



# A new ferrocenophane with amide and triazole donors for recognition of dihydrogenphosphate anion

You-Hui Zhang<sup>a</sup>, Hongwei Huang<sup>b</sup>, Si-Si Yang<sup>a</sup>, Qian-Yong Cao<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Nanchang University, Nanchang, 330031, China

<sup>b</sup> College of Chemistry and Bio-engineering, Yichun University, Yichun, 336000, China

## ARTICLE INFO

### Article history:

Received 4 April 2018

Received in revised form

30 June 2018

Accepted 7 July 2018

Available online 9 July 2018

### Keywords:

Ferrocene

Macrocyclic receptor

Electrochemical sensing

Dihydrogenphosphate anion

## ABSTRACT

A new ferrocenophane **1** incorporation amide and triazole donors has been conveniently prepared via 'click' reactions in the cyclization step. The probe shows exclusive electrochemical sensing of  $\text{H}_2\text{PO}_4^-$  with a large potential shift. The  $^1\text{H}$  NMR titrations and DFT calculation results show that the amide NH, the triazole CH, the endocyclic benzene CH and the  $\alpha$ -position cyclopentadiene CH protons of **1** play a key role for binding with the guest  $\text{H}_2\text{PO}_4^-$  anion.

© 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

Anions play an important role in a wide range of chemical and biological processes. Thus, the development of anion selective receptors has been actively investigated [1–2]. Over the past decade, a number of anion receptors with different anion binding sites and signaling unit have been reported [3–7]. Among them, the macrocyclic receptors have attracted much attention for their high degree of preorganization and rigidity, providing their higher affinity and selectivity in anions complexation. Thus, various of macrocycles containing amide, ammonium, urea, thiourea, pyrrole, indole or imidazolium donors have been successfully developed for anions sensing [8–17]. However, compared to acyclic systems, examples on cyclic anion receptors are quite limited for their complicated synthetic pathways.

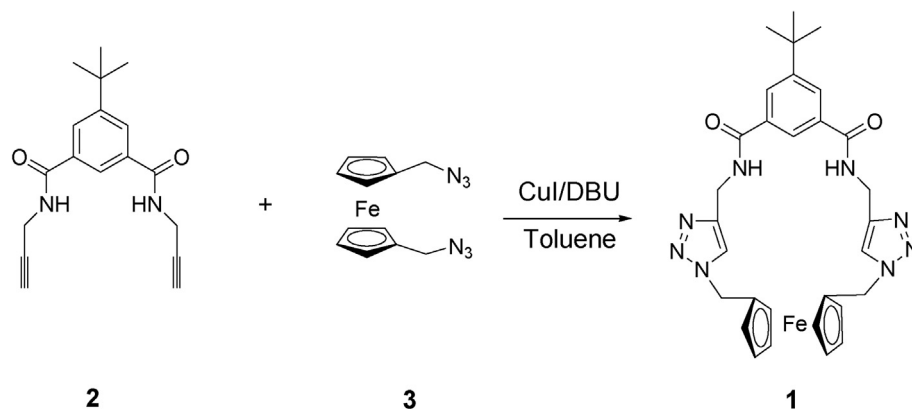
Recently, Cu(I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction has been widely applied for the efficient formation of rigid or shape-persistent, preorganized macrocyclic species, due to its high efficiency, mild reaction conditions and technical simplicity [18–20]. Some research results revealed that these 1,2,3-triazoles containing macrocycles are good candidates for recognition and sensing of anions, in which the acidic C5-H protons of the

heterocyclic ring act as efficient hydrogen-bonding donors in the complexation of anions [21–22]. In the pioneering work, Flood and coworkers have reported shape persistent [3<sub>4</sub>] triazolophanes, with an unexpectedly high affinity for chloride that rivaled many synthetic receptors with NH and OH hydrogen bond donors [23–24]. Sessler et al. have reported a pyrrolyl-based triazolophane, which exhibits a preference for pyrophosphate anions [25]. More recently, Kubik et al. have reported a cyclic pseudopeptide containing four amide NH and four triazole CH groups, which can bind with a dihydrogenphosphate tetramer and a dihydrogenpyrophosphate dimer in 2.5 vol% water/DMSO solution [26]. Despite their success, click macrocycles for anion binding with high selectivity are still rare. In addition, these click-derived macrocycles are absent easily detectable optical and/or electrochemical units, which can readily get discernible changes in these signals after binding with a given guest species, also limited them in practical applications.

Ferrocene-based receptors have enjoyed considerable popularity for electrochemical anion sensors due to the readily accessible ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox potential and easy functionalization [27]. Normally, a large cathodic potential shift of the  $\text{Fc}/\text{Fc}^+$  redox couple can be observed upon binding the anions guest [28]. We and other groups have reported acyclic and cyclic ferrocene-containing receptors for anions recognition [29–39]. Here in we design and synthesize a new ferrocenophane **1** (Scheme 1) containing two amide NH and two triazole CH donors. We found this preorganized and rigid cycle receptor shows high binding

\* Corresponding author.

E-mail address: [cqyong@ncu.edu.cn](mailto:cqyong@ncu.edu.cn) (Q.-Y. Cao).



Scheme 1. The syntheses route of probe 1.

affinity for dihydrogenphosphate anion with a large electrochemical potential shift. The binding mechanism between probe **1** and anions was detailedly investigated by  $^1\text{H}$  NMR titration and density functional theory (DFT) calculations.

## 2. Results and discussion

The synthetic route of **1** is shown in Scheme 1. Firstly, the two precursors biamide-containing alkyne **2** and 1,1'-bis(azidomethyl)ferrocene **3** were prepared by the literature methods [40–41]. Then by some previously reported conditions for CuAAC (Copper Catalyzed Azide-Alkyne Cycloaddition) macrocyclizations, with the dry toluene as solvent and under high dilution condition, coupling reaction of **2** and **3** with CuI/DBU (8-diaza [5.4.0] bicycloundec-7-ene) as catalysts gets ferrocenophane **1** in a good yield (40%). The chemical structure of **1** was confirmed by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, HR-TOF-MS and elemental analysis.

The recognition ability of **1** towards some selected monovalence anions with different geometries (sphere:  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ; trigonal planar  $\text{AcO}^-$  and  $\text{NO}_3^-$ , liner:  $\text{N}_3^-$ , tetrahedron:  $\text{H}_2\text{PO}_4^-$  and  $\text{HSO}_4^-$ ) in the form of their corresponding tetrabutylammonium (TBA) salts was investigated by absorption and electrochemical measurements. The free probe shows a typical weak ferrocenyl-based metal-to-ligand charge transition (MLCT) band absorption at 400–500 nm, and strong absorption at  $\lambda < 330$  nm which can be assigned to the  $\pi$ - $\pi^*$  transition of benzene and/or cyclopentadiene rings. Upon addition of various anions, probe **1** shows barely absorption changes (Fig. S1). In contrast, probe **1** exhibits a good

electrochemical response toward anions.

The electrochemical sensing ability of **1** toward anions was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in  $\text{CH}_3\text{CN}$  solution with  $\text{TBAPF}_6$  (0.1 M) as a supporting electrolyte. Probe **1** shows a reversible one-electron redox couple with the half wave potential at 0.387 V (vs.  $\text{Ag}/\text{AgNO}_3$ ). Upon addition equal amount of various anions (3 equivalents), probe **1** shows exclusive sensing of  $\text{H}_2\text{PO}_4^-$  over anions. As shown in Fig. 1, the DPV potential of free probe **1** shift from 360 mV to 200 mV ( $\Delta E_p = -160$  mV) upon binding with  $\text{H}_2\text{PO}_4^-$ . In addition, the addition of  $\text{AcO}^-$  gives a 40 mV cathodic potential shift, while the addition of other anions shows little electrochemical response.

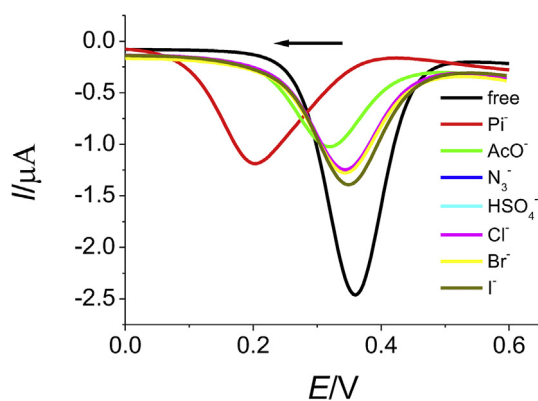


Fig. 1. DPVs profile of **1** (0.2 mM) before and after adding 3 equivalents anions in  $\text{CH}_3\text{CN}$  solution. Reference electrode  $\text{Ag}/\text{AgNO}_3$ ; supporting electrolyte  $[\text{n-Bu}_4\text{N}]\text{PF}_6$  (0.1 M); scan rate =  $100 \text{ mV s}^{-1}$ .

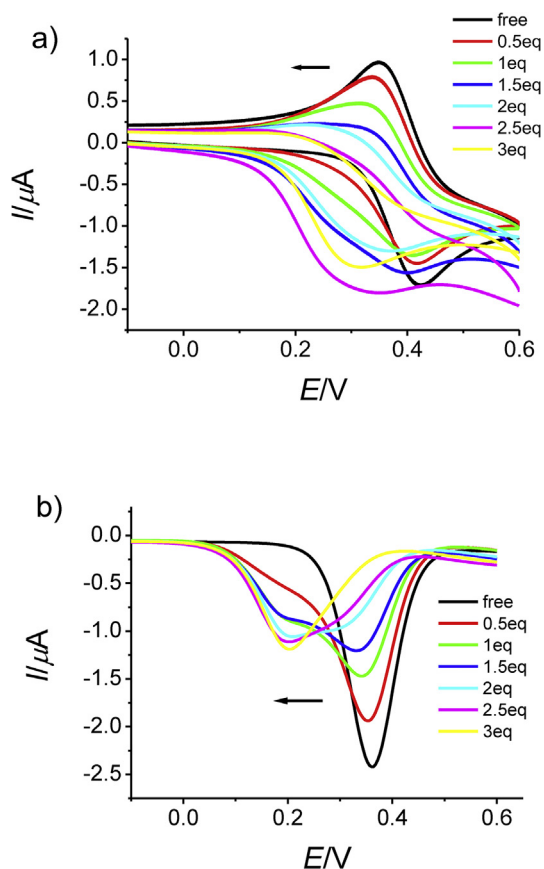


Fig. 2. The CVs (a) and DPVs (b) profile of **1** (0.2 mM) with increasing the concentration of  $\text{H}_2\text{PO}_4^-$  in  $\text{CH}_3\text{CN}$  solution.

Download English Version:

<https://daneshyari.com/en/article/7755702>

Download Persian Version:

<https://daneshyari.com/article/7755702>

[Daneshyari.com](https://daneshyari.com)