Electronic Supplementary Information

Insights into the spontaneous multi-scale supramolecular assembly in ionic liquid based extraction system

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Supplementary Figures and Tables

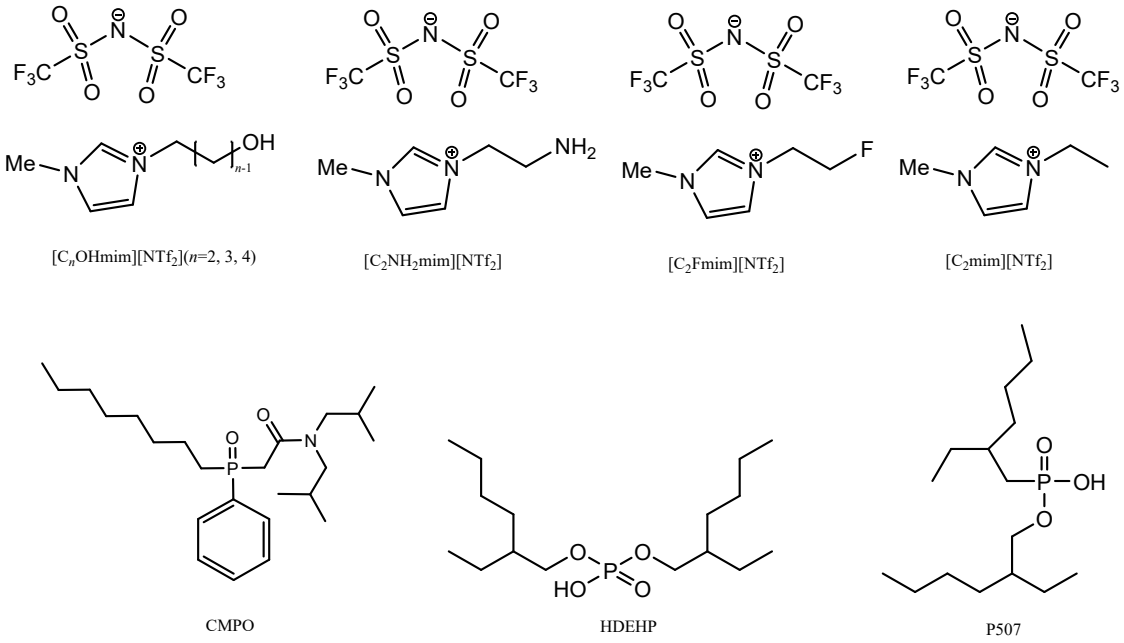

Figure S1 Structures of ILs and extractants involved in this work.

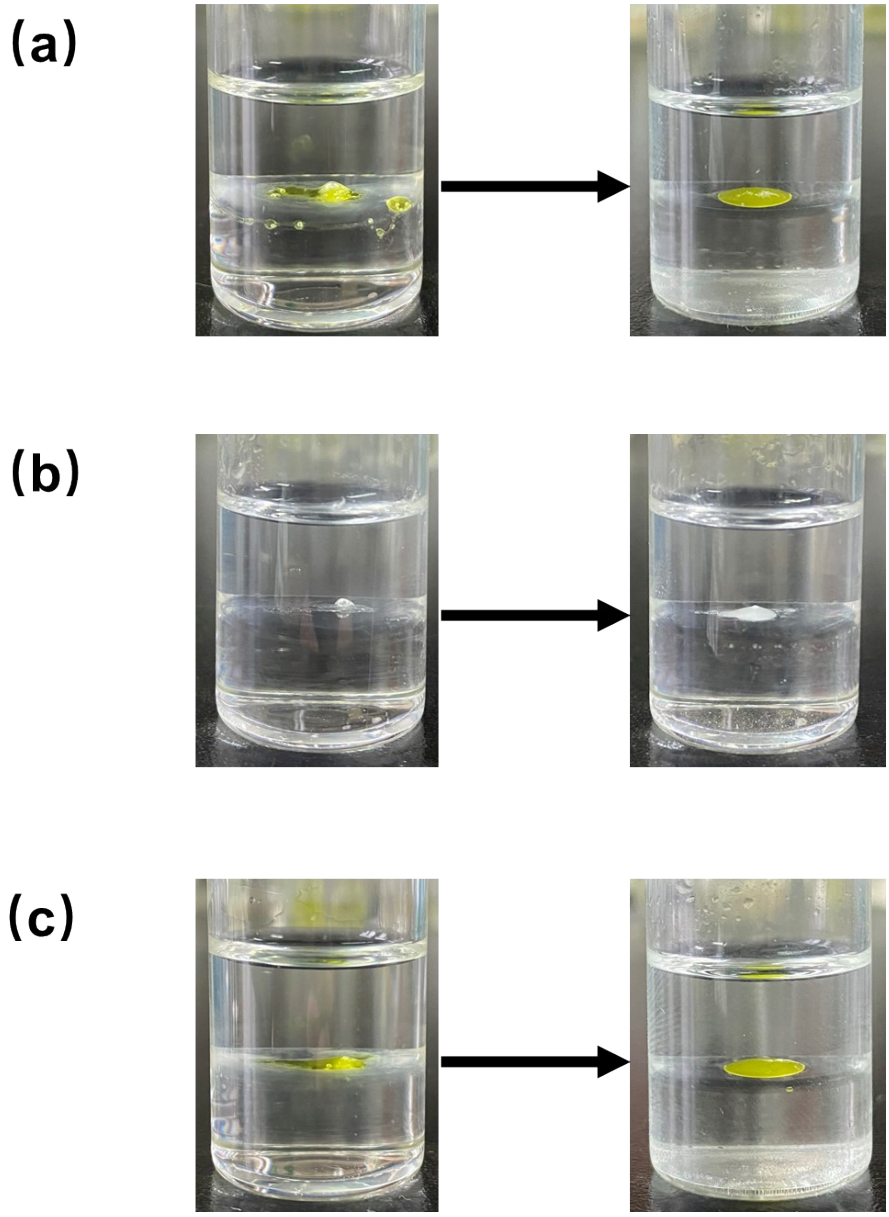

Figure S2 The pictures of the MSSA systems left for one day and one week at 10 °C. The aqueous solutions of metal ions (a. 10 mM UO_2^{2+}, b. 10 mM Al^{3+}, c. 10 mM UO_2^{2+} and 10 mM Al^{3+}) with 0.1 M nitric acid were mixed with the solutions of 60 mM CMPO in C_2OHmimNTf_2. Left: one day. Right: one week. Several macroscopic assemblies were formed in the IL-water interface and then they aggregated into the single MA sphere. From the pictures of U-MSSA system and Al-MSSA system left for 1d, we can see the rate of the U-MSSA process is higher than that of the Al-MSSA process.

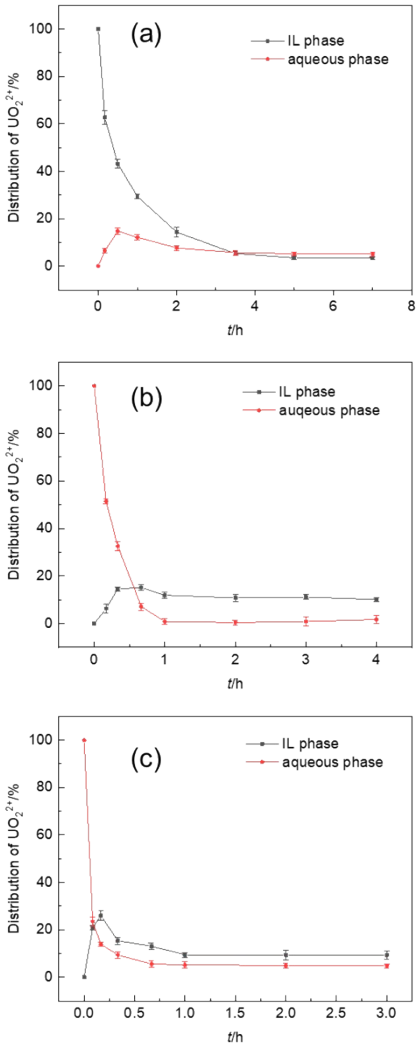

Figure S3 Distribution of UO_2^{2+} in aqueous phase and IL phase against time in the initial stage of the MSSA process at different temperatures: (a) 25 °C. (b) 30 °C. (c) 40 °C. 10 mM UO_2^{2+} solutions with 0.1 M HNO_3 were mixed with 60 mM CMPO/C_2OHmimNTf_2 at different temperatures. The uranyl content in the aqueous phase declines sharply, while that in the IL phase is enhanced at first and then goes down. Both of them reach a platform at about 1 to 2 h depending on the temperature. This result indicates that uranyl can be extracted to the IL phase and then uranyl would move to the interface. The first step of the MSSA process is the cation exchange.

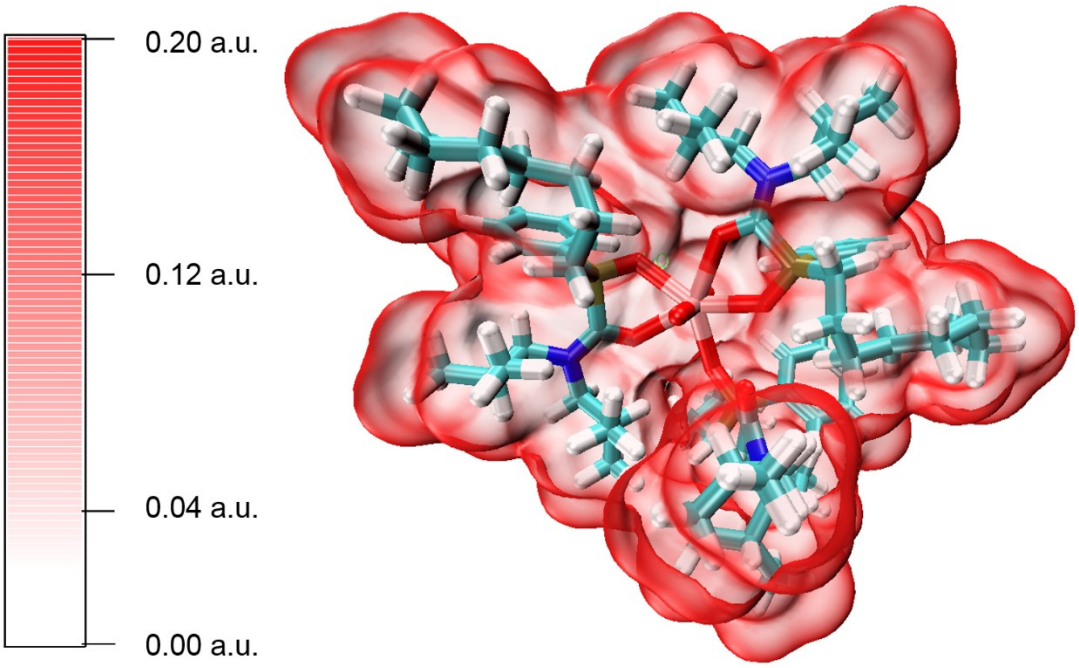

Figure S4 The molecular electrostatic potential of $[UO_2(CMPO)_3]^{2+}$. The red cover means that $[UO_2(CMPO)_3]^{2+}$ has positive electrostatic potential. On the surface of $[UO_2(CMPO)_3]^{2+}$, the deeper red colour means the more positive electrostatic potential. The $[UO_2(CMPO)_3]^{2+}$ has hydrophobic organic chains with positive electrostatic potential which is essential in construction of the EBB.

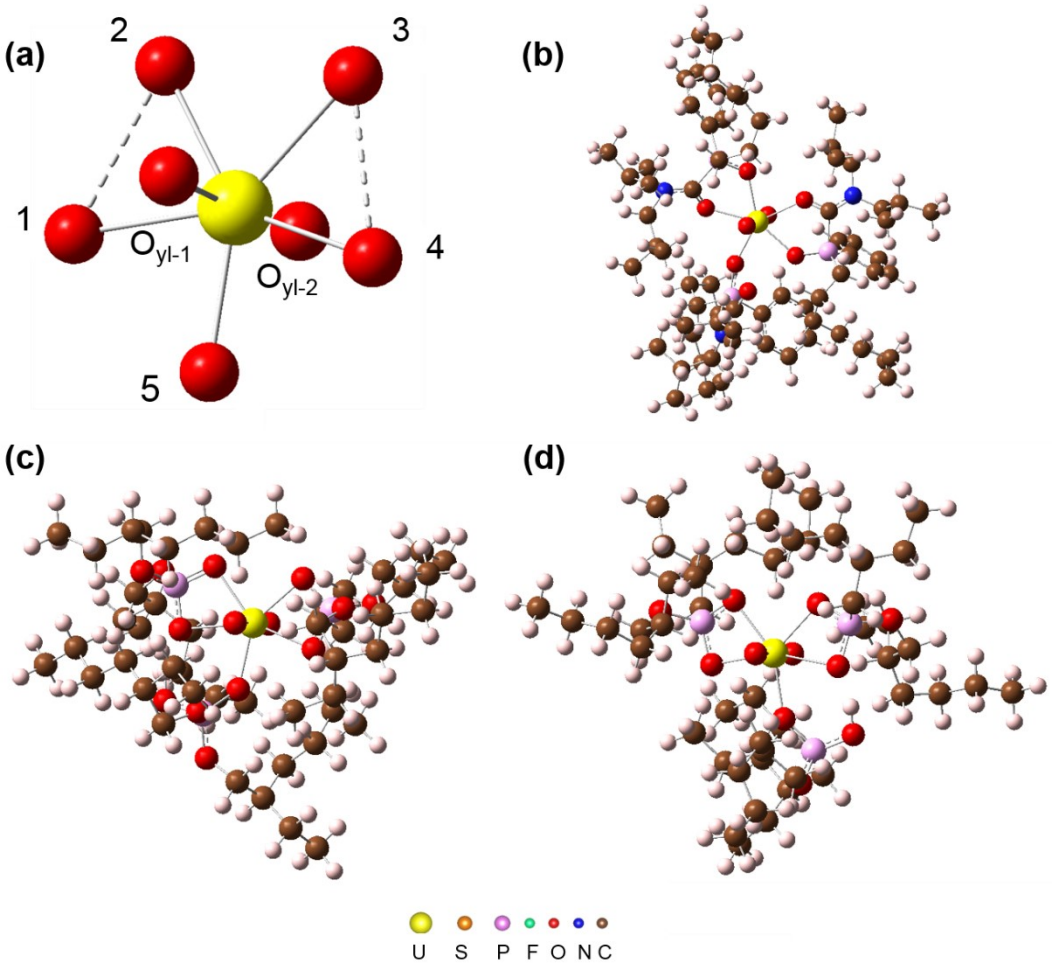

Figure S5 (a) Coordination between uranyl and three bidentate ligands. Oxygen atoms **1** and **2** are from the first ligand while **3** and **4** from the second ligand respectively. Oxygen atom **5** is from the third ligand. (b, c, d) The 1:3 complex structures between uranyl and CMPO, HDEHP, P507, respectively.

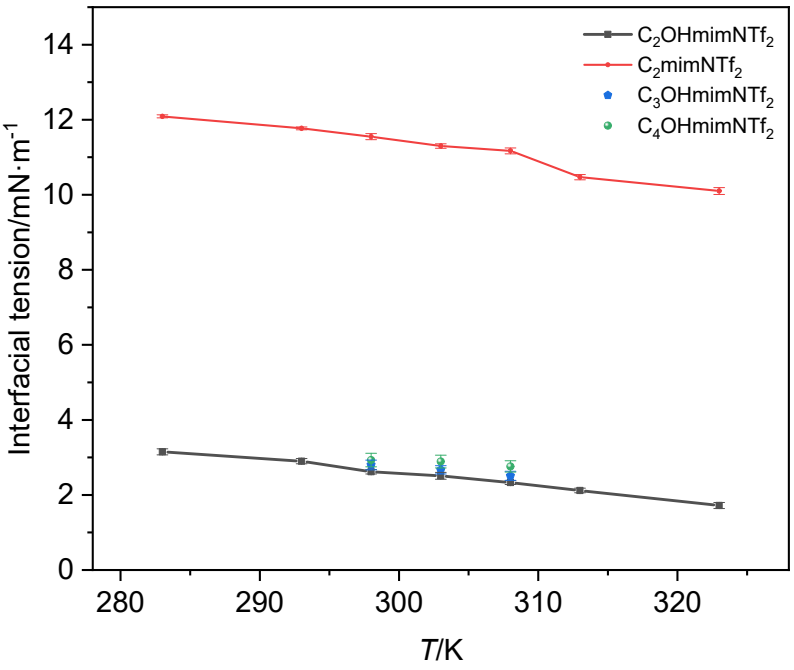

Figure S6 The interfacial tension for C_2mimNTf_2-water and C_nOHmimNTf_2 (n=2, 3, 4)-water interfaces against the temperature.

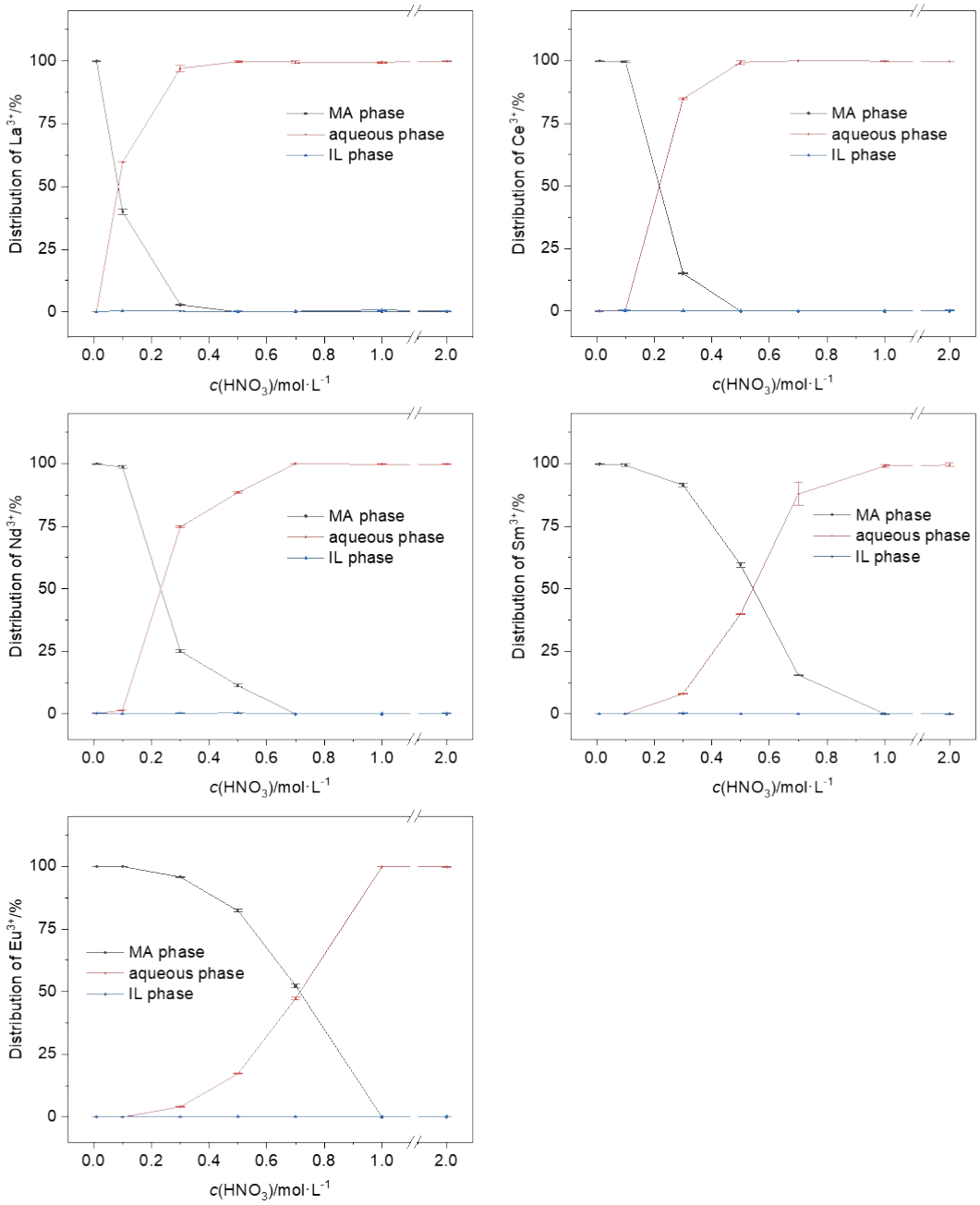

Figure S7 MSSA-based separation of La^{3+}(a), Ce^{3+}(b), Nd^{3+}(c), Sm^{3+}(d), Eu^{3+}(e) under different HNO_3 concentrations in HDEHP-C_2OHmimNTf_2 system. Aqueous solutions of 10 mM M^{3+} with different concentrations of nitric acid are mixed with 60 mM HDEHP/C_2OHmimNTf_2 and MSSA-based separation experiments last for 3 days. La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} exhibited similar behaviors at different concentration of nitric acid. All of them remained in the aqueous phase when the concentration of nitric acid was greater than 1 M.

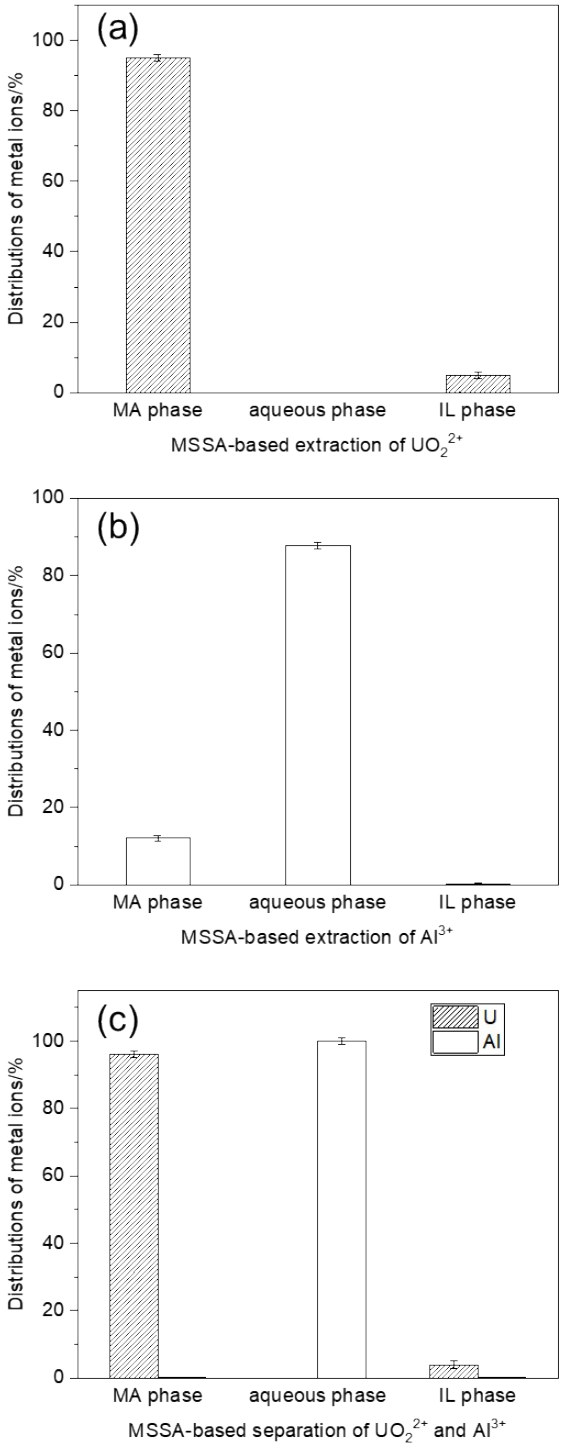

Figure S8 MSSA-based separation of UO_2^{2+} and Al^{3+} at 10 °C . The distributions of metal ions when they are extracted from the solution of 10 mM UO_2^{2+} with 0.1 M nitric acid (a), the solution of 10 mM Al^{3+} with 0.1 M nitric acid (b), the mixed solution of 10 mM UO_2^{2+} and Al^{3+} with 0.1 M nitric acid (c). MSSA-based separation experiments lasted for 7 days at 10 °C. In the mixed solution of UO_2^{2+} and Al^{3+}, almost all Al^{3+} ions still remain in the aqueous phase while UO_2^{2+} can be selectively extracted into the MA phase.

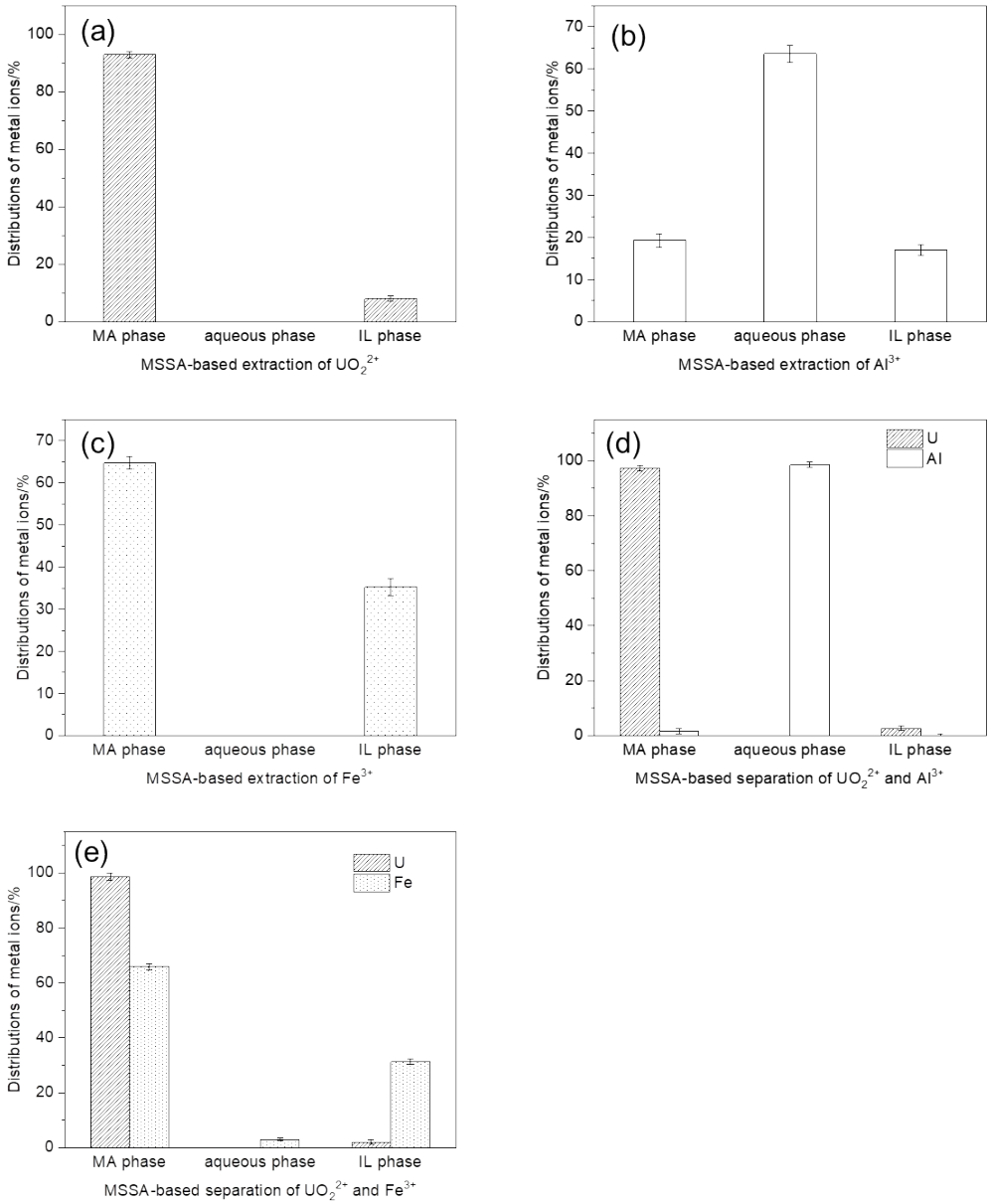

Figure S9 MSSA-based separation of UO_2^{2+} and Al^{3+}, Fe^{3+} at 20 °C . The distributions of metal ions when they are extracted from the solution of 10 mM UO_2^{2+} with 0.1 M nitric acid (a), the solution of 10 mM Al^{3+} with 0.1 M nitric acid (b), the solution of 10 mM Fe^{3+} with 0.1 M nitric acid (c), the mixed solution of 10 mM UO_2^{2+} and Al^{3+} with 0.1 M nitric acid (d) and the mixed solution of 10 mM UO_2^{2+} and Al^{3+} with 0.1 M nitric acid (e). MSSA-based separation experiments lasted for 7 days at 20 °C. In the mixed solution of UO_2^{2+} and Al^{3+}, almost all Al^{3+} ions still remain in the aqueous phase while UO_2^{2+} can be selectively extracted into the MA phase. The amount of Al^{3+} extracted to the MA phase and IL phase is very small if any. But in the mixed solution of UO_2^{2+} and Fe^{3+}, both UO_2^{2+} and Fe^{3+} can be extracted to the MA phase and IL phase.

Table S1. The axial O=U=O bond angles and bond lengths of U-O coordination bonds of 1:3 complex structures between uranyl and CMPO, HDEHP, P507, respectively.

Structural parameter	CMPO	HDEHP	P507
O=U=O/deg	176.0	177.1	178.3
U-$O_{\mathbf{1}}$/pm	247	240	259
U-$O_{\mathbf{2}}$/pm	238	240	253
U-$O_{\mathbf{3}}$/pm	248	241	254
U-$O_{\mathbf{4}}$/pm	235	262	251
U-$O_{\mathbf{5}}$/pm	231	235	255
U-$O_{yl\text{-}1}$/pm	177	177	176
U-$O_{yl\text{-}2}$/pm	177	177	174

The numbers of oxygen atoms are consistent with those in Fig. S5, ESI†.

Table S2. Diameters of EBB, the cavity in EBB capturing imidazolium cation and length of imidazolium cations for different IL system.

	C_2mimNTf_2	C_2OHmimNTf_2	C_3OHmimNTf_2
Diameters of EBB/nm	2.8	2.3	3.0
Diameters of the cavity/pm	980	972	1198
Length of imidazolium cation/pm	751	839	965

Table S3. Elemental analysis results of the Fe-MA.

Batch	C/%	H/%	N/%
A	42.98	5.84	4.51
B	43.04	5.83	4.50
cal	42.97	5.79	4.35

The Fe-MA was taken out with a tweezer and placed in a petri dish with an air-drying for a week. The results are quite close to that of assembly made up of $[Fe(CMPO)_3]^{3+}$:$[C_2OHmim]^{+}$:$[NTf_2]^{-}$ in a molar ratio of 3:1:10.