SUPPORTING INFORMATION

Structures and thermodynamics of dinuclear species forming in the uranyl(VI)–malic acid system: a multi-technique approach

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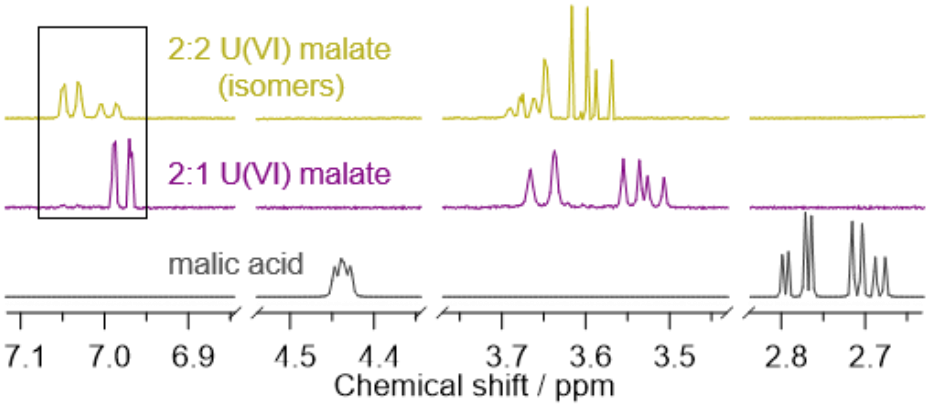

Figure S1. Single-component ^{1}H NMR spectra of the malate species relevant in this study: free malic acid at pD 3.0 (bottom), uranyl(VI) malate 2:1 complex (middle), as well as the uranyl(VI) malate 2:2 complex occurring as two isomeric forms (top).

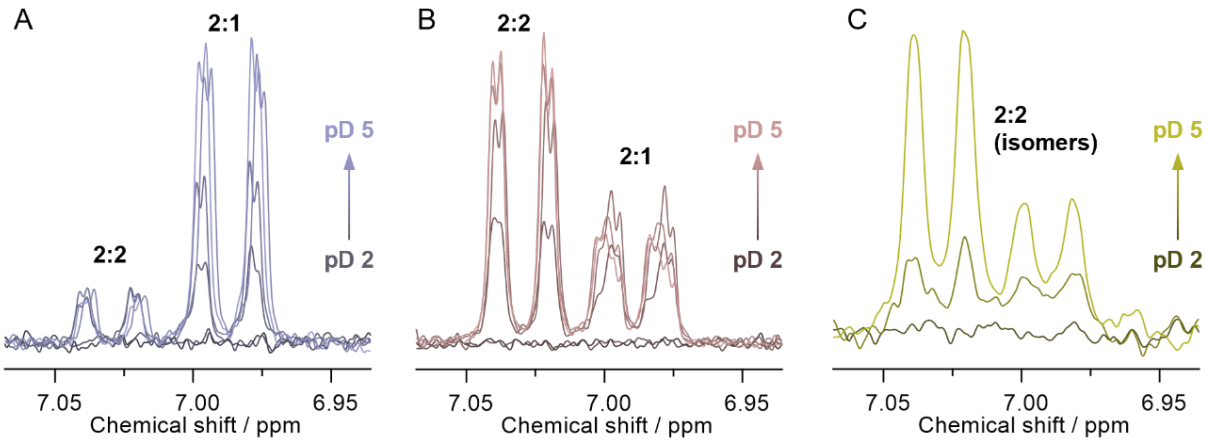

Figure S2. Representative ^{1}H NMR pD-titration spectra obtained at different given uranyl(VI) to malate ratios: (A) 100 µM U(VI) and 50 µM malate; (B) 100 µM each in U(VI) and malate; (C) 10 µM U(VI) and 100 µM malate.

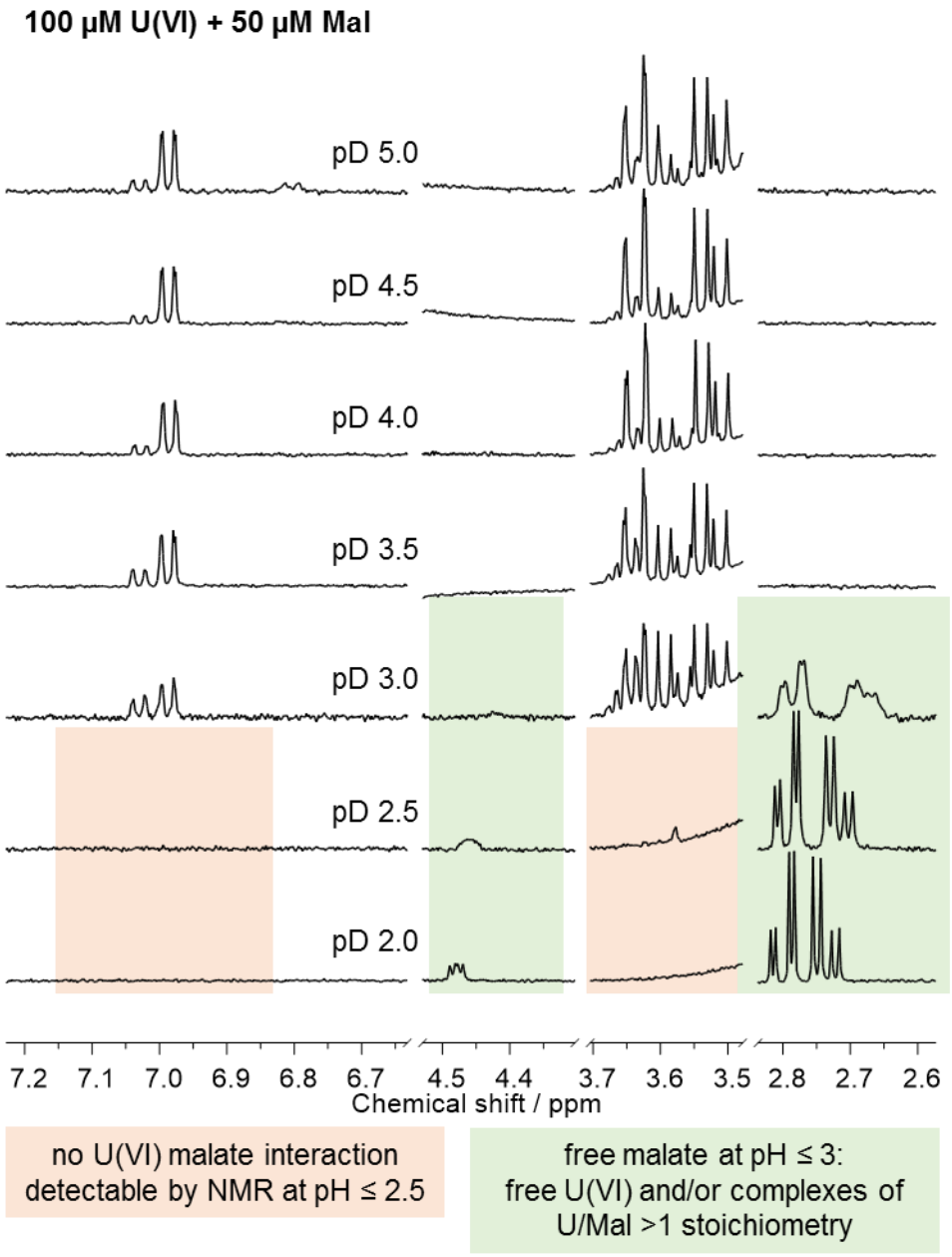

Figure S3. ^{1}H NMR spectra showing signal regions of interest for solutions 100 µM in uranyl(VI) and 50 µM in malic acid, in the pD range 2.0 – 5.0.

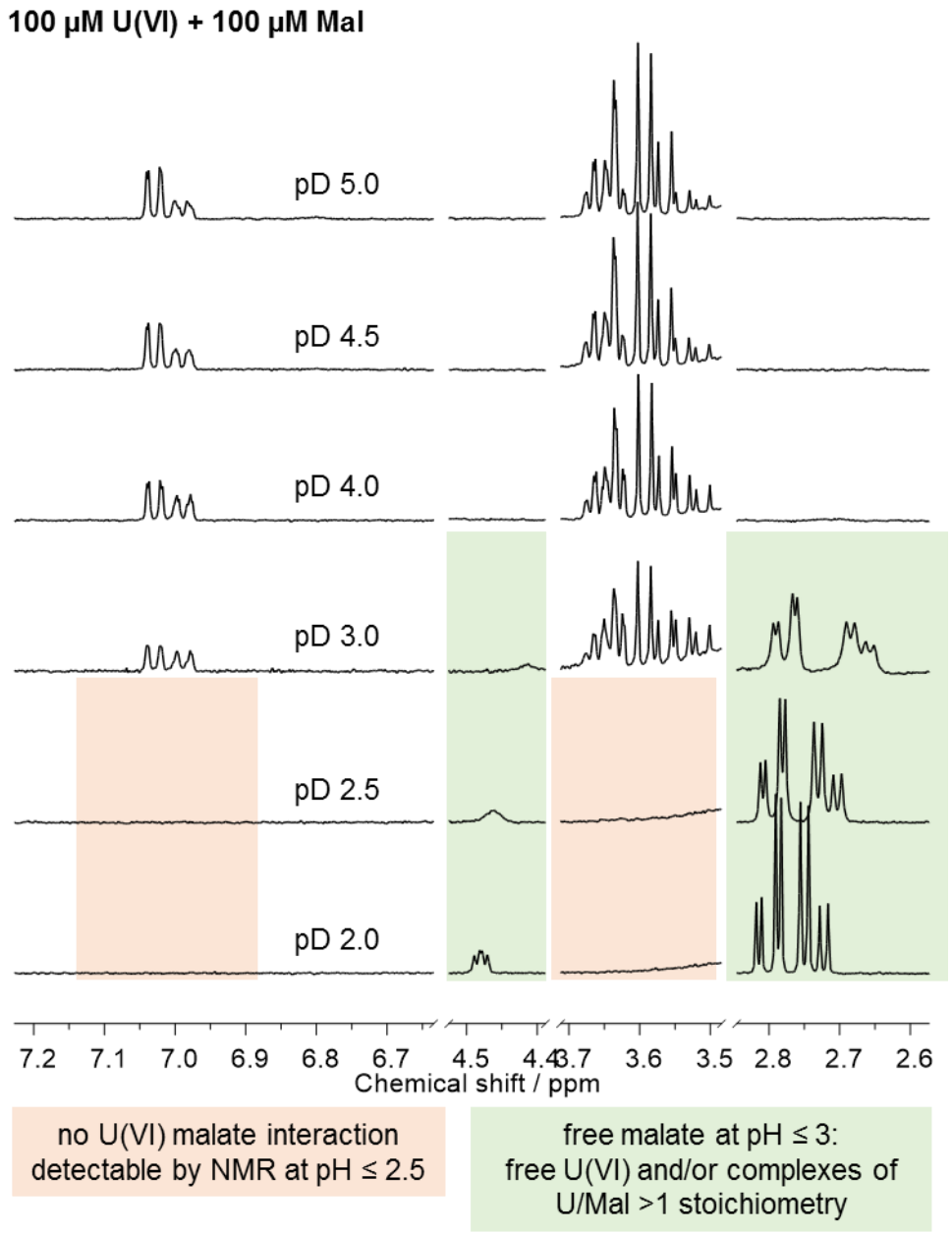

Figure S4. ^{1}H NMR spectra showing signal regions of interest for solutions 100 µM in each uranyl(VI) and malic acid, in the pD range 2.0 – 5.0.

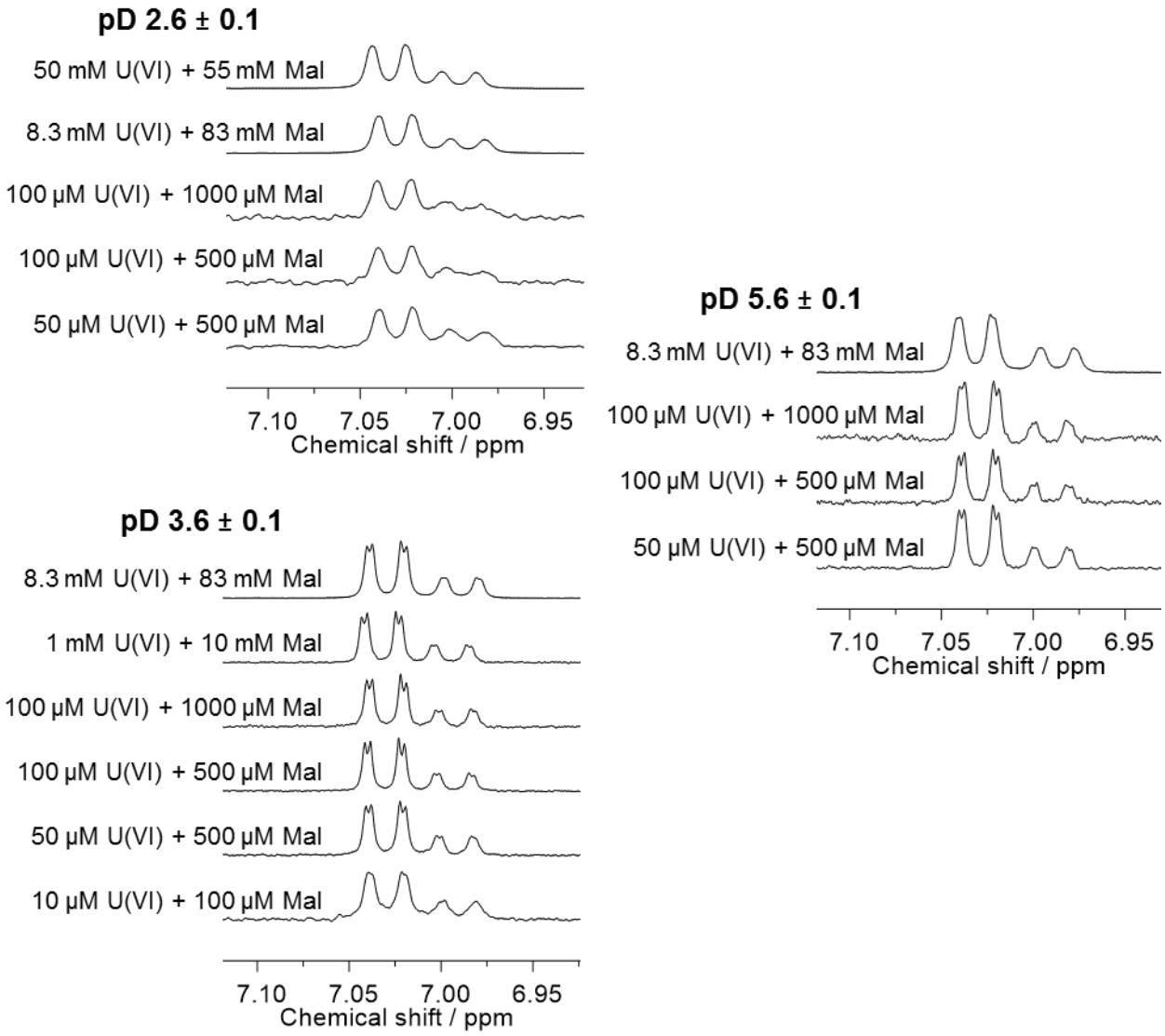

Figure S5. ^{1}H NMR spectra showing the representative CH signal region associated with uranyl(VI) malate complexes obtained at different pD values and concentrations covering the micromolar and millimolar range.

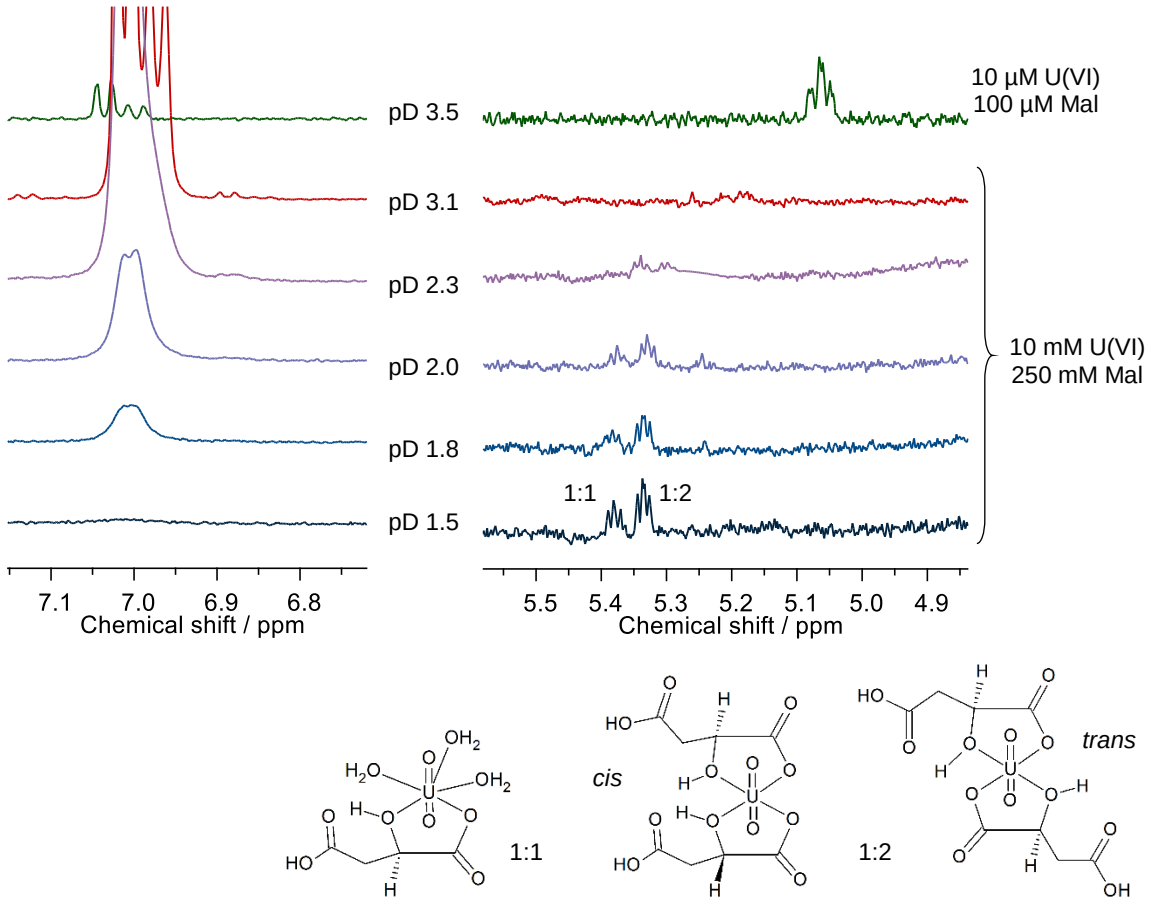

Figure S6. ^{1}H NMR spectra showing the CH (2-H) region associated with dinuclear complexes (left) and mononuclear complexes (right), obtained from D_2O ligand excess solutions with U(VI) in the millimolar range under very acidic conditions as well as with U(VI) in the micromolar range at somewhat less acidic conditions. In millimolar solutions, upon successively increasing pD, the signals of the mononuclear complexes – already very weak in intensity – decrease and practically disappear. Note that under such acidic conditions most of the U(VI) is unbound. Therefore, along the pD series, the fraction of the 2:2 complex species increases notably stronger in contrast to the displacement of the mononuclear species. Additionally, the signals shift upfield upon increasing pD owing to successive deprotonation of the unbound CH_2COOH residue, particularly clear for the very diluted and least acidic solution. In the latter, we assume that only one of the two mononuclear species is present. Assignment of the CH (2-H) signals to the 1:1 and 1:2 complexes is tentative, and is based on pure electrostatic reasons. That is, the uranyl ion's +2 charge is somewhat more shielded (compensated) upon coordination by the two $HMal^-$ ligands in the 1:2 complex than is the case in the 1:1 complex bearing one ligand only. Furthermore, formation of two isomers of the 1:2 complexes is conceivable, i.e., the two malate ligands can be *cis* or *trans* oriented to one another. In this context, we also performed some supplementary DFT calculations on these 1:2 complex isomers. Accordingly, the energy difference is only 2.4 kJ/mol, slightly favoring the *cis* conformation. Taking into account the accuracy of calculations at this level of theory, both isomers are as likely to occur.

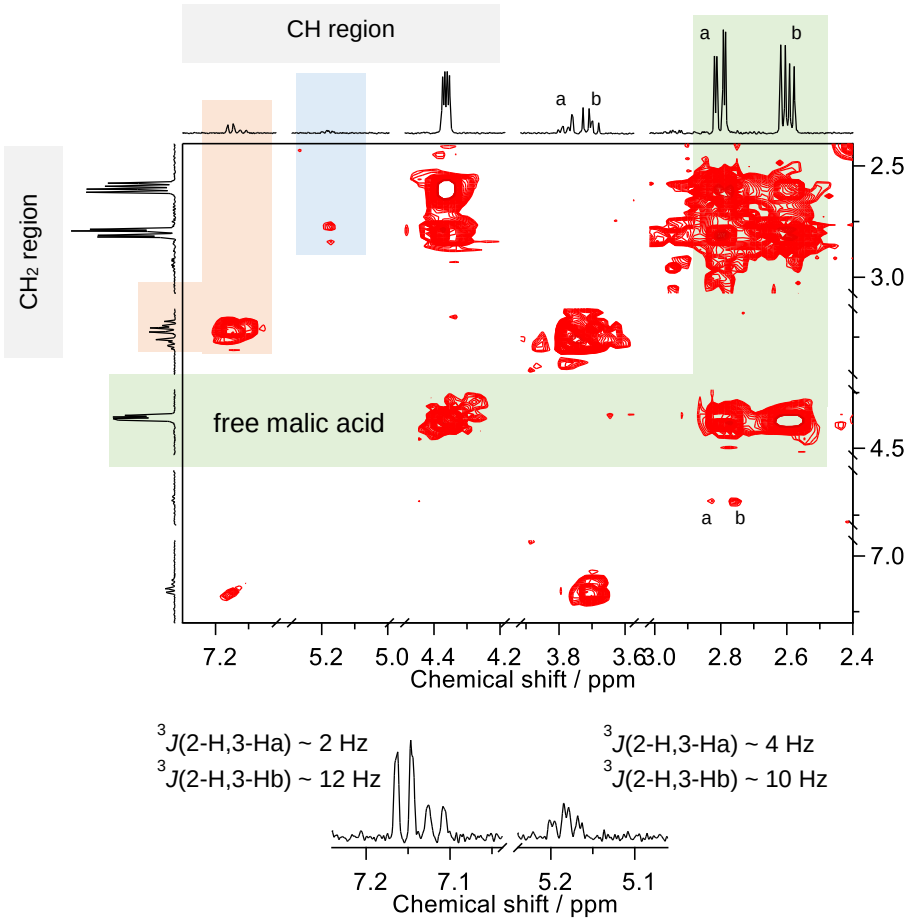

Figure S7. $^{1}H,^{1}H$-COSY NMR spectrum of the D_2O pD 3.5 solution 10 µM in U(VI) and 100 µM in malic acid (cf. Figure S6, top spectrum), acquired upon accumulating 1024 (!) transitions per F1 increment. The correlations between the CH and the CH_2 hydrogens (corresponding to 2-H and 3-H(a/b), respectively) are highlighted. The insert depicts the CH signals to scale along with the vicinal coupling constants. Although the sample is of micromolar solution, the dinuclear 2:2 complex species are clearly present. Within the limits of NMR detectability (the ^{1}H NMR spectrum was obtained upon accumulation of over 14k (!) scans), dinuclear and mononuclear species are present in similar quantities.

Three major spectral features support the assignment to mononuclear species:

a) The CH signal of the mononuclear species is not so drastically shifted as for the 2:2 complexes (δ_H 5.18 *vs.* 7.15/7.12 ppm compared to 4.36 ppm in free malic acid).

b) CH_2 signals of the observed mononuclear complex reveal only very small shifts compared to corresponding signals in free malic acid: δ_H, Ha 2.83 *vs.* 2.80 and Hb 2.75 *vs*. 2.59 ppm for mononuclear species *vs*. free malic acid, respectively. In all the complexes, owing to the larger coupling constant, the correlation between 2-H and 3-Hb is better detectable than that involving 3-Ha which reveals the smaller coupling.

c) The coupling constants (and their differences) between CH and the two neighboring methylene group's hydrogen atoms are significantly different: when the CH_2COO residue is fixed in a six-membered ring in the 2:2 complex species, the respective coupling constants are 2 and 12 Hz, whereas in the mononuclear species where the unbound $CH_2COO(H)$ residue is more flexible and its hydrogen atoms possess less distinct environments, these values amount to 4 and 10 Hz (4.1 and 8.4 Hz in free malic acid).

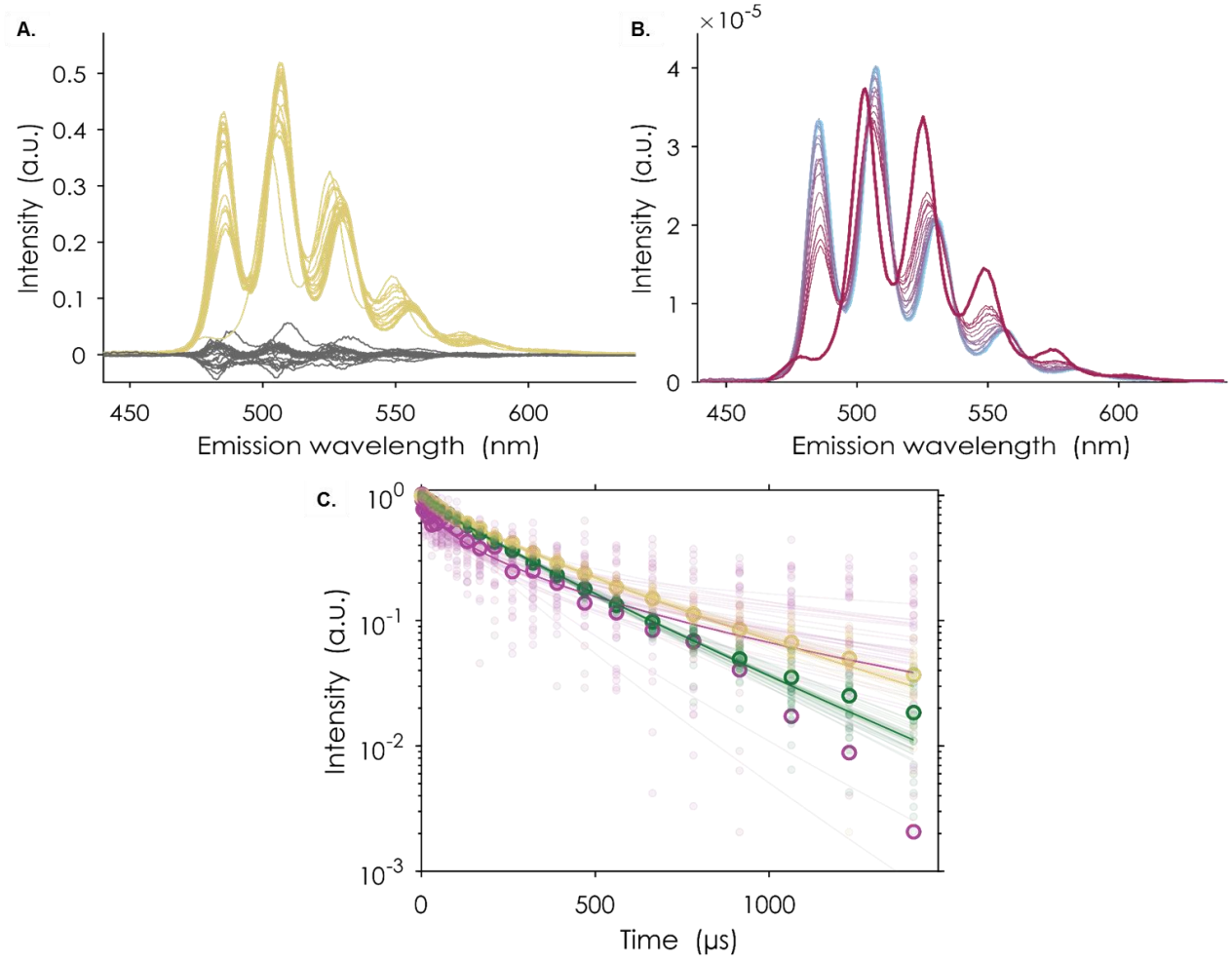

Figure S8. PARAFAC results of the three independent TRLFS series of uranyl(VI) complexation at different malate concentrations. [U(VI)] = 50 µM, [malate] = 0–100 mM, [$NaClO_4$] = 0.1 M, pH = 4. Raw data of the TRLFS series (A), normalized emission spectra at t = 0 µs (B), and luminescence decays of the U(VI) species (C) with green for the uranyl(VI) aquo ion, magenta for the 2:1 uranyl(VI) malate complex, and yellow for the 2:2 uranyl(VI) malate complex, and luminescence decay times of 257, 130, and 320 µs, respectively.

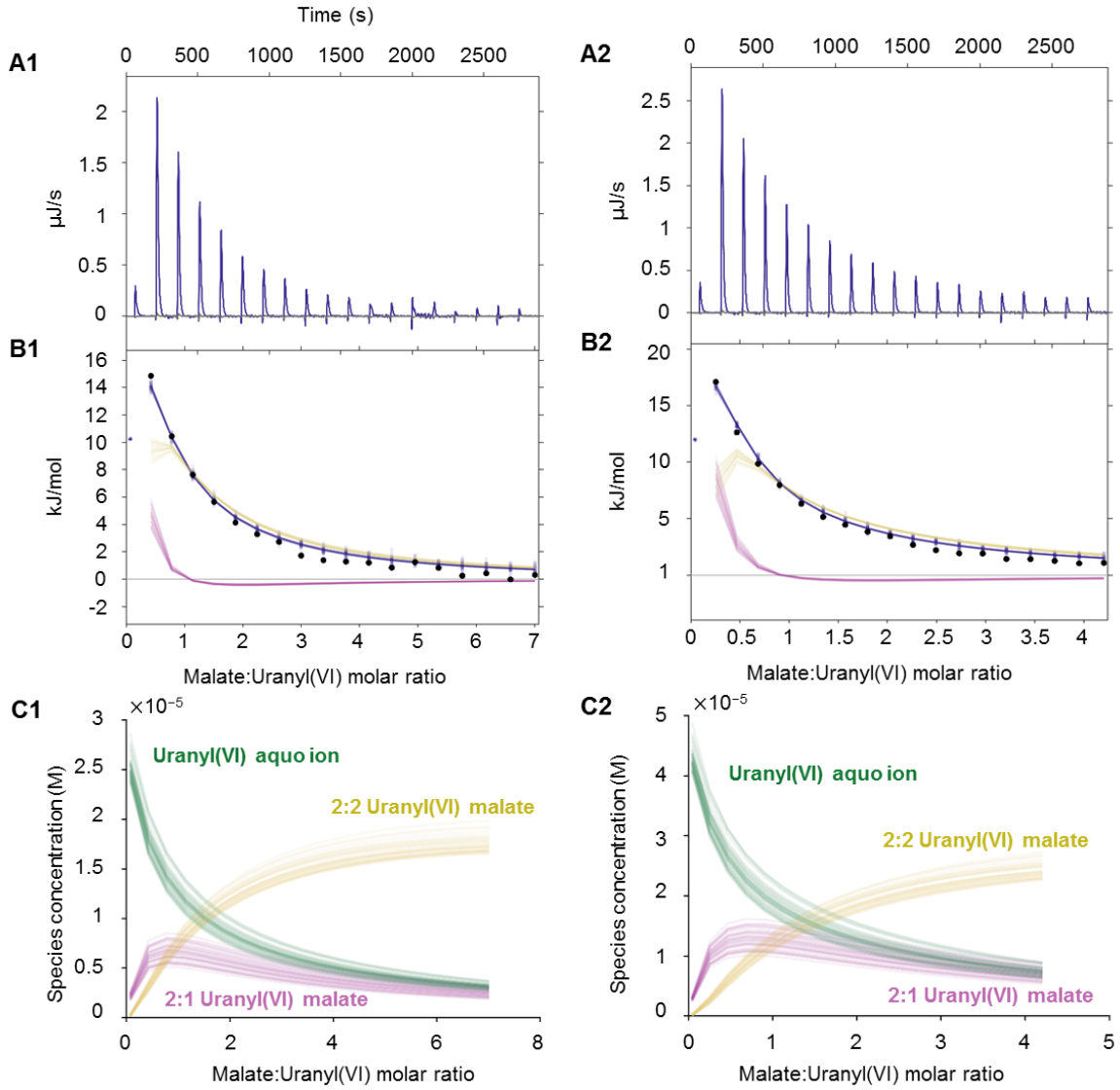

Figure S9. ITC titrations of malic acid with uranyl(VI) with different U(VI) concentrations. $[U(VI)]_{initial}$ = 30 µM, [malate] = 0–220 µM, $[NaClO_4]$ = 0.1 M (A1–C1) and $[U(VI)]_{initial}$ = 50 µM, [malate] = 0–220 µM, $[NaClO_4]$ = 0.1 M (A2–C2), all at pH 4. Thermogram obtained from the titration (A1–A2), integrated heat and best fit (blue line) (B1-B2) and species distribution of the different complexes; yellow: 2:2 uranyl(VI) malate complex, magenta: 2:1 uranyl(VI) malate complex, and green: uranyl(VI) aquo ion (C1 –C2).

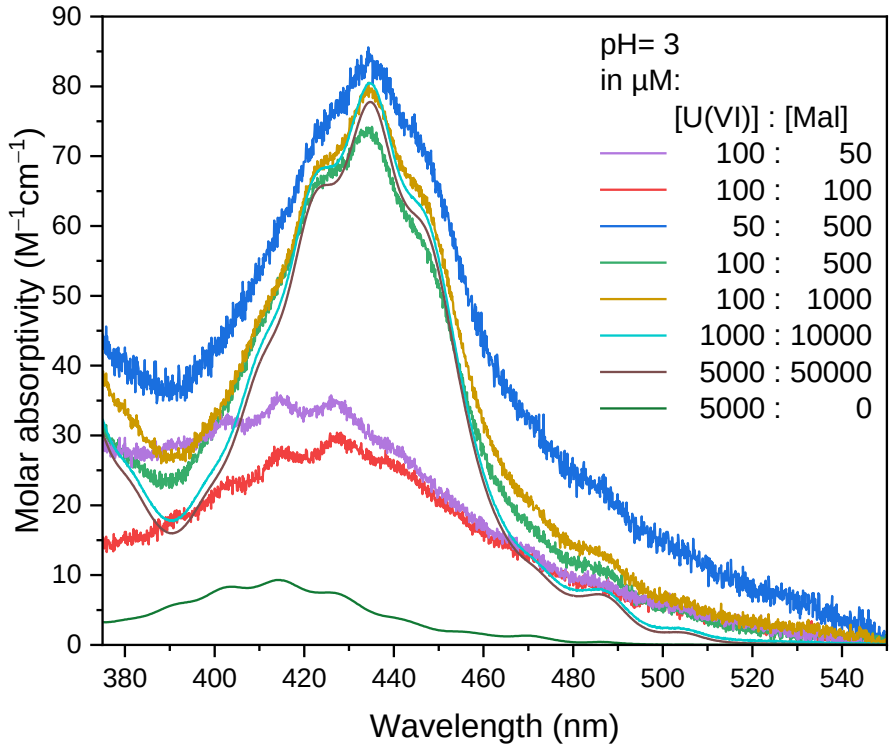

Figure S10. UV-vis absorption spectra obtained from pH 3 solutions of varying uranyl(VI) nitrate and malic acid concentrations.

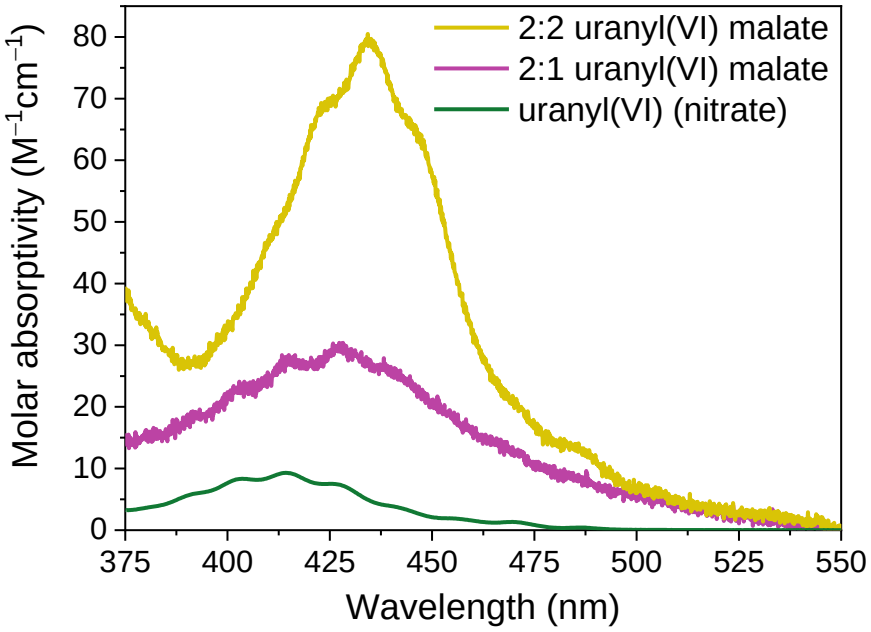

Figure S11. Single-component spectra obtained from UV-vis spectrophotometry results of the complexation of malic acid with uranyl(VI) nitrate at pH 3.