

# A Bisferrocene-Benzobisimidazole Triad as a Multichannel Ditopic Receptor for Selective Sensing of Hydrogen Sulfate and Mercury Ions

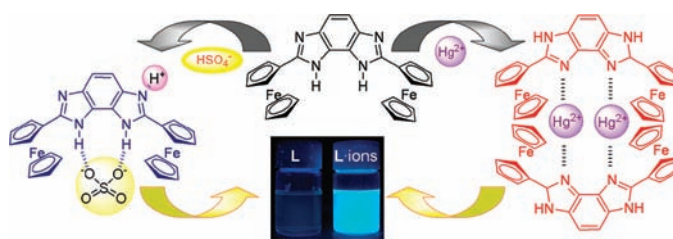
María Alfonso, Alberto Tárraga,\* and Pedro Molina\*

Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, E-30100, Murcia, Spain

pmolina@um.es; atarraga@um.es

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## ABSTRACT



The bisferrocene-benzobisimidazole triad behaves as a selective redox and fluorescent chemosensor for  $\text{HSO}_4^-$  and  $\text{Hg}^{2+}$  ions, exhibiting an easily detectable signal change in both the redox potential of the ferrocene/ferrocinium redox couple and in the emission band which is red-shifted ( $\Delta\lambda = 10\text{--}13\text{ nm}$ ) and enhanced in intensity (Chelation Enhanced Fluorescence, CHEF =  $486\text{--}225$ ) upon complexation with these ions, in EtOH solutions.

The design of receptors that contain two quite different binding sites for the complexation of cationic and anionic guest species is a new emerging and topical field of supramolecular chemistry.<sup>1</sup>

On the other hand, the development of sulfate selective anion receptors is currently an area of intense interest due to the important roles this anion plays in biological systems and disease<sup>2</sup> and the appreciation of the role they could play in radioactive waste remediation.<sup>3</sup> Considerable effort has been devoted of late to the synthesis of receptors that

might allow the removal of sulfate from the highly basic nitrate-rich mixtures produced by pretreatment of the original radioactive waste with NaOH.<sup>4</sup> Consequently, one of the current challenges in anion recognition chemistry involves the preparation of receptors that show high sulfate/nitrate selectivity.<sup>5</sup> Tripodal tris-urea based systems have been developed as selective receptors for the sulfate anion.<sup>6</sup> Macrocyclic sulfate receptors include cyclo-[8]pyrrole,<sup>7</sup> a cyclic tetraamide/amine based receptor,<sup>8</sup> and cyclic peptide based molecular oysters,<sup>9</sup> whereas acyclic

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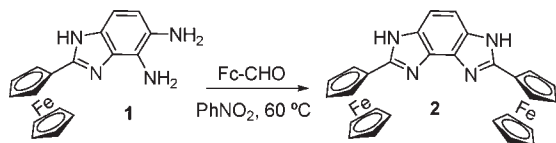
receptors consist of diindolylurea groups appended with amido functionalities.<sup>10</sup>

Additionally, the design and synthesis of artificial receptors for sensing and recognition of heavy and transition-metal ions have also received considerable attention.<sup>11</sup> Mercury ions are especially toxic: they contaminate the environment and cause serious problems for human health and ecology.<sup>12</sup> Fluorescent chemical sensors have consequently been developed as a means of detecting Hg(II) ions in environmental and biological samples.<sup>13–17</sup>

Here we present the synthesis of the nonreadily available  $\pi$ -extended 2,7-biferrocenyl-1,6-dihydrobenzobisimidazole,<sup>18</sup> as a binding site<sup>19</sup> which features two angular opposed imidazole ring systems annulated to a common arene backbone. This new receptor binds, in an ethanolic solution, a hydrogen sulfate anion with high selectivity relative to a nitrate anion, as well as mercury cations.

Scheme 1 illustrates the synthesis of receptor **2**. The required diamine **1** was initially formed through the thiadiazole ring opening of the 7-ferrocenyl-imidazo[4,5-*e*]-2,1,3-benzothiadiazole<sup>20</sup> by treatment with NaBH<sub>4</sub> in the presence of CoCl<sub>2</sub>.<sup>21</sup> Subsequent reaction of **1** with ferrocenecarboxaldehyde (Fc-CHO) provided the bisferrocene-benzobisimidazole **2** in 43% yield.

**Scheme 1.** Preparation of Compound **2**



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The chemosensor behavior of **2** toward a variety of cations (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, and Pb<sup>2+</sup>) and anions (F<sup>−</sup>, Cl<sup>−</sup>, Br<sup>−</sup>, AcO<sup>−</sup>, NO<sub>3</sub><sup>−</sup>, HSO<sub>4</sub><sup>−</sup>, H<sub>2</sub>PO<sub>4</sub><sup>−</sup>, and HP<sub>2</sub>O<sub>7</sub><sup>3−</sup>) was investigated by cyclic (CV) and Osteryoung square-wave (OSW) voltammeteries as well as through spectrophotometric and <sup>1</sup>H NMR techniques. The titration experiments were further analyzed using the computer program Specfit.<sup>22</sup> The CV of receptor **2** shows a reversible two-electron oxidation wave at  $E_{1/2} = 623$  mV, calculated versus the decamethylferrocene (DMFc) redox couple, indicating that the two metal centers are electronically decoupled.

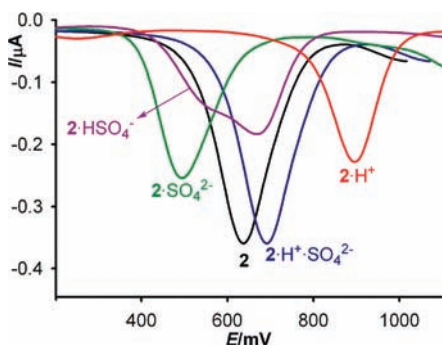
Titration studies with addition of those anions to an electrochemical solution of receptor **2** in CH<sub>3</sub>CN demonstrate that while addition of AcO<sup>−</sup>, HSO<sub>4</sub><sup>−</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>−</sup> anions promotes remarkable responses, addition of Cl<sup>−</sup>, Br<sup>−</sup>, and NO<sub>3</sub><sup>−</sup> anionic species had no effect on the CV or OSW of this receptor even when present in a large excess. Yet, F<sup>−</sup> and HP<sub>2</sub>O<sub>7</sub><sup>3−</sup> induced deprotonation (Supporting Information, SI). Nevertheless, the results obtained on the stepwise addition of AcO<sup>−</sup>, HSO<sub>4</sub><sup>−</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>−</sup> revealed three different electrochemical behaviors. For AcO<sup>−</sup> a typical “two-wave behavior” was observed, with the appearance of a second peak at a more negative potential ( $\Delta E_{1/2} = -136$  mV) together with the corresponding free receptor. In the case of H<sub>2</sub>PO<sub>4</sub><sup>−</sup> a “shifting behavior” was observed, appearing as a second redox peak, negatively shifted ( $\Delta E_{1/2} = -193$  mV), compared to the free receptor. Remarkably, for HSO<sub>4</sub><sup>−</sup> a new oxidation peak emerged at a more positive potential ( $\Delta E_{1/2} = 44$  mV). The electrochemical behavior observed for HSO<sub>4</sub><sup>−</sup> is consistent with a guest-to-host proton transfer reaction by the moderately strong acidic HSO<sub>4</sub><sup>−</sup>, accompanied by H-bonding and electrostatic interaction with the guest anion: proton transfer is followed by H-bond formation and subsequent anion coordination.<sup>23</sup> This assumption is supported by the following results: (a) upon protonation of receptor **2** with HCl the redox peak was shifted anodically to  $E_{1/2} = 893$  mV ( $\Delta E_{1/2} = 270$  mV); (b) when SO<sub>4</sub><sup>2−</sup> was added, the redox peak was shifted cathodically to  $E_{1/2} = 495$  mV ( $\Delta E_{1/2} = -128$  mV); and (c) upon addition of SO<sub>4</sub><sup>2−</sup> to the electrochemical solution of the protonated receptor [**2**·H<sup>+</sup>] a cathodically shifted oxidation peak appears at  $E_{1/2} = 677$  mV, virtually the same potential as that observed for the [**2**·HSO<sub>4</sub><sup>−</sup>] complex:  $E_{1/2} = 667$  mV (Figure 1).

Yet, the results obtained on the stepwise addition of substoichiometric amounts of the above-mentioned metal ions show that only the addition of Hg<sup>2+</sup> and Zn<sup>2+</sup> induced the appearance, in the OSW, of a new oxidation peak at a remarkably more positive potential  $E_{1/2} = 870$  mV

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**Figure 1.** Evolution of the OSWV of **2** ( $c = 1 \times 10^{-4}$  M) in  $\text{CH}_3\text{CN}/n\text{-Bu}_4\text{NPF}_6$  scanned at  $0.1 \text{ V s}^{-1}$  in the presence of  $\text{HSO}_4^-$  (purple),  $\text{HCl}$  (red), and  $\text{SO}_4^{2-}$  (green); initial addition of  $\text{HCl}$  followed by addition of  $\text{SO}_4^{2-}$  (blue).

( $\Delta E_{1/2} = +247 \text{ mV}$ ) for  $\text{Hg}^{2+}$  and at a more slightly shifted potential  $E_{1/2} = 690 \text{ mV}$  ( $\Delta E_{1/2} = +67 \text{ mV}$ ) for  $\text{Zn}^{2+}$  (SI).

Ion recognition properties of the receptor **2** toward metal cations and anions have also been studied by using absorption and emission techniques. The UV-vis spectrum of **2** in  $\text{CH}_3\text{CN}$  ( $c = 5 \times 10^{-5} \text{ M}$ ) and  $\text{EtOH}$  at the same concentration exhibits two bands at  $\lambda = 304 \text{ nm}$  ( $\epsilon = 1721 \text{ M}^{-1} \text{ cm}^{-1}$ ) and  $445 \text{ nm}$  ( $\epsilon = 68 \text{ M}^{-1} \text{ cm}^{-1}$ ). The addition of  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Pb}^{2+}$  elicited the same optical response: the progressive appearance of a new LE band red-shifted by  $\Delta\lambda = 12 \text{ nm}$ . However, in an  $\text{EtOH}$  solution only the addition of  $\text{Hg}^{2+}$  induced the red shift of the LE band by  $\Delta\lambda = 10 \text{ nm}$ . Three well-defined isosbestic points at  $\lambda = 250, 319, \text{ and } 337 \text{ nm}$ , indicative of the presence of only two absorbing species in the solution, were found. Binding assays using the method of continuous variations (Job's plot) suggest a 1:1 binding model with an association constant  $K_a$  of  $9.46 \times 10^4 \text{ M}^{-1}$ . Titration studies of **2** toward the set of anions under study revealed that only  $\text{F}^-$ ,  $\text{AcO}^-$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{HP}_2\text{O}_7^{3-}$  decrease in the intensity of the HE absorption band (SI).

Assessments of the ion affinities also came from observing the extent to which the fluorescence intensity of receptor **2** was affected in the presence of cations and anions (SI). As expected, **2** showed a weak fluorescence in  $\text{EtOH}$  ( $c = 10^{-5} \text{ M}$ ), revealing that the excitation spectrum at  $\lambda = 330 \text{ nm}$  is an ideal excitation wavelength. The emission spectrum displays a structureless band centered at  $\lambda = 405 \text{ nm}$ , with a rather low quantum yield ( $\Phi = 10^{-3}$ ). Receptor **2** in  $\text{EtOH}$  did not undergo any considerable change in its emission spectra upon addition of  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  cations. However, it showed a large CHEF (Chelation-Enhanced Fluorescence Effect)<sup>24</sup> when  $\text{Hg}^{2+}$  was added. Thus addition of 1 equiv of  $\text{Hg}^{2+}$  induced a red shift of the emission band from 405 to 415 nm ( $\Delta\lambda = 10 \text{ nm}$ )

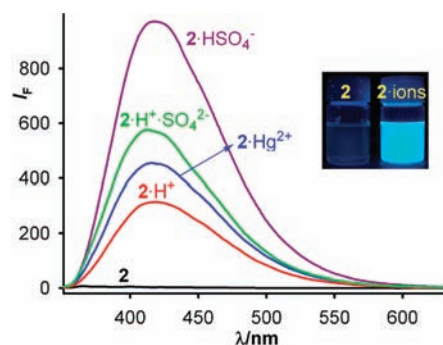
(24) CHEF is defined as  $I_{\text{max}}/I_0$ , where  $I_{\text{max}}$  corresponds to the maximum emission intensity of the receptor-metal complex, while  $I_0$  is the maximum emission intensity of the free receptor.

which is also accompanied by a remarkable increase in the intensity of the emission band (CHEF = 225) and by a 60-fold increase in the quantum yield ( $\Phi = 6 \times 10^{-2}$ ) (Figure 2). From the fluorescence titration data, a 1:1 binding mode is deduced and the association constant was calculated to be  $3.95 \times 10^5 \text{ M}^{-1}$ . The detection limit was found to be  $6.58 \times 10^{-6} \text{ M}$ .

After addition of 1 equiv of  $\text{HSO}_4^-$  to a solution of receptor **2** in  $\text{EtOH}$ , the emission band was red-shifted from 405 to 418 nm ( $\Delta\lambda = 13 \text{ nm}$ ), with a concomitant increase in the intensity of the emission band (CHEF = 486) and in the fluorescence quantum yield which increased by a factor of 100 ( $\Phi = 10^{-1}$ ) (SI). The stoichiometry of the complex was also determined by the changes in the fluorogenic response of **2** and  $\text{HSO}_4^-$ , the results indicating the formation of a 1:1 complex with association constant  $K_a = 4.19 \times 10^4 \text{ M}^{-1}$  and a detection limit of  $1.57 \times 10^{-6} \text{ M}$ . No changes in the emission spectrum of receptor **2** were observed in the presence of the remaining tested anions.

Interestingly, the protonated species [**2**· $\text{H}^+$ ], formed by addition of 1 equiv of  $\text{HBF}_4$  to the free ligand, showed the same emission spectrum as those obtained by addition of both  $\text{Hg}^{2+}$  and  $\text{HSO}_4^-$ , although with a CHEF = 156. Moreover, the emission band of [**2**· $\text{H}^+$ ] undergoes a gradual increase in intensity only upon addition of  $\text{SO}_4^{2-}$ , reaching a maximum when 1 equiv of this anion was added (CHEF = 1.83). This result clearly indicates that the protonated species [**2**· $\text{H}^+$ ] could be used for the selective detection of  $\text{SO}_4^{2-}$  ions, taking into account that the addition of only this anion to the free ligand does not promote any change in its emission spectrum (Figure 2).

The stoichiometries proposed from absorption and fluorescent data were further confirmed by mass spectrometry. The ESI-MS spectrum of receptor **2** in the presence of  $\text{HSO}_4^-$  shows a peak at  $m/z$  623.5 corresponding to the 1:1 complex, whereas the ESI-MS and ESI-TOF in the presence of  $\text{Hg}^{2+}$  show a peak at  $m/z$  1451 corresponding to the complex [**2**· $\text{Hg}^{2+}$ ]<sub>2</sub>. The relative abundance of the isotopic clusters was in good agreement with the simulated spectra of the complexes (SI).

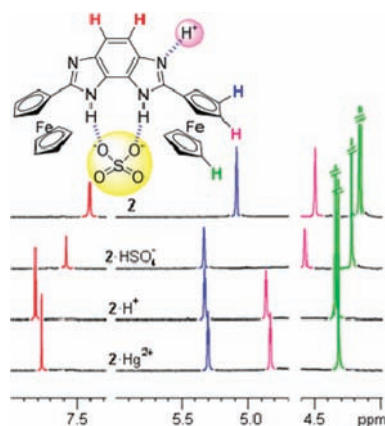


**Figure 2.** Evolution of the emission spectrum of **2** (black), upon addition of  $\text{HSO}_4^-$  (purple) and  $\text{HBF}_4$  (red); initial addition of  $\text{HBF}_4$  followed by addition of  $\text{SO}_4^{2-}$  (green); and addition of  $\text{Hg}^{2+}$  (blue).

To gain some insight about the plausible binding modes operating in these recognition processes, a  $^1\text{H}$  NMR titration study of **2** upon addition of  $\text{Hg}^{2+}$  and  $\text{HSO}_4^-$  ions was also carried out. However, such studies were developed in  $\text{CH}_3\text{OD}$  solutions because solubility problems at NMR concentration were encountered when  $\text{CD}_3\text{CN}$  solutions were used (Figure 3). The results obtained in this study demonstrated a similar trend upon addition of both  $\text{Hg}^{2+}$  and  $\text{HSO}_4^-$  ions to the free ligand. Thus, the progressive addition of  $\text{Hg}^{2+}$  to the solution of **2** in  $\text{CH}_3\text{OD}$  causes the simultaneous downfield shift of the following signals: (i) those corresponding to the protons present within the unsubstituted cyclopentadienyl (Cp) unit of the ferrocene moiety; (ii) signals attributed to the  $\text{H}_\alpha$  and  $\text{H}_\beta$  protons of the unsubstituted Cp unit of the metallocene; and (iii) those associated to the protons of the fused phenyl ring. The maximum downfield shifts were observed when addition of 1 equiv of  $\text{Hg}^{2+}$  was reached:  $\Delta\delta\text{H}_{\text{Cp}} = 0.19$  ppm,  $\Delta\delta\text{H}_\alpha = 0.21$  ppm,  $\Delta\delta\text{H}_\beta = 0.36$  ppm, and  $\Delta\delta\text{H}_{\text{Ph}} = 0.36$  ppm. More importantly, similar changes in the chemical shifts of these protons were also observed when  $\text{HSO}_4^-$  was added, which indicate that this anion interacts with the free ligand promoting a protonation process on the imidazole nitrogen atoms. Similar behavior was also observed when electrochemical techniques were applied, as it was already described above. Moreover, the  $^1\text{H}$  NMR spectra of **2** upon addition of increasing amounts of  $\text{HBF}_4$  also displayed the same set of signals than those observed for the species formed upon addition of both  $\text{Hg}^{2+}$  and  $\text{HSO}_4^-$  ions. Interestingly, the only significant differences between the chemical shift data of the species formed upon addition of  $\text{Hg}^{2+}$  or  $\text{HSO}_4^-$  ions is the magnitude of the downfield shift observed for these signals in each case (SI).

It is worth noting that all attempts carried out to achieve the simultaneous recognition of the  $\text{Hg}^{2+}/\text{HSO}_4^-$  ion pair failed.

In conclusion, the bisferrocene-benzobisimidazole triad acts as a dual selective redox and fluorescent molecular sensor for  $\text{HSO}_4^-$  anions and  $\text{Hg}^{2+}$  cations. The recognition



**Figure 3.** Evolution of the  $^1\text{H}$  NMR spectrum of **2** upon addition 1 equiv of  $\text{HSO}_4^-$ ,  $\text{HBF}_4$ , and  $\text{Hg}(\text{OTf})_2$ . Inset: proposed binding mode with the  $\text{HSO}_4^-$  anion.

event of the  $\text{HSO}_4^-$  anion, which probably involves proton transfer followed by hydrogen bond formation and subsequent anion coordination, has been studied by electrochemical and optical techniques and  $^1\text{H}$  NMR spectroscopy.

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**Supporting Information Available.** General experimental comments.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **2**. Electrochemical, UV-vis, fluorescence, and  $^1\text{H}$  NMR titration data. This material is available free of charge via the Internet at <http://pubs.acs.org>.