SUPPORTING INFORMATION

Directed Nucleation of Monomeric and Dimeric Uranium(VI) Complexes with a Room Temperature Carboxyl-Functionalized Phosphonium Ionic Liquid

Xiao-Yan Chen, George S. Goff,* Mauricio Quiroz-Guzman, Daniel P. Fagnant Jr., Joan F. Brennecke, Brian L. Scott, and Wolfgang Runde*

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Experimental Section

Materials. Trimethylphosphine and bromoacetic acid were purchased from Aldrich. Anhydrous acetonitrile was used as received from VWR. Anhydrous deuterated dimethyl sulfoxide (DMSO-d_6) was obtained from Cambridge Isotope Laboratories. Anhydrous deuterated acetonitrile (CD_3CN) was purchased from Acros. $LiTf_2N$ was purchased from 3M. All other chemicals were purchased from Fisher Scientific, Inc.. The deionized water has a specific resistance $\geq$ 18.0 MΩ·cm. UO_2CO_3 was prepared in a manner similar to that reported for PuO_2CO_3.[1] Crystals of $UO_2(NO_3)_2\cdot 6H_2O$ were dissolved into water and the pH was adjusted to 7 with NH_4OH. CO_2 was sparged through the solution and solution was periodically exchanged for fresh deionized water. The reaction was monitored by changes in the O=U=O Raman frequency until no additional changes were observed with the final value of 885 cm^{-1}.[2] The solid was triply rinsed with deionized water, re-suspended in distilled deionized water, sparged with CO_2 for another day and stored under CO_2 atmosphere. Aliquats were removed for each experiment. [Hbet][Tf_2N] was prepared according to literature method.[3] [HCTMP][Tf_2N] was prepared by a modified method.[4-6]

Synthesis of [HCTMP]Br. Inside the glove box, bromoacetic acid (45.8257 g, 329.8 mmol) dissolved in anhydrous CH_3CN (80 mL) was transferred into an addition funnel with leveling arm. The addition funnel was fitted into a 100 mL Schlenk flask in which trimethyl phosphine (34 mL, 329 mmol) was dissolved in CH_3CN (30 mL). The assembled equipment was brought outside to an ice bath and charged with a positive dry nitrogen flow. Bromoacetic acid was added dropwise into trimethyl phosphine over one hour under vigorous stirring. The temperature was then slowly increased to RT. After stirring overnight, CH_3CN was eveporated to get a white solid, which was dispersed in isopropanol and filtered through a fine frit, repeated 3 times in total. The white solid was air dried in frit under a nitrogen atmosphere, and then in vacuum line at 45°C. ^1H NMR (DMSO-d_6): $\delta = 1.95$ (d, 15.3 Hz, 9H, P(CH_3)$_3$), 3.75 (d, 14.9 Hz, 2H, CH_2COOH), 13.56 (s, 1H, COOH). ^{31}P NMR (DMSO-d_6): $\delta = 26.86$ (s, P(CH$_3$)$_3$).

Synthesis of [HCTMP][Tf_2N]. [HCTMP]Br (23.8369 g, 110.85 mmol), LiTf_2N (30.1887 g, 133.02 mmol) and millipore water (200 mL) were added into a 500 mL round bottom flask. After stirring overnight at RT, the reaction mixture was washed five times with millipore water (50 mL each time). The resulting pale pink ionic liquid was dried in vacuum line at 60°C for 2 weeks. ^1H NMR (DMSO-d_6): $\delta = 1.89$ (d, 1.89, 15.11 Hz, 9H, P(CH_3)$_3$), 3.59 (d, 14.65 Hz, 2H, CH_2COOH), 13.31 (s, 1H, COOH). ^{13}C NMR (DMSO-d_6): $\delta = 7.9$ (d, 55.13 Hz, P(CH$_3$)$_3$), 30.5 (d, 56.8 Hz, CH$_2$COOH), 119.7 (q, 321.7 Hz, SO$_2$$CF_3$), 167.3 (d, 4.9 Hz, CH$_2$$C$OOH). ^{31}P NMR (DMSO-d_6): $\delta = 26.72$ (s, P(CH$_3$)$_3$).

Synthesis of [$UO_2(CTMP)_3(H_2O)_2$][Tf_2N]$_2$ (1). [HCTMP][Tf_2N] (0.5 mmol, 207.6 mg) was dissolved in 5 mL of deionized water in a 20 mL borosilicate scintillation vial at around 90°C. UO_2CO_3 (0.17 mmol, 56 mg) was added into the above solution and stirred for 30 minutes to get a clear solution. Water was added to bring the final volume to 5 mL and the final pH was 3. The solution was filtered through a 0.45 μm polyamide syringe filter and transferred to a 20 mL borosilicate scintillation vial, allowing for slow evaporation at RT. After one week, yellow needle-like crystals suitable for single crystal analysis were obtained (51 mg, yield: 23.6%). Mp. 172°C. Crystal data for **1**: $C_{19}H_{37}F_{12}N_2O_{18}P_3S_4U$, $M_r = 1268.69$, triclinic space group P-1, $a = 8.3319(7)$ Å, $b = 21.0439(19)$ Å, $c = 24.947(2)$ Å, $\alpha = 100.891(1)^o$, $\beta = 90.379(1)^o$, $\gamma = 96.996(1)^o$, $V = 4261.4(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.977$ g cm^{-3}, $T = 120(1)$ K, F(000) = 2472, $\mu(Mo_{k\alpha})$

= 4.237 mm^{-1}, yellow needle-like crystal, 47416 reflections measured, 18927 unique (R_{int} = 0.0384), R_1 = 0.0326 ($I > 2\sigma(I)$), wR_2 = 0.0651 (all data), GOF = 1.024.

Synthesis of [UO$_2$(CTMP)$_3$]$_2$[NTf$_2$]$_4$ (2). [HCTMP][Tf$_2$N] (1.0 mmol, 415.2 mg) was dissolved in 5 mL of deionized water in a 20 mL borosilicate scintillation vial at around 90°C. UO_2CO_3 (0.33 mmol, 109 mg) was added into the above solution and stirred 45 min to get a clear solution. Water was added to bring the final volume to 5 mL and the final pH was 2.2. The solution was filtered through a 0.45 µm polyamide syringe filter and transferred to a 20 mL borosilicate scintillation vial, allowing for slow evaporation at RT. After one week, yellow block crystals suitable for single crystal analysis were obtained (127 mg, yield: 31.2%). Mp. 153°C. Crystal data for **2**: $C_{38}H_{66}F_{24}N_4O_{32}P_6S_8U_2$, M_r = 2465.31, triclinic space group P-1, a = 14.9671(7) Å, b = 17.1019(8) Å, c = 17.3543(8) Å, α = 87.020(1)°, β = 77.318(1)°, γ = 74.0413(4)°, V = 4166.5(3)Å^3, Z = 2, ρ_{calcd} = 1.965 g cm^{-3}, T = 120(1) K, F(000) = 2392, $\mu(\mathrm{Mo}_{\mathrm{k}\alpha})$ = 4.327 mm^{-1}, yellow block crystal, 47312 reflections measured, 19106 unique (R_{int} = 0.0287), R_1 = 0.0237 ($I > 2\sigma(I)$), wR_2 = 0.0535 (all data), GOF = 1.060.

General Methods. Raman spectra were collected with Nicolet Magna-IR 560 ESD with a Raman accessory. NMR spectra in DMSO-d_6 were measured on a Varian VXR-300 for ^{31}P or a Varian INOVA-500 spectrometer for ^{1}H and ^{13}C. NMR spectra in CD_3CN were obtained at room temperature using a Bruker ARX-300 spectrometer equipped with 5- and 10-mm multinuclear probes (^{1}H and ^{13}C). The electrochemical experiments were performed using a computer-controlled Solartron 273A Potentiostat/Galvanostat (EG&G, Princeton Applied Research). All the electrodes (diameter 1 mm) were purchased from Cypress Systems. Water content was measured by Karl-Fisher titration using an 852 Titrando (Metrohm USA, Inc.). The water contents of [Hbet][Tf$_2$N] and [HCTMP][Tf$_2$N] for electrochemical measurement were 0.095 wt. % and 0.46 wt.%, respectively. The melting point determined with a Buchi M-560 Melting Point apparatus. Thermal gravimetric analyses were recorded in a Mettler Toledo TGA 851e where products were heated at a rate of 10°C/min from 25 to 500°C (dynamic decomposition) under a N_2 atmosphere. The glass transition temperature was determined with a Mettler Toledo DSC822e differential scanning calorimeter at a ramp rate of 10°C/min from -120 to 110°C under N_2. Density measurements were taken with a Anton Paar DMA 4500 oscillating u-tube densitometer. Uncertainty for density is estimated to be $\pm 5 \times 10^{-5}$ g cm^{-1}. Temperature is controlled with two internal Pt 100 thermometers with an uncertainty of ± 0.01 K. Viscosity measurements were done using a Reologica Viscoanalyser parallel plate viscometer with an uncertainty (Less than or within) ± 5% and temperature precision of 0.1 K.

Crystallography. Single crystals were mounted using a nylon cryoloop and Paratone-N oil. The data were collected on a Bruker D8 diffractometer, with an APEX II charge-coupled-device (CCD) detector, and a Bruker Kryoflex low temperature device at 120 K using a liquid nitrogen vapor stream. The instrument was equipped with a graphite monochromatized Mo Kα X-ray source (λ=0.71073 Å). A hemisphere of data was collected using ω scans, with 10-s frame exposures and 0.5^o frame widths. Data collection and initial indexing and cell refinement were handled using APEX II software.[4] Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.[5] The data were corrected for absorption using redundant reflections and the SADABS program.[6] Decay of reflection intensity was not observed as monitored via analysis of redundant frames. The structure was solved using direct methods and difference Fourier techniques. The tertiary and secondary hydrogen atom positions were idealized, but were not refined on water molecules. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, and creation of publication materials were performed using SHELXTL.[7] CCDC reference numbers CCDC 904329 (**1**) and CCDC 904330 (**2**) contain the supplementary crystallographic data. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retreving.html or from the Cambridge Crystallographic Data Center, 12 union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

Table S1. Selected crystal data and structure refinements for $[UO_2(CTMP)_3(H_2O)_2][Tf_2N]_2$ (**1**) and $[UO_2(CTMP)_3]_2[NTf_2]_4$ (**2**).

	1	**2**
formula	$C_{19}H_{37}F_{12}N_2O_{18}P_3S_4U$	$C_{38}H_{66}F_{24}N_4O_{32}P_6S_8U_2$
fw	1268.69	2465.31
crystal system	triclinic	triclinic
space group	*P*-1	*P*-1
a (Å)	8.3319(7)	14.9671(7)
b (Å)	21.0439(19)	17.1019(8)
c (Å)	24.947(2)	17.3543(8)

α (deg)	100.891(1)	87.020(1)
β (deg)	90.379(1)	77.318(1)
γ (deg)	96.996(1)	74.0413(4)
V (Å^3)	4261.4(6)	4166.5(3)
Z	4	2
ρ (g/cm^3)	1.977	1.965
μ (mm^{-1})	4.237	4.327
F(000)	2472	2392
crystal size (mm)	0.28 × 0.10 × 0.06	0.20 × 0.18 × 0.08
θ (deg)	1.99 to 27.45	1.84 to 28.44
Index ranges	$-10 \le h \le 10$	$-19 \le h \le 19$
	$-27 \le k \le 27$	$-22 \le k \le 21$
	$-32 \le l \le 32$	$-23 \le l \le 22$
Min. and max. transmission	0.3833 and 0.7581	0.4782 and 0.7234
GOF on F^2	1.024	1.060
R_1, R_2 [I > 2σ (I)]	0.0326, 0.0603	0.0237, 0.0509
R_1, R_2 (all data)	0.0501, 0.0651	0.0321, 0.0535
Largest diff. peak and hole (e·Å^{-3})	1.122 and -1.115	0.968 and -0.547

Table S2. Selected bond lengths (Å) and angles (deg) of $[UO_2(CTMP)_3(H_2O)_2][Tf_2N]_2$ (**1**) and $[UO_2(CTMP)_3]_2[NTf_2]_4$ (**2**).

1					
Bond lengths (Å)					
U1-O1	1.754(3)	U1-O2	1.769(3)	U1-O4	2.349(3)
U1-O7	2.354(3)	U1-O8	2.395(3)	U1-O10	2.428(3)
U1-O11	2.443(3)	O8-C11	1.267(4)	O9-C11	1.237(4)
O14-C16	1.274(4)	O15-C16	1.243(4)	O16-C26	1.276(4)
O18-C21	1.277(4)	O17-C26	1.235(5)	O19-C21	1.232(5)
Bond angles (°)					
O1-U1-O2	179.49(13)	O1-U1-O4	91.51(11)	O2-U1-O4	88.22(11)
O1-U1-O7	92.47(11)	O2-U1-O7	88.01(11)	O4-U1-O7	142.08(9)
O1-U1-O8	91.31(11)	O4-U1-O8	142.02(9)	O7-U1-O8	75.55(9)

O2-U1-O8	88.64(10)	O1-U1-O10	90.48(11)	O2-U1-O10	89.02(11)
O4-U1-O10	70.10(9)	O7-U1-O10	147.49(9)	O8-U1-O10	72.01(9)
2					
Bond lengths (Å)					
U1-O2	1.7617(19)	U1-O1	1.7681(19)	U1-O7	2.3028(19)
U1-O3	2.3155(17)	U1-O8	2.3930(17)	U1-O5	2.4584(17)
U1-O6	2.4971(18)	U2-O9	1.7664(19)	U2-O10	1.7683(19)
U2-O13	2.3167(17)	U2-O15	2.3215(18)	U2-O16	2.3987(18)
U2-O11	2.4663(18)	U2-O12	2.4732(17)	O4-C1	1.216(3)
O3-C1	1.288(3)	O5-C6	1.263(3)	O6-C6	1.262(3)
O7-C11	1.234(3)	O8-C11	1.260(3)	O11-C16	1.259(3)
Bond angles (º)					
O2-U1-O1	179.19(8)	O2-U1-O7	89.33(8)	O1-U1-O7	90.55(9)
O2-U1-O3	92.07(8)	O1-U1-O3	88.33(8)	O2-U1-O5	89.06(7)
O3-U1-O5	73.53(6)	O7-U1-O5	127.12(6)	O1-U1-O5	90.37(8)
O2-U1-O6	89.52(7)	O1-U1-O6	89.67(7)	O7-U1-O6	74.55(6)

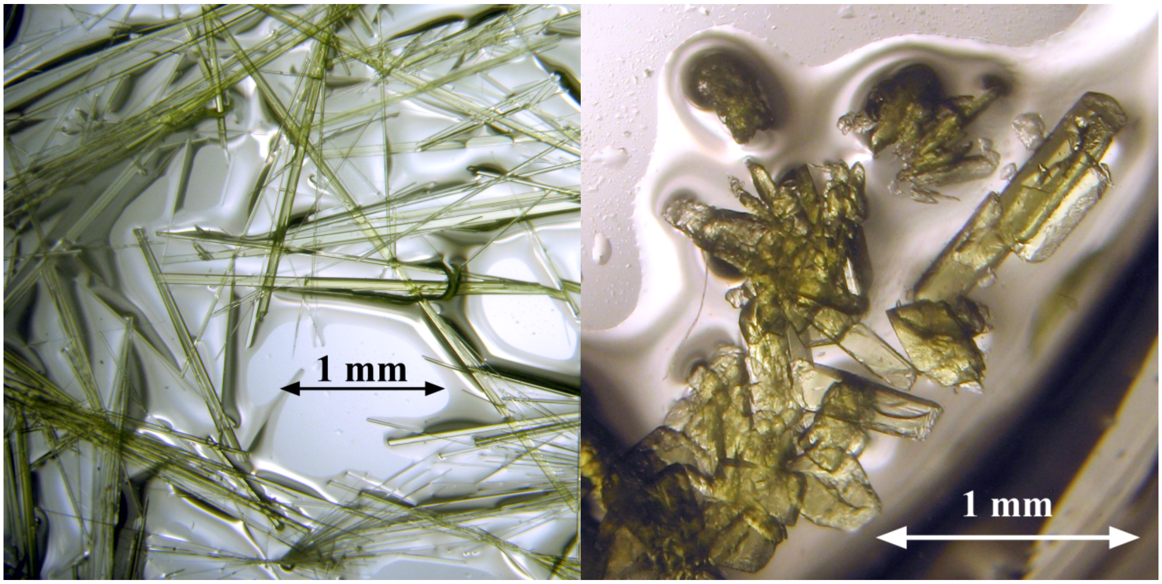

Figure S1. Photographs of single crystals $[UO_2(CTMP)_3(H_2O)_2][Tf_2N]_2$ (**1**) and $[UO_2(CTMP)_3]_2[NTf_2]_4$ (**2**).

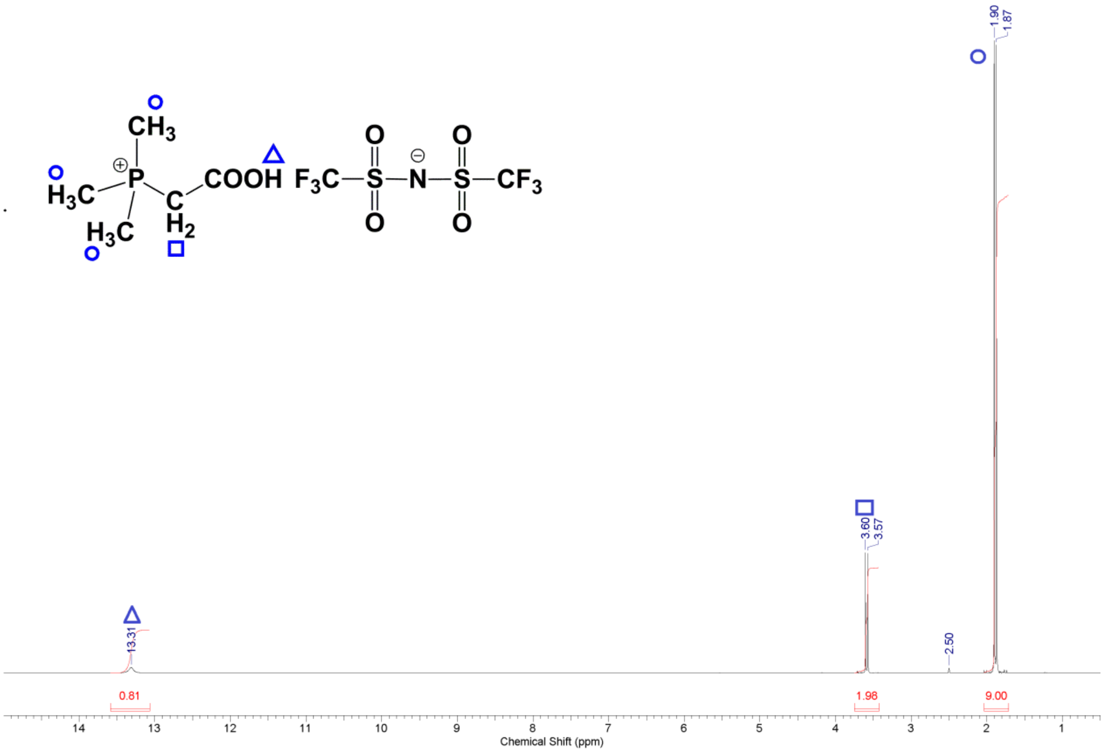

Figure S2. ^{1}H-NMR of $[HCTMP][Tf_2N]$ in DMSO-d_6.

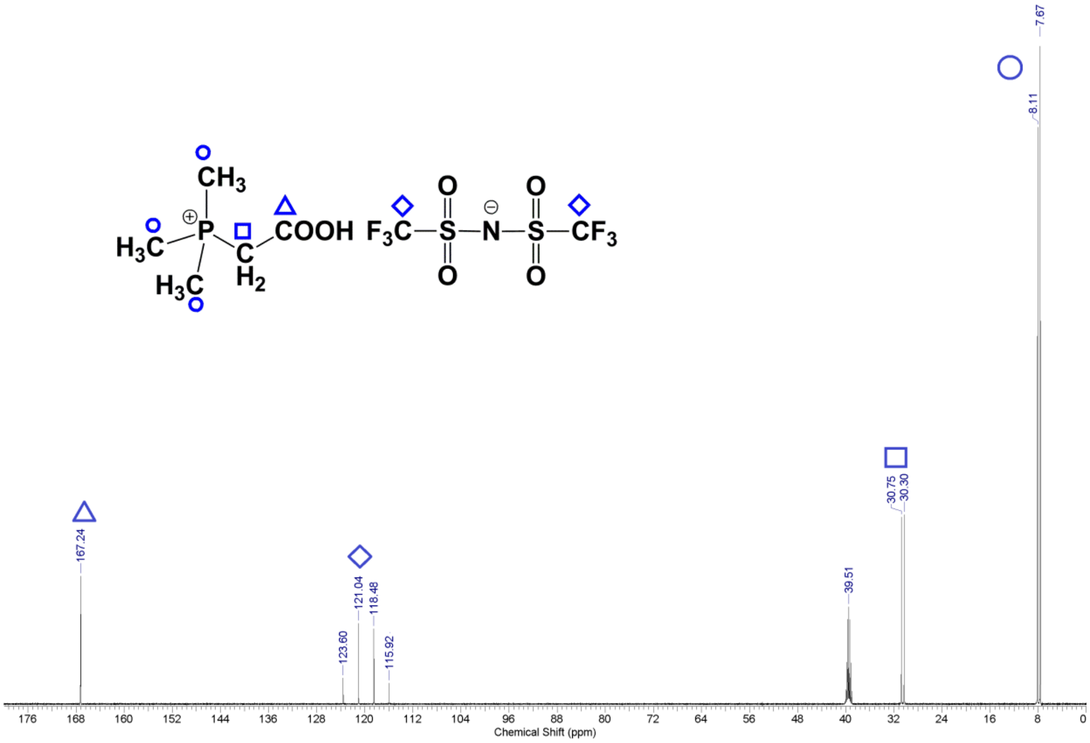

Figure S3. ^{13}C-NMR of [HCTMP][Tf_2N] in DMSO-d_6.

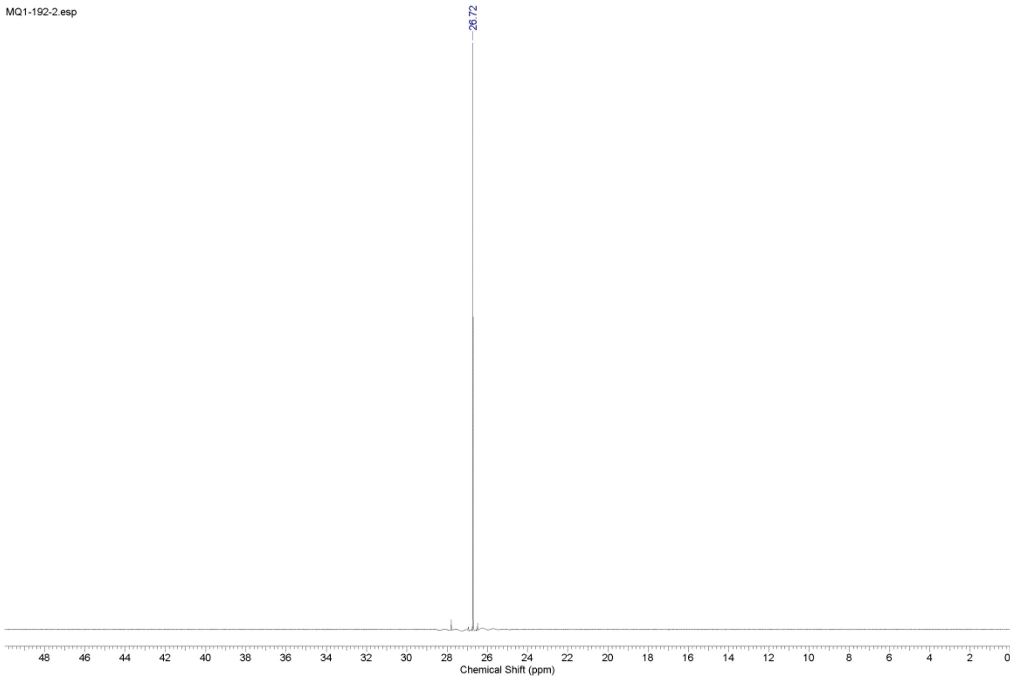

Figure S4. ^{31}P-NMR of [HCTMP][Tf_2N] in DMSO-d_6.

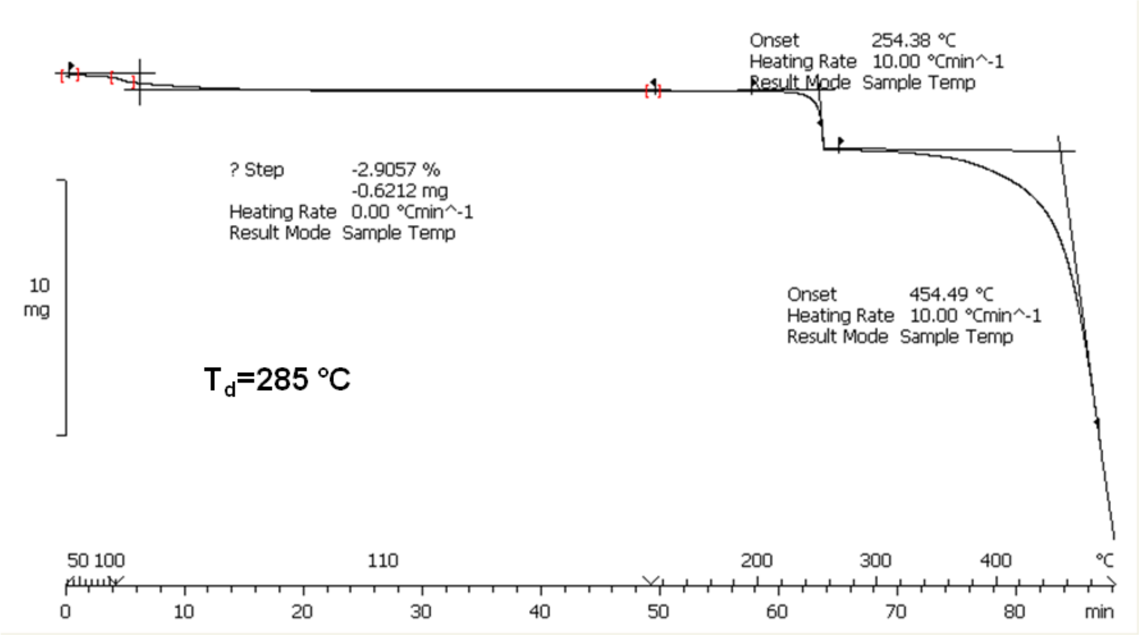

Figure S5. Thermogravimetric analysis of [HCTMP][Tf_2N].

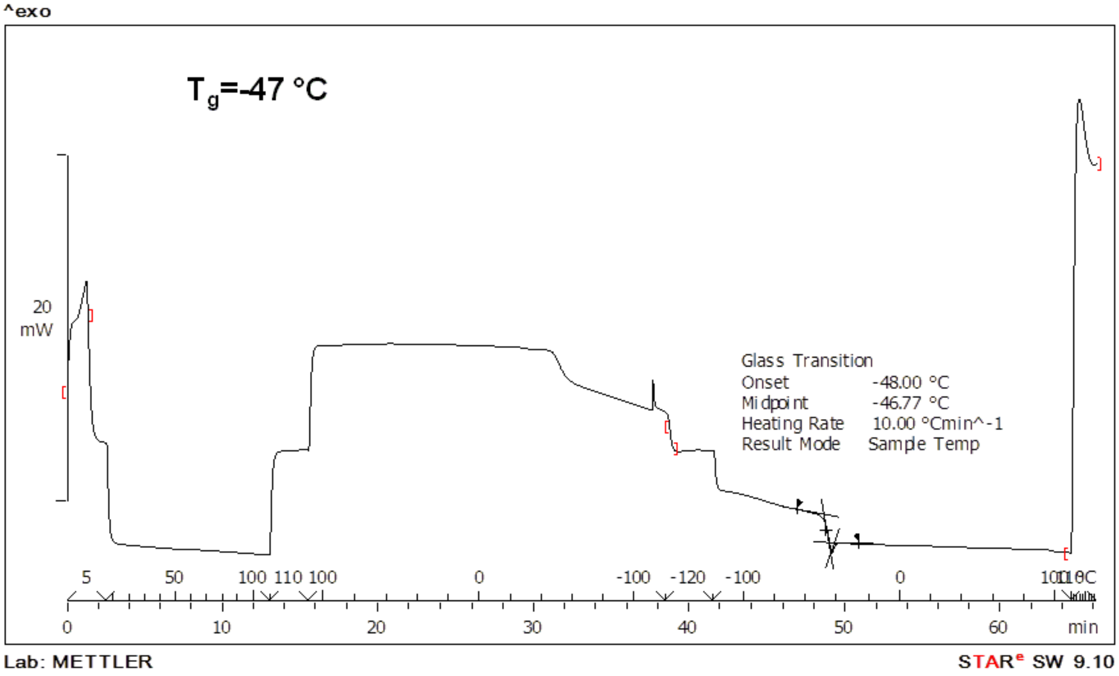

Figure S6. Differential scanning calorimetry of [HCTMP][Tf_2N].

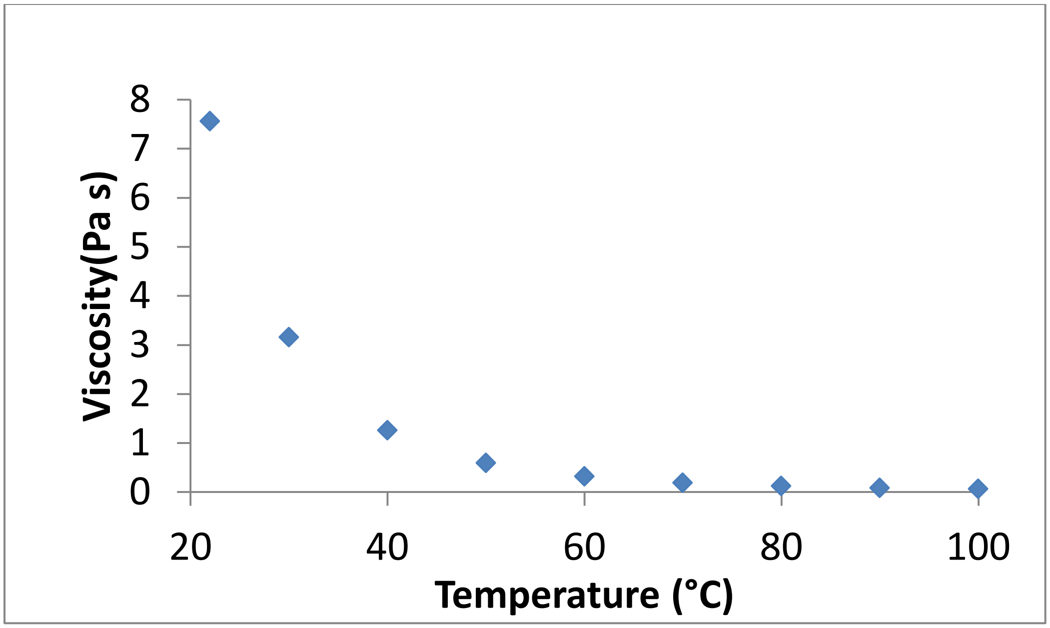

Figure S7. Viscosity data of [HCTMP][Tf_2N] at different temperatures.

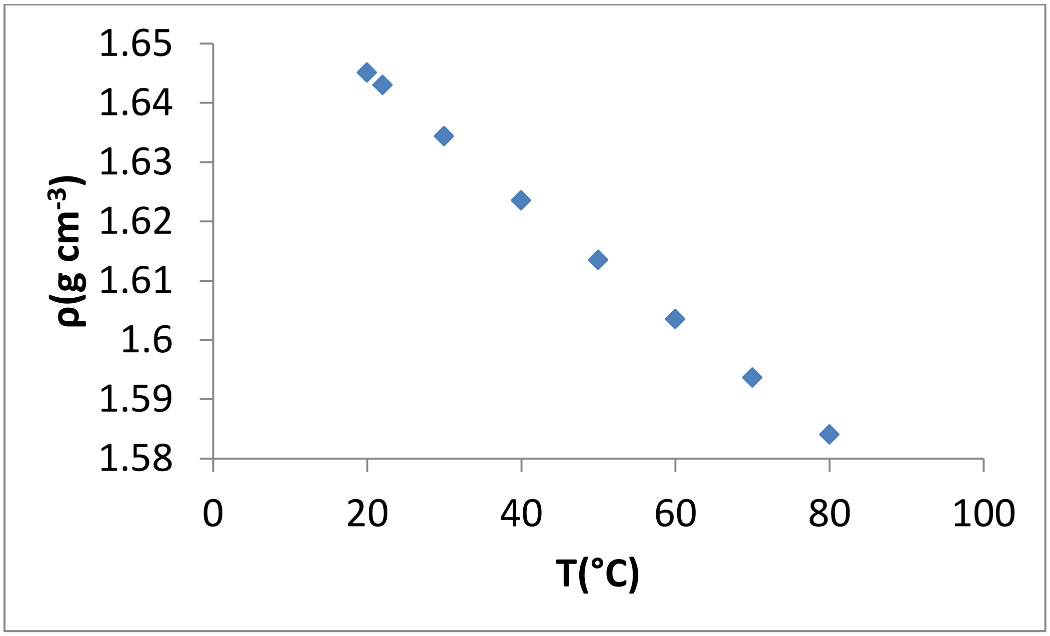

Figure S8. Density data of [HCTMP][Tf_2N] at different temperatures.

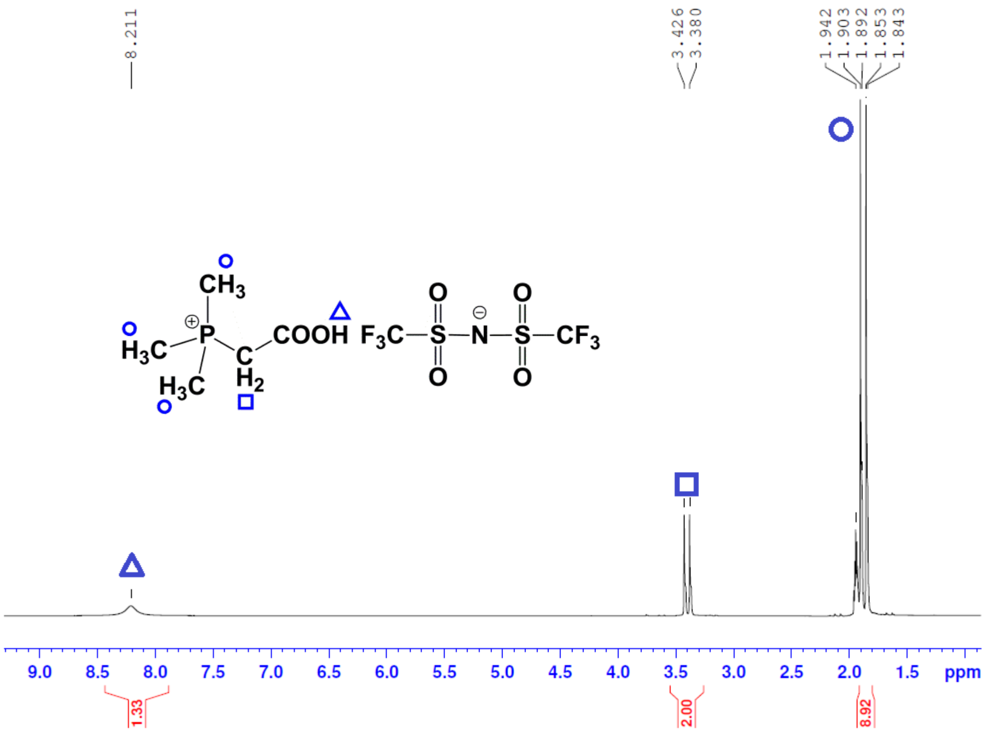

Figure S9. ^{1}H-NMR of [HCTMP][Tf$_2$N] in CD$_3$CN.

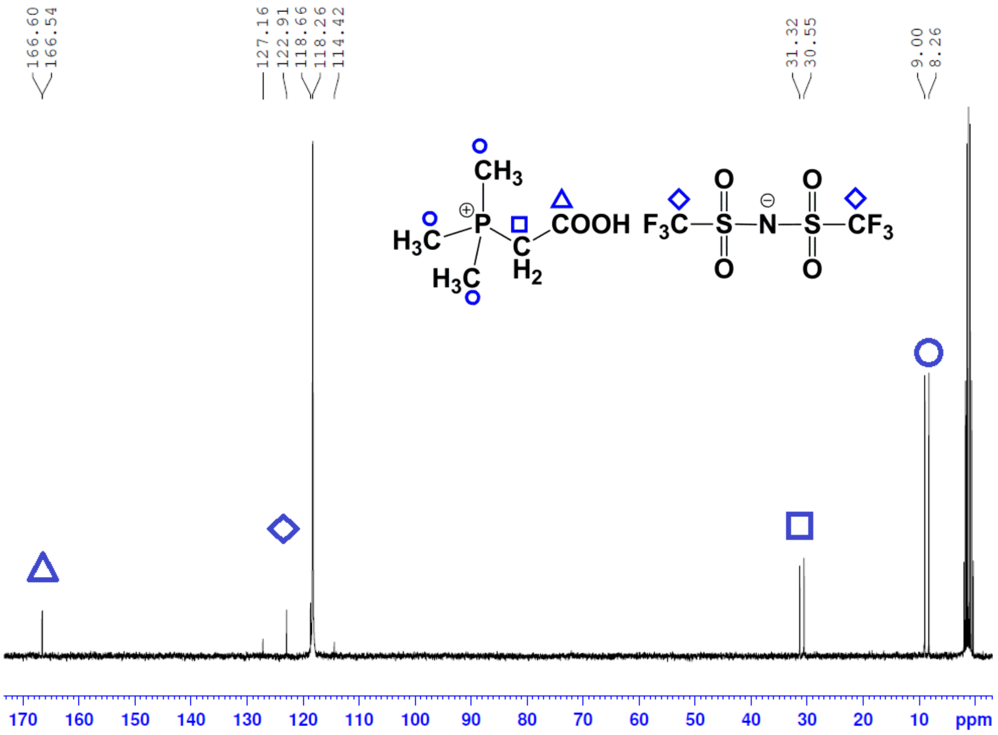

Figure S10. ^{13}C-NMR of [HCTMP][Tf$_2$N] in CD$_3$CN.

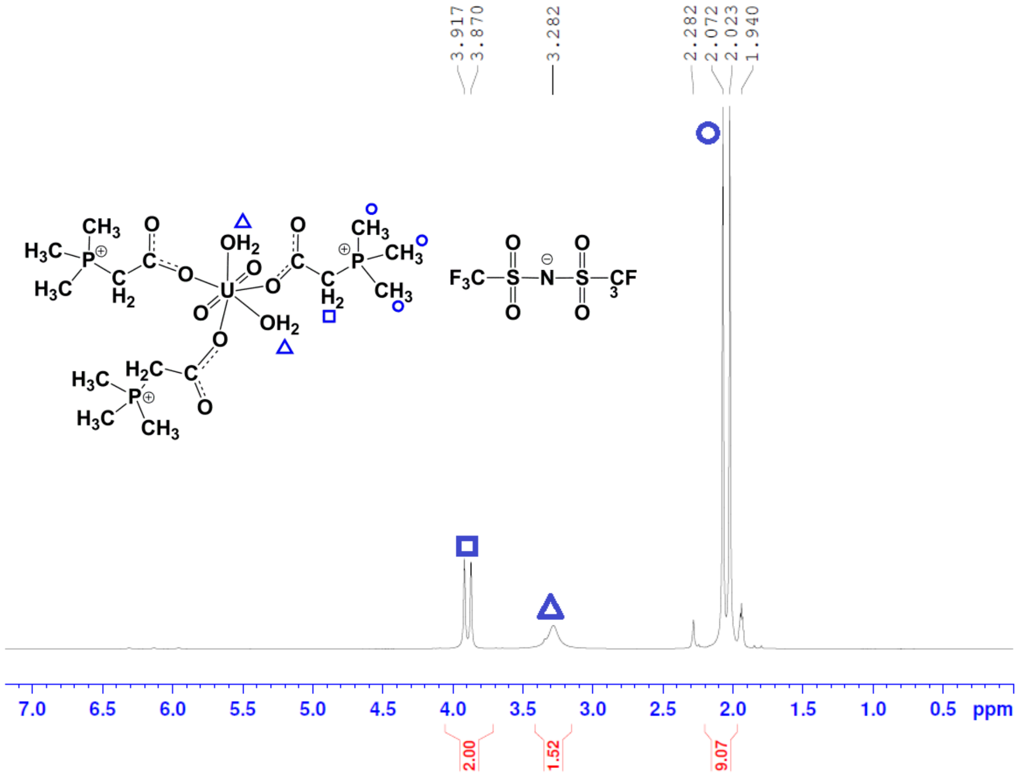

Figure S11. ^{1}H-NMR of $[UO_2(CTMP)_3(H_2O)_2][Tf_2N]_2$ (**1**) in CD_3CN.

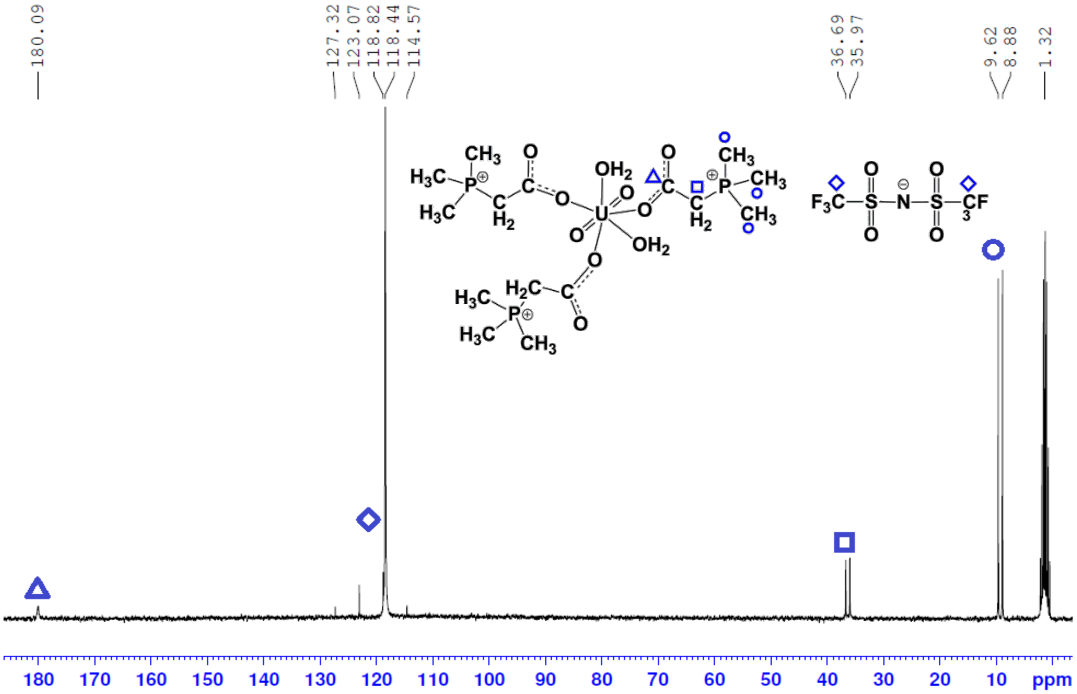

Figure S12. ^{13}C-NMR of $[UO_2(CTMP)_3(H_2O)_2][Tf_2N]_2$ (**1**) in CD_3CN.

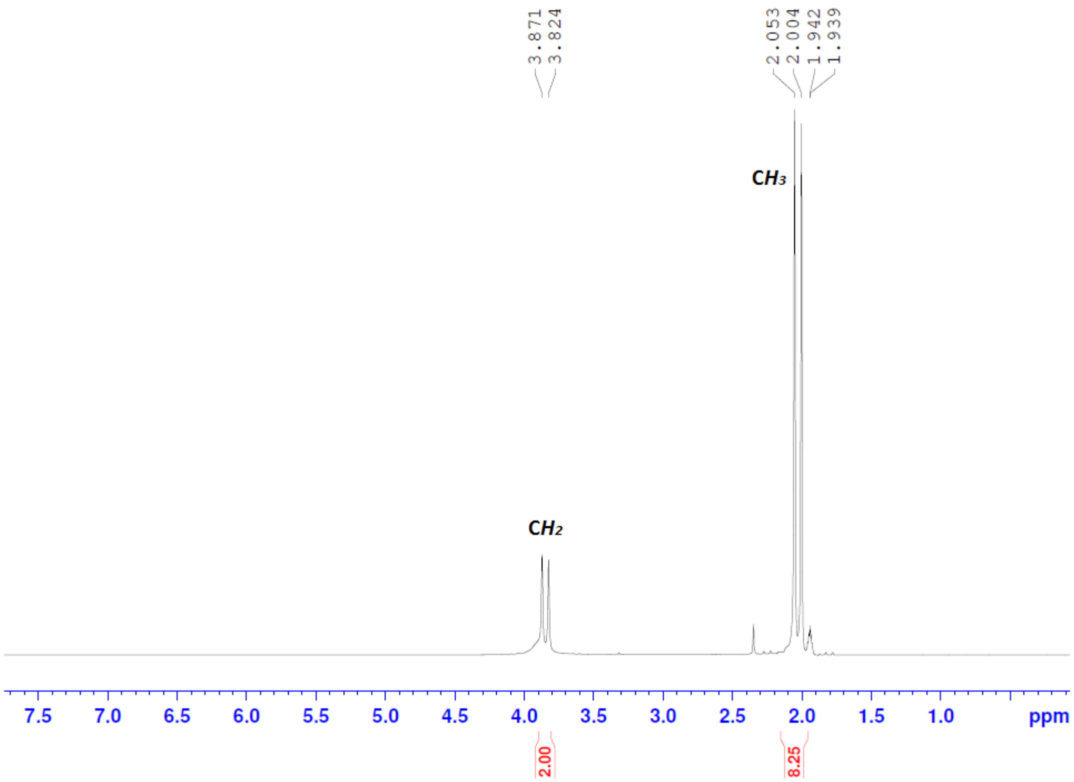

Figure S13. ^{1}H-NMR of $[UO_2(CTMP)_3]_2[NTf_2]_4$ (**2**) in CD_3CN.

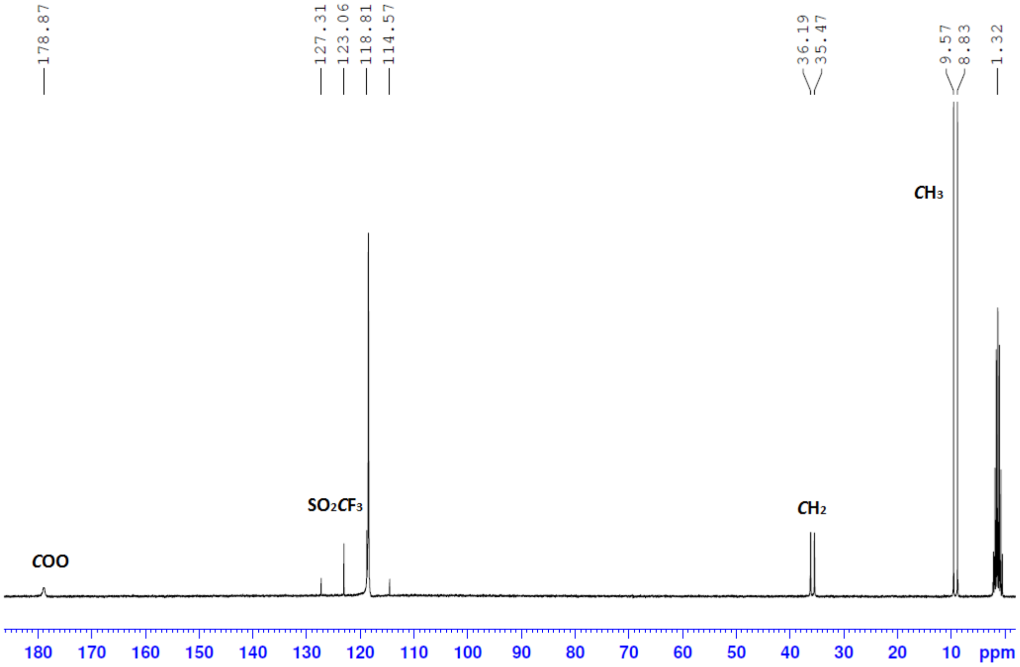

Figure S14. ^{13}C-NMR of $[UO_2(CTMP)_3]_2[NTf_2]_4$ (**2**) in CD_3CN.

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