Supporting information

Rare-Earth Chalcogenidotetrachloride Clusters (RE_3ECl_4, RE = Dy, Gd, Y; E = S, Se, Te): Syntheses and Materials Properties

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Table S1 Crystal data and structure refinement for **Dy_3SCl_4**, **Dy_3SeCl_4**, and **Dy_3TeCl_4**.

Identification code	**Dy_3SCl_4**	**Dy_3SeCl_4**	**Dy_3TeCl_4**
Empirical formula	$C_{42}H_{69}Cl_4Dy_3O_3S$	$C_{42}H_{69}Cl_4Dy_3O_3Se$	$C_{42}H_{69}Cl_4Dy_3O_3Te$
Formula weight	1283.33	1330.23	1378.87
Temperature/K	100	100	100
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	12.4410(7)	12.4872(9)	12.6415(8)
b/Å	19.9615(12)	19.9721(15)	20.0788(14)
c/Å	18.8018(10)	18.7396(13)	18.6221(13)
α/°	90	90	90
β/°	90.463(2)	90.542(3)	91.076(3)
γ/°	90	90	90
Volume/Å^3	4669.1(5)	4673.4(6)	4725.9(6)
2Θ range for data collection/°	5.618 to 105.95	4.404 to 50.052	4.61 to 50.052
Index ranges	$-14 \le h \le 14$, $-23 \le k \le 23$, $-22 \le l \le 22$	$-14 \le h \le 14$, $-23 \le k \le 23$, $-22 \le l \le 21$	$-15 \le h \le 14$, $-23 \le k \le 23$, $-22 \le l \le 22$
Reflections collected	40689	57524	37722
Independent reflections	8209 [R_{int} = 0.0794, R_{sigma} = 0.0651]	8198 [R_{int} = 0.0695, R_{sigma} = 0.0459]	8323 [R_{int} = 0.0430, R_{sigma} = 0.0371]
Data/restraints/parameters	8209/317/492	8198/1771/459	8323/859/493
Goodness-of-fit on F^2	1.056	1.274	1.253
Final R indexes [I>=2σ (I)]	R_1 = 0.0748, wR_2 = 0.1905	R_1 = 0.0901, wR_2 = 0.1961	R_1 = 0.0906, wR_2 = 0.1952
Final R indexes [all data]	R_1 = 0.0822, wR_2 = 0.1954	R_1 = 0.0954, wR_2 = 0.1985	R_1 = 0.0930, wR_2 = 0.1963

Table S2 Crystal data and structure refinement for **Gd_3SCl_4**, **Gd_3SeCl_4**, and **Gd_3TeCl_4**.

Identification code	**Gd_3SCl_4**	**Gd_3SeCl_4**	**Gd_3TeCl_4**
Empirical formula	$C_{42}H_{69}Cl_4Gd_3O_3S$	$C_{42}H_{69}Cl_4Gd_3O_3Se$	$C_{42}H_{69}Cl_4Gd_3O_3Te$
Formula weight	1267.58	1314.48	1363.12
Temperature/K	200	100	100
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	12.6429(6)	12.5326(6)	12.7229(6)
b/Å	20.1652(10)	20.0475(12)	20.1326(9)
c/Å	18.8257(10)	18.8177(11)	18.5683(9)
α/°	90	90	90
β/°	90.135(2)	91.071(2)	91.302(2)
γ/°	90	90	90
Volume/Å^3	4799.5(4)	4727.1(5)	4755.0(4)
2Θ range for data collection/°	4.582 to 50.054	4.604 to 50.054	4.832 to 50.054
Index ranges	$-14 \le h \le 15$, $-23 \le k \le 24$, $-22 \le l \le 22$	$-14 \le h \le 14$, $-23 \le k \le 23$, $-22 \le l \le 22$	$-13 \le h \le 15$, $-23 \le k \le 20$, $-22 \le l \le 22$
Reflections collected	39723	63627	34015
Independent reflections	8443 [R_{int} = 0.0526, R_{sigma} = 0.0401]	8190 [R_{int} = 0.1249, R_{sigma} = 0.0794]	8387 [R_{int} = 0.0946, R_{sigma} = 0.0776]
Data/restraints/parameters	8443/318/491	8190/1251/491	8387/326/490
Goodness-of-fit on F^2	1.222	1.051	1.122
Final R indexes [I>=2σ (I)]	R_1 = 0.0543, wR_2 = 0.1172	R_1 = 0.0779, wR_2 = 0.1627	R_1 = 0.0757, wR_2 = 0.1470
Final R indexes [all data]	R_1 = 0.0634, wR_2 = 0.1207	R_1 = 0.1071, wR_2 = 0.1793	R_1 = 0.1076, wR_2 = 0.1597

Table S3 Crystal data and structure refinement for Y_3SCl_4, Y_3SeCl_4, and Y_3TeCl_4.

Identification code	Y_3SCl_4	Y_3SeCl_4	Y_3TeCl_4
Empirical formula	$C_{42}H_{69}Cl_4O_3SY_3$	$C_{42}H_{69}Cl_4O_3SeY_3$	$C_{42}H_{69}Cl_4O_3TeY_3$
Formula weight	1062.56	1109.46	1158.10
Temperature/K	100	100	200
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	12.4185(7)	12.5114(9)	12.7624(11)
b/Å	19.9574(11)	20.0184(14)	20.192(4)
c/Å	18.7827(11)	18.8023(13)	18.727(4)
α/°	90	90	90
β/°	90.671(3)	90.768(2)	91.396(5)
γ/°	90	90	90
Volume/Å^3	4654.8(5)	4708.8(6)	4824.3(14)
2Θ range for data collection/°	5.622 to 105.954	5.61 to 105.962	4.584 to 55.036
Index ranges	$-14 \le h \le 14$, $-23 \le k \le 23$, $-22 \le l \le 22$	$-14 \le h \le 14$, $-23 \le k \le 23$, $-22 \le l \le 22$	$-15 \le h \le 16$, $-25 \le k \le 26$, $-24 \le l \le 24$
Reflections collected	62841	47339	48142
Independent reflections	8194 [R_{int} = 0.0866, R_{sigma} = 0.0531]	8184 [R_{int} = 0.0694, R_{sigma} = 0.0539]	11079 [R_{int} = 0.0938, R_{sigma} = 0.0854]
Data/restraints/parameters	8194/771/504	8184/637/534	11079/939/493
Goodness-of-fit on F^2	1.167	1.095	1.013
Final R indexes [I>=2σ (I)]	R_1 = 0.0929, wR_2 = 0.2047	R_1 = 0.0966, wR_2 = 0.2693	R_1 = 0.0522, wR_2 = 0.1165
Final R indexes [all data]	R_1 = 0.0972, wR_2 = 0.2066	R_1 = 0.0984, wR_2 = 0.2720	R_1 = 0.1032, wR_2 = 0.1392

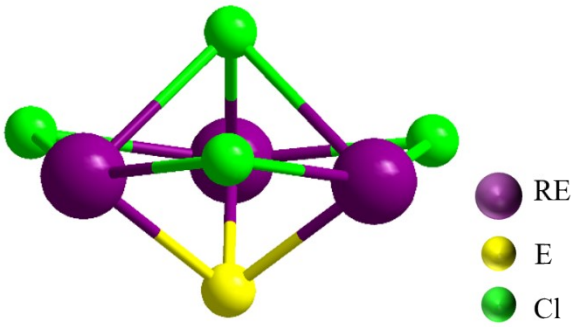

Figure S1. Ball-and-stick depictions of the core of $\mathbf{Dy_3ECl_4}$ (E = S, Se, Te).

Table S4 Selected bond distances (Å) for **Gd_3SCl_4**, **Gd_3SeCl_4**, and **Gd_3TeCl_4**

Bond Distance (Å)	**Gd_3SCl_4**	**Gd_3SeCl_4**	**Gd_3TeCl_4**
Gd1-S/Se/Te	2.718(2)	2.8510(18)	3.0663(13)
Gd2-S/Se/Te	2.717(2)	2.8362(18)	3.0602(13)
Gd3-S/Se/Te	2.731(2)	2.8336(18)	3.0564(12)
Average	2.722(8)	2.8403(9)	3.0609(5)
Gd1-Gd2	3.8442(7)	3.8901(10)	3.9536(11)
Gd2-Gd3	3.8422(7)	3.8770(12)	3.9571(10)
Gd3-Gd1	3.8568(7)	3.8747(11)	3.9564(10)
Average	3.8477(8)	3.8806(8)	3.9557(2)

Table S5 Selected bond distances (Å) for **Y_3SCl_4**, **Y_3SeCl_4**, and **Y_3TeCl_4**

Bond Distance (Å)	**Y_3SCl_4**	**Y_3SeCl_4**	**Y_3TeCl_4**
Y1-S/Se/Te	2.6860(3)	2.8140(2)	3.0329(8)
Y2-S/Se/Te	2.6740(3)	2.8331(9)	3.0341(7)
Y3-S/Se/Te	2.6960(3)	2.8259(9)	3.0450(8)
Average	2.6850(11)	2.8243(9)	3.0373(7)
Y1-Y2	3.7870(14)	3.8430(8)	3.9353(8)
Y2-Y3	3.7890(16)	3.8586(9)	3.9374(8)
Y3-Y1	3.8090(15)	3.8500(2)	3.9302(10)
Average	3.7950(12)	3.8505(8)	3.9343(4)

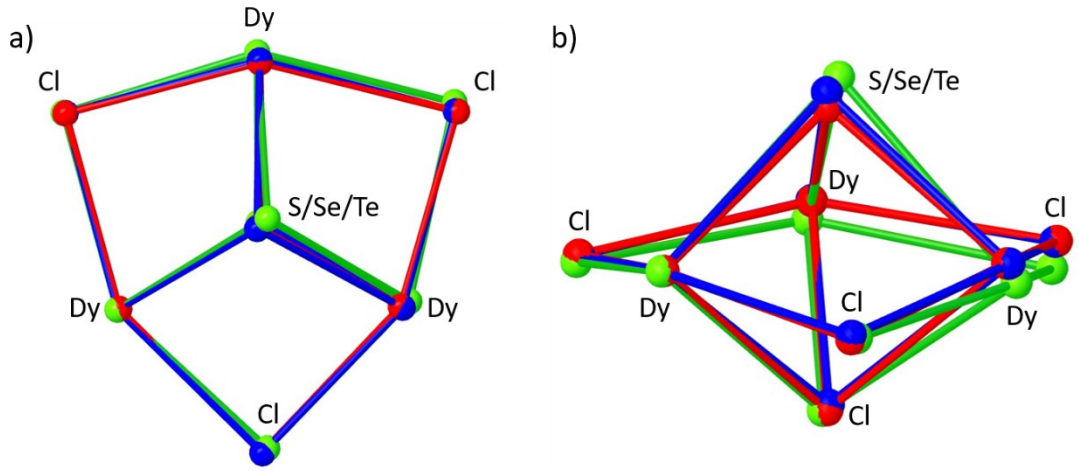

Figure S2. Overlay (a) top view and (b) front view of the core in $\mathbf{Dy_3SCl_4}$ (red), $\mathbf{Dy_3SeCl_4}$ (blue), and $\mathbf{Dy_3TeCl_4}$ (green). Other atoms are omitted for clarity.

Table S6 Selected bond distances (Å) for **Dy_3SCl_4**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Dy1-Cl1	2.739(3)	Dy2-Cl1	2.755(3)	Dy3-Cl2	2.752(3)
Dy1-Cl2	2.745(3)	Dy2-Cl3	2.740(3)	Dy3-Cl3	2.753(3)
Dy1-Cl4	2.861(3)	Dy2-Cl4	2.855(3)	Dy3-Cl4	2.874(3)
Dy1-C1	2.655(11)	Dy2-C11	2.627(16)	Dy3-C21	2.633(15)
Dy1-C2	2.628(11)	Dy2-C12	2.615(13)	Dy3-C22	2.634(15)
Dy1-C3	2.644(12)	Dy2-C13	2.664(15)	Dy3-C23	2.658(17)
Dy1-C4	2.665(13)	Dy2-C14	2.643(13)	Dy3-C24	2.663(16)
Dy1-C5	2.712(14)	Dy2-C15	2.619(15)	Dy3-C25	2.641(16)
Dy1-$Cp_{centroid}$	2.377	Dy2-$Cp_{centroid}$	2.359	Dy3-$Cp_{centroid}$	2.374

Table S7 Selected bond distances (Å) for **Dy_3SeCl_4**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Dy1-Cl1	2.742(5)	Dy2-Cl1	2.763(5)	Dy3-Cl2	2.746(5)
Dy1-Cl3	2.749(5)	Dy2-Cl2	2.751(4)	Dy3-Cl3	2.748(5)
Dy1-Cl4	2.845(4)	Dy2-Cl4	2.867(4)	Dy3-Cl4	2.852(4)
Dy1-C1	2.693(16)	Dy2-C11	2.670(2)	Dy3-C21	2.630(2)
Dy1-C2	2.702(15)	Dy2-C12	2.665(17)	Dy3-C22	2.630(2)
Dy1-C3	2.673(16)	Dy2-C13	2.673(16)	Dy3-C23	2.630(3)
Dy1-C4	2.610(2)	Dy2-C14	2.686(15)	Dy3-C24	2.650(3)
Dy1-C5	2.670(2)	Dy2-C15	2.656(19)	Dy3-C25	2.680(2)
Dy1-$Cp_{centroid}$	2.378	Dy2-$Cp_{centroid}$	2.384	Dy3-$Cp_{centroid}$	2.354

Table S8 Selected bond distances (Å) for **Dy_3TeCl_4**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Dy1-Cl1	2.774(5)	Dy2-Cl1	2.746(5)	Dy3-Cl2	2.764(5)
Dy1-Cl3	2.775(5)	Dy2-Cl2	2.766(4)	Dy3-Cl3	2.769(5)
Dy1-Cl4	2.863(5)	Dy2-Cl4	2.828(4)	Dy3-Cl4	2.821(4)
Dy1-C1	2.672(16)	Dy2-C11	2.640(2)	Dy3-C21	2.612(16)
Dy1-C2	2.648(14)	Dy2-C12	2.620(2)	Dy3-C22	2.597(15)
Dy1-C3	2.629(16)	Dy2-C13	2.630(2)	Dy3-C23	2.685(17)
Dy1-C4	2.620(2)	Dy2-C14	2.630(3)	Dy3-C24	2.720(2)
Dy1-C5	2.650(2)	Dy2-C15	2.620(2)	Dy3-C25	2.670(19)
Dy1-$Cp_{centroid}$	2.354	Dy2-$Cp_{centroid}$	2.356	Dy3-$Cp_{centroid}$	2.369

Table S9 Selected bond distances (Å) for **Gd_3SCl_4**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Gd1-Cl1	2.780(3)	Gd2-Cl1	2.770(3)	Gd3-Cl2	2.777(2)
Gd1-Cl3	2.773(3)	Gd2-Cl2	2.773(2)	Gd3-Cl3	2.767(3)
Gd1-Cl4	2.918(2)	Gd2-Cl4	2.888(2)	Gd3-Cl4	2.893(2)
Gd1-C1	2.667(12)	Gd2-C11	2.692(14)	Gd3-C21	2.650(12)
Gd1-C2	2.655(12)	Gd2-C12	2.682(15)	Gd3-C22	2.648(11)
Gd1-C3	2.654(14)	Gd2-C13	2.663(12)	Gd3-C23	2.654(11)
Gd1-C4	2.684(13)	Gd2-C14	2.648(10)	Gd3-C24	2.675(11)
Gd1-C5	2.675(11)	Gd2-C15	2.677(12)	Gd3-C25	2.671(11)
Gd1-$Cp_{centroid}$	2.397	Gd2-$Cp_{centroid}$	2.396	Gd3-$Cp_{centroid}$	2.386

Table S10 Selected bond distances (Å) for **Gd_3SeCl_4**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Gd1-Cl1	2.770(4)	Gd2-Cl1	2.783(4)	Gd3-Cl2	2.771(5)
Gd1-Cl3	2.779(4)	Gd2-Cl2	2.790(4)	Gd3-Cl3	2.769(4)
Gd1-Cl4	2.882(4)	Gd2-Cl4	2.899(4)	Gd3-Cl4	2.885(4)
Gd1-C1	2.669(13)	Gd2-C11	2.700(14)	Gd3-C21	2.677(13)
Gd1-C2	2.678(15)	Gd2-C12	2.680(16)	Gd3-C22	2.627(13)
Gd1-C3	2.681(14)	Gd2-C13	2.680(19)	Gd3-C23	2.660(16)
Gd1-C4	2.693(12)	Gd2-C14	2.673(16)	Gd3-C24	2.75(2)
Gd1-C5	2.667(12)	Gd2-C15	2.713(13)	Gd3-C25	2.768(15)
Gd1-$Cp_{centroid}$	2.393	Gd2-$Cp_{centroid}$	2.410	Gd3-$Cp_{centroid}$	2.414

Table S11 Selected bond distances (Å) for **Gd_3TeCl_4**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Gd1-Cl1	2.770(4)	Gd2-Cl1	2.786(4)	Gd3-Cl2	2.783(4)
Gd1-Cl3	2.792(4)	Gd2-Cl2	2.804(4)	Gd3-Cl3	2.794(4)
Gd1-Cl4	2.864(4)	Gd 2-Cl4	2.889(4)	Gd3-Cl4	2.853(3)
Gd1-C1	2.66(2)	Gd2-C11	2.65(2)	Gd3-C21	2.663(18)
Gd1-C2	2.65(2)	Gd2-C12	2.65(2)	Gd3-C22	2.69(2)
Gd1-C3	2.655(19)	Gd2-C13	2.66(3)	Gd3-C23	2.657(18)
Gd1-C4	2.638(19)	Gd2-C14	2.659(16)	Gd3-C24	2.627(17)
Gd1-C5	2.666(19)	Gd2-C15	2.675(17)	Gd3-C25	2.642(19)
Gd1-$Cp_{centroid}$	2.382	Gd2-$Cp_{centroid}$	2.383	Gd3-$Cp_{centroid}$	2.386

Table S12 Selected bond distances (Å) for $\mathbf{Y_3SCl_4}$.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Y1-Cl1	2.742(3)	Y2-Cl1	2.729(3)	Y3-Cl2	2.737(4)
Y1-Cl3	2.741(2)	Y2-Cl2	2.733(3)	Y3-Cl3	2.736(3)
Y1-Cl4	2.873(3)	Y2-Cl4	2.865(3)	Y3-Cl4	2.863(3)
Y1-C1	2.61(3)	Y2-C11	2.654(16)	Y3-C21	2.650(16)
Y1-C2	2.62(2)	Y2-C12	2.714(13)	Y3-C22	2.616(15)
Y1-C3	2.66(2)	Y2-C13	2.728(14)	Y3-C23	2.625(15)
Y1-C4	2.62(2)	Y2-C14	2.660(18)	Y3-C24	2.615(15)
Y1-C5	2.65(2)	Y2-C15	2.592(19)	Y3-C25	2.610(15)
$Y1\text{-}Cp_{centroid}$	2.345	$Y2\text{-}Cp_{centroid}$	2.381	$Y3\text{-}Cp_{centroid}$	2.332

Table S13 Selected bond distances (Å) for $\mathbf{Y_3SeCl_4}$.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Y1-Cl1	2.7400(3)	Y2-Cl1	2.7410(16)	Y3-Cl2	2.7397(19)
Y1-Cl3	2.7362(18)	Y2-Cl2	2.7301(18)	Y3-Cl3	2.7509(18)
Y1-Cl4	2.838(4)	Y2-Cl4	2.8460(16)	Y3-Cl4	2.8559(18)
Y1-C1	2.699(11)	Y2-C11	2.626(8)	Y3-C21	2.641(9)
Y1-C2	2.654(14)	Y2-C12	2.631(8)	Y3-C22	2.641(9)
Y1-C3	2.653(17)	Y2-C13	2.644(8)	Y3-C23	2.623(9)
Y1-C4	2.652(19)	Y2-C14	2.651(8)	Y3-C24	2.658(11)
Y1-C5	2.720(12)	Y2-C15	2.628(8)	Y3-C25	2.648(9)
$Y1\text{-}Cp_{centroid}$	2.393	$Y2\text{-}Cp_{centroid}$	2.363	$Y3\text{-}Cp_{centroid}$	2.361

Table S14 Selected bond distances (Å) for $\mathbf{Y_3TeCl_4}$.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Y1-Cl1	2.7651(16)	Y2-Cl1	2.7532(17)	Y3-Cl2	2.7582(15)
Y1-Cl3	2.7525(17)	Y2-Cl2	2.7591(17)	Y3-Cl3	2.7417(16)
Y1-Cl4	2.8565(15)	Y2-Cl4	2.8271(16)	Y3-Cl4	2.8462(15)
Y1-C1	2.651(6)	Y2-C11	2.647(7)	Y3-C21	2.638(6)
Y1-C2	2.634(6)	Y2-C12	2.663(7)	Y3-C22	2.625(6)
Y1-C3	2.654(6)	Y2-C13	2.649(6)	Y3-C23	2.637(6)
Y1-C4	2.658(6)	Y2-C14	2.624(6)	Y3-C24	2.661(6)
Y1-C5	2.656(6)	Y2-C15	2.622(6)	Y3-C25	2.641(6)
$Y1\text{-}Cp_{centroid}$	2.365	$Y2\text{-}Cp_{centroid}$	2.361	$Y3\text{-}Cp_{centroid}$	2.359

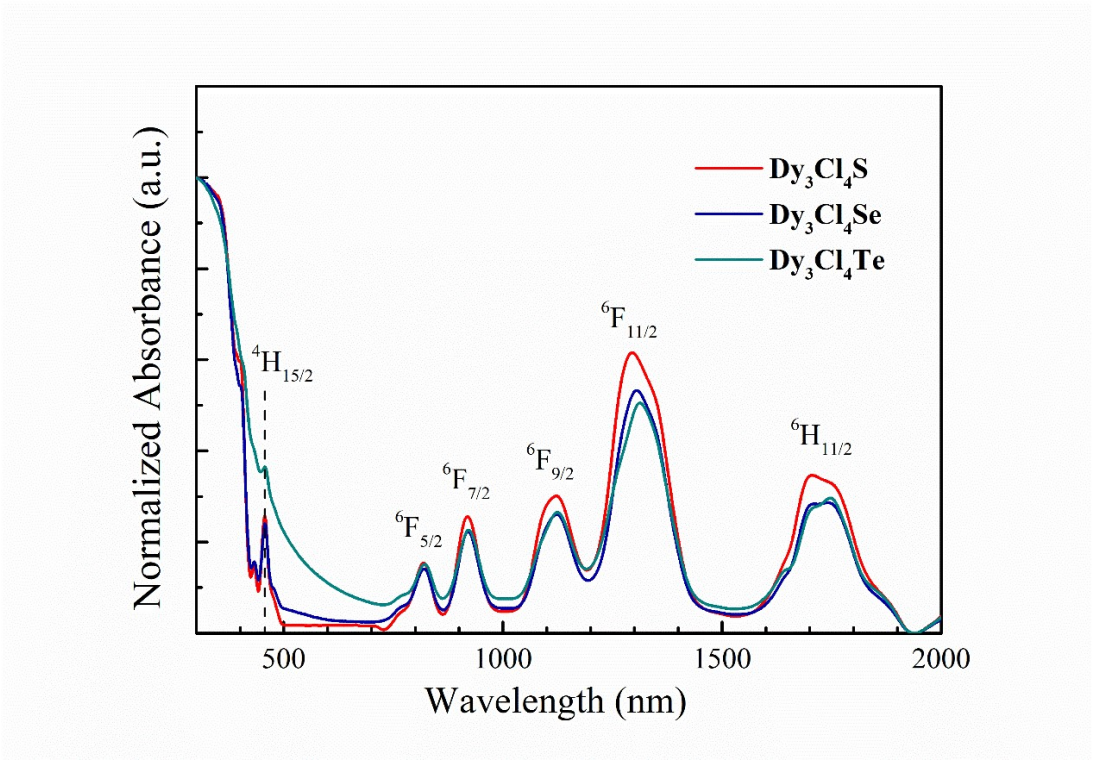

Figure S3. Absorption spectrum of Dy_3SCl_4, Dy_3SeCl_4, and Dy_3TeCl_4 with standard assignments for the various spectral transitions.

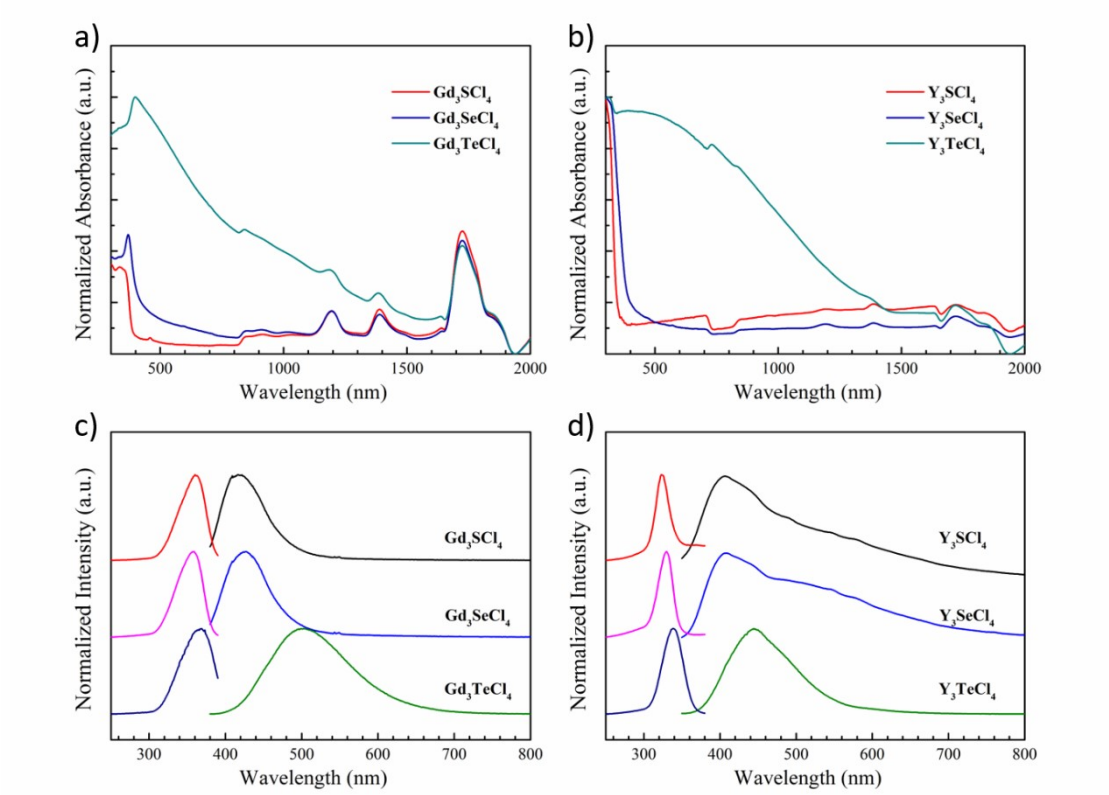

Figure S4. Absorption spectra of (a) **Gd_3ECl_4** and (b) **Y_3ECl_4** (E=S, Se, and Te). Room-temperature (c) excitation (λ_{ex} = 360 nm) and emission (λ_{em} = 418 nm and 504 nm) spectra of **Gd_3ECl_4** (E = S, Se, and Te); (d) excitation (λ_{ex} = 324 nm) and emission (λ_{em} = 407 nm and 445 nm) spectra of **Y_3ECl_4** (E = S, Se, and Te).

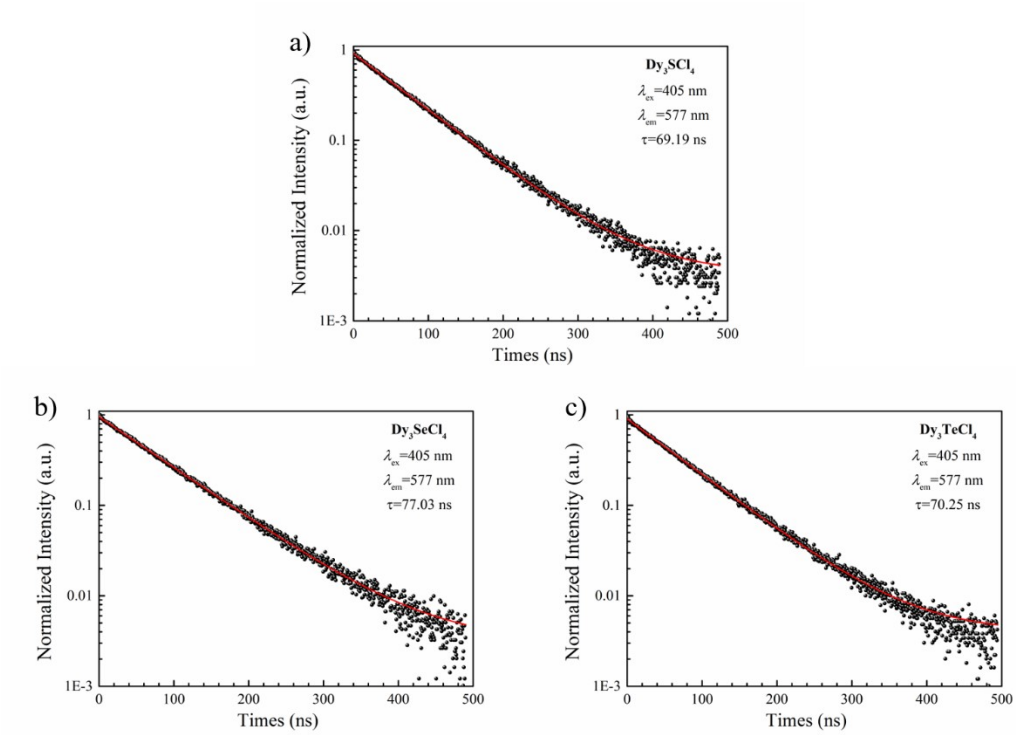

Figure S5. Photoluminescence decay curves of (a) Dy_3SCl_4, (b) Dy_3SeCl_4, and (c) Dy_3TeCl_4 complex under 405 nm laser excitation. The solid lines are the fit curve.

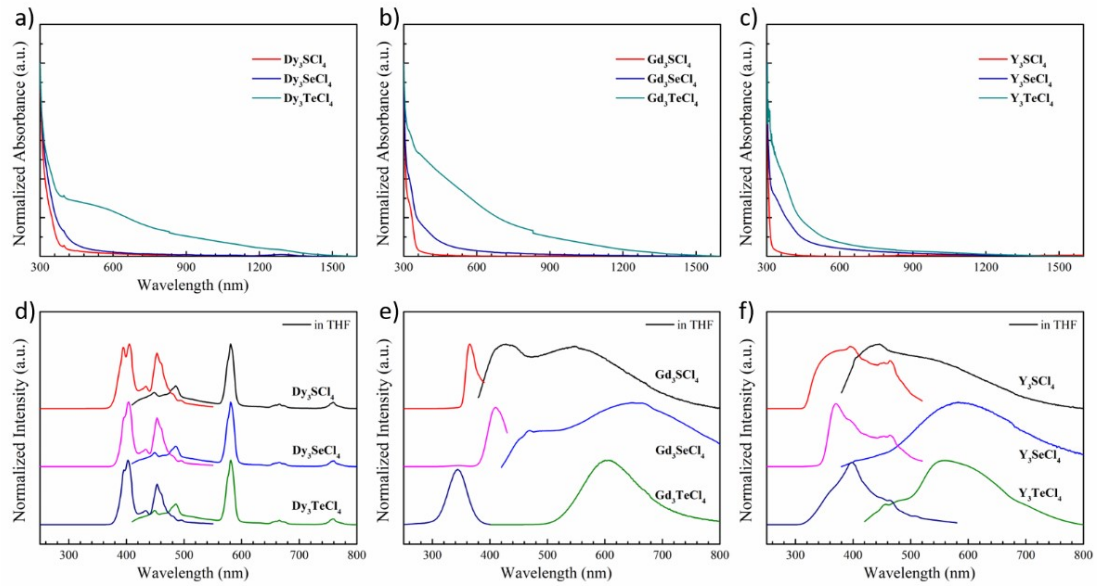

Figure S6. Absorption spectra (a-c) and room-temperature excitation and emission spectra (d-f) of RE_3ECl_4 (RE=Dy, Gd, Y; E=S, Se, and Te) in THF.

Table S15. Electronic structure of **Dy1** in Dy_3SCl_4 calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet.

Energy (cm^{-1})	g1	g2	g3	Wavefunction
0.00	6.15×10^{-2}	0.14	19.58	96.3%| ± 15/2⟩
84.521	0.76	0.95	18.20	19.0%| ± 5/2⟩+17.7%| ± 9/2⟩+15.6%| ± 7/2⟩+14.3%| ± 3/2⟩...
159.147	4.21	6.11	10.75	43.8%| ± 13/2⟩+15.3%| ± 7/2⟩+11.4%| ± 11/2⟩+10.8%| ± 9/2⟩...
212.036	0.16	3.21	8.71	35.7%| ± 13/2⟩+27.4%| ± 11/2⟩+13.8%| ± 7/2⟩+9.3%| ± 1/2⟩...
272.498	1.13	1.99	12.13	38.7%| ± 11/2⟩+30.6%| ± 9/2⟩+9.8%| ± 3/2⟩+7.1%| ± 7/2⟩...
315.170	0.38	0.58	16.13	34.4%| ± 7/2⟩+25.9%| ± 9/2⟩+22.9%| ± 5/2⟩+11.2%| ± 11/2⟩...
390.862	5.54×10^{-2}	0.13	18.18	31.7%| ± 5/2⟩+31.7%| ± 3/2⟩+16.8%| ± 7/2⟩ +14.5%| ± 1/2⟩...
421.524	5.25×10^{-2}	0.16	19.09	53.9%| ± 1/2⟩+28.3%| ± 3/2⟩+8.9%| ± 5/2⟩+3%| ± 9/2⟩...

Table S16. Electronic structure of **Dy2** in Dy_3SCl_4 calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet.

Energy (cm^{-1})	g1	g2	g3	Wavefunction
0.00	0.15	0.47	18.72	85.1%| ± 15/2⟩+8.1%| ± 11/2⟩+2.9%| ± 7/2⟩
49.914	0.33	0.65	19.95	23.0%| ± 13/2⟩+21.8%| ± 9/2⟩+13.4%| ± 5/2⟩+13.1%| ± 7/2⟩...
147.550	3.88	6.08	11.47	31.6%| ± 13/2⟩+16.5%| ± 3/2⟩+15.1%| ± 7/2⟩ +11.2%| ± 1/2⟩...
202.003	1.31	2.93	8.60	30.6%| ± 13/2⟩+28.6%| ± 11/2⟩+15.9%| ± 5/2⟩+10.0%| ± 1/2⟩...
264.957	0.21	1.50	12.09	34.4%| ± 11/2⟩+28.1%| ± 9/2⟩+10.9%| ± 13/2⟩ +10.5%| ± 3/2⟩...
311.195	0.57	0.86	16.01	32.3%| ± 7/2⟩+28.8%| ± 9/2⟩+21.7%| ± 5/2⟩+9.8%| ± 11/2⟩...
381.584	9.94×10^{-3}	0.13	18.62	31.3%| ± 3/2⟩+29.5%| ± 5/2⟩+17.0%| ± 1/2⟩ +16.3%| ± 7/2⟩...
416.981	4.91×10^{-2}	0.11	19.39	50.6%| ± 1/2⟩+28.4%| ± 3/2⟩+11.0%| ± 5/2⟩+4.8%| ± 7/2⟩...

Table S17. Electronic structure of **Dy3** in Dy_3SCl_4 calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet.

Energy (cm^{-1})	g1	g2	g3	Wavefunction
0.00	5.23×10^{-2}	0.12	19.56	94.7%| ± 15/2⟩+2.6%| ± 11/2⟩
85.745	0.59	0.70	18.02	20.6%| ± 9/2⟩+19.2%| ± 13/2⟩+14.6%| ± 7/2⟩+14.5%| ± 5/2⟩…
168.274	9.63	7.10	3.86	53.2%| ± 13/2⟩+12.6%| ± 3/2⟩+12.2%| ± 7/2⟩ +8.3%| ± 1/2⟩…
219.525	0.78	3.41	8.58	35.2%| ± 11/2⟩+20.5%| ± 13/2⟩+14.8%| ± 5/2⟩+11.5%| ± 9/2⟩…
276.030	0.73	1.78	12.27	34.8%| ± 11/2⟩+32.7%| ± 9/2⟩+13.7%| ± 7/2⟩ +8.1%| ± 3/2⟩…
308.733	0.57	0.70	16.70	33.5%| ± 7/2⟩+26.8%| ± 5/2⟩+24.8%| ± 9/2⟩+7.7%| ± 3/2⟩…
383.596	0.16	0.22	16.92	33.8%| ± 3/2⟩+30.8%| ± 5/2⟩+15.7%| ± 1/2⟩ +15.0%| ± 7/2⟩…
404.676	9.66×10^{-2}	0.36	17.93	54.1%| ± 1/2⟩+28.2%| ± 3/2⟩+8.1%| ± 5/2⟩+4.7%| ± 7/2⟩…

Table S18. Electronic structure of **Dy1** in Dy_3SeCl_4 calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet.

Energy (cm^{-1})	g1	g2	g3	Wavefunction
0.00	3.12×10^{-2}	6.46×10^{-2}	19.68	97.4%| ± 15/2⟩
101.261	0.62	0.91	18.21	20.0%| ± 9/2⟩+16.3%| ± 13/2⟩+16.4%| ± 5/2⟩+16.2%| ± 7/2⟩…
173.140	3.97	6.60	10.41	51.4%| ± 13/2⟩+12.7%| ± 7/2⟩+12.1%| ± 11/2⟩ +10.1%| ± 3/2⟩…
221.851	0.15	3.89	8.85	30.0%| ± 11/2⟩+23.9%| ± 13/2⟩+14.2%| ± 9/2⟩+13.2%| ± 5/2⟩…
281.513	0.98	2.08	12.11	33.6%| ± 11/2⟩+28.7%| ± 9/2⟩+13.3%| ± 7/2⟩ +6.5%| ± 13/2⟩…
320.661	0.43	0.63	17.07	31.8%| ± 7/2⟩+24.7%| ± 5/2⟩+24.4%| ± 9⟩+10.2%| ± 11/2⟩…
389.818	0.10	0.21	18.20	32.5%| ± 13/2⟩+26.0%| ± 5/2⟩+24.5%| ± 1/2⟩ +12.4%| ± 7/2⟩…
424.790	9.18×10^{-2}	0.29	18.92	47.0%| ± 1/2⟩+28.0%| ± 3/2⟩+12.6%| ± 5/2⟩+6.5%| ± 7/2⟩…

Table S19. Electronic structure of **Dy2** in Dy_3SeCl_4 calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet.

Energy (cm^{-1})	g1	g2	g3	Wavefunction
0.00	5.91×10^{-2}	0.14	19.63	97.0%| ± 15/2⟩
85.920	0.93	1.31	18.13	20.3%| ± 5/2⟩+16.7%| ± 1/2⟩+16.6%| ± 3/2⟩+15.9%| ± 9/2⟩…
150.528	4.21	4.54	11.58	39.9%| ± 13/2⟩+17.8%| ± 7/2⟩+13.9%| ± 11/2⟩+8.9%| ± 3/2⟩…
206.853	8.44	4.88	1.23	41.6%| ± 13/2⟩+24.1%| ± 11/2⟩+12.6%| ± 5/2⟩+9.3%| ± 1/2⟩…
269.273	1.55	2.23	12.00	40.3%| ± 11/2⟩+30.9%| ± 9/2⟩+10.3%| ± 3/2⟩+8.4%| ± 13/2⟩…
314.774	0.35	0.47	16.05	34.8%| ± 7/2⟩+26.5%| ± 9/2⟩+21.7%| ± 5/2⟩+12.0%| ± 11/2⟩…
390.175	3.42×10^{-2}	0.10	18.11	32.1%| ± 5/2⟩+30.6%| ± 3/2⟩+17.6%| ± 7/2⟩+14.0%| ± 1/2⟩…
419.298	3.28×10^{-2}	0.12	19.09	53.1%| ± 1/2⟩+28.8%| ± 3/2⟩+9.2%| ± 5/2⟩+3.5%| ± 7/2⟩…

Table S20. Electronic structure of **Dy3** in Dy_3SeCl_4 calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet.

Energy (cm^{-1})	g1	g2	g3	Wavefunction
0.00	3.35×10^{-2}	7.26×10^{-2}	19.72	97.9%| ± 15/2⟩
103.652	0.92	1.52	18.10	19.8%| ± 5/2⟩+16.9%| ± 9/2⟩+15.3%| ± 3/2⟩+15.1%| ± 1/2⟩…
162.566	4.27	4.86	11.11	45.1%| ± 13/2⟩+16.5%| ± 7/2⟩+13.9%| ± 11/2⟩+10.7%| ± 9/2⟩…
214.768	0.57	4.51	8.62	35.9%| ± 13/2⟩+25.7%| ± 11/2⟩+13.6%| ± 5/2⟩+8.7%| ± 1/2⟩…
273.421	1.80	2.32	12.14	39.2%| ± 11/2⟩+30.6%| ± 9/2⟩+9.5%| ± 3/2⟩+8.0%| ± 7/2⟩…
317.398	0.20	0.34	16.02	33.5%| ± 7/2⟩+25.8%| ± 9/2⟩+22.5%| ± 5/2⟩+11.6%| ± 11/2⟩…
385.394	1.08×10^{-2}	9.54×10^{-2}	18.90	31.5%| ± 5/2⟩+28.2%| ± 3/2⟩+21.4%| ± 1/2⟩+14.3%| ± 7/2⟩…
430.855	2.16×10^{-2}	6.60×10^{-2}	19.56	47.1%| ± 1/2⟩+28.6%| ± 3/2⟩+12.6%| ± 5/2⟩+5.9%| ± 7/2⟩…

Table S21. Electronic structure of **Dy1** in Dy_3TeCl_4 calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet.

Energy (cm^{-1})	g1	g2	g3	Wavefunction
0.00	4.48×10^{-3}	8.33×10^{-3}	19.84	99.5%| ± 15/2⟩
168.402	11.04	8.81	1.89	52.2%| ± 13/2⟩+16.0%| ± 9/2⟩+13.2%| ± 5/2⟩+6.3%| ± 1/2⟩…
196.994	5.50	4.93	1.49	27.2%| ± 13/2⟩+24.0%| ± 11/2⟩+22.6%| ± 7/2⟩ + 14.1%| ± 3/2⟩…
245.736	8.16	6.33	7.45×10^{-2}	30.2%| ± 11/2⟩+26.2%| ± 9/2⟩+18.0%| ± 13/2⟩+12.7%| ± 5/2⟩…
299.713	2.31	3.97	11.78	37.6%| ± 11/2⟩+28.5%| ± 9/2⟩+17.7%| ± 7/2⟩+11.2%| ± 3/2⟩…
332.135	0.80	1.04	16.22	33.1%| ± 7/2⟩+31.6%| ± 5/2⟩+21.8%| ± 9/2⟩+9.2%| ± 3/2⟩…
413.894	0.23	0.30	16.60	34.8%| ± 3/2⟩+30.7%| ± 5/2⟩+17.2%| ± 1/2⟩+13.2%| ± 7/2⟩…
440.325	0.12	0.51	17.95	55.5%| ± 1/2⟩+27.5%| ± 3/2⟩+8.1%| ± 5/2⟩+4.7%| ± 7/2⟩…

Table S22. Electronic structure of **Dy2** in Dy_3TeCl_4 calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet.

Energy (cm^{-1})	g1	g2	g3	Wavefunction
0.00	7.98×10^{-3}	1.48×10^{-2}	19.83	98.4%| ± 15/2⟩
152.061	1.51	4.27	15.88	25.1%| ± 13/2⟩+18.3%| ± 5/2⟩+17.8%| ± 9/2⟩+11.5%| ± 1/2⟩…
186.563	2.59	4.84	8.16	47.4%| ± 13/2⟩+18.8%| ± 7/2⟩+17.2%| ± 11/2⟩ + 10.2%| ± 3/2⟩…
232.725	8.27	5.80	0.63	27.5%| ± 11/2⟩+24.3%| ± 13/2⟩+20.9%| ± 9/2⟩+13.6%| ± 5/2⟩…
284.017	2.64	3.84	11.77	41.2%| ± 11/2⟩+28.3%| ± 9/2⟩+13.5%| ± 7/2⟩+8.5%| ± 3/2⟩…
318.948	0.51	0.66	15.92	33.0%| ± 7/2⟩+31.6%| ± 5/2⟩+24.0%| ± 9/2⟩+7.7%| ± 3/2⟩…
388.706	2.42×10^{-2}	0.13	18.74	33.2%| ± 3/2⟩+27.4%| ± 5/2⟩+22.5%| ± 1/2⟩+12.8%| ± 7/2⟩…
434.592	2.69×10^{-2}	8.43×10^{-2}	19.46	48.4%| ± 1/2⟩+28.3%| ± 3/2⟩+12.0%| ± 5/2⟩+5.8%| ± 7/2⟩…

Table S23. Electronic structure of **Dy3** in Dy_3TeCl_4 calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet.

Energy (cm^{-1})	g1	g2	g3	Wavefunction
0.00	1.11×10^{-2}	2.13×10^{-2}	19.81	99.1%| ± 15/2⟩
134.983	1.54	4.03	16.21	19.1%| ± 13/2⟩+18.7%| ± 5/2⟩+17.4%| ± 9/2⟩+13.0%| ± 3/2⟩…
171.416	2.41	4.87	8.54	42.8%| ± 13/2⟩+18.9%| ± 7/2⟩+16.1%| ± 11/2⟩ + 10.5%| ± 3/2⟩…
222.549	8.04	5.86	0.16	33.8%| ± 13/2⟩+24.5%| ± 11/2⟩+14.7%| ± 9/2⟩+13.6%| ± 5/2⟩…
280.918	2.92	3.49	11.60	43.0%| ± 11/2⟩+28.7%| ± 9/2⟩+9.9%| ± 7/2⟩+9.4%| ± 3/2⟩…
323.738	0.33	0.47	15.85	34.2%| ± 7/2⟩+26.4%| ± 9/2⟩+24.7%| ± 5/2⟩+7.9%| ± 11/2⟩…
405.698	5.87×10^{-2}	0.11	16.80	35.2%| ± 5/2⟩+33.0%| ± 3/2⟩+18.3%| ± 7/2⟩+8.7%| ± 1/2⟩…
432.372	2.80×10^{-2}	0.16	18.32	60.7%| ± 1/2⟩+28.4%| ± 3/2⟩+5.5%| ± 5/2⟩…