Electronic Supplementary Information

Insights at the molecular level into the formation of oxo-bridged trinuclear uranyl complexes

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1 General Remarks

General Considerations: All reported compounds were fully characterized by multinuclear NMR spectroscopy, IR- and Raman spectroscopy and elemental analysis as well as single crystal X-ray crystallography where applicable. Manipulations were performed under ambient conditions or, when stated, in a Glovebox MB Unilab or using Schlenk techniques under an atmosphere of purified argon. Dry, oxygen-free solvents (pyridine, MeCN and NEt_3 distilled from CaH_2) were employed. All distilled solvents were stored over molecular sieves (3 Å). The water content of solvents was monitored via coulometric Karl- Fischer-titration using an Aqua 40.00 titrator (Elektroktrochemie Halle GmbH) and is quoted in ppm (MeCN: 5.2 ppm, NEt_3: 9.5 ppm). Deuterated dimethyl sulfoxide (DMSO-d_6, 99.9%) was purchased from Sigma Aldrich, deuterated acetonitrile (MeCN-d_3, 99.8%) was purchased from Eurisotope and used without further purification. Anhydrous DMSO-d_6 was prepared from freshly opened DMSO-d_6, degassed and stored over molecular sieves (3 Å) under a nitrogen atmosphere. All glassware was oven-dried at 160 °C prior to use. Compounds H**L**(Ac) and its precursors **I**-**III** were prepared according to procedures given in the literature[1-4]. MeCN (LC-MS) and ethanol (for synthesis) were purchased from Fisher, acetone (for synthesis) was purchased from Sigma Aldrich, pyridine was purchased from Acros, benzonitrile (99%) was purchased from abcr and used without further purification. Glucosamine hydrochloride (98%) and *p*-anisaldehyde (99%) was purchased from TCI Japan, acetic anhydride (Ac_2O) was purchased from Merck, hydrochloric acid (HCl, 37%) was purchased from VWR, perchloric acid ($HClO_4$, 70%) was purchased from Fluka, 2-hydroxy-1-naphthaldehyde 98% were purchased from Alfa Aesar, triethylamine 99.5% was purchased from Roth and used without further purification. Uranyl acetate dihydrate ($UO_2(OAc)_2{\cdot}2H_2O$) was purchased from Merck. Water ^{18}O (97%) was purchased from Deutoro.

NMR spectra were measured on a Bruker AVANCE III HDX, 500 MHz Ascend (^1H (500.13 MHz), ^{13}C (125.75 MHz) instrument, recorded at 300 K. All ^{13}C NMR spectra were exclusively recorded with composite pulse decoupling. Reported numbers assigning atoms in the ^{13}C spectra were indirectly deduced from the cross-peaks in 2D correlation experiments (HMBC, HSQC). Chemical shifts were referenced to δ_{TMS} = 0.00 ppm (^1H, ^{13}C, externally) and are reported in ppm. Coupling constants (*J*) are reported in Hz.

Melting points (m.p.) were recorded on an electrothermal melting point apparatus (Büchi Switzerland, Melting point M-560) in capillaries and are uncorrected. Infrared (IR) and Raman spectra were recorded at ambient temperature using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd-YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parenthesis. An ATR unit (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parenthesis using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong. Elemental analyses were performed on a Vario MICRO cube Elemental Analyzer (Elementar Analysatorsysteme GmbH) in CHNS modus. **Note:** Uranyl complexes **1**·1.5EtOH·0.25H_2O and $[HNEt_3]_2$[**2**] were analysed in the presence of excess WO_3 to ensure the complete burning of the analyte.

UV/Vis data were recorded on a Perkin Elmer LAMBDA 25 double beam spectrometer at room temperature against blank solvent. The UV/Vis-titration experiment was performed as a batch titration. To 500 µl of a stock solution of **1** in MeCN (c(**1**) = 0.2 mM) defined volumes (0-500 µl) of a NEt_3 solution ($c(NEt_3)$ = 0.4 mM in MeCN) were added, with the MeCN solution diluted to 1 ml and shaken overnight. UV/Vis spectra were recorded at room temperature using quartz cuvettes with 10 mm path lengths.

High resolution MS-data were recorded on an Agilent 6545 Q-TOF mass spectrometer coupled with an Agilent 1260 Infinity HPLC system. A constant solvent flow of 0.1 ml/min MeCN, containing 0.1% NEt_3, was provided via a HPLC pump. Samples were injected via the HPLC autosampler (Injection volume = 4 µl) directly into the mass spectrometer. Data were recorded in ESI negative mode in a range of 100-3000 Da/e at 1 spectra/s. The following parameters were set for the mass spectrometer: Gas temperature: 250 °C, Drying Gas 8 l/min, Nebulizer: 35 psig, Sheath Gas temperature: 280 °C, Sheath Gas flow: 11 l/min, VCap: 3500 V, Nozzle Voltage: 0V, Fragmentor: 175 V, Skimmer1: 65 V, Oct 1 RF Vpp: 750 V, Collision Energy: 0 eV.

LC-MS-data were recorded on a Waters ACQUITY UPLC H-class system consisting of Waters ACQUITY Quaternary Solvent Manager, Waters ACQUITY Sample Manager FTN, Waters ACQUITY Column Manager, Waters ACQUITY PDA detector and a Waters ACQUITY tandem quadrupole detector (TQD) with Zspray ESI/APCI/ESCi ion source. Nitrogen, provided by a CMC instruments membrane nitrogen generator (NGM-11-LC/MS), was used as both the desolvation and the cone gas. For CID experiments, argon was used as the collision gas. The spectrometer was calibrated using sodium iodide (2 µg/µl) / cesium iodide (50 ng/µl) in 50/50 iso-propanol/water solution via Acquity Intellistart software.

2 Additional spectroscopic data

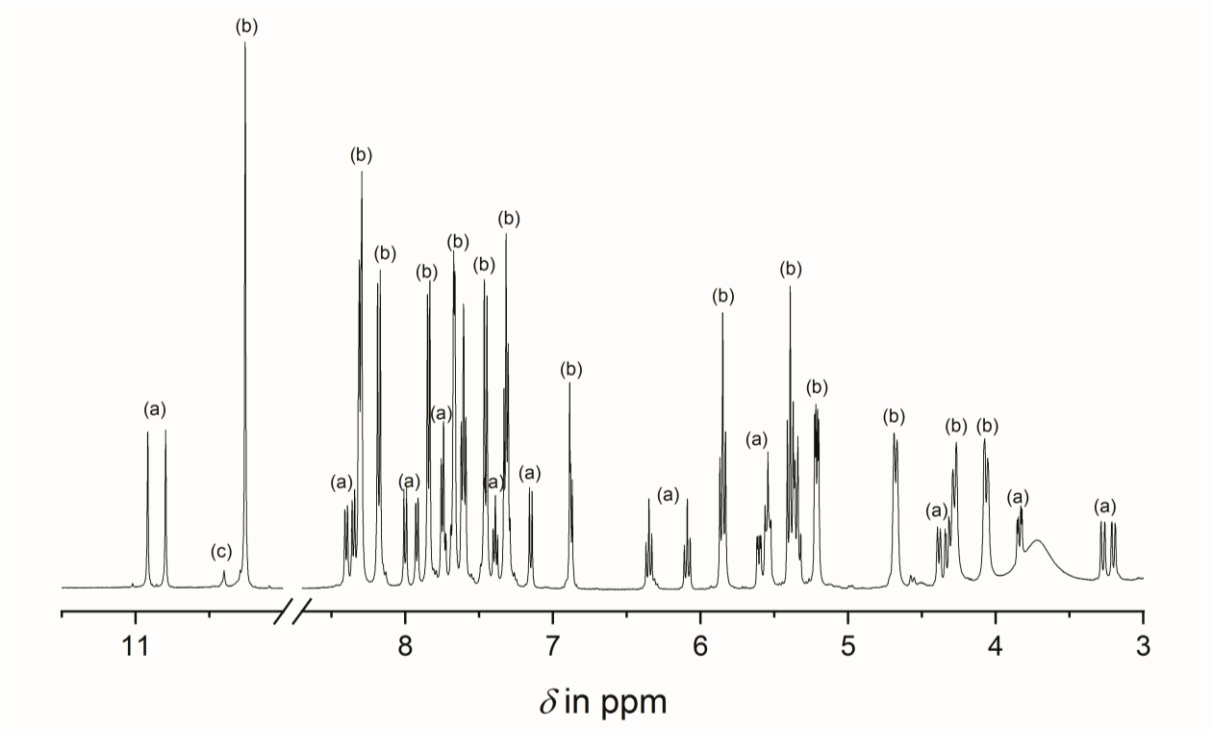


Fig. S1. 1H-NMR (500 MHz, CD_3CN) of **1**·1.5EtOH·0.25H_2O; (a) resonances attributed to [**1**(H_2O)(CD_3CN)], (b) resonances attributed to [**1**(CD_3CN)$_2$], (c) resonances attributed to H**2**$^-$.

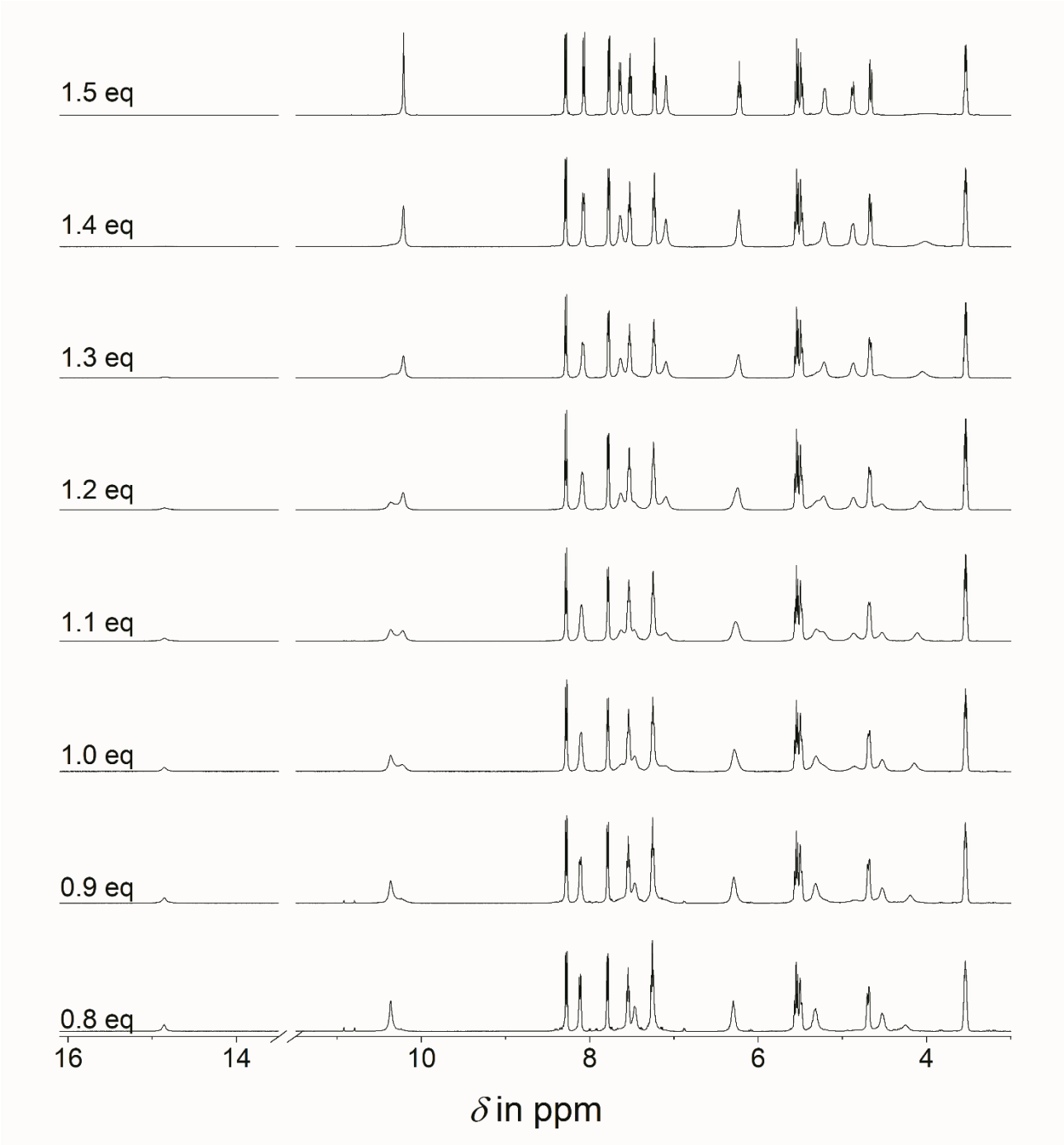


Fig. S2. ^{1}H-NMR (500 MHz, CD_3CN) spectra of **1**·1.5EtOH·0.25H_2O with increasing NEt_3, as marked on the left hand side, from 0.8 eq. to 1.5 eq.

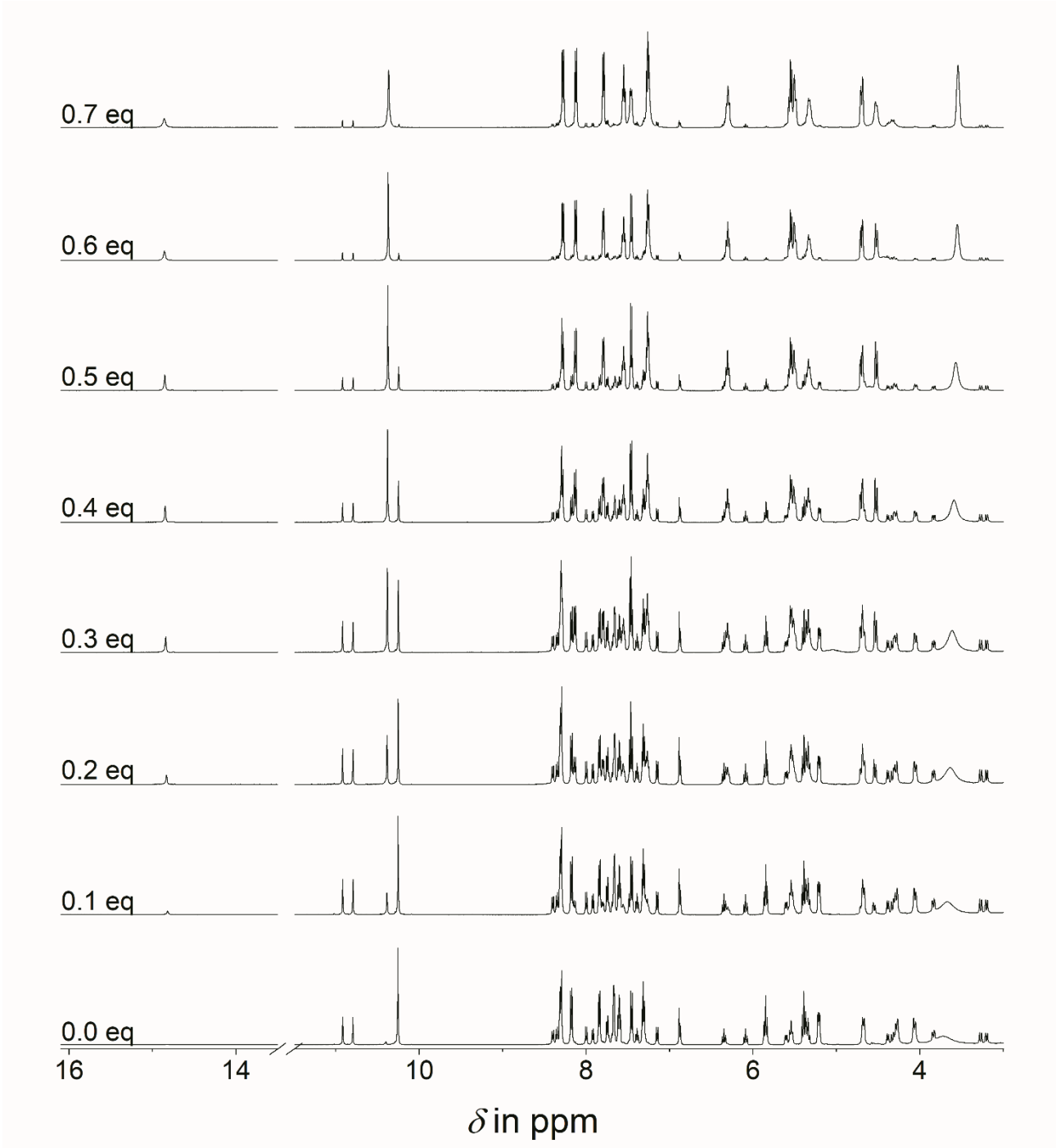


Fig. S3. ^{1}H-NMR (500 MHz, CD_3CN) spectra of **1**·1.5EtOH·0.25H_2O with increasing NEt_3, as marked on the left hand side, from 0.0 eq. to 0.7 eq.

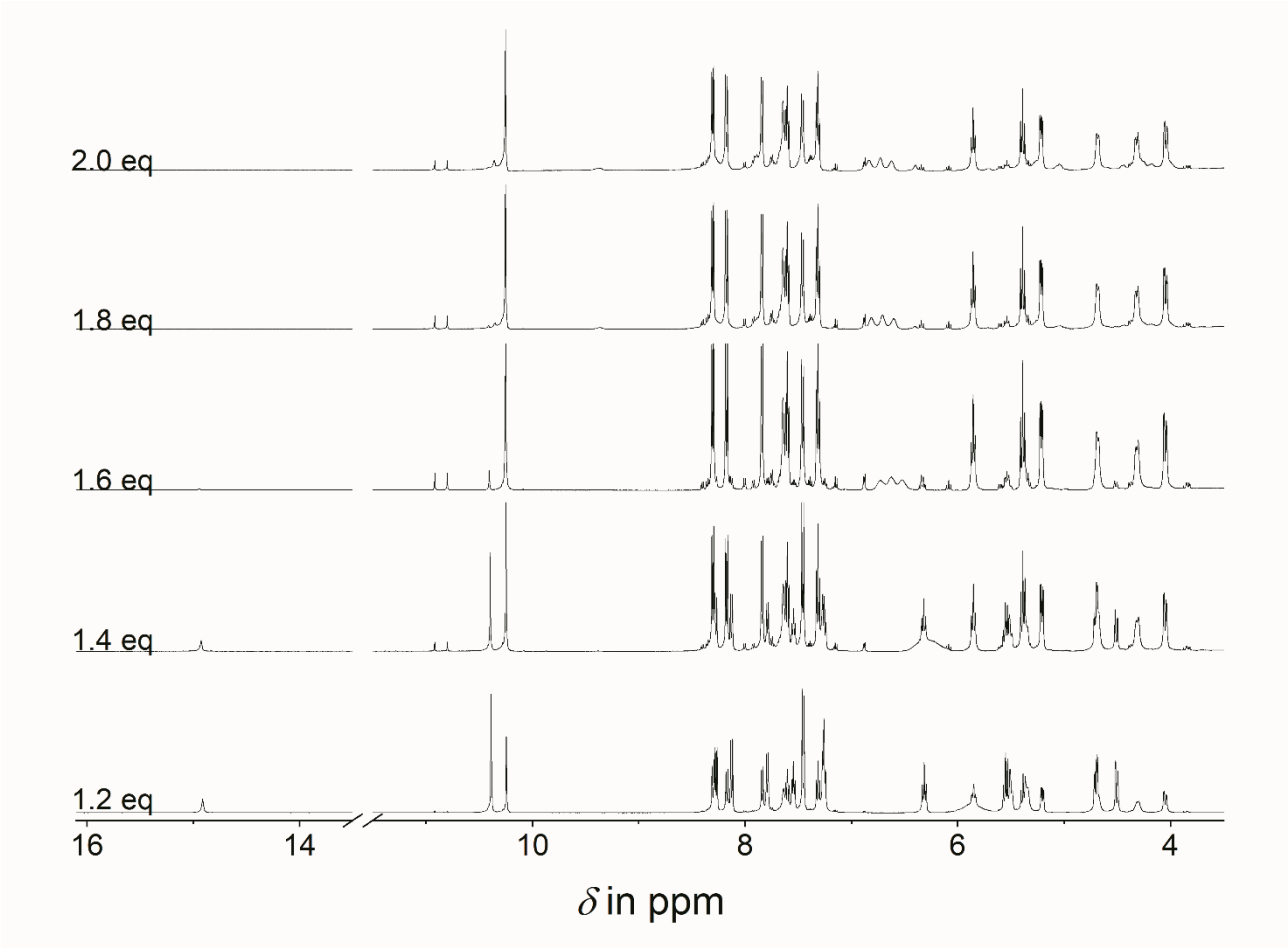


Fig. S4. ^{1}H-NMR (500 MHz, CD_3CN) spectra of $[HNEt_3]_2$[**2**] with increasing $HClO_4$, as marked on the left hand side, from 1.2 eq. to 2.0 eq.

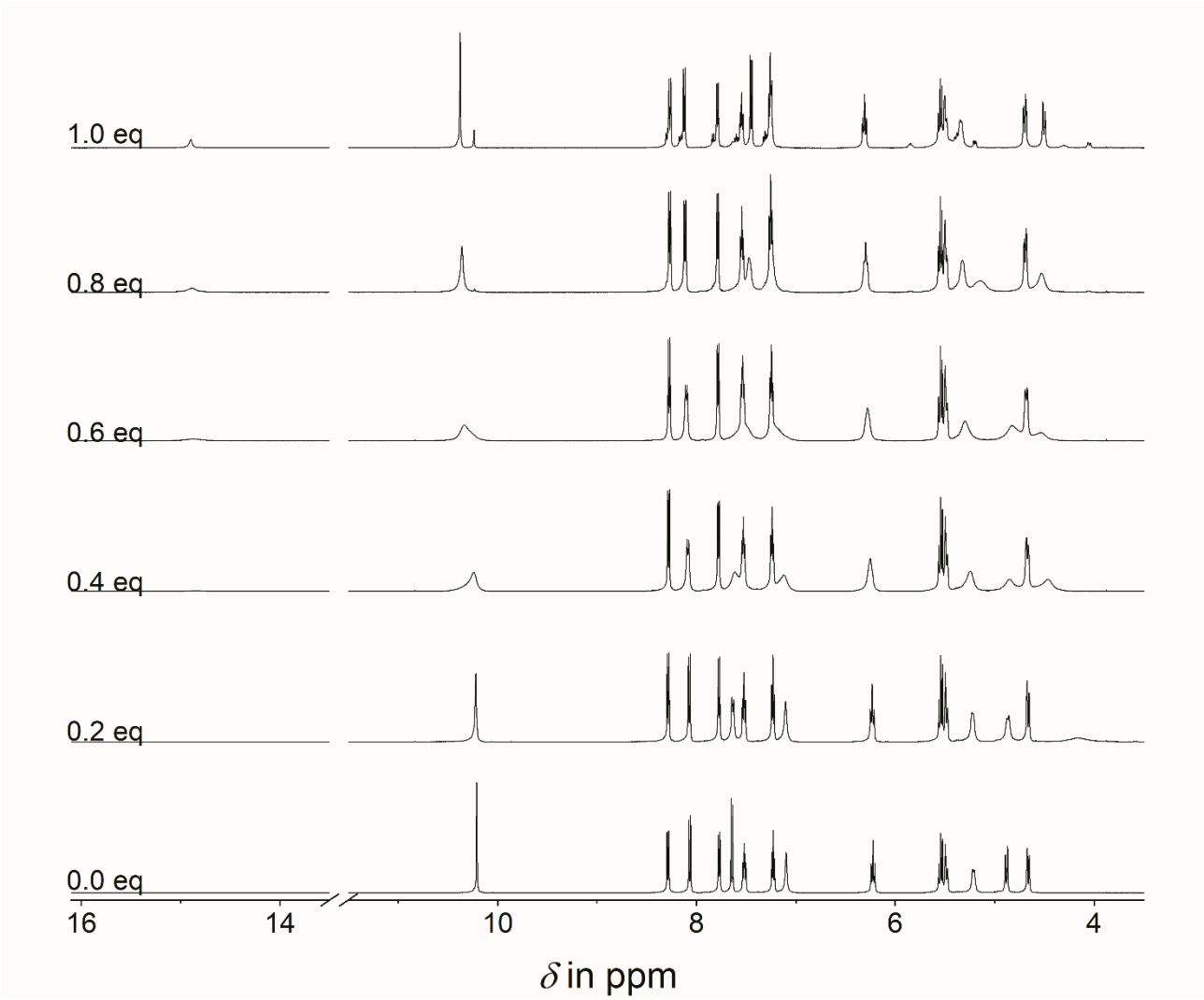


Fig. S5. ^{1}H-NMR (500 MHz, CD_3CN) spectra of $[HNEt_3]_2$[**2**] with increasing $HClO_4$, as marked on the left hand side, from 1.2 eq. to 2.0 eq.

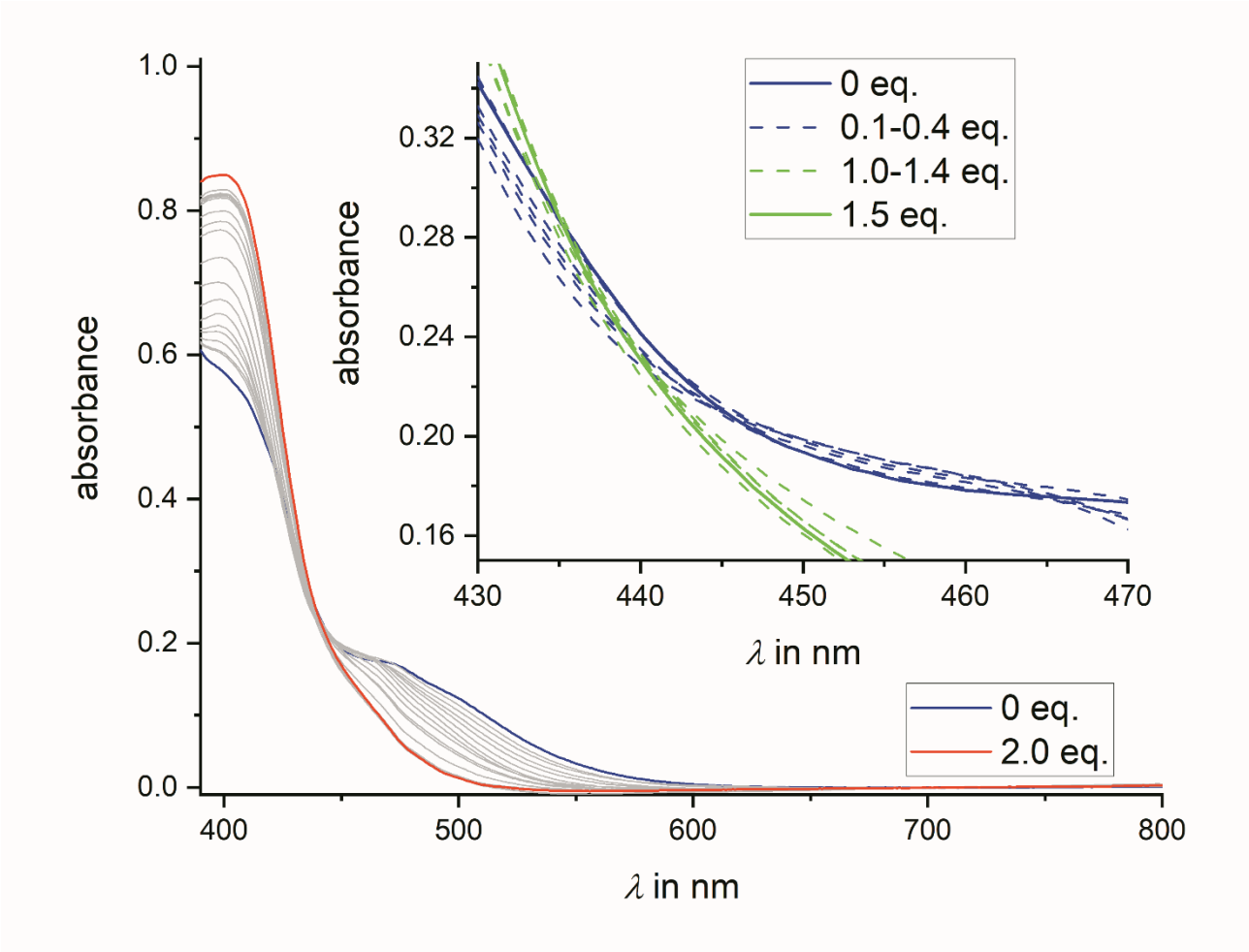


Fig. S6. UV/Vis spectra of 0.1 mmol/l **1**·1.5EtOH·0.25H_2O in MeCN with varying NEt_3 concentration, including a magnification of the spectra at 430 to 470 nm, displaying the spectra at selected NEt_3 concentration (bue: 0.0 to 0.4 eq., green: 1.0 to 1.5 eq.).

3 Determination of benzamide contained in benzonitrile

The amount of benzamide contained in benzonitrile was quantified via UPLC-MS/MS according to a modified literature procedure.[5] UPLC analysis was performed on a Waters ACQUITY UPLC H-class system (see above). The method parameters are listed in Table S1.

Table S1. Operating conditions for the measurement of benzamide by UPLC-MS/MS.

UPLC	Column	ACQUITY BEH C18 (Waters) 50 mm x 2.1 mm, 1.7 µm, including ACQUITY UPLC BEH C18 VanGuard Pre-column (5 mm x 2.1 mm, 1.7 µm)
	Column temperature	40 °C
	Samplemanager temperature	10 °C
	Mobile phase	A: 0.1 % formic acid in water B: MeOH
	Gradient	Isocratic 25% B for 3 min
	Flow rate	0.5 ml/min
	Injection volume	1.0 µl
UV/Vis	PDA	Chromatogramm: 220 nm UV/Vis spectra: 200-800 nm
ESI^+	Desolvation gas	800 l/h
	Cone gas	100 l/h
	Collision gas	0.10 ml/h
	Desolvation temperature	500 °C
	Source temperature	150 °C
	Capillary voltage	3 kV
MS/MS	MRM	See **Table S2**

Appropriate MRM transitions for benzamide in ESI^+ mode were determined automatically using Intellistart software and are displayed in Table S2. Data were acquired using Mass Lynx[6], evaluation and quantification of the chromatograms were carried out using Quan Lynx Software[7]. The retention times were determined as t_{ret}(benzamide) = 0.78 min and t_{ret}(benzonitrile) = 2.09 min (see Fig. S7b).

Table S2. MRM parameter for the quantification of benzamide. The transition marked as *Q* was used for quantification, transition marked as *q* used to confirm the presence of the analyte.

Parent ion	Daughter ion	Cone voltage (V)	Collision Energy (eV)	Dwell time (s)
121.96	78.88 (*Q*)	22	12	0.245
121.96	104.88 (*q*)	22	16	0.245

The linearity of the method was established by external calibration using benzamide in methanol stock solutions between 50 ng/ml and 2.0 µg/ml (see Fig. S7a). The amount of benzamide contained in benzonitrile was determined via three point standard addition according to Table S3. For each sample a three-fold determination was performed. Fig. S7b shows the chromatogram for sample 1. The total amount of benzamide contained in benzonitrile was calculated to be (606±93) µg/g.

Table S3. Sample preparation for the quantification of benzamide; V_1: methanolic solution of benzonitrile (*c* = 1.055 mg/ml), V_2: methanolic solution of benzamide (*c* = 1.0 µg/ml), V_3: methanol.

Sample	V_1 (µl)	V_2 (µl)	V_3 (µl)
1	100	0	900
2	100	450	450
3	100	900	0

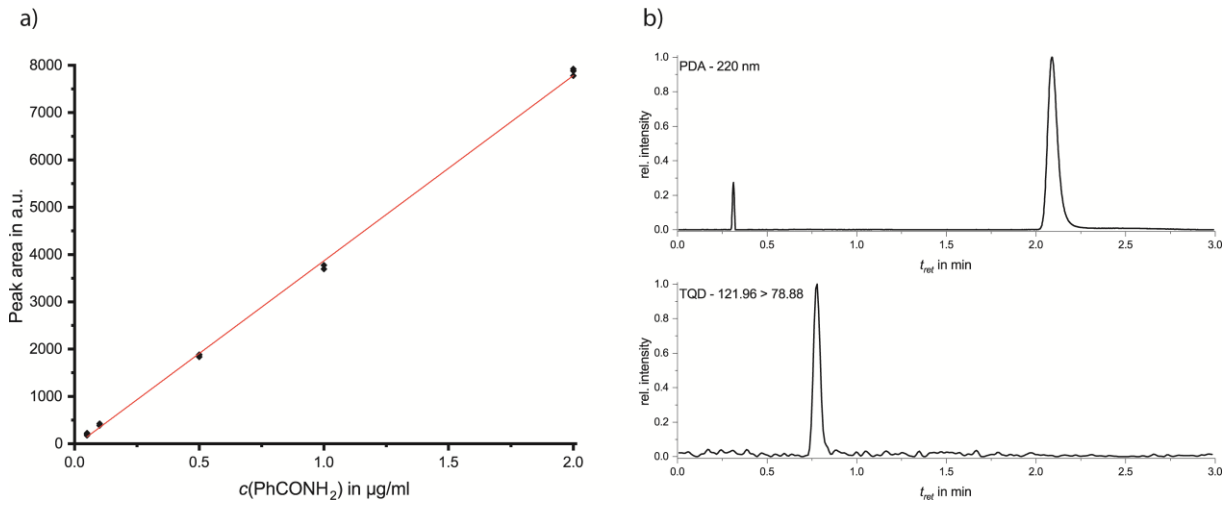
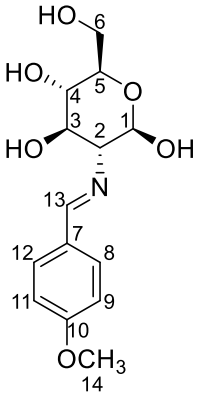


Fig. S7. a) External calibration of benzamide between 0.050 µg/ml and 2.0 µg/ml; b) Chromatogram of Sample 1, UV/Vis trace at λ = 220 nm (top) and MS *Q*-trace (bottom).

4 Synthesis of Ligands

4.1 Synthesis of *N*-anisylidene glucosamine (I)



I was prepared according to the literature procedure.[1] Glucosamine hydrochloride (5.05 g, 23.4 mmol, 1.0 eq.) was dissolved in aqueous sodium hydroxide solution (1 M, 30 ml). *p*-Anisaldehyde (3.70 ml, 4.14 g, 30.4 mmol, 1.3 eq.) was added and the resulting emulsion was stirred at room temperature for 17 h. The precipitate was filtered off, washed with ice water (3 x 20 ml), dichloromethane (3 x 30 ml) and diethyl ether (3 x 30 ml). The target compound was obtained as a colourless solid.

Yield: 4.77 g (69%), **m. p.:** 170.2 °C (decomp.), **Raman** (100 mW, 1000 scans, 300 K, [cm^{-1}]): 3070 (7), 3027 (6), 2974 (5), 2931 (17), 2896 (9), 2844 (9), 1642 (58), 1603 (100), 1575 (8), 1441 (5), 1425 (6), 1371 (6), 1315 (12), 1268 (7), 1225 (17), 1170 (26), 1118 (7), 1060 (7), 1017 (9), 988 (6), 871 (14), 786 (10), 724 (7), 633 (10), 506 (9), 462 (10), 426 (11), 394 (11), 326 (9), **IR** (ATR, 300 K, [cm^{-1}]): 3487 (w), 3323 (w), 3211 (w), 2971 (vw), 2932 (vw), 2896 (vw), 2846 (vw), 1639 (w), 1605 (s), 1516 (m), 1453 (w), 1429 (w), 1385 (w), 1371 (w), 1314 (m), 1268 (s), 1250 (w), 1215 (vw), 1172 (m), 1151 (w), 1104 (m), 1063 (vs), 1030 (vs), 988 (s), 973 (w), 887 (w), 870 (w), 835 (s), 709 (w), 658 (m), 646 (w), 631 (m), 581 (m), 559 (m), 528 (s), 504 (m), 472 (w), 428 (m), **^{1}H-NMR** (500 MHz, DMSO-d^6): δ [ppm] = 2.80 (1H, *pseudo*-t, $^{3}J_{1H,2H}$ = 7.1 Hz, $^{3}J_{2H,3H}$ = 9.7 Hz, 2-H), 3.13-3.17 (1H, m, 4-H), 3.23-3.26 (1H, m, 5-H), 3.41-3.45 (1H, m, 3-H), 3.47-3.52 (1H, m, 6-H), 3.72-3.75 (1H, m, 6-H'), 3.80 (3H, s, 14-CH_3), 4.54 (1H, *pseudo*-t, $^{3}J_{6H,6OH} \approx {}^{3}J_{6H',6OH} \approx$ 5.1 Hz, 6-OH), 4.70 (1H, pseudo-t, $^{3}J_{1H,1OH}$ = 5.8 Hz, $^{3}J_{1H,2H}$ = 7.1 Hz, 1-H), 4.80 (1H, d, $^{3}J_{3H,3OH}$ = 5.6 Hz, 3-OH), 4.90 (1H, d, $^{3}J_{4H,4OH}$ = 4.8 Hz, 4-OH), 6.51 (1H, d, $^{3}J_{1H,1OH}$ = 5.8 Hz), 6.98 (2H, d, $^{3}J_{8H,9H}$ = 8.2 Hz, 9-H, 11-H), 7.68 (2H, d, $^{3}J_{8H,9H}$ = 8.2 Hz, 8-H, 12-H), 8.12 (1H, s, 13-H), **^{13}C{^{1}H}-NMR** (125 MHz, DMSO-d_6): δ [ppm] = 55.27 (1C, s, 14-C), 61.28 (1C, s, 6-C), 70. 37 (1C, s, 4-C), 74.60 (1C, s, 3-C), 76.85 (1C, s, 5-C), 78.18 (1C, s, 2-C), 95.63 (1C, s, 1-C), 113.90 (2C, s, 9-C, 11-C), 129.10 (1C, s, 7-C), 129.62 (2C, s, 8-C, 12-C), 161.05 (1C, s, 10-C), 161.24 (1C, s, 13-C), **Elemental Analysis:** calculated for $C_{14}H_{19}NO_6$, C: 56.56%, H: 6.44%, N: 4.71%, found C: 56.42%, H: 6.420%, N: 4.77%.

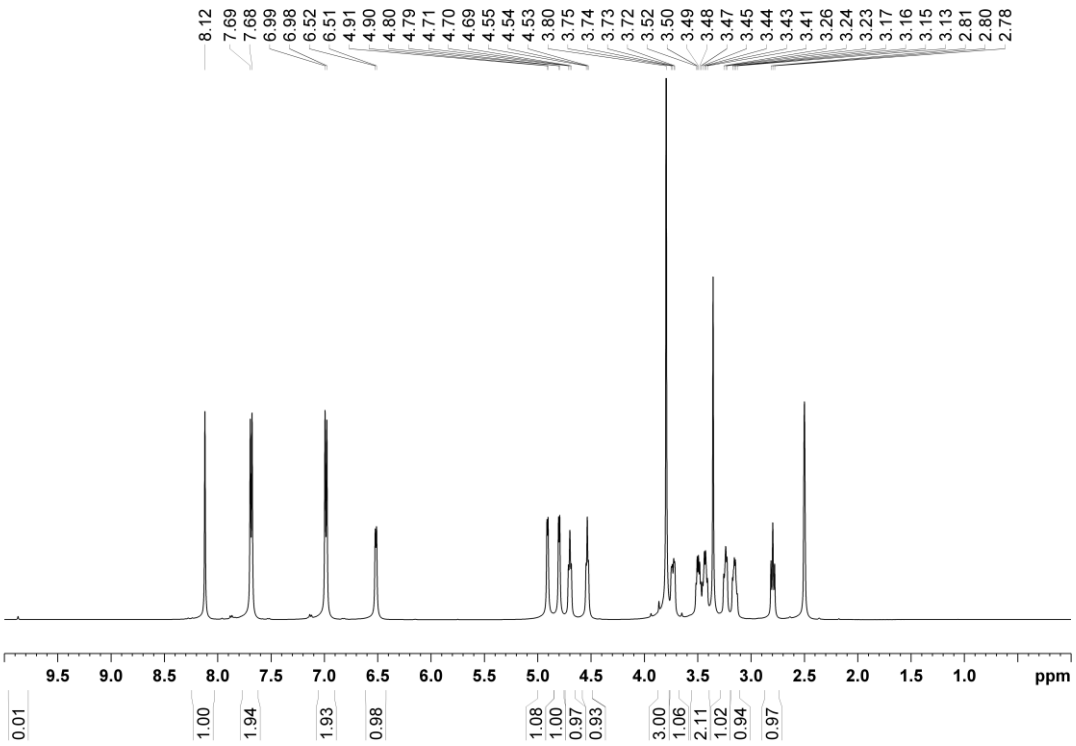


Fig. S8. ^{1}H-NMR (500 MHz, DMSO-d_6) of **I**.

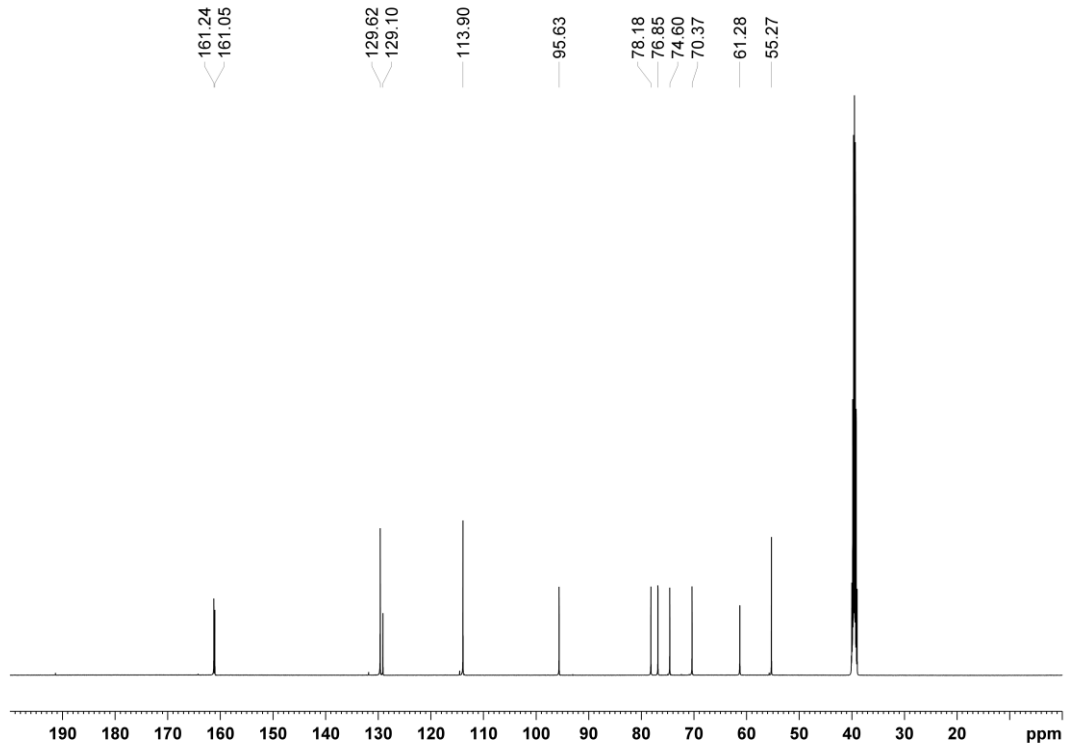
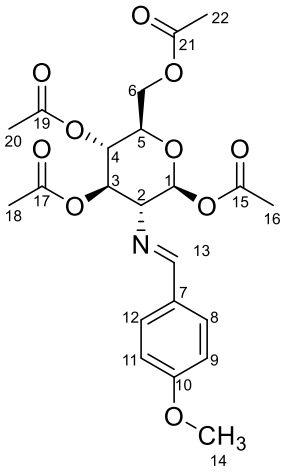


Fig. S9. ^{13}C{^{1}H}-NMR (125 MHz, DMSO-d_6) of **I**.

4.2 Synthesis of 1,3,4,6-tetra-*O*-acetyl-*N*-anisylidene glucosamine (II)



II was prepared according to a literature procedure.[2] *N*-Anisylidene glucosamine (**I**, 5.01 g, 16.9 mmol, 1.0 eq.) was dissolved in anhydrous pyridine (170 ml) under a N_2-atmosphere and chilled to about 0 °C. Acetic anhydride (13 ml, 138 mmol, 8.2 eq.) was added and the reaction solution was stirred for 24 h, while slowly warming to room temperature. The solution was poured onto ice water (1 l) and stored overnight in a refrigerator to allow complete precipitation. The resulting colourless solid was filtered off, washed with ice water (3 x 100 ml), petroleum ether (40-60 °C, 3 x 100 ml) and dried in vacuo. The target compound was isolated as a colourless solid. Crystals of **II** suitable for single crystal x-ray diffraction were obtained by allowing pentane vapour to diffuse into a dichloromethane solution of the product at -30 °C.

Yield: 3.24 g (41%), **m. p.:** 234.9 °C (decomp.), **Raman** (100 mW, 1000 scans, 300 K, [cm^{-1}]): 3079 (8), 3056 (8), 3017 (11), 2960 (16), 2940 (35), 2895 (16), 2846 (8), 1747 (7), 1650 (57), 1604 (100), 1580 (7), 1423 (5), 1376 (5), 1308 (9), 1254 (6), 1223 (14), 1164 (21), 1109 (8), 913 (5), 864 (6), 777 (5), **IR** (ATR, 300 K, [cm^{-1}]): 2970 (vw), 2921 (vw), 1747 (s), 1736 (s), 1648 (w), 1605 (m), 1514 (w), 1445 (vw), 1364 (m), 1307 (w), 1249 (s), 1214 (vs), 1163 (m), 1144 (w), 1128 (w), 1108 (w), 1080 (s), 1050 (s), 1028 (vs), 956 (m), 930 (w), 913 (w), 895 (m), 877 (w), 863 (w), 834 (m), 822 (m), 777 (w), 667 (w), 650 (w), 638 (w), 596 (m), 564 (w), 549 (m), 524 (m), 494 (w), 455 (w), 415 (w), **^{1}H-NMR** (500 MHz, DMSO-d_6): δ [ppm] = 1.82 (3H, s, 16-CH_3/18-CH_3/20-CH_3/22-CH_3), 1.98 (6H, s, 16-CH_3/18-CH_3/20-CH_3/22-CH_3), 2.02 (3H, s, 16-CH_3/18-CH_3/20-CH_3/22-CH_3), 3.44 (1H, *pseudo*-t, $^3J_{1H\text{-}2H}$ = 8.2 Hz, $^3J_{2H\text{-}3H}$ = 9.8 Hz , 2-H), 3.79 (3H, s, 14-CH_3), 4.01 (1H, d, $^3J_{5H\text{-}6H}$ = 11.9 Hz, 6-H), 4.20-4.28 (2H, m, 5-H, 6-H'), 4.97 (1H, *pseudo*-t, $^3J_{3H\text{-}4H}$ = 9.5 Hz, $^3J_{4H\text{-}5H}$ = 9.8 Hz, 4-H), 5.44 (1H, *pseudo*-t, $^3J_{2H\text{-}3H}$ = 9.8 Hz, $^3J_{3H\text{-}4H}$ = 9.5 Hz, 3-H), 6.06 (1H, d, $^3J_{1H\text{-}2H}$ = 8.2 Hz, 1-H), 6.99 (2H, d, $^3J_{8H\text{-}9H}$ = $^3J_{11H\text{-}12H}$ = 8.6 Hz, 9-H, 11-H), 7.65 (2H, d, $^3J_{8H\text{-}9H}$ = $^3J_{11H\text{-}12H}$ = 8.6 Hz, 8-H, 12-H), 8.28 (1H, s, 13-H), **^{13}C{^{1}H}-NMR** (125 MHz, DMSO-d_6): δ [ppm] = 20.16 (1C, s, 16-CH_3/18-CH_3/20-CH_3/22-CH_3), 20.40 (1C, s, 16-CH_3/18-CH_3/20-CH_3/22-CH_3), 20.41 (1C, s, 16-CH_3/18-CH_3/20-CH_3/22-CH_3), 20.50 (1C, s, 16-CH_3/18-CH_3/20-CH_3/22-CH_3), 55.34 (1C, s, 14-C), 61.62 (1C, s, 6-C), 67.79 (1C, s, 4-C), 71.50 (1C, s, 5-C), 72.20 (1C, s, 3-C), 72.32 (1C, s, 2-C), 92.50 (1C, s, 1-C), 114.17 (2C, s, 9-C, 11-C), 128.23 (1C, s, 7-C), 129.88 (2C, s, 8-C, 12-C), 161.79 (1C, s, 10-C), 164.41 (1C, s, 13-C), 168.55 (1C, s, 15-C), 168.94 (1C, s, 17-C), 169.40 (1C, s, 19-C), 170.00 (1C, s, 21-C), **Elemental Analysis:** calculated for $C_{22}H_{27}NO_{10}$ C: 56.77%, H: 5.85%, N: 3.01%, found C: 56.38%, H: 5.677% N: 3.18%.

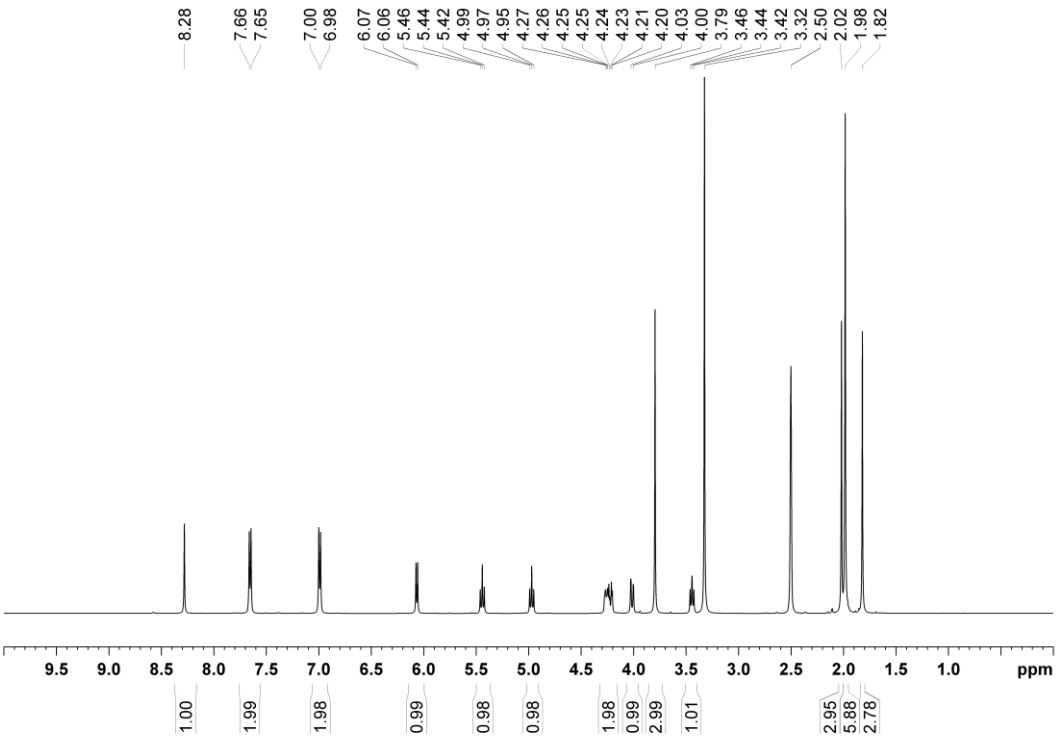


Fig. S10. ^{1}H-NMR (500 MHz, DMSO-d_6) of **II**.

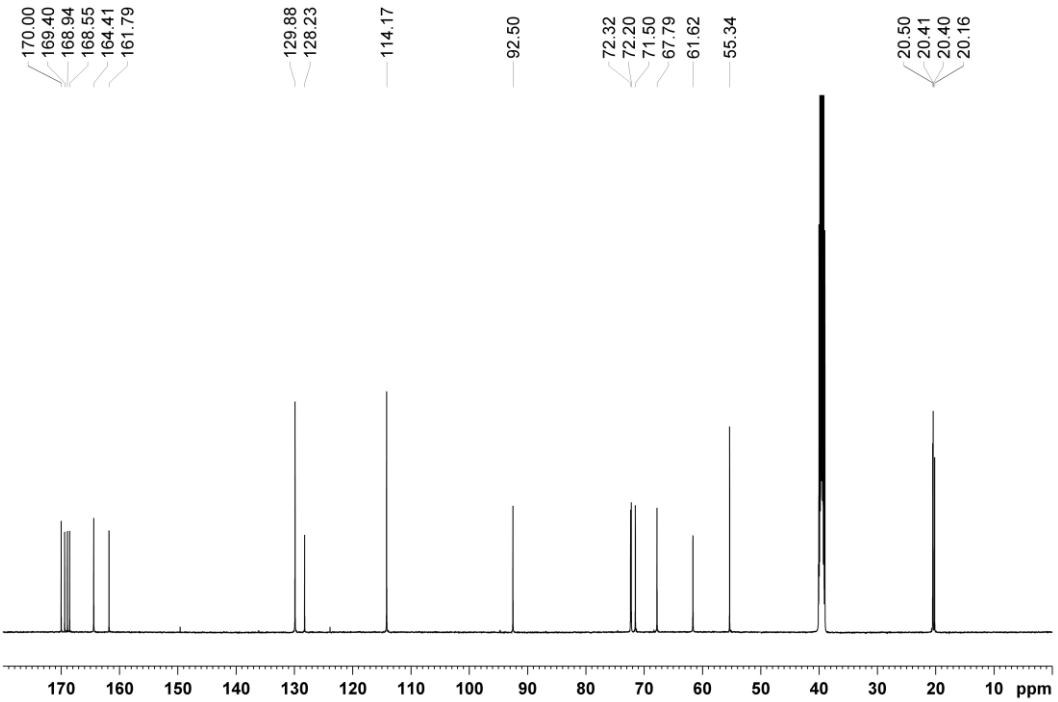
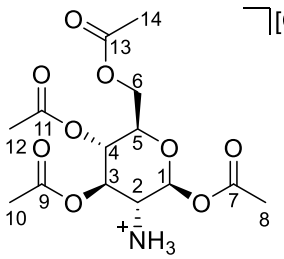


Fig. S11. ^{13}C{^{1}H}-NMR (125 MHz, DMSO-d_6) of **II**.

4.3 Synthesis of 1,3,4,6-tetra-*O*-acetyl-glucosamine hydrochloride (III)



III was prepared according to a literature procedure.[2] 1,3,4,6-Tetra-O-acetyl-N-anisylidene glucosamine (**II**, 2.01 g, 4.32 mmol, 1.0 eq.) was dissolved in acetone (15 ml) and the solution was heated to reflux. Upon addition of HCl (4 N, 2 ml) a white solid started to precipitate. The reaction mixture was first cooled to room temperature and then stored overnight at -30 °C to complete precipitation. The colourless solid was filtered off, washed with ice-cold acetone (3 x 10ml), petroleum ether (40-60 °C, 3x 10ml) and dried in vacuo. The target compound was isolated as a colourless solid.

Yield: 1.55 g (94%), **m. p.:** 234.9 °C (decomp.), **Raman** (100 mW, 1000 scans, 300 K, [cm^{-1}]): 3000 (25), 2974 (31), 2942 (100), 2897 (38), 1749 (27), 1616 (8), 1436 (21), 1387 (21), 1369 (17), 1328 (10), 1252 (10), 1172 (13), 1140 (19), 1117 (19), 1059 (17), 1043 (21), 1001 (17), 970 (17), 912 (17), 867 (21), 699 (17), 663 (23), 637 (29), 601 (23), 553 (25), 530 (38), 493 (29), 470 (27), 452 (27), 412 (31), 345 (27), 301 (29), **IR** (ATR, 300 K, [cm^{-1}]): 2829 (w), 2747 (vw), 2686 (vw), 1757 (vs), 1747 (s), 1596 (w), 1571 (vw), 1520 (w), 1509 (w), 1434 (vw), 1383 (w), 1365 (m), 1246 (s), 1204 (vs), 1149 (w), 1081 (vs), 1059 (vs), 1037 (vs), 973 (w), 956 (w), 920 (w), 897 (m), 699 (vw), 664 (vw), 648 (vw), 637 (vw), 600 (w), 580 (w), 558 (w), 493 (w), 470 (vw), 412 (w), **^{1}H-NMR** (500 MHz, DMSO-d_6): δ [ppm] = 1.97 (3H, s, 10-CH_3/12-CH_3/14-CH_3), 1.99 (3H, s, 10-CH_3/12-CH_3/14-CH_3), 2.03 (3H, s, 10-CH_3/12-CH_3/14-CH_3), 2.17 (3H, s, 8-CH_3), 3.54 (1H, dd, $^{3}J_{1H\text{-}2H}$ = 8.7 Hz, $^{3}J_{2H\text{-}3H}$ = 10.4 Hz, 3.98-4.04 (2H, m, 5-H, 6-H), 4.18 (1H, dd, $^{2}J_{6H,6H'}$ = 4.3 Hz, $^{3}J_{5H,6H}$ = 12.4Hz, 6-H'), 4.92 (1H, *pseudo*-t, $^{3}J_{3H,4H}$ = 9.2 Hz, $^{3}J_{4H,5H}$ = 10.0 Hz, 4-H), 5.37 (1H, *pseudo*-t, $^{3}J_{2H,3H}$ = 10.4 Hz, $^{3}J_{3H,4H}$ = 9.2 Hz, 3-H), 5.92 (1H, d, $^{3}J_{1H\text{-}2H}$ = 8.7 Hz, 1-H), 8.88 (3H, s, 2-NH_3^+), **^{13}C{^{1}H}-NMR** (125 MHz, DMSO-d_6): δ [ppm] = 20.32 (1C, s, 8-C/10-C/12-C/14-C), 20.46 (1C, s, 8-C/10-C/12-C/14-C), 20.84 (1C, s, 8-C/10-C/12-C/14-C), 20.93 (1C, s, 8-C/10-C/12-C/14-C), 52.13 (1C, s, 2-C), 61.24 (1C, s, 6-C), 67.78 (1C, s, 4-C), 70.31 (1C, s, 3-C), 71.58 (1C, s, 5-C), 90.07 (1C, s, 1-C), 168.61 (1C, s, 7-C), 169.29 (1C, s, 11-C), 169.74 (1C, s, 9-C), 169.94 (1C, s, 13-C), **Elemental Analysis:** calculated for $C_{14}H_{22}NO_9Cl$ C: 43.82%, H: 5.78%, N: 3.65%, found C: 43.46%, H: 5.490% N: 3.73%.

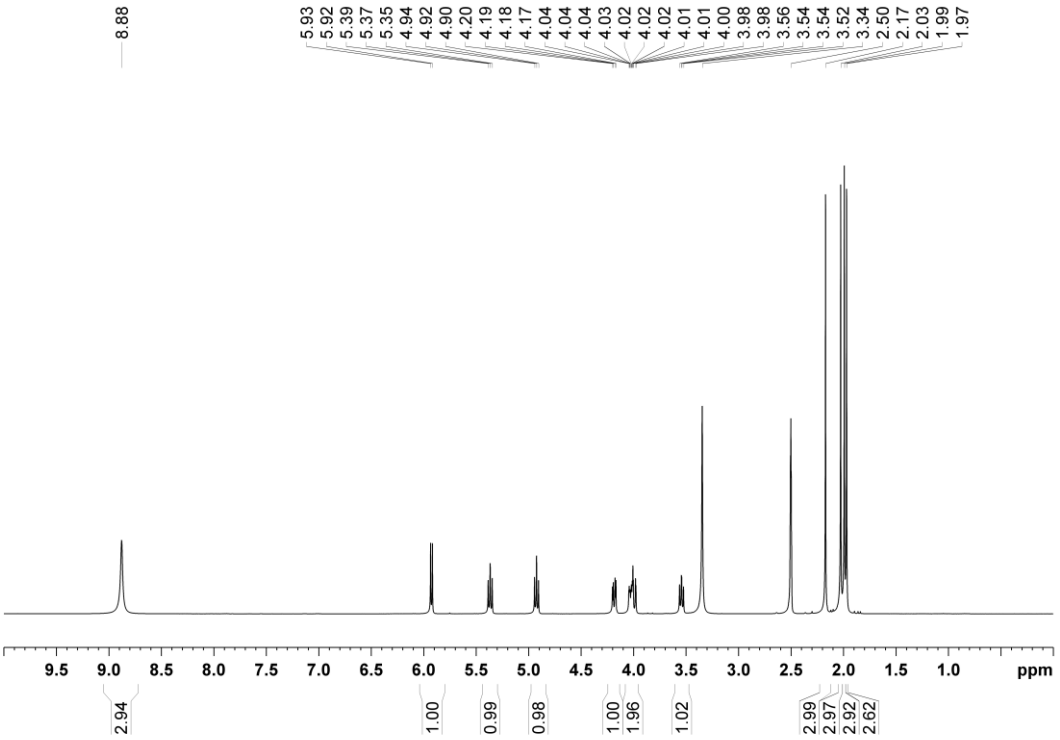


Fig. S12. ^{1}H-NMR (500 MHz, DMSO-d_6) of **III**.

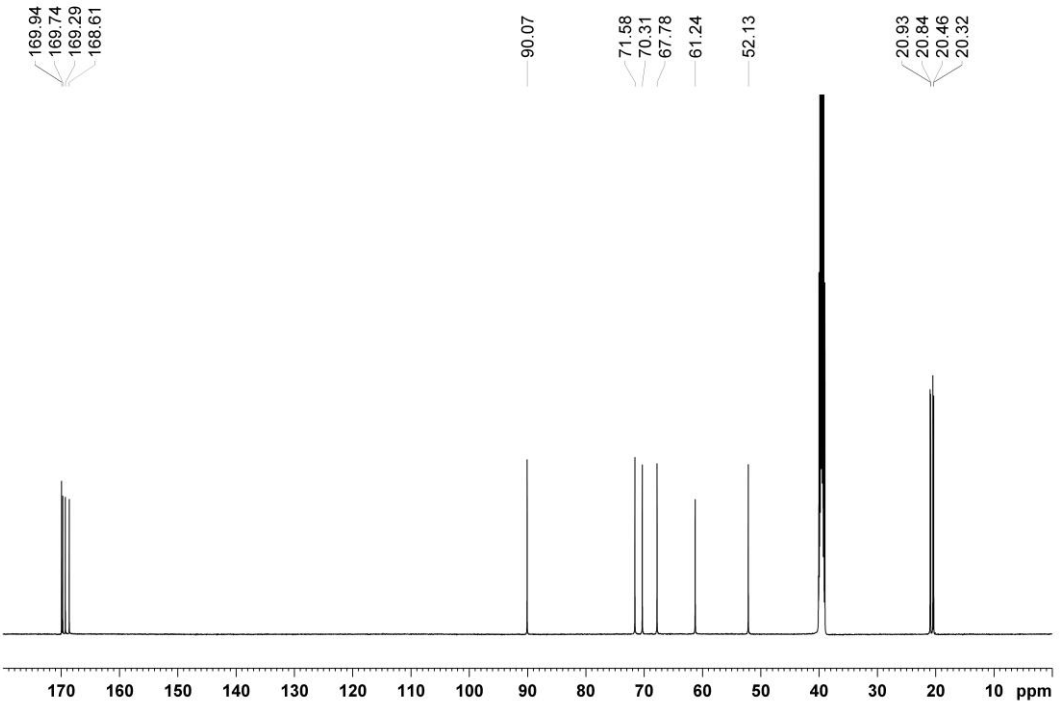
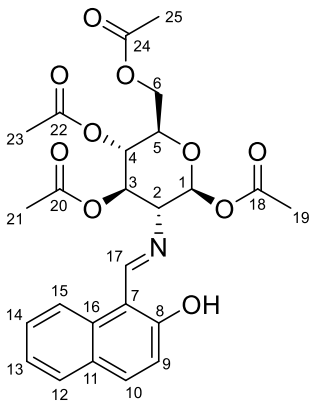


Fig. S13. ^{13}C{^{1}H}-NMR (125 MHz, DMSO-d_6) of **III**.

4.4 Synthesis of 1,3,4,6-Tetra-*O*-acetyl-*N*-(2-Hydroxy)-naphthylidene glucosamine (HL(Ac))



H**L**(Ac) was prepared according to modified literature procedures.[3,4] 1,3,4,6-Tetra-*O*-acetyl-glucosamine hydrochloride (**III**, 1.00 g, 2.61 mmol, 1.0 eq.) and triethyl amine (363 µl, 264 mg, 2.61 mmol, 1.0 eq) were dissolved in a mixture of ethanol (10 ml) and water (5 ml). 2-Hydroxy-naphthyl aldehyde (450 mg, 2.61 mmol, 1.0 eq.) was added and the reaction mixture was stirred at room temperature for 19 h. The yellow precipitate was filtered off, washed with ice water (3 x 10 ml) and n-pentane (3 x 10 ml), and dried in vacuo. The target compound was isolated as a yellow solid.

Yield: 1.12 g (86%), **m.p.:** 172°C, **Raman** (100 mW, 1000 scans, 300 K, [cm^{-1}]): 3069 (12), 2940 (32), 2889 (9), 1750 (8), 1627 (28), 1609 (48), 1585 (70), 1523 (12), 1432 (47), 1370 (97), 1334 (26), 1281 (11), 1245 (6), 1210 (8), 1188 (6), 1162 (6), 1140 (12), 1100 (10), 1036 (12), 958 (10), 879 (8), 785 (23), 530 (15), 437 (23), 149 (26), 105 (84), 91 (100), **IR** (ATR, 300 K, [cm^{-1}]): 1743 (s), 1626 (m), 1582 (m), 1471 (w), 1418 (w), 1372 (m), 1333 (w), 1212 (vs), 1127 (m), 1092 (s), 1034 (vs), 904 (m), 820 (s), 746 (s), 724 (w), 648 (w), 625 (w), 595 (w), 562 (m), 527 (w), 497 (w), 470 (w), **^{1}H-NMR** (500 MHz, DMSO-d_6): δ [ppm] = 1.83 (3H, s, 21-H), 1.99 (3H, s, 19-H/23-H/25-H), 2.01 (3H, s, 19-H/23-H/25-H), 2.04 (3H, s, 19-H/23-H/25-H), 3.90 (1H, *pseudo*-t, $^{3}J_{1H,2H}$ = 8.2 Hz, $^{3}J_{2H,3H}$ = 8.7 Hz, 2-H), 4.05 (1H, d, $^{2}J_{6H,6H'}$ = 11.8 Hz, 6-H), 4.25 (1H, dd, $^{2}J_{6H,6H'}$ = 11.8 Hz, $^{3}J_{5H,6H'}$ = 4.0 Hz, 6-H'), 4.28-4.33 (1H, m, 5-H), 5.02 (1H, *pseudo*-t, $^{3}J_{3H,4H}$ = 10.6 Hz, $^{3}J_{4H,5H}$ = 8.7 Hz, 4-H), 5.71 (1H, *pseudo*-t, $^{3}J_{2H,3H}$ = 8.7 Hz, $^{3}J_{3H,4H}$ = 10.6 Hz, 3-H), 6.24 (1H, d, $^{3}J_{1H,2H}$ = 8.2 Hz, 1-H), 7.00 (1H, d, $^{3}J_{9H,10H}$ = 9.1 Hz, 9-H), 7.34 (1H, *pseudo*-t, $^{3}J_{12H,13H}$ = 7.8 Hz, $^{3}J_{13H,14H}$ = 6.8 Hz, 13-H), 7.55 (1H, *pseudo*-t, $^{3}J_{13H,14H}$ = 6.8 Hz, $^{3}J_{14H,15H}$ = 8.1 Hz, 14-H), 7.80 (1H, d, $^{3}J_{12H,13H}$ = 7.8 Hz, 12-H), 7.89 (1H, d, $^{3}J_{9H,10H}$ = 9.1 Hz, 10-H), 8.29 (1H, d, $^{3}J_{14H,15H}$ = 8.1 Hz, 15-H), 9.43 (1H, s, 17-H), 14.09 (1H, s, 8-OH), **^{13}C{^{1}H}-NMR** (125MHz, DMSO-d_6): δ [ppm] = 20.14 (1C, s, 21-C), 20.36 (1C, s, 19-C/23-C/25-C), 20.39 (1C, s, 19-C/23-C/25-C), 20.50 (1C, s, 19-C/23-C/25-C), 61.52 (1C, s, 6-C), 67.72 (1C, s, 4-C), 68.41 (1C, s, 2-C), 71.47 (1C, s, 5-C), 72.15 (1C, s, 3-C), 92.03 (1C, s, 1-C), 107.79 (1C, s, 7-C), 119.52 (1C, s, 15-C), 121.04 (1C, s, 9-C), 123.32 (1C, s, 13-C), 126.75 (1C, s, 11-C), 128.16 (1C, s, 14-C), 129.00 (1C, s, 12-C), 132.87 (1C, s, 16-C), 135.75 (1C, s, 10-C), 164.24 (1C, s, 17-C), 166.62 (1C, s, 8-C), 168.62 (1C, s, 18-C), 169.26 (1C, s, 20-C), 169.41 (1C, s, 22-C), 170.00 (1C, s, 24-C), **Elemental analysis:** calculated for $C_{25}H_{27}NO_{10}$, C: 59.88%, H: 5.43%, N: 2.79%, found C: 59.48%, H: 5.311%, N: 2.77%.

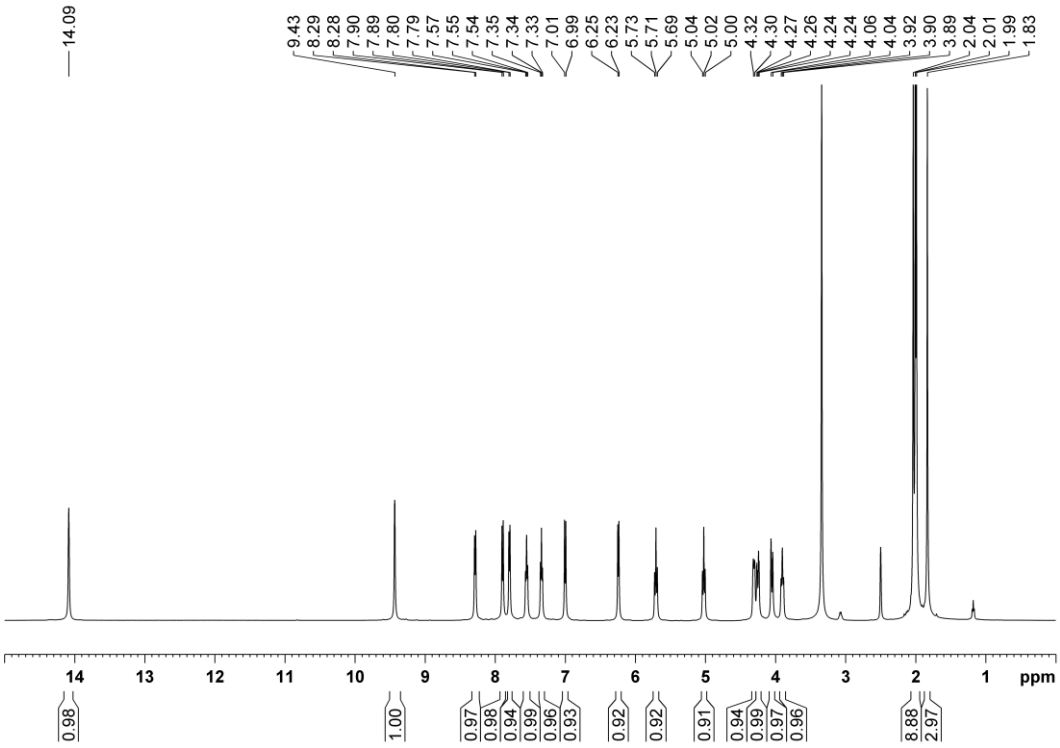


Fig. S14. ^{1}H-NMR (500 MHz, DMSO-d_6) of H**L**(Ac).

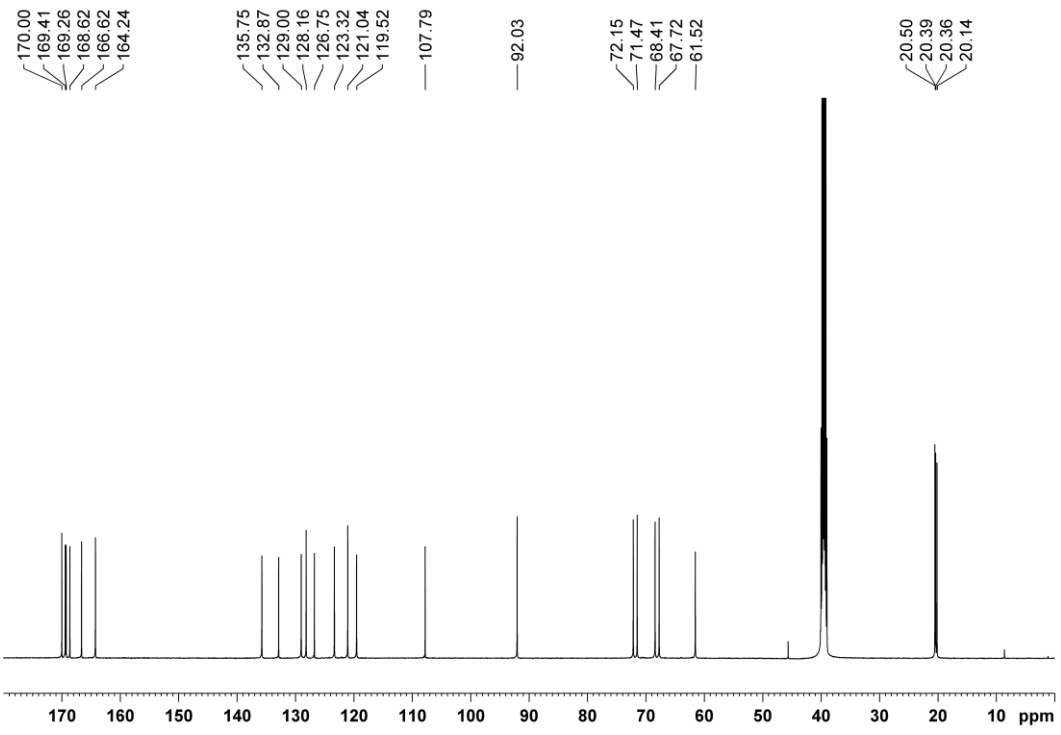
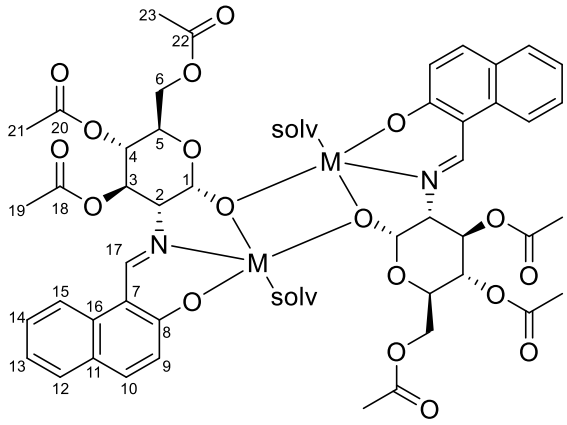


Fig. S15. ^{13}C{^{1}H}-NMR (125 MHz, DMSO-d_6) of H**L**(Ac).

5 Synthesis of uranyl complexes

5.1 Synthesis of $[(UO_2)_2(L)_2]\cdot 1.5\ EtOH\cdot 0.25H_2O$ (1·1.5EtOH·0.25H$_2$O)



H**L**(Ac) (501 mg, 1.00 mmol, 2.0 eq.) and uranyl acetate (420 mg, 0.99 mmol, 2.0 eq.) were suspended in ethanol (20 ml) and the reaction mixture was refluxed for 2 h. The red precipitate that formed was filtered off, washed with diethyl ether (5 x 2 ml), and dried in vacuo. The target compound was isolated as a red solid.

Single crystals of 2[**1**$(DMSO)_2$]·DMSO·H_2O suitable for x-ray analysis were obtained by slow diffusion of water vapour into a DMSO solution of the crude product.

Single crystals of $[H_3O][H\mathbf{2}]\cdot[\mathbf{1}(H_2O)(PhCONH_2)]\cdot 2PhCN\cdot Et_2O$ suitable for x-ray analysis were obtained by slow diffusion of water vapour into a benzonitrile (PhCN) solution of the crude product.

Yield: 582 mg (77%), **m.p.:** 224 °C (decomp.), **Raman** (100 mW, 1000 scans, 300 K, [cm^{-1}]): 3071 (15), 3043 (15), 2932 (38), 1740 (11), 1611 (42), 1545 (55), 1438 (70), 1392 (100), 1369 (42), 1348 (39), 1045 (13), 959 (11), 828 (35), 767 (16), 651 (9), 543 (11), 516 (14), 352 (11), 194 (13), 79 (49), 838 (30), **IR** (ATR, 300 K, [cm^{-1}]): 3394 (vw), 2979 (vw), 1751 (s), 1713 (w), 1619 (m), 1607 (m), 1543 (m), 1509 (vw), 1456 (w), 1420 (w), 1392 (w), 1366 (m), 1344 (m), 1306 (w), 1284 (w), 1230 (vs), 1211 (s), 1188 (m), 1141 (m), 1108 (w), 1093 (w), 1032 (s), 1006 (s), 992 (s), 967 (m), 947 (m), 918 (vs), 903 (vs), 880 (m), 829 (m), 801 (w), 756 (m), 745 (m), 666 (w), 648 (w), 612 (w), 574 (m), 559 (m), 540 (m), 514 (m), 494 (w), 473 (s), 437 (m), 414 (m), **^{1}H-NMR** (500 MHz, DMSO-$d_{6,\ anhydrous}$): δ [ppm] = 1.06 (6H, t, $^3J_{CH3,CH2}$ = 7.0 Hz, EtOH-CH_3), 1.77 (6H, s, 19-H), 1.90 (6H, s, 21-H), 2.10 (6H, s, 23-H), 3.32 (2H, s, H_2O) 3.41-3.47 (6H, m, EtOH-CH_2), 4.18 (2H, d, $^2J_{6H,6H'}$ = 10.0 Hz, 6-H), 4.33-4.37 (3H, m, 6-H', EtOH-OH), 4.70 (2H, dd, $^3J_{1H,2H}$ = 2.9 Hz, $^3J_{2H,3H}$ = 9.3 Hz, 2-H), 4.79-4.82 (2H, m, 5-H), 5.07 (2H, *pseudo*-t, $^3J_{3H,4H}$ = 9.6 Hz, $^3J_{4H,5H}$ = 10.1 Hz, 4-H), 5.70 (2H, *pseudo*-t, $^3J_{2H,3H}$ = 9.3 Hz, $^3J_{3H,4H}$ = 9.7 Hz, 3-H), 6.96 (2H, d, $^3J_{1H,2H}$ = 2.9 Hz, 1-H), 7.24 (2H, *pseudo*-t, $^3J_{12H,13H}$ = 7.9 Hz, $^3J_{13H,14H}$ = 6.6 Hz, 13-H), 7.28 (2H, d, $^3J_{9H,10H}$ = 9.0 Hz, 9-H), 7.53 (2H, *pseudo*-t, $^3J_{13H,14H}$ = 6.6 Hz, $^3J_{14H,15H}$ = 8.7 Hz, 14-H), 7.80 (2H, d, $^3J_{12H,13H}$ = 7.9 Hz, 12-H), 8.06 (2H, d, $^3J_{9H,10H}$ = 9.0 Hz, 10-H), 8.32 (2H, d, $^3J_{14H,15H}$ = 8.7 Hz, 15-H), 9.98 (2H, s, 17-H), **^{13}C{^{1}H}-NMR** (125 MHz, DMSO-$d_{6,\ anhydrous}$): δ [ppm] = 18.53 (1C, s, EtOH-CH_3), 20.28 (2C, s, 19-C), 20.43 (2C, s, 21-C), 20.65 (2C, s, 23-C), 55.98 (2C, s, EtOH-CH_2), 62.93 (2C, s, 6-C), 66.02 (2C, s, 5-C), 69.50 (2C, s, 4-C), 73.16 (2C, s, 3-C), 79.78 (2C, s, 2-C), 99.20 (2C, s, 1-C), 112.48 (2C, s, 16-C), 119.49 (2C, s, 15-C), 121.86 (2C, s, 13-C), 124.68 (2C, s, 9-C), 126.54 (2C, s, 7-C), 127.37 (2C, s, 14-C), 128.70 (2C, s, 12-C), 134.68 (2C, s, 11-C), 135.31 (2C, s, 10-C), 162.62 (2C, s, 17-C), 169.08 (2C, s, 18-C), 169.59 (2C, s, 20-C), 170.22 (2C, s, 22-C), 170.71 (2C, s, 8-C), **Elemental analysis:** calculated for $C_{46}H_{46}N_2O_{22}U_2\cdot 1.5\ C_2H_6O\cdot 0.25\ H_2O$, C: 38.50%, H: 3.66%, N: 1.83%; found C: 38.11%, H: 3.303%, N: 1.84%.

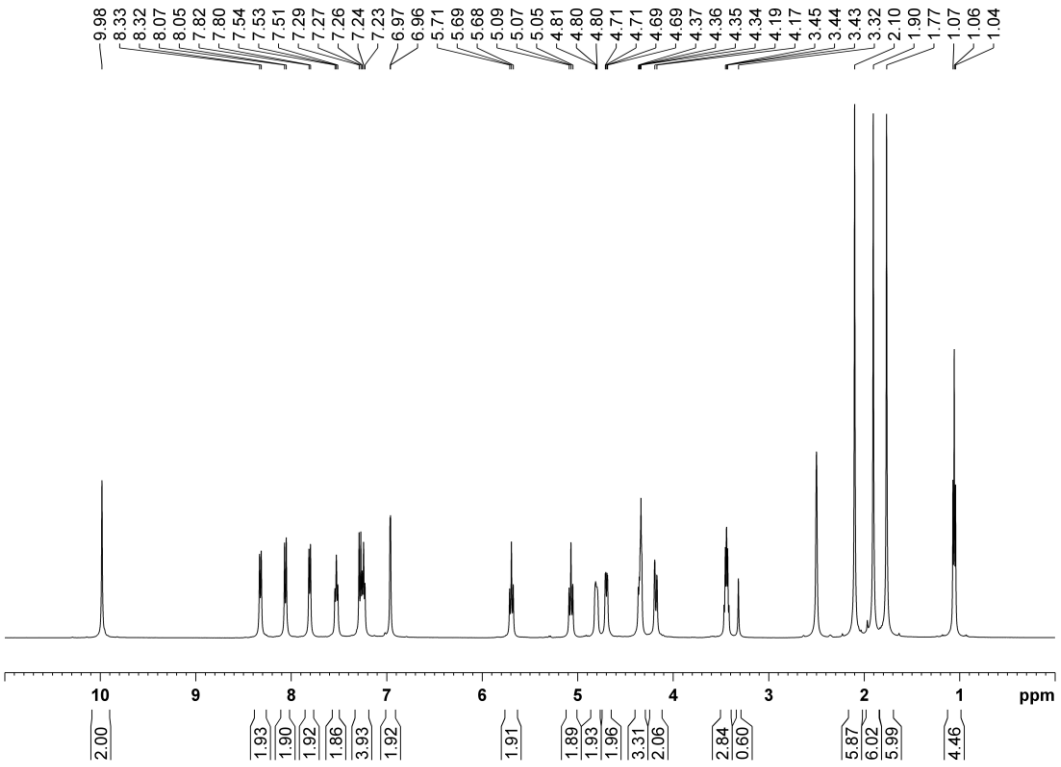


Fig. S16. ^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **1**·1.5EtOH·0.25H_2O.

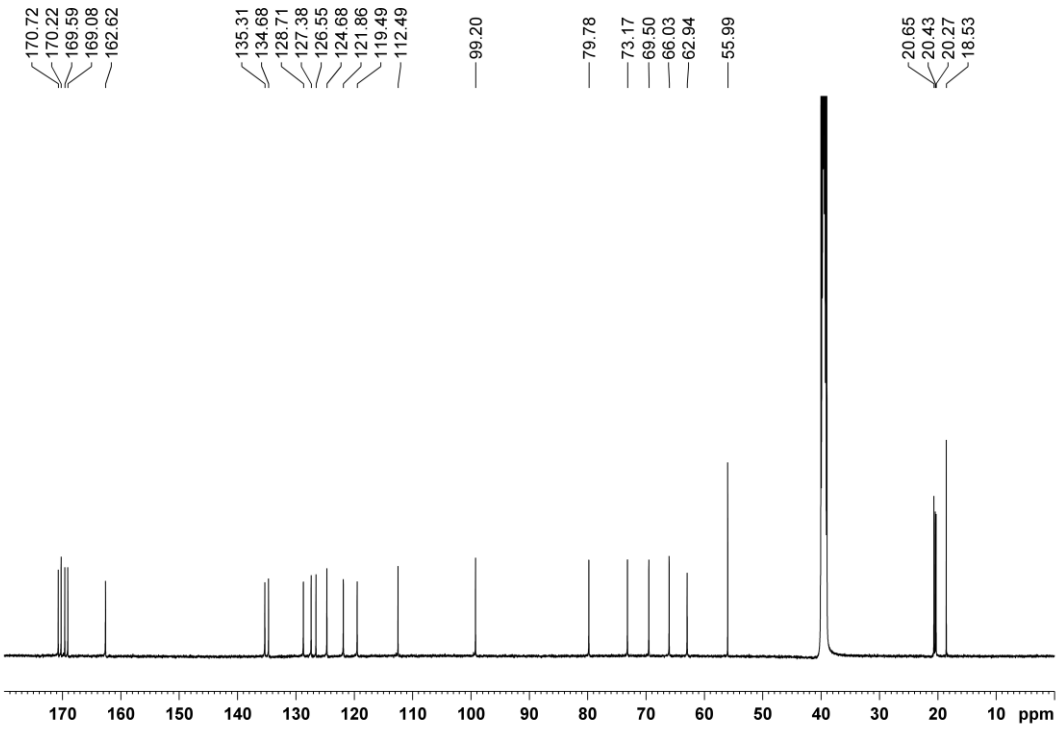
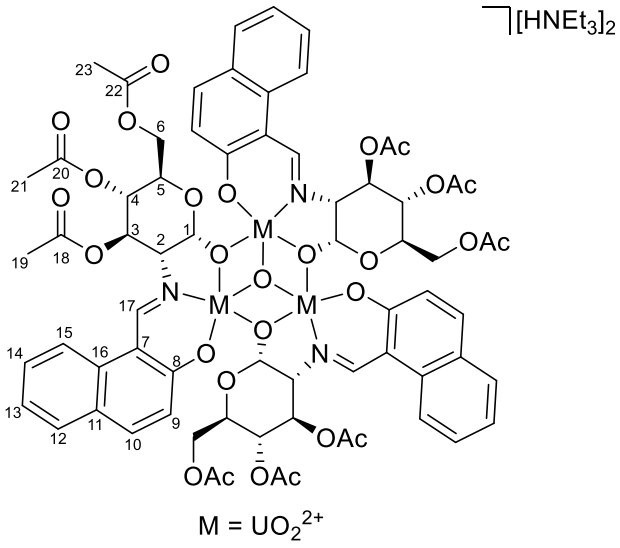


Fig. S17. ^{13}C{^{1}H}-NMR (125 MHz, DMSO-d_6) spectrum of **1**·1.5EtOH·0.25H_2O.

5.2 Synthesis of $[HNEt_3]_2[(UO_2)_3(\mu_3\text{-}O)(L)_3]$ ($[HNEt_3]_2$[2])



To prepare $[HNEt_3]_2$[**2**], **1**·1.5EtOH·0.25H_2O (102 mg, 66.7 µmol, 1.5 eq.) was dissolved in 2 ml MeCN and triethylamine (940 µl, 682 mg, 6.74 mmol, 101 eq.) was added. Then diethyl ether was allowed to diffuse into this solution over 5 days. The orange crystals obtained were filtered off, washed with diethyl ether (3 x 2 ml), and dried in vacuo. The target compound was isolated as a yellow solid.

Yield: 95 mg (39.5 µmol, 89%), **m.p.:** 214°C (decomp.), **Raman** (100 mW, 100 scans, 300 K, [cm^{-1}]): 3066 (8), 2939 (22), 1610 (40), 1542 (47), 1437 (100), 1394 (86), 1347 (48), 1039 (10), 957 (8), 806 (32), 767 (10), 540 (7), 515 (7), 192 (9), 92 (46), **IR** (ATR, 300 K, [cm^{-1}]): 3454 (vw), 2881 (vw), 1607 (s), 1539 (m), 1506 (w), 1455 (m), 1434 (m), 1417 (m), 1391 (m), 1361 (s), 1345 (m), 1311 (w), 1294 (w), 1230 (vs), 1182 (m), 1145 (m), 1118 (m), 1088 (w), 1067 (m), 1021 (vs), 981 (s), 913 (w), 879 (vs), 832 (s), 799 (m), 764 (m), 743 (s), 686 (w), 666 (w), 648 (w), 608 (w), 573 (m), 558 (m), 455 (vs), 429 (s), **^{1}H-NMR** (500 MHz, MeCN-d_3): δ [ppm] = 0.48 (18H, t, $^3J_{CH3,CH2}$ = 7.4 Hz, $HNEt_3^+$), 1.87 (9H, s, 19-CH_3, 21-CH_3), 1.93-1.95 (9H, m, 19-CH_3, 21-CH_3), 2.05 (12H, q, $^3J_{CH3,CH2}$ = 7.4 Hz, $HNEt_3^+$), 2.18 (9H, s, 23-CH_3), 4.67 (3H, dd, $^2J_{6H,6H'}$ = 11.8 Hz, $^3J_{5H,6H}$ = 2.8 Hz, 6-H), 4.88 (3H, d, $^2J_{6H,6H'}$ = 11.8 Hz, 6-H'), 5.20-5.22 (3H, m, 2-H), 5.48-5.57 (6H, m, 4-H, 5-H), 6.23 (3H, pseudo-t, $^3J_{2H,3H}$ = 9.2 Hz, $^3J_{3H,4H}$ = 9.3 Hz, 3-H), 7.10 (3H, s(br., $v_{1/2}$ = 11 Hz, 1-H), 7.23 (3H, *pseudo*-t, $^3J_{12H,13H}$ = 8.0 Hz, $^3J_{13H,14H}$ = 6.7 Hz, 13-H), 7.52 (3H, *pseudo*-t, $^3J_{13H,14H}$ = 6.7 Hz, $^3J_{14H,15H}$ = 8.5 Hz, 14-H), 7.65 (3H, d, $^3J_{9H,10H}$ = 9.0 Hz, 9-H), 7.78 (3H, d, $^3J_{12H,13H}$ = 8.0 Hz, 12-H), 8.07 (3H, d, $^3J_{9H,10H}$ = 9.0 Hz, 10-H), 8.29 (3H, d, $^3J_{14H,15H}$ = 8.5 Hz, 15-H), 10.21 (3H, s, 17-H), **^{13}C{^{1}H}-NMR** (125 MHz, MeCN-d_3): δ [ppm] = 9.00 (6C, s, $HNEt_3^+$), 21.06 (3C, s, 19-C/21-C/23-C), 21.18 (6C,s, 19-C/21-C/23-C), 46.65 (6C, s, $HNEt_3^+$), 63.55 (3C, s, 5-C), 67.96 (3C, s, 5-C), 70.90 (3C, s, 4-C), 74.95 (3C, s, 3-C), 81.57 (3C, s, 2-C), 102.42 (3C, s, 1-C), 113.59 (3C, s, 16-C), 120.86 (3C, s, 15-C), 122.94 (3C, s, 13-C), 125.85 (3C, s, 9-C), 128.11 (3C, s, 11-C), 128.18 (3C, s, 14-C), 129.73 (3C, s, 12-C), 135.86 (3C, s, 7-C), 136.21 (3C, s, 10-C), 171.01 (3C, s, 18-C/20-C), 171.04 (3C, s, 18-C/20-C), 171.91 (3C, s, 22-C), 173.51 (3C, s, 8-C), **Elemental analysis:** calculated for $C_{81}H_{101}N_5O_{34}U_3$ C: 40.49%, H: 4.24%, N: 2.91%, found C: 40.27%, H: 3.875%, N:3.06%.

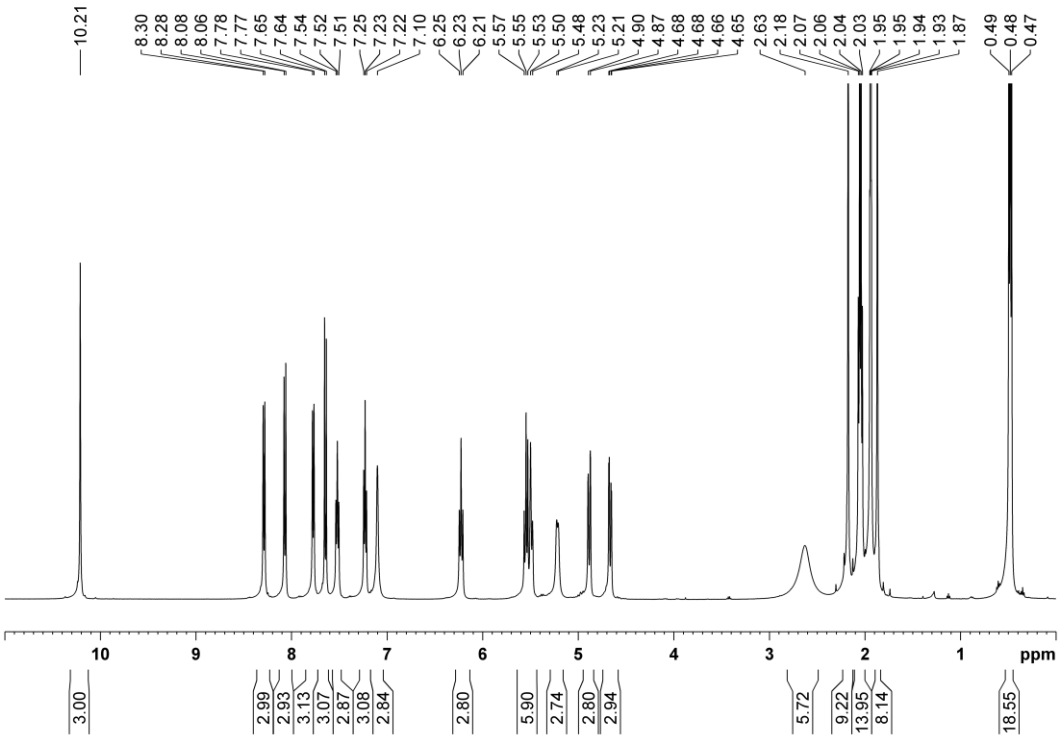


Fig. S18. ^{1}H-NMR (500 MHz, CD_3CN) of $[HNEt_3]_2$[**2**].

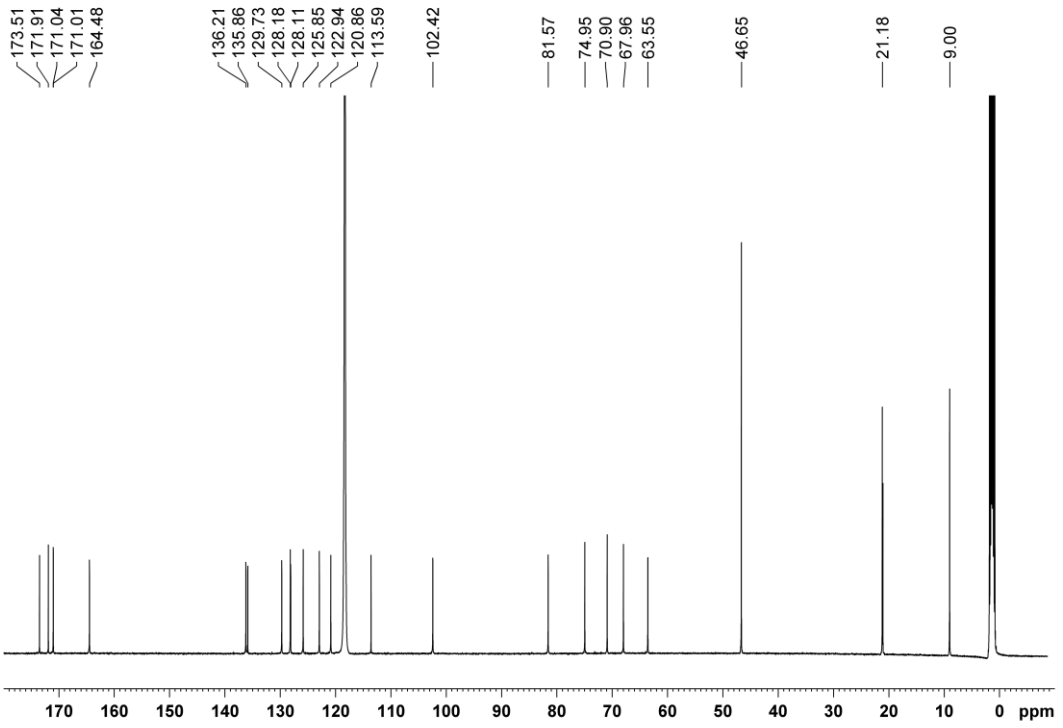


Fig. S19. $^{13}C\{^{1}H\}$-NMR (125 MHz, CD_3CN) of $[HNEt_3]_2$[**2**].

6 High resolution mass measurement

6.1 In situ preparation and measurement of 2^{2-}.

Water (20 µl) was added to a solution of **1**·1.5EtOH·0.25H_2O (12 mg, 8.2 µmol, 1.5 eq.) in MeCN (1 ml) and the mixture was stirred for 5 min. Anhydrous NEt_3 (10 µl, 72 µmol, 9.0 eq.) was added and the reaction mixture was stirred for another 5 min. An aliquot of 10 µl of the reaction solution was diluted to 1 ml in MeCN and mixed rigorously. From this solution another aliquot of 100 µl was again diluted to 1 ml, resulting in a total dilution of 1:1000 (c(**2**$^{2-}$) = 12 µg/ml). The sample was filtered through a syringe filter (PTFE, 0.2 µm) and injected into the mass spectrometer.

HRMS (ESI$^-$): m/z 1098.7577 (**2**$^{2-}$, calc. $C_{69}H_{69}N_3O_{34}U_3^{2-}$ = 1098.7648), 2198.5198 ({**2**+H}$^-$, calc. $C_{69}H_{70}N_3O_{34}U_3^-$ = 2198.5370)

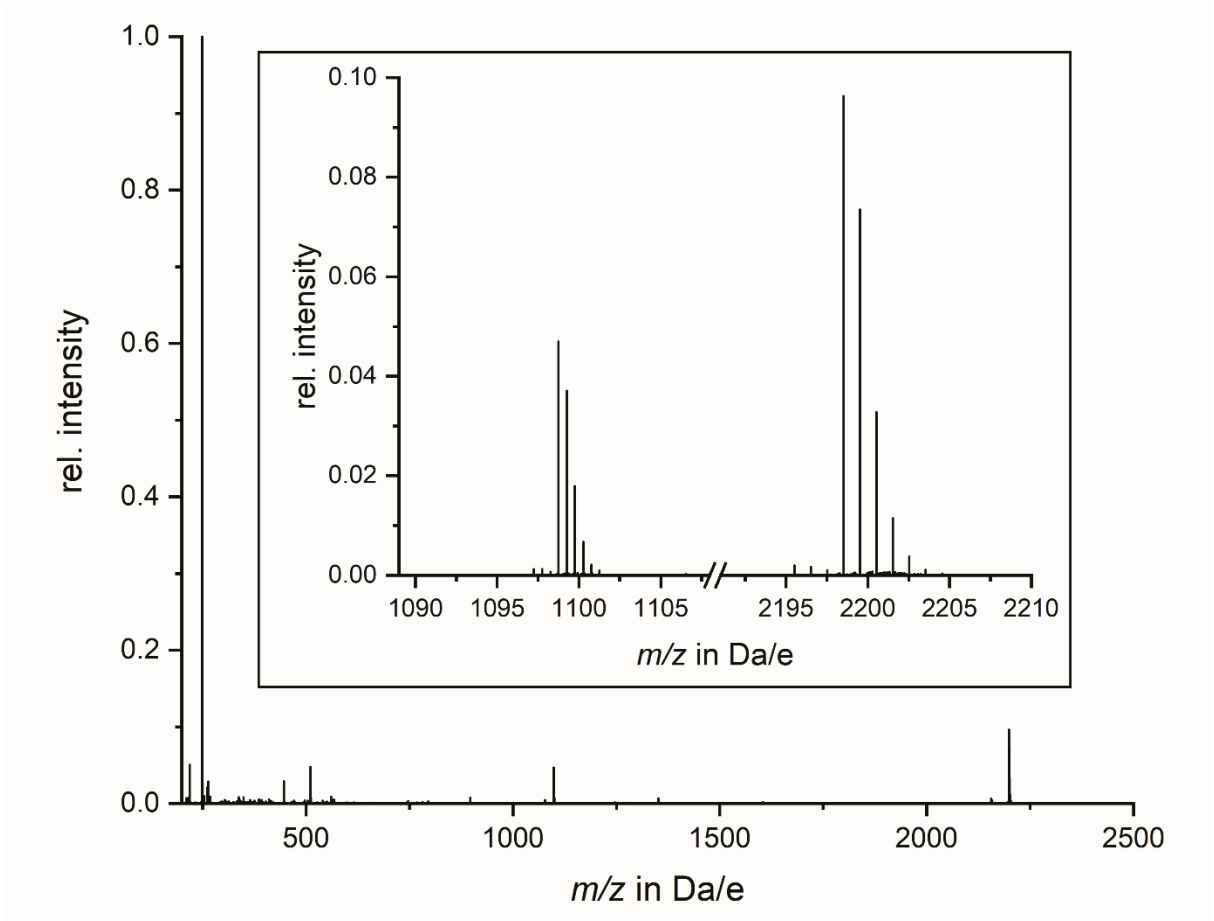


Fig. S20. Mass spectrum of **2**$^{2-}$ prepared in situ, showing a magnification of the molecular peaks for **2**$^{2-}$ and {**2**+H}$^-$.

6.2 In situ preparation and measurement of $[(UO_2)_3(\mu_3\text{-}^{18}O)(L)_3]^{2-}$ (2^{*2-}).

$H_2{}^{18}O$ (20 µl) was added to a solution of **1**·1.5EtOH·0.25H_2O (12 mg, 8.2 µmol, 1.5 eq.) in dry MeCN (1 ml) and the mixture was stirred for 5 min. Anhydrous NEt_3 (10 µl, 72 µmol, 9.0 eq.) was added and the reaction mixture was stirred for another 5 min. An aliquot of 10 µl of the reaction solution was diluted to 1 ml in MeCN under atmospheric conditions and mixed rigorously. From this solution another aliquot of 100 µl was again diluted to 1 ml, resulting in a total dilution of 1:1000 (c(**2***$^{2-}$) = 12 µg/ml). The sample was filtered through a syringe filter (PTFE, 0.2 µm) and injected into the mass spectrometer.

HRMS (ESI$^-$): m/z 1099.7591 (**2***$^{2-}$, calc. $C_{69}H_{69}N_3O_{33}{}^{18}OU_3{}^{2-}$ = 1099.7670), 2200.5231 ({**2***+H}$^-$, calc. $C_{69}H_{70}N_3O_{33}{}^{18}OU_3{}^-$ = 2200.5412)

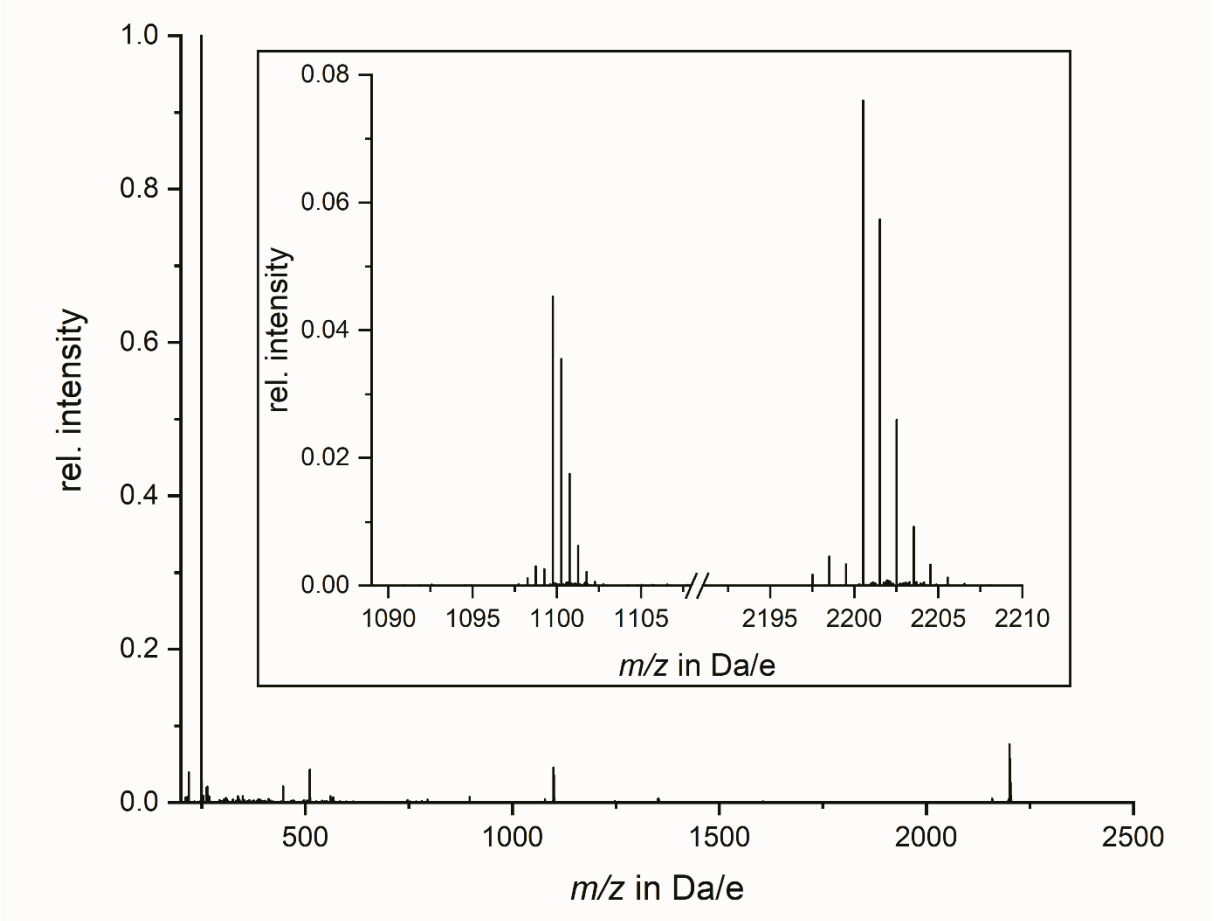


Fig. S21. Mass spectrum of in situ prepared **2***$^{2-}$, showing a magnification of the molecular peaks for **2***$^{2-}$ and {**2***+H}$^-$.

7 Crystallographic details

Suitable single crystals were coated with Paratone-N oil or Fomblin Y25 PFPE oil, mounted using a glass fiber and frozen in the cold nitrogen stream. X-ray diffraction data were collected at 100 K on a Rigaku Oxford Diffraction SuperNova diffractometer using Cu Kα radiation (λ = 1.54184 Å) generated by a micro-focus source. The data reduction and absorption correction were performed using CrysAlisPro.[8] For further crystal and data collection details see Table S4. The structures were solved using Olex2[9] with the SHELXT package[10] and were refined with SHELXS[11]. Images of the structures were produced with Olex2[9] software.

The structure containing DMSO was refined using SQUEEZE to account for disordered water molecules in the lattice. The SQUEEZE program of PLATON[12] has identified 8 voids of about 25 A^2 each containing 5-8 electrons which accounts for fractional occupied water molecules. The total electron count of 54 electrons per cell accounts for about 6 water molecules, i.e. 1.5 per formula unit. Furthermore some DMSO molecules had to be restrained by SIMU and RIGU commands to yield a converging refinement.

The structure containing benzonitrile was refined as an inversion twin with a minor component of only 4%. The SQUEEZE program of PLATON has identified a void of about 6345 A^2 containing 1823 electrons which accounts for disordered solvent molecules of benzonitrile and diethyl ether. The total electron count of 455 electrons per a.u. for one molecule of benzonitrile and one molecule of diethyl ether, which could be identified in the difference fourier map and approximately another 7 undefined molecules of this type. In order to yield a converging refinement some DFIX, SADI, SIMU and EADP restraints and constraints had to be applied. The hydrogen positions of the hydronium ion and the hydroxo ligand were modelled and refined in positions appropriate for the hydrogen bonding network.

Table S4. Crystallographic data and details of the structure refinements for compounds **II**, 2[**1**$(DMSO)_2$]·DMSO·H_2O, $[H_3O][H\mathbf{2}]\cdot[\mathbf{1}(H_2O)(PhCONH_2)]\cdot 2PhCN\cdot Et_2O$.

	II	2[**1**$(DMSO)_2$]·DMSO·H_2O	$[H_3O][H\mathbf{2}]\cdot[\mathbf{1}(H_2O)(PhCONH_2)]\cdot 2PhCN\cdot Et_2O$
Empirical formula	$C_{22}H_{27}NO_{10}$	$C_{102}H_{124}N_4O_{50}S_5U_4$	$C_{140}H_{148}N_8O_{60}U_5$
FW (g mol^{-1})	465.44	3318.46	4092.81
Temperature (K)	100.00(10)	100.03(19)	100.00(10)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
***a* (Å)**	5.74940(10)	12.89840(10)	20.89580(10)
***b* (Å)**	14.25760(10)	21.5255(3)	23.13860(10)
***c* (Å)**	28.6021(3)	42.4726(4)	40.88710(10)
***α* (°)**	90	90	90
***β* (°)**	90	90	90
***γ* (°)**	90	90	90
***V* (Å^3)**	2344.59(5)	11792.3(2)	19768.89(14)
Z	4	4	4
ρ_{calc} (g cm^{-3})	1.319	1.869	1.375
μ (mm^{-1})	0.889	16.892	11.985
F(000)	984.0	6448.0	7936.0
Crystal size (mm^{-3})	0.415 x 0.156 x 0.126	0.235 x 0.075 x 0.059	0.196 x 0.152 x 0.134
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection (°)	6.18 to 153.254	4.602 to 153.562	4.75 to 153.394
Index ranges	-6 ≤ h ≤ 7, -17 ≤ k ≤ 14, -36 ≤ l ≤ 29	-16 ≤ h ≤ 10, -27 ≤ k ≤ 24, -52 ≤ l ≤ 53	-23 ≤ h ≤ 26, -29 ≤ k ≤ 27, -51 ≤ l ≤ 47
Reflections collected	10772	107491	210322
Independent reflections	4828 [R_{int} = 0.0414, R_{sigma} = 0.0496]	24579 [R_{int} = 0.0664, R_{sigma} = 0.0536]	41376 [R_{int} = 0.0342, R_{sigma} = 0.0249]
Data/restraints/ parameters	4828/0/304	24579/98/1536	41376/107/1745
Goodness-of-fit on F^2	1.047	1.043	1.055
Final R indexes [I ≥ 2σ (I)]	R_1 = 0.0433, wR_2 = 0.1155	R_1 = 0.0422, wR_2 = 0.1080	R_1 = 0.0352, wR_2 = 0.0916
Final R indexes [all data]	R_1 = 0.0444, wR_2 = 0.1174	R_1 = 0.0470, wR_2 = 0.1118	R_1 = 0.0353, wR_2 = 0.0916
Largest diff. peak/hole (*e* Å^{-3})	0.26/-0.28	1.93/-1.90	1.34/-2.19
CCDC	2119924	2119925	2119926

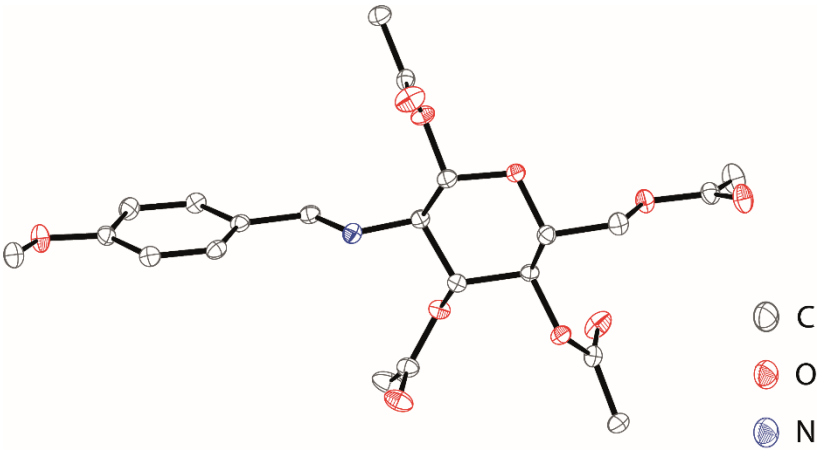


Fig. S22. Crystal structure of **II**. Ellipsoids drawn at 50% probability. H-atoms omitted for clarity.

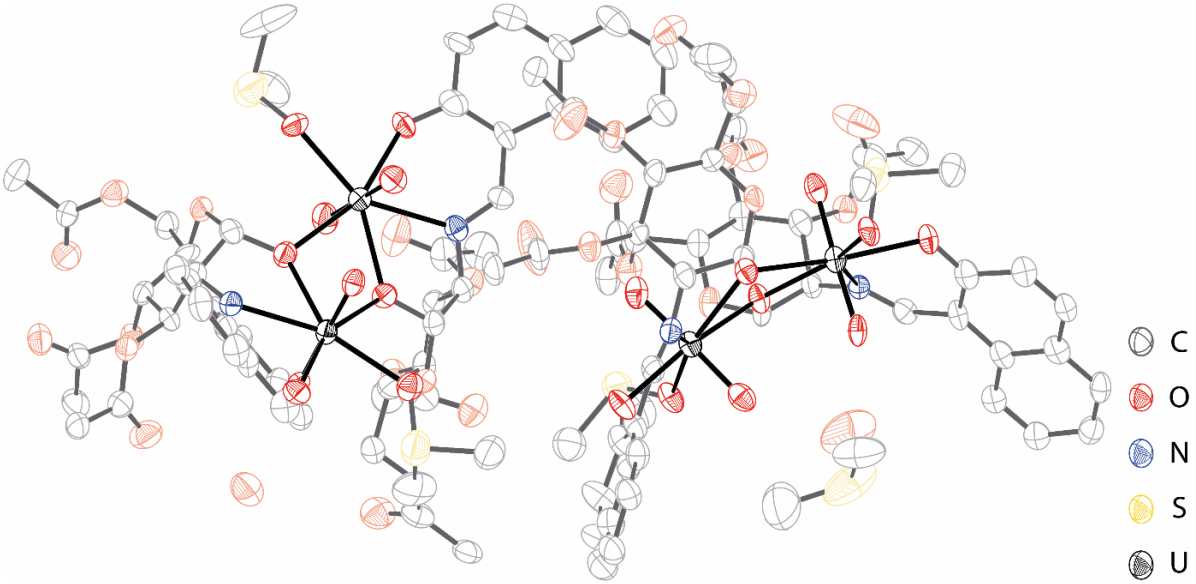


Fig. S23. Crystal structure of 2[**1**$(DMSO)_2$]·DMSO·H_2O. The central uranyl coordination environment is emphasized for better visibility. Ellipsoids drawn at 50% probability. H-atoms omitted for clarity.

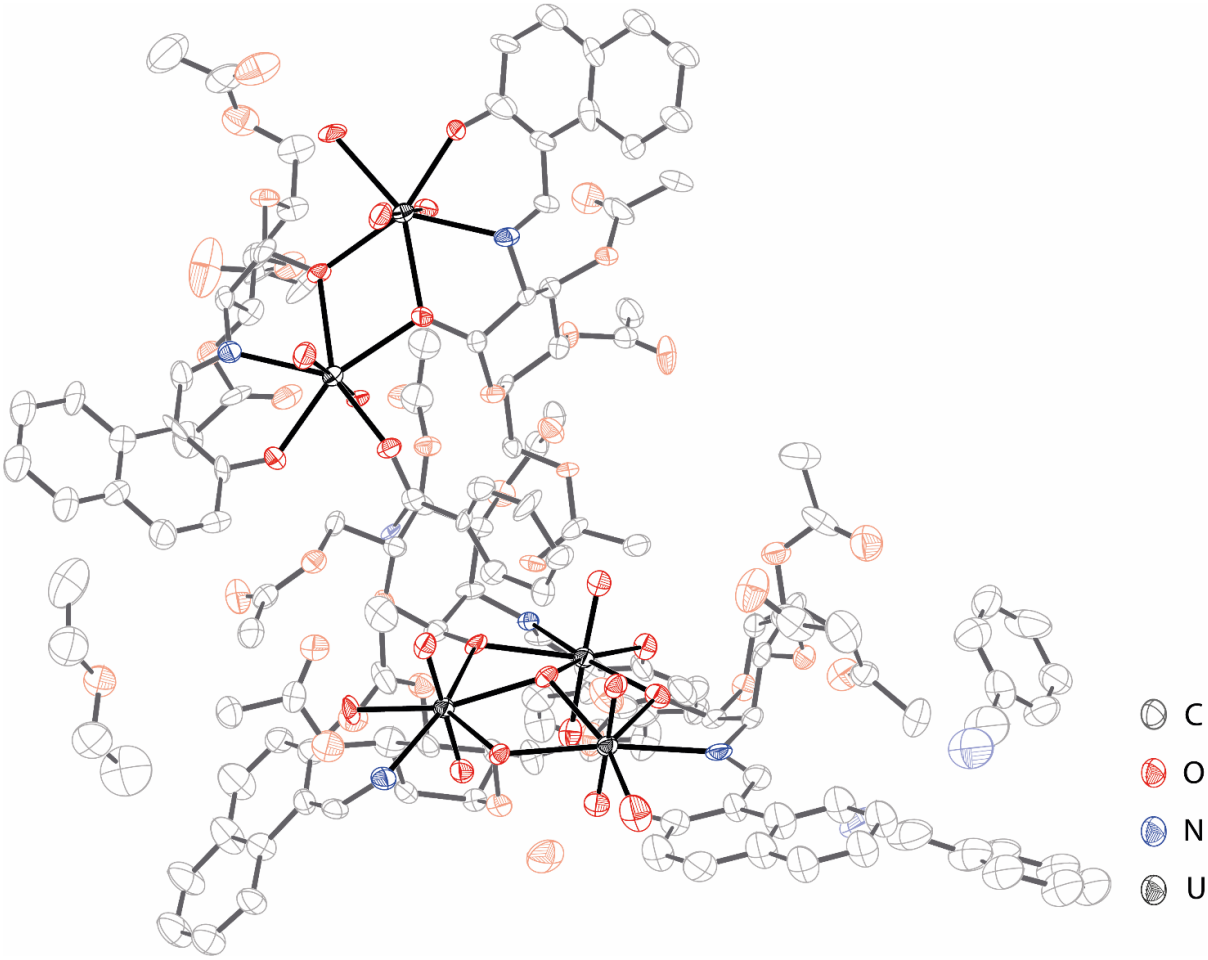


Fig. S24. Crystal structure of $[H_3O][H\mathbf{2}]\cdot[\mathbf{1}(H_2O)(PhCONH_2)]\cdot 2PhCN\cdot Et_2O$. The central uranyl coordination environment is emphasized for better visibility. Ellipsoids drawn at 50% probability. H-atoms omitted for clarity.

7.1 Bond valence sum analysis of μ_3-OH in $[H_3O][H2]\cdot[1(H_2O)(PhCONH_2)]\cdot 2PhCN\cdot Et_2O$

Bond valence sum (BVS) calculations were done for the central μ_3-OH ligand in $[H_3O][H\mathbf{2}]\cdot[\mathbf{1}(H_2O)(PhCONH_2)]\cdot 2PhCN\cdot Et_2O$ according to literature.[13] The valency of a bond i-j can be calculated according to (Eq. 1), with the total valence of the atom I being a sum of all its bonds (Eq. 2).

$$v_{ij} = exp\left(\frac{R_{ij}^0 - d_{ij}}{b}\right) \quad (1)$$

$$\sum_j v_{ij} = V_i \quad (2)$$

With: v_{ij} Valence of the bond between i and j

V_i Valence of the atom i

R_{ij}^0 Bond valence parameter

d_{ij} Observed bond length

b Empirical parameter = 0.37

Given the observed bond lengths d_{UO} = 2.4090(6) Å, 2.3816(6) Å, 2.4026(10) Å and the bond valence parameter R_{UO}^{0}= 2.075 from literature,[13] the valence of the U-O bond was calculated as $v_{UO} \approx 0.42$. Likewise, the H-O valence was calculated as $v_{HO} \approx 0.77$, with dd_{HO} = 0.9 Å and R_{HO}^{0}= 0.805, giving a total valence for the hydroxo ligand of V_O = 2.03.

8 References

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