

Supporting Information (SI)

Heteroditopic ligands based on ferrocenyl benzimidazoles fused to an additional diaza heterocyclic ring system

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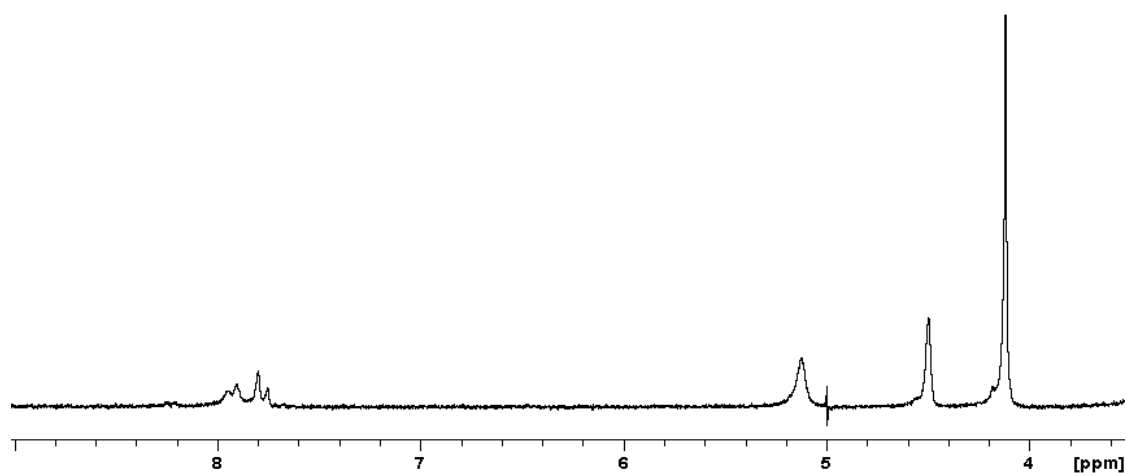
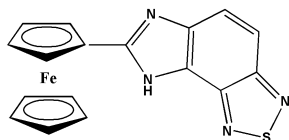
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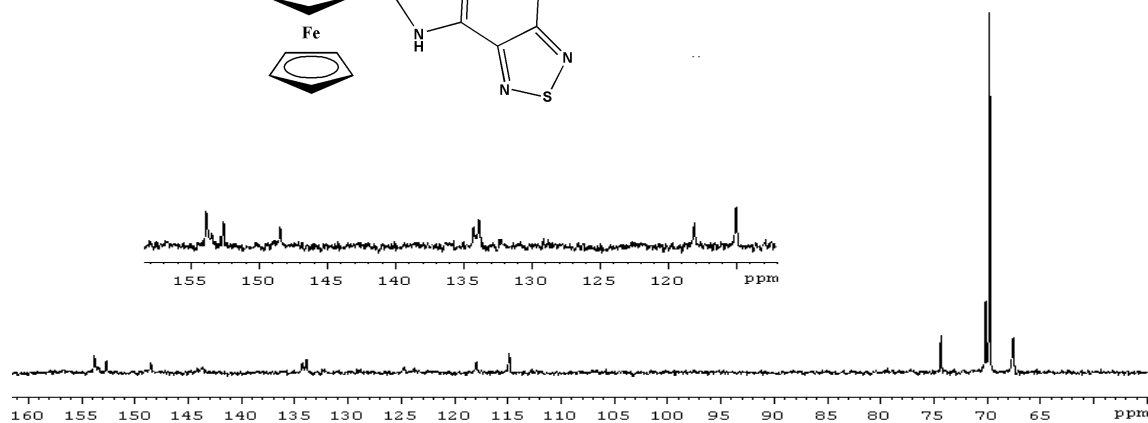
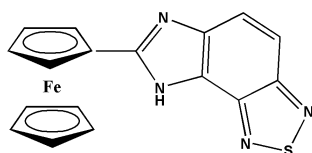
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7-Ferrocenyl-8*H*-imidazo [4,5-*e*]-2,1,2-benzothiadiazole, [2]

¹H NMR (200MHz, DMSO)

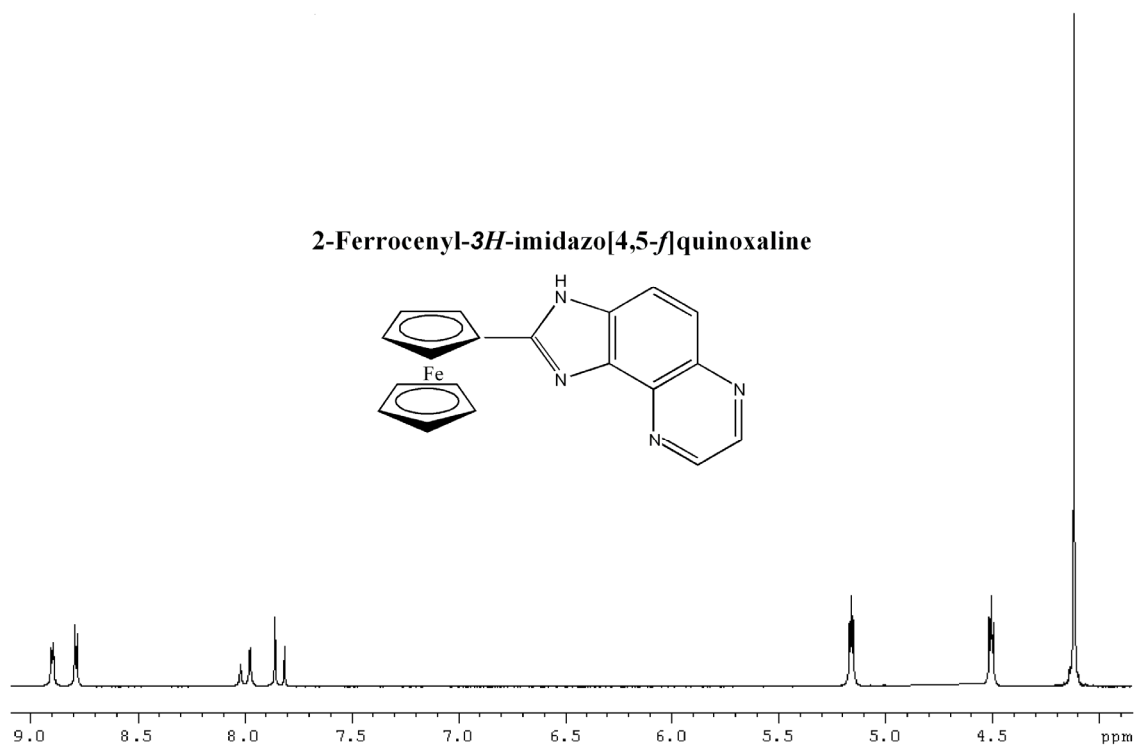


¹³C NMR (50 MHz, DMSO)



2-Ferrocenyl-3*H*-imidazo [4,5-*f*]quinoxaline, [3]

¹H NMR (300 MHz, CD₃OD):



¹³C NMR (75 MHz, CD₃OD):

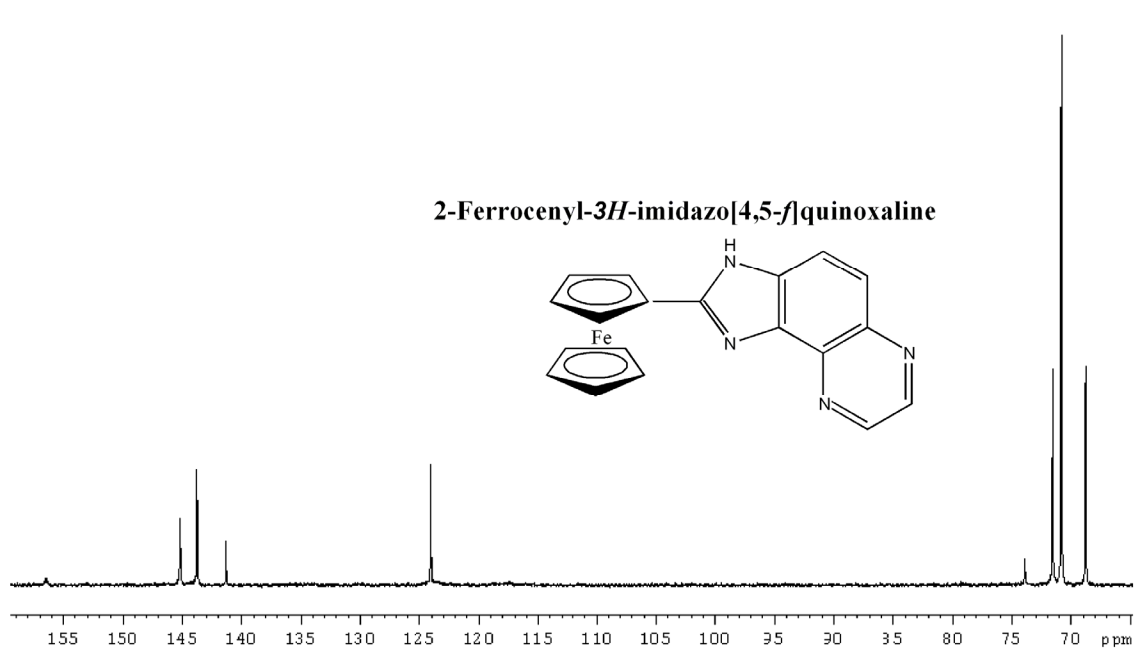


Table S1. Electrochemical data of the receptors **2** and **3** and their metal complexes formed

Comp.	$E_{1/2}$ (mV)	ΔE (mV) ^a	K_{red}/K_{ox} (BEF) ^b
2	520	-	-
2 · Pb ²⁺	720	200	2800
3 ·	580	-	
3 · Cd ²⁺	650	73	17
3 · Zn ²⁺	670	88	31
3 · Hg ²⁺	730	150	340
3 · Pb ²⁺	650	67	13

a) $\Delta E = E_{1/2}$ (complex) - $E_{1/2}$ (free ligand); b) BEF = Binding Enhancement Factor, calculated using the equation $\ln(K_{red}/K_{ox}) = \Delta E^\circ(nF/RT)$, where the equilibrium constants K_{ox} and K_{red} correspond to the complexation processes by the oxidized and reduced form of the ligand

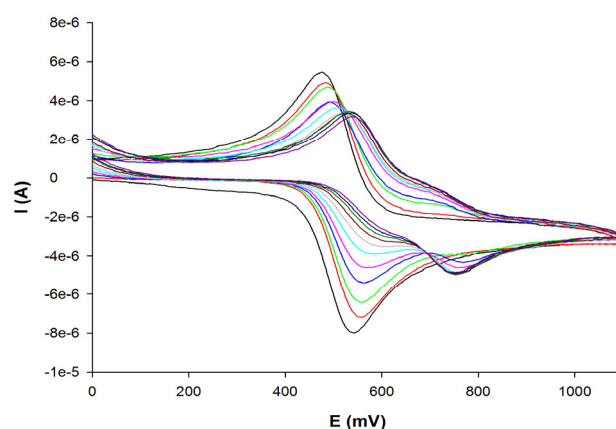


Figure SI 1. Evolution of the CV of **2** (1 mM) in CH₃CN/[(*n*-Bu)₄]ClO₄ scanned at 0.1 V s⁻¹ in the presence of increasing amounts of Pb²⁺: the initial (black) is that of **2** and the final one (purple), after addition of 1 equivalent of Pb²⁺.

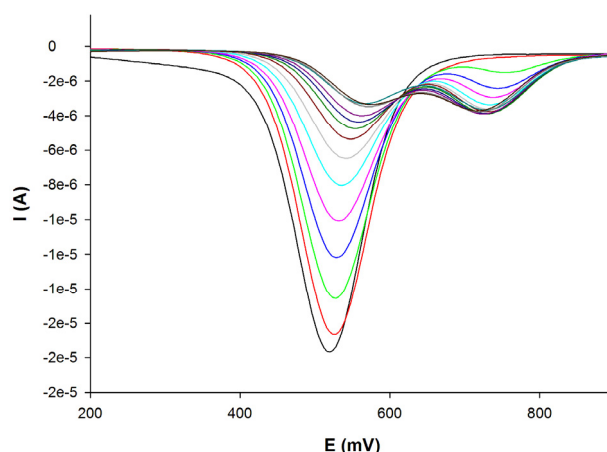


Figure SI 2. Evolution of the SWV of **2** (1 mM) in CH₃CN/[(*n*-Bu)₄]ClO₄ scanned at 0.1 V s⁻¹ in the presence of increasing amounts of Pb²⁺: the initial (black) is that of **2** and the final one (purple), after addition of 1 equivalent of Pb²⁺.

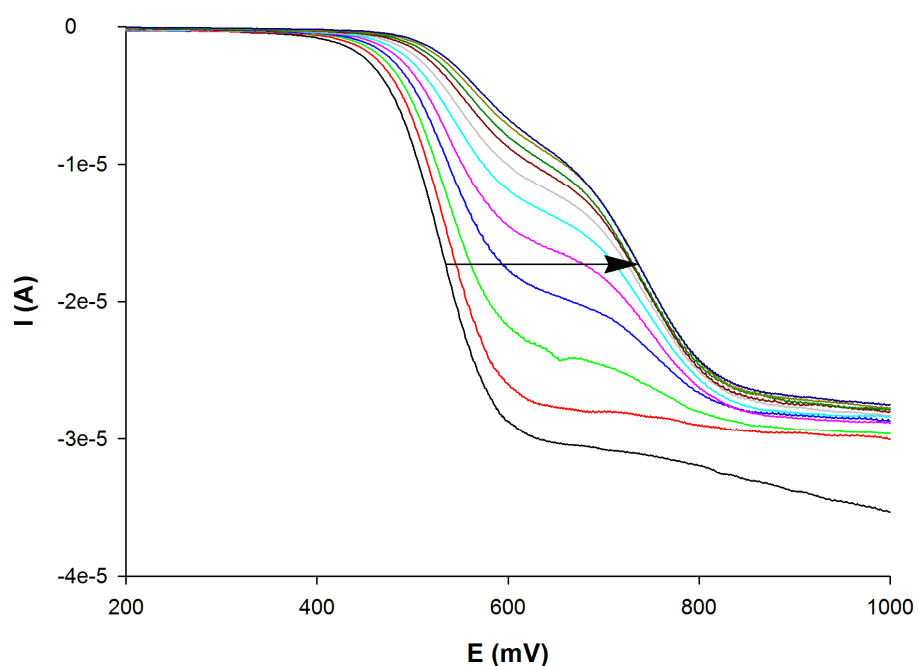


Figure SI 3. Evolution of the LSW in the presence of increasing amounts of Pb^{+2} : the initial (black) is that of **2** (1 mM) and the final one (deep blue), after addition of 1 equivalent of Pb^{+2} , $[(n\text{-Bu})_4]\text{ClO}_4$ 0.1 M as supporting electrolyte, obtained using a rotating disk electrode at 100 mVs^{-1} and 1000 rpm.

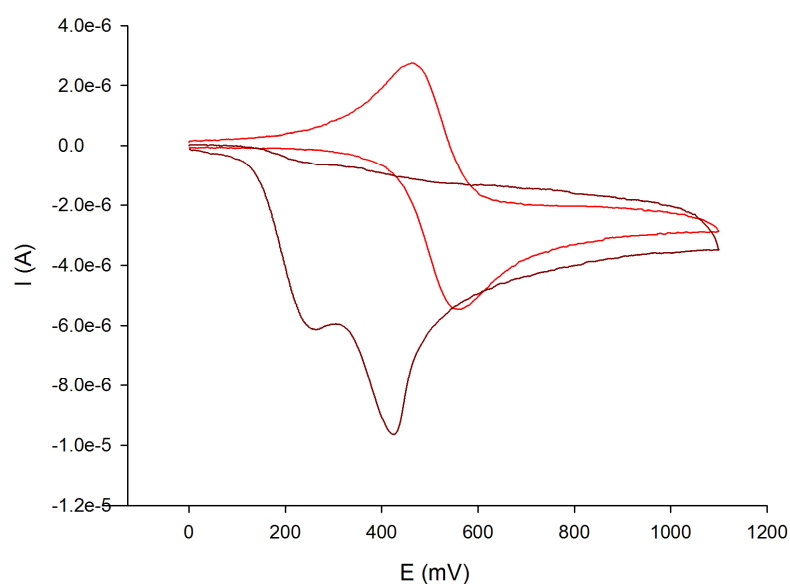


Figure SI 4. CV of **2** (red) (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ scanned at 0.1 V s^{-1} and in the presence 1 equiv of $\text{HP}_2\text{O}_7^{3-}$ (purple).

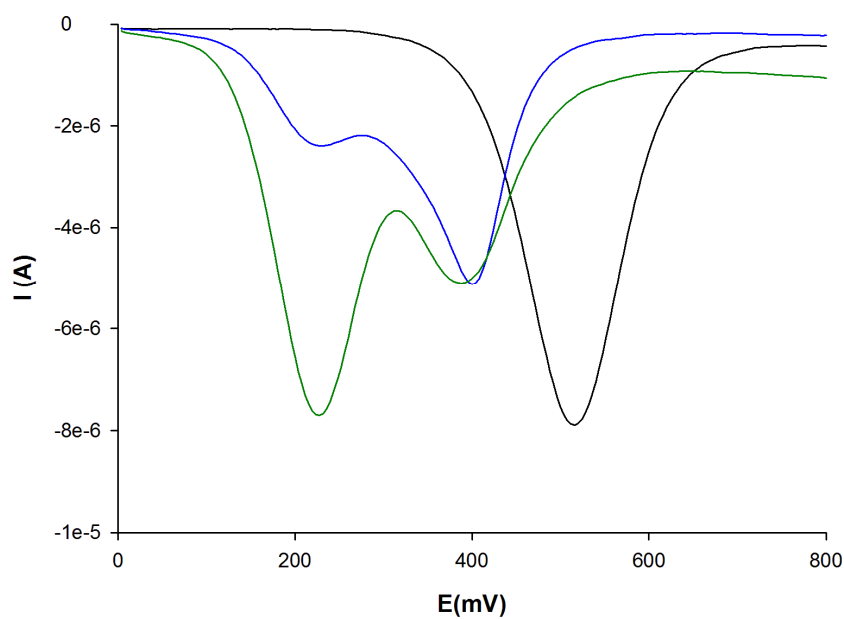


Figure SI 5. SWV of **2** (black) (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ scanned at 0.1 V s^{-1} and in the presence 0.4 equiv of $\text{HP}_2\text{O}_7^{3-}$ (blue) and in the presence 1.6 equiv of $\text{HP}_2\text{O}_7^{3-}$ (green).

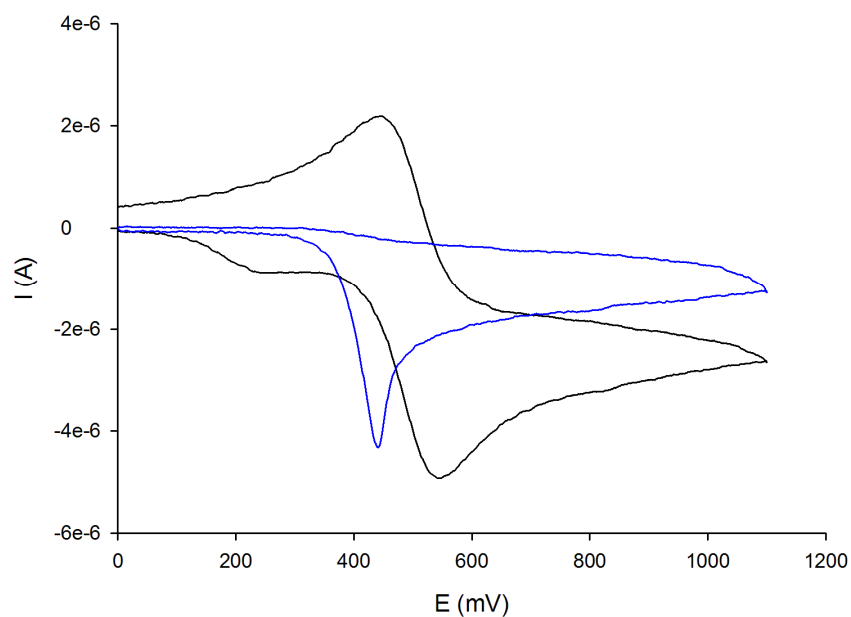


Figure SI 6. CV of **2** (black) (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ scanned at 0.1 V s^{-1} and in the presence 1 equiv of $\text{HP}_2\text{O}_7^{3-}$ (blue) and 20 equiv of acetic acid in CH_3CN .

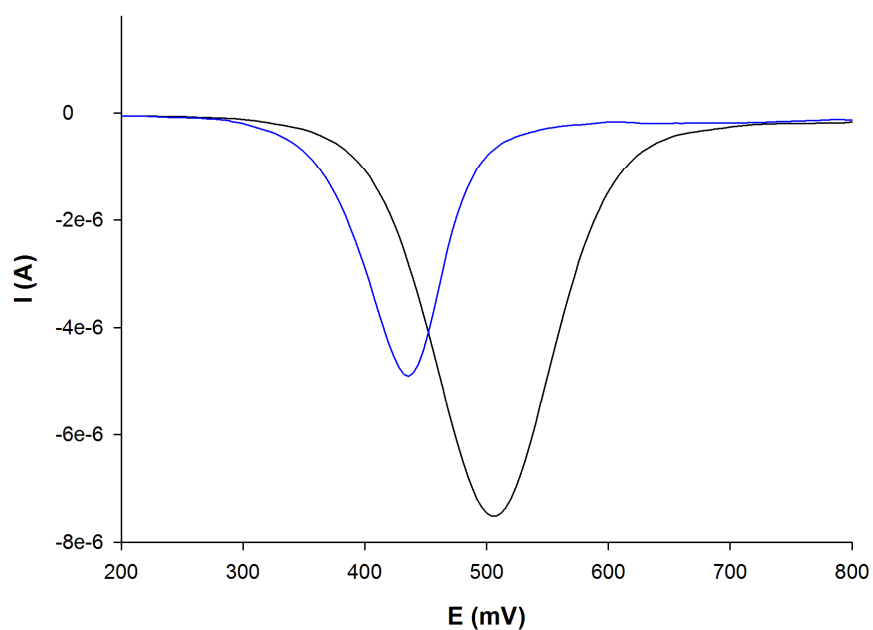


Figure SI 7. SWV of **2** (black) (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ scanned at 0.1 V s^{-1} and in the presence 2 equiv of $\text{HP}_2\text{O}_7^{3-}$ (blue) and 20 equiv of acetic acid in CH_3CN .

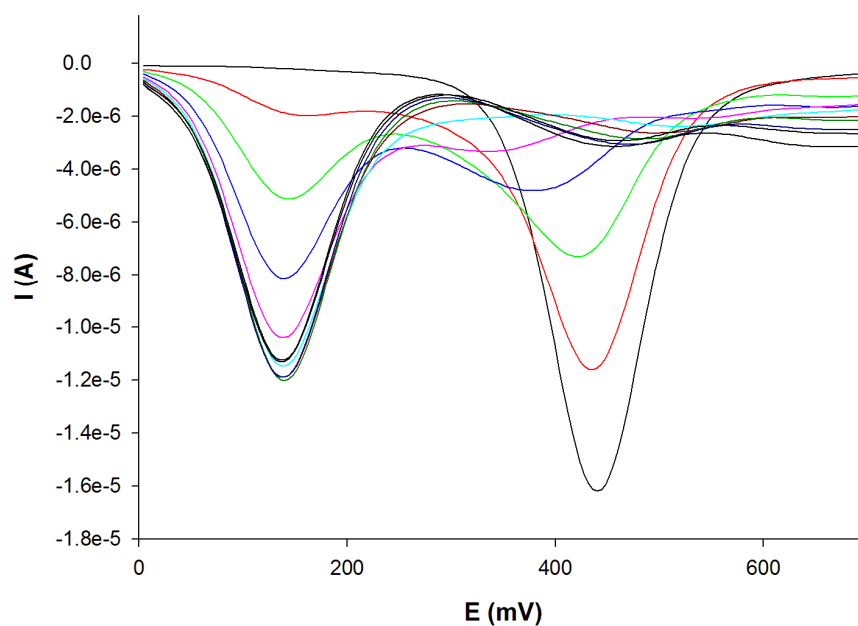


Figure SI 8. Evolution of the OSWV of **2** (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ scanned at 0.1 V s^{-1} in the presence of increasing amounts of F^- : the initial (black) is that of **2** and the final one (deep green), after addition of 5 equivalent of F^- .

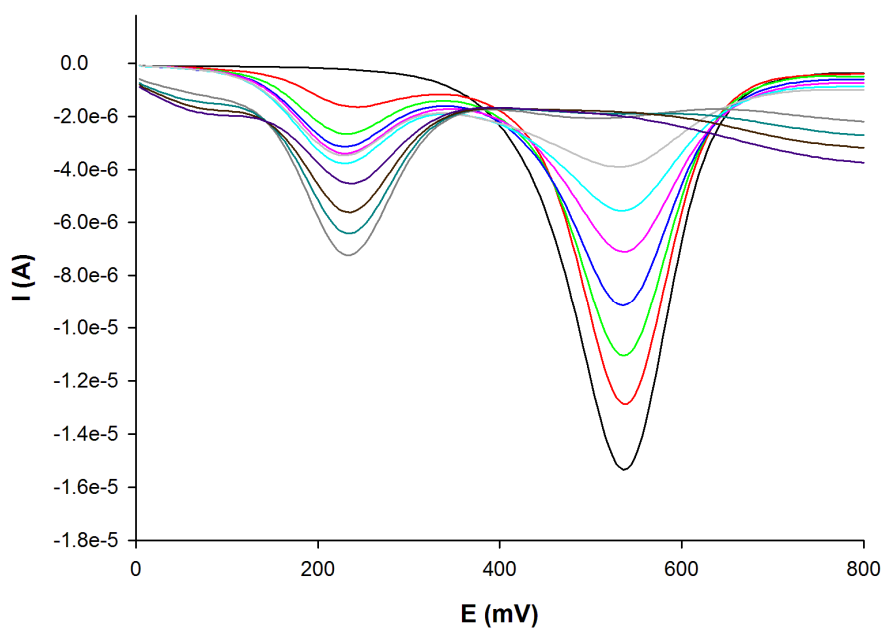


Figure SI 9. Evolution of the OSWV of **2** (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ scanned at 0.1 V s^{-1} in the presence of increasing amounts of OH^- : the initial (black) is that of **2** and the final one (gray), after addition of 2 equivalent of OH^- .

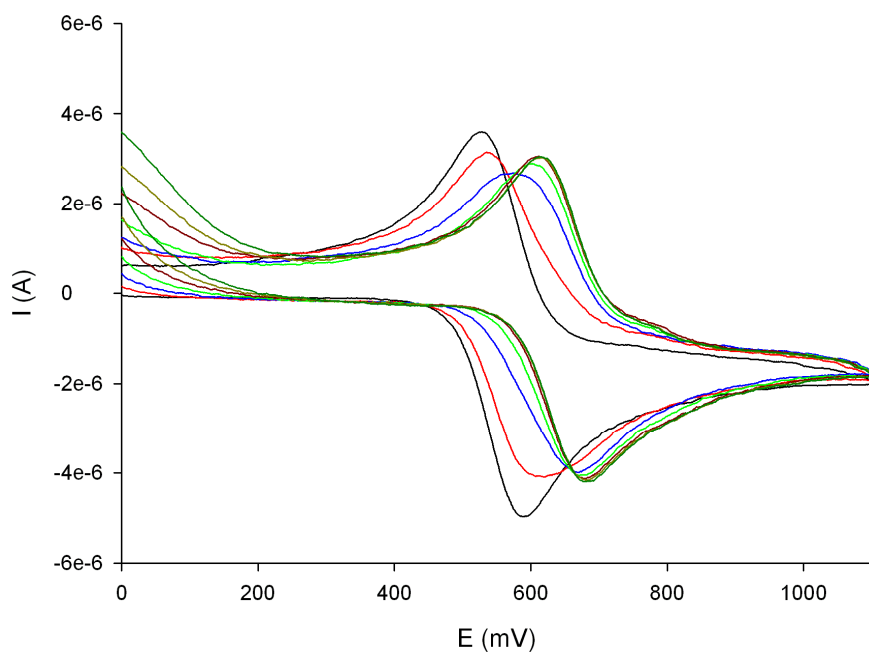


Figure SI 10. Evolution of the CV of **3** (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ scanned at 0.1 V s^{-1} in the presence of increasing amounts of Pb^{2+} : the initial (black) is that of **3** and the final one (deep green), after addition of 0.5 equivalent of Pb^{2+} .

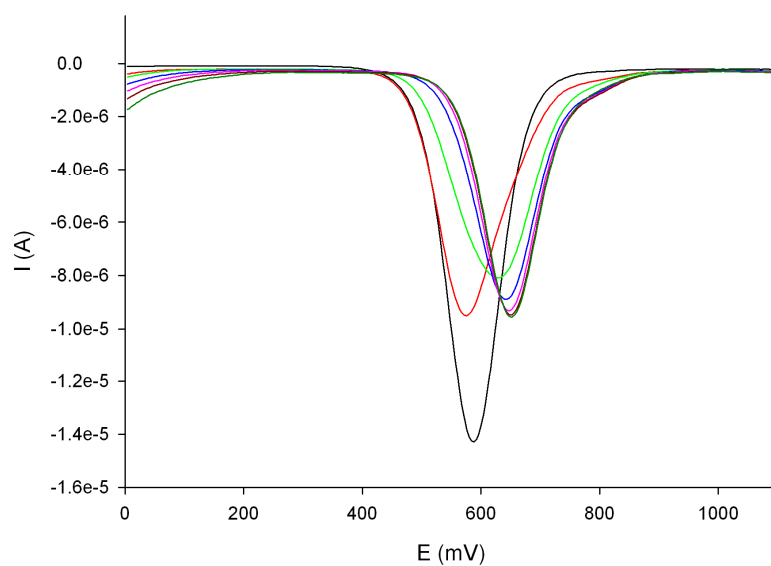


Figure SI 11. Evolution of the OSWV of **3** (1 mM) in CH₃CN/[*n*-Bu)₄]ClO₄ scanned at 0.1 V s⁻¹ in the presence of increasing amounts of Pb²⁺: the initial (black) is that of **3** and the final one (deep green), after addition of 0.5 equivalent of Pb²⁺.

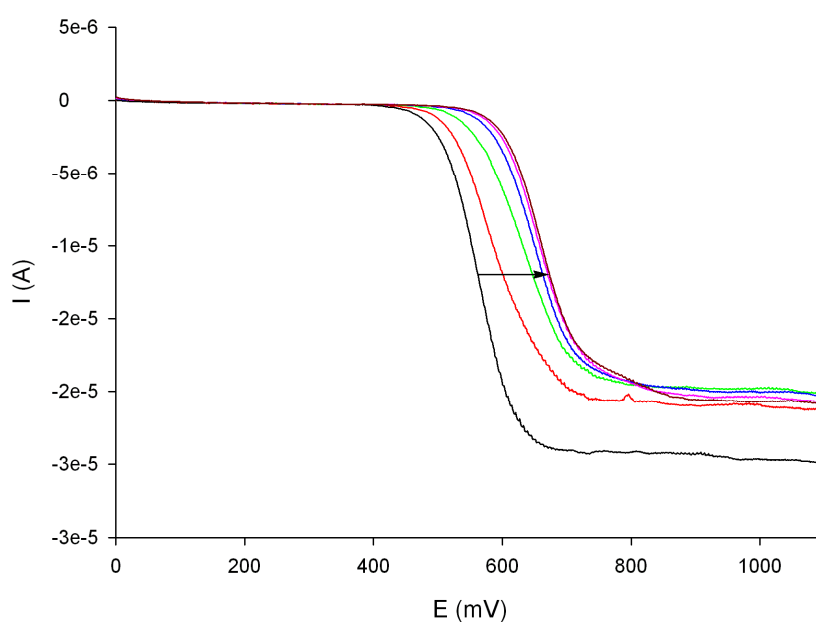


Figure SI 12. Evolution of the LSW in the presence of increasing amounts of Pb²⁺: the initial (black) is that of **3** (1 mM in CH₃CN) and the final one (deep red), after addition of 0.5 equivalent of Pb²⁺, [(*n*-Bu)₄]ClO₄ 0.1 M as supporting electrolyte, obtained using a rotating disk electrode at 100 mVs⁻¹ and 1000 rpm.

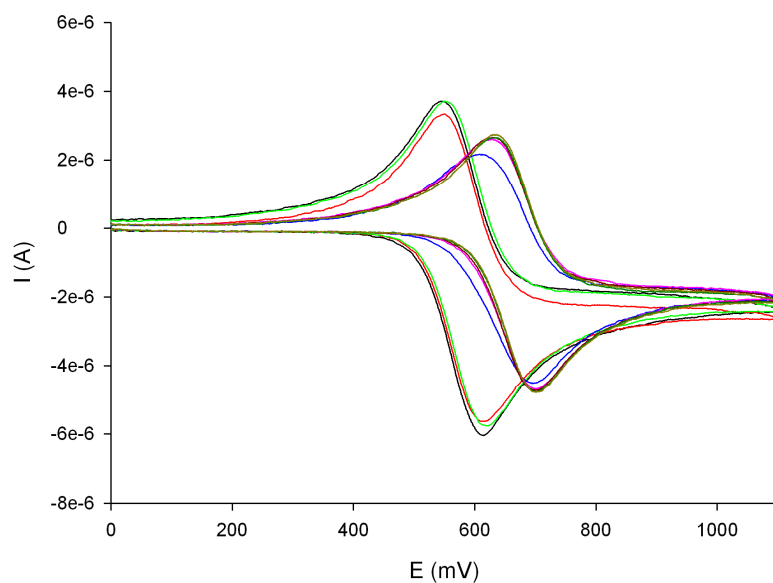


Figure SI 13. Evolution of the CV of **3** (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ scanned at 0.1 V s^{-1} in the presence of increasing amounts of Zn^{2+} : the initial (black) is that of **3** and the final one (deep yellow), after addition of 1 equivalent of Zn^{2+} .

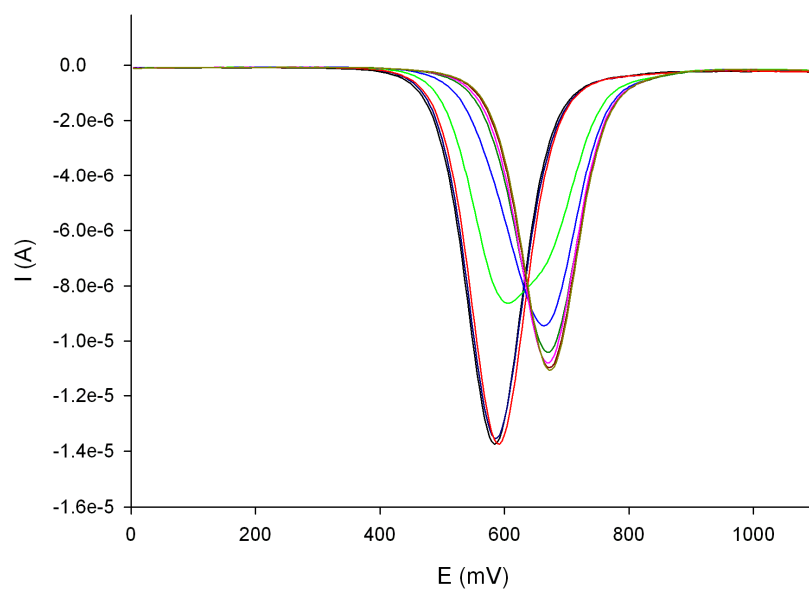


Figure SI 14. Evolution of the OSWV of **3** (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ scanned at 0.1 V s^{-1} in the presence of increasing amounts of Zn^{2+} : the initial (black) is that of **3** and the final one (deep yellow), after addition of 1 equivalent of Zn^{2+} .

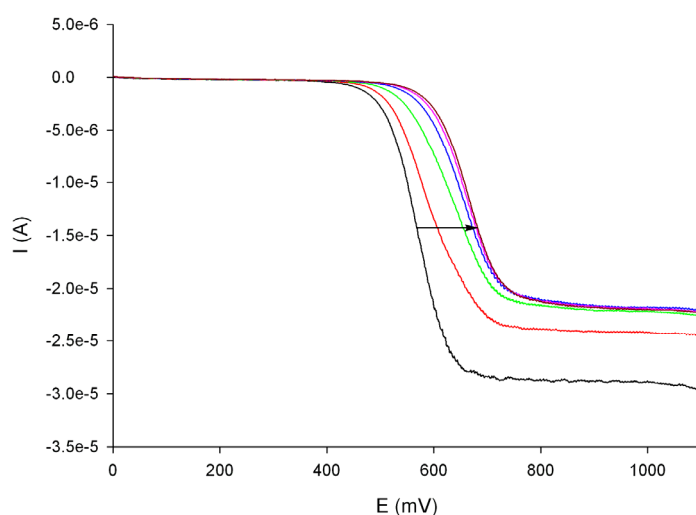


Figure SI 15. Evolution of the LSW in the presence of increasing amounts of Zn^{2+} : the initial (black) is that of **3** (1 mM in CH_3CN) and the final one (deep red), after addition of 1 equivalent of Zn^{2+} $[(n\text{-Bu})_4]\text{ClO}_4$ 0.1 M as supporting electrolyte, obtained using a rotating disk electrode at 100 mVs^{-1} and 1000 rpm.

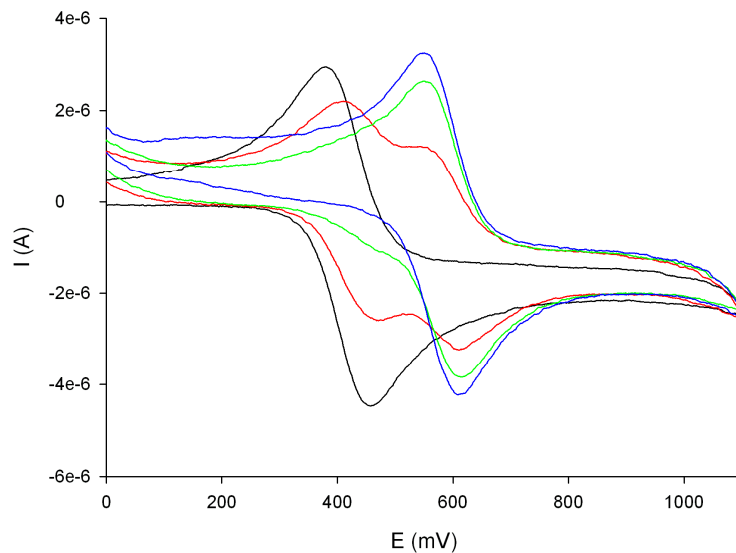


Figure SI 16. Evolution of the CV of **3** (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ scanned at 0.1 V s^{-1} in the presence of increasing amounts of Hg^{2+} : the initial (black) is that of **3** and the final one (blue), after addition of 0.5 equivalent of Hg^{2+} .

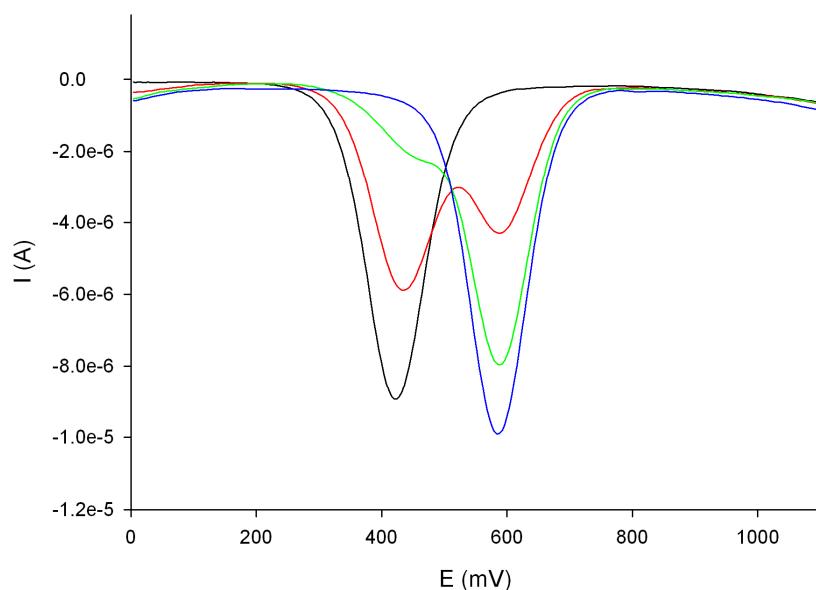


Figure SI 17. Evolution of the OSWV of **3** (1 mM) in CH₃CN/[*n*-Bu₄]ClO₄ scanned at 0.1 V s⁻¹ in the presence of increasing amounts of Hg²⁺: the initial (black) is that of **3** and the final one (blue), after addition of 0.5 equivalent of Hg²⁺.

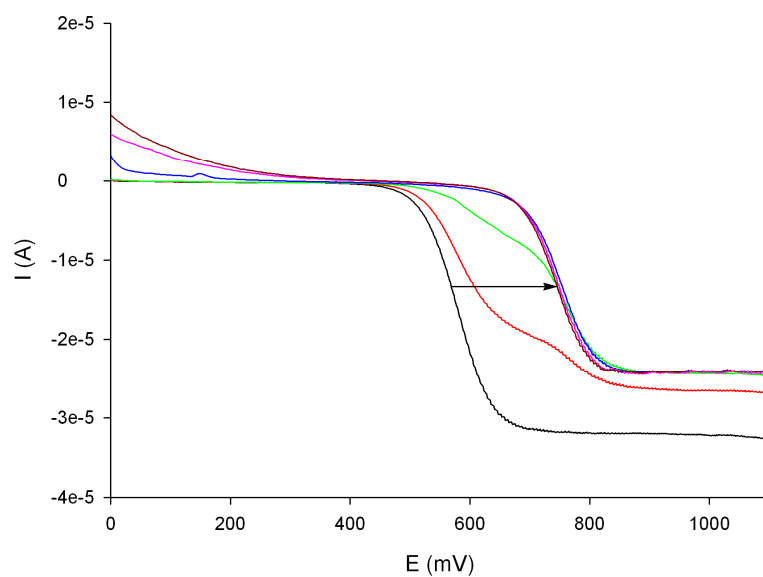


Figure SI 18. Evolution of the LSW in the presence of increasing amounts of Hg²⁺: the initial (black) is that of **3** (1 mM in CH₃CN) and the final one (deep red), after addition of 0.5 equivalent of Hg²⁺ [(*n*-Bu₄)ClO₄ 0.1 M as supporting electrolyte, obtained using a rotating disk electrode at 100 mVs⁻¹ and 1000 rpm.

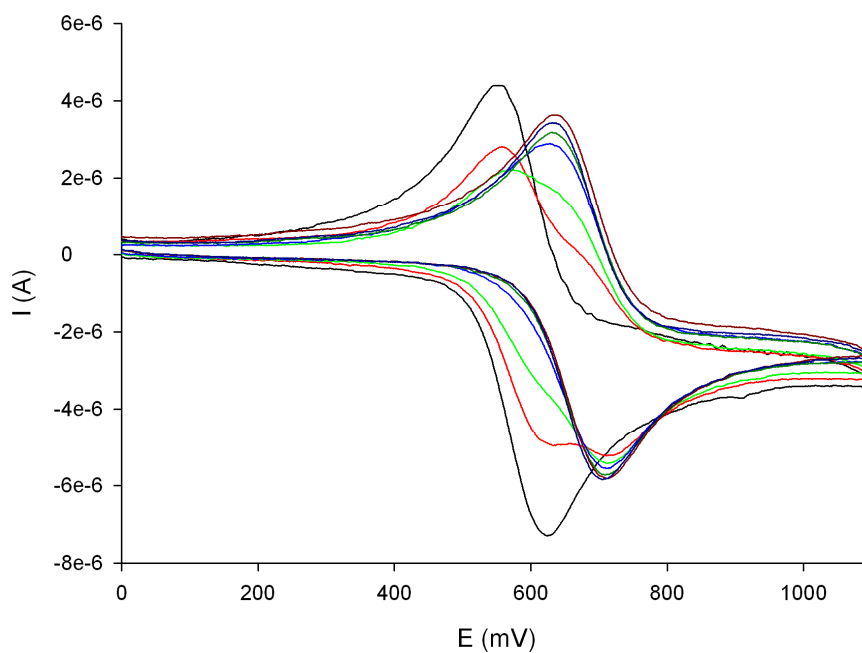


Figure SI 19. Evolution of the CV of **3** (1 mM) in CH₃CN/[*n*-Bu)₄]ClO₄ scanned at 0.1 V s⁻¹ in the presence of increasing amounts of Cd²⁺: the initial (black) is that of **3** and the final one (deep blue), after addition of 1 equivalent of Cd²⁺.

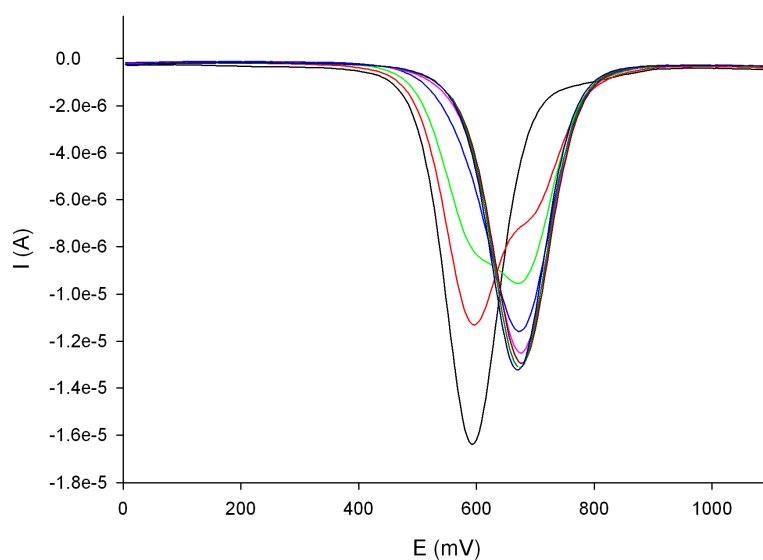


Figure SI 20. Evolution of the OSWV of **3** (1 mM) in CH₃CN/[*n*-Bu)₄]ClO₄ scanned at 0.1 V s⁻¹ in the presence of increasing amounts of Cd²⁺: the initial (black) is that of **3** and the final one (deep blue), after addition of 1 equivalent of Cd²⁺.

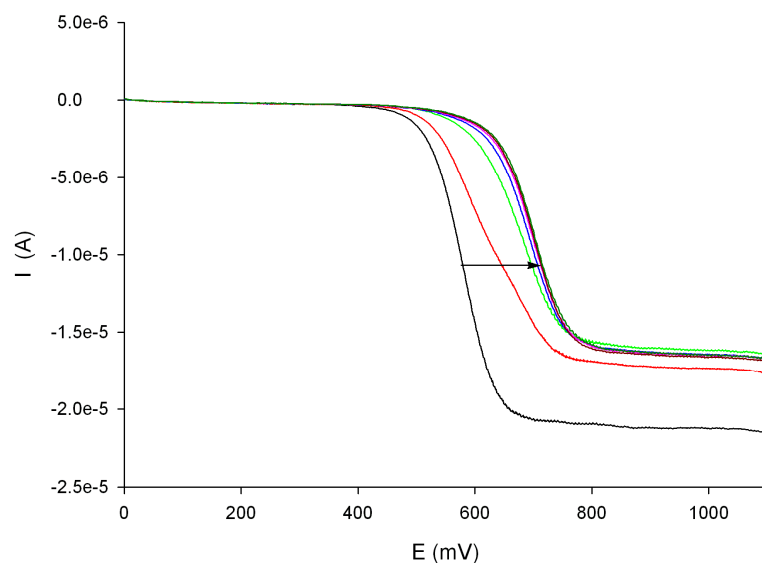


Figure SI 21. Evolution of the LSW in the presence of increasing amounts of Cd^{2+} : the initial (black) is that of **3** (1 mM in CH_3CN) and the final one (deep red), after addition of 1 equivalent of Cd^{2+} , $[(n\text{-Bu})_4]\text{ClO}_4$ 0.1 M as supporting electrolyte, obtained using a rotating disk electrode at 100 mVs^{-1} and 1000 rpm.

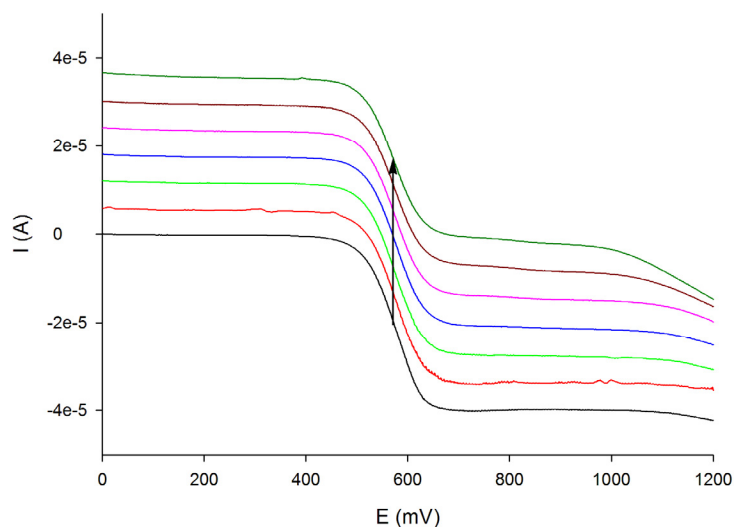


Figure SI 22. Evolution of the LSW in the presence of increasing amounts of Cu^{2+} : the initial (black) is that of **3** and the final one (deep green), after addition of 2 equivalents of Cu^{2+} $[(n\text{-Bu})_4]\text{ClO}_4$ 0.1 M as supporting electrolyte, obtained using a rotating disk electrode at 100 mVs^{-1} and 1000 rpm.

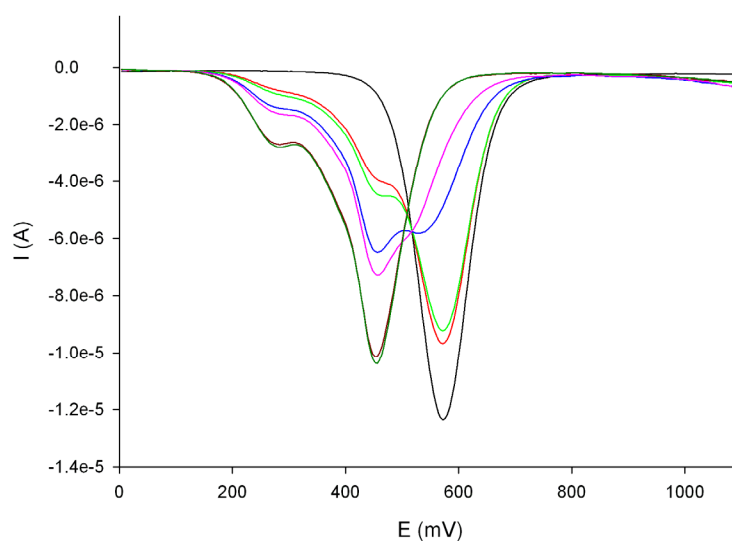


Figure SI 23. Evolution of the OSWV of **3** (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ scanned at 0.1 V s^{-1} in the presence of increasing amounts of $\text{HP}_2\text{O}_7^{3-}$: the initial (black) is that of **3** and the final one (deep green), after addition of 3 equivalent of $\text{HP}_2\text{O}_7^{3-}$.

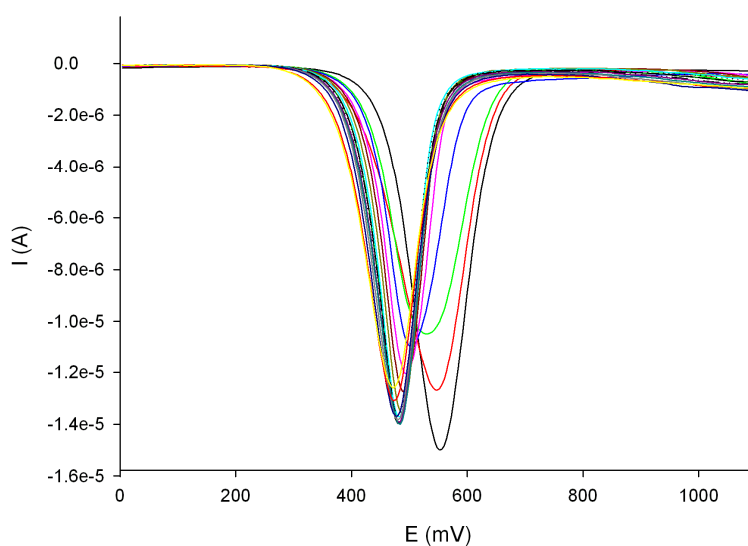


Figure SI 24. Evolution of the OSWV of **3** (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ in the presence of 20 mM AcOH, scanned at 0.1 V s^{-1} upon addition of increasing amounts of $\text{HP}_2\text{O}_7^{3-}$ the initial (black) is that of **3** and the final one (deep pink), after addition of 3 equivalents of $\text{HP}_2\text{O}_7^{3-}$.

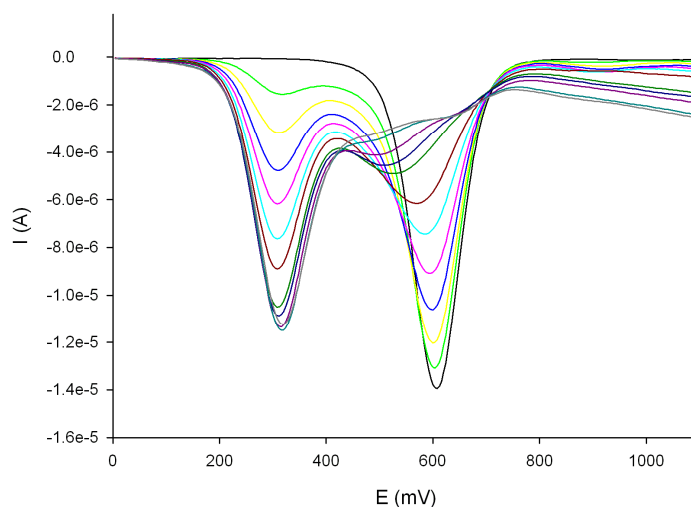


Figure SI 25. Evolution of the OSWV of **3** (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ scanned at 0.1 V s^{-1} in the presence of increasing amounts of F^- : the initial (black) is that of **3** and the final one (deep gray), after addition of 2 equivalents of F^- .

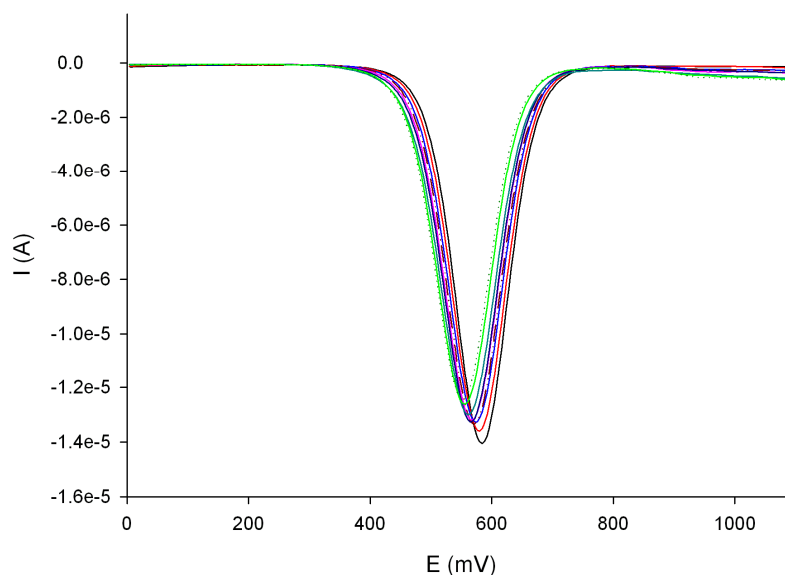


Figure SI 26. Evolution of the OSWV of **3** (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4]\text{ClO}_4$ in the presence of 20 mM AcOH, scanned at 0.1 V s^{-1} upon addition of increasing amounts of $\text{HP}_2\text{O}_7^{3-}$ the initial (black) is that of **3** and the final one (green), after addition of 2 equivalents of F^- .

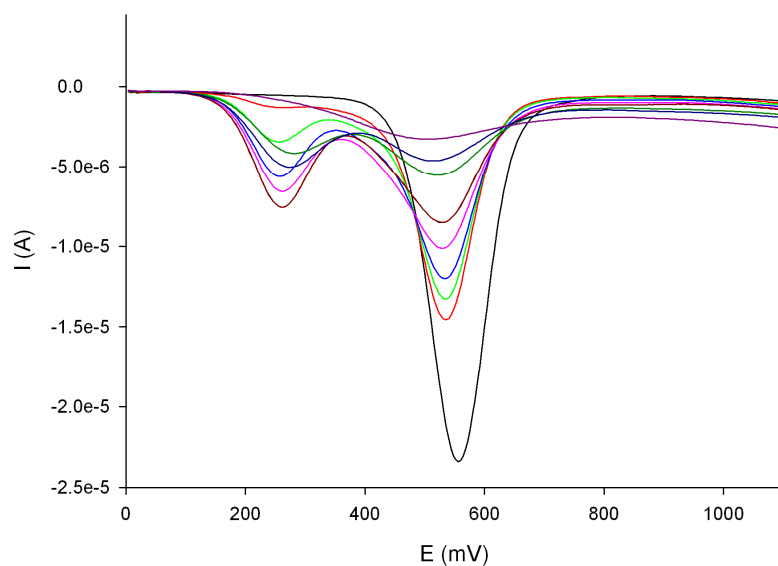


Figure SI 27. Evolution of the OSWV of **3** (1 mM) in CH₃CN/[*n*-Bu)₄]ClO₄ scanned at 0.1 V s⁻¹ in the presence of increasing amounts of OH⁻: the initial (black) is that of **3** and the final one (deep red), after addition of 2 equivalents of OH⁻.

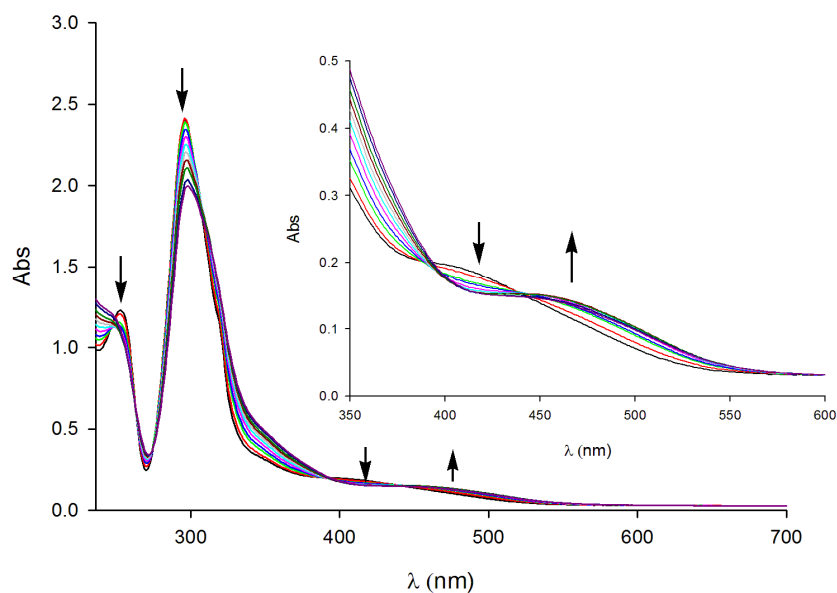


Figure SI 28. Changes in the absorption spectra of **2** (black) ($c = 1 \cdot 10^{-4}$ M in CH₃CN) upon addition of increasing amounts of Pb²⁺ metal cation, until 1 equiv was added (purple). Arrows indicate absorption that increase or decrease during the experiment.

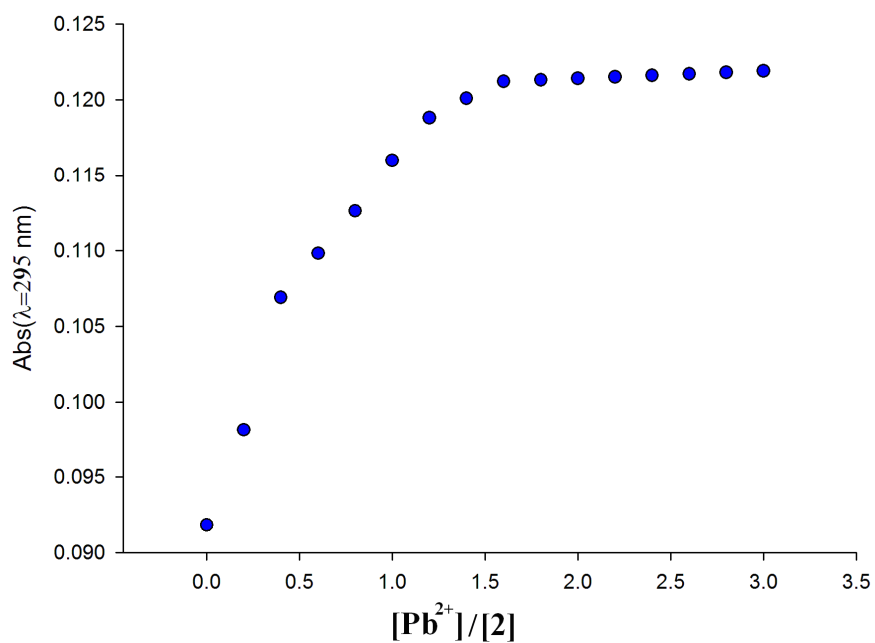


Figure SI 29. Change of absorbance of **2** ($c = 1 \cdot 10^{-4}$ M in CH_3CN) at $\lambda = 295$ nm upon addition of Pb^{2+} , indicating the formation of 1:1 complex.

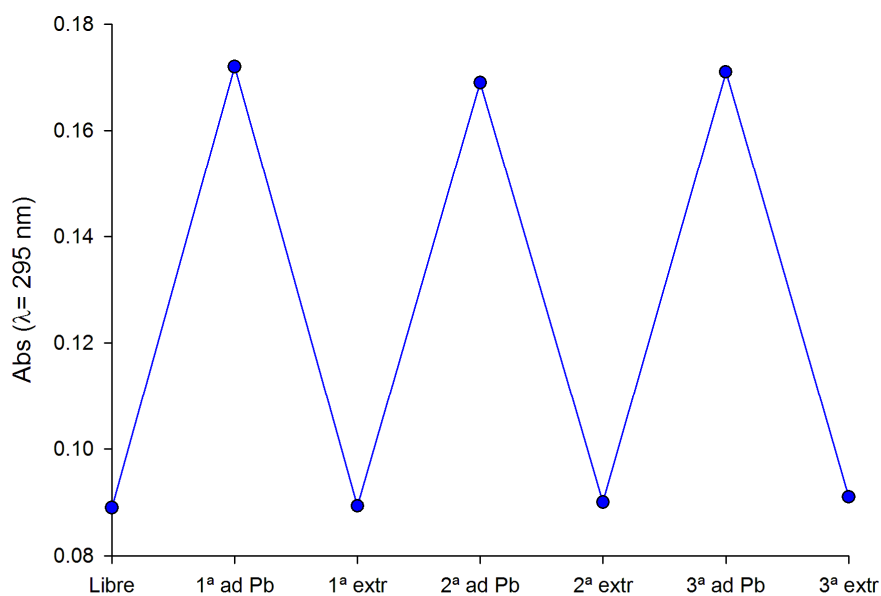


Figure SI 30. Stepwise complexation (addition of Pb^{2+}) /decomplexation (extraction with H_2O) cycles of ligand **2** ($1 \cdot 10^{-4}$ M in CH_2Cl_2) and Pb^{2+} , carried out by UV/Vis analysis.

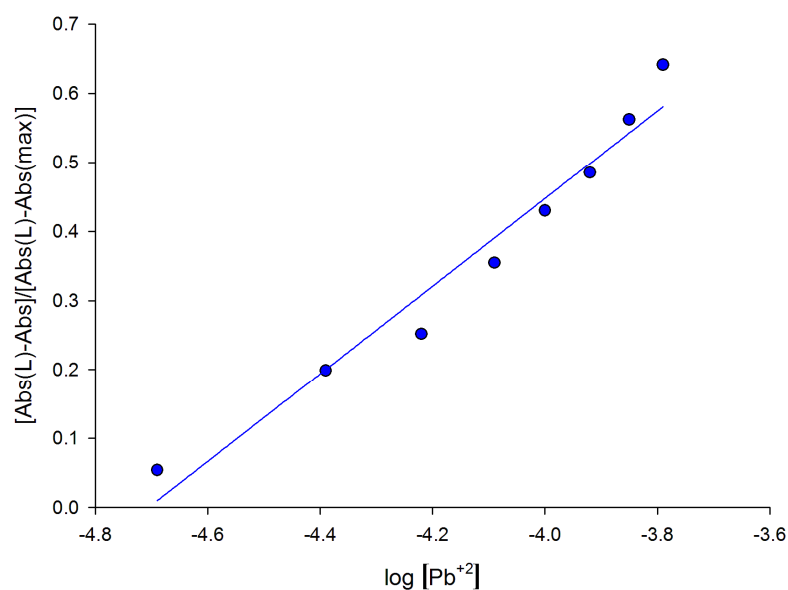


Figure SI 31. Absorbance of **2** ($c = 1 \cdot 10^{-4}$ M in CH_3CN) at each concentration of Pb^{2+} added, normalized between the minimum absorbance, found at zero equiv of Pb^{2+} ; and the maximum absorbance, found at $[\text{Pb}^{2+}] = 2 \cdot 10^{-5}$ M.

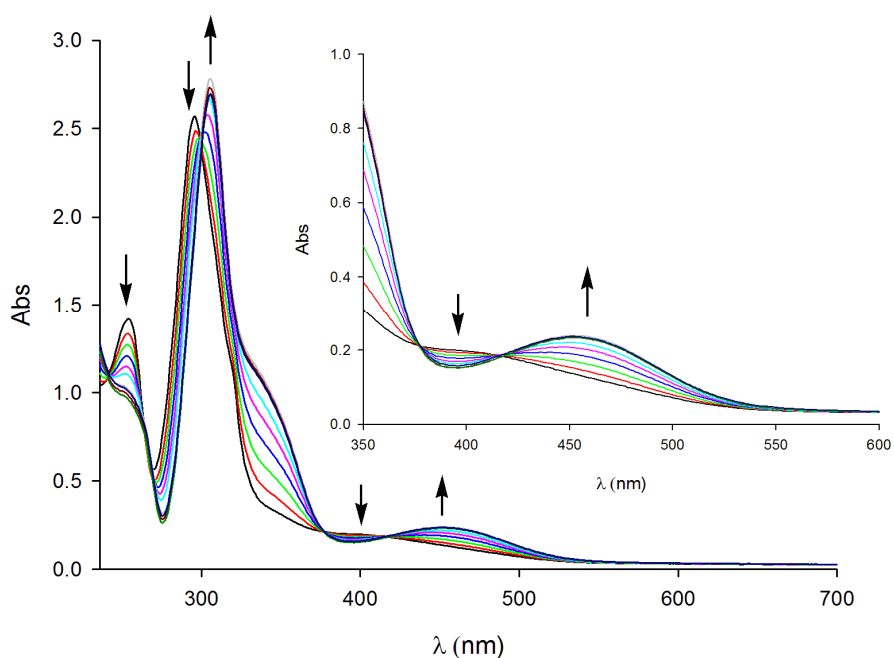


Figure 32. Changes in the absorption spectra of **2** (black) ($c = 1 \cdot 10^{-4}$ M in CH_3CN) upon addition of increasing amounts of $\text{HP}_2\text{O}_7^{3-}$ anion, until 1 equiv was added (gray). Arrows indicate absorption that increase or decrease during the experiment.

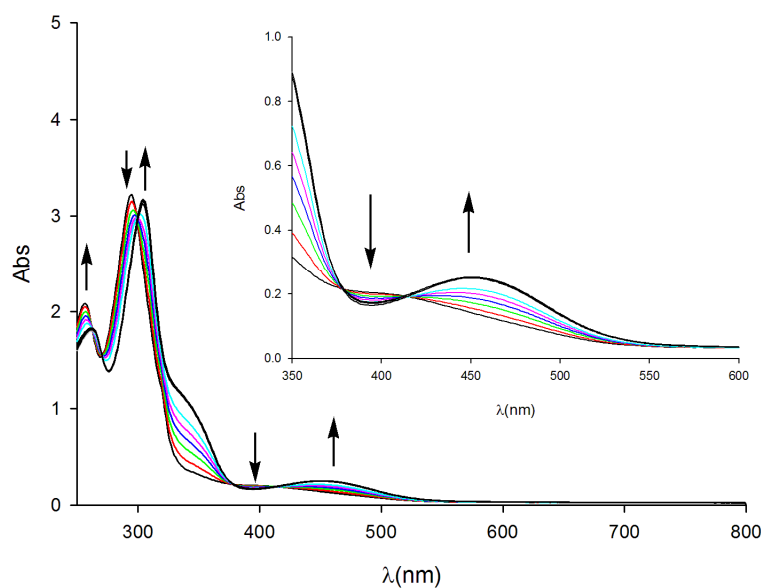


Figure SI 33. Changes in the absorption spectra of **2** (black) ($c = 1 \cdot 10^{-4} \text{M}$ in CH_3CN) upon addition of increasing amounts of OH^- anion, until 1 equiv was added (gray). Arrows indicate absorption that increase or decrease during the experiment.

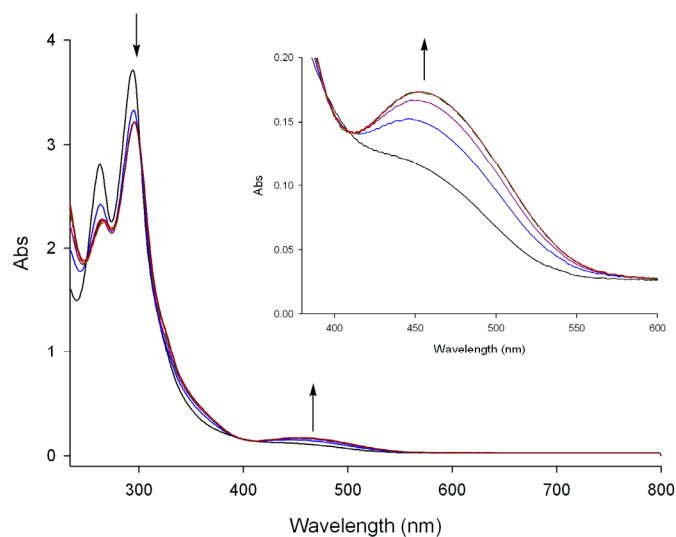


Figure SI 34. Changes in the absorption spectra of **3** (black) ($c = 1 \cdot 10^{-4} \text{M}$ in CH_3CN) upon addition of increasing amounts of Pb^{2+} metal cation, until 0.5 equiv was added (deep red). Arrows indicate absorption that increase or decrease during the experiment.

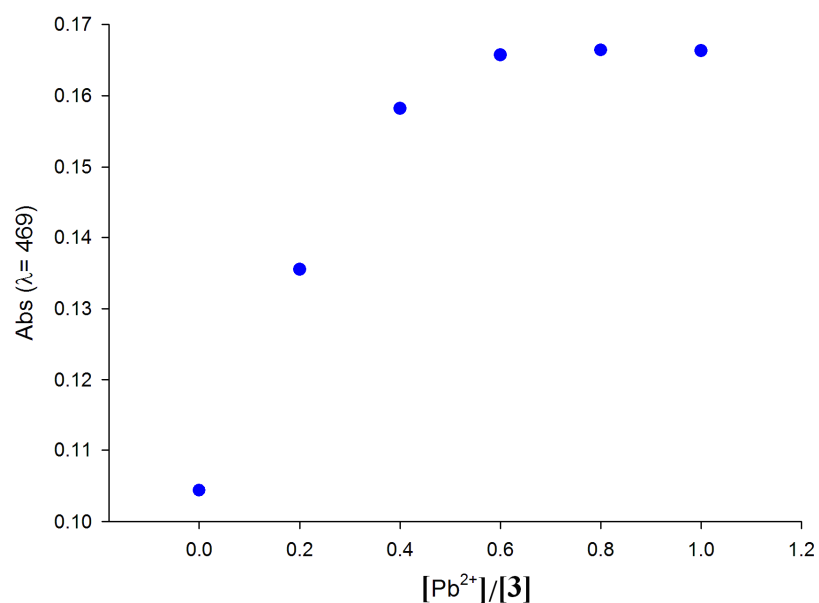


Figure SI 35. Change of absorbance of **3** ($c = 1 \cdot 10^{-4} \text{M}$ in CH_3CN) at $\lambda = 469 \text{ nm}$ upon addition of Pb^{2+} , indicating the formation of 2:1 complex.

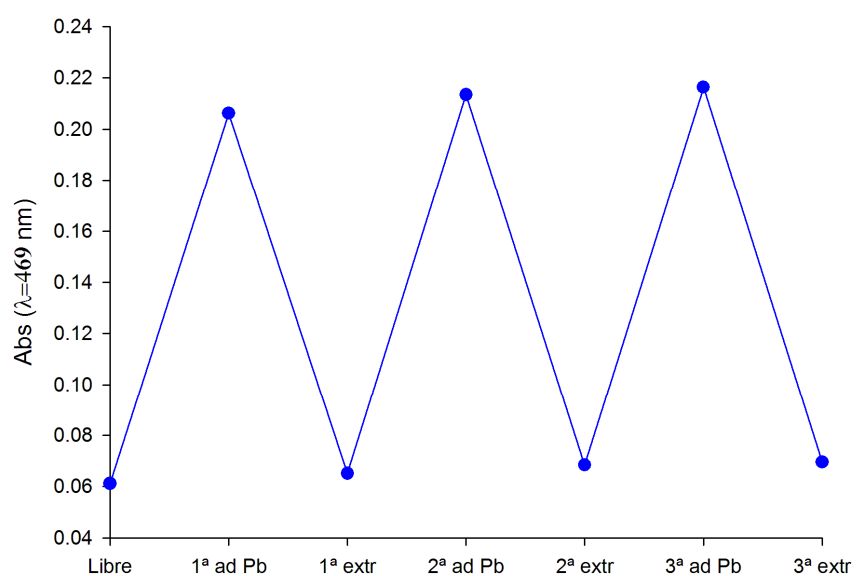


Figure SI 36. Stepwise complexation (addition of Pb^{2+}) /decomplexation (extraction with H_2O) cycles of ligand **3** ($c = 1 \cdot 10^{-4} \text{M}$ in CH_3CN) and Pb^{2+} , carried out by UV/Vis analysis.

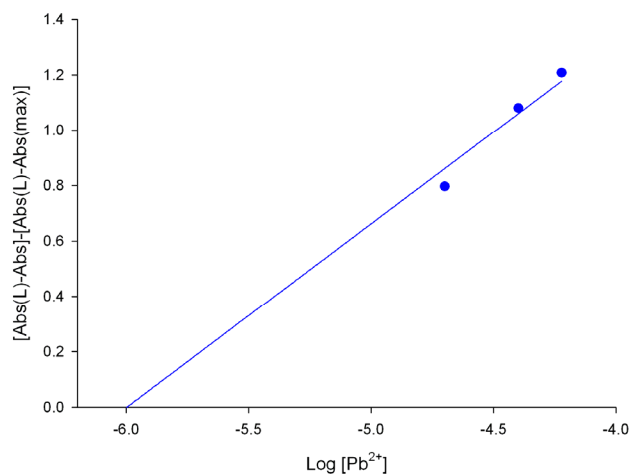


Figure SI 37. Absorbance of **3** ($c = 1 \cdot 10^{-4}$ M in CH_3CN) at each concentration of Pb^{2+} added, normalized between the minimum absorbance, found at zero equiv of Pb^{2+} ; and the maximum absorbance, found at $[\text{Pb}^{2+}] = 1.0035 \cdot 10^{-6}$ M.

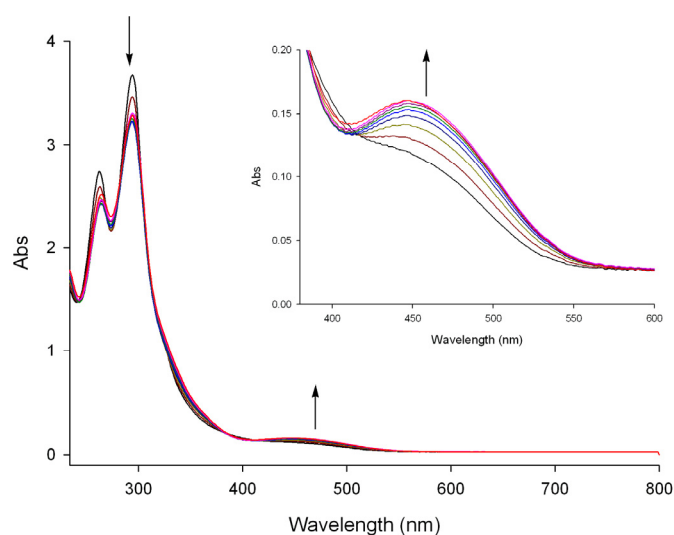


Figure SI 38. Changes in the absorption spectra of **3** (black) ($c = 1 \cdot 10^{-4}$ M in CH_3CN) upon addition of increasing amounts of Zn^{2+} metal cation, until 1 equiv was added (red). Arrows indicate absorption that increase or decrease during the experiment.

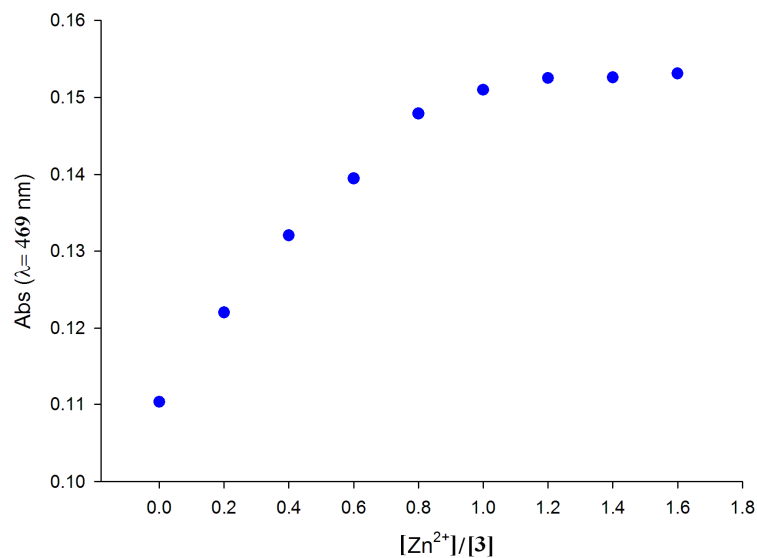


Figure SI 39. Change of absorbance of **3** ($c = 1 \cdot 10^{-4}$ M in CH_3CN) at $\lambda = 469$ nm upon addition of Zn^{2+} , indicating the formation of 1:1 complex.

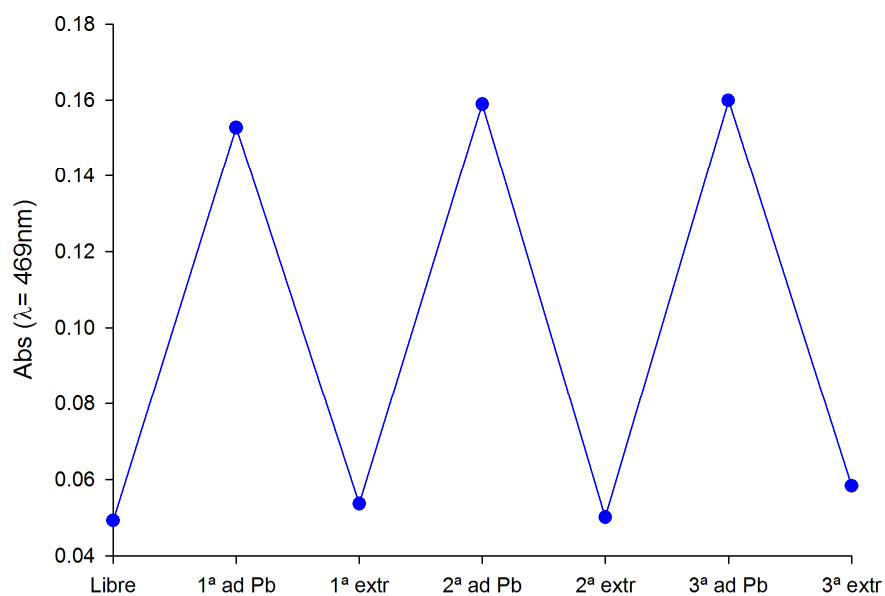


Figure SI 40. Stepwise complexation (addition of Zn^{2+}) /decomplexation (extraction with H_2O) cycles of ligand **3** ($1 \cdot 10^{-4}$ M in CH_2Cl_2) and Zn^{2+} , carried out by UV/Vis analysis.

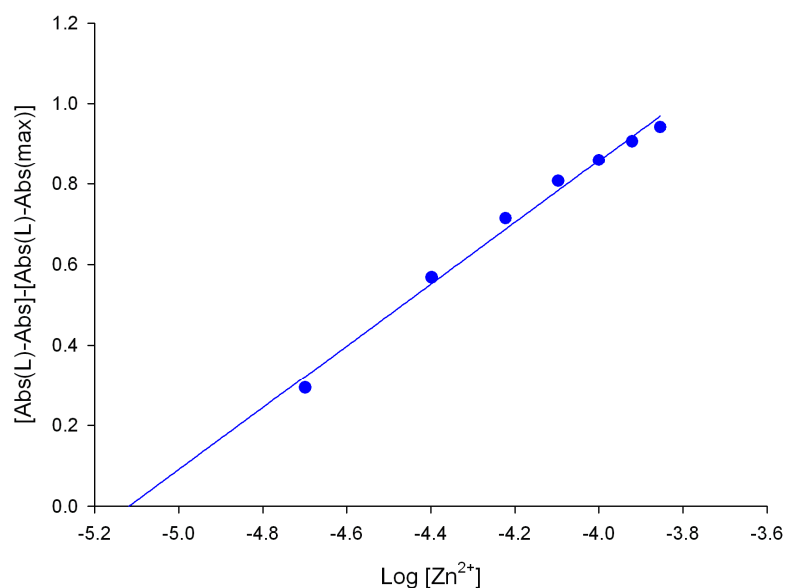


Figure SI 41. Absorbance of **3** ($c = 1 \cdot 10^{-4} \text{ M}$ in CH_3CN) at each concentration of Zn^{2+} added, normalized between the minimum absorbance, found at zero equiv of Zn^{2+} ; and the maximum absorbance, found at $[\text{Zn}^{2+}] = 7.6079 \cdot 10^{-6} \text{ M}$.

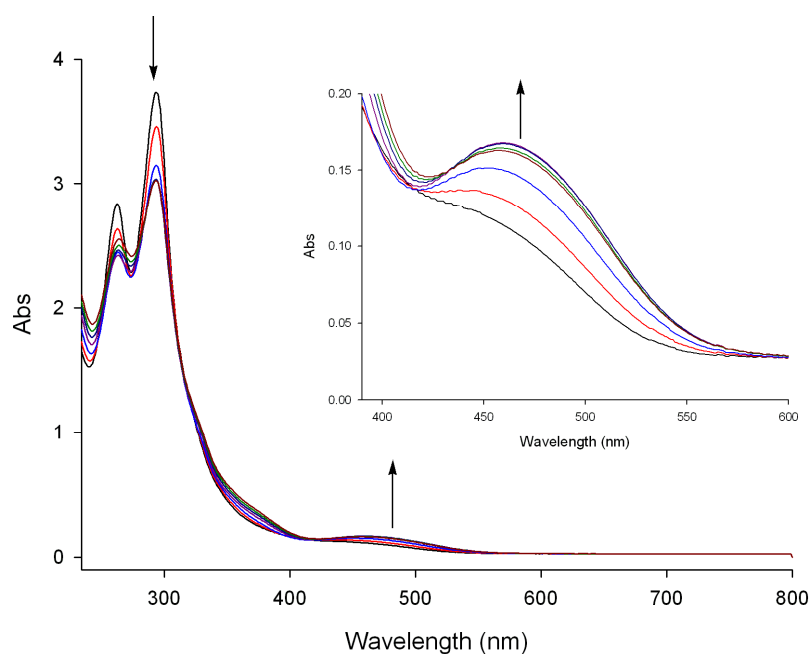


Figure SI 42. Changes in the absorption spectra of **3** (black) ($c = 1 \cdot 10^{-4} \text{ M}$ in CH_3CN) upon addition of increasing amounts of Hg^{2+} metal cation, until 0.5 equiv was added (deep red). Arrows indicate absorption that increase or decrease during the experiment.

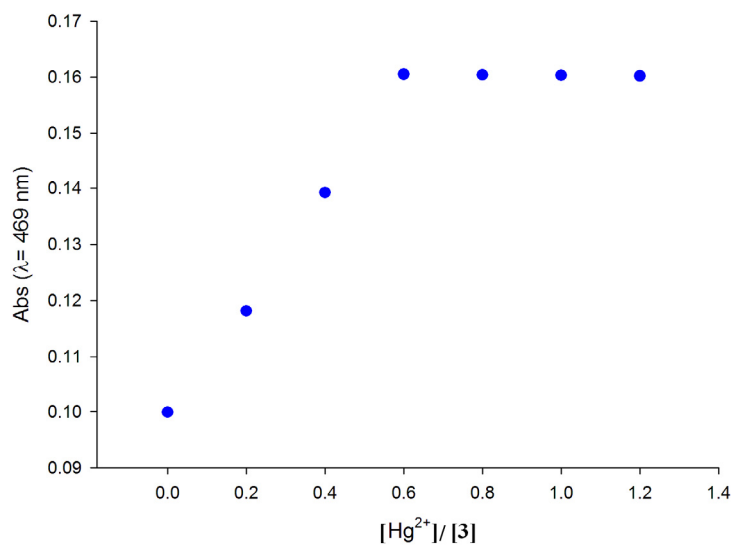


Figure SI 43. Change of absorbance of **3** ($c = 1 \cdot 10^{-4}$ M in CH₃CN) at $\lambda = 469$ nm upon addition of Hg²⁺, indicating the formation of 2:1 L/M complex.

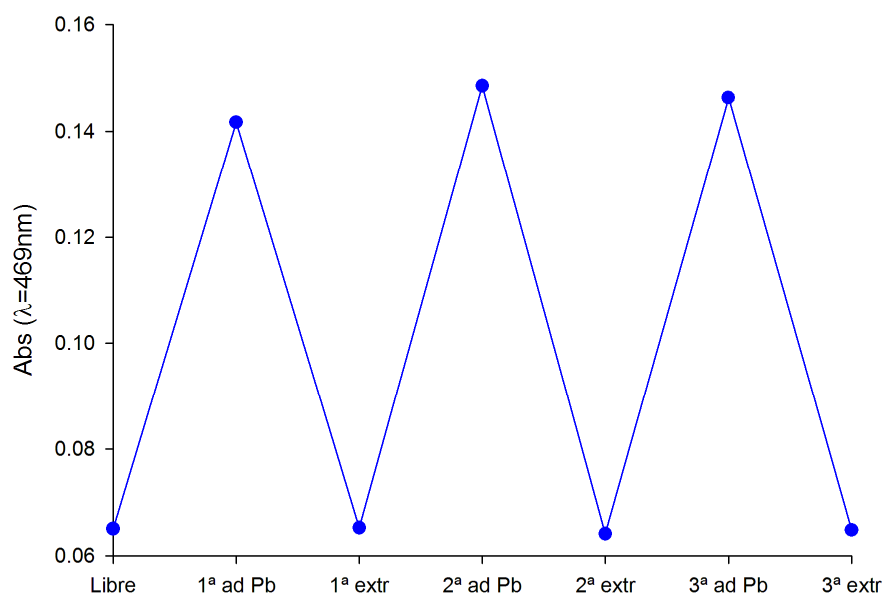


Figure SI 44. Stepwise complexation (addition of Hg²⁺) /decomplexation (extraction with H₂O) cycles of ligand **3** ($1 \cdot 10^{-4}$ M in CH₂Cl₂) and Hg²⁺, carried out by UV/Vis analysis.

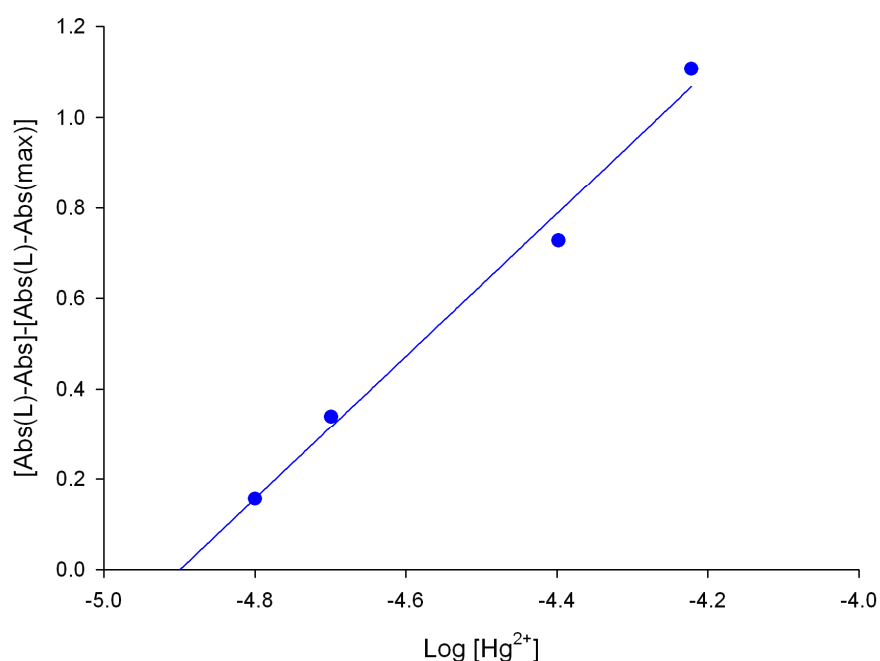


Figure SI 45. Absorbance of **3** ($c = 1 \cdot 10^{-4} \text{ M}$ in CH_3CN) at each concentration of Hg^{2+} added, normalized between the minimum absorbance, found at zero equiv of Hg^{2+} ; and the maximum absorbance, found at $[\text{Hg}^{2+}] = 1.2614 \cdot 10^{-5} \text{ M}$.

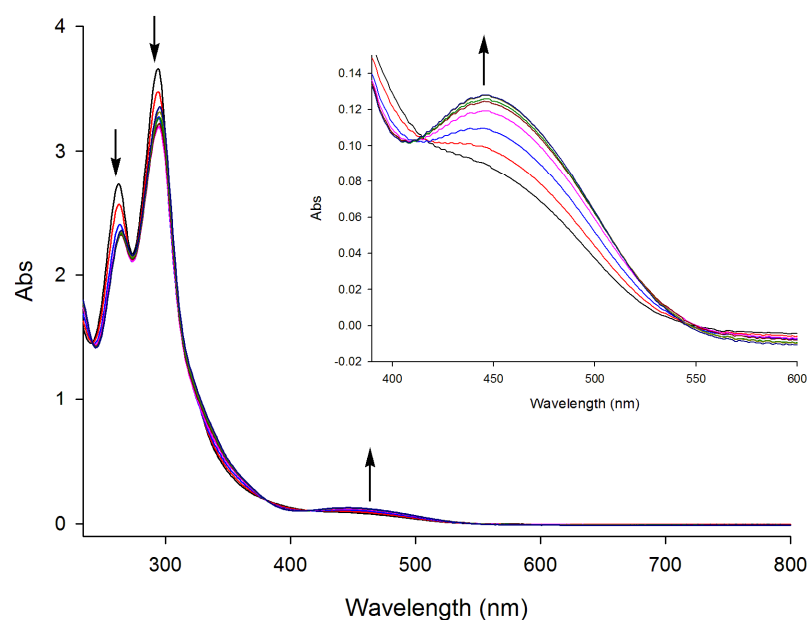


Figure SI 46. Changes in the absorption spectra of **3** (black) ($c = 1 \cdot 10^{-4} \text{ M}$ in CH_3CN) upon addition of increasing amounts of Cd^{2+} metal cation, until 1 equiv was added (deep blue). Arrows indicate absorption that increase or decrease during the experiment.

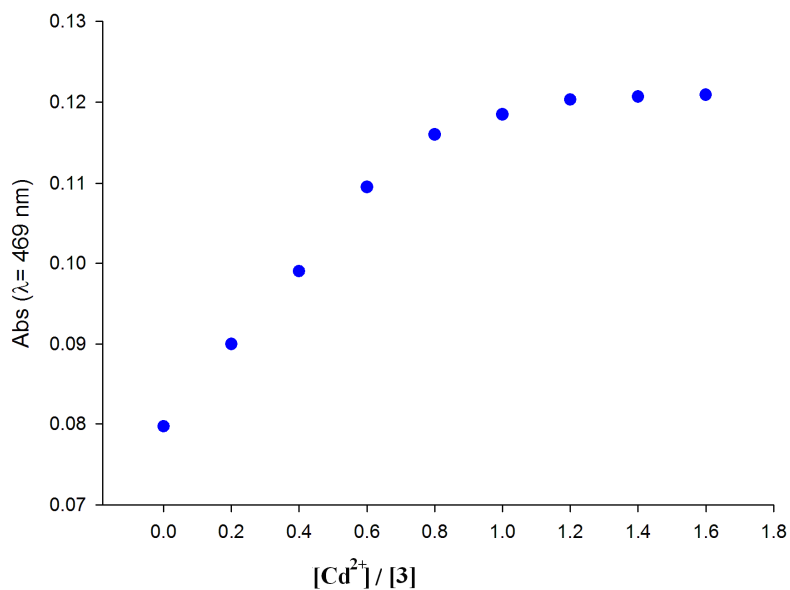


Figure SI 47. Change of absorbance of **3** ($c = 1 \cdot 10^{-4} \text{ M}$ in CH_3CN) at $\lambda = 469 \text{ nm}$ upon addition of Cd^{2+} , indicating the formation of 1:1 L/M complex.

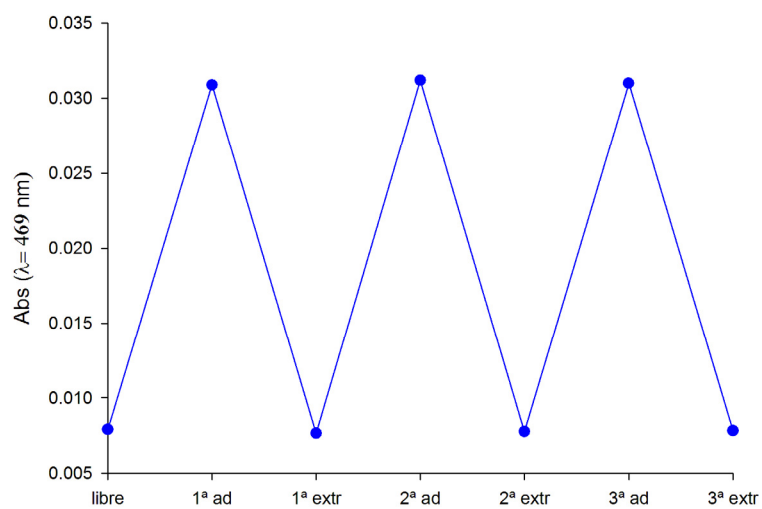


Figure SI 48. Stepwise complexation (addition of Hg^{2+}) /decomplexation (extraction with H_2O) cycles of ligand **3** ($1 \cdot 10^{-4} \text{ M}$ in CH_2Cl_2) and Hg^{2+} , carried out by UV/Vis analysis.

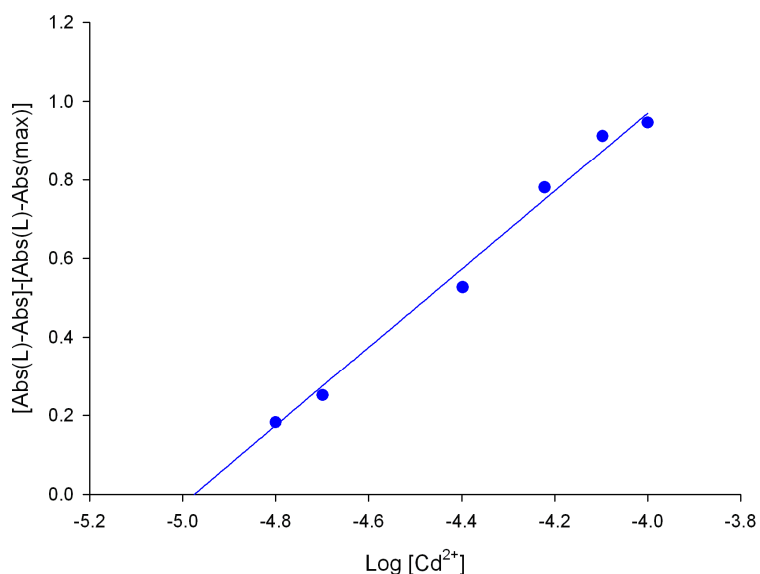


Figure SI 49. Absorbance of **3** ($c = 1 \cdot 10^{-4}$ M in CH_3CN) at each concentration of Cd^{2+} added, normalized between the minimum absorbance, found at zero equiv of Cd^{2+} ; and the maximum absorbance, found at $[\text{Cd}^{2+}] = 1.0173 \cdot 10^{-5}$ M.

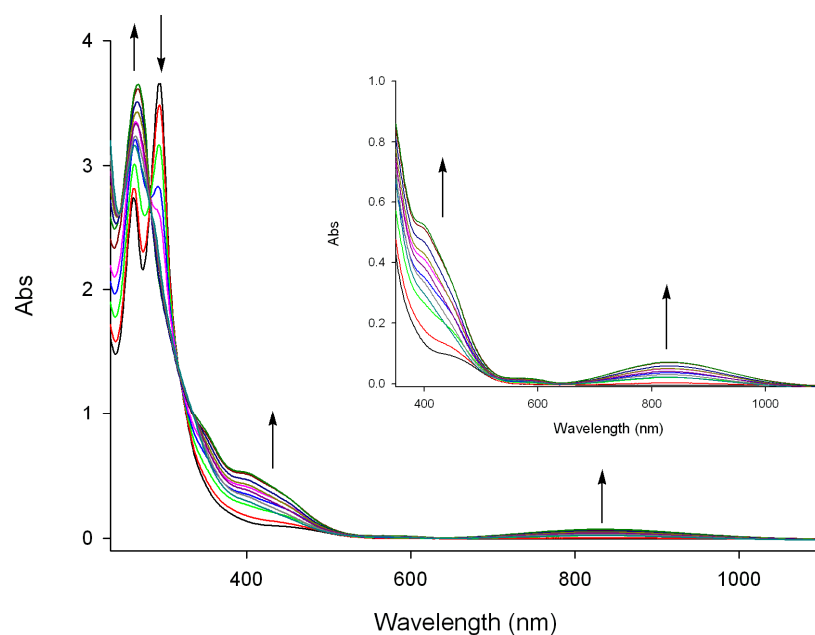


Figure SI 50. Changes in the absorption spectra of **3** (black) (1×10^{-4} M) in CH_3CN upon addition of increasing amounts of Cu^{2+} metal cation, until 2 equiv was added (deep cyan). Arrows indicate absorption that increase or decrease during the experiment.

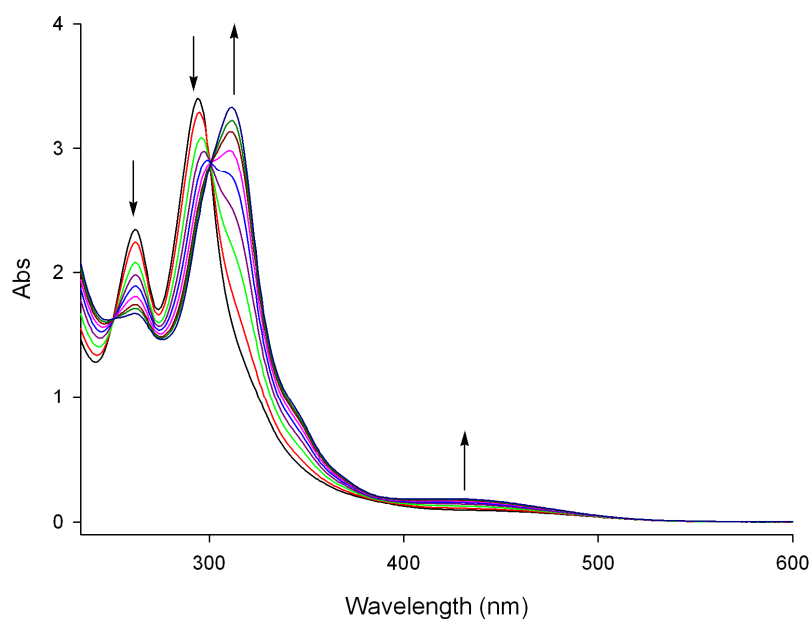


Figure SI 51. Changes in the absorption spectra of **3** (black) ($c = 1 \cdot 10^{-4} \text{M}$ in CH_3CN) upon addition of increasing amounts of $\text{HP}_2\text{O}_7^{3-}$ anion, until 4 equiv was added (deep blue). Arrows indicate absorption that increase or decrease during the experiment.

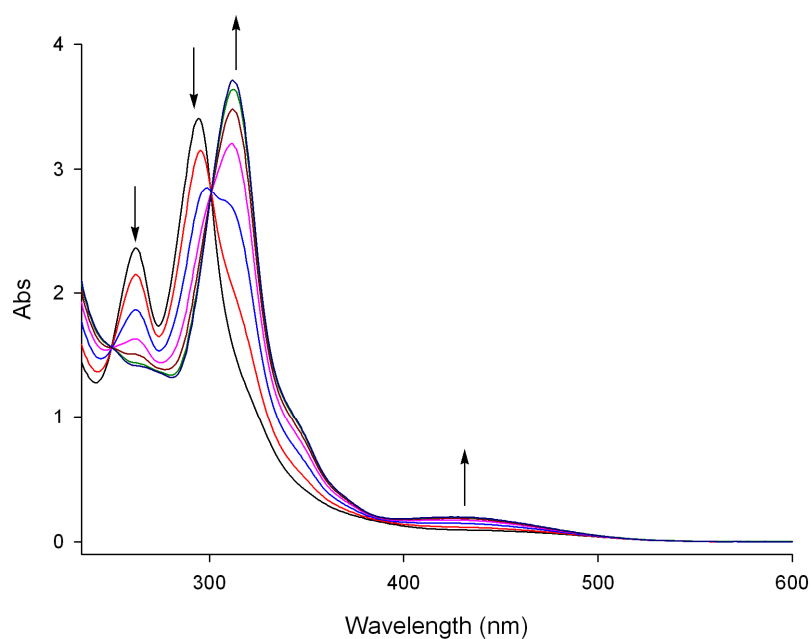


Figure SI 52. Changes in the absorption spectra of **3** (black) ($c = 1 \cdot 10^{-4} \text{M}$ in CH_3CN) upon addition of increasing amounts of F^- metal anion, until 3 equiv was added (deep blue). Arrows indicate absorption that increase or decrease during the experiment.

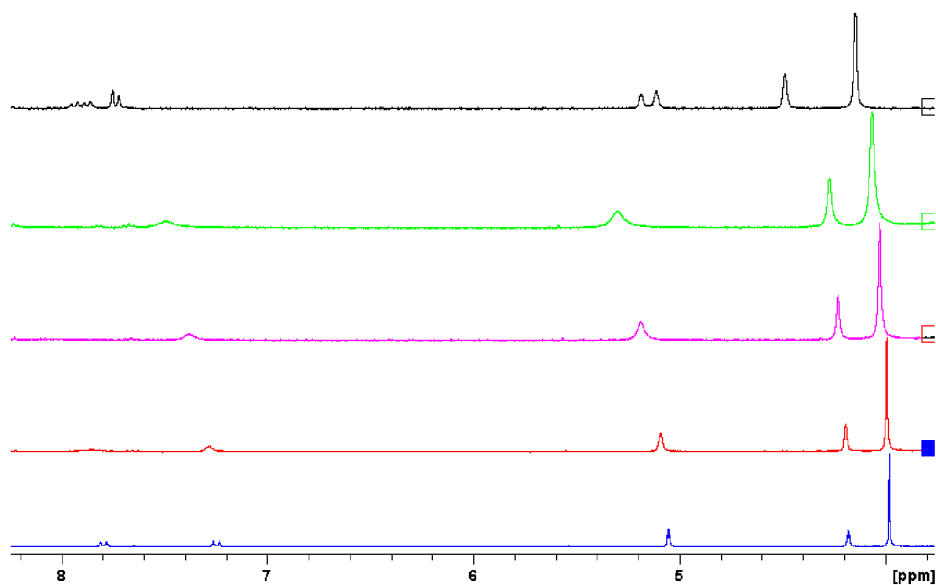


Figure SI 53. Changes in the ^1H -NMR spectrum of **3** (top) in acetone upon addition of increasing amounts of $\text{HP}_2\text{O}_7^{3-}$ until 2 equiv (bottom).

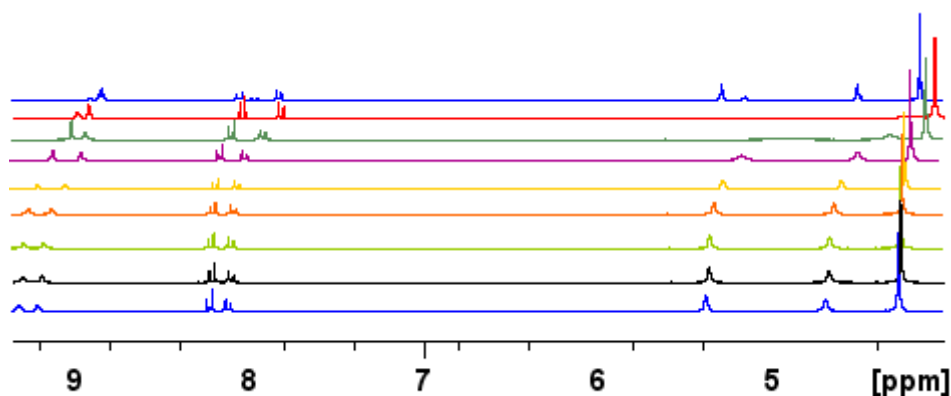


Figure SI 54. Changes in the ^1H -NMR spectrum of **3** (top) in acetone upon addition of increasing amounts of Pb^{2+} until 0.5 equiv (bottom).

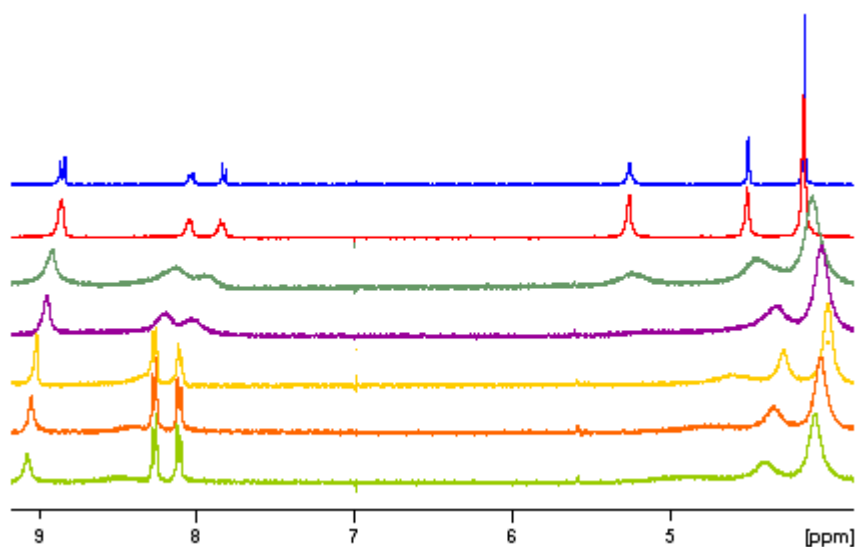


Figure SI 55. Changes in the ¹H-NMR spectrum of **3** (top) in acetone upon addition of increasing amounts of Zn²⁺ until 1 equiv (bottom).

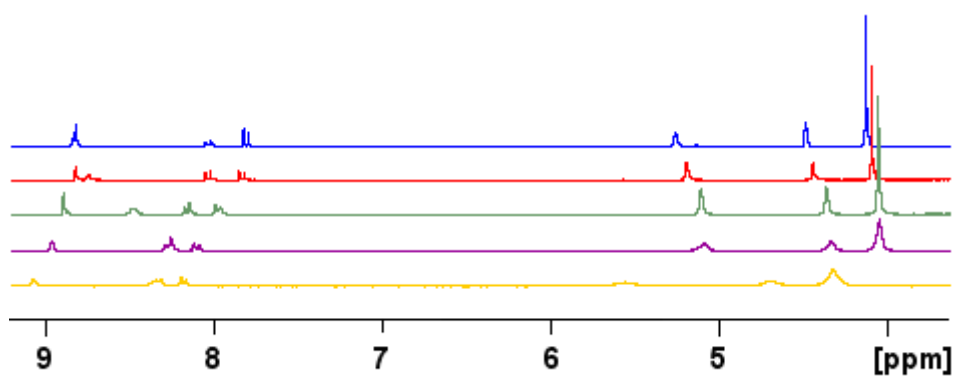


Figure SI 56. Changes in the ¹H-NMR spectrum of **3** (top) in acetone upon addition of increasing amounts of Hg²⁺ until 0.5 equivalent (bottom).

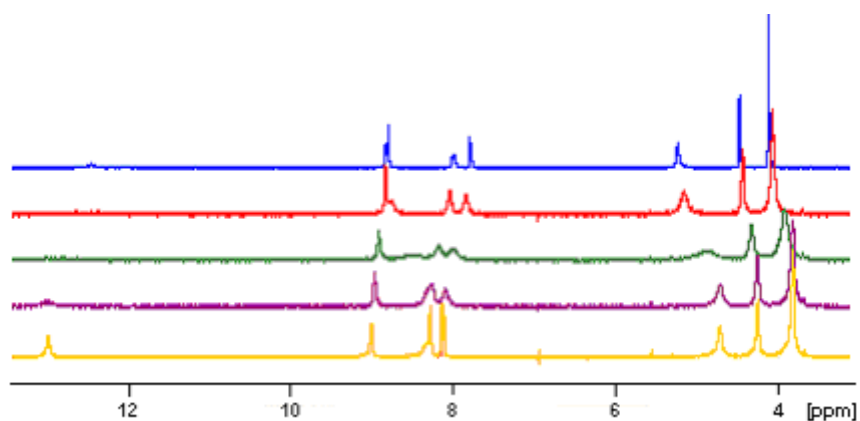


Figure SI 57. Changes in the ¹H-NMR spectrum of **3** (top) in acetone upon addition of increasing amounts of Cd²⁺ until 1. equiv (bottom).

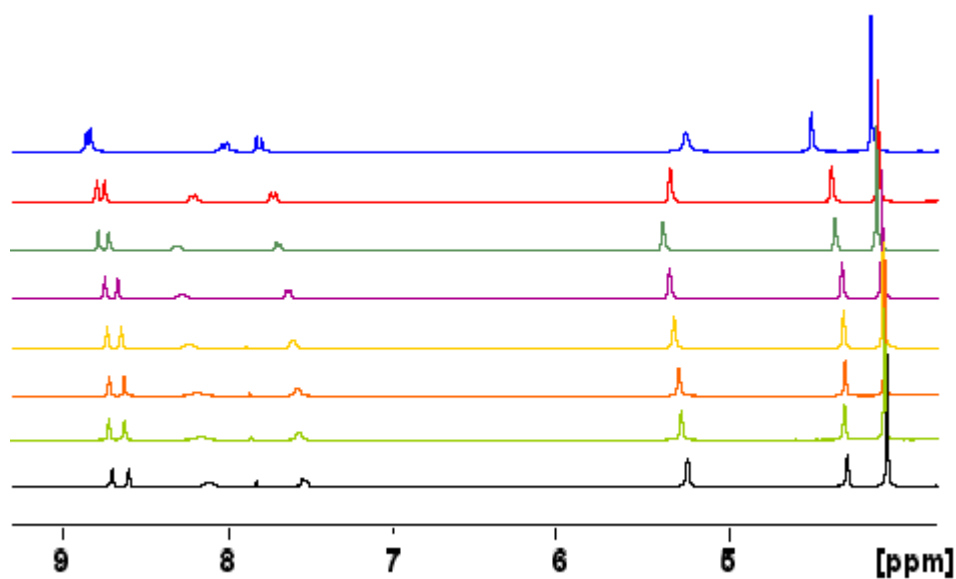


Figure SI 58. Changes in the ^1H -NMR spectrum of **3** (top) in acetone upon addition of increasing amounts of $\text{HP}_2\text{O}_7^{3-}$ until 1.4 equivalents (bottom).

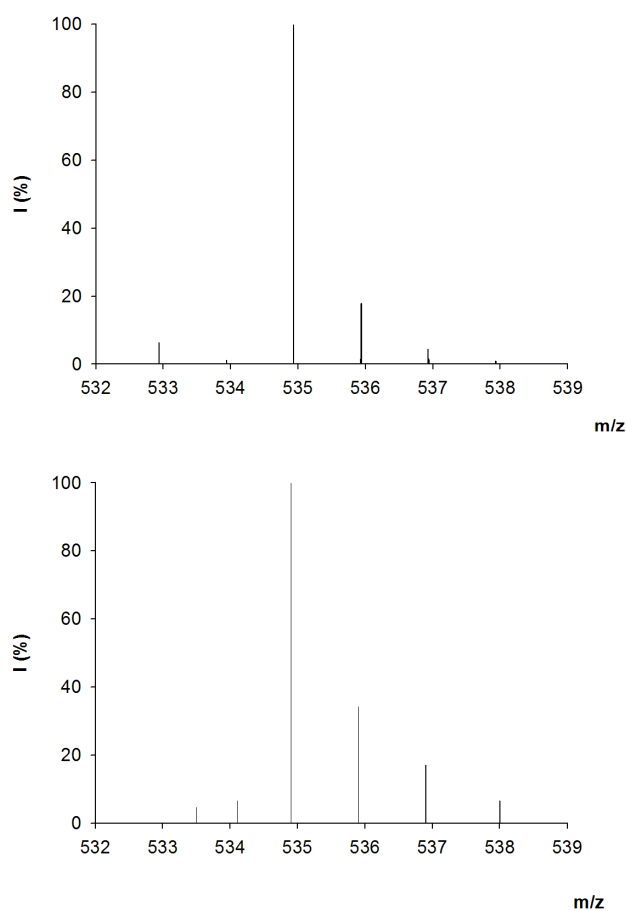


Figure SI 59. Relative abundance of the isotopic cluster for $2 \cdot \text{HP}_2\text{O}_7^{3-}$ (top) experimental (in CH_3CN); (bottom) simulated.

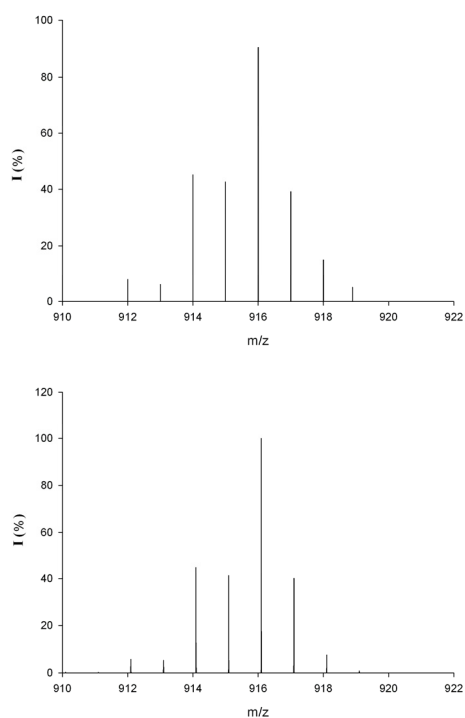


Figure SI 60. Relative abundance of the isotopic cluster for 3_2Pb^{2+} (top) experimental (in CH_3CN); (bottom) simulated.

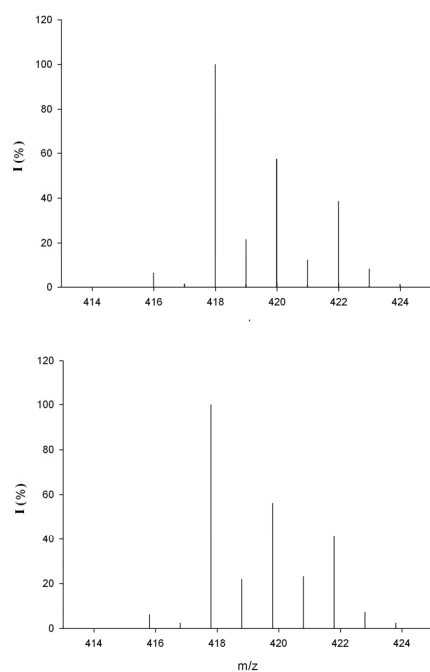


Figure SI 61. Relative abundance of the isotopic cluster for 3Zn^{2+} (top) experimental (in CH_3CN); (bottom) simulated.

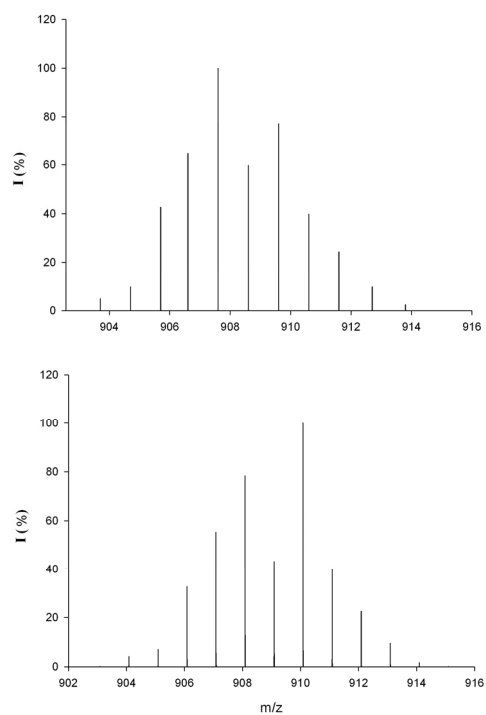


Figure SI 62. Relative abundance of the isotopic cluster for 3_2Hg^{2+} (top) experimental (in CH_3CN); (bottom) simulated.

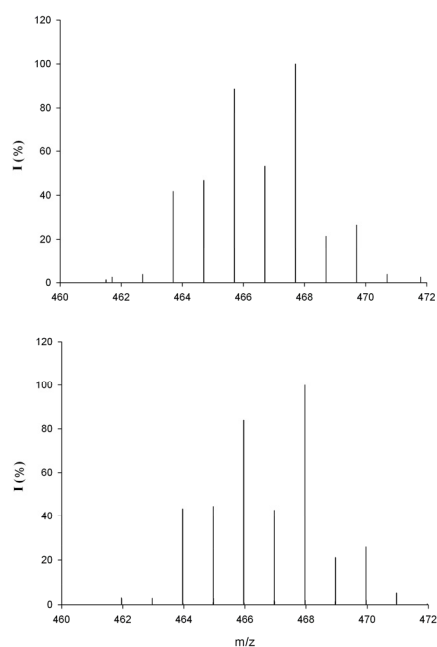


Figure SI 63. Relative abundance of the isotopic cluster for 3Cd^{2+} (top) experimental (in CH_3CN); (bottom) simulated.