Supplementary Information

Structure, Equilibrium and Ligand Exchange Dynamics in the Binary and Ternary Dioxouranium(VI)-Glyphosate-Fluoride System. A Multinuclear NMR study.

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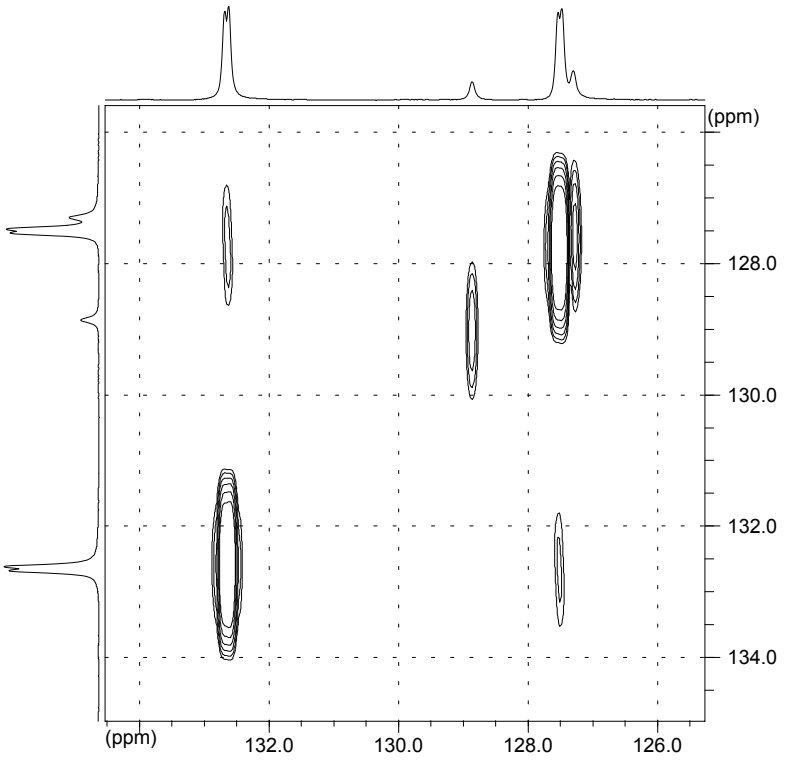


Figure S1 ^{19}F-^{19}F homonuclear correlation (COSY) spectrum for complex **1** in the ternary uranium(VI)-glyphosate-fluoride system measured at –5 °C using $[UO_2^{2+}]_{tot}$= 50 mM, $[PMG]_{tot}$= 100 mM and $[F^-]_{tot}$= 500 mM at pH=9.5.

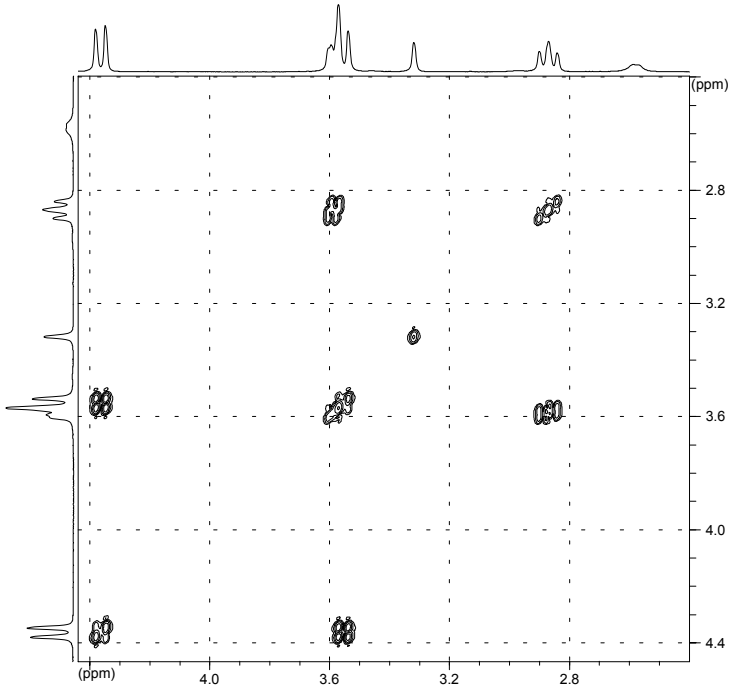


Figure S2 ^{1}H-^{1}H homonuclear correlation (COSY-45) spectrum for complex **1** in the ternary uranium(VI)-glyphosate-fluoride system measured at –5 °C using $[UO_2^{2+}]_{tot}$= 20 mM, $[PMG]_{tot}$= 20 mM and $[F^-]_{tot}$= 800 mM at pH=8.8.

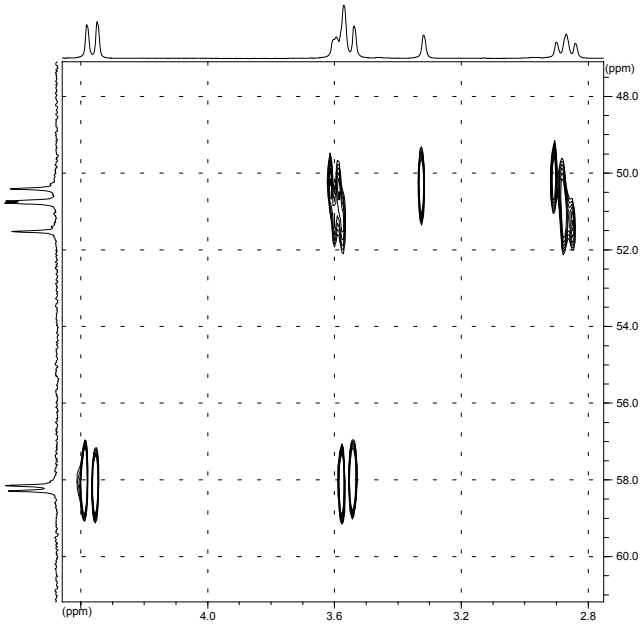


Figure S3 ^{1}H-^{13}C heteronuclear correlation spectrum for complex **1** in the ternary uranium(VI)-glyphosate-fluoride system measured at –5 °C using $[UO_2^{2+}]_{tot}$= 20 mM, $[PMG]_{tot}$= 20 mM and $[F^-]_{tot}$= 800 mM at pH=8.8.

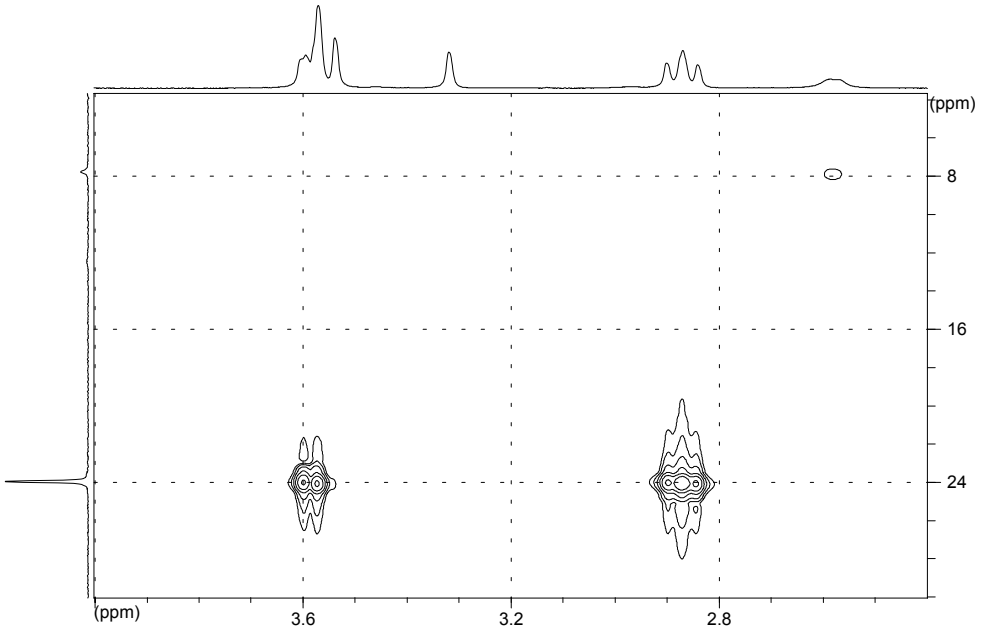


Figure S4 ^{1}H-^{31}P heteronuclear correlation spectrum for complex **1** in the ternary uranium(VI)-glyphosate-fluoride system measured at –5 °C using $[UO_2^{2+}]_{tot}$= 20 mM, $[PMG]_{tot}$= 20 mM and $[F^-]_{tot}$= 800 mM at pH=8.8.

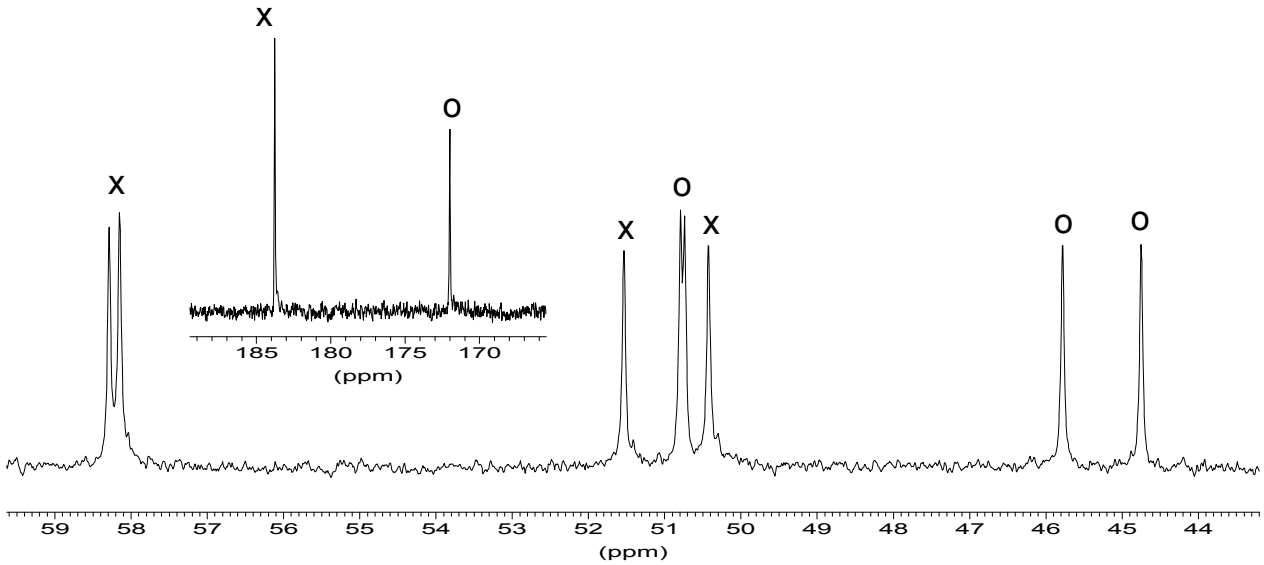


Figure S5 Proton decoupled ^{13}C-NMR spectrum in the ternary uranium(VI)-glyphosate-fluoride system measured at –5 °C using $[UO_2^{2+}]_{tot}$= 20 mM, $[PMG]_{tot}$= 35 mM and $[F^-]_{tot}$= 800 mM at pH=9.5. x: signals for the chelated glyphosate in complex **1**, o: signals for the free glyphosate. The inset shows the carbonyl carbons.

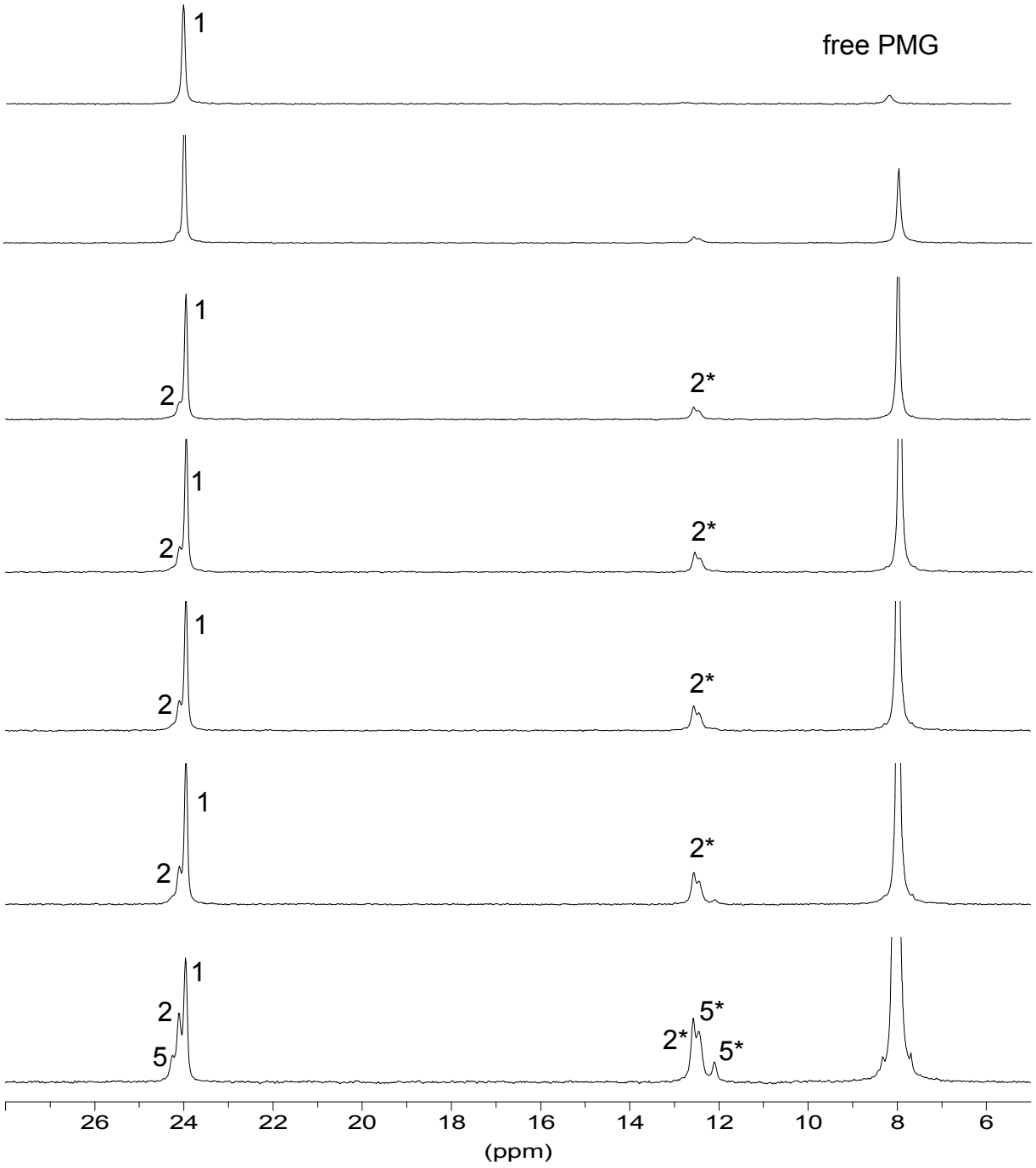


Figure S6 Proton decoupled ^{31}P-NMR spectra for the ternary uranium(VI)-glyphosate-fluoride system as a function of the total glyphosate concentration measured at –5 °C using $[UO_2^{2+}]_{tot}$=20 mM and $[F^-]_{tot}$=800 mM at pH=8.8. The total glyphosate concentrations from top to bottom: 20.2, 38.4, 54.7, 69.5, 82.7, 94.6 and 202 mM. Star indicates the peaks from the non-chelated glyphosates in complexes **2** and **5**.

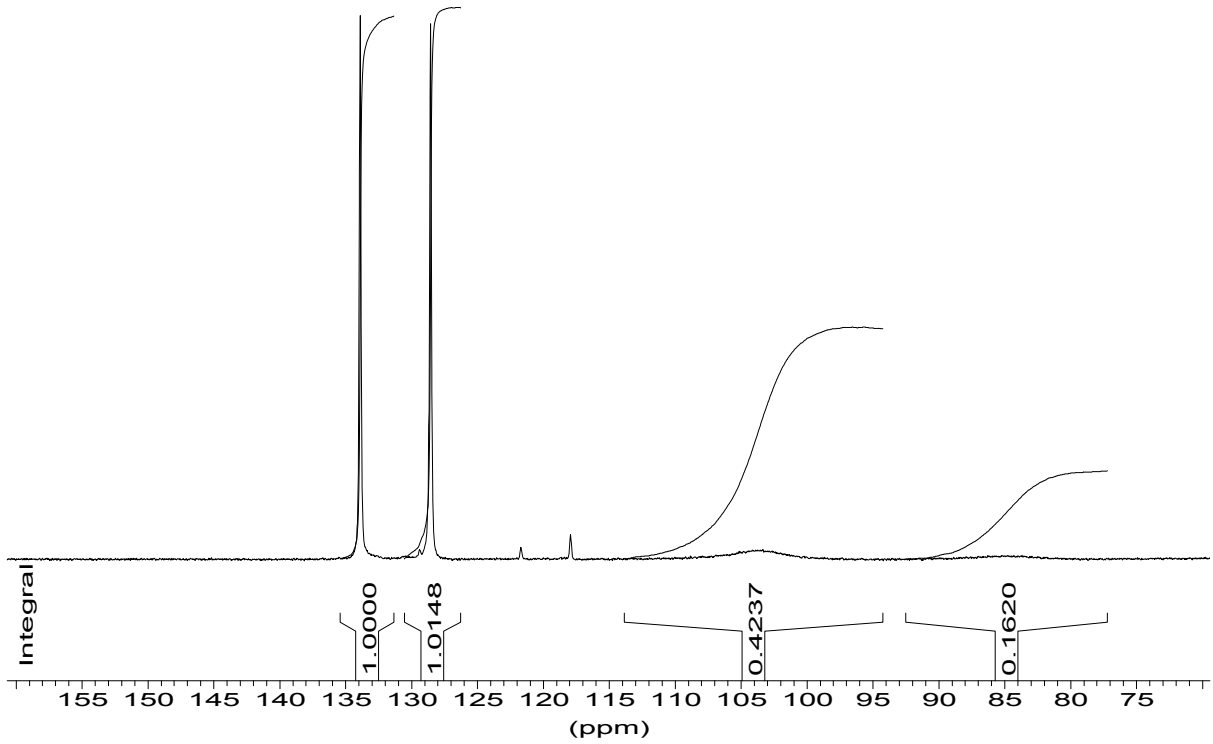


Figure S7 ^{19}F-NMR spectrum in the ternary uranium(VI)-glyphosate-fluoride system showing two coupled signals for complex **1** (134 and 128.5 ppm), and signals for the binary complexes $UO_2F_4^{2-}$ (~105 ppm) and $UO_2F_5^{3-}$ (~85 ppm). The spectrum was recorded at –5 °C using $[UO_2^{2+}]_{tot}$= 20 mM, $[PMG]_{tot}$= 20.2 mM and $[F^-]_{tot}$= 800 mM at pH=8.8

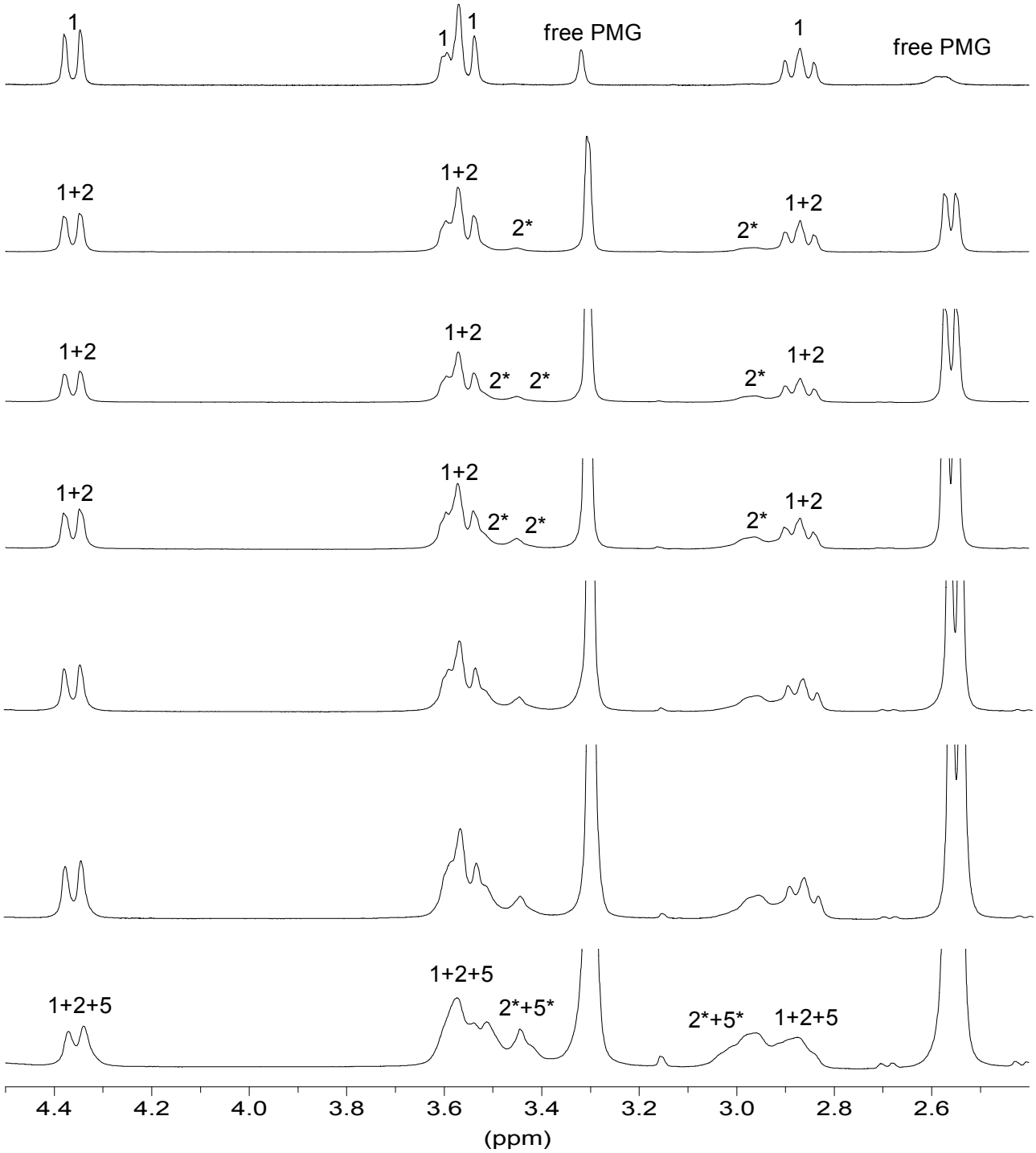


Figure S8 ^{1}H-NMR spectra for the ternary uranium(VI)-glyphosate-fluoride system as a function of the total glyphosate concentration measured at –5 °C using $[UO_2^{2+}]_{tot}$=20 mM and $[F^-]_{tot}$=800 mM at pH=8.8. The total glyphosate concentrations are from top to bottom: 20.2, 38.4, 54.7, 69.5, 82.7, 94.6 and 202 mM. Star indicates the peaks for the non-chelated glyphosates in complexes **2** and **5**.

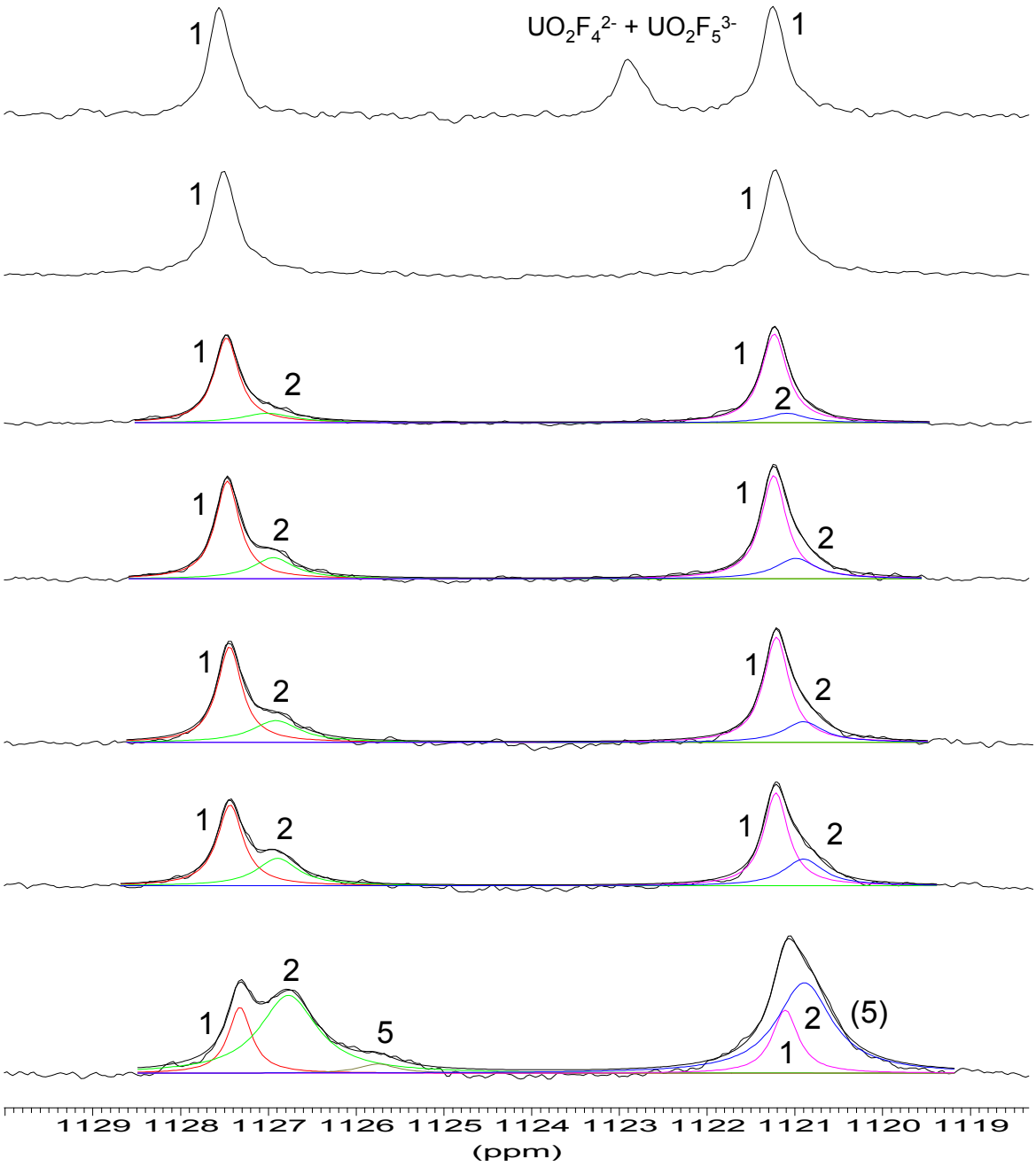
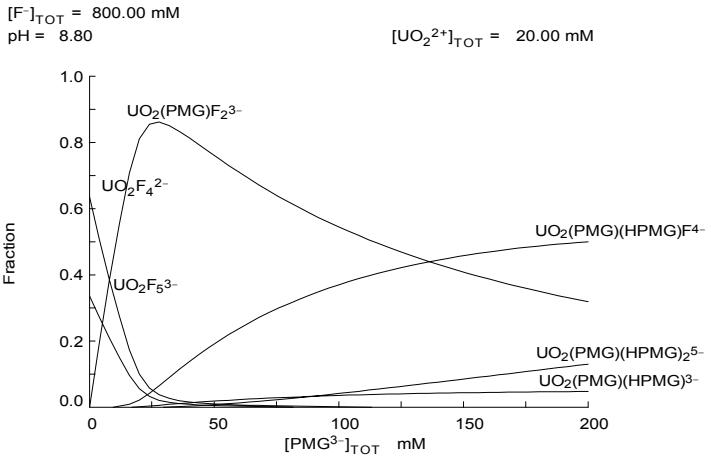
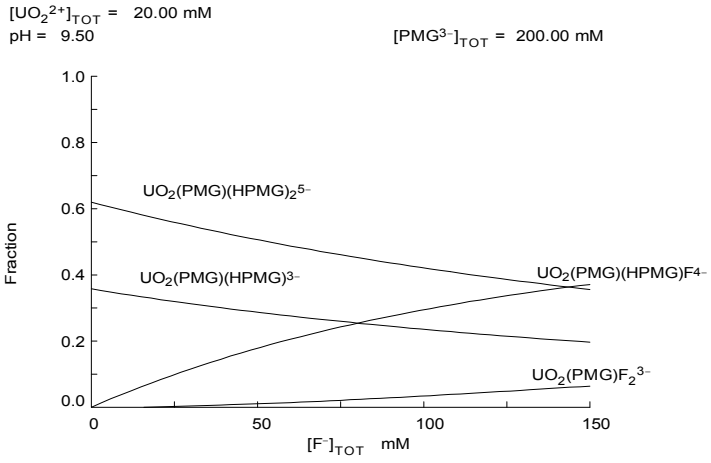


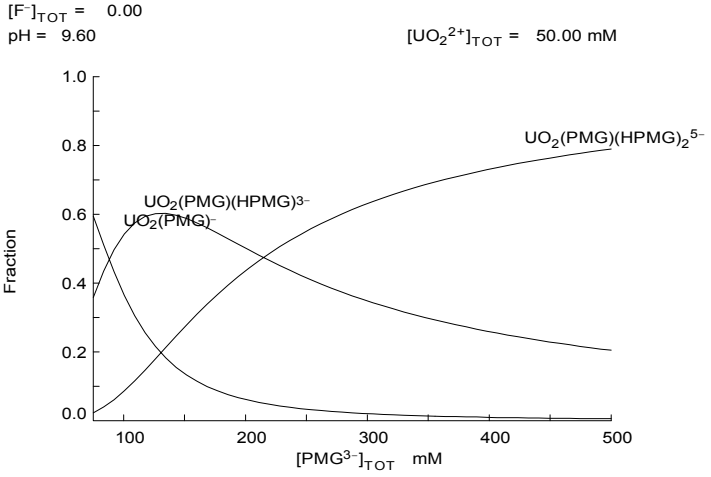
Figure S9 ^{17}O-NMR spectra for the ternary uranium(VI)-glyphosate-fluoride system as a function of the total glyphosate concentration measured at –5 °C using $[UO_2^{2+}]_{tot}$=20 mM and $[F^-]_{tot}$=800 mM at pH=8.8. The total glyphosate concentrations are from top to bottom: 20.2, 38.4, 54.7, 69.5, 82.7, 94.6 and 202 mM. The peak at 1123 ppm is from the binary fluoride complexes, $UO_2F_4^{2-}$ and $UO_2F_5^{3-}$ present in the solution. The deconvoluted peaks are for complexes **1** (1121.3 and 1127.4 ppm) and **2** (1120.8 and 1126.8). Only one of the peaks can be resolved for complex **5** at 1125.7 ppm.



a.)



b.)



c.)

Figure S10 Equilibrium distribution diagrams for the ternary uranium(VI)-glyphosate-fluoride system as a function of the total glyphosate concentration at pH=8.8, $[UO_2^{2+}]_{tot}$=20 mM, $[F^-]_{tot}$=800 mM (a), and as a function of the total fluoride concentration at pH=9.5, $[UO_2^{2+}]_{tot}$=20 mM and $[PMG]_{tot}$=200 mM (b). Distribution diagram for the binary uranium(VI)-glyphosate system as a function of the total glyphosate concentration using$[UO_2^{2+}]_{tot}$=50 mM at pH=9.6 (c). PMG: $OOC\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}PO_3^{3-}$

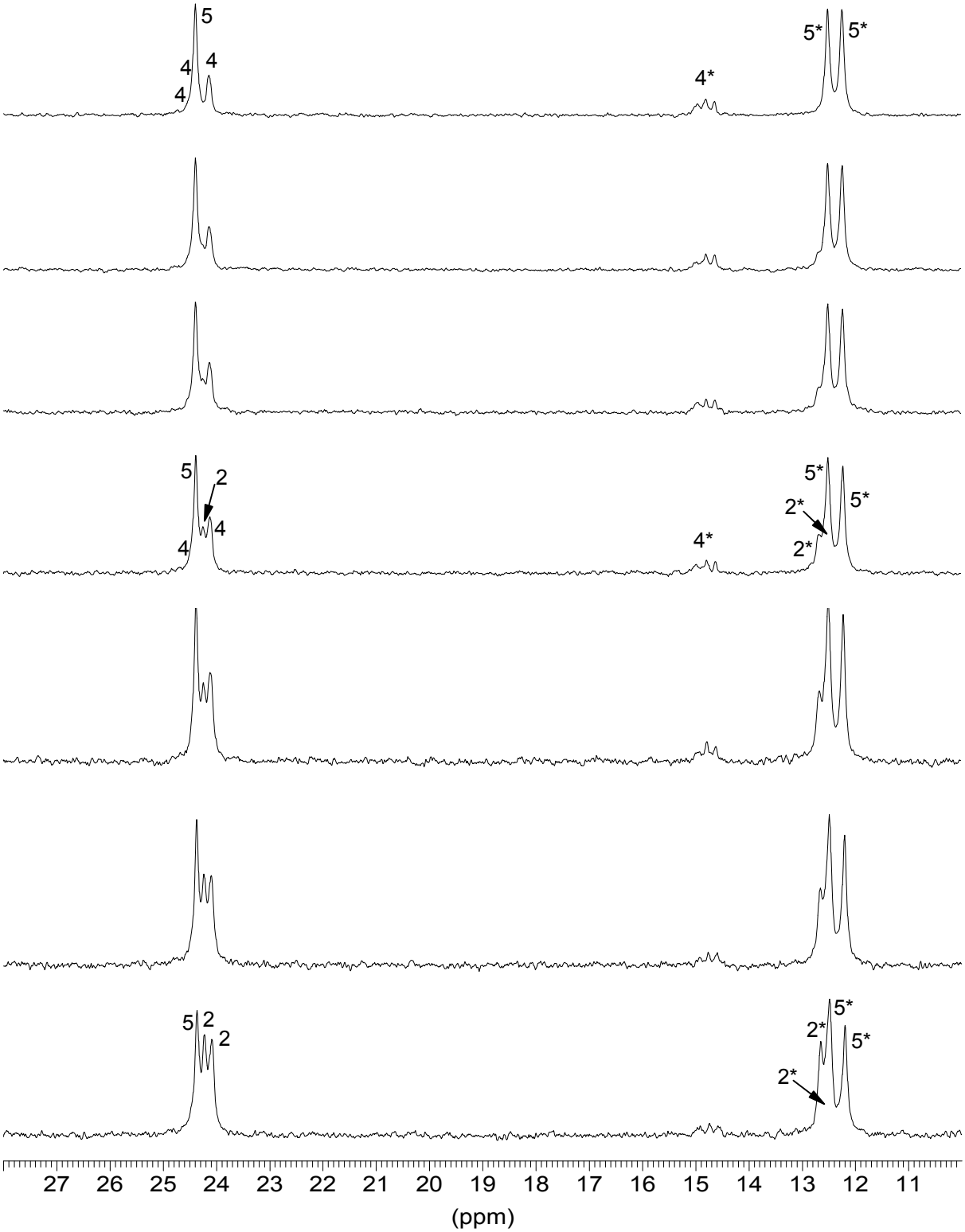
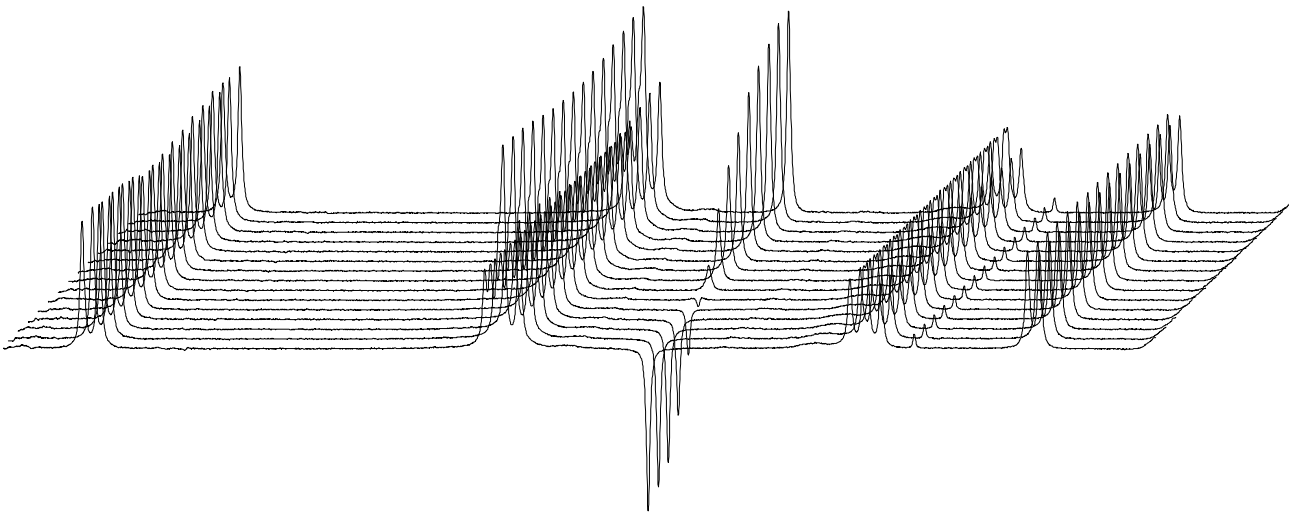
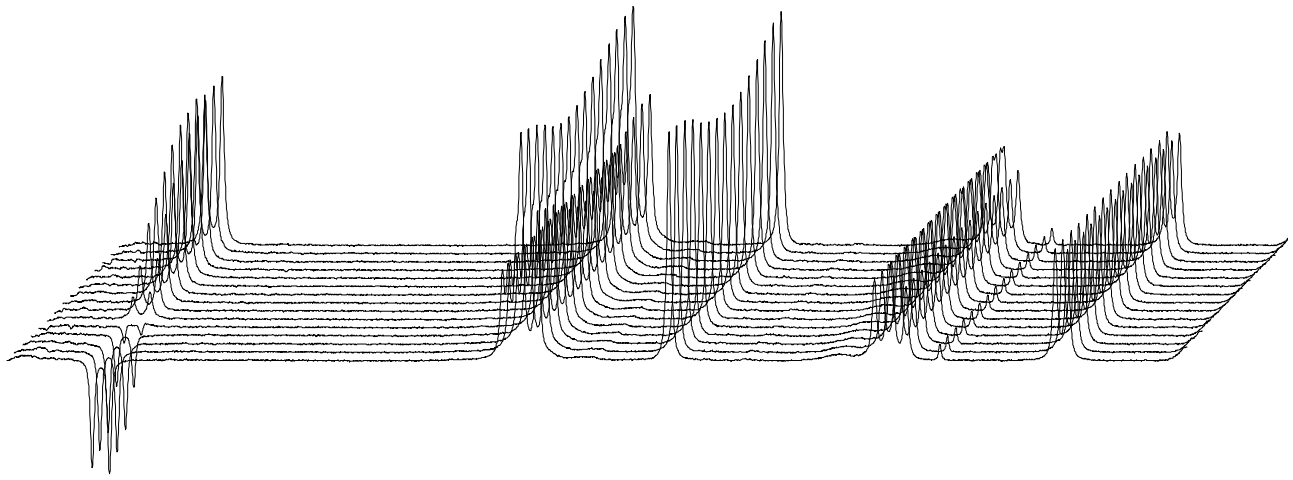


Figure S11 Proton decoupled ^{31}P-NMR spectra for the ternary uranium(VI)-glyphosate-fluoride system as a function of the total fluoride concentration measured at –5 °C using $[UO_2^{2+}]_{tot}$=20 mM and $[PMG]_{tot}$=200 mM at pH=9.5. The total fluoride concentrations are from top to bottom: 0, 8.4, 17.0, 34.7, 52.6, 88.9, 123.9 157.5. Star indicates the peaks for the non-chelated glyphosates in complexes **2**, **4** and **5**.

Figure S12 Proton decoupled ^{31}P-NMR spectra for the binary uranium(VI)-glyphosate system as a function of the total glyphosate concentration measured at –5 °C, using $[UO_2^{2+}]_{tot}$=50 mM at pH=9.6. The total glyphosate concentrations are from top to bottom: 75.0, 97.3, 123.8 157.6, 196, 257.5 and 500 mM. Star indicates the peaks for the non-chelated glyphosates in complexes **4** and **5**.



a.)



b.)

Figure S13 ^{1}H-NMR inversion transfer experiments to study the exchange between the free and coordinated glyphosate in complex **1**. The spectra were recorded at –5 °C with increasing delays after selective inversion of the CH_2 protons (at 3.3 ppm) in the free (a), and one of the CH_2 protons (at 4.4 ppm) in the coordinated glyphosate.