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Anion receptors of *N*-ferrocenylmethylene-substituted bis-imidazolium salts linked by xylene spacers

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ABSTRACT

A series of xylyl (*ortho*, *meta*, and *para*) linked *N*-ferrocenylmethylene-substituted bis-imidazolium salts (**3a**–**3c**) and bis-benzimidazolium salts (**4a**–**4c**) were synthesized and structurally characterized. Their binding properties for anions were investigated by electrochemistry and ^{1}H NMR spectroscopy. The structure of **3b**, **3c**, **4a** and **4b** were confirmed by X-ray crystallography. As expected, all salts were good electrochemistry-signaling receptors for several anions (F^-, AcO^-, HSO_4^-, Cl^-, Br^- and I^-), that in one receptor the imidazolium/benzimidazolium units offer binding sites for anion and the ferrocenyl units offer electrochemistry response sites. Furthermore, the results showed that they were highly selective and sensitive to F^- and receptors **3b** and **4b** featuring a *meta*-xylene spacer were more effective receptors for F^- compared to receptors linked by an *orth* or a *para*-xylene spacer. ^{1}H NMR titrations demonstrated that fluoride ion was recognized by receptors through $(C{-}H)^+\cdots X^-$ hydrogen bonds.

1. Introduction

Anions play a fundamental role in a wide range in medicine, biology, catalysis and environment [1–3]. The synthesis of artificial receptors designed to coordinate anions is an area of intense current research activity [4–8]. Fluoride is widespread in daily life as additive in drinking water that it displays special physical and chemical properties among the inorganic anions [9,10]. Due to its possible toxicity, the development of synthetic sensors for its detection has been an area of immense research interest to the scientific community [11–15]. Fluoride is also the smallest anion with a high charge density and a hard Lewis basic nature, which can take place strong interactions with electron-deficient Lewis acid coordination via orbital overlap [16,17]. In a number of cases, the receptors containing boron [16–25] and silicon [26–28] utilize the characteristics as binding mechanism to realize the purpose of recognize fluoride. Hydrogen bonding between receptor and fluoride is the uppermost mechanism of fluoride recognition [29,30], typically the binding sites of the receptors containing amide, urea, thiourea, guanidinium, or pyrole functionalities are capable of hydrogen bonding with the fluoride [31–34]. The imidazolium/benzimidazolium group is an attractive building block for fluoride receptors because strong attractive electrostatic forces in positively charged hosts are also of significant importance to the fluoride recognition process [35]. Various signaling groups, such as optical, fluorescent, or electrochemical sensing units have been installed on imidazolium/benzimidazolium receptors to realize the convenient detection of fluoride [34–36]. The recognition of the host is introduced by the presence of directional hydrogen-bonding $(C{-}H)^+\cdots F^-$ functionality as well as the electrostatic force between the imidazolium/benzimidazolium moieties and fluoride [37,38].

Ferrocene and their derivatives are found to be very convenient building blocks for redox-active ligands [39–42]. Suitable signaling chemical receptors can be built by combining ferrocene with imidazolium/benzimidazolium moieties utilizing both redox-active and hydrogen bond interactions to recognize anion [43,44]. In such ferrocene-based receptors, the binding sites are interacting with anions based on several types of interaction such as electrostatic interactions and hydrogen bonding interactions, which induces a negative shift in the redox potential of the ferrocene/ferrocenium couple and the magnitude of the electrochemical shift

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upon complexation represents a quantitative measurement of the perturbation of the redox center [32,45–47]. In our previous work, we have reported a series of receptors of ferrocene-based imidazolium/benzimidazolium salts showing marked electrochemical sensing to fluoride ion [48–50]. As an extension of our work, it is necessary to understand the unique host–guest interaction of the sensor with fluoride ion from other anions. Herein, we designed and synthesized a serious of ferrocene-based imidazolium salts **3a**–**3c** and ferrocene-based benzimidazolium salts **4a**–**4c** (Scheme 1), in which imidazolium/benzimidazolium moieties behaved as the anion binding sites and ferrocene groups behaved as the signaling units. Its anion binding ability was investigated by monitoring the substrate-induced changes in its electrochemical signaling (cyclic voltammetry (CV), differential pulse voltammetry (DPV)) and ^{1}H NMR spectroscopy.

2. Result and discussion

2.1. Synthesis

As shown in Scheme 1, key precursor 1-(ferrocenylmethylene) imidazole **1** and 1-(ferrocenylmethylene)benzimidazole **2** were synthesized according to the literature [51,52]. Receptors **3a**–**3c** were prepared in medium yield by reacting **1** with 0.5 mol equivalent corresponding bromides followed an anion exchange with NH_4PF_6 in CH_3OH. Receptors **4a**–**4c** were obtained in the manner analogous to **3a**–**3c**. NMR spectra of all receptors were obtained in DMSO-d_6 at room temperature (Figs. S1–S12). The characteristic resonances for acidic protons in ^{1}H NMR appeared at 9.12–9.25 ppm for imidazolium receptors **3a**–**3c** and 9.66–9.84 ppm for benzimidazolium receptors **4a**–**4c,** which were consistent with those of reported corresponding salts [35–38].

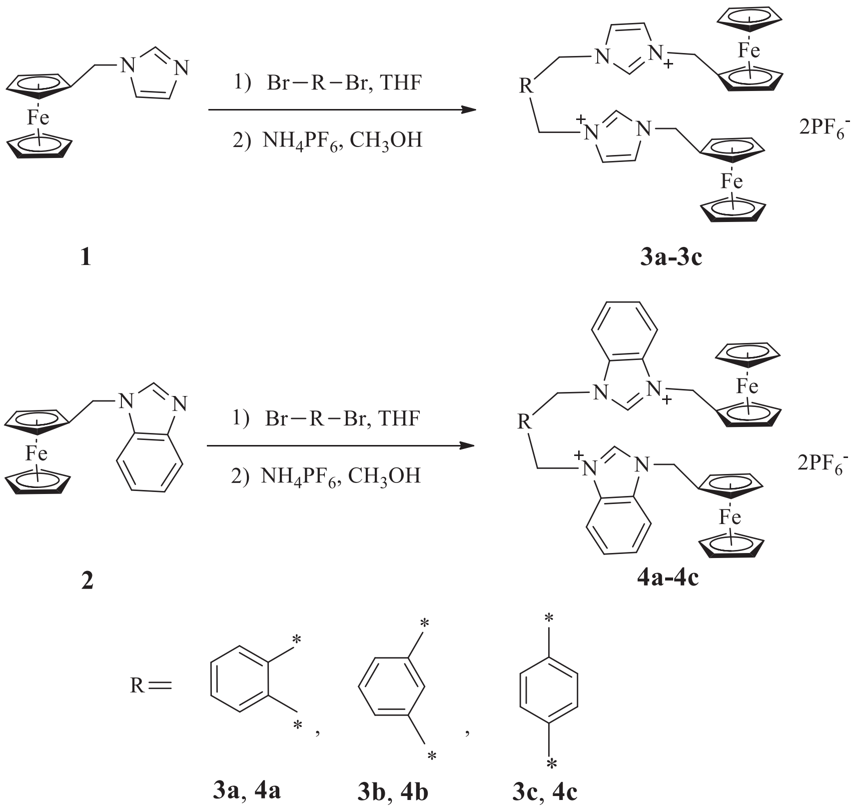
2.2. Crystal structures

These receptors are stable in their solid form and in solution. Orange crystals of **3b**, **3c**, **4a** and **4b** were obtained by diffusion of diethyl ether into solutions of the compounds in acetonitrile, and the spatial structures of them were confirmed by X-ray crystallography. The crystallographic data and collection parameters were summarized in Table 1. Selected bond lengths and angles were given in Tables S1–S4.

The structural descriptions of **3b**, **3c**, **4a** and **4b** were summarized in Fig. 1. In the structure of **3b** and **3c**, the cation of the molecule is centrosymmetric configuration. Two 1-(ferrocenylmethylene)imidazolium moieties adopt a ‘trans’ conformation with respect to the benzene ring. The cyclopentadiene (Cp) rings of the ferrocenyl moieties slightly tilt toward each other and exhibit an eclipsed conformation (pseudo-torsion angles of Fc is 5.88° for **3b** and 4.84° for **3c**, respectively) [53]. However, two ferrocenyl moieties in **4a** and **4b** are not crystallographically identical and the pseudo-torsion angles of each ferrocenyl moieties are listed in Table 2. The spatial structures of crystals **3b**, **3c**, **4a** and **4b** are stacked through C–H···F hydrogen bonds in the solid state, the data of hydrogen bonds are given in Table S5. Interactions of molecules lead to a stable spatial structure (Fig. 2, Figs S13–S15).

2.3. Electrochemical studies of receptors

The CV of receptors **3a**–**3c** and **4a**–**4c** ($c = 10^{-3}$ M) were studied in their CH_3CN solution using $TBAPF_6$ ($c = 10^{-1}$ M) as supporting electrolyte, respectively. The results exhibited that there was a reversible one-electron redox wave with a half wave potential ($E_{1/2}$) value of 628–642 mV in each CV (Fig. 3), indicating the two ferrocenyl units in each receptor were electrochemical equivalent



Scheme 1. The synthesis of receptors **3a**–**3c** and **4a**–**4c**.