Supporting Information

β-Perhalogenated Porphyrins Enable Sensitive Cryogenic NIR Lanthanide Thermometry

Li-Jun Guo,[‡a] Meng-Xin Wang,[‡a], Zhe-Ming Wang[a] and Jun-Long Zhang[*a]

[a] *Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China.*

[‡] *These authors contributed equally to this work.*

** Correspondence to: Jun-long Zhang, e-mail: zhangjunlong@pku.edu.cn;*

Table of Contents

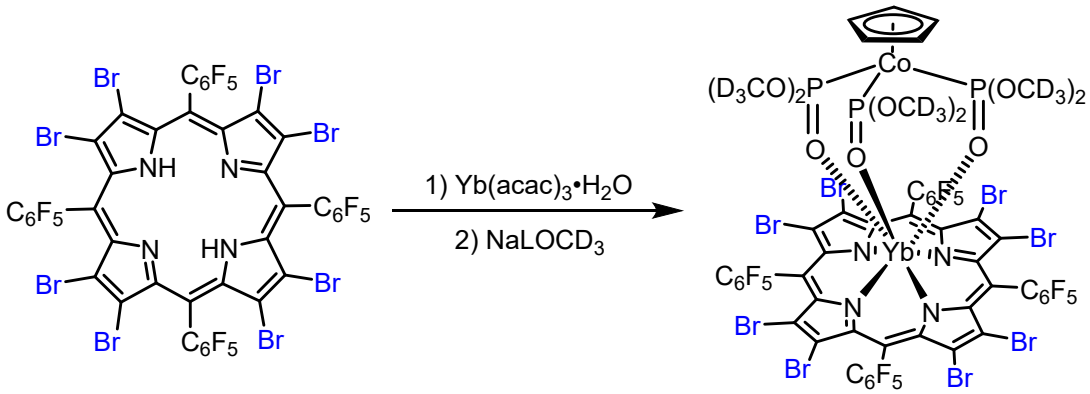
Supporting Methods

Chemicals reagents and instruments

Column chromatography was carried out on silica gel (200-300 mesh, Qingdao Ocean Chemicals) with the indicated eluents. All other reagents and solvents were used as received. The compound **X-1** (X=H, F, Cl, Br) and the complex **X-1-Er** (X=H, F, Cl, Br) was synthesized according to literature methods.[1] ^{1}H and ^{19}F NMR spectra were recorded using a Bruker DPX 400 MHz spectrometer and the chemical shifts were reported relative to internal $SiMe_4$. ESI mass spectra were recorded using a Bruker APEX IV FTICR mass spectrometer. Electronic absorption spectra were recorded using an Agilent 8453 UV/Vis spectrometer. The luminescence emission and fluorescence spectra were recorded using an Edinburgh FLS1000 spectrometer. The singlet crystal data were recorded using a Rigaku XtaLAB PRO 007HF(Mo) Single crystal X-ray diffractometer. The differential scanning calorimetry (DSC) spectra were recorded using PE LN2-DSC8500 DSC8500 Differential Scanning Calorimeter (liquid nitrogen).

Synthesis procedures

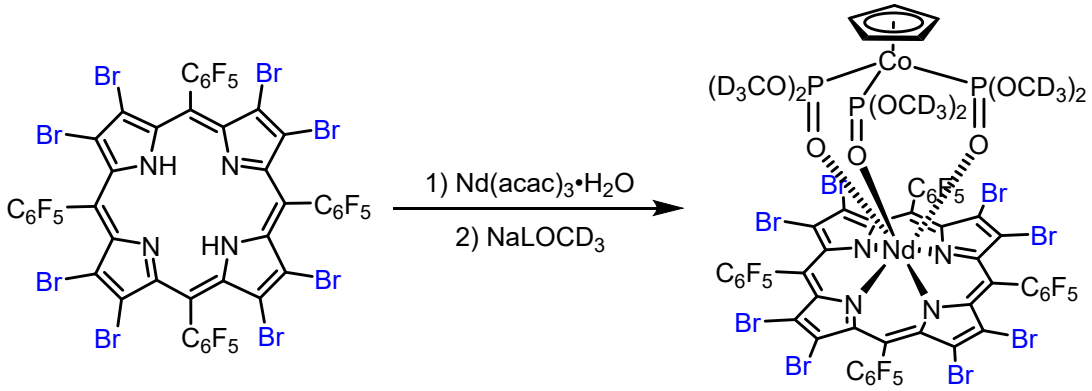
Synthesis of **Br-1**, **H-1-Er**, **F-1-Er**, **Cl-1-Er**, **Br-1-Er**, **H-1-Yb** and **H-1-Nd** were synthesized according to the previously reported literature. [1]



Br-1 **Br-1-Yb**

Synthesis of complex Br-1-Yb：The ligand **Br-1** (0.03 mmol) and $Yb(acac)_3 \cdot nH_2O$ (0.15 mmol) were dissolved in 8 mL of anhydrous 1,2,4-trichlorobenzene (TCB) and refluxed for 2 hours under a nitrogen atmosphere. During

this period, the luminescence of the free ligand gradually diminished. Upon cooling to ambient temperature, silica gel chromatography was performed using sequential elution with petroleum ether, dichloromethane, and a dichloromethane/methanol mixture (v/v = 5/1), yielding TCB, unreacted porphyrin ligand, and ytterbium porphyrin complexes. The ytterbium complex was subsequently reacted with 1.2 equivalents of deuterated Klaui ligand in 10 mL of a chloroform/methanol solution (v/v = 4/1) at room temperature for 24 hours. The resulting product was purified by silica gel column chromatography and recrystallized from a dichloromethane/n-hexane mixture, ultimately affording the target compound Br-1-Yb as a green solid. **Br-1-Yb**: Yield: 87%. ESI-HR-MS: [M+H$^+$] *m/z* calcd. for $C_{55}H_6D_{18}Br_8CoYbF_{20}N_4O_9P_3$: 2239.371886; Found: 2239.374872.



Br-1 **Br-1-Nd**

Synthesis of complex Br-1-Nd：Ligand **Br-1** (0.03 mmol) and Nd(acac)$_3$·nH$_2$O (0.15 mmol) were added to 8 mL of anhydrous 1,2,4-trichlorobenzene (TCB) and refluxed under N_2 for 2 h. During the reaction, the luminescence of the free ligand gradually disappeared. After cooling to room temperature, the mixture was successively eluted with petroleum ether, CH_2Cl_2, and CH_2Cl_2/MeOH (v/v = 5/1), and the TCB, unreacted porphyrin ligand, and neodymium porphyrin complex were obtained through silica gel chromatography. The neodymium complex was reacted with 1.2 equivalents of deuterated Klaui ligand in a 10 mL $CHCl_3$/MeOH (v/v = 4/1) mixed solution at room temperature overnight. Then, the product was separated by silica gel column chromatography and recrystallized from CH_2Cl_2/hexane to obtain the final product as a green solid. **Br-1-Nd**: Yield: 82%. ESI-HR-MS: [M+H$^+$] *m/z* calcd. for

$C_{55}H_6D_{18}Br_8CoNdF_{20}N_4O_9P_3$: 2207.345445; Found: 2207.343734.

Preparation of PMMA Film

Two poly(methyl methacrylate) (PMMA) beads with a diameter of approximately 3 mm were dissolved in 1 mL of dichloromethane to prepare a 10% PMMA dichloromethane solution. A small amount of the sample was then dissolved in the aforementioned solution to achieve a final concentration of 0.1% for the sample. The solution was subsequently dropped onto the surface of a glass slide with a diameter of 1 cm. After allowing the solvent to evaporate at room temperature for 2 hours, the glass slide was placed in a vacuum drying chamber for an additional 2 hours of drying, resulting in a PMMA film with uniformly dispersed sample.

Near infrared emission spectrum and lifetime

The excitation and emission spectra of all complexes were measured by the Edinburgh FLS1000 steady state/transient fluorescence spectrometer. The source of excitation and emission spectrum is 450 W xenon lamp, and the source of lifetime detection is subtle pulse lamp. The detection system includes near infrared photomultiplier tube (R5509 near infrared PMT (500-1700 nm)) and cooling device (C9940-02 Hamamatsu, -80 ℃). During the test, an 850 nm long wave pass filter was added at the transmitting end. An additional variable temperature attachment and control system (Oxford Optistat DN2) is used for variable temperature fluorescence testing. The absorbance of the samples at excitation wavelength is 0.1. Lifetime τ is obtained by fitting a single exponential decay function.

Calculation of relative thermal sensitivity Sr

The temperature measurement parameter Δ (T) used in this section is the ratio between the intensity of a single band and the intensity of two transmitting bands, and the relative thermal sensitivity Sr is calculated by the Equation 1:

$$S_r(T) = \frac{1}{\Delta(T)}\left|\frac{\partial\Delta}{\partial T}\right| \qquad \text{Equation 1}$$

Singlet oxygen ($^1O_2$) test of Br-1-Nd

Singlet oxygen fluorescence probe (SOSG, 10 μM) was used at different time points in water /DMF= 1:1 solution under irradiation of 460 nm (10 mW/cm^2).

Dielectric permittivity measurements

The temperature-dependent ac (alternate current) dielectric permittivity measurements were performed on a TH2828 Precision LCR meter against capacitors made of powder samples. The samples were ground, and pressed into tablets under the pressure of 1.3 GPa. The capacitors were made by painting the two faces of tablet pieces with silver conducting paste and copper wires as the electrodes. These capacitors were kept vacuum-dried over silica gel more than ten days and finally coated by AB glue before dielectric measurements, in order to avoid the influence of moisture. The area and thickness of the capacitors were measured under a microscope with a Phenix CCD eye and the software. The dielectric permittivity measurements were performed on cooling-warming cycle under dried N_2 flow, with the applied voltage of 1.0 V and the temperature sweeping rates of ca.2 Kmin^{-1} using a home-made temperature control system.

Supporting figures and tables

^{19}F NMR

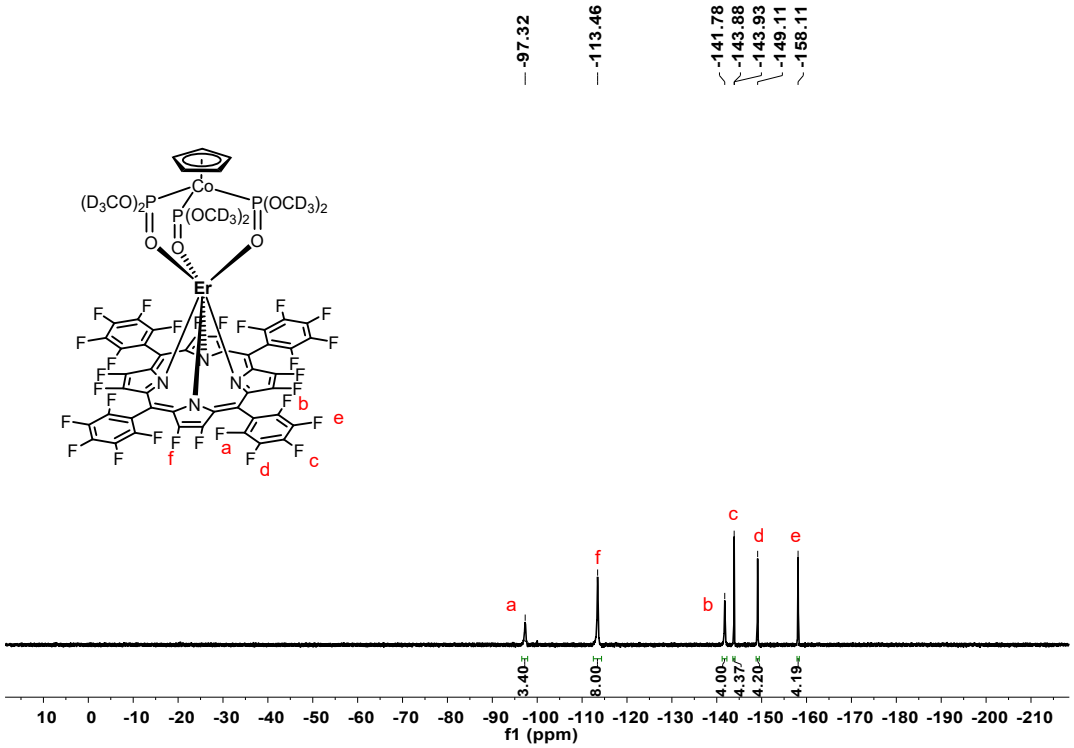


Figure S1 ^{19}F NMR spectrum of **F-1-Er** (471 MHz, $CDCl_3$).

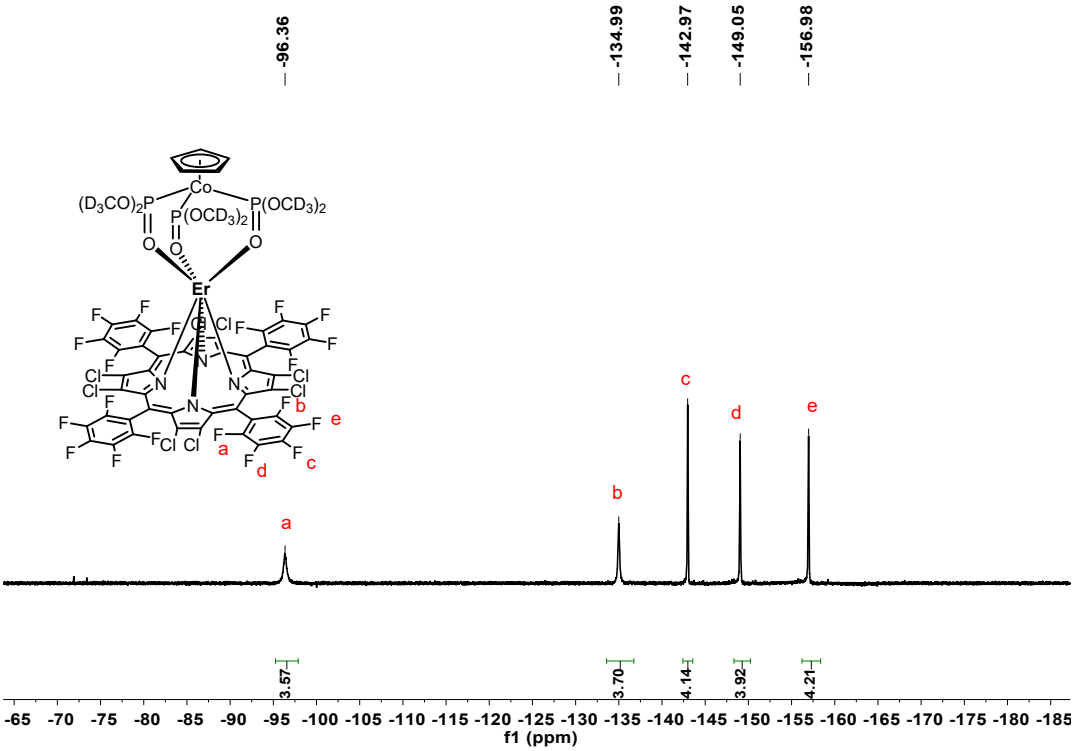


Figure S2 ^{19}F NMR spectrum of **Cl -1-Er** (471 MHz, $CDCl_3$).

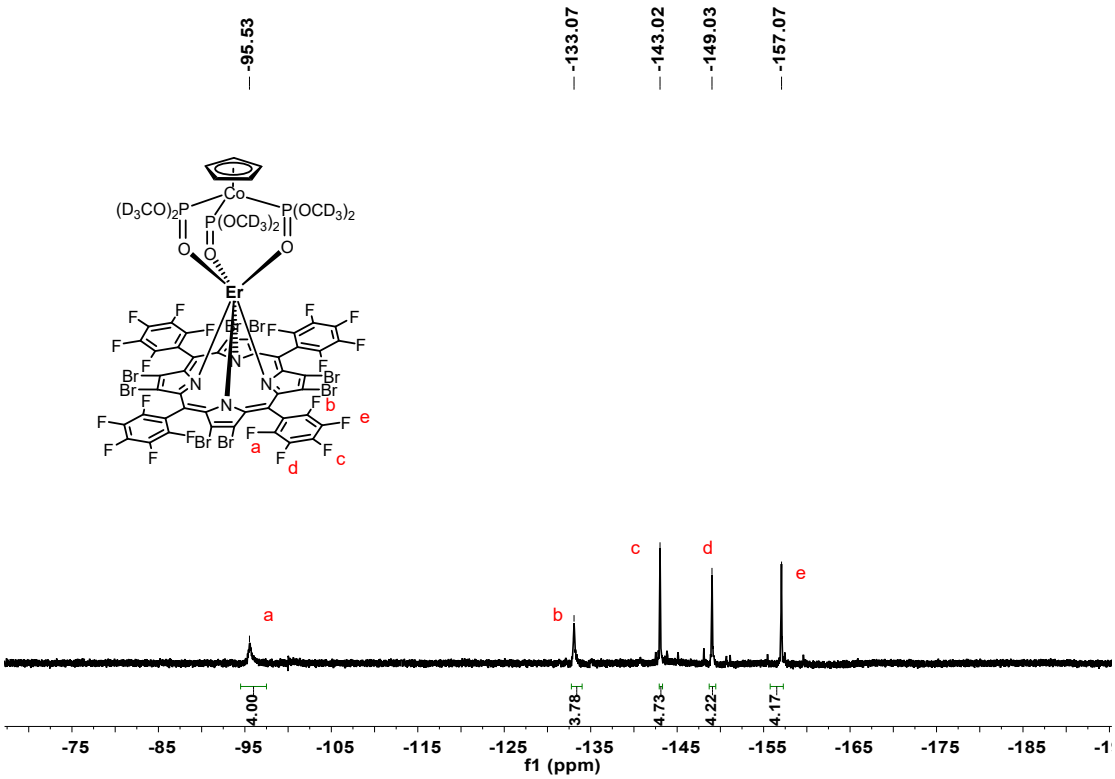


Figure S3 ^{19}F NMR spectrum of **Br-1-Er** (471 MHz, $CDCl_3$).

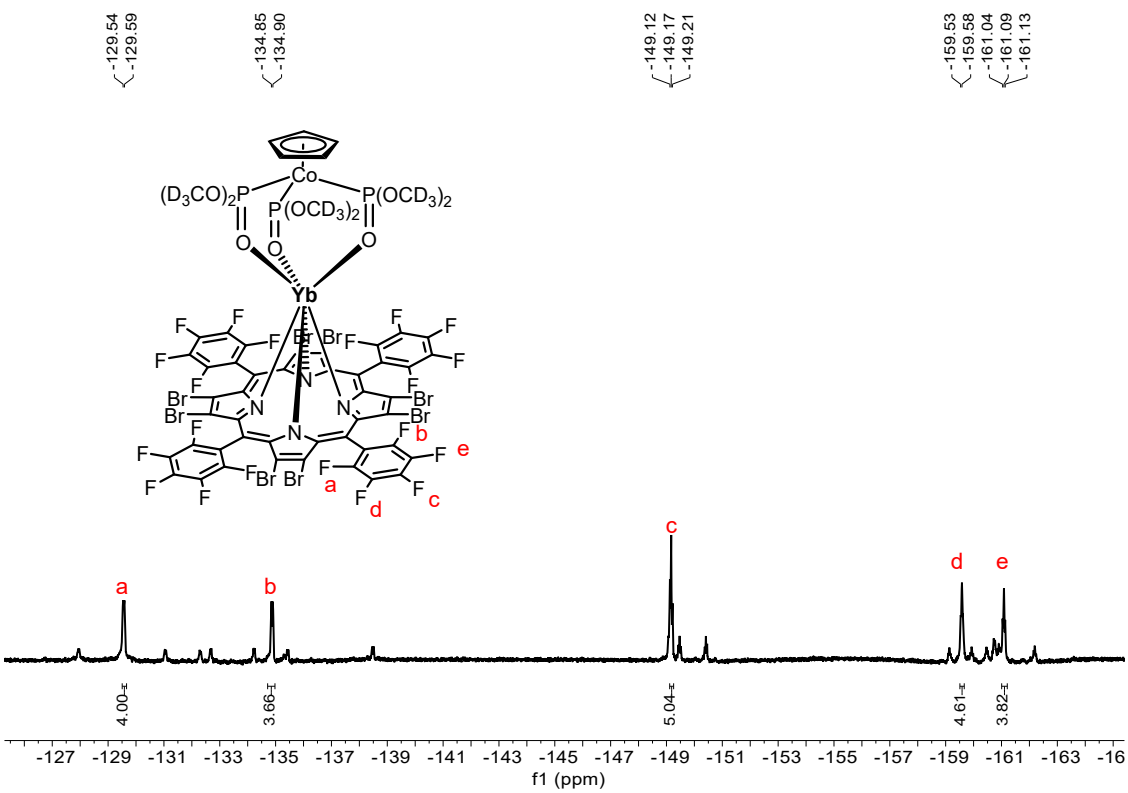


Figure S4 ^{19}F NMR spectrum of **Br-1-Yb** (471 MHz, $CDCl_3$).

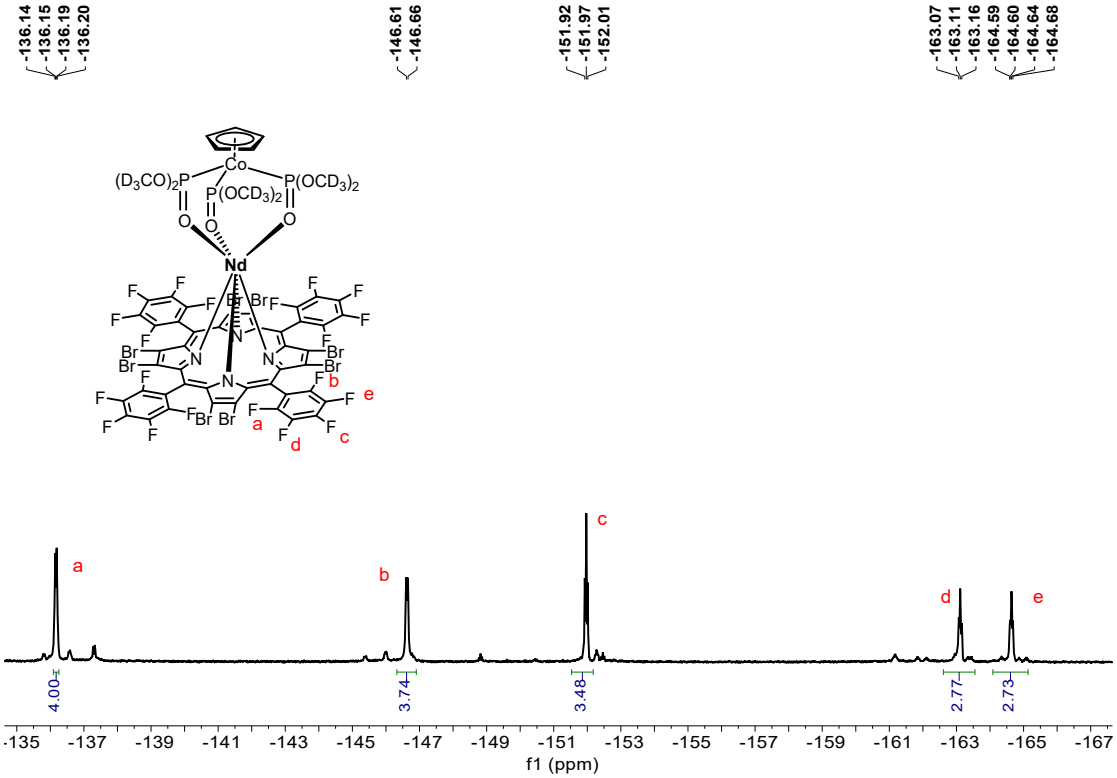


Figure S5 ^{19}F NMR spectrum of **Br-1-Nd** (471 MHz, $CDCl_3$).

Mass spectra

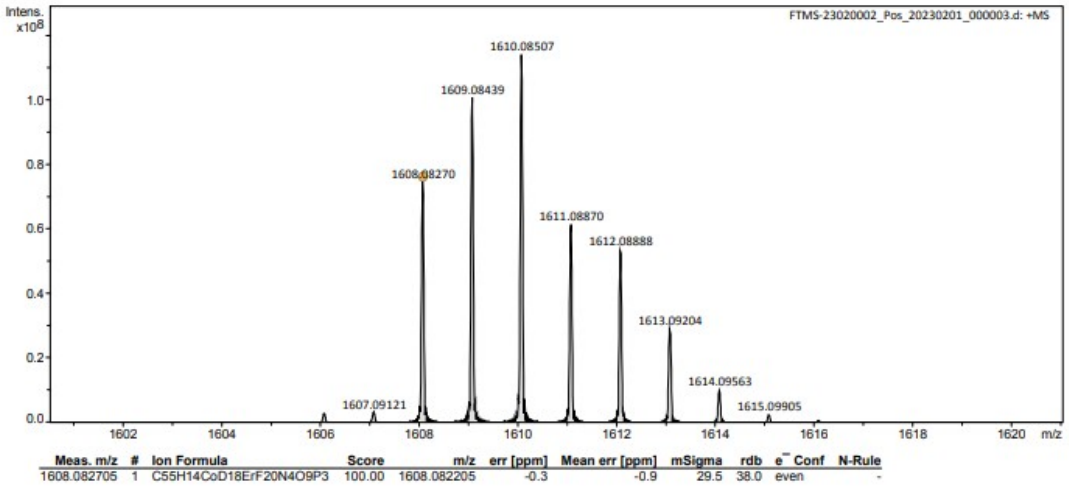


Figure S6 ESI-HRMS of **H-1-Er**.

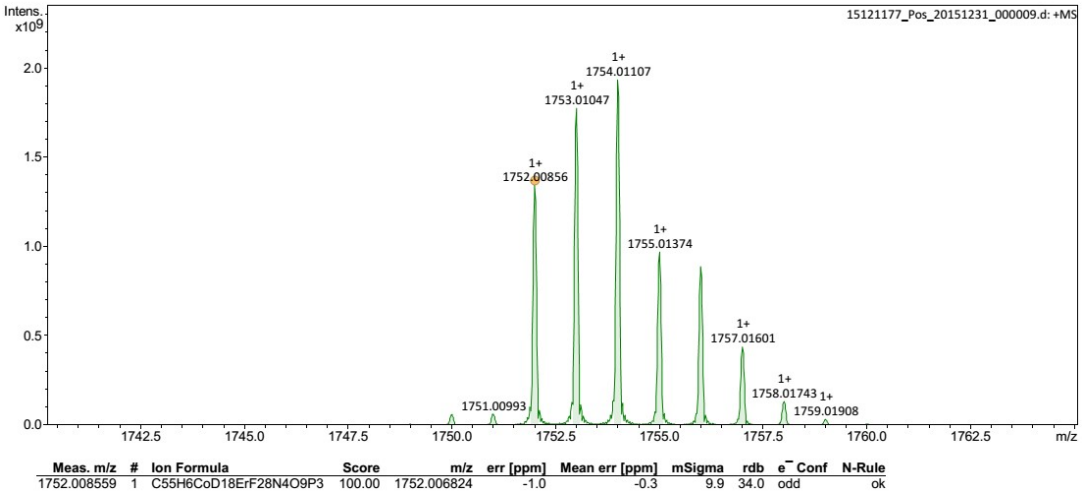


Figure S7 ESI-HRMS of **F-1-Er**.

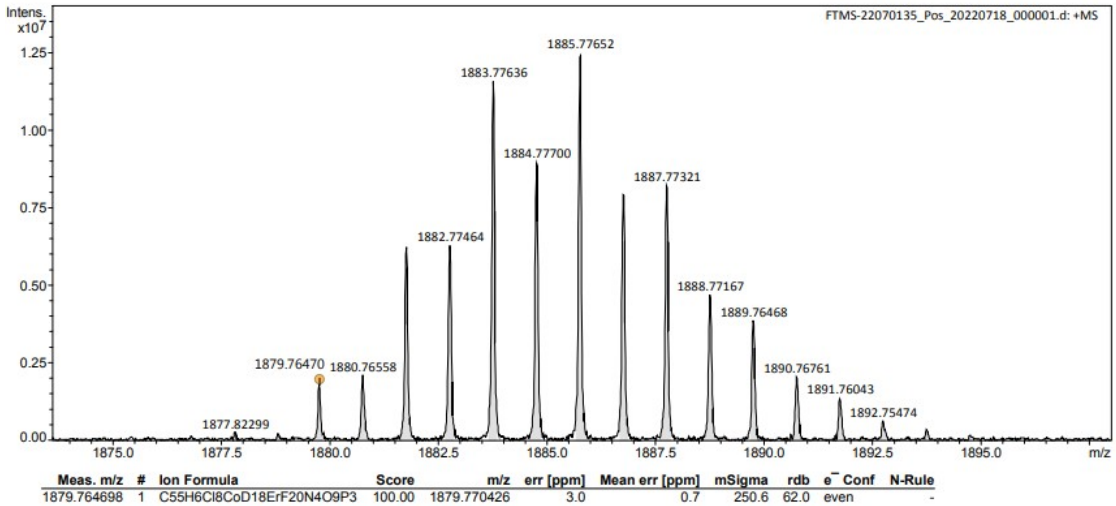
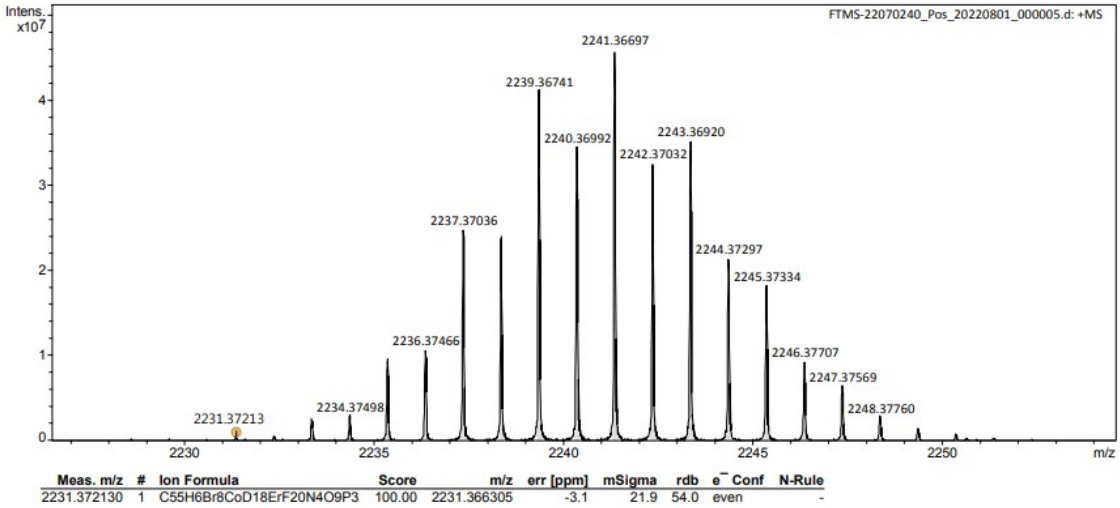
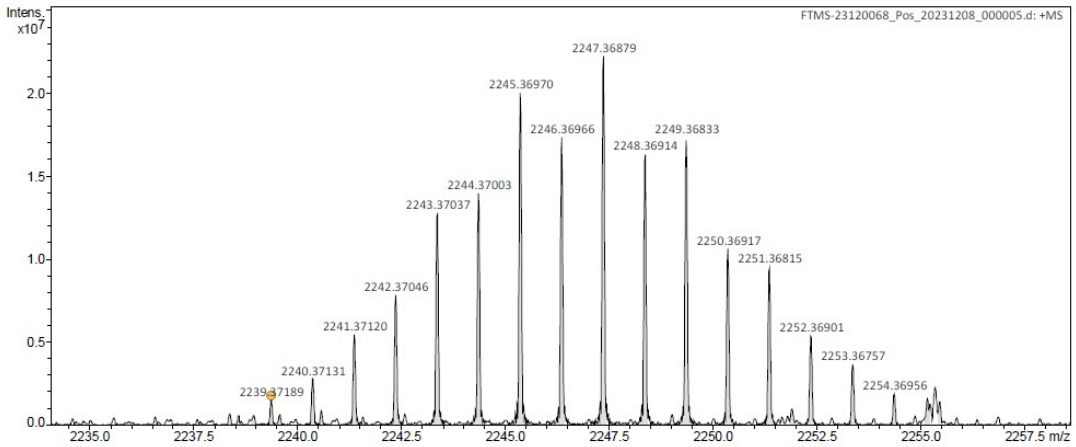


Figure S8 ESI-HRMS of **Cl-1-Er**.



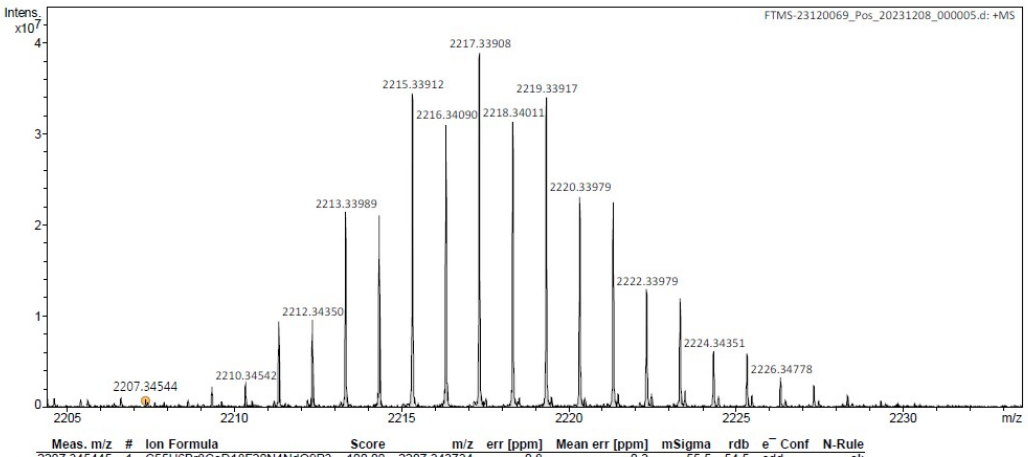
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
2231.372130	1	C55H6Br8CoD18ErF20N4O9P3	100.00	2231.366305	-3.1	21.9	54.0	even	-

Figure S9 ESI-HRMS of **Br-1-Er**.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
2239.371886	1	C55H6Br8CoD18F20N4O9P3Yb	100.00	2239.374872	-0.5	-0.4	19.8	54.0	even	-

Figure S10 ESI-HRMS of **Br-1-Yb**.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
2207.345445	1	C55H6Br8CoD18F20N4NdO9P3	100.00	2207.343734	-0.8	0.3	55.5	54.5	odd	ok

Figure S11 ESI-HRMS of **Br-1-Nd**.

IR spectra

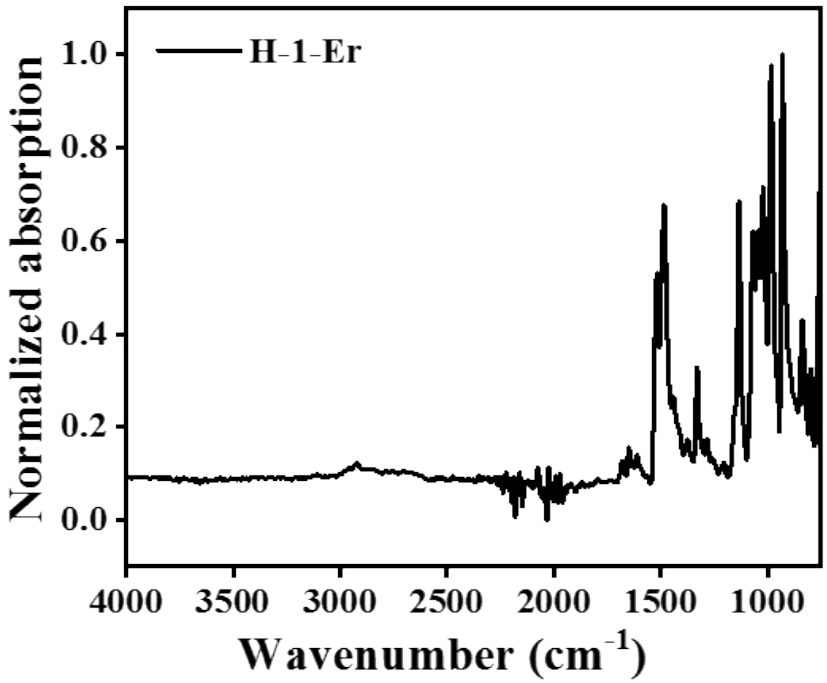


Figure S12 Normalized IR spectrum of **H-1-Er** (KBr pellet) recorded at room temperature.

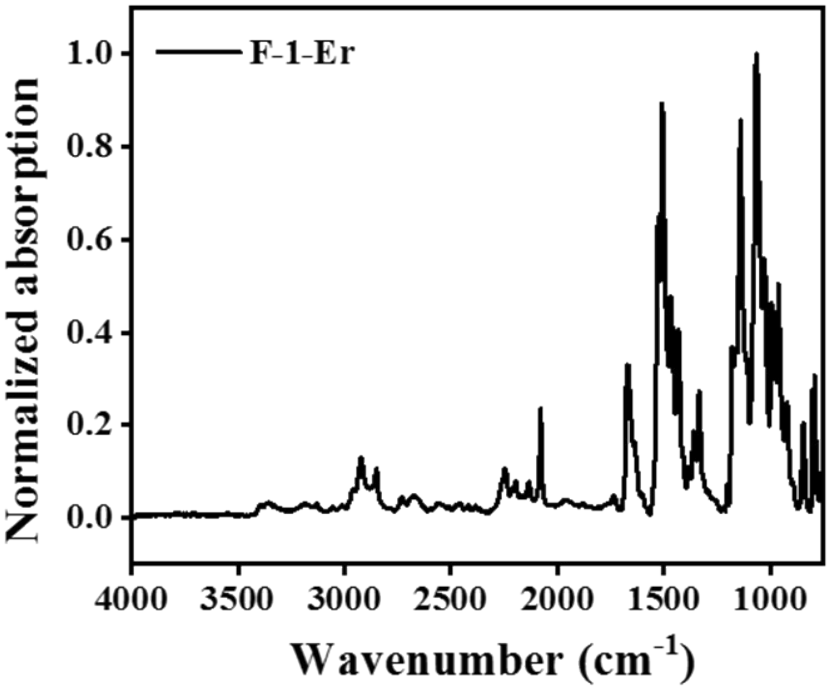


Figure S13 Normalized IR spectrum of **F-1-Er** (KBr pellet) recorded at room temperature.

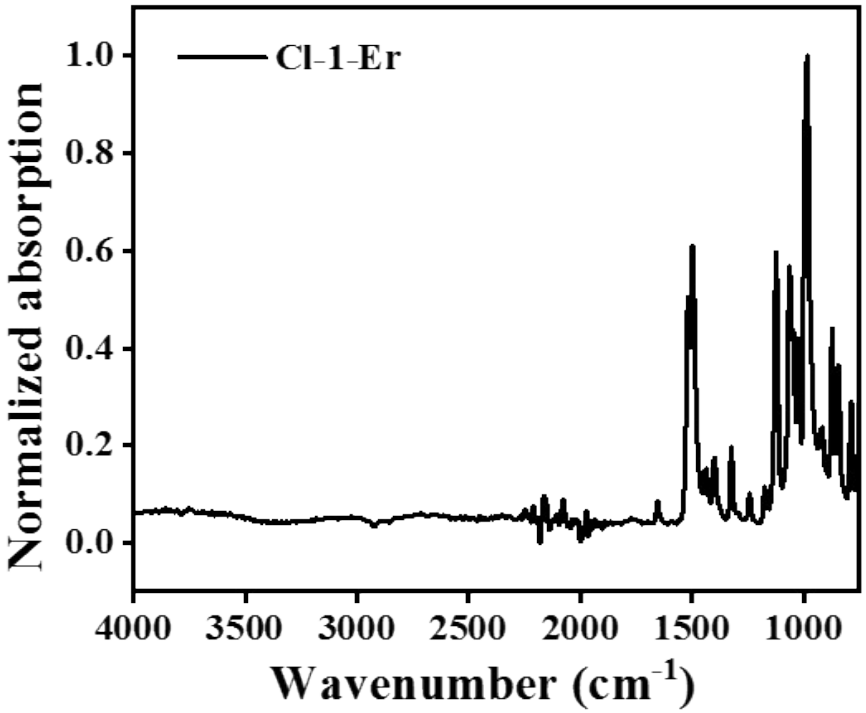


Figure S14 Normalized IR spectrum of **Cl-1-Er** (KBr pellet) recorded at room temperature.

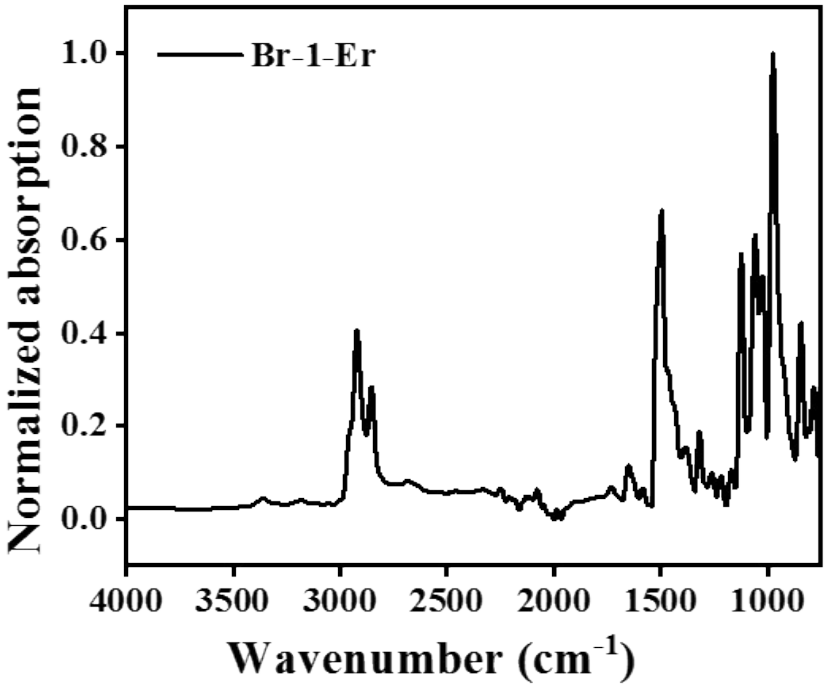


Figure S15 Normalized IR spectrum of **Br-1-Er** (KBr pellet) recorded at room temperature.

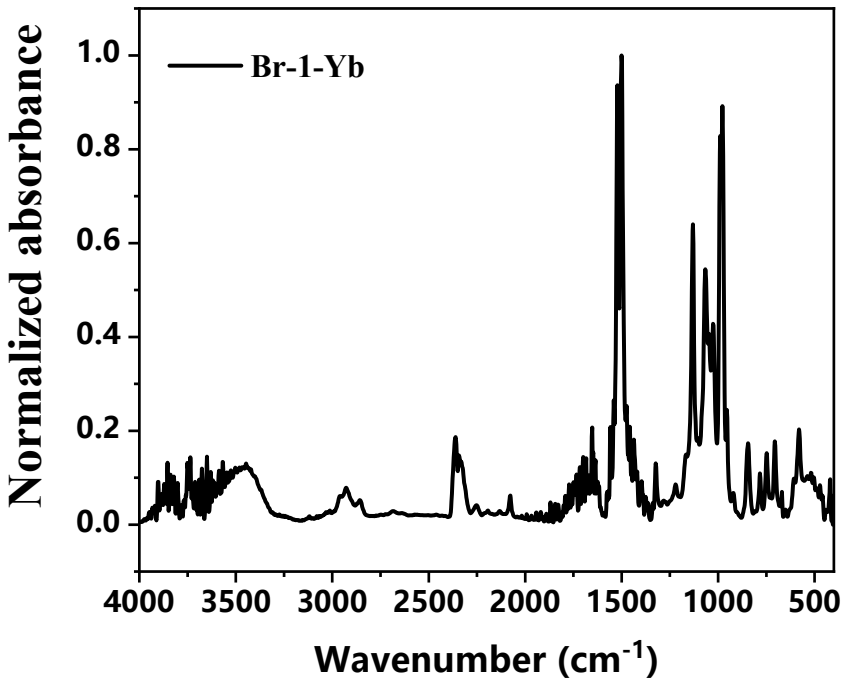


Figure S16 Normalized IR spectrum of **Br-1-Yb** (KBr pellet) recorded at room temperature.

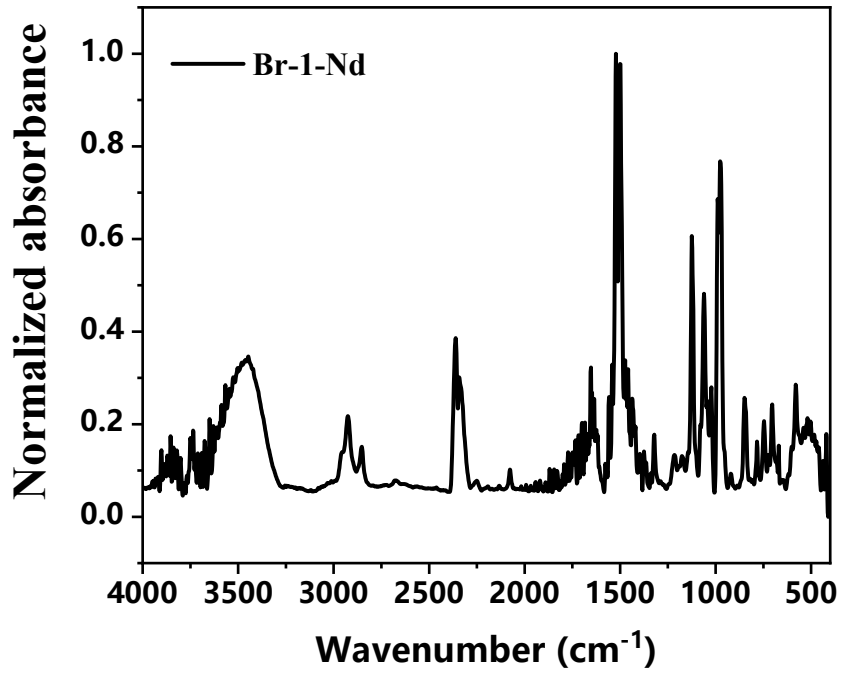


Figure S17 Normalized IR spectrum of **Br-1-Nd** (KBr pellet) recorded at room temperature.

UV spectra

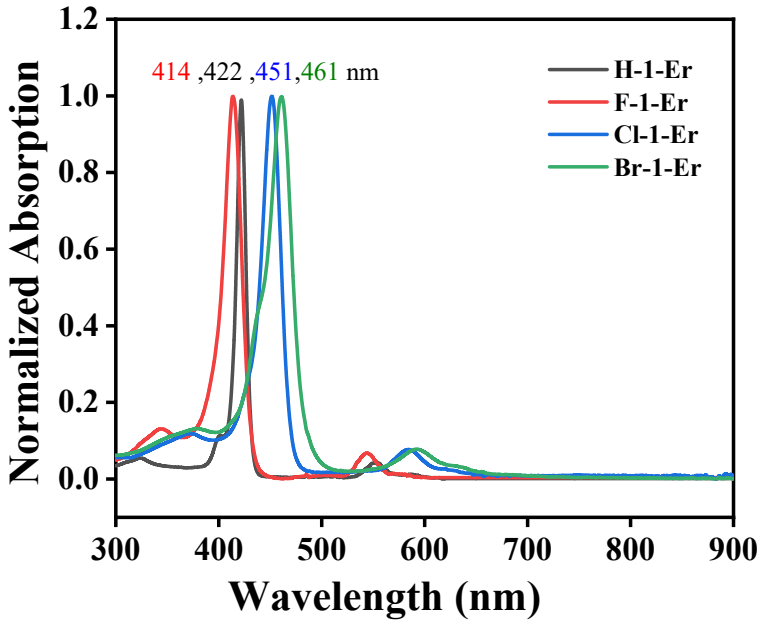


Figure S18 Normalized UV-visible absorption spectra of **X-1-Er** (X = H, F, Cl, Br) in dichloromethane solution at room temperature.

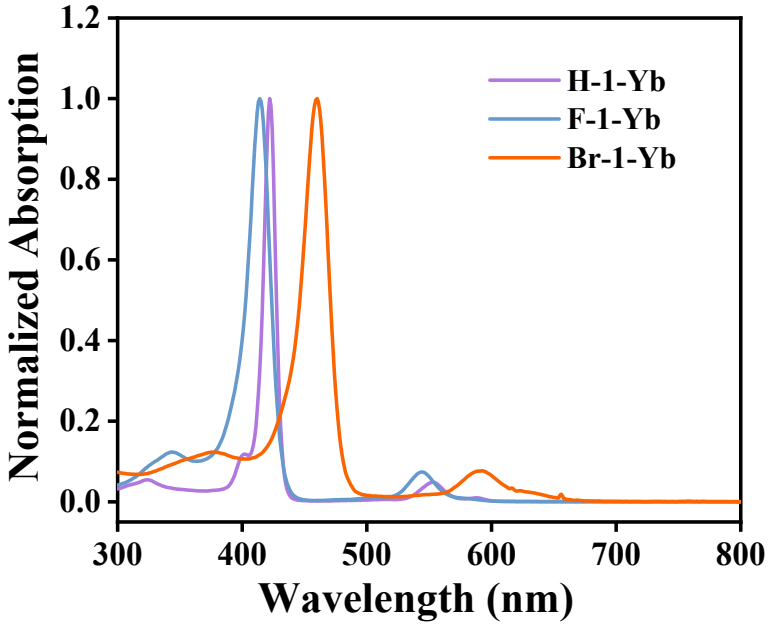


Figure S19 Normalized UV-visible absorption spectra of **X-1-Yb** (X = H, F, Br) in dichloromethane solution at room temperature.

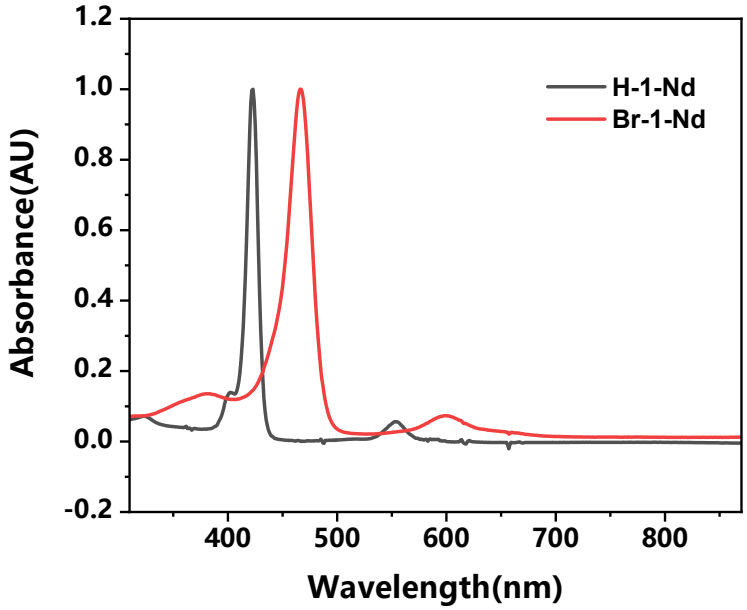


Figure S20 Normalized UV-visible absorption spectra of **X-1-Nd** (X = H, Br) in dichloromethane solution at room temperature.

Summary of crystallographic data

Table S1 Crystal data and structure refinement for Br-1-Er-90K (CCDC: 2451473).

Identification code	**Br-1-Er-90K**
Molecular formula	$C_{55}H_5D_{18}Br_8CoErF_{20}N_4O_9P_3$
Formula wt. (g mol^{-1})	2240.23
Temperature (K)	90
Radiation (λ, Å)	0.71073
Crystal system	tetragonal
Space group	*P-4*
a (Å)	20.7534(2)
b (Å)	20.7534(2)
c (Å)	10.24650(10)
α (º)	90
β (º)	90
γ (º)	90
Volume (Å^3)	4413.20(10)
Z	2
ρ_{calcd} (g cm^{-3})	1.672
μ (mm^{-1})	4.894
F (000)	2106.0
Crystal size (mm^3)	0.6×0.15×0.05
Theta range	2.194 to 29.511º
Reflections collected	61402
Independent reflections	11447 [R(int) = 0.0482]
Completeness	95%
Goodness-of-fit on F^2	1.059
Final R indices	$R1^a$ = 0.0368
[R > 2σ (I)]	$wR2^b$= 0.0939
R indices (all data)	$R1^a$= 0.0418 $wR2^b$= 0.0956

Largest diff. peak and hole (e $Å^{-3}$)	1.57 and -1.00

Table S2 Crystal data and structure refinement for H-1-Er-90K (CCDC: 2451475).

Identification code	**H-1-Er-90K**
Empirical formula	$C_{55}H_{31}CoErF_{20}N_4O_9P_3$
Formula weight	1590.94
Temperature/K	90.8(3)
Crystal system	orthorhombic
Space group	*Pnma*
a/Å	19.6546(2)
b/Å	22.8703(3)
c/Å	15.5652(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6996.66(15)
Z	4
ρ_{calc}g/cm^3	1.510
μ/mm^{-1}	1.600
F(000)	3124.0
Crystal size/mm^3	0.4 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.166 to 61.62
Index ranges	-27 ≤ h ≤ 26, -32 ≤ k ≤ 28, -20 ≤ l ≤ 21
Reflections collected	84715
Independent reflections	10202 [R_{int} = 0.0329, R_{sigma} = 0.0224]
Data/restraints/parameters	10202/24/490
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0276, wR_2 = 0.0709
Final R indexes [all data]	R_1 = 0.0400, wR_2 = 0.0772
Largest diff. peak/hole / e Å^{-3}	1.13/-0.87

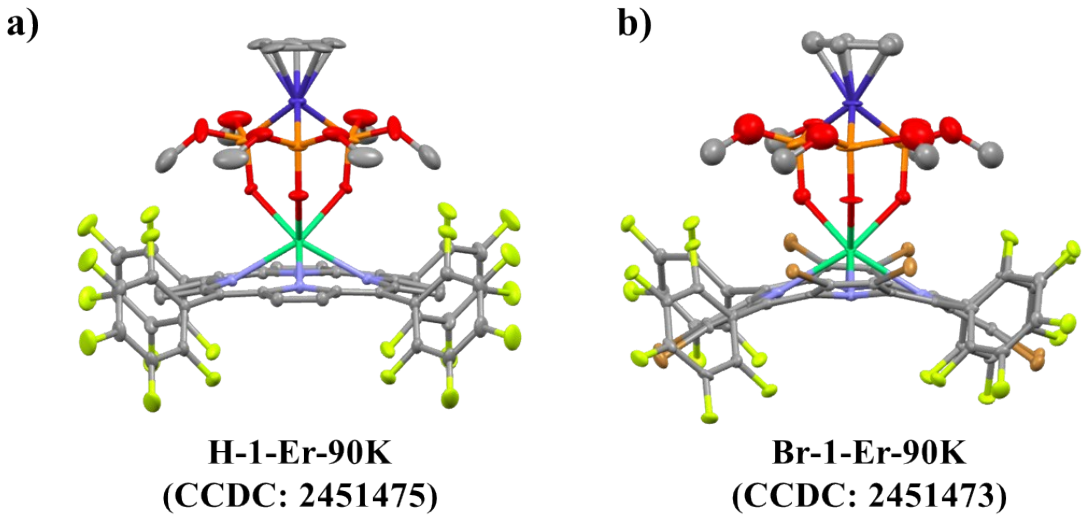


Figure S21 Single crystal structure of (a) **H-1-Er-90K** and (b) **Br-1-Er-90K** measured at 90 K. The crystal was grown by slow evaporation from a mixed solution of dichloromethane and n-hexane.

Other spectra

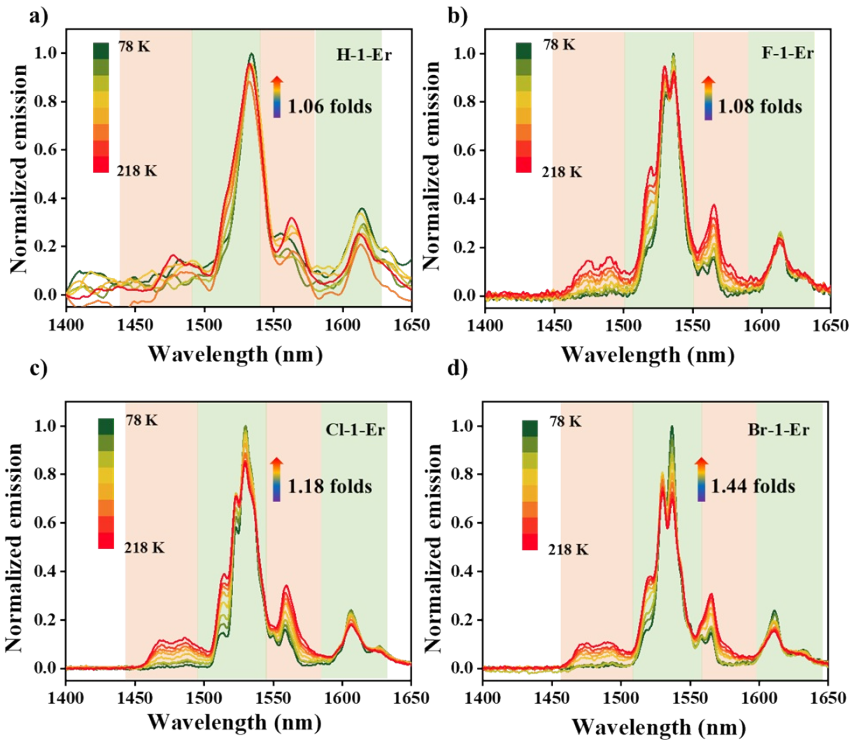


Figure S22 Emission spectra of complex a) **H-1-Er** (λ_{ex}=414 nm), b) **F-1-Er** (λ_{ex}=422 nm), c) **Cl-1-Er** (λ_{ex}=451 nm), d) **Br-1-Er** (λ_{ex}=461 nm) in PMMA from 78-218 K.

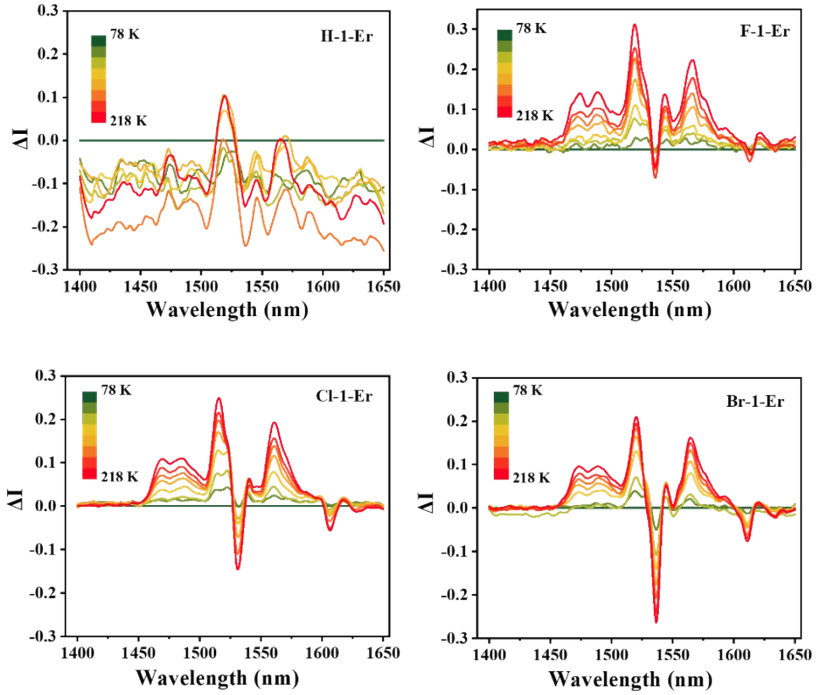


Figure S23 Differential emission spectra of complex a) **H-1-Er** (λ_{ex}=414 nm), b) **F-1-Er** (λ_{ex}=422 nm), c) **Cl-1-Er** (λ_{ex}=451 nm), d) **Br-1-Er** (λ_{ex}=461 nm) in PMMA from 78-218 K.

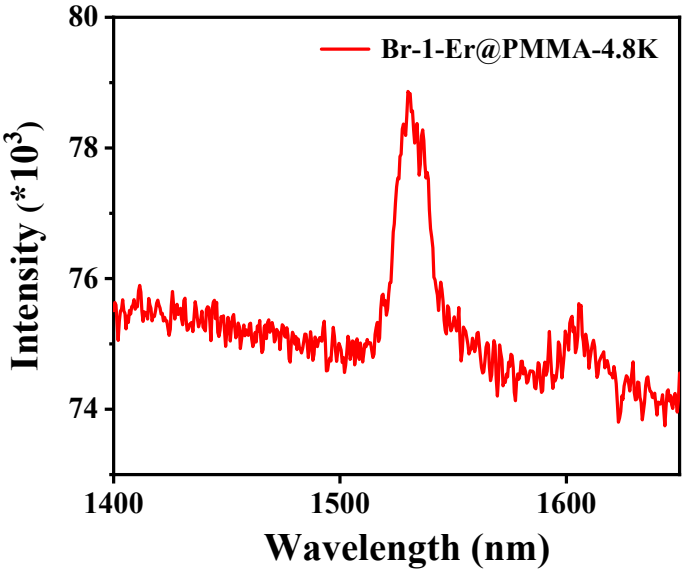


Figure S24 Emission spectrum of **Br-1-Er** in PMMA at 4.8 K (λ_{ex}=460 nm).

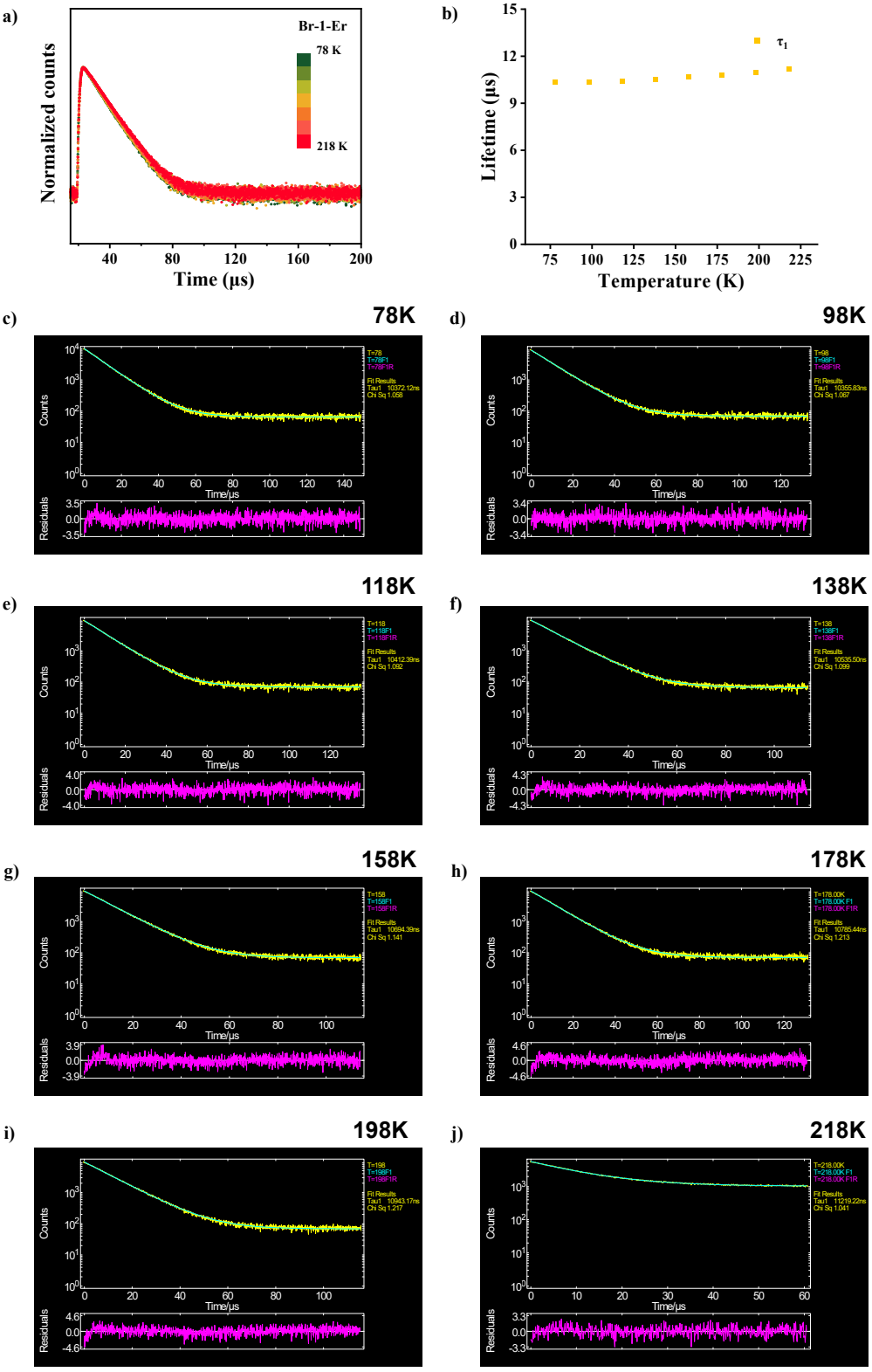


Figure S25 a) PL decay curves of the complex **Br-1-Er** in PMMA at different temperatures (λ_{ex}=461 nm) (y-axis is shown on a logarithmic scale); b) Plot of lifetime variations of the complex **Br-1-Er** in PMMA from 78-218 K. c-j) Fitting results of **Br-1-Er** at various temperatures in PMMA (λ_{ex} = 461 nm, λ_{em} = 1537 nm).

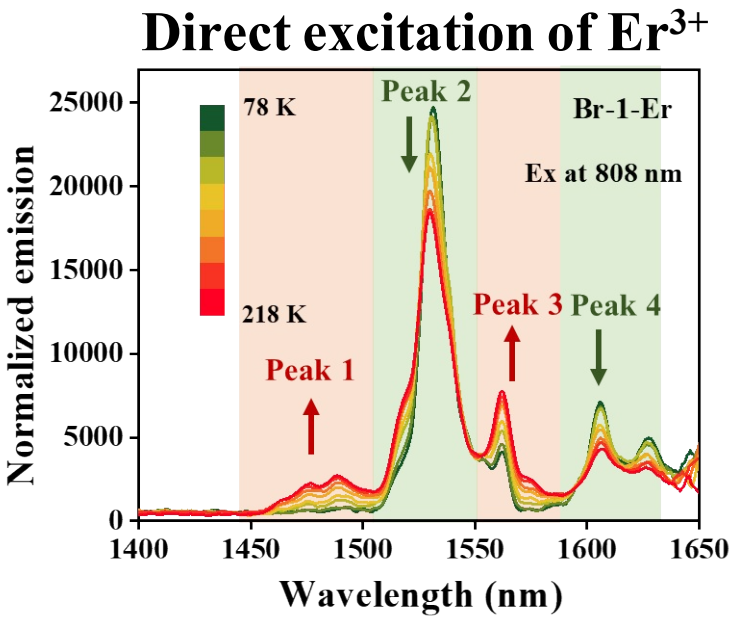


Figure S26 Luminescence spectra of the complex **Br-1-Er** in PMMA under excitation at 808 nm from 78-218 K (λ_{ex}=808 nm).

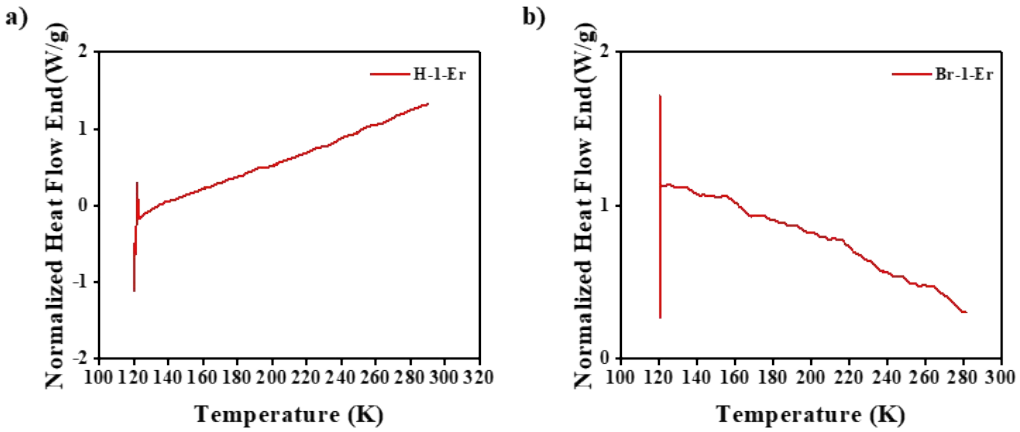


Figure S27 DSC curves of the complexes a) **H-1-Er** and b) **Br-1-Er**.

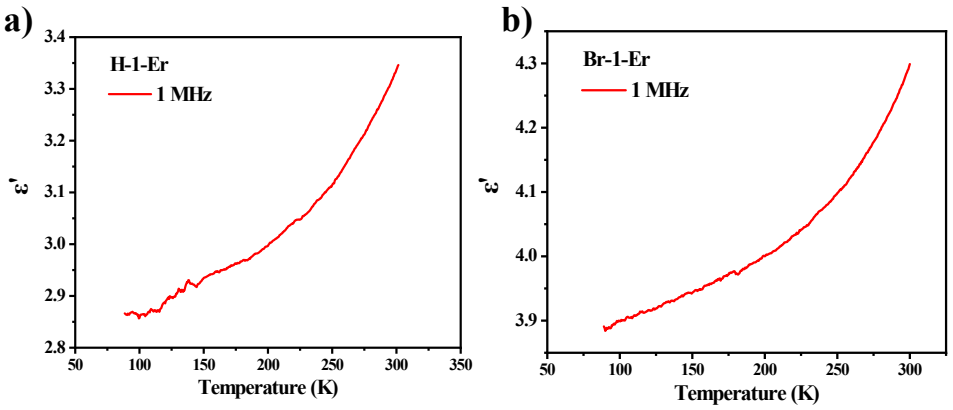


Figure S28 Temperature-dependent ac (alternate current) dielectric permittivity measurements of a) **H-1-Er** and b) **Br-1-Er** from 78-298 K.

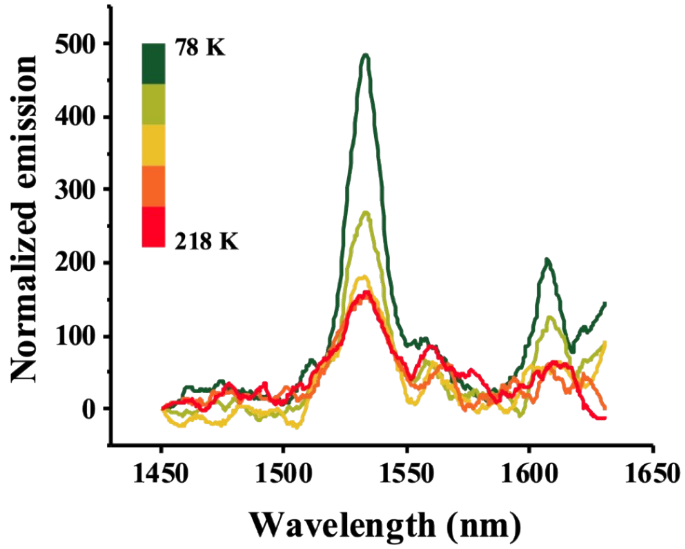


Figure S29 Variable temperature spectra of **Br-1-Er** in 2-methyltetrahydrofuran solution from 78-218 K (λ_{ex}=461 nm,), the absorbance of excitation wavelength was fixed at 0.1.

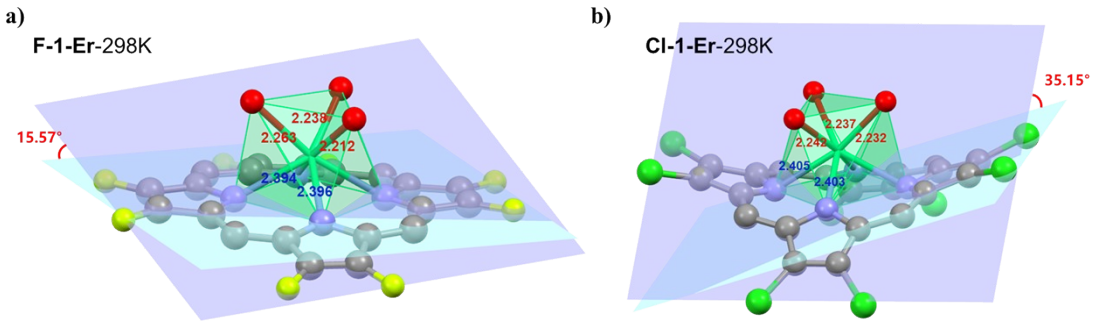


Figure S30 Single X-ray crystal structures of **F-1-Er** (a) and **Cl-1-Er** (b). To observe the distortion of the porphyrin ring, partial atoms are omitted for clarity.

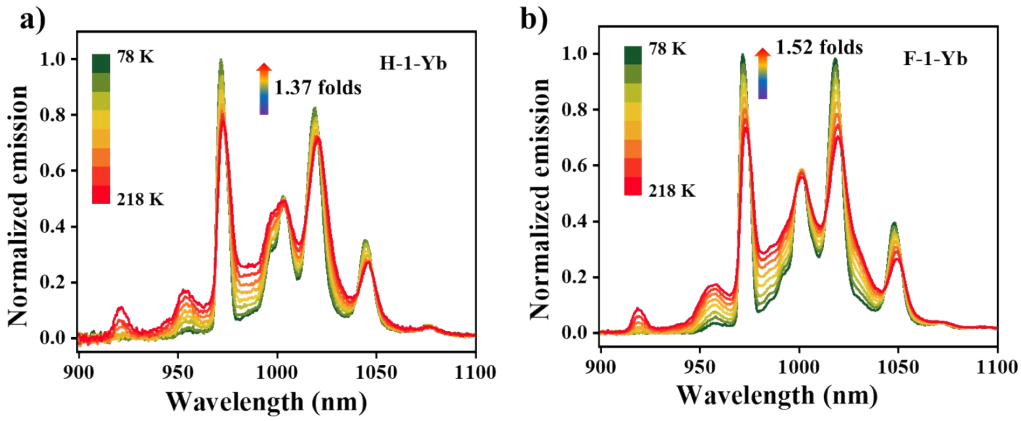


Figure S31 a) Normalized emission spectra of **H-1-Yb** in PMMA from 78-218 K upon excitation at 422 nm; b) Normalized emission spectra of **F-1-Yb** in PMMA from 78-218 K upon excitation at 414 nm.

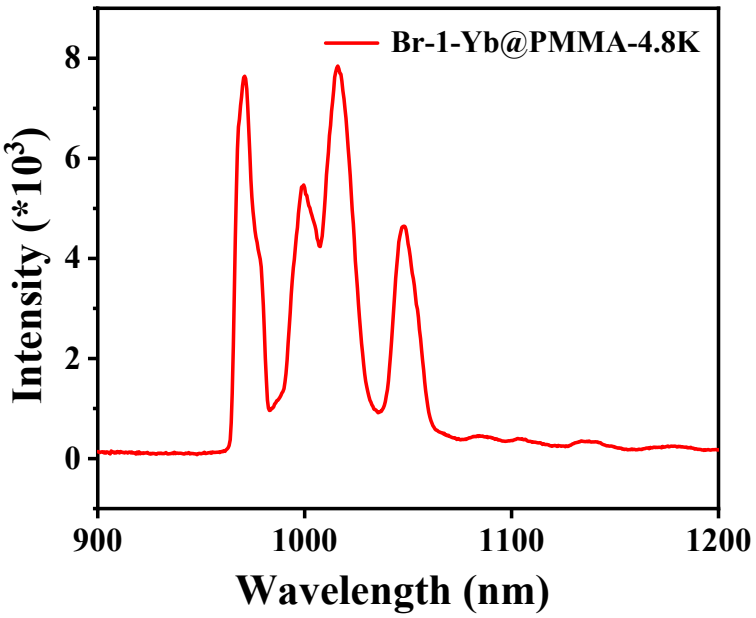


Figure S32 Emission spectrum of **Br-1-Yb** in PMMA at 4.8 K upon excitation at 460 nm.

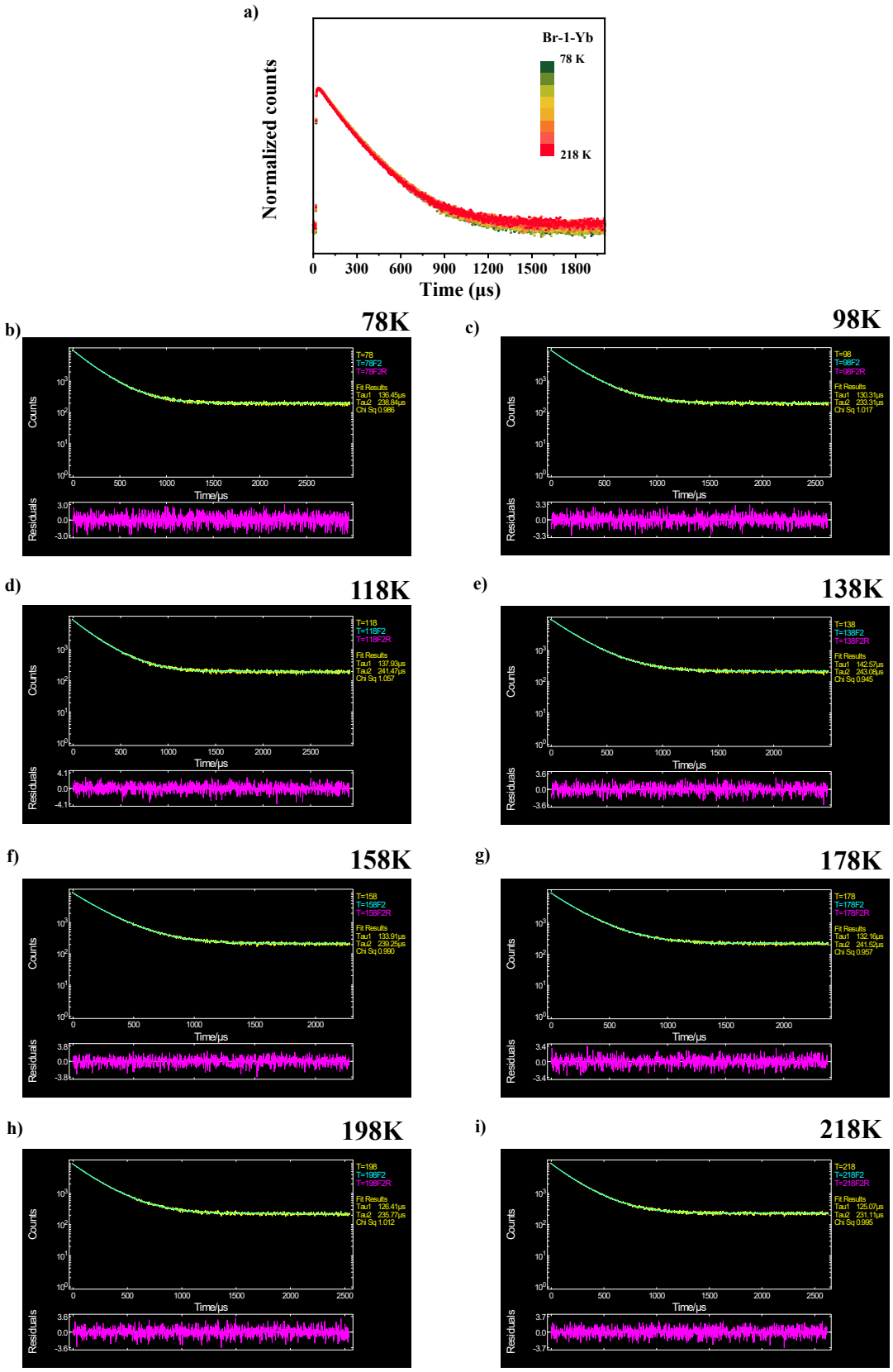


Figure S33 (a) PL decay curves of the complex **Br-1-Yb** in PMMA from 78-218 K upon excitation at 460 nm (y-axis is shown on a logarithmic scale); b-i) Fitting results of **Br-1-Yb** at various temperatures in PMMA (λex=460 nm, λem=977 nm).

.

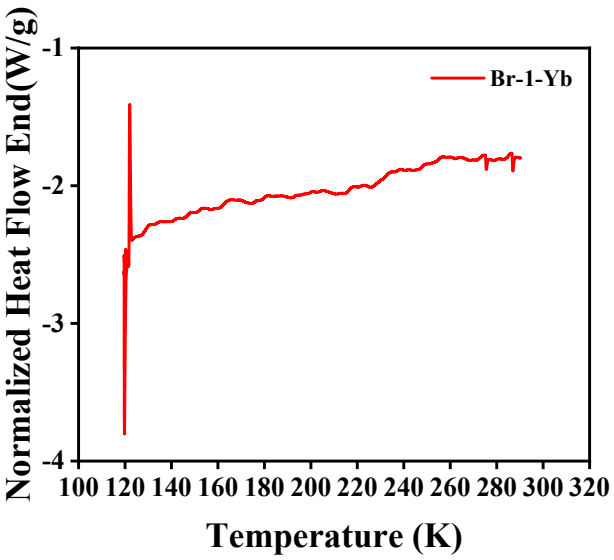


Figure S34 DSC curves of the complex **Br-1-Yb**.

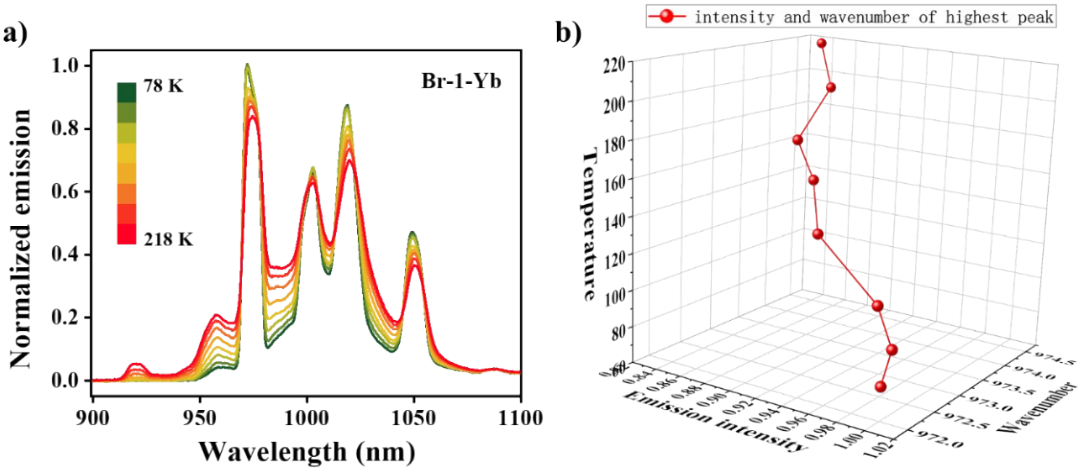


Figure S35 a) Luminescence emission diagram of the complex **Br-1-Yb** in 2-methyltetrahydrofuran from 78-218 K upon excitation at 460 nm; b) Luminescence emission peaking intensity and wavelength changes of the complex **Br-1-Yb** in 2-methyltetrahydrofuran at about 970 nm from 78-218 K.

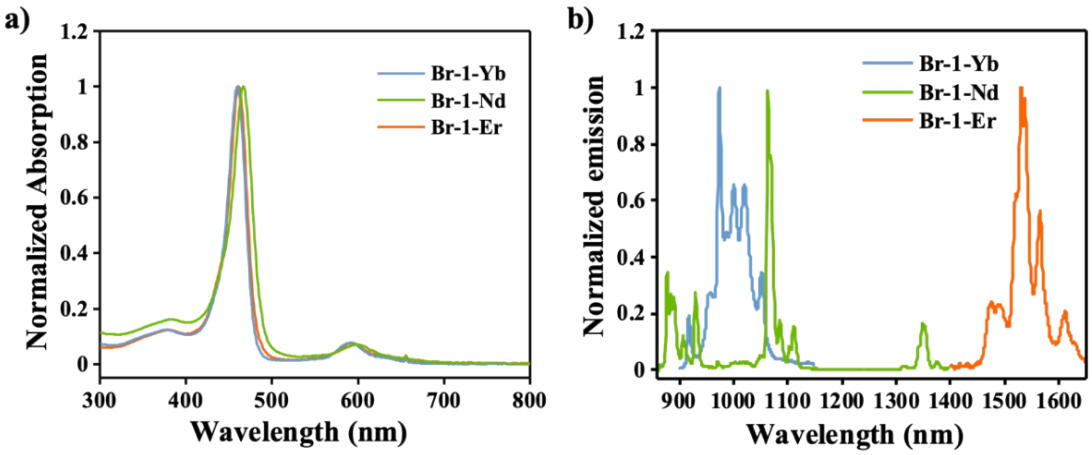


Figure S36 a) UV-visible absorption spectra and b) luminescence emission spectra of complexes **Br-1-Er**, **Br-1-Yb** and **Br-1-Nd** in dichloromethane solution upon excitation at 460 nm from 78-218 K.

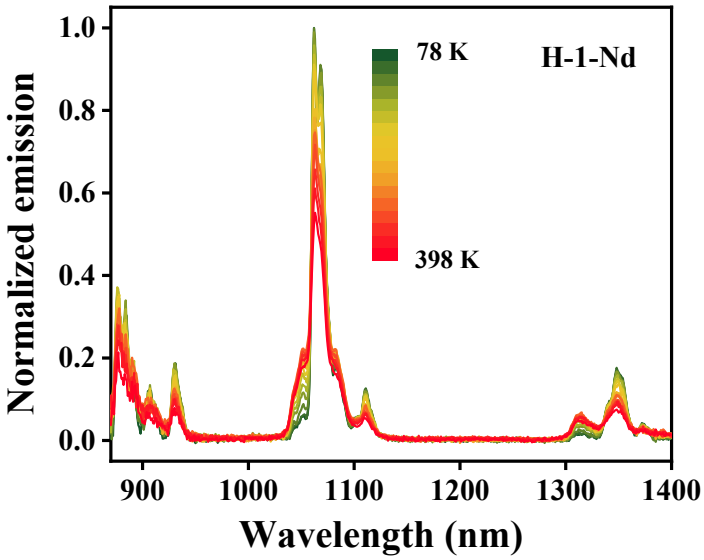


Figure S37 Luminescence spectra of the complex **H-1-Nd** in PMMA under excitation at 420 nm from 78-398 K.

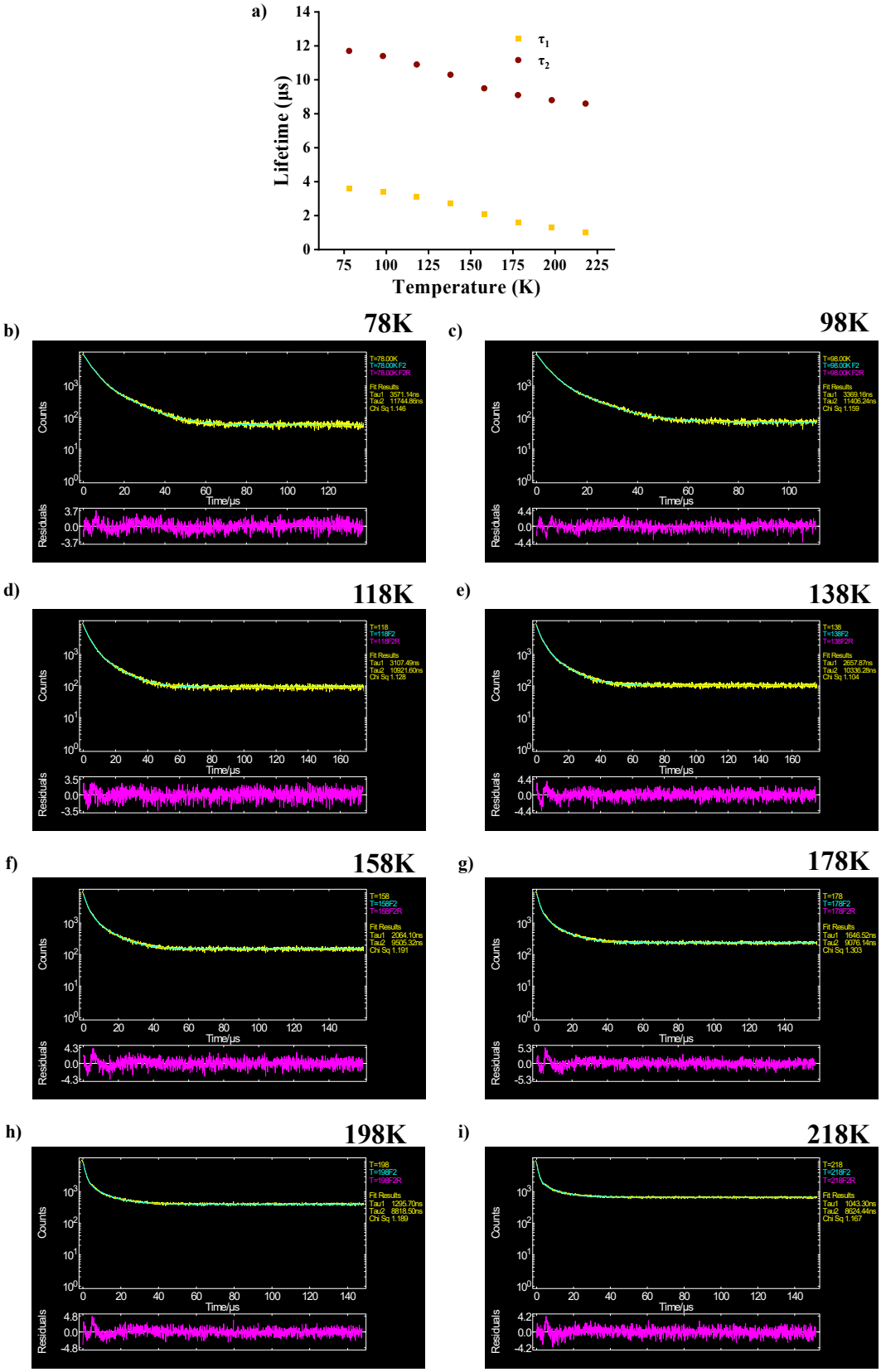


Figure S38 Plot of lifetime variations of the complex **Br-1-Nd** in PMMA upon excitation at 460 nm from 78-218 K. a-h) Fitting results of **Br-1-Nd** at various temperatures in PMMA (λ_{ex} = 461 nm, λ_{em} = 1063 nm).

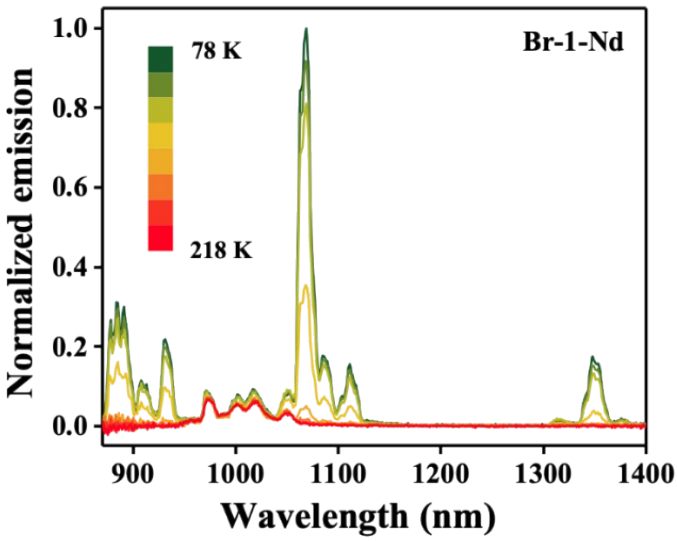


Figure S39 Temperature change spectra of **Br-1-Nd** in 2-methyltetrahydrofuran solution upon excitation at 460 nm from 78-218 K, the absorbance of excitation wavelength was fixed at 0.1.

.

Supporting reference

[1] Guo, L.-J.; Zhang, J.-L. Highly NIR-II luminescent erbium porphyrinoids. *J. Porphyrins Phthalocyanines* **2023**, *27*, 1348-1356.