

Synthesis and spectroscopic characterisation of L^{1c-1e} , L^{2b2-e} , L^{3b-3d} and the metal complexes isolated.

Synthesis of L^{1c} . It was obtained as a colourless oil starting from L^{1b} and using the same procedure described for L^{4c} (see paper). Yield: 76%. $^1\text{H-NMR}$ (300 MHz, 298 K, CDCl_3): δ_{H} 1.43-1.47 (2H, m), 2.00 (2H, br), 2.41 (2H, t, $J = 7.2\text{Hz}$), 2.57-2.74 (16H, m), 3.63 (2H, t, $J = 4.6\text{Hz}$). $^{13}\text{C-NMR}$ (300 MHz, 298 K, CDCl_3): δ_{C} 27.58, 30.16, 31.06, 40.17, 51.14, 53.00, 74.17. Concentrated HClO_4 was added to a solution of L^{1c} in dry EtOH to give a white precipitate. This solid was filtered off, dried under reduced pressure and crystallised from $\text{dmf}/\text{Et}_2\text{O}$ to give the salt $(\text{H}_2\text{L}^{1c})(\text{ClO}_4)_2 \cdot \text{dmf}$. Elem. Anal.: found (calc. for $\text{C}_{14}\text{H}_{33}\text{Cl}_2\text{N}_3\text{O}_{10}\text{S}_2$): C, 31.20 (31.23); H, 6.15 (6.18); N, 7.84 (7.80); S, 11.85 (11.91).

Synthesis of L^{1d} . It was obtained as a yellow solid starting from L^{1c} and using the same procedure described for L^{4d} (see paper). Yield: 73%. Mp: 90-92°C. Elem. Anal.: found (calc. for $\text{C}_{23}\text{H}_{35}\text{N}_3\text{S}_3\text{O}_3$): C, 55.54 (55.50); H, 7.30 (7.09); N, 8.60 (8.44); S, 19.30 (19.33). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ_{H} 1.51-1.53 (2H, m), 2.43 (2H, t, $J = 5.8\text{ Hz}$), 2.65-2.69 (8H, m), 2.78-2.81 (8H, m), 2.84 (6H, s), 2.95 (2H, t, $J = 4\text{ Hz}$), 7.14 (1H, d, $J = 8\text{ Hz}$), 7.47 (1H, t, $J = 8\text{ Hz}$), 7.53 (1H, t, $J = 8\text{ Hz}$), 8.19 (1H, d, $J = 8\text{ Hz}$), 8.32 (1H, d, $J = 8\text{ Hz}$), 8.47 (1H, d, $J = 8\text{ Hz}$). $^{13}\text{C NMR}$ (400 MHz, CDCl_3): δ_{C} 25.08, 27.18, 30.35, 43.49, 45.19, 50.80, 54.63, 74.39, 114.84, 118.88, 122.90, 127.91, 129.23, 129.48, 129.58, 129.82, 134.74, 151.60. Mass Spectrum EI^+ : m/z 497 ($[\text{C}_{23}\text{H}_{35}\text{N}_3\text{S}_3\text{O}_3]^+$).

Synthesis of L^{1e} . It was obtained as a yellow solid starting from L^{1c} and using the same procedure described for L^{4e} (see paper). Yield: 45%. M.p.: 126-127°C. Elem. Anal.: found (calc. for $\text{C}_{26}\text{H}_{34}\text{N}_2\text{S}_2\text{O}$): C, 68.57 (68.68); H, 7.30 (7.54); N, 5.97 (6.16); S, 14.24 (14.10). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ_{H} 1.23-1.25 (2H, m), 1.74-1.77 (2H, m), 2.46-2.49 (2H, m), 2.62-2.70 (10H, m), 2.95-2.97 (2H, m), 3.65 (4H, s), 4.54 (1H, br), 4.81 (2H, s), 7.46-7.49 (2H, m), 7.55-7.59 (2H, m), 8.00 (2H, d, $J = 8\text{Hz}$), 8.33 (2H, d, $J = 8.8\text{Hz}$), 8.42 (1H, s). $^{13}\text{C NMR}$ (400 MHz, CDCl_3): δ_{C} 26.35, 27.28, 30.27, 44.90, 48.94, 50.89, 54.10, 74.41, 123.83, 124.96, 126.44, 127.74, 129.13, 130.32, 131.35. Mass Spectrum EI^+ : m/z 455 ($[\text{C}_{26}\text{H}_{34}\text{N}_2\text{S}_2\text{O}]^+$).

Synthesis of L^{2b} . Acrylonitrile (5 ml) was added to a solution of L^{2a} (0.5 g, 2.2 mmol) in $\text{H}_2\text{O}:\text{EtOH}$ (40 mL, 1:1 v/v). The mixture was refluxed for 24 hours under N_2 . After cooling the volume of the mixture was reduced to 15 mL under reduced pressure. After 12 hours at 0°C a white solid formed. (0.48 g, 1.7 mmol, 77% yield). M.p.: 84-85°C. Elem. Anal.: found (calc. for $\text{C}_{11}\text{H}_{20}\text{N}_2\text{S}_3$): C, 47.85 (47.79); H, 7.51 (7.29); N, 10.18 (10.13); S, 34.52 (34.79). $^1\text{H-NMR}$ (400 MHz, 298 K, CDCl_3): δ_{H} 2.49-2.51 (2H, m), 2.64-2.65 (4H, m), 2.77-2.80 (14H, m). $^{13}\text{C-NMR}$ (400 MHz, 298 K, CDCl_3): δ_{C} 16.84, 26.61, 27.95, 29.03, 50.06, 52.93, 118.70.

Synthesis of L^{2c} . It was obtained as a colourless oil starting from L^{2b} and using the same procedure described for L^{4c} (see paper). Yield: 87%. $^1\text{H-NMR}$ (400 MHz, 298 K, CDCl_3): δ_{H} 1.55-1.58 (2H, m), 1.76 (2H, br), 2.44-2.76 (20H, m). $^{13}\text{C-NMR}$ (300 MHz, 298 K, CDCl_3): δ_{C} 26.17, 28.08, 28.90, 31.04, 40.26, 52.16, 52.38.

Synthesis of L^{2d} . It was obtained as a yellow solid starting from L^{2c} and using the same procedure described for L^{4d} (see paper). Yield: 46%. Mp: 110-112°C. Elem. Anal.: found (calc. for $\text{C}_{23}\text{H}_{35}\text{N}_3\text{S}_4\text{O}_2$): C, 54.64 (53.77); H, 7.88 (6.87); N, 8.00 (8.18); S, 23.52 (24.96). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ_{H} 1.50-1.56 (2H, m), 2.35 (2H, t, $J = 4\text{ Hz}$), 2.48-2.56 (8H, m), 2.64-2.68 (8H, m), 2.85 (6H, s), 2.96 (2H, t, $J = 4\text{ Hz}$), 6.15 (1H, br), 7.14 (1H, d, $J = 7.2\text{ Hz}$), 7.46-7.54 (2H, m), 8.20 (1H, d, $J = 7.6\text{ Hz}$), 8.28 (1H, d, $J = 8.8\text{ Hz}$), 8.49 (1H, d, $J = 8.4\text{ Hz}$). $^{13}\text{C NMR}$ (400 MHz,

CDCl₃): δ_C 25.07, 25.56, 27.72, 28.33, 42.42, 45.17, 51.14, 52.57, 114.88, 118.56, 122.97, 127.98, 129.38, 129.45, 129.59, 130.05, 134.48, 151.75. Mass Spectrum EI⁺: m/z 514 ([C₂₃H₃₅N₃S₄O₂]⁺).

Synthesis of L^{2e}. It was obtained as a yellow solid starting from L^{2c} and using the same procedure described for L^{4c} (see paper). Yield: 49%. Mp.: 120-121°C. Elem. Anal: found (calc. for C₂₆H₃₄N₂S₃): C, 66.01 (66.33); H, 7.68 (7.28); N, 5.46 (5.95); S, 19.97 (20.43). ¹H NMR (400 MHz, CDCl₃): δ_H 1.69-1.73 (2H, m), 2.43-2.46 (6H, m), 2.55-2.69 (12H, m), 2.89-2.93 (2H, m), 4.74 (2H, s), 7.43-7.47 (2H, m), 7.51-7.55 (2H, m), 7.99 (2H, d, J = 8.4Hz), 8.32 (2H, d, J = 8.8 Hz), 8.40 (1H, s). ¹³C NMR (300 MHz, CDCl₃): δ_C 26.06, 27.31, 28.07, 28.84, 45.60, 48.64, 52.30, 52.75, 124.02, 124.95, 126.18, 127.36, 129.20, 130.26, 131.14, 131.49. Mass Spectrum EI⁺: m/z 471 ([C₂₆H₃₄N₂S₃]⁺).

Synthesis of L^{3b}. It was obtained as a colourless oil starting from L^{3a} and using the same procedure described for L^{4b} (see paper). Yield: 83%. Elem. Anal.: found (calc. for C₁₄H₂₄N₄SO): C, 56.43 (56.73); H, 8.82 (8.16); N, 18.66 (18.90); S, 10.29 (10.82). ¹H-NMR (300 MHz, 298 K, CDCl₃): δ_H 2.47-2.50 (4H, m), 2.52-2.54 (4H, m), 2.73-2.84 (12H, m), 3.47-3.52 (4H, m). ¹³C-NMR (400 MHz, 298 K, CDCl₃): δ_C 18.00, 32.57, 48.73, 53.47, 55.42, 69.5, 117.6.

Synthesis of L^{3c}. It was obtained as a yellow solid starting from L^{3b} and using the same procedure described for L^{4c} (see paper). Yield: 65%. ¹H-NMR (400 MHz, 298 K, CDCl₃): δ_H 2.03-2.12 (4H, m), 2.73-3.87 (24H, m). ¹³C-NMR (300 MHz, 298 K, CDCl₃): δ_C 26.23, 31.11, 40.09, 53.65, 53.87, 54.39, 70.93.

Synthesis of L^{3d}. It was obtained as a yellow solid starting from L^{3c} and using the same procedure described for L^{4d} (see paper). Yield: 44%. M.p.: 82-84°C. Elem. Anal.: found (calc. for C₃₈H₅₄N₆S₃O₅): C, 59.34 (59.19); H, 7.58 (7.06); N, 10.08 (10.90); S, 11.78 (12.47). ¹H NMR (400 MHz, CDCl₃): δ_H 1.19 (4H, t, J = 7.2Hz), 1.51-1.56 (4H, m), 2.41-2.44 (4H, m), 2.57-2.64 (4H, m), 2.75-2.77 (4H, m), 2.86 (12H, s), 2.97-3.00 (4H, m), 3.43-3.48 (4H, m), 3.55 (2H, br), 7.16 (2H, d, J = 7.2Hz), 7.44-7.56 (4H, m), 8.21 (2H, d, J = 7.2Hz), 8.31 (2H, d, J = 8.4Hz), 8.50 (2H, d, J = 8.4 Hz). ¹³C NMR (300 MHz, CDCl₃): δ_C 25.37, 26.02, 42.94, 45.28, 52.73, 54.12, 54.53, 69.91, 115.00, 118.86, 123.04, 128.03, 129.31, 129.53, 129.67, 129.99, 134.82, 151.74. Mass Spectrum EI⁺: m/z 514 ([C₃₈H₅₄N₆S₃O₅]⁺).

Synthesis of [Zn(L^{1c})](ClO₄)₂ (3)

To a solution of L^{1c} (40 mg, 0.15 mmol) in 5 cm³ of MeCN 56.4 mg (0.15 mmol) of Zn(ClO₄)₂ · 6 H₂O. The resulting colourless solution was stirred for four hours at room temperature. The solvent was partially removed under reduced pressure and the product crystallised by diffusion of Et₂O vapour into the remaining solution. Colourless crystals were obtained (28 mg, 0.062 mmol, 41% yield). Mp.: up to 250 °C. Elem. Anal: found (calc. for C₁₁H₂₄N₂S₂O₉Cl₂Zn): C, 25.66 (24.99); H, 4.76 (4.58); N, 5.48 (5.30); S, 12.65 (12.13).

Synthesis of [Cd(L^{1c})](NO₃)](NO₃) (4)

This complex was obtained as colourless crystals using the same procedure described for **3**. Yield: 51%. Mp.: 249-250°C. Elem. Anal: found (calc. for C₁₁H₂₄N₄S₂O₇Cd): C, 26.73 (26.38); H, 4.55 (4.83); N, 11.21 (11.19); S, 12.45 (12.80).

Synthesis of [Hg(L^{2c})](ClO₄)₂ (5)

This complex was obtained as colourless crystals using the same procedure described for **3**. Yield: 56%. Mp.: 266-267°C. Elem. Anal: found (calc. for C₁₁H₂₄N₂S₃O₈Cl₂Hg): C, 19.66 (19.43); H, 3.89 (3.56); N, 4.23 (4.12); S, 14.82 (14.15).

Synthesis of [Cd(L^{3a})(NO₃)₂] (1)

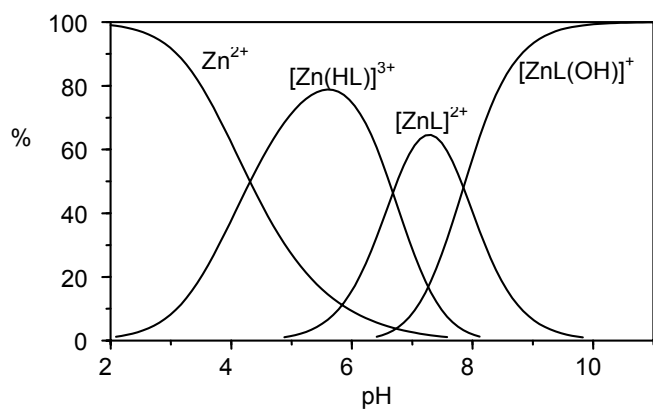
This complex was obtained as colourless crystals using the same procedure described for **3**. Yield: 27%. Mp.: up to 250°C. Elem. Anal: found (calc. for C₈H₁₈N₄SO₇Cd): C, 22.73 (22.52); H, 4.32 (4.25); N, 13.05 (13.13); S, 7.45 (7.51).

Synthesis of [Cu(L^{4a})(dmf)](ClO₄)₂ (2)

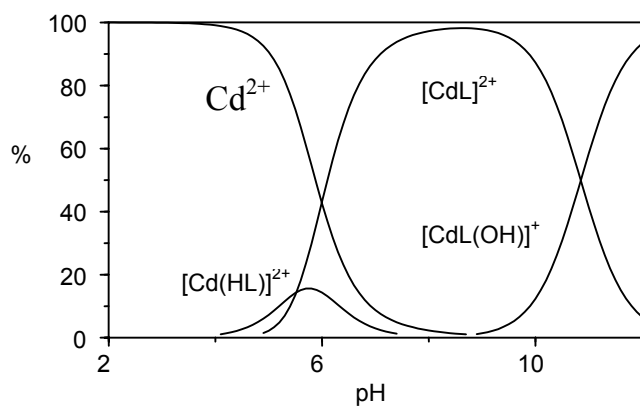
This complex was obtained as blue crystals using the same procedure described for **3**. After reaction, the solvent was removed under reduced pressure and the resulting residue was crystallised by diffusion of Et₂O vapours into a dmf solution. Yield: 24%. M.p.: 182-183°C. Anal: found (calc. for C₁₃H₂₈N₂S₂O₁₁Cl₂Cu): C, 26.38 (26.60); H, 4.85 (4.81); N, 4.80 (4.77); S, 11.15 (10.92).

Table S1. Protonation constants (log *K*) of L^{3a}, L^{1c}, L^{2c}, L^{3c}, and L^{4c} (*I* = 0.1 M, 298.1 K).

reaction	L ^{3a}	L ^{1c}	L ^{2c}	L ^{3c}	L ^{4c}
L + H ⁺ ⇌ (HL) ⁺	9.14(3)	9.98(3)	9.66(1)	10.01(2)	10.11(2)
(HL) ⁺ + H ⁺ ⇌ (H ₂ L) ²⁺	6.80(3)	6.93(5)	5.80(1)	9.69(3)	3.19(3)
(H ₂ L) ²⁺ + H ⁺ ⇌ (H ₃ L) ³⁺				7.18(3)	
(H ₃ L) ³⁺ + H ⁺ ⇌ (H ₄ L) ⁴⁺				5.35(3)	



(a)



(b)

Figure S1. Distribution diagrams for the systems Zn^{II}/L^{1c} (a), and Cd^{II}/L^{1c} (b) ($[M^{II}] = [L^{1c}] = 1 \times 10^{-3}$ M, 298.1 K, $I = 0.1$ M).

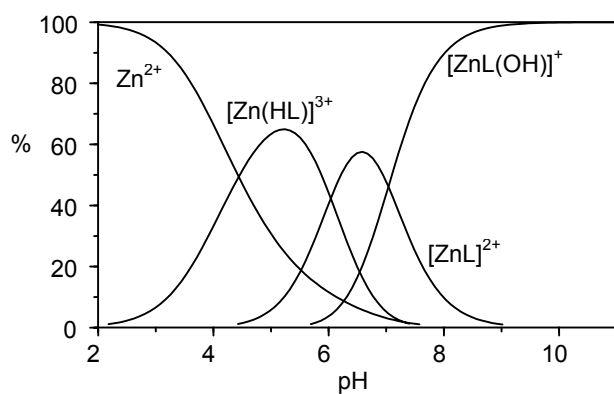
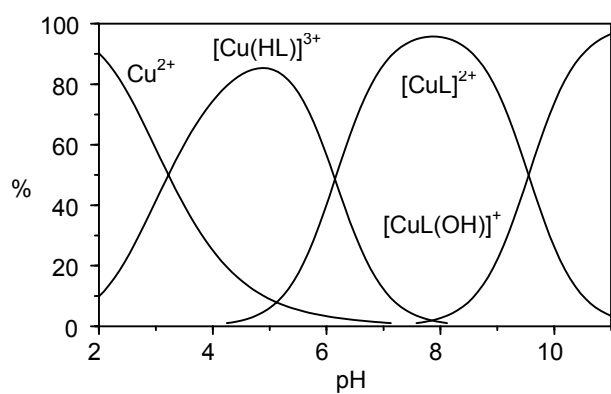
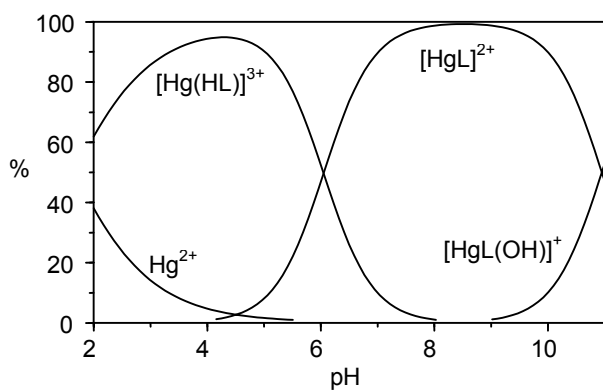


Figure S2. Distribution diagram for the system Zn^{II}/L^{2c} ($[M^{II}] = [L^{2c}] = 1 \times 10^{-3}$ M, 298.1 K, $I = 0.1$ M).

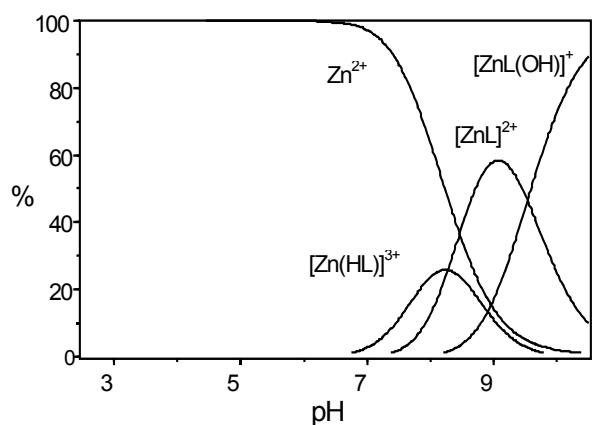


(a)

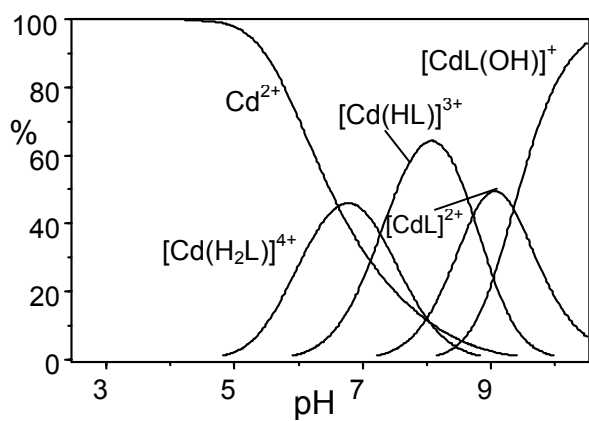


(b)

Figure S3. Distribution diagrams for the systems Cu^{II}/L^{2c} (a), and Hg^{II}/L^{2c} (b) ($[M^{II}] = [L^{2c}] = 1 \times 10^{-3}$ M, $T = 298.1$ K, $I = 0.1$ M)



(a)



(b)

Figure S4. Distribution diagram for the systems Zn^{II}/L^{3c} (a), and Cd^{II}/L^{3c} (b) ($[M^{II}] = [L^{3c}] = 1 \times 10^{-3}$ M, 298.1 K, $I = 0.1$ M).

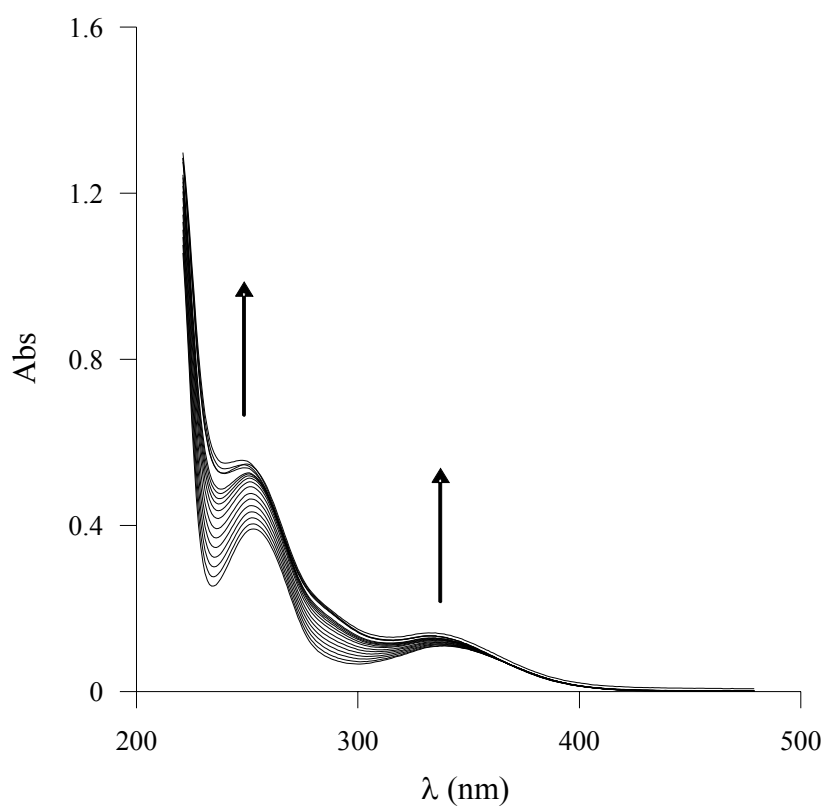


Figure S5. Changes in the UV-Vis spectrum of L^{4d} [2.5×10^{-5} M, MeCN/H₂O (4:1 v/v), pH = 7.0] upon addition of increasing amounts of Hg^{II} up to a Hg^{II}/L^{4d} molar ratio of 2.

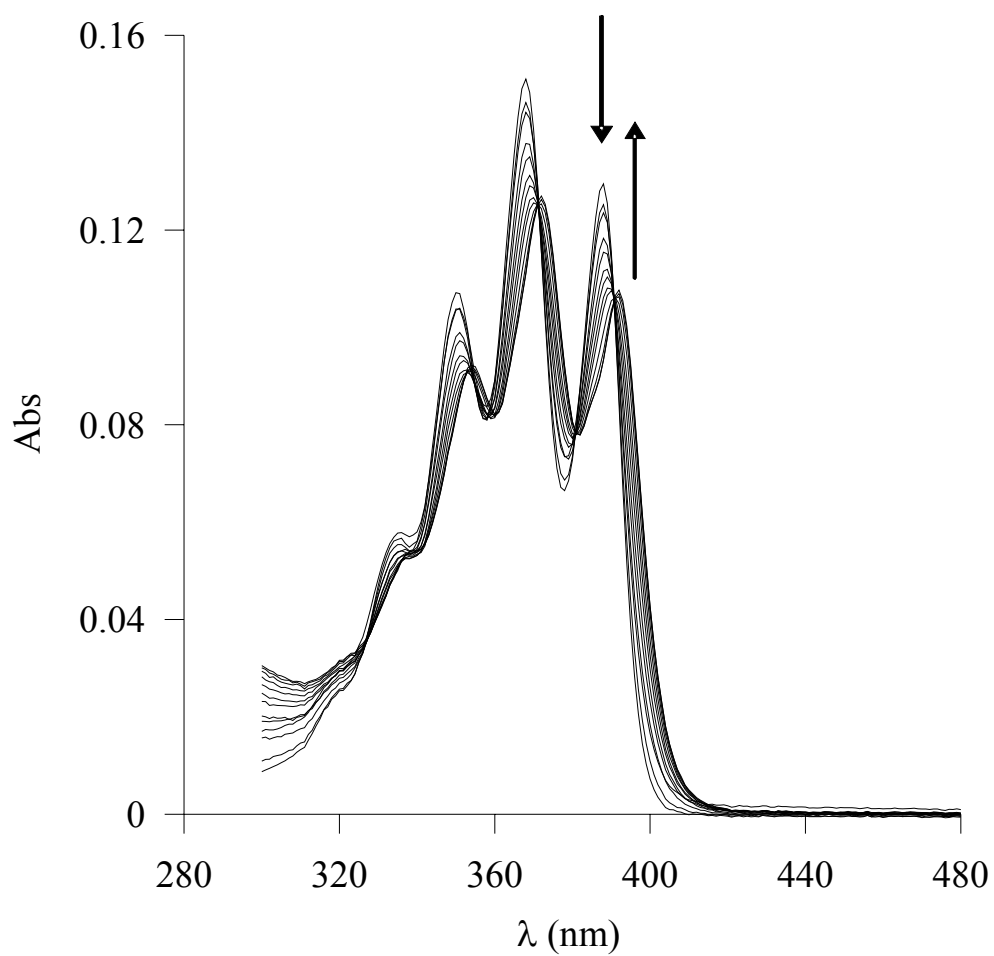


Figure S6. Changes in the UV-Vis spectrum of L^{2e} [2.5×10^{-5} M, MeCN/ H_2O (4:1 v/v), pH = 7.0] upon addition of increasing amounts of Hg^{II} up to a Hg^{II}/L^{2e} molar ratio of 2.