Supporting Information

Tailored ternary hydrophobic deep eutectic solvents for synergistic separation of yttrium from heavy rare earth elements

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1 Experimental

1.1 Reagents and Materials

The information of the chemicals and materials used in the experiments are shown in **Table S1**. All the chemicals were used as received from the supplier without further purification. Concentrated HCl was used to dissolve rare earth oxide (REO), followed by evaporation excess HCl to obtain rare earth chloride ($RECl_3$).

Table S1 Chemicals and materials used in the experiments.

Compound	Supplier	CAS	Purity, wt%
Bis(2-ethylhexyl)amine (BEA)	Energy Chemical	106-20-7	98%
1-Decanol (DL)	Adamas-beta®	112-30-1	97%
Decanoic acid (DA)	Adamas-beta®	334-48-5	99%
Oleic acid (OA)	Adamas-beta®	112-80-1	≥ 90%
2-Hexyldecanoic acid (HDA)	Energy Chemical	25354-97-6	98%
Gemfibrozil (GE)	Adamas-beta®	25812-30-0	98%
NaCl	Adamas-beta®	7647-14-5	≥ 99%
HCl	Xiya Reagent	7647-01-0	36-38%
NaOH	Greagent	1310-73-2	≥ 98%
Sodium oxalate	Adamas-beta®	62-76-0	≥ 99%
Sulfonated kerosene	Shanghai Laiyashi Chemical Co., Ltd.	-	-
Rare earth oxides (REO)	Fujian Changting Golden Dragon Rare Earth Co., Ltd.	-	≥ 99%
Rare earth chloride ($RECl_3$)	Prepared in our lab		> 99%
$RECl_3$ solution	Synthetic	-	-
Industrial yttrium-enriched solution	Ganzhou Rare Earth Group Co., Ltd	-	-
Deionized water	Prepared by Shanghai Hetai Smart-S30UV ultrapure water system	-	The resistivity is 18.2 MΩ*cm

1.2 Instrumentation and analysis methods

The metal ion concentrations in the aqueous sample were determined by inductively coupled plasma-atomic emission spectroscopy instrument (ICP-OES, JY-Horiba ICP-OES Ultima 2). The chloride ion concentration in the aqueous sample was determined by an ion chromatography HIC-ESP. The concentrations of metal ions and chloride ion loaded in the HDES phase were calculated by mass balance. The densities of HDESs were determined by a Biolin Automatic Surface Tensiometer Sigma 701 with a density precision of $\pm 0.001\ \text{g}\cdot\text{cm}^{-3}$. The viscosities of HDESs were measured using a rotary viscometer (NDJ-5S, Shanghai, China). The solubilities of HDESs in water were measured by total organic carbon analyser (TOC, TOC-L CPH). The water contents dissolved in HDESs were determined by a Karl Fischer moisture titrator (MCU-610, Kyoto Electronics Manufacturing Co. Ltd.). Fourier transform infrared spectra (FT-IR) with a wavenumber range of 400-4000 cm^{-1} were measured for HDESs before and after the extraction of REEs. ^{1}H NMR spectra of HDESs before and after the extraction of REEs were recorded in $CDCl_3$ by an AV III-500 BRUKER spectrometer. The pH of the sample was measured by a pHS-3C (the accuracy is ± 0.01 pH) digital pH meter made in Shanghai Rex Instruments Factory. The thermal stabilities of HDESs before and after the extraction of REEs were analyzed using Mettler-Toledo TGA/DSC3+ series system.

1.3 Computational methods

The initial structures of HBDs, BEA and DL were constructed by the GaussView 5.0 program. The density functional theory calculations (DFT) at B3LYP/6-311G (d, p) level coupled with the van der Waals semiempirical contribution from the DFT-D3(BJ) method by Grimme was selected for geometric optimization to obtain the stable configuration. The frequency analyses of the optimized structures were performed on the same basis set to confirm that there are no imaginary frequency. The wave function analyses were performed using Multiwfn 3.8 [1]. The color mapped isosurface graphs of the electrostatic potentials were obtained using the Multiwfn 3.8 program in conjunction with VMD 1.9.3 program [2, 3].

1.4 HDES preparation and characterization

All the HDESs were prepared at room temperature without heating. According to the molar ratio of HBA, HBD and DL components, accurately weigh the required sample mass of each component into a 20 mL glass vial, stirring at room temperature (25±2 °C) until a homogeneous transparent liquid was formed. HDESs without solid precipitation after standing at room temperature for 48 h were used for subsequent experiments. The FT-IR spectra and ^{1}H NMR spectra were used to analyze the chemical stabilities of HDESs. The viscosities and densities of HDESs were also determined. The hydrophobicities of HDESs were comprehensively evaluated by the degree of cross-contamination between the HDES phase and the aqueous phase. Specifically, HDES and deionized water with a volume ratio of 1:1 was thoroughly mixed at room temperature for 1 h, followed by centrifugation at 4000 rpm to separate the HDES phase and the water phase. Finally, the water content in the HDES and the total nitrogen (TN) and total organic carbon content (TOC) in the water phase were analyzed respectively. The higher the values of water content, TN and TOC, the worse the hydrophobicity of HDES.

1.5 Extraction experiments

Unless otherwise specified, all the liquid-liquid extraction experiments were carried out at room temperature (25±2 °C), the initial pH value of the feed solution was 3.0, the concentration of each rare earth element (La-Lu and Y) in the feed solution was 0.002 mol/L, and 0.04 mol/L NaCl was used as the salting-out agent. The volume ratio of HDES phase to aqueous phase is O/A = 1/1, and stirred at 300 rpm for 30 min. In order to avoid accidental errors in the experiment results, all experiments were carried out in parallel for three times. After extraction, the metal ion concentrations in the raffinate were determined by ICP-OES. The saturated loading of HDESs were determined by calculating the total concentrations of loaded ions in the HDESs phase after repeated contact of the HDESs phase with the feed solution (0.1 mol/L $HoCl_3$ and 0.04 mol/L NaCl) until the ion concentration in the raffinate remained constant or a third phase appeared, the phase ratio of O/A was 2/5. Taking Ho and Dy as examples, the stoichiometric ratio of RE^{3+} and Cl^- loaded into HDES was calculated to determine the mechanism of the HDES extraction of REEs. The effects of the initial pH (1.0-5.3) of the feed solution and the concentration of the salting-out agent (c(NaCl) = 0-0.10 mol/L) on the extraction performance of HDES were also investigated. The extraction and separation performance of DL:OA:BEA (9:1:5) HDES for HREEs (Dy-Lu) and Y in industrial Y-enriched solution were evaluated under optimal conditions, pH = 3, c(NaCl) = 0.10 mol/L, O/A = 1/1-5/1. The stripping performance of HREEs from the loaded DL:OA:BEA (9:1:5) HDES using $Na_2C_2O_4$ (0-0.2 mol/L), H_2O (A/O = 1/1-5/1), and HCl (0.5 mol/L-3 mol/L) were compared. And the stabilities of HDES cycled 5 times were investigated.

The extraction percentage (E%), distribution ratio (D), separation factor (β) and stripping percentage (S%) are defined as the following Eq. (1-4) :

$$E\% = \frac{c_i - c_e}{c_i} \times 100\% \tag{1}$$

$$D = \frac{c_o}{c_e} \tag{2}$$

$$\beta = \frac{D_1}{D_2} \tag{3}$$

$$S\% = \frac{m_l - m_s}{m_l} \times 100\% \tag{4}$$

where c_i, c_e and c_o represent the elemental concentrations in the feed solution, raffinate solution and HDES, respectively. m_l and m_s represent the moles of REEs loaded in the HDES phase before and after stripping, respectively. D_1 and D_2 represent the distribution ratio of element 1 and element 2, respectively.

Table S2 Relevant properties of the used materials.

Compound	**M. P. (°C)** [4]	**Aqueous solubility (mg/L, 20 °C)** [4, 5]	**LD50* (oral, rat) (mg/kg)** [4]
DA	27-32	61.8	> 2000
OA	13-14	none	25000
HDA	18	< 500	> 2020
GE	61-63	11	1414
DL	5-7	21.1	> 5000
BEA	-60	14	1008

***Note:** LD50 is median lethal dose.

Table S3 The prepared HDESs and their properties (stored at 25±2 °C for more than 48 h).

NO.	Composition of HDES	Molar ratio	Characteristic	NO.	Composition of HDES	Molar ratio	Characteristic
1	DL:DA:BEA	5:3:1	Clear liquid	**23**	DL:HDA:BEA	5:3:1	Clear liquid
2	DL:DA:BEA	5:2:1	Clear liquid	**24**	DL:HDA:BEA	5:2:1	Clear liquid
3	DL:DA:BEA	5:1:1	Clear liquid	**25**	DL:HDA:BEA	5:1:1	Clear liquid
4	DL:DA:BEA	5:1:2	Clear liquid	**26**	DL:HDA:BEA	5:1:2	Clear liquid
5	DL:DA:BEA	5:1:3	Clear liquid	**27**	DL:HDA:BEA	5:1:3	Clear liquid
6	DL:DA:BEA	5:1:4	Clear liquid	**28**	DL:HDA:BEA	5:1:4	Clear liquid
7	DL:DA:BEA	5:1:5	Clear liquid	**29**	DL:HDA:BEA	5:1:5	Clear liquid
8	DL:DA:BEA	0:1:5	Clear liquid	**30**	DL:HDA:BEA	0:1:5	Clear liquid
9	DL:DA:BEA	3:1:5	Clear liquid	**31**	DL:HDA:BEA	3:1:5	Clear liquid
10	DL:DA:BEA	7:1:5	Clear liquid	**32**	DL:HDA:BEA	7:1:5	Clear liquid
11	DL:DA:BEA	9:1:5	Clear liquid	**33**	DL:HDA:BEA	9:1:5	Clear liquid
12	DL:OA:BEA	5:3:1	Clear liquid	**34**	DL:GE:BEA	5:3:1	Clear liquid
13	DL:OA:BEA	5:2:1	Clear liquid	**35**	DL:GE:BEA	5:2:1	Clear liquid
14	DL:OA:BEA	5:1:1	Clear liquid	**36**	DL:GE:BEA	5:1:1	Clear liquid
15	DL:OA:BEA	5:1:2	Clear liquid	**37**	DL:GE:BEA	5:1:2	Clear liquid
16	DL:OA:BEA	5:1:3	Clear liquid	**38**	DL:GE:BEA	5:1:3	Clear liquid
17	DL:OA:BEA	5:1:4	Clear liquid	**39**	DL:GE:BEA	5:1:4	Clear liquid
18	DL:OA:BEA	5:1:5	Clear liquid	**40**	DL:GE:BEA	5:1:5	Clear liquid
19	DL:OA:BEA	0:1:5	Clear liquid	**41**	DL:GE:BEA	0:1:5	Clear liquid
20	DL:OA:BEA	3:1:5	Clear liquid	**42**	DL:GE:BEA	3:1:5	Clear liquid
21	DL:OA:BEA	7:1:5	Clear liquid	**43**	DL:GE:BEA	7:1:5	Clear liquid
22	DL:OA:BEA	9:1:5	Clear liquid	**44**	DL:GE:BEA	9:1:5	Clear liquid

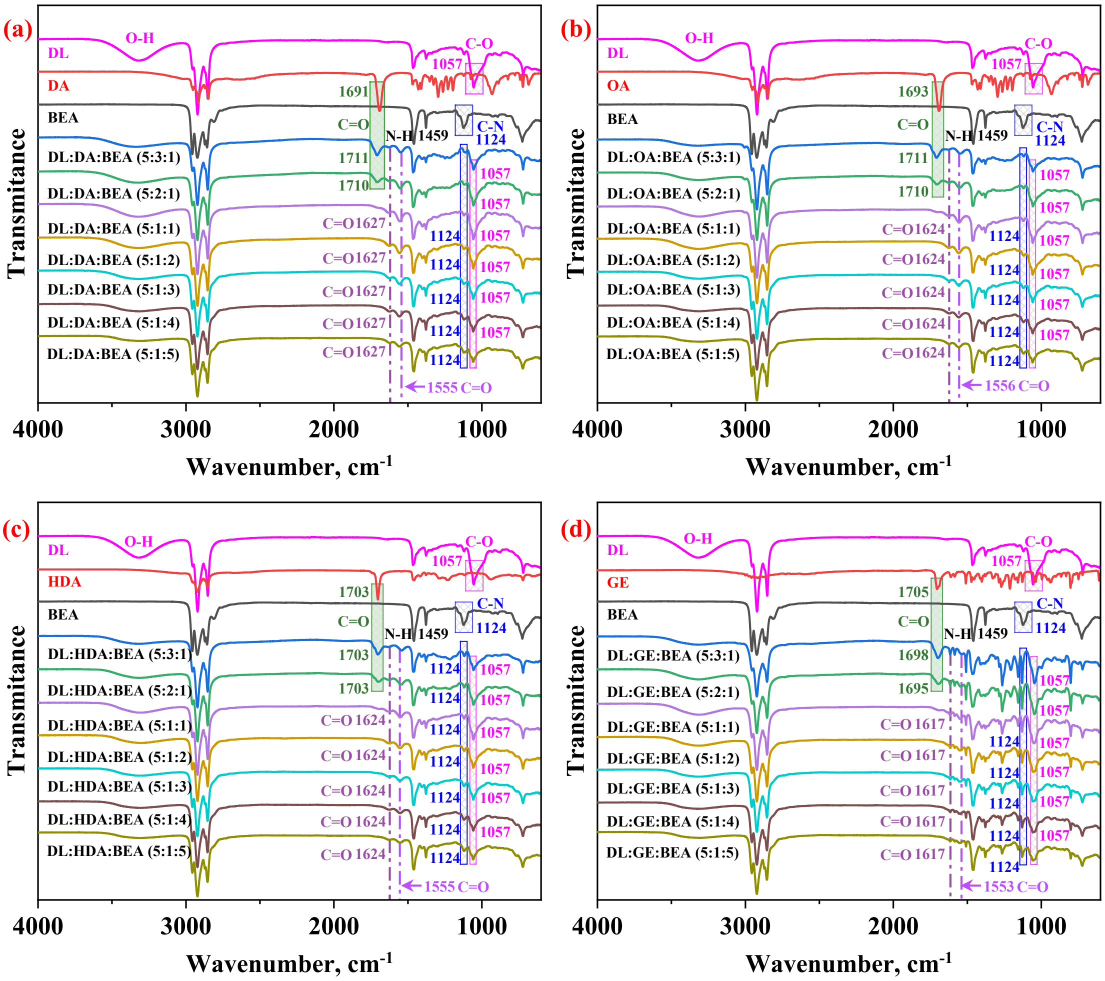


Fig. S1 FT-IR of (a) DL:DA:BEA HDESs, (b) DL:OA:BEA HDESs, (c) DL:HDA:BEA HDESs and (d) DL:GE:BEA HDESs. The molar ratios of DL:HBD:HBA are ranged from 5:3:1 to 5:1:5.

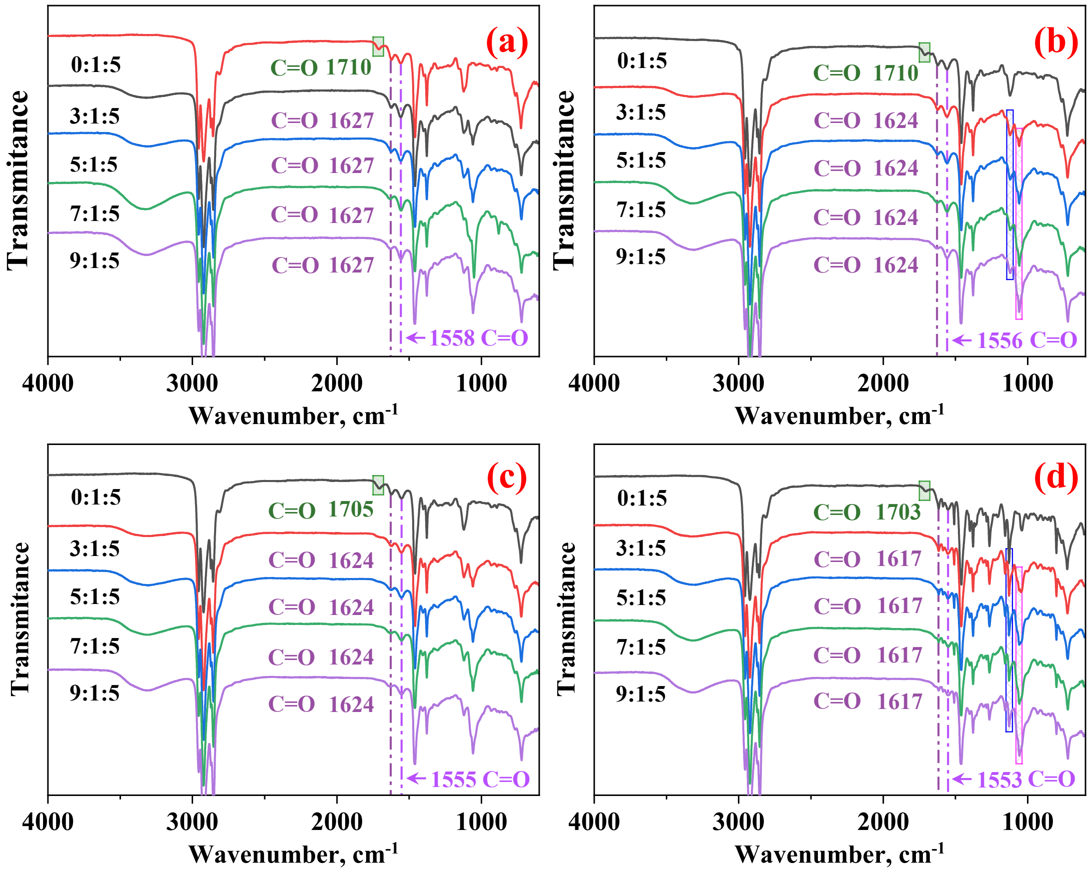


Fig. S2 FT-IR of (a) DL:DA:BEA HDESs, (b) DL:OA:BEA HDESs, (c) DL:HDA:BEA HDESs and (d) DL:GE:BEA HDESs. The molar ratios of DL:HBD:HBA are ranged from 0:1:5 to 9:1:5.

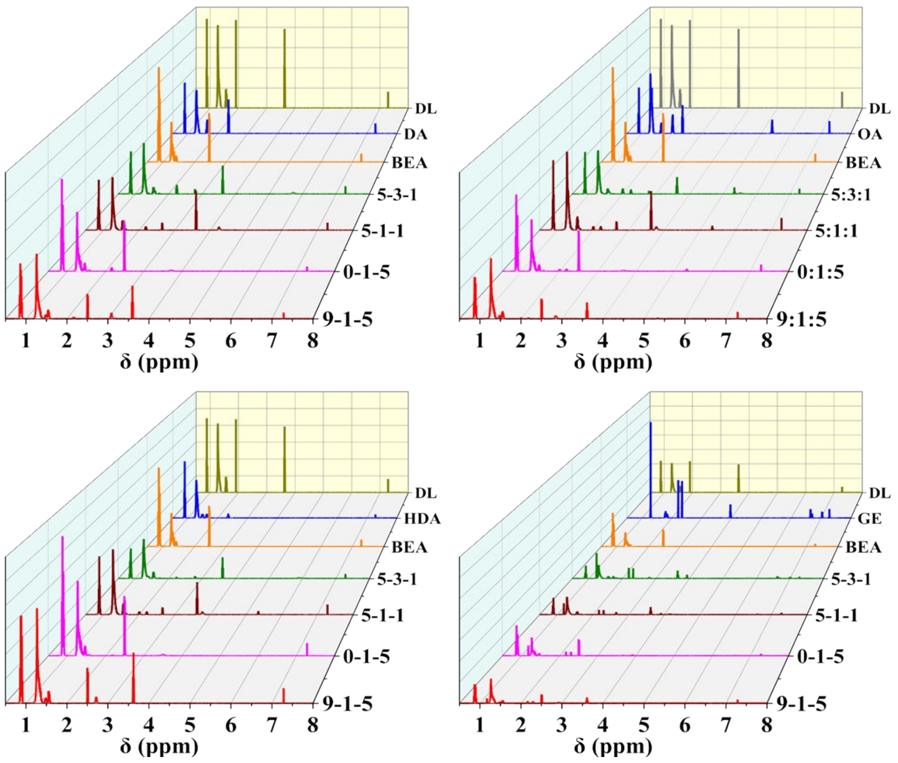
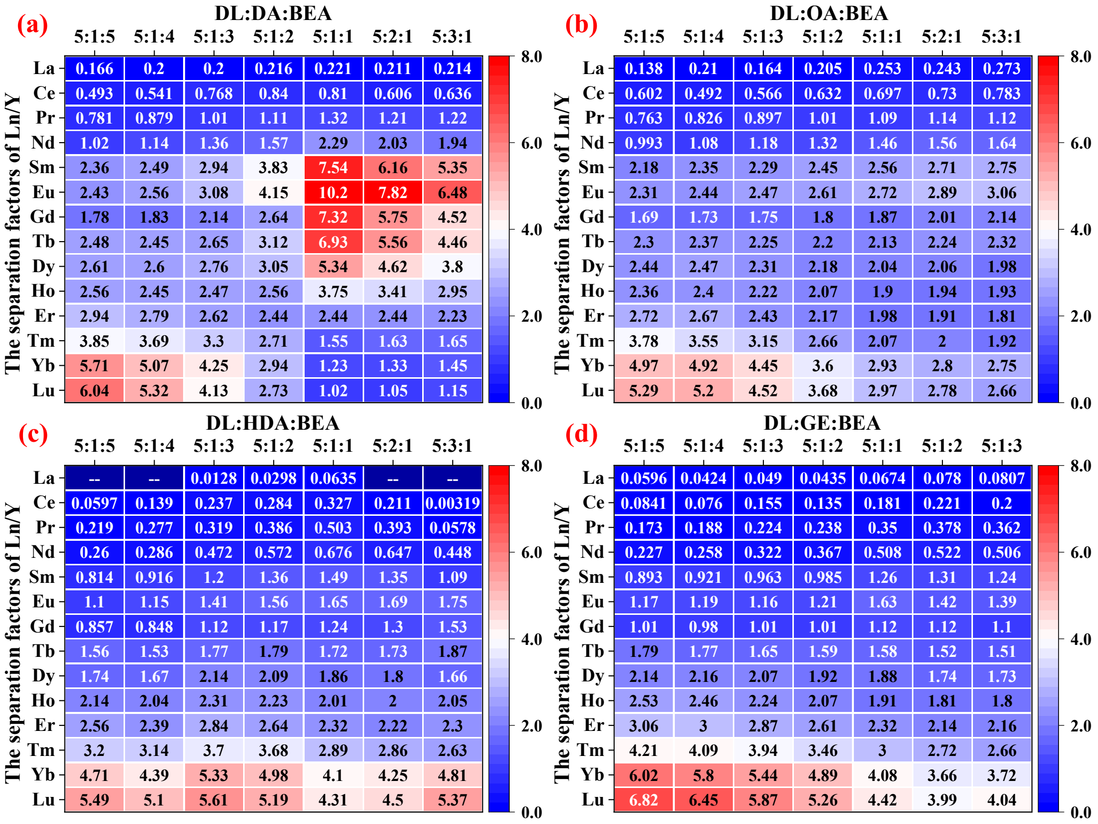


Fig. S3 ^{1}H NMR of (a) DL:DA:BEA HDESs, (b) DL:OA:BEA HDESs, (c) DL:HDA:BEA HDESs and (d) DL:GE:BEA HDESs.



(a) DL:DA:BEA

	5:1:5	5:1:4	5:1:3	5:1:2	5:1:1	5:2:1	5:3:1
La	0.166	0.2	0.2	0.216	0.221	0.211	0.214
Ce	0.493	0.541	0.768	0.84	0.81	0.606	0.636
Pr	0.781	0.879	1.01	1.11	1.32	1.21	1.22
Nd	1.02	1.14	1.36	1.57	2.29	2.03	1.94
Sm	2.36	2.49	2.94	3.83	7.54	6.16	5.35
Eu	2.43	2.56	3.08	4.15	10.2	7.82	6.48
Gd	1.78	1.83	2.14	2.64	7.32	5.75	4.52
Tb	2.48	2.45	2.65	3.12	6.93	5.56	4.46
Dy	2.61	2.6	2.76	3.05	5.34	4.62	3.8
Ho	2.56	2.45	2.47	2.56	3.75	3.41	2.95
Er	2.94	2.79	2.62	2.44	2.44	2.44	2.23
Tm	3.85	3.69	3.3	2.71	1.55	1.63	1.65
Yb	5.71	5.07	4.25	2.94	1.23	1.33	1.45
Lu	6.04	5.32	4.13	2.73	1.02	1.05	1.15

(b) DL:OA:BEA

	5:1:5	5:1:4	5:1:3	5:1:2	5:1:1	5:2:1	5:3:1
La	0.138	0.21	0.164	0.205	0.253	0.243	0.273
Ce	0.602	0.492	0.566	0.632	0.697	0.73	0.783
Pr	0.763	0.826	0.897	1.01	1.09	1.14	1.12
Nd	0.993	1.08	1.18	1.32	1.46	1.56	1.64
Sm	2.18	2.35	2.29	2.45	2.56	2.71	2.75
Eu	2.31	2.44	2.47	2.61	2.72	2.89	3.06
Gd	1.69	1.73	1.75	1.8	1.87	2.01	2.14
Tb	2.3	2.37	2.25	2.2	2.13	2.24	2.32
Dy	2.44	2.47	2.31	2.18	2.04	2.06	1.98
Ho	2.36	2.4	2.22	2.07	1.9	1.94	1.93
Er	2.72	2.67	2.43	2.17	1.98	1.91	1.81
Tm	3.78	3.55	3.15	2.66	2.07	2	1.92
Yb	4.97	4.92	4.45	3.6	2.93	2.8	2.75
Lu	5.29	5.2	4.52	3.68	2.97	2.78	2.66

(c) DL:HDA:BEA

	5:1:5	5:1:4	5:1:3	5:1:2	5:1:1	5:2:1	5:3:1
La	--	--	0.0128	0.0298	0.0635	--	--
Ce	0.0597	0.139	0.237	0.284	0.327	0.211	0.00319
Pr	0.219	0.277	0.319	0.386	0.503	0.393	0.0578
Nd	0.26	0.286	0.472	0.572	0.676	0.647	0.448
Sm	0.814	0.916	1.2	1.36	1.49	1.35	1.09
Eu	1.1	1.15	1.41	1.56	1.65	1.69	1.75
Gd	0.857	0.848	1.12	1.17	1.24	1.3	1.53
Tb	1.56	1.53	1.77	1.79	1.72	1.73	1.87
Dy	1.74	1.67	2.14	2.09	1.86	1.8	1.66
Ho	2.14	2.04	2.31	2.23	2.01	2	2.05
Er	2.56	2.39	2.84	2.64	2.32	2.22	2.3
Tm	3.2	3.14	3.7	3.68	2.89	2.86	2.63
Yb	4.71	4.39	5.33	4.98	4.1	4.25	4.81
Lu	5.49	5.1	5.61	5.19	4.31	4.5	5.37

(d) DL:GE:BEA

	5:1:5	5:1:4	5:1:3	5:1:2	5:1:1	5:1:2	5:1:3
La	0.0596	0.0424	0.049	0.0435	0.0674	0.078	0.0807
Ce	0.0841	0.076	0.155	0.135	0.181	0.221	0.2
Pr	0.173	0.188	0.224	0.238	0.35	0.378	0.362
Nd	0.227	0.258	0.322	0.367	0.508	0.522	0.506
Sm	0.893	0.921	0.963	0.985	1.26	1.31	1.24
Eu	1.17	1.19	1.16	1.21	1.63	1.42	1.39
Gd	1.01	0.98	1.01	1.01	1.12	1.12	1.1
Tb	1.79	1.77	1.65	1.59	1.58	1.52	1.51
Dy	2.14	2.16	2.07	1.92	1.88	1.74	1.73
Ho	2.53	2.46	2.24	2.07	1.91	1.81	1.8
Er	3.06	3	2.87	2.61	2.32	2.14	2.16
Tm	4.21	4.09	3.94	3.46	3	2.72	2.66
Yb	6.02	5.8	5.44	4.89	4.08	3.66	3.72
Lu	6.82	6.45	5.87	5.26	4.42	3.99	4.04

Fig. S4 The separation factors (β) of REEs/Y by different HDESs. (a) DL:DA:BEA HDESs, (b) DL:OA:BEA HDESs, (c) DL:HDA:BEA HDESs and (d) DL:GE:BEA HDESs. The molar ratio of DL:HBD:HBA is ranged from from 5:3:1 to 5:1:5.

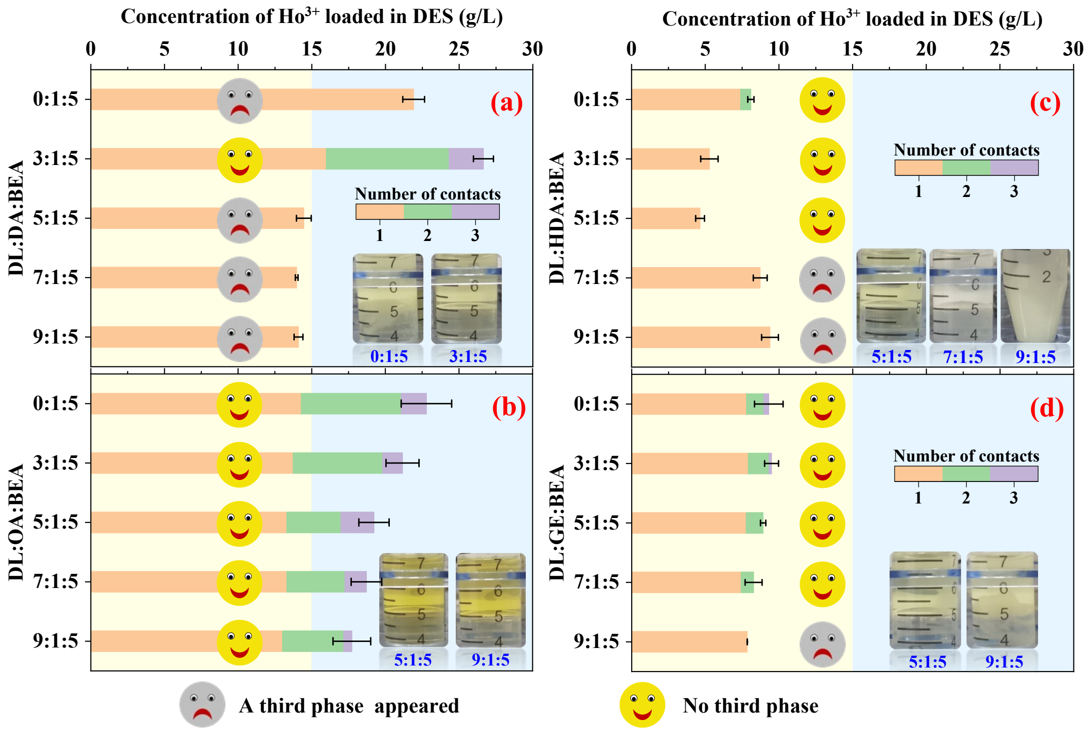


Fig. S5 Effect of the proportion of DL in HDESs on the saturated loading capacities. (a) DL:DA:BEA HDESs, (b) DL:OA:BEA HDESs, (c) DL:HDA:BEA HDESs and (d) DL:GE:BEA HDESs. The molar ratios of DL:HBD:HBA are ranged from 0:1:5 to 9:1:5.

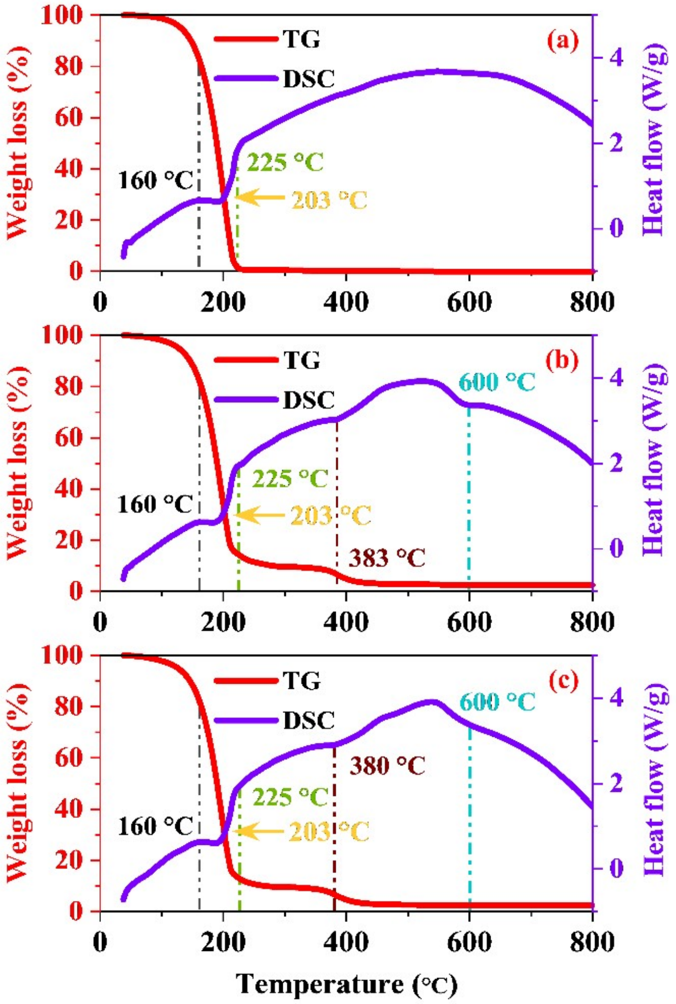


Fig. S6 The TGA-DSC analyses of (a) DL:OA:BEA (9:1:5) HDES, (b) DL:OA:BEA (9:1:5) HDES loaded with Dy^{3+} and (c) DL:OA:BEA (9:1:5) HDES loaded with Ho^{3+}.

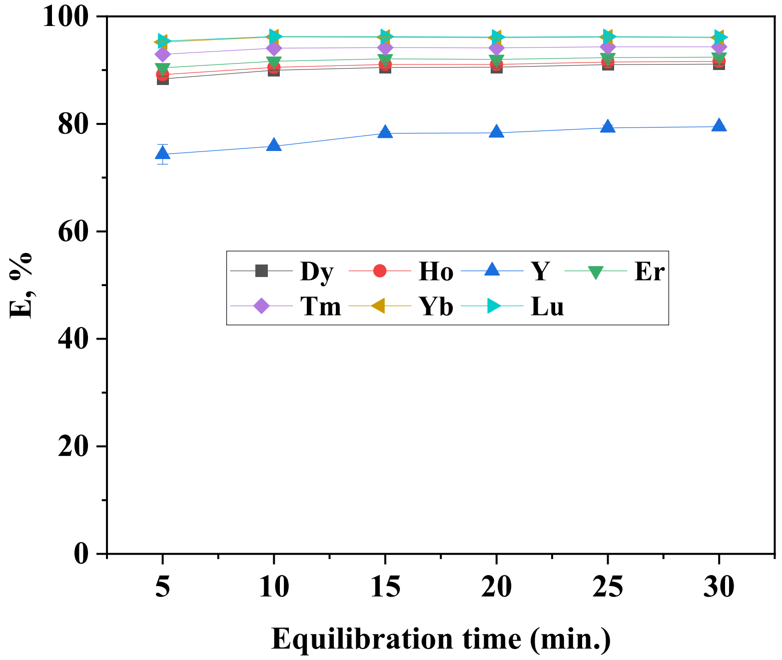


Fig. S7 Equilibrium time of HREEs and Y extracted by DL:OA:BEA (9:1:5) HDES, O/A = 2/1, pH = 3, c(NaCl) = 0.1 mol/L.

Table S4 The composition of industrial Y-enriched solution.

Ingredients	**Dy**	**Ho**	**Y**	**Er**	**Tm**	**Yb**	**Lu**	**Total**
Concentration (mg/L)	221.2	1032.6	22927.5	2038.3	281.1	1248.7	149.3	27898.8
wt. %	0.8	3.7	82.2	7.3	1.0	4.5	0.5	100

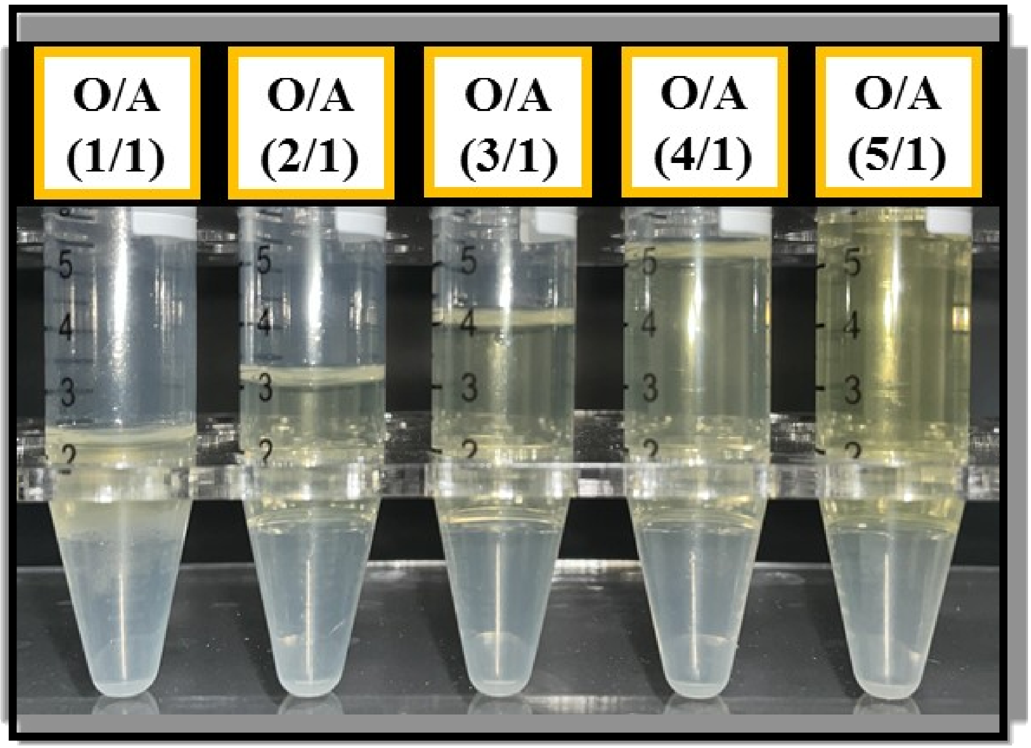


Fig. S8 The photo of HDES after extraction of HREEs and Y from industrial Y-enriched solution.

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