Electronic Supplementary Information for

Environmentally friendly separation of dysprosium and neodymium by fractional precipitation of coordination polymers

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1. Changes in precipitation yield of [Nd(dehp)$_3$] and [Dy(dehp)$_3$] with ethanol-water composition

The reagents listed in Table S1 were mixed in the amounts shown to form [Nd(dehp)$_3$] and [Dy(dehp)$_3$]. The resulting ethanol-water compositions are also tabulated. All the initial Nadehp/Ln (= Nd or Dy) ratios were 3:1. After ca. 20 h, the precipitates were filtered and washed several times with binary ethanol-water mixtures. The Ln^{3+} concentrations in the filtrates were measured by means of ICP-OES, and the precipitation yields (Y/%) were calculated. Figure S1 shows the Ys as a function of the ethanol concentration in the solutions. The Ys for Dy shown in Figure S1 are 100% irrespective of the ethanol concentration, while the Ys for Nd decrease with an increase in the ethanol concentration. As a result, a higher ethanol concentration is likely preferable for Nd/Dy separation.

Table S 1: Volumes of the mixed solution to form [Ln(dehp)$_3$] and resulting ethanol concentration

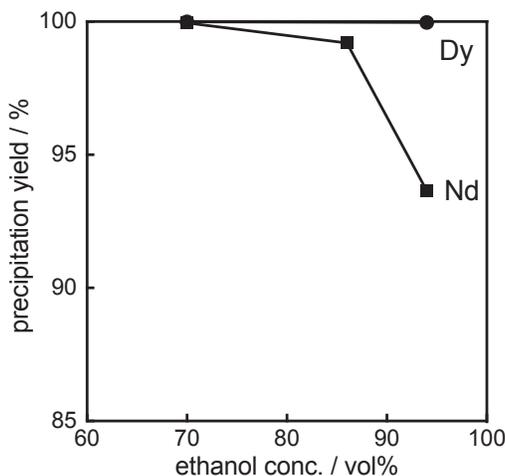| water / mL	ethanol / mL	1 M NdCl$_3$ or DyCl$_3$ in aqueous solution	0.3 M Na dehp in 80:20 vol% aqueous solution	ethanol concentration / vol%
4.8	10.8	0.40	4.0	70
1.6	14.0	0.40	4.0	86
-	15.6	0.40	4.0	94

Figure S1. Change in precipitation yield of [Nd(dehp)$_3$] and [Dy(dehp)$_3$] with ethanol concentration.

2. Quantification of precipitates and filtrates

The dried precipitate ($\sim$0.015 g) was accurately weighed and then decomposed in a mixture of 60 % HNO_3 (3 mL) and H_2O_2 (0.3 mL) using irradiation from a 200 W microwave for 3 min, first with 100 mL water and then for 5 min without water. The concentrations of P and Nd and/or Dy were measured by ICP-OES, and their compositions (Q/mmol$\cdot$g^{-1}) were determined. The filtrate (1-2 mL) was evaporated to dryness, and then decomposed and quantifide in the same way. Table S2 lists the Q(Ln) and Q(P) of the solids and Q(P)/Q(Ln) ratios at various pH of the filtrate.

All the Q(Ln), Q(P), and Q(P)/Q(Ln) values are very close to the calculated values based on the chemical formula [Ln(dehp)$_3$], indicating that Ln precipitates as the coordination polymer [Ln(dehp)$_3$] from binary ethanol-water solutions. Figure S2 shows c^{tot}(P) (/ M) and c(Ln^{3+}) (/ M) in the filtrates. All the c^{tot}(P) and c^{tot}(Ln^{3+}) decrease with increases in pH. This is consistent with the change in Y shown in Figure 1 (in the main text).

Table S 2: Q(Ln), Q(P), and Q(P)/Q(Ln) of the precipitates from LnCl$_3$ solutions at various pH

(A) [Nd(dehp)$_3$]				(B) [Dy(dehp)$_3$]			
pH	Q(Nd) / mmol$\cdot$g^{-1}	Q(P) / mmol$\cdot$g^{-1}	Q(P)/Q(Nd)	pH	Q(Dy) / mmol$\cdot$g^{-1}	Q(P) / mmol$\cdot$g^{-1}	Q(P)/Q(Dy)
5.6	1.0	2.7	2.7	3.7	0.93	2.6	2.8
3.6	0.92	2.6	2.8	1.9	0.90	2.6	2.9
1.9	0.92	2.7	2.9	1.5	0.95	2.7	2.8
1.6	0.91	2.6	2.9	0.70	0.92	2.7	2.9
calc.	0.91	2.7	3.0	0.27	0.91	2.7	3.0
				calc.	0.89	2.7	3.0
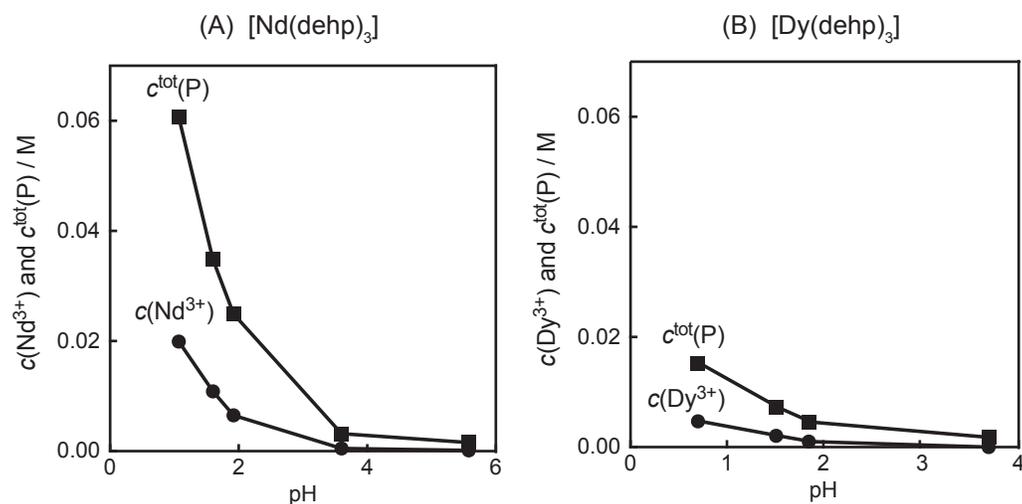
Figure S2. Change in c^{tot}(P) and c(Ln^{3+} in the filtrates of precipitation of [Nd(dehp)$_3$] (A) and [Dy(dehp)$_3$] (B) (*c.f.* Figure 1 in the main text).

3. Estimation of apparent solubility product (K_{sp}^a) from $c^{tot}(P)$ and $c(Ln^{3+})$

K_{sp} cannot be precisely determined because the solution includes many components and the ionic strength is too high to determine γ values by conventional means, *e.g.* according to the Debye–Hückel equation. Therefore, we employed an apparent solubility product, K_{sp}^a. In order to estimate K_{sp}^a, chemical equilibrium in a solution must be taken into account. We investigated the possibility of forming mononuclear complexes by means of X-ray absorption fine structural analysis (XAFS) as mentioned in the following section, and concluded that the amount of Hdehp–complexed species were negligible. From the mass balance of P;

$$c^{tot}(P) = c(dehp^-) + c(Hdehp) \tag{S-1}$$

and the acid dissociation of Hdehp (Eq. 3 in the main text), K_{sp}^a is given by

$$K_{sp}^a = \left[\frac{c^{tot}(P)}{1 + a(H^+)/K_a} \right]^3 \cdot c(Ln^{3+}) \tag{S-2}$$

where

$$
\begin{aligned}
K_a &= \frac{a(H^+) \cdot a(dehp^-)}{a(Hdehp)} \\
&= \frac{a(H^+) \cdot \left[\gamma(dehp^-) \cdot c(dehp^-) \right]}{\gamma(Hdehp) \cdot c(Hdehp)}
\end{aligned}
\tag{S-3}
$$

$a(H^+)$ is obtained by pH measurement, and K_a is an acid dissociation constant of Hdehp determined by titration (following section 5 for details). Table S3 lists the K_{sp}^a values. Although K_{sp} shoud be constant, it varies especially when pH is small. A high ionic strength in a solution and uncertainty of pH measurement possibly result in variety of K_{sp}^a values in the low pH region.

Table S 3: K_{sp}^a estimated from $c^{tot}(P)$ and $c(Ln^{3+})$ shown in Figure S2.

(A) [Nd(dehp)$_3$]		(B) [Dy(dehp)$_3$]	
pH	K_{sp}^a / mol^3·L^{-3}	pH	K_{sp}^a / mol^3·L^{-3}
3.8	3.8×10^{-12}	2.0	1.9×10^{-15}
2.1	3.3×10^{-12}	1.7	1.6×10^{-15}
1.8	1.7×10^{-12}	0.87	1.3×10^{-16}

4. XAFS measurement

XAFS analysis was performed in order to confirm whether a mononuclear complex of Hdehp and Nd^{3+} is formed in an ethanol-water binary solution or not. XAFS spectra at the K-edge of Nd (43575.27 keV) for 0.1 M $NdCl_3$ in 86:14 vol% ethanol-water (i), $NdCl_3$ and Hdehp in 86:14 vol% ethanol-water (ii) and Hdehp in hexane solution that extracted Nd^{3+} from an aqueous solution (iii) were collected in transmission mode at beamline BL11XU of SPring-8 (Harima, Japan). Solution (ii) was the filtrate from the recovery of precipitated $[Nd(dehp)_3]$ discussed in the main text, and solution (iii) was prepared by the solvent extraction method as a reference for the complex of Nd-and-Hdehp. The operating energy and the ring current were 8 GeV and 99 mA, respectively. Si(311) was used as a monochromator. The optics and EXAFS measurement systems in the beamline are described in ref.1.[1] The intensities of incident (I_0) and fluorescent (I_f) X-rays were detected by using ionization chambers filled with Ar(50%)+N_2(50%).

The EXAFS oscillation $\chi(k)$ was extracted from the EXAFS spectra using the Athena software package[2] for XAS analysis; and involved subtraction of a linear pre-edge background, normalization, and conversion to k-space, followed by μ_0 fitting using a cubic spline. The $\chi(k)$ function was Fourier transformed using k^3 weighting and a Gaussian window, and all fitting was done in R-space using the program Artemis and theoretical backscattering amplitudes and phase shifts were calculated using FEFF6.[3] The range of k and R for curve fittings was 3.2 to 13.5 $\AA^{-1}$ and 1.3 to 2.3 $\AA^{-1}$ (1.3 to 3.7 $\AA^{-1}$ only for solution (iii)), respectively. Figures. S4–S6 are the normalized μ_0, the extracted EXAFS oscillations ($\chi(k)k^3$), and the Fourier-transformed structure functions, respectively. Table S4 lists curve-fits parameters.

The most intense peak at $R + \Delta R = ca.2\AA$ in all the Fourier transforms (FT, Figure S6) is due to the oxygen atoms that coordinate with Nd. The Nd–O distance ($\Delta R + R$) and the coordination number (CN) for the solution (b) are 2.48 $\AA$ and 9.1, respectively, which is the same as those for the solution (i). This indicates that the local structure of Nd in the solutions (i) and (ii) are very similar. On the other hand, the $\Delta R + R$ and the CN for the solution (iii) are 2.35 $\AA$ and 6.2, respectively. It has been known that Ln^{3+} is six-fold coordinated with Hdehp in organic phases. Therefore, the another intense peak at $R + \Delta R = ca.3.2\,\AA$ in the FT for the solution (iii) can be attributed to Nd–P. In this regard, the FT for the filtrate (ii) shows no peak attributed to P. From these result, it is suggested that the local coordination structure of Nd in the filtrate in the presence of Hdehp is very similar to that in 86:14 vol% ethanol-water in the absence of Hdehp. Although EXAFS measurement gives an averaged signal, we regard that the effect of Nd–Hdehp complex formation on the precipitation equilibria is negligible.
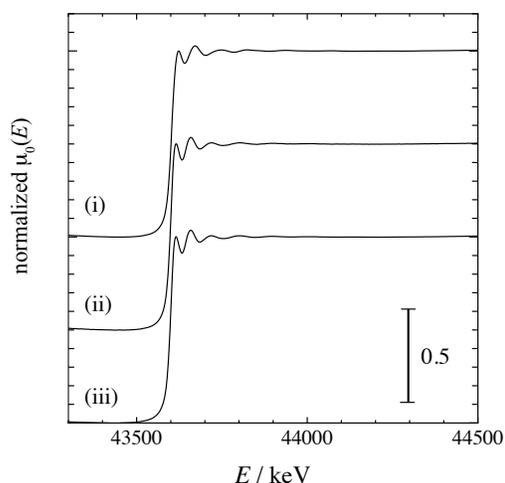

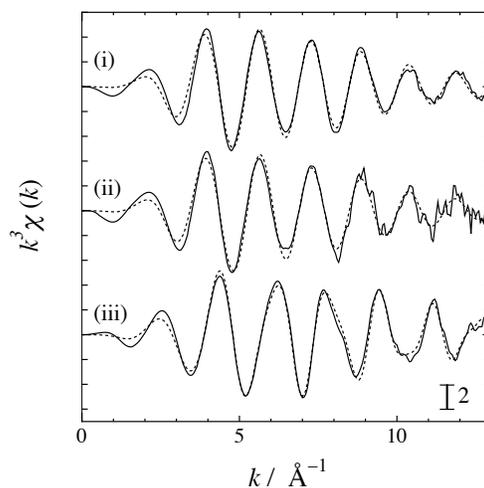Fig. S 3: Normalized $\mu_0(E)$ for solutions (i)–(iii) at Nd K edge.

Fig. S 4: Normalized, background-subtracted EXAFS spectra weighed by k^3 for solutions (i)–(iii) at Nd K edge. Dotted lines represent the result of curve fitting.
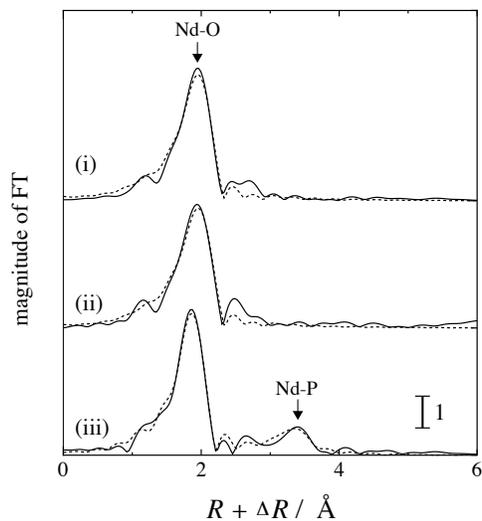
Fig. S 5: Fourier transform magnitudes in R-space (not corrected for phase shifts) corresponding to those in Fig. S4. Dotted lines represent the result of curve fitting.

Table S 4: EXAFS curve-fits parameters

		$R+\Delta R$ / Å	$s_0^2 \cdot CN^a$	ΔE /eV	σ^2 / Å
(i)	Nd–O	2.48	9.1	-6.3	0.0080
(ii)	Nd–O	2.48	9.1	-5.2	0.0086
(iii)	Nd–O	2.35	6.2	-1.5	0.0058
	Nd–P	3.89	6.2	-25	0.0058

$R+\Delta R$: bonding distance;
s_0^2: amplitude reduction factor;
CN: coordination number;
ΔE: phase shift;
σ^2: Debye-Waller factor.
[a] The s_0^2 was set as 1.0.

5. Acid dissociation constant (K_a) of Hdehp in 86:14 vol% ethanol-water

Accurately weighed Hdehp (∼0.5 g) was dissolved in an 86:14 vol % ethanol-water (ca. 40 mL) and titrated with KOH solution (0.43 mol·L^{-1}) of the same composition using an automatic titrator (TOA, AUTO TITRATOR AUT-501). Titration was conducted three times. Figure S7 shows the titration curves. Based on the Henderson-Hasselbalch equation,

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{c(\mathrm{dehp}^-)}{c(\mathrm{Hdehp})} \tag{S-4}$$

$\mathrm{p}K_a$, which is the half-equivalence point on the titration curves, is determined as 3.4. As a reference, $\mathrm{p}K_a$ in water is 1.70.[4]
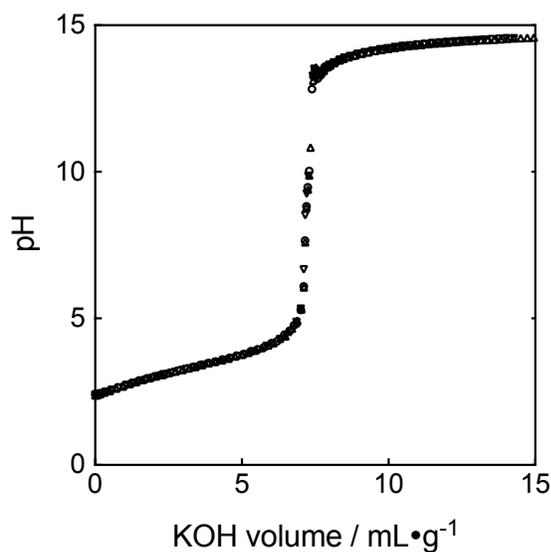

Figure S7. titration curves of Hdehp in 86:14 vol% ethanol-water.

References

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[4] R. K. Biswas, M. A. Habib and M. N. Islam, <u>Ind. Eng. Chem. Res.</u>, 2000, **39**, 155–160.