Supporting Information (SI)

Highly selective mercury(II) cations detection in mixed/aqueous media by a ferrocene-based fluorescent receptor

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Calculated structures. Cartesian coordinates (in Å) and energies for all computed species.
2-Ferrocenyl-3H-imidazo[4,5-h]phenanthro[4,5-abc]phenazine (3):

$^1$H NMR (400 MHz, DMF-d$_7$)

Figure S1. $^1$H NMR spectra of 3.
\[ ^{13}C \text{ NMR (100 MHz, DMF-d}_7) \]

Figure S2. \[ ^{13}C \] NMR spectra of 3.
Figure S3. CV (a) and OSWV (b) of 3 (1x10^{-4} M) in CH_{3}CN using [(n-Bu)_{4}N]PF_{6} as supporting electrolyte.

Figure S4. Evolution of the CV of 3 (1x10^{-4} M) in CH_{3}CN in the presence of increasing amounts of Zn (OTf)_{2} using [(n-Bu)_{4}N]PF_{6} as supporting electrolyte.
Figure S5. Evolution of the OSWC of 3 (1x10^{-4} M) in CH₃CN in the presence of increasing amounts of Zn (OTf)₂ using [(n-Bu)₄N]PF₆ as supporting electrolyte.

Figure S6. Evolution of the LSW of 3 (1x10^{-4} M in CH₃CN) in the presence of increasing amounts of Cu(OTf)₂ obtained by using a rotating disk electrode at 100 mVs⁻¹ and 1000 rpm and [(n-Bu)₄N]PF₆ 0.1 M as supporting electrolyte.
Figure S7. Changes in the absorption spectra of 3 (c = 5 x 10^{-5} M in CH₃CN) upon addition of increasing amounts of Cu(OTf)₂, from 0 (black) to 1 equiv (deep red). Arrows indicate absorptions that increase or decrease during the experiment.

Figure S8. Evolution of the LSW of 3 (1x10⁻⁴ M in CH₃CN) in the presence of increasing amounts of Zn(OTf)₂ obtained by using a rotating disk electrode at 100 mVs⁻¹ and 1000 rpm and [(n-Bu)₄ N]PF₆ 0.1 M as supporting electrolyte.
**Figure S9.** Evolution of the LSW of 3 (1x10^{-4} M in CH$_3$CN) in the presence of increasing amounts of Hg(OTf)$_2$ obtained by using a rotating disk electrode at 100 mVs$^{-1}$ and 1000 rpm and [(n-Bu)$_4$ N]PF$_6$ 0.1 M as supporting electrolyte.

**Figure S10.** Changes in the absorption spectra of 3 (c = 5 x 10^{-5} M in CH$_3$CN) upon addition of increasing amounts of Hg(OTf)$_2$, from 0 (black) to 0.5 equiv (deep red). Arrows indicate absorptions that increase or decrease during the experiment.
Figure S11. Changes in the absorption spectra of 3 (c = 5 x 10^-5 M in CH3CN) upon addition of increasing amounts of Zn(OTf)2, from 0 (black) to 1.0 equiv (deep red). Arrows indicate absorptions that increase or decrease during the experiment.

Figure S12. Job’s plot for 3 [c = 1 x 10^-3 M in CH3CN] and Hg(OTf)2 [0.1 mM in CH3CN], indicating the formation of a 2:1 complex.

Figure S113. Titration profile showing the absorbance change as a function of the equivalents of Zn(OTf)2 added.
Figure S14. Changes in the fluorescence emission spectrum of 3 (c = 1 x 10^{-5} M) in CH$_3$CN upon titration with Zn(OTf)$_2$: the initial (black) is that of 3 and the final one (deep gray), after addition of 1 equiv of Zn(OTf)$_2$ (c = 1 x 10^{-2} M in CH$_3$CN). Emission is monitored at $\lambda_{exc} = 300$ nm.

Figure S15. Changes in the fluorescence emission spectrum of 3 (c = 1 x 10^{-5} M) in CH$_3$CN upon titration with Pb(ClO$_4$)$_2$: the initial (black) is that of 3 and the final one (deep gray), after addition of 1 equiv of Pb(ClO$_4$)$_2$ (c = 1 x 10^{-2} M in CH$_3$CN). Emission is monitored at $\lambda_{exc} = 300$ nm.
Figure S16. Changes in the fluorescence emission spectrum of 3 (c = 1 x 10⁻⁵ M) in CH₃CN upon titration with Hg(OTf)₂: the initial (black) is that of 3 and the final one (deep yellow), after addition of 0.5 equiv of Hg(OTf)₂ (c = 1 x 10⁻² M in CH₃CN). Emission is monitored at λₑₓc = 300 nm.

Figure S17. Visual changes observed in the fluorescence of CH₃CN solution of 3 (left) after addition of the cations (right).

Figure S18. Fluorescence intensity of ligand 3 in CH₃CN/EtOH (70/30), after addition of 1 equiv. of several metal cations. Emission monitored at λₑₓc = 300 nm.
**Figure S19.** (a) Changes in the fluorescence emission spectrum of 3 (c = 1x10^{-5} M in CH_{3}CN/EtOH (70/30)) upon titration with Hg(OTf)_{2}: the initial (black) is that of 3 and the final one (deep cyan), after addition of 0.5 equiv. of Hg(OTf)_{2} (c = 1x10^{-2} M in CH_{3}CN). Emission is monitored at $\lambda_{\text{exc}} = 300$ nm. (b) Visual changes observed in the fluorescence of CH_{3}CN/EtOH (70/30) solutions of 3 (left) and after addition of Hg(OTf)_{2} (right).

**Figure S20.** Fluorescence intensity of 3 (c = 1·10^{-4}M in CH_{3}CN/EtOH (70/30)) at each concentration of Hg(OTf)_{2} added, normalized between the minimum fluorescence intensity, found at zero equiv of metal cation, and the maximum fluorescence intensity, found at [Hg^{2+}] = 4.10 ppm.
Figure S21. Fluorescence intensity of 3 (c = 1·10^{-4}M in CH$_3$CN/EtOH/H$_2$O (65/25/10) at each concentration of Hg(OTf)$_2$ added, normalized between the minimum fluorescence intensity, found at zero equiv of metal cation, and the maximum fluorescence intensity, found at [Hg$^{2+}$] = 1.52 ppm.

Figure S22. ESI-MS spectra of a CH$_3$CN/EtOH (70/30) solution of an equimolecular amount of Hg(OTf)$_2$ and ligand 3.
**Figure S23.** Relative abundance of the isotopic cluster for \(3_2\cdot Hg^{2+}\) (top) simulated; (bottom) experimental.

**Figure S24.** Stepwise complexation/decomplexation (extraction with H\(_2\)O) cycles of ligand 3 (c = 1·10\(^{-4}\)M in CH\(_2\)Cl\(_2\)) in the presence of Hg(OTf)\(_2\), carried out by UV/Vis analysis.
**Figure S25.** Fluorescence emission intensity of 3 upon addition of 0.5 equiv. of Hg(OTf)$_2$ in the presence of 1 equiv. of interference metal ions in CH$_3$CN/EtOH (7/3).

**Figure S26.** Fluorescence emission intensity of 3 upon addition of 0.5 equiv. of Hg(OTf)$_2$ in the presence of 1 equiv. of interference metal ions in CH$_3$CN/EtOH/H$_2$O (65/25/10).
Figure S27. Calculated (vdw-RIJCOSX-B3LYP/def2-TZVP-ecp) structure for the most stable $C_2$-symmetric [4$_2$·Hg(TfO)$_2$] model complex.
Figure S28. Side view for NCI isosurfaces in the calculated (vdw-RIJCOSX-
B3LYP/def2-TZVP-ecp) structure for the most stable $C_2$-symmetric
$[4_2\cdot\text{Hg(TfO)}_2]$ model complex highlighting $\pi$ stacking.

Figure S29. Front view for NCI isosurfaces in the calculated (vdw-RIJCOSX-
B3LYP/def2-TZVP-ecp) structure for the most stable $C_2$-symmetric
$[4_2\cdot\text{Hg(TfO)}_2]$ model complex highlighting hydrogen bonds with lateral anions and ferrocene interpenetration.
**Calculated structures:** cartesian coordinates (in Å) and energies for all computed species.

**Complex 4**\(^2\)\(\text{Hg(TfO)}_2\)\(^2\) (\(C_2\))

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E = -7120.815314304 au

E = -7119.82311389 au (RIJCOXS-3LYP/def2-TZVP-f)

**Electronic Supplementary Material (ESI) for Dalton Transactions**

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Complex 4: Hg(TfO)$_2$-no-interp. (qC$_2$) E = -7119.810012 au (RIJCOSX-B3LYP/def2-TZVP-f)
F  2.63042484  0.62572330  2.83773620
O -5.49316674  -6.39864984  -0.05429921
S -6.75623022  -5.78873913  -0.53874612
O -7.1807069    -4.67347836  0.29313649
O -7.74553609   -6.72744175  -0.98434068
C -6.17502311  -4.92431922  -2.08730020
F -7.17143878  -4.28484777   -2.9911918
F -5.62060898  -5.78277224  -2.95522923
F -5.22508037  -4.00404696  -1.77013