

Beyond Copper: Examining the Significance of His-Mutations in Mycobacterial GroEL1 HRCT for Ni(II) Complex Stability and Formation

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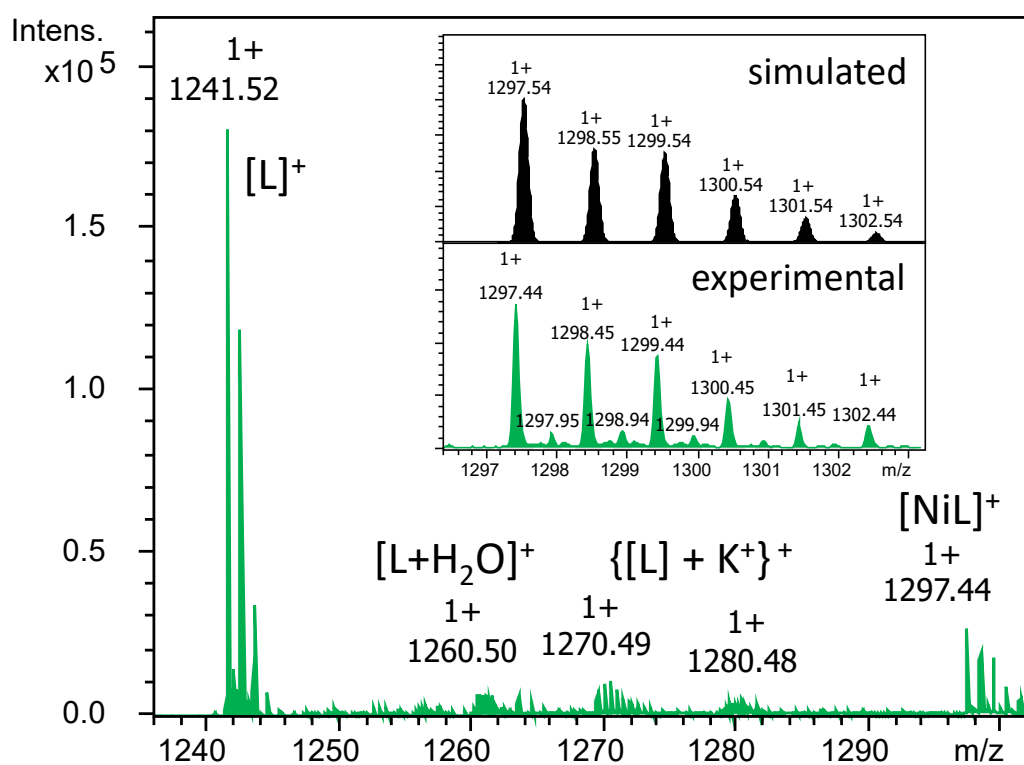


Figure S1. ESI-MS spectrum of a Ni(II)-Ac-DHDHHHGHAAH (L1) system in the m/z 1235–1300 range at pH 7.5 [M/L = 1:1]. The simulated and experimental isotopic distribution spectra of the peak at m/z = 1297.44 are presented in the middle.

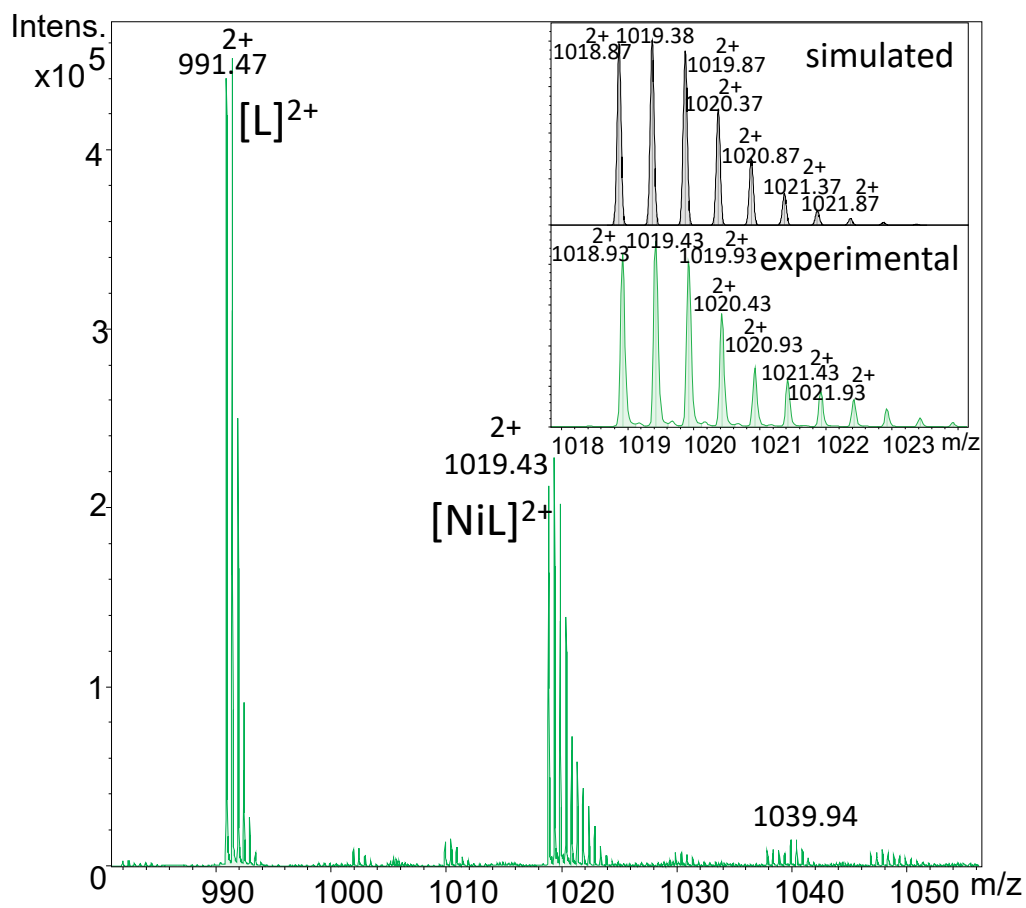


Figure S2. ESI-MS spectrum of a Ni(II)-Ac-DKPAKAEDHDDHHGHAH (L2) system in the m/z 980–1060 range at pH 7.5 [$M/L = 1:1$]. The simulated and experimental isotopic distribution spectra of the peak at $m/z = 1019.43$ are presented in the middle.

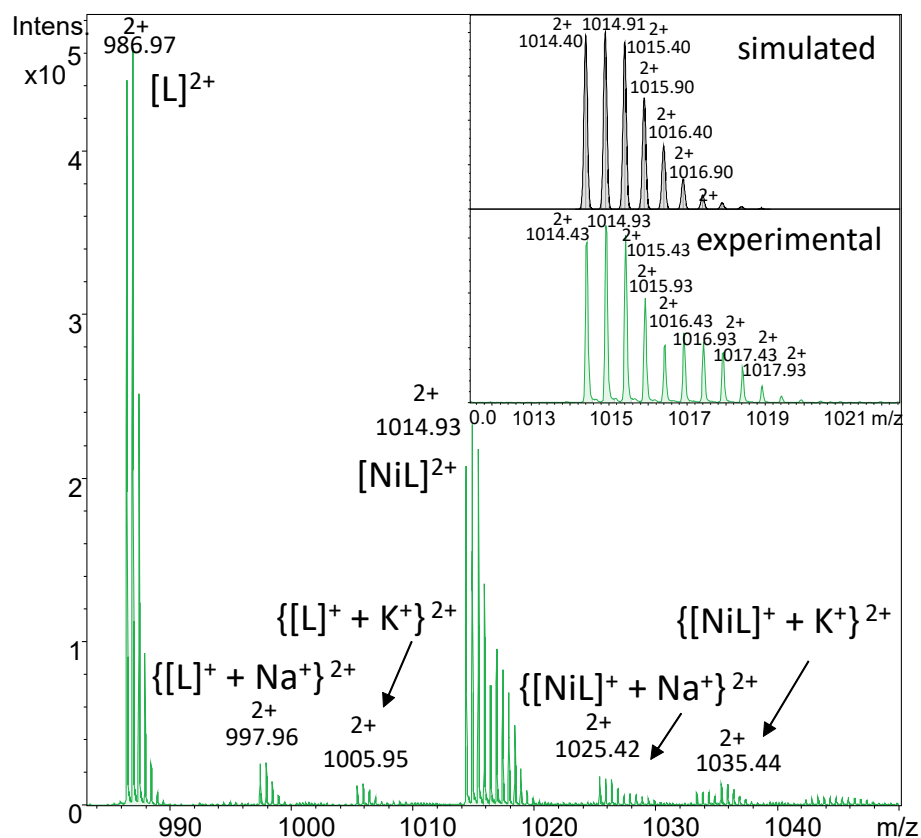


Figure S3. ESI-MS spectrum of a Ni(II)-Ac-DKPAKAEDQDHHHGHAAH (L3) system in the m/z 970–1060 range at pH 7.5 [$M/L = 1:1$]. The simulated and experimental isotopic distribution spectra of the peak at $m/z = 1017.43$ are presented in the middle. The spectrum is identical in case of all studied mutants.

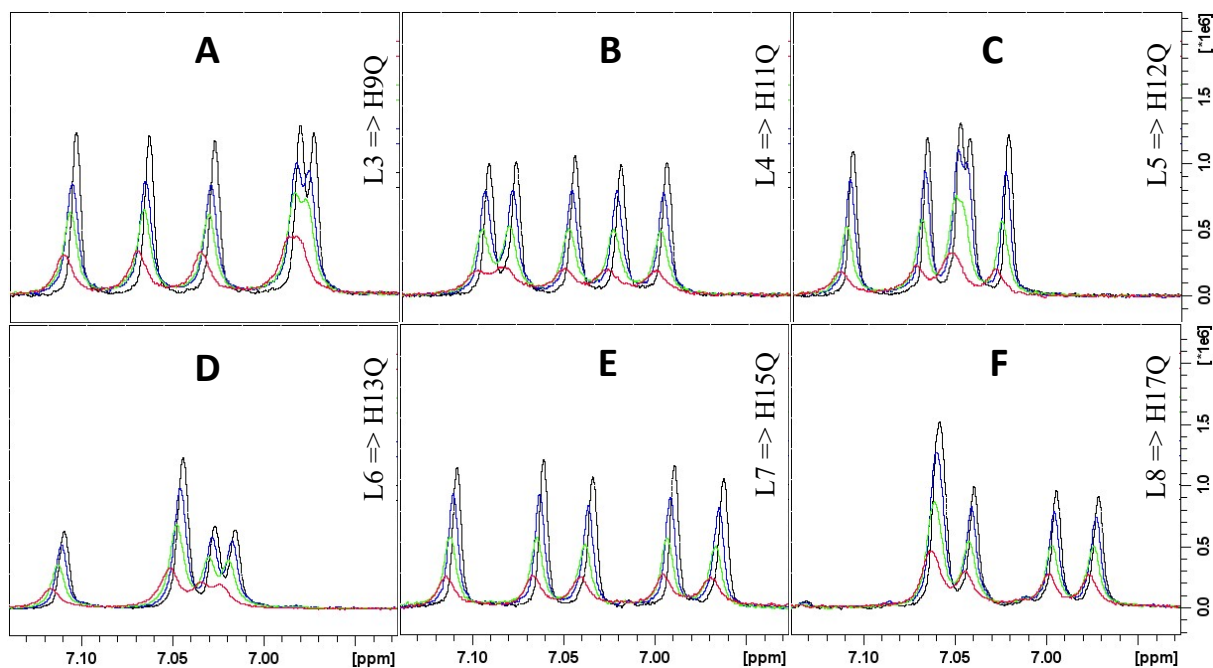


Figure S4. Superimposition of selected regions of ^1H 1D NMR spectra of His/Gln substituted peptides (L3-L8) 1.0 mM in absence (black) and in presence of different Ni(II):L ratio: 0.05 (blue), 0.1 green, 0.2 (red). T =298 K, pH 7.1, $\text{H}_2\text{O}/\text{D}_2\text{O}$ 9/1.

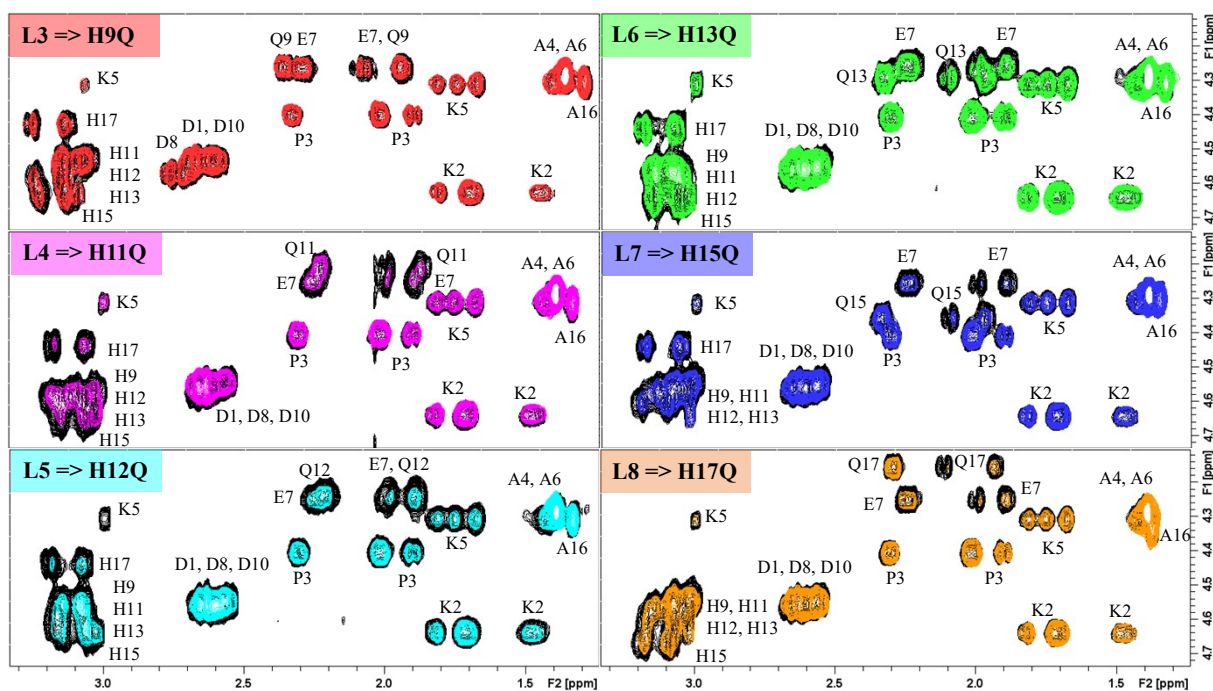


Figure S5. Superimposition of selected regions of the ^1H - ^1H TOCSY spectra of His/Gln substituted peptides 1.0 mM in absence (black) and in presence of 0.2 Ni(II) eqs. (coloured contours). T =298 K, pH 7.1, $\text{H}_2\text{O}/\text{D}_2\text{O}$ 9/1.

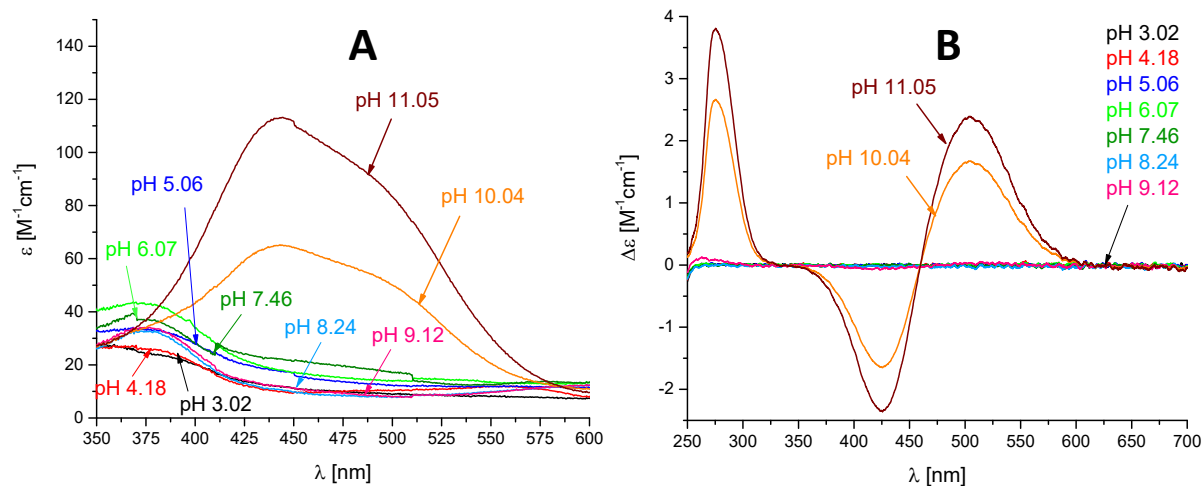


Figure S6. UV-Vis (A) and CD (B) spectra of Ni(II)-L3 system over the pH range 2–11. Conditions: T = 298 K and metal to ligand ratio = 1:0.8; $[\text{Ni(II)}] = 4 \times 10^{-4}$ M.

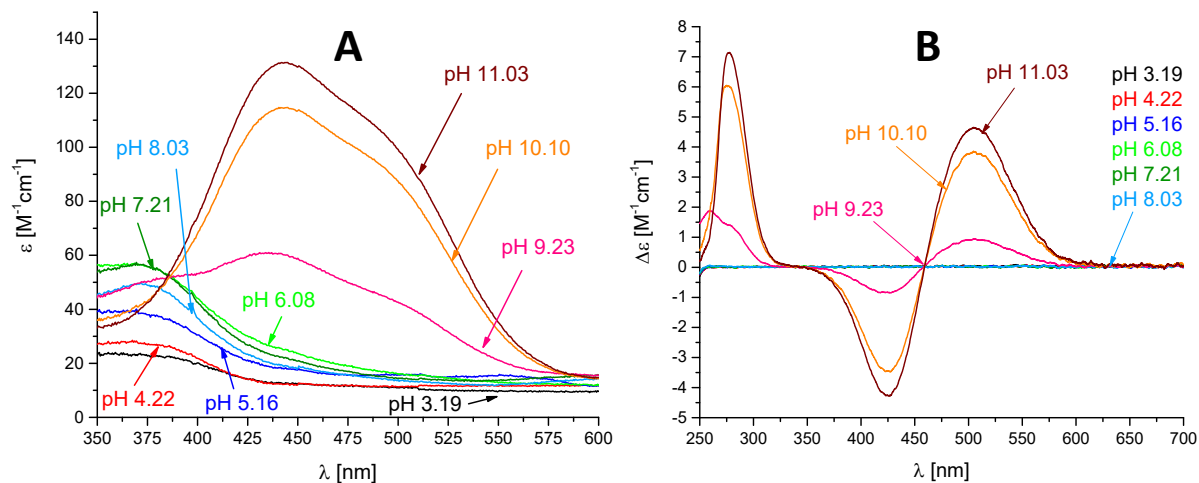


Figure S7. UV-Vis (A) and CD (B) spectra of Ni(II)-L4 system over the pH range 2–11. Conditions: T = 298 K and metal to ligand ratio = 1:0.8; $[\text{Ni(II)}] = 4 \times 10^{-4}$ M.

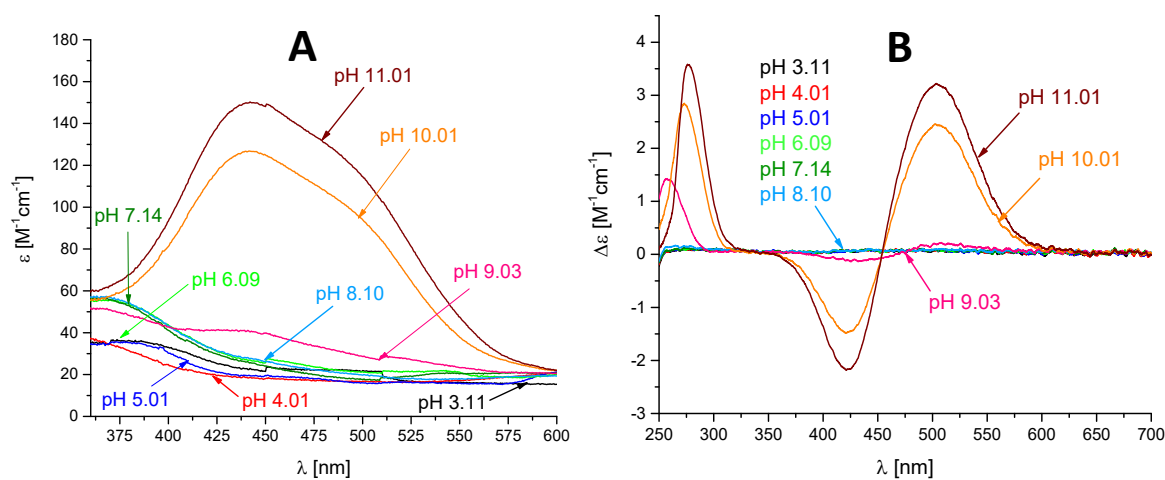


Figure S8. UV-Vis (A) and CD (B) spectra of Ni(II)-L5 system over the pH range 2–11. Conditions: T = 298 K and metal to ligand ratio = 1:0.8; $[\text{Ni(II)}] = 4 \times 10^{-4}$ M.

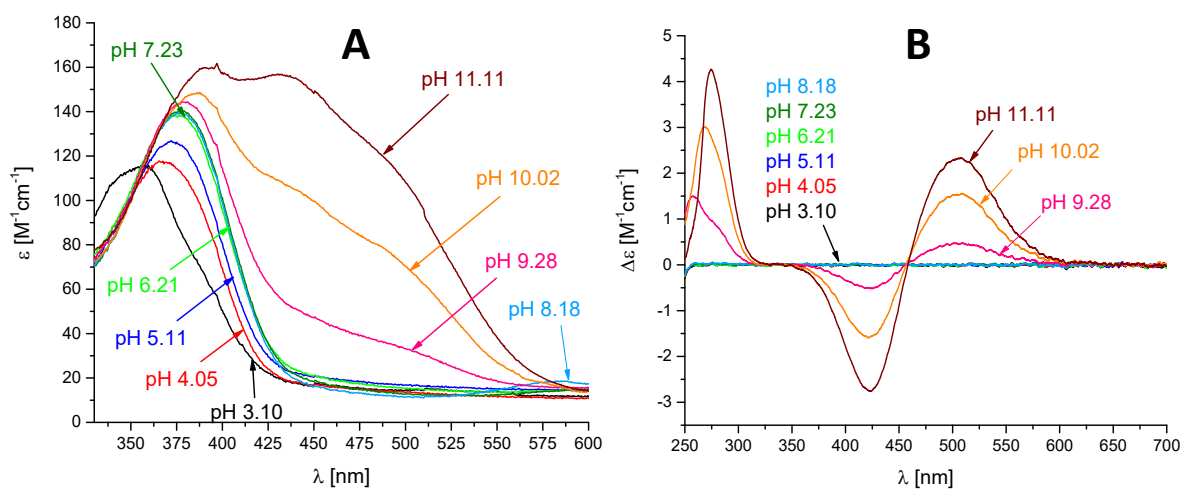


Figure S9. UV-Vis (A) and CD (B) spectra of Ni(II)-L6 system over the pH range 2–11. Conditions: T = 298 K and metal to ligand ratio = 1:0.8; $[\text{Ni(II)}] = 4 \times 10^{-4} \text{ M}$.

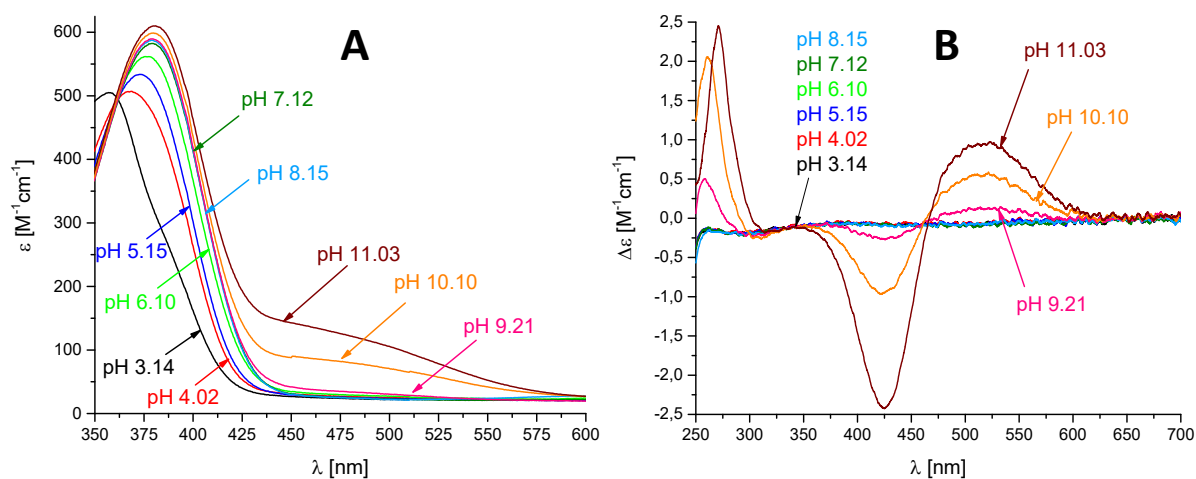


Figure S10. UV-Vis (A) and CD (B) spectra of Ni(II)-L7 system over the pH range 2–11. Conditions: T = 298 K and metal to ligand ratio = 1:0.8; $[\text{Ni(II)}] = 4 \times 10^{-4} \text{ M}$.

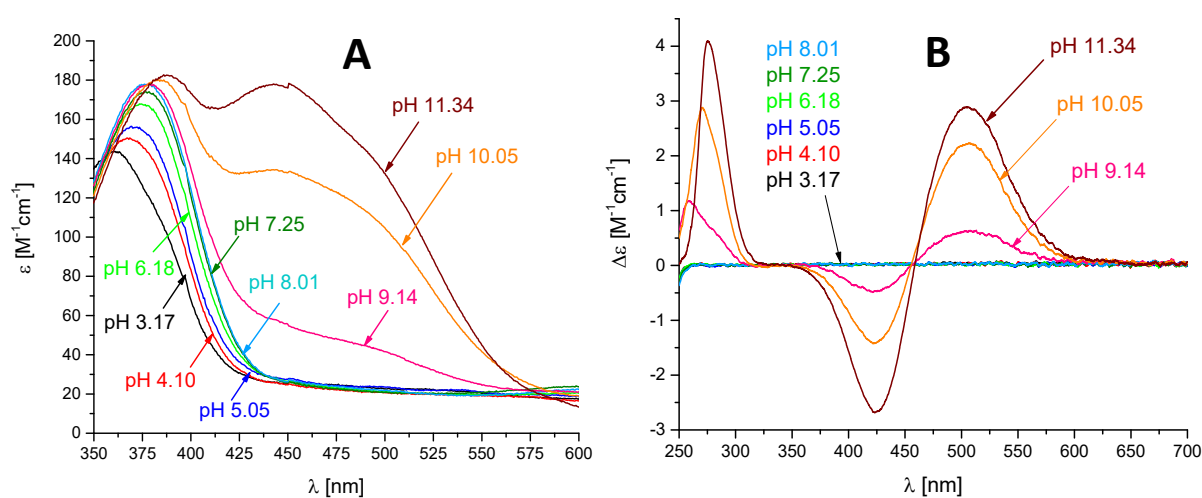


Figure S11. UV-Vis (A) and CD (B) spectra of Ni(II)-L8 system over the pH range 2–11. Conditions: T = 298 K and metal to ligand ratio = 1:0.8; $[\text{Ni(II)}] = 4 \times 10^{-4} \text{ M}$.

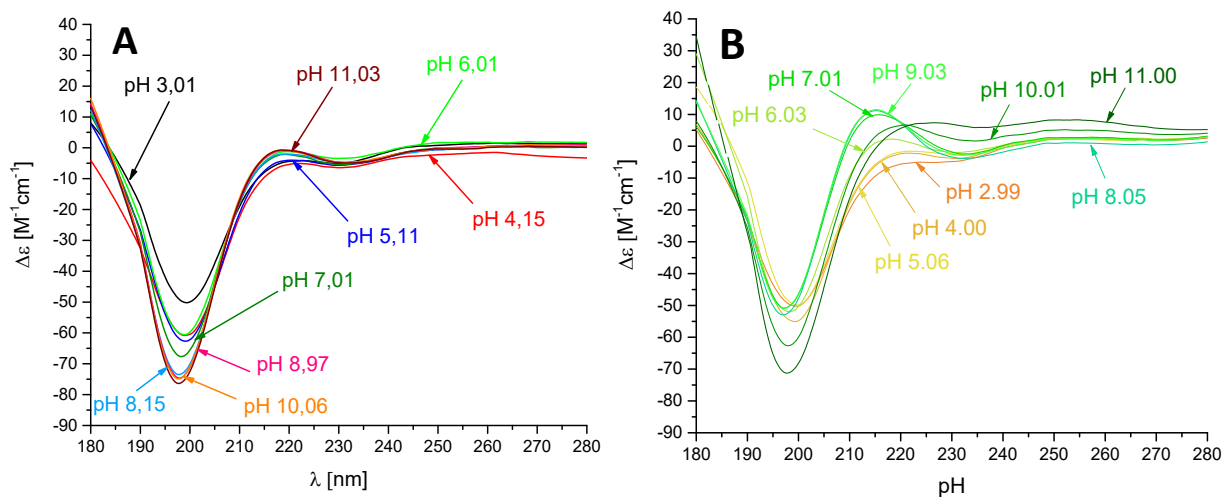


Figure S12. CD spectra of (A) L2: Ac-DKPAKAEDHDHGHGHAH peptide, (B) Ni(II)-L2 system over the pH range 2–11, 180–280 nm. Conditions: T = 298 K and metal to ligand ratio = 0.8:1; [Ni(II)] = 4×10^{-4} M.