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# Aldimines generated from aza-Wittig reaction between bis(iminophosphoranes) derived from 1,1'-diazidoferrocene and aromatic or heteroaromatic aldehydes: electrochemical and optical behaviour towards metal cations<sup>†</sup>

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Aldimine **4** bearing a 2-quinolyl group was prepared by aza-Wittig reaction between the triphenyliminophosphorane derived from the 1,1'-diazidoferrocene and 2-formylquinoline. However, aldimine **5**, bearing a pyrene ring, was prepared using the most reactive tributyliminophosphorane derivative and the corresponding 1-formylpyrene. On the other hand, formation of aldimine **8** involves a tandem process, Staudinger reaction/intramolecular aza-Wittig reaction, by using directly 1,1'-diazidoferrocene and 2-(diphenylphosphonyl)benzaldehyde. Aldimine **4** behaves as chemosensor molecule for Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup> cations through two different channels: electrochemical ( $\Delta E_{1/2} = 222-361$  mV) and chromogenic ( $\Delta \lambda = 122-153$  nm), which can be used for the "naked eye" detection of these metal cations. Aldimine **5** behaves as a highly selective redox (in CH<sub>3</sub>CN) and fluorescent (in CH<sub>3</sub>Cl–DMF) probe for Hg<sup>2+</sup> metal cations even in the presence of a large excess of the other metal cations tested. Aldimine **8** displays electrochemical affinity ( $\Delta E_{1/2} = 60-288$  mV) to Li<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> metal cations, with the phosphorus oxide functionality as a binding site. From the <sup>1</sup>H NMR titration data as well as DFT calculations, different tentative binding modes have been established, for these structurally related ferrocenyl derivatives.

# Introduction

The development of ligands that are capable of binding and sensing different target species is currently a topic of major interest. Thus, considerable efforts have been made to design new molecular systems able to bind and sense environmentally and biologically important ionic species. Such receptors are generally formed by two components, namely a binding site and a signalling subunit which can be either independent species or covalently linked in one molecule. They are designed to exhibit a reversible easy-to-observe output (*e.g.* electrochemical, optical or fluorescent) by the signalling subunit when the interaction between the binding site and the target species takes place.<sup>1</sup> Another approach developed for the selective recognition of target analytes is based on the used of synthetic chemodosimeters. Such molecules are used to detect an analyte through a irreversible chemical reaction between them and the target analyte, giving rise to a concomitant human-

observable signal, associated with the spectroscopic properties of the new species formed.<sup>2</sup>

In this context, the ferrocene unit has largely proved to be a simple and remarkable signalling unit. Thus, the preparation and sensing properties of ferrocene derivatives containing nitrogen functionalities have been recently reviewed.<sup>3</sup> In such ferrocene-containing ligands, cation binding at an adjacent receptor site induces a positive shift in the redox potential of the ferrocene/ferrocenium couple by through-space electrostatic communication, and the complexation ability of the ligand can be switched on and off by varying the applied electrochemical potential. In addition, binding at a proximate site can also affect the UV/Vis properties of the ferrocene unit. In general, metal complexation induces bathochromic shifts in the lower-energy, spin-allowed ferrocene absorption band.

The importance of colorimetric sensors is closely related to their ability to allow the so-called "naked-eye" detection in a straightforward and inexpensive manner, offering qualitative and quantitative information without using expensive equipment. However, fluorescence sensors make the best choice, since they are qualified with high sensitivity, fast response and inexpensive installation. As fluorogenic groups, pyrenyl substituents are very attractive because of their strong and well characterized emissions, and their chemical stability.<sup>4</sup>

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On the other hand, imine-based ligands have attracted much attention in recent years in selective detection of metal ions and anions.<sup>5</sup> For this reason, the construction of new types of ligands that contain the imino functionality seems promising in a research field focused on ion detection.

In spite of the well-known ability of the aldiminic group to act as a binding site for metal cations, aldimines derived from 1,1'-diaminoferrocene have barely been studied,<sup>6</sup> probably due to difficulties found in the synthesis of the precursor 1.1'diaminoferrocene.<sup>7</sup> Nevertheless, there has been a very recently reported more efficient route for the preparation of this functionality through an aza-Wittig reaction, involving the use of the bis(iminophosphorane) derived from the 1,1'-diazidoferrocene.8 The combined effect of the binding capability of the aldimine moieties and the close proximity to the redox center makes this structural motif a likely candidate for displaying selective redox cation-sensing properties. Only recently 1,1'-N-substituted ferrocenediyl ligands derived from 1,1'-diaminoferrocene in which zirconium,9 titanium,9,10 magnesium,10a,b tin,11 and palladium12 fill the gap between the two nitrogen atoms have been reported, and a significant number of such metal complexes have recently been highlighted.13

In the context of this work, a series of aldimine derivatives have been developed owing to their good binding ability towards metal ions by exhibiting changes in their electrochemical, absorption and emission properties. Moreover, quinoline and phosphine oxide moieties have been appended in compounds **4** and **8**, respectively, in order to demonstrate the binding ability of these units in conjunction with the imine moiety, while in compound **5** a pyrene unit has been connected to the imine function due to its many interesting fluorescence properties.

### **Results and discussion**

#### Synthesis

Compounds 4 and 5 were readily synthesized starting from the 1,1'-bis(*N*-triphenylphosphoranylidenamino)ferrocene 2 or 1,1'-bis[*N*-tri(*n*-butyl)phosphoranylidenamino]ferrocene 3, readily available by a Staudinger reaction between 1,1'-diazidoferrocene 1 and triphenyl- or tributylphosphine, respectively.<sup>14</sup> These metallocenyl bis(iminophosphoranes) display the typical reactivity showed by aromatic and heteroaromatic bis(iminophosphoranes) in aza-Wittig-type reactions towards carbonyl compounds.<sup>15</sup> Thus, an aza-Wittig reaction of 2 with an equimolecular amount of 2-quinolinecarbaldehyde provided the bis(aldimine)ferrocene 4 in a moderate 46% yield. Similarly, reaction of 3 with 1-pyrenecarbaldehyde gave rise to the formation of 5 in 63% yield (Scheme 1).

By contrast, compound **8** was prepared in a moderate 40% yield following a Staudinger ligation-like procedure<sup>16</sup> by using 2-(diphenylphosphino)benzaldehyde and the 1,1'-diazidoferrocene **1**. Thus, the bis(iminophosphorane) intermediate **6**, initially formed by Staudinger reaction between the azide groups and the diphenylphosphine substituent, undergoes an intramolecular aza-Wittig reaction<sup>17</sup> through the formyl substituents and the preformed iminophosphoranes moieties, giving rise to the intermediate **7** which, in turn, undergoes ring-opening to give **8**, where a stable imine bond is formed (Scheme 2).



Scheme 1 Synthesis of receptors 4 and 5. Reagents and conditions: (a)  $Ph_3P$ , dry  $CH_2Cl_2$ , 3 h, rt,  $N_2$ ; (b) 2-quinolinecarbaldehyde, dry toluene, reflux, 10 h; (c)  $Bu_3P$ , dry THF, 1.5 h, rt,  $N_2$ ; (d) 1-pyrenecarbaldehyde, dry THF, reflux 12 h.



Scheme 2 Synthesis of receptor 8.

The structure of these aldimine derivatives **4**, **5** and **8**, was determined by means of standard spectroscopic techniques (<sup>1</sup>H and <sup>13</sup>C NMR), mass spectrometry and elemental analyses, all data being in agreement with the proposed structures

#### Electrochemical and optical sensing properties

The chemosensor behaviour of compounds **4**, **5** and **8** towards 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>), as their perchlorate or triflate salts,<sup>18</sup> was investigated by linear sweep voltammetry (LSV), cyclic voltammetry (CV), and Osteryoung square-wave voltammetry (OSWV)<sup>19</sup> as well as through UV-vis, fluorescent and <sup>1</sup>H NMR spectroscopic techniques.

Table 1	Electrochemical data for the complexes formed between	ligands
4, 5 and 8	and the corresponding metal cations	

Cation	$E_{1/2} \ [4 \cdot \mathbf{M}^{n+}]^a \ (\Delta E_{1/2})^c$	$E_{1/2} [5 \cdot \mathbf{M}^{n+}]^{b} \ (\Delta E_{1/2})^{c}$	$E_{1/2}  [8 \cdot \mathbf{M}^{n+}]^a  (\Delta E_{1/2})^c$
Li+	_		537 (60)
Ca <sup>2+</sup>			584 (107)
$Mg^{2+}$			563 (86)
Ni <sup>2+</sup>	799 (224)		_ `
Zn <sup>2+</sup>	908 (333)		683 (206)
Cd <sup>2+</sup>	849 (274)		_ `
Hg <sup>2+</sup>	936 (361)	730 (260)	
Pb <sup>2+</sup>	857 (282)		765 (288)

(9:1); <sup>*c*</sup>  $E_{1/2}$  and  $\Delta E_{1/2}$  [ $\Delta E_{1/2} = E_{1/2}$ (complex) –  $E_{1/2}$ (free ligand)], in mV.

**Electrochemical titrations.** The electrochemical responses of the ferrocene units present in **4**, **5** and **8** were investigated upon addition of varying concentrations of the above mentioned set of metal cations to the appropriate electrochemical solution of each free ligand, containing 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> (TBAHFP) as supporting electrolyte. While the electrochemical titrations using receptors **4** and **8** were carried out in CH<sub>3</sub>CN solutions ( $c = 1 \times 10^{-4}$  M), the poor solubility of **5** in the common organic solvents at the required concentration for these studies, forced us to used a mixture of CHCl<sub>3</sub>–DMF (9 : 1) ( $c = 5 \times 10^{-4}$  M).

Thus, under such conditions, each free receptor exhibited a reversible one-electron redox wave, typical of a ferrocene derivative, at the half-wave potential value of  $E_{1/2} = 575$  mV for 4,  $E_{1/2} = 470$  mV for 5, and  $E_{1/2} = 477$  mV for 8, calculated *vs*. the decamethylferrocene (DMFc) redox couple. The criteria applied for reversibility was a separation of 60 mV between cathodic and anodic peaks, a ratio for the intensities of the cathodic and anodic currents  $I_c/I_a$  of 1.0, and no shift of the half-wave potentials with varying scan rates.

The results obtained on the stepwise addition of the metal cations to acetonitrile solutions of receptors **4** and **8** are summarized in Table 1. These results clearly demonstrate a common general feature for ligands **4** and **8** which is their good binding capacity towards the divalent metal cations  $Zn^{2+}$ , and  $Pb^{2+}$  (Fig. 1a). Moreover, the presence of the nitrogen atom in the quinoline moiety allows the coordination of ligand **4** with Ni<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> metal cations (Fig. 1b and ESI<sup>†</sup>). On the other hand, while **4** does not undergo any perturbation on its corresponding CV or OSWV upon the addition of alkali or alkaline-earth metal ions, ligand **8** shows binding ability for coordinating Li<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> metal cations (see ESI<sup>†</sup>), although the anodic shifts promoted on the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple of **8** are significantly smaller than those promoted by the transition metal cations.

On the other hand, electrochemical titration experiments carried out upon addition of aliquots of the above mentioned set of metal cations to a solution of **5** in CHCl<sub>3</sub>–DMF (9:1) ( $c = 5 \times 10^{-4}$  M) demonstrate that only the addition of Hg<sup>2+</sup> causes significant changes in the redox potential of this receptor. Thus, a clear evolution of the oxidation peak to  $E_{1/2} = 730$  mV ( $\Delta E_{1/2} = 260$  mV) was observed, with a maximum perturbation of the DPV obtained when 1.4 equiv. of Hg<sup>2+</sup> ions were added. From this result we can conclude that the competitive character of DMF compared to CHCl<sub>3</sub> increases the selectivity of ligand **5**.



**Fig. 1** Evolution of the OSWV of **4** ( $c = 10^{-4}$  M) in CH<sub>3</sub>CN–n-Bu<sub>4</sub>NPF<sub>6</sub> scanned at 0.1 V s<sup>-1</sup> in the presence of increasing amounts of (a) Pb<sup>2+</sup> and (b) Hg<sup>2+</sup>; the initial black trace is that of **4** and the final blue trace, that after addition of 1 equivalent of Pb<sup>2+</sup> (a) and Hg<sup>2+</sup> (b).

The binding ability of these receptors to the selected metal cations was also demonstrated by using linear sweep voltammetry (LSV). Thus, LSV studies carried out upon addition of  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  or  $Pb^{2+}$  metal cations to the appropriate receptor revealed a shift of the linear sweep voltammogram toward more positive potentials, which is in agreement with the complexation processes as previously observed by CV and OSWV (see ESI<sup>†</sup>). However, a different effect was promoted upon addition of  $Cu^{2+}$  to receptors 4 and 5 or upon addition of  $Cu^{2+}$  and  $Hg^{2+}$  cations to 8. In such cases a significant shift of the sigmoidal voltammetric wave toward cathodic currents was mainly observed, which is consistent with the fact that those metal cations promote the oxidation of the free receptors.

UV-vis spectral titrations. One of the most important attributes of receptors 4, 5 and 8 is the presence of one ferrocene moiety in proximity to the cation-binding nitrogen atom of the imine functionality. Previous studies on ferrocene-based ligands have shown that their characteristic low-energy bands (LE) are perturbed by complexation.<sup>20</sup> Therefore, the metal coordination properties of these ligands toward the above mentioned set of metal cations were also evaluated by UV/VIS spectroscopy (Table 2), and the titration experiments were further analyzed quantitatively.<sup>21</sup>

The absorption spectrum of the free ligand 4 ( $c = 1 \times 10^{-4}$  M) in CH<sub>3</sub>CN (Table 2) exhibited two main absorption bands at 262 and 309 nm which can safely be ascribed to a  $\pi - \pi^*$  excitation, mainly within the imine bridge. In addition to this band, another weaker absorption is visible at 455 nm which is assigned to another localized excitation with a lower energy produced either by two nearly degenerate transitions, a Fe<sup>II</sup> d–d transition<sup>22</sup> or by a metalto-ligand charge transfer (MLCT) process ( $d_{\pi} - \pi^*$ ) (LE band).<sup>23</sup> Such spectral characteristics confer a red color to this species.

Titration experiments carried out upon addition of increasing amounts of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> metal cations to CH<sub>3</sub>CN solutions of receptor **4** ( $c = 1 \times 10^{-4}$  M) do not show any

 Table 2
 UV-Vis data for compounds 4, 5 and 8 and for their corresponding metal complexes

	$\lambda_{\rm max}/{\rm nm}~(10^{-3}\varepsilon/{ m M}^{-1}~{ m cm}^{-1})$	Isos. pt. <sup>a</sup>	$K_{ m as}$	$D_{\lim}{}^{b}/\mathrm{M}$
4	262 (30.86), 309 (25.80), 455 (3.46)			
<b>4</b> ·Ni <sup>2+</sup>	255 (35.91), 343 (17.06), 577 (2.33)	516, 415, 333	$3.60 \times 10^{7 d}$	$2.5 \times 10^{-5}$
$4 \cdot Zn^{2+}$	258 (29.27), 353 (19.92), 605 (2.45)	523, 419, 336	$7.04  imes 10^{6 c}$	$2.5 \times 10^{-5}$
$4 \cdot Cd^{2+}$	257 (36.43), 347 (18.89), 585 (2.87)	510, 410, 332	$6.56 \times 10^{5}$ c	$2.6 \times 10^{-5}$
4·Hg <sup>2+</sup>	254 (33.07), 360 (16.81), 608 (3.14)	513, 426, 336	$1.12 \times 10^{6}$ c	$2.8 \times 10^{-5}$
$4 \cdot Pb^{2+}$	262 (30.83), 340 (16.62), 380 (sh, 11.00), 577 (3.22)	512, 414, 333	$7.78 \times 10^{6}$ c	$2.3 \times 10^{-5}$
$5 \cdot Zn^{2+}$	479 (23.76), 651 (3.46)	416, 343, 303	$3.09 \times 10^{5}$ c	$2.9 \times 10^{-5}$
5⋅Hg <sup>2+</sup>	479 (28.46), 650 (4.06)	418, 344, 303	$1.05 \times 10^{5}$ c	$3.1 \times 10^{-5}$
5.Pb <sup>2+</sup>	484 (23.37), 662 (3.62)	416, 342, 303	$1.07 \times 10^{5 c}$	$2.8 \times 10^{-5}$
8 · Li⁺	266 (14.90), 274 (16.46), 286 (15.99), 446 (2.89)	481, 414, 318	$2.93 \times 10^{6}$ d	$1.3 \times 10^{-5}$
8.Ca <sup>2+</sup>	266 (14.99), 274 (17,06), 288 (15.86), 416 (2.76)	500, 435, 318	$1.80  imes 10^{6}$ d	$1.7 \times 10^{-5}$
8·Mg <sup>2+</sup>	266 (15.05), 274 (15.02), 297 (14.42)	329	$1.56 \times 10^{7 d}$	$1.2 \times 10^{-5}$
$8 \cdot Zn^{2+}$	266 (13.99), 274 (14.26), 291 (14.22), 462 (2.10)	316, 284	$4.81 \times 10^{7 d}$	$1.1 \times 10^{-5}$
8·Pb <sup>2+</sup>	266 (13.07), 274 (13.07), 294 (12.97), 462 (2.19)	316, 286	$6.55 \times 10^{7 d}$	$1.3 \times 10^{-5}$

<sup>&</sup>lt;sup>a</sup> Isosbestic points. <sup>b</sup> Detection limit. <sup>c</sup> In M<sup>-1</sup>. <sup>d</sup> In M<sup>-2</sup>.



**Fig. 2** Evolution of the OSWV of **5** ( $c = 10^{-4}$  M) in CHCl<sub>3</sub>–DMF (9:1), using *n*-BuN<sub>4</sub>PF<sub>6</sub> as supporting electrolyte, scanned at 0.1 V s<sup>-1</sup> in the presence of increasing amounts of Hg<sup>2+</sup> from 0 (black) to 1 equiv. (blue).

obvious absorption changes, even when they were added in a large excess. However, significant modifications were observed for the tested transition-metal ions Ni2+, Zn2+, Cd2+, Hg2+ and Pb<sup>2+</sup>. Thus, addition of such divalent metal cations caused the progressive appearance of a new low-energy band located in the region  $\lambda = 577-608$  nm as well as a decrease in the intensity of the initial band at  $\lambda = 309$  nm. These changes take place with the concomitant appearance of a new band in the region  $\lambda = 340-360$  nm, absorption value of which is dependent on the metal cation used (Table 2). The presence of well defined isosbestic points during the titration process clearly indicates that a neat interconversion between the uncomplexed and complexed species occurs. The new low-energy band is responsible for the change of color from red to blue (Zn<sup>+</sup> and Hg<sup>2+</sup>) or purple (Ni<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>). As a consequence, these changes of color can be used for a "naked eye" detection of these metals (Fig. 3 and ESI<sup>†</sup>). From analysis of the spectral titration data a 1:1 (receptor: cation) binding stoichiometries were observed for Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup> and 2:1 for Ni<sup>2+</sup>. By using the already mentioned software, the corresponding binding constants



**Fig. 3** (a) Changes in the absorption spectra of **4** (black) ( $c = 10^{-4}$  M) in CH<sub>3</sub>CN upon addition of increasing amounts of Hg<sup>2+</sup> metal cation, until 1 equiv. was added (magenta); (b) visual changes promoted upon complexation; (c) Job's plot indicating the 1:1 stoichiometry for the complex [**4**·Hg<sup>2+</sup>] formed.

were determined (Table 2). Similarly, the detection limits<sup>24</sup> were calculated are also summarized in Table 2.

For the reported constants to be taken with confidence, we have proved the reversibility of the complexation processes between receptor **4** and the above mentioned divalent metal cations. If the sensing system is reversible, depletion of the cation that coordinates the corresponding receptor must produce a change of the absorption spectra, causing it to revert to the original spectrum of the free receptor. The reversibility was tested by addition of water to the dichloromethane solutions of the complexes  $[4 \cdot M]^{2+}$ . The UV-vis spectra were recorded after the metal extraction was completed and they were identical to those of the free ligands. This process was repeated over several cycles and the optical spectra were recorded after each step, demonstrating the high degree of reversibility of the recognition process (see ESI<sup>†</sup>).

On the other hand, the optical detection capability of ligand 5 in CHCl<sub>3</sub> ( $c = 5 \times 10^{-5}$  M) toward the above mentioned set of metal cations, upon addition of increasing amounts of such ions, demonstrates that only the presence of Zn<sup>2+</sup>, Hg<sup>2+</sup> Pb<sup>2+</sup> cations led to modifications of the UV-vis spectrum of the free ligand (Table 2). By contrast, the UV-vis spectra recorded on addition of the other metal cations tested were similar to that showed by the free ligand. In fact, the long-wavelength absorption band at  $\lambda =$ 510 nm, with a molecular absorption coefficient of  $\varepsilon = 3100 \text{ M}^{-1}$ cm<sup>-1</sup>, gradually disappeared as increasing amounts of these metal cations were added. At the same time, a new red-shifted band  $(\Delta \lambda = 140 \text{ nm for } \text{Zn}^{2+} \text{ and } \text{Hg}^{2+}, \text{ and } \Delta \lambda = 152 \text{ nm for } \text{Pb}^{2+}) \text{ slowly}$ appeared, reaching the maximum absorbance when 1.6 equiv. of the metal cations were added. Meanwhile, the absorbance values at 291 and 373 nm were reduced in intensity and simultaneously a new absorbance band at around  $\lambda = 480$  nm was developed gradually (Fig. 4a and ESI<sup>†</sup>). The new LE band, which appears in the visible light region, causes a change in the colour of the solution from red to yellow which could be easily detected by the naked eye. The presence of well defined isosbestic points (Table 2) indicated the existence of a two-state equilibrium, which means that there is only one stable complex in solution.



**Fig. 4** Changes in the absorption spectra of **5** (black) ( $c = 5 \times 10^{-5}$  M) in (a) CHCl<sub>3</sub> and (b) CHCl<sub>3</sub>–DMF (9:1), upon addition of increasing amounts of Hg<sup>2+</sup> metal cation, until 1.5 equiv. (magenta) were added; (c) visual changes promoted during the complexation process.

Binding assays using the method of continuous variations (Job's plot)<sup>25</sup> suggest that **5** forms complexes with a 1:1 (receptor: cation) stoichiometry with these metal cations. The association constants and detection limits were further calculated and collected in Table 2.

Titration experiments using receptor **5** were also carried out in CHCl<sub>3</sub>–DMF (9:1) ( $c = 5 \times 10^{-5}$  M). Interestingly, under these conditions, only the addition of Hg<sup>2+</sup> promotes significant changes in the absorption spectrum of the free ligand. Nevertheless, the UV-vis spectrum of the complex formed, after addition of 1.6 equiv. of this metal cation, show identical shape, almost identical absorption coefficients and, as a consequence, the same visual changes as those observed in pure CHCl<sub>3</sub> (Fig. 4b). Thus, receptor **5** could be used as a highly selective chromogenic chemosensor for Hg<sup>2+</sup> under these conditions. The calculated detection limit  $(1.2 \times 10^{-5} \text{ M})$  was of the same order than that obtained in CHCl<sub>3</sub> solution.

With regard to receptor **8**, addition of the metal cations tested demonstrates that the stepwise addition of Li<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> metal cations promote only very slight changes in the UV-vis spectrum of the free ligand. As a consequence no change or perceptible intensification in the colour of the solution was observed. Nevertheless, these changes occur at around well-defined isosbestic points suggesting that only one spectral distinct complex is present (Fig. 5a and ESI†). The titration profiles obtained by the UV-vis experiments indicated that a 1 : 2 (receptor : metal) (Fig. 5b) adducts were formed between this receptor and those metal cations. The reversibility of the complexation/decomplexation process was also proved (see ESI†) and the apparent association constants and detection limits<sup>24</sup> were calculated (Table 2).



**Fig. 5** (a) Changes in the absorption spectra of **8** (black) ( $c = 7.5 \times 10^{-5}$  M) in CH<sub>3</sub>CN upon addition of increasing amounts of Li<sup>+</sup> metal cation, until 1 equiv. was added (magenta); (b) extended visible region of the spectrum upon Li<sup>+</sup> complexation; (c) titration profile indicating the 1:2 (metal : receptor) stoichiometry of the complex formed.

It is worth mentioning that in the cases of ligands **4** and **8** the stoichiometries proposed from absorption data have further been confirmed by either electrospray mass spectrometry ESMS) or high-resolution mass spectrometry (HRMS). The ESMS spectra of receptor **4** in the presence of  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$  metal cations show the peaks at a value of m/z corresponding to the 1:1 metal: ligand complex while the species formed between receptor **4** and Ni<sup>2+</sup> shows the molecular ion peak corresponding to the 2:1 metal: ligand complex. Moreover, the relative abundance of the isotopic clusters was in good agreement with the simulated spectrum of the corresponding complex (see ESI†). Similarly, the HRMS obtained upon addition of Li<sup>+</sup> and Ca<sup>2+</sup> metal cations also show peaks at a value of m/z corresponding to the 1:1 metal: ligand complex (see ESI†).

By contrast, the ESMS experiments carried out upon addition of metal cations to ligand **5** did not support the results obtained

through the UV/Vis titration experiments. In this case, the expected molecular ion peaks of the complexes formed did not appear and only the molecular ion peak of the naked ligand was observed. These results suggest that binding energies within these complexes are very weak, which make them unstable even in the soft ionization conditions in which the ESMS experiments were developed.

**Fluorescence titrations.** As it has already been mentioned, the synthetic method used for the preparation of these receptors, has allowed the direct connection of fluorogenic subunits onto the imine group, without drastic changes in the chromogenic properties of the ferrocene moiety.

Thus, the photophysical responses of receptors 4 and 5, upon addition of the metal cations tested, were also studied. While compound 4 ( $c = 1 \times 10^{-5}$  M in CH<sub>3</sub>CN) did not show any fluorescence emission, compound 5 ( $c = 1 \times 10^{-5}$  M both in CHCl<sub>3</sub> and in CHCl<sub>3</sub>–DMF (9:1)) exhibited a very weak emission ( $\lambda_{em} = 432$  nm,  $\Phi_0 = 1 \times 10^{-3}$ ) when excited at  $\lambda_{exc} = 290$  nm. The observed fluorescence quenching in both ligands could be due to the combination of two effects: a photoinduced electron transfer (PET) from the lone pair of the imine nitrogen to the photo-excited fluorophore and a intramolecular charger transfer process from the electron-donor ferrocene unit on the fluorescent unit.

Remarkably, none of the metal cations used above promoted the appearance of any emission band either in CH<sub>3</sub>CN solutions of **4** or in CHCl<sub>3</sub> or CHCl<sub>3</sub>–DMF (9:1) solutions of **5**, when up to 3 equiv. of metal cations were added. As we have already mentioned, a clear change in the colour, from red to yellow, was observed upon addition of Zn<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup> cations to CHCl<sub>3</sub> solutions of **5** and upon addition of Hg<sup>2+</sup> to CHCl<sub>3</sub>–DMF (9:1) solutions of the same receptor. These results clearly indicate that formation of the corresponding complexes is taking place.

Regarding receptor 5, the following experimental observations should also be noticed: (i) once Zn2+, Hg2+ and Pb2+ metal complexes are formed in the CHCl<sub>3</sub> solution, they started to discolour after 2 h; (ii) similar behaviour is also observed with the [5·Hg]<sup>2+</sup> complex, formed in the CHCl<sub>3</sub>–DMF (9:1) solution; (iii) as the solution is decoloured, a remarkable enhancement of the fluorescence was observed, giving rise to a new emission band at  $\lambda_{em} = 425$  nm ( $\Phi = 8 \times 10^{-3}$ ) when excited at  $\lambda_{exc} = 290$  (Fig. 6); (iv) the emission as well as the UV-vis spectra of such discoloured solutions are identical to those of the 1-pyrenecarbaldehyde in the same solvent (ESI<sup>†</sup>), which indicates that after 2 h such complexes started to decompose by hydrolysis of the imine unit; (v) the breakup of the imine moiety speeds up if water is added to the CHCl<sub>3</sub>-DMF (9:1) solution of [5·Hg]<sup>2+</sup> complex; (vi) moreover, such break-up is only induced once the corresponding metal complexes are formed, because the free ligand remains stable even when water was added to its CHCl<sub>3</sub>-DMF (9:1) solution.

Taking into account these observations it could be concluded that receptor **5** behaves as a chemodosimeter<sup>2</sup> for the fluorescent detection of  $Hg^{2+}$  metal cations in  $CHCl_3$ –DMF (9:1) solution: in a first step, the metal cation is complexed by the free receptor and in a second step, the  $Hg^{2+}$  cation catalyzes an irreversible chemical reaction which involves the hydrolysis of the imine functionality. As the final compound is chemically different to the original one, the spectroscopic characteristics of the solution are completely



**Fig. 6** (a) Changes in the emission spectra of **5** ( $c = 1 \times 10^{-5}$  M) in CHCl<sub>3</sub>–DMF (9:1), upon addition of increasing amounts of Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup> metal cations, until 1 equiv. was added; (b) Comparison of the emission spectra, in CHCl<sub>3</sub>–DMF (9:1), of the free receptor **5** (black) and those obtained upon addition of Hg<sup>2+</sup> metal cation to **5** (blue) and pyrene carbaldehyde (magenta).

different to those of the free receptor and, consequently, the determination of the cation is shown.

<sup>1</sup>H NMR spectral titrations. The binding of Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup> cations for receptor 4 was also clear from the <sup>1</sup>H NMR spectral titrations carried out in CD<sub>3</sub>CN. In this deuterated solvent, compound 4 showed five different signals before the addition of these metal cations: one associated with the imine CH=N proton, at  $\delta = 8.46$  ppm; two pseudo-triplets at  $\delta =$ 4.85 and 4.37 ppm, corresponding to the H $\alpha$  and H $\beta$  protons, respectively, of the monosubstituted cyclopentadienyl (Cp) rings present in the ferrocene moiety, and two multiplets centered at  $\delta = 7.57$  and 7.41 ppm associated with the protons of the heterocyclic ring. Upon addition of increasing amounts of the above-mentioned metal cations, the following common features were observed: (i) the hydrogen atom within the imine group showed a significant downfield shift, demonstrating that this unit is involved in the ligand-cation binding event; (ii) downfield shifts were also observed for the H $\alpha$  and H $\beta$  protons of the Cp rings; (iii) the signals associated with the heterocyclic ring are much better resolved and downfield shifted, which could also be related to the participation of the quinoline nitrogen atom in the binding process. These changes in the aromatic region can be easily observed in Fig. 7 (see also the ESI<sup>†</sup>) where four doublets, attributable to H4 ( $\delta$  = 9.12 ppm), H3 ( $\delta$  = 8.39 ppm), H8 ( $\delta$  = 8.32 ppm) and H5 ( $\delta$  = 8.15 ppm), and two triplets, attributable to H7 ( $\delta$  = 7.96 ppm) and H6 ( $\delta$  = 7.83 ppm), appeared.

<sup>1</sup>H NMR experiments were also performed to study the recognition process of receptor **5** with  $Zn^{2+}$ ,  $Hg^{2+}$  and  $Pb^{2+}$  cations. In the free ligand, eight different doublets and one triplet appear, associated with the pyrene ring protons, as well as a singlet and two pseudo-triplets, corresponding to the protons within CH==N and the monosubstituted Cp moieties present in this ferrocene derivative. The most remarkable features observed during the formation of the 1 : 1 complexes with  $Zn^{2+}$  and  $Pb^{2+}$  metal cations



Fig. 7 Evolution of the <sup>1</sup>H NMR spectra, in the ferrocene and aromatic regions, of 4 (top) in CD<sub>3</sub>CN upon addition of aliquots of  $Hg^{2+}$  until 1 equiv. was reached (bottom).

are the downfield shifting of H $\alpha$  ( $\Delta\delta$  = 0.50 ppm for Zn<sup>2+</sup> and  $\Delta\delta$  = 0.39 ppm for Pb<sup>2+</sup>) and H $\beta$  ( $\Delta\delta$  = 0.15 ppm for Zn<sup>2+</sup> and  $\Delta\delta$  = 0.22 ppm for Pb<sup>2+</sup>) signals together with the signal attributed to the H10 proton of the pyrene ring ( $\Delta\delta$  = 0.10 ppm for both metal cations) (Fig. 8 and ESI<sup>†</sup>).

By contrast, the most relevant interaction-induced chemical shift during the titration with Hg<sup>2+</sup> metal cations, which promoted the formation of complexes with a 1:1 stoichiometry, was found to be the bigger downfield shift of the H4, H5 and H7, within the 1-pyrenyl substituent, and the downfield shift of the H $\alpha$  ( $\Delta\delta$ =0.91 ppm), H $\beta$  ( $\Delta\delta$ =0.29 ppm) and H10 proton of the pyrene ring ( $\Delta\delta$ = 0.26 ppm). It is important to note that while the signal associated with the imine proton was almost unaffected by Zn<sup>2+</sup> and Pb<sup>2+</sup> metal cations, it was downfield shifted by Hg<sup>2+</sup>. Moreover, while in the case of Zn<sup>2+</sup> and Pb<sup>2+</sup> it appears as a singlet, when Hg<sup>2+</sup> is the metal cation added, this signal is split into two different singlets (Fig. 9).

The binding capability of receptor **8** toward the metal cations selected was also studied by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopies. Once again, these results clearly demonstrate a high affinity of this receptor towards Li<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> metal cations. However, these titration experiments evidenced a different evolution for the CH==N proton than that observed for ligands **4** and **5**. In fact, the singlet associated with this group is now shifted upfield by  $\Delta \delta = -0.37$  ppm (Li<sup>+</sup>),  $\Delta \delta = -0.53$  ppm (Ca<sup>2+</sup>),  $\Delta \delta = -0.64$  ppm (Mg<sup>2+</sup>),  $\Delta \delta = -0.74$  ppm (Zn<sup>2+</sup>), and  $\Delta \delta = -0.61$  ppm (Pb<sup>2+</sup>). Similarly, the signals corresponding to the H3 and H6 protons within the benzylidene unit experienced also an upfield shifting although in a less extent, while the other aromatic signals are broadened during the titrations. Moreover, the H $\alpha$  and H $\beta$  ferrocene signals were shifted downfield as the complexes were formed (Fig. 10 and ESI<sup>+</sup>).



Fig. 8 Evolution of the <sup>1</sup>H NMR spectra, in the ferrocene and aromatic regions, of 5 (top) in CDCl<sub>3</sub> upon addition of aliquots of  $Zn^{2+}$  until 1 equiv. was reached (bottom).



**Fig. 9** Evolution of the <sup>1</sup>H NMR spectra, in the ferrocene and aromatic regions, of **5** (top) in CDCl<sub>3</sub> upon addition of aliquots of  $Hg^{2+}$  until 1 equiv. was reached (bottom).

As far as the <sup>31</sup>P NMR titrations are concerned, it is worth mentioning that the signal of the P=O group in the metal complexes formed is deshielded with reference to that of the free receptor by  $\Delta\delta$ =4.8 ppm (Li<sup>+</sup>),  $\Delta\delta$ =6.7 ppm (Ca<sup>2+</sup>),  $\Delta\delta$ =13.8 ppm (Zn<sup>2+</sup>) and  $\Delta\delta$  = 12.0 ppm (Pb<sup>2+</sup>) (Fig. 11 and ESI†). The upfield shifting of the CH=N signals along with the downfield shifting of



Fig. 10 Evolution of the <sup>1</sup>H NMR spectra, in the ferrocene and aromatic regions, of 8 (top) in CD<sub>3</sub>CN upon addition of aliquots of Li<sup>+</sup> until 1 equiv. was reached (bottom).



Fig. 11 Evolution of the  ${}^{31}$ P NMR spectra of 8 (top) in CD<sub>3</sub>CN upon addition of 1 equiv. of Li<sup>+</sup> (bottom).

the P=O signals could indicate that the recognition process of this receptor takes place through the phosphoryl oxygen atom instead of the imine nitrogen atom.

Interestingly, <sup>7</sup>Li NMR spectroscopic studies carried out upon addition of LiClO<sub>4</sub> to a solution of receptor **8** also indicates the formation of the proposed  $[8 \cdot Li]^+$  complex (see ESI<sup>†</sup>).

In spite of the closely related structures of receptors 4, 5 and 8, these spectroscopic studies could be used to suggest three different tentative binding modes of these receptors towards the metal cations. In receptor 4 the remarkable downfield shift observed for the aldiminic proton as well as those within the heteroaromatic ring clearly suggest that the aldiminic and the pyridine-like nitrogen atoms are involved in the recognition event. In receptor 5 important perturbations of some of the pyrene and cyclopentadienyl protons, along with a small shift of the aldiminic protons suggests an appreciable interaction between the metal cation and the pyrene and ferrocene units during the recognition process. However, in receptor 8, the upfield shift of the aldiminic

Theoretical calculations. OC calculations (see Computational details) were undertaken in order to obtain some additional insight into the stoichiometries and binding modes of the complexes mentioned so far. 1:1 Complexes of Zn<sup>2+</sup> and Hg<sup>2+</sup> with receptors 4 and 5 as well as model ligand 9 (analogous to 8 but with methyl instead of phenyl substituted at phosphorus) were studied as well as the 1:2 metal: ligand complex resulting upon complexation of 4 with  $Ni(ClO_4)_2$ . The most significant geometrical and bonding features are collected in Table 3. The 4·[Ni(ClO<sub>4</sub>)<sub>2</sub>]<sub>2</sub> complex shows a most stable quintuplet, and thus paramagnetic, electronic configuration with overall  $C_i$ -symmetry and the Ni<sup>2+</sup> cation is hexacoordinated by two receptor N atoms and four perchlorate O atoms. Most likely this stoichiometry is preferred due to its low ligand strain (8.05 kcal mol<sup>-1</sup> per Ni<sup>2+</sup> ion) in comparison to an hypothetical 1:1 complex with ligand 4 using its four N donor atoms to wrap the small Ni<sup>2+</sup> cation ( $L_{\text{strain}} = 27.63 \text{ kcal mol}^{-1}$ for  $1 \cdot [Ni(ClO_4)_2]$ ). On the contrary, the same ligand 4 can easily furnish the required convergent tetrahedral environment around Zn<sup>2+</sup> and the larger Hg<sup>2+</sup> cation, the latter requiring very little ligand deformation (Fig. 12). In all three cases the bond between the metal and the imine N atoms are weaker than those with the other quinoleine N atoms.



Fig. 12 Calculated structure for the complex [4·Hg]<sup>2+</sup>.

Similar behaviour is observed in the case of complexes with the model phosphine-oxide **9**, whose  $[9 \cdot Zn]^{2+}$  complex also displays stronger M–O bonds. The high computed ligand strain energy can be partially attributed to the existence of two components which in principle are common to all the cations. On the one hand, there is the required energy to break two hydrogen bonds at every side-arm of the free ligand **9**, between the oxide O atom and two H atoms, which is estimated to amount to 2.25 kcal mol<sup>-1</sup>.<sup>26</sup> On the other hand, the high strain energy can be also attributed to the distorted P–O bond length in the chelate (1.529 Å) in comparison to the free ligand **9** (1.487 Å). Ligand strain energies become significantly lower when these two effects are corrected.

	$4 \cdot [\mathrm{Ni}(\mathrm{ClO}_4)_2]_2$	$[4 \cdot Zn]^{2+}$	<b>[4</b> ·Hg] <sup>2+</sup>	<b>[9</b> ⋅ <b>Z</b> n] <sup>2+</sup>	$[5\cdot\mathbf{Zn}(\mathbf{OTf})_2]$	<b>[5</b> ·Hg] <sup>2+</sup>
$d_{\rm NM}/{\rm \AA}$	2.079	2.075	2.403	2.049	2.063	2.331
$10^2 \rho(\mathbf{r}_c)_{\rm NM} / e a_0^{-3}$	7.38	7.57	5.97	7.92	7.71	6.85
WBINM	0.255	0.230	0.224	0.186	0.197	0.232
LBO <sub>N-M</sub>	0.502	0.511	0.390	0.533	0.523	0.437
$d_{\rm Do-M}/{\rm \AA}$	$2.061, 2.134^{a}$	2.039	2.242	1.986	1.976	2.237
$10^2 \rho(\mathbf{r}_c)_{\rm Do-M}/e a_0^{-3}$	7.68, 22.74	8.25	8.40	7.73	8.01	7.21
WBI <sub>Do-M</sub>	$0.263, 0.952^{b}$	0.254	0.326	0.183	0.192	0.209
LBO	$0.519, 2.067^{b}$	0.563	0.528	0.689	0.715	0.565
$L_{\rm strain}/\rm kcal\ mol^{-1}$	16.10	21.25	17.85	16.12	33.59 (28.82) <sup>c</sup>	31.42 (26.83) <sup>c</sup>

Table 3 Relevant geometric and bonding parameters for all studied complexes

" Average of four Ni–O bonds. " Sum of four Ni–O bonds. " Corrected values (see text).

The complexation of "naked" cations giving rise to complexes  $[L \cdot M]^{2+}$  (for L = 4, M = Zn or Hg and for L = 9, M = Zn) in which the first coordination sphere around the cation M<sup>2+</sup> is exclusively occupied by donor atoms belonging to the receptor L, promotes an strong polarization of the later – a significant electronic inductive withdrawing effect of M<sup>2+</sup> onto ligand L – which accounts for the downfield shift of many relevant signals as observed in <sup>1</sup>H NMR spectra (Fig. 7 and ESI<sup>†</sup>)

On the contrary, the 1-pyrenyl appended ligand **5**, featuring only two typical donor atoms, displays a behaviour strongly dependent on the metal cation. Thus, towards zinc(II) ditriflate, only the two imine N atoms in the receptor are involved in the complexation event, the other two coordinative positions required to saturate the tetrahedral environment around the  $Zn^{2+}$  cation being occupied by triflate O atoms. This results in an small polarization effect of the whole Zn(OTf)<sub>2</sub> unit on the receptor unit, which in turn is reflected in the very slight shifts observed in the <sup>1</sup>H NMR spectrum (Fig. 8). In this [ $5 \cdot Zn(OTf)_2$ ] complex the overall host–guest linkage is reinforced by three sets of supplementary interactions between the receptor and triflate O atoms.<sup>27</sup>

Conversely,  $Hg^{2+}$  cations exhibit a well-known preference for a linear dicoordination<sup>28</sup> in this case between an imine N atom and a pyrene C-10 atom<sup>29</sup> belonging to the other side-arm. As a consequence, the resulting structure is asymmetric, the Hg atom retaining weak additional bonding interactions with the other two donor positions (the other imine N atom and the other pyrene C-10 atom) that very likely constitute the strong bonding positions in another equivalent structure. The interconversion between both degenerate minima should proceed through a tetracoordinated (presumably  $C_2$ -symmetric) transition state, high enough in energy to make the process slow in the NMR time-scale, therefore accounting for the observed splitting in the iminic H atoms (and other) signals (Fig. 13).

# Conclusions

In summary, we describe a type of readily synthesized neutral ferrocene-based receptors and examined their binding properties towards various metal cations guest by using electrochemical and spectral techniques as well as DFT calculations. The receptor **4**, bearing a quinoline ring behaves as chemosensor molecule for Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup>. cations acting through two different channels: electrochemical and chromogenic. On the other hand, receptor **5**, bearing a pyrene ring, behaves as



Fig. 13 Calculated structure for the complex [5·Hg]<sup>2+</sup>.

a dual redox and optical chemosensor molecule for  $Zn^{2+}$ ,  $Hg^{2+}$ and  $Pb^{2+}$  metal cations in CHCl<sub>3</sub>: the oxidation redox peak is anodically shifted (up to 200 mV) and the low energy band is increased in the presence of these metal cations. However, by using CHCl<sub>3</sub>–DMF (9:1) as solvent, receptor **5** behaves as a fluorometric chemodosimeter which selectively senses the presence of  $Hg^{2+}$  even in the presence of a large excess of the other metal cations tested. Finally, electrochemical and spectroscopies studies carried out on the receptor **8** showed the affinity of this receptor towards metal cations such as Li<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> metal cations

The spectral data obtained during the titration of these receptors were used to establish the stoichiometries of the metal complexes formed and through <sup>1</sup>H NMR titration data and DFT calculations plausible binding modes between the receptors and the metals have also been proposed.

# Experimental

#### General methods

All reactions were carried out under  $N_2$  and using solvents which were dried by routine procedures. Melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on Bruker AC300 and 400 spectrometers. The following abbreviations for stating the multiplicity of the signals have been used; s (singlet), d (doublet), pt (pseudotriplet), q (quaternary carbon). Chemical shifts refer to signals of tetramethylsilane in the case of <sup>1</sup>H and <sup>13</sup>C spectra. The electron impact (EI) and electrospray (ESI) mass spectra were recorded on a Fisons AUTOSPEC 500 VG spectrometer. Microanalyses were performed on a Carlo Erba 1108 instrument. CV and OSWV techniques were performed with a conventional three-electrode configuration consisting of a carbon working and platinum auxiliary electrodes and a Ag/AgCl reference electrode. The experiments were carried out with a 10<sup>-4</sup> M solution of sample in CH<sub>3</sub>CN or CHCl<sub>3</sub> containing 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> (TBAPF<sub>6</sub>) as supporting electrolyte. All the potential values reported are relative to the decamethylferrocene (DMFc) couple at room temperature. Deoxygenation of the solutions was achieved by bubbling nitrogen for at least 10 min and the working electrode was cleaned after each run. The cyclic voltammograms were recorded with a scan rate increasing from 0.05 to 1.00 V s<sup>-1</sup>, while the OSWV were recorded at a scan rate of 100 mV s<sup>-1</sup> with a pulse height of 10 mV and a step time of 50 ms. Typically, receptor  $(1 \times 10^{-4} \text{ M})$  was dissolved in the appropriate solvent (5 mL) and  $TBAPF_{6}$  (base electrolyte) (0.190 g) added. The guest under investigation was then added as a  $2.5 \times 10^{-2}$  M solution in appropriate solvent using a microsyringe whilst the cyclic voltammetric properties of the solution were monitored. DMFc was used as an external reference both for potential calibration and for reversibility criteria. Under similar conditions DMFc has E = -0.07 V vs. SCE and the anodiccathodic peak separation is 67 mV.

UV-vis and fluorescence spectra were carried out in the solvents and concentrations stated in the text and in the corresponding figure captions. Quantum yield values were measured with respect to anthracene as standard ( $\Phi = 0.27 \pm 0.01$ ),<sup>30</sup> using the equation  $\Phi_x/\Phi_s = (S_x/S_s)[(1-10^{-4s})/(1-10^{-4s})]$ ,<sup>2</sup> where x and s indicate the unknown and standard solution, respectively,  $\Phi$  is the quantum yield, S is the area under the emission curve and A is the absorbance at the excitation wavelength.

Synthesis of 1,1'-bis[(2-quinolyl)methyleneamino]ferrocene, 4. To a solution of 2-quinolinecarbaldehyde (0.1 g, 0.63 mmol) in dry toluene (20 ml) a solution of 1,1'-bis(Ntriphenylphosphoranaylidenamino)ferrocene 2 (0.23 g, 0.31 mol) in the same solvent (40 ml) was added. The reaction mixture was heated under reflux temperature for 10 h. On cooling, the solvent was removed under reduced pressure and the resulting crude product was chromatographed on a silica gel column using  $CH_2Cl_2$ -MeOH (9:1) as eluent to give compound 4 in 46% yield (0.07 g). Mp 236–240 °C (decomp.). Found: C 72.61, H, 4.28, N, 11.58. Calc. for C<sub>30</sub>H<sub>22</sub>FeN<sub>4</sub>: C 72.89, H 4.49, N 11.33%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.36 (pt, 2H), 4.80 (pt, 2H), 7.31 (1 H, d, J = 8.0 Hz), 7.36 (1 H, d, J = 8.4 Hz), 7.39 (1 H, t, J = 8.0 Hz), 7.53 (1 H, t, J = 8.0 Hz), 7.75 (1 H, d, J = 8.4 Hz), 7.81 (1 H, d, J = 8.4 Hz), 8.55 (1H, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  65.0 (2 × CH), 69.3 (2 × CH), 103.0 (q), 117.6 (CH), 126.6 (CH), 127.4 (CH), 127.9 (q), 128.9 (CH), 129.3 (CH), 135.3 (CH), 147.4 (q), 154.9 (q), 158.6 (CH=N). EI MS (70 eV): m/z (%): 494 (M<sup>+</sup>, 57), 339 (100).

Synthesis of 1,1'-bis[(1-pyrenyl)methyleneamino]ferrocene, 5. To a solution of 1,1'-diazidoferrocene 1<sup>8</sup> (0.1 g, 0.37 mmol) in dry THF (30 ml),  $Bu_3P$  (0.31 ml, 1.2 mmol) was added. The resulting solution was stirred at room temperature and under nitrogen for 1.5 h. Then, 1-pyrenecarbaldehyde (0.17 g, 0.74 mmol) was added and the reaction mixture was refluxed for 12 h. On cooling, the solvent was removed under vacuum and the resulting crude was crystallized from CH<sub>2</sub>Cl<sub>2</sub> to give **5** as a purple solid in 63% yield (0.150 g). Mp 280–282 °C (decomp.). Found: C 82.74, H, 4.64, N, 4.21. Calc. for C<sub>44</sub>H<sub>28</sub>FeN<sub>2</sub>: C 82.50, H 4.41, N 4.37%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  4.41 (pt, 2H), 4.89 (pt, 2H), 7.30 (1 H, d, J = 8.7 Hz), 7.38 (1 H, d, J = 8.1 Hz), 7.46 (1 H, d, J = 9.3 Hz), 7.55 (1 H, d, J = 8.7 Hz), 7.65 (1 H, d, J = 7.5 Hz), 7.67 (1 H, t, J = 7.5 Hz), 7.83 (1 H, d, J = 7.5 Hz), 8.21 (1 H, d, J = 8.1 Hz), 8.24 (1 H, d, J = 9.3 Hz), 9.20 (1H, s). <sup>13</sup>C NMR was impossible to register due to the very low solubility of this compound in the common deuterated solvents. ESI MS: m/z (%): 641 (M<sup>+</sup> + 1, 40).

Synthesis of 1,1'-bis[(2-diphenylphosphoryl)benzylideneamino]ferrocene, 8. To a solution of 1,1'-diazidoferrocene 1 (0.1 g, 0.37 mmol) in dry THF (15 ml), a solution of 2-(diphenylphosphino)benzaldehyde (0.22 g, 0.74 mmol) in the same solvent (30 ml) was added. The reaction mixture was first stirred at room temperature for 2 h and afterwards it was refluxed for 16 h. Then, the solvent was eliminated under reduced pressure and the resulting product was recrystallized in CH2Cl2-n-hexane (6:4) to give 8 as a reddish solid in 40% yield (0.120 g). Mp 220-224 °C (decomp.). Found: C 72.51, H 4.59, N 3.79. Calc. for C48H38FeN2O2P2: C 72.74, H 4.83, N 3.53%. 1H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.86 (pt, 2H), 4.20 (pt, 2H), 7.05 (1H, d,  ${}^{3}J_{PH} = 7.8$ Hz,  ${}^{3}J_{HH} = 7.6$  Hz), 7.29 (2H, t, J = 7.6 Hz), 7.53 (10H, m), 8.23  $(1H, d, {}^{3}J_{HH} = 7.6 \text{ Hz}, {}^{3}J_{PH} = 3.6 \text{ Hz}), 9.33 (1 \text{ H}, \text{ s}). {}^{13}\text{C} \text{ NMR}$  (75) MHz, CDCl<sub>3</sub>):  $\delta$  64.4 (2 × CH), 69.7 (2 × CH), 104.8 (q), 127.8 (CH,  ${}^{2}J_{PC} = 9.3$  Hz), 128.8 (CH,  ${}^{3}J_{PC} = 12.2$  Hz), 129.1 (CH,  ${}^{3}J_{PC} =$ 11.5 Hz), 130.9 (q), 131.9 (CH,  $J_{PC} = 9.8$  Hz), 132.1 (CH,  ${}^{4}J_{PC} =$ 2.5 Hz), 132.2 (CH), 133.3 (CH,  ${}^{3}J_{PC} = 11.5$  Hz), 136.6 (q), 140.8  $(q, {}^{2}J_{PC} = 6.3 \text{ Hz}), 156.8 \text{ (CH=N, }{}^{3}J_{PC} = 6.4 \text{ Hz}). {}^{31}\text{P} \text{ NMR} (121)$ MHz, CDCl<sub>3</sub>): δ 32.15. ESI MS: *m*/*z* (%): 815 (M<sup>+</sup> + 23, 51), 793  $(M^+ + 1, 71)$ 

Computational details. Quantum chemical calculations were performed with the ORCA electronic structure program package.<sup>31</sup> All geometry optimizations were run without symmetry constraints, with tight convergence criteria,32 first at the B3LYP33 together with the new efficient RIJCOSX algorithm<sup>34</sup> and the def2-SVP35 basis set and thereafter refined with the def2-TZVP basis set.<sup>36</sup> For Hg atoms the [OLD-SD(60,MDF)] effective core potencial<sup>37</sup> (ECP) was used. In all optimizations a semiempirical correction accounting for the major part of the contribution of dispersion forces to the energy was included.<sup>38</sup> From these gasphase optimized geometries all reported data were obtained by means of single-point (SP) calculations using the more extended def2-TZVPP basis set.<sup>39</sup> Reported energies are uncorrected for the zero-point vibrational term. Ligand strain energies are obtained comparing the energy of the optimized free ligand with those of the frozen ligands after removing the metallic units. Löwdin bond orders (LBO) were obtained upon Löwdin population analysis<sup>40</sup> as implemented in the ORCA program. The topological analysis of the electronic charge density was conducted using the AIM2000 software<sup>41</sup> and the wavefunctions generated with the Gaussian09 software package.<sup>42</sup> Wiberg's Bond Indices (WBI)<sup>43</sup> were obtained from the Natural Bond Orbital (NBO) analysis.44 Fig. 12 and 13 were generated with VMD.45

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