

## Electronic Supporting Information

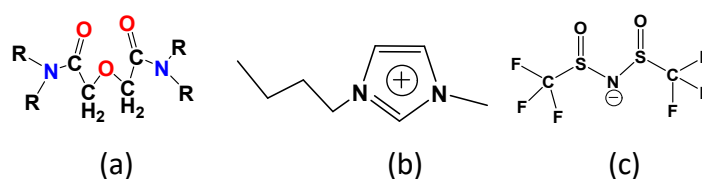
### First example of a solid, homoleptic $\text{UO}_2^{2+}$ - diglycolamide complex from a room temperature ionic liquid: X-ray crystallography and complexation studies

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## 1. Materials

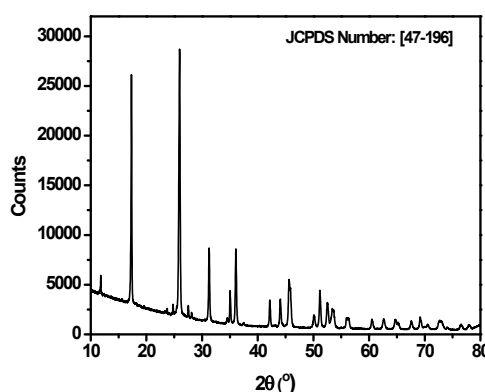
*N,N,N',N'*-tetramethyl diglycolamide (TMDGA; **Fig. S1**) was synthesized by reacting diglycolyl chloride with dimethylamine as reported earlier.<sup>1</sup> The material was characterized by <sup>1</sup>H-NMR, FT-IR and mass spectrometry. 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (denoted as C<sub>4</sub>mim·Tf<sub>2</sub>N; **Fig. S1**), having a purity >99%, was procured from Iolitec, Germany. No attempt was made to dry the C<sub>4</sub>mim·Tf<sub>2</sub>N, and it was used as received. The water content of C<sub>4</sub>mim·Tf<sub>2</sub>N was about 1000 ppm as estimated by Karl Fischer titration. Trifluoromethanesulfonylimide (HTf<sub>2</sub>N) was procured from Sigma Aldrich (CAS 82113-65-3). Other chemicals used were of analytical reagent grade.



**Fig. S1** (a) Molecular structure of TMDGA (R = -CH<sub>3</sub>), and (b) structure of the cation, and (c) anion of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (C<sub>4</sub>mim·Tf<sub>2</sub>N).

## 2. Preparation of UO<sub>3</sub>

UO<sub>3</sub> was prepared by heating ammonium diuranate (ADU) in the air as per a reported procedure.<sup>2</sup> For synthesis of ADU, a NH<sub>4</sub>OH solution was slowly added to an aqueous 100 g/L solution of uranyl nitrate hexahydrate at pH 2 with constant stirring. The addition of NH<sub>4</sub>OH was continued till the pH was about 11 and a completely yellow precipitate appeared. The yellow precipitate was subsequently filtered and washed with water and dried to get the ADU product. Subsequently, it was heated in the air at 600 °C for 6 h to give the product uranium trioxide (UO<sub>3</sub>). The UO<sub>3</sub> was characterized by the XRD and the spectrum given below (**Fig. S2**).

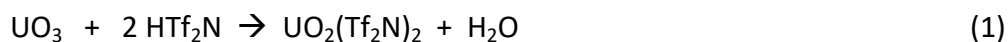


**Fig. S2** XRD spectrum of UO<sub>3</sub> recorded on a Rigaku Ultima IV instrument.

## 3. Preparation of UO<sub>2</sub>(Tf<sub>2</sub>N)<sub>2</sub> salt

UO<sub>2</sub>(Tf<sub>2</sub>N)<sub>2</sub> salt was prepared by reaction of uranium trioxide with HTf<sub>2</sub>N as per a procedure described earlier.<sup>3,4</sup> A known amount of HTf<sub>2</sub>N (5 g) was dissolved in 20 mL MilliQ water. A stoichiometric amount of solid UO<sub>3</sub> was dissolved in this solution by stirring for 1 hour at 80

°C. After complete dissolution, a little excess of  $\text{UO}_3$  was added to ensure complete consumption of the entire amount of  $\text{HTf}_2\text{N}$  to form the water soluble  $\text{UO}_2(\text{Tf}_2\text{N})_2$  salt as per the following reaction:



The  $\text{UO}_2(\text{Tf}_2\text{N})_2$  salt solution containing un-reacted  $\text{UO}_3$  was filtered through a Whatman filter 42 (2.5  $\mu\text{m}$ ). The clear filtrate containing  $\text{UO}_2(\text{Tf}_2\text{N})_2$  was evaporated to dryness, and finally vacuum dried to give a yellow residue of  $\text{UO}_2(\text{Tf}_2\text{N})_2$ . A stock solution of the uranyl ion in ionic liquid medium ( $\text{C}_4\text{mim}\cdot\text{Tf}_2\text{N}$ ) was prepared by dissolving the appropriate amount of the  $\text{UO}_2(\text{Tf}_2\text{N})_2$  salt, and its concentration in the IL solution was confirmed by volumetric titration using Davis gray method.<sup>5</sup>

#### 4. Spectrophotometric titration

Absorption spectra of  $\text{UO}_2^{2+}$  in  $\text{C}_4\text{mim}\cdot\text{Tf}_2\text{N}$  were recorded in the wavelength region 370 - 510 nm (0.1 nm interval) on a double beam Jasco V-530 spectrophotometer using 10 mm path length quartz cells. The initial concentration of  $\text{UO}_2^{2+}$  in the cell was  $\sim 30$  mmol/L. In each titration, appropriate aliquots of the titrant solution (100 mmol/L TMDGA solution in  $\text{C}_4\text{mim}\cdot\text{Tf}_2\text{N}$ ) were added into the cell and mixed thoroughly for about 5 minutes before the spectrum was recorded. Usually, a set of 20-25 spectra were recorded in each titration. Based on the equations (2) and (3), the stability constants of the  $\text{UO}_2^{2+}/\text{L}$  complexes were calculated by nonlinear least-squares regression analysis using the HypSpec<sup>®</sup> program.<sup>6</sup>



$$\beta_i = \frac{[(\text{UO}_2\text{L}_i)^{3+}]}{[\text{UO}_2^{2+}][\text{L}]^i} \quad (3)$$

Where  $\beta_i$  is the stability constant of the  $i^{\text{th}}$  complex, and L = TMDGA.

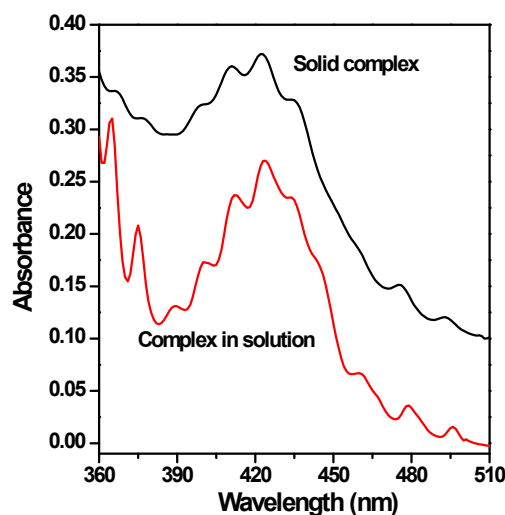
#### 5. Preparation of solid complex (crystals) for XRD

A light yellow coloured solid complex of  $\text{UO}_2^{2+}/\text{TMDGA}$  was obtained in  $\text{C}_4\text{mim}\cdot\text{Tf}_2\text{N}$  by mixing 0.5 mmol of  $\text{UO}_2(\text{Tf}_2\text{N})_2$  salt solution with 1.5 mmol of the ligand (TMDGA) solution in a closed cap fluorescence cell (Total volume = 3 mL). After mixing the ligand solution in the uranium solution, a clear solution was obtained which was stirred thoroughly with the help of magnetic stirring bar for about 10 minutes. This solution was then kept undisturbed for two days when solid complexes appeared in the solution. This solid complex was isolated and re-dissolved in about 1 mL  $\text{C}_4\text{mim}\cdot\text{Tf}_2\text{N}$  with the help of same magnetic stirring bar, and then the solution was kept undisturbed. After few days, bright yellow needle shape crystals were obtained, which were directly analysed by X-ray crystallography.

Similarly, a light yellow coloured crystals of  $\text{UO}_2^{2+}/\text{TMDGA}$  was also obtained in water by mixing 0.5 mmol of  $\text{UO}_2(\text{Tf}_2\text{N})_2$  salt solution in water with 1.5 mmol of TMDGA (both,

UO<sub>2</sub>(Tf<sub>2</sub>N)<sub>2</sub> salt and TMDGA are water soluble). After mixing the ligand solution in the uranium solution, a clear solution was obtained which was kept undisturbed for two days when bright yellow coloured needle shape crystals appeared in the solution. The crystals were isolated and directly mounted for XRD analysis.

FT-IR spectrum of the UO<sub>2</sub><sup>2+</sup>/TMDGA solid complex was recorded in ATR mode using an Alpha FTIR spectrometer (Bruker, Germany), and the spectra was compared with those obtained in solution by spectrophotometric titration. As shown in **Fig S3**, the absorbance spectra of the solid complex and the complex present in liquid IL medium was same.



**Fig. S3** Comparison of the UV-vis spectra of the solid complex and that of the solution spectra corresponding to the ML<sub>2</sub> species.

## 6. X-ray crystallography

The crystallographic data were collected using Cu K<sub>α</sub> radiation ( $\lambda = 1.54184 \text{ \AA}$ ) from a single crystal at 298(2) K on a XtaLAB Synergy, Dualflex, HyPix four-circle diffractometer with a micro-focus sealed X-ray tube using a mirror as monochromator and a HyPix detector. All data were integrated, and a multi-scan absorption correction was applied using CrysAlis PRO.<sup>7</sup> The structure was solved by direct methods using SIR-2014,<sup>8</sup> and refined by full-matrix least-squares methods against  $F^2$  by SHELXL-2017/1.<sup>9</sup> Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 2115403 for the crystals obtained in IL medium and CCDC No. 2115404 for the same isolated from the aqueous solution). The ORTEP was employed for the final data presentation and structure plots.<sup>10</sup>

The crystallography data for the crystals isolated from the IL medium are given in **Table S1**, and those for aqueous medium are given in **Table S2**. A table comparing the important bond length and bond angles for the UO<sub>2</sub>(L)<sub>2</sub>·(Tf<sub>2</sub>N)<sub>2</sub> isolated from IL and water

media are given in **Table S3**.

**Table S1** Crystal data and structure refinement for  $C_{16}H_{32}N_4O_8U$ ,  $2(C_2F_6NO_4S_2)$ .  
(For crystal obtained in IL medium)

CCDC number	2115403
Empirical formula	$C_{20}H_{32}F_{12}N_6O_{16}S_4U$
Formula weight	1206.78
Temperature [K]	298(2)
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
$a$ [Å]	10.9388(2)
$b$ [Å]	28.0055(5)
$c$ [Å]	13.24770(10)
$\alpha$ [°]	90
$\beta$ [°]	90.9710(10)
$\gamma$ [°]	90
Volume [Å <sup>3</sup> ]	4057.80(11)
$Z$	4
$\rho_{\text{calc}}$ [g/cm <sup>3</sup> ]	1.975
$\mu$ [mm <sup>-1</sup> ]	?
$F(000)$	2344
Crystal size [mm <sup>3</sup> ]	0.200×0.050×0.050
Crystal colour	Colourless (Translucent)
Crystal shape	needles
Radiation	Cu $K_\alpha$ ( $\lambda=1.54184$ Å)
$2\theta$ range [°]	6.31 to 166.78 (0.78 Å)
Index ranges	$-13 \leq h \leq 13$ $-35 \leq k \leq 35$ $-12 \leq l \leq 16$
Reflections collected	83879
Independent reflections	8567 $R_{\text{int}} = 0.0795$ $R_{\text{sigma}} = 0.0353$
Completeness to $\theta = 67.684^\circ$	100.0 %
Data / Restraints / Parameters	8567/0/541
Goodness-of-fit on $F^2$	1.058
Final $R$ indexes	$R_1 = 0.0476$
[ $I \geq 2\sigma(I)$ ]	$wR_2 = 0.1280$
Final $R$ indexes	$R_1 = 0.0524$
[all data]	$wR_2 = 0.1329$
Largest peak/hole [eÅ <sup>3</sup> ]	2.25/-1.44

**Table S2** Crystal data and structure refinement for  $C_{16}H_{32}N_4O_8U$ ,  $2(C_2F_6NO_4S_2)$

(For crystal obtained in water medium)

CCDC number	2115404
Empirical formula	C <sub>20</sub> H <sub>32</sub> F <sub>12</sub> N <sub>6</sub> O <sub>16</sub> S <sub>4</sub> U
Formula weight	1206.78
Temperature [K]	298(2)
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (14)
<i>a</i> [Å]	10.93520(10)
<i>b</i> [Å]	28.0044(3)
<i>c</i> [Å]	13.2553(2)
$\alpha$ [Å]	90
$\beta$ [Å]	90.9590(10)
$\gamma$ [Å]	90
Volume [Å <sup>3</sup> ]	4058.65(8)
<i>Z</i>	4
$\rho_{\text{calc}}$ [g/cm <sup>3</sup> ]	1.975
$\mu$ [mm <sup>-1</sup> ]	14.347
<i>F</i> (000)	2344
Crystal size [mm <sup>3</sup> ]	0.100×0.050×0.020
Crystal colour	colourless
Crystal shape	plate
Radiation	Cu <i>K</i> <sub>α</sub> ( $\lambda$ =1.54184 Å)
2 $\theta$ range [°]	6.31 to 154.46 (0.79 Å)
Index ranges	-13 ≤ <i>h</i> ≤ 13 -35 ≤ <i>k</i> ≤ 35 -13 ≤ <i>l</i> ≤ 16
Reflections collected	86008
Independent reflections	8543 <i>R</i> <sub>int</sub> = 0.0735 <i>R</i> <sub>sigma</sub> = 0.0364
Completeness to $\theta = 67.684^\circ$	99.9 %
Data / Restraints / Parameters	8543/0/540
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.049
Final <i>R</i> indexes	<i>R</i> <sub>1</sub> = 0.0437
[ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>wR</i> <sub>2</sub> = 0.1231
Final <i>R</i> indexes	<i>R</i> <sub>1</sub> = 0.0467
[all data]	<i>wR</i> <sub>2</sub> = 0.1264
Largest peak/hole [eÅ <sup>3</sup> ]	1.99/-1.61

**Table S3** Selected bond lengths (Å) and bond angle (°) in UO<sub>2</sub>(L)<sub>2</sub>·(Tf<sub>2</sub>N)<sub>2</sub> complexes obtained in IL and in water medium.

<b>Bonds / Angles</b>	<b>IL medium</b>	<b>Water medium</b>
U=O (axial)	1.749(5), 1.752(5)	1.749(5), 1.752(5)
U-O (amide)	2.399(4), 2.419(4), 2.417(4), 2.417(4)	2.399(4), 2.417(4), 2.417(4), 2.419(4),
U-O (ether)	2.663(4), 2.634(4)	2.663(4), 2.634(4)
Angle O=U=O	179.4(2)	179.4(2)

**Table S4** Selected bond lengths and angles for C<sub>16</sub>H<sub>32</sub>N<sub>4</sub>O<sub>8</sub>U, 2(C<sub>2</sub>F<sub>6</sub>NO<sub>4</sub>S<sub>2</sub>)

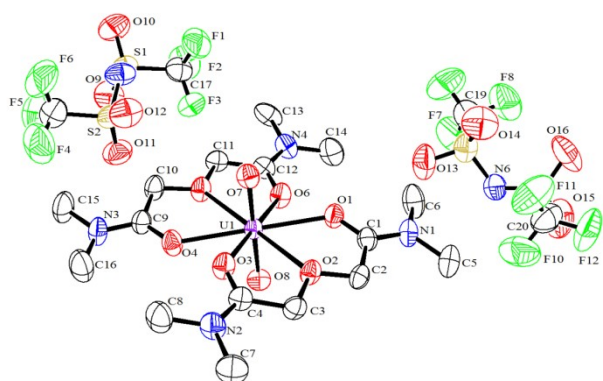
(For crystal obtained in IL medium)

	Length [Å] /Angle [°]		Length [Å] /Angle [°]
O1–U1	2.399(4)	O5–U1	2.634(4)
O2–U1	2.663(4)	O6–U1	2.417(4)
O3–U1	2.419(4)	O7–U1	1.749(5)
O4–U1	2.417(4)	O8–U1	1.752(5)
O7–U1–O8	179.4(2)	O4–U1–O3	65.64(15)
O7–U1–O1	86.9(2)	O7–U1–O5	82.7(2)
O8–U1–O1	93.0(2)	O8–U1–O5	97.9(2)
O7–U1–O6	94.7(2)	O1–U1–O5	122.60(15)
O8–U1–O6	85.8(2)	O6–U1–O5	58.24(15)
O1–U1–O6	66.72(16)	O4–U1–O5	58.55(15)
O7–U1–O4	93.2(2)	O3–U1–O5	121.88(15)
O8–U1–O4	86.9(2)	O7–U1–O2	97.3(2)
O1–U1–O4	178.84(15)	O8–U1–O2	82.12(19)
O6–U1–O4	114.40(15)	O1–U1–O2	57.74(15)
O7–U1–O3	85.6(2)	O6–U1–O2	122.09(15)
O8–U1–O3	94.0(2)	O4–U1–O2	121.11(15)
O1–U1–O3	113.23(15)	O3–U1–O2	57.78(14)
O6–U1–O3	179.70(18)	O5–U1–O2	179.66(12)

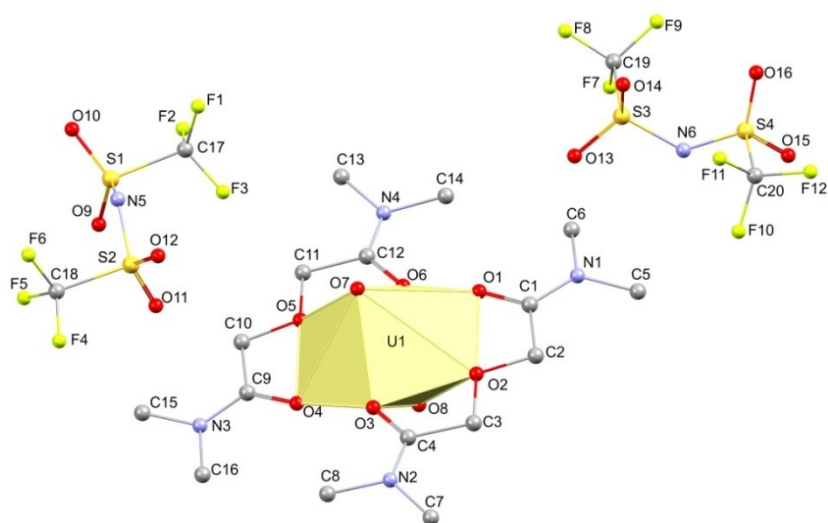
(For crystal obtained in water medium)

	Length [Å] /Angle [°]		Length [Å] /Angle [°]
O1–U1	2.399(4)	O5–U1	2.634(4)
O2–U1	2.663(4)	O6–U1	2.417(4)
O3–U1	2.419(4)	O7–U1	1.749(5)
O4–U1	2.417(4)	O8–U1	1.752(5)
O7–U1–O8	179.4(2)	O4–U1–O3	65.64(15)
O7–U1–O1	86.9(2)	O7–U1–O5	82.7(2)
O8–U1–O1	93.0(2)	O8–U1–O5	97.9(2)
O7–U1–O6	94.7(2)	O1–U1–O5	122.60(15)
O8–U1–O6	85.8(2)	O6–U1–O5	58.24(15)
O1–U1–O6	66.72(16)	O4–U1–O5	58.55(15)
O7–U1–O4	93.2(2)	O3–U1–O5	121.88(15)
O8–U1–O4	86.9(2)	O7–U1–O2	97.3(2)
O1–U1–O4	178.84(15)	O8–U1–O2	82.12(19)
O6–U1–O4	114.40(15)	O1–U1–O2	57.74(15)
O7–U1–O3	85.6(2)	O6–U1–O2	122.09(15)
O8–U1–O3	94.0(2)	O4–U1–O2	121.11(15)
O1–U1–O3	113.23(15)	O3–U1–O2	57.78(14)
O6–U1–O3	179.70(18)	O5–U1–O2	179.66(12)

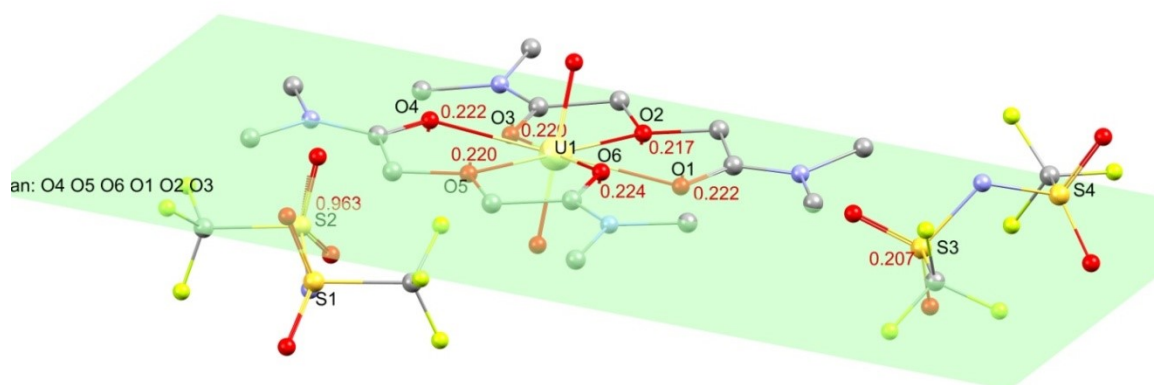




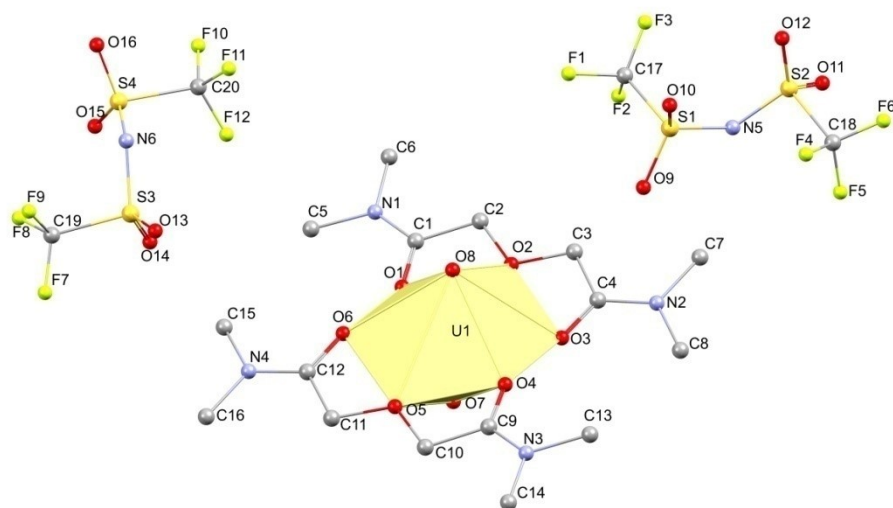
**Fig. S4** ORTEP diagram of the complex (probability 35%, hydrogens omitted for clarity).



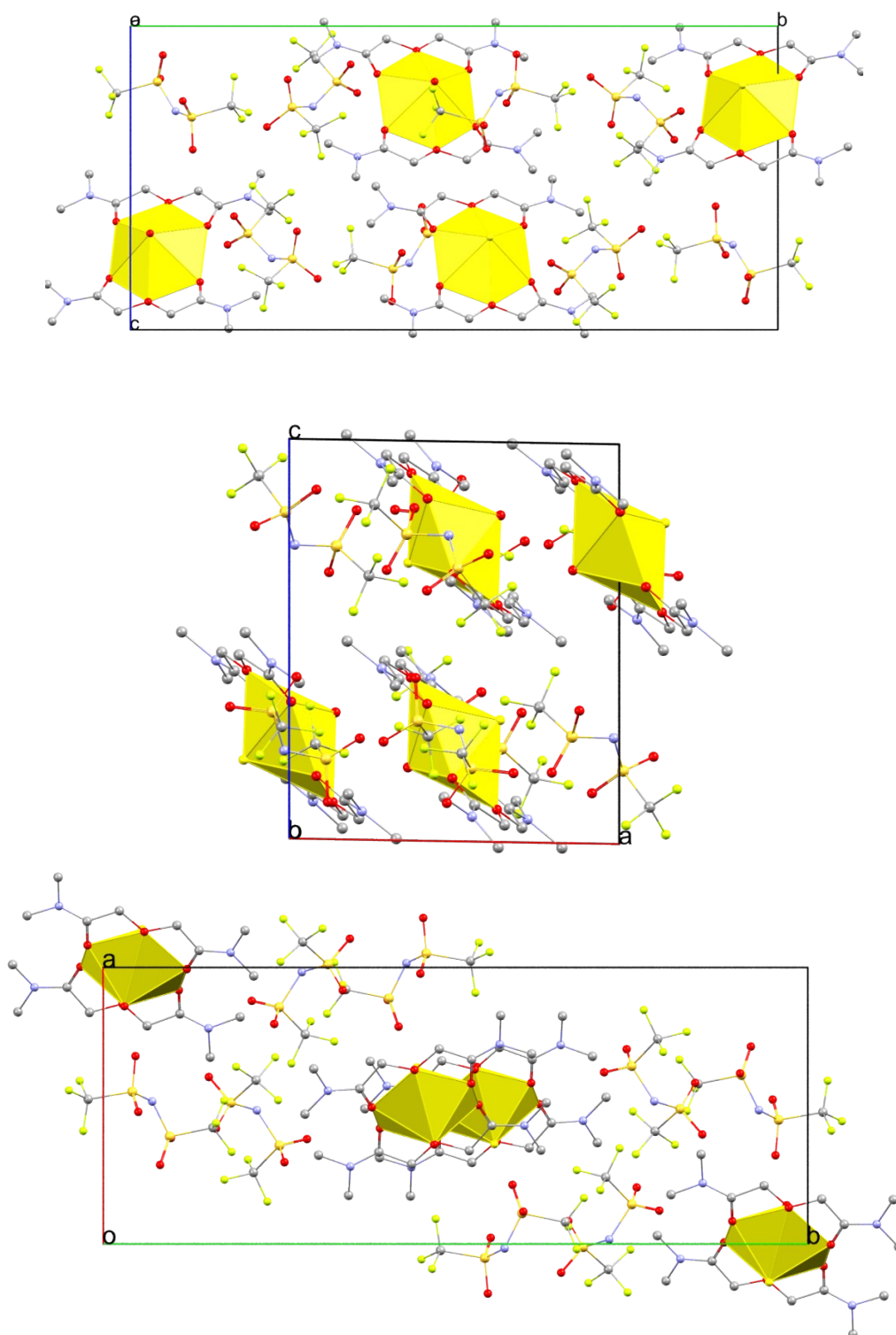
**Fig. S5.** Crystal structure of the complex in ionic liquid.



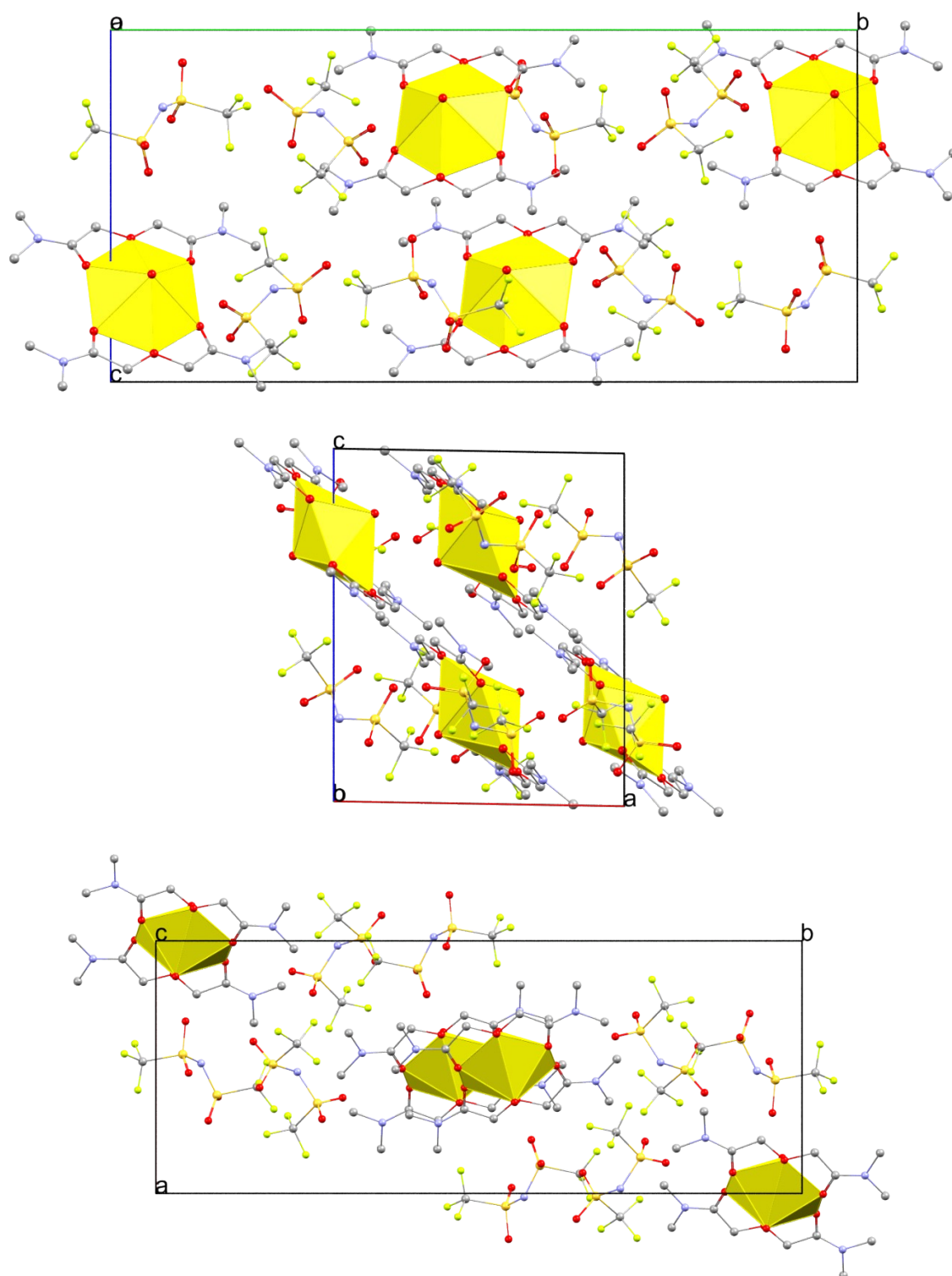
**Fig. S6** Relative position of the atoms in the complex isolated from ionic liquid. The red balls are the 'O' atoms above the plane and the buff coloured balls represent the 'O' atoms below the plane (shaded in green). Similarly, the 'S' atoms are also not in the plane.



**Fig. S7** Crystal structure of the complex in water.



**Fig. S8** Packing diagram of the complex in ionic liquid along the a-axis (top), b-axis (middle) and c-axis (bottom).



**Fig. S9** Packing diagram of the complex in water along the a-axis (top), b-axis (middle), and c-axis (bottom). The  $\text{UO}_2(\text{TMDGA})_2$  complexes are presented as yellow polyhedral.

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