraviolet and visible region, and was wildly used in fluorescence chemosensors [44–46]. The anion binding properties of **1** and **2** were detailedly investigated by electrochemical (cyclic voltammetry (CV) and differential pulse voltammetry (DPV)), fluorescent, and ^1H NMR titration techniques.

2. Experimental section

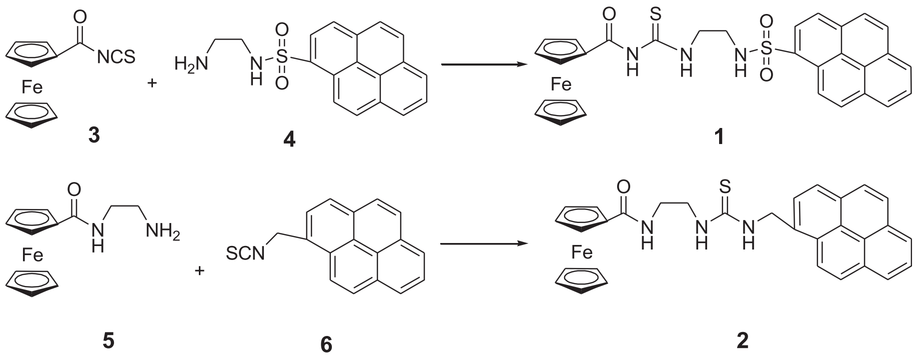
2.1. General instrumentations and reagents

Ferrocene, pyrene and the anions (F^-, Cl^-, Br^-, I^-, AcO^-, HSO4$^-$ and $H_2PO_4{}^-$) in their tetrabutylammonium salts were purchased form J &K Scientific Ltd. (Beijing, China). Other reagents were purchased from China National Pharmaceutical Group Corporation. These reagents

---

[*] Corresponding authors.
E-mail addresses: huanghongwei816@163.com (H. Huang), cqyong@ncu.edu.cn (Q.-Y. Cao).

https://doi.org/10.1016/j.ica.2018.08.055
Received 14 June 2018; Received in revised form 28 August 2018; Accepted 30 August 2018



Scheme 1. The synthesis route towards target compounds **1** and **2**.

were analytical pure and used without further purification. Acetonitrile for CVs, DPVs and emission titration measurements was dried with CaH_2 and distilled prior to use. The four important intermediates, ferrocenoyl isothiocyanate (**3**), *N*-(2-aminoethyl)-1-pyrenesulfonamide (**4**) [((2-aminoethyl)amino)carbonyl]-ferrocene (**5**) and 1-(isothiocyanatomethyl)-pyrene (**6**), were prepared by literature methods [29,47,48]. Emission spectra were recorded on a Hitachi F-4500 spectrophotometer. Electrochemical measurements were performed with a CHI 624C instruments. NMR spectra were recorded using Varian instruments (400 MHz). The anions were tetrabutylammonium (TBA) salts.

2.2. Preparation of emission and electrochemical titration solutions

Stock solutions of anions and receptors were first prepared in CH_3CN solution with the concentration of 0.01 M. The concentration of **1** and **2** for emission checking was 10 μM. During the emission titration, the high concentration anion solution was dropped into a solution of **1** or **2** (2 mL) with a micro injector, which makes the volume of the final system constant because the volume of the anion solution added is negligible compared to that of receptor.

The CV and DPV 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 supported electrolyte was a 0.10 M CH_3CN solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$). The concentrations of **1** and **2** for CV/DPV titrations were 0.3 mM. The potentials were recorded in CH_3CN and quoted relative to Ag/$AgNO_3$.

2.3. X-ray crystallographic analysis

Single crystals of **1** were obtained by slow diffusion of hexane into its CH_2Cl_2/MeOH (95:5, v/v) solution. The single crystal data were collected on 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 [49]. The refinement and all further calculations were carried out using SHELXL-97 [50]. The non-H atoms were refined anisotropically, using weighted full matrix least-squares on F^2.

2.4. Synthesis of 1

Under nitrogen, ferrocenoyl isothiocyanate **3** (0.271 g, 1 mmol), N-(2-aminoethyl)- 1-pyrenesulfonamide **4** (0.324 g, 1 mmol) and triethylamine (0.6 mL) 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 (9:1, v/v) as the eluent to yield **1** as an yellow solid (0.457 g, 77% yield). ^1H NMR ($CDCl_3$/DMSO-d_6, 8/2, v/v, 400 MHz): δ 10.52 (br, 1H), 8.78 (d, 1H, J = 9.2 Hz), 8.72 (br, 1H), 8.40 (d, 1H, J = 9.2 Hz), 7.78–8.05 (m, 7H), 7.59 (br, 1H), 4.45 (t, 2H, J = 2.0 Hz), 4.19 (t, 2H, J = 2.0 Hz), 3.92 (s, 5H); 3.48 (dd, 2H, J = 6.0), 2.98 (dd, 2H, J = 6.0). ^{13}C NMR ($CDCl_3$/DMSO-d_6, 8/2, v/v, 101 MHz): 180.5, 171.4, 134.5, 131.8, 130.8, 130.0, 129.7, 127.9, 127.1, 127.0, 126.8, 126.7, 72.3, 72.2, 70.1, 69.0, 44.6, 41.2 ppm.

2.5. Synthesis of 2

This compound was prepared by a similar procedure as that of **1** by condensation of **4** and **5**. Yield: 82%. ^1H NMR (DMSO-d_6, 400 MHz): δ 8.39 (br, 1H), 8.02–8.27 (m, 8H), 7.85 (s, 1H), 7.59 (br, 1H), 5.37 (s, 2H), 4.72 (s, 2H), 4.29 (s, 2H), 4.11 (s, 5H); 3.35 (s, 2H), 3.28 (s, 2H). ^{13}C NMR (DMSO-d_6, 101 MHz): 180.5, 171.4, 134.5, 131.8, 130.8, 130.0, 129.7, 127.9, 127.1, 127.0, 126.8, 126.7, 72.3, 72.2, 70.1, 69.0, 44.6, 41.2 ppm.

3. Results and discussion

The synthesis route of receptors **1** and **2** is shown in Scheme 1. With commercially available ferrocenecarboxylic acid and pyrene as the starting materials, the four precursors ferrocenoyl isothiocyanate (**3**), *N*-(2-aminoethyl)-1-pyrenesulfonamide (**4**) [((2-aminoethyl)amino) carbonyl]-ferrocene (**5**) and 1-(isothiocyanatomethyl)-pyrene (**6**) were prepared by literature methods . The target receptors **1** and **2** were then obtained by condensation of **3** and **4**, or **5** and **6**, with triethylamine as the catalyst in CH_2Cl_2 solution. The molecular structures of **1** and **2** were characterized by ^1H NMR and ^{13}C NMR spectra. In addition, the structure of **1** was further confirmed by single crystal X-ray analysis. In the ^1H NMR spectra of **1**, one of the NH proton is located at far downfield (10.87 ppm in DMSO-d_6 solution (Fig. 6), and at 10.52 ppm in $CDCl_3$/DMSO (8/2, V/V) solution (Fig. S7), which can be assigned to the acylthiourea NH proton involving in an intramolecular hydrogen bond [51].

The strong intramolecular hydrogen bond in **1** was also confirmed by the X-ray crystal analysis. The single crystals of **1** for X-ray analysis were obtained by slow diffusion of hexane to its CH_2Cl_2/MeOH (95:5, v/v) solution. The ORTEP diagram of **1** is shown in Fig. 1. The ferrocenyl substituent adopts a sandwiched conformation, with the iron atom lying in the center between the two cyclopentadienyl rings. The distances of the iron atoms to the two cyclopentadienyl rings are within the normal rang [52]. Intramolecular N−H⋯O hydrogen bonding exists between the carbonyl oxygen and the acylthiourea NH proton (N2−H⋯O1, 2.01 Å, 2.674(3) Å, 133°), which forms a stable six-membered ring (O1-C11-N1-C12-N2-H2a). This ring is approximately in the same plane as the attached cyclopentadienyl ring (the dihedral angle is 3.2°). This intramolecular hydrogen bonding mode is observed in related ferrocene-containing acyl-thiourea derivatives [29,52,53]. In addition, moderate intermolecular hydrogen bonding was also observed via N2−H2a⋯O3 (2.39 Å, 3.011(3) Å, 130°) and N3−H3b⋯O1 2.29 Å,