Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for: UO_2^{2+} Structure in Solvent Extraction Phases Resolved at Molecular and Supramolecular Scales: A Combined Molecular Dynamics, EXAFS and SWAXS Approach

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S1 Figures

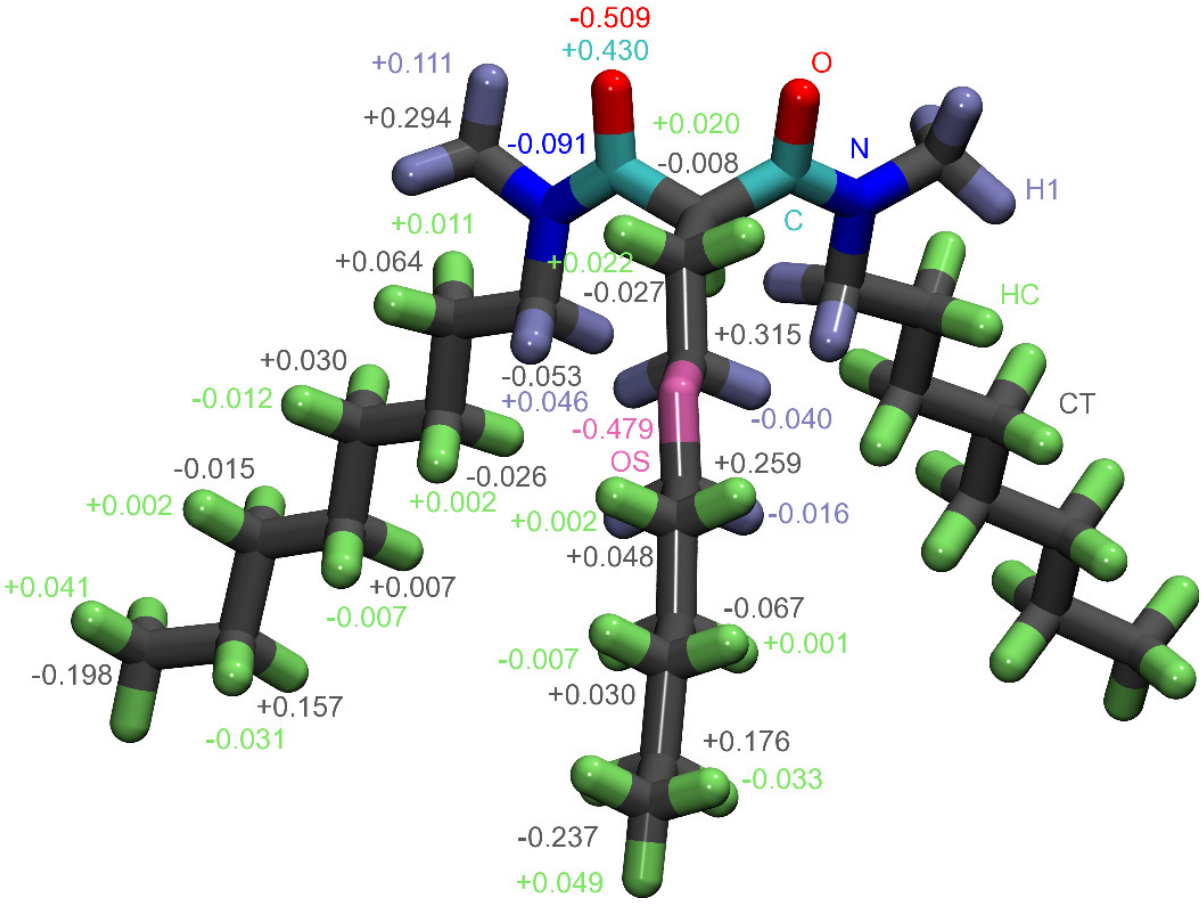

Fig. S1 Atom types and partial atomic charges of the DMDOHEMA molecule. For clarity, partial atomic charges have been written in the same color as the atom type, i.e., C (cyan): sp2 C carbonyl group; CT (gray): sp3 aliphatic C; HC (green): H aliphatic bonded to C without electron-withdrawing group; H1 (purple): H aliphatic bonded to C with 1 electron-withdrawing group; N (blue): sp2 nitrogen in amide groups; O (red): carbonyl group oxygen; OS (pink): ether oxygen.

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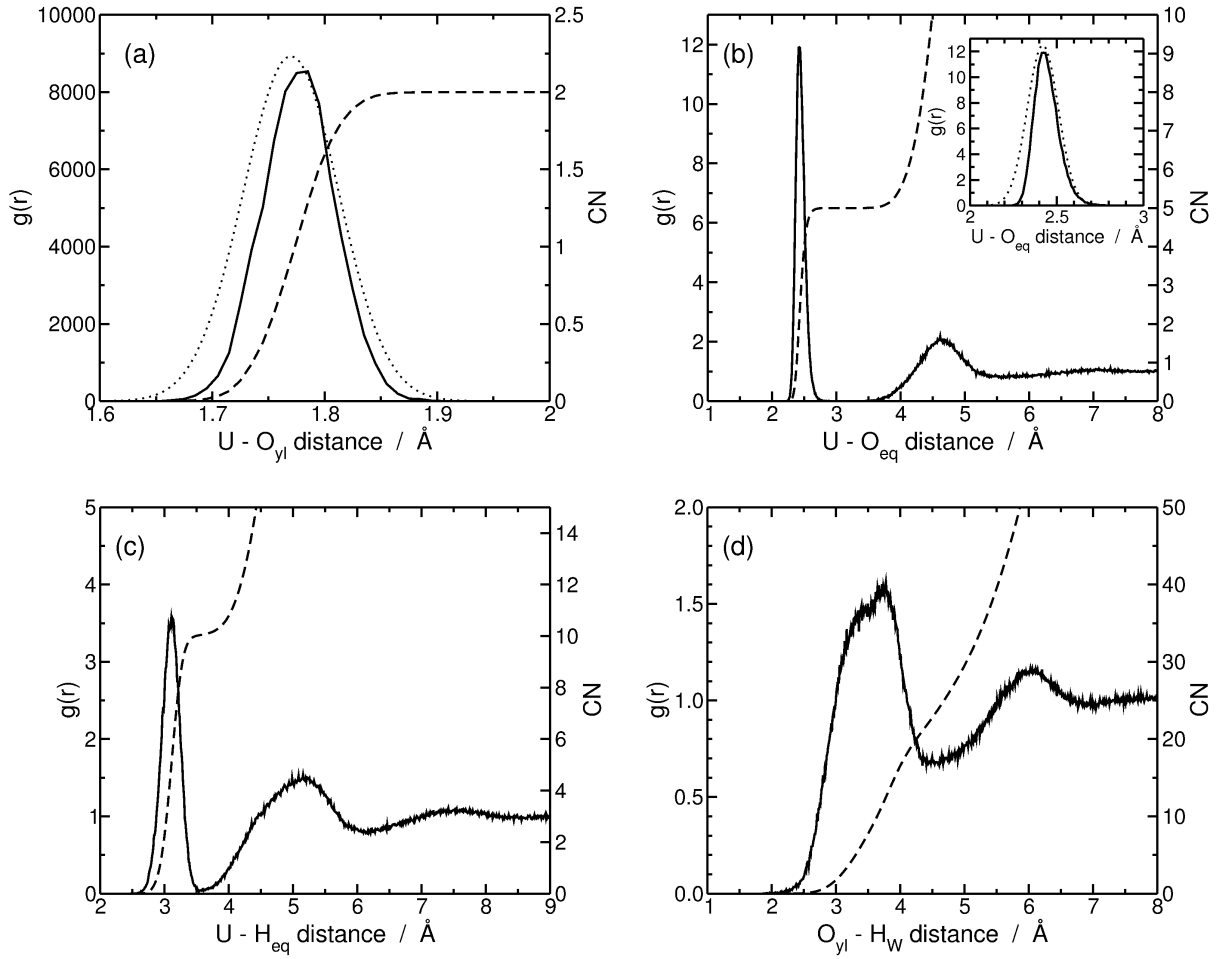

Fig. S2 Radial distribution functions (solid line) and corresponding coordination numbers (dashed line) calculated for (a) U – O_{eq}, (b) U – H_{eq}, (c) U – O_{yl}, and (d) O_{yl} – H_W. Theoretical radial distribution functions calculated from the experimental metrical parameters are also plotted (dashed dotted line).

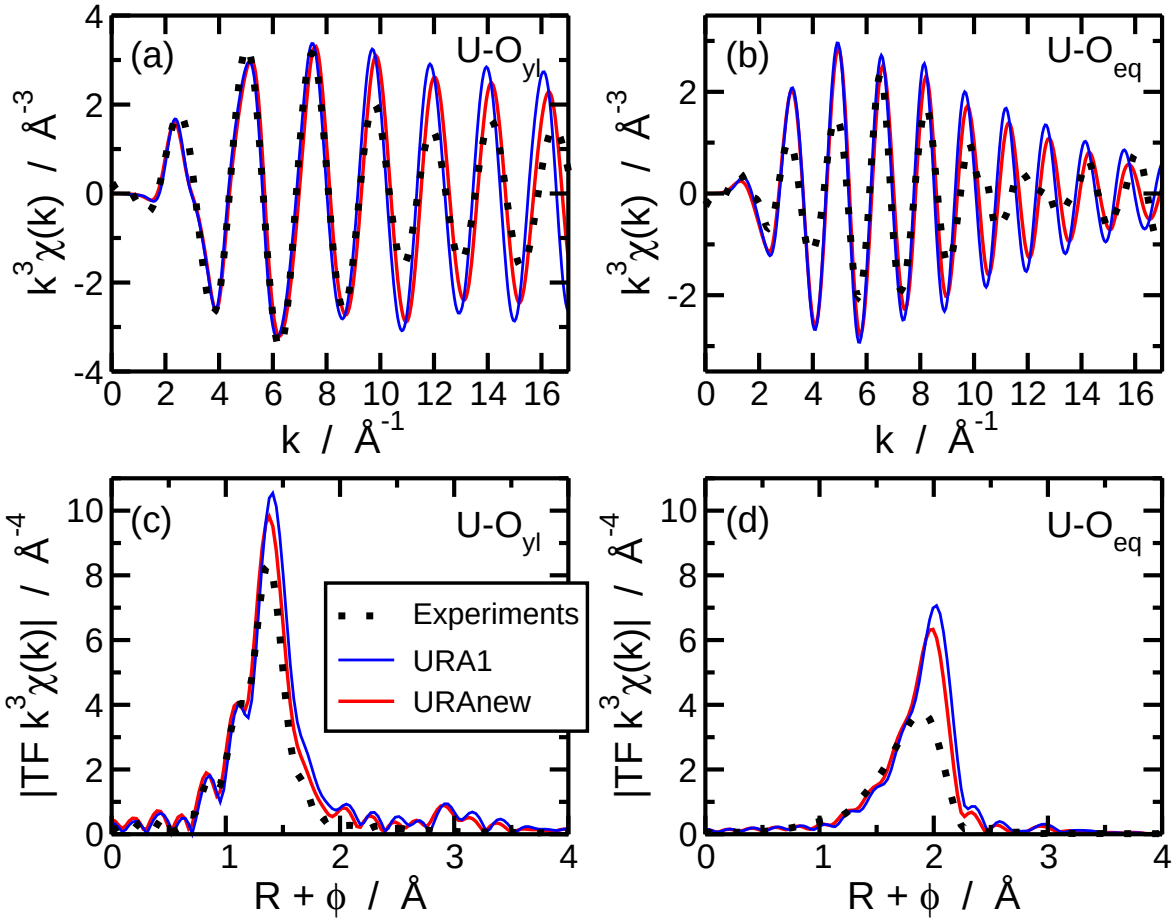

Fig. S3 (Top) k^3-weighted EXAFS spectra corresponding to the (a) U – O_{yl} and (b) U – O_{eq} distances and (bottom) Fourier transform (FT) obtained from k^3-weighted EXAFS spectra for a k range of 1.7 to 16.9 Å^{-1} corresponding to the (c) U – O_{yl} and (d) U – O_{eq} distances. The experimental results are presented in black and the theoretical results are presented in blue and red for the URA1 and URAnew models, respectively.

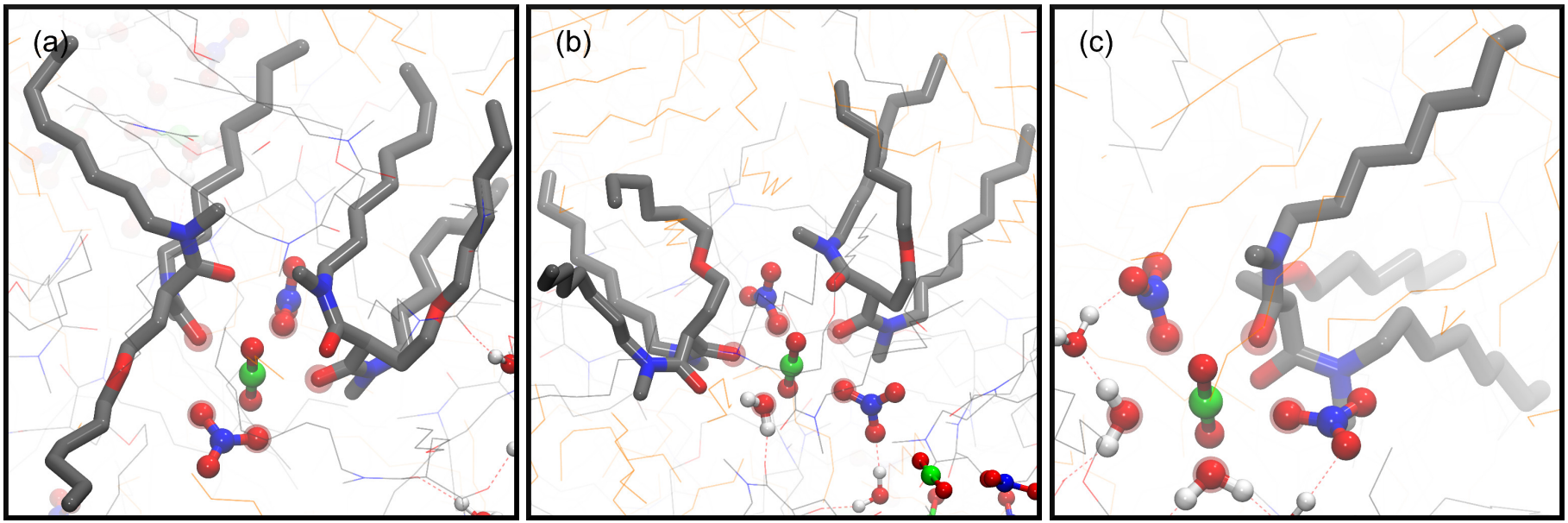

Fig. S4 Snaphsots issued from MD simulations presenting the average configurations calculated in Table S3 with (a) 0, (b) 1, and (c) 2 water molecules in the complexe. For the illustrations, uranium atoms are colored in green, oxygen atoms are in red, nitrogen atoms are in blue, carbon atoms are in grey, and hydrogen atoms are in white, and n-heptane molecules are colored in orange. Oxygen atoms in th eequatorial plane of the UO_2^{2+} cation are representated by a transparent red sphere.

S2 Tables

Table S1 UO_2^{2+} – H_2O first shell structural parameters calculated from MD simulations using the URAnew model for UO_2^{2+} as a function of the simulation temperature

	EXAFS	298.15[a]	400[a]	500[a]	550[a]	600[a]
$N(O_{yl})$[b]	2	2	2	2	2	2
$R(O_{yl})$[c]	1.77	1.78	1.78	1.78	1.78	1.77
$\sigma^2(O_{yl})$[d]	0.0018	0.0010	0.0013	0.0017	0.0018	0.0020
$N(O_{eq})$[b]	5.3 ± 0.5	5	5	5	5	5
$R(O_{eq})$[c]	2.42	2.43	2.43	2.43	2.43	2.43
$\sigma^2(O_{eq})$[d]	0.0080	0.0044	0.0060	0.0078	0.0086	0.0094

[a] Temperature (in K). [b] Number of oxygen atoms. [c] Distance (in Å). [d] Debye-Waller Factor (in $Å^2$).

Table S2 Configurations in organic phase calculated from MD simulations at 298.15 K

Configuration	% (number)
0 water molecule	
$UO_2(NO_3)_2(DMDOHEMA)_2(H_2O)_0$	13.95% (6)
$UO_2(NO_3)_2(DMDOHEMA)_3(H_2O)_0$	4.65% (2)
$[UO_2(NO_3)_3(DMDOHEMA)_1(H_2O)_0]^-$	2.33% (1)
$[UO_2(NO_3)_3(DMDOHEMA)_2(H_2O)_0]^-$	4.65% (2)
1 water molecule	
$UO_2(NO_3)_2(DMDOHEMA)_1(H_2O)_1$	2.33% (1)
$UO_2(NO_3)_2(DMDOHEMA)_{1.5}(H_2O)_1$	9.30% (4)
$UO_2(NO_3)_2(DMDOHEMA)_2(H_2O)_1$	23.26% (10)
$[UO_2(NO_3)_3(DMDOHEMA)_0(H_2O)_1]^-$	2.33% (1)
$[UO_2(NO_3)_3(DMDOHEMA)_1(H_2O)_1]^-$	9.30% (4)
$[UO_2(NO_3)_4(DMDOHEMA)_0(H_2O)_1]^{2-}$	2.33% (1)
2 water molecules	
$UO_2(NO_3)_2(DMDOHEMA)_0(H_2O)_2$	2.33% (1)
$UO_2(NO_3)_2(DMDOHEMA)_1(H_2O)_2$	16.28% (7)
3 water molecules	
$[UO_2(NO_3)_1(DMDOHEMA)_1(H_2O)_3]^+$	2.33% (1)
$UO_2(NO_3)_2(DMDOHEMA)_0(H_2O)_3$	2.33% (1)
4 water molecules	
$[UO_2(NO_3)_1(DMDOHEMA)_0(H_2O)_4]^+$	2.33% (1)

Table S3 UO_2^{2+} first shell structural parameters calculated in organic phase from MD simulations at 298.15 K as a function of the number of water molecules in the UO_2^{2+} first coordination shell

	0 H_2O (11 confs)			1 H_2O (21 confs)			2 H_2O (8 confs)			3 H_2O (2 confs)			4 H_2O (1 conf)		
Atom	N[a]	R[b]	σ^{2c}	N[a]	R[b]	σ^{2c}	N[a]	R[b]	σ^{2c}	N[a]	R[b]	σ^{2c}	N[a]	R[b]	σ^{2c}
O_{yl}	2	1.77	0.0010	2	1.77	0.0010	2	1.77	0.0010	2	1.78	0.0010	2	1.78	0.0010
O_{H_2O}	0.03	2.37	0.0027	0.99	2.38	0.0030	2.01	2.39	0.0033	2.85	2.40	0.0034	3.73	2.41	0.0037
$O_{(NO_3^-)_{bi}}$	1.30	2.55	0.0089	0.99	2.54	0.0073	0.77	2.57	0.0088	0.59	2.57	0.0073	-	-	-
$O_{(NO_3^-)_{mono}}$	1.78	2.45	0.0036	1.57	2.45	0.0033	1.45	2.47	0.0037	1.06	2.48	0.0040	1.07	2.51	0.0061
$O_{(NO_3^-)}$	**3.08**	**2.49**	-	**2.56**	**2.48**	-	**2.22**	**2.50**	-	**1.65**	**2.51**	-	**1.07**	**2.51**	-
$N_{(NO_3^-)_{bi}}$	**0.71**	**2.95**	**0.0041**	**0.21**	**2.96**	**0.0038**	**0.16**	**2.99**	**0.0043**	**0.03**	**3.00**	**0.0059**	**0.01**	**3.12**	**0.0033**
$N_{(NO_3^-)_{mono}}$	1.33	3.39	0.0371	1.30	3.40	0.0215	0.96	3.38	0.0221	0.60	3.58	0.0333	0.32	3.44	0.0611
	0.26	3.63	0.0061	0.81	3.66	0.0091	0.88	3.66	0.0112	0.98	3.66	0.0096	0.73	3.62	0.0071
$N_{(NO_3^-)_{mono}}$	**1.59**	**3.43**	-	**2.11**	**3.50**	-	**1.84**	**3.51**	-	**1.58**	**3.63**	-	**1.05**	**3.57**	-
$O_{DMDOHEMA}$	**2.09**	**2.45**	**0.0061**	**1.49**	**2.46**	**0.0067**	**0.81**	**2.50**	**0.0083**	**0.49**	**2.54**	**0.0156**	**0.20**	**2.53**	**0.0107**
$C_{DMDOHEMA}$	**2.10**	**3.60**	**0.0101**	**1.50**	**3.66**	**0.0082**	**0.88**	**3.69**	**0.0095**	**0.50**	**3.69**	**0.0141**	**0.21**	**3.74**	**0.0114**
$O2_{(NO_3^-)_{bi}}$	1.34	4.20	0.0105	1.41	4.24	0.0250	1.56	4.32	0.0569	1.76	4.08	0.0658	1.42	3.99	0.0227
	1.49	4.51	0.0111	1.97	4.55	0.0118	1.30	4.56	0.0105	2.10	4.59	0.0186	3.08	4.67	0.0432
$O2_{(NO_3^-)_{bi}}$	**2.83**	**4.36**	-	**3.38**	**4.42**	-	**2.86**	**4.43**	-	**3.86**	**4.36**	-	**4.50**	**4.46**	-
$C^{central,bi}_{DMDOHEMA}$	0.34	4.07	0.0099	< 0.1	-	-	-	-	-	-	-	-	-	-	-
$C^{central,mono}_{DMDOHEMA}$	1.41	4.52	0.0144	1.49	4.55	0.0151	0.82	4.60	0.0232	0.50	4.53	0.0119	0.21	4.71	0.0180

[a] Number of atoms. [b] Distance (in Å). [c] Debye-Waller Factor (in $Å^2$).