

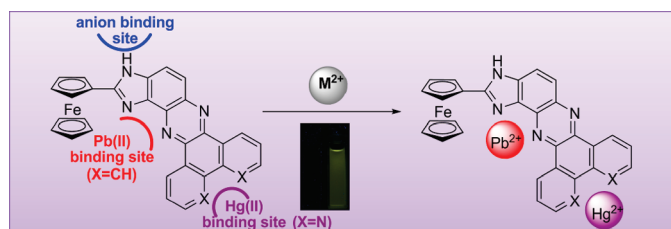
## Ferrocene-Based Heteroditopic Receptors Displaying High Selectivity toward Lead and Mercury Metal Cations through Different Channels

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The synthesis and electrochemical, optical, and ion-sensing properties of ferrocene–imidazophenazine dyads are presented. Dyad **4** behaves as a highly selective chemosensor molecule for  $\text{Pb}^{2+}$  cations in  $\text{CH}_3\text{-CN}/\text{H}_2\text{O}$  (9:1). The emission spectrum ( $\lambda_{\text{exc}} = 317$  nm) undergoes an important chelation-enhanced fluorescence effect (CHEF = 47) in the presence of  $\text{Pb}^{2+}$  cations, a new low-energy band appeared at 502 nm, in its UV/vis spectrum, and the oxidation redox peak is anodically shifted ( $\Delta E_{1/2} = 230$  mV). The presence of  $\text{Hg}^{2+}$  cations also induced a perturbation of the redox potential although in less extension than those found with  $\text{Pb}^{2+}$  cations. Dyad **7**, bearing two fused pyridine rings, has shown its ability for sensing  $\text{Hg}^{2+}$  cations selectively through three channels: electrochemical, optical, and fluorescent; the oxidation redox peak is anodically shifted ( $\Delta E_{1/2} = 200$  mV), a new low-energy band of the absorption spectrum appeared at 485 nm, and the emission spectrum ( $\lambda_{\text{exc}} = 340$  nm) is red-shifted by 32 nm accompanied by a remarkable chelation-enhanced fluorescent effect (CHEF = 165). Linear sweep voltammetry revealed that  $\text{Cu}^{2+}$  cations induced oxidation of the ferrocene unit in both dyads.  $^1\text{H}$  NMR studies have been carried out to obtain information about the molecular sites which are involved in the binding process.

### Introduction

Mercury is a notoriously toxic element that exists at 0.08 ppm in the Earth's crust. Every year, 2700–6000 tons of elemental mercury is released to the atmosphere through volcanic activity and 2000–3000 tons through coal combustion, gold production, and industrial waste.<sup>1</sup> Once released, it can be converted to organic mercury by the bacteria in lakes and oceans and inorganic mercury in the liver. Three forms of mercury exist in the environment: elemental, inorganic, and organic, all of which are highly toxic. Mercury damages DNA, impairs mitosis, and disrupts the central nervous and endocrine systems.<sup>2</sup> Mercury is one of the most frequently found and second most common toxic heavy

metals on the planet, after only plutonium.<sup>3</sup> It can accumulate in vital organs and tissues, such as liver and heart muscle, and has lethal effects on living systems.<sup>4</sup> Contamination of the environment with mercury is an important concern throughout the world.<sup>5</sup> Driven by the need to detect trace amounts of mercury in environmental samples, many laboratories have focused on “colorimetric”,<sup>6</sup> redox active,<sup>7</sup> and/or fluorescent<sup>8</sup> highly selective mercury responsive small-molecule chemosensor, conjugated polymers,<sup>9</sup> microcantilevers,<sup>10</sup> oligonucleotides,<sup>11</sup> semiconductor quantum dots,<sup>12</sup> DNAszymes,<sup>13</sup> proteins,<sup>14</sup> metal nanoparticles,<sup>15</sup> and carbon nanotubes.<sup>16</sup> Most of these systems,

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however, have limitations with respect to either sensitivity, selectivity, or simplicity.<sup>17</sup>

Among heavy metals, lead is the most abundant and ranks third in the list of toxic substances and is often encountered due to its wide distribution in the environment as well as its current and previous use in batteries, gasoline, and pigments. Lead pollution is an ongoing danger to human health, particularly in children (memory loss, irritability, anemia, muscle paralysis, and mental retardation),<sup>18</sup> and the environment, as most of the 300 million tons of this heavy metal

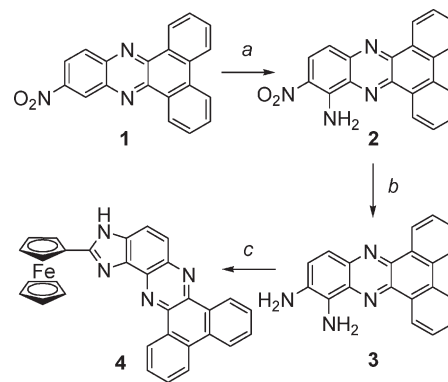
mined to date are still circulating in soil and groundwater.<sup>19</sup> Despite effort to reduce global emissions, lead poisoning remains the world's most common environmentally caused disease.<sup>20</sup> Thus, the level of this detrimental ion, which is present in tap water as a result of dissolution from household plumbing systems, is the object of several official norms. The World Health Organization established in 1996 guidelines for drinking-water quality,<sup>21</sup> which included a lead maximal value of  $10 \mu\text{g L}^{-1}$ . The US Center for Disease Control (CDC) set standards stating that a  $10\text{--}19 \mu\text{g dL}^{-1}$  level of lead in blood poses a potential threat and that diagnostic testing is recommended.<sup>22</sup> Thus, keeping in view the role of  $\text{Pb}^{2+}$ , the detection and monitoring of this metal cation by methods which allow the development of selective and sensitive assays becomes very important. As many of the heavy metals are known as fluorescence quenchers via enhanced spin-orbital coupling,<sup>23</sup> energy or electron transfer,<sup>24</sup> development of fluorescent sensors for  $\text{Pb}^{2+}$  presents a challenge. In this context, considerable efforts have been undertaken to develop fluorescent chemosensors for  $\text{Pb}^{2+}$  ions based on peptide,<sup>25</sup> protein,<sup>26</sup> DNAzyme,<sup>27</sup> polymer,<sup>28</sup> and small-molecule<sup>29</sup> scaffolds. There is, however, a paucity of use of multichannel receptors as potential guest reporters via multiple signaling patterns. Specifically, as we report here, the development of multichannel (chromogenic/fluorogenic/electrochemical)  $\text{Pb}^{2+}$  selective chemosensors is, as far as we know, an unexplored subject,<sup>30</sup> and only a few dual chromogenic and redox receptors have been recently described.<sup>31</sup>

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Ferrocene-based ligands have been found to be useful for incorporating redox functions into supramolecular complexes to bind and allow the electrochemical sensing of cations, anions, and neutral molecules by change in the oxidation potential of Fe(II)/Fe(III) redox couple.<sup>32</sup> In this context, we have found that a number of ferrocene–azaheterocycle dyads selectively sense transition metal cation through several channels.<sup>33</sup> Recently, new chemosensor molecules based on ferrocene–imidazoquinoxalines have been reported, which effectively recognize metal transition cations, and one of them behaves as a highly selective redox, chromogenic, and fluorescent chemosensor molecule for Pb(II) cations in acetonitrile solutions.<sup>34</sup> With these considerations in mind, we decided to annulate an additional polycyclic ring (phenanthrene or phenanthroline) to the imidazoquinoxaline core, which could impart interesting sensing properties. In these new structural motifs the added ring system could cooperate either with the nitrogen atoms of the preexisting ring or generate a new binding site and consequently enhance not only the binding affinity toward metal cations but also the selectivity. In addition, several different heterocyclic ring systems containing a pyrrolic NH group have been reported in the literature as hydrogen bond donors to anions, as demonstrated in calixpyrroles,<sup>35</sup> expanded porphyrinoids,<sup>36</sup> pyrrole derivatives,<sup>37</sup> indoles,<sup>38</sup> bisindoles,<sup>39</sup> bisimidazoles,<sup>40</sup> indolocarbazoles,<sup>41</sup> and benzimidazoles.<sup>42</sup> Keeping in mind these results, we describe the synthesis and electrochemical and sensing properties of the new receptors **4** and **7** in which a

### SCHEME 1. Synthesis of Receptor 4<sup>a</sup>



<sup>a</sup>Reagents and conditions: (a)  $(\text{CH}_3)_3\text{N}^+-\text{NH}_2^-$ ,  $\text{K}^t\text{BuO}$ , DMSO, 120 °C (32%); (b)  $\text{N}_2\text{H}_4$ , Pd/C, EtOH, 50 °C (62%); (c) ferrocenecarboxaldehyde,  $\text{C}_6\text{H}_5\text{NO}_2$ , AcOH, 60 °C (28%).

nitrogen-rich polycyclic system (metal transition binding site) is linked to a ferrocene unit through a imidazole ring (anion binding site). The multiresponsive character of the receptors and the ability of the previously unreported polycyclic ring system to act as favorable binding for cations and anions in the recognition event are most noteworthy.

### Results and Discussion

**Synthesis.** The receptor **4** was prepared from **1**, available by condensation of the 4-nitro-*o*-phenyldiamine and phenanthrene-9,10-dione,<sup>43</sup> by initial amination at position 6 of the quinoxaline ring with *N,N,N*-trimethylhydrazinium iodide in the presence of  $\text{K}^t\text{BuO}$  in DMSO at 120 °C to give **2** in 32% yield, followed by reduction of the nitro group with hydrazine in the presence of Pd on charcoal to afford **3** in 62% yield. Finally, imidazole-ring formation by reaction of **3** with ferrocenecarboxaldehyde in nitrobenzene provided **4** in 28% yield (Scheme 1).

The previously reported<sup>34a</sup> compound **5** was used as starting material for the preparation of the receptor **7**. Ring-opening of the thiadiazole ring in compound **5** by reduction with  $\text{NaBH}_4$  in the presence of  $\text{CoCl}_2$  provided the diamine **6** in 65% yield, which was converted in the receptor **7** in 47% yield by reaction with 1,10-phenanthroline-5,6-dione (Scheme 2).

**Electrochemical and Optical Properties.** The redox chemistry of receptors **4** and **7** was investigated by linear sweep voltammetry (LSV), cyclic voltammetry (CV), and Osteryoung square wave voltammetry (OSWV) in a  $\text{CH}_3\text{CN}$  solution containing 0.1 M  $[\text{n-Bu}_4\text{N}]\text{PF}_6$  (TBAHFP) as supporting electrolyte. Each receptor exhibited in the range 0–1.1 V a reversible one-electron redox wave, typical of a ferrocene derivative, at the half-wave potential value of  $E_{1/2} = 0.580$  V and  $E_{1/2} = 0.520$  V versus decamethylferrocene (DMFc), for **4** and **7**, respectively (Figure 1). The criteria applied for reversibility was a separation of 60 mV between cathodic and anodic peaks, a ratio of  $1.0 \pm 0.1$  for the intensities of the cathodic and anodic currents  $I_c/I_a$ , and no shift of the half-wave potential with varying scan rates.

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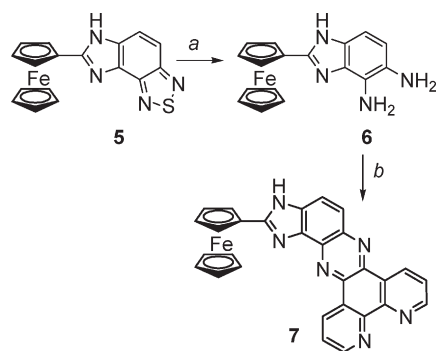
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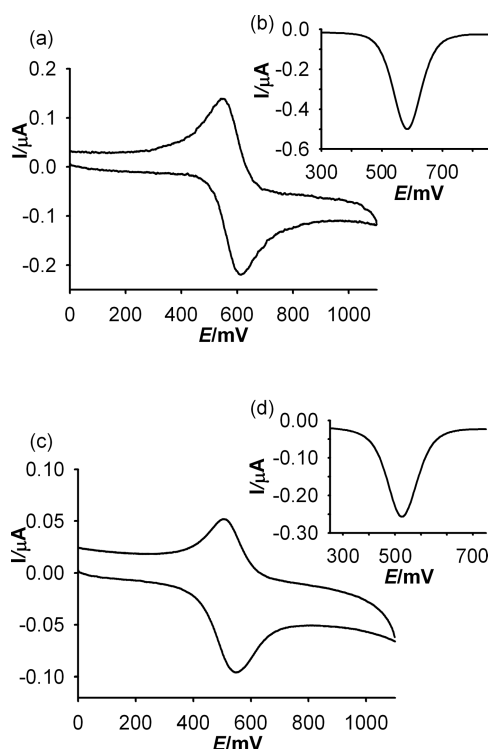
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SCHEME 2. Synthesis of Receptor 7<sup>a</sup>

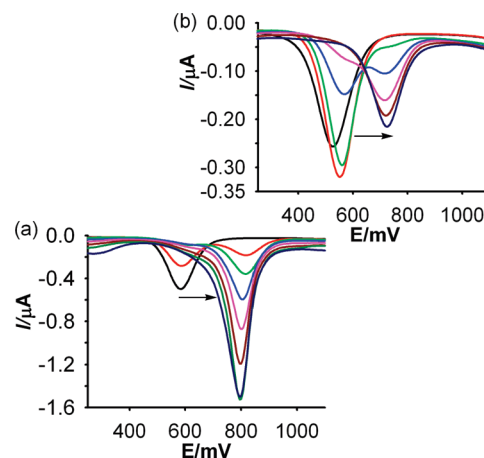
<sup>a</sup>Reagents and conditions: (a) NaBH<sub>4</sub>, EtOH, CoCl<sub>2</sub>·6H<sub>2</sub>O (65%); (b) 1,10-phenanthroline-5,6-dione, AcOH, 50 °C (47%).



**FIGURE 1.** CV (a) and OSWV (b) of **4** (0.5 mM) and CV (c) and OSWV (d) of **7** (0.1 mM) in CH<sub>3</sub>CN, using [(*n*-Bu)<sub>4</sub>N]PF<sub>6</sub> as supporting electrolyte, scanned at 0.1 V s<sup>-1</sup>.

The UV–vis data obtained in CH<sub>3</sub>CN ( $c = 5 \times 10^{-5}$  M) for receptors **4** and **7** are consistent with most ferrocenyl chromophores in that they exhibit two charge-transfer bands in the UV–vis region.<sup>44</sup> These spectra contain a prominent absorption band with a maximum at 320 ( $\epsilon = 1700 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 323 nm ( $\epsilon = 2450 \text{ M}^{-1} \text{ cm}^{-1}$ ) for **4** and **7**, respectively, which can safely be ascribed to a high-energy ligand-centered  $\pi$ – $\pi^*$  electronic transition (L– $\pi^*$ ) (HE band). In addition to this band, two weaker absorptions are visible at 375 ( $\epsilon = 450 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 396 nm ( $\epsilon = 500 \text{ M}^{-1} \text{ cm}^{-1}$ ) for **4** and only one low-energy band at 385 nm ( $\epsilon = 535 \text{ M}^{-1} \text{ cm}^{-1}$ ) for receptor **7**, which are assigned to

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**FIGURE 2.** (a) Evolution of the OSWV of **4** ( $5 \times 10^{-4}$  M) in CH<sub>3</sub>CN/[(*n*-Bu)<sub>4</sub>]PF<sub>6</sub> scanned at 0.1 V s<sup>-1</sup> in the presence of increasing amounts of Hg(OTf)<sub>2</sub>, from 0 (black) to 1.0 equiv (deep blue). (b) Evolution of the OSWV of **7** ( $1 \times 10^{-4}$  M) in CH<sub>3</sub>CN/[(*n*-Bu)<sub>4</sub>]PF<sub>6</sub> scanned at 0.1 V s<sup>-1</sup>, in the presence of increasing amounts of Hg(OTf)<sub>2</sub>, from 0 (black) to 0.5 equiv (deep blue).

another localized excitation with a lower energy produced by either of two nearly degenerate transitions: an Fe(II) d–d transition<sup>45</sup> or by a metal–ligand charge transfer (MLCT) process (d<sub>π</sub>–π\*) (LE band).<sup>46</sup>

Receptors **4** and **7** exhibit very weak fluorescence in CH<sub>3</sub>CN ( $c = 1 \times 10^{-5}$  M), with the excitation spectrum revealing  $\lambda_{\text{exc}} = 317$  and 340 nm, as an ideal excitation wavelength for **4** and **7**, respectively. The emission spectra show broad and structureless bands at 520 and 512 nm, with rather low quantum yield ( $\Phi = 3.9 \times 10^{-4}$  and  $1 \times 10^{-3}$ , for **4** and **7** respectively).

**Ion Sensing Properties.** The response of the receptors **4** and **7** with cationic and anionic guest has been investigated by electrochemistry, spectroscopic measurements (absorption and emission), and <sup>1</sup>H NMR spectroscopy.

The metal cation complexing properties of receptors **4** and **7** toward Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Hg<sup>2+</sup> reveal that the univalent metal ions do not cause significant changes in either redox potential, absorption, or the fluorescence emission spectrum, whereas redox shift, absorption perturbations, and increased emission bands are observed upon addition of Pb<sup>2+</sup> and Hg<sup>2+</sup> metal cations.

On stepwise addition of Hg<sup>2+</sup> cations to an electrochemical solution of the receptor **4** in CH<sub>3</sub>CN ( $c = 5 \times 10^{-4}$  M) a clear anodic shift of the oxidation potential from  $E_{1/2} = 0.58$  V to  $E_{1/2} = 0.79$  V ( $\Delta E_{1/2} = 210$  mV) was observed, and maximum perturbation of the CV was obtained with 0.5 equiv of added Hg<sup>2+</sup> cations (Figure 2a). Receptor **4** also showed perturbation of the oxidation wave in the presence of Pb<sup>2+</sup> cations. Upon addition of small amounts of this metal cation, a new oxidation wave at  $E_{1/2} = 0.81$  V ( $\Delta E_{1/2} = 230$  mV) anodically shifted appeared. The CV analysis of the complexes **4**·Pb<sup>2+</sup> (see Figure 1 in the Supporting Information) shows that one reduction process takes place at almost

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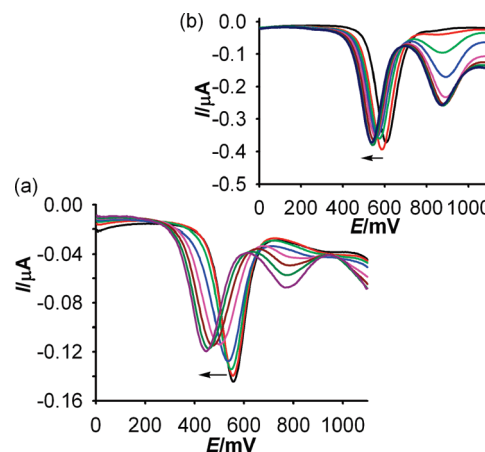
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the same reduction potential shown by the uncomplexed ligand **4**. This fact suggests that after the electronic oxidation of the complex  $4 \cdot \text{Pb}^{2+}$  it starts to be disrupted and the subsequent reduction takes place on the  $4^+$  species. This behavior means that this receptor is not only able to monitor binding but it is also able to behave as an electrochemically induced switchable chemosensor for  $\text{Pb}^{2+}$  through the progressive electrochemical release of this metal cation. This electrochemical induced complexation/decomplexation process has already been described in some other ferrocene derivatives<sup>7,33c,47</sup> and it is associated with a decrease of the association constant when the ligand is oxidized, giving rise to a destabilization of the complex formed.

Remarkably, linear sweep voltammetry (LSV) studies carried out upon addition of  $\text{Cu}^{2+}$  to a  $\text{CH}_3\text{CN}$  solution of **4** showed a significant shift of the sigmoidal voltammetric wave toward cathodic current, indicating that this metal promotes the oxidation of the free receptor. The presence of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$  metal cations had no effect on either OSWV or CV of the receptor **4**, even when present in large excess.

Receptor **7** only exhibits selectivity toward  $\text{Hg}^{2+}$  cations over the tested metal cations. The oxidation potential of **7** is only shifted from  $E_{1/2} = 0.52 \text{ V}$  to  $E_{1/2} = 0.72 \text{ V}$  ( $\Delta E_{1/2} = 200 \text{ mV}$ ) by addition of 2 equiv of  $\text{Hg}^{2+}$  metal cations (Figure 2b). Addition of  $\text{Cu}^{2+}$  induced oxidation of the ferrocene/ferrocenium redox couple, as indicated by the shift toward cathodic currents of the sigmoidal voltammetric wave, when LSV experiments were carried out in the presence of variable amounts of this metal cation (see the Supporting Information).

The binding and recognition ability of the receptors **4** and **7** toward various anions  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{AcO}^-$ ,  $\text{NO}_3^-$ ,  $\text{HSO}_4^-$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{HP}_2\text{O}_7^{3-}$ , in the form of their corresponding tetrabutylammonium salts ( $\text{TBA}^+$ ), was also evaluated by electrochemical techniques. Only in recent years have alternative mechanisms for several types of anion–receptor interaction<sup>48</sup> been developed. If the basicity of the anion is insufficient to induce deprotonation of the receptor, one observes formation of a hydrogen-bonded complex manifested in a red-shift of the receptor absorption band and a downfield shift or often disappearance of NMR signals of the receptors



**FIGURE 3.** Evolution of the OSWV of **4** ( $5 \times 10^{-4} \text{ M}$ ) in  $\text{CH}_3\text{CN}/[\text{n-Bu}]_4\text{PF}_6$  scanned at  $0.1 \text{ V s}^{-1}$  in the presence of increasing amounts of (a)  $\text{AcO}^-$  from 0 (black) to 3 equiv (deep blue), and (b) from 0 (black) to 3 equiv (deep blue) of  $\text{AcO}^-$  but in the presence of 20 equiv of acetic acid.

protons involved in the hydrogen bonding. If basicity of the anion is high enough to deprotonate the receptor, one observes the appearance of a new intense absorption band in the visible region of the electronic spectrum, and the disappearance of NMR signals of abstracted receptor protons, and an upfield shift of the signals of adjacent receptor protons.<sup>49</sup> A possible way to reveal the formation of hydrogen-bonded complexes under conditions of electrochemical titration is to suppress deprotonation by adding a small amount of acetic acid.<sup>50</sup>

On stepwise addition of  $\text{F}^-$  anion to a solution of receptor **4** in  $\text{CH}_3\text{CN}$ , a remarkable cathodic shift ( $\Delta E_{1/2} = -290 \text{ mV}$ ) of the oxidation potential is observed. In particular, this large cathodically shifted oxidation peak reaches the maximum current intensity value at 3 equiv of anion added. OSWV titration also showed a measurable change in the oxidation potential (see the Supporting Information). Receptor **4** also showed a perturbation of the oxidation peak in the presence of  $\text{HP}_2\text{O}_7^{3-}$  anion. Upon addition of 1 equiv of this anion a new oxidation peak, cathodically shifted, at  $0.46 \text{ V}$  ( $\Delta E_{1/2} = -120 \text{ mV}$ ) appeared. However, in the presence of an excess of  $\text{HP}_2\text{O}_7^{3-}$  anion, a remarkable cathodic shift ( $\Delta E_{1/2} = -290 \text{ mV}$ ) of the oxidation potential is observed (see the Supporting Information). It is worth noting that addition of  $\text{AcO}^-$  and  $\text{H}_2\text{PO}_4^-$  anions also induced cathodic shift by  $-120$  and  $-110 \text{ mV}$ , respectively (Figure 3a). Titration with the strong base  $\text{Bu}_4\text{NOH}$ , which definitely leads to deprotonation, also induced a strong cathodic shift of the oxidation peak ( $\Delta E_{1/2} = -290 \text{ mV}$ ) (see the Supporting Information). In preliminary experiments, we found that addition of up to 20 equiv of acetic acid did not affect either the CV or the OSWV of receptor **4** in  $\text{CH}_3\text{CN}$ . Addition of  $\text{HP}_2\text{O}_7^{3-}$  anion to an electrochemical solution of receptor **4** in  $\text{CH}_3\text{CN}$  in the presence of 20 equiv of acetic acid induced a cathodic shift of the oxidation peak ( $\Delta E_{1/2} = -80 \text{ mV}$ ) considerably smaller than that observed in the absence of acid ( $\Delta E_{1/2} = -290 \text{ mV}$ ), whereas the addition of  $\text{F}^-$  anion under these conditions does not induce perturbation in the

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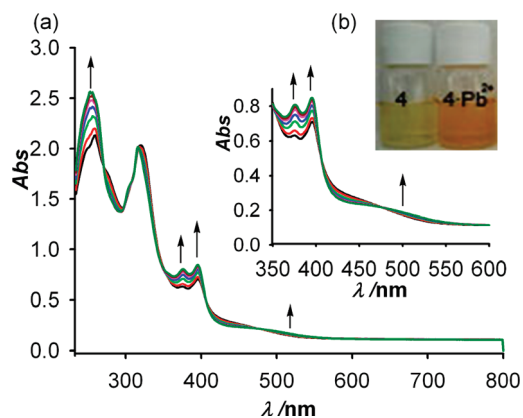
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oxidation potential of the receptor **4** (see the Supporting Information). Results of titrations carried out in the presence of 20 equiv of acetic acid indeed show smaller but significant oxidation potential shifts for  $\text{AcO}^-$  ( $\Delta E_{1/2} = -70$  mV) and  $\text{H}_2\text{PO}_4^-$  anions ( $\Delta E_{1/2} = -70$  mV). Remarkably, the presence of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ , and  $\text{HSO}_4^-$  had no effect on the OSWV, even when present in large excess.

With regard to receptor **7**, the OSWV remains unchanged in the presence of acetic acid. Addition of  $\text{F}^-$ ,  $\text{AcO}^-$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{HP}_2\text{O}_7^{3-}$  anions with and without the presence of acid induced the same kind of perturbation in the oxidation potential as those observed with receptor **4** (Table 1 in the Supporting Information). These electrochemical data show that the voltammetric techniques are able not only to study anion–receptor interactions but also to discriminate between deprotonation and simple association. The electrochemical data suggest that the interaction between receptors **4** and **7** with  $\text{AcO}^-$  and  $\text{H}_2\text{PO}_4^-$  anions involve both formation of hydrogen-bonded complex and deprotonation. Interestingly, the oxidation potential found with or without added acid in the presence of 1 equiv of  $\text{HP}_2\text{O}_7^{3-}$  anion could be due to the complex  $[\text{LHP}_2\text{O}_7^{3-}]$  formation, which in the presence of an excess of anion undergoes deprotonation. Clearly,  $\text{F}^-$  anion induced deprotonation.

Interestingly, upon addition of 1 equiv of  $\text{Pb}^{2+}$  cation to the electrochemical solution of the  $[\text{4}\cdot\text{H}_2\text{PO}_4^-]$  complex a slight shift of 55 mV was observed, whereas such addition on the  $[\text{4}\cdot\text{AcO}^-]$  species promotes the appearance of the redox peak ascribed to the free receptor **4** (see the Supporting Information). For receptor **7**, however, addition of 0.5 equiv of  $\text{Hg}^{2+}$  cation to an electrochemical solution of the  $[\text{7}\cdot\text{AcO}^-]$  complex induced an anodic shift of 70 mV, whereas such addition on the  $[\text{7}\cdot\text{H}_2\text{PO}_4^-]$  complex had no effect (see the Supporting Information). These results clearly show the ability of the electrochemical DPV technique for detecting the formation of the ion pair  $[\text{4}\cdot\text{Pb}(\text{H}_2\text{PO}_4)_2]$  and  $[\text{7}\cdot\text{Hg}(\text{AcO})_2]$  complexes.

Ion recognition properties of the receptors **4** and **7** toward metal cations and anions were also evaluated by UV–vis spectroscopy. Titration experiments carried out with  $\text{CH}_3\text{CN}$  solutions of these receptors ( $c = 5 \times 10^{-5}$  M) and the corresponding ions were performed and analyzed quantitatively.<sup>51</sup> It is worth mentioning that no changes were observed in the UV–vis upon addition of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$  metal ions, even in a large excess; however, significant modifications were observed upon addition of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  to a solution of receptor **4**. The addition of  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  elicited the same optical response. In both cases, addition of such divalent metal cations caused the progressive appearance of a new LE band located at  $\lambda = 502$  nm ( $\epsilon = 1700 \text{ M}^{-1} \text{ cm}^{-1}$  for  $\text{Pb}^{2+}$  and  $\epsilon = 1800 \text{ M}^{-1} \text{ cm}^{-1}$  for  $\text{Hg}^{2+}$ ) as well as a decrease in the intensity of the initial HE band (Figure 4 and the Supporting Information). Three well-defined isosbestic points (271, 364, and 414 nm for  $\text{Pb}^{2+}$  and 271, 364, and 488 nm for  $\text{Hg}^{2+}$ )



**FIGURE 4.** Changes in the absorption spectra of **4** ( $c = 5 \times 10^{-5}$  M in  $\text{CH}_3\text{CN}$ ) upon addition of increasing amounts of  $\text{Pb}(\text{ClO}_4)_2$ , from 0 (black) to 1 equiv (deep green). Arrows indicate absorptions that increase or decrease during the experiment.

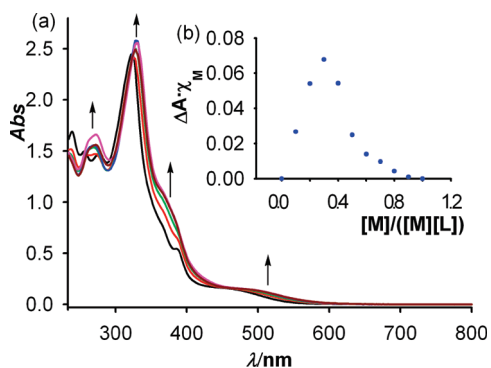
indicated that a neat interconversion between the uncomplexed and complexed species occurs. The new LE band is responsible for the change of color, from yellow to orange, which can be used for a “naked eye” detection of these metals. From analysis of the spectral titration data 1:1 and 2:1 (receptor/cation) binding stoichiometries were observed for  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ , respectively (see the Supporting Information), and the corresponding binding constants were determined by using the already mentioned software:  $K_a = 1.72 \times 10^6 \text{ M}^{-1}$  for  $\text{Pb}^{2+}$  and  $\beta = 1.72 \times 10^{12} \text{ M}^{-2}$  for  $\text{Hg}^{2+}$ . By contrast, addition of  $\text{Cu}^{2+}$  metal ion to a solution of **4** produces the same perturbations in its absorption spectrum as those observed when **4** was electrochemically oxidized: a new ligand-to-metal band at  $\lambda 820$  nm appears (see the Supporting Information). The stoichiometry of the complexes has also been confirmed by ESI-MS, where peaks at  $m/z$  1209.2 ( $[\text{4}_2\cdot\text{Hg}]^{2+}$ ) and 711.0 ( $[\text{4}\cdot\text{Pb}]^{2+}$ ) are observed.

In comparison to the above-mentioned results obtained with receptor **4**, the titration studies of receptor **7** toward the same set of metal cations and under the same conditions revealed a different behavior than **4** upon addition of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$ . In this case,  $\text{Cu}^{2+}$  induces again the oxidation of the receptor, which is confirmed by comparison of the absorption spectrum resulting from the electrochemical oxidation of **7** and that obtained upon addition of  $\text{Cu}^{2+}$  metal cations (see the Supporting Information). Whereas no changes were observed in the absorption spectrum upon addition of  $\text{Pb}^{2+}$  cations, the addition of increasing amounts of  $\text{Hg}^{2+}$  cations caused a progressive appearance of two weak low-energy bands at  $\lambda = 362$  and 485 nm, respectively, as well as an increase of the initial high-energy bands intensities (Figure 5). Binding assays using the method of continuous variations (Job’s plot) suggest that **4** complexes  $\text{Hg}^{2+}$  cations with a 2:1 (receptor:cation) stoichiometry.

Receptors **4** did not show any obvious spectral change upon addition of  $\text{AcO}^-$  and  $\text{H}_2\text{PO}_4^-$  anions. However, upon addition of small amounts of  $\text{HP}_2\text{O}_7^{3-}$  anion the two energy bands are red-shifted by 41 and 29 nm, respectively, and at the same time, a new weak low-energy band at 500 nm increases in intensity reaching a maximum when 3 equiv of this anion was added (see the Supporting Information). The absorption spectrum of **4** in the presence of either  $\text{F}^-$  or  $\text{Bu}_4\text{NOH}$  displayed the same changes as those observed with

(51) Specfit/32 Global Analysis System, 1999–2004 Spectrum Software Associates (SpecSoft@compuserve.com). The Specfit program was acquired from Biologic, SA (www.bio-logic.info) in January 2005. The equation to be adjusted by nonlinear regression, using the above-mentioned software was the following:  $\Delta A/b = \{K_{11}\Delta\epsilon_{\text{HG}}[\text{H}]_{\text{tot}}[\text{G}]\}/\{1 + K_{11}[\text{G}]\}$ , where H = host, G = guest, HG = complex,  $\Delta A$  = variation in the absorption,  $b$  = cell width,  $K_{11}$  = association constant for a 1:1 model, and  $\Delta\epsilon_{\text{HG}}$  = variation of molar absorptivity.





**FIGURE 5.** (a) Changes in the absorption spectra of **7** ( $c = 5 \times 10^{-5}$  M in  $\text{CH}_3\text{CN}$ ) upon addition of increasing amounts of  $\text{Hg}(\text{OTf})_2$ , from 0 (black) to 2 equiv (red). Arrows indicate absorptions that increase or decrease during the experiment. (b) Job's plot for **7** ( $1 \times 10^{-4}$  M in  $\text{CH}_3\text{CN}$ ), and  $\text{Hg}(\text{OTf})_2$  ( $1 \times 10^{-5}$  M in  $\text{CH}_3\text{CN}$ ), indicating the formation of a 2:1 complex.

the  $\text{HP}_2\text{O}_7^{3-}$  anion (see the Supporting Information). These results indicate that deprotonation takes place in the presence of these anions. Similar behavior was found with receptor **7** in the presence of the above-mentioned anions: no changes in the presence of  $\text{AcO}^-$  and  $\text{H}_2\text{PO}_4^-$  anions and deprotonation by the action of  $\text{HP}_2\text{O}_7^{3-}$  and  $\text{F}^-$  anions (see the Supporting Information).

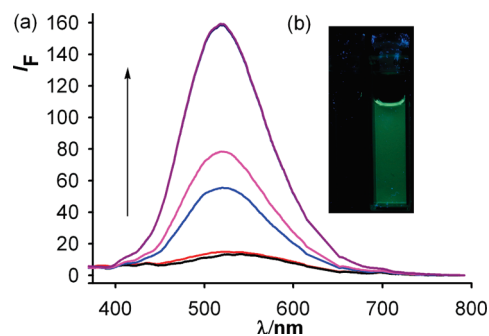
Assessment of the cation affinity also came from observing the extent to which the fluorescence intensity of receptors **4** and **7** was affected in the presence of the selected cations. Receptor **4** in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (9:1) did not undergo any considerable change in its emission spectrum upon addition of  $\text{Hg}^{2+}$  metal cations. However, in the presence of  $\text{Pb}^{2+}$  metal cations it showed a remarkable increase of the intensity of the emission band ( $\text{CHEF}^{52} = 47$ ) and the quantum yield ( $\Phi = 1.8 \times 10^{-2}$ ) resulted in a 50-fold increase (Figure 6). From the fluorescence binding isotherm, the association constant was calculated to be  $K_a = 3.57 \times 10^6 \text{ M}^{-1}$ .

For receptor **7**, fluorescent titration experiments demonstrate that only  $\text{Hg}^{2+}$  cation induced a red-shift of the emission band from 512 to 544 nm ( $\Delta\lambda = 32$  nm) accompanied by an intense enhancement of the emission band ( $\text{CHEF} = 165$ ). The stoichiometry of the complex was also determined by the changes in the fluorogenic response of the receptor **7** in the presence of varying concentrations of this metal cation and the results obtained indicate the formation of a 2:1 complex, the global association constant being  $\beta = 1.38 \times 10^{12} \text{ M}^{-2}$ . The increase in quantum yield of **7** induced by  $\text{Hg}^{2+}$  ( $\Phi = 3.7 \times 10^{-2}$ ) was 37-fold (Figure 7).

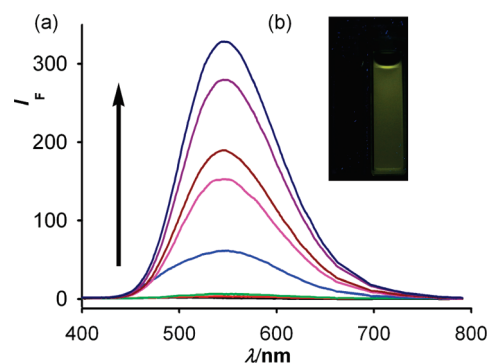
The selectivity of receptor **4** for  $\text{Pb}^{2+}$  over  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Hg}^{2+}$  is particularly important because  $\text{Pb}^{2+}$  targets  $\text{Ca}^{2+}$ -binding sites *in vivo*<sup>53</sup> and  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  are metal cations that frequently interfere with  $\text{Pb}^{2+}$  analysis. Therefore, the selective binding ability of **4** for  $\text{Pb}^{2+}$  and **7** for  $\text{Hg}^{2+}$  over other metal ions was investigated by the competition-based fluorescence experiments (see the Supporting Information).

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

(53) (a) Goldstein, G. W. *Neurotoxicology* **1993**, *14*, 97–102. (b) Simonos, T. J. B. *Neurotoxicology* **1993**, *14*, 77–86. (c) Goyer, R.-A. *Health Perspect.* **1990**, *86*, 177–182.



**FIGURE 6.** (a) Changes in the fluorescence emission spectrum of **4** ( $c = 1 \times 10^{-5}$  M in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  90/10) upon addition of  $\text{Pb}(\text{ClO}_4)_2$  ( $c = 2.5 \times 10^{-3}$  M in  $\text{CH}_3\text{CN}$ ): black line, 0 equiv added; blue line, after addition of 0.3 equiv; pink line, after addition of 0.6 equiv; deep purple line, after addition of 1 equiv. Emission is monitored at  $\lambda_{\text{exc}} = 317$  nm. (b) Visual changes observed in the fluorescence of  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (90/10) solutions of **4** (left) and after addition of  $\text{Pb}(\text{ClO}_4)_2$  (right).

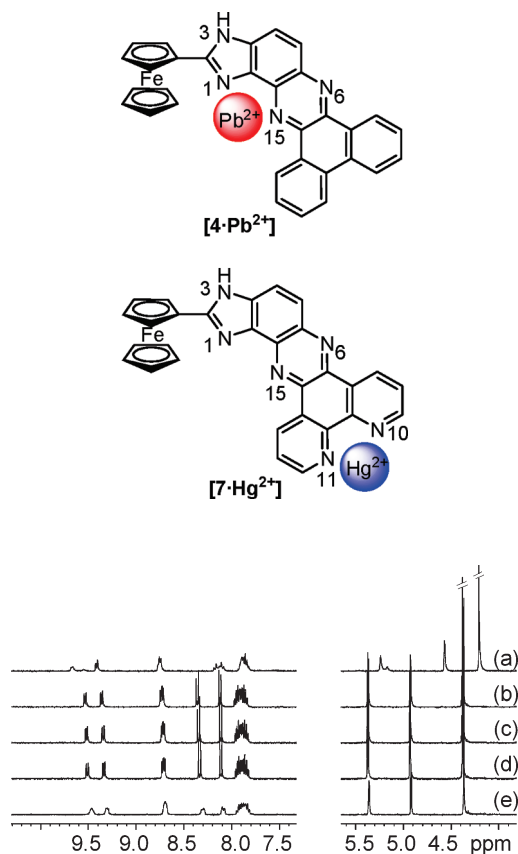


**FIGURE 7.** (a) Changes in the fluorescence emission spectrum of **7** ( $c = 1 \times 10^{-5}$  M in  $\text{CH}_3\text{CN}$ ) upon titration with  $\text{Hg}(\text{OTf})_2$ : the initial (black) is that of **7** and the final one (deep blue), after addition of 2 equiv of  $\text{Hg}(\text{OTf})_2$  ( $c = 2.5 \times 10^{-3}$  M in  $\text{CH}_3\text{CN}$ ). Emission is monitored at  $\lambda_{\text{exc}} = 340$  nm. (b) Visual changes observed in the fluorescence of  $\text{CH}_3\text{CN}$  solutions of **7** (left) and after addition of  $\text{Hg}(\text{OTf})_2$  (right).

For the reported constant to be taken with confidence, we have proved the reversibility of the complexation process by carrying out the following experimental test: 1 equiv of  $\text{Pb}(\text{ClO}_4)_2$  was added to a solution of the receptor **4** in  $\text{CH}_2\text{Cl}_2$  to obtain the complex  $[\mathbf{4} \cdot \text{Pb}^{2+}]$ , whose UV–vis spectrum and  $^1\text{H}$  NMR were recorded. The  $\text{CH}_2\text{Cl}_2$  solution of the complex was washed several times with water. The organic layer was dried, and the optical spectrum and  $^1\text{H}$  NMR spectrum were recorded and they were found to be the same as that of the free receptor **4**. Afterward, 1 equiv of  $\text{Pb}(\text{ClO}_4)_2$  was added to this solution, and the initial UV–vis and  $^1\text{H}$  NMR spectra of the complex  $[\mathbf{4} \cdot \text{Pb}^{2+}]$  were fully recovered. This experiment was carried out over several cycles, and the optical spectrum was recorded after each step, thus demonstrating the high degree of the reversibility of the complexation/decomplexation process. Similar studies were carried out by using the receptor **7** and  $\text{Hg}^{2+}$  metal cation, which confirm the reversibility of this process between this receptor and such cationic metal species (see the Supporting Information).

To support the results obtained by electrochemical and spectroscopic (absorption and emission) experiments, and to

**CHART 1. Schematic Representation of the Binding Sites Where the Corresponding Metal Cations Are Bound to the Receptors 4 and 7**



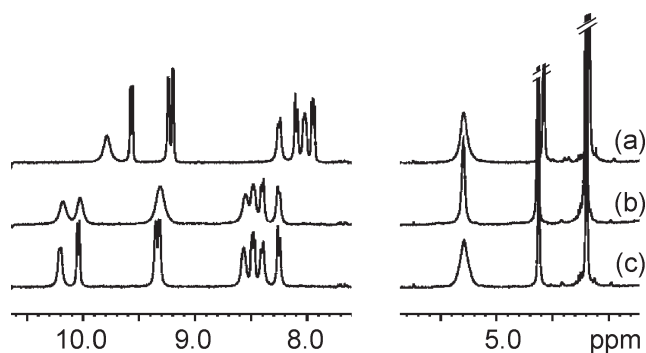
**FIGURE 8.** Changes in the  $^1\text{H}$  NMR spectrum (in  $\text{CD}_3\text{CN}$ ) of **4** upon addition of increasing amounts of  $\text{Pb}(\text{ClO}_4)_2$ : from 0 (a) to 1.0 equiv (e).

achieve additional information about the coordination mode of both metal cations and anions by receptors **4** and **7**, we also performed a  $^1\text{H}$  NMR spectroscopic analysis in  $\text{CD}_3\text{CN}$  or  $\text{DMSO}-d_6$  solutions, respectively.

Metal ion-induced chemical shift changes in the  $^1\text{H}$  NMR spectra of **4** and **7** support that  $\text{Pb}^{2+}$  is linked to the N1 and N15 of the imidazo-phenazine framework present in **4** while  $\text{Hg}^{2+}$  is bound to the N10 and N11 atoms present within the phenantroline subunits existing in **7** (Chart 1).

Thus, addition of  $\text{Pb}^{2+}$  to ligand **4** promotes not only a downfield shifting of the  $\text{H}\beta$  and the Cp protons of the ferrocene moiety ( $\Delta\delta = +0.35$  ppm for  $\text{H}\beta$  and  $\Delta\delta = +0.15$  ppm for the Cp singlet), but also a change in the peak shapes of the  $\text{H}\alpha$  and  $\text{H}\alpha'$  protons which gave rise only to a pseudo-triplet at  $\delta$  5.35 ppm while in the free ligand they appeared as two different pseudotriplets at  $\delta$  5.24 and 5.17 ppm, respectively (Figure 8). Moreover, a simultaneous downfield shifting is also observed in the signal corresponding to the H5 ( $\Delta\delta = +0.10$  ppm) while the protons present in the phenanthrene moiety remained essentially unaffected during the complexation process.

By contrast, the most prominent changes observed in the  $^1\text{H}$  NMR of **7** upon addition of  $\text{Hg}^{2+}$  cation are the appearance of very significant downfield shifts of the  $^1\text{H}$  NMR signals corresponding to the H9 ( $\Delta\delta = +0.93$  ppm), H12



**FIGURE 9.** Changes in the  $^1\text{H}$  NMR spectrum (in  $\text{DMSO}-d_6$ ) of **7** (top) upon addition from 0 (a) to 0.5 equiv of  $\text{Hg}(\text{OTf})_2$  (c).

( $\Delta\delta = +0.47$  ppm), H8 ( $\Delta\delta = +0.40$  ppm), and H13 ( $\Delta\delta = +0.39$  ppm). Moreover, the formation of the complexed species was not accompanied by any shift of the ferrocene signals (Figure 9).

The interactions between the  $\text{AcO}^-$  and  $\text{H}_2\text{PO}_4^-$  anions with ligands **4** and **7** were also investigated by  $^1\text{H}$  NMR spectra studies. However, in both cases the complexations are accompanied by very slight upfield shifts of the signals present in the free ligands (see the Supporting Information), which might be attributed to a weak binding affinity between such ligands and those anions.

On the other hand and on the basis of the electrochemical results showing the capability of these two ligands to bind and recognize the above-mentioned cations and anions, a study of the ability of this receptor toward the simultaneous binding of these types of ions was also carried out through  $^1\text{H}$  NMR titration experiments. Thus, additions of the corresponding metal cations to the deuterated solutions of the free ligands followed by additions of the appropriate anions were analyzed by  $^1\text{H}$  NMR spectroscopy. However, the low solubility of the species formed during these experiments in the commonly used deuterated solvents prevented the success of this study. Nevertheless, it is worth mentioning that the electrospray mass spectrum obtained from the species formed by sequential addition of  $\text{H}_2\text{PO}_4^-$  and  $\text{Pb}^{2+}$  to the free receptor **4** gave rise to a peak at  $m/z$  806.1 indicating the simultaneous recognition of both ions (see the Supporting Information).

## Conclusion

The synthesis and electrochemical, optical, and ion sensing properties of ferrocene-imidazophenazine dyads are presented. The binding events are strongly affected by the nature of the aromatic ring fused to this ring system. Dyad **4** behaves as a highly selective redox/chromogenic/fluorescent chemosensor molecule for  $\text{Pb}^{2+}$  cations in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (9:1). In addition, dyad **4** also exhibited a redox-induced complexation/decomplexation type signaling pattern that can be used for the construction of more elaborate supramolecular switching systems. Dyad **7**, bearing two fused pyridine rings, displays the same type of sensing properties but now toward  $\text{Hg}^{2+}$  cations. In both dyads,  $\text{Cu}^{2+}$  cations induced oxidation of the ferrocenyl end group, which is confirmed by spectroelectrochemical studies and linear sweep voltammetry (LSV) data. The changes in the absorption spectra are accompanied



by a color change from yellow to orange which allows the potential for “naked eye” detection.

On the other hand, electrochemical data suggest that the interaction between receptors **4** and **7** with  $\text{AcO}^-$  and  $\text{H}_2\text{PO}_4^-$  anions involves both formation of hydrogen-bonded complex and deprotonation. However,  $\text{HP}_2\text{O}_7^{3-}$  and  $\text{F}^-$  anions induced deprotonation. The electrochemical OSWV technique shows its ability for detecting the formation of the ion-pair [**4**· $\text{Pb}(\text{H}_2\text{PO}_4)_2$ ] and [**7**· $\text{Hg}(\text{AcO})_2$ ] complexes, which were also detected by electrospray mass spectrometry.

## Experimental Section

**6-Amino-7-nitrodibenzo[*a,c*]phenazine, 2.** To a solution of 7-nitrodibenzo[*a,c*]phenazine (0.5 g, 1.5 mmol) and trimethylhydrazinium iodide (0.34 g, 1.66 mmol) in DMSO (70 mL) was added *K*tBuOK (0.20 g, 1.79 mmol) and the reaction mixture was heated at 120 °C overnight. After cooling at 0 °C, HCl was added until pH 3. Then, the solution was poured into a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (30 mL) and the resulting brown precipitate was filtered and purified by column chromatography on silica gel with dichloromethane/*n*-hexane (7:3) as eluent. Mp 191–193 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  7.24 (d,  $J = 9.6$  Hz, 1H), 7.81 (m, 2H), 7.90 (m, 2H), 8.33 (d,  $J = 9.6$  Hz, 1H), 8.76 (m, 2H), 8.85 (s, 2H), 9.20 (d,  $J = 8$  Hz, 1H), 9.58 (d,  $J = 8$  Hz, 1H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ ) 114.3 (CH), 123.3 (CH), 123.5 (CH), 125.4 (Cq), 125.8 (CH), 126.1 (CH), 126.5 (CH), 128.2 (CH), 128.6 (Cq), 128.8 (Cq), 130.8 (CH), 131.4 (CH), 132.2 (Cq), 133.5 (Cq), 143.7 (Cq), 145.3 (Cq). MS (EI)  $m/z$  (rel intensity) 340 ( $\text{M}^+$ , 100), 294 (70), 266 (29), 176 (39), 133 (35). Anal. Calcd for  $\text{C}_{20}\text{H}_{12}\text{N}_4\text{O}_2$ : C, 70.58; H, 3.55; N, 16.46. Found: C, 70.29; H, 3.31; N, 16.70.

**6,7-Diaminodibenzo[*a,c*]phenazine, 3.** To a solution of 6-amino-7-nitrodibenzo[*a,c*]phenazine (0.2 g, 0.56 mmol) in ethanol (100 mL) heated at 50 °C was added Pd/C (10 mol %). Then, hydrazine hydrate (0.2 mL 3.92 mmol) was added dropwise. Afterward, a new portion of Pd/C (10 mol %) was added and the reaction mixture was refluxed for 1 h. The hot solution was filtered over a Celite pad and the solvent was removed under reduced pressure giving rise to a red solid that was washed with *n*-pentane and crystallized from ethanol/*n*-hexane. Mp 222–223 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  7.50 (d,  $J = 9.2$  Hz, 1H), 7.57 (d,  $J = 8.8$  Hz, 1H), 7.79 (m, 4H), 8.72 (d,  $J = 4$  Hz, 1H), 8.74 (d,  $J = 4.8$  Hz, 1H), 9.18 (dd,  $J = 7.2, 2$ , 1H), 9.47 (dd,  $J = 7.6, 1.6$ , 1H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  117.3 (CH), 123.4 (CH), 123.5 (CH), 124.2 (CH), 124.6 (CH), 126.0 (CH), 127.9 (CH), 128.0 (CH), 129.3 (CH), 129.9 (CH), 130.2 (Cq), 130.3 (Cq), 130.5 (Cq), 131.2 (Cq), 133.4 (Cq), 136.8 (Cq), 137.1 (Cq), 138.8 (Cq). MS (EI)  $m/z$  (rel intensity) 310 ( $\text{M}^+$ , 100), 282 (35), 155 (45), 140 (36). Anal. Calcd for  $\text{C}_{20}\text{H}_{14}\text{N}_4$ : C, 77.40; H, 4.55; N, 18.05. Found: C, 77.65; H, 4.29; N, 18.30.

**2-Ferrocenyl-3*H*-dibenzo[*a,c*]imidazo[4,5-*h*]phenazine, 4.** To a solution of 5,6-diamino-2,3-di(2-pyridil)quinoxaline (0.2 g, 0.64 mmol) in nitrobenzene (20 mL) was added acetic acid (0.5 mL). The resulting mixture was stirred at 60 °C for 15 h and then neutralized to pH 7 with a  $\text{NaHCO}_3$  solution. Then  $\text{H}_2\text{O}$  (50 mL) was added and the solution was extracted with  $\text{CHCl}_3$  (2 × 50 mL). The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated to dryness to give a brown residue that was purified by column chromatography on silica gel with dichloromethane/methanol (9/1) as eluent. Mp 224–225 °C.  $^1\text{H}$  NMR

(DMSO- $d_6$ )  $\delta$  4.18 (s, 5H), 4.56 (s, 2H), 5.21 (s, 1H), 5.35 (s, 1H), 7.89 (m, 4H), 8.05 (d,  $J = 8.8$  Hz, 1H), 8.21 (d,  $J = 8.8$  Hz, 1H), 8.81 (m, 2H), 9.93 (d,  $J = 8.0$  Hz, 1H), 9.64 (d,  $J = 8.0$  Hz, 1H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  67.6 (CH), 69.5 (CH), 70.0 (CH), 74.1 (Cq), 123.0 (CH), 123.6 (CH), 125.1 (CH), 126.0 (CH), 128.0 (CH), 128.3 (CH), 129.9 (CH), 130.1 (CH), 130.5 (Cq), 130.9 (Cq), 131.4 (Cq), 139.0 (Cq), 139.6 (Cq). MS (EI)  $m/z$  (rel intensity) 504 ( $\text{M}^+$ , 100), 252 (47), 66 (52). Anal. Calcd for  $\text{C}_{31}\text{H}_{20}\text{FeN}_4$ : C, 73.82; H, 4.00; N, 11.11. Found: C, 73.60; H, 4.17; N, 11.32.

**2-Ferrocenyl-4,5-diamino-1*H*-benzo[*d*]imidazole, 6.** To a solution of 2-ferrocenyl-8*H*-imidazo[4,5-*e*]-2,1,3-benzothiadiazole (0.25 g, 0.69 mmol) in EtOH (50 mL) were added  $\text{NaBH}_4$  (6.95 g, 37.83 mmol) and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (30 mol %). The reaction mixture was stirred at reflux temperature for 1 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was treated with  $\text{H}_2\text{O}$  (50 mL) and extracted with ethyl acetate (2 × 25 mL). The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated to dryness to give a red solid that was washed with *n*-pentane and purified by a silica gel column chromatography with dichloromethane/methanol (9:1). Mp 190 °C dec.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  4.09 (s, 5H), 4.39 (t,  $J = 1.6$  Hz, 2H), 4.93 (s, 2H), 6.52 (d,  $J = 8.0$  Hz, 1H), 6.59 (d,  $J = 8.0$  Hz, 1H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  112.6 (CH), 75.27 (Cq), 69.1 (CH), 68.9 (CH), 66.6 (CH). MS (EI)  $m/z$  (rel intensity) 332 ( $\text{M}^+$ , 100), 266 (46), 166 (29), 149 (41), 121 (23). Anal. Calcd for  $\text{C}_{17}\text{H}_{16}\text{FeN}_4$ : C, 61.47; H, 4.85; N, 16.87. Found: C, 61.24; H, 5.02; N, 16.70.

**2-Ferrocenyl-3*H*-dipyrido[3,2-*a*:2',3'-*c*]imidazo[4,5-*h*]phenazine, 7.** To a solution of 1,10-phenanthroline-5,6-dione (0.10 g, 0.47 mmol) in ethanol (50 mL) was slowly added a solution of 2-ferrocenyl-4,5-diamino-1*H*-benzo[*d*]imidazole (0.15 g, 0.47 mmol). The mixture was stirred at reflux temperature for 10 h. After cooling to room temperature, the brown solid formed was filtered, washed with EtOH (4 × 10 mL) and crystallized from ethanol. Mp 300 °C dec.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  4.18 (s, 5H), 4.57 (t,  $J = 1.6$  Hz, 2H), 5.29 (s, 2H), 7.94 (dd,  $J = 8.0, 4.4$  Hz, 1H), 8.00 (dd,  $J = 8.0$  Hz,  $J = 4.4$  Hz, 1H), 8.10 (d,  $J = 9.0$  Hz, 1H), 8.24 (d,  $J = 9.0$  Hz, 1H), 9.20 (dd,  $J = 4.4$  Hz,  $J = 1.6$  Hz, 1H), 9.24 (dd,  $J = 4.4$  Hz,  $J = 1.6$  Hz, 1H), 9.58 (dd,  $J = 4.4$  Hz,  $J = 1.6$  Hz, 1H), 9.81 (d,  $J = 8.0$  Hz, 1H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  67.7 (CH), 69.5 (CH), 70.02 (CH), 74.19 (Cq), 123.0 (CH), 124.2 (Cq), 124.4 (CH), 127.3 (Cq), 127.4 (Cq), 132.5 (CH), 133.3 (CH), 138.0 (Cq), 140.1 (Cq), 147.4 (Cq), 147.8 (Cq), 151.6 (CH), 152.1 (CH). MS (EI)  $m/z$  (rel intensity) 506 ( $\text{M}^+$ , 100), 386 (15), 253 (45), 121 (11). Anal. Calcd for  $\text{C}_{29}\text{H}_{18}\text{FeN}_6$ : C, 68.79; H, 3.58; N, 16.60. Found: C, 68.55; H, 3.70; N, 16.33.

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**Supporting Information Available:** NMR spectra, electrochemical titration data, NMR, UV–vis, and emission spectral data, titration profiles, competition experiments, detection limit calculations, and Experimental Section: General Comments. This material is available free of charge via the Internet at <http://pubs.acs.org>.