Supporting Information

Contents

1. Experimental details

1.1 General procedure

Dysprosium(III) trifluoromethanesulfonate $(Dy(CF_3SO_3)_3)$ and neodymium(III) trifluoromethanesulfonate $(Nd(CF_3SO_3)_3)$ were purchased from Sigma-Aldrich. Dysprosium(III) nitrate pentahydrate $(Dy(NO_3)_3 \cdot 5H_2O)$, neodymium(III) nitrate hexahydrate $(Nd(NO_3)_3 \cdot 6H_2O)$, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), methanol, ethanol, isopropyl alcohol (IPA) were purchased from Kanto Chemical Co., Inc. Tris(2-aminoethyl)amine (tren), 5-methylsalicylaldehyde (5-MeSal), *N,N*-diisopropylethylamine (DIEA), and dimethyl sulfoxide-d₆ (DMSO-d₆) were obtained from Tokyo Chemical Industry Co., Ltd. Diethyl ether was purchased from FUJIFILM Wako Pure Chemical Corp. Isopropyl alcohol-d₈ (IPA-d₈) was purchased from Sigma-Aldrich. All chemicals purchased were used without further purification. Elemental analysis was performed using an NM-10 (J-Science Lab Co., Ltd.) and a vario EL cube (Elementar Japan K.K.). ¹H-NMR spectra were recorded using an AV400 NMR spectrometer (Bruker Corp.). The absorption spectra were recorded with a UV-1800 UV-vis spectrometer (SHIMADZU Corp.) using a quartz cuvette with an optical path length of 1 cm. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed using an iCAP6500 (Thermo Fisher Scientific K.K.). Scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDX) was conducted using an S-4800 scanning electron microscope (Hitachi High-Tech Corp.) with the EDX analysis system EMAXEvolution X-max (HORIBA, Ltd.). Powder X-ray diffraction (PXRD) data were recorded using a MiniFlex instrument (Rigaku Corp.).

1.2 Synthesis

Synthesis of H₃L

An ethanol solution (25 mL) containing 0.745 g (5.0 mmol) of tren was added to a diethyl ether solution (25 mL) containing 2.043 g (15.0 mmol) of 5-MeSal. The resultant solution was stirred at 60 °C for 10 min. The reaction mixture was cooled in an ice bath for 2 h and gave yellow crystals of H₃L, which were filtered, washed with diethyl ether, and dried under reduced

pressure overnight. Yield: 1.490 g (59.5%). Elemental analysis calcd for $C_{30}H_{36}N_4O_3$: C, 71.97; H, 7.25; N, 11.19. Found: C, 71.96; H, 7.34; N, 11.36. Mass spectrum (FAB) m/z = 501 ($[(H_4L)]^+$).

Synthesis of DyL.

$Dy(CF_3SO_3)_3$ (1.219 g, 2 mmol) was dissolved in methanol (40 mL) at 60 °C. A methanol solution (8 mL) containing 0.585 g (4 mmol) of tren was added to a solution containing $Dy(CF_3SO_3)_3$. The resulting mixture was stirred for 10 min at 60 °C. A methanol solution (8 mL) containing 0.817 g (6 mmol) of 5-MeSal was subsequently added to the reaction mixture and stirred for 10 min at 60 °C. After cooling to room temperature, the product was collected by filtration and dried under reduced pressure. The crude product (1.040 g) was dissolved in 75 mL of hot DMF, and the resulting solution was filtered. The addition of 35 mL of methanol to the filtrate yielded pale yellow crystals. The crystals were collected by filtration and washed with methanol. After heating the obtained crystals to 100 °C under reduced pressure for 10 h, pale yellow crystals of DyL were obtained. Yield: 0.415 g (31.4%). Elemental analysis calcd (%) for $C_{30}H_{33}N_4O_3Dy$: C 54.59, H 5.04, N 8.49; found: C 54.30, H 5.11, N 8.39. Mass spectrum (FAB) m/z = 662 ($[Dy(HL)]^+$).

Synthesis of NdL.

Methanol was dried over molecular sieves prior to the use in the synthesis of the Nd^{3+} complex. A methanol solution (20 mL) containing $Nd(CF_3SO_3)_3$ (0.5916 g, 1 mmol) and H_3L (0.5008 g, 1 mmol) was stirred at 50 °C for 5 min. To this reaction mixture, DIEA (528 μl, 3 mmol) was added and stirred for 2 min at 50 °C. The reaction mixture immediately gave the precipitates of NdL, which were collected by filtration, washed with a methanol, and dried under reduced pressure. Yield: 0.503 g (78.4%). Elemental analysis calcd. for $C_{30}H_{33}N_4O_3Nd$: C, 56.18; H, 5.18; N, 8.73. Found: C, 55.92; H, 5.11; N, 8.79. Mass spectrum (FAB): m/z = 640 ($[Nd(HL)]^+$).

1.3 Determination of s_{NdL} and s_{DyL}.

DMSO and IPA were dried over molecular sieves prior to use in this experiment. Saturated DMSO/IPA (1:1, 1:3, and 1:6 by volume) solutions of DyL and NdL were prepared. The supernatants were then diluted with nitric acid. The Dy^{3+} and Nd^{3+} concentrations of the diluted

solutions were quantitatively determined by ICP-AES. The solubility of DyL and NdL were calculated from these concentrations.

1.4 Crystallization from the DMSO/IPA mixture containing NdL and DyL.

DMSO and IPA were dried over molecular sieves prior to use in this experiment. IPA (1.2 ml) was added to a DMSO solution (400 μl) in which both DyL (6.0 μmol) and NdL (6.0 μmol) were dissolved. Standing the solution for 1 day at room temperature gave crystals, which were filtered, washed with a DMSO/IPA mixture (1:3 by volume) and diethyl ether, and dried in air overnight. The Nd/Dy ratio in the crystals was semi-quantitatively analysed using SEM-EDX. PXRD patterns were measured of the obtained crystals.

1.5 Determination of K'_{NdL} and K'_{DyL}.

The conditional formation constants K'_{NdL} and K'_{DyL} were calculated using Equation 3 in the main text. The equilibrium concentrations of the chemical species were determined using UV-vis absorption measurements. DMSO and IPA were dried over molecular sieves prior to use in this experiment. DMSO/IPA (1:3 by volume) solutions containing $Ln(NO_3)_3$ (Ln = Nd or Dy, 3×10^{-5} mol/L), H_3L (3×10^{-5} mol/L), and x equivalents of DIEA (x = 1.5, 3, and 6) were prepared using volumetric flasks. Air was removed from the headspace of the flasks using argon gas. UV-vis absorption spectra were recorded (Figure S5) after leaving these solutions to stand for 24 h. As the amount of DIEA increased, the absorption band at 330 nm, assigned to the absorption by the protonated form of the ligand, decreased. Instead, an absorption band appeared at 370 nm. This absorption band is ascribed to the absorption of the deprotonated ligand coordinated to Nd^{3+} or Dy^{3+}. The equilibrium concentrations of H_3L and LnL were determined by the linear system of the following equations for absorbance at 330 nm (A_{330}) and 370 nm (A_{370}):

$$A_{330} = \varepsilon_{H3L,330}[H_3L] + \varepsilon_{LnL,330}[LnL] \quad \text{(S1)}$$

$$A_{370} = \varepsilon_{H3L,370}[H_3L] + \varepsilon_{LnL,370}[LnL] \quad \text{(S2)}$$

where $\varepsilon_{H3L,330}$, $\varepsilon_{H3L,370}$, $\varepsilon_{LnL,330}$ and $\varepsilon_{LnL,370}$ denote the molar absorption coefficients of H_3L and LnL at 330 and 370 nm in M^{-1} cm^{-1}, respectively. These molar absorption coefficients were calculated from the absorption spectra of H_3L (Figure S6) and the complexes (Figure S7). The equilibrium concentration for Ln^{3+} was calculated as the difference between the total Ln^{3+} concentration (c_{Ln}) and the equilibrium concentration of LnL as follows:

$$[Ln^{3+}] = c_{Ln} - [LnL] \quad \text{(S3)}$$

In this calculation, we assume that proton dissociation without coordination to the Ln^{3+} ion is negligible. This assumption is supported by the absorption spectra of H_3L (Figure S6). Even in the presence of an excess amount of DIEA, no changes in the absorption spectra were observed, suggesting that the acid dissociation of H_3L was negligible in DMSO/IPA. This is not surprising considering that the conjugated base of H_3L tends to show weak solvation in the DMSO/IPA mixture.

1.6 Crystallization-based Nd^{3+}/Dy^{3+} separation

DMSO and IPA were dried over molecular sieves prior to use in this experiment. DMSO/IPA solutions (1:3 by volume) were prepared by dissolving $Nd(NO_3)_3 \cdot 6H_2O$, $Dy(NO_3)_3 \cdot 5H_2O$, H_3L in a x:1:2 molar ratio ([$Nd(NO_3)_3$] = 8 mmol/L for x = 1, [$Nd(NO_3)_3$] = 16 mmol/L for x = 2, [$Dy(NO_3)_3$] = 8 mmol/L, [H_3L] = 16 mmol/L). To the solutions, DIEA was added in a $Nd(NO_3)_3$:$Dy(NO_3)_3$:H_3L:DIEA = x:1:2:y molar ratio ([DIEA] = 24 mmol/L for y =3, [DIEA] = 48 mmol/L for y =6). Each solution (4 mL) was stored at 25 °C for 3 days in a screw-capped vial of which air in the headspace was removed using argon gas. The obtained crystals were filtered, washed with DMSO/IPA (1:3 by volume) and diethyl ether, and dried in air overnight. The crystals were dissolved in nitric acid. The filtrate and washed solution were collected and diluted with nitric acid. We quantitatively analysed the Nd/Dy ratios in these solutions using ICP-AES to determine the separation factors ($S_{Nd/Dy}$). The $S_{Nd/Dy}$ value was calculated as follows:

$$S_{Nd/Dy} = \left(\frac{n_{Dy}}{n_{Nd}}\right)_c \left(\frac{n_{Nd}}{n_{Dy}}\right)_s \qquad \text{(S4)}$$

where n_{Nd} and n_{Dy} represents the molar masses of Nd and Dy, respectively. The subscripts c and s represents the crystalline and solution phases, respectively. The crystallization yield for Dy^{3+} is given as:

$$crystallization\ yield = 1 - \left(\frac{n_{Dy}}{n_{Dy,0}}\right)_s \qquad \text{(S5)}$$

where $n_{Dy,0}$ represents the initial molar mass of Dy determined by ICP-AES analysis.
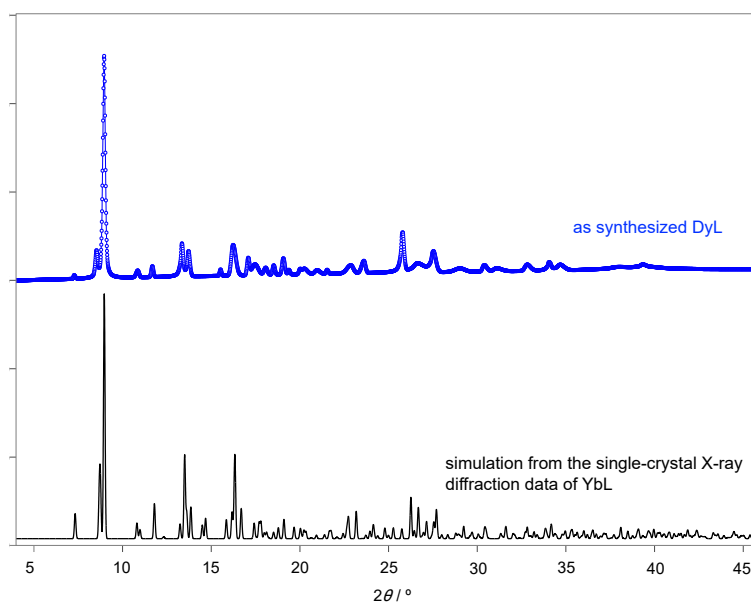
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2. Additional data

Figure S1. PXRD pattern of the as-synthesized DyL (blue line) and that simulated from the single-crystal X-ray diffraction data of YbL, which was reported in *ChemistryOpen*, **2021**, *10*, 46 (black line).
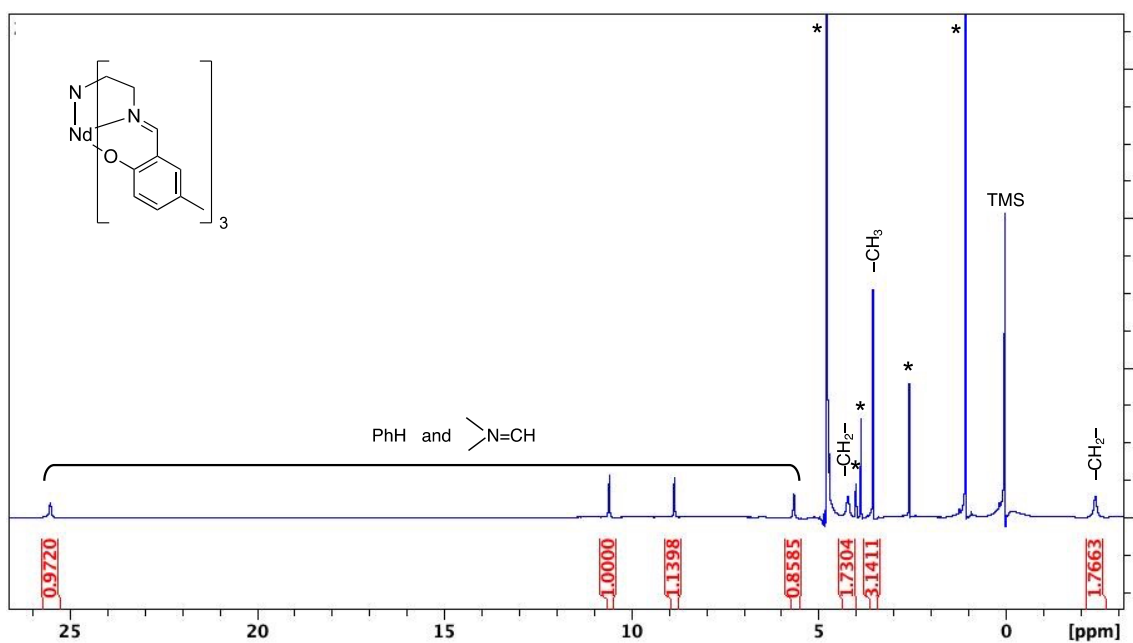

Figure S2. ^{1}H-NMR spectrum of a DMSO-d$_6$/IPA-d$_8$ mixture (1:3) containing NdL. Chemical shifts are referenced to tetramethylsilane (TMS) added to the solution and set to 0.0 ppm. The peaks indicated by stars represent the residual solvent signals.
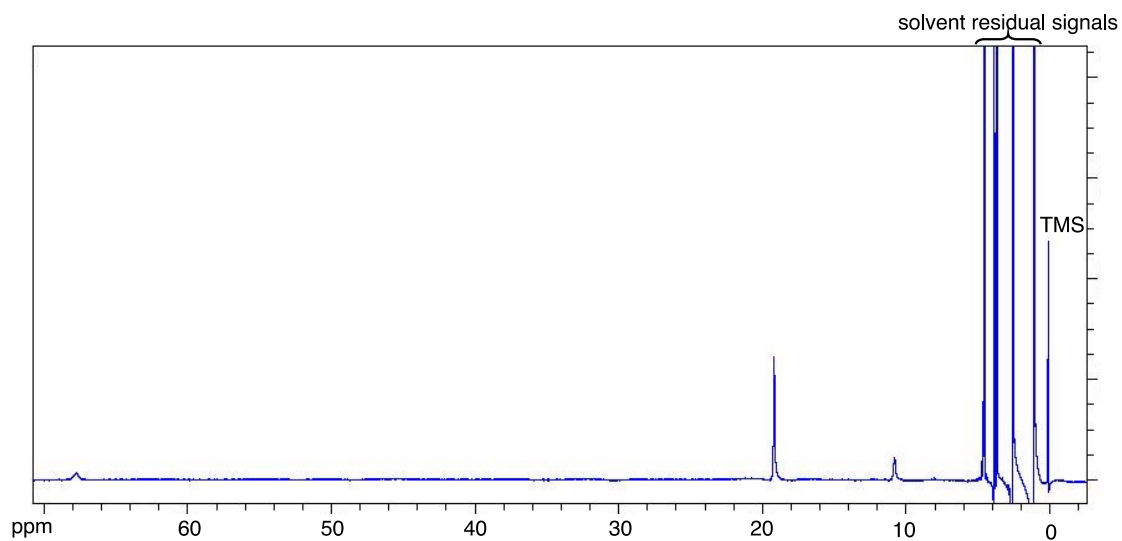
Figure S3. ^{1}H-NMR spectrum of a DMSO-d_6/IPA-d_8 mixture (1:1) containing DyL. Chemical shifts are referenced to TMS added to the solution and set to 0.0 ppm.
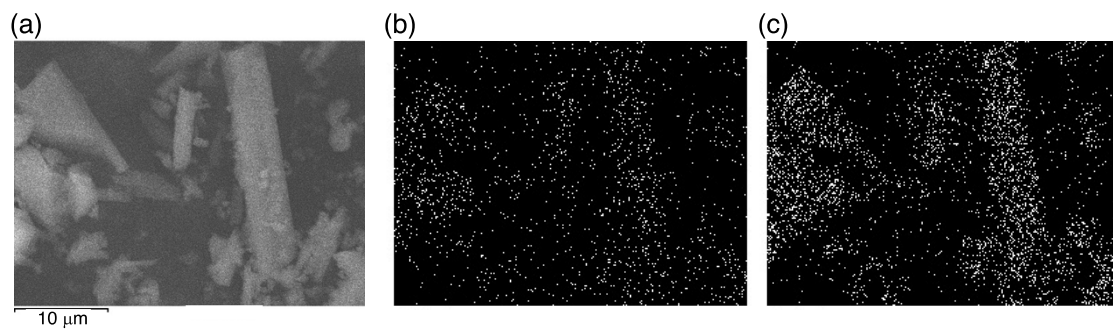

Figure S4. SEM-EDX images of the crystals grown from the DMSO/IPA mixture containing NdL and DyL. (a) Electron micrograph, (b) EDX map of Nd Lα and (c) EDX map of Dy Lα.

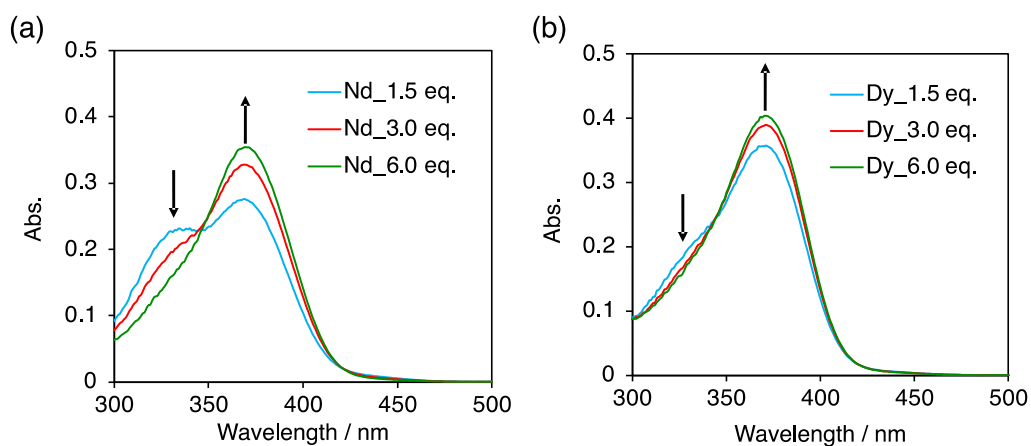Figure S5. Absorption spectra of the DMSO/IPA (1:3) solution containing $Ln(NO_3)_3$ (3×10^{-5} mol/L), H_3L (3×10^{-5} mol/L), and a x equivalent of DIEA to $Ln(NO)_3$ (x = 1.5, 3 and 6). (a) Ln = Nd, (b) Ln = Dy.
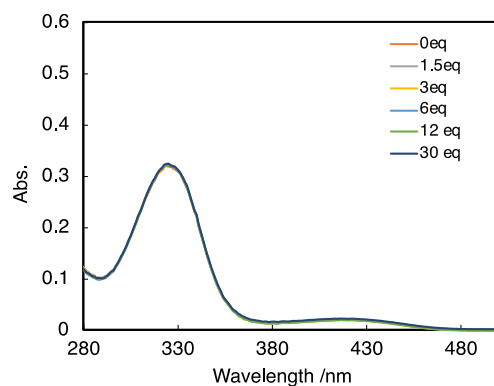

Figure S6. Absorption spectrum of the DMSO/IPA (1:3) solution containing H_3L (3×10^{-5} mol/L) and a x equivalent of DIEA to H_3L (x = 0, 1.5, 3, 6, 12 and 30).
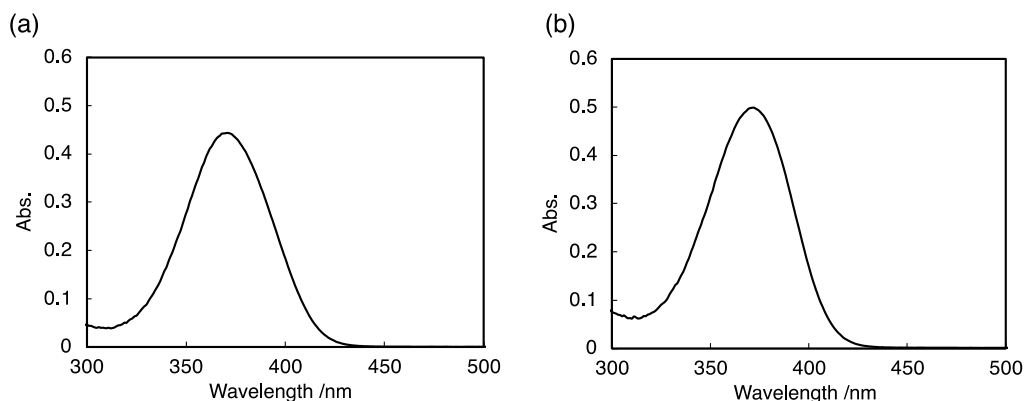
Figure S7. Absorption spectra of the DMSO/IPA (1:3 by volume) solution containing (a) NdL and (b) DyL, respectively. ([NdL] = [DyL] = 3×10^{-5} mol/L).

Table S1. Summary of the s_{LnL} (Ln = Nd and Dy, mM) values for the DMSO/IPA solvent mixtures (1:1, 1:3 and 1:6 by volume). All values are described as the average of three measurements with an uncertainty of $\pm 2\sigma$.

DMSO:IPA	s_{NdL}	s_{DyL}
1:1	18 ± 2	3.1 ± 0.7
1:3	5.5 ± 0.9	0.6 ± 0.1
1:6	1.2 ± 0.3	0.20 ± 0.01

Table S2. Atomic percentage (%) for Nd and Dy in crystals obtained from the DMSO/IPA mixture (1:3 by volume) containing NdL and DyL in a 1:1 molar ratio. Each atomic percentage is shown as the average of three measurements with an uncertainty of $\pm 2\sigma$.

	Atomic percentage
Nd	18 ± 4
Dy	82 ± 4

Table S3. Summary of $\log K'_{LnL}$ (Ln = Nd and Dy) in DMSO/IPA (1:3 by volume) at a given amount of DIEA. All values are described as the average of three measurements with an uncertainty of $\pm 2\sigma$.

Ln:H$_3$L:DIEA	$\log K'_{NdL}$	$\log K'_{DyL}$
1:1:1.5	5.0 ± 0.1	5.47 ± 0.03
1:1:3	5.35 ± 0.01	5.78 ± 0.04
1:1:6	5.6 ± 0.1	5.9 ± 0.1