

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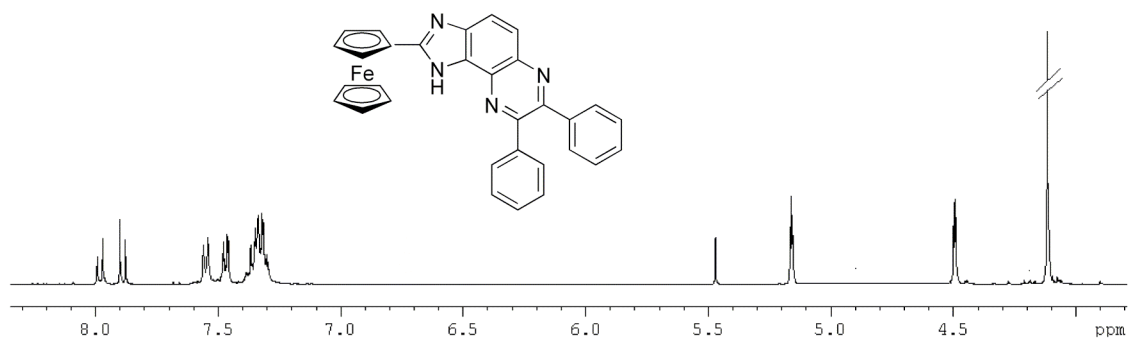
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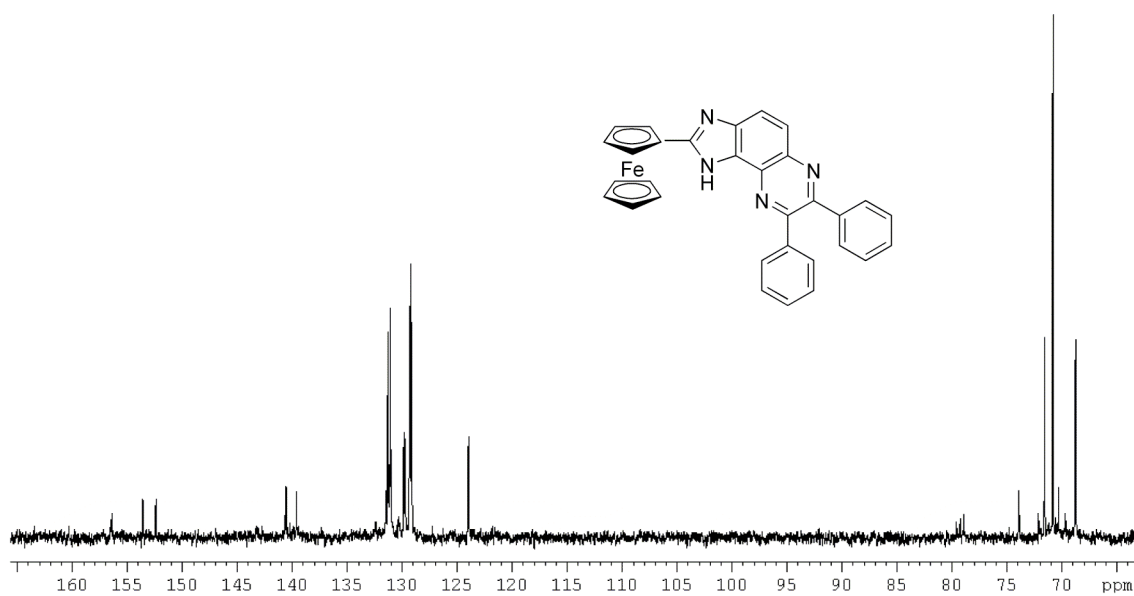
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2-Ferrocenyl-7,8-Diphenyl-3*H*-imidazo[4,5-*f*]quinoxalines, [6a]

^1H NMR (400MHz, MeOD)

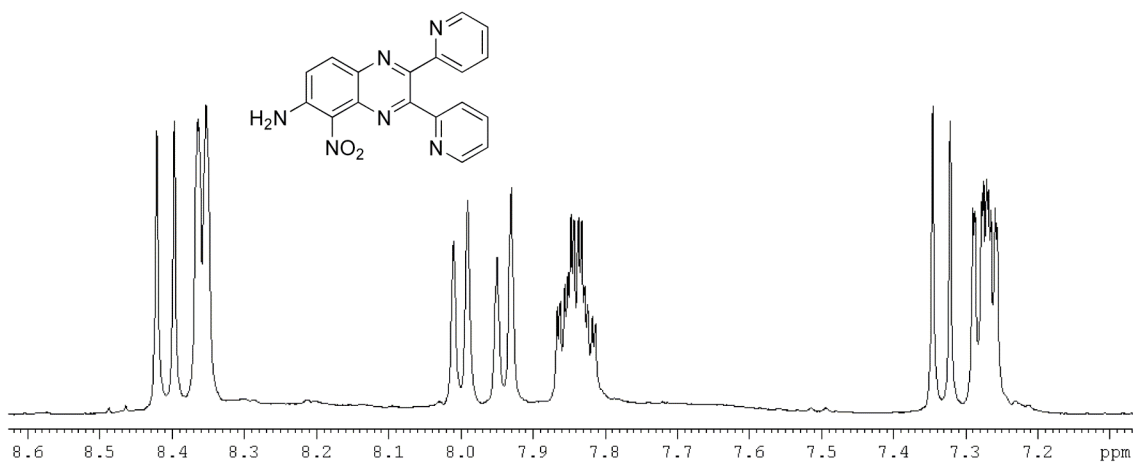


^{13}C NMR (100 MHz, CDCl_3):

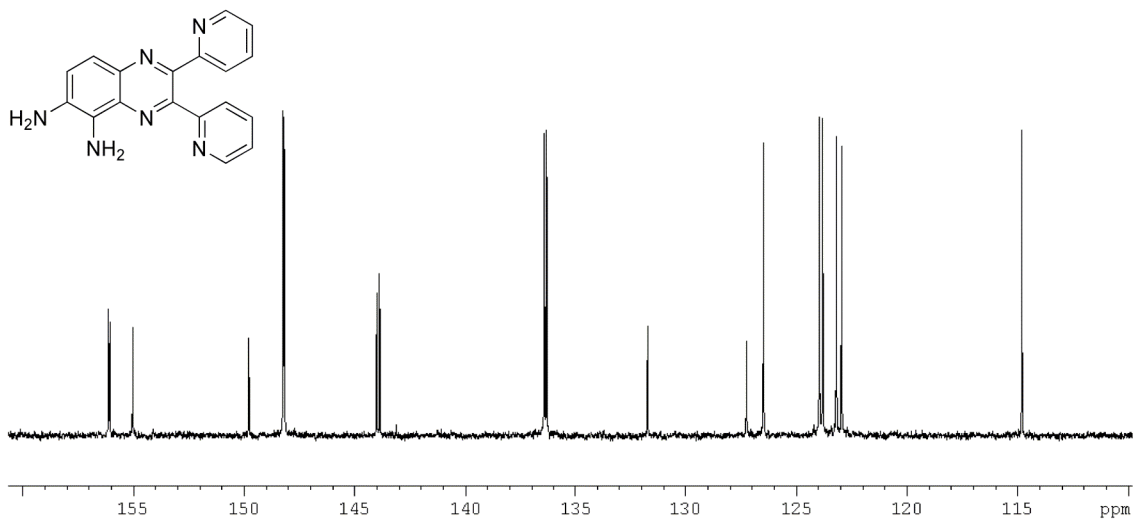


5-amino-6-nitro-2,3-di(2-pyridyl)quinoxaline, [4b]

^1H NMR (400MHz, CDCl_3)

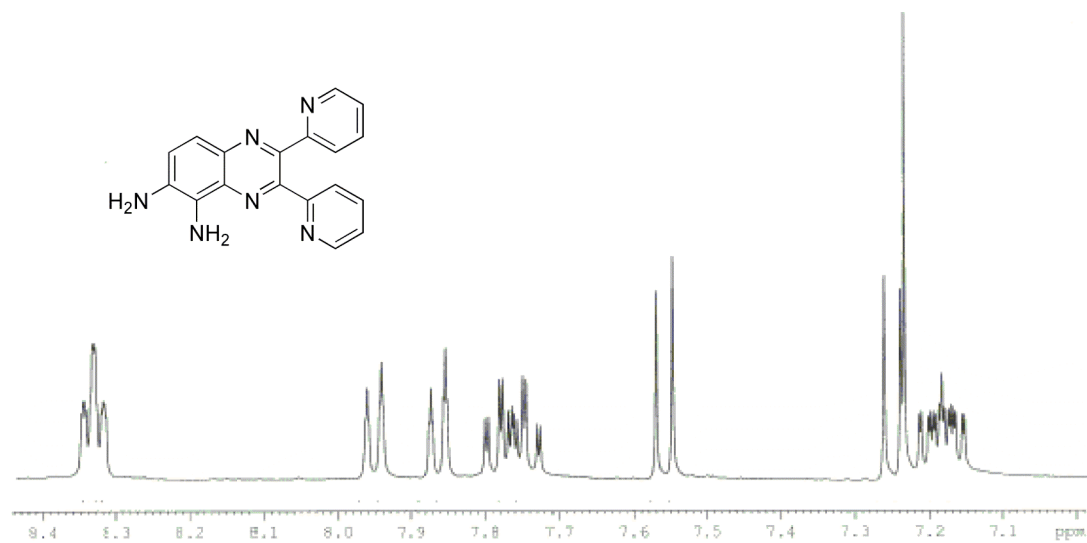


^{13}C NMR (100 MHz, CDCl_3):

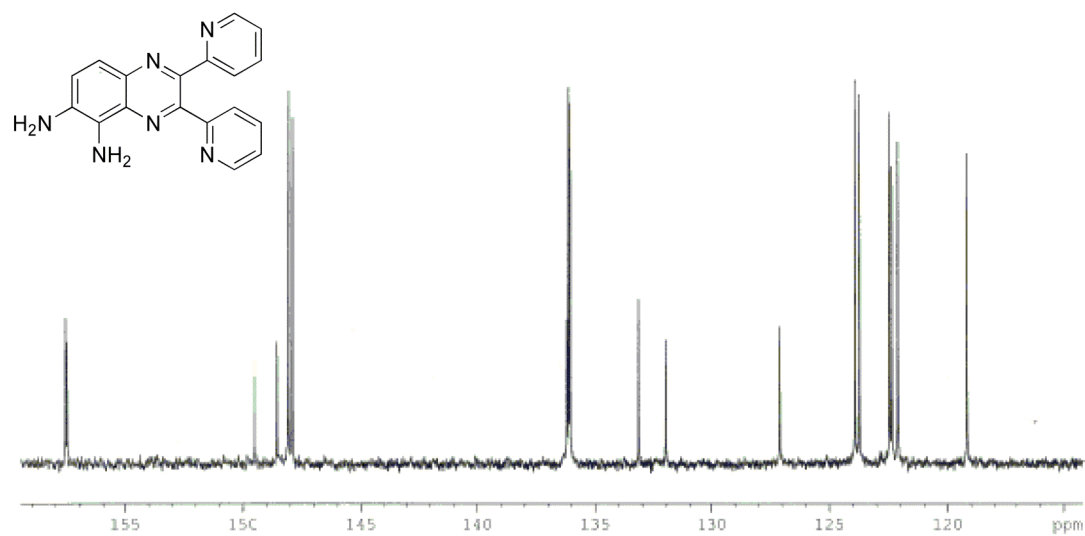


5,6-diamino-2,3-di(2-pyridyl)quinoxaline, [5b]

^1H NMR (400MHz, CDCl_3):

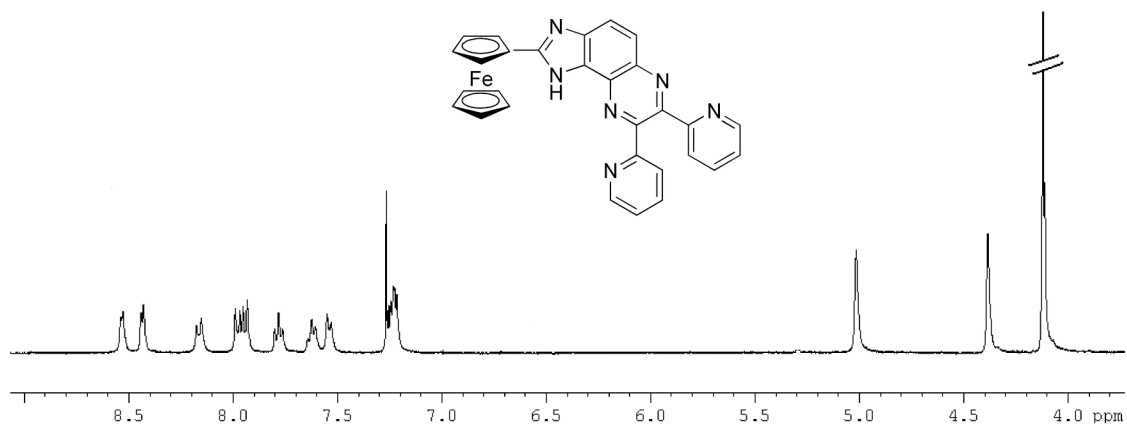


^{13}C NMR (100 MHz, CDCl_3):

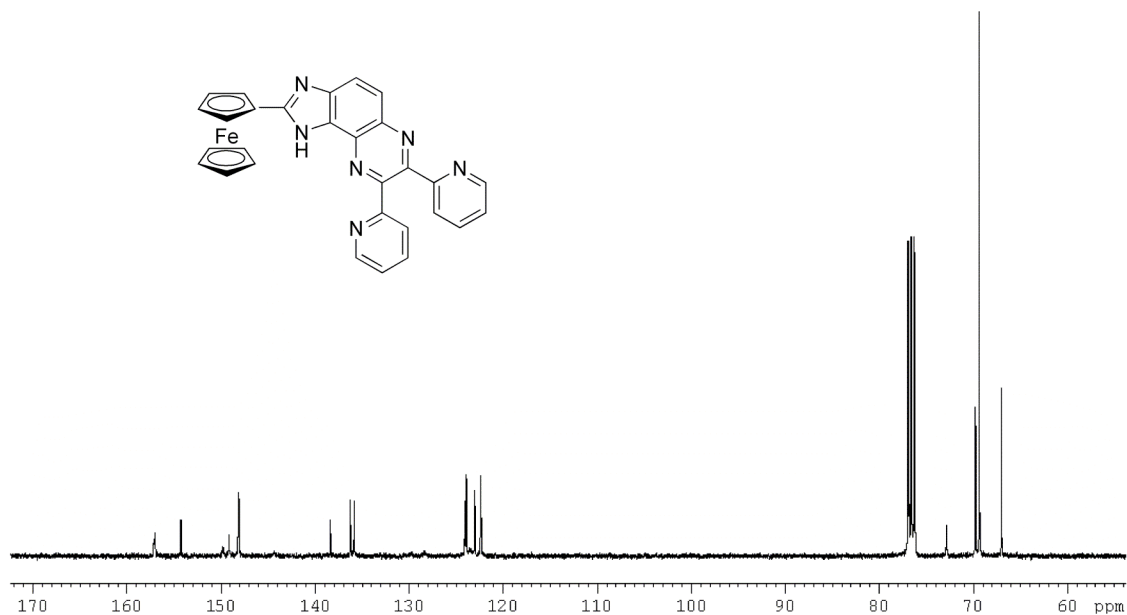


2-Ferrocenyl-7,8-Di-(2-pyridyl)-3H-imidazo[4,5-f]quinoxalines, [6b]

^1H NMR (400MHz, CDCl_3):



^{13}C NMR (100 MHz, CDCl_3):



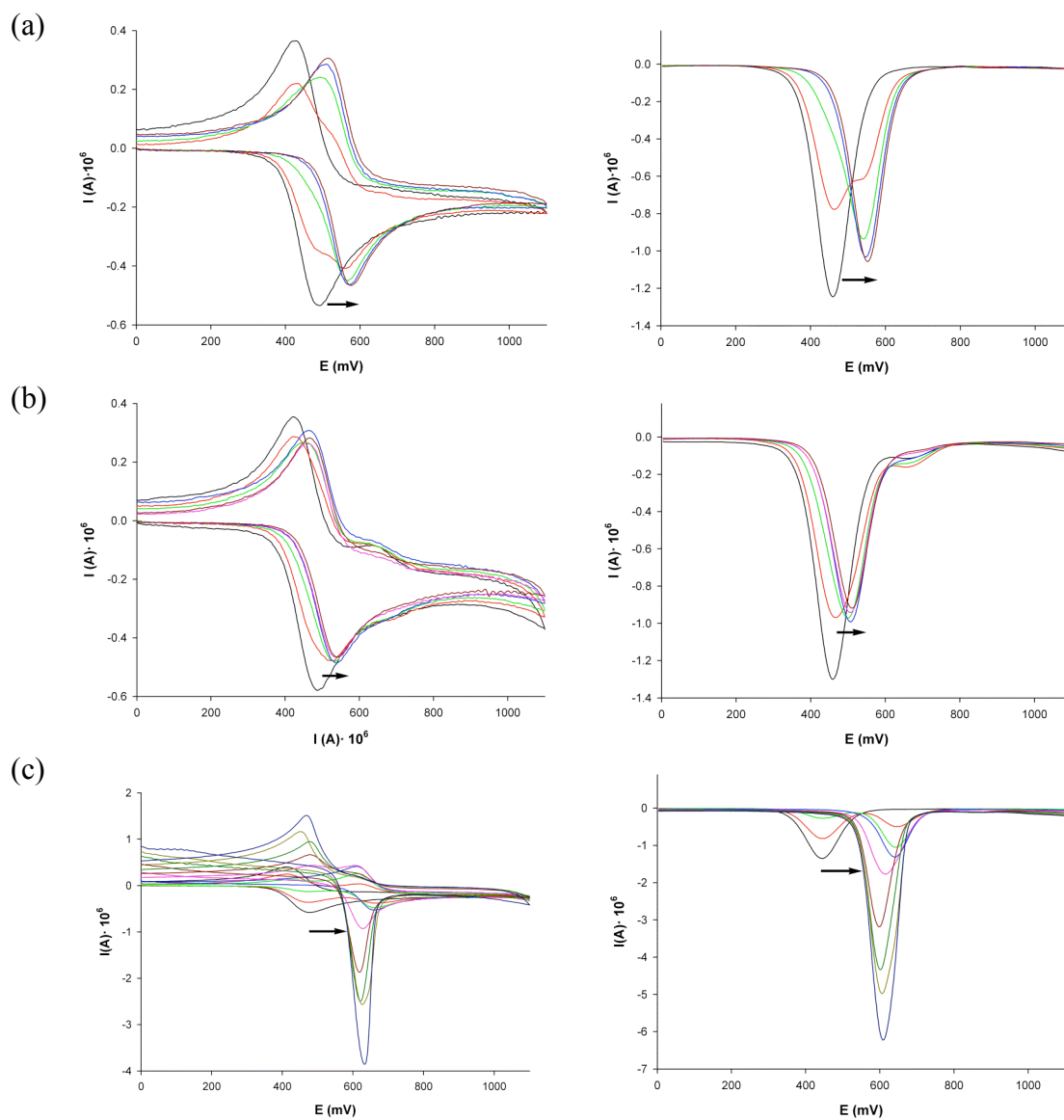


Figure SI 1. Evolution of the CV (left) and OSWV (right) of **6a** (1 mM) in $\text{CH}_3\text{CN}/[(n\text{-Bu})_4\text{ClO}_4]$ scanned at 0.1 V s^{-1} in the presence of increasing amounts of: (a) Cd^{2+} ; (b) Zn^{2+} ; (c) Hg^{2+} .

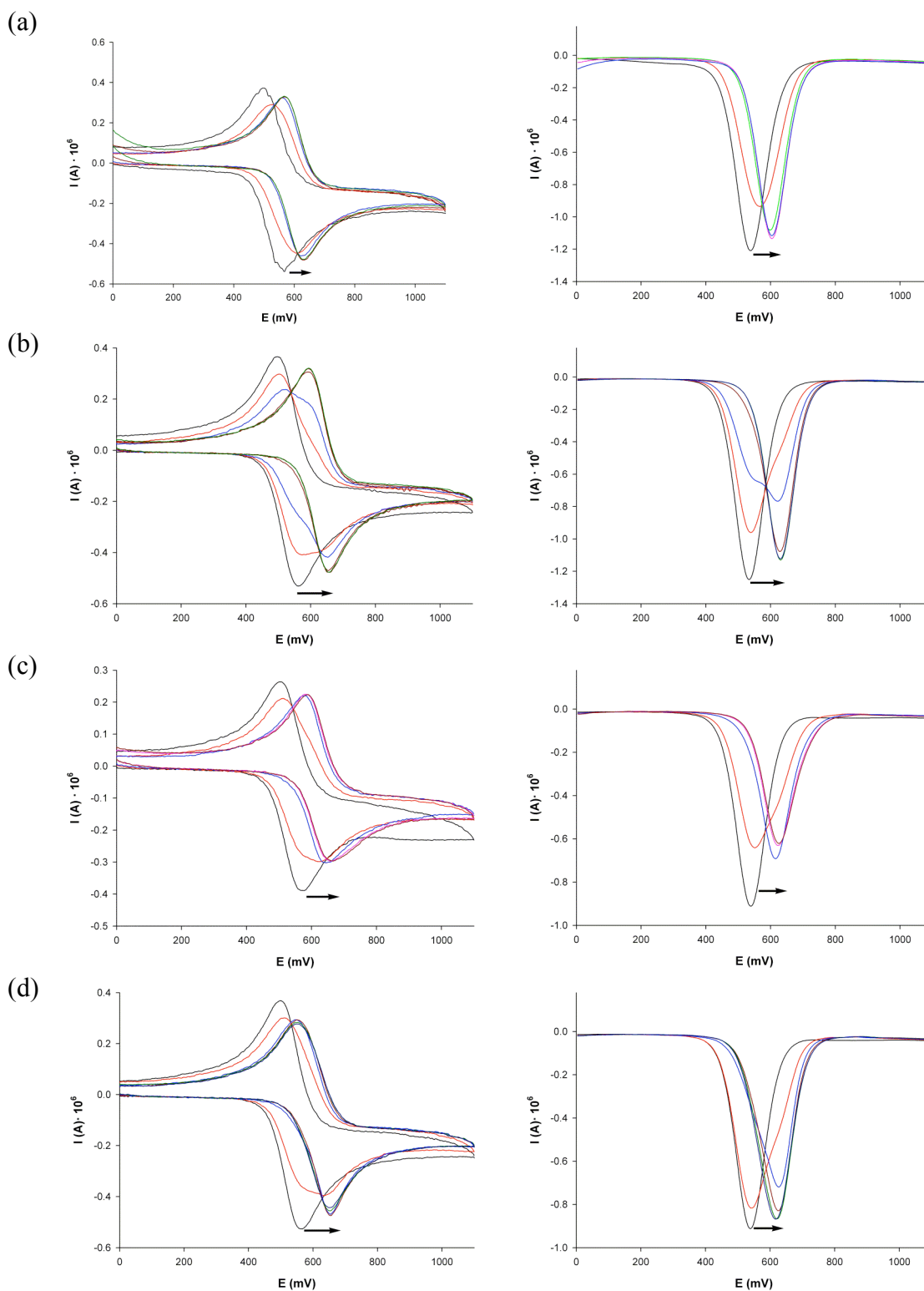


Figure SI 2. Evolution of the CV (left) and OSWV (right) of **6b** (1 mM) in CH₃CN/[*n*-Bu)₄]ClO₄ scanned at 0.1 V s⁻¹ in the presence of increasing amounts of: (a) Pb²⁺; (b) Cd²⁺; (c) Zn²⁺; (d) Ni²⁺.

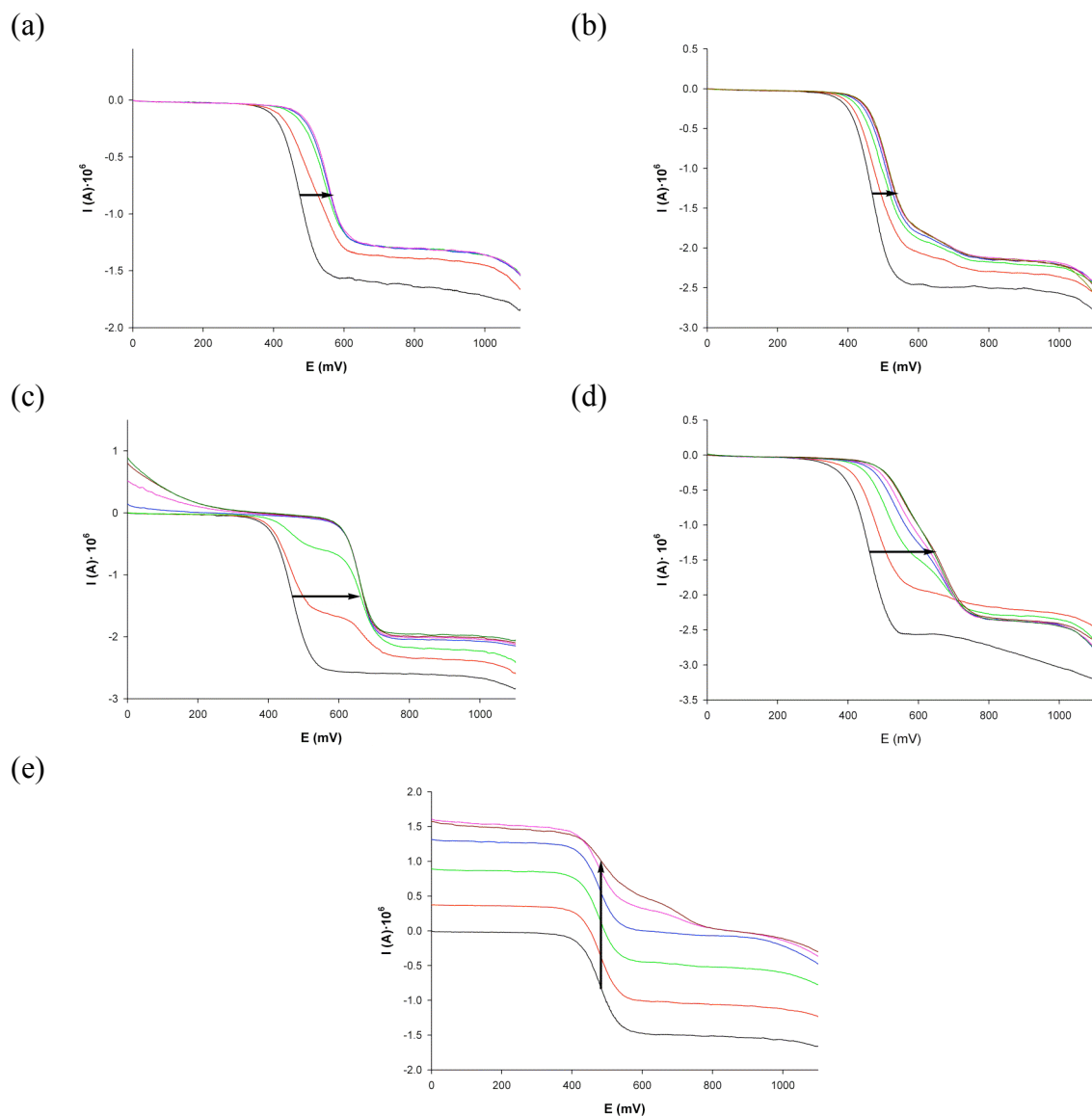


Figure SI 3. Evolution of the LSW of **6a** (1mM) in the presence of increasing amounts of (a) Cd²⁺; (b) Cd²⁺; (c) Hg²⁺; (d) Pb²⁺; (e) Cu²⁺, obtained using a rotating disk electrode at 100 mVs⁻¹ and 1000 rpm and [(*n*-Bu)₄]ClO₄ 0.1 M as supporting electrolyte.

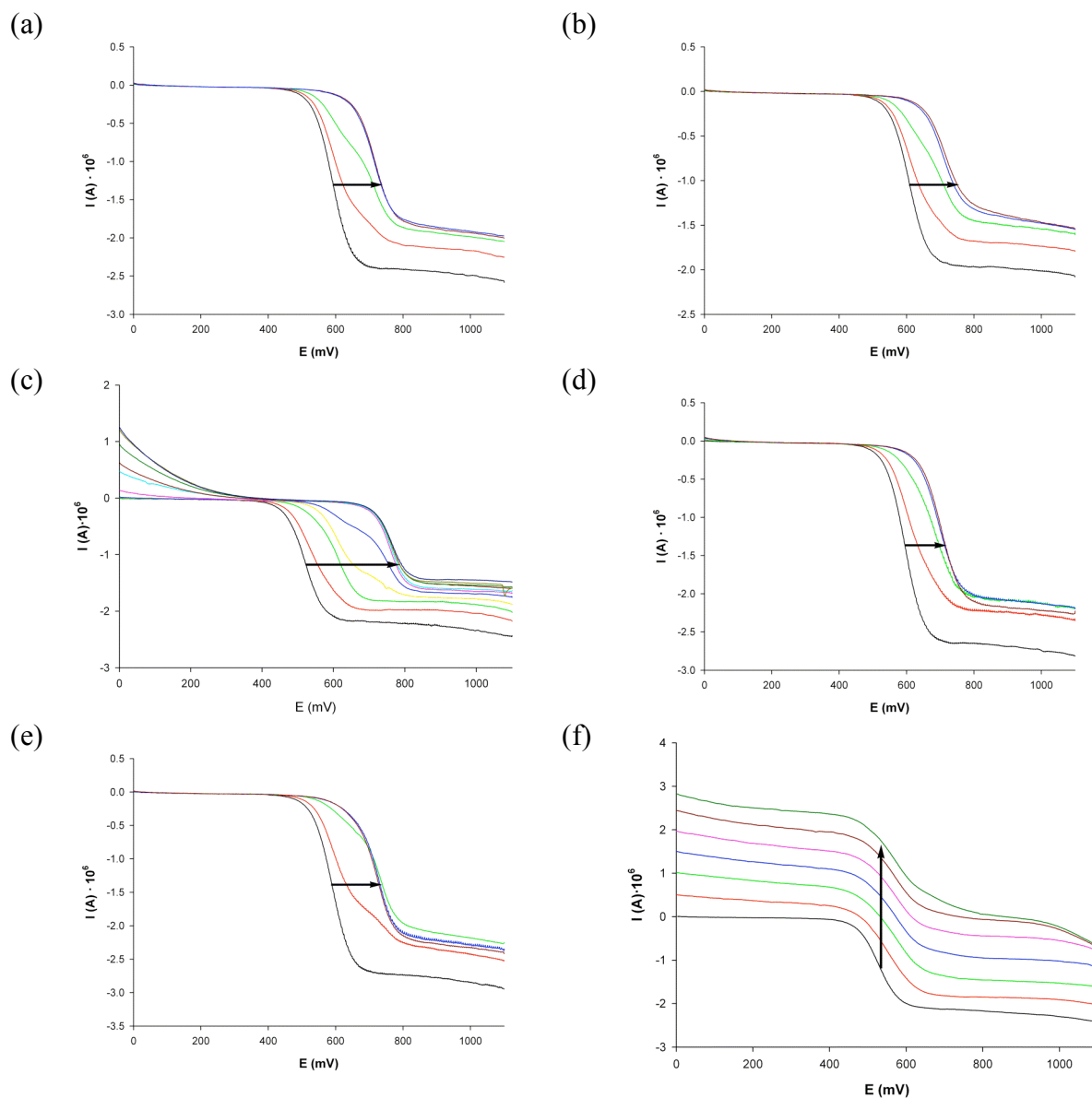


Figure SI 4. Evolution of the LSW of **6b** (1mM) in the presence of increasing amounts of (a) Cd^{2+} ; (b) Zn^{2+} ; (c) Hg^{2+} ; (d) Pb^{2+} ; (e) Ni^{2+} ; (g) Cu^{2+} , obtained using a rotating disk electrode at 100 mVs^{-1} and 1000 rpm and $[(n\text{-Bu})_4]\text{ClO}_4$ 0.1 M as supporting electrolyte.

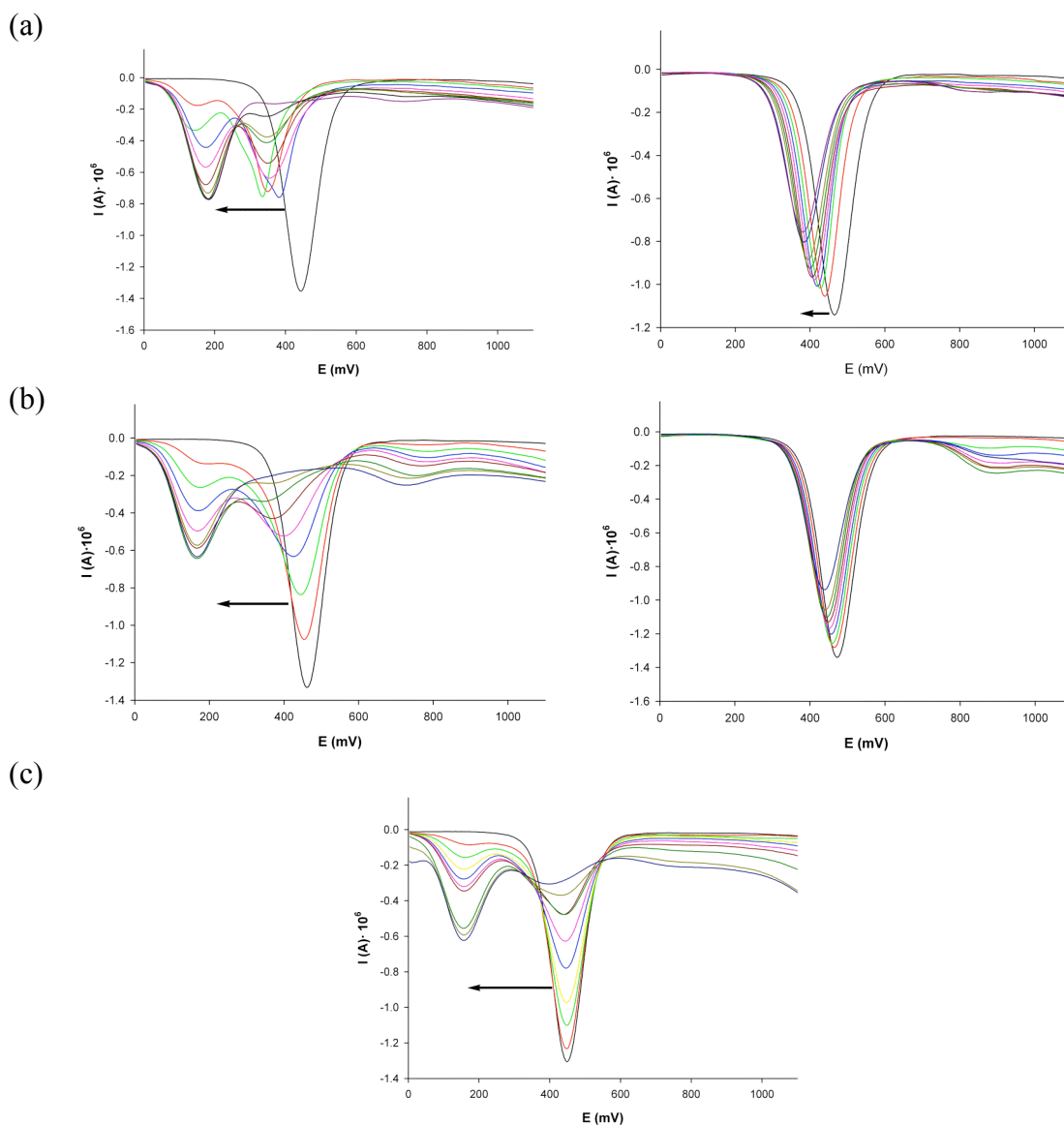


Figure SI 5. (a) Evolution of the OSWV of **6a** (1 mM) in CH₃CN/[*n*-Bu)₄]ClO₄ scanned at 0.1 V s⁻¹ in the presence of increasing amounts of (a) HP₂O₇³⁻ (left) until 2 equiv and in the presence of 2 equiv of HP₂O₇³⁻ and 20 equiv of acetic acid in CH₃CN (right); (b) F⁻ (left) until 2 equiv and in the presence of 2 equiv of F⁻ and 20 equiv of acetic acid in CH₃CN (right). (c) Evolution of the OSWV of **6a** (1 mM) in CH₃CN/[*n*-Bu)₄]ClO₄ scanned at 0.1 V s⁻¹ in the presence of increasing amounts of OH⁻ until 2 equiv.

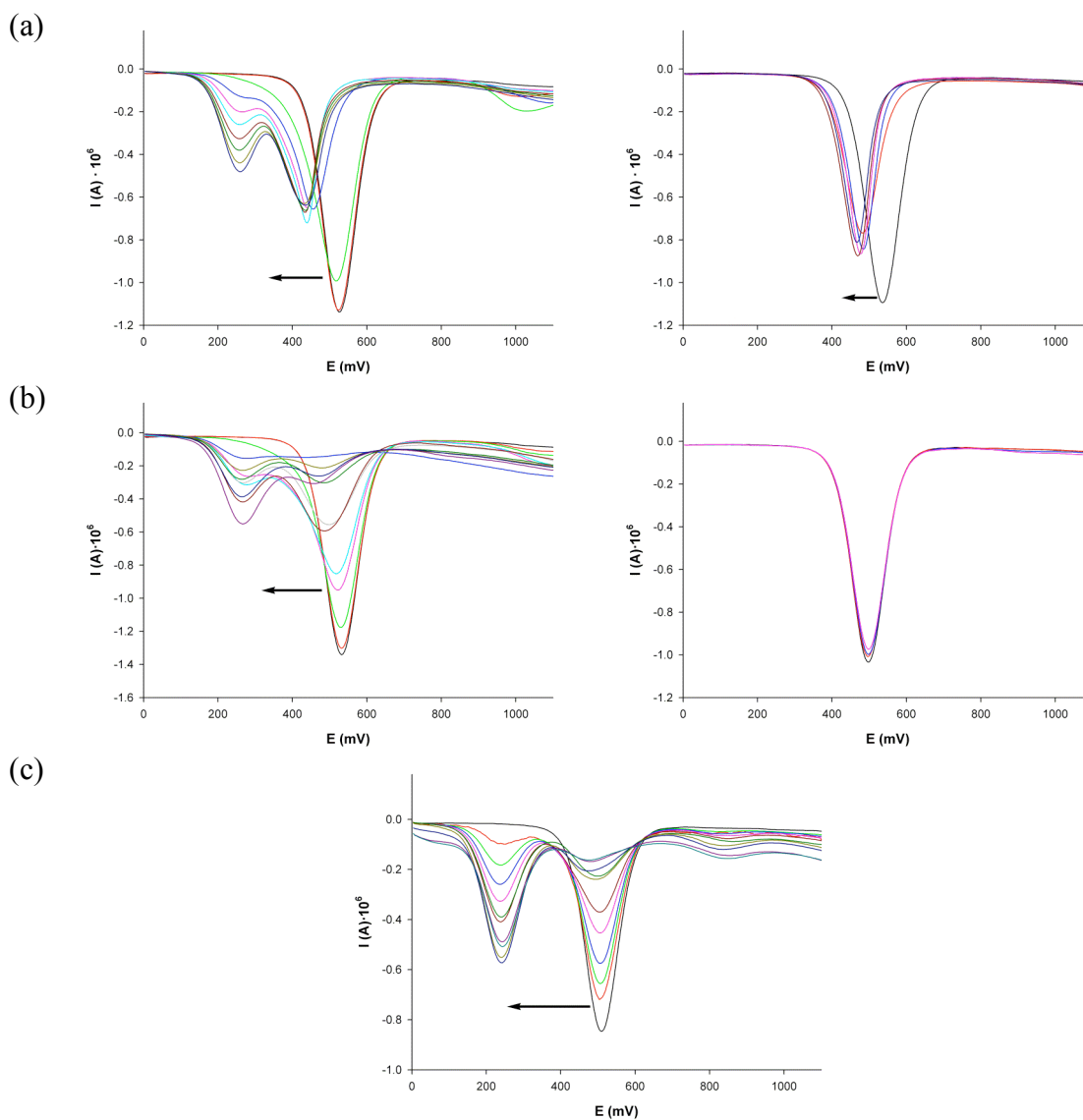


Figure SI 6. (a) Evolution of the OSWV of **6b** (1 mM) in CH₃CN/[*n*-Bu₄]₄ClO₄ scanned at 0.1 V s⁻¹ in the presence of increasing amounts of (a) HP₂O₇³⁻ (left) until 2 equiv and in the presence of 2 equiv of HP₂O₇³⁻ and 20 equiv of acetic acid in CH₃CN (right); (b) F⁻ (left) until 2 equiv and in the presence of 2 equiv of F⁻ and 20 equiv of acetic acid in CH₃CN (right). (c) Evolution of the OSWV of **6b** (1 mM) in CH₃CN/[*n*-Bu₄]₄ClO₄ scanned at 0.1 V s⁻¹ in the presence of increasing amounts of OH⁻ until 2 equiv.

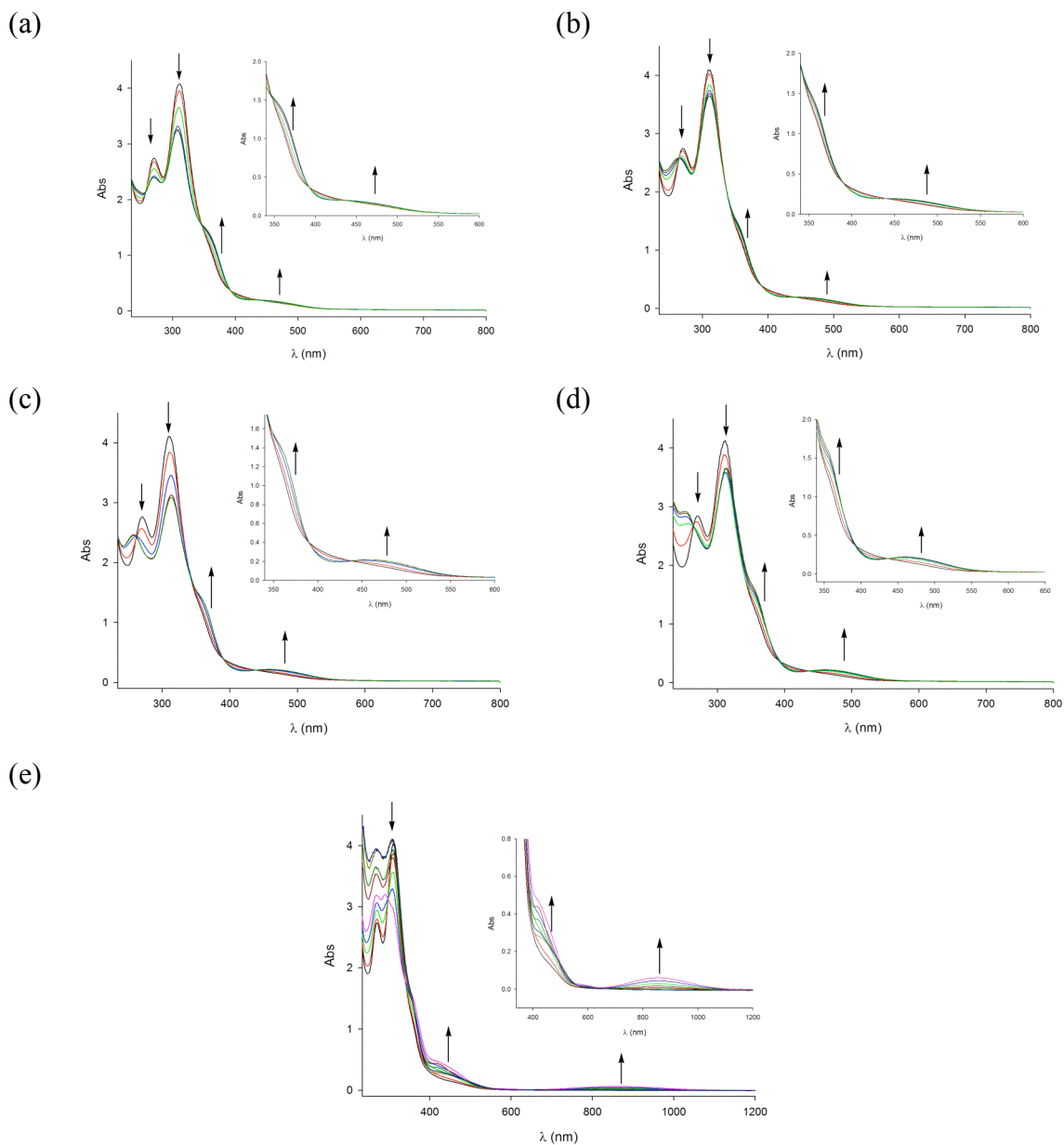


Figure SI 7. Changes in the absorption spectra of **6a** ($c = 1 \cdot 10^{-4}$ M in CH_3CN) upon addition of increasing amounts of (a) Cd^{2+} ; (b) Zn^{2+} ; (c) Hg^{2+} ; (d) Pb^{2+} ; (e) Cu^{2+} metal cation, until 1 equiv was added. Arrows indicate absorptions that increase or decrease during the experiment.

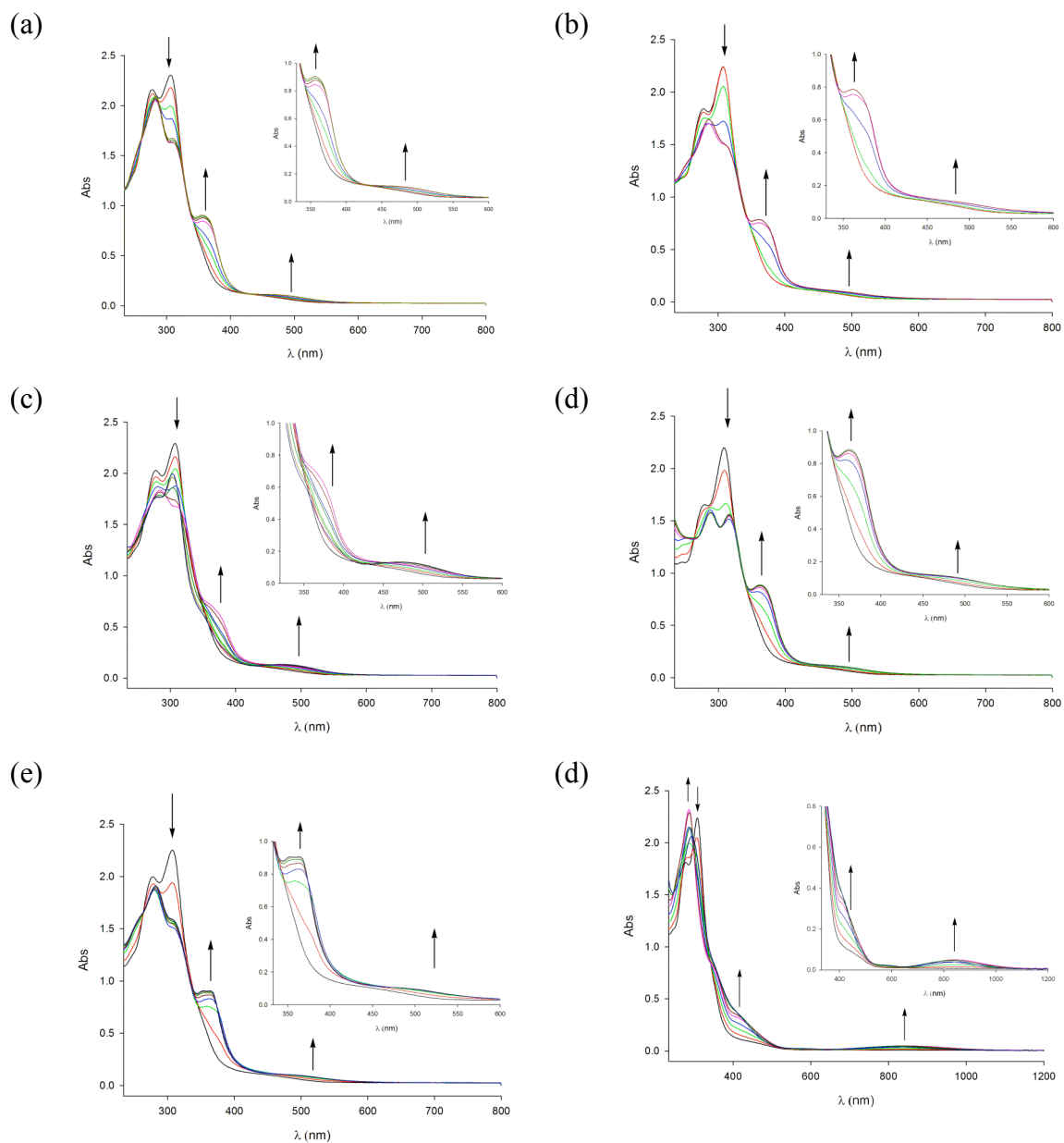


Figure SI 8. Changes in the absorption spectra of **6b** ($c = 5 \cdot 10^{-5}$ M in CH_3CN) upon addition of increasing amounts of (a) Cd^{2+} ; (b) Zn^{2+} ; (c) Hg^{2+} ; (d) Pb^{2+} ; (e) Ni^{2+} ; (d) Cu^{2+} metal cation, until 1 equiv was added. Arrows indicate absorptions that increase or decrease during the experiment.

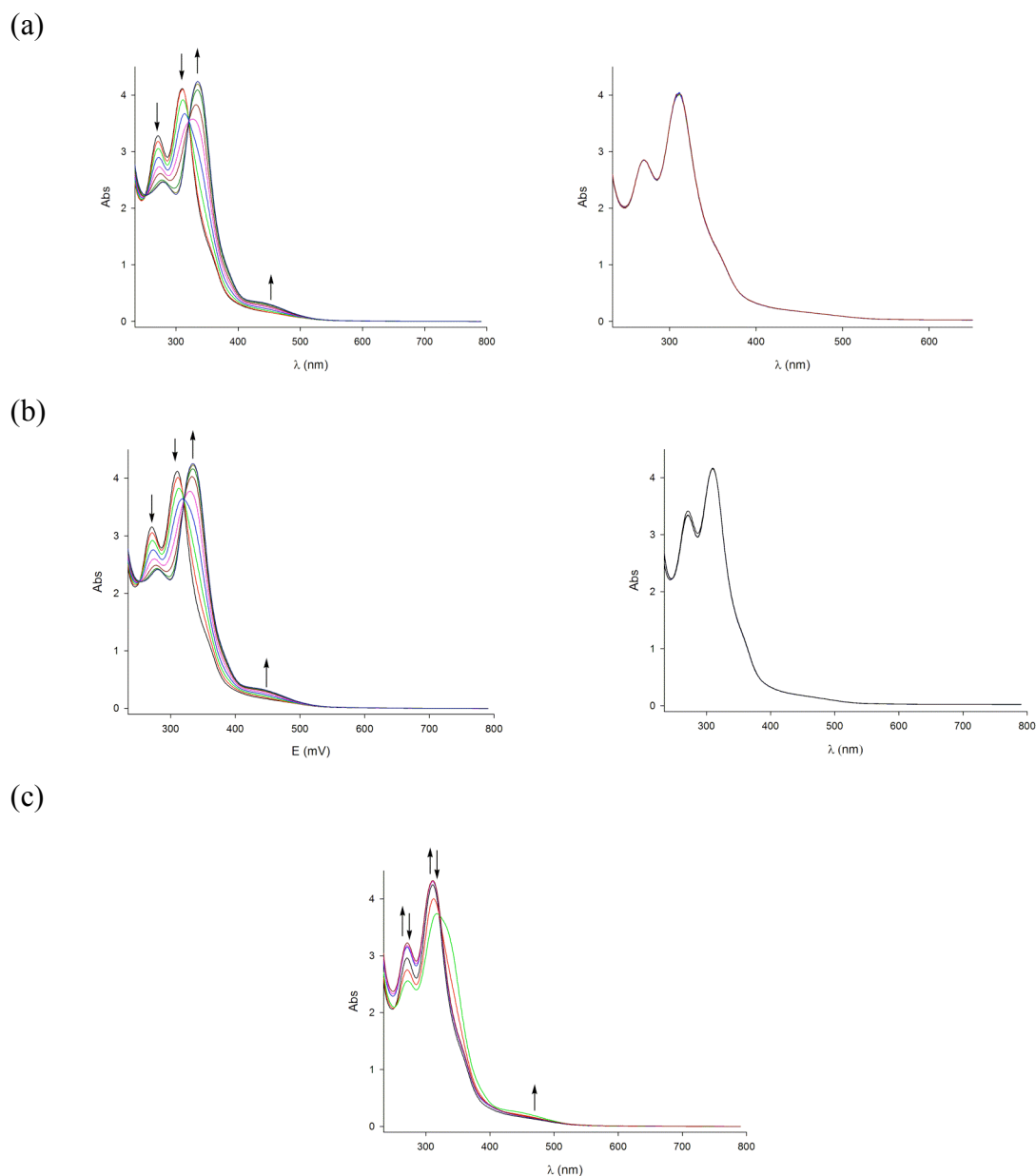


Figure SI 9. Changes in the absorption spectra of **6a** ($c = 1 \cdot 10^{-4} \text{ M}$ in CH_3CN) upon addition of increasing amounts of (a) $\text{HP}_2\text{O}_7^{3-}$ anion; (b) F^- anion, until 2 equiv (left) and in the present of 20 equiv of acetic acid (right). (c) Changes in the absorption spectra of **6a** ($c = 1 \cdot 10^{-4} \text{ M}$ in CH_3CN) upon addition of increasing amounts of (a) OH^- anion. Arrows indicate absorptions that increase or decrease during the experiment.

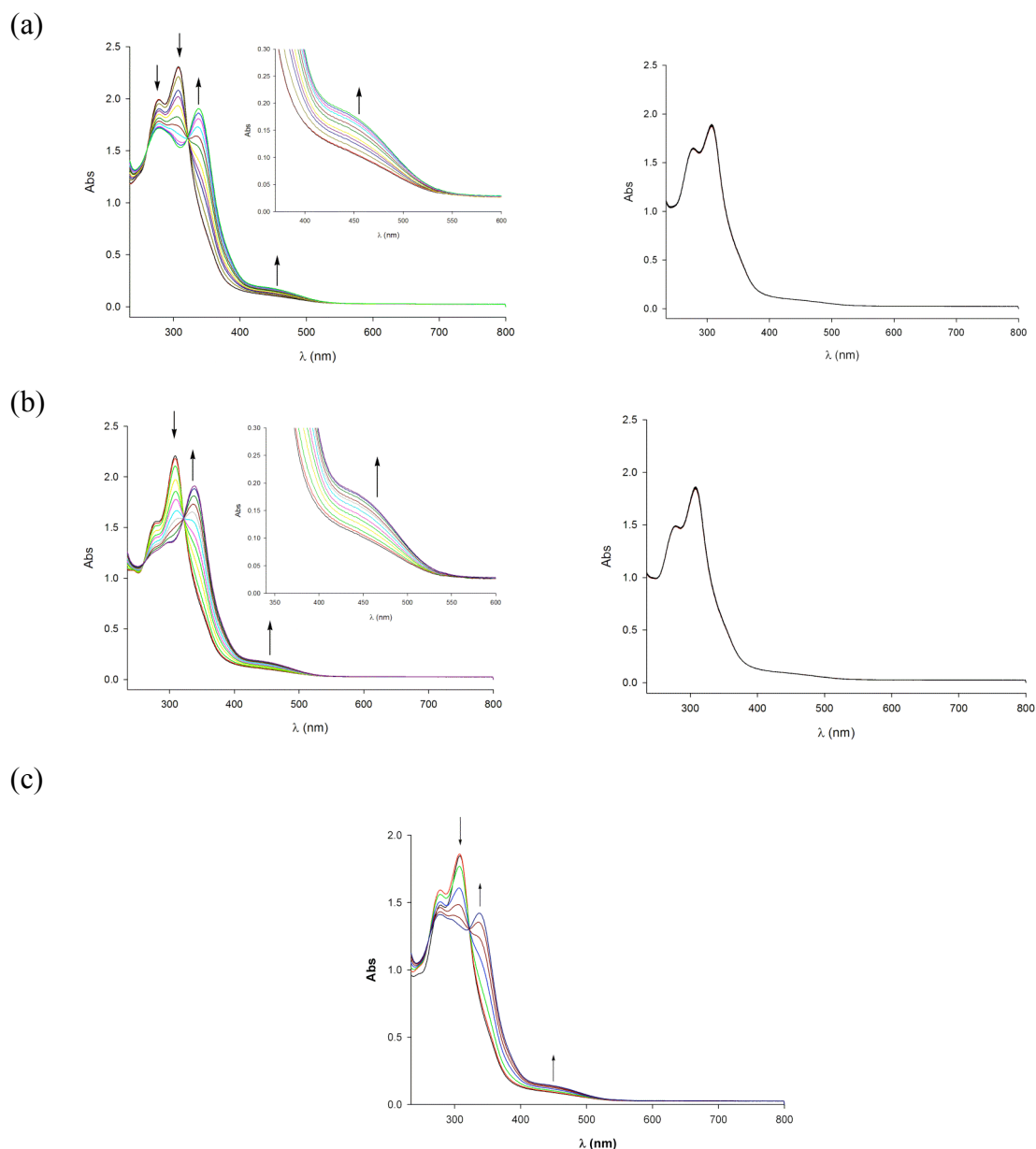


Figure SI 10. Changes in the absorption spectra of **6b** ($c = 1 \cdot 10^{-4} \text{ M}$ in CH_3CN) upon addition of increasing amounts of (a) $\text{HP}_2\text{O}_7^{3-}$ anion; (b) F^- anion, until 2 equiv (left) and in the present of 20 equiv of acetic acid (right). (c) Changes in the absorption spectra of **6b** ($c = 1 \cdot 10^{-4} \text{ M}$ in CH_3CN) upon addition of increasing amounts of (a) OH^- anion. Arrows indicate absorptions that increase or decrease during the experiment.

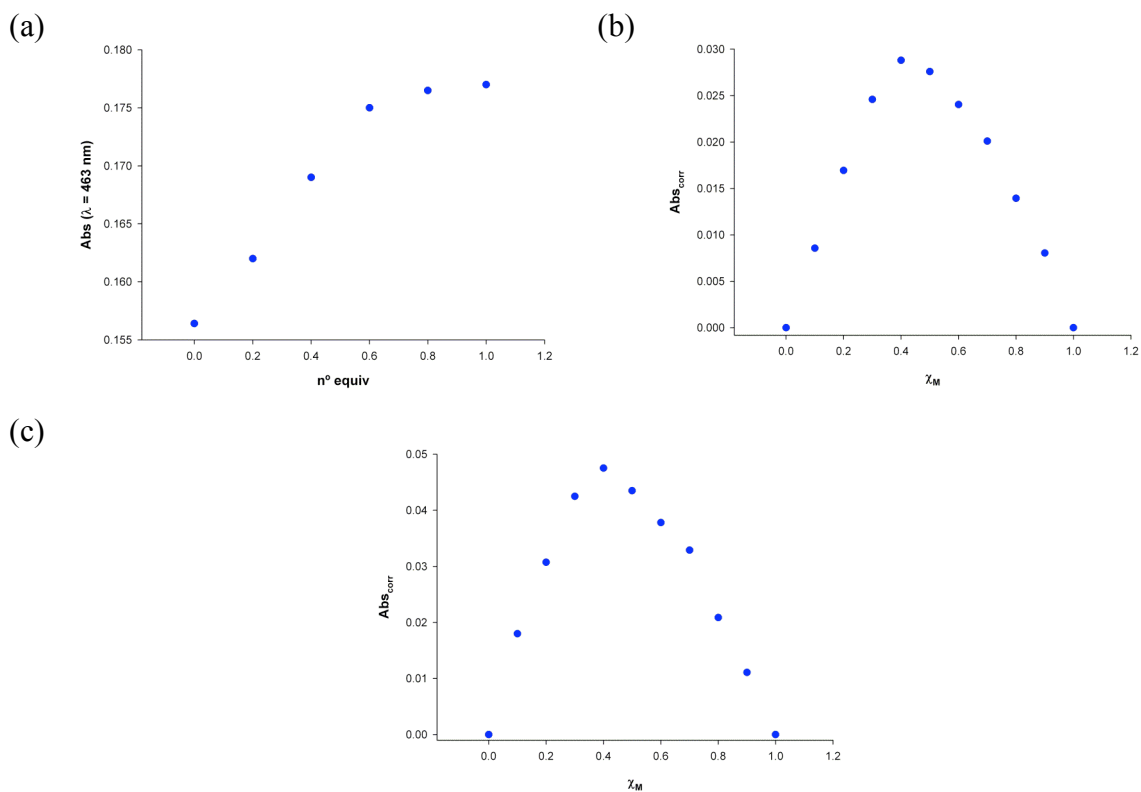


Figure SI 11. (a) Titration profile showing the change in absorbance of **6a** ($c = 1 \cdot 10^{-4} \text{ M}$ in CH_3CN), at $\lambda = 463 \text{ nm}$, upon addition of Cd^{2+} , indicating the formation of 2:1 complex. (b) Job's plot for **6a** ($1 \times 10^{-4} \text{ M}$ in CH_3CN) and Zn^{2+} , indicating the formation of a 2:1 complex. (c) Job's plot for **6a** ($1 \times 10^{-4} \text{ M}$ in CH_3CN) and Hg^{2+} ($1 \times 10^{-4} \text{ M}$ in CH_3CN), indicating the formation of a 2:1 complex.

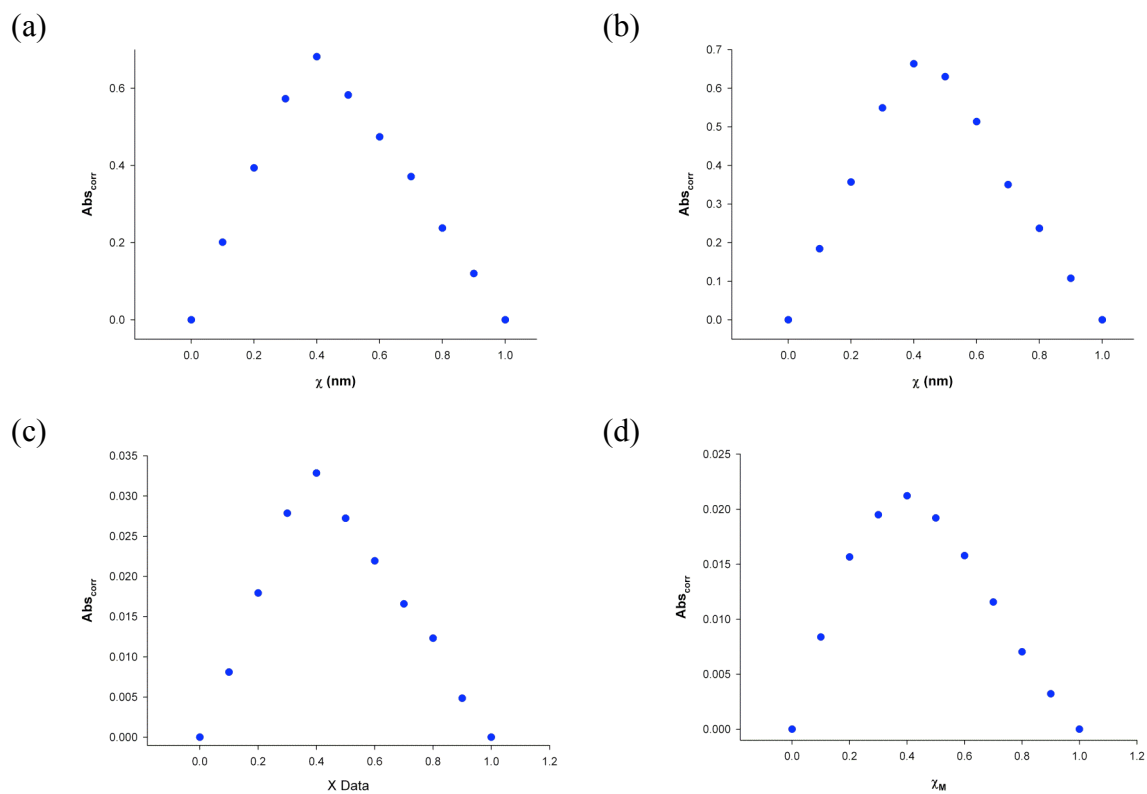


Figure SI 12. Job's plot for **6b** (1×10^{-4} M in CH₃CN), and (a) Cd²⁺; (b) Zn²⁺; (c) Pb²⁺; (d) Ni²⁺ (1×10^{-5} M in CH₃CN), indicating the formation of 2:1 complexes.

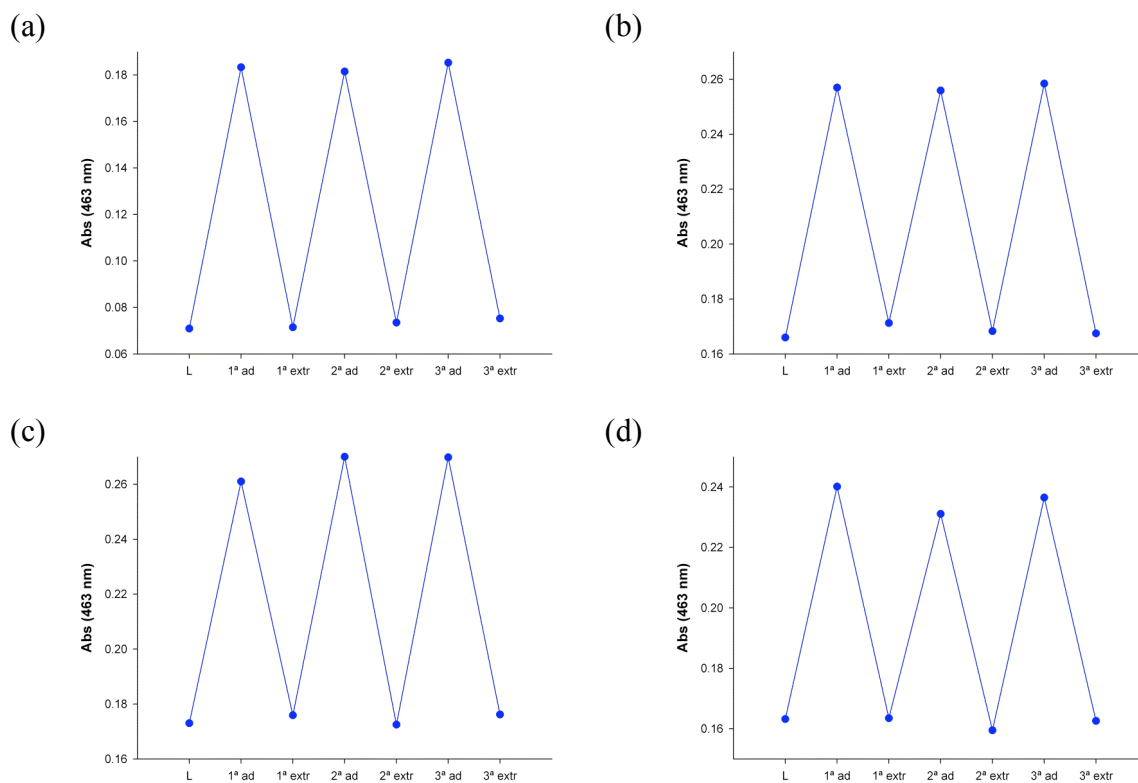


Figure SI 13. Stepwise complexation [by addition of (a) Cd²⁺; (b) Zn²⁺; (c) Hg²⁺; (d) Pb²⁺]/decomplexation (extraction with H₂O) cycles of ligand **6a** ($c = 1 \times 10^{-4} \text{M}$ in CH₂Cl₂) carried out by UV/Vis analysis.

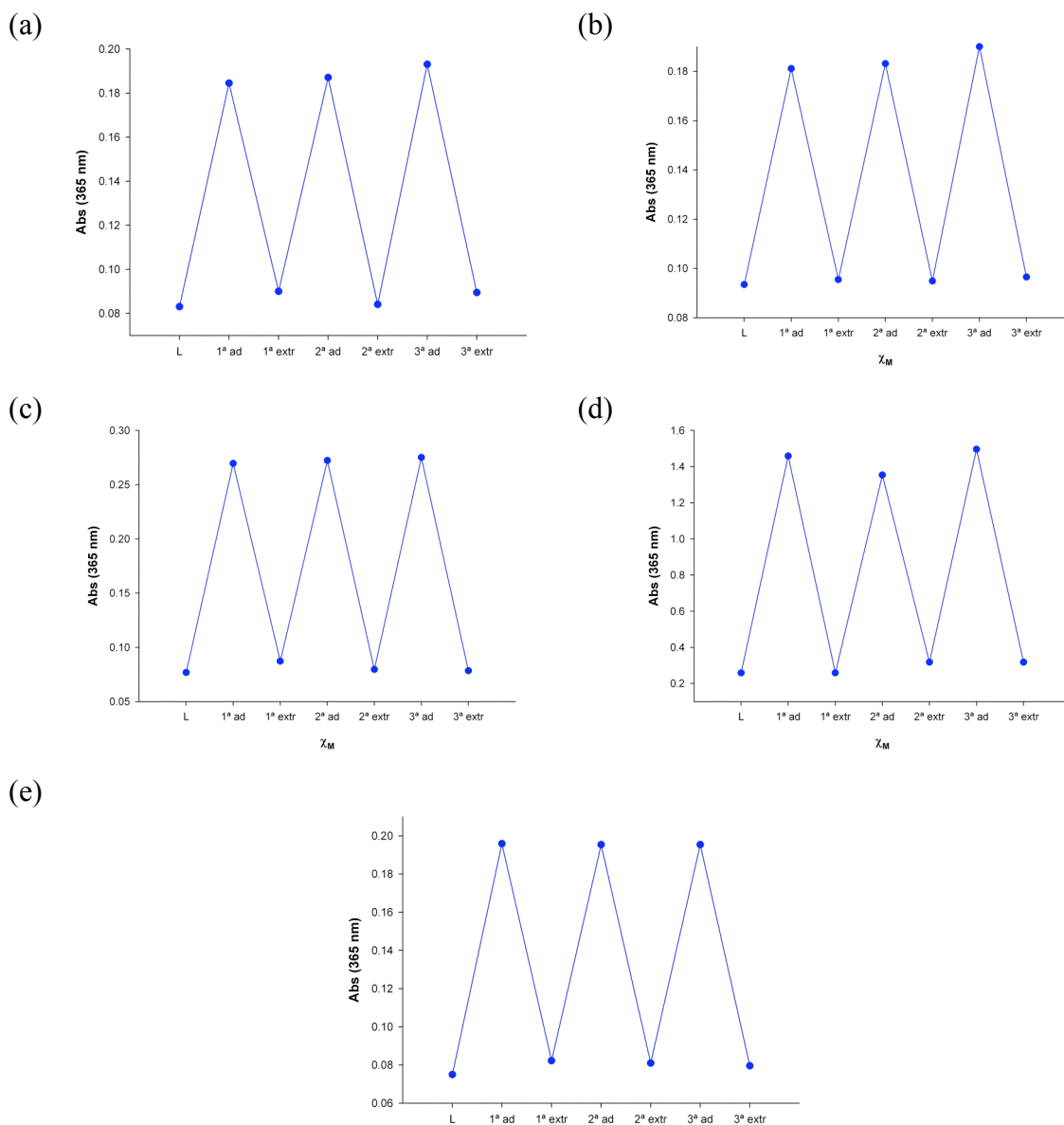


Figure SI 14. Stepwise complexation [addition of (a) Cd^{2+} ; (b) Zn^{2+} ; (c) Hg^{2+} ; (d) Pb^{2+} ; (e) Ni^{2+}]/decomplexation (extraction with H_2O) cycles of ligand **6b** ($c = 1 \times 10^{-4} \text{M}$ in CH_2Cl_2) carried out by UV/Vis analysis.

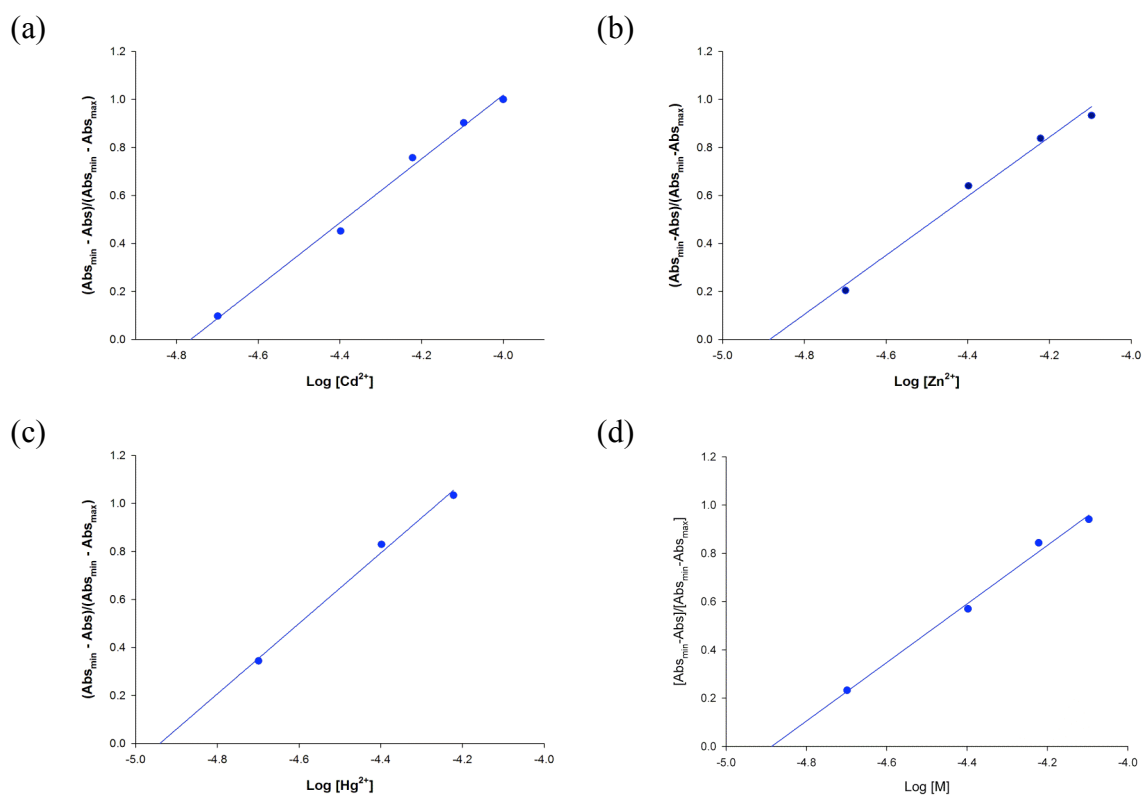


Figure SI 15. Absorbance of **6a** ($c = 1 \cdot 10^{-4}$ M in CH_3CN) at each concentration of cation added (a) Cd^{2+} ; (b) Zn^{2+} ; (c) Hg^{2+} ; (d) Pb^{2+} , normalized between the minimum absorbance, found at zero equiv of metal cation; and the maximum absorbance, found at (a) $[Cd^{2+}] = 1.72 \cdot 10^{-5}$ M; (b) $[Zn^{2+}] = 1.31 \cdot 10^{-5}$ M; (c) $[Hg^{2+}] = 1.15 \cdot 10^{-5}$ M; (d) $[Pb^{2+}] = 1.30 \cdot 10^{-5}$ M.

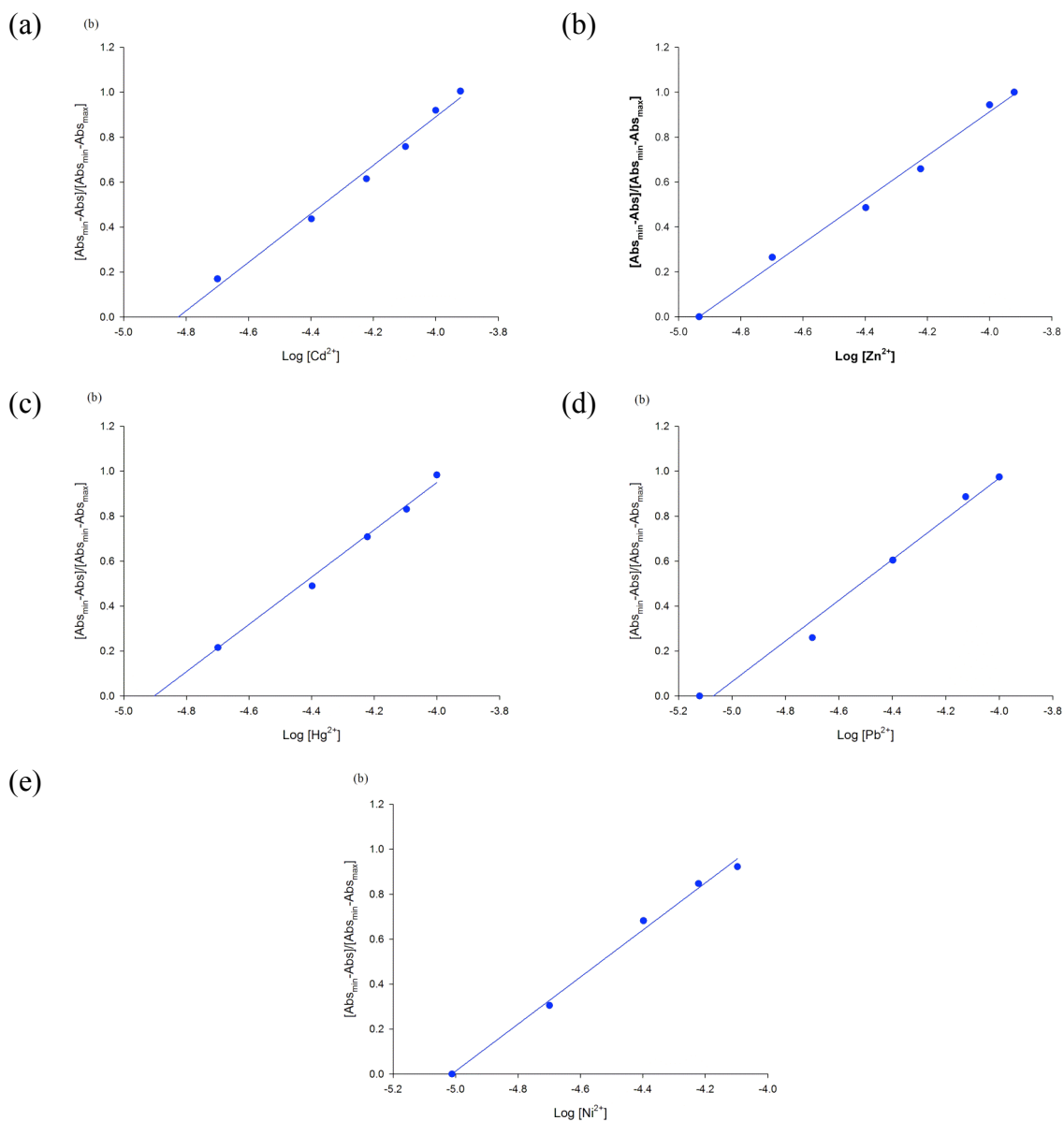


Figure SI 16. Absorbance of **6b** ($c = 1 \cdot 10^{-4}$ M in CH_3CN) at each concentration of cation added (a) Cd^{2+} ; (b) Zn^{2+} ; (c) Hg^{2+} ; (d) Pb^{2+} ; (e) Ni^{2+} normalized between the minimum absorbance, found at zero equiv of metal cation; and the maximum absorbance, found at (a) $[\text{Cd}^{2+}] = 1.50 \cdot 10^{-5}$ M; (b) $[\text{Zn}^{2+}] = 1.16 \cdot 10^{-5}$ M; (c) $[\text{Hg}^{2+}] = 1.25 \cdot 10^{-5}$ M; (d) $[\text{Pb}^{2+}] = 7.58 \cdot 10^{-6}$ M; (e) $[\text{Ni}^{2+}] = 9.74 \cdot 10^{-6}$ M.

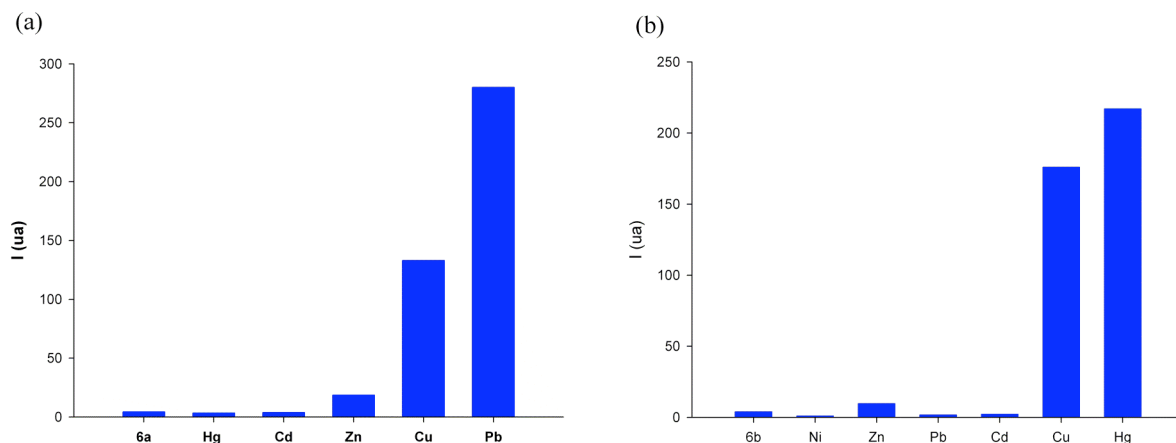


Figure SI 17. Fluorescence intensity of ligand (a) **6a**; (b) **6b**, in CH_3CN , after addition of 1 equiv of several cations. Emission monitored at (a) $\lambda_{\text{exc}} = 330$ nm; (b) $\lambda_{\text{exc}} = 310$ nm.

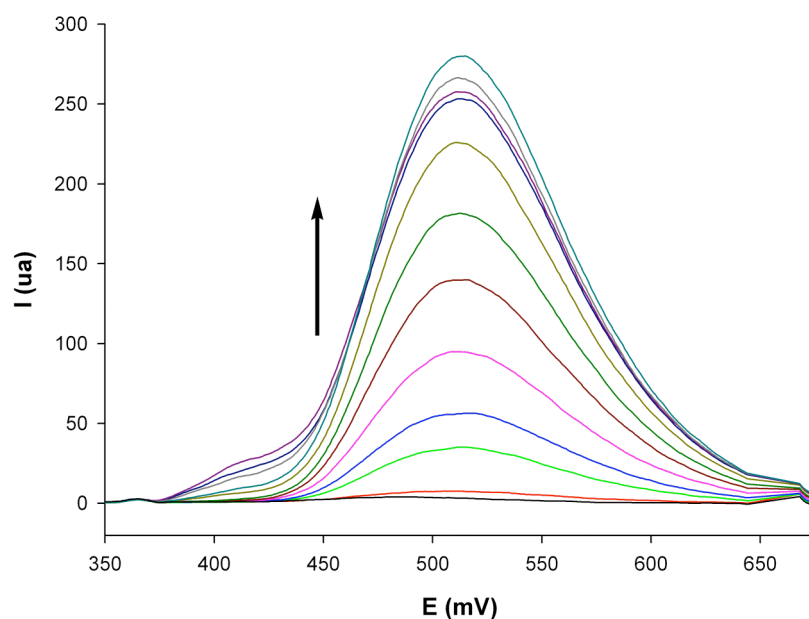


Figure SI 18. Changes in the fluorescence emission spectrum of **6a** ($c = 1 \times 10^{-5}$ M in CH_3CN) upon titration with Pb^{2+} : the initial (black) is that of **6a** and the final one (deep cyan), after addition of 1.4 equiv of Pb^{2+} ($c = 2.5 \times 10^{-3}$ M in CH_3CN). Emission is monitored at $\lambda_{\text{exc}} = 330$ nm.

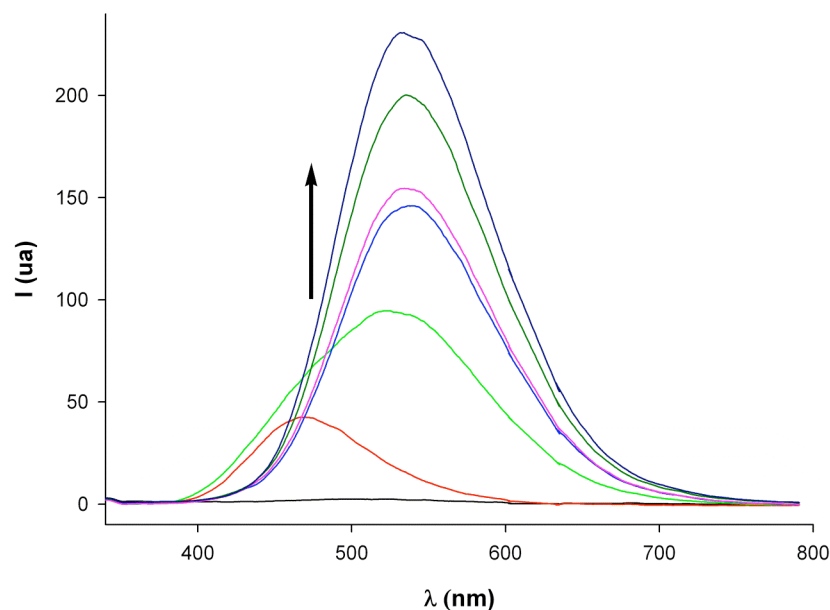


Figure SI 19. Changes in the fluorescence emission spectrum of **6b** ($c = 1 \times 10^{-5}$ M in CH₃CN) upon titration with Hg²⁺: the initial (black) is that of **6b** and the final one (deep blue), after addition of 1.2 equiv of Hg²⁺ ($c = 2.5 \times 10^{-3}$ M in CH₃CN). Emission is monitored at $\lambda_{\text{exc}} = 310$ nm.

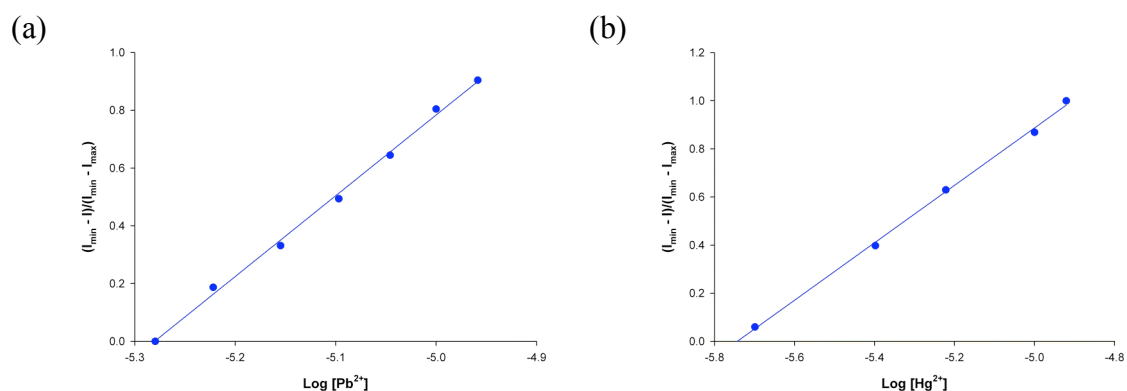


Figure SI 20. Fluorescence intensity of (a) **6a**; (b) **6b** (1×10^{-5} M in CH₃CN), at each concentration of (a) Pb²⁺; (b) Hg²⁺ added, normalized between the minimum fluorescence intensity, found at zero equiv of cation, and the maximum fluorescence intensity, found at (a) [Pb²⁺]= 5.25×10^{-6} M; (b) [Hg²⁺]= 1.81×10^{-6} M.

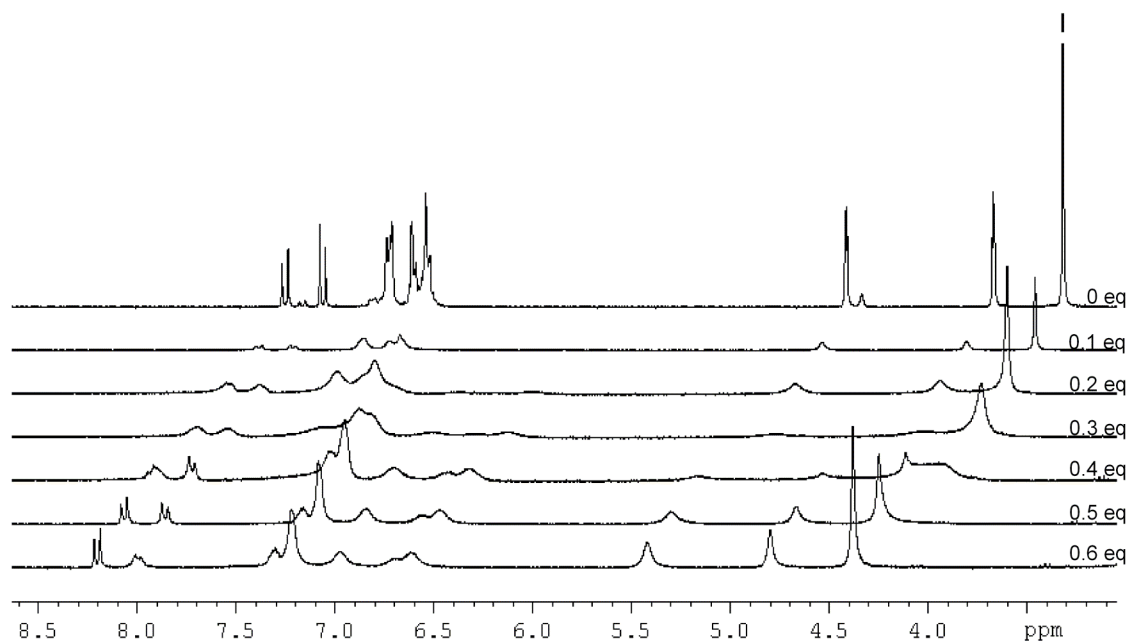


Figure SI 21. Changes in the ¹H-NMR (in acetone-d₆) spectrum of **6a** (top) in acetone upon addition of increasing amounts of Cd²⁺ until 0.6 equiv (bottom).

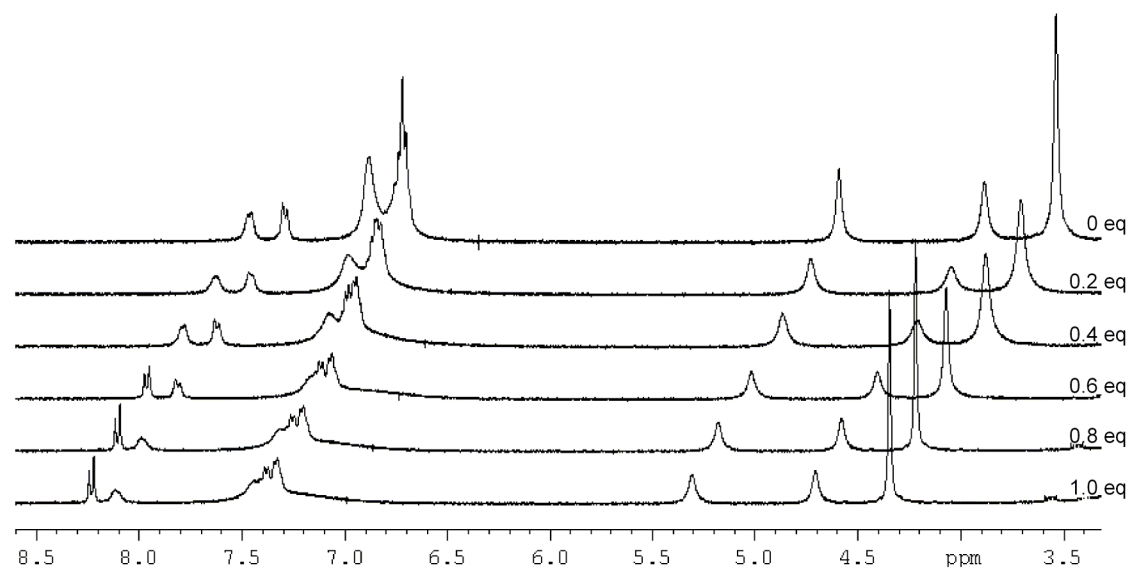


Figure SI 22. Changes in the ¹H-NMR (in acetone-d₆) spectrum of **6a** (top) in acetone upon addition of increasing amounts of Zn²⁺ until 1.0 equiv (bottom).

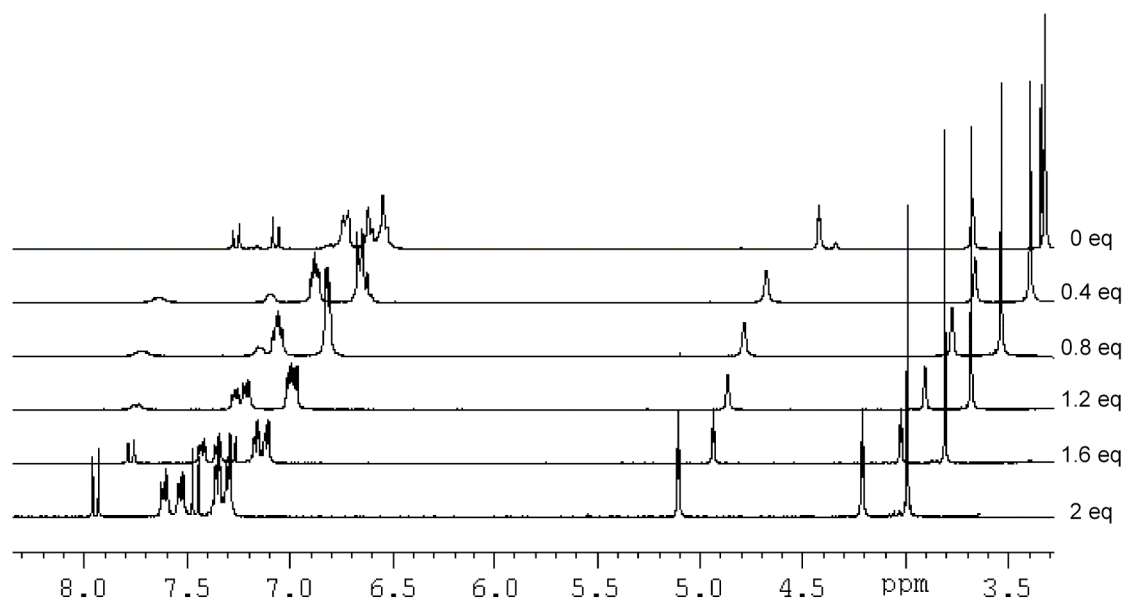


Figure SI 23. Changes in the ¹H-NMR (in acetone-*d*₆) spectrum of **6a** (top) in acetone upon addition of increasing amounts of HP₂O₇³⁻ until 2.0 equiv (bottom).

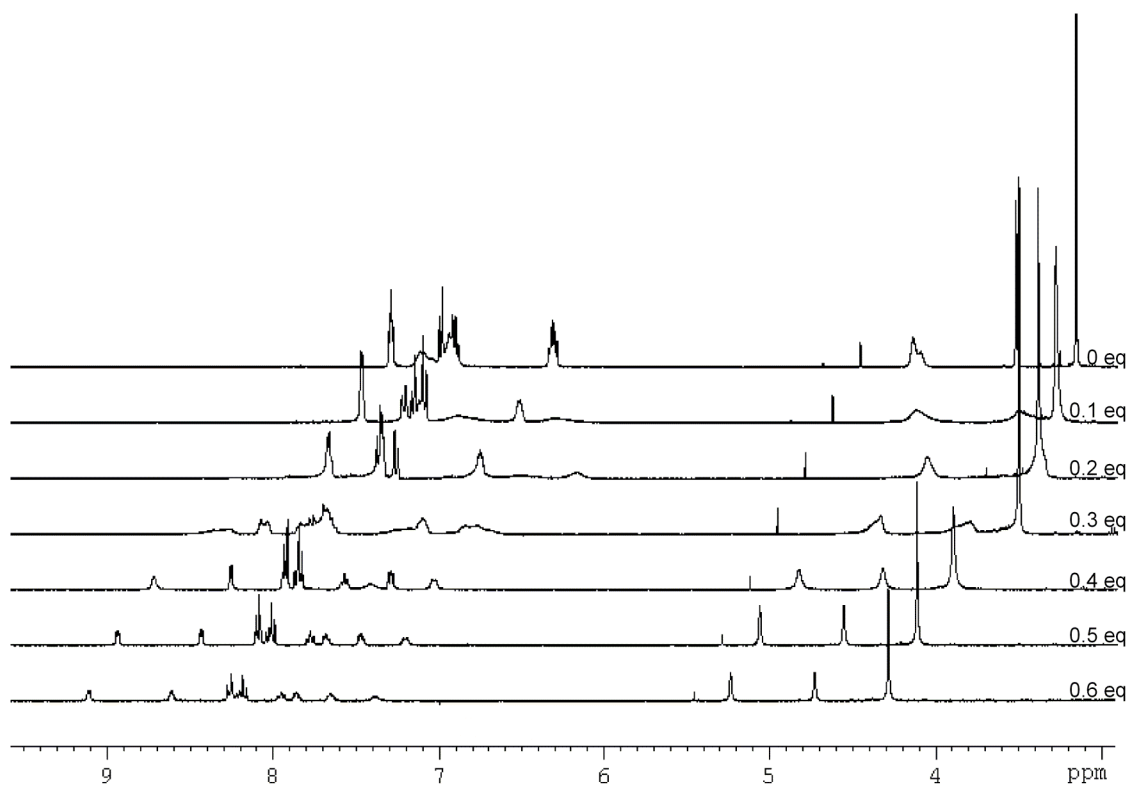


Figure SI 24. Changes in the ¹H-NMR (in acetonitrile-*d*₃) spectrum of **6b** (top) in acetone upon addition of increasing amounts of Pb²⁺ until 0.6 equiv (bottom).

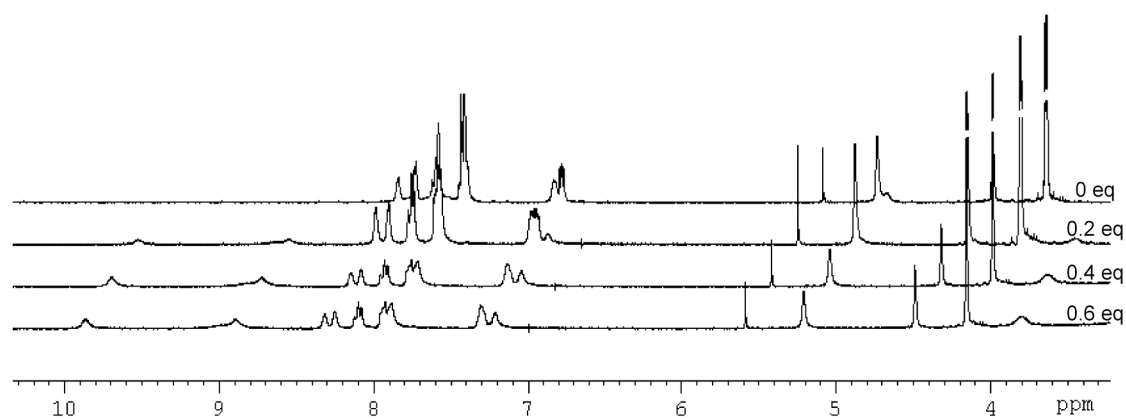


Figure SI 25. Changes in the ¹H-NMR (in acetone-*d*₆) spectrum of **6b** (top) in acetone upon addition of increasing amounts of Ni²⁺ until 0.6 equiv (bottom).

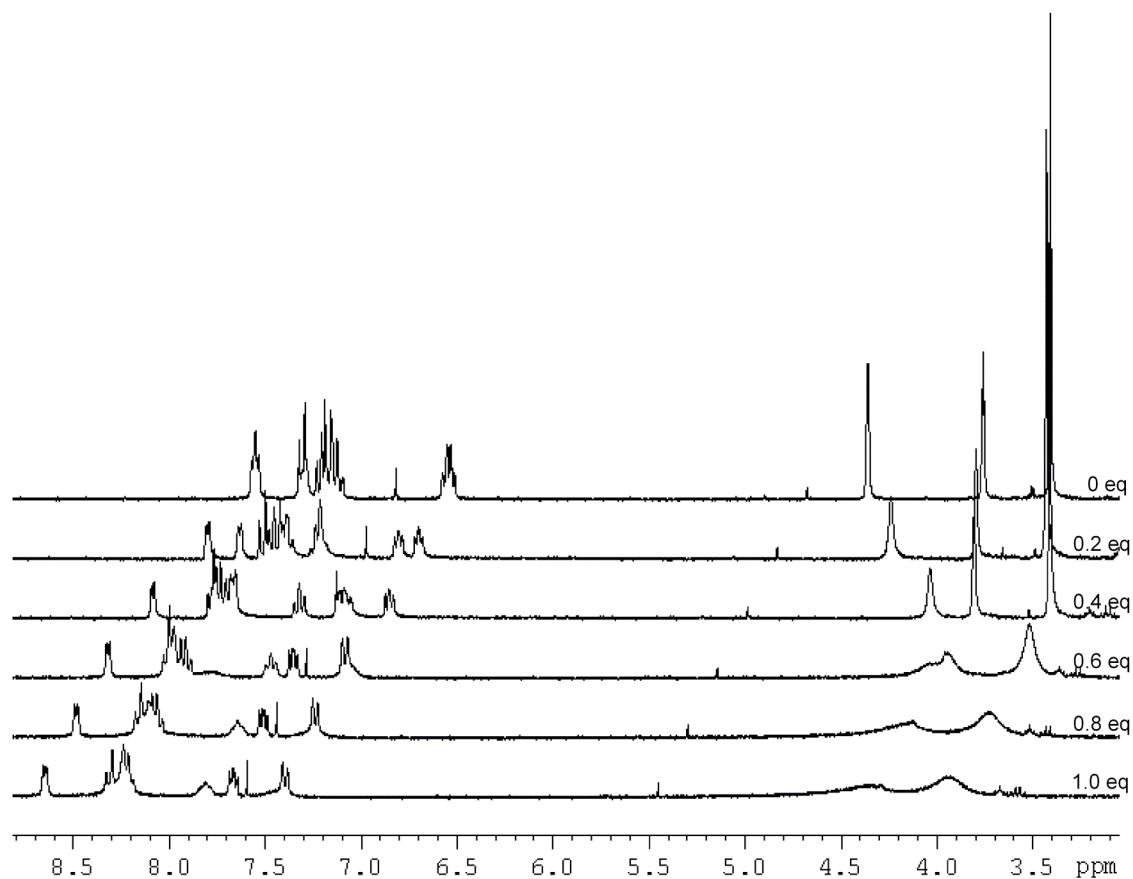


Figure SI 26. Changes in the ¹H-NMR (in acetonitrile-*d*₃) spectrum of **6b** (top) in acetone upon addition of increasing amounts of Cd²⁺ until 1.0 equiv (bottom).

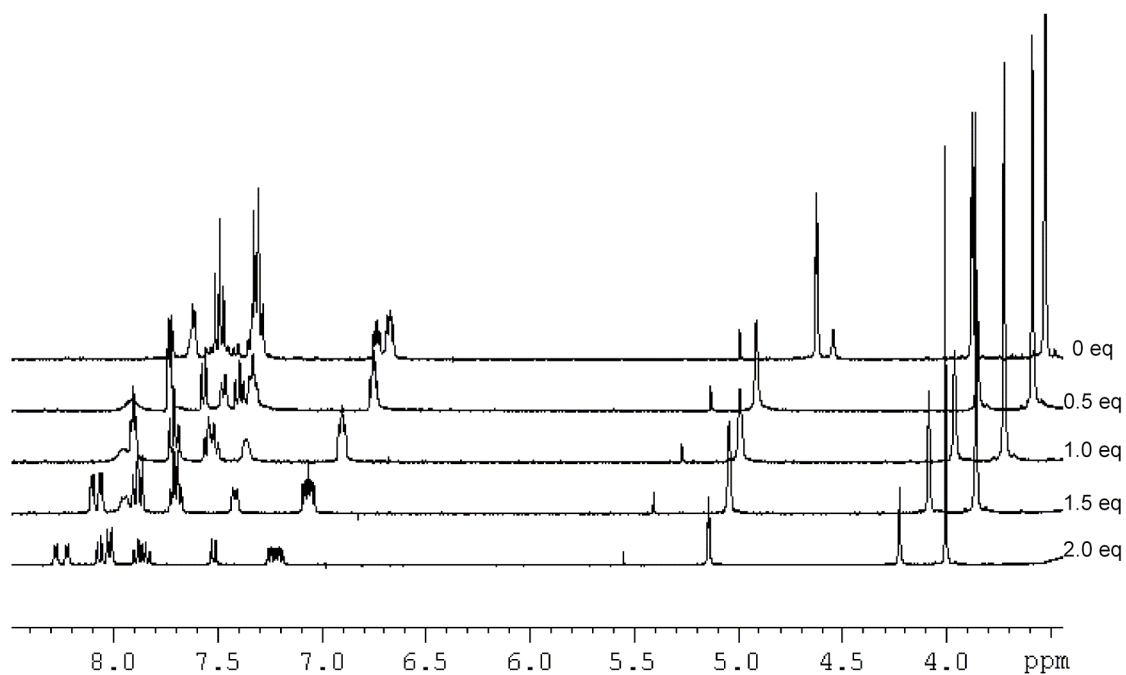


Figure SI 27. Changes in the ¹H-NMR (in acetone-*d*₆) spectrum of **6b** (top) in acetone upon addition of increasing amounts of HP₂O₇³⁻ until 2.0 equiv (bottom).

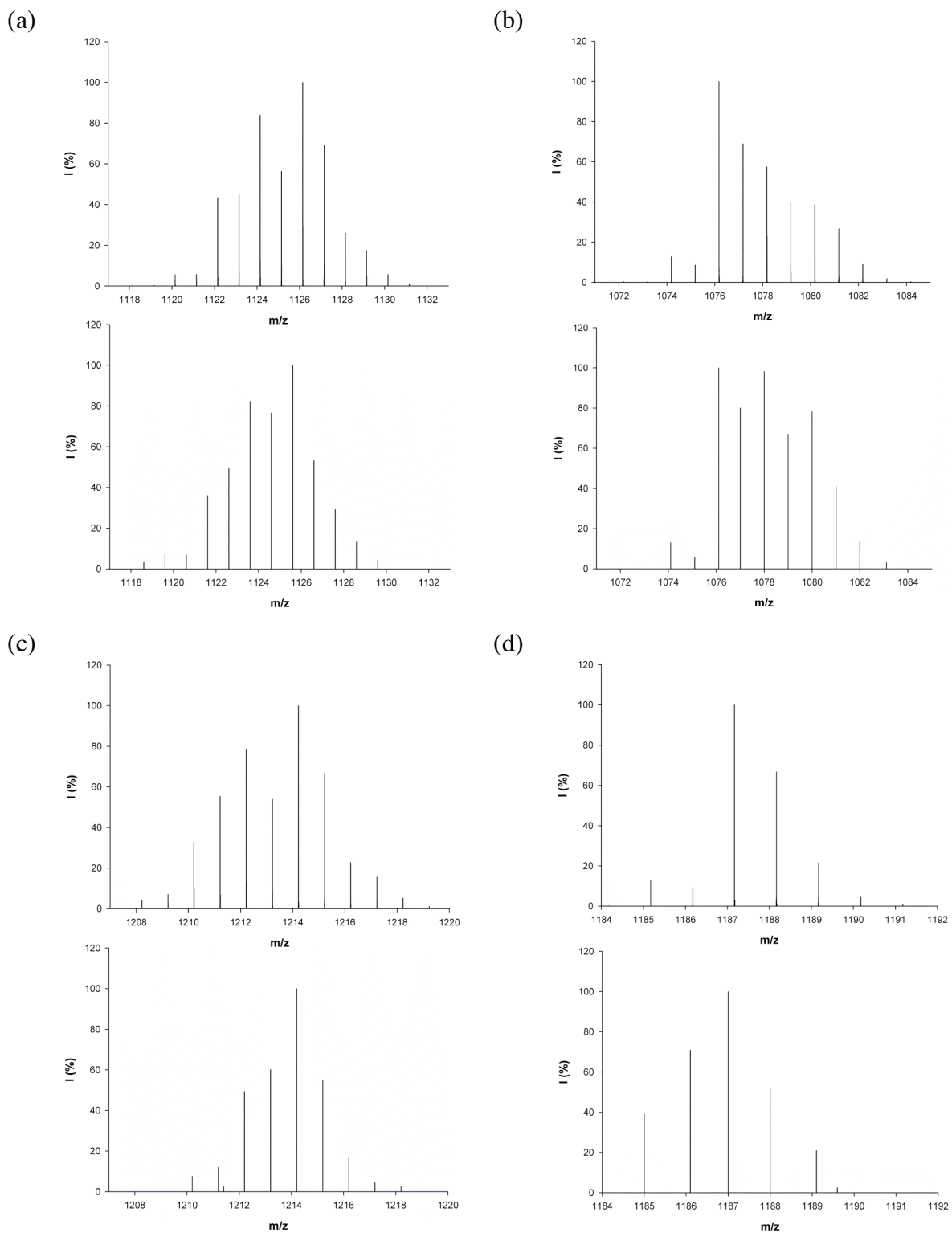


Figure SI 28. Relative abundance of the isotopic cluster for (a) $6a_2 \cdot Cd^{2+}$; (b) $6a_2 \cdot Zn^{2+}$; (c) $6a_2 \cdot Hg^{2+}$; (d) $6a_2 \cdot HP_2O_7^{3-}$ (top) simulated; (bottom) experimental.

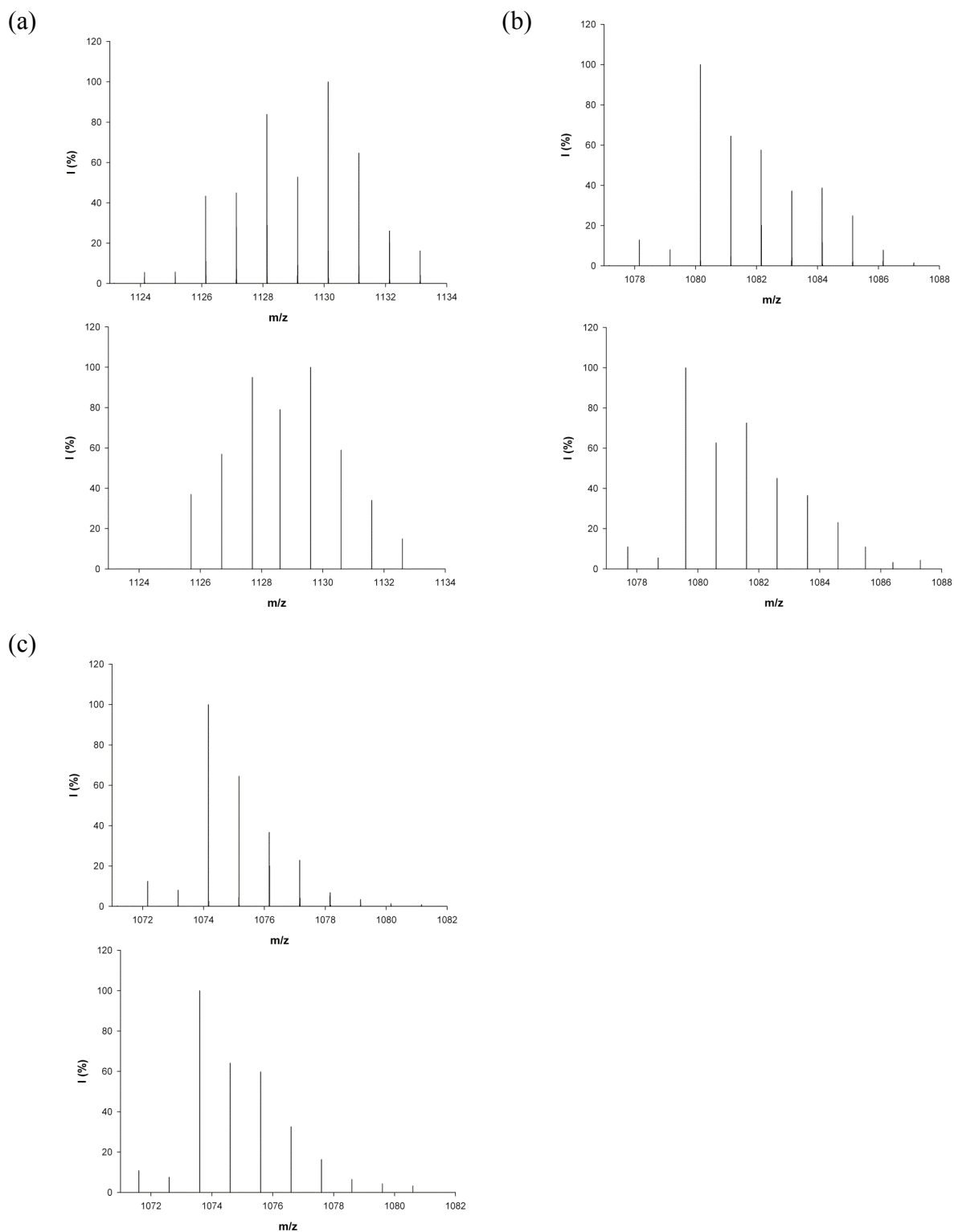


Figure SI 29. Relative abundance of the isotopic cluster for (a) $6b_2 \cdot Cd^{2+}$; (b) $6b_2 \cdot Zn^{2+}$; (c) $6c_2 \cdot Ni^{2+}$ (top) simulated; (bottom) experimental.