Supporting Information

Unexpected Deprotonation from a Chemically Inert OH Group Promoted by Metal Ions in Lanthanide-Erythritol Complexes

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List of Supporting Information

Part 1 Description of the structure of HoE(I)

The ORTEP diagram of HoE(I) is shown in **Figure S1-1**. The packing diagram is shown in **Figure S1-2**. Crystallographic data and structure refinement summary are listed in **Table S1-1**. Selected bond lengths and bond angles are listed in **Table S1-2**. Hydrogen bonds of the complex are listed in **Table S1-3**.

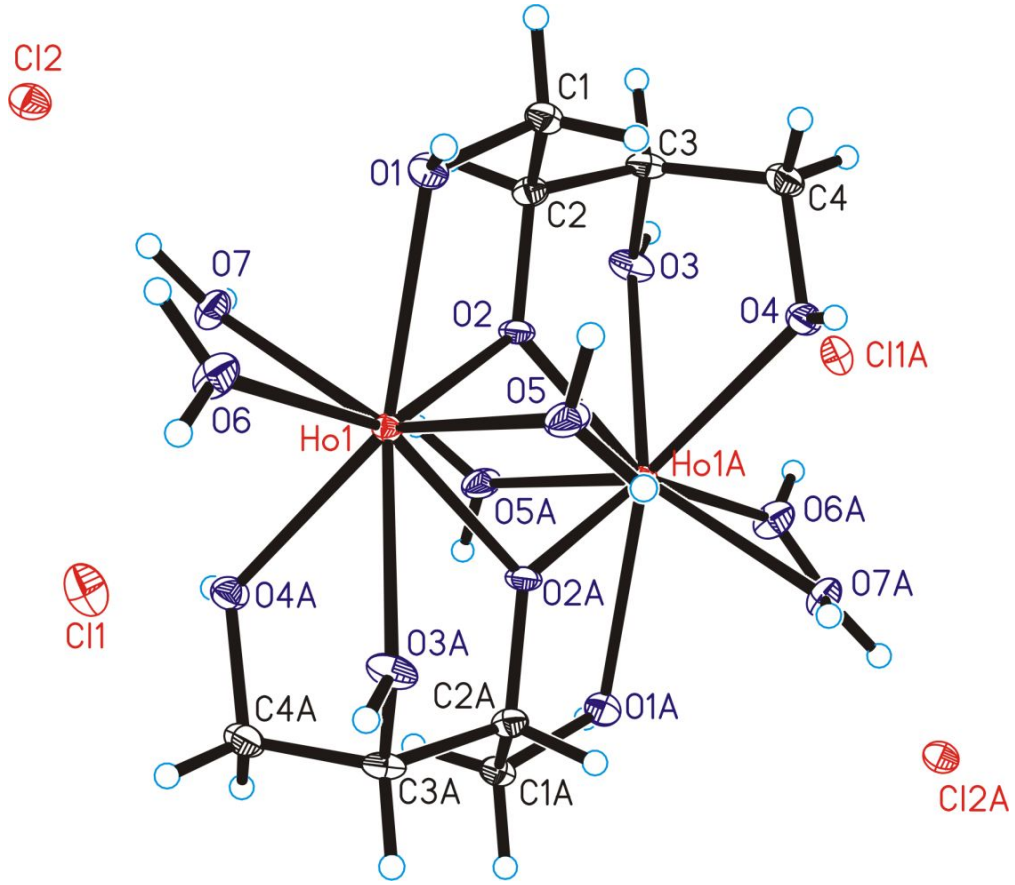

Figure S1-1. The ORTEP diagram of HoE(I)

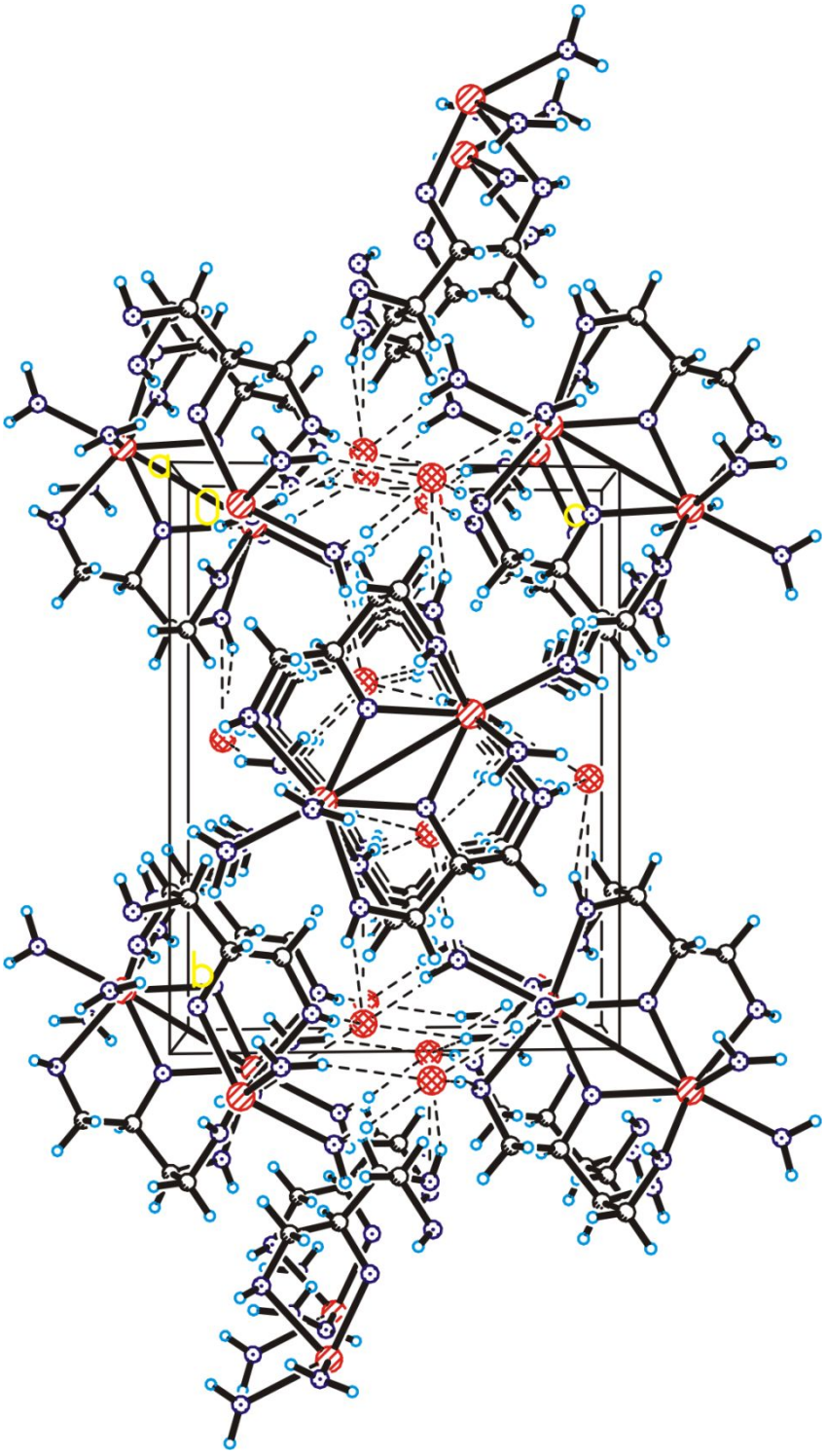

Figure S1-2. The packing diagram of HoE(I)

Table S1-1. Crystallographic Data and Structure Refinement Summary for HoE(I).

Identification code	HoE(I)
CCDC No.	1974395
Formula	$C_8H_{30}Cl_4Ho_2O_{14}$
formula weight	821.98
crystal system	Monoclinic
space group, Z	$P2_1/n$, 2
a (Å)	8.4653(2)
b (Å)	13.1179(3)
c (Å)	10.2051(3)
α (deg)	90
β (deg)	99.540(2)
γ (deg)	90
V (Å^3)	1117.57(5)
ρ_{calc} (g/cm^3)	2.443
μ (mm^{-1})	7.566
reflections collected	7541
data/restraints/parameters	2559/12/154
R(int)	0.0285
goodness of fit	1.053
$R_1[I>2\sigma(I)]$	0.0196
$wR_2[I>2\sigma(I)]$	0.0393
R_1(all data)	0.0243
wR_2 (all data)	0.0403

Table S1-2. Selected Bond Lengths and Bond Angles of the Complex HoE(I).

Bond Lengths (Å)			
Ho1–O2	2.215(2)	O2–C2	1.414(4)
Ho1–O2[1]	2.226(2)	O2–Ho1[1]	2.226(2)
Ho1–O6	2.321(2)	O3–C3	1.459(3)
Ho1–O5	2.344(2)	O3–Ho1[1]	2.470(2)
Ho1–O7	2.385(2)	O4–C4	1.445(4)
Ho1–O4[1]	2.420(2)	O4–Ho1[1]	2.420(2)
Ho1–O3[1]	2.470(2)	C1–C2	1.514(4)
Ho1–O1	2.471(2)	C2–C3	1.536(4)
Ho1–Ho1[1]	3.6867(3)	C3–C4	1.499(4)
O1–C1	1.456(4)		
Bond Angles (°)			
O2–Ho1–O2[1]	67.79(8)	O7–Ho1–O1	74.53(7)
O2–Ho1–O6	142.71(8)	O4[1]–Ho1–O1	144.65(7)
O2[1]–Ho1–O6	149.10(8)	O3[1]–Ho1–O1	142.08(7)
O2–Ho1–O5	95.25(8)	O2–Ho1–Ho1[1]	33.99(5)
O2[1]–Ho1–O5	86.94(8)	O2[1]–Ho1–Ho1[1]	33.80(5)
O6–Ho1–O5	85.22(8)	O6–Ho1–Ho1[1]	175.00(6)
O2–Ho1–O7	81.60(8)	O5–Ho1–Ho1[1]	91.30(6)
O2[1]–Ho1–O7	120.97(7)	O7–Ho1–Ho1[1]	102.88(5)
O6–Ho1–O7	78.38(8)	O4[1]–Ho1–Ho1[1]	94.39(5)
O5–Ho1–O7	147.10(8)	O3[1]–Ho1–Ho1[1]	99.55(5)
O2–Ho1–O4[1]	111.88(7)	O1–Ho1–Ho1[1]	98.78(5)
O2[1]–Ho1–O4[1]	75.87(7)	C1–O1–Ho1	113.53(17)
O6–Ho1–O4[1]	90.60(8)	C2–O2–Ho1	123.71(17)
O5–Ho1–O4[1]	138.48(7)	C2–O2–Ho1[1]	123.13(17)
O7–Ho1–O4[1]	70.60(7)	Ho1–O2–Ho1[1]	112.21(8)
O2–Ho1–O3[1]	132.89(7)	C3–O3–Ho1[1]	105.84(16)
O2[1]–Ho1–O3[1]	66.27(7)	C4–O4–Ho1[1]	118.93(16)
O6–Ho1–O3[1]	82.87(8)	O1–C1–C2	106.1(2)
O5–Ho1–O3[1]	72.62(7)	O2–C2–C1	107.9(2)
O7–Ho1–O3[1]	132.05(8)	O2–C2–C3	110.3(2)
O4[1]–Ho1–O3[1]	65.88(7)	C1–C2–C3	113.1(2)
O2–Ho1–O1	67.64(7)	O3–C3–C4	106.4(2)
O2[1]–Ho1–O1	129.15(7)	O3–C3–C2	103.7(2)
O6–Ho1–O1	76.81(8)	C4–C3–C2	116.2(3)
O5–Ho1–O1	74.05(7)	O4–C4–C3	108.4(2)

Symmetry transformations used to generate equivalent atoms: [1]1-X, 1-Y, 1-Z

Table S1-3. The Hydrogen Bond Data of the Complex HoE(I).

D–H···A	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	∠D–H···A/°
O1–H1···Cl2[1]	0.803(17)	2.36(2)	3.111(2)	157(3)
O3–H3···Cl2[2]	0.805(18)	2.38(2)	3.127(2)	154(3)
O4–H4···Cl1[3]	0.819(17)	2.275(19)	3.070(2)	164(3)
O5–H5A···Cl1[4]	0.928(17)	2.174(17)	3.101(2)	178(3)
O5–H5B···Cl2[1]	0.911(17)	2.285(17)	3.173(2)	165(3)
O6–H6A···Cl2	0.927(17)	2.165(17)	3.084(2)	171(3)
O6–H6B···Cl1	0.929(17)	2.094(17)	3.020(2)	175(3)
O7–H7A···Cl2	0.922(16)	2.489(18)	3.320(2)	150(2)
O7–H7B···Cl1[2]	0.929(17)	2.188(17)	3.114(2)	174(3)

[1]1-X, 1-Y, -Z; [2]1/2-X, -1/2+Y, 1/2-Z; [3]3/2-X, -1/2+Y, 1/2-Z; [4]1/2+X, 3/2-Y, 1/2+Z

Part 2 Spectroscopic study of HoE(I)

The FTIR spectrum of HoE(I) is shown in **Figure S2-1**. Its FIR spectrum is shown in **Figure S2-2**. The THz spectrum of HoE(I) is shown in **Figure S2-3**.

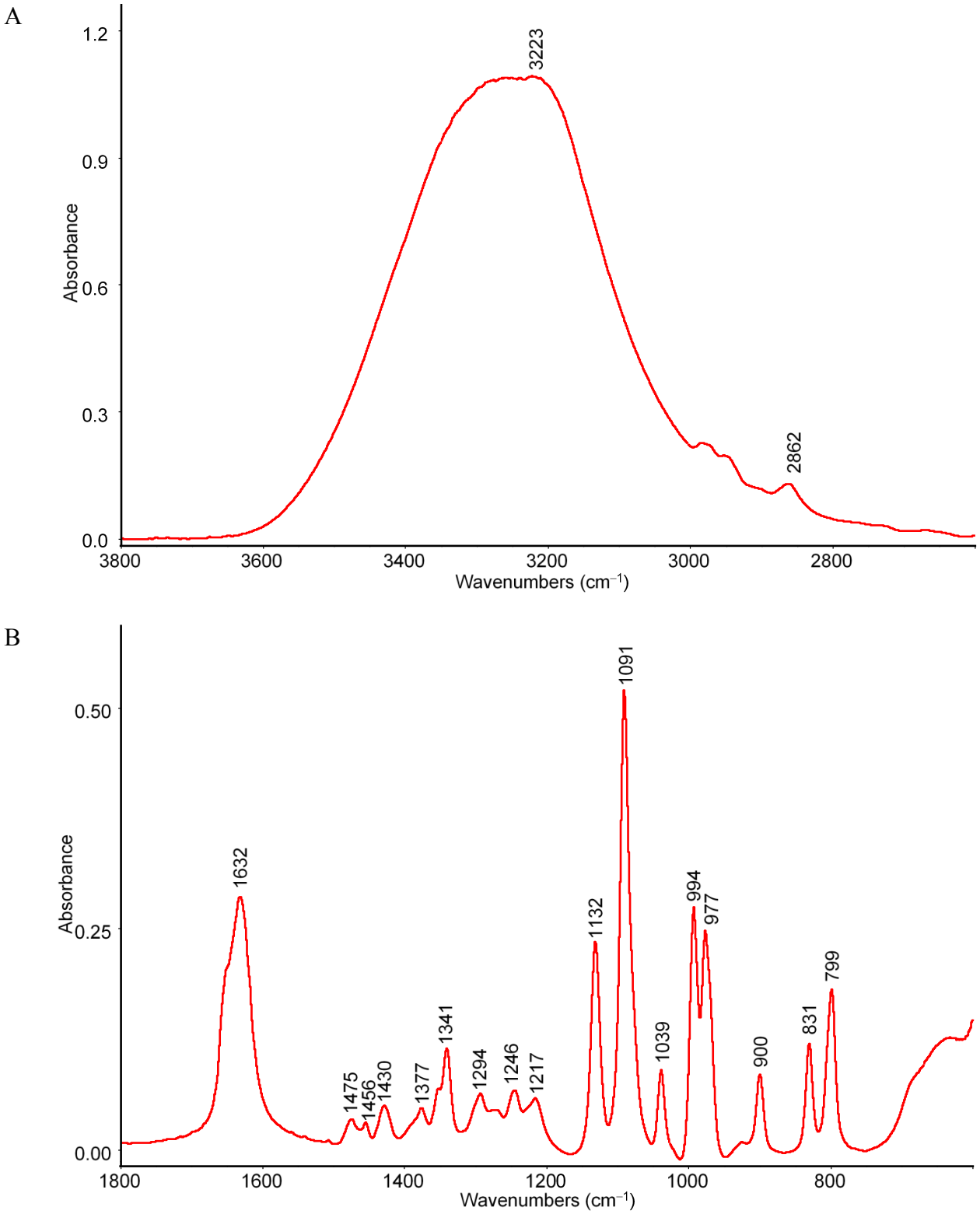

Figure S2-1. FTIR spectrum of HoE(I) in the 3800–2600 (A) and 1800–600 cm^{-1} (B) region

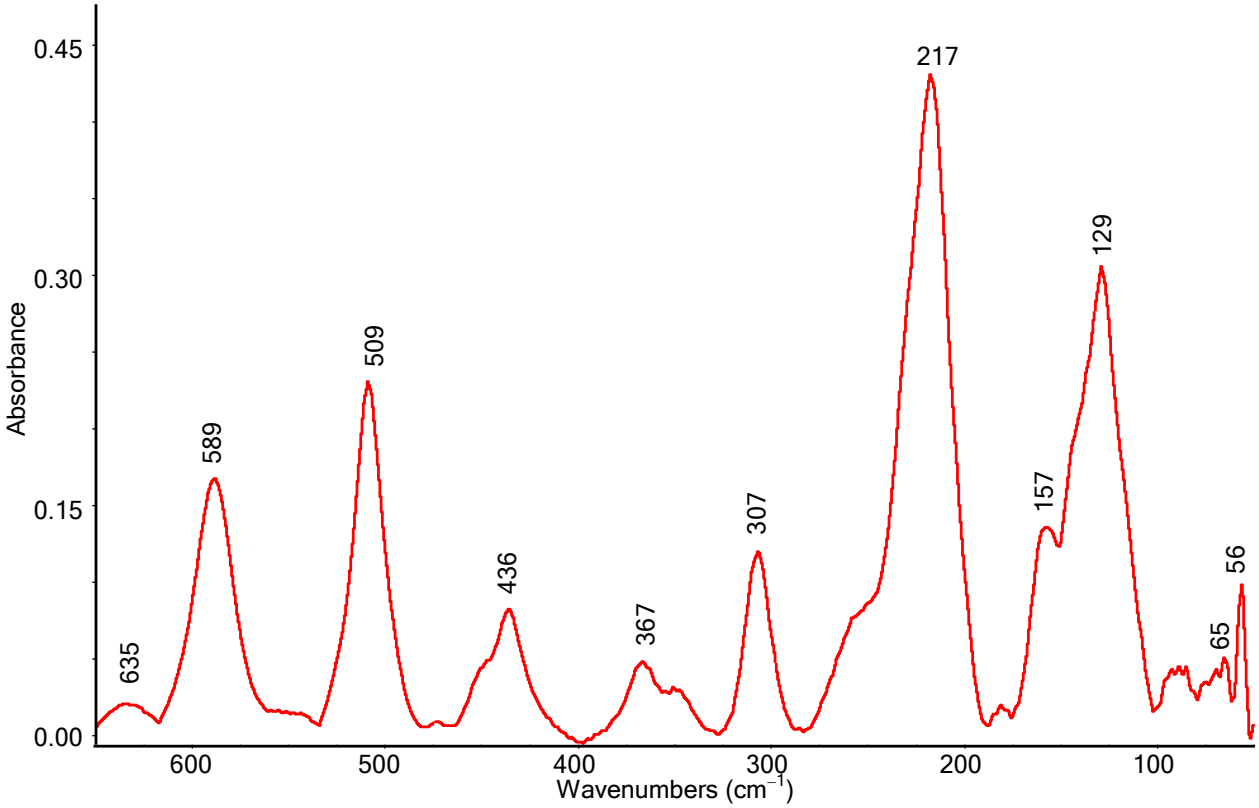

Figure S2-2. FIR spectrum of HoE(I) in the 650–50 cm^{-1} region

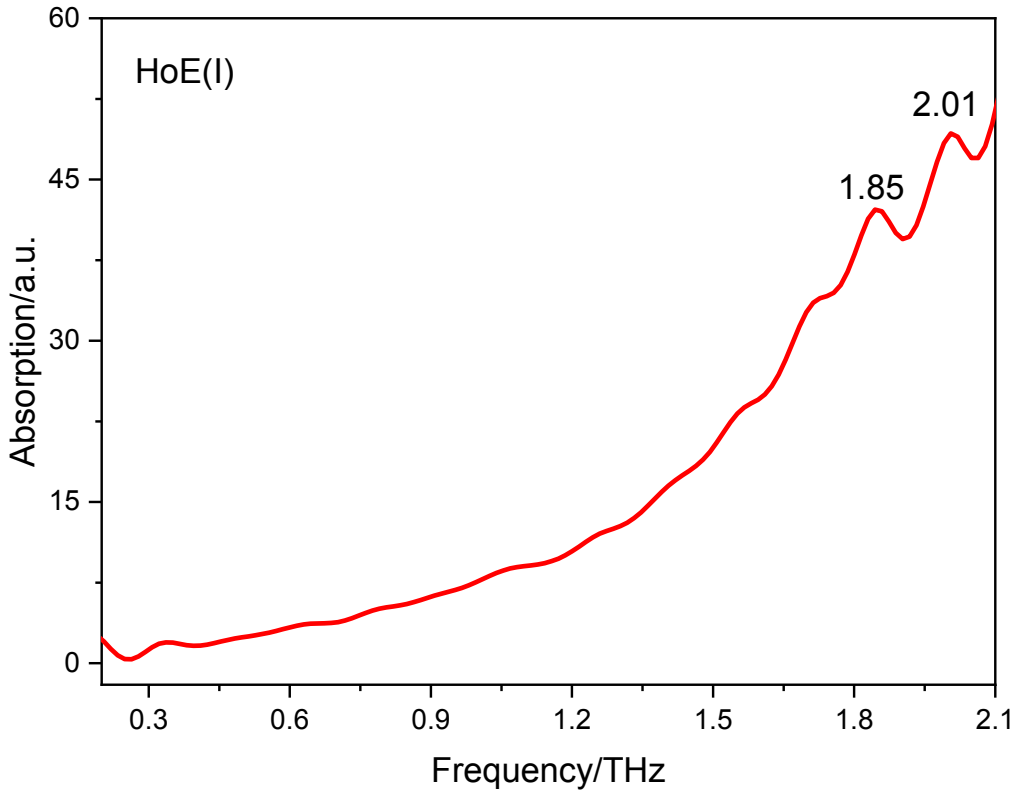

Figure S2-3. THz spectrum of HoE(I) in the 0.2–2.1 THz region

Part 3 Description of the structure of ErEN(I)

The ORTEP diagram of ErEN(I) is shown in **Figure S3-1**. The packing diagram is shown in **Figure S3-2**. Crystallographic data and structure refinement summary are listed in **Table S3-1**. Selected bond lengths and bond angles are listed in **Table S3-2**. Hydrogen bonds of the complex are listed in **Table S3-3**.

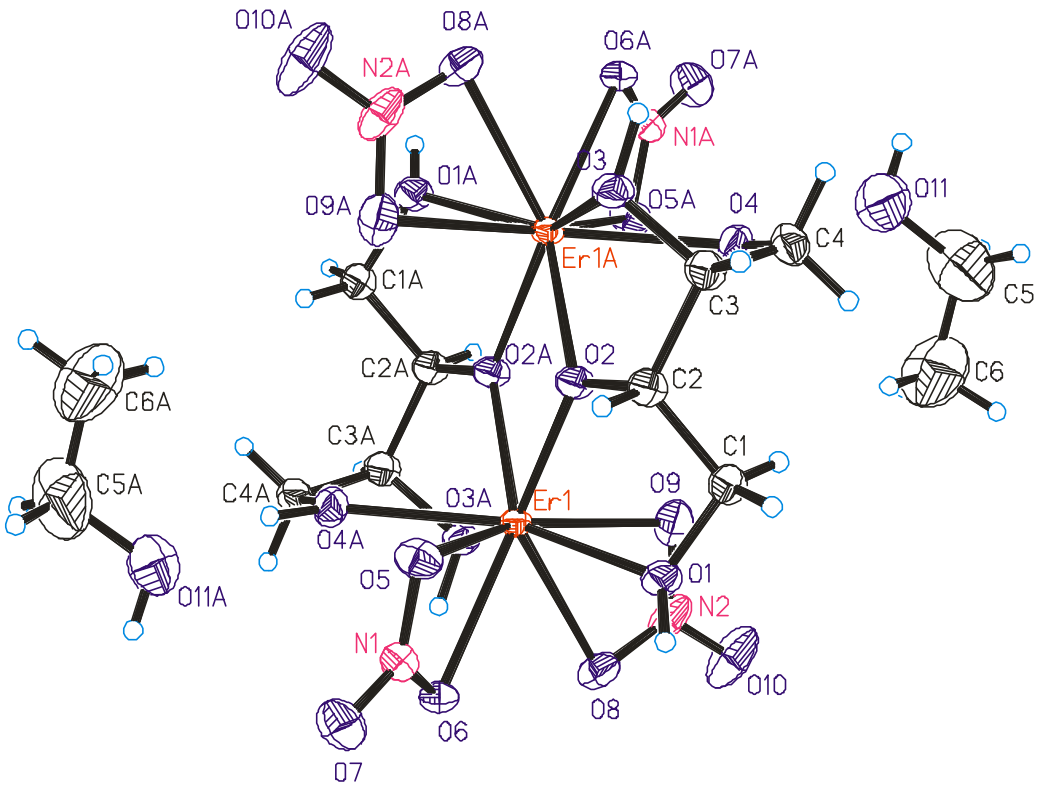

Figure S3-1. The ORTEP diagram of ErEN(I)

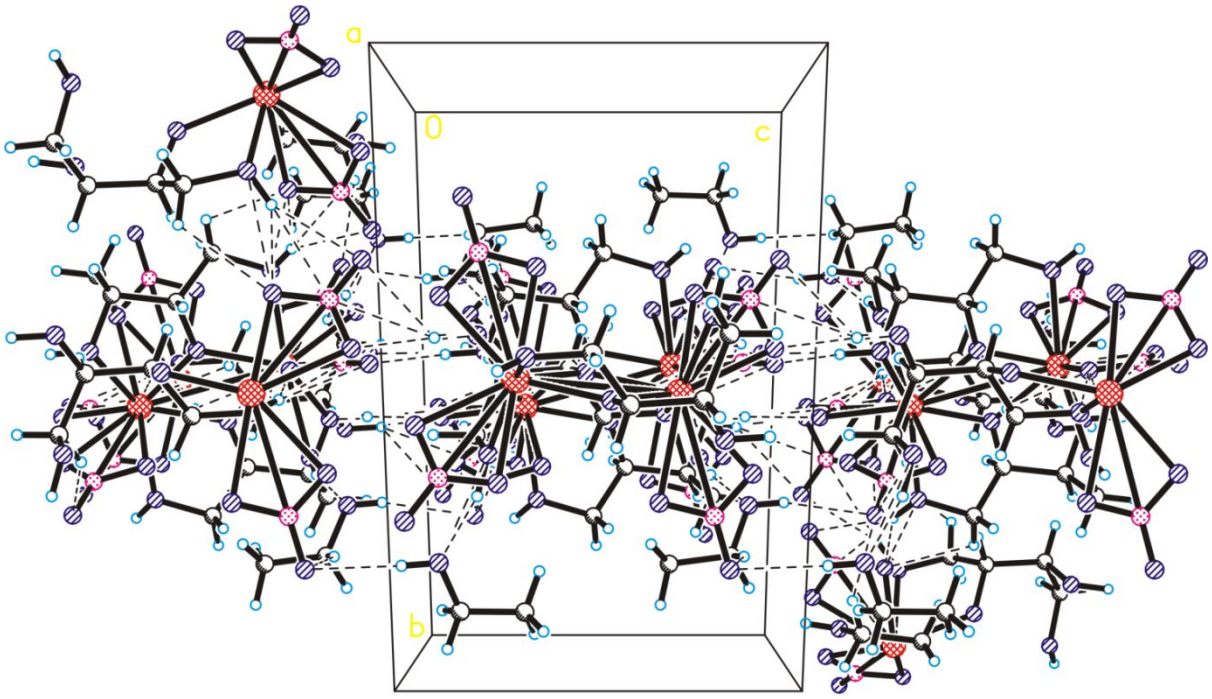

Figure S3-2. The packing diagram of ErEN(I)

Table S3-1. Crystallographic Data and Structure Refinement Summary for ErEN(I).

Identification code	ErEN(I)
CCDC No.	1974396
Formula	$C_{12}H_{30}Er_2N_4O_{22}$
formula weight	916.92
crystal system	trigonal
space group, Z	$P\bar{3}$, 3
a (Å)	16.0782(2)
b (Å)	16.0782(2)
c (Å)	9.3265(2)
α (deg)	90
β (deg)	90
γ (deg)	120
V (Å^3)	2087.97(7)
ρ_{calc} (g/cm^3)	2.188
μ (mm^{-1})	6.085
reflections collected	26740
data/restraints/parameters	3188/3/192
R(int)	0.0528
goodness of fit	1.086
$R_1[I>2\sigma(I)]$	0.0283
$wR_2[I>2\sigma(I)]$	0.0735
R_1(all data)	0.0315
wR_2 (all data)	0.0750

Table S3-2. Selected Bond Lengths and Bond Angles of the Complex ErEN(I).

Bond Lengths (Å)			
Er1–O2	2.207(3)	O3–C3	1.445(6)
Er1–O2[1]	2.234(3)	O3–Er1[1]	2.457(3)
Er1–O4[1]	2.381(3)	O4–C4	1.424(6)
Er1–O1	2.425(3)	O4–Er1[1]	2.381(3)
Er1–O8	2.434(3)	O5–N1	1.258(5)
Er1–O9	2.437(4)	O6–N1	1.254(5)
Er1–O3[1]	2.457(3)	O7–N1	1.225(5)
Er1–O6	2.485(3)	O8–N2	1.251(6)
Er1–O5	2.491(3)	O9–N2	1.272(6)
Er1–N2	2.834(4)	O10–N2	1.237(6)
Er1–N1	2.901(4)	C1–C2	1.513(7)
Er1–Er1[1]	3.6923(3)	C2–C3	1.543(6)
O1–C1	1.451(6)	C3–C4	1.497(8)
O2–C2	1.416(5)	O11–C5	1.369(12)
O2–Er1[1]	2.234(3)	C5–C6	1.433(15)
Bond Angles (°)			
O2–Er1–O2[1]	67.52(13)	O8–Er1–N1	93.56(11)
O2–Er1–O4[1]	108.53(13)	O9–Er1–N1	139.28(12)
O2[1]–Er1–O4[1]	74.62(12)	O3[1]–Er1–N1	116.54(11)
O2–Er1–O1	68.37(11)	O6–Er1–N1	25.46(10)
O2[1]–Er1–O1	129.36(11)	O5–Er1–N1	25.55(10)
O4[1]–Er1–O1	143.99(12)	N2–Er1–N1	117.22(13)
O2–Er1–O8	134.01(13)	O2–Er1–Er1[1]	33.99(8)
O2[1]–Er1–O8	123.46(12)	O2[1]–Er1–Er1[1]	33.53(8)
O4[1]–Er1–O8	117.46(13)	O4[1]–Er1–Er1[1]	91.69(9)
O1–Er1–O8	74.73(13)	O1–Er1–Er1[1]	99.39(8)
O2–Er1–O9	90.19(14)	O8–Er1–Er1[1]	138.49(9)
O2[1]–Er1–O9	83.27(13)	O9–Er1–Er1[1]	86.05(10)
O4[1]–Er1–O9	142.11(13)	O3[1]–Er1–Er1[1]	99.52(8)
O1–Er1–O9	73.23(12)	O6–Er1–Er1[1]	150.81(7)
O8–Er1–O9	52.65(13)	O5–Er1–Er1[1]	100.27(8)
O2–Er1–O3[1]	133.02(11)	N2–Er1–Er1[1]	112.50(11)
O2[1]–Er1–O3[1]	66.37(11)	N1–Er1–Er1[1]	125.57(8)
O4[1]–Er1–O3[1]	66.98(13)	C1–O1–Er1	113.7(2)
O1–Er1–O3[1]	142.48(12)	C2–O2–Er1	124.2(3)
O8–Er1–O3[1]	69.61(12)	C2–O2–Er1[1]	122.0(3)
O9–Er1–O3[1]	76.10(13)	Er1–O2–Er1[1]	112.48(13)
O2–Er1–O6	126.36(11)	C3–O3–Er1[1]	105.8(3)
O2[1]–Er1–O6	149.01(11)	C4–O4–Er1[1]	119.4(3)
O4[1]–Er1–O6	74.54(11)	N1–O5–Er1	95.7(2)
O1–Er1–O6	79.47(11)	N1–O6–Er1	96.1(2)
O8–Er1–O6	69.81(11)	N2–O8–Er1	95.1(3)
O9–Er1–O6	120.64(12)	N2–O9–Er1	94.4(3)
O3[1]–Er1–O6	98.47(10)	O7–N1–O6	121.8(4)
O2–Er1–O5	79.04(12)	O7–N1–O5	121.1(4)

O2[1]–Er1–O5	118.86(12)	O6–N1–O5	117.1(4)
O4[1]–Er1–O5	69.60(13)	O7–N1–Er1	177.1(3)
O1–Er1–O5	74.73(12)	O6–N1–Er1	58.4(2)
O8–Er1–O5	116.77(12)	O5–N1–Er1	58.7(2)
O9–Er1–O5	147.94(13)	O10–N2–O8	121.1(5)
O3[1]–Er1–O5	132.42(12)	O10–N2–O9	121.1(6)
O6–Er1–O5	50.99(10)	O8–N2–O9	117.8(4)
O2–Er1–N2	113.38(15)	O10–N2–Er1	179.6(5)
O2[1]–Er1–N2	103.91(13)	O8–N2–Er1	58.8(2)
O4[1]–Er1–N2	133.69(15)	O9–N2–Er1	59.0(2)
O1–Er1–N2	72.55(13)	O1–C1–C2	107.9(4)
O8–Er1–N2	26.08(14)	O2–C2–C1	107.0(4)
O9–Er1–N2	26.58(14)	O2–C2–C3	110.4(4)
O3[1]–Er1–N2	70.33(13)	C1–C2–C3	114.8(4)
O6–Er1–N2	95.14(13)	O3–C3–C4	107.5(4)
O5–Er1–N2	136.58(13)	O3–C3–C2	103.2(4)
O2–Er1–N1	103.18(11)	C4–C3–C2	114.5(4)
O2[1]–Er1–N1	137.42(12)	O4–C4–C3	108.3(4)
O4[1]–Er1–N1	69.39(11)	O11–C5–C6	113.9(9)
O1–Er1–N1	76.39(11)		

Symmetry transformations used to generate equivalent atoms: [1]1-X, 1-Y, 1-Z

Table S3-3. The Hydrogen Bond Data of the Complex ErEN(I).

D–H···A	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	∠D–H···A/°
O1–H1···O5[1]	0.95(2)	2.01(4)	2.854(5)	146(5)
O3–H3···O6[2]	0.953(19)	1.85(2)	2.798(4)	175(5)
O4–H4···O11	0.95(2)	1.68(3)	2.606(6)	164(6)
O11–H11···O10[2]	0.82	2.16	2.959(9)	164.2

[1]1-Y, +X-Y, +Z; [2]+X, +Y, -1+Z

Part 4 Spectroscopic study of ErEN(I)

The FTIR spectrum of ErEN(I) is shown in **Figure S4-1**. The FIR spectrum is shown in **Figure S4-2**. The THz spectrum is shown in **Figure S4-3**.

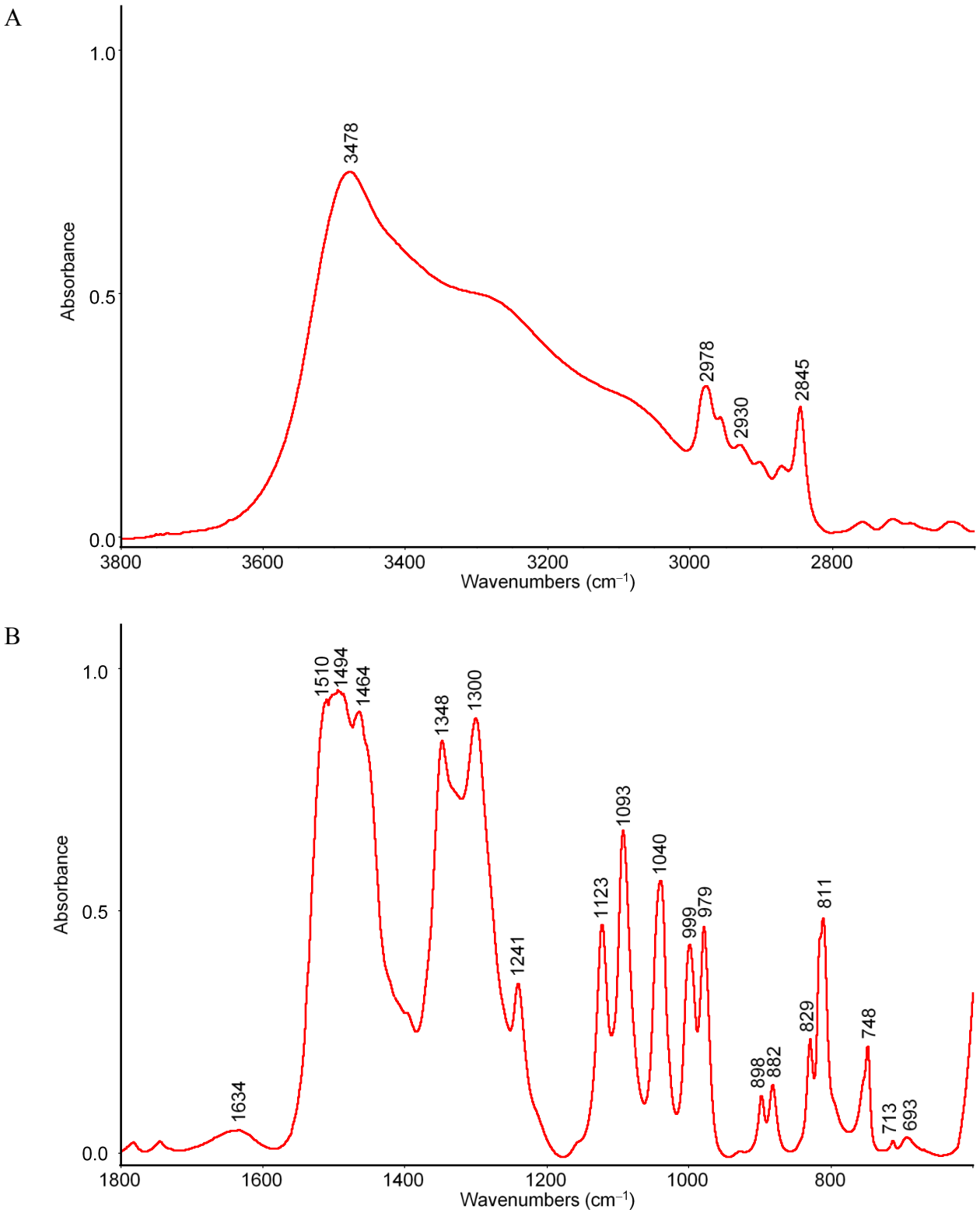

Figure S4-1. FTIR spectrum of ErEN(I) in the 3800–2600 (A) and 1800–600 cm^{-1} (B)

region

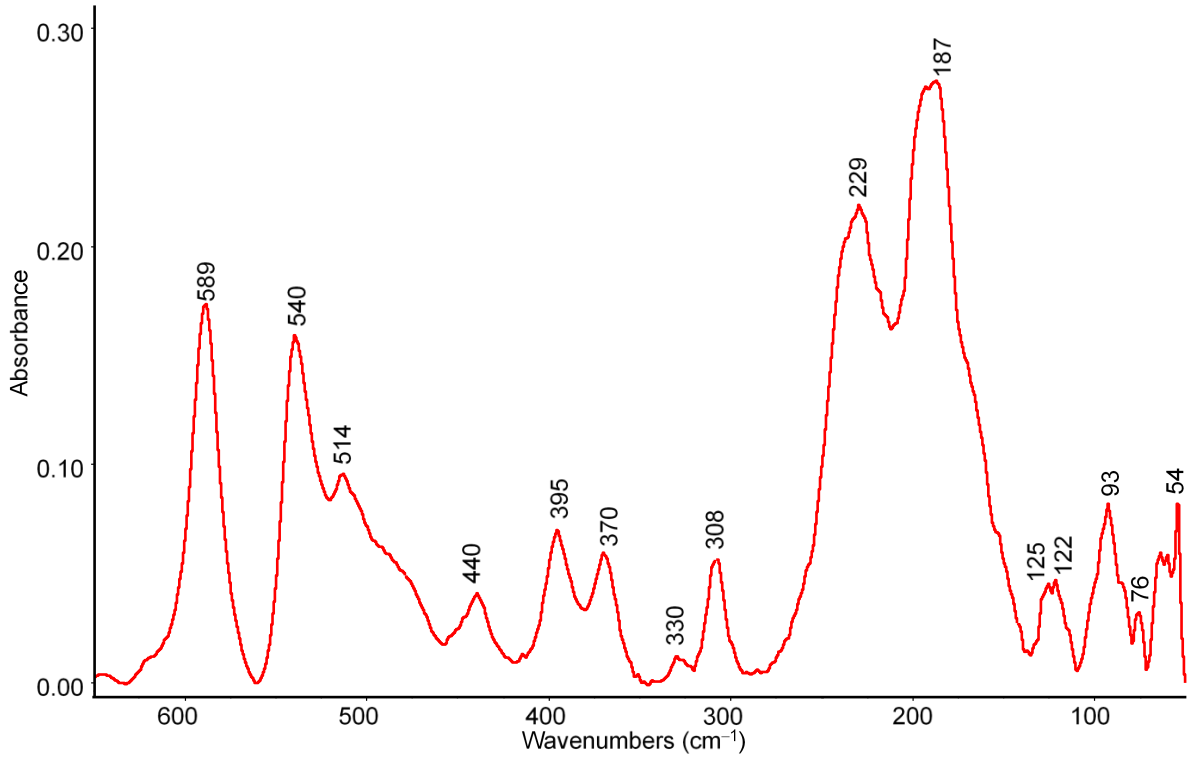

Figure S4-2. FIR spectrum of ErEN(I) in the 650–50 cm^{-1} region

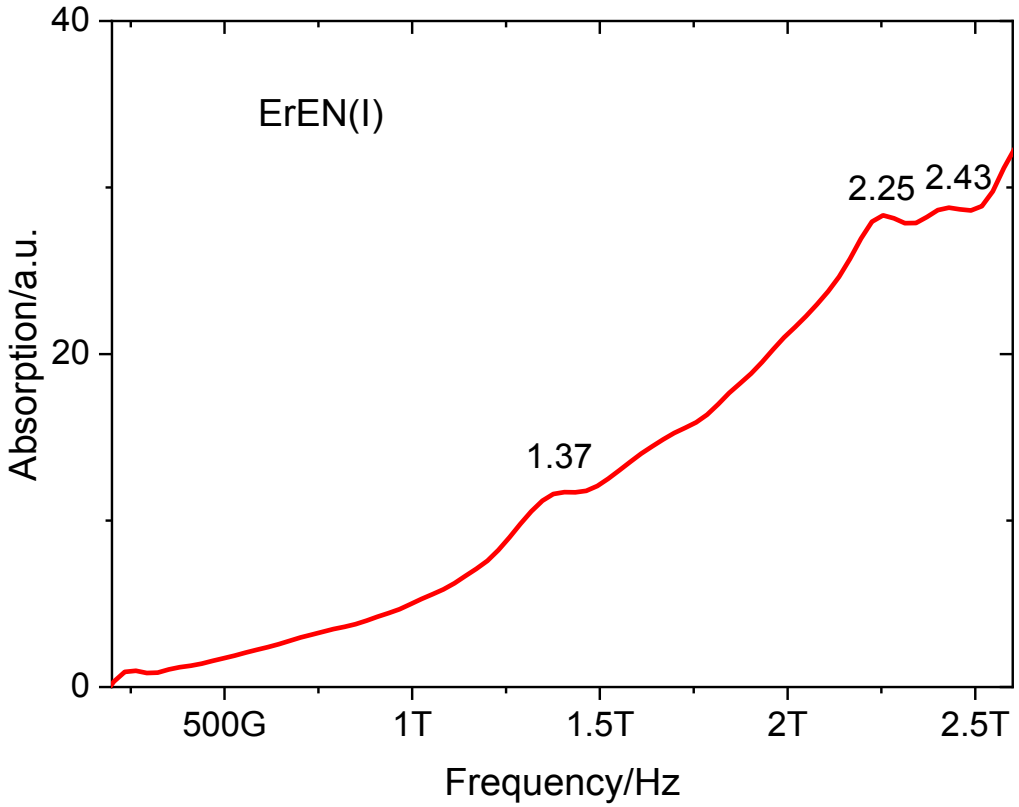

Figure S4-3. THz spectrum of ErEN(I) in the 0.2–2.6 THz region

Part 5 Description of the structure of DyE(I)

The ORTEP diagram of DyE(I) is shown in **Figure S5-1**. The packing diagram is shown in **Figure S5-2**. Crystallographic data and structure refinement summary are listed in **Table S5-1**. Selected bond lengths and bond angles are listed in **Table S5-2**. Hydrogen bonds of the complex are listed in **Table S5-3**.

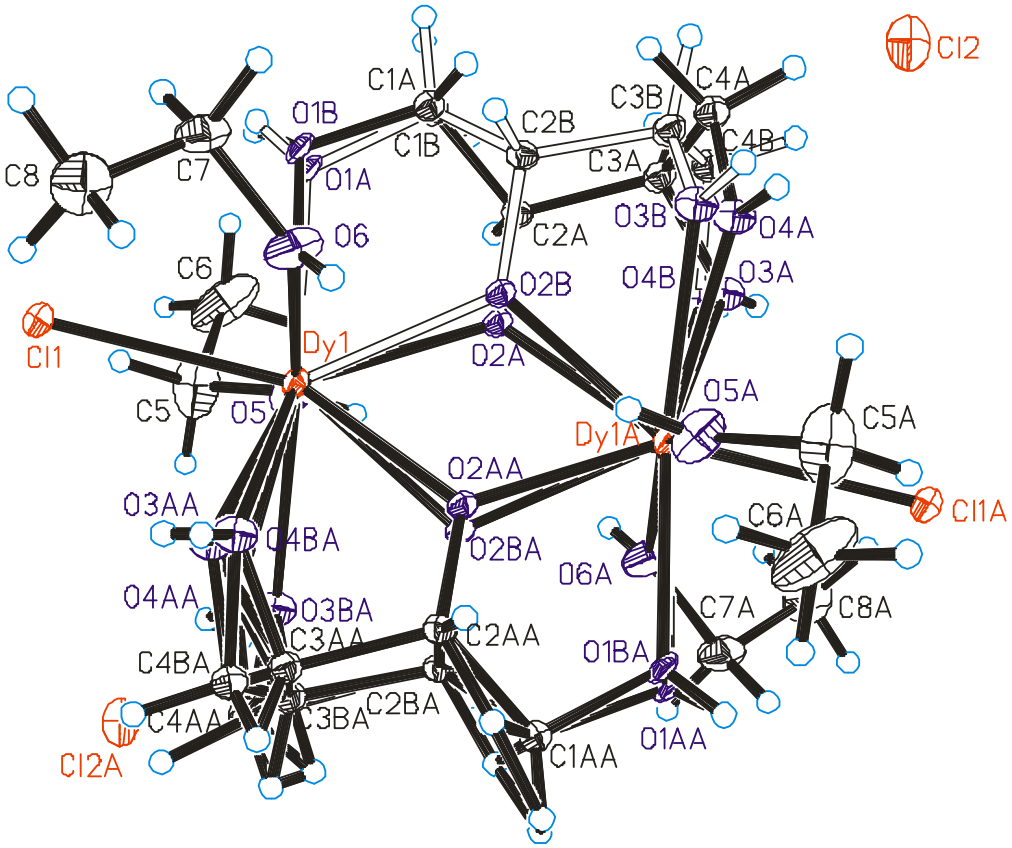

Figure S5-1. The ORTEP diagram of the complex DyE(I)

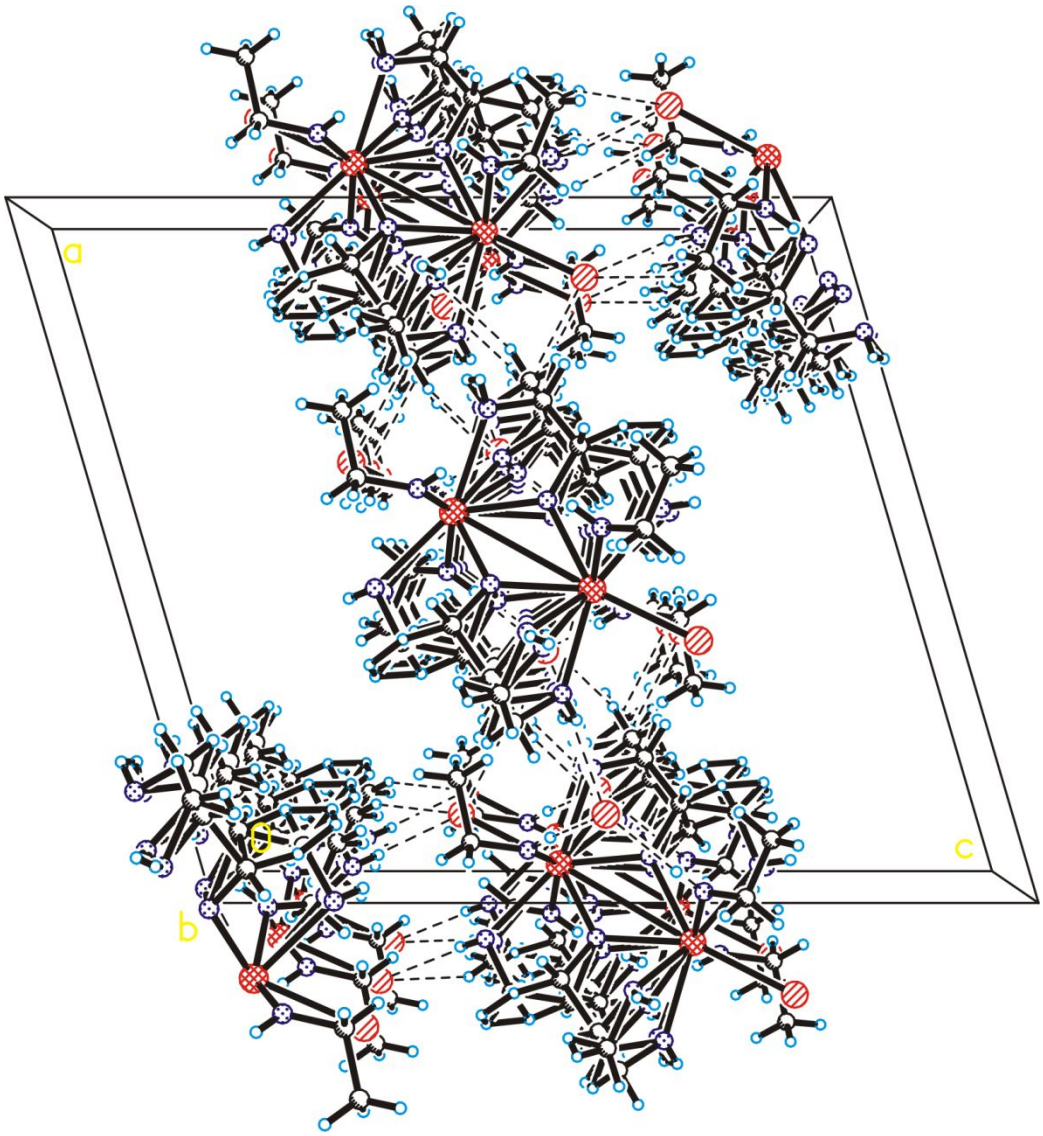

Figure S5-2. The packing diagram of DyE(I)

Table S5-1. Crystallographic Data and Structure Refinement Summary for DyE(I).

Identification code	DyE(I)
CCDC No.	1974394
Formula	$C_{16}H_{42}Cl_4Dy_2O_{12}$
formula weight	893.29
crystal system	monoclinic
space group, Z	*C2/c*, 4
a (Å)	17.1352(4)
b (Å)	9.3207(2)
c (Å)	19.2651(4)
α (deg)	90
β (deg)	106.356(2)
γ (deg)	90
V (Å^3)	2952.35(12)
ρ_{calc} (g/cm^3)	2.010
μ (mm^{-1})	5.435
reflections collected	18310
data/restraints/parameters	3382/124/199
R(int)	0.0333
goodness of fit	1.056
$R_1[I>2\sigma(I)]$	0.0175
$wR_2[I>2\sigma(I)]$	0.0410
R_1(all data)	0.0225
wR_2 (all data)	0.0419

Table S5-2. Selected Bond Lengths and Bond Angles of the Complex DyE(I).

Bond Lengths (Å)			
Dy1–O2B[1]	2.235(4)	O3A–C3A	1.424(8)
Dy1–O2A	2.255(3)	O3A–Dy1[1]	2.439(6)
Dy1–O2B	2.263(4)	O3B–C3B	1.406(11)
Dy1–O2A[1]	2.271(2)	O3B–Dy1[1]	2.490(8)
Dy1–O6	2.3693(19)	O4A–C4A	1.399(7)
Dy1–O1B	2.39(2)	O4A–Dy1[1]	2.393(5)
Dy1–O4A[1]	2.393(5)	O4B–C4B	1.474(10)
Dy1–O5	2.413(2)	O4B–Dy1[1]	2.521(10)
Dy1–O3A[1]	2.439(6)	O5–C5	1.449(4)
Dy1–O3B[1]	2.490(8)	O6–C7	1.441(3)
Dy1–O1A	2.505(14)	C1A–C2A	1.538(15)
Dy1–O4B[1]	2.521(10)	C1B–C2B	1.550(18)
O1A–C1A	1.434(11)	C2A–C3A	1.545(6)
O1B–C1B	1.450(17)	C2B–C3B	1.538(9)
O2A–C2A	1.409(4)	C3A–C4A	1.490(8)
O2A–Dy1[1]	2.271(2)	C3B–C4B	1.500(12)
O2B–C2B	1.414(7)	C5–C6	1.469(6)
O2B–Dy1[1]	2.235(4)	C7–C8	1.491(5)
Bond Angles (°)			
O2B[1]–Dy1–O2B	65.47(18)	O6–Dy1–O4B[1]	69.24(19)
O2A–Dy1–O2A[1]	66.54(11)	O1B–Dy1–O4B[1]	146.5(5)
O2B[1]–Dy1–O6	107.74(12)	O5–Dy1–O4B[1]	139.56(15)
O2A–Dy1–O6	94.99(9)	O3B[1]–Dy1–O4B[1]	72.4(3)
O2B–Dy1–O6	72.88(13)	C1A–O1A–Dy1	111.4(9)
O2A[1]–Dy1–O6	85.41(9)	C1B–O1B–Dy1	118.1(16)
O2B[1]–Dy1–O1B	127.5(5)	C2A–O2A–Dy1	122.4(2)
O2B–Dy1–O1B	67.6(6)	C2A–O2A–Dy1[1]	123.2(2)
O6–Dy1–O1B	79.0(4)	Dy1–O2A–Dy1[1]	113.46(11)
O2A–Dy1–O4A[1]	115.43(11)	C2B–O2B–Dy1[1]	123.2(3)
O2A[1]–Dy1–O4A[1]	78.18(14)	C2B–O2B–Dy1	122.2(3)
O6–Dy1–O4A[1]	134.98(11)	Dy1[1]–O2B–Dy1	114.53(18)
O2B[1]–Dy1–O5	93.52(13)	C3A–O3A–Dy1[1]	108.7(5)
O2A–Dy1–O5	75.83(9)	C3B–O3B–Dy1[1]	105.9(6)
O2B–Dy1–O5	97.63(13)	C4A–O4A–Dy1[1]	124.1(4)
O2A[1]–Dy1–O5	115.83(9)	C4B–O4B–Dy1[1]	114.2(6)
O6–Dy1–O5	149.42(7)	C5–O5–Dy1	133.41(19)
O1B–Dy1–O5	70.6(5)	C7–O6–Dy1	132.93(16)
O4A[1]–Dy1–O5	73.67(12)	O1A–C1A–C2A	113.5(12)
O2A–Dy1–O3A[1]	132.14(16)	O1B–C1B–C2B	107.7(19)
O2A[1]–Dy1–O3A[1]	66.05(17)	O2A–C2A–C1A	107.9(7)
O6–Dy1–O3A[1]	75.23(13)	O2A–C2A–C3A	109.1(3)
O4A[1]–Dy1–O3A[1]	59.77(18)	C1A–C2A–C3A	112.9(7)
O5–Dy1–O3A[1]	132.31(11)	O2B–C2B–C3B	108.8(6)
O2B[1]–Dy1–O3B[1]	57.2(2)	O2B–C2B–C1B	105.5(11)
O2B–Dy1–O3B[1]	119.12(19)	C3B–C2B–C1B	113.7(11)

O6–Dy1–O3B[1]	141.52(17)	O3A–C3A–C4A	105.5(5)
O1B–Dy1–O3B[1]	139.3(5)	O3A–C3A–C2A	105.0(4)
O5–Dy1–O3B[1]	68.70(18)	C4A–C3A–C2A	115.9(4)
O2A–Dy1–O1A	69.6(3)	O3B–C3B–C4B	126.0(9)
O2A[1]–Dy1–O1A	128.0(3)	O3B–C3B–C2B	85.3(6)
O6–Dy1–O1A	71.8(3)	C4B–C3B–C2B	115.5(7)
O4A[1]–Dy1–O1A	148.1(3)	O4A–C4A–C3A	105.5(5)
O5–Dy1–O1A	77.7(3)	O4B–C4B–C3B	110.3(9)
O3A[1]–Dy1–O1A	142.1(3)	O5–C5–C6	112.9(4)
O2B[1]–Dy1–O4B[1]	74.1(3)	O6–C7–C8	111.2(3)
O2B–Dy1–O4B[1]	110.8(2)		

Symmetry transformations used to generate equivalent atoms: [1]1-X, 1-Y, 1-Z

Table S5-3. The Hydrogen Bond Data of the Complex DyE(I).

D–H···A	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	∠D–H···A/°
O1A–H1A···Cl1[1]	0.82(2)	2.35(5)	3.116(16)	156(10)
O1B–H1B···Cl1[1]	0.82(2)	2.34(7)	3.13(3)	163(20)
O3A–H3A···Cl2[2]	0.809(19)	2.35(3)	3.132(8)	162(6)
O3B–H3B···Cl2	0.82(2)	2.24(3)	3.051(10)	172(8)
O4A–H4A···Cl2	0.821(19)	2.27(3)	3.070(6)	163(6)
O4B–H4B···Cl2[2]	0.81(2)	2.38(4)	3.098(13)	148(7)
O5–H5···Cl2[3]	0.791(18)	2.34(2)	3.109(2)	163(3)
O6–H6···Cl2[4]	0.789(18)	2.288(19)	3.063(2)	167(3)

[1]1-X, +Y, 3/2-Z; [2]3/2-X, 1/2-Y, 1-Z; [3]+X, 1+Y, +Z; [4]1-X, -Y, 1-Z

Part 6 Spectroscopic study of DyE(I)

The FTIR spectrum of DyE(I) is shown in **Figure S6-1**.

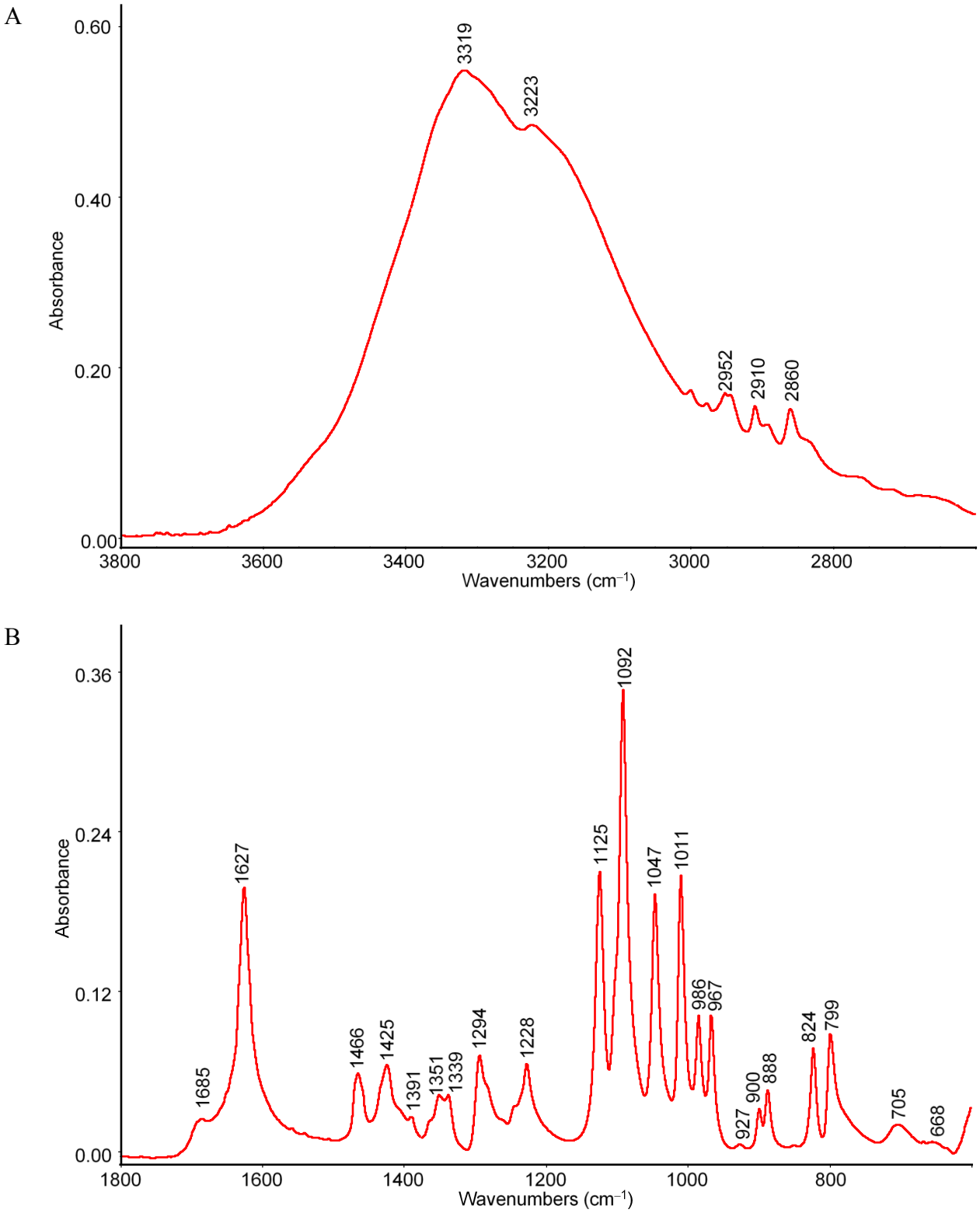

Figure S6-1. FTIR spectrum of DyE(I) in the 3800–2600 (A) and 1800–600 cm^{-1} (B) region

Part 7 Description of the structure of TbE(II)

The ORTEP diagram of TbE(II) is shown in **Figure S7-1**. The packing diagram is shown in **Figure S7-2**. Crystallographic data and structure refinement summary are listed in **Table S7-1**. Selected bond lengths and bond angles are listed in **Table S7-2**. Hydrogen bonds of the complex are listed in **Table S7-3**.

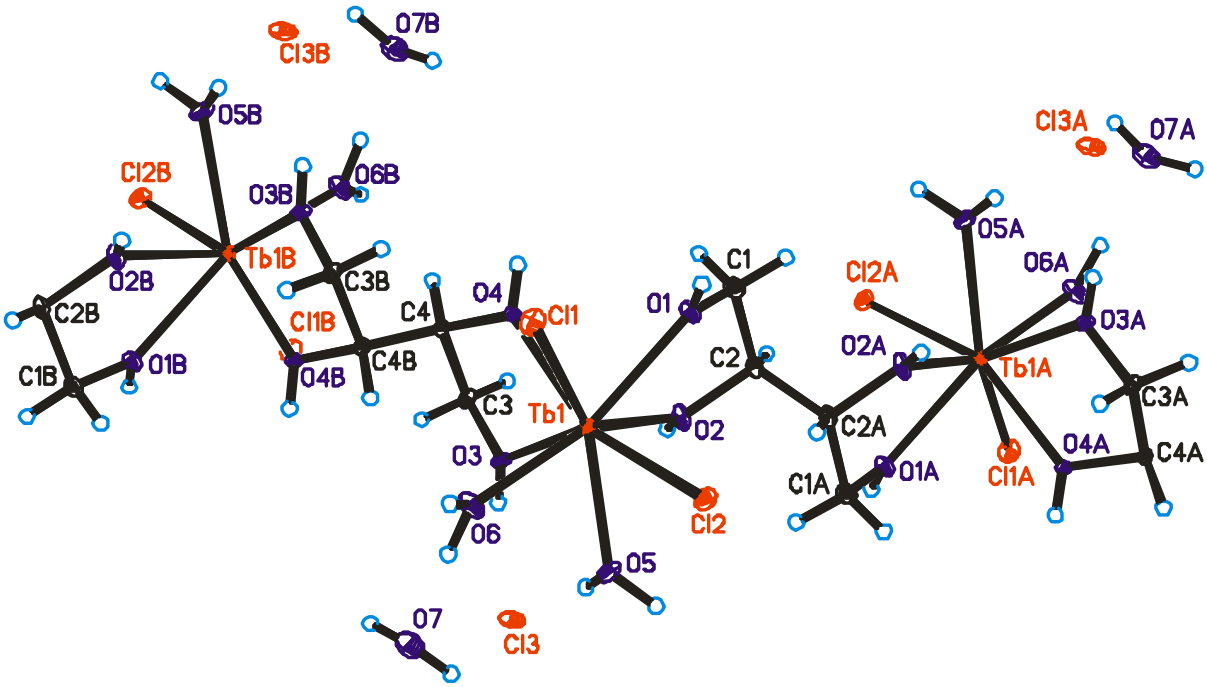

Figure S7-1. The ORTEP diagram of TbE(II)

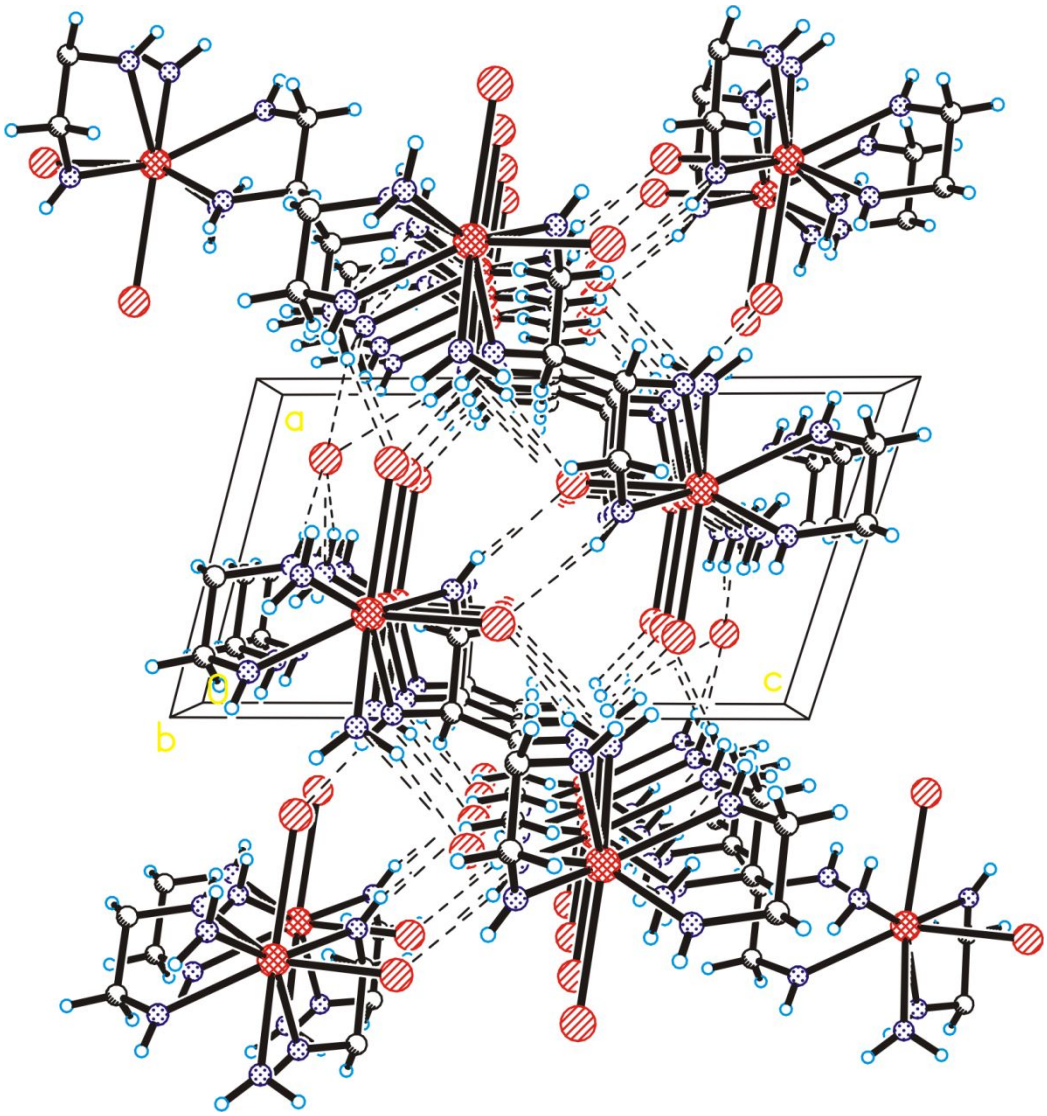

Figure S7-2. The packing diagram of TbE(II)

Table S7-1. Crystallographic Data and Structure Refinement Summary for TbE(II).

Identification code	TbE(II)
CCDC No.	1974397
Formula	$C_4H_{16}Cl_3O_7Tb$
formula weight	441.44
crystal system	triclinic
space group, Z	$P\bar{1}$, 2
a (Å)	7.3881(2)
b (Å)	8.0296(2)
c (Å)	12.5100(3)
α (deg)	85.869(2)
β (deg)	73.473(2)
γ (deg)	66.780(2)
V (Å^3)	653.17(3)
ρ_{calc} (g/cm^3)	2.245
μ (mm^{-1})	6.038
reflections collected	8006
data/restraints/parameters	3259/13/166
R(int)	0.0188
goodness of fit	1.042
$R_1[I>2\sigma(I)]$	0.0161
$wR_2[I>2\sigma(I)]$	0.0408
R_1(all data)	0.0166
wR_2 (all data)	0.0410

Table S7-2. Selected Bond Lengths and Bond Angles of the Complex TbE(II).

Bond Lengths (Å)			
Tb1–O6	2.3227(16)	O1–C1	1.439(3)
Tb1–O4	2.3837(15)	O2–C2	1.439(3)
Tb1–O1	2.3955(16)	O3–C3	1.442(3)
Tb1–O2	2.4123(15)	O4–C4	1.446(2)
Tb1–O5	2.4204(16)	C1–C2	1.515(3)
Tb1–O3	2.4260(15)	C2–C2[1]	1.535(4)
Tb1–Cl2	2.6959(6)	C3–C4	1.508(3)
Tb1–Cl1	2.7578(5)	C4–C4[2]	1.535(4)
Bond Angles (°)			
O6–Tb1–O4	99.77(6)	O3–Tb1–Cl2	143.06(4)
O6–Tb1–O1	150.34(6)	O6–Tb1–Cl1	75.57(4)
O4–Tb1–O1	77.40(6)	O4–Tb1–Cl1	75.09(4)
O6–Tb1–O2	145.70(6)	O1–Tb1–Cl1	75.20(4)
O4–Tb1–O2	86.92(6)	O2–Tb1–Cl1	138.11(4)
O1–Tb1–O2	63.96(5)	O5–Tb1–Cl1	143.45(5)
O6–Tb1–O5	75.21(6)	O3–Tb1–Cl1	124.10(4)
O4–Tb1–O5	131.46(6)	Cl2–Tb1–Cl1	84.897(18)
O1–Tb1–O5	128.82(6)	C1–O1–Tb1	122.75(13)
O2–Tb1–O5	75.31(6)	C2–O2–Tb1	122.77(12)
O6–Tb1–O3	76.78(6)	C3–O3–Tb1	122.78(12)
O4–Tb1–O3	63.12(5)	C4–O4–Tb1	123.06(12)
O1–Tb1–O3	124.93(6)	O1–C1–C2	106.70(18)
O2–Tb1–O3	76.53(5)	O2–C2–C1	106.11(18)
O5–Tb1–O3	68.87(6)	O2–C2–C2[1]	108.0(2)
O6–Tb1–Cl2	91.30(5)	C1–C2–C2[1]	113.6(2)
O4–Tb1–Cl2	153.75(4)	O3–C3–C4	105.66(16)
O1–Tb1–Cl2	81.23(4)	O4–C4–C3	104.73(16)
O2–Tb1–Cl2	97.26(4)	O4–C4–C4[2]	108.9(2)
O5–Tb1–Cl2	74.32(4)	C3–C4–C4[2]	113.1(2)

Symmetry transformations used to generate equivalent atoms: [1]-X, 1-Y, 1-Z; [2]1-X, 1-Y, -Z

Table S7-3. The Hydrogen Bond Data of the Complex TbE(II).

D–H···A	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	∠D–H···A/°
O1–H1···Cl2[1]	0.759(17)	2.392(19)	3.1136(17)	159(3)
O2–H2···Cl1[2]	0.811(17)	2.240(19)	3.0162(16)	160(3)
O3–H3···Cl3	0.797(17)	2.242(18)	3.0301(16)	170(3)
O4–H4···Cl3[3]	0.814(17)	2.236(18)	3.0420(16)	171(3)
O5–H5A···Cl2[4]	0.920(16)	2.209(19)	3.0912(18)	160(2)
O5–H5B···Cl3	0.906(16)	2.280(16)	3.1779(18)	171(3)
O6–H6A···Cl3[5]	0.920(16)	2.25(2)	3.1237(17)	157(2)
O6–H6B···O7	0.927(16)	1.758(16)	2.684(3)	178(3)
O7–H7A···Cl1[6]	0.929(17)	2.81(2)	3.560(2)	139(2)
O7–H7A···Cl3	0.929(17)	2.83(3)	3.435(2)	124(2)
O7–H7B···Cl3[7]	0.957(17)	2.378(17)	3.318(2)	167(3)

[1]1-X, 1-Y, 1-Z; [2]-1+X, +Y, +Z; [3]1+X, -1+Y, +Z; [4]-X, 2-Y, 1-Z; [5]1+X, +Y, +Z; [6]-1+X, 1+Y, +Z; [7]-X, 2-Y, -Z

Part 8 Spectroscopic study of TbE(II)

The FTIR spectrum of TbE(II) is shown in **Figure S8-1**.

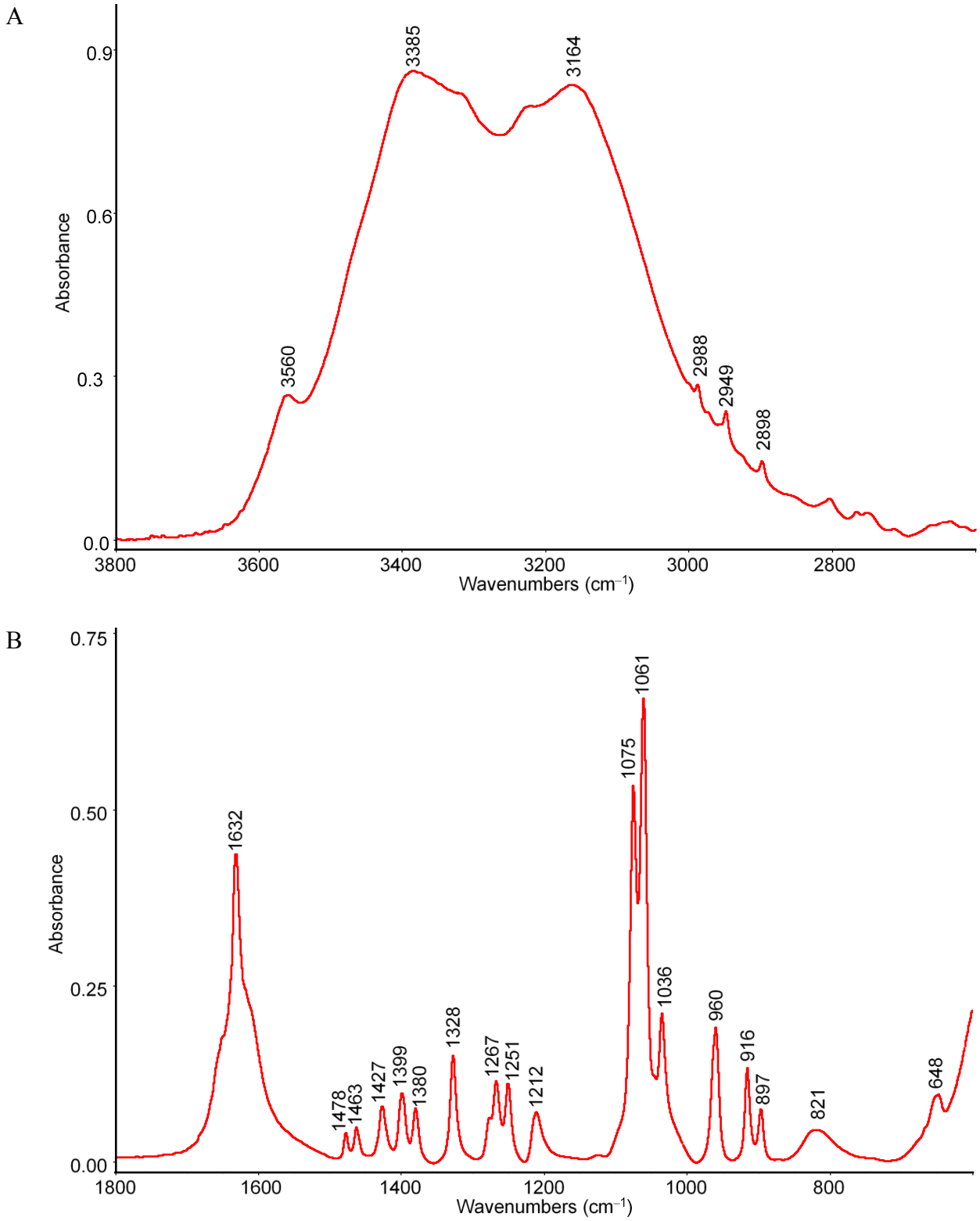

Figure S8-1. FTIR spectrum of TbE(II) in the 3800–2600 (A) and 1800–600 cm^{-1} (B) region

Part 9 Description of the structure of DyE(II)

The ORTEP diagram of DyE(II) is shown in **Figure S9-1**. The packing diagram is shown in **Figure S9-2**. Crystallographic data and structure refinement summary are listed in **Table S9-1**. Selected bond lengths and bond angles are listed in **Table S9-2**. Hydrogen bonds of the complex are listed in **Table S9-3**.

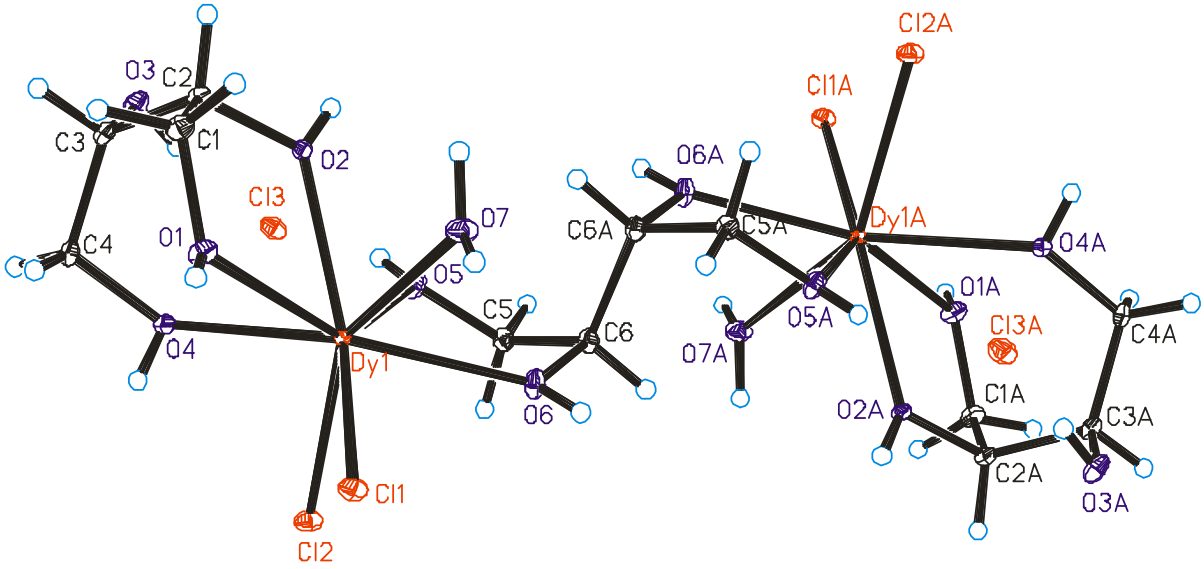

Figure S9-1. The ORTEP diagrams of the complex DyE(II)

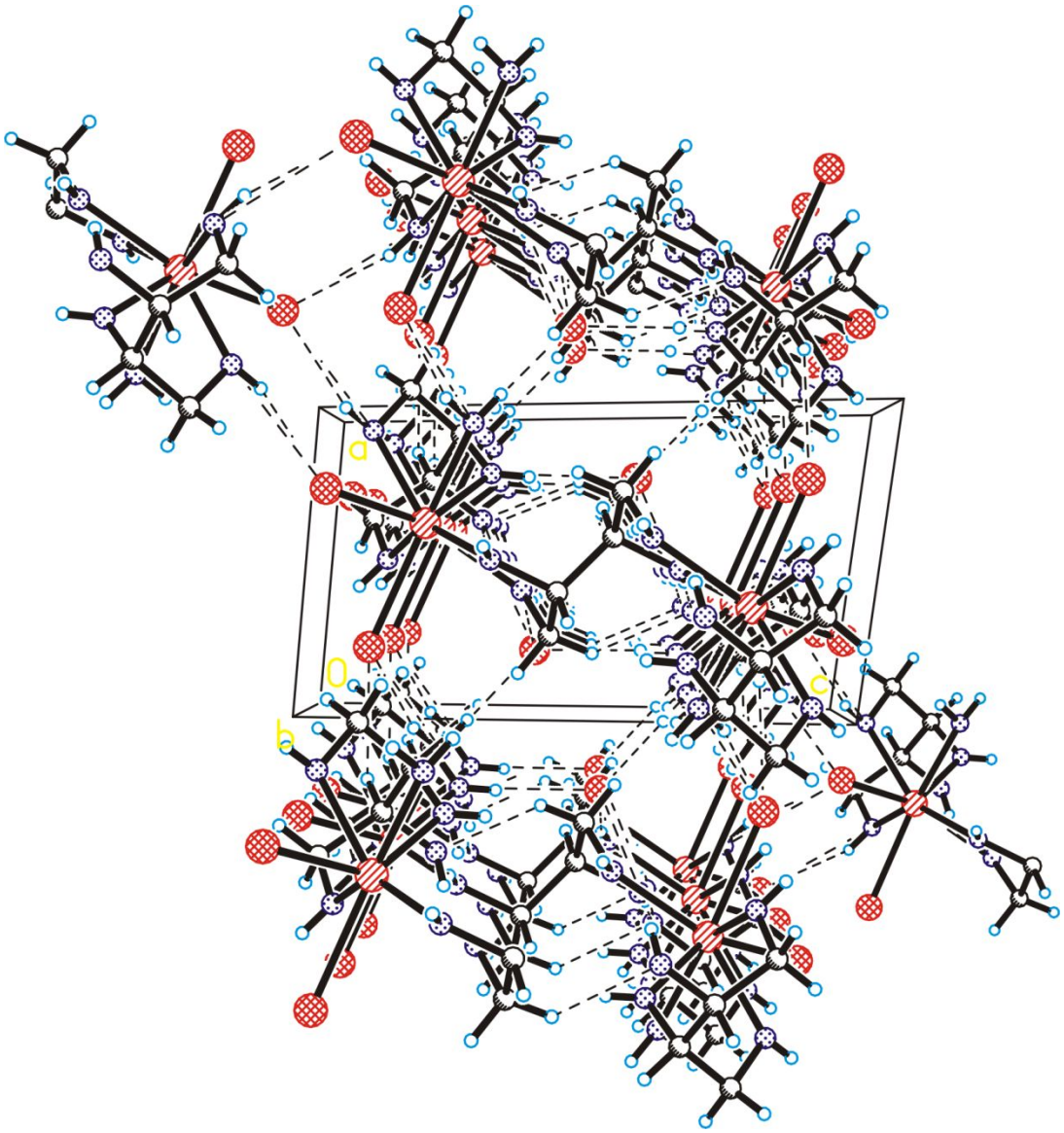

Figure S9-2. The packing diagram of the complex DyE(II)

Table S9-1. Crystallographic Data and Structure Refinement Summary for DyE(II).

Identification code	DyE(II)
CCDC No.	1974392
Formula	$C_{12}H_{34}Cl_6Dy_2O_{14}$
formula weight	940.09
crystal system	triclinic
space group, Z	$P\bar{1}$, 1
a (Å)	7.11360(10)
b (Å)	8.7233(2)
c (Å)	12.4902(2)
α (deg)	70.093(2)
β (deg)	76.583(2)
γ (deg)	66.910(2)
V (Å^3)	666.01(2)
ρ_{calc} (g/cm^3)	2.344
μ (mm^{-1})	6.228
reflections collected	7562
data/restraints/parameters	3062/9/186
R(int)	0.0154
goodness of fit	1.010
$R_1[I>2\sigma(I)]$	0.0140
$wR_2[I>2\sigma(I)]$	0.0364
R_1(all data)	0.0144
wR_2 (all data)	0.0366

Table S9-2. Selected Bond Lengths and Bond Angles of the Complex DyE(II).

Bond Lengths (Å)			
Dy1–O2	2.3582(15)	O3–C3	1.428(3)
Dy1–O5	2.3758(16)	O4–C4	1.448(3)
Dy1–O1	2.3979(16)	O5–C5	1.437(3)
Dy1–O6	2.4062(15)	O6–C6	1.448(3)
Dy1–O7	2.4195(16)	C1–C2	1.521(3)
Dy1–O4	2.4400(16)	C2–C3	1.532(3)
Dy1–Cl1	2.6707(5)	C3–C4	1.517(3)
Dy1–Cl2	2.6940(6)	C5–C6	1.509(3)
O1–C1	1.442(3)	C6–C6[1]	1.541(4)
O2–C2	1.440(3)		
Bond Angles (°)			
O2–Dy1–O5	69.71(5)	O1–Dy1–Cl2	124.53(4)
O2–Dy1–O1	65.64(5)	O6–Dy1–Cl2	82.93(4)
O5–Dy1–O1	134.23(5)	O7–Dy1–Cl2	148.67(4)
O2–Dy1–O6	113.27(5)	O4–Dy1–Cl2	71.46(4)
O5–Dy1–O6	64.19(5)	Cl1–Dy1–Cl2	82.608(17)
O1–Dy1–O6	145.29(6)	C1–O1–Dy1	121.28(13)
O2–Dy1–O7	75.21(6)	C2–O2–Dy1	120.56(12)
O5–Dy1–O7	102.93(6)	C4–O4–Dy1	128.44(13)
O1–Dy1–O7	75.19(6)	C5–O5–Dy1	119.72(13)
O6–Dy1–O7	71.39(6)	C6–O6–Dy1	121.85(13)
O2–Dy1–O4	70.70(5)	O1–C1–C2	106.68(18)
O5–Dy1–O4	85.30(5)	O2–C2–C1	106.51(17)
O1–Dy1–O4	71.24(5)	O2–C2–C3	109.23(17)
O6–Dy1–O4	143.08(5)	C1–C2– C3	114.18(18)
O7–Dy1–O4	139.47(6)	O3–C3–C4	112.12(19)
O2–Dy1–Cl1	139.33(4)	O3–C3–C2	108.81(18)
O5–Dy1–Cl1	147.08(4)	C4–C3–C2	115.91(19)
O1–Dy1–Cl1	78.32(4)	O4–C4–C3	110.63(18)
O6–Dy1–Cl1	85.78(4)	O5–C5–C6	104.98(17)
O7–Dy1–Cl1	78.01(4)	O6–C6–C5	104.39(17)
O4–Dy1–Cl1	115.72(4)	O6–C6–C6[1]	109.6(2)
O2–Dy1–Cl2	133.15(4)	C5–C6–C6[1]	113.2(2)
O5–Dy1–Cl2	80.68(4)		

Symmetry transformations used to generate equivalent atoms: [1]1-X, 1-Y, 1-Z

Table S9-3. The Hydrogen Bond Data of the Complex DyE(II).

D–H···A	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	∠D–H···A/°
O1–H1···Cl1[1]	0.811(18)	2.33(2)	3.0870(17)	156(3)
O2–H2···Cl3[2]	0.792(18)	2.206(18)	2.9918(16)	172(3)
O3–H3···Cl3	0.795(17)	2.36(2)	3.1055(18)	156(3)
O4–H4···Cl1[3]	0.791(18)	2.48(2)	3.2109(17)	155(3)
O5–H5···Cl3	0.810(17)	2.204(19)	2.9931(17)	164(3)
O6–H6···O3[4]	0.828(18)	1.834(18)	2.661(2)	177(4)
O7–H7A···Cl3[5]	0.904(17)	2.211(18)	3.1132(18)	176(3)
O7–H7B···Cl2[5]	0.928(17)	2.31(2)	3.2078(18)	162(3)

[1]2-X, 1-Y, -Z; [2]1-X, -Y, 1-Z; [3]1-X, 1-Y, -Z; [4]+X, 1+Y, +Z; [5]1+X, +Y, +Z

Part 10 Spectroscopic study of DyE(II)

The FTIR spectrum of DyE(II) is shown in **Figure S10-1**. The FIR spectrum is shown in **Figure S10-2**. The THz spectrum is shown in **Figure S10-3**.

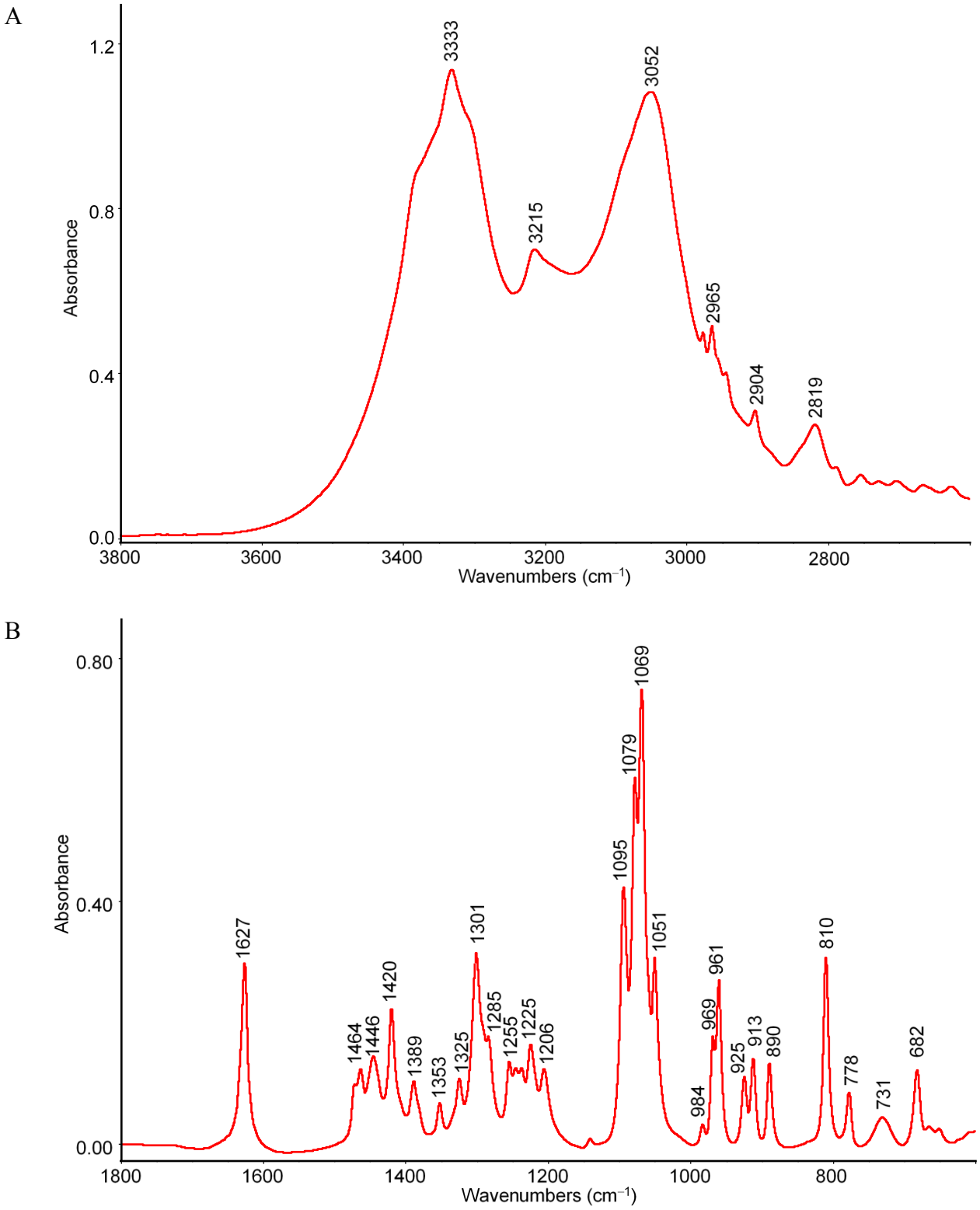

Figure S10-1. FTIR spectrum of DyE(II) in the 3800–2600 (A) and 1800–600 cm^{-1} (B)

region

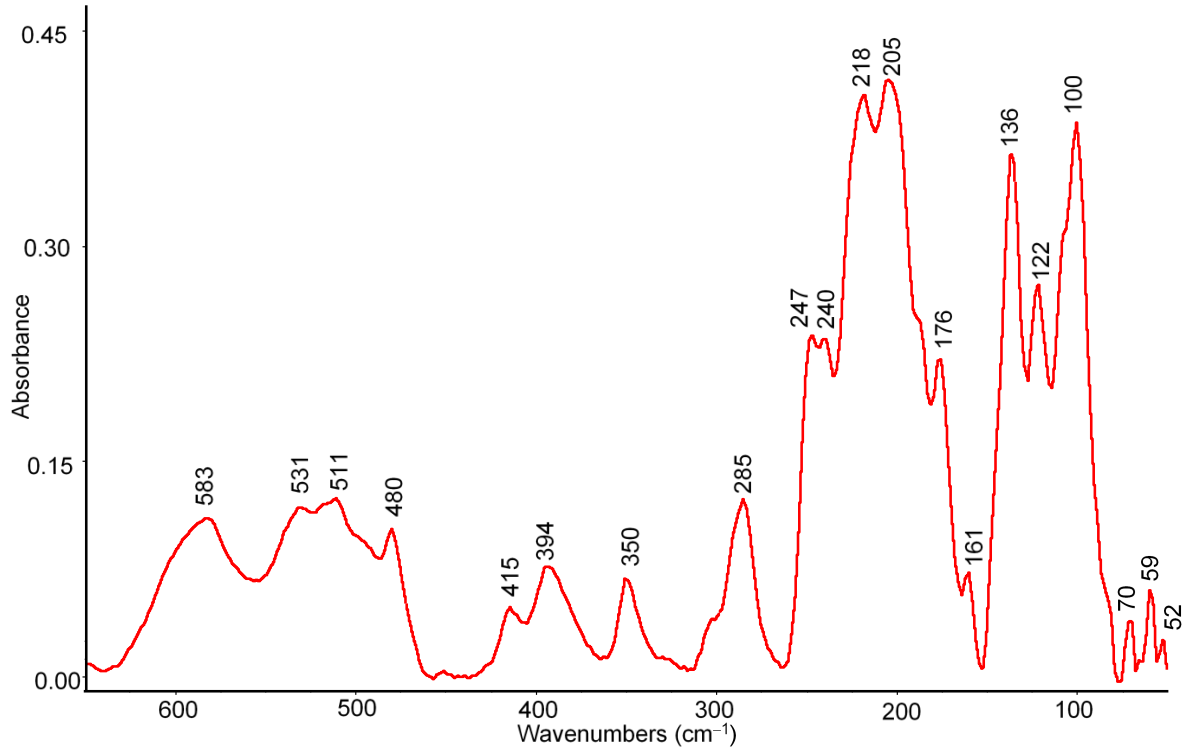

Figure S10-2. FIR spectrum of DyE(II) in the 650–50 cm^{-1} region

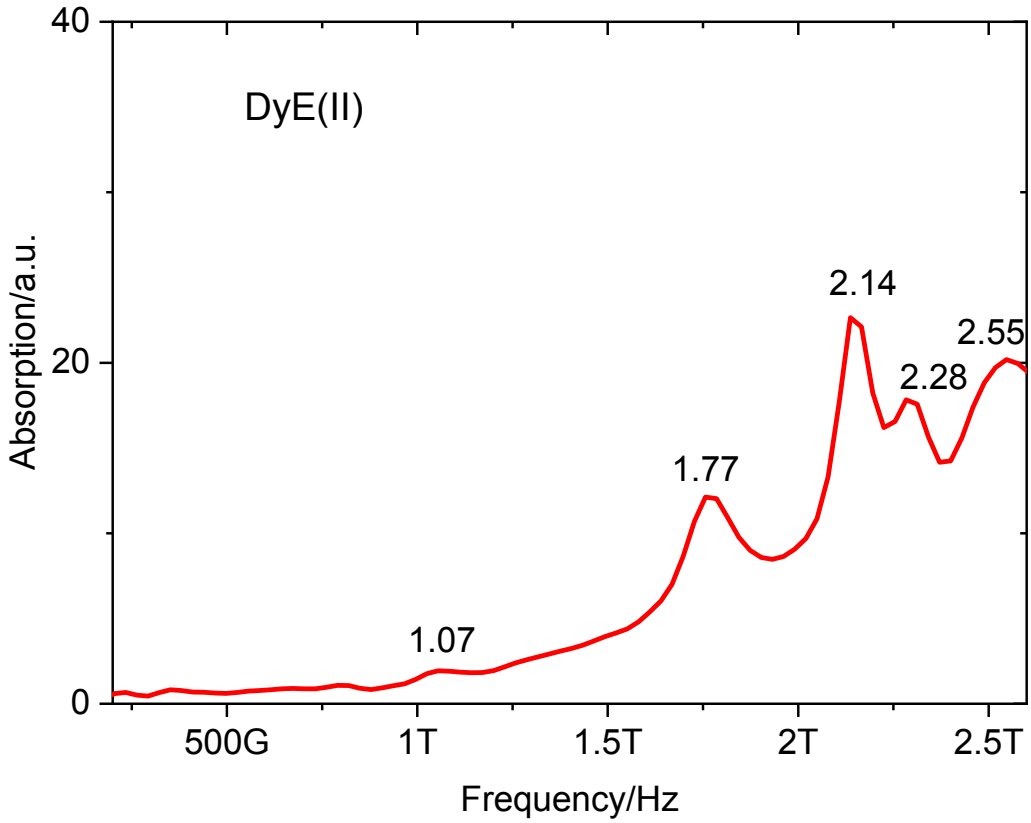

Figure S10-3. THz spectrum of DyE(II) in the 0.2–2.6 THz region

Part 11 The structure of ErE

The structure of ErE was published in reference 11. The structure of ErE is also shown here in **Figure S11-1 and S11-2**. Crystallographic data and structure refinement summary are listed in Table S11-1, selected bond lengths and bond angles of ErE are listed in Table S11-2.

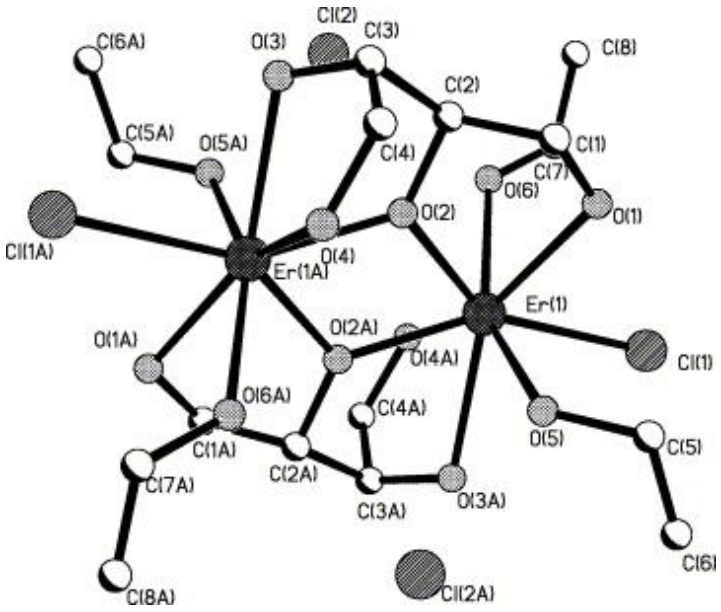

Figure S11-1. The structure and atom numbering of $ErCl_2 \cdot C_4H_9O_4 \cdot 2C_2H_5OH$.

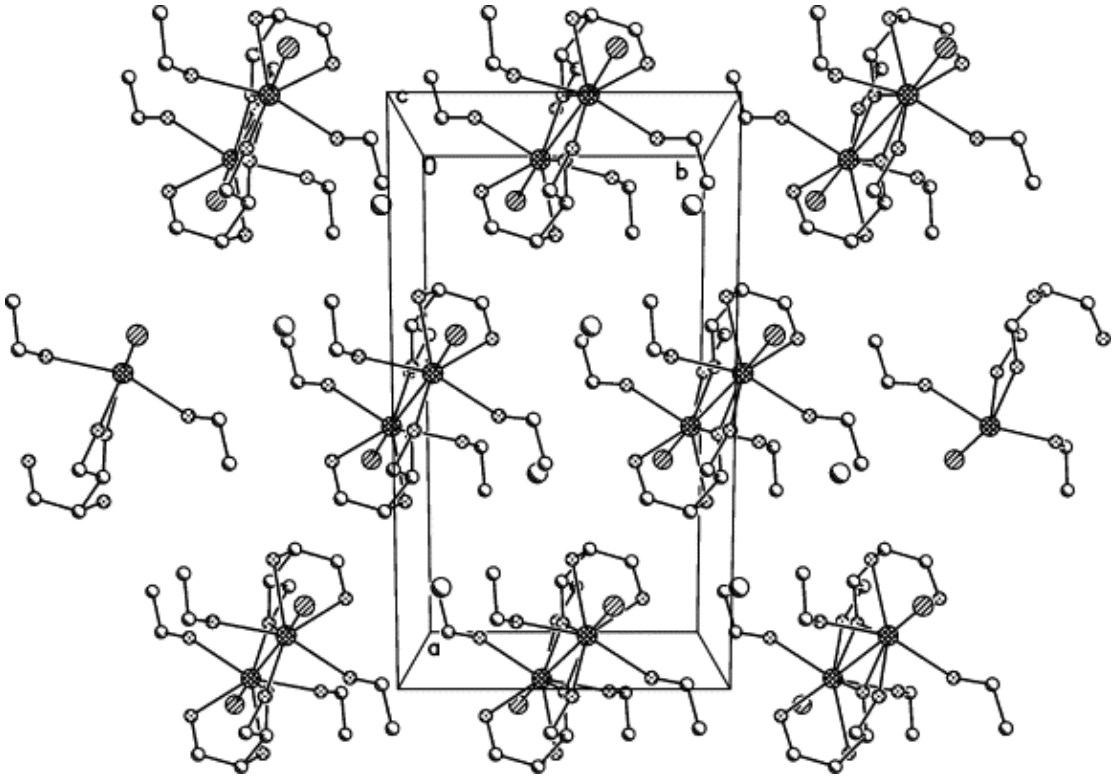

Figure S11-2. The projection of the cell of $ErCl_2 \cdot C_4H_9O_4 \cdot 2C_2H_5OH$.

Table S11-1. Crystallographic Data and Structure Refinement Summary for ErE.

Identification code	ErE
CCDC No.	273169
Formula	$C_8H_{21}Cl_2ErO_6$
formula weight	451.41
crystal system	monoclinic
space group, Z	*C2/c*, 8
a (Å)	17.050(3)
b (Å)	9.3352(19)
c (Å)	19.271(4)
α (deg)	90
β (deg)	106.79(3)
γ (deg)	90
V (Å^3)	2936.6(10)
ρ_{calc} (g/cm^3)	2.042
μ (mm^{-1})	6.090
reflections collected	8794
data/restraints/parameters	3236/2/163
R(int)	0.0928
goodness of fit	0.919
$R_1[I>2\sigma(I)]$	0.0523
$wR_2[I>2\sigma(I)]$	0.1146
R_1(all data)	0.0790
wR_2 (all data)	0.1204

Table S11-2. Selected Bond Lengths and Bond Angles of the Complex ErE.

Bond Lengths (Å)			
Er1–O2[1]	2.200(7)	O3–C3	1.383(13)
Er1–O2	2.210(7)	O3–Er1[1]	2.466(7)
Er1–O5	2.351(7)	O4–C4	1.413(11)
Er1–O6	2.388(8)	O4–Er1[1]	2.396(7)
Er1–O4[1]	2.396(7)	O5–C5	1.455(14)
Er1–O1	2.421(6)	O6–C7	1.462(16)
Er1–O3[1]	2.466(7)	C1–C2	1.472(16)
Er1–Cl1	2.669(2)	C2–C3	1.670(18)
Er1–Er1[1]	3.7381(11)	C3–C4	1.397(16)
O1–C1	1.445(11)	C5–C6	1.443(16)
O2–C2	1.482(13)	C7–C8	1.41(2)
O2–Er1[1]	2.200(7)		
Bond Angles (°)			
O2[1]–Er1–O2	64.1(3)	O3[1]–Er1–Cl1	83.45(19)
O2[1]–Er1–O5	87.3(4)	O2[1]–Er1–Er1[1]	32.12(18)
O2–Er1–O5	91.4(4)	O2–Er1–Er1[1]	31.96(17)
O2[1]–Er1–O6	113.9(4)	O5–Er1–Er1[1]	89.27(19)
O2–Er1–O6	80.6(4)	O6–Er1–Er1[1]	98.1(2)
O5–Er1–O6	150.2(3)	O4[1]–Er1–Er1[1]	93.4(2)
O2[1]–Er1–O4[1]	74.0(3)	O1–Er1–Er1[1]	99.44(16)
O2–Er1–O4[1]	112.1(3)	O3[1]–Er1–Er1[1]	97.87(19)
O5–Er1–O4[1]	138.1(3)	Cl1–Er1–Er1[1]	174.04(6)
O6–Er1–O4[1]	70.5(3)	C1–O1–Er1	114.7(5)
O2[1]–Er1–O1	129.6(3)	C2–O2–Er1[1]	123.5(7)
O2–Er1–O1	69.1(2)	C2–O2–Er1	120.6(6)
O5–Er1–O1	76.0(3)	Er1[1]–O2–Er1	115.9(3)
O6–Er1–O1	74.3(3)	C3–O3–Er1[1]	109.4(6)
O4[1]–Er1–O1	143.9(3)	C4–O4–Er1[1]	118.0(7)
O2[1]–Er1–O3[1]	66.7(3)	C5–O5–Er1	131.4(7)
O2–Er1–O3[1]	128.8(3)	C7–O6–Er1	133.4(8)
O5–Er1–O3[1]	72.9(3)	O1–C1–C2	109.7(8)
O6–Er1–O3[1]	133.6(3)	C1–C2–O2	106.8(9)
O4[1]–Er1–O3[1]	65.3(3)	C1–C2–C3	116.4(11)
O1–Er1–O3[1]	144.1(3)	O2–C2–C3	106.7(9)
O2[1]–Er1–Cl1	150.1(2)	O3–C3–C4	115.0(10)
O2–Er1–Cl1	145.06(17)	O3–C3–C2	98.8(9)
O5–Er1–Cl1	85.6(2)	C4–C3–C2	105.1(10)
O6–Er1–Cl1	85.0(2)	C3–C4–O4	113.2(10)
O4[1]–Er1–Cl1	92.4(2)	C6–C5–O5	110.1(10)
O1–Er1–Cl1	76.45(16)	C8–C7–O6	116.3(14)

Symmetry transformations used to generate equivalent atoms: [1]-X, 1-Y, 1-Z

Part 12 The coordination structure summary of lanthanide-polyol complexes

Table S12-1. The coordination structures of lanthanide-polyol complexes.

Formula		CN	CNNBO	CNAL	reference
$ErCl_2 \cdot C_4H_9O_4 \cdot 2C_2H_5OH$	ErE	8	3	3	1
$DyCl_2 \cdot C_4H_9O_4 \cdot 2C_2H_5OH$	DyE(I)	8	3	3	
$HoCl_2 \cdot C_4H_9O_4 \cdot 3H_2O$	HoE(I)	8	3	3	
$Er(NO_3)_2 \cdot C_4H_9O_4 \cdot C_2H_5OH$	ErEN(I)	9	3	4	
$PrCl_3 \cdot C_6H_{12}O_6 \cdot 9H_2O$	PrI	9	2	7	2
$NdCl_3 \cdot C_6H_{12}O_6 \cdot 9H_2O$	NdI	9	2	7	3
$La(NO_3)_3 \cdot 0.5C_4H_{10}O_4 \cdot 4H_2O$	LaEN	11	2	9	1
$PrCl_3 \cdot 0.5C_6H_{14}O_6 \cdot 7H_2O$	PrG	9	3	6	4
$NdCl_3 \cdot 0.5C_6H_{14}O_6 \cdot 7H_2O$	NdG	9	3	6	5
$SmCl_3 \cdot 0.5C_6H_{14}O_6 \cdot 7H_2O$	SmG	9	3	6	6
$EuCl_3 \cdot 0.5C_6H_{14}O_6 \cdot 7H_2O$	EuG	9	3	6	7
$TbCl_3 \cdot 0.5C_6H_{14}O_6 \cdot 7H_2O$	TbG	9	3	6	8
$HoCl_3 \cdot 0.5C_6H_{14}O_6 \cdot 7H_2O$	HoG	9	3	6	9
$GdCl_3 \cdot 0.5C_6H_{14}O_6 \cdot 7H_2O$	GdG	9	3	6	10
$PrCl_3 \cdot C_5H_{10}O_5 \cdot 5H_2O$	PrR	9	3	6	11, 12
$NdCl_3 \cdot C_5H_{10}O_5 \cdot 5H_2O$	NdR	9	3	6	13, 14
$SmCl_3 \cdot C_5H_{10}O_5 \cdot 5H_2O$	SmR	9	3	6	15
$LaCl_3 \cdot C_5H_{10}O_5 \cdot 5H_2O$	LaR	9	3	6	16
$CeCl_3 \cdot C_5H_{10}O_5 \cdot 5H_2O$	CeR	9	3	6	16
$EuCl_3 \cdot C_5H_{10}O_5 \cdot 5H_2O$	EuR	9	3	6	17
$LaCl_3 \cdot 0.5C_6H_{14}O_6 \cdot 5H_2O$	LaG(II)	9	3	6	18
$Nd(NO_3)_3 \cdot C_4H_{10}O_4 \cdot C_2H_5OH$	NdEN	10	3	7	19
$Y(NO_3)_3 \cdot C_4H_{10}O_4 \cdot C_2H_5OH$	YEN	10	3	7	20
$Gd(NO_3)_3 \cdot C_4H_{10}O_4 \cdot C_2H_5OH$	GdEN	10	3	7	20
$Tb(NO_3)_3 \cdot C_4H_{10}O_4 \cdot C_2H_5OH$	TbEN	10	3	7	20
$Sm(NO_3)_3 \cdot C_4H_{10}O_4 \cdot C_2H_5OH$	SmEN	10	3	7	21
$Er(NO_3)_3 \cdot C_4H_{10}O_4 \cdot C_2H_5OH$	ErEN	10	3	7	22
$Ho(NO_3)_3 \cdot C_4H_{10}O_4 \cdot C_2H_5OH$	HoEN	10	3	7	23
$Eu(NO_3)_3 \cdot C_4H_{10}O_4 \cdot C_2H_5OH$	EuEN	10	3	7	24
$Nd(NO_3)_3 \cdot 0.5C_6H_{14}O_6 \cdot 4H_2O$	NdGN(I)	10	3	7	25
$[La(L1)_2(NO_3)_2]La(L1)(NO_3)_4](H_2O)$	LaL1N	11	3	8	26

$Pr(NO_3)_3 \cdot C_4H_{10}O_4 \cdot 2H_2O$	PrEN	11	3	8	20
$Ce(NO_3)_3 \cdot C_4H_{10}O_4 \cdot 2H_2O$	CeEN	11	3	8	20
$TbCl_3 \cdot C_4H_{10}O_4 \cdot 3H_2O$	TbE(II)	8	4	4	
$2EuCl_3 \cdot 2C_4H_{10}O_4 \cdot 7H_2O$	EuE	8	4	4	27
$LaCl_3 \cdot C_4H_{10}O_4 \cdot 5H_2O$	LaE(I)	9	4	5	28
$LaCl_3 \cdot C_4H_{10}O_4 \cdot 3H_2O$	LaE(II)	9	4	5	28
$2EuCl_3 \cdot 2C_4H_{10}O_4 \cdot 7H_2O$	EuE	9	4	5	27
$PrCl_3 \cdot C_4H_{10}O_4 \cdot 6H_2O$	PrE	9	4	5	19
$NdCl_3 \cdot C_4H_{10}O_4 \cdot 6H_2O$	NdE	9	4	5	19
$TbCl_3 \cdot 1.5C_4H_{10}O_4 \cdot H_2O$	TbE(I)	8	5	3	20
$DyCl_3 \cdot 1.5C_4H_{10}O_4 \cdot H_2O$	DyE(II)	8	5	3	
$LaCl_3 \cdot 1.5C_4H_{10}O_4$	LaE(III)	9	5	4	28
$[Y\{(HOCH_2)_3CCH_3\}_2Cl_2]$ Cl·MeOH		8	6	2	29
$Tb(NO_3)_3 \cdot C_6H_{14}O_6 \cdot 3H_2O$		9	6	3	30
$Pr(L2)_2(NO_3)_2](NO_3)$		9	6	3	26
$Nd(L2)_2(NO_3)_2](NO_3)$		9	6	3	26
$Eu(L2)_2(NO_3)_2](NO_3)$		9	6	3	31
$[Pr(L1)_2(NO_3)_2](NO_3)(CH_3CN)$		9	6	3	26
$[Nd(L1)_2(NO_3)_2](NO_3)(CH_3CN)$		9	6	3	26
$[Eu(L1)2(NO_3)(H_2O)](NO_3)_2$		9	6	3	31
$[Yb(L1)_2(NO_3)(H_2O)](NO_3)_2$		9	6	3	26
$[Ho(L1)_2(NO_3)(H_2O)](NO_3)_2$		9	6	3	26
$[Tb(NO_3)(H_3L^{Et})_2(H_2O)](NO_3)_2$		9	6	3	32
$[Dy(NO_3)(H_3L^{Et})_2(H_2O)](NO_3)_2$		9	6	3	33
$[Y\{(HOCH_2)_3CCH_3\}_2(NO_3)(H_2O)]$ $(NO_3)_2$		9	6	3	29
$LaCl_3 \cdot C_6H_{14}O_6 \cdot 6H_2O$		10	6	4	34
$Nd(NO_3)_3 \cdot C_6H_{14}O_6$		10	6	4	25
$Tb(NO_3)_3 \cdot C_6H_{14}O_6$		10	6	4	30
$Sm(NO_3)_3 \cdot C_6H_{14}O_6$		10	6	4	30
$[La(L1)_2(NO_3)_2](NO_3) \cdot 0.5CH_3CN$		10	6	4	31
$[Tb(NO_3)_2(H_3L^{Et})_2]NO_3 \cdot 0.5C_4H_{10}O_2$		10	6	4	32
$[La(L1)_2(NO_3)_2]La(L1)(NO_3)_4]$ (H_2O)		10	6	4	26
$La(NO_3)_3 \cdot C_6H_{14}O_6 \cdot 4H_2O$		12	6	6	35
$NdCl_3 \cdot 2.5\ C_4H_{10}O_4 \cdot C_2H_5OH$		9	8	1	36

CN: Coordination Number;

CNNBO: Coordination number contributed from non-bridging OH group;

CNAL: The coordination number contributed from auxiliary ligands.

G stands for galactitol;

R stands for D-ribose;

I stands for *myo*-inositol;

L1 stands for *cis,cis*-1,3,5-trihydroxycyclohexane;

L2 stands for *cis,cis*-1,2,3-trihydroxycyclohexane;

H_3L^{Et} stands for 1,1,1-tris(hydroxymethyl)propane.

The related references in **Table S12-1** are as follows:

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