Electronic Supplementary Information

Ferrocene-based multichannel molecular chemosensors with high selectivity and sensitivity for Pb(II) and Hg(II) metal cations

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2-Ferrocenil-7,8-Diphenyl-3H-imidazo[4,5-f]quinoxalines, [6a]

$^1$H NMR (400MHz, MeOD)

$^{13}$C NMR (100 MHz, CDCl$_3$):
5-amino-6-nitro-2,3-di(2-pyridyl)quinoxaline, [4b]

$^1$H NMR (400MHz, CDCl$_3$): 

$^{13}$C NMR (100 MHz, CDCl$_3$):
5,6-diamino-2,3-di(2-pyridyl)quinoxaline, [5b]

$^1$H NMR (400MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
2-Ferrocenyl-7,8-Di-(2-pyridyl)-3H-imidazo[4,5-f]quinoxalines, [6b]

$^1$H NMR (400MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
Figure SI 1. Evolution of the CV (left) and OSWV (right) of 6a (1 mM) in CH$_3$CN/[(n-Bu)$_4$]ClO$_4$ scanned at 0.1 V s$^{-1}$ in the presence of increasing amounts of: (a) Cd$^{2+}$; (b) Zn$^{2+}$; (c) Hg$^{2+}$. 
Figure SI 2. Evolution of the CV (left) and OSWV (right) of 6b (1 mM) in CH$_3$CN/[(n-Bu)$_4$]ClO$_4$ scanned at 0.1 V s$^{-1}$ in the presence of increasing amounts of: (a) Pb$^{2+}$; (b) Cd$^{2+}$; (c) Zn$^{2+}$; (d) Ni$^{2+}$. 
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Figure SI 14. Stepwise complexation [addition of (a) Cd$^{2+}$; (b) Zn$^{2+}$; (c) Hg$^{2+}$; (d) Pb$^{2+}$; (e) Ni$^{2+}$]/decomplexation (extraction with H$_2$O) cycles of ligand 6b (c = 1x10$^{-4}$M in CH$_2$Cl$_2$) carried out by UV/Vis analysis.
Figure SI 15. Absorbance of 6a (c = 1·10^{-4}M in CH$_3$CN) at each concentration of cation added (a) Cd$^{2+}$; (b) Zn$^{2+}$; (c) Hg$^{2+}$; (d) Pb$^{2+}$, normalized between the minimum absorbance, found at zero equiv of metal cation; and the maximum absorbance, found at (a) [Cd$^{2+}$]=1.72·10^{-5} M; (b) [Zn$^{2+}$]=1.31·10^{-5} M; (c) [Hg$^{2+}$]=1.15·10^{-5} M; (d) [Pb$^{2+}$]=1.30·10^{-5} M.
Figure SI 16. Absorbance of 6b (c = 1·10^{-4}M in CH$_3$CN) at each concentration of cation added (a) Cd$^{2+}$; (b) Zn$^{2+}$; (c) Hg$^{2+}$; (d) Pb$^{2+}$; (e) Ni$^{2+}$ normalized between the minimum absorbance, found at zero equiv of metal cation; and the maximum absorbance, found at (a) [Cd$^{2+}$]=1.50·10^{-5} M; (b) [Zn$^{2+}$]=1.16·10^{-5} M; (c) [Hg$^{2+}$]=1.25·10^{-5} M; (d) [Pb$^{2+}$]=7.58·10^{-6} M; (e) [Ni$^{2+}$]=9.74·10^{-6} M.
**Figure SI 17.** Fluorescence intensity of ligand (a) 6a; (b) 6b, in CH$_3$CN, after addition of 1 equiv of several cations. Emission monitored at (a) $\lambda_{\text{exc}}$ = 330 nm; (b) $\lambda_{\text{exc}}$ = 310 nm.

**Figure SI 18.** Changes in the fluorescence emission spectrum of 6a ($c = 1 \times 10^{-5}$ M in CH$_3$CN) upon titration with Pb$^{2+}$: the initial (black) is that of 6a and the final one (deep cyan), after addition of 1.4 equiv of Pb$^{2+}$ ($c = 2.5 \times 10^{-3}$ M in CH$_3$CN). Emission is monitored at $\lambda_{\text{exc}}$ = 330 nm.
Figure SI 19. Changes in the fluorescence emission spectrum of 6b (c = 1 x 10^{-5} M in CH$_3$CN) upon titration with Hg$^{2+}$: the initial (black) is that of 6b and the final one (deep blue), after addition of 1.2 equiv of Hg$^{2+}$ (c = 2.5x10^{-3} M in CH$_3$CN). Emission is monitored at $\lambda_{\text{exc}} = 310$ nm.

Figure SI 20. Fluorescence intensity of (a) 6a; (b) 6b (1x10^{-5} M in CH$_3$CN), at each concentration of (a) Pb$^{2+}$; (b) Hg$^{2+}$ added, normalized between the minimum fluorescence intensity, found at zero equiv of cation, and the maximum fluorescence intensity, found at (a) [Pb$^{2+}$]= 5.25x10^{-6} M; (b) [Hg$^{2+}$]= 1.81x10^{-6} M.
Figure SI 21. Changes in the $^1$H-NMR (in acetone-d$_6$) spectrum of 6a (top) in acetone upon addition of increasing amounts of Cd$^{2+}$ until 0.6 equiv (bottom).

Figure SI 22. Changes in the $^1$H-NMR (in acetone-d$_6$) spectrum of 6a (top) in acetone upon addition of increasing amounts of Zn$^{2+}$ until 1.0 equiv (bottom).
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Figure SI 24. Changes in the $^1$H-NMR (in acetonitrile-$d_3$) spectrum of $6b$ (top) in acetone upon addition of increasing amounts of Pb$^{2+}$ until 0.6 equiv (bottom).
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Figure SI 26. Changes in the $^1$H-NMR (in acetonitrile-d$_3$) spectrum of 6b (top) in acetone upon addition of increasing amounts of Cd$^{2+}$ until 1.0 equiv (bottom).
Figure SI 27. Changes in the $^1$H-NMR (in acetone-d$_6$) spectrum of 6b (top) in acetone upon addition of increasing amounts of HP$_2$O$_7$ until 2.0 equiv (bottom).
Figure SI 28. Relative abundance of the isotopic cluster for (a) $6a_2$·Cd$^{2+}$; (b) $6a_2$·Zn$^{2+}$; (c) $6a_2$·Hg$^{2+}$; (d) $6a_2$·HP$\text{O}_7$$^{3-}$ (top) simulated; (bottom) experimental.
Figure SI 29. Relative abundance of the isotopic cluster for (a) $6b_2 \cdot Cd^{2+}$; (b) $6b_2 \cdot Zn^{2+}$; (c) $6c_2 \cdot Ni^{2+}$ (top) simulated; (bottom) experimental.