SUPPORTING INFORMATION

Coordination structures of uranium(VI) and plutonium(IV) in organic solutions with amide derivatives

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Sample compositions

Table S1. Compositions of **TBU**, **THU**, **TOU** and **MOEHA** organic solutions for UV-visible and infra-red analysis

	C_{amide}^{org} (± 5 %) mol•L^{-1}	$C_{actinide}^{org}$ (± 10 %) mol•L^{-1}	C_{HNO3}^{org} (± 10 %) mol•L^{-1} [a]
TBU-H4	1.28	-	0.92
THU-H4	1.27	-	1.04
TOU-H4	1.18	-	1.03
MOEHA-H4	1.29	-	0.83
U-TBU-H0.5	1.28	0.27	0.20
U-THU-H0.5	1.27	0.31	0.19
U-TOU-H0.5	1.18	0.31	0.19
U-MOEHA-H0.5	1.29	0.24	0.19
U-TBU-H4 [b]	1.28	*0.34*	0.58
U-THU-H4	1.27	0.30	0.64
U-TOU-H4	1.18	0.29	0.66
U-MOEHA-H4	1.29	0.30	0.50
Pu-TBU-H0.5	1.18	$5.60.10^{-3}$	0.13
Pu-THU-H0.5	1.21	$8.20.10^{-3}$	0.10
Pu-TOU-H0.5	1.18	$1.04.10^{-2}$	0.07
Pu-MOEHA-H0.5	1.29	$1.04.10^{-3}$	0.15
Pu-TBU-H4 [b]	1.18	*$3.01.10^{-2}$*	0.86
Pu-THU-H4	1.21	$2.70.10^{-2}$	0.94
Pu-TOU-H4	1.18	$2.84.10^{-2}$	0.93
Pu-MOEHA-H4	1.29	$3.04.10^{-2}$	0.84

[a] Determined from the differences between concentrations measured in the aqueous phase before and after equilibration and extraction. [b] a 3rd phase formation was observed after uranium and plutonium extraction, the 3rd phases were dissolved by addition of 10 µL of fresh solvent.

Table S2. Compositions of **TBU** solutions for EXAFS measurements.

	$C_{HNO3}^{aq,ini}$ (mol•L^{-1})	C_{amide}^{org} (mol•L^{-1})	$C_{Pu(IV)}^{org,eq}$ (mmol•L^{-1})
Pu-TBU-1	1.2	1.5	3.1
Pu- TBU-4	4	1.5	5.2

Crystal data

Table S3. Crystal data and final refinement

Compound	T*i*BU-U(VI)	T*i*BU-Pu(IV)
Formula	$UC_{34}H_{36}N_6O_{10}$	$PuC_{34}H_{72}N_8O_{14}$
Temperature	150	190
Formula weight (g·mol^{-1})	926.72	1058.99
Crystal size (µm)	100 x 80 x 50	400 x 100 x 100
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/n$
A (Å)	24.6931(6)	11.3686(12)
b (Å)	12.8371(3)	27.380(3)
c (Å)	17.5175(4)	15.9956(17)
Beta (°)	126.8774(10)	99.438(2)
Volume (Å^3)	4441.83(19)	4911.6(9)
Z	8	4
ρ_{calc} (g·cm^{-3})	2.772	1.432
R[I>2sigma(I)]	0.0244/0.0502	0.0312/0.0711
R indices (all data)	0.0415/0.0555	0.0460/0.0798

Infra-red and Raman spectroscopy of solid state compounds

Table S4. Infra-red and Raman main attributions for the free ligand, **T*i*BU**-Pu(IV) and **T*i*BU**-U(VI).

Free T*i*BU		T*i*BU-Pu(IV)		T*i*BU-U(VI)		Attribution
IR	Raman	IR	Raman	IR	Raman	
1633	1630	1536	1573	1544	1568	ν(C=O)
		1495	1514	1497	1505	ν(N=O)
1469		1470		1470		$\delta_{asym}(CH_2, CH_3)$ + ν(C-N)
	1444-1458		1444-1458		1444-1458	$\delta_{asym}(CH_2, CH_3)$ (butyl)
1394-1363	1280-1314		1304		1306	$\delta_{asym}(CH_2, CH_3)$ (butyl)
		1266	1270	1280	1265	$\nu_{asym}(NO_3)$
	1206		1219		1205	ν(C-N)
1138	1165	1151	1171	1147	1172	$\delta(C\text{-}CH_3)$ (butyl)
		1019	1025	1032	1031	$\nu_{sym}(NO_3)$
930-983	919-960	909-945	914-977		914-977	ν(C-C) + $\delta(C\text{-}CH_3)$ (butyl)
				933	855	$\nu(UO_2^{2+})$
819		818		816		ν(C-C)
781		790		791		$\nu(NR_2)$
			797		789	$\delta(NO_2)$

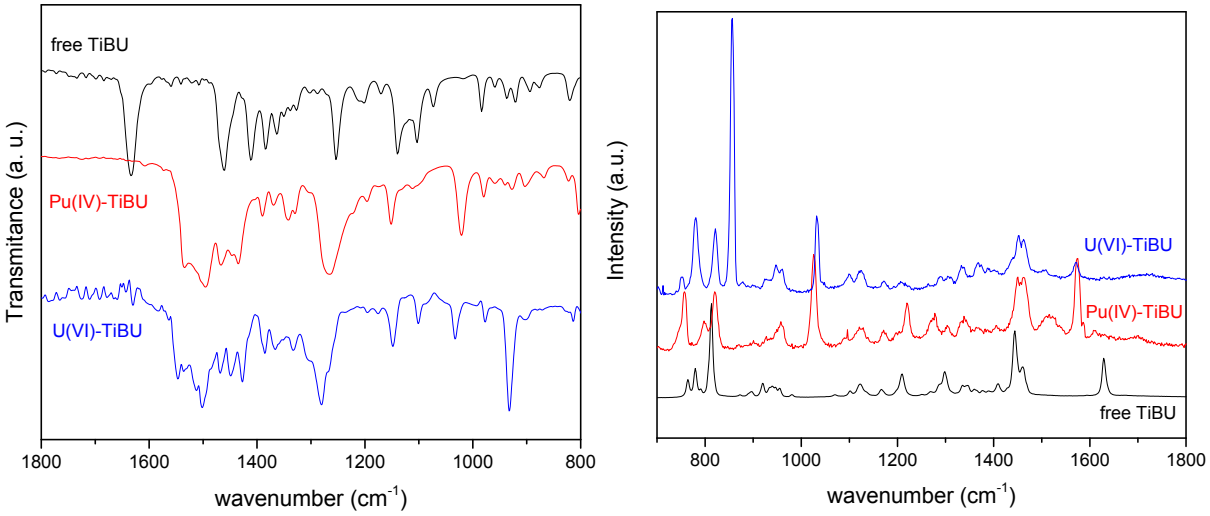
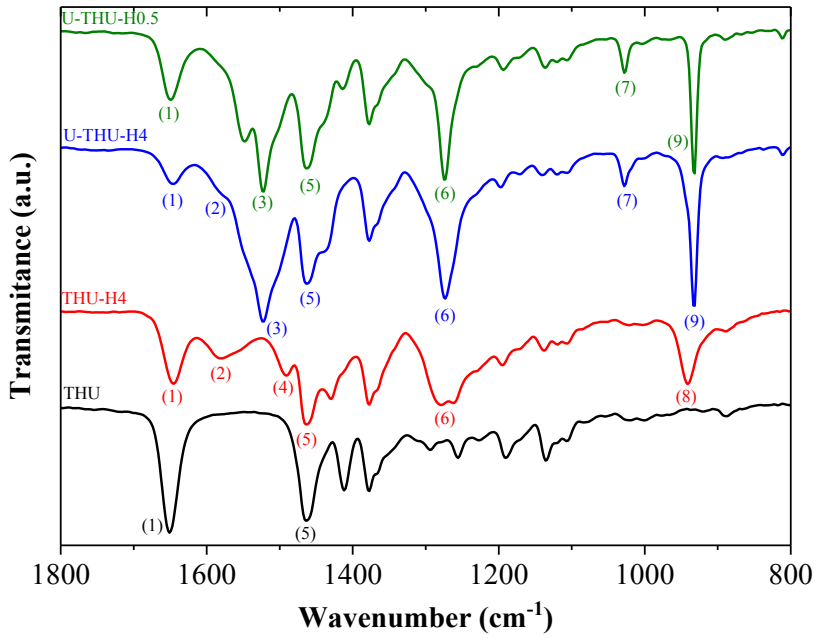


Figure S1. Infra-red (left) and Raman (right) spectra of $UO_2(NO_3)_2$**T*i*BU**$_2$, $Pu(NO_3)_4$**T*i*BU**$_2$ and free **T*i*BU** crystals compared to the free ligand ones.

Infra-red spectroscopy of solvent extraction organic phase



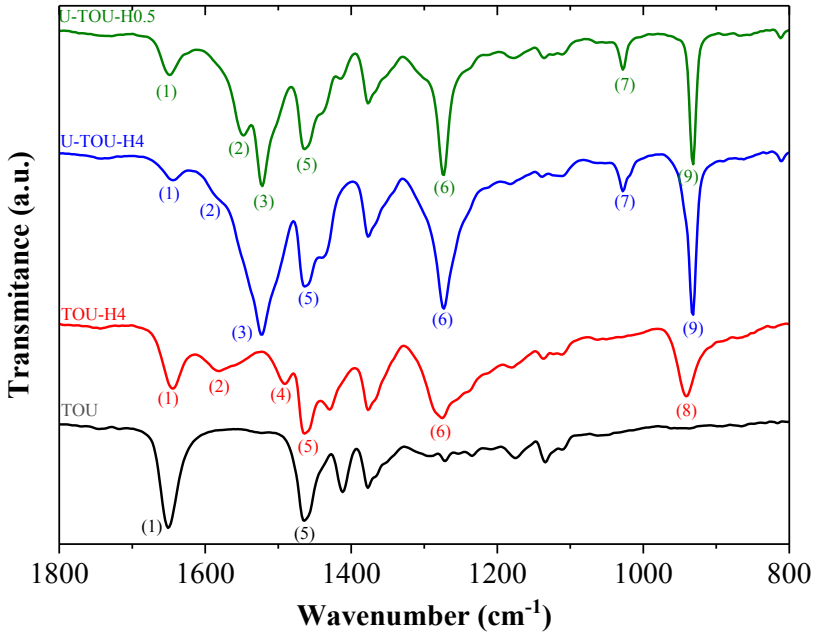


Figure S2. Infra-red spectra of organic phase with free ligand (**THU** and **TOU** 1.2 $mol \cdot L^{-1}$ in TPH), ligands contacted with nitric acid (**THU**-H4 and **TOU**-H4) and contacted with

uranium(VI) solutions (U-**THU**-H4, U-**TOU**-H4, U-**THU**-H0.5 and U-**TOU**-H0.5). (Composition of the sample are reported in **Table1**)

Table S5. Wavenumbers of vibrational bands observed on infra-red spectra of organic phases with **THU** and **TOU** 1.2 mol•L^{-1} in TPH after contact with HNO_3 4 mol•L^{-1} and uranium(VI). (composition of the sample are reported in Table1)

	Wavenumbers (cm^{-1})								
	THU				**TOU**				
	Free	**HNO_3**	**U-H4**	**U-H0.5**	**Free**	**HNO_3**	**U-H4**	**U-H0.5**	**Attribution**
(1)	1649	1645	1647	1649	1651	1645	1643	1649	$\nu(C{=}O)_{free}$
(2)		1581	1581			1583	1587		$\nu(C{=}O)_{HNO3}$
(3)		1490	1523	1521		1490	1523	1521	$\nu(C{=}O)_{Uranyl}$
(4)									$\nu_1(NO_3^-)$
(5)	1464	1464	1462	1464	1464	1464	1462	1464	$\delta_{as}(CH_2, CH_3) + \nu(CN)$
(6)		1278	1273	1273		1275	1272	1275	$\nu_4(NO_3^-)$
(7)			1028	1028			1028	1028	$\nu_2(NO_3^-)$
(8)		941				941			ν (NO')
(9)			932	932			932	932	$\nu_{asym}(UO_2^{2+})$

UV-visible spectroscopy of solvent extraction organic phases

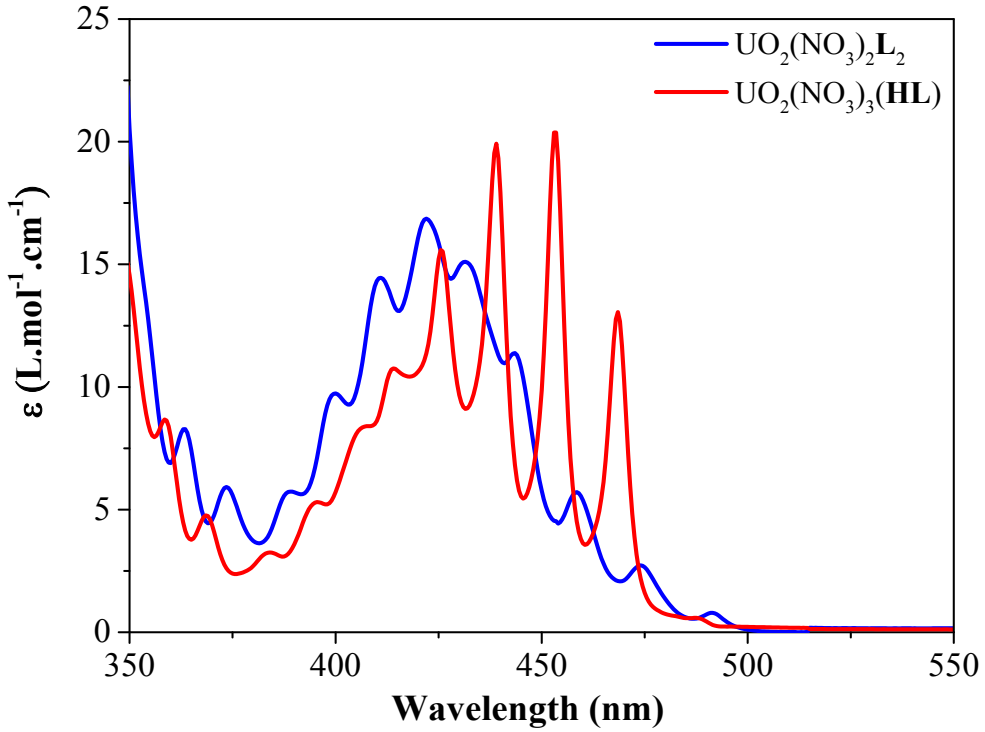


Figure S3. UV-visible spectra of $UO_2(NO_3)_2$**L**$_2$ and $UO_2(NO_3)_3$(**HL**) species (L = **MOEHA** 1.2 in TPH or 3.2 mol•L^{-1}) in organic phases.

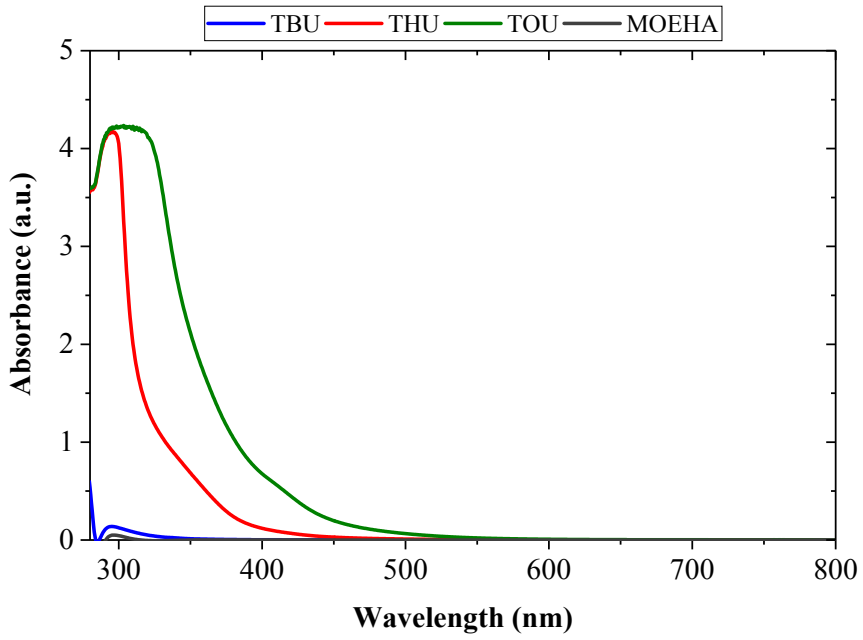


Figure S4. UV-Vis spectra of free ligands at 1.2 $mol \cdot L^{-1}$ in TPH and of organic phase containing **TBU**, **THU**, **TOU** and **MOEHA**. Path cell: 1 cm