

Supporting information for

Metastable precipitation and ion-extractant transport in liquid-liquid separations of trivalent elements

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This PDF file includes:

Supporting text
Figures S1 to S23
Tables S1 to S3
Legends for Movies S1 to S10

Other supporting materials for this manuscript include the following:

Movies S1 to S10



Figure S1. The illustration of setup used to record the evolution process of precipitation.

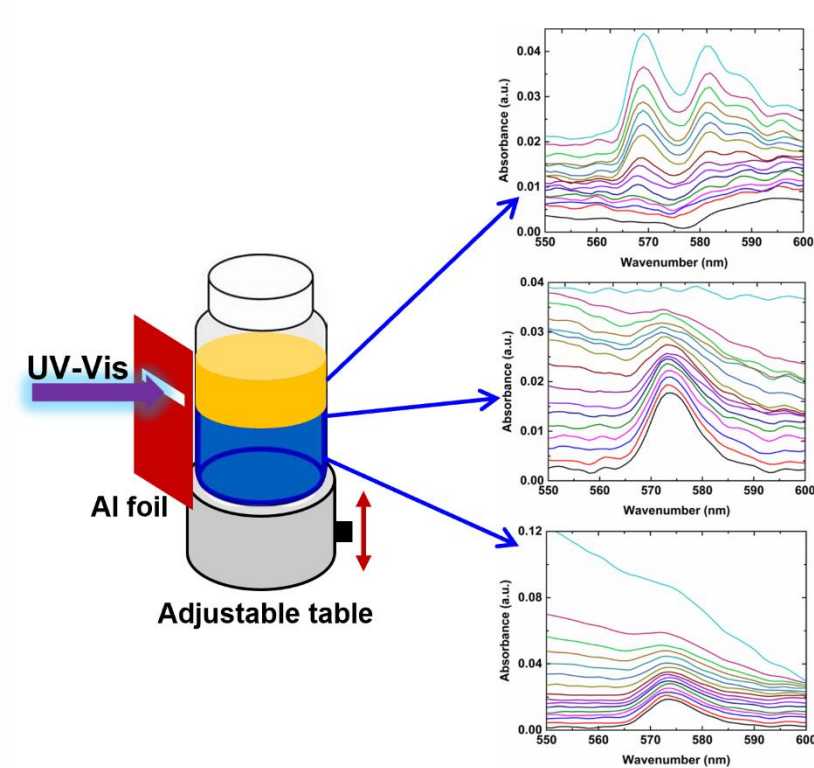


Figure S2. Illustration of the setup used to measure UV-Vis spectra of Nd^{3+} during the evolution of the precipitation. The beam is $2 \times 2 \text{ mm}^2$. The regions near the interface are centered 2 mm below and above it, and the far region is centered 2 mm above the bottom of the sample vial.

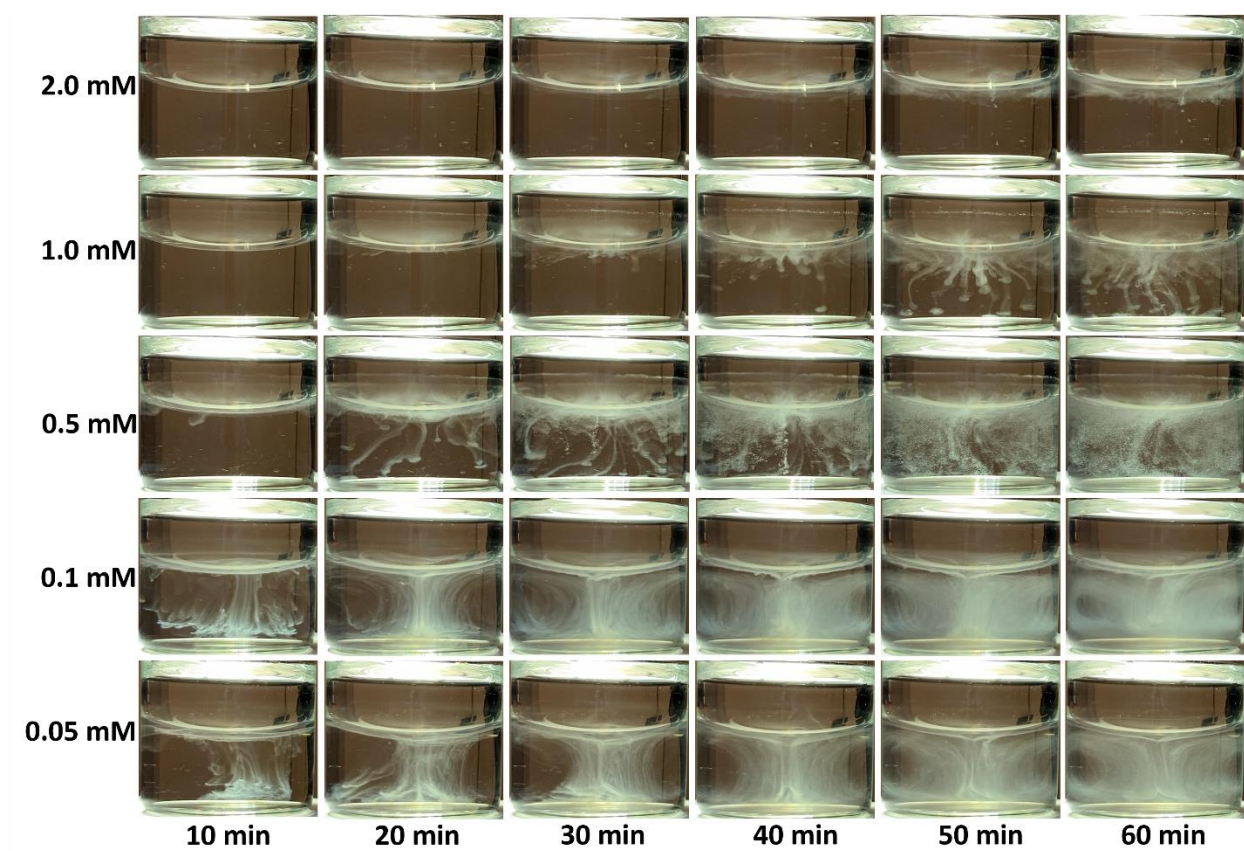


Figure S3. True color version of panel A in Figure 1 of the main paper. The evolution of precipitation in the 0.2 M HDEHP-dodecane/aqueous solution containing various concentrations of Nd at pH 4.5.

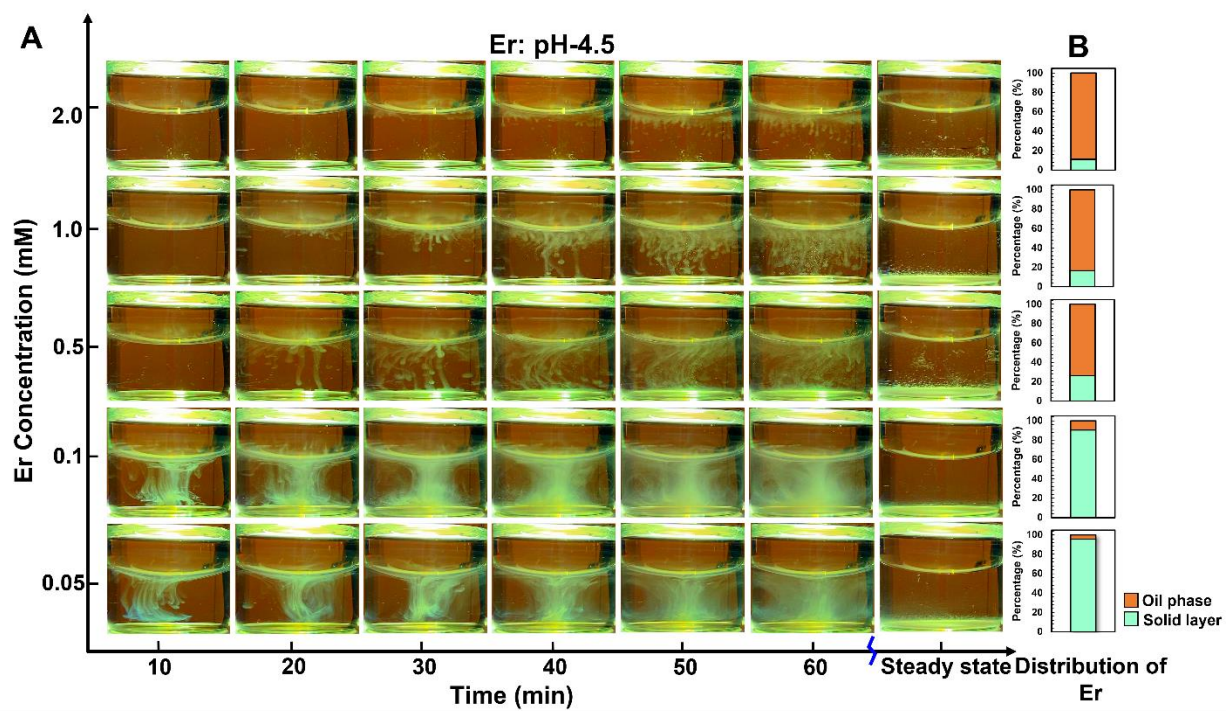


Figure S4. The evolution of precipitation (A) and 48 hour (steady state) distribution of Er (B) in the 0.2 M HDEHP-dodecane/aqueous solution containing various concentrations of Er at pH 4.5.

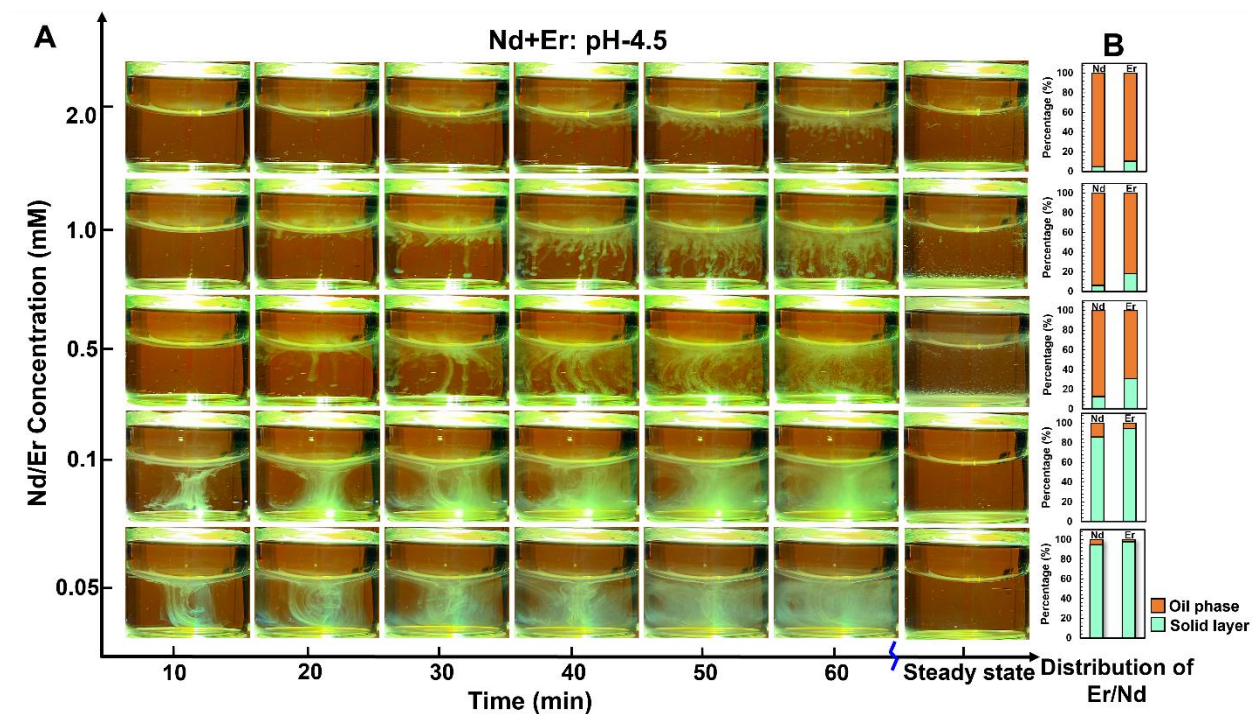


Figure S5. The evolution of precipitation (A) and 48 hour (steady state) distribution of Er/Nd (B) in the 0.2 M HDEHP-dodecane/aqueous solution containing various concentrations of Er/Nd (1:1) at pH 4.5.

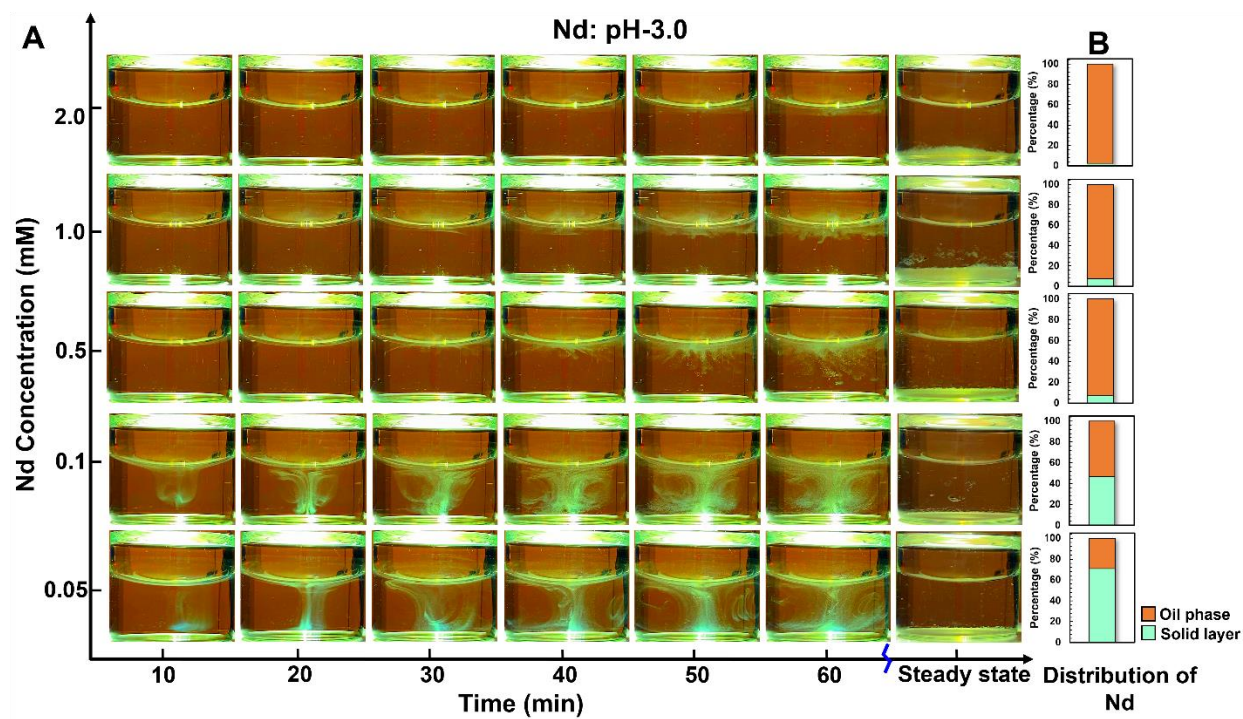


Figure S6. The evolution of precipitation (A) and 48 hour (steady state) distribution of Nd (B) in the 0.2 M HDEHP-dodecane/aqueous solution containing various concentrations of Er at pH 3.0.

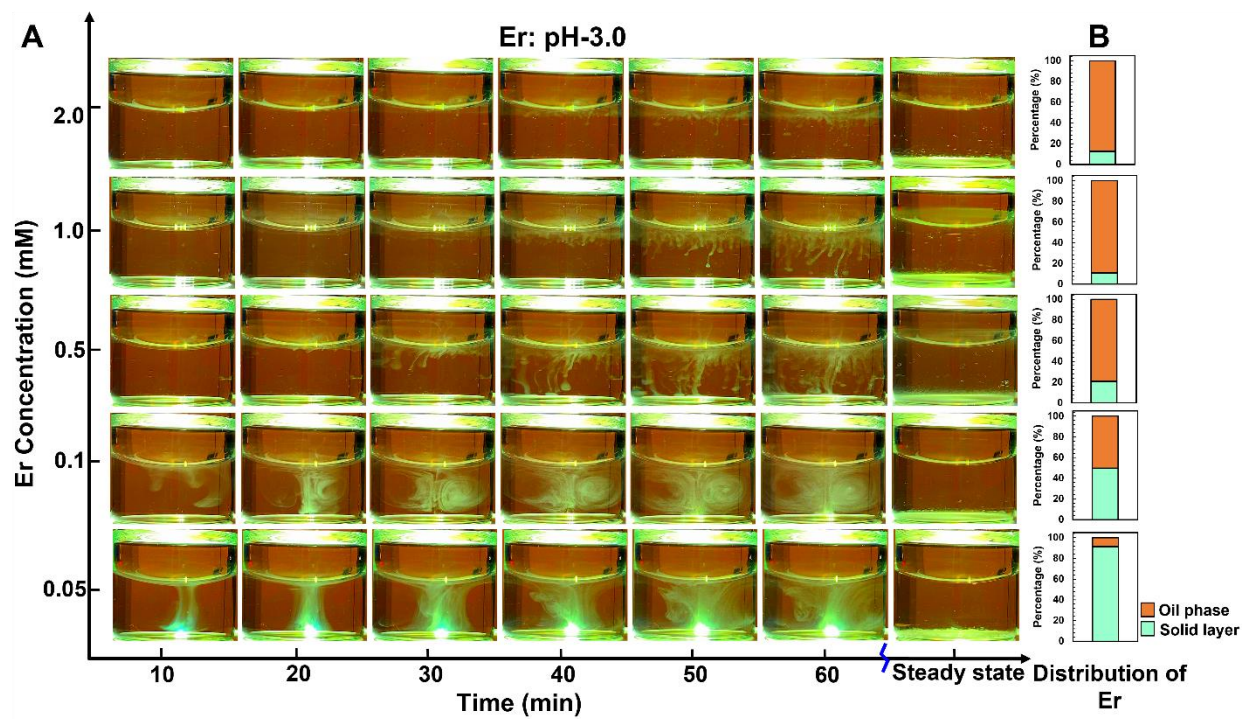


Figure S7. The evolution of precipitation (A) and 48 hour (steady state) distribution of Er (B) in the 0.2 M HDEHP-dodecane/aqueous solution containing various concentrations of Er at pH 3.0.

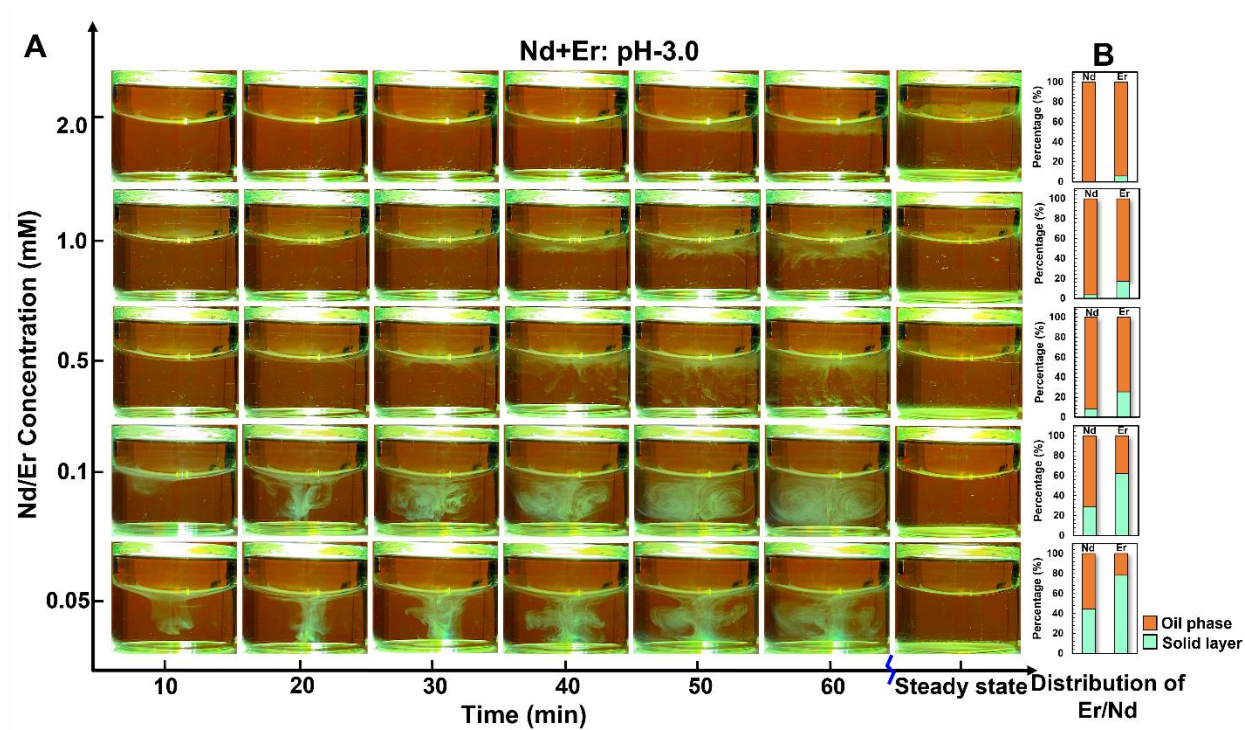


Figure S8. The evolution of precipitation (A) and 48 hour (steady state) distribution of Er/Nd (B) in the 0.2 M HDEHP-dodecane/aqueous solution containing various concentrations of Er/Nd(1:1) at pH 3.0.

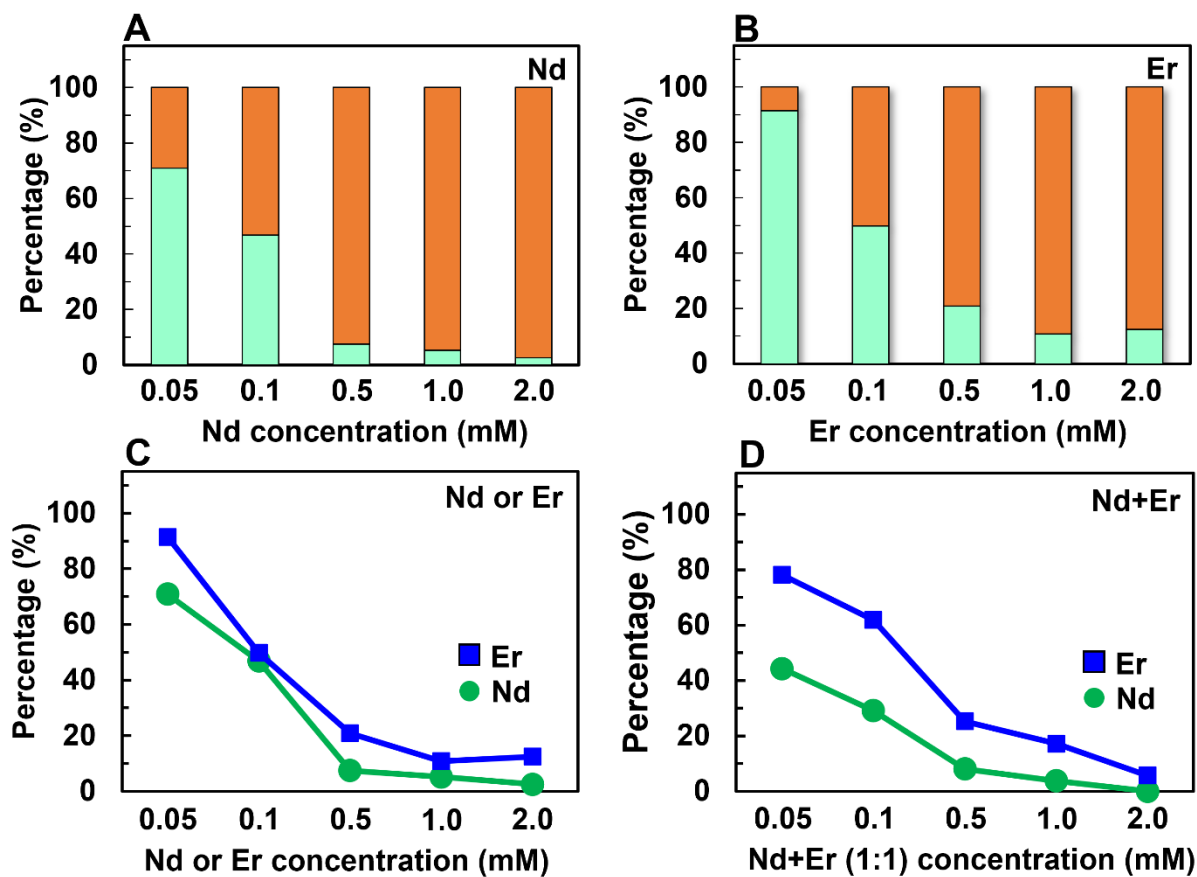


Figure S9. The equilibrium distribution of Nd (A) and Er(B) in the organic phase and solid layer; (C) The percentage of Nd or Er in the solid layer after equilibrium in the 0.2M HDEHP-dodecane/aqueous solution containing various concentration of Nd or Er at pH of 3.0. (D) The percentage of Nd and Er in the solid layer after equilibrium in the 0.2M HDEHP-dodecane/aqueous solution containing various concentrations of Nd and Er mixture (1:1) at pH 3.0.

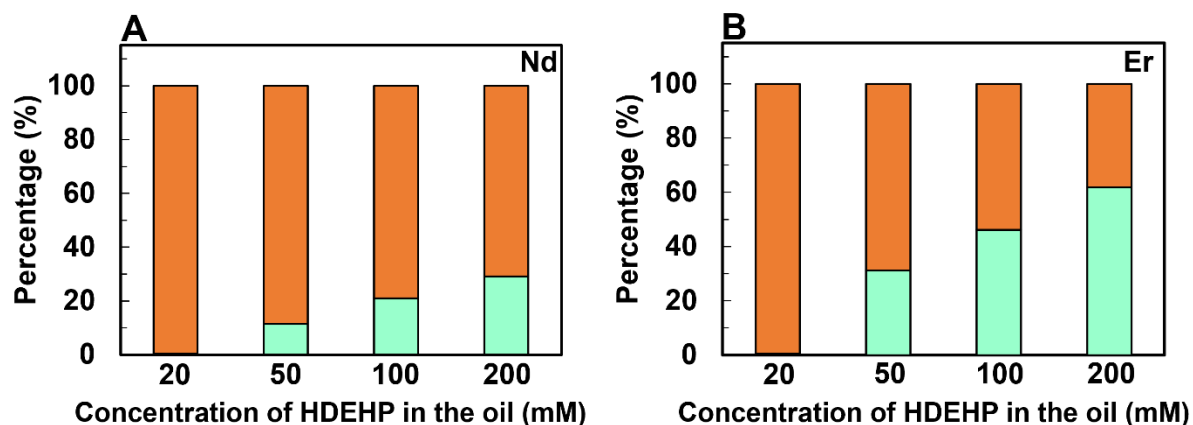


Figure S10. The effect of the HDEHP concentration in the organic phase on the equilibrium distribution of (A) Nd and (B) Er in HDEHP-dodecane/aqueous solution at pH 3.0 with a 1:1 NdCl₃:ErCl₃ mixture with total metal ion concentration of 0.1 mM.

Table S1. The mass of Nd and Er in mg in the precipitate after 48 hours.

Total initial ion concentration of REEs (mM)	pH=3.0				pH=4.5			
	Nd (mg)	Er (mg)	Nd(mix) (mg)	Er(mix) (mg)	Nd (mg)	Er (mg)	Nd(mix) (mg)	Er(mix) (mg)
0.05	0.0100	0.0153	0.00313	0.00641	0.0132	0.0160	0.00670	0.00802
0.1	0.0122	0.0167	0.00411	0.0101	0.0250	0.0302	0.00862	0.01550
0.5	0.0136	0.0350	0.00574	0.0208	0.0467	0.0441	0.00895	0.02517
1	0.0147	0.0363	0.00541	0.0282	0.0480	0.0560	0.01214	0.02999
2	0.0145	0.0833	0.00571	0.0389	0.0525	0.0744	0.01438	0.03497

Using the results of our EXAFS measurements that the ratio of HDEHP to rare earth ions is roughly 6, we estimated the mass of HDEHP in the precipitate in different samples as shown in Table S2. The mass of HDEHP in the precipitate increases with initial concentration of rare earths in the aqueous solution. More HDEHP is present in the precipitate when Er is in the samples. In addition, higher pH increases the amount of HDEHP in the precipitate. These calculations have not considered the possible co-precipitation of free HDEHP with ion-HDEHP complexes. Therefore, the real content of HDEHP in the precipitates may be higher than the values in Table S2.

Table S2. The mass of HDEHP in mg in the precipitate after 48 hours.

Total initial ion concentration of REEs (mM)	pH=3.0			pH=4.5		
	Nd (mg)	Er (mg)	Mix (mg)	Nd (mg)	Er (mg)	Mix (mg)
0.05	0.1344	0.1772	0.1281	0.1775	0.1855	0.1829
0.1	0.1776	0.1931	0.1915	0.3360	0.3502	0.3427
0.5	0.1422	0.4047	0.3553	0.6268	0.5102	0.4119
1	0.1980	0.4205	0.4515	0.6442	0.6481	0.4632
2	0.1945	0.9652	0.4552	0.3025	0.8618	0.5983

*Total mass of HDEHP in each sample is 64.5 mg.

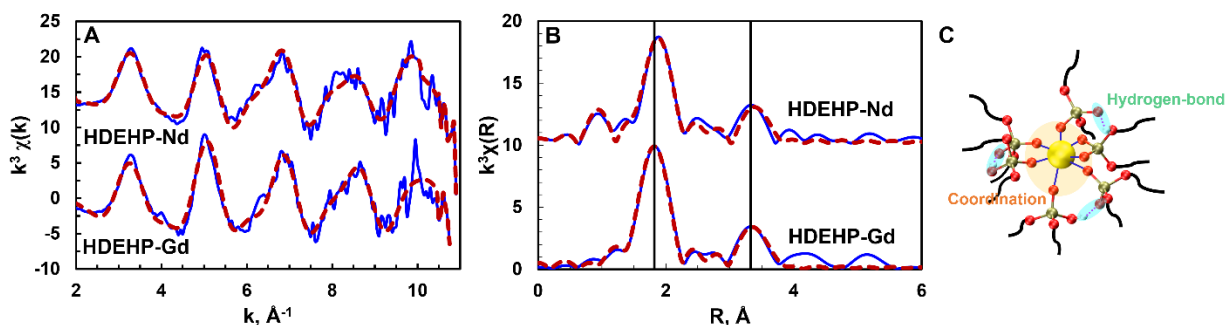


Figure S11. k^3 -weighted (A) and Fourier-transformed k^3 -weighted (B) EXAFS data in k space of the Nd (upper) or Gd (bottom) L_3 -edge in the precipitate collected from the 0.1 mM NdCl_3 or GdCl_3 aqueous solution (pH =3.0)/0.2 M HDEHP-dodecane solution; Blue lines represent experimental data; red dash lines represent the model fit. (C) Proposed structure of rare earth ion-HDHEP complex.

Table S3. k^3 -Weighted EXAFS Fit Results for the Nd or Gd L_3 -edge in the precipitate collected from the 0.1 mM NdCl_3 or GdCl_3 aqueous solution (pH =3.0)/0.2 M HDEHP-dodecane solution

Rare earth- HDEHP precipitates	Potential	$R/\text{\AA}$	CN	$\sigma^2 \times 10^{-3} / \text{\AA}^{-1}$	$\Delta E_0/\text{eV}$
Nd	O	2.303+/-0.013	4.89+/-0.8	2.53+/-2.58	1.33+/-1.02
	P	3.869+/-0.032	6.65+/-3.9	10.5+/-9.21	
Gd	O	2.273+/-0.008	6.00+/-0.5	3.32+/-1.41	0.09+/-0.62
	P	3.853+/-0.019	8.59+/-2.7	11.5+/-5.2	

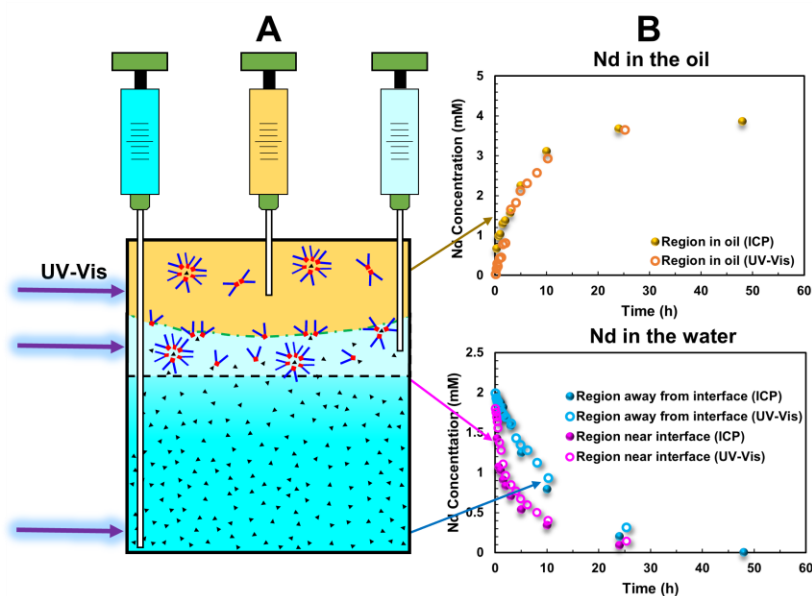


Figure S12. The transfer kinetics of Nd^{3+} into the organic phase and solid layer. (Aqueous phase, 2 mM NdCl_3 , pH=3.0; organic phase: 0.2 M HDEHP in dodecane) A: Illustration of the setup for measuring the kinetics of ion transfer. B: The concentration of Nd in three different regions: organic phase, region in the water side near the interface and away from the interface.

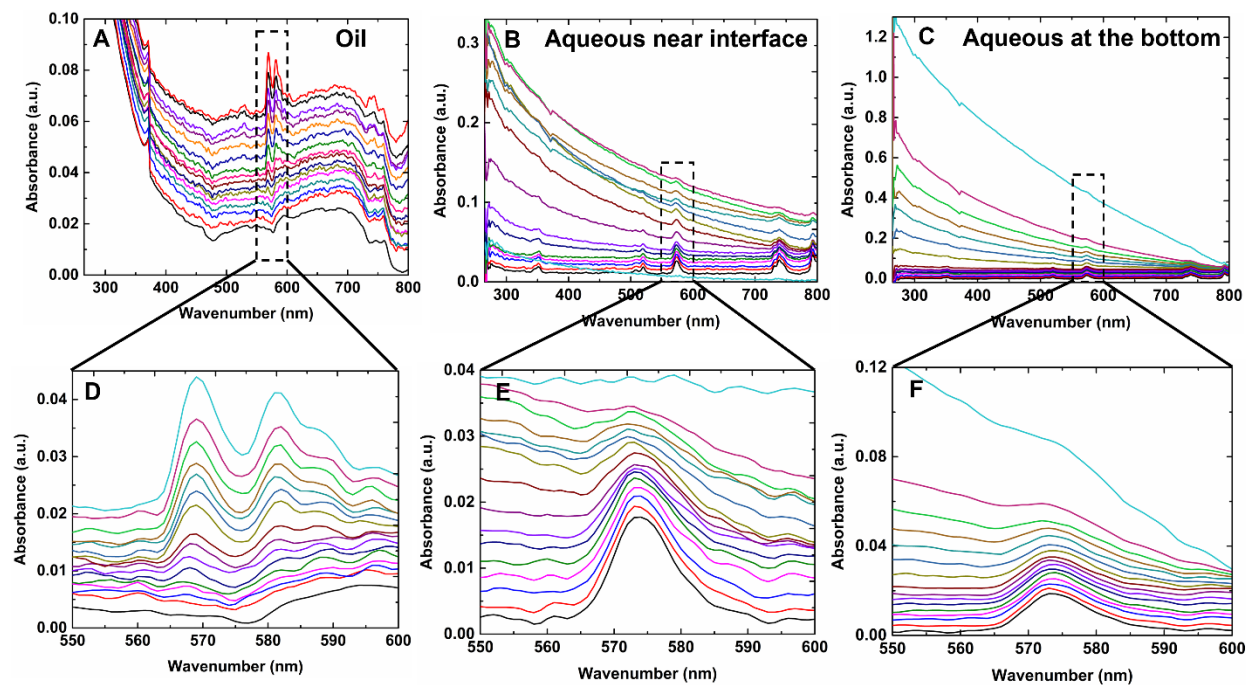


Figure S13. Time dependent in-situ UV-Vis spectra of Nd in the system. From bottom to top: 2 min, 10 min, 17 min, 24 min, 31 min, 50 min, 1 h 10 min, 1 h 31 min, 2 h, 3 h 4 min, 4 h, 4 h 52min, 6 h 12 min, 8 h 3 min, 10 h 12 min, 25 h 18 min. (0.1 M HDEHP in the dodecane, 2,0 mM NdCl₃ in the aqueous phase with pH of 3.0).

A range of monovalent and divalent cations, by themselves, do not exhibit precipitation at pH 3.0 (Fig. S14), though weak effects were observed at pH 4.5 (Fig. S15).

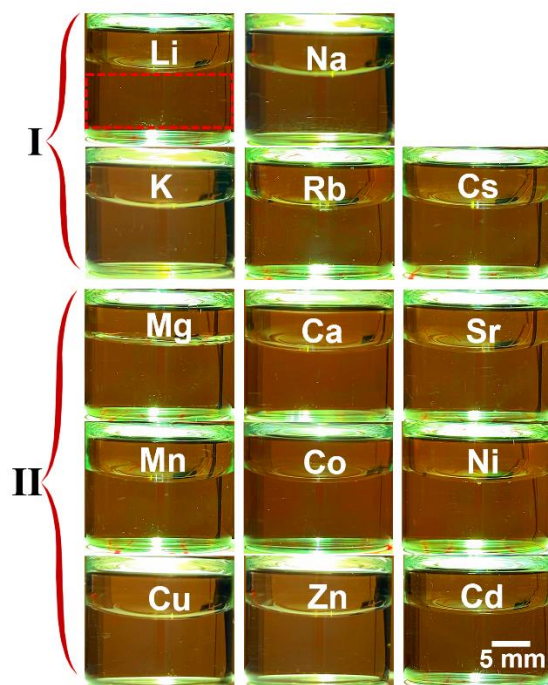


Figure S14. Patterns of precipitation in the systems containing 0.1 mM metal ions (monovalent and divalent) at pH of 3.0.

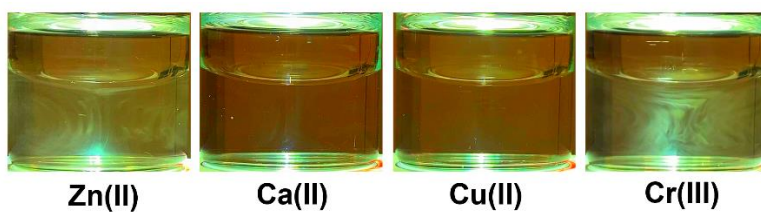


Figure S15. The pictures of system containing 0.1 mM different metal ions (Zn(II), Ca(II), Cu(II), Cr(III)) at aqueous pH of 4.5. The pictures were taken after 1 h.

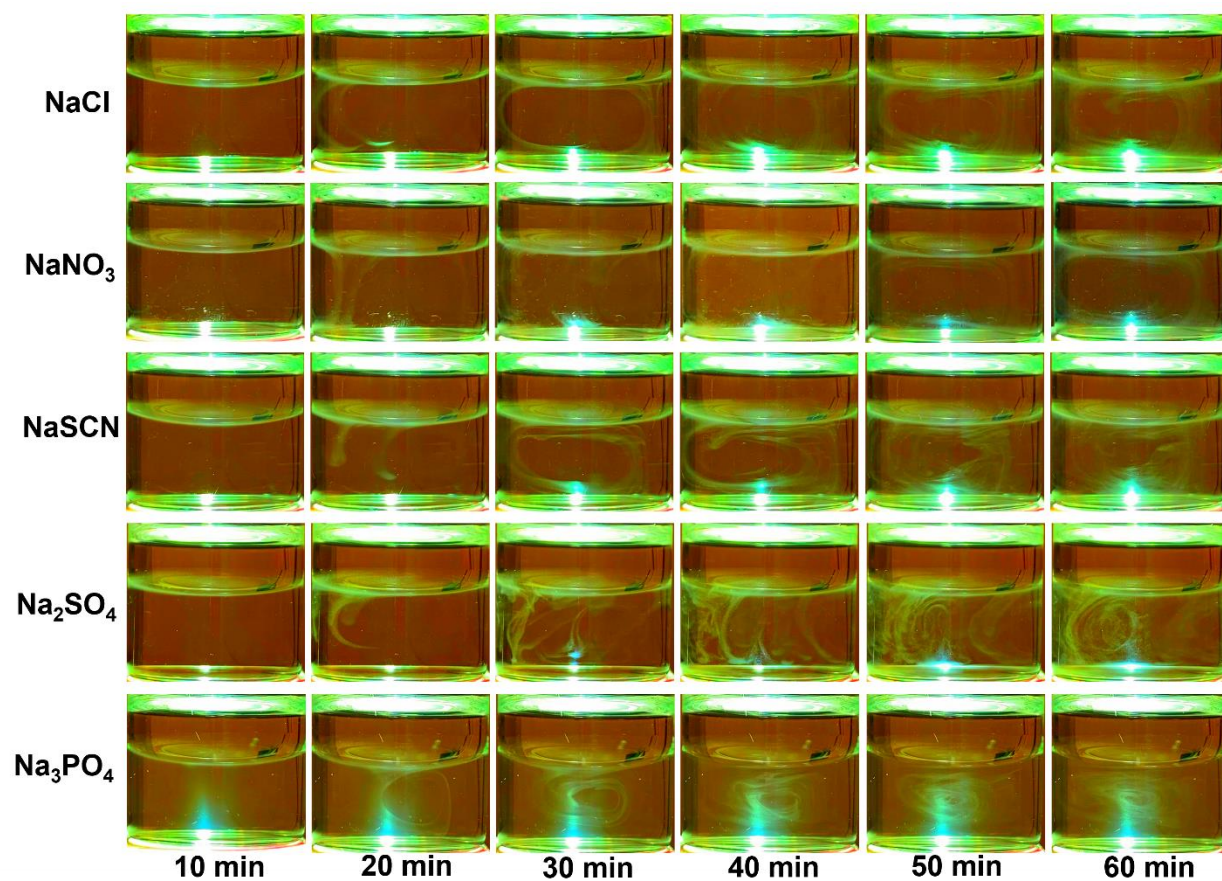


Figure S16. The effect of inorganic salts (50 mM) on the evolution of the precipitation in the system containing 0.1mM Nd³⁺ at aqueous pH of 3.0 in the first hour. A weak dependence was observed for a range of anions, Cl⁻, NO₃⁻, SCN⁻, SO₄²⁻, and PO₄⁻.

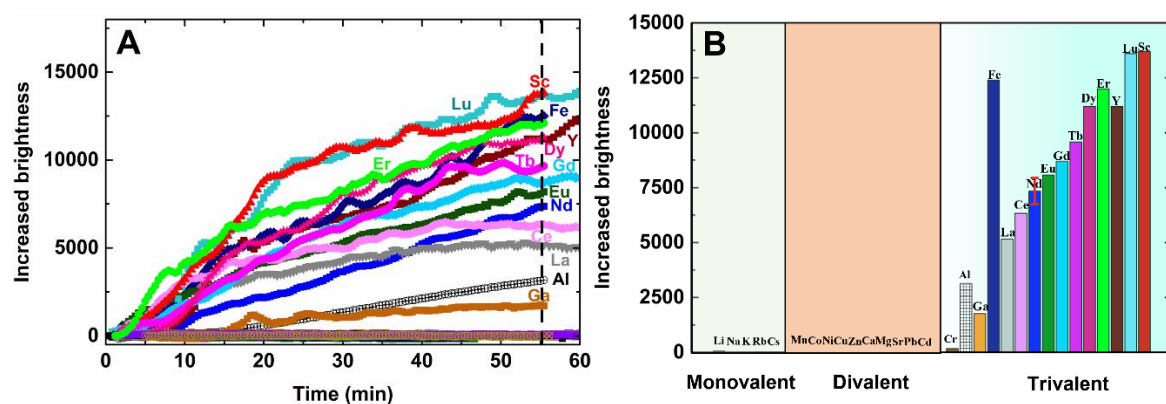


Figure S17. The formation of precipitation in the presence of various metal ions. A: Time evolution of increased brightness of water phase; B: Increased brightness of water phase at 55 min for different metal ions.

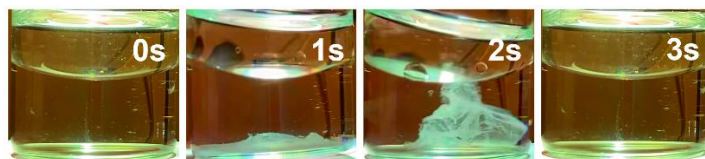


Figure S18. Transfer of the precipitates from aqueous to organic phase by shaking after equilibrium for the system containing 0.1 mM NdCl_3 at aqueous pH of 3.0.

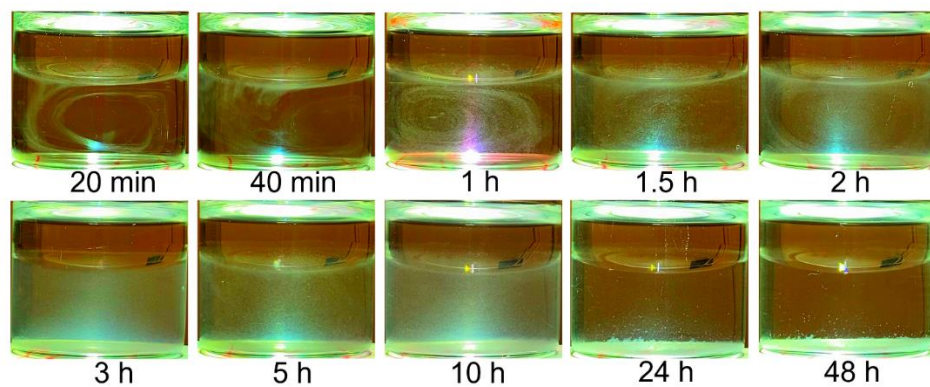


Figure S19. The long-time evolution process of the precipitate in the system containing 0.1 mM Nd at aqueous pH of 3.0.

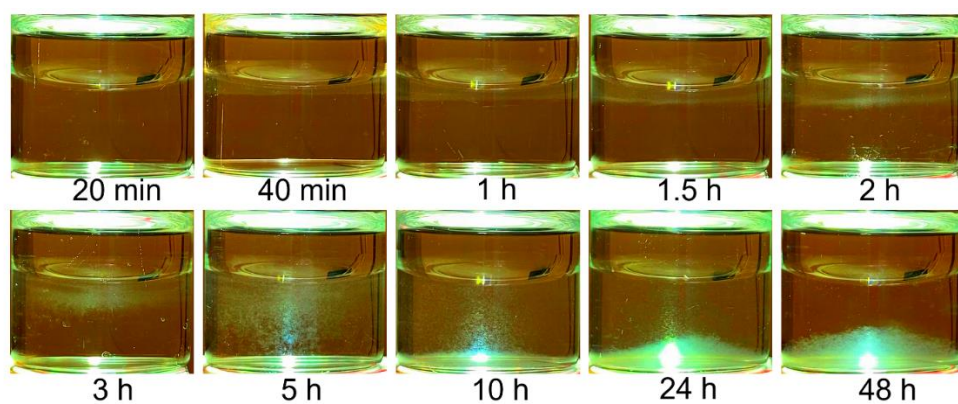


Figure S20. The long-time evolution process of the precipitate in the system containing 2.0 mM Nd at aqueous pH of 3.0.

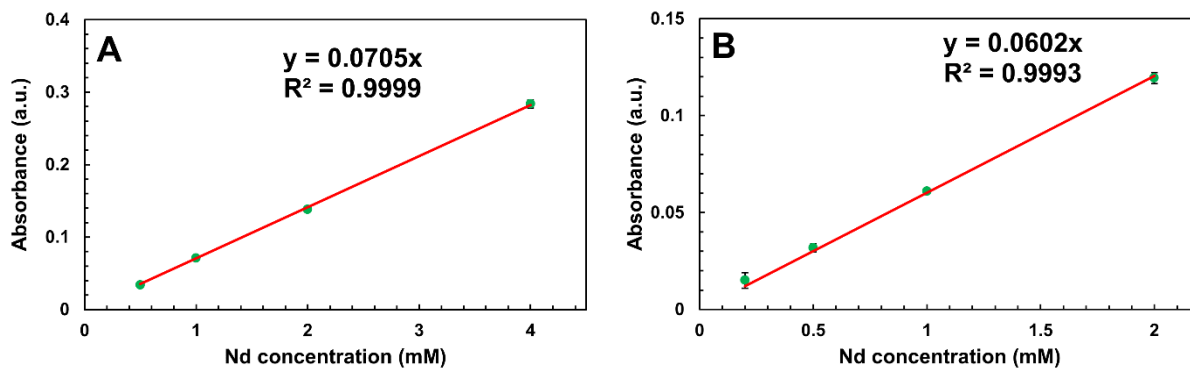


Figure S21. Calibration of UV-Vis absorbance of Nd to the concentration of Nd in the organic phase (A) and aqueous phase (B). The organic phases (0.2 M HDEHP in dodecane) with different concentration of Nd were prepared by extraction of known amount of Nd into organic phase.

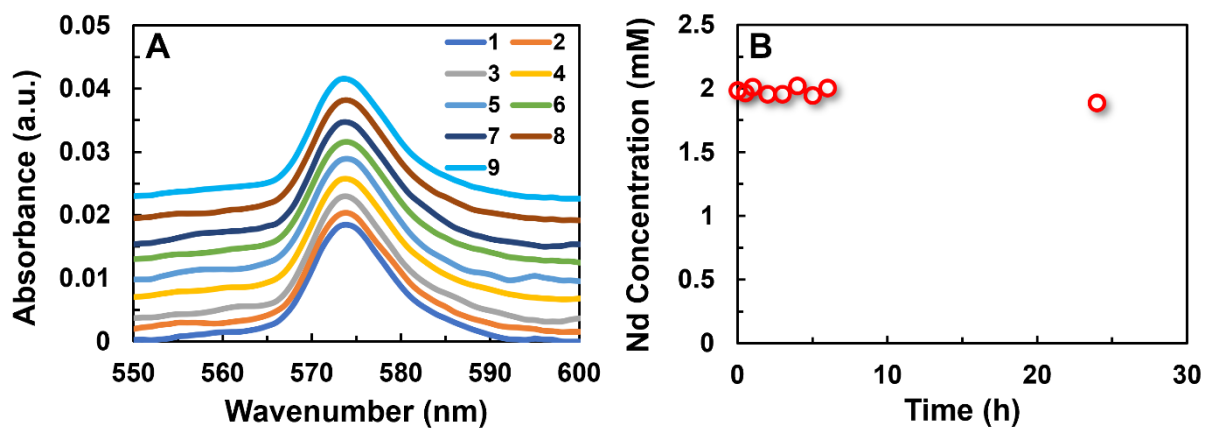


Figure S22. (A) Time dependent in-situ UV-Vis spectra of Nd in the system. From 1 to 9: 1 min, 30 min, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 24 h. (organic phase is pure dodecane, 2.0 mM NdCl_3 in the aqueous phase with pH of 3.0) (B) Time dependence of Nd-concentration obtained from the peak area of UV-Vis spectra in (A).

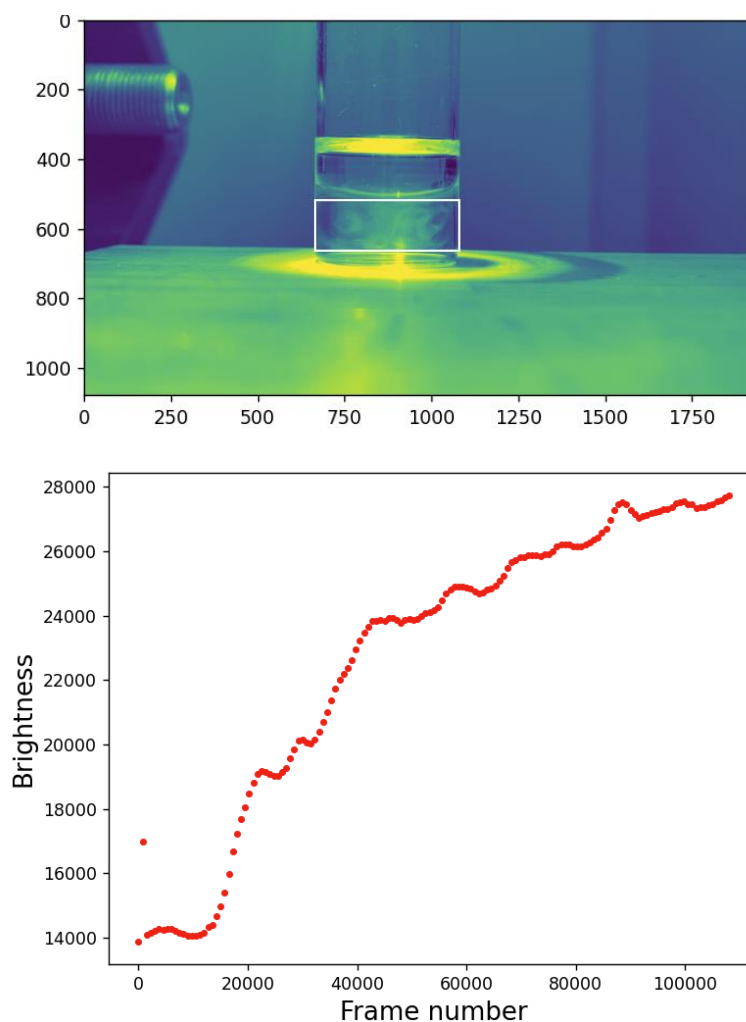


Figure S23. (Top) A grayscale frame from a system with Lu-ions in the aqueous phase. The region of interest selects the area of the aqueous phase where the brightness from the pixels were averaged over. (Bottom) The averaged brightness is plotted as a function of the frame number.

Movie S1 (separate file). Video illustrating the evolution process of precipitate in sample that contain initially 0.2 M HDEHP in n-dodecane and 0.05 mM NdCl_3 in water adjusted to pH 4.5 with HCl. The video was taken for the first hour after contacting the organic phase with the aqueous phase and was compressed into 11 second.

Movie S2 (separate file). Video illustrating the evolution process of precipitate in sample that contain initially 0.2 M HDEHP in n-dodecane and 0.1 mM NdCl_3 in water adjusted to pH 4.5 with HCl. The video was taken for the first hour after contacting the organic phase with the aqueous phase and was compressed into 11 second.

Movie S3 (separate file). Video illustrating the evolution process of precipitate in sample that contain initially 0.2 M HDEHP in n-dodecane and 0.5 mM NdCl_3 in water adjusted to pH 4.5 with HCl. The video was taken for the first hour after contacting the organic phase with the aqueous phase and was compressed into 11 second.

Movie S4 (separate file). Video illustrating the evolution process of precipitate in sample that contain initially 0.2 M HDEHP in n-dodecane and 1 mM NdCl_3 in water adjusted to pH 4.5 with HCl. The video was taken for the first hour after contacting the organic phase with the aqueous phase and was compressed into 11 second.

Movie S5 (separate file). Video illustrating the evolution process of precipitate in sample that contain initially 0.2 M HDEHP in n-dodecane and 2 mM NdCl_3 in water adjusted to pH 4.5 with HCl. The video was taken for the first hour after contacting the organic phase with the aqueous phase and was compressed into 11 second.

Movie S6 (separate file). Video illustrating the microscopy observation of precipitate in sample that contain initially 0.2 M HDEHP in n-dodecane and 0.1 mM NdCl_3 in water adjusted to pH 4.5 with HCl. The video was taken for the first 10 minutes after contacting the organic phase with the aqueous phase and was compressed into 2 second.

Movie S7 (separate file). Video illustrating spontaneous fluctuations of precipitate in an equilibrium sample lead to its contact with the upper dodecane phase and subsequent absorption and dissolution. Aqueous phase contains 2 mM GdCl_3 initially at pH of 3.0. Organic phase contains 200 mM HDEHP in dodecane. The video last 25 second in real time and was compressed into 11 second.

Movie S8 (separate file). Video illustrating adsorption of precipitate into organic phase by mechanical disturbance for an equilibrium sample. Aqueous phase contains 0.1 mM NdCl_3 initially at pH of 3.0. Organic phase contains 200 mM HDEHP in dodecane. The video last 3 second in real time and was compressed into 1 second.

Movie S9 (separate file). Video illustrating adsorption of precipitate into organic phase by mechanical disturbance for an equilibrium sample. Aqueous phase contains 2 mM NdCl_3 initially at pH of 3.0. Organic phase contains 200 mM HDEHP in dodecane. The video last 26 second in real time and was compressed into 1 second.

Movie S10 (separate file). Video illustrating the formation of Nd-HDEHP precipitates in the aqueous region between two convex organic phase regions that mimic two oil drops. Sample composition is 0.2 M HDEHP in dodecane and 0.1 mM NdCl_3 in water at pH 3.0. The video was taken

for the first hour after contacting the organic phase with the aqueous phase and was compressed into 8 second.