**Supplementary Information**

# *Aspergillus fumigatus* ZrfC Zn(II) transporter scavengers zincophore-bound Zn(II)

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The signals: m/z = 826.34, z = 1+ and m/z = 1258.52, z = 2+ correspond to the free ligand for Ac-TGCHSHGS-$NH_2$ and Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$, respectively. The assignment peaks were compared to simulated isotopic patterns, which fit perfectly to experimental data (Fig. S1 and 2, ESI†). In all measured mass spectra, the signals corresponding to the sodium and potassium adducts of the free ligands were observed. The signals: m/z = 848.32, z = 1+ correspond to the Ac-TGCHSHGS-$NH_2$ adduct with sodium atom (Fig. S1A and S1B, ESI†). In the case of Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$ mass spectra the signals: m/z = 1269.52, z = 2+ correspond to ligand adduct with sodium atom and the signals: m/z = 1277.51, z = 2+ correspond to ligand adduct with potassium atom (Fig. S2A and S2B, ESI†).
In the mass spectra of Zn(II)-Ac-TGCHSHGS-$NH_2$ (Fig. S1A, ESI†) beside the signals from the ligand and its sodium adduct, we observe a signals which comes from the zinc complex (m/z = 885.25, z = 1+) and its adducts with potassium atom (m/z = 926.30, z = 1+). In the case of Ni(II)-Ac-TGCHSHGS-$NH_2$ (Fig. S1B, ESI†) the signal (m/z = 882.24, z = 1+) correspond to the equimolar Ni(II) complex. In the Zn(II)-Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$ spectra, aside from the signals which comes from the free ligand and its adducts, a equimolar Zn(II) complex (m/z = 1289.98, z = 2+), its sodium adduct (m/z = 1300.97, z = 2+), potassium adduct (m/z = 1308.97, z = 2+) and sodium and potassium adduct (m/z = 1320.95, z = 2+) can be observed (Fig. S2A, ESI†). In the spectra of the same ligand with Ni(II) (Fig. S2B, ESI†), the signals can be assigned to the nickel complex (m/z = 1286.99, z = 2+) and a nickel complex with a sodium adduct (m/z = 1297.98, z = 2+).

Figure 1. ESI-MS spectrum of A) Zn(II)-Ac-TGCHSHGS-$NH_2$; B) Ni(II)-Ac-TGCHSHGS-$NH_2$ - M(II)/L molar ratio = 1 : 1

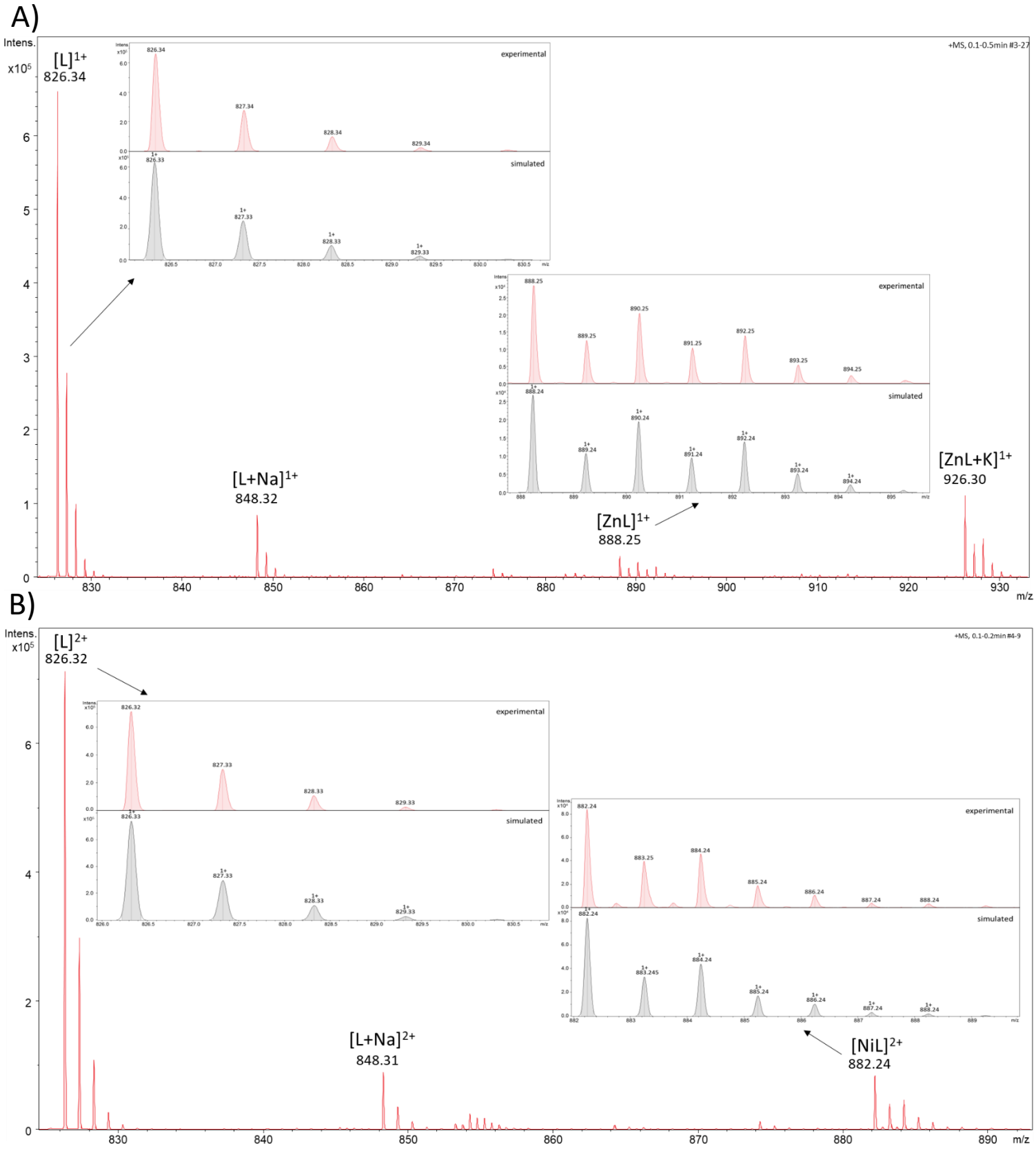


Figure 2. ESI-MS spectrum of A) Zn(II)-Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$; B) Ni(II)-Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$ - M(II)/L molar ratio = 1 : 1

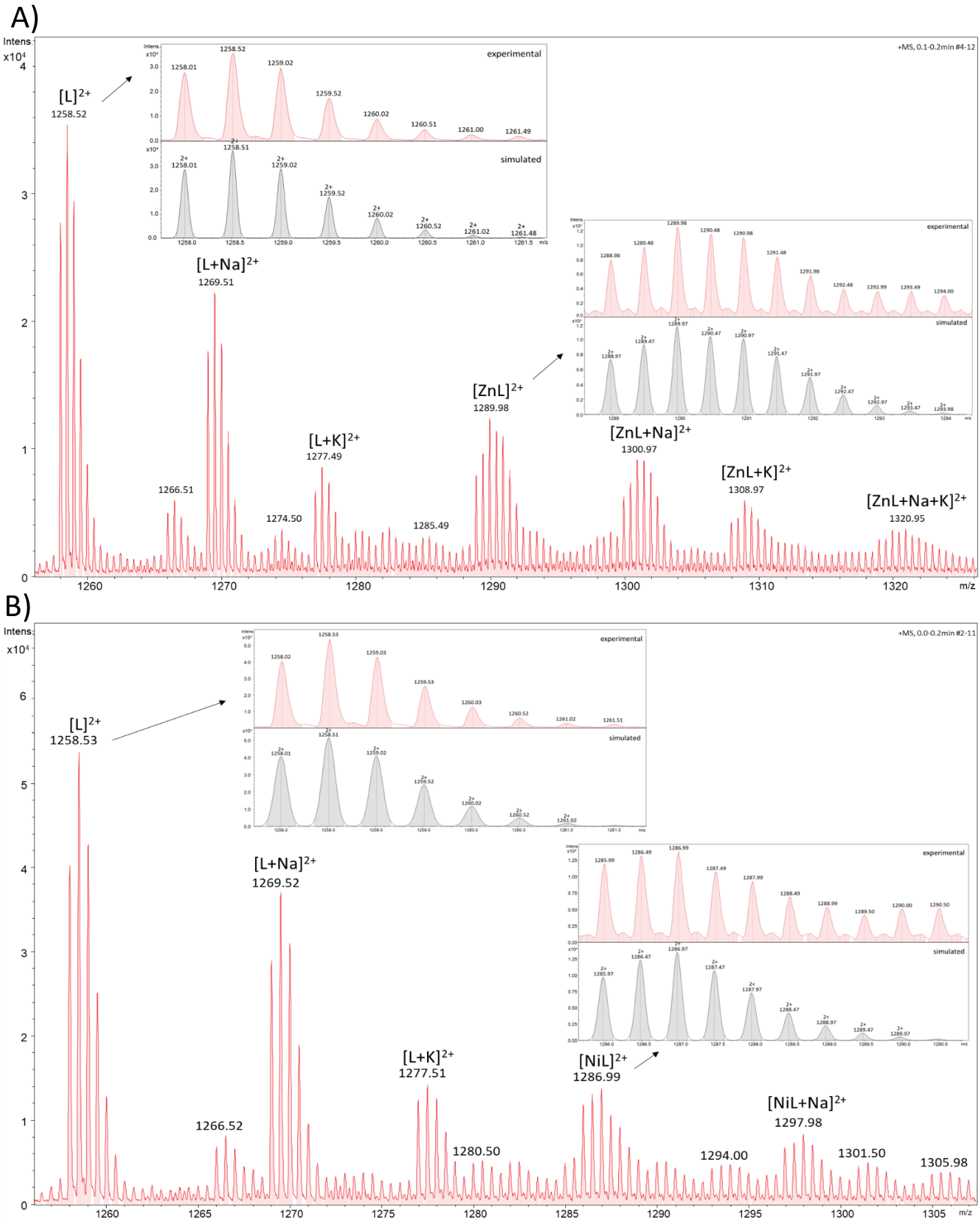


Figure 3. Species distribution diagrams for the formation of A) Zn(II) complexes with the Ac-TGCHSHGS-$NH_2$ ZrfC fragment; B) Zn(II) complexes with the Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$ ZrfC fragment; T = 298 K; I = 0.1 M; [L] = 0.0005 M; M(II)/L molar ratio = 1 : 1

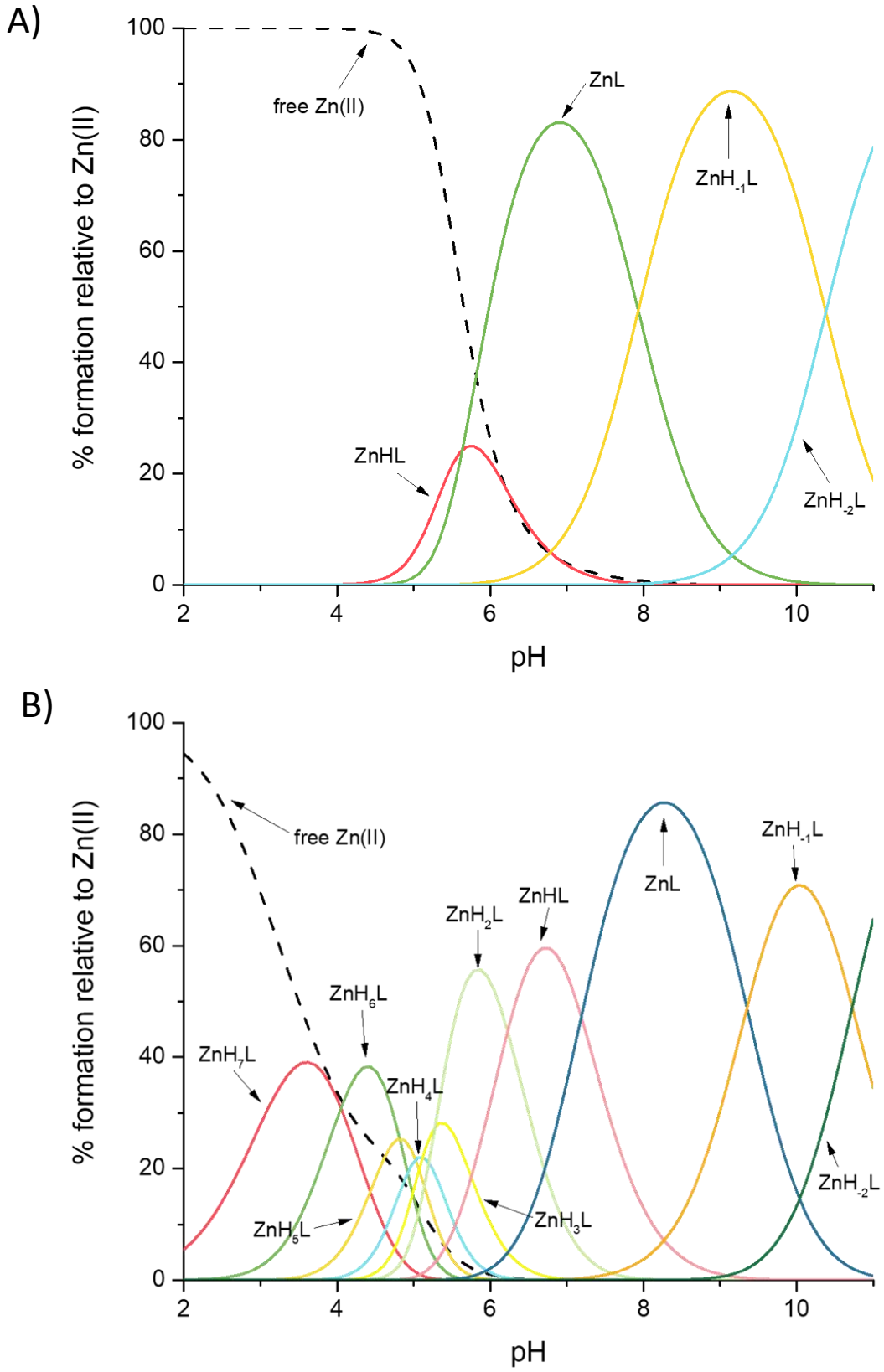


Figure 4. Distribution diagrams for the formation of A) Ni(II) complexes with the Ac-TGCHSHGS-$NH_2$ ZrfC fragment; B) Ni(II) complexes with the Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$ ZrfC fragment; T = 298 K; I = 0.1 M; [L] = 0.0005 M; M(II)/L molar ratio = 1 : 1

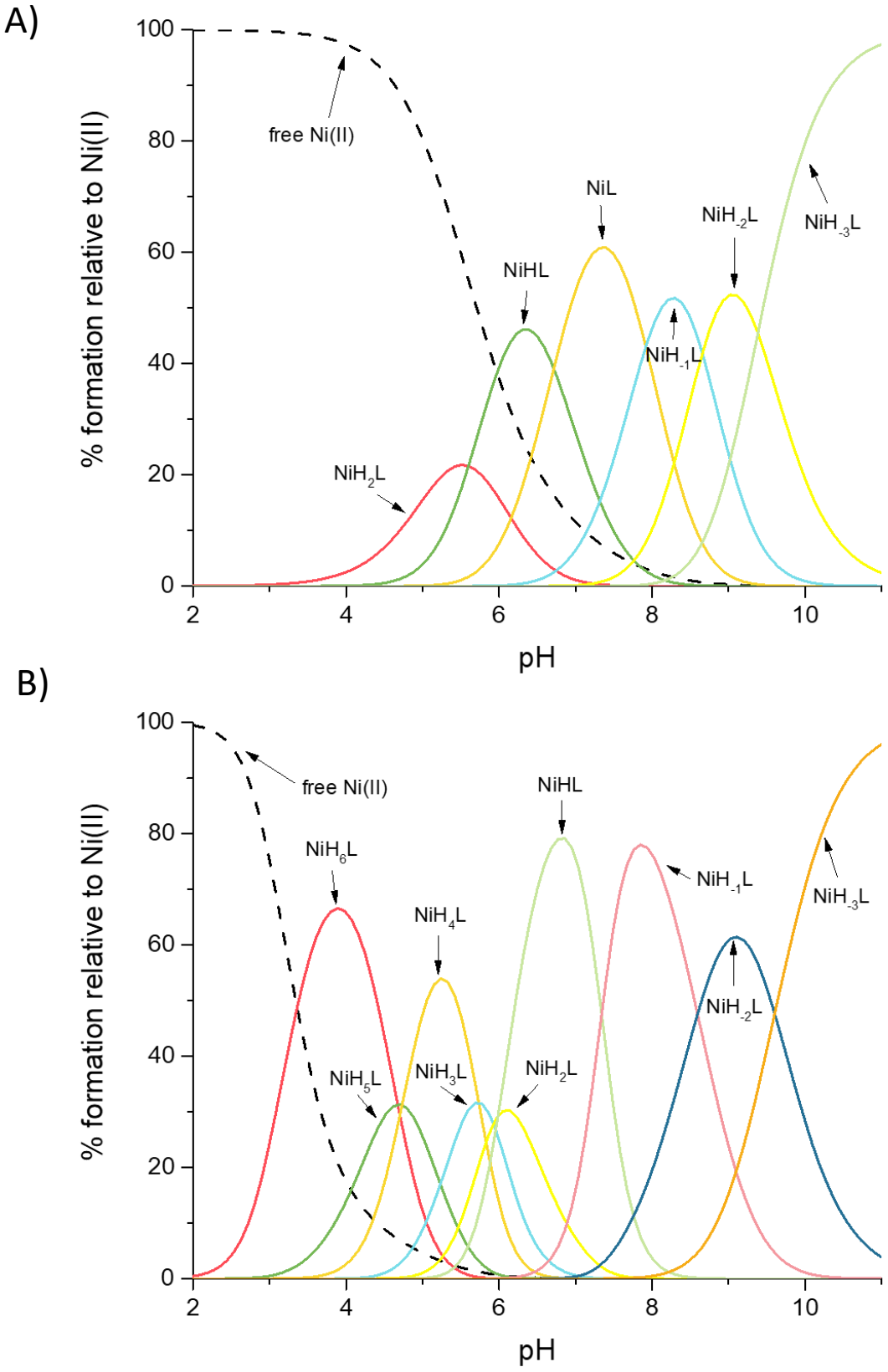
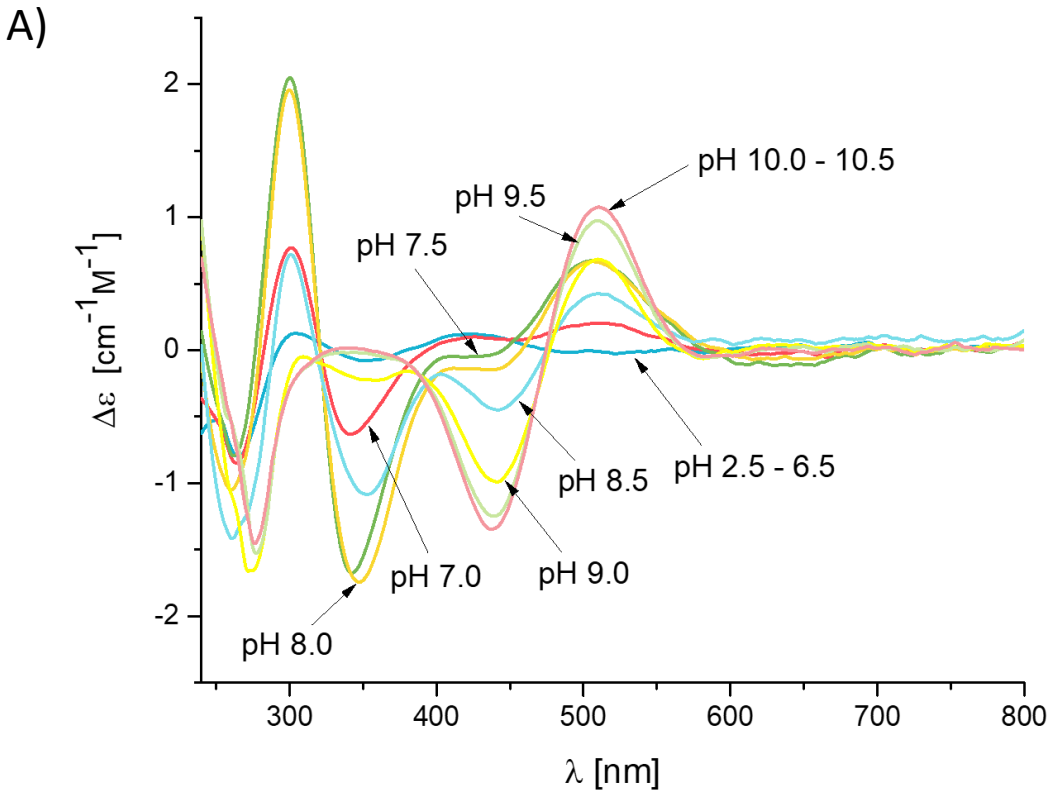


Figure 5. CD spectra of Ni(II) complexes with A) the Ac-TGCHSHGS-$NH_2$ fragment from ZrfC protein; B) the Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$ fragment from ZrfC protein in the range 240 - 800 nm and pH range 2,5 – 10.5; T = 298 K; optical path = 1 cm; [L] = 0.0005 M; M(II)/L = 1 : 1



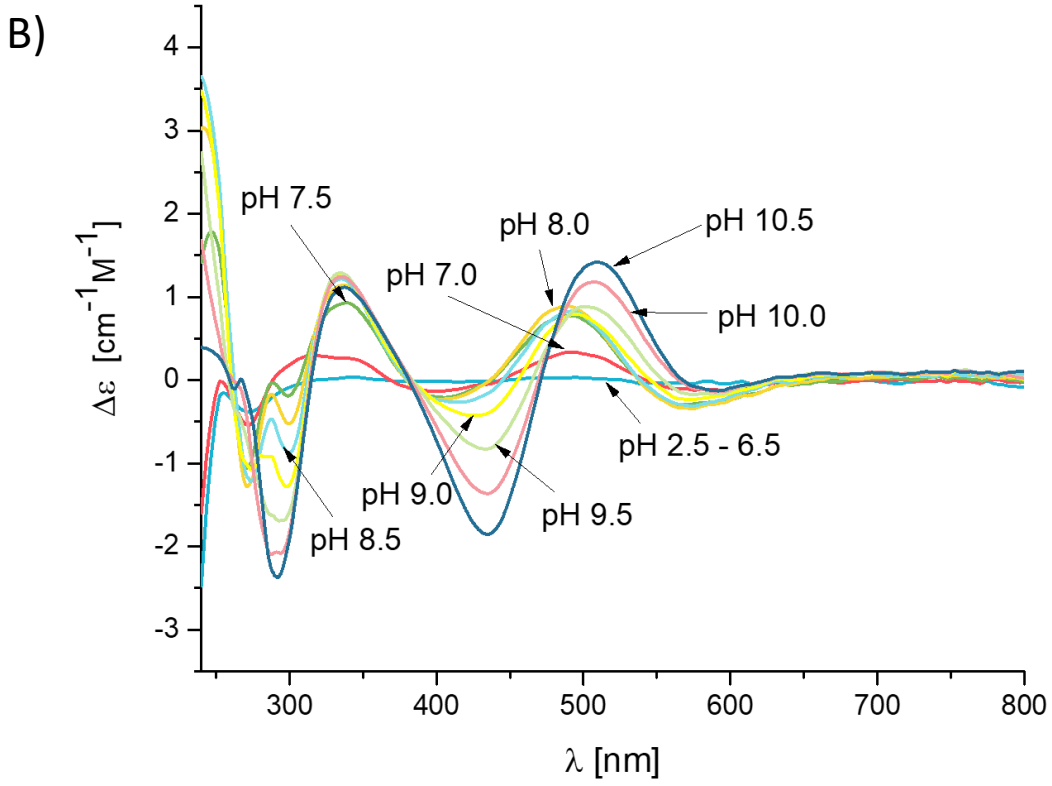



Figure 6. UV-Vis spectra of Ni(II) complexes with A) the Ac-TGCHSHGS-$NH_2$ fragment from ZrfC protein; B) the Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$ fragment from ZrfC protein in the range 200 - 800 nm and pH range 2.5 – 10.5; T = 298 K; optical path = 1 cm; [L] = 0.0005 M; M(II)/L = 1 : 1

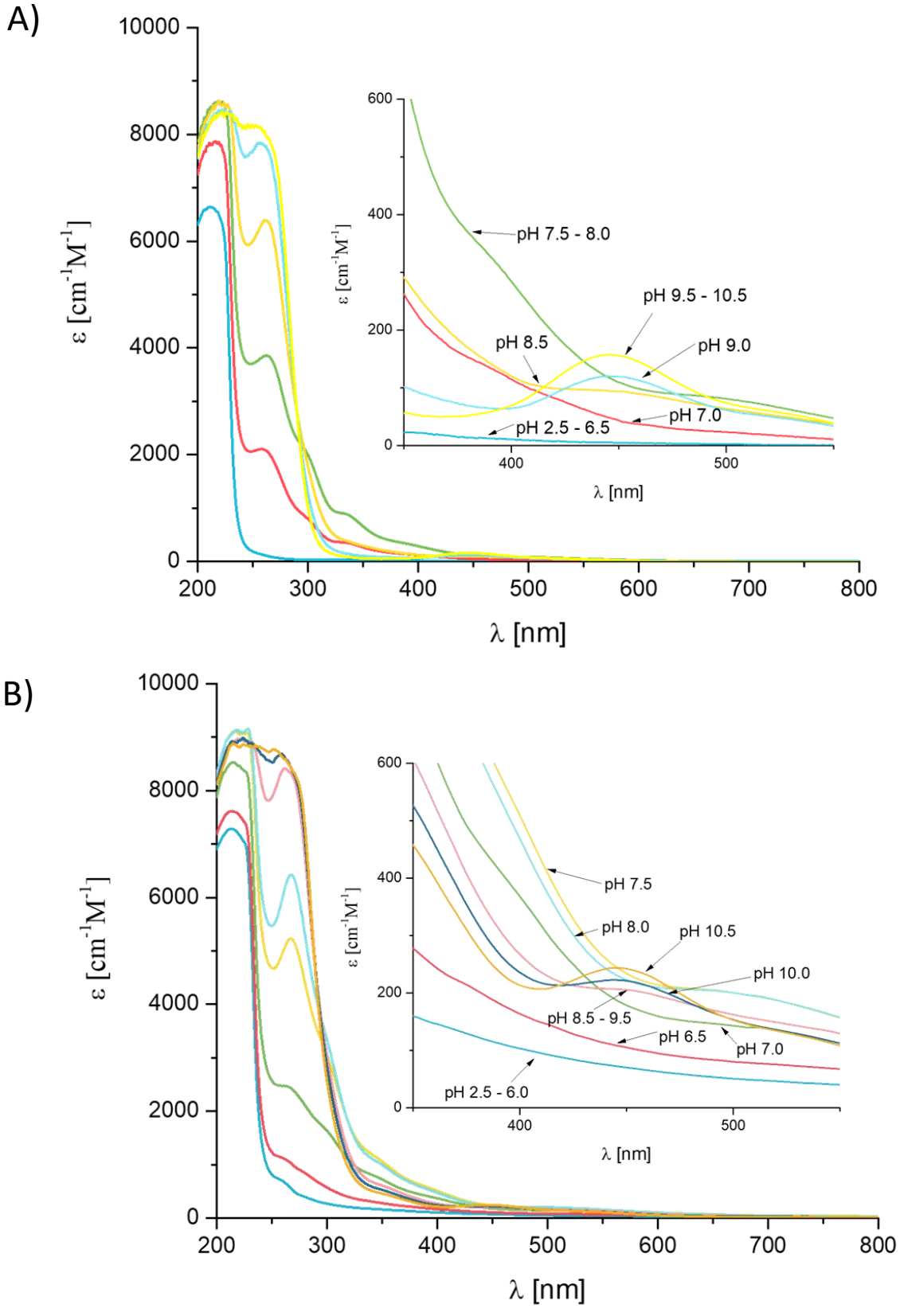


Figure 7. Far UV CD spectra of A) the Ac-TGCHSHGS-$NH_2$ fragment, B) Zn(II)-Ac-TGCHSHGS-$NH_2$ complex, C) Ni(II)-Ac-TGCHSHGS-$NH_2$ in the range 180 - 280 nm and pH range 3.5 – 11.5; T = 298 K; optical path = 0.01 cm; [L] = 0.0005 M; M(II)/L = 1 : 1

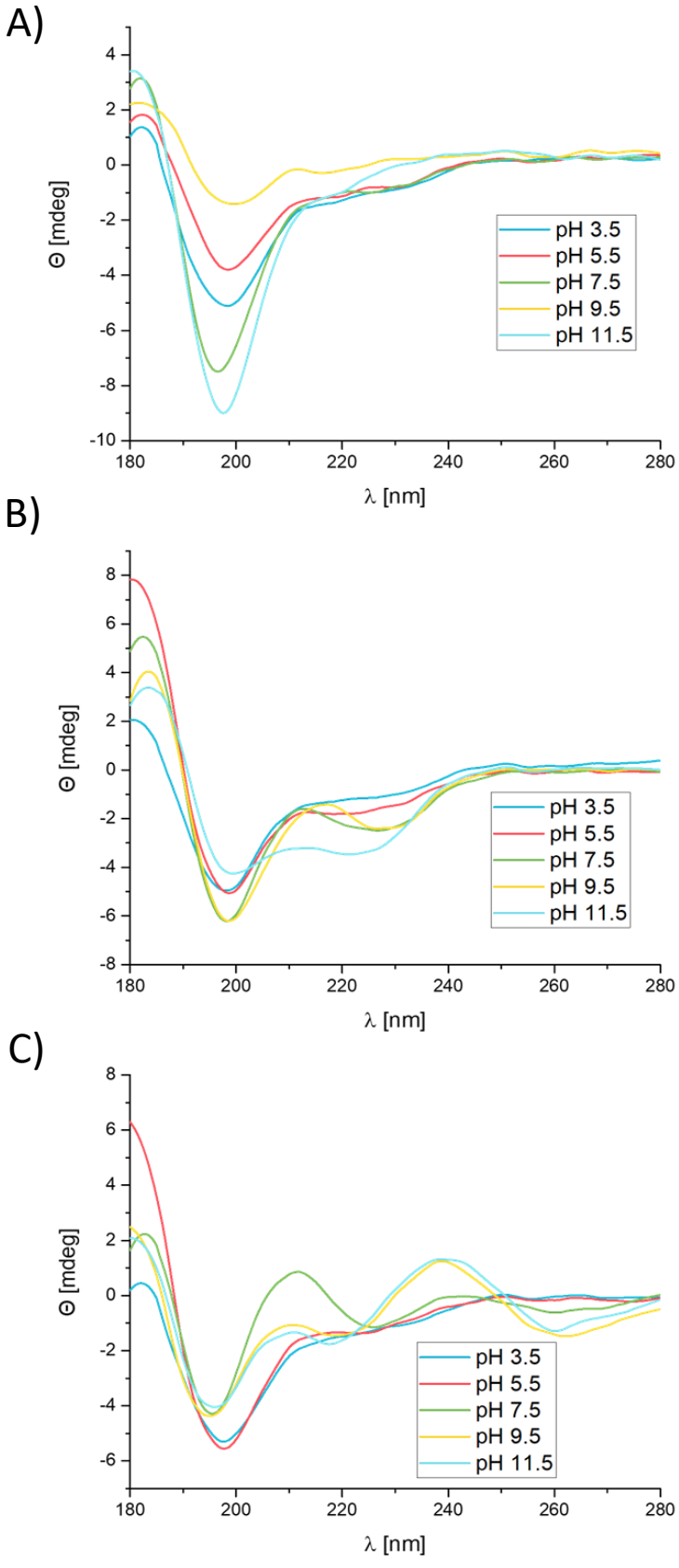


Figure 8. Far UV CD spectra of A) the Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$ fragment, B) Zn(II)- Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$ complex, C) Ni(II)- Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$ complex in the range 180 - 280 nm and pH range 3.5 – 11.5; T = 298 K; optical path = 0.01 cm; [L] = 0.0005 M; M(II)/L = 1 : 1

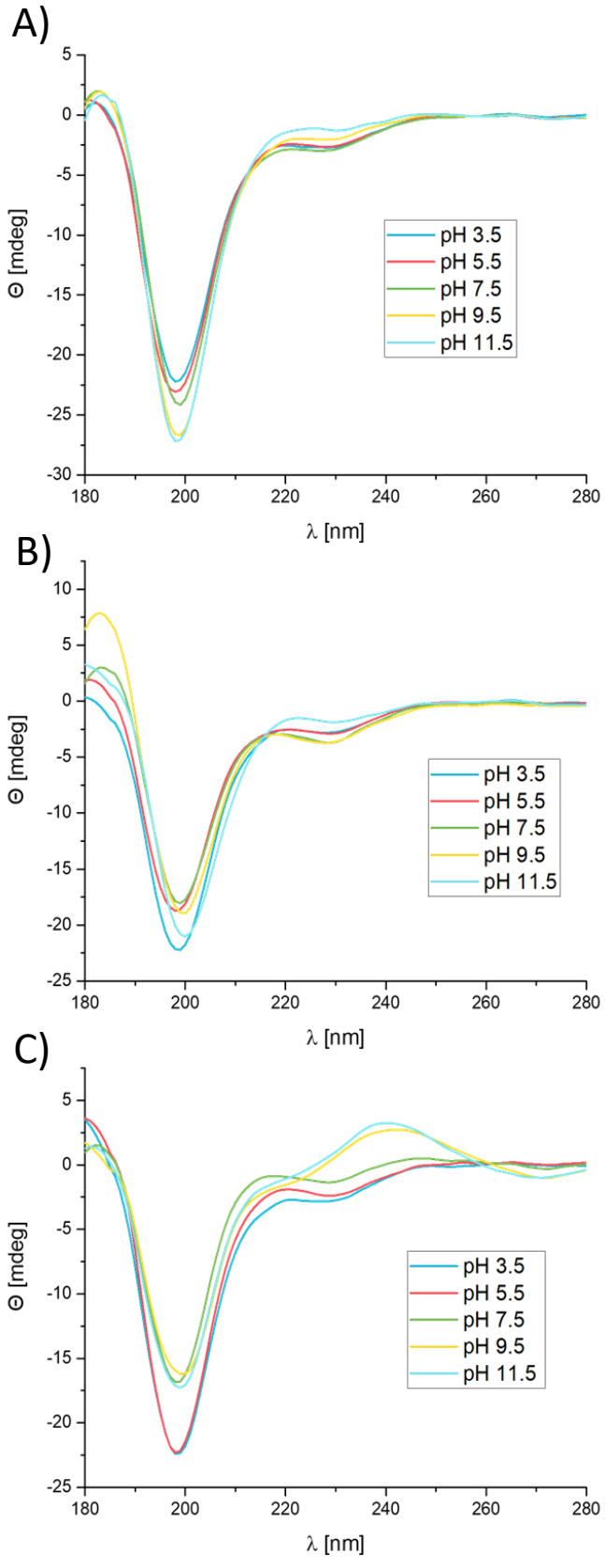


Figure 9. A competition plot between ZrfC fragments: Ac-TGCHSHGS-$NH_2$, Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$ and A) Zn(II), B) Ni(II), describes complex formation at different pH values in a hypothetical situation in which equimolar amounts of all reagents are mixed. Calculations are based on binding constants from Table 1. Conditions: T=298 K, I=0.1 M $NaClO_4$, A) [Zn(II)], B) [Ni(II)] = [Ac-TGCHSHGS-$NH_2$] = [Ac-MNCHFHAGVEHCIGAGESESGSSQ-$NH_2$] = 0.001 M

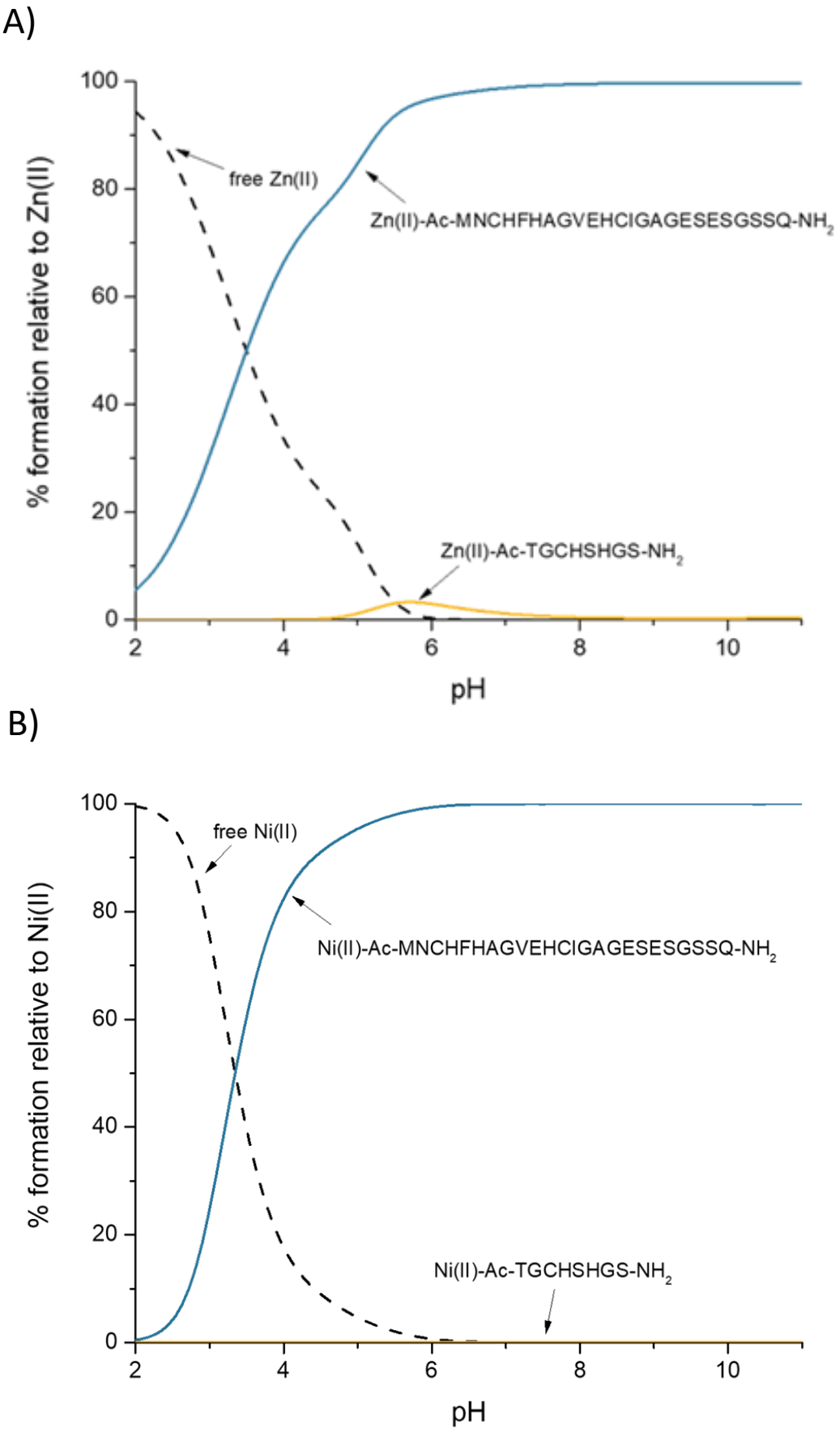


Figure 10. A competition plot between ZrfC fragment: Ac-TGCHSHGS-$NH_2$, Zn(II) and Ni(II), describes complex formation at different pH values in a hypothetical situation in which equimolar amounts of all reagents are mixed. Calculations are based on binding constants from Table 1. Conditions: T=298 K, I=0.1 M $NaClO_4$, [Zn(II)] = [Ni(II)] = [Ac-TGCHSHGS-$NH_2$] = 0.001 M