Supplementary Material

Selective Hydrolysis of Transferrin Promoted by Zr-Substituted Polyoxometalates

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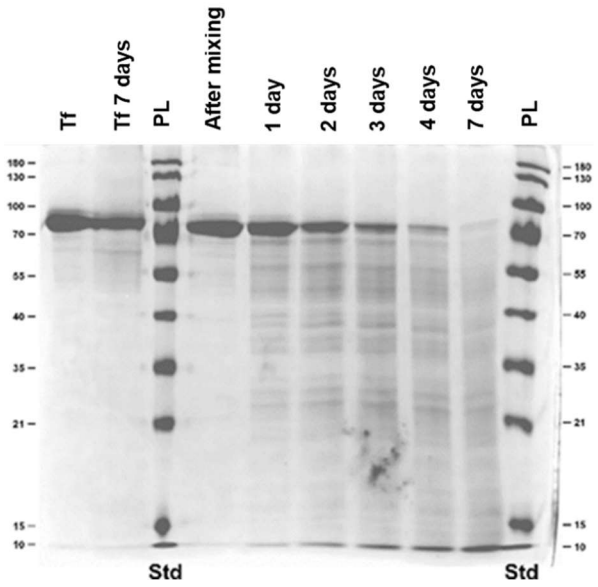

Figure S1. SDS-PAGE gel of transferrin (7.5 μM) in water (lane 1), transferrin (7.5 μM) incubated in phosphate buffer (10 mM, pH 7.4) for 7 days at 60 °C (lane 2) and transferrin (7.5 μM) incubated in phosphate buffer (10 mM, pH 7.4) with **Zr-WD 1:2** (0.75 mM) at 60 °C for different time increments (lanes 4–9).

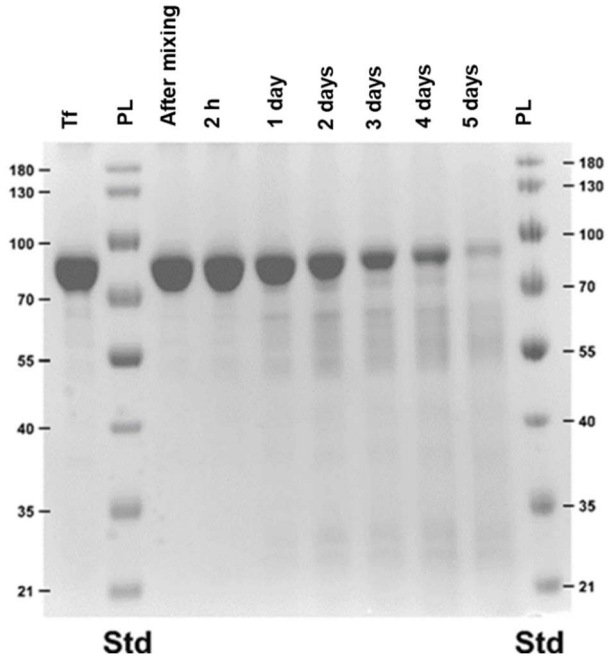

Figure S2. SDS-PAGE gel of transferrin (7.5 μM) in water (lane 1) and transferrin (7.5 μM) incubated in phosphate buffer (10 mM, pH 7.4) with **Zr-WD 4:2** (0.75 mM) at 60 °C for different time increments (lanes 3–9).

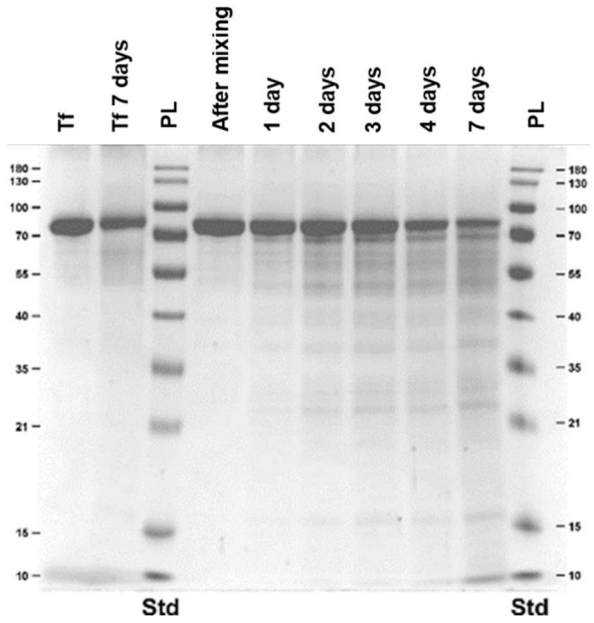

Figure S3. SDS-PAGE gel of transferrin (7.5 μM) in water (lane 1), transferrin (7.5 μM) incubated in phosphate buffer (10 mM, pH 7.4) for 7 days at 60 °C (lane 2) and transferrin (7.5 μM) incubated in phosphate buffer (10 mM, pH 7.4) with **Zr-K 1:2** (0.75 mM) at 60 °C for different time increments (lanes 4–9).

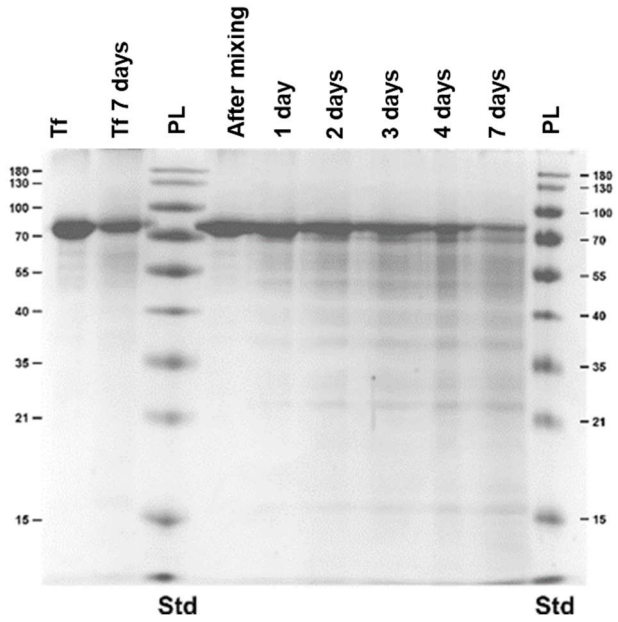

Figure S4. SDS-PAGE gel of transferrin (7.5 μM) in water (lane 1), transferrin (7.5 μM) incubated in phosphate buffer (10 mM, pH 7.4) for 7 days at 60 °C (lane 2) and transferrin (7.5 μM) incubated in phosphate buffer (10 mM, pH 7.4) with **Zr-K 2:2** (0.75 mM) at 60 °C for different time increments (lanes 4–9).

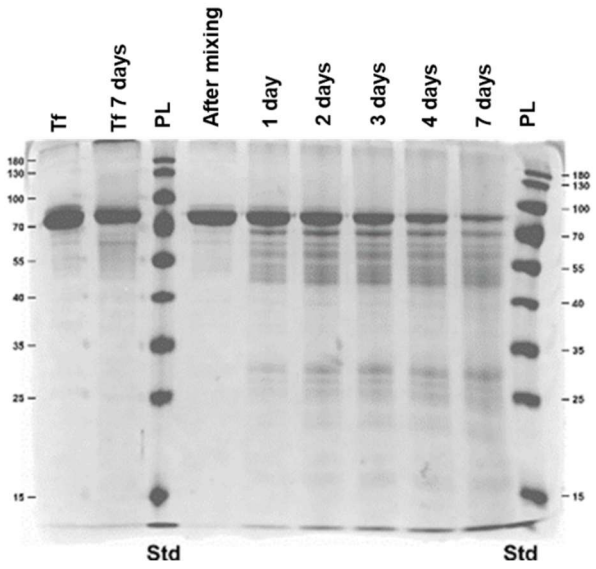

Figure S5. SDS-PAGE gel of transferrin (7.5 μM) in water (lane 1), transferrin (7.5 μM) incubated in phosphate buffer (10 mM, pH 7.4) for 7 days at 60 °C (lane 2) and transferrin (7.5 μM) incubated in phosphate buffer (10 mM, pH 7.4) with **Zr-L 1:1** (0.75 mM) at 60 °C for different time increments (lanes 4–9).

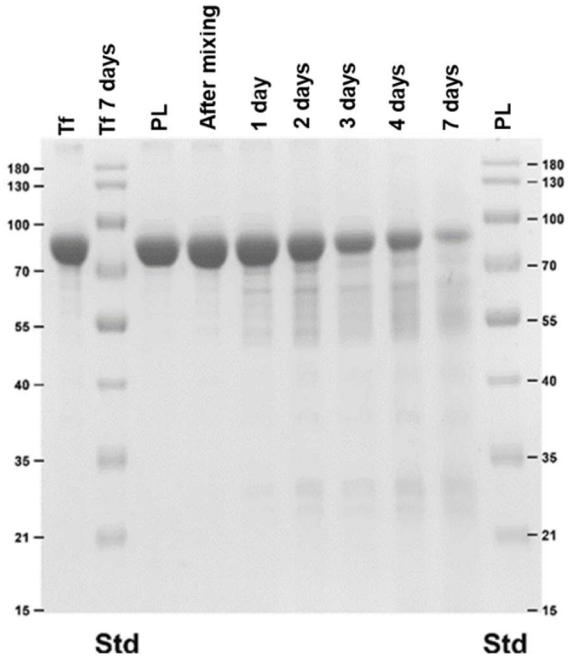

Figure S6. SDS-PAGE gel of transferrin (7.5 μM) in water (lane 1) and transferrin (7.5 μM) incubated in phosphate buffer (10 mM, pH 7.4) with **Zr-L 2:2** (0.75 mM) at 60 °C for different time increments (lanes 3–9).

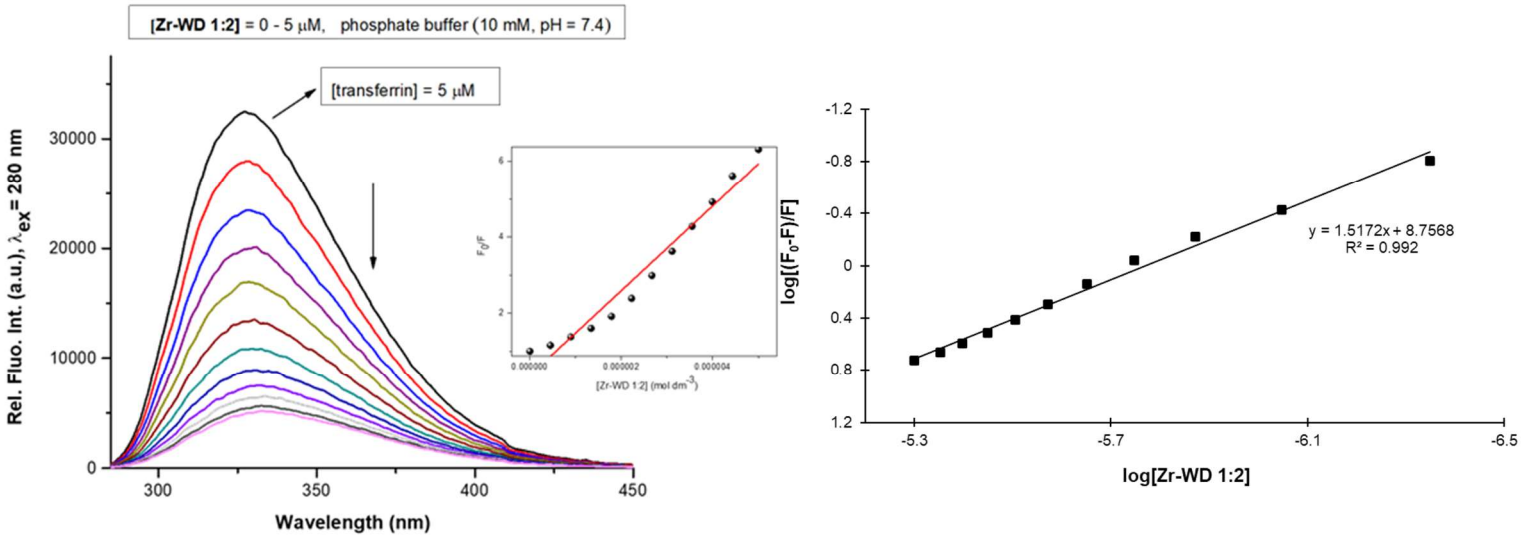

Figure S7. Tryptophan fluorescence quenching spectra of transferrin (5 μM) in phosphate buffer (10 mM, pH 7.4) with increasing concentrations of **Zr-WD 1:2** (0–5 μM). The insert shows a plot of F_0/F versus the POM concentration. (Right) Derived Stern-Volmer plot used to calculate the association constant.

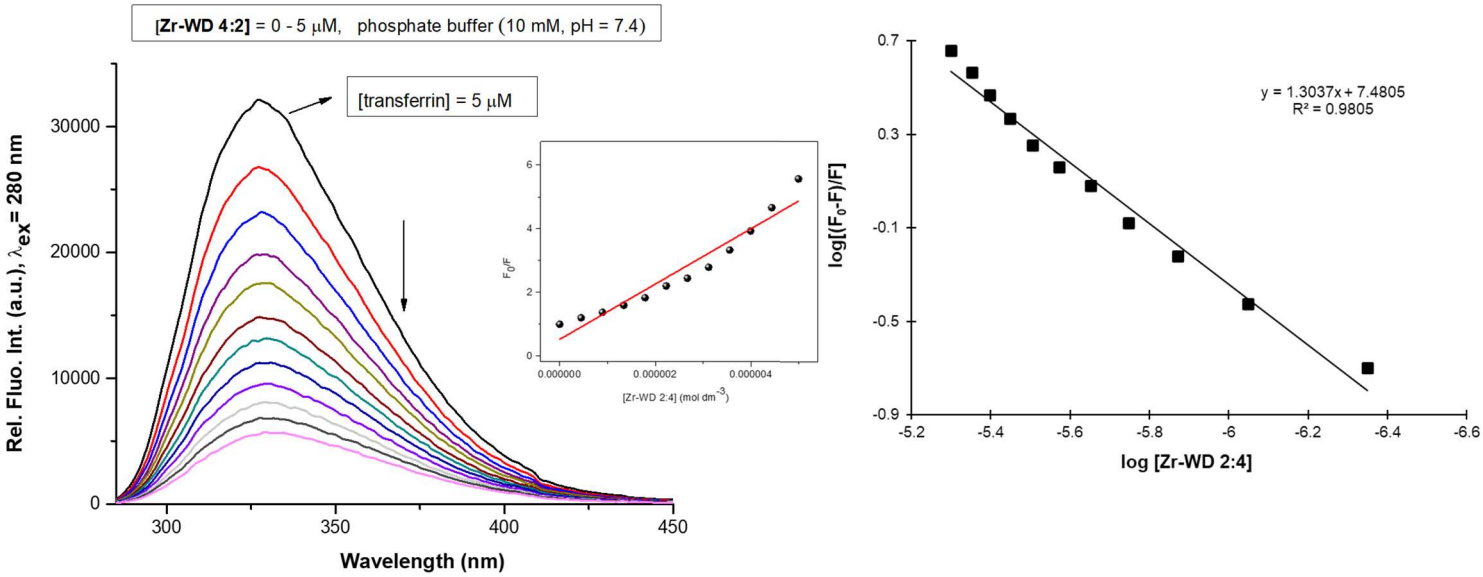

Figure S8. Tryptophan fluorescence quenching spectra of transferrin (5 μM) in phosphate buffer (10 mM, pH 7.4) with increasing concentrations of **Zr-WD 4:2** (0–5 μM). The insert shows a plot of F_0/F versus the POM concentration. (Right) Derived Stern-Volmer plot used to calculate the association constant.

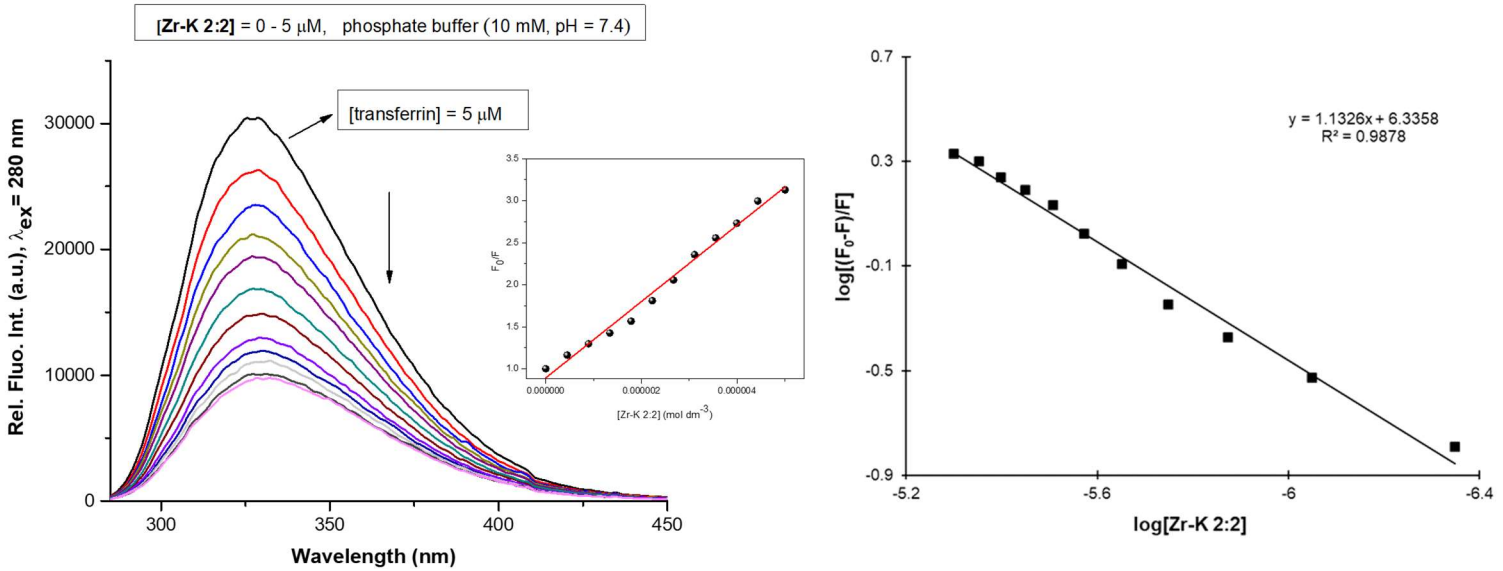

Figure S9. Tryptophan fluorescence quenching spectra of transferrin (5 μM) in phosphate buffer (10 mM, pH 7.4) with increasing concentrations of **Zr-K 2:2** (0–5 μM). The insert shows a plot of F_0/F versus the POM concentration. (Right) Derived Stern-Volmer plot used to calculate the association constant.

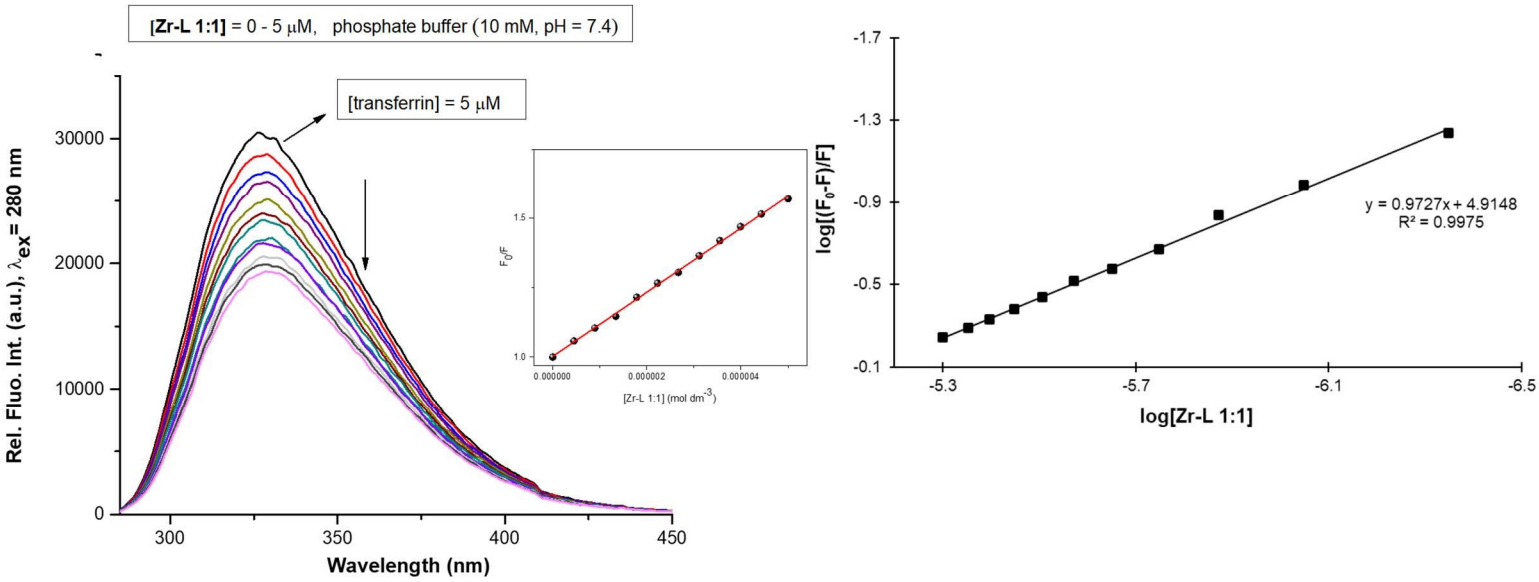

Figure S10. Tryptophan fluorescence quenching spectra of transferrin (5 μM) in phosphate buffer (10 mM, pH 7.4) with increasing concentrations of **Zr-L 1:1** (0–5 μM). The insert shows a plot of F_0/F versus the POM concentration. (Right) Derived Stern-Volmer plot used to calculate the association constant.

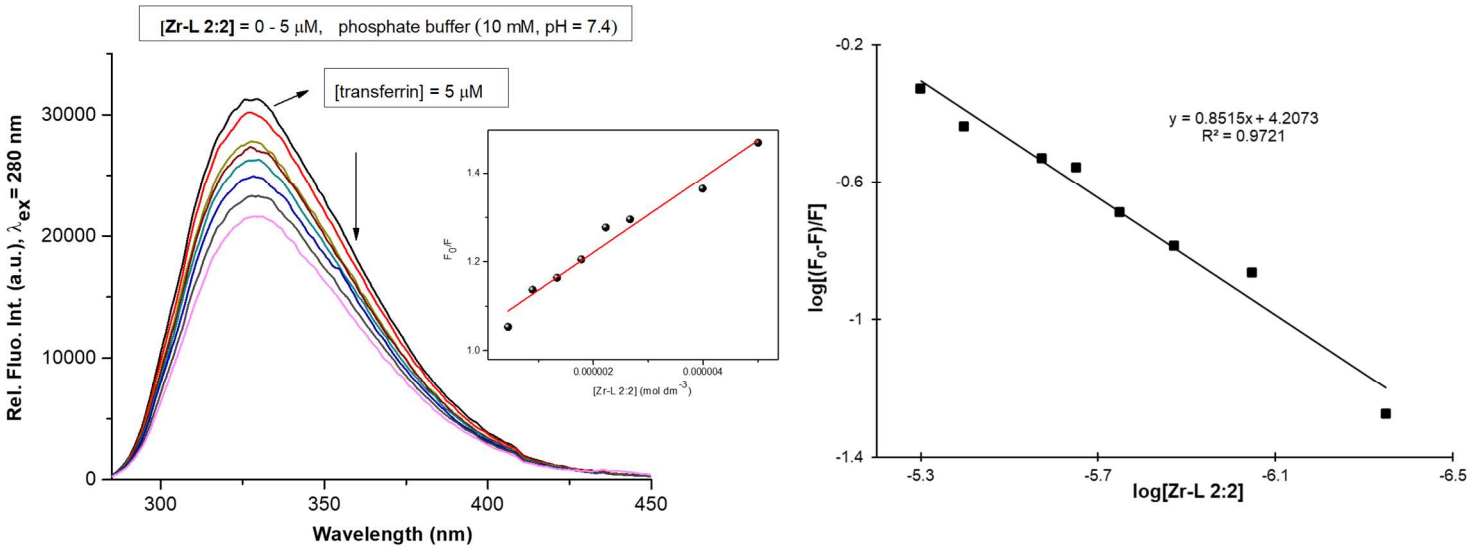

Figure S11. Tryptophan fluorescence quenching spectra of transferrin (5 μM) in phosphate buffer (10 mM, pH 7.4) with increasing concentrations of **Zr-L 2:2** (0–5 μM). The insert shows a plot of F_0/F versus the POM concentration. (Right) Derived Stern-Volmer plot used to calculate the association constant.

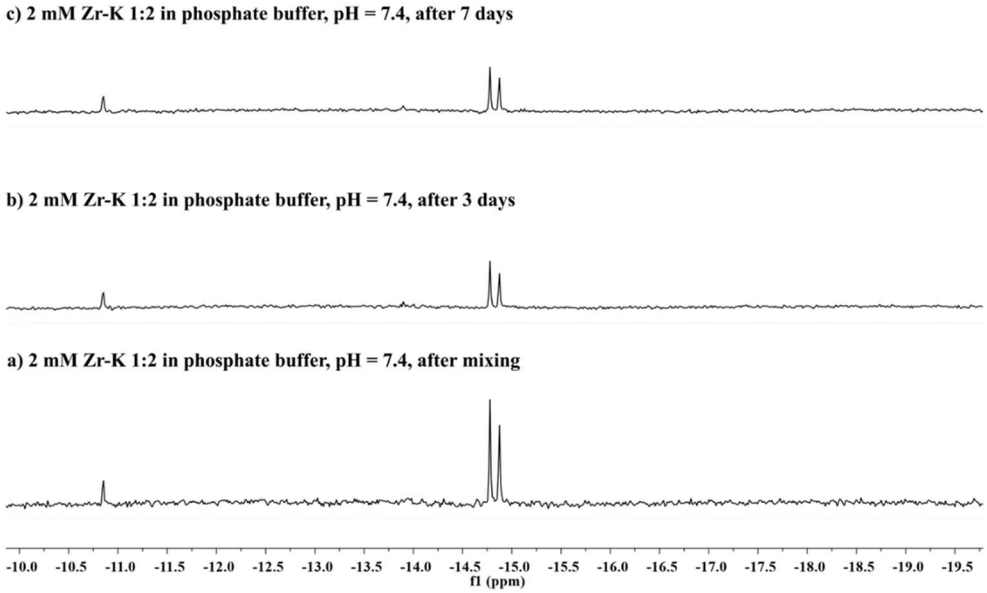

Figure S12. ^{31}P NMR of **Zr-K 1:2** (2 mM) in phosphate buffer (10 mM, pH 7.4) at room temperature. The **Zr-K 1:2** structure (−14.78 and −14.83 ppm) remains largely stable over time, the signal at −10.85 ppm is attributed to the lacunary Keggin.

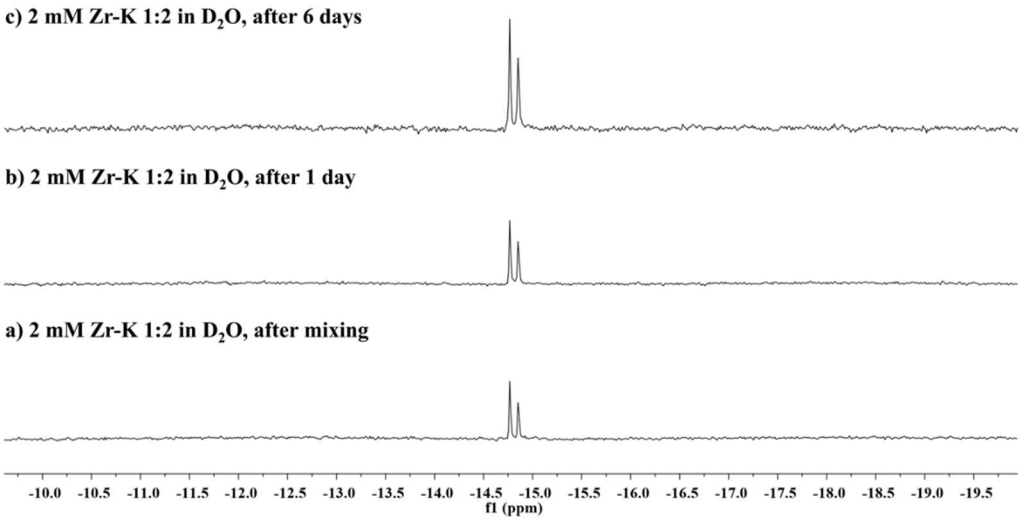

Figure S13. ^{31}P NMR of **Zr-K 1:2** (2 mM) in D_2O at room temperature. The **Zr-K 1:2** structure (−14.78 and −14.83 ppm) remains largely stable over time.

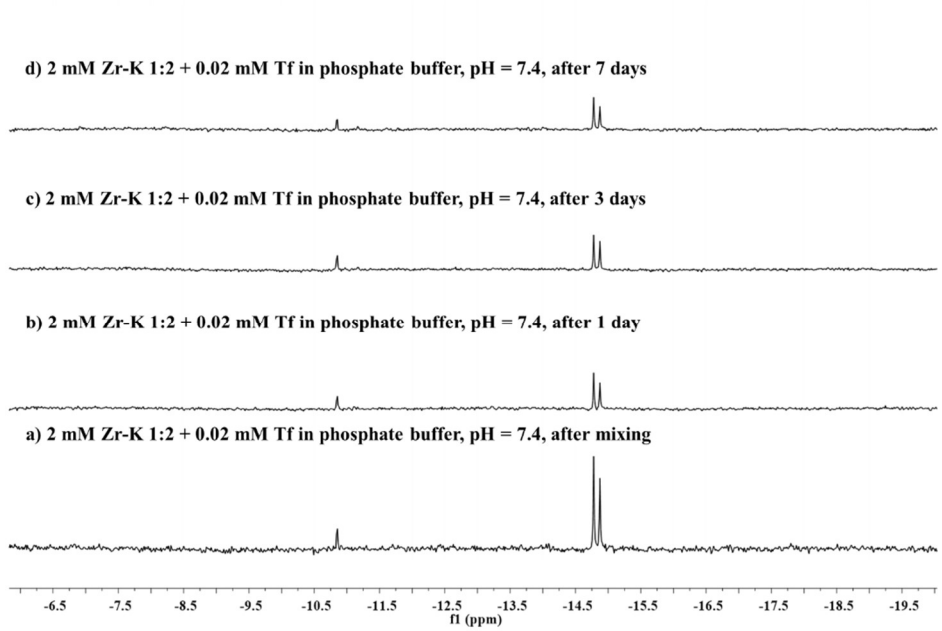

Figure S14. ^{31}P NMR of **Zr-K 1:2** (2 mM) in the presence of transferrin (20 μM) incubated in phosphate buffer (10 mM, pH 7.4) at 60 °C. The **Zr-K 1:2** structure (−14.78 and −14.83 ppm) remains largely stable over time, the signal at −10.85 ppm is attributed to the lacunary Keggin.

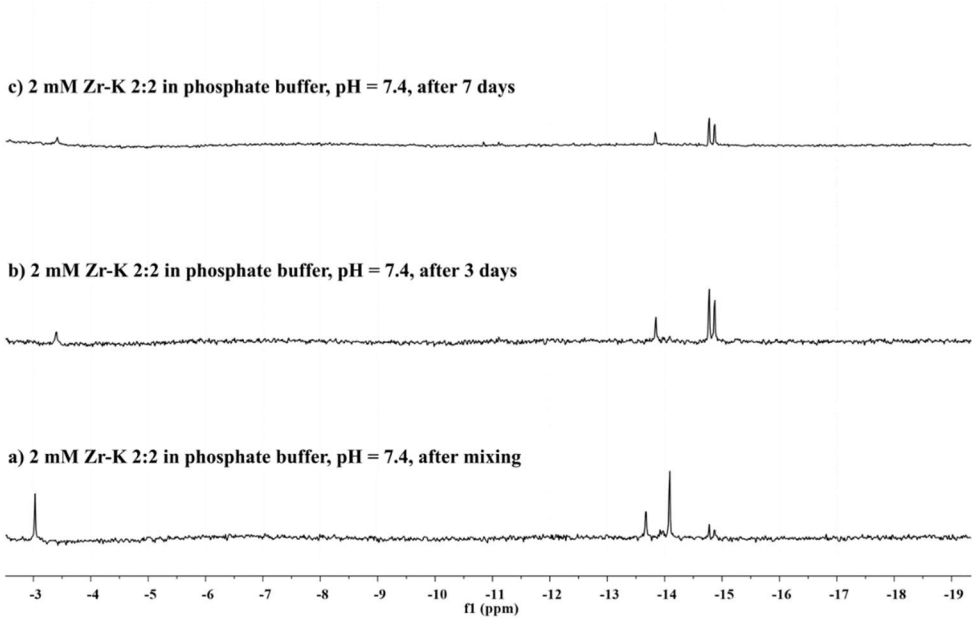

Figure S15. ^{31}P NMR of **Zr-K 2:2** (2 mM) in phosphate buffer (10 mM, pH 7.4) at room temperature. The peak corresponding to intact **Zr-K 2:2** appears at −13.69 ppm in buffer solution. Simultaneously, 2 peaks corresponding to **Zr-K 1:2** appeared around −14.77 and 14.86 ppm. Additional peaks appeared around −14 ppm and one around −3 ppm.

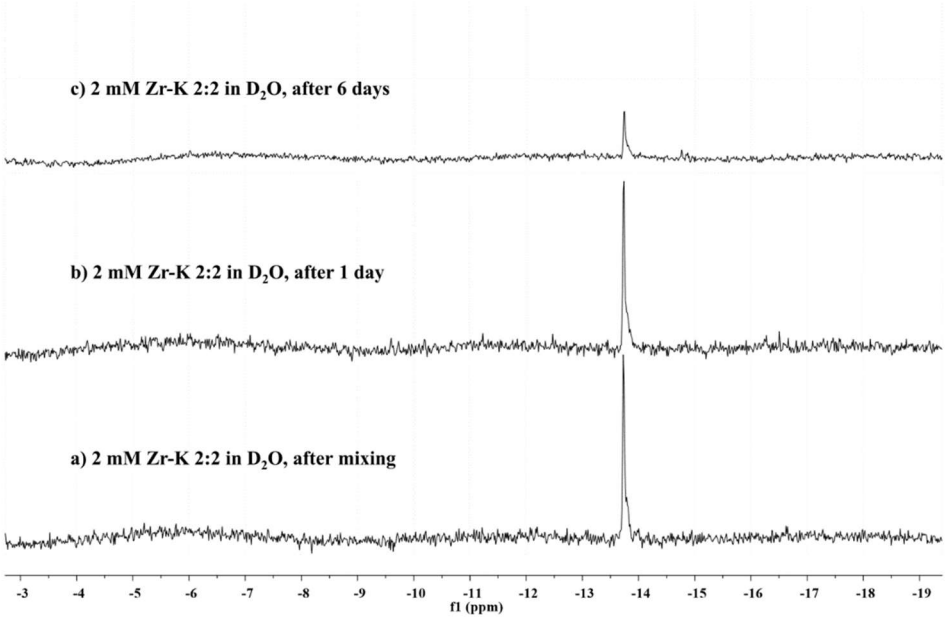

Figure S16. ^{31}P NMR of **Zr-K 2:2** (2 mM) incubated in D_2O at room temperature. The **Zr-K 2:2** structure (−14.78 and −14.83 ppm) remains largely stable over time.

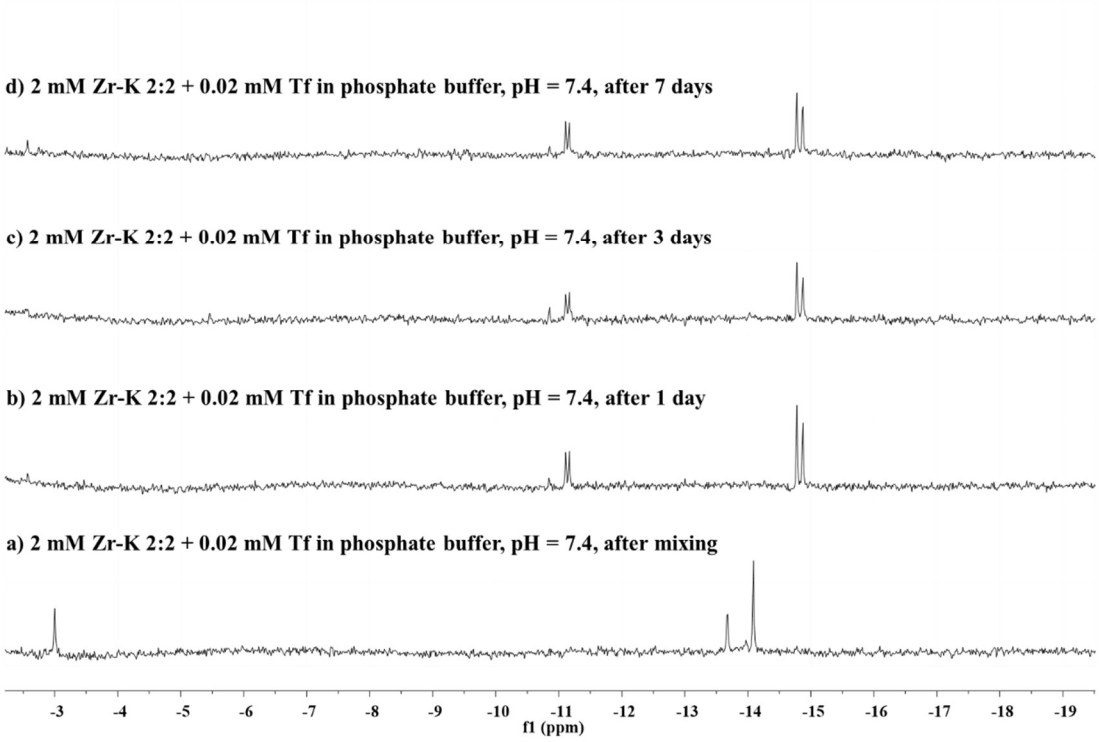

Figure S17. ^{31}P NMR of **Zr-K 2:2** (2 mM) incubated in phosphate buffer (10 mM, pH 7.4) at 60 °C in the presence of transferrin (20 μM). The peak corresponding to intact **Zr-K 2:2** appears at −13.69 ppm in buffer solution, this peak disappeared after 1 day of incubation. Simultaneously, 2 peaks corresponding to **Zr-K 1:2** appeared around −14.77 and 14.86 ppm. Additional peaks appeared around −14 ppm and one around −3 ppm immediately after mixing. In all conditions, **Zr-K 2:2** was quickly converted to **Zr-K 1-2** upon incubation. Other unknown peaks appeared around −11 ppm.

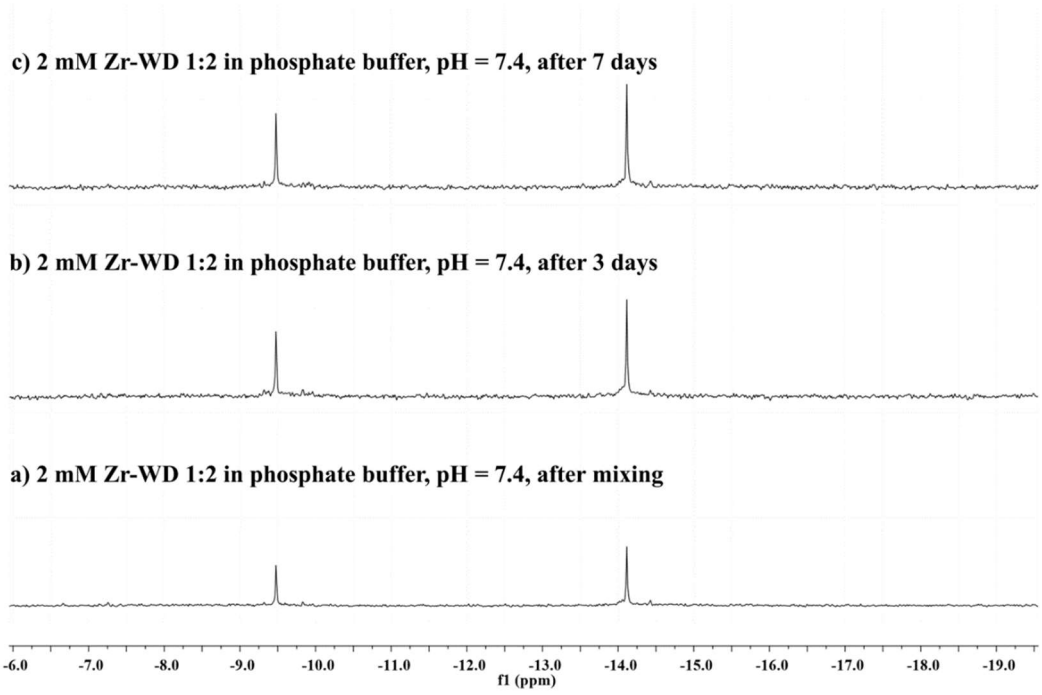

Figure S18. ^{31}P NMR of **Zr-WD 1:2** (2 mM) in phosphate buffer (10 mM, pH 7.4) at room temperature. The **Zr-WD 1:2** structure (−14.11 and −9.48 ppm) remains largely stable over time.

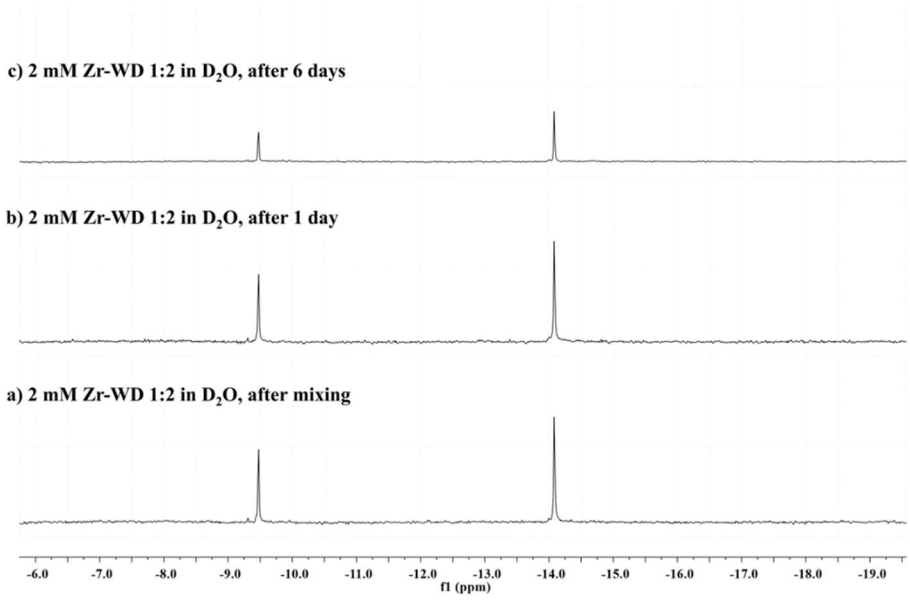

Figure S19. ^{31}P NMR of **Zr-WD 1:2** (2 mM) in D_2O at room temperature. The **Zr-WD 1:2** structure (−14.08 and −9.47 ppm) remains largely stable over time.

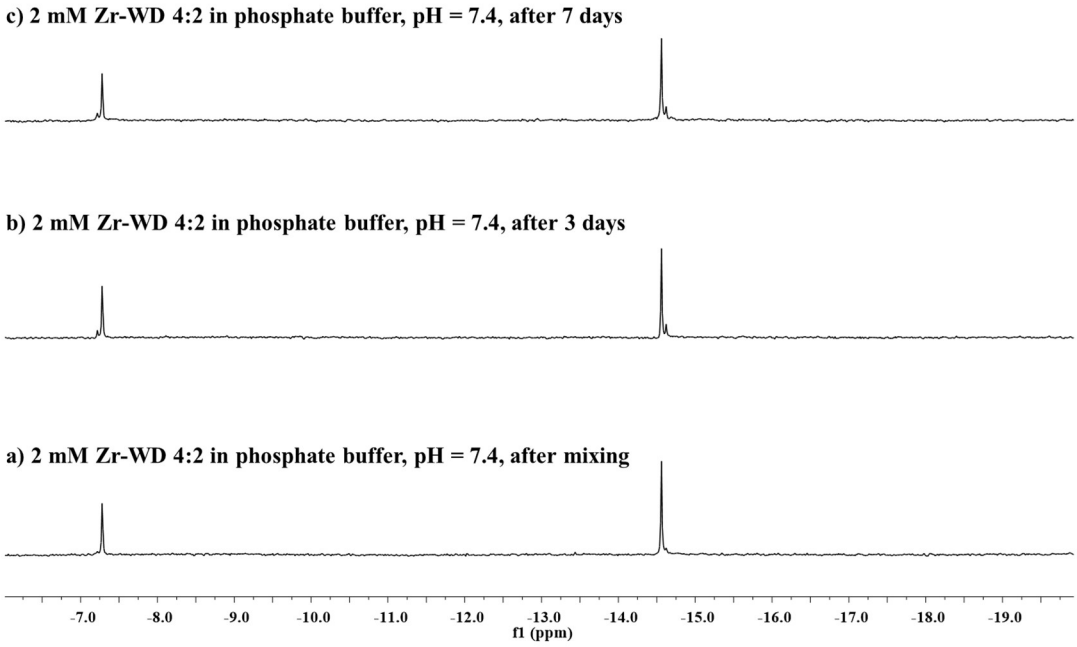

Figure S20. ^{31}P NMR of **Zr-WD 4:2** (2 mM) in phosphate buffer (10 mM, pH 7.4) at room temperature. The **Zr-WD 4:2** structure (−14.59 and −7.28 ppm) remains largely stable over time.

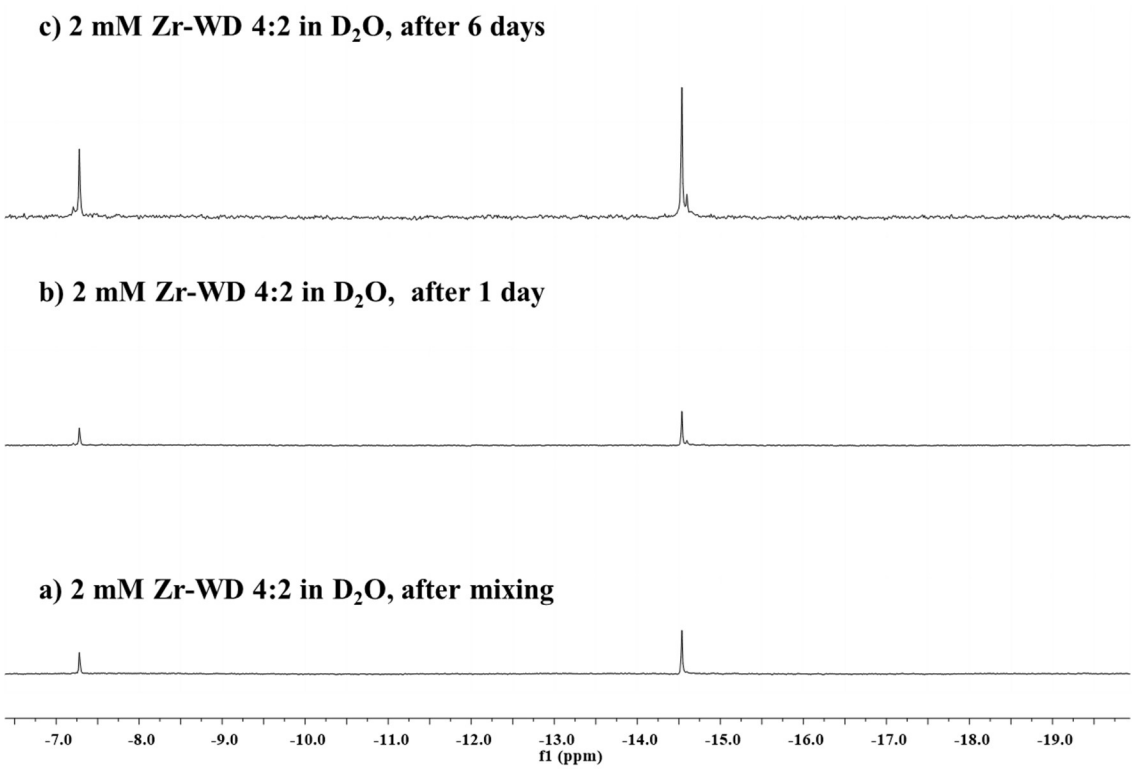

Figure S21. ^{31}P NMR of **Zr-WD 4:2** (2 mM) in D_2O at room temperature. The **Zr-WD 4:2** structure (−14.59 and −7.28 ppm) remains largely stable over time.

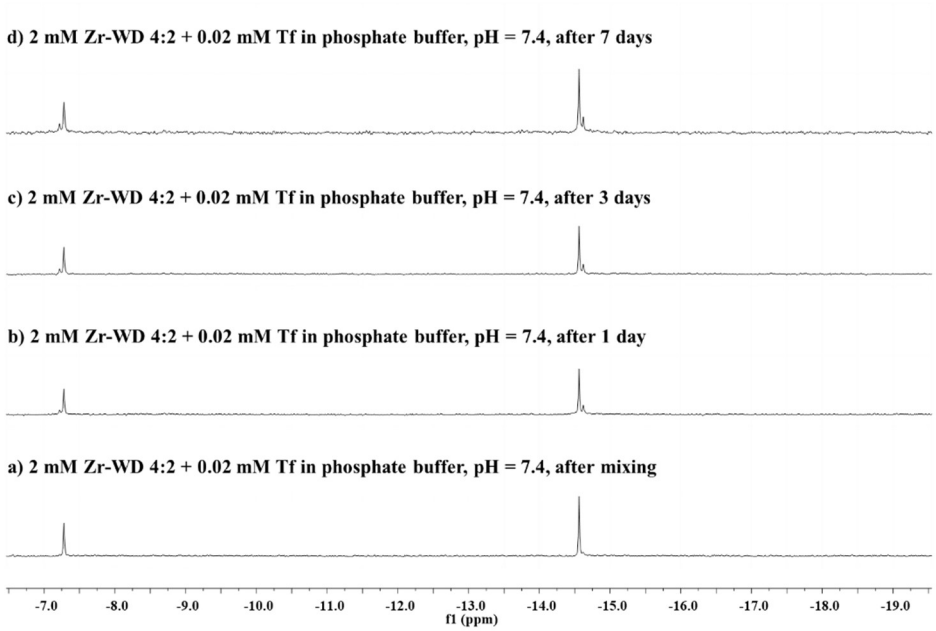

Figure S22. ^{31}P NMR of **Zr-WD 4:2** (2 mM) incubated in phosphate buffer (10 mM, pH 7.4) at 60 °C in the presence of transferrin (20 μM). The **Zr-WD 4:2** structure (−14.59 and −7.28 ppm) remains largely stable over time.

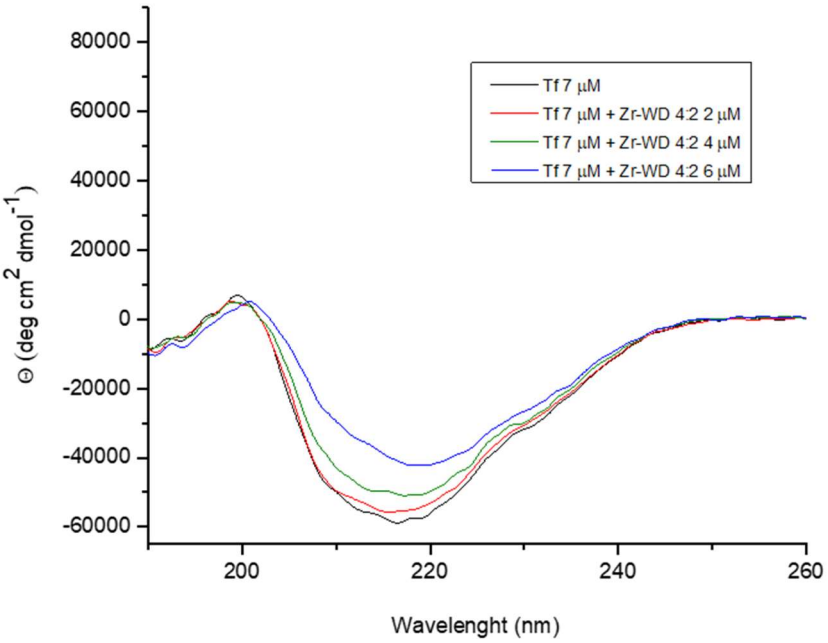

Figure S23. CD spectra of transferrin (7 μM) in phosphate buffer (10 mM, pH 7.4) with increasing concentrations (0–10 μM) of **Zr-WD 4:2**.

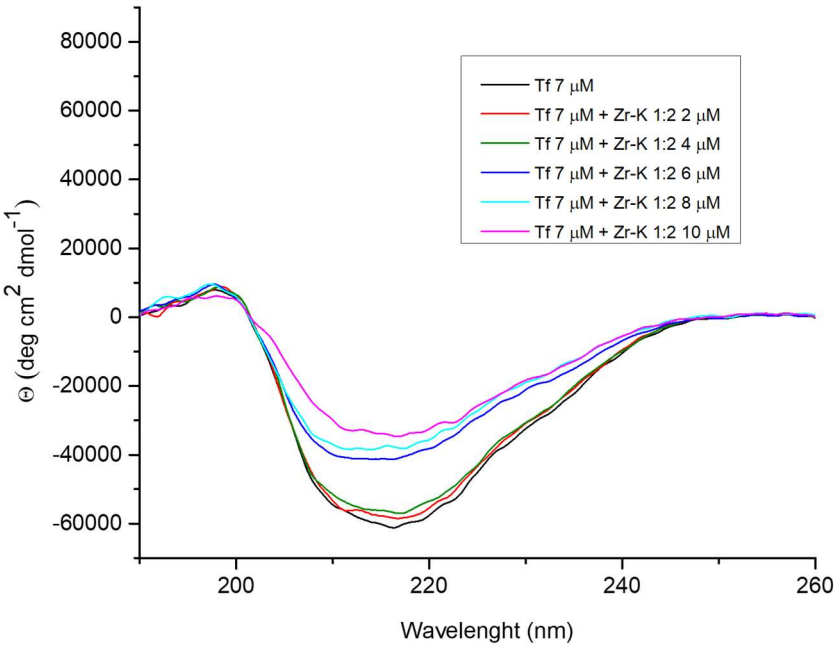

Figure S24. CD spectra of transferrin (7 μM) in phosphate buffer (10 mM, pH 7.4) with increasing concentrations (0–10 μM) of **Zr-K 1:2**.

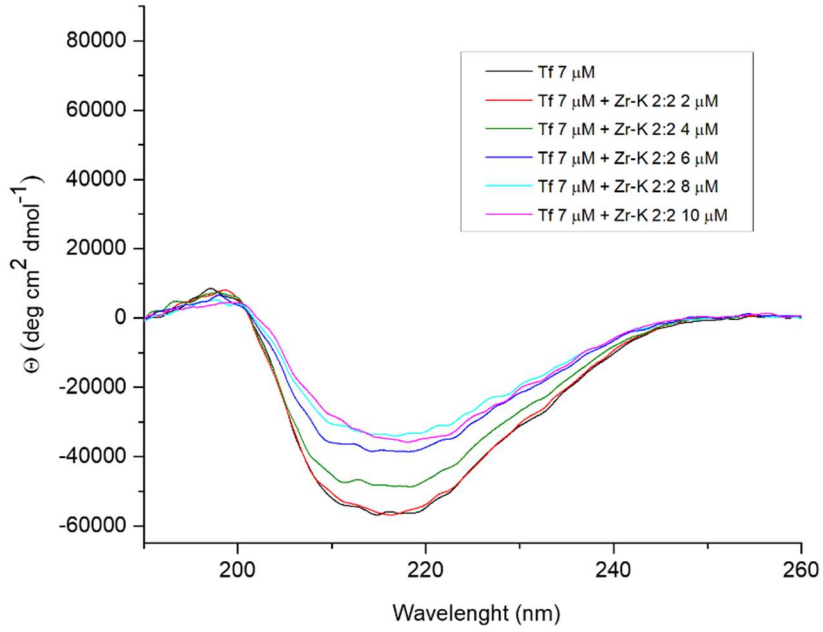

Figure S25. CD spectra of transferrin (7 μM) in phosphate buffer (10 mM, pH 7.4) with increasing concentrations (0–10 μM) of **Zr-K 2:2**.

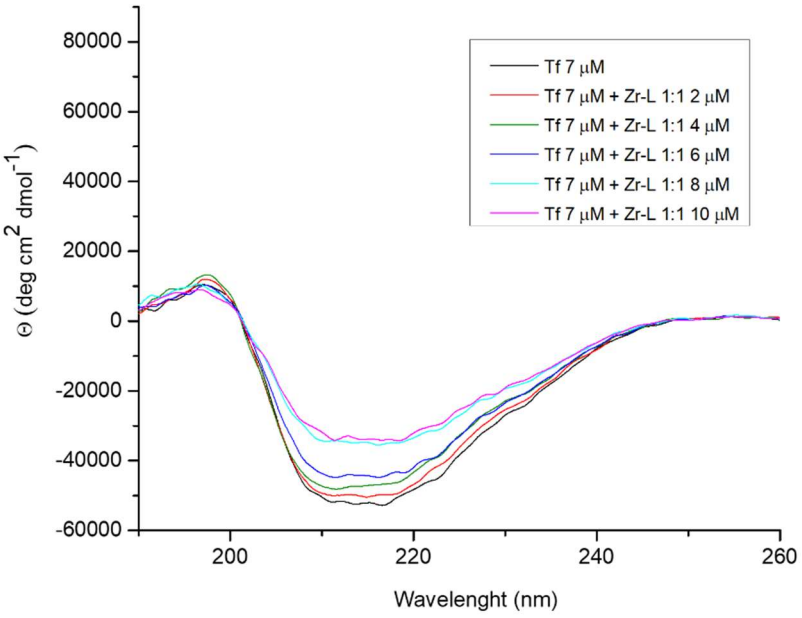

Figure S26. CD spectra of transferrin (7 μM) in phosphate buffer (10 mM, pH 7.4) with increasing concentrations (0–10 μM) of **Zr-L 1:1**.

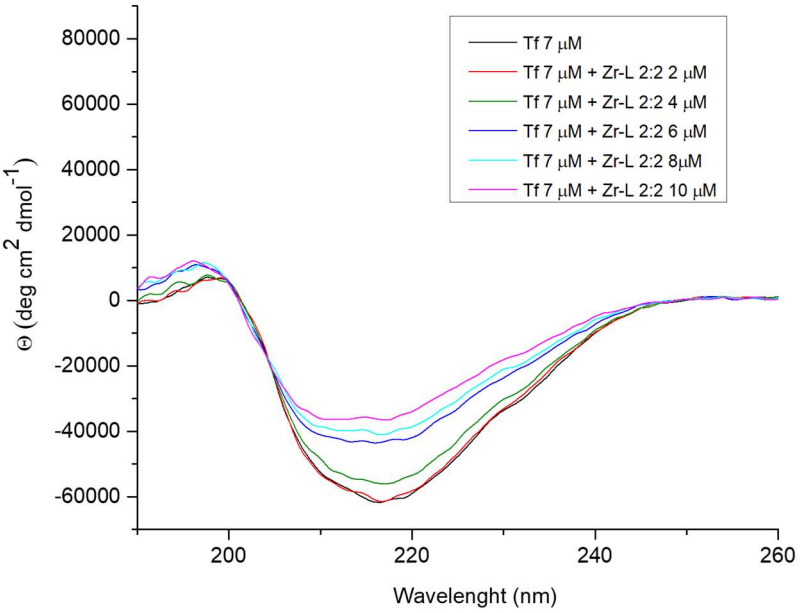

Figure S27. CD spectra of transferrin (7 μM) in phosphate buffer (10 mM, pH 7.4) with increasing concentrations (0–10 μM) of **Zr-L 2:2**.