Electronic Supplementary Information (ESI)

Data-driven efficient synthetic exploration of lanthanide-based metal–organic frameworks

Yu Kitamura,[a] Yuiga Nakamura,[b] Kunihisa Sugimoto,[c] Hirofumi Yoshikawa,[d] and Daisuke Tanaka*[a]

a. *Department of Chemistry, School of Science, Kwansei Gakuin University, 1 Gakuen-Uegahara, Sanda, Hyogo 669-1330, Japan*
b. *Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan*
c. *Department of Chemistry, Kindai University, 3-4-1Kowakae, Higashi-osaka, Osaka 577-8502, Japan*
d. *Program of Materials Science, School of Engineering, School of Science and Technology, Kwansei Gakuin University, 1 Gakuen-Uegahara, Sanda, Hyogo 669-1330, Japan*

**Corresponding Author. E-mail: dtanaka@kwansei.ac.jp.*

Table of Contents

S1. General information

Chemicals. All reagents were purchased and used without further purification. Terephthalic acid (H_2BDC, 95.0%), *N,N*-dimethylformamide (DMF, 99.95%), and triethylamine (tea) were purchased from FUJIFILM Wako Pure Chemical Corporation, Japan. *N*-Methyldiethanolamine (meda, >99.0%) was purchased from Tokyo Chemical Industry Co., Ltd., Japan. Lanthanide nitrates were purchased from various companies: $Gd(NO_3)_3 \cdot 6H_2O$ (99.95%) and $Tb(NO_3)_3 \cdot 6H_2O$ (99.95%) were purchased from Kanto Chemical Co., Inc., Japan; $Eu(NO_3)_3 \cdot 6H_2O$ (99.9%) was purchased from Kishida Chemical Co., Ltd., Japan; and $La(NO_3)_3 \cdot 6H_2O$ (99.999%), $Ce(NO_3)_3 \cdot 6H_2O$ (99.99%), $Pr(NO_3)_3 \cdot 6H_2O$ (99.9%), $Nd(NO_3)_3 \cdot 6H_2O$ (99.9%), $Sm(NO_3)_3 \cdot 6H_2O$ (99.9%), $Eu(NO_3)_3 \cdot 5H_2O$ (99.9%), $Gd(NO_3)_3 \cdot 6H_2O$ (99.9%), $Tb(NO_3)_3 \cdot 6H_2O$ (99.999%), $Dy(NO_3)_3 \cdot nH_2O$ (99.9%), $Ho(NO_3)_3 \cdot 5H_2O$ (99.99%), $Er(NO_3)_3 \cdot 5H_2O$ (99.9%), $Tm(NO_3)_3 \cdot 5H_2O$ (99.9%), $Yb(NO_3)_3 \cdot 5H_2O$ (99.999%), $Lu(NO_3)_3 \cdot nH_2O$ (99.999%), and $Y(NO_3)_3 \cdot 6H_2O$ (99.8%) were purchased from Sigma-Aldrich Co. LLC, Japan.

Characterization. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku MiniFlex600 diffractometer at 40 kV and 15 mA using a Cu target tube. The samples were examined without grinding, and the data were collected for 2θ values of 2°–30° using Cu Kα radiation. The excitation and emission spectra were obtained using a HITACHI F-7000 spectrofluorophotometer. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed using a JEOL JSM-7001FA or JCM-6000 microscope. Crystals were coated with osmium or gold for SEM observations. Thermogravimetry (TG) was performed using a Shimadzu DTG-60 instrument in the temperature range of 30–500 °C at 10 °C min^{-1} under a nitrogen atmosphere. The PXRD patterns were simulated based on single-crystal data using the diffraction crystal module of the Mercury software program (version 3.10), which is available free of charge at http://www.iucr.org.

Crystal structure determination. Crystallographic data for KGF-15(Gd, Er, Y) were collected with a CCD diffractometer using Mo Kα radiation. The CrysAlisPro 1.171.40.53 program (Rigaku, 2019) was used to integrate the diffraction profiles. The crystal structure was solved by direct methods using the SHELXT program and refined using SHELXL. Triethylammonium cations were disordered. One terminal methyl group was not visible. Anisotropic thermal parameters were used to refine all non-H atoms (CCDC number: 2169872, 2169876, 2169877).

Synchrotron crystal structure determination. Crystallographic data for KGF-15(Sm, Eu, Tb, Dy, Ho) were collected on a CCD diffractometer with synchrotron radiation (λ = 0.41760, 0.41310, 0.41260, or 0.41340 Å) at the BL02B1 beamline of the SPring-8 synchrotron radiation facility. The CrysAlisPro 1.171.40.53 program (Rigaku, 2019) was used to integrate the diffraction profiles. The crystal data were solved by direct methods using the SHELXT program and were refined with SHELXL. Triethylammonium cations were disordered. One terminal methyl group was not visible. Anisotropic thermal parameters were used to refine all non-H atoms (CCDC number: 2169870, 2169871, 2169873–2169875).

Machine-learning analysis. Cluster analysis was carried out using PDXL 2.8 (Rigaku)[1]. Powder patterns were compared with each other using a weighted mean of the Pearson and Spearman coefficients with every measured intensity data point. The Pearson coefficient is defined as

$$r_{xy} = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}\left((y_i - \bar{y})\right)^2}}$$

where x_i and y_i are the measured data points for the two patterns. The Spearman coefficient is defined as

$$\rho_{xy} = \frac{\sum_{i=1}^{n} R(x_i)R(y_i) - n\left(\frac{n+1}{2}\right)^2}{\sqrt{\sum_{i=1}^{n} R(x_i)^2 - n\left(\frac{n+1}{2}\right)^2}\sqrt{\sum_{i=1}^{n} R(y_i)^2 - n\left(\frac{n+1}{2}\right)^2}}$$

where x_i and y_i are the measured data points for the two patterns.
Decision tree analysis (Partition) was performed using JMP® Pro 15.2.1 (SAS Institute Inc., Cary, NC, USA) with the default settings, and the minimum degree of branching was set to 6.

S2. Synthesis

Synthetic conditions 1 (initial screening : exploratory experiments). $Dy(NO_3)_3 \cdot nH_2O$ (0.005–0.25 mmol) was dissolved in MeOH (0.25–1.75 mL, 2–125 mM), and H_2BDC (0.01–0.18 mmol) was separately dissolved in DMF (0.25–1.75 mL, 5–88 mM). The two solutions were mixed in a 4 mL Teflon-lined stainless-steel container. Subsequently, tea (140 or 400 μL) and meda (1 drop (40) or 60, 200, or 400 μL) were added, and the reaction mixture was heated at 130, 150, or 170 °C for 48 or 120 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h.

Synthetic conditions 2 (additional screening : detailed exploratory experiments). $Ln(NO_3)_3 \cdot nH_2O$ (Ln = La–Lu, excluding Pm) (0.005–0.15 mmol) was dissolved in MeOH (0.25–1.75 mL, 5–25 mM), and H_2BDC (0.02–0.12 mmol) was separately dissolved in DMF (0.25–1.75 mL, 15–61 mM). The two solutions were mixed in a 4 mL Teflon-lined stainless-steel container. Subsequently, tea (400 μL) and meda (1 drop (40 μL)) were added, and the reaction mixture was heated at 170 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h.

Synthetic conditions 3 (optimized synthetic conditions). $Ln(NO_3)_3 \cdot xH_2O$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, or Y) (0.12 mmol) was dissolved in MeOH (0.25 mL), and H_2BDC (0.035 mmol) was separately dissolved in DMF (1.75 mL). The two solutions were mixed in a 4 mL Teflon-lined stainless-steel container, and the reaction mixture was heated at 170 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h.

Synthetic conditions 4 (optimized synthetic conditions for bulk synthesis A). $Ln(NO_3)_3 \cdot xH_2O$ (Ln = Eu, Gd, Tb, or Dy) (0.3 mmol) was dissolved in MeOH (6.3 mL), and H_2BDC (0.9 mmol) was separately dissolved in DMF (44.0 mL). The two solutions were mixed in a 100 mL Teflon-lined stainless-steel container. Subsequently, tea (10 mL) was added, and the reaction mixture was heated at 170 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h. The obtained residue was washed with MeOH (× 3).

$Ln(NO_3)_3 \cdot nH_2O$ (Ln = Ho or Lu) (0.15 mmol) was dissolved in MeOH (3.0 mL), and H_2BDC (0.42 mmol) was separately dissolved in DMF (21.0 mL). The two solutions were mixed in a 50 mL Teflon-lined stainless-steel container. Subsequently, tea (5 mL) was added, and the reaction mixture was heated at 170 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h. The obtained residue was washed with MeOH (× 3).

$Er(NO_3)_3 \cdot 5H_2O$ (0.013 mmol) was dissolved in MeOH (0.25 mL), and H_2BDC (0.035 mmol) was separately dissolved in DMF (1.75 mL). The two solutions were mixed in a 4 mL Teflon-lined stainless-steel container. Subsequently, tea (400 μL) was added, and the reaction mixture was heated at 170 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h. The obtained residue was washed with MeOH (× 3).

Synthetic conditions 5 (optimized synthetic conditions for bulk synthesis B).
$Sm(NO_3)_3 \cdot 6H_2O$ (0.12 mmol) was dissolved in MeOH (12.6 mL), and H_2BDC (3.06 mmol) was separately dissolved in DMF (38.0 mL). The two solutions were mixed in a 100 mL Teflon-lined stainless-steel container. Subsequently, tea (10 mL) was added, and the reaction mixture was heated at 170 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h. The obtained residue was washed with MeOH (× 3).

Synthetic conditions 6 (optimized synthetic conditions for bulk synthesis C).
$Ln(NO_3)_3 \cdot 5H_2O$ (Ln = Tm or Yb) (0.13 mmol) was dissolved in MeOH (6.8 mL), and H_2BDC (0.88 mmol) was separately dissolved in DMF (44.0 mL). The two solutions were mixed in a 100 mL Teflon-lined stainless-steel container. Subsequently, tea (10 mL) was added, and the reaction mixture was heated at 170 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h. The obtained residue was washed with MeOH (× 3).

Synthetic conditions 7 (preparation of a single crystal of KGF-15(Sm)).
$Sm(NO_3)_3 \cdot 6H_2O$ (0.005 mmol) was dissolved in MeOH (0.25 mL), and H_2BDC (0.1225 mmol) was dissolved in DMF (1.75 mL). The solutions were then mixed in a 4 mL Teflon-lined stainless-steel container. Subsequently, tea (400 μL) and meda (1 drop) were added, and the reaction mixture was heated at 170 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h.

Synthetic conditions 8 (preparation of a single crystal of KGF-15(Eu, Gd, Tb, Er, or Y)). $Ln(NO_3)_3 \cdot nH_2O$ (Ln = Eu, Gd, Tb, Er, or Y) (0.025 mmol) was dissolved in MeOH (0.5 mL), and H_2BDC (0.045 mmol) was dissolved in DMF (1.5 mL). The solutions were then mixed in a 4 mL Teflon-lined stainless-steel container. Subsequently, tea (400 μL) and meda (1 drop) were added, and the reaction mixture was heated at 170 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h.

Synthetic conditions 9 (preparation of a single crystal of KGF-15(Ho)). $Ho(NO_3)_3 \cdot 5H_2O$ (0.025 mmol) was dissolved in MeOH (0.5 mL), and H_2BDC (0.045 mmol) was dissolved in DMF (1.5 mL). The solutions were then mixed in a 4 mL Teflon-lined stainless-steel container. Subsequently, tea (400 μL) was added, and the reaction mixture was heated at 170 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h.

Synthetic conditions 10 (preparation of a single crystal of KGF-15(Dy)). $Dy(NO_3)_3 \cdot nH_2O$ (0.015 mmol) was dissolved in MeOH (0.75 mL), and H_2BDC (0.0875 mmol) was dissolved in DMF (1.25 mL). The solutions were then mixed in a 4 mL Teflon-lined stainless-steel container. Subsequently, tea (400 μL) and meda (1 drop) were added, and the reaction mixture was heated at 170 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h.

S3. Synthetic conditions for previous Ln-BDC-MOFs

Table S1. Previously reported conditions for the synthesis of Ln-BDC-MOFs

No.	Formula	Ln	Metal source	BDC source	H_2O / %	DMF / %	Alcohol / %	Temp. / °C	Reference
1	$Ln_2(BDC)_3(DMF)_2(H_2O)_2$	Gd	$LnCl_3$	H_2BDC	17	83	0	55	[2]
2		Eu, Dy, Y	$Ln(NO_3)_3{\cdot}nH_2O$	Na_2BDC	50	50	0	30	[3]
3		Tb	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	50	50	0	100	[4]
4		Er, Tm	$LnCl_3$	H_2BDC	0	67	33	110	[5]
5		Er, Tm	$LnCl_3$	H_2BDC	0	67	33	110	[6]
6		Eu	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	50	50	0	115	[7]
7		Gd, Tb	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	50	50	0	80	[8]
8		Yb	$LnCl_3$	H_2BDC	50	50	0	100	[9, 10]
9		Er	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	25	38	38	80	[11]
10	$Ln(BDC)_{1.5}(H_2O){\cdot}(DMF)(H_2O)$	Tb	$[Tb_6O(OH)_8(NO_3)_6(H_2O)_{12}]^{2+}$	H_2BDC	0	100	0	30	[12]
11	$Ln_2(BDC)_3(H_2O)_4$	Nd, Er	Ln_2O_3	H_2BDC	100	0	0	170	[13]
12		Ce, Eu, Tb	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	100	0	0	120	[14]
13		La–Tm, Y (excluding Pm)	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	100	0	0	140	[15-21]
14	$Ln(BDC)(NO_3)(DMF)_2$	Eu	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	0	50	50	80	[22]
15		Gd	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	0	100	0	85	[23]
16		Tb	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	0	50	50	30	[24]

No.	Formula	Ln	Metal source	BDC source	H_2O / %	DMF / %	Alcohol / %	Temp. / °C	Reference
17	$Ln_4(BDC)_6(H_2O)_6$	Er	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	91	0	9	160	[25]
18		Er	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	100	0	0	180	[26]
19	$Ln_2(BDC)(OH)_4$	Eu	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	100	0	0	250	[27]
20	$Ln_2(BDC)_3(H_2O)_6$	Lu	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	100	0	0	180	[28]
21		Yb	Ln_2O_3	H_2BDC	100	0	0	170	[29]
22		Yb	Ln_2O_3	H_2BDC	100	0	0	170	[13]
23		Er	$LnCl_3$	Na_2BDC	100	0	0	30	[30, 31]
24	$Ln_2(BDC)_3(H_2O)_6{\cdot}(H_2O)_2$	Er	$LnCl_3$	Na_2BDC	100	0	0	30	[31]
25	$Ln_2(BDC)_3(H_2O)_8{\cdot}(H_2O)_2$	Yb	Ln_2O_3	H_2BDC	100	0	0	170	[13]
26		Yb	$LnCl_3$	H_2BDC	100	0	0	180	[32]
27		Er	$LnCl_3$	Na_2BDC	100	0	0	30	[31]
28	$Ln_2(BDC)_3(H_2O)_6{\cdot}(H_2O)_2$	Er	$LnCl_3$	Na_2BDC	100	0	0	30	[31]
29	$Ln_2(BDC)_3(H_2O)_6{\cdot}H_2O$	Er	$LnCl_3$	Na_2BDC	100	0	0	30	[31]
30	$Ln_3(BDC)_{4.5}(DMF)_2(H_2O)_3{\cdot}(DMF)(H_2O)$	Er	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	14	71	14	55	[31]
31	$Ln_3(BDC)_{4.5}(DMF)_2(H_2O)_3{\cdot}(DMF)(EtOH)_{0.5}(H_2O)_{0.5}$	Dy, Ho, Er	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	14	71	14	55	[31]
32	$Ln_3(BDC)_{4.5}(DMF)_2(H_2O)_3{\cdot}(DMF)_2$	Yb	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	0	83	17	60	[33]
33	$Ln_3(BDC)_{3.5}(OH)_2(H_2O)_2{\cdot}(H_2O)$	Er, Yb, Y	$LnCl_3$	H_2BDC	100	0	0	190	[34]
34	$Ln_2(BDC)_3(MeOH)_4{\cdot}(MeOH)_8$	Eu	$LnCl_3$	H_2BDC	0	0	100	heat	[35]
35	$Ln_2(BDC)_3(MeOH)_4{\cdot}(Cl)(MeOH)(H_2O)_{0.25}$	Eu, Gd, Tb	$LnCl_3$	H_2BDC	0	0	100	heat	[35]
36	$Ln_2(BDC)_3(NO_3)(MeOH)_2{\cdot}(MeCN)(H_2O)$	Eu, Gd	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	0	0	100	heat	[35]

No.	Formula	Ln	Metal source	BDC source	H_2O / %	DMF / %	Alcohol / %	Temp. / °C	Reference
37	$Ln(BDC)_{1.5}(DEF)$	La, Ce, Nd	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	2	98	0	130	[36]
38	$Ln_2(BDC)_3(DMF)_2{\cdot}(H_2O)$	Yb	$LnCl_3$	H_2BDC	3	97	0	100	[9, 37]
39	$Ln_2(BDC)_3(DMF)_2$	Er	$LnCl_3$	H_2BDC	0	100	0	85	[38]
40	$Ln_2(BDC)_3(DMF)_2$	Yb	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	50	50	0	100	[39]
41	$Ln_6(BDC)_9(DMF)_6(H2O)_3{\cdot}(DMF)_3$	La, Ce, Nd	$Ln(NO_3)_3{\cdot}nH_2O$	Na_2BDC	50	50	0	30	[3]
42	$Ln_2(BDC)_3(H_2O)_2$	Yb	Ln_2O_3	H_2BDC	100	0	0	170	[13]
43	$Ln_2(BDC)_3(DMF)_2(H_2O)_2{\cdot}(DMF)(H_2O)$	Pr, Nd, Sm, Eu	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	14	71	14	60	[40]
44	$Ln_3(BDC)_{4.5}(H_2O)(DMF)_2$	Tb	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	50	50	0	100	[4]
45	$Ln_2(BDC)_3(DMF)_2{\cdot}(H_2O)_{0.7}$	Eu	$LnCl_3$	H_2BDC	0	100	0	120	[41]
46	$Ln_2(BDC)_3(DMF)_2{\cdot}(H_2O)$	Gd	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	0	100	0	110	[42]
47	$Ln_2(BDC)_3(DMF)_2(DMSO)_2$	Ce	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	0	80	0	120	[43]
48	$Ln_4(BDC)_6(H_2O)_2(DMF)(EtOH){\cdot}(DMF)_2(H_2O)_2$	Tm	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	33	33	33	30	[6]
49	$Ln(BDC)(HCOO)$	Dy, Er	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	0	100	0	180	[44]
50		Eu, Gd, Tb	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	60	40	0	160	[45]
51		Yb	$LnCl_3$	H_2BDC	50	50	0	120	[9]
52		Gd	Ln_2O_3	H_2BDC	50	50	0	180	[46]
53	$Ln(BDC)_{1.5}(H_2O){\cdot}(DMF)_{0.5}(EtOH)(H_2O)_2$	Tm	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	13	63	25	50	[6]
54	$Ln_6(BDC)_6(OH)_4O_4$	Ce	$Ln(NH_4)_2(NO_3)_6$	H_2BDC	0	100	0	100	[47]
55	$Ln_2(BDC)(OH)_4(H_2O)_2$	Eu	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	100	0	0	180	[48]
56	$Ln_5(BDC)_{7.5}(DMF)_4$	Ce	$Ln(NH_4)_2(NO_3)_6$	H_2BDC	0	100	0	150	[49]

No.	Formula	Ln	Metal source	BDC source	H_2O / %	DMF / %	Alcohol / %	Temp. / °C	Reference
57	$Ln_6(BDC)_7(OH)_4(H_2O)_4$	Yb	$LnCl_3$	MOF	100	0	0	200	[10]
58	$Ln_2(BDC)_3$	Yb	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	100	0	0	200	[10]
59	$[(CH_3)_2NH_2]{\cdot}Ln_3(BDC)_3(HCOO)_3(OH)$	Tb, Er, Y	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	19	81	0	105	[10]
60	$Ln_{10}(BDC)_3(HCOO)_4(OH)_{12}(CO_3)_4(H_2O)_2$	Dy, Ho, Y	$Ln(NO_3)_3{\cdot}nH_2O$	H_2BDC	60	40	0	150	[50]

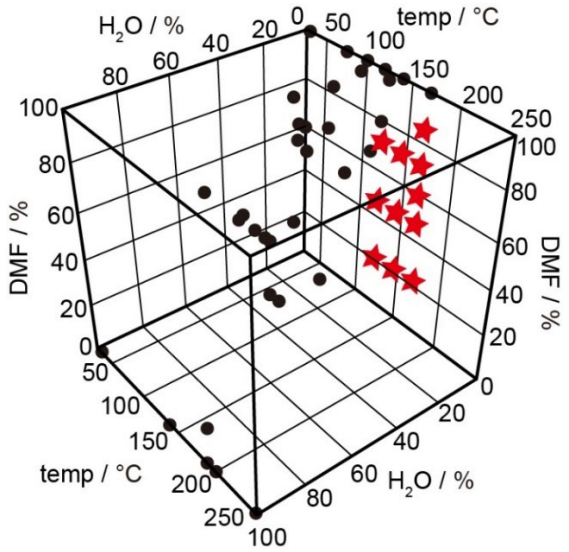


Fig. S1. 3D plot of synthetic conditions, focusing on DMF, H_2O, and reaction temperature. Red stars indicate the synthetic conditions used in this study, and black circles indicate previously reported synthetic conditions. The data of No. 19 and 34-36 are excluded from the synthetic conditions of Table S1, and the same solvent and reaction temperature, but different concentrations, etc., are described in the same plot.

S4. Initial and additional synthetic screening

Table S2. Initial synthetic screening conditions

Experiment No.	PXRD (cluster)	M /mM	L /mM	L/M	EtOH /mL	DMF /mL	DMF /EtOH	Metal source	Meda /μL	Tea /μL	Rising time	Reaction time	Cooling time	Reaction temp.	Reaction vessel /mL
YU343_3	1	19	25	1.3	1.5	0.5	0.33	Dy	60	140	5	120	12	130	4
YU343_4	1	13	50	3.8	1.0	1.0	1.00	Dy	60	140	5	120	12	130	4
YU343_6	5	19	13	0.7	1.5	0.5	0.33	Dy	60	140	5	120	12	130	4
YU343_7	1	13	25	1.9	1.0	1.0	1.00	Dy	60	140	5	120	12	130	4
YU343_11	1	94	25	0.3	1.5	0.5	0.33	Dy	60	140	5	120	12	130	4
YU343_12	7	63	50	0.8	1.0	1.0	1.00	Dy	60	140	5	120	12	130	4
YU343_13	4	31	75	2.4	0.5	1.5	3.00	Dy	60	140	5	120	12	130	4
YU343_14	1	94	13	0.1	1.5	0.5	0.33	Dy	60	140	5	120	12	130	4
YU343_15	1	63	25	0.4	1.0	1.0	1.00	Dy	60	140	5	120	12	130	4
YU343_16	7	13	38	2.9	0.5	1.5	3.00	Dy	60	140	5	120	12	130	4
YU343_19	1	94	13	0.1	1.5	0.5	0.33	Dy	60	140	5	120	12	130	4
YU343_20	7	63	25	0.4	1.0	1.0	1.00	Dy	60	140	5	120	12	130	4
YU343_21	4	31	38	1.2	0.5	1.5	3.00	Dy	60	140	5	120	12	130	4
YU343_22	1	94	6	0.1	1.5	0.5	0.33	Dy	60	140	5	120	12	130	4
YU343_23	1	63	13	0.2	1.0	1.0	1.00	Dy	60	140	5	120	12	130	4
YU343_24	7	31	19	0.6	0.5	1.5	3.00	Dy	60	140	5	120	12	130	4
YU344_1	8	38	5	0.1	1.5	0.5	0.33	Dy	200	400	5	48	12	130	4
YU344_2	1	25	10	0.4	1.0	1.0	1.00	Dy	200	400	5	48	12	130	4

Experiment No.	PXRD (cluster)	M /mM	L /mM	L/M	EtOH /mL	DMF /mL	DMF /EtOH	Metal source	Meda /μL	Tea /μL	Rising time	Reaction time	Cooling time	Reaction temp.	Reaction vessel /mL
YU344_3	2	13	15	1.2	0.5	1.5	3.00	Dy	200	400	5	48	12	130	4
YU344_4	1	38	13	0.3	1.5	0.5	0.33	Dy	200	400	5	48	12	130	4
YU344_5	2	25	25	1.0	1.0	1.0	1.00	Dy	200	400	5	48	12	130	4
YU344_6	2	13	38	2.9	0.5	1.5	3.00	Dy	200	400	5	48	12	130	4
YU344_7	8	38	5	0.1	1.5	0.5	0.33	Dy	400	400	5	48	12	130	4
YU344_8	1	25	10	0.4	1.0	1.0	1.00	Dy	400	400	5	48	12	130	4
YU344_9	1	13	15	1.2	0.5	1.5	3.00	Dy	400	400	5	48	12	130	4
YU344_10	1	38	13	0.3	1.5	0.5	0.33	Dy	400	400	5	48	12	130	4
YU344_11	2	25	25	1.0	1.0	1.0	1.00	Dy	400	400	5	48	12	130	4
YU344_12	2	13	38	2.9	0.5	1.5	3.00	Dy	400	400	5	48	12	130	4
YU344_13	2	15	25	1.7	1.5	0.5	0.33	Dy	200	400	5	48	12	130	4
YU344_14	2	10	50	5.0	1.0	1.0	1.00	Dy	200	400	5	48	12	130	4
YU344_15	7	5	75	15	0.5	1.5	3.00	Dy	200	400	5	48	12	130	4
YU344_16	2	15	10	0.7	1.5	0.5	0.33	Dy	200	400	5	48	12	130	4
YU344_17	2	10	20	2.0	1.0	1.0	1.00	Dy	200	400	5	48	12	130	4
YU344_18	2	5	30	6.0	0.5	1.5	3.00	Dy	200	400	5	48	12	130	4
YU344_19	2	15	25	1.7	1.5	0.5	0.33	Dy	400	400	5	48	12	130	4
YU344_20	2	10	50	5.0	1.0	1.0	1.00	Dy	400	400	5	48	12	130	4
YU344_21	2	5	75	15	0.5	1.5	3.00	Dy	400	400	5	48	12	130	4
YU344_22	1	15	10	0.7	1.5	0.5	0.33	Dy	400	400	5	48	12	130	4
YU344_23	2	10	20	2.0	1.0	1.0	1.00	Dy	400	400	5	48	12	130	4

Experiment No.	PXRD (cluster)	M /mM	L /mM	L/M	EtOH /mL	DMF /mL	DMF /EtOH	Metal source	Meda /μL	Tea /μL	Rising time	Reaction time	Cooling time	Reaction temp.	Reaction vessel /mL
YU344_24	2	5	30	6.0	0.5	1.5	3.00	Dy	400	400	5	48	12	130	4
YU345_1	1	38	5	0.1	1.5	0.5	0.33	Dy	200	400	5	48	12	150	4
YU345_2	2	25	10	0.4	1.0	1.0	1.00	Dy	200	400	5	48	12	150	4
YU345_3	2	13	15	1.2	0.5	1.5	3.00	Dy	200	400	5	48	12	150	4
YU345_4	2	38	13	0.3	1.5	0.5	0.33	Dy	200	400	5	48	12	150	4
YU345_5	2	25	25	1.0	1.0	1.0	1.00	Dy	200	400	5	48	12	150	4
YU345_6	2	13	38	2.9	0.5	1.5	3.00	Dy	200	400	5	48	12	150	4
YU345_7	2	38	5	0.1	1.5	0.5	0.33	Dy	400	400	5	48	12	150	4
YU345_8	1	25	10	0.4	1.0	1.0	1.00	Dy	400	400	5	48	12	150	4
YU345_9	1	13	15	1.2	0.5	1.5	3.00	Dy	400	400	5	48	12	150	4
YU345_10	1	38	13	0.3	1.5	0.5	0.33	Dy	400	400	5	48	12	150	4
YU345_11	1	25	25	1.0	1.0	1.0	1.00	Dy	400	400	5	48	12	150	4
YU345_12	2	13	38	2.9	0.5	1.5	3.00	Dy	400	400	5	48	12	150	4
YU345_13	2	15	25	1.7	1.5	0.5	0.33	Dy	200	400	5	48	12	150	4
YU345_14	2	10	50	5.0	1.0	1.0	1.00	Dy	200	400	5	48	12	150	4
YU345_15	3	5	75	15	0.5	1.5	3.00	Dy	200	400	5	48	12	150	4
YU345_16	1	15	10	0.7	1.5	0.5	0.33	Dy	200	400	5	48	12	150	4
YU345_17	2	10	20	2.0	1.0	1.0	1.00	Dy	200	400	5	48	12	150	4
YU345_18	2	5	30	6.0	0.5	1.5	3.00	Dy	200	400	5	48	12	150	4
YU345_19	2	15	25	1.7	1.5	0.5	0.33	Dy	400	400	5	48	12	150	4
YU345_20	2	10	50	5.0	1.0	1.0	1.00	Dy	400	400	5	48	12	150	4

Experiment No.	PXRD (cluster)	M /mM	L /mM	L/M	EtOH /mL	DMF /mL	DMF /EtOH	Metal source	Meda /μL	Tea /μL	Rising time	Reaction time	Cooling time	Reaction temp.	Reaction vessel /mL
YU345_21	2	5	75	15	0.5	1.5	3.00	Dy	400	400	5	48	12	150	4
YU345_22	1	15	10	0.7	1.5	0.5	0.33	Dy	400	400	5	48	12	150	4
YU345_23	2	10	20	2.0	1.0	1.0	1.00	Dy	400	400	5	48	12	150	4
YU345_24	2	5	30	6.0	0.5	1.5	3.00	Dy	400	400	5	48	12	170	4
YU346_1	2	38	5	0.1	1.5	0.5	0.33	Dy	200	400	5	48	12	170	4
YU346_2	2	25	10	0.4	1.0	1.0	1.00	Dy	200	400	5	48	12	170	4
YU346_3	6	13	15	1.2	0.5	1.5	3.00	Dy	40	400	5	48	12	170	4
YU346_4	1	38	13	0.3	1.5	0.5	0.33	Dy	40	400	5	48	12	170	4
YU346_5	4	25	25	1.0	1.0	1.0	1.00	Dy	40	400	5	48	12	170	4
YU346_6	3	13	38	2.9	0.5	1.5	3.00	Dy	40	400	5	48	12	170	4
YU346_7	1	38	5	0.1	1.5	0.5	0.33	Dy	400	400	5	48	12	170	4
YU346_8	1	25	10	0.4	1.0	1.0	1.00	Dy	400	400	5	48	12	170	4
YU346_9	1	13	15	1.2	0.5	1.5	3.00	Dy	400	400	5	48	12	170	4
YU346_10	1	38	13	0.3	1.5	0.5	0.33	Dy	400	400	5	48	12	170	4
YU346_11	1	25	25	1.0	1.0	1.0	1.00	Dy	400	400	5	48	12	170	4
YU346_12	2	13	38	2.9	0.5	1.5	3.00	Dy	400	400	5	48	12	170	4
YU346_13	1	15	25	1.7	1.5	0.5	0.33	Dy	200	400	5	48	12	170	4
YU346_14	3	10	50	5.0	1.0	1.0	1.00	Dy	200	400	5	48	12	170	4
YU346_15	3	5	75	15	0.5	1.5	3.00	Dy	40	400	5	48	12	170	4
YU346_16	1	15	10	0.7	1.5	0.5	0.33	Dy	40	400	5	48	12	170	4
YU346_17	3	10	20	2.0	1.0	1.0	1.00	Dy	40	400	5	48	12	170	4

Experiment No.	PXRD (cluster)	M /mM	L /mM	L/M	EtOH /mL	DMF /mL	DMF /EtOH	Metal source	Meda /μL	Tea /μL	Rising time	Reaction time	Cooling time	Reaction temp.	Reaction vessel /mL
YU346_18	3	5	30	6.0	0.5	1.5	3.00	Dy	40	400	5	48	12	170	4
YU346_19	2	15	25	1.7	1.5	0.5	0.33	Dy	400	400	5	48	12	170	4
YU346_20	2	10	50	5.0	1.0	1.0	1.00	Dy	400	400	5	48	12	170	4
YU346_21	2	5	75	15	0.5	1.5	3.00	Dy	400	400	5	48	12	170	4
YU346_22	1	15	10	0.7	1.5	0.5	0.33	Dy	400	400	5	48	12	170	4
YU346_23	2	10	20	2.0	1.0	1.0	1.00	Dy	400	400	5	48	12	170	4
YU346_24	2	5	30	6.0	0.5	1.5	3.00	Dy	400	400	5	48	12	170	4
YU347_1	3	6	18	3.0	0.25	1.75	7.00	Dy	40	400	5	48	12	170	4
YU347_2	3	13	16	1.2	0.5	1.5	3.00	Dy	40	400	5	48	12	170	4
YU347_5	2	13	16	1.2	0.5	1.5	3.00	Dy	200	400	5	48	12	170	4
YU347_6	2	19	13	0.7	0.75	1.25	1.67	Dy	200	400	5	48	12	170	4
YU347_7	3	6	27	4.5	0.25	1.75	7.00	Dy	40	400	5	48	12	170	4
YU347_8	3	13	23	1.8	0.5	1.5	3.00	Dy	40	400	5	48	12	170	4
YU347_9	3	19	19	1.0	0.75	1.25	1.67	Dy	40	400	5	48	12	170	4
YU347_10	3	6	27	4.5	0.25	1.75	7.00	Dy	200	400	5	48	12	170	4
YU347_11	2	13	23	1.8	0.5	1.5	3.00	Dy	200	400	5	48	12	170	4
YU347_12	2	19	19	1.0	0.75	1.25	1.67	Dy	200	400	5	48	12	170	4
YU347_13	3	6	35	5.8	0.25	1.75	7.00	Dy	40	400	5	48	12	170	4
YU347_14	3	13	30	2.3	0.5	1.5	3.00	Dy	40	400	5	48	12	170	4
YU347_15	3	19	25	1.3	0.75	1.25	1.67	Dy	40	400	5	48	12	170	4
YU347_16	3	6	35	5.8	0.25	1.75	7.00	Dy	200	400	5	48	12	170	4

Experiment No.	PXRD (cluster)	M /mM	L /mM	L/M	EtOH /mL	DMF /mL	DMF /EtOH	Metal source	Meda /μL	Tea /μL	Rising time	Reaction time	Cooling time	Reaction temp.	Reaction vessel /mL
YU347_17	2	13	30	2.3	0.5	1.5	3.00	Dy	200	400	5	48	12	170	4
YU347_18	2	19	25	1.3	0.75	1.25	1.67	Dy	200	400	5	48	12	170	4
YU347_19	3	6	44	7.3	0.25	1.75	7.00	Dy	40	400	5	48	12	170	4
YU347_20	3	13	37	2.8	0.5	1.5	3.00	Dy	40	400	5	48	12	170	4
YU347_21	3	19	31	1.6	0.75	1.25	1.67	Dy	40	400	5	48	12	170	4
YU347_22	2	6	44	7.3	0.25	1.75	7.00	Dy	200	400	5	48	12	170	4
YU347_23	2	13	37	2.8	0.5	1.5	3.00	Dy	200	400	5	48	12	170	4
YU347_24	2	19	31	1.6	0.75	1.25	1.67	Dy	200	400	5	48	12	170	4
YU347_25	3	3	88	29.3	0.25	1.75	7.00	Dy	40	400	5	48	12	170	4
YU347_26	1	5	75	15.0	0.5	1.5	3.00	Dy	40	400	5	48	12	170	4
YU347_27	1	8	63	7.9	0.75	1.25	1.67	Dy	40	400	5	48	12	170	4
YU347_28	2	3	88	29.3	0.25	1.75	7.00	Dy	200	400	5	48	12	170	4
YU347_29	2	5	75	15.0	0.5	1.5	3.00	Dy	200	400	5	48	12	170	4
YU347_30	2	8	63	7.9	0.75	1.25	1.67	Dy	200	400	5	48	12	170	4
YU347_31	3	3	61	20.3	0.25	1.75	7.00	Dy	40	400	5	48	12	170	4
YU347_32	3	5	53	10.6	0.5	1.5	3.00	Dy	40	400	5	48	12	170	4
YU347_34	2	3	61	20.3	0.25	1.75	7.00	Dy	200	400	5	48	12	170	4
YU347_35	2	5	53	10.6	0.5	1.5	3.00	Dy	200	400	5	48	12	170	4
YU347_36	2	8	44	5.5	0.75	1.25	1.67	Dy	200	400	5	48	12	170	4
YU347_37	3	3	44	14.7	0.25	1.75	7.00	Dy	40	400	5	48	12	170	4
YU347_38	3	5	37	7.4	0.5	1.5	3.00	Dy	40	400	5	48	12	170	4

Experiment No.	PXRD (cluster)	M /mM	L /mM	L/M	EtOH /mL	DMF /mL	DMF /EtOH	Metal source	Meda /μL	Tea /μL	Rising time	Reaction time	Cooling time	Reaction temp.	Reaction vessel /mL
YU347_40	2	3	44	14.7	0.25	1.75	7.00	Dy	200	400	5	48	12	170	4
YU347_41	2	5	37	7.4	0.5	1.5	3.00	Dy	200	400	5	48	12	170	4
YU347_42	2	8	31	3.9	0.75	1.25	1.67	Dy	200	400	5	48	12	170	4
YU347_43	3	3	35	11.7	0.25	1.75	7.00	Dy	40	400	5	48	12	170	4
YU347_44	3	5	30	6.0	0.5	1.5	3.00	Dy	40	400	5	48	12	170	4
YU347_45	3	8	25	3.1	0.75	1.25	1.67	Dy	40	400	5	48	12	170	4
YU347_46	3	3	35	11.7	0.25	1.75	7.00	Dy	200	400	5	48	12	170	4
YU347_47	2	5	30	6.0	0.5	1.5	3.00	Dy	200	400	5	48	12	170	4
YU347_48	2	8	25	3.1	0.75	1.25	1.67	Dy	200	400	5	48	12	170	4

Table S3. Additional synthetic screening conditions

Experiment No.	PXRD (cluster)	M /mM	L /mM	L/M	EtOH /mL	DMF /mL	DMF /EtOH	Metal source	Meda /μL	Tea /μL	Rising time	Reaction time	Cooling time	Reaction temp.	Reaction vessel /mL
YU348_1	3	13	44	3.4	0.25	1.75	7.00	Dy	40	400	5	48	12	170	4
YU348_2	9	25	38	1.5	0.50	1.50	3.00	Dy	40	400	5	48	12	170	4
YU348_11	1	18	38	2.1	0.50	1.50	3.00	Dy	40	400	5	48	12	170	4
YU349_1	3	12	44	3.7	0.25	1.75	7.00	Er	40	400	5	48	12	170	4
YU349_2	10	25	38	1.5	0.50	1.50	3.00	Er	40	400	5	48	12	170	4
YU349_11	3	17	38	2.2	0.50	1.50	3.00	Er	40	400	5	48	12	170	4
YU349_18	1	17	22	1.3	0.50	1.50	3.00	Er	40	400	5	48	12	170	4
YU351_1	3	6	18	3.0	0.25	1.75	7.00	Er	40	400	5	48	12	170	4
YU351_7	3	6	26	4.3	0.25	1.75	7.00	Er	40	400	5	48	12	170	4
YU351_14	3	5	53	10.6	0.50	1.50	3.00	Er	40	400	5	48	12	170	4
YU351_15	3	8	44	5.5	0.75	1.25	1.67	Er	40	400	5	48	12	170	4
YU351_19	3	3	44	14.7	0.25	1.75	7.00	Er	40	400	5	48	12	170	4
YU351_20	3	5	38	7.6	0.50	1.50	3.00	Er	40	400	5	48	12	170	4
YU351_21	3	8	31	3.9	0.75	1.25	1.67	Er	40	400	5	48	12	170	4
YU356_1	3	13	23	1.8	0.50	1.50	3.00	Dy	40	400	5	48	12	170	4
YU356_2	3	11	23	2.1	0.50	1.50	3.00	Er	40	400	5	48	12	170	4
YU356_4	3	2	61	30.5	0.25	1.75	7.00	Dy	40	400	5	48	12	170	4
YU356_5	3	2	61	30.5	0.25	1.75	7.00	Er	40	400	5	48	12	170	4
YU356_13	3	7	32	4.6	0.75	1.25	1.67	Dy	40	400	5	48	12	170	4
YU356_14	3	7	32	4.6	0.75	1.25	1.67	Er	40	400	5	48	12	170	4

Experiment No.	PXRD (cluster)	M /mM	L /mM	L/M	EtOH /mL	DMF /mL	DMF /EtOH	Metal source	Meda /μL	Tea /μL	Rising time	Reaction time	Cooling time	Reaction temp.	Reaction vessel /mL
YU356_17	3	7	44	6.3	0.75	1.25	1.67	Er	40	400	5	48	12	170	4
YU356_19	3	18	38	2.1	0.50	1.50	3.00	Dy	40	400	5	48	12	170	4
YU356_20	3	17	38	2.2	0.50	1.50	3.00	Er	40	400	5	48	12	170	4
YU356_23	3	11	15	1.4	0.50	1.50	3.00	Er	40	400	5	48	12	170	4
YU357_1	13	2	61	30.5	0.25	1.75	7.00	La	40	400	5	48	12	170	4
YU357_2	13	2	61	30.5	0.25	1.75	7.00	Ce	40	400	5	48	12	170	4
YU357_3	3	3	61	20.3	0.25	1.75	7.00	Pr	40	400	5	48	12	170	4
YU357_4	3	3	61	20.3	0.25	1.75	7.00	Nd	40	400	5	48	12	170	4
YU357_5	3	3	61	20.3	0.25	1.75	7.00	Sm	40	400	5	48	12	170	4
YU357_6	3	3	61	20.3	0.25	1.75	7.00	Eu	40	400	5	48	12	170	4
YU357_7	3	3	61	20.3	0.25	1.75	7.00	Gd	40	400	5	48	12	170	4
YU357_8	3	2	61	30.5	0.25	1.75	7.00	Tb	40	400	5	48	12	170	4
YU357_9	3	2	61	30.5	0.25	1.75	7.00	Ho	40	400	5	48	12	170	4
YU357_10	3	2	61	30.5	0.25	1.75	7.00	Tm	40	400	5	48	12	170	4
YU357_11	3	3	61	20.3	0.25	1.75	7.00	Yb	40	400	5	48	12	170	4
YU357_12	3	3	61	20.3	0.25	1.75	7.00	Lu	40	400	5	48	12	170	4
YU357_13	13	12	23	1.9	0.50	1.50	3.00	La	40	400	5	48	12	170	4
YU357_14	13	12	23	1.9	0.50	1.50	3.00	Ce	40	400	5	48	12	170	4
YU357_15	13	13	23	1.8	0.50	1.50	3.00	Pr	40	400	5	48	12	170	4
YU357_16	13	13	23	1.8	0.50	1.50	3.00	Nd	40	400	5	48	12	170	4
YU357_17	11	13	23	1.8	0.50	1.50	3.00	Sm	40	400	5	48	12	170	4

Experiment No.	PXRD (cluster)	M /mM	L /mM	L/M	EtOH /mL	DMF /mL	DMF /EtOH	Metal source	Meda /μL	Tea /μL	Rising time	Reaction time	Cooling time	Reaction temp.	Reaction vessel /mL
YU357_18	3	13	23	1.8	0.50	1.50	3.00	Eu	40	400	5	48	12	170	4
YU357_19	3	13	23	1.8	0.50	1.50	3.00	Gd	40	400	5	48	12	170	4
YU357_20	3	12	23	1.9	0.50	1.50	3.00	Tb	40	400	5	48	12	170	4
YU357_21	3	13	23	1.8	0.50	1.50	3.00	Ho	40	400	5	48	12	170	4
YU357_22	12	12	23	1.9	0.50	1.50	3.00	Tm	40	400	5	48	12	170	4
YU357_23	12	12	23	1.9	0.50	1.50	3.00	Yb	40	400	5	48	12	170	4
YU357_24	12	12	23	1.9	0.50	1.50	3.00	Lu	40	400	5	48	12	170	4

S5. Crystallographic data

Table S4. Crystallographic parameters and data for KGF-15(Ln)

Compound	KGF-15(Sm)	KGF-15(Eu)	KGF-15(Gd)	KGF-15(Tb)	KGF-15(Dy)	KGF-15(Ho)	KGF-15(Er)	KGF-15(Y)
Formula	$C_{42.5}H_{38.5}Sm_2N_2O_{16}$	$C_{42.5}H_{38.5}Eu_2N_2O_{16}$	$C_{42.5}H_{38.5}Gd_2N_2O_{16}$	$C_{42.5}H_{38.5}Tb_2N_2O_{16}$	$C_{42.5}H_{38.5}Dy_2N_2O_{16}$	$C_{42.5}H_{38.5}Ho_2N_2O_{16}$	$C_{42.5}H_{38.5}Er_2N_2O_{16}$	$C_{42.5}H_{38.5}Y_2N_2O_{16}$
Formula weight	1133.95	1137.17	1147.75	1151.09	1158.25	1163.11	1167.77	1011.07
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*Iba*2	*Iba*2	*Iba*2	*Iba*2	*Iba*2	*Iba*2	*Iba*2	*Iba*2
a / Å	47.1720(8)	47.3677(3)	47.5920(11)	47.3077(4)	17.26240(10)	17.0266(2)	47.3291(14)	17.0356(5)
b / Å	17.2138(4)	17.29520(10)	17.2469(4)	17.1468(2)	47.8338(4)	47.1777(5)	16.9949(5)	47.4052(16)
c / Å	11.23970(10)	11.31890(10)	11.4052(2)	11.34970(10)	11.47730(10)	11.35380(10)	11.4233(3)	11.4193(4)
V / $Å^3$	9126.7(3)	9272.83(11)	9361.6(3)	9206.60(16)	9477.11(13)	9120.24(17)	9188.4(5)	9222.0(5)
Z	8	8	8	8	8	8	8	8
ρ_{calc} / g cm^{-3}	1.651	1.629	1.629	1.661	1.624	1.694	1.688	1.456
μ / mm^{-1}	0.627	0.655	2.877	0.742	0.789	0.846	3.698	2.574
F(000)	4476	4492	4508	4524	4540	4556	4572	4108
Temperature / K	100	100	150	100	100	100	150	150
GOF	0.968	1.053	0.982	1.037	1.047	0.941	0.980	1.050
$R_1[I>2\sigma(I)]$	0.0493	0.0255	0.0271	0.0433	0.0493	0.0487	0.0480	0.0671
$wR_2[I>2\sigma(I)]$	0.1386	0.0759	0.0995	0.1118	0.1316	0.1240	0.1259	0.1910
CCDC number	2169870	2169871	2169872	2169873	2169874	2169875	2169876	2169877

S6. Cluster analysis

The cluster analysis results were verified by the authors. The classification produced by the automated analysis was consistent with the intuition of the researchers, except for three data points among the 132 patterns. Specifically, experiment numbers YU344–1 and YU344–7 were changed from cluster 2 to cluster 8, and experiment number YU345–16 was changed from cluster 2 to cluster 1.

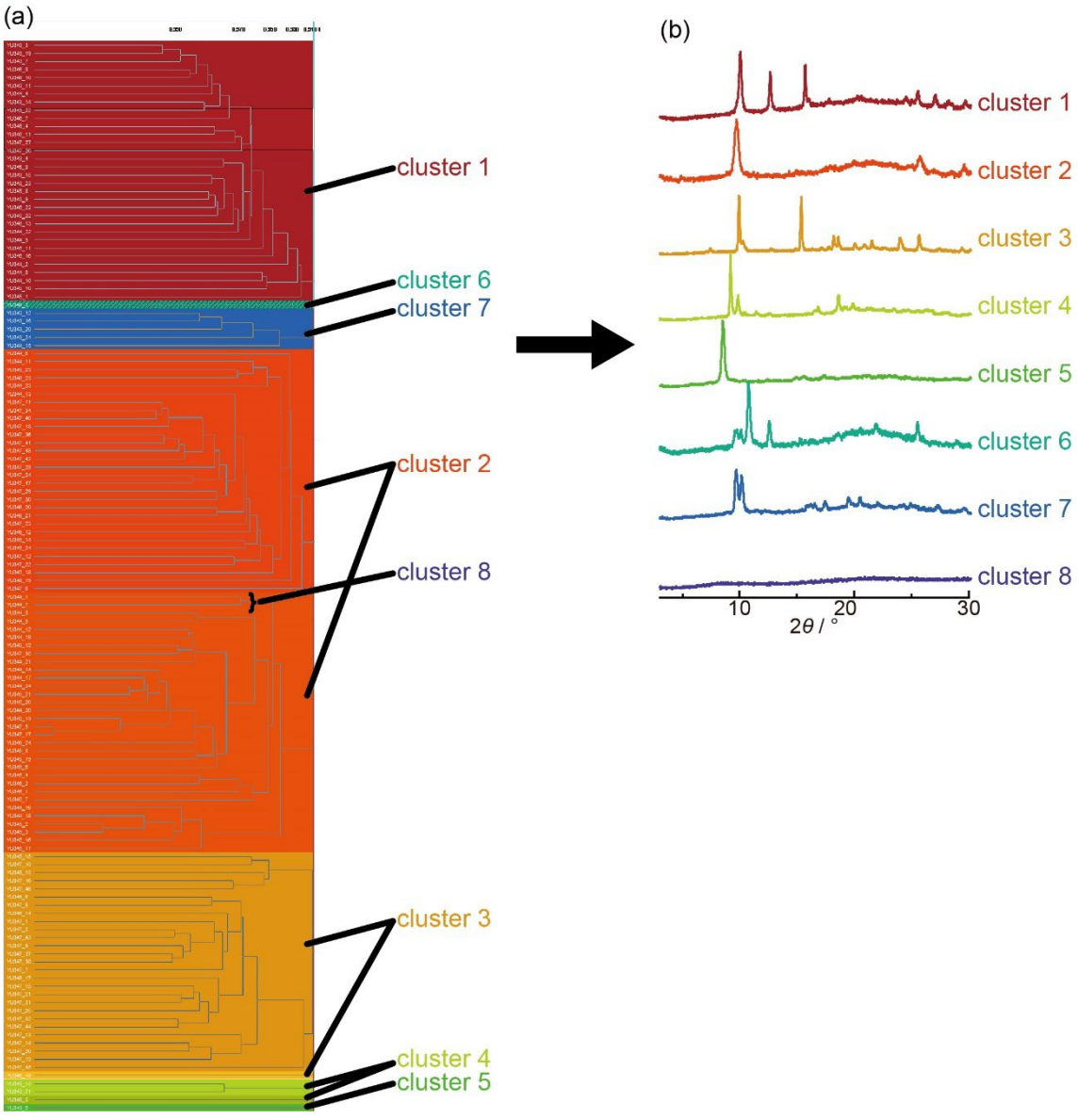
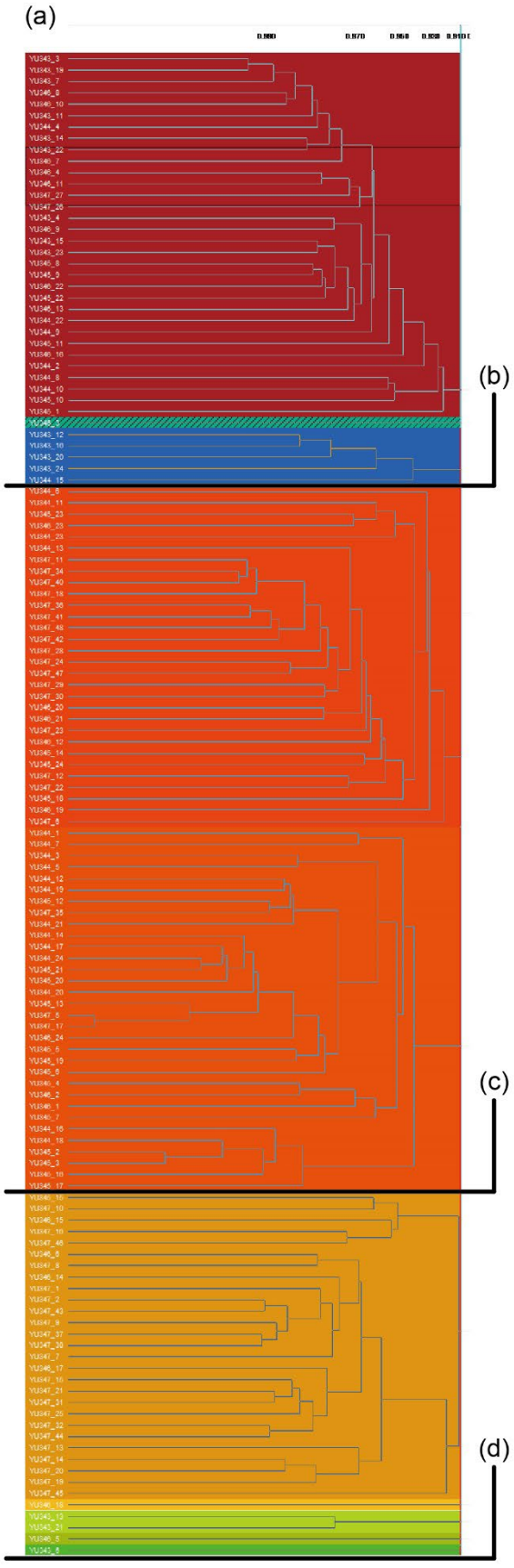
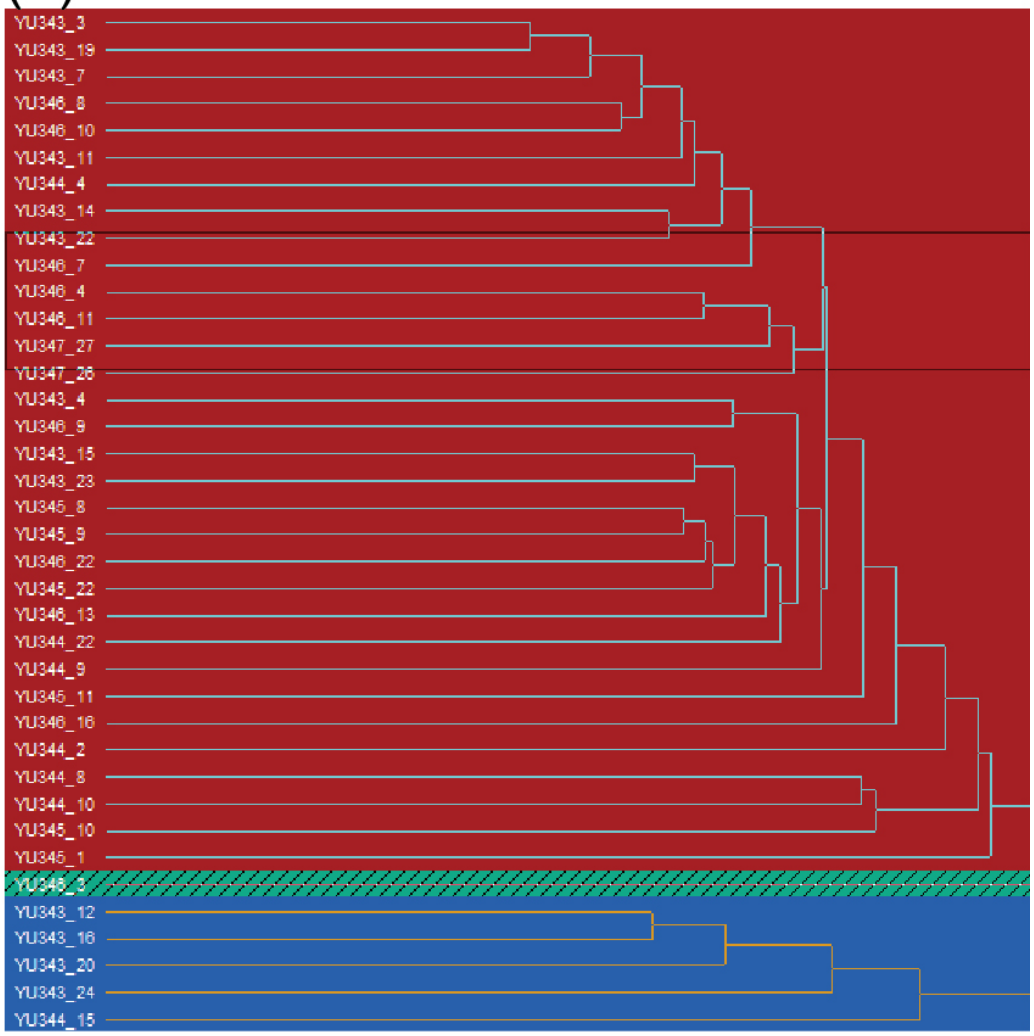


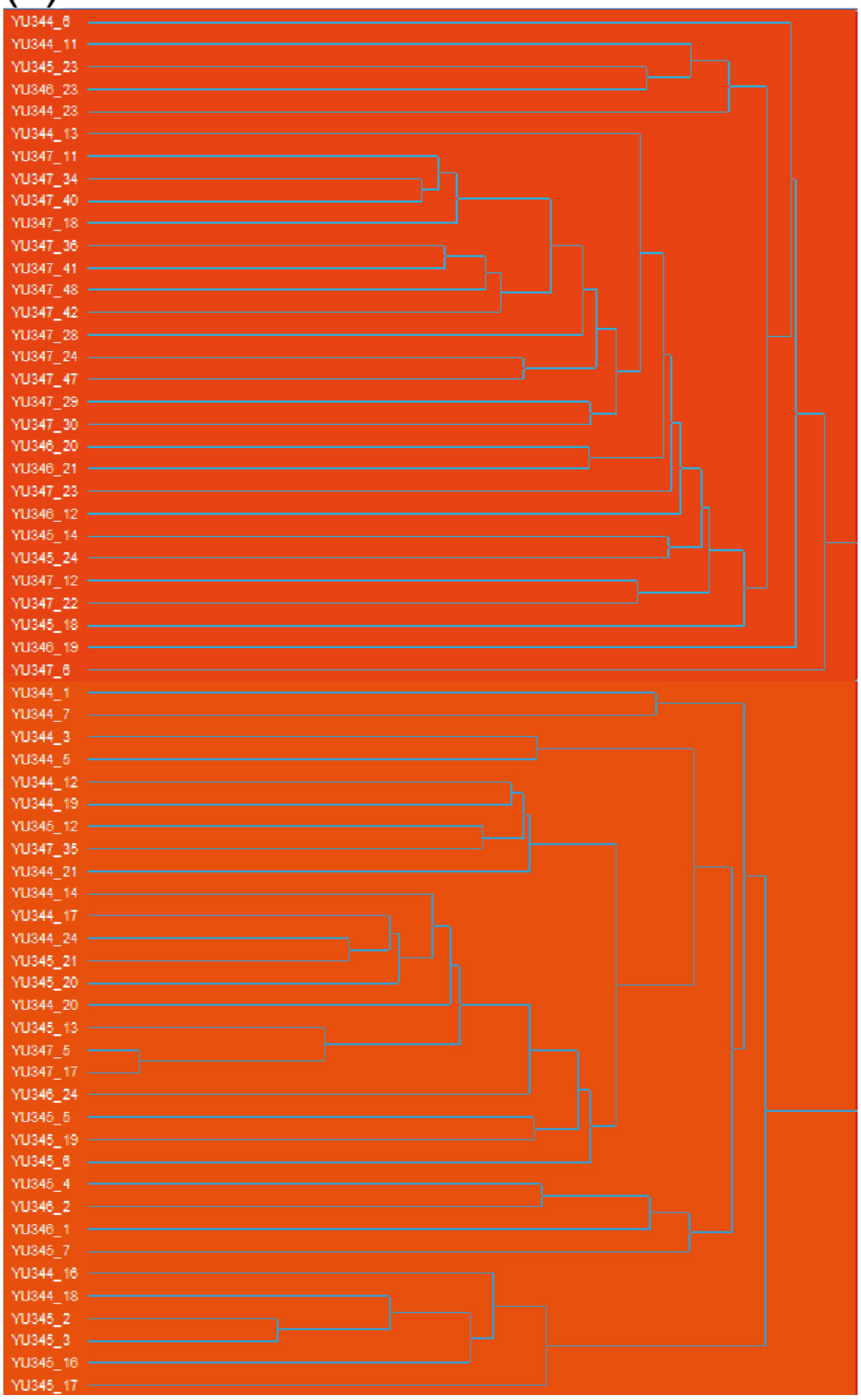
Fig. S2. Cluster analysis results. (a) Cluster analysis by PDXL (Rigaku). (b) PXRD patterns assigned according to the PDXL analysis.


(a)
(b)
(c)
(d)

(b)


YU343_3
YU343_19
YU343_7
YU346_8
YU346_10
YU343_11
YU344_4
YU343_14
YU343_22
YU346_7
YU346_4
YU346_11
YU347_27
YU347_26
YU343_4
YU346_9
YU343_15
YU343_23
YU345_8
YU345_9
YU346_22
YU345_22
YU346_13
YU344_22
YU344_9
YU345_11
YU346_16
YU344_2
YU344_8
YU344_10
YU345_10
YU345_1
YU345_3
YU343_12
YU343_16
YU343_20
YU343_24
YU344_15

(c)


YU344_8
YU344_11
YU345_23
YU346_23
YU344_23
YU344_13
YU347_11
YU347_34
YU347_40
YU347_18
YU347_36
YU347_41
YU347_48
YU347_42
YU347_28
YU347_24
YU347_47
YU347_29
YU347_30
YU346_20
YU346_21
YU347_23
YU346_12
YU345_14
YU345_24
YU347_12
YU347_22
YU345_18
YU346_19
YU347_6
YU344_1
YU344_7
YU344_3
YU344_5
YU344_12
YU344_19
YU345_12
YU347_35
YU344_21
YU344_14
YU344_17
YU344_24
YU345_21
YU345_20
YU344_20
YU345_13
YU347_5
YU347_17
YU346_24
YU345_5
YU345_19
YU345_8
YU345_4
YU346_2
YU346_1
YU345_7
YU344_16
YU344_18
YU345_2
YU345_3
YU345_16
YU345_17

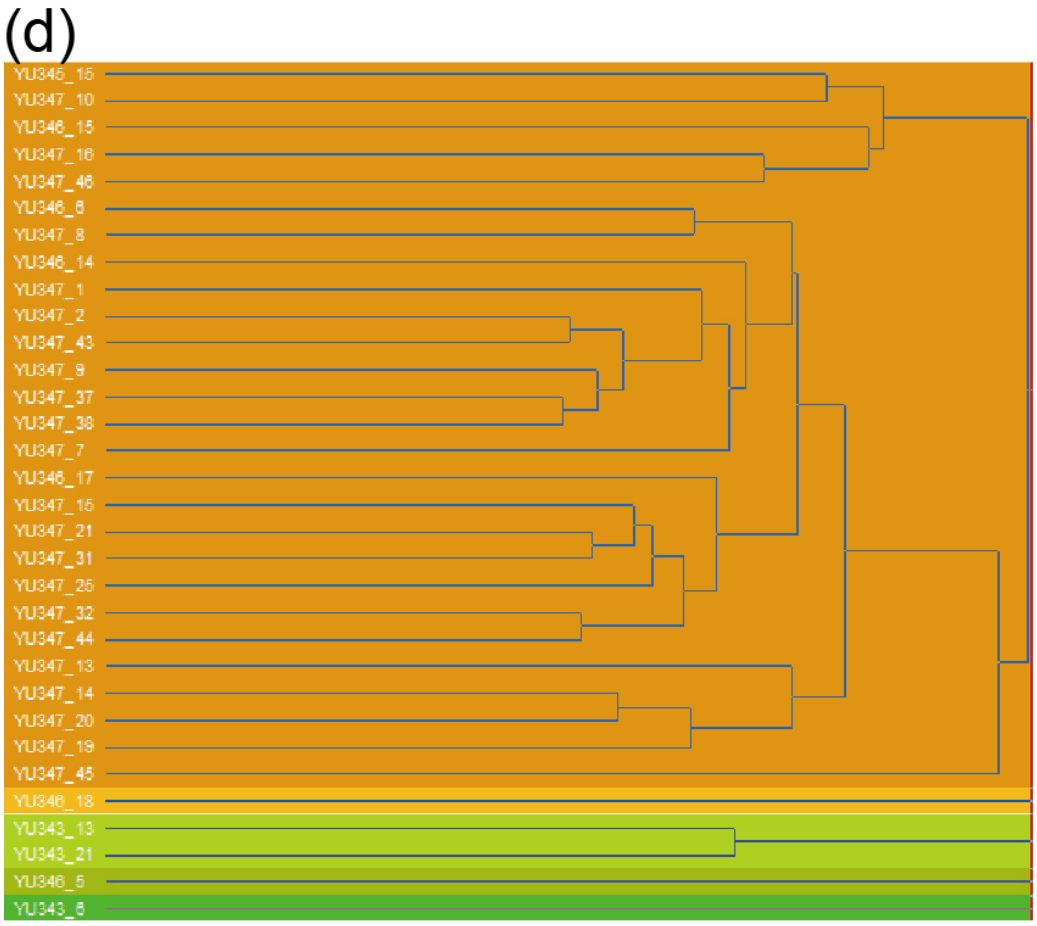


Fig. S3. Custer analysis results for 132 PXRD patterns. (a) Entirety of the cluster analysis results and (b–e) corresponding subparts.

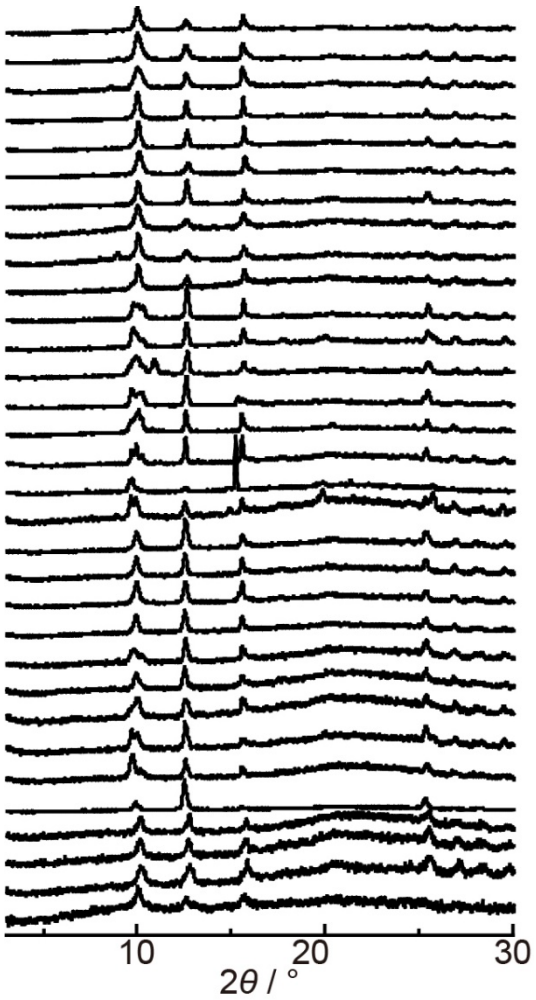


Fig. S4. PXRD patterns classified as cluster 1.

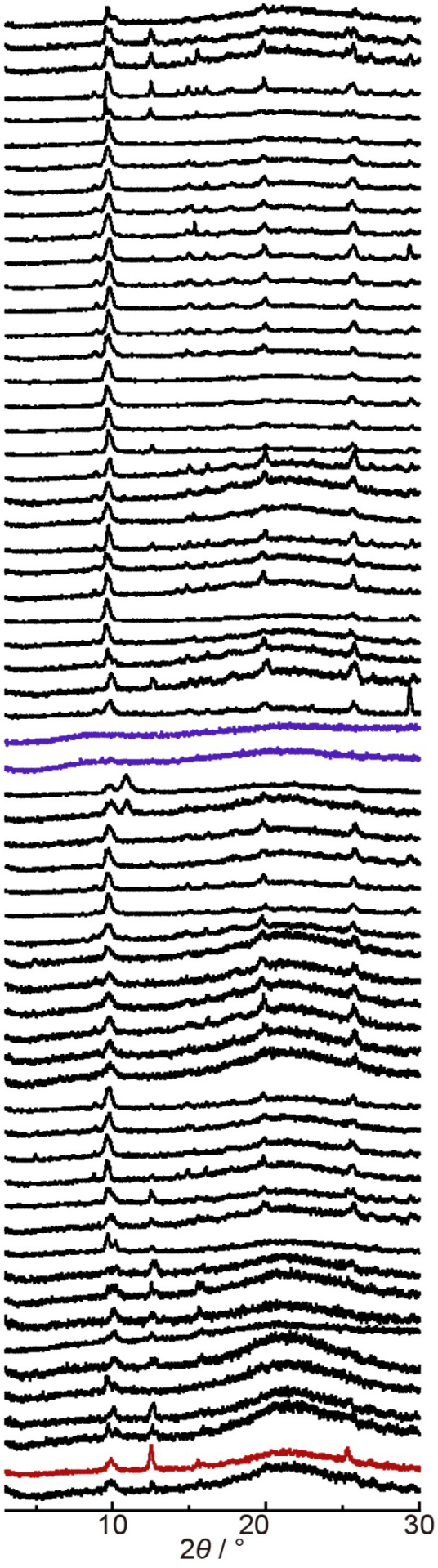

10
20
30
2θ / °

Fig. S5. PXRD patterns classified as cluster 2. The purple patterns were changed from cluster 2 to cluster 8, and the red pattern was changed from cluster 2 to cluster 1 by the researcher (author).

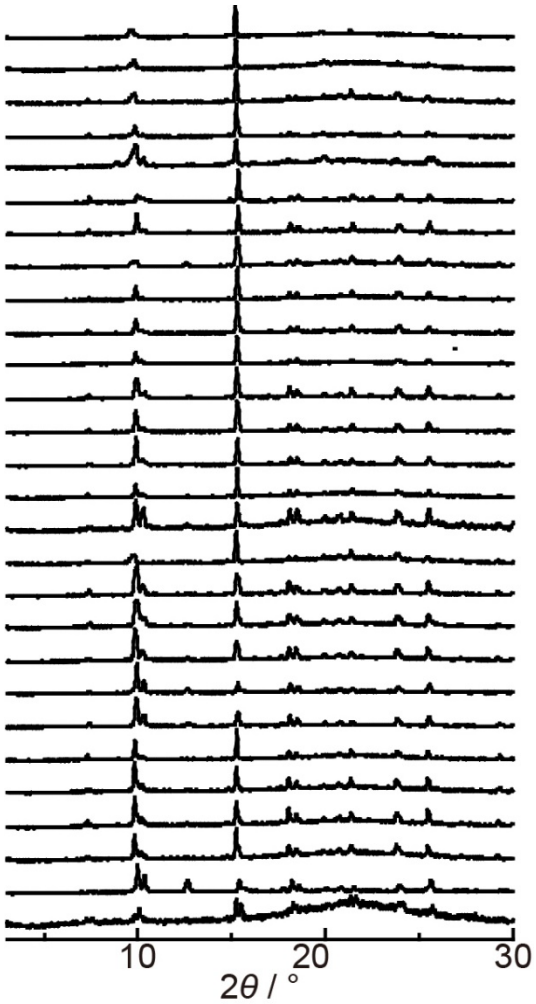


Fig. S6. PXRD patterns classified as cluster 3.

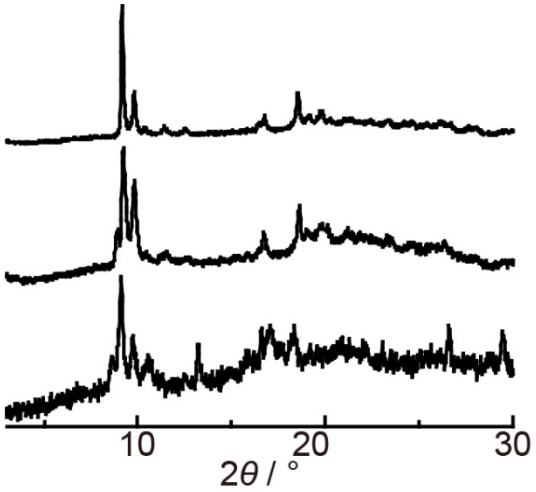


Fig. S7. PXRD patterns classified as cluster 4.

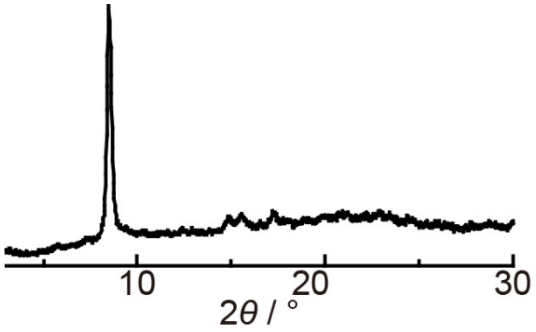


Fig. S8. PXRD patterns classified as cluster 5.

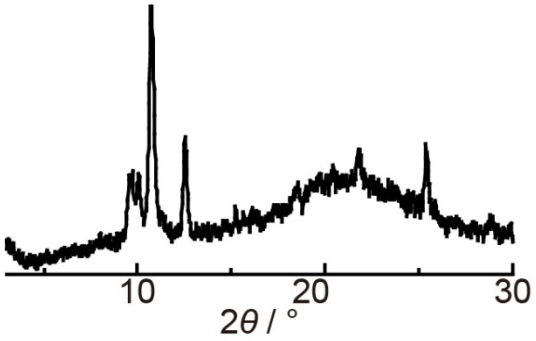


Fig. S9. PXRD patterns classified as cluster 6.

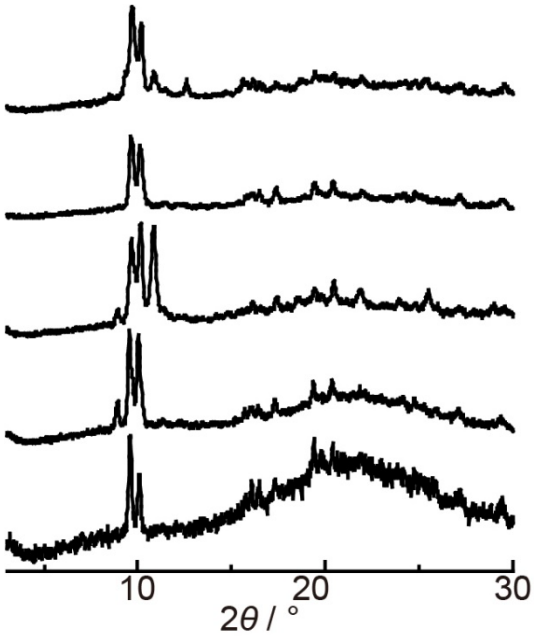


Fig. S10. PXRD patterns classified as cluster 7.

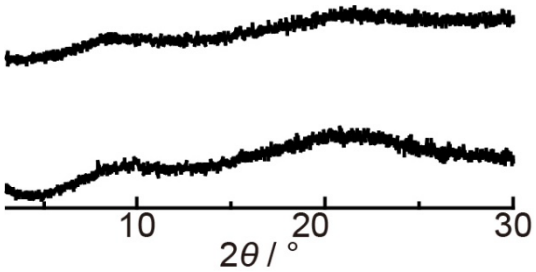


Fig. S11. PXRD patterns classified as cluster 8.

S7. Decision tree analysis

The objective variable (the variable we wished to predict) was obtained by classifying the obtained PXRD patterns using cluster analysis. The detailed chemical descriptors (explanatory variables) for the machine-learning models were the concentrations of the metal solution (3–94 mM) and ligand solution (5–88 mM), metal-to-ligand solution ratio (0.1–29.3), volumes of EtOH (0.25–1.5 mL) and DMF (0.5–1.75 mL), DMF-to-EtOH ratio (0.33–7), amounts of meda (1 drop (40 μL), 60, 200, or 400 μL) and tea (140 or 400 μL), reaction time (48 or 120 h), and reaction temperature (130, 150 or 170 °C). Decision tree analysis was performed on the dataset without any special treatment. Please see the details in the csv file for further information.

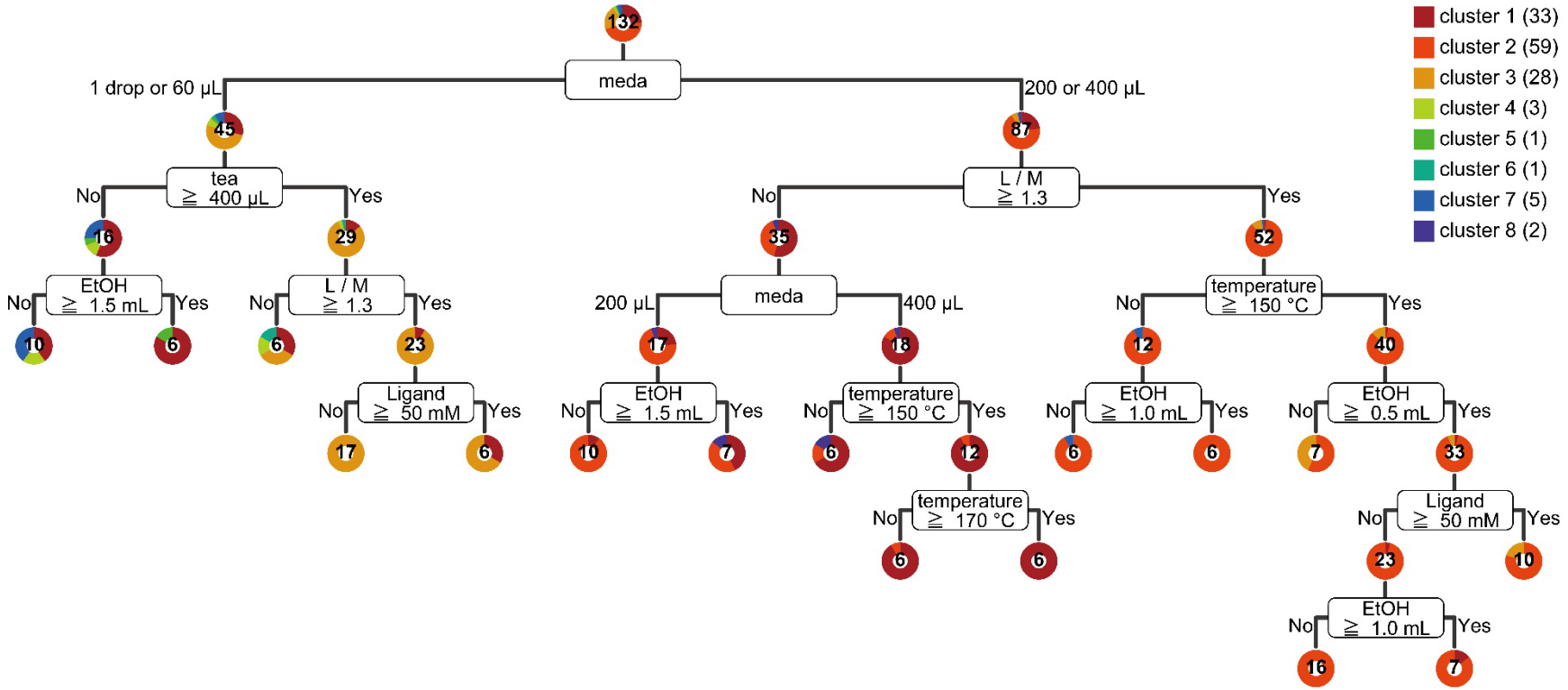


Fig. S12. Overview of the decision tree analysis process. The values in parentheses indicate the number of PXRD patterns. This decision tree is a complete decision tree with no pruning.

S8. Crystal Structure

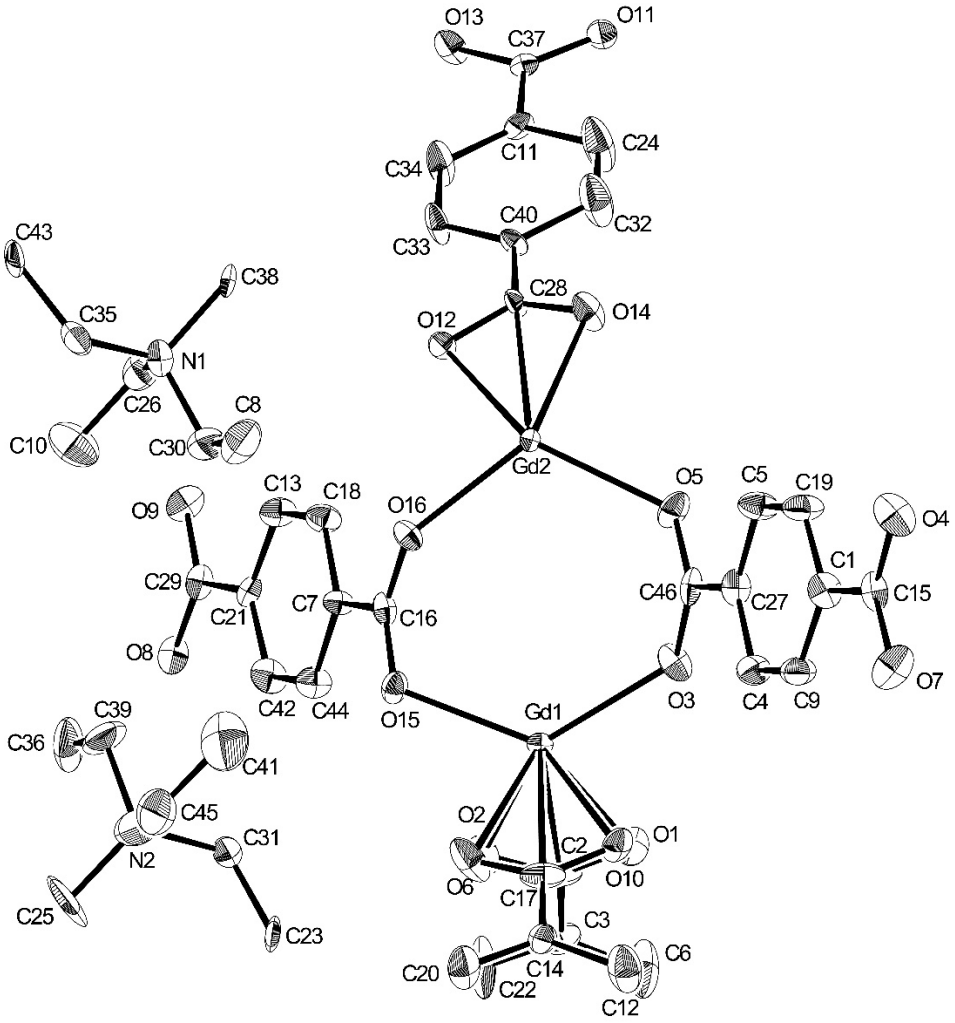


Fig. S13. ORTEP drawing of KGF-15 along the b-axis.

S9. Optimized synthetic conditions using various trivalent lanthanide metal ions

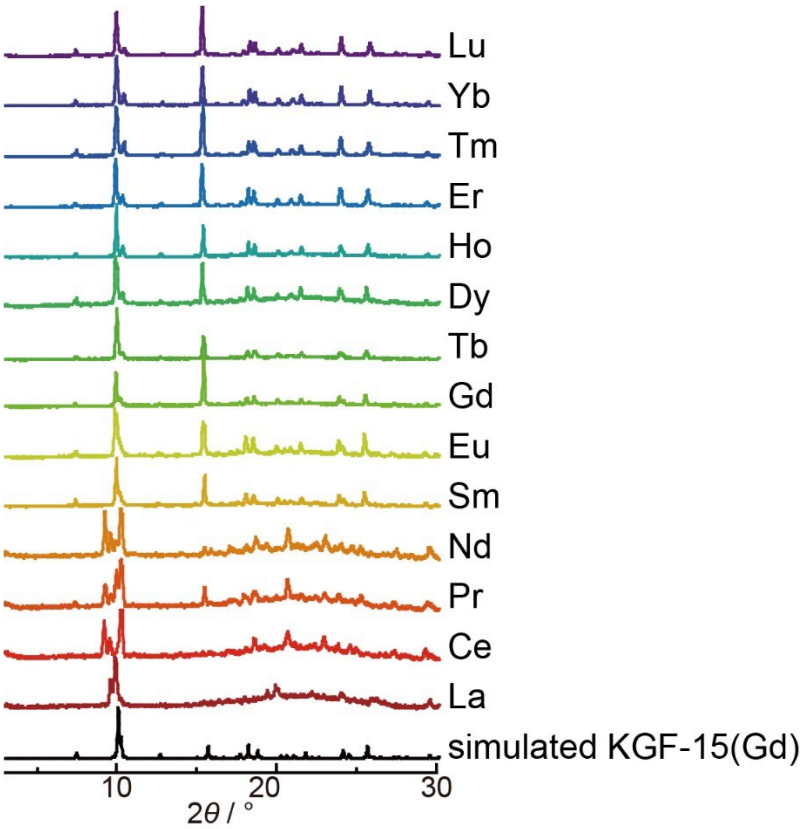


Fig. S14. PXRD patterns acquired under optimized synthetic condition 3.

S10. Elemental analysis

Table S5. Elemental analysis of KGF-15(Ln).

	KGF-15(Ln^{3+})	Synthetic condition	C / %	H / %	N / %	Yield / g	Yield / %
obs.	Sm	5	45.70	4.03	2.26	0.0643	88.7
	Eu	4	45.48	4.23	2.31	0.1651	86.7
	Gd	4	45.18	4.05	2.33	0.1758	93.8
	Tb	4	45.01	4.12	2.26	0.1810	98.4
	Dy	4	44.75	4.15	2.38	0.1368	73.4
	Ho	4	44.47	4.06	2.27	0.0772	86.0
	Er	4	44.20	3.94	2.39	0.0070	90.0
	Tm	6	45.04	4.32	2.22	0.0636	84.7
	Yb	6	45.77	4.21	2.33	0.0674	76.4
	Lu	4	44.71	4.11	2.25	0.1587	87.5
calc. $[NH(C_2H_5)_3]_2 \cdot Ln_2(BDC)_4$	Sm		45.50	4.17	2.41		
	Eu		45.37	4.15	2.41		
	Gd		44.96	4.12	2.38		
	Tb		44.83	4.10	2.38		
	Dy		44.56	4.08	2.36		
	Ho		44.38	4.06	2.27		
	Er		44.21	4.05	2.34		
	Tm		44.09	4.04	2.34		
	Yb		43.79	4.01	2.32		
	Lu		43.65	4.00	2.31		

S11. Stability Evaluation

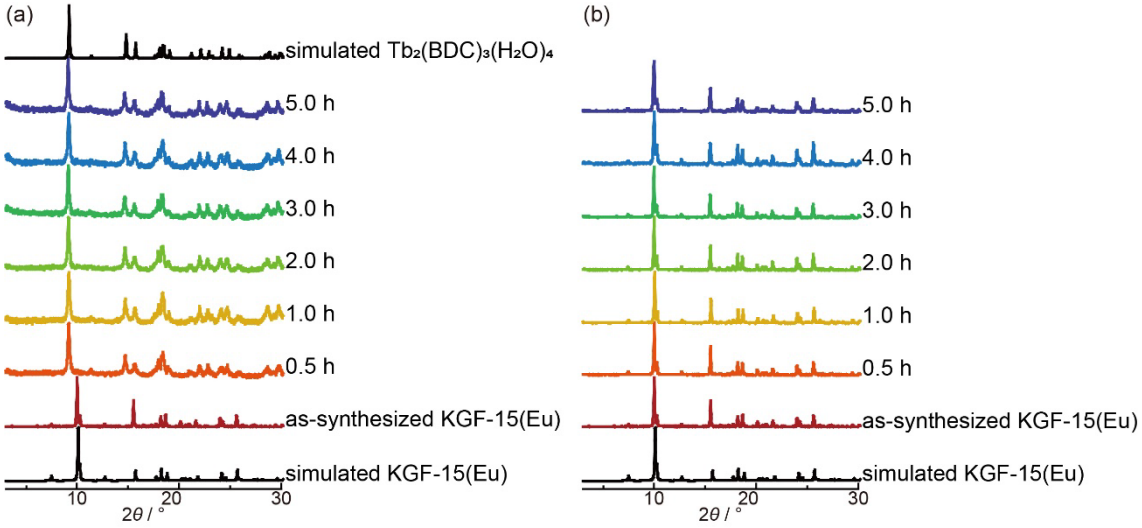


Fig. S15. Stability evaluation of KGF-15 in various solvents. (a) PXRD patterns of KGF-15 soaked in H_2O and simulated patterns of single crystal structures. The patterns for $Tb_2(BDC)_3(H_2O)_4$ were simulated from the reported crystal structures.[15] (b) PXRD patterns of KGF-15 soaked in MeOH.

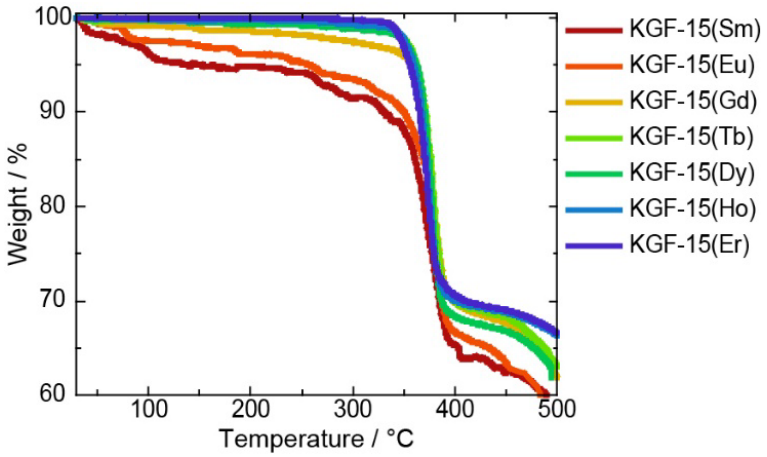


Fig. S16. TG curves of KGF-15(Ln).

S12. Sensing of metal cations

The sensing ability of KGF-15(Eu) for metal cations (K^+, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) was investigated. Elemental analysis after soaking in the Cu^{2+} solution revealed a decrease in the nitrogen content, indicating that partial Cu^{2+} substitution occurred. In addition, the SEM-EDX results suggest that Cu^{2+} may be adsorbed on the MOF surface.

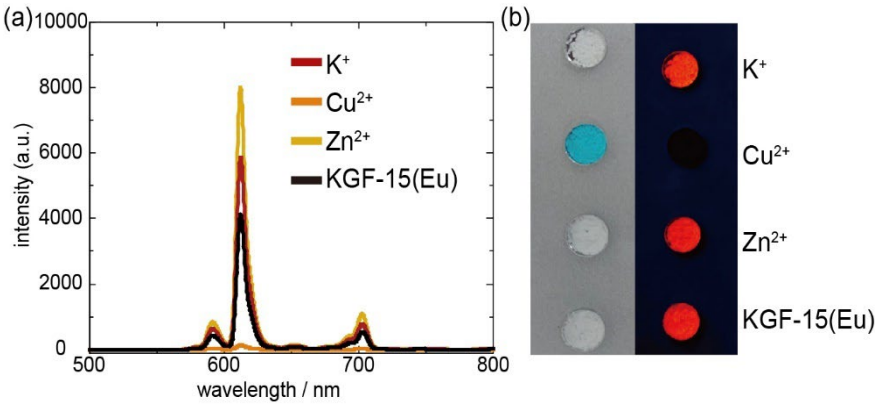


Fig. S17. (a) Emission spectra of KGF-15(Eu) in the presence of different cations. The excitation wavelength was 300 nm. (b) Digital photographs of KGF-15(Eu) in the presence of different metal cations.

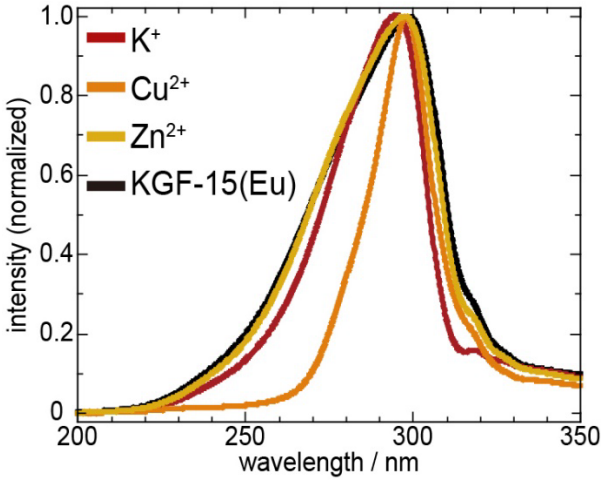


Fig. S18. Solid-state excitation spectra of KGF-15(Eu) after soaking in solutions of different metal cations. The emission wavelength was 612 nm.

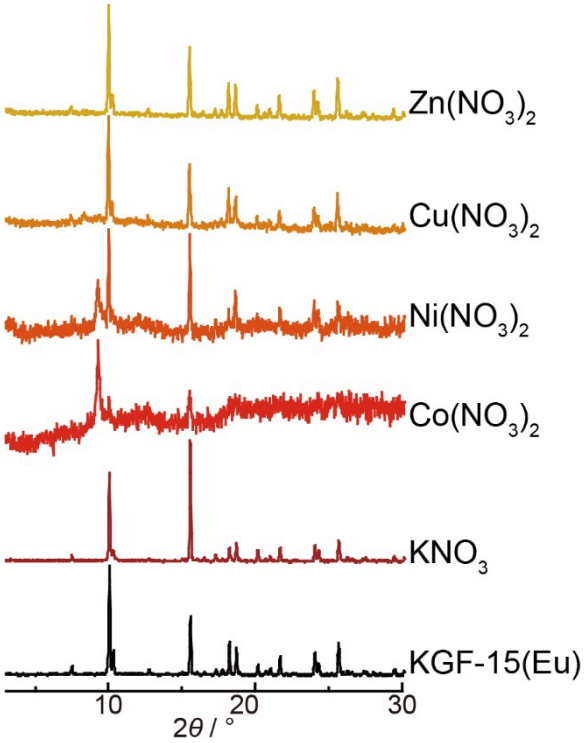


Fig. S19. PXRD patterns of KGF-15(Eu) after soaking in solutions of different metal cations.

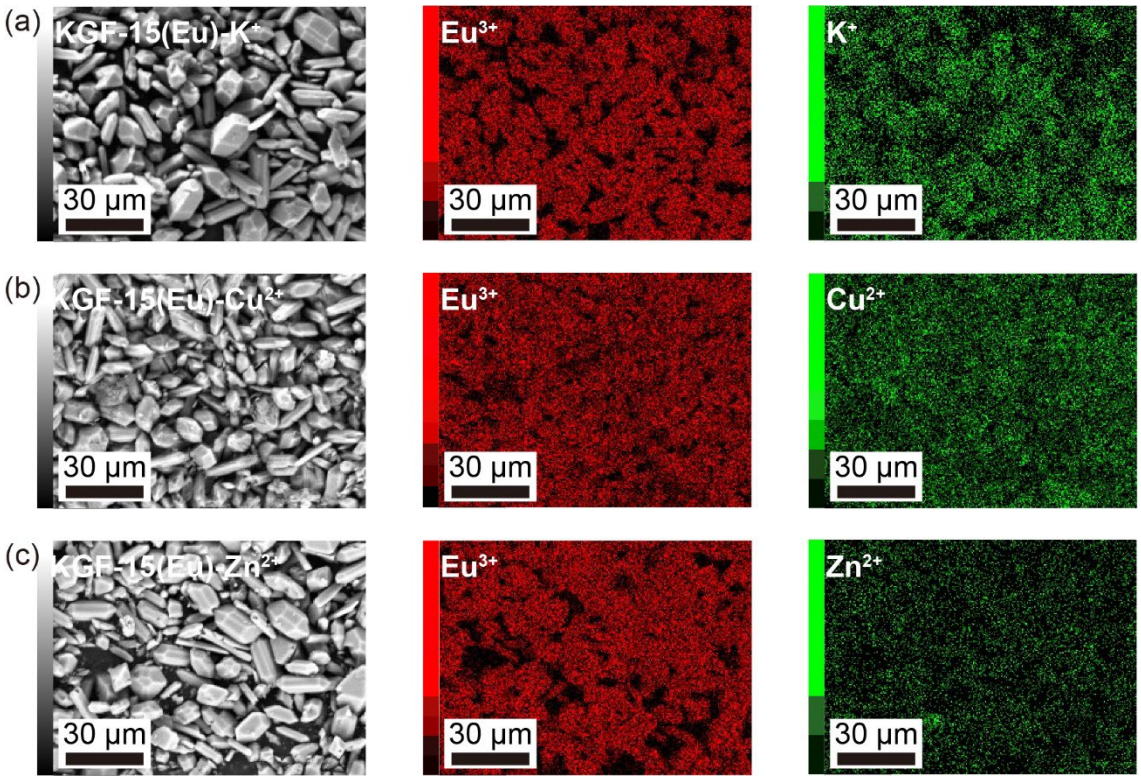


Fig. S20. SEM-EDS elemental mapping images of KGF-15(Eu) after soaking in solutions of various metal cations: (a) K^+, (b) Cu^{2+}, and (c) Zn^{2+}

Table S6. Metal content ratios of KGF-15(Eu) after cation sensing

KGF-15(Eu)-cation	Content ratio	
	Eu^{3+}	Cation
KGF-15(Eu)-K^+	99	1
KGF-15(Eu)-Cu^{2+}	51	49
KGF-15(Eu)-Zn^{2+}	93	7

Table S7. Elemental analysis of KGF-15(Eu) after cation sensing

	Cation	C / %	H / %	N / %
obs.	K^+	45.33	4.21	2.42
	Cu^{2+}	42.41	3.39	1.71
	Zn^{2+}	45.46	4.14	2.68
calc.	$[NH(C_2H_5)_3]_2 \cdot Eu_2(BDC)_4$	45.37	4.15	2.41
	$Cu \cdot Eu_2(BDC)_4$	37.54	1.58	0.00

References

1. G. Barr, W. Dong, C. Gilmore and J. Faber, *J Appl Crystallogr*, 2004, **37**, 635-642.
2. W.-Z. Zhang, *Acta Crystallogr. Sect. E: Struct. Rep. Online*, 2006, **62**, m1600–m1602.
3. Y. Han, X. Li, L. Li, C. Ma, Z. Shen, Y. Song and X. You, *Inorg. Chem.*, 2010, **49**, 10781–10787.
4. Q. Lei, Q.-Y. Liu, Y.-L. Wang, L.-L. Chen and S.-G. Yin, *Chin. J. Struct. Chem.*, 2016, **35**, 566–576.
5. H. He, D. Yuan, H. Ma, D. Sun, G. Zhang and H. C. Zhou, *Inorg. Chem.*, 2010, **49**, 7605–7607.
6. H. He, H. Ma, D. Sun, L. Zhang, R. Wang and D. Sun, *Cryst. Growth Des.*, 2013, **13**, 3154–3161.
7. Z.-H. Zhang, S.-Y. Wan, T.-a. Okamura, W.-Y. Sun and N. Ueyama, *Z. Anorg. Allg. Chem.*, 2006, **632**, 679–683.
8. H.-J. Zhang, R.-Q. Fan, P. Wang, X.-M. Wang, W. Chen, X.-B. Zheng, K. Li and Y.-L. Yang, *J. Inorg. Organomet. Polym. Mater.*, 2014, **24**, 624–632.
9. M. I. Breeze, T. W. Chamberlain, G. J. Clarkson, R. P. de Camargo, Y. Wu, J. F. de Lima, F. Millange, O. A. Serra, D. O'Hare and R. I. Walton, *CrystEngComm*, 2017, **19**, 2424–2433.
10. D. L. Burnett, R. Oozeerally, R. Pertiwi, T. W. Chamberlain, N. Cherkasov, G. J. Clarkson, Y. K. Krisnandi, V. Degirmenci and R. I. Walton, *Chem. Commun.*, 2019, **55**, 11446–11449.
11. B. Chen, Y. Yang, F. Zapata, G. Qian, Y. Luo, J. Zhang and E. B. Lobkovsky, *Inorg. Chem.*, 2006, **45**, 8882–8886.
12. F. Le Natur, G. Calvez, S. Freslon, C. Daiguebonne, K. Bernot and O. Guillou, *J. Mol. Struct.*, 2015, **1086**, 34–42.
13. R. A. Zehnder, R. A. Renn, E. Pippin, M. Zeller, K. A. Wheeler, J. A. Carr, N. Fontaine and N. C. McMullen, *J. Mol. Struct.*, 2011, **985**, 109–119.
14. M. Zhu, W. Fu and G. Zou, *J. Coord. Chem.*, 2012, **65**, 4108–4114.
15. T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1999, **121**, 1651–1657.
16. C. Daiguebonne, N. Kerbellec, O. Guillou, J. C. Bünzli, F. Gumy, L. Catala, T. Mallah, N. Audebrand, Y. Gérault, K. Bernot and G. Calvez, *Inorg. Chem.*, 2008, **47**, 3700–3708.

17. V. Haquin, F. Gumy, C. Daiguebonne, J. C. Bünzli and O. Guillou, *Eur. J. Inorg. Chem.*, 2009, DOI: 10.1002/ejic.200900549, 4491–4497.
18. N. Kerbellec, D. Kustaryono, V. Haquin, M. Etienne, C. Daiguebonne and O. Guillou, *Inorg. Chem.*, 2009, **48**, 2837–2843.
19. A. Cadiau, C. D. S. Brites, P. M. F. J. Costa, R. A. S. Ferreira, J. Rocha and L. D. Carlos, *ACS Nano*, 2013, **7**, 7213–7218.
20. V. Haquin, M. Etienne, C. Daiguebonne, S. Freslon, G. Calvez, K. Bernot, L. Le Pollès, S. E. Ashbrook, M. R. Mitchell, J. C. Bünzli, S. V. Eliseeva and O. Guillou, *Eur. J. Inorg. Chem.*, 2013, **2013**, 3464-3476.
21. A. Y. Grishko, V. V. Utochnikova, A. A. Averin, A. V. Mironov and N. P. Kuzmina, *Eur. J. Inorg. Chem.*, 2015, DOI: 10.1002/ejic.201403071, 1660–1664.
22. D. Aulakh, J. R. Varghese and M. Wriedt, *Inorg. Chem.*, 2015, **54**, 8679–8684.
23. L. Liao, C. W. Ingram, D. Vandeveer, K. Hardcastle, K. M. Solntsev, D. Sabo, Z. J. Zhang and R. T. Weber, *Inorg. Chim. Acta*, 2012, **391**, 1–9.
24. T. M. Reineke, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Angew. Chem. Int. Ed.*, 1999, **38**, 2590–2594.
25. L. Pan, N. Zheng, Y. Wu, S. Han, R. Y. Yang, X. Huang and J. Li, *Inorg. Chem.*, 2001, **40**, 828–830.
26. J. Zhang, J. Li, Z. G. Sun, Y. Zhao, Y. Y. Zhu, N. Zhang, L. Liu and X. Lu, *Z. Anorg. Allg. Chem.*, 2008, **634**, 2629–2633.
27. C. Serre, F. Millange, J. Marrot and G. Férey, *Chem. Mater.*, 2002, **14**, 2409–2415.
28. S.-L. Xie, B.-Q. Xie, X.-Y. Tang, N. Wang and S.-T. Yue, *Z. Anorg. Allg. Chem.*, 2008, **634**, 842–844.
29. S. Feng, *Acta Crystallogr. Sect. E: Struct. Rep. Online*, 2010, **66**, m33.
30. A. Deluzet, W. Maudez, C. Daiguebonne and O. Guillou, *Cryst. Growth Des.*, 2003, **3**, 475–479.
31. C. Daiguebonne, N. Kerbellec, K. Bernot, Y. Gérault, A. Deluzet and O. Guillou, *Inorg. Chem.*, 2006, **45**, 5399–5406.
32. J.-c. Yao, X.-x. Cao, L. Zhang, Y.-f. Wang, J.-b. Guo and C.-p. Fan, *J. Chem. Crystallogr.*, 2011, **41**, 1400–1405.
33. L. Na, R. Hua, L. Zhang, W. Zhang and G. Ning, *J. Chem. Crystallogr.*, 2009, **39**, 688–691.
34. D. Weng, X. Zheng and L. Jin, *Eur. J. Inorg. Chem.*, 2006, **2006**, 4184–4190.

35. X. P. Yang, R. A. Jones, J. H. Rivers and P.-j. Lai, *Dalton Trans.*, 2007, DOI: 10.1039/b706823a, 3936–3942.
36. L.-Q. Yu, R.-D. Huang, Y.-Q. Xu, T.-F. Liu, W. Chu and C.-W. Hu, *Inorg. Chim. Acta*, 2008, **361**, 2115–2122.
37. Y. Wu, M. I. Breeze, G. J. Clarkson, F. Millange, D. O'Hare and R. I. Walton, *Angew. Chem. Int. Ed.*, 2016, **55**, 4992–4996.
38. Y. Zhang, J. Yang, G.-D. Li, F. Zhang and J.-S. Chen, *J. Coord. Chem.*, 2008, **61**, 945–955.
39. J.-J. Wang, Y. Chen, M.-J. Liu, R.-Y. Fan, P.-P. Si, J. Yang, Y.-Y. Pan, Y. Chen, S.-S. Zhao and J. Xu, *Polyhedron*, 2018, **154**, 411–419.
40. R. Decadt, K. Van Hecke, D. Depla, K. Leus, D. Weinberger, I. Van Driessche, P. Van Der Voort and R. Van Deun, *Inorg. Chem.*, 2012, **51**, 11623–11634.
41. H. F. Clausen, J. Overgaard, R. D. Poulsen, W. Morgenroth and B. B. Iversen, *Acta Crystallogr. Sect. E: Struct. Rep. Online*, 2006, **62**, m3333–m3335.
42. R. D. Poulsen, J. Overgaard, M. A. Chevallier, H. F. Clausen and B. B. Iversen, *Acta Crystallogr. Sect. E: Struct. Rep. Online*, 2005, **61**, m1337–m1339.
43. A. Abbasi, F. Mohammadnezhad and S. Geranmayeh, *J. Inorg. Organomet. Polym. Mater.*, 2014, **24**, 1021–1026.
44. Z. Min, M. A. Singh-Wilmot, C. L. Cahill, M. Andrews and R. Taylor, *Eur. J. Inorg. Chem.*, 2012, **2012**, 4419–4426.
45. G. Huang, P. Yang, N. Wang, J.-Z. Wu and Y. Yu, *Inorg. Chim. Acta*, 2012, **384**, 333–339.
46. R. Sibille, T. Mazet, B. Malaman and M. Francois, *Chem. Eur. J.*, 2012, **18**, 12970–12973.
47. M. Lammert, M. T. Wharmby, S. Smolders, B. Bueken, A. Lieb, K. A. Lomachenko, D. D. Vos and N. Stock, *Chem. Commun.*, 2015, **51**, 12578–12581.
48. C. Serre, F. Millange, J. Marrot and G. Ferey, *Chem. Mater.*, 2002, **14**, 2409–2415.
49. L. D'Arras, C. Sassoye, L. Rozes, C. Sanchez, J. Marrot, S. Marre and C. Aymonier, *New J. Chem.*, 2014, **38**, 1477–1483.
50. Y. Kitamura, E. Terado, Z. Zhang, H. Yoshikawa, T. Inose, H. Uji-i, M. Tanimizu, A. Inokuchi, Y. Kamakura and D. Tanaka, *Chem. Eur. J.*, 2021, **27**, 16347–16353.