Electronic Supplementary Information

Determination of Ligand Field Splitting in Lanthanide(III) Monoporphyrinato Complexes

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Contents:

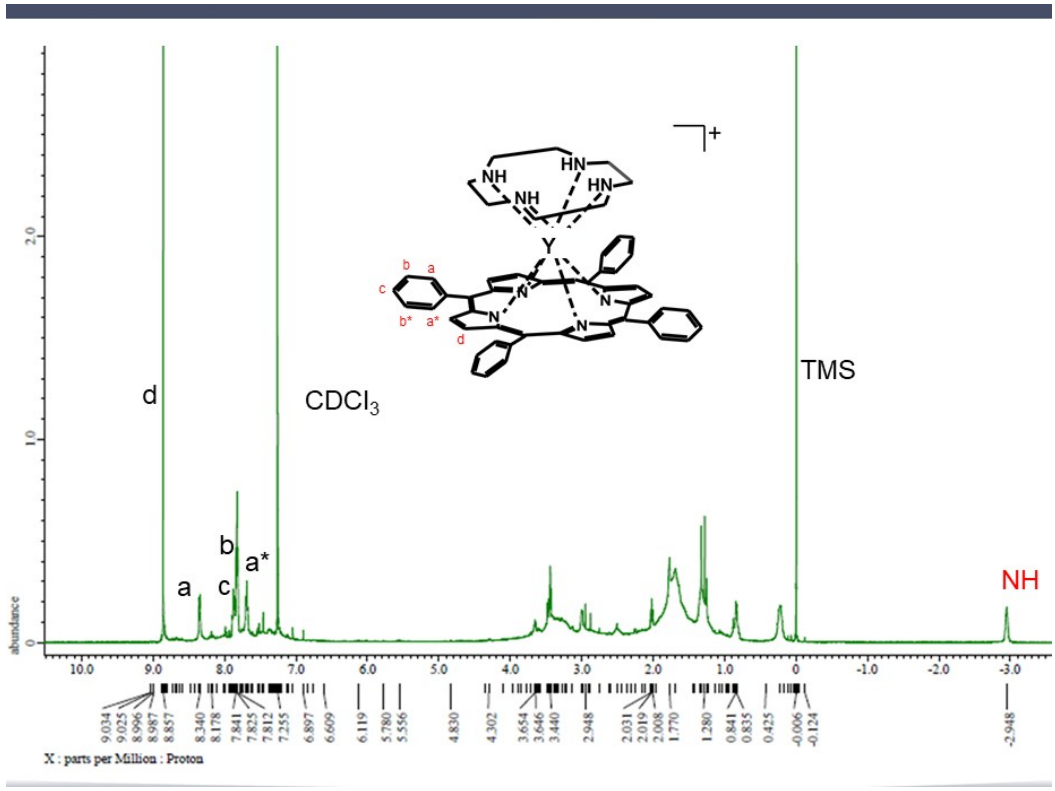


Figure S1. ^{1}H NMR spectrum of [Y(TPP)(cyclen)]Cl in deuterated chloroform, $CDCl_3$, measured at 298 K

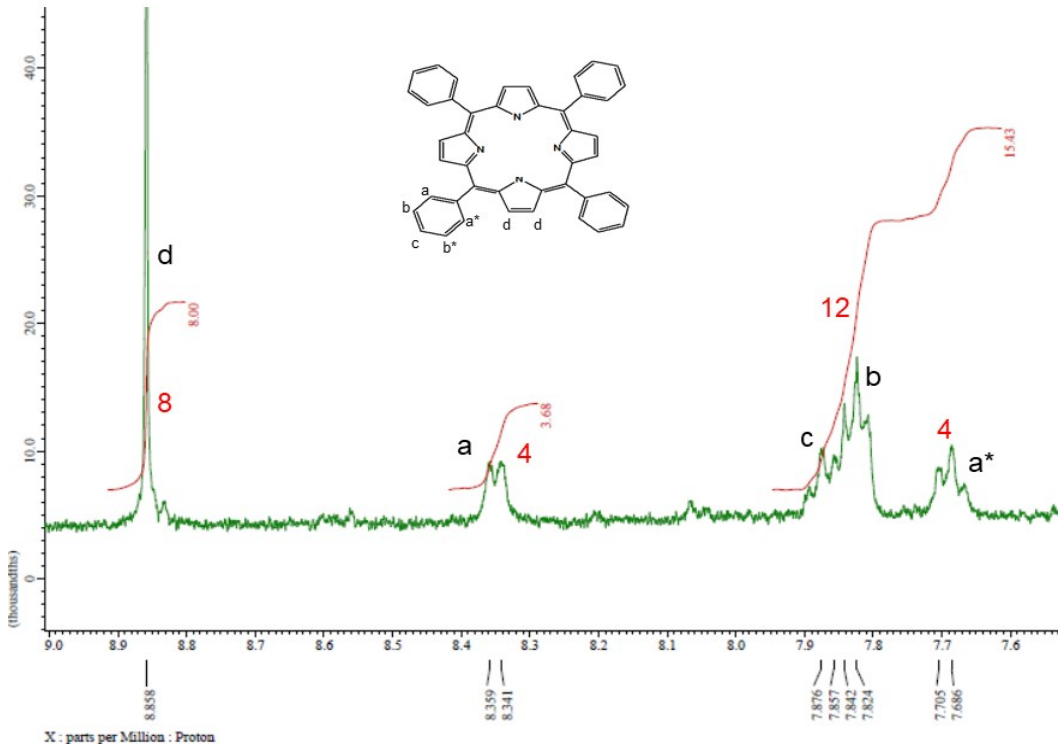


Figure S2. The peak integration for porphyrin moiety of [Y(TPP)(cyclen)]Cl

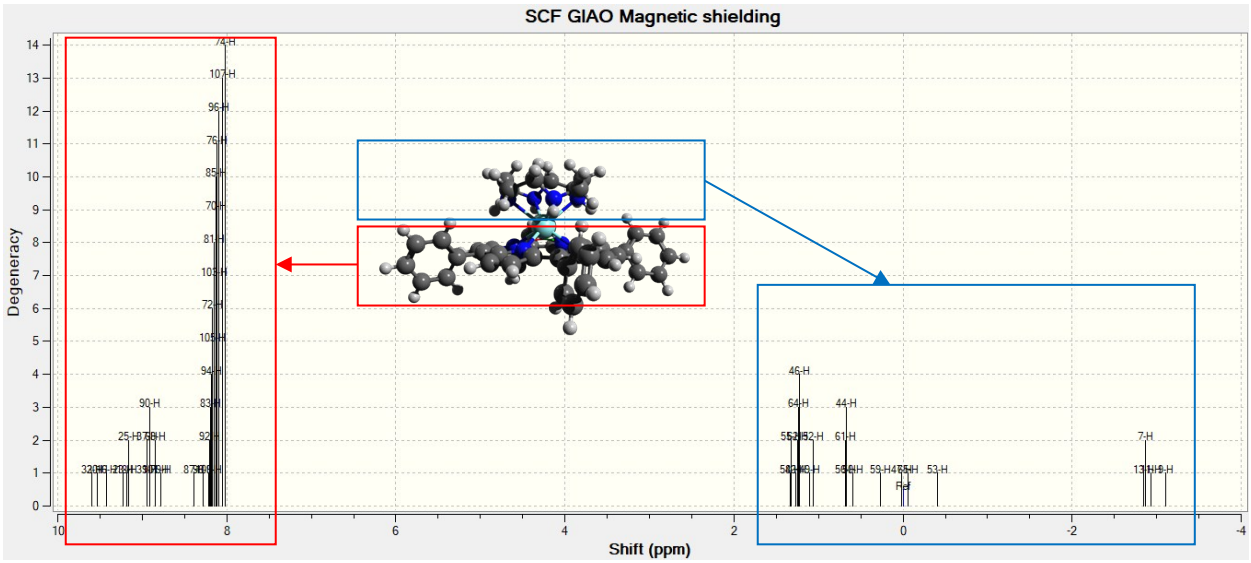


Figure S3. The theoretical calculation for ^{1}H NMR spectrum of [Y(TPP)(cyclen)]Cl. Ref shielding: 31.8821 ppm (TMS B3LYP/6-311+G(2d,p))

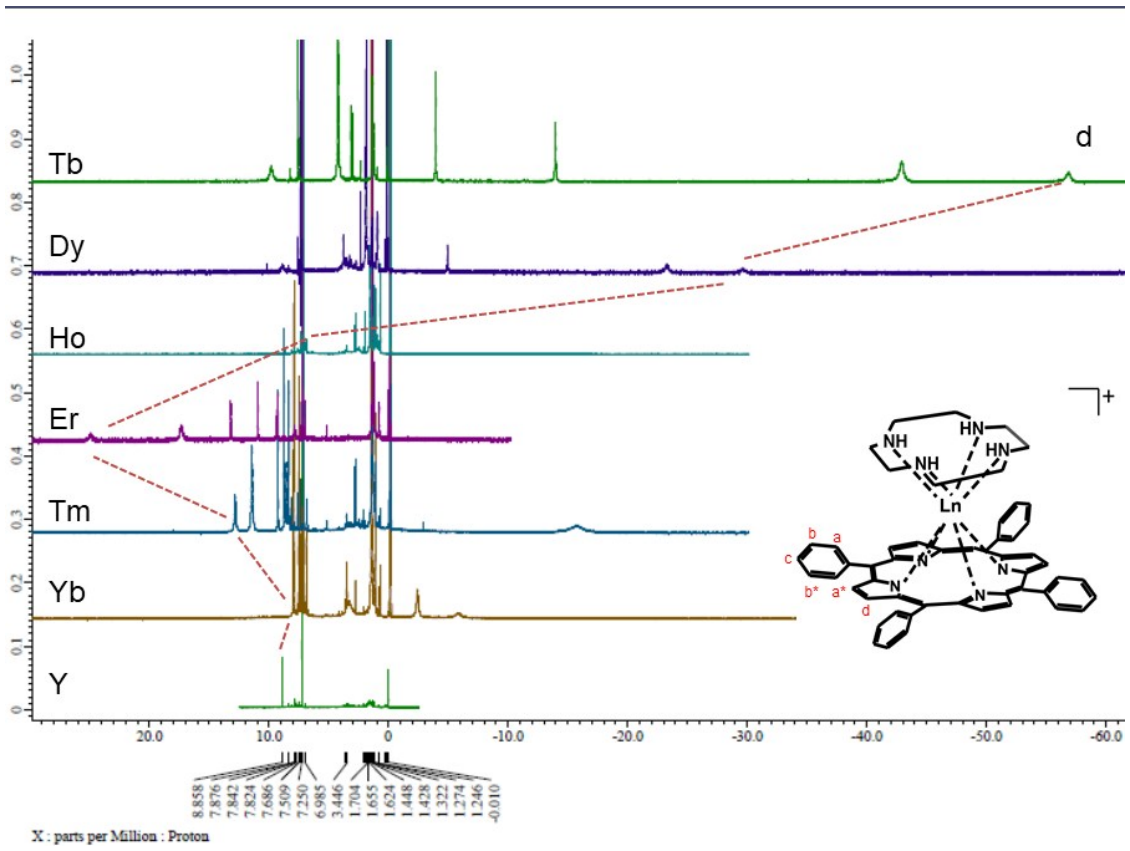


Figure S4. ^{1}H NMR spectrum of [Ln(TPP)(cyclen)]Cl in deuterated chloroform, $CDCl_3$, measured at 298

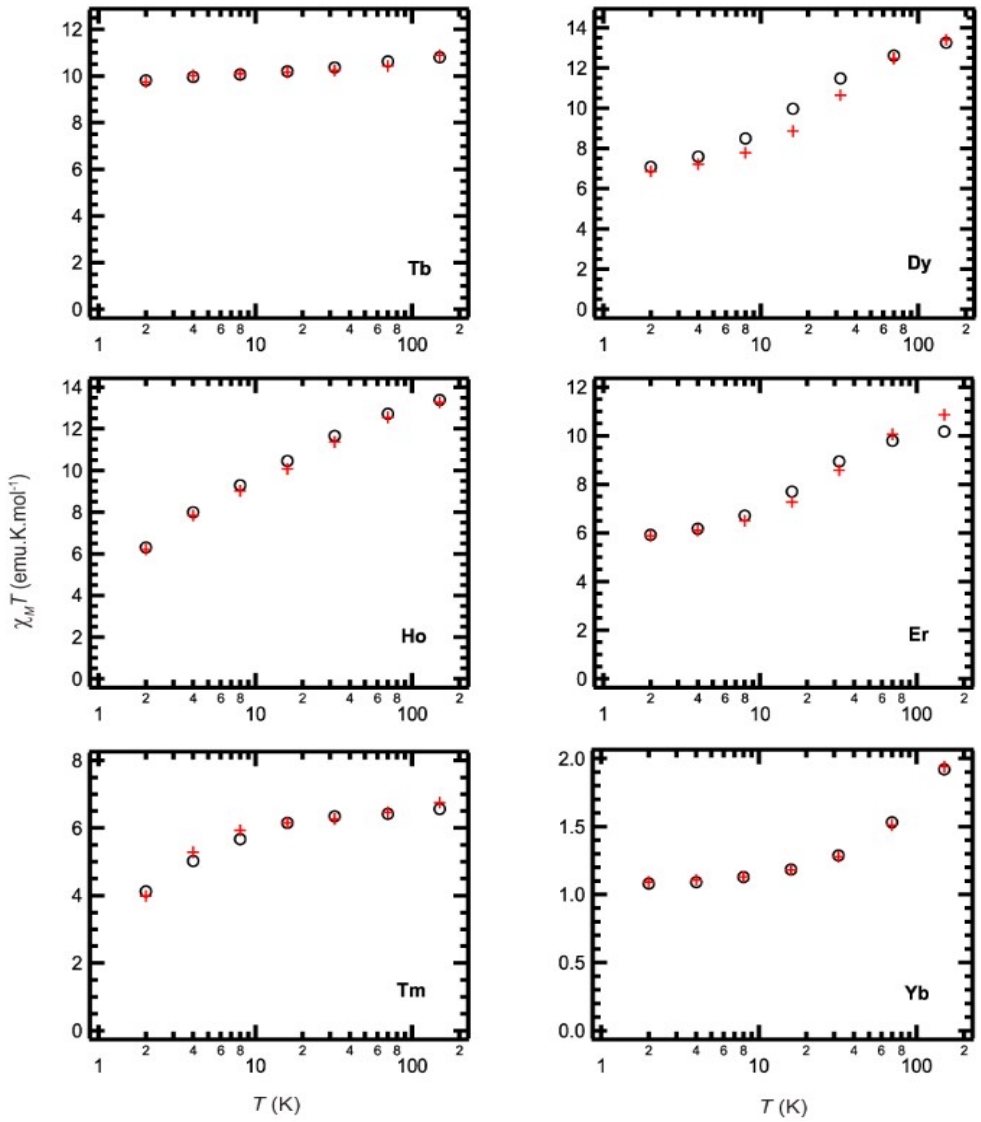


Figure S5. Magnetic susceptibility, $\chi_m T$, values against temperature for [Ln(TPP)(cyclen)]Cl (Ln = Tb, Dy, Ho, Er, Tm, and Yb). Red cross and black circles indicate theoretical and experimental for fitting, repectively.

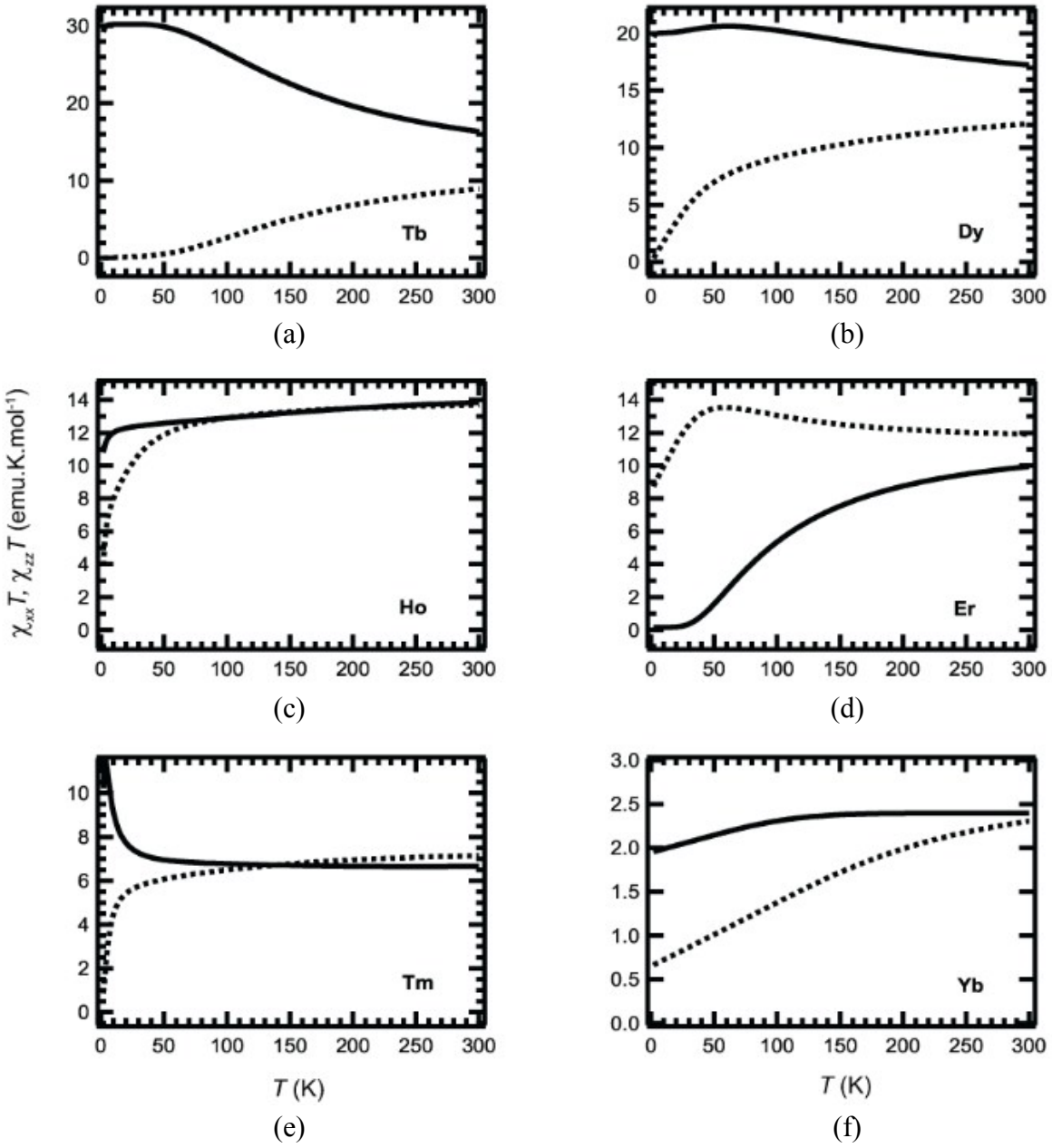
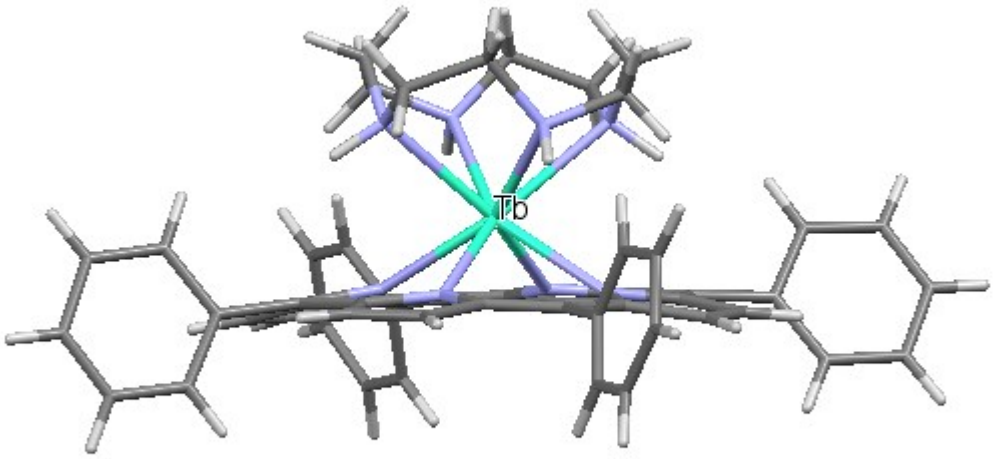
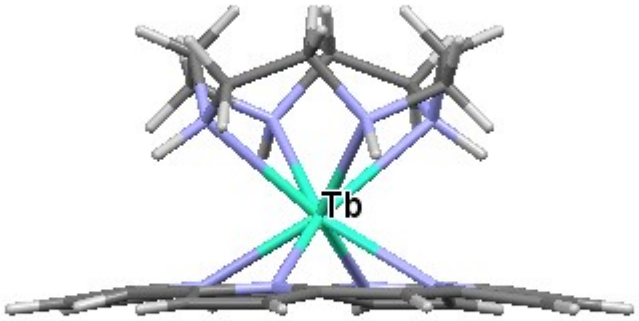


Figure S6. Plots of the principal magnetic susceptibilities $\chi_{zz}T$ (solid lines) and $\chi_{xx}T = \chi_{yy}T$ (dash lines) vs temperature (T) for [Ln(TPP)(cyclen)]Cl (Produced by LF terms with C_4 symmetry).



(a)



(b)

Figure S7. The molecular structure of terbium(III) monoporphyrinato cyclen complex: (a) obtained by single crystal x-ray diffraction, and (b) simplified by replacing phenyl rings to the hydrogen atoms.

Table S1. Assignments of the ^{1}H NMR signal of the proton chemical shift δ, paramagnetic shifts Δδ, and components of geometrical factor (R = Ln-H distance; θ = the angle of proton to the z-axis) for [Ln(TPP)(cyclen)]Cl (Ln = Tb, Dy, Ho, Er, Tm, and Yb)

		Y	Tb	Dy	Ho	Er	Tm	Yb
H^{a}	δ	8.36	-43.21	-23.38	7.45	17.40	11.50	7.96
	Δδ	0.00	-51.57	-31.74	-0.91	9.04	3.14	-0.40
	R	5.34	5.34	5.37	5.35	5.35	5.36	5.37
	§θ	*N.A*	65.50	66.30	65.50	62.20	65.60	62.50
	C	*N.A*	-1.59×10^{-3}	-1.66×10^{-3}	-1.58×10^{-3}	-1.14×10^{-3}	-1.58×10^{-3}	-1.16×10^{-3}
	Δδ/*C*	*N.A*	3.25×10^{4}	1.91×10^{4}	5.75×10^{2}	-7.96×10^{3}	-1.98×10^{3}	3.45×10^{2}
H^{a*}	δ	7.69	9.52	8.76	7.72	7.95	8.48	7.54
	Δδ	0.00	1.83	1.07	0.03	0.26	0.79	-0.15
	R	6.16	6.16	6.17	6.16	6.16	6.18	6.15
	§θ	*N.A*	54.20	54.21	54.22	55.04	58.50	59.00
	C	*N.A*	5.67×10^{-5}	5.54×10^{-5}	-5.47×10^{-5}	-3.21×10^{-5}	-3.84×10^{-4}	-4.40×10^{-3}
	Δδ/*C*	*N.A*	3.23×10^{4}	1.93×10^{4}	5.84×10^{2}	-8.06×10^{3}	-2.06×10^{3}	3.43×10^{2}
H^{b}	δ	7.82	-4.24	0.78		11.00	8.88	7.65
	Δδ	0.00	-12.06	-7.04		3.18	1.06	-0.17
	R	7.66	7.65	7.66		7.65	7.62	7.66
	§θ	*N.A*	61.80	61.70		62.45	65.50	64.80
	C	*N.A*	-3.68×10^{-4}	-3.63×10^{-4}		-3.99×10^{-4}	-5.46×10^{-4}	-5.07×10^{-4}
	Δδ/*C*	*N.A*	3.27×10^{4}	1.94×10^{4}		-7.97×10^{3}	-1.94×10^{3}	3.45×10^{2}
H^{b*}	δ	7.82	0.96	3.66	7.69	9.39	8.75	
	Δδ	0.00	-6.86	-4.16	-0.13	1.57	0.93	
	R	8.23	8.23	8.22	8.22	8.22	8.22	
	§θ	*N.A*	59.70	59.80	59.60	59.30	65.00	
	C	*N.A*	-2.12×10^{-4}	-2.17×10^{-4}	-2.09×10^{-4}	-1.96×10^{-5}	-4.19×10^{-4}	
	Δδ/*C*	*N.A*	3.24×10^{4}	1.92×10^{4}	5.99×10^{2}	-7.98×10^{3}	-2.22×10^{3}	
H^{c}	δ	7.88	-14.25	-5.09	7.48	13.26	9.35	7.62
	Δδ	0.00	-22.13	-12.97	-0.40	5.38	1.47	-0.26
	R	8.76	8.76	8.78	8.78	8.77	8.79	8.77
	θ	79.90	79.71	79.06	79.87	79.69	79.49	79.40
	C	-6.44×10^{-4}	-6.73×10^{-4}	-6.58×10^{-4}	-6.70×10^{-4}	-6.70×10^{-4}	-6.62×10^{-4}	-6.67×10^{-4}
	Δδ/*C*	*N.A*	3.29×10^{4}	1.97×10^{4}	5.97×10^{2}	-8.03×10^{3}	-2.20×10^{3}	3.86×10^{2}
H^{d}	δ	8.86	-57.14	-29.80	7.69	24.95	12.84	8.12
	Δδ	0.00	-66.00	-38.66	-1.17	16.09	3.98	-0.74
	R	5.45	5.44	5.44	5.45	5.44	5.44	5.41
	θ	71.47	70.45	70.27	70.30	70.01	70.59	71.00
	C	-2.20×10^{-3}	-2.06×10^{-3}	-2.04×10^{-3}	-2.04×10^{-3}	-2.02×10^{-3}	-2.08×10^{-3}	-2.16×10^{-3}
	Δδ/*C*	*N.A*	3.21×10^{4}	1.90×10^{4}	5.74×10^{2}	-7.97×10^{3}	-1.92×10^{3}	3.45×10^{2}

Table S2. Magnetic susceptibility χT (cm^3 K mol^{-1}) and calculated paramagnetic shift Δδ (ppm) using equation 1. Simulation 1 and 2 are produced by LF terms with the C_4 and D_{4d} symmetry, respectively. Ab Initio 1 and 2 are produced by CASSCF calculation with experimental and symmetrized-C_4 geometry, respectively. $\chi_{AV}T$ = Average of principal magnetic susceptibility

Method	[Tb(TPP)(cyclen)]Cl			Method	[Dy(TPP)(cyclen)]Cl		
	$\chi_{ZZ}T$	$\chi_{AV}T$	Δδ		$\chi_{ZZ}T$	$\chi_{AV}T$	Δδ
Simulation 1	16.3620	11.4227	-60.0201	Simulation 1	17.235	13.8137	-38.6129
Simulation 2	16.3840	11.5460	-58.7887	Simulation 2	17.5640	13.9287	-41.0281
Ab Initio 1	15.0831	11.7809	-40.1269	Ab Initio 1	16.5731	14.0984	-27.9293
Ab Initio 2	14.9941	11.78457	-35.4289	Ab Initio 2	16.5349	14.0937	-27.0594
Method	[Ho(TPP)(cyclen)]Cl			Method	[Er(TPP)(cyclen)]Cl		
	$\chi_{ZZ}T$	$\chi_{AV}T$	Δδ		$\chi_{ZZ}T$	$\chi_{AV}T$	Δδ
Simulation 1	13.8390	13.7430	-1.1736	Simulation 1	9.9440	11.2553	15.9927
Simulation 2	14.0010	13.9050	-1.1736	Simulation 2	10.1360	11.3553	14.8707
Ab Initio 1	14.3258	14.0083	-3.8820	Ab Initio 1	10.6319	11.4081	9.4660
Ab Initio 2	14.1498	13.9905	-2.0564	Ab Initio 2	10.3527	11.4103	11.7227
Method	[Tm(TPP)(cyclen)]Cl			Method	[Yb(TPP)(cyclen)]Cl		
	$\chi_{ZZ}T$	$\chi_{AV}T$	Δδ		$\chi_{ZZ}T$	$\chi_{AV}T$	Δδ
Simulation 1	6.6640	6.9820	3.8956	Simulation 1	2.3950	2.3343	-0.7376
Simulation 2	6.7150	7.0443	4.0344	Simulation 2	2.4870	2.4257	-0.7457
Ab Initio 1	6.6486	7.0938	5.4534	Ab Initio 1	2.4334	2.5093	0.9232
Ab Initio 2	7.0090	7.1007	1.1601	Ab Initio 2	2.6136	2.5309	-0.9919

Table S3. Electronic structures of [Ln(TPP)(cyclen)]Cl generated by LF parameters with C_4 symmetry (Energies and wave functions).

[Tb(TPP)(cyclen)]Cl						
Energy (cm^{-1})	Wave Function					
0.00	$+0.71\|+6\rangle$	$+0.71\|-6\rangle$	$-0.05\|+2\rangle$	$-0.05\|-2\rangle$		
0.39	$+0.71\|+6\rangle$	$-0.71\|-6\rangle$	$-0.03\|+2\rangle$	$+0.03\|-2\rangle$		
150.73	$+0.99\|0\rangle$	$+0.09\|+4\rangle$	$+0.09\|-4\rangle$			
184.07	$-0.69\|+1\rangle$	$-0.69\|-1\rangle$	$-0.16\|+3\rangle$	$-0.16\|-3\rangle$		
184.07	$+0.69\|+1\rangle$	$-0.69\|-1\rangle$	$-0.16\|+3\rangle$	$+0.16\|-3\rangle$		
238.74	$+0.71\|+2\rangle$	$+0.71\|-2\rangle$	$+0.05\|+6\rangle$	$+0.05\|-6\rangle$		
399.80	$-0.71\|+2\rangle$	$+0.71\|-2\rangle$	$-0.03\|+6\rangle$	$+0.03\|-6\rangle$		
490.84	$-0.69\|+3\rangle$	$+0.69\|-3\rangle$	$-0.16\|+1\rangle$	$+0.16\|-1\rangle$	$-0.03\|+5\rangle$	$+0.03\|-5\rangle$
490.84	$-0.69\|+3\rangle$	$-0.69\|-3\rangle$	$+0.16\|+1\rangle$	$-0.16\|-1\rangle$	$+0.03\|+5\rangle$	$+0.03\|-5\rangle$
515.74	$+0.71\|+5\rangle$	$+0.71\|-5\rangle$	$+0.03\|+3\rangle$	$+0.03\|-3\rangle$		
515.74	$-0.71\|+5\rangle$	$+0.71\|-5\rangle$	$+0.03\|+3\rangle$	$-0.03\|-3\rangle$		
589.38	$-0.71\|+4\rangle$	$+0.71\|-4\rangle$				
596.29	$-0.70\|+4\rangle$	$-0.70\|-4\rangle$	$+0.12\|0\rangle$			
[Dy(TPP)(cyclen)]Cl						
Energy (cm^{-1})	Wave Function					
0.00	$+0.99\|+11/2\rangle$	$+0.15\|-11/2\rangle$	$+0.05\|+3/2\rangle$			
0.00	$-0.99\|-11/2\rangle$	$+0.15\|+11/2\rangle$	$-0.05\|-3/2\rangle$			
67.18	$+0.98\|+13/2\rangle$	$+0.21\|+5/2\rangle$	$-0.07\|-3/2\rangle$	$+0.04\|-13/2\rangle$		
67.18	$+0.98\|-13/2\rangle$	$+0.21\|-5/2\rangle$	$-0.07\|+3/2\rangle$	$-0.04\|+13/2\rangle$		
106.59	$+0.79\|-9/2\rangle$	$+0.59\|+9/2\rangle$	$-0.09\|-1/2\rangle$	$-0.07\|+1/2\rangle$	$+0.05\|-7/2\rangle$	
106.59	$+0.79\|+9/2\rangle$	$-0.59\|-9/2\rangle$	$-0.09\|+1/2\rangle$	$+0.07\|-1/2\rangle$	$-0.05\|+7/2\rangle$	
222.22	$-0.91\|+7/2\rangle$	$+0.29\|-1/2\rangle$	$+0.23\|-7/2\rangle$	$-0.14\|+15/2\rangle$	$+0.10\|-9/2\rangle$	$-0.07\|+1/2\rangle$ $+0.04\|-15/2\rangle$

222.22	$-0.91\|-7/2\rangle$	$+0.29\|+1/2\rangle$	$-0.23\|+7/2\rangle$	$-0.14\|-15/2\rangle$	$+0.10\|+9/2\rangle$	$+0.07\|-1/2\rangle$	$-0.04\|+15/2\rangle$
304.19	$+0.73\|+5/2\rangle$	$-0.57\|-3/2\rangle$	$+0.25\|-5/2\rangle$	$-0.20\|+13/2\rangle$	$-0.19\|+3/2\rangle$	$-0.07\|-13/2\rangle$	$+0.04\|-11/2\rangle$
304.19	$-0.73\|-5/2\rangle$	$+0.57\|+3/2\rangle$	$+0.25\|+5/2\rangle$	$+0.20\|-13/2\rangle$	$-0.19\|-3/2\rangle$	$-0.07\|+13/2\rangle$	$-0.04\|+11/2\rangle$
541.19	$-0.80\|-1/2\rangle$	$+0.49\|+1/2\rangle$	$-0.24\|+7/2\rangle$	$-0.18\|+15/2\rangle$	$+0.14\|-7/2\rangle$	$+0.11\|-15/2\rangle$	$-0.07\|-9/2\rangle$
541.19	$-0.80\|+1/2\rangle$	$-0.49\|-1/2\rangle$	$-0.24\|-7/2\rangle$	$-0.18\|-15/2\rangle$	$-0.14\|+7/2\rangle$	$-0.11\|+15/2\rangle$	$-0.07\|+9/2\rangle$
569.63	$+0.80\|-3/2\rangle$	$+0.60\|+5/2\rangle$	$-0.07\|+13/2\rangle$	$-0.03\|-11/2\rangle$			
569.63	$+0.80\|+3/2\rangle$	$+0.60\|-5/2\rangle$	$-0.07\|-13/2\rangle$	$-0.03\|+11/2\rangle$			
636.16	$-0.97\|+15/2\rangle$	$+0.20\|+7/2\rangle$	$+0.16\|-1/2\rangle$				
636.16	$+0.97\|-15/2\rangle$	$-0.20\|-7/2\rangle$	$-0.16\|+1/2\rangle$				
[Ho(TPP)(cyclen)]Cl							
Energy (cm^{-1})	Wave Function						
0.00	$-0.68\|+4\rangle$	$-0.68\|-4\rangle$	$+0.21\|+8\rangle$	$+0.21\|-8\rangle$	$+0.04\|0\rangle$		
0.72	$+0.68\|+4\rangle$	$-0.68\|-4\rangle$	$-0.21\|+8\rangle$	$+0.21\|-8\rangle$			
5.10	$+0.70\|+5\rangle$	$-0.70\|-5\rangle$	$-0.11\|+1\rangle$	$+0.11\|-1\rangle$	$+0.04\|+3\rangle$	$-0.04\|-3\rangle$	
5.10	$-0.70\|+5\rangle$	$-0.70\|-5\rangle$	$+0.11\|+1\rangle$	$+0.11\|-1\rangle$	$+0.04\|+3\rangle$	$+0.04\|-3\rangle$	
57.84	$+0.61\|+6\rangle$	$+0.61\|-6\rangle$	$-0.35\|+2\rangle$	$-0.35\|-2\rangle$			
70.38	$-0.61\|+3\rangle$	$-0.61\|-3\rangle$	$+0.36\|+7\rangle$	$+0.36\|-7\rangle$	$-0.05\|+5\rangle$	$-0.05\|-5\rangle$	
70.38	$+0.61\|+3\rangle$	$-0.61\|-3\rangle$	$-0.36\|+7\rangle$	$+0.36\|-7\rangle$	$-0.05\|+5\rangle$	$+0.05\|-5\rangle$	
76.21	$+0.65\|+6\rangle$	$-0.65\|-6\rangle$	$-0.27\|+2\rangle$	$+0.27\|-2\rangle$			
333.25	$+0.61\|+2\rangle$	$+0.61\|-2\rangle$	$+0.35\|+6\rangle$	$+0.35\|-6\rangle$			
373.22	$+0.67\|+8\rangle$	$+0.67\|-8\rangle$	$+0.21\|+4\rangle$	$+0.21\|-4\rangle$	$-0.05\|0\rangle$		
373.50	$-0.68\|+8\rangle$	$+0.68\|-8\rangle$	$-0.21\|+4\rangle$	$+0.21\|-4\rangle$			
378.11	$+0.60\|+7\rangle$	$+0.60\|-7\rangle$	$+0.34\|+3\rangle$	$+0.34\|-3\rangle$	$+0.14\|+1\rangle$	$+0.14\|-1\rangle$	
378.11	$-0.60\|+7\rangle$	$+0.60\|-7\rangle$	$-0.34\|+3\rangle$	$+0.34\|-3\rangle$	$+0.14\|+1\rangle$	$-0.14\|-1\rangle$	
409.10	$+0.65\|+2\rangle$	$-0.65\|-2\rangle$	$+0.27\|+6\rangle$	$-0.27\|-6\rangle$			
458.28	$+0.68\|+1\rangle$	$+0.68\|-1\rangle$	$-0.11\|+3\rangle$	$-0.11\|-3\rangle$	$+0.11\|+5\rangle$	$+0.11\|-5\rangle$	
458.28	$-0.68\|+1\rangle$	$+0.68\|-1\rangle$	$-0.11\|+3\rangle$	$+0.11\|-3\rangle$	$-0.11\|+5\rangle$	$+0.11\|-5\rangle$	
492.54	$-1.00\|0\rangle$	$-0.04\|+4\rangle$	$-0.04\|-4\rangle$				
[Er(TPP)(cyclen)]Cl							
Energy (cm^{-1})	Wave Function						
0.00	$+1.00\|+1/2\rangle$	$+0.11\|+9/2\rangle$	$+0.04\|-7/2\rangle$				
0.00	$-1.00\|-1/2\rangle$	$-0.11\|-9/2\rangle$	$-0.04\|+7/2\rangle$				
77.91	$+0.84\|+3/2\rangle$	$+0.43\|-3/2\rangle$	$+0.26\|+11/2\rangle$	$+0.13\|-11/2\rangle$	$-0.10\|-5/2\rangle$	$-0.09\|-13/2\rangle$	
77.91	$-0.84\|-3/2\rangle$	$+0.43\|+3/2\rangle$	$-0.26\|-11/2\rangle$	$+0.13\|+11/2\rangle$	$+0.10\|+5/2\rangle$	$+0.09\|+13/2\rangle$	
113.04	$+0.82\|-13/2\rangle$	$+0.55\|-5/2\rangle$	$+0.14\|+3/2\rangle$	$+0.05\|+11/2\rangle$			
113.04	$-0.82\|+13/2\rangle$	$-0.55\|+5/2\rangle$	$-0.14\|-3/2\rangle$	$-0.05\|-11/2\rangle$			
121.84	$+0.96\|-15/2\rangle$	$+0.27\|-7/2\rangle$	$-0.03\|+1/2\rangle$				
121.84	$+0.96\|+15/2\rangle$	$+0.27\|+7/2\rangle$	$-0.03\|-1/2\rangle$				
327.70	$-0.83\|-5/2\rangle$	$+0.56\|-13/2\rangle$	$-0.06\|+11/2\rangle$				
327.70	$-0.83\|+5/2\rangle$	$+0.56\|+13/2\rangle$	$-0.06\|-11/2\rangle$				
376.12	$+0.95\|+11/2\rangle$	$-0.30\|+3/2\rangle$	$-0.04\|-5/2\rangle$	$+0.04\|-11/2\rangle$			
376.12	$+0.95\|-11/2\rangle$	$-0.30\|-3/2\rangle$	$-0.04\|+5/2\rangle$	$-0.04\|+11/2\rangle$			
420.86	$-0.96\|+7/2\rangle$	$+0.27\|+15/2\rangle$	$+0.06\|-9/2\rangle$				
420.86	$-0.96\|-7/2\rangle$	$+0.27\|-15/2\rangle$	$+0.06\|+9/2\rangle$				
446.02	$+0.99\|+9/2\rangle$	$-0.11\|+1/2\rangle$	$-0.09\|-9/2\rangle$	$+0.06\|-7/2\rangle$			
446.02	$+0.99\|-9/2\rangle$	$-0.11\|-1/2\rangle$	$+0.09\|+9/2\rangle$	$+0.06\|+7/2\rangle$			
[Tm(TPP)(cyclen)]Cl							
Energy (cm^{-1})	Wave Functions						
0.00	$-0.61\|+6\rangle$	$-0.61\|-6\rangle$	$-0.36\|+2\rangle$	$-0.36\|-2\rangle$			
2.87	$-0.71\|+6\rangle$	$+0.71\|-6\rangle$					

7.52	$-0.97\|-0\rangle$	$-0.16\|+4\rangle$	$-0.16\|-4\rangle$			
7.61	$-0.66\|+1\rangle$	$+0.66\|-1\rangle$	$+0.26\|+3\rangle$	$-0.26\|-3\rangle$	$-0.05\|+5\rangle$	$+0.05\|-5\rangle$
7.61	$+0.66\|+1\rangle$	$+0.66\|-1\rangle$	$+0.26\|+3\rangle$	$+0.26\|-3\rangle$	$+0.05\|+5\rangle$	$+0.05\|-5\rangle$
11.37	$-0.61\|+2\rangle$	$-0.61\|-2\rangle$	$+0.36\|+6\rangle$	$+0.36\|-6\rangle$		
204.68	$-0.71\|+2\rangle$	$+0.71\|-2\rangle$				
264.52	$-0.66\|+3\rangle$	$-0.66\|-3\rangle$	$+0.26\|+1\rangle$	$+0.26\|-1\rangle$	$+0.04\|+5\rangle$	$+0.04\|-5\rangle$
264.52	$-0.66\|+3\rangle$	$+0.66\|-3\rangle$	$-0.26\|+1\rangle$	$+0.26\|-1\rangle$	$-0.04\|+5\rangle$	$+0.04\|-5\rangle$
390.21	$+0.71\|+4\rangle$	$-0.71\|-4\rangle$				
410.39	$+0.69\|+4\rangle$	$+0.69\|-4\rangle$	$-0.22\|0\rangle$			
443.39	$-0.70\|+5\rangle$	$+0.70\|-5\rangle$	$+0.06\|+1\rangle$	$-0.06\|-1\rangle$		
443.39	$+0.70\|+5\rangle$	$+0.70\|-5\rangle$	$-0.06\|+1\rangle$	$-0.06\|-1\rangle$		
[Yb(TPP)(cyclen)]Cl						
Energy (cm^{-1})	Wave Functions					
0.00	$+0.93\|+5/2\rangle$	$-0.35\|-3/2\rangle$				
0.00	$-0.93\|-5/2\rangle$	$+0.35\|+3/2\rangle$				
306.87	$-0.93\|+3/2\rangle$	$-0.35\|-5/2\rangle$				
306.87	$+0.93\|-3/2\rangle$	$+0.35\|+5/2\rangle$				
353.66	$-0.87\|-1/2\rangle$	$+0.50\|+7/2\rangle$				
353.66	$+0.87\|+1/2\rangle$	$-0.50\|-7/2\rangle$				
551.81	$-0.87\|+7/2\rangle$	$-0.50\|-1/2\rangle$				
551.81	$+0.87\|-7/2\rangle$	$+0.50\|+1/2\rangle$				

Table S4. Electronic structures of [Ln(TPP)(cyclen)]Cl generated by LF parameters with D_{4d} symmetry (Energies and wave functions).

[Tb(TPP)(cyclen)]Cl			[Dy(TPP)(cyclen)]Cl			[Ho(TPP)(cyclen)]Cl	
Energy (cm^{-1})	Wave function		Energy (cm^{-1})	Wave function		Energy (cm^{-1})	Wave function
0.00	+0.85|+6> +0.52 |–6>		0.00	+0.28|+5.5> +0.96|–5.5>		0.00	+1.00|+5> –0.03|–5>
0.00	+0.85|–6> +0.52 |+6>		0.00	–0.96|+5.5> +0.28|–5.5>		0.00	–0.03|+5> –1.00|–5>
166.45	–1.00 |0>		48.12	+0.98|+6.5> +0.18|–6.5>		9.63	–0.74|+4> –0.67|–4>
197.44	–0.71|+1> –0.71|–1>		48.12	+0.18|+6.5> –0.98|–6.5>		9.63	+0.67|+4> –0.74|–4>
197.44	+0.71|+1> –0.71|–1>		106.91	+0.02|+4.5> –1.00|–4.5>		99.91	+0.71|+6> +0.70|–6>
284.01	–0.71|+2> +0.71|–2>		106.91	+1.00|+4.5> +0.02|–4.5>		99.91	+0.70|+6> –0.71|–6>
284.01	+0.71|+2> +0.71|–2>		237.16	+1.00|+3.5> –0.04|–3.5>		111.51	+0.71|+3> +0.71|–3>
401.44	+0.71|+3> +0.71|–3>		237.16	+0.04|+3.5> +1.00|–3.5>		111.51	+0.71|+3> –0.71|–3>
401.44	+0.71|+3> –0.71|–3>		336.89	–1.00|–2.5>		248.55	–0.08 |+7> –1.00|–7>
430.21	–1.00|–5>		336.89	–1.00|+2.5>		248.55	+1.00|+7> –0.08|–7>
430.21	+1.00|+5>		395.78	+1.00|+1.5> +0.03|–1.5>		250.50	–0.66|+2> +0.75|–2>
490.49	–0.71|+4> +0.70|–4>		395.78	+0.03|+1.5> –1.00|–1.5>		250.50	–0.75|+2> –0.66|–2>
490.49	–0.70|+4> –0.71|–4>		421.22	+0.85|+0.5> –0.53|–0.5>		257.84	+1.00|–8>
			421.22	+0.53|+0.5> +0.85|–0.5>		257.84	–1.00|+8>
			503.70	+1.00|+7.5>		364.85	–0.71|+1> +0.71|–1>
			503.70	+1.00|–7.5>		364.85	–0.71|+1> –0.71|–1>
						408.57	+1.00|0>
[Er(TPP)(cyclen)]Cl			[Tm(TPP)(cyclen)]Cl			[Yb(TPP)(cyclen)]Cl	
Energy (cm^{-1})	Wave function		Energy (cm^{-1})	Wave function		Energy (cm^{-1})	Wave function
0.00	–0.73|+0.5> –0.69|–0.5>		0.00	–1.00|0>		0.00	–0.90|+2.5> +0.44|–2.5>
0.00	+0.69|+0.5> –0.73|–0.5>		0.13	+0.71|+6> –0.71|–6>		0.00	+0.44|+2.5> +0.90|–2.5>

83.66	+0.29|+1.5> +0.96|–1.5>		0.13	+0.71|+6> +0.71|–6>		180.95	+1.00|–1.5>
83.66	–0.96|+1.5> +0.29|–1.5>		18.72	+0.71|+1> –0.71|–1>		180.95	+1.00|+1.5>
122.37	+1.00|–7.5>		18.72	+0.71|+1> +0.71|–1>		325.18	–0.52|+0.5> +0.86|–0.5>
122.37	+1.00|+7.5>		80.85	–0.70|+2> +0.71|–2>		325.18	+0.86|+0.5> +0.52|–0.5>
149.90	–0.03|+6.5> +1.00|–6.5>		80.85	+0.71|+2> +0.70|–2>		405.22	–1.00|+3.5>
149.90	–1.00|+6.5> –0.03|–6.5>		192.66	+0.71|+3> +0.71|–3>		405.22	+1.00|–3.5>
214.31	–0.16|+2.5> +0.99|–2.5>		192.66	–0.71|+3> +0.71|–3>			
214.31	–0.99 |+2.5> –0.16|–2.5>		325.94	+0.71|+4> +0.71|–4>			
291.33	–1.00|+5.5>		325.94	–0.71|+4> +0.71|–4>			
291.33	–1.00|–5.5>		359.93	–1.00|–5.0>			
330.01	+1.00|–3.5>		359.93	–1.00|+5>			
330.01	–1.00|+3.5>						
366.47	–1.00|+4.5> +0.02|–4.5>						
366.47	–0.02|+4.5> –1.00|–4.5>						

Ab initio Calculation details

Apart from geometry optimization, all calculations were employed on MOLCAS 8.0 such as SCF, CASSCF, RASSI and SINGLE_ANISO type. Four basis set approximations have been used for calculations. The details of basis sets are summarized in Table S5.

Table S5. The employed basis sets for theoretical calculations.

Basis set 1	**Basis set 2**
Ln.ANO-RCC…7s6p4d2f1g	Ln.ANO-RCC…8s7p5d3f2g1h
N.ANO-RCC…3s2p1d	N.ANO-RCC…3s2p1d
C.ANO-RCC…2s1p	C.ANO-RCC…2s1p
H.ANO-RCC…1s	H.ANO-RCC…1s

Table S6. Ab initio ligand-field parameters B_n^m (in cm^{-1}) of the $[Tb(TPP)(cyclen)]^+$

n	m	Experimental Geometry		Symmetrized-C_4 Geometry	
		Real part	Imaginary part	Real part	Imaginary part
2	0	**124.80**	**0.00**	**124.00**	**0**
	1	-15.17	-15.17	0.00	0
	2	-13.73	16.44	-0.01	0
4	0	**-126.58**	**0.00**	**-121.20**	**0**
	1	-6.69	1.78	0.00	0
	2	-4.11	-4.11	-0.02	0
	3	9.58	0.85	0.00	0
	4	**57.71**	**54.74**	**-85.94**	**20**
	0	**8.06**	**0.00**	**7.61**	**0**
6	1	1.88	-0.97	0.00	0
	2	-0.38	-1.70	0.00	0
	3	3.52	3.52	0.00	0
	4	**-0.55**	**-12.31**	**11.90**	**5**
	5	1.34	-2.28	0.00	0
	6	-0.62	1.95	0.00	0

Table S7. CASSCF/RASSI calculated energies and wave functions of the $[Tb(TPP)(cyclen)]^+$ with an absolute coefficient larger than 0.04.

Symmetrized-C_4			
Basis Set 1		Basis Set 2	
Energy (cm^{-1})	Wave Function	Energy (cm^{-1})	Wave Function
0.00	|±6⟩, |±2⟩	0.00	|±6⟩, |±2⟩
0.26	|±6⟩, |±2⟩	0.25	|±6⟩, |±2⟩
126	|0⟩, |±4⟩	138	|0⟩, |±4⟩
130	|±1⟩, |±5⟩, |±3⟩	142	|±1⟩, |±5⟩, |±3⟩
130	|±1⟩, |±5⟩, |±3⟩	142	|±1⟩, |±5⟩, |±3⟩
148	|±2⟩, |±6⟩	162	|±2⟩, |±6⟩
190	|±5⟩, |±3⟩, |±1⟩	200	|±5⟩, |±3⟩, |±1⟩
190	|±5⟩, |±3⟩, |±1⟩	200	|±5⟩, |±3⟩, |±1⟩
216	|±2⟩, |±6⟩	233	|±2⟩, |±6⟩
235	|±3⟩, |±1⟩, |±5⟩	252	|±3⟩, |±1⟩, |±5⟩
235	|±3⟩, |±1⟩, |±5⟩	252	|±3⟩, |±1⟩, |±5⟩
239	|±4⟩	254	|±4⟩
257	|±4⟩, |0⟩	273	|±4⟩, |0⟩
Experimental geometry			
Basis Set 2			
Energy (cm^{-1})	Wave Function		
0.00	|±6⟩, |±2⟩		
0.17	|±6⟩, |±2⟩		
140	|0⟩, |±1⟩, |±5⟩, |±3⟩, |±4⟩, |±2⟩		
142	|0⟩, |±1⟩, |±4⟩, |±2⟩, |±5⟩, |±3⟩		
155	|±1⟩, |±5⟩, |±3⟩		
171	|±2⟩, |0⟩, |±5⟩, |±4⟩, |±3⟩, |±6⟩		
204	|±5⟩, |±1⟩, |±3⟩, |±2⟩, |±4⟩		
206	|±5⟩, |±1⟩, |±3⟩, |±2⟩		
232	|±2⟩, |±5⟩, |±4⟩, |±1⟩, |±3⟩		
250	|±3⟩, |±4⟩, |±1⟩, |±5⟩		
255	|±3⟩, |±1⟩, |±4⟩, |±2⟩, |±5⟩		
267	|±4⟩, ±3⟩, |±1⟩, |±2⟩, |±5⟩		
279	|±4⟩, |0⟩, ±3⟩		

Table S8. Composition of wave functions for $[Tb(Por)(cyclen)]^+$ as extracted from CASSCF/RASSI/Single_Aniso calculations with basis set 1.

M_J	Wave Functions and Energies					
	1		2		3	
	0.00 cm^{-1}		0.26 cm^{-1}		126 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	0.702568-0.054416i	**0.704672**	-0.703732+0.054503i	**0.705839**	-0.000027+0.000006i	0.000028
–5	0	0.000000	0	0.000000	0	0.000000
–4	0.000021-0.000001i	0.000021	-0.000021+0.000001i	0.000021	-0.24786+0.012483i	0.248174
–3	0	0.000000	0	0.000000	0	0.000000
–2	0.058611+0.001527i	0.058631	-0.042306-0.001082i	0.042320	0.000403-0.000031i	0.000404
–1	0	0.000000	0	0.000000	0	0.000000
0	-0.000002	0.000002	0.000001i	0.000001	-0.930349+0.106157i	**0.936386**
1	0	0.000000	0	0.000000	0	0.000000
2	0.058318-0.006049i	0.058631	0.042096-0.004345i	0.042320	0.0004-0.000061i	0.000405
3	0	0.000000	0	0.000000	0	0.000000

4	0.000021-0.000001i	0.000021	0.000021-0.000001i	0.000021	-0.2443+0.043675i	0.248173
5	0	0.000000	0	0.000000	0	0.000000
6	0.704672	**0.704672**	0.705839	**0.705839**	-0.000028	0.000028

M_J	4		5		6	
	130 cm^{-1}		130 cm^{-1}		148 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	0	0.000000	0	0.000000	-0.058469+0.004356i	0.058631
–5	-0.261199+0.069708i	0.270341	-0.145483-0.228011i	0.270471	0	0.000000
–4	0	0.000000	0	0.000000	0.000175+0.000005i	0.000175
–3	0.22338-0.02647i	0.224943	-0.092763-0.204925i	0.224943	0	0.000000
–2	0	0.000000	0	0.000000	0.704374+0.020475i	**0.704672**
–1	-0.595294+0.148125i	**0.613446**	-0.321152-0.522597i	**0.613389**	0	0.000000
0	0	0.000000	0	0.000000	0.000518-0.000019i	0.000518
1	0.596866-0.14166i	**0.613446**	-0.315465-0.52605i	**0.613390**	0	0.000000
2	0	0.000000	0	0.000000	0.700906-0.072749i	**0.704671**
3	-0.210606+0.079022i	0.224943	-0.139007-0.176851i	0.224943	0	0.000000
4	0	0.000000	0	0.000000	0.000174-0.000018i	0.000175
5	0.264052-0.057968i	0.270340	-0.135164-0.234276i	0.270471	0	0.000000
6	0	0.000000	0	0.000000	-0.058631	0.058631

M_J	7		8		9	
	190 cm^{-1}		190 cm^{-1}		216cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	0	0.000000	0	0.000000	0.042207-0.003088i	0.042320
–5	0.621901-0.147189i	**0.639082**	0.534861+0.349751i	**0.639063**	0	0.000000
–4	0	0.000000	0	0.000000	-0.000063-0.000009i	0.000064
–3	0.225101-0.043119i	0.229194	-0.186145-0.133534i	0.229088	0	0.000000
–2	0	0.000000	0	0.000000	-0.705528-0.020975i	**0.705840**
–1	-0.193041+0.042179i	0.197595	-0.163637-0.111085i	0.197780	0	0.000000
0	0	0.000000	0	0.000000	-0.000013i	0.000013
1	0.188441-0.059447i	0.197595	-0.173003-0.095849i	0.197780	0	0.000000
2	0	0.000000	0	0.000000	0.702116-0.072401i	**0.705839**
3	-0.21672+0.074581i	0.229194	-0.203196-0.105797i	0.229089	0	0.000000
4	0	0.000000	0	0.000000	0.000062-0.000014i	0.000064
5	-0.612706+0.181707i	**0.639082**	0.55357+0.319315i	**0.639063**	0	0.000000
6	0	0.000000	0	0.000000	-0.04232	0.042320

M_J	10		11		12	
	235 cm^{-1}		235 cm^{-1}		239 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	0	0.000000	0	0	-0.000017-0.000001i	1.7E-05
–5	-0.097405+0.094638i	0.135809	-0.008382-0.135719i	0.135978	0	0
–4	0	0.000000	0	0	0.703315+0.073133i	**0.707107**
–3	-0.443058+0.447905i	**0.630015**	0.051263+0.627887i	**0.629976**	0	0
–2	0	0.000000	0	0	-0.000064-0.000006i	6.43E-05
–1	0.211809-0.199432i	0.290923	0.013351+0.290623i	0.29093	0	0
0	0	0.000000	0	0	0.000012-0.000315i	0.000315
1	0.179419-0.229009i	0.290923	-0.056912-0.285308i	0.290929	0	0
2	0	0.000000	0	0	0.000064-0.000001i	6.4E-05
3	-0.405915+0.481822i	**0.630015**	-0.101195-0.621796i	**0.629977**	0	0
4	0	0.000000	0	0	-0.706892+0.017435i	**0.707107**
5	-0.085422+0.10558i	0.135809	0.024493+0.133753i	0.135977	0	0
6	0	0.000000	0	0	0.000017	0.000017

M_J	13	
	257 cm^{-1}	
	c	|c|
–6	-0.000017-0.000001i	0.000017
–5	0	0.000000
–4	0.658564+0.068581i	**0.662125**
–3	0	0.000000
–2	-0.000037	0.000037
–1	0	0.000000
0	-0.350697-0.013863i	0.350971
1	0	0.000000
2	-0.000037-0.000003i	0.000037
3	0	0.000000
4	0.661923-0.016382i	**0.662126**
5	0	0.000000
6	-0.000017	0.000017

Table S9. Composition of wave functions for [Tb(Por)(cyclen)]$^+$ as extracted from CASSCF/RASSI/Single_Aniso calculations with basis set 2.

M_J	Wave Functions and Energies					
	1		2		3	
	0.00 cm^{-1}		0.25 cm^{-1}		138 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	0.579254+0.401511i	**0.704802**	-0.580129-0.402122i	**0.70587**	-0.000013-0.000006i	1.43E-05
–5	0	0	0	0	0	0
–4	0.000012+0.000007i	1.39E-05	-0.000012-0.000007i	1.39E-05	-0.224453-0.121722i	0.255334
–3	0	0	0	0	0	0
–2	0.050614+0.02631i	0.057044	-0.037118-0.019272i	0.041823	0.000225+0.000084i	0.00024
–1	0	0	0	0	0	0
0	0	0	0.000001i	0.000001	-0.912106-0.194091i	**0.932528**
1	0	0	0	0	0	0
2	0.056586+0.00721i	0.057043	0.041484+0.005307i	0.041822	0.00024+0.000015i	0.00024
3	0	0	0	0	0	0
4	0.000014+0.000001i	1.4E-05	0.000014+0.000001i	1.4E-05	-0.254566+0.019789i	0.255334
5	0	0	0	0	0	0
6	0.704802	**0.704802**	0.705869	**0.705869**	-0.000015	0.000015

M_J	4		5		6	
	142 cm^{-1}		142 cm^{-1}		162 cm^{-1}	
	c	|c|	c		c	|c|
–6	0	0	0	0	-0.046781-0.032641i	0.057043
–5	-0.008953-0.297412i	0.297547	0.092031-0.283048i	0.297634	0	0
–4	0	0	0	0	0.000089+0.000061i	0.000108
–3	-0.001416+0.220643i	0.220648	0.075842-0.207203i	0.220647	0	0
–2	0	0	0	0	0.624324+0.327055i	**0.704802**
–1	-0.142684-0.585168i	**0.602312**	0.063283-0.598936i	**0.60227**	0	0
0	0	0	0	0	0.000291+0.000092i	0.000305
1	0.196376+0.569401i	**0.602313**	0.007426-0.602224i	**0.60227**	0	0
2	0	0	0	0	0.699156+0.089033i	**0.704802**
3	-0.120494-0.184842i	0.220648	-0.051007-0.21467i	0.220647	0	0
4	0	0	0	0	0.000108+0.000001i	0.000108

5	0.15328+0.255027i	0.297546	-0.058186-0.291891i	0.297634	0	0
6	0	0	0	0	-0.057043	0.057043

M_J	7		8		9	
	200 cm^{-1}		200 cm^{-1}		233cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	0	0	0	0	-0.034267-0.023978i	0.041823
–5	0.38641-0.496096i	**0.628827**	0.182662+0.601691i	**0.628806**	0	0
–4	0	0	0	0	0.000026+0.000028i	3.82E-05
–3	0.127494-0.193149i	0.231433	-0.084322-0.215465i	0.231377	0	0
–2	0	0	0	0	0.62505+0.327968i	**0.705869**
–1	-0.098848+0.203084i	0.225863	-0.109037-0.197935i	0.225981	0	0
0	0	0	0	0	-0.000002+0.000006i	6.32E-06
1	0.054512-0.219186i	0.225863	-0.147769-0.170973i	0.225981	0	0
2	0	0	0	0	-0.700154-0.08964i	**0.705869**
3	-0.026166+0.229949i	0.231433	-0.172788-0.153882i	0.231377	0	0
4	0	0	0	0	-0.000037+0.000008i	3.79E-05
5	-0.021999+0.628443i	**0.628828**	0.50085+0.380193i	**0.628806**	0	0
6	0	0	0	0	0.041823	0.041823

M_J	10		11		12	
	252 cm^{-1}		252 cm^{-1}		254 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	0	0	0	0	-0.000008-0.000008i	1.13E-05
–5	-0.124225-0.024186i	0.126558	-0.096283+0.082288i	0.126656	0	0
–4	0	0	0	0	0.551135+0.443001i	**0.707107**
–3	-0.63069-0.003165i	**0.630698**	0.394801-0.491818i	**0.630676**	0	0
–2	0	0	0	0	-0.000032-0.00002i	3.77E-05
–1	0.293556-0.005295i	0.293604	0.178476-0.233135i	0.293608	0	0
0	0	0	0	0	0.000123-0.0003i	0.000324
1	0.277395-0.096203i	0.293603	-0.097231+0.277041i	0.293608	0	0
2	0	0	0	0	0.000037+0.000009i	3.81E-05
3	-0.590958+0.220338i	**0.630698**	-0.195095+0.599742i	**0.630676**	0	0
4	0	0	0	0	-0.703512-0.071214i	**0.707107**
5	-0.108278+0.065518i	0.126557	0.016079-0.125631i	0.126656	0	0
6	0	0	0	0	0.000012	0.000012

M_J	13	
	273 cm^{-1}	
	c	|c|
–6	-0.000008-0.000008i	1.13E-05
–5	0	0
–4	0.50753+0.420972i	**0.659397**
–3	0	0
–2	-0.000023-0.000008i	2.44E-05
–1	0	0
0	-0.331994-0.142024i	0.361097
1	0	0
2	-0.000022-0.000011i	2.46E-05
3	0	0
4	0.654964+0.076334i	**0.659397**
5	0	0
6	-0.000011	0.000011

Table S10. Composition of wave functions for [Tb(TPP)(cyclen)]$^+$ as extracted from CASSCF/RASSI/Single_Aniso calculations with basis set 2.

M_J	Wave Functions and Energies					
	1		2		3	
	0.00 cm^{-1}		0.17 cm^{-1}		140 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	0.585074+0.393945i	**0.705300**	0.585676+0.39435i	**0.706065**	0.010495-0.001964i	0.010677
–5	0.000306-0.00068i	0.000700	0.000272-0.000649i	0.000704	-0.181665+0.074244i	0.196251
–4	-0.003416+0.00538i	0.006400	-0.003055+0.004905i	0.005777	0.078112-0.112122i	0.136649
–3	-0.004844-0.001474i	0.005100	-0.005193-0.001645i	0.005447	0.040453-0.16723i	0.172053
–2	-0.003103-0.049067i	0.049200	-0.002383-0.037329i	0.037405	0.062479+0.083615i	0.104380
–1	0.001097+0.000555i	0.001200	0.002773-0.00084i	0.002897	0.429255+0.175515i	**0.463751**
0	0.004185+0.001278i	0.004400	-0.000495+0.001621i	0.001695	-0.609162+0.05652i	**0.611778**
1	-0.00122-0.000152i	0.001200	0.001831+0.002246i	0.002898	-0.389636+0.251494i	**0.463752**
2	-0.029979+0.038968i	0.049200	0.022826-0.029633i	0.037405	0.046029-0.093683i	0.104800
3	0.004841+0.001483i	0.005100	-0.005226-0.001536i	0.005447	-0.070529-0.156933i	0.172053
4	0.000172-0.00637i	0.006400	-0.000206+0.005775i	0.005779	0.097407+0.095837i	0.136649
5	0.000126-0.000735i	0.000700	-0.000137+0.00069i	0.000703	0.192223+0.039554i	0.196250
6	0.70534	**0.705300**	-0.706065	**0.706065**	0.010677	0.010677

M_J	4		5		6	
	142 cm^{-1}		155 cm^{-1}		171 cm^{-1}	
	c	|c|	c		c	|c|
–6	0.011321+0.010842i	0.015675	-0.003057+0.000832i	0.003168	0.036921+0.026594i	0.045502
–5	0.157263-0.010297i	0.157600	-0.269128+0.143488i	0.304990	-0.015016-0.058011i	0.059923
–4	0.162942-0.056455i	0.172445	-0.006734-0.015082i	0.016517	-0.051308+0.02472i	0.056953
–3	-0.07446+0.121586i	0.142574	-0.061502+0.169826i	0.180619	0.016393-0.048722i	0.051406
–2	0.016971+0.169962i	0.170807	-0.01584-0.020821i	0.026161	0.013212+0.672239i	**0.672369**
–1	-0.265266-0.316808i	**0.413199**	0.568584+0.223755i	**0.611027**	0.034405-0.00883i	0.03552
0	-0.622419-0.249961i	**0.670735**	-0.001129-0.008446i	0.008521	0.252195+0.081371i	0.264997
1	0.410704-0.045342i	**0.413199**	0.48983-0.365268i	**0.611027**	-0.022756-0.027273i	0.035520
2	0.129811-0.111015i	0.170808	0.009813-0.024251i	0.026161	0.403615-0.537749i	**0.672368**
3	-0.030316+0.139314i	0.142574	-0.103957-0.147704i	0.180620	0.015175-0.049115i	0.051406
4	0.078636+0.153472i	0.172445	0.002535-0.016321i	0.016517	-0.027185-0.050046i	0.056953
5	-0.10646-0.116207i	0.157600	-0.297371-0.067745i	0.304990	0.046089-0.038295i	0.059923
6	0.015675	0.015675	0.003168	0.003168	0.045502	0.045502

M_J	7		8		9	
	204 cm^{-1}		206 cm^{-1}		232 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	0.000128+0.0051i	0.005102	-0.002598+0.002508i	0.003611	-0.030667-0.020385i	0.036824
–5	-0.102342-0.622856i	**0.631208**	-0.620716-0.12265i	**0.632718**	-0.06519-0.093795i	0.114225
–4	0.001685+0.04632i	0.046351	0.026669+0.013975i	0.030109	-0.074285+0.079092i	0.108507
–3	0.077652-0.187989i	0.203395	0.190036+0.082241i	0.207068	0.011033+0.054301i	0.055411
–2	-0.078841+0.089938i	0.119603	-0.027248-0.041942i	0.050016	-0.039921-0.67989i	**0.681061**
–1	0.120653-0.168812i	0.207496	-0.094586-0.210446i	0.230725	-0.011577-0.080221i	0.081052
0	-0.025625+0.026279i	0.036705	0.015333-0.006193i	0.016537	0.007536-0.02495i	0.026063
1	-0.165719+0.124867i	0.207496	-0.078109-0.217101i	0.230725	-0.054051+0.060398i	0.081052
2	-0.087924+0.081081i	0.119603	0.009526+0.0491i	0.050016	0.409626-0.544105i	**0.681061**
3	-0.185974+0.082363i	0.203396	-0.079606+0.191155i	0.207069	0.039249-0.039114i	0.055411
4	-0.046348-0.000518i	0.046351	0.009481-0.028576i	0.030108	0.018079+0.10699i	0.108507
5	-0.625236-0.08662i	**0.631208**	0.361401-0.519346i	**0.632717**	-0.106213+0.042023i	0.114224
6	-0.005101	0.005101	-0.003611	0.003611	0.036824	0.036824

M_J	10		11		12	
	250 cm^{-1}		255 cm^{-1}		267 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	-0.007687+0.00081i	0.007730	-0.007618-0.001165i	0.007707	-0.000344-0.000733i	0.000810
–5	-0.018794-0.121823i	0.123264	0.049026+0.057201i	0.075336	-0.015109-0.080042i	0.081456
–4	0.25347+0.197617i	0.321402	0.222922-0.015202i	0.223440	-0.142765-0.577127i	**0.594523**
–3	-0.556645-0.132682i	**0.572240**	-0.538705-0.28892i	**0.611292**	-0.042225-0.322042i	0.324798
–2	-0.029412-0.016168i	0.033563	-0.056338-0.077504i	0.095817	-0.093103-0.048279i	0.104876
–1	0.109615-0.201724i	0.229582	-0.133804+0.204839i	0.244668	0.052386-0.142295i	0.151632
0	-0.017515+0.00092i	0.017539	-0.004311+0.056731i	0.056895	-0.024519-0.015581i	0.029051
1	-0.130145-0.189131i	0.229583	-0.101313-0.222706i	0.244668	0.106576-0.10786i	0.151632
2	-0.027556+0.01916i	0.033563	0.067402-0.0681i	0.095816	-0.083249-0.063785i	0.104876
3	0.539682-0.190267i	**0.572240**	-0.576179+0.204196i	**0.611292**	0.309488-0.098545i	0.324798
4	0.231373-0.223084i	0.321403	-0.218065-0.048714i	0.223440	-0.583124+0.115859i	**0.594522**
5	0.005928-0.123122i	0.123265	0.057107-0.049135i	0.075336	0.078881-0.020315i	0.081455
6	-0.007729	0.007729	0.007706	0.007706	-0.00081	0.000810

M_J	13	
	279 cm^{-1}	
	c	|c|
–6	-0.002292-0.002713i	0.003552
–5	-0.024821+0.010765i	0.027055
–4	-0.615552+0.218139i	**0.653061**
–3	-0.119831+0.080263i	0.144228
–2	-0.034616+0.013976i	0.037331
–1	-0.003674+0.033775i	0.033974
0	-0.285146-0.132389i	0.314380
1	-0.02343+0.024603i	0.033975
2	-0.011663-0.035463i	0.037332
3	0.016017+0.143335i	0.144227
4	-0.230597-0.610994i	**0.653061**
5	0.007794+0.025907i	0.027054
6	-0.003551	0.003551

Table S11. Ab initio ligand-field parameters B_n^m (in cm^{-1}) of the [Dy(TPP)(cyclen)]$^+$

n	m	Experimental Geometry		Symmetrized-C_4 Geometry	
		Real part	Imaginary part	Real part	Imaginary part
2	0	**87.71**	**0.00**	**37.31**	**0.00**
	1	**82.37**	**82.37**	0.00	0.00
	2	**11.66**	**19.99**	0.00	0.00
4	0	**-18.25**	**0.00**	**-129.00**	**0.00**
	1	**-160.13**	**-49.59**	0.00	0.00
	2	**-64.36**	**-64.36**	0.00	0.00
	3	**-31.53**	**-70.20**	0.00	0.00
	4	**-15.52**	**55.44**	**85.08**	**-38.64**
6	0	**-5.19**	**0.00**	**28.36**	**0.00**
	1	**13.87**	**8.97**	0.00	0.00
	2	**24.86**	**12.85**	0.00	0.00
	3	**5.32**	**5.32**	0.00	0.00
	4	**1.61**	**7.33**	**-3.79**	**-17.19**
	5	**0.48**	**2.78**	0.00	0.00
	6	**2.35**	**-0.71**	0.00	0.00

Table S12. CASSCF/RASSI calculated energies and wave functions of the [Dy(Por)(cyclen)]$^+$ with an absolute coefficient larger than 0.05.

Basis Set 2	
Energy (cm^{-1})	Wave Function
0.00	$\|+11/2\rangle, \|+3/2\rangle, \|-5/2\rangle, \|-11/2\rangle, \|-13/2\rangle$
0.00	$\|-11/2\rangle, \|-3/2\rangle, \|+5/2\rangle, \|+11/2\rangle, \|+13/2\rangle$
15.6	$\|-13/2\rangle, \|-5/2\rangle, \|+11/2\rangle$
15.6	$\|+13/2\rangle, \|+5/2\rangle, \|-11/2\rangle$
47.0	$\|+9/2\rangle, \|-9/2\rangle, \|+1/2\rangle, \|-7/2\rangle, \|-1/2\rangle, \|+7/2\rangle$
47.0	$\|-9/2\rangle, \|+9/2\rangle, \|-1/2\rangle, \|+7/2\rangle, \|+1/2\rangle, \|-7/2\rangle$
102.6	$\|-7/2\rangle, \|+1/2\rangle, \|+9/2\rangle, \|+7/2\rangle, \|-15/2\rangle$
102.6	$\|+7/2\rangle, \|-1/2\rangle, \|-9/2\rangle, \|-7/2\rangle, \|+15/2\rangle$
131.3	$\|-5/2\rangle, \|+3/2\rangle, \|+5/2\rangle, \|-3/2\rangle, \|+11/2\rangle, \|+13/2\rangle$
131.3	$\|+5/2\rangle, \|-3/2\rangle, \|-5/2\rangle, \|+3/2\rangle, \|-11/2\rangle, \|-13/2\rangle$
222.5	$\|+1/2\rangle, \|-7/2\rangle, \|-1/2\rangle, \|+9/2\rangle, \|+7/2\rangle, \|-9/2\rangle$
222.5	$\|-1/2\rangle, \|+7/2\rangle, \|+1/2\rangle, \|-9/2\rangle, \|-7/2\rangle, \|+9/2\rangle$
229.3	$\|-3/2\rangle, \|+5/2\rangle, \|-11/2\rangle, \|+3/2\rangle, \|+13/2\rangle, \|-5/2\rangle$
229.3	$\|+3/2\rangle, \|-5/2\rangle, \|+11/2\rangle, \|-3/2\rangle, \|-13/2\rangle, \|+5/2\rangle$
254.7	$\|-15/2\rangle, \|-7/2\rangle, \|+1/2\rangle$
254.7	$\|+15/2\rangle, \|+7/2\rangle, \|-1/2\rangle$

Table S13. Composition of wave functions for [Dy(Por)(cyclen)]$^+$ as extracted from CASSCF/RASSI/Single_Aniso calculations with basis set 2.

M_J	Wave Functions and Energies					
	1		2		3	
	0.00 cm^{-1}		0.00 cm^{-1}		15.6 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	0	0.000000	0	0.000000	0.000005i	0.000005
−13/2	-0.063054+0.002577i	0.063107	0.004332-0.002668i	0.005088	0.680989-0.71187i	**0.985142**
−11/2	-0.076729-0.018286i	0.078878	-0.942482+0.267401i	**0.979681**	-0.000285+0.000091i	0.000299
−9/2	0	0.000000	-0.000006-0.000003i	0.000007	0	0.000000
−7/2	0	0.000000	0	0.000000	0.000001i	0.000001
−5/2	-0.054931-0.011972i	0.056220	0.004331-0.001321i	0.004528	0.128377-0.078729i	0.150595
−3/2	-0.012974-0.002092i	0.013142	-0.153288+0.056056i	0.163216	0.000112-0.000041i	0.000119
−1/2	0	0.000000	-0.000001-0.000001i	0.000001	0	0.000000
1/2	0.000001-0.000001i	0.000001	0	0.000000	0	0.000000
3/2	-0.148543+0.067635i	0.163216	0.007775-0.010595i	0.013142	0.010197-0.027661i	0.029481
5/2	-0.004012+0.002098i	0.004527	-0.030733+0.047077i	0.056221	0.000313-0.000513i	0.000601
7/2	0	0.000000	0	0.000000	0	0.000000
9/2	0.000002-0.000006i	0.000006	0	0.000000	0	0.000000
11/2	-0.859095+0.470885i	**0.979682**	0.041831-0.066872i	0.078878	-0.022862+0.07354i	0.077012
13/2	-0.004959+0.00114i	0.005088	-0.04673+0.042412i	0.063107	0.002833-0.002725i	0.003931
15/2	0	0.000000	0	0.000000	0	0.000000

M_J	4		5		6	
	15.6 cm^{-1}		47.0 cm^{-1}		47.0 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	0	0.000000	0.000481-0.002169i	0.002222	0.002537-0.011441i	0.011719
−13/2	-0.002793+0.002766i	0.003931	0	0.000000	0	0.000000
−11/2	-0.074074+0.021068i	0.077012	0.000006-0.000003i	0.000007	-0.000001	0.000001

–9/2	0	0.000000	-0.880318-0.293192i	**0.927858**	0.16686+0.055578i	0.175873
–7/2	0	0.000000	0.022855-0.022336i	0.031957	0.120596-0.117803i	0.168585
–5/2	-0.000521+0.000301i	0.000602	0	0.000000	0.000001	0.000001
–3/2	0.027901-0.009522i	0.029481	0.000002-0.000002i	0.000003	0	0.000000
–1/2	0	0.000000	-0.275194+0.010326i	0.275388	0.052163-0.001954i	0.052200
1/2	0	0.000000	0.013202-0.050503i	0.052200	0.069667-0.26643i	0.275388
3/2	-0.000043+0.000111i	0.000119	0.000001	0.000001	0.000002-0.000001i	0.000002
5/2	0.081826-0.126425i	0.150595	-0.000001i	0.000001	0	0.000000
7/2	0.000001	0.000001	-0.141121+0.092228i	0.168586	0.026755-0.017476i	0.031957
9/2	0	0.000000	-0.01813-0.174936i	0.175873	-0.095626-0.922917i	**0.927858**
11/2	0.000098-0.000283i	0.000299	0.000001-0.000001i	0.000001	0.000004-0.000005i	0.000006
13/2	0.728215-0.663482i	**0.985142**	0	0.000000	0	0.000000
15/2	0.000005	0.000005	-0.011719	0.011719	0.002221	0.002221

M_J	7		8		9	
	102.6 cm^{-1}		102.6cm^{-1}		131.3 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–15/2	0.001028+0.000958i	0.001405	-0.063449-0.059114i	0.086719	0	0.000000
–13/2	0	0.000000	-0.000001i	0.000001	0.010354-0.001105i	0.010413
–11/2	0.000002-0.000001i	0.000002	0	0.000000	0.128168-0.039547i	0.134131
–9/2	-0.247562-0.082779i	0.261035	-0.004005-0.001337i	0.004222	0.000001	0.000001
–7/2	0.0034+0.014277i	0.014676	-0.209959-0.881369i	**0.906032**	0	0.000000
–5/2	0	0.000000	0.000004-0.000007i	0.000008	-0.054376-0.008266i	0.055001
–3/2	-0.000002+0.000002i	0.000003	0	0.000000	-0.554749+0.214311i	0.594706
–1/2	0.321156-0.00654i	0.321223	0.005206-0.000106i	0.005207	-0.000005-0.000002i	0.000005
1/2	0.003737+0.003626i	0.005207	-0.230517-0.22371i	0.321223	0	0.000000
3/2	0	0.000000	-0.000003i	0.000003	-0.036827+0.020535i	0.042165
5/2	-0.000002+0.000007i	0.000007	0	0.000000	-0.400536+0.664329i	**0.775733**
7/2	0.754425-0.501734i	**0.906032**	0.01222-0.008128i	0.014676	-0.000006+0.000002i	0.000006
9/2	-0.003842-0.001752i	0.004223	0.237558+0.108191i	0.261035	0	0.000000
11/2	0	0.000000	0.000001+0.000002i	0.000002	0.007964-0.005197i	0.009510
13/2	0	0.000000	0	0.000000	0.105328-0.102348i	0.146864
15/2	0.086719	0.086719	0.001405	0.001405	0.000001	0.000001

M_J	10		11		12	
	131.3 cm^{-1}		222.5 cm^{-1}		222.5 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–15/2	-0.000001i	0.000001	-0.161681-0.05805i	0.171786	-0.014625-0.005251i	0.015539
–13/2	-0.138746+0.048154i	0.146865	-0.000001i	0.000001	0	0.000000
–11/2	0.00822-0.004783i	0.009510	0	0.000000	-0.000001+0.000001i	0.000001
–9/2	0	0.000000	-0.016951-0.005719i	0.017890	0.187426+0.063231i	0.197805
–7/2	-0.000005+0.000005i	0.000007	-0.20774-0.290129i	0.356834	-0.01879-0.026242i	0.032275
–5/2	0.773442-0.059575i	**0.775733**	-0.000004i	0.000004	0.000001-0.000003i	0.000003
–3/2	-0.034884+0.023684i	0.042164	-0.000003+0.000003i	0.000004	0.000006-0.000006i	0.000008
–1/2	0	0.000000	0.080623-0.003299i	0.080690	-0.891395+0.036509i	**0.892142**
1/2	0.000005i	0.000005	0.826622+0.33558i	**0.892142**	0.074765+0.030349i	0.080690
3/2	0.440593-0.399442i	0.594707	0.000004+0.000008i	0.000009	0.000002+0.000004i	0.000004
5/2	-0.017031+0.052297i	0.055000	-0.000003i	0.000003	-0.000001+0.000003i	0.000003
7/2	0	0.000000	-0.026553+0.018349i	0.032276	0.29356-0.202863i	0.356835
9/2	-0.000001i	0.000001	-0.197768-0.003823i	0.197805	-0.017886-0.000345i	0.017889
11/2	-0.092888+0.096762i	0.134131	-0.000001-0.000001i	0.000001	-0.000001i	0.000001
13/2	0.005637-0.008755i	0.010413	0	0.000000	-0.000001+0.000001i	0.000001
15/2	0	0.000000	-0.015539	0.015539	0.171786	0.171786

M_J	13	14	15

	229.3 cm^{-1}		229.3 cm^{-1}		254.7 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–15/2	0.000001	0.000001	0	0.000000	0	0.000000
–13/2	-0.010526-0.008055i	0.013254	0.004388-0.059985i	0.060145	0	0.000000
–11/2	0.066189-0.071735i	0.097606	-0.021218-0.003533i	0.021510	0	0.000000
–9/2	0.000001	0.000001	0.000001	0.000001	-0.022091-0.007471i	0.023320
–7/2	0.000001i	0.000001	-0.000002-0.000005i	0.000005	0	0.000000
–5/2	0.080138+0.103365i	0.130792	-0.192945+0.561265i	0.593503	0	0.000000
–3/2	-0.473635+0.603294i	**0.767003**	0.168414+0.014413i	0.169030	-0.000001+0.000001i	0.000001
–1/2	-0.000009+0.000002i	0.000009	-0.000003+0.000001i	0.000003	0.125555-0.005739i	0.125686
1/2	-0.000002-0.000002i	0.000003	0.000007+0.000005i	0.000009	0.000001+0.000001i	0.000001
3/2	-0.16369-0.042148i	0.169029	-0.247231-0.726065i	**0.767003**	0	0.000000
5/2	0.003722-0.593492i	0.593504	-0.109836+0.071011i	0.130792	-0.000001i	0.000001
7/2	0.000004-0.000004i	0.000006	-0.000001i	0.000001	-0.120267+0.081311i	0.145174
9/2	0.000001	0.000001	-0.000001	0.000001	-0.000001	0.000001
11/2	0.021191+0.00369i	0.021510	0.038711+0.0896i	0.097605	0	0.000000
13/2	-0.015715+0.058056i	0.060145	0.012599-0.004117i	0.013255	-0.000004+0.000003i	0.000005
15/2	0	0.000000	0.000001	0.000001	0.981113	**0.981113**

M_J	16	
	254.7 cm^{-1}	
	c	|c|
–15/2	-0.934265-0.299554i	**0.981113**
–13/2	-0.000002-0.000004i	0.000004
–11/2	0	0.000000
–9/2	-0.000001	0.000001
–7/2	0.089698+0.114148i	0.145174
–5/2	0.000001i	0.000001
–3/2	0	0.000000
–1/2	0.000001	0.000001
1/2	-0.117808-0.043799i	0.125686
3/2	-0.000001-0.000001i	0.000001
5/2	0	0.000000
7/2	0	0.000000
9/2	0.023317-0.00037i	0.023320
11/2	0	0.000000
13/2	0	0.000000
15/2	0	0.000000

Table S14. CASSCF/RASSI calculated energies and wave functions of the [Dy(TPP)(cyclen)]$^+$ with an absolute coefficient larger than 0.05.

Basis set 2	
Energy (cm^{-1})	Wave Function
0.00	|+15/2⟩,|+13/2⟩,|+7/2⟩,|+11/2⟩,|+5/2⟩,|+9/2⟩,|+3/2⟩
0.00	|–15/2⟩,|–13/2⟩,|–7/2⟩,|–11/2⟩,|–5/2⟩,|–9/2⟩,|–3/2⟩
16.1	|+9/2⟩,|+7/2⟩,|+11/2⟩,|+15/2⟩,|+5/2⟩, |+13/2⟩,|+3/2⟩, |+1/2⟩
16.1	|–9/2⟩,|–7/2⟩,|–11/2⟩,|–15/2⟩,|–5/2⟩, |–13/2⟩,|–5/2⟩, |–1/2⟩
63.4	|+5/2⟩,|+11/2⟩,|+13/2⟩,|+3/2⟩,|+7/2⟩, |+9/2⟩,|+15/2⟩, |+1/2⟩
63.4	|–5/2⟩,|–11/2⟩,|–13/2⟩,|–3/2⟩,|–7/2⟩, |–9/2⟩,|–15/2⟩, |–1/2⟩
131.4	|+3/2⟩,|–11/2⟩,|+1/2⟩,|–3/2⟩,|+7/2⟩,|+9/2⟩,|+13/2⟩,|–9/2⟩, |–1/2⟩, |–11/2⟩, |–7/2⟩,|+5/2⟩, |–5/2⟩,|+15/2⟩

131.4	|−3/2⟩,|−11/2⟩,|−1/2⟩,|+3/2⟩,|−7/2⟩,|−9/2⟩,|−13/2⟩,|+9/2⟩, |+1/2⟩, |+11/2⟩, |+7/2⟩,|−5/2⟩, |+5/2⟩,|−15/2⟩
176.7	|−1/2⟩,|−9/2⟩,|−11/2⟩,|−7/2⟩,|+5/2⟩,|+7/2⟩,|−5/2⟩,|−3/2⟩, |+3/2⟩, |+1/2⟩, |−13/2⟩,|+13/2⟩, |−15/2⟩,|+11/2⟩
176.7	|+1/2⟩,|+9/2⟩,|+11/2⟩,|+7/2⟩,|−5/2⟩,|−7/2⟩,|+5/2⟩,|+3/2⟩, |−3/2⟩, |−1/2⟩, |+13/2⟩,|−13/2⟩, |+15/2⟩,|−11/2⟩
229.2	|+13/2⟩,|+15/2⟩,|+11/2⟩,|+9/2⟩,|−15/2⟩,|−13/2⟩,|+7/2⟩,|−11/2⟩,|−9/2⟩, |+3/2⟩
229.2	|−13/2⟩,|−15/2⟩,|−11/2⟩,|−9/2⟩,|+15/2⟩,|+13/2⟩,|−7/2⟩,|+11/2⟩,|+9/2⟩, |−3/2⟩
261.6	|+3/2⟩,|+1/2⟩,|+5/2⟩,|+9/2⟩,|+7/2⟩,|−3/2⟩,|−7/2⟩,|−5/2⟩,|+11/2⟩,|−1/2⟩,|−9/2⟩
261.6	|−3/2⟩,|−1/2⟩,|−5/2⟩,|−9/2⟩,|−7/2⟩,|+3/2⟩,|+7/2⟩,|+5/2⟩,|−11/2⟩,|+1/2⟩,|+9/2⟩
271.6	|−5/2⟩,|−7/2⟩,|−1/2⟩,|+7/2⟩, |−3/2⟩,|+3/2⟩,|+5/2⟩,|−9/2⟩,|+1/2⟩,|+9/2⟩,|−11/2⟩,|+11/2⟩,|−13/2⟩,|+13/2⟩
271.6	|+5/2⟩,|+7/2⟩,|+1/2⟩,|−7/2⟩, |+3/2⟩,|−3/2⟩,|−5/2⟩,|+9/2⟩,|−1/2⟩,|−9/2⟩,|+11/2⟩,|−11/2⟩,|+13/2⟩,|−13/2⟩

Table S15. Composition of wave functions for [Dy(TPP)(cyclen)]$^+$ as extracted from CASSCF/RASSI/Single_Aniso calculations with basis set 2.

M_J	Wave Functions and Energies					
	1		2		3	
	0.00 cm^{-1}		0.00 cm^{-1}		16.1 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	-0.008843-0.00411i	0.009751	-0.604298-0.280873i	**0.666383**	-0.003067-0.005734i	0.006503
−13/2	-0.001308+0.004927i	0.005098	0.423875+0.392457i	0.577661	-0.019448-0.006548i	0.020521
−11/2	0.004299+0.000183i	0.004303	0.157483+0.237367i	0.284858	0.005574+0.005454i	0.007798
−9/2	0.006761+0.01618i	0.017536	-0.052949-0.063805i	0.082914	0.015097+0.047188i	0.049544
−7/2	0.010383+0.004205i	0.011202	0.04707-0.290656i	0.294443	0.011263+0.020706i	0.023571
−5/2	-0.008761+0.010446i	0.013634	0.060033-0.185999i	0.195447	-0.014866+0.029691i	0.033205
−3/2	0.027823+0.000961i	0.027840	0.037028-0.067051i	0.076596	0.03735+0.000241i	0.037351
−1/2	-0.036988-0.001438i	0.037016	0.008267-0.022103i	0.023598	-0.074532-0.003148i	0.074598
1/2	-0.00182+0.023528i	0.023598	0.034148+0.014286i	0.037016	0.050544+0.026058i	0.056866
3/2	-0.005317-0.076411i	0.076596	0.025636+0.010856i	0.027840	-0.017707-0.082438i	0.084318
5/2	-0.023956+0.193973i	0.195447	0.003541+0.013166i	0.013634	-0.040927+0.228802i	0.232434
7/2	0.079824-0.283416i	0.294443	0.011188+0.000564i	0.011202	0.180485-0.458482i	0.492728
9/2	-0.074909+0.035543i	0.082914	-0.012951+0.011823i	0.017536	-0.378844+0.483642i	**0.614355**
11/2	-0.242859+0.148875i	0.284858	0.003975+0.001646i	0.004302	0.342004-0.201874i	0.397140
13/2	0.5498-0.177234i	0.577661	-0.00089+0.00502i	0.005098	0.161796-0.034861i	0.165509
15/2	0.666382	**0.666382**	-0.009752	0.009752	-0.344539	0.344539

M_J	4		5		6	
	16.1 cm^{-1}		63.4 cm^{-1}		63.4 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	0.162497+0.303812i	0.344539	-0.000003-0.000001i	0.000003	-0.145727-0.047053i	0.153135
−13/2	0.045569+0.159112i	0.165509	0.000906+0.011503i	0.011539	0.330733+0.245661i	0.411987
−11/2	0.016709-0.396788i	0.397140	-0.011857-0.042514i	0.044136	-0.289385-0.361689i	0.463209
−9/2	0.247795-0.562166i	**0.614356**	-0.006916+0.047826i	0.048323	-0.076682-0.153918i	0.171962
−7/2	0.319163-0.375388i	0.492728	0.023203-0.007662i	0.024435	0.032305+0.255887i	0.257918
−5/2	0.182454-0.144i	0.232434	-0.056935+0.019526i	0.060190	-0.174423+0.539798i	**0.567279**
−3/2	0.081044-0.023267i	0.084318	0.142255-0.02978i	0.145339	-0.153963+0.315188i	0.350782
−1/2	0.046816+0.032279i	0.056865	-0.035668-0.037305i	0.051613	-0.094217+0.100037i	0.137420
1/2	0.037928+0.064237i	0.074598	0.058922+0.124147i	0.137420	-0.045405+0.024541i	0.051613
3/2	0.017828+0.032821i	0.037350	-0.049668-0.347248i	0.350782	-0.126223-0.07205i	0.145339

5/2	-0.01917+0.027112i	0.033205	0.000124+0.567279i	**0.567279**	-0.048181-0.036076i	0.060190
7/2	0.02357+0.000166i	0.023571	0.109367-0.233582i	0.257918	-0.019726-0.014421i	0.024435
9/2	-0.048731+0.008943i	0.049545	0.120266-0.122911i	0.171962	0.008114-0.047638i	0.048324
11/2	0.007438+0.002342i	0.007798	-0.38652+0.255273i	0.463208	0.024347-0.036814i	0.044137
13/2	0.014946+0.014061i	0.020521	-0.390217+0.132154i	0.411988	0.004396-0.010669i	0.011539
15/2	-0.006502	0.006502	-0.153135	0.153135	0.000003	0.000003

M_J	7		8		9	
	131.4 cm^{-1}		131.4 cm^{-1}		176.7 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	-0.005614-0.01279i	0.013968	-0.032834-0.074808i	0.081696	0.062113-0.006262i	0.062428
−13/2	-0.01016-0.004452i	0.011093	-0.133896+0.162956i	0.210909	0.026734+0.070673i	0.075560
−11/2	0.097981+0.0533i	0.111540	0.31214-0.374287i	0.487362	-0.078056-0.287573i	0.297978
−9/2	-0.063262-0.163382i	0.175202	-0.234182+0.130135i	0.267911	-0.052319+0.466623i	0.469547
−7/2	-0.064188+0.085119i	0.106608	-0.267746+0.053945i	0.273126	0.07543-0.282062i	0.291974
−5/2	0.09275-0.007696i	0.093069	0.101618-0.007439i	0.101890	0.056637-0.128355i	0.140295
−3/2	-0.154755+0.233358i	0.280009	0.462587+0.189451i	**0.499878**	0.118713+0.044071i	0.126629
−1/2	0.042423+0.151441i	0.157271	0.303517+0.214342i	0.371571	-0.664412+0.093067i	**0.670898**
1/2	-0.318253-0.191781i	0.371571	0.155722-0.022018i	0.157271	-0.056649+0.102383i	0.117010
3/2	0.359391+0.347443i	**0.499879**	-0.151486+0.235493i	0.280009	0.040531+0.117443i	0.124240
5/2	-0.034029-0.09604i	0.101890	0.030229+0.088023i	0.093069	-0.08184-0.204322i	0.220103
7/2	-0.058211-0.266851i	0.273126	-0.052145+0.092986i	0.106609	-0.077754-0.129007i	0.150627
9/2	-0.025045+0.266738i	0.267911	-0.175031+0.007736i	0.175202	-0.007329-0.044282i	0.044884
11/2	-0.217279+0.436247i	0.487362	-0.088184-0.068299i	0.111540	-0.044583+0.038262i	0.058751
13/2	-0.095403+0.188098i	0.210909	-0.00816-0.007515i	0.011093	-0.054812+0.036141i	0.065655
15/2	-0.081697	0.081697	0.013968	0.013968	0.004339	0.004339

M_J	10		11		12	
	176.7 cm^{-1}		229.2 cm^{-1}		229.2 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	0.004317-0.000435i	0.004339	-0.164758-0.008483i	0.164976	-0.610432-0.03143i	0.611241
−13/2	0.058161+0.030461i	0.065655	-0.143993-0.063586i	0.157408	-0.565845-0.234104i	**0.612360**
−11/2	-0.048196-0.033597i	0.058750	-0.078334-0.040528i	0.088197	-0.299513-0.198078i	0.359086
−9/2	0.00285-0.044794i	0.044885	-0.030588-0.081384i	0.086942	-0.101594-0.160812i	0.190215
−7/2	-0.064421+0.136155i	0.150626	-0.012171+0.022336i	0.025437	-0.022738-0.093832i	0.096548
−5/2	0.060933-0.211501i	0.220103	0.013864-0.030854i	0.033826	0.027389-0.027187i	0.038591
−3/2	0.028547-0.120916i	0.124240	0.006162+0.000148i	0.006164	-0.052851-0.023689i	0.057917
−1/2	0.066632+0.096185i	0.117010	-0.027517+0.026093i	0.037921	-0.038799+0.002314i	0.038868
1/2	-0.670396-0.025954i	**0.670898**	-0.038629-0.004306i	0.038868	0.026139+0.027473i	0.037921
3/2	-0.113694+0.055757i	0.126630	0.053999-0.02094i	0.057917	0.006161+0.000169i	0.006163
5/2	0.069226+0.122027i	0.140296	0.025955+0.02856i	0.038592	-0.012259-0.031526i	0.033826
7/2	-0.103342-0.273073i	0.291973	0.027533-0.092539i	0.096548	-0.011006-0.022932i	0.025436
9/2	-0.09886-0.459022i	0.469547	-0.109729+0.155375i	0.190215	0.034732-0.079703i	0.086942
11/2	0.048817-0.293952i	0.297978	0.309302-0.182415i	0.359086	-0.080314+0.036446i	0.088197
13/2	0.01951-0.072998i	0.075560	-0.577134+0.204699i	**0.612360**	0.147072-0.056098i	0.157408
15/2	-0.062428	0.062428	0.611241	0.611241	-0.164976	0.164976

M_J	13		14		15	
	261.6 cm^{-1}		261.6 cm^{-1}		271.6 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	-0.010881-0.009202i	0.014250	0.008802+0.007444i	0.011528	0.036002+0.019742i	0.041060
−13/2	-0.043646-0.004096i	0.043838	-0.000968+0.046853i	0.046863	-0.061756+0.04371i	0.075660
−11/2	-0.000635+0.042748i	0.042753	0.193792+0.039836i	0.197844	0.123269-0.054295i	0.134697
−9/2	0.121375-0.037549i	0.127050	-0.16722-0.296101i	0.340056	-0.103312+0.199887i	0.225007
−7/2	-0.15047-0.177241i	0.232499	-0.158771+0.297182i	0.336935	0.001707-0.350998i	0.351002

–5/2	0.047168+0.204117i	0.209496	0.285678+0.234088i	0.369336	0.092399+0.477593i	**0.486449**
–3/2	0.220556+0.105965i	0.244691	0.053045-0.475887i	**0.478834**	-0.157586-0.276569i	0.318314
–1/2	-0.176242-0.062674i	0.187054	-0.386595+0.036299i	0.388295	0.300569+0.174515i	0.347559
1/2	-0.27175-0.277355i	0.388296	0.175042+0.065951i	0.187054	-0.012837+0.177362i	0.177826
3/2	0.266794-0.397621i	**0.478833**	0.236833+0.06151i	0.244690	0.293729-0.027909i	0.295052
5/2	0.369291+0.005732i	0.369335	-0.167821+0.125397i	0.209495	0.210273-0.17352i	0.272624
7/2	-0.07067+0.32944i	0.336935	-0.229344+0.03817i	0.232499	0.22029-0.244013i	0.328740
9/2	-0.318886+0.118111i	0.340057	-0.068431-0.107047i	0.127051	0.087232-0.149346i	0.172956
11/2	-0.173696-0.094721i	0.197844	0.027119-0.03305i	0.042752	0.013536-0.079518i	0.080662
13/2	0.029515-0.036401i	0.046863	0.035972+0.025057i	0.043839	-0.044076-0.04927i	0.066108
15/2	-0.011528	0.011528	-0.01425	0.014250	0	0.000000

M_J	16	
	271.6 cm^{-1}	
	c	|c|
–15/2	0	0.000000
–13/2	0.062336-0.022009i	0.066107
–11/2	-0.026365+0.076232i	0.080662
–9/2	-0.00468-0.172892i	0.172955
–7/2	0.075832+0.319875i	0.328741
–5/2	-0.100943-0.253248i	0.272624
–3/2	0.24413+0.165699i	0.295052
–1/2	-0.074021+0.161688i	0.177826
1/2	0.347455-0.008503i	0.347559
3/2	0.271153-0.166734i	0.318315
5/2	0.310648-0.374339i	**0.486448**
7/2	0.167266-0.308585i	0.351002
9/2	0.005521-0.224939i	0.225007
11/2	-0.08198-0.106876i	0.134697
13/2	-0.033133-0.068019i	0.075660
15/2	-0.041059	0.041059

Table S16. Ab initio ligand-field parameters B_n^m (in cm^{-1}) of the [Ho(TPP)(cyclen)]$^+$

n	m	Experimental Geometry		Symmetrized-C_4 Geometry	
		Real part	Imaginary part	Real part	Imaginary part
2	0	**30.71**	**0.00**	**53.87**	**0.00**
	1	**-52.22**	**-52.22**	0.00	0.00
	2	**31.89**	**-25.01**	0.00	0.00
4	0	**38.05**	**0.00**	**-111.81**	**0.00**
	1	**17.14**	**9.37**	0.00	0.00
	2	**-13.16**	**-13.16**	0.00	0.00
	3	**18.54**	**-74.94**	0.00	0.00
	4	**51.12**	**2.28**	**43.31**	**-46.09**
6	0	**-0.53**	**0.00**	**26.06**	**0.00**
	1	**14.04**	**-10.45**	0.00	0.00
	2	**1.04**	**2.04**	0.00	0.00
	3	**4.03**	**4.03**	0.00	0.00
	4	**-12.71**	**-9.29**	**1.32**	**6.72**
	5	**11.90**	**0.84**	0.00	0.00
	6	**-6.30**	**0.72**	0.00	0.00

Table S17. CASSCF/RASSI calculated energies and wave functions of the $[Ho(TPP)(cyclen)]^+$ with an absolute coefficient larger than 0.05.

Basis set 2	
Energy (cm^{-1})	Wave Function
0.00	|±8⟩, |±2⟩, |±7⟩, |±6⟩, |±5⟩, |±4⟩, |±3⟩, |±1⟩, |0⟩
1.90	|±8⟩, |±6⟩, |±7⟩, |±4⟩, |0⟩, |±1⟩, |±5⟩, |±2⟩, |±3⟩
5.24	|±1⟩, |±2⟩, |±6⟩, |±5⟩, |±4⟩, |0⟩, |±8⟩, |±3⟩, |±7⟩
7.71	|0⟩, |±3⟩, |±1⟩, |±5⟩, |±7⟩, |±2⟩, |±8⟩, |±6⟩, |±4⟩
45.2	|±4⟩, |±7⟩, |±5⟩, |±1⟩, |±2⟩, |±6⟩, |0⟩, |±8⟩
50.5	|±3⟩, |±7⟩, |±2⟩, |±5⟩, |0⟩, |±6⟩, |±1⟩, |±8⟩
55.5	|0⟩, |±8⟩, |±2⟩, |±4⟩, |±5⟩, |±1⟩, |±7⟩, |±6⟩, |±3⟩
57.7	|±1⟩, |±8⟩, |±2⟩, |±5⟩, |±6⟩, |±4⟩, |0⟩, |±7⟩
102	|±4⟩, |±3⟩, |±7⟩, |±2⟩, |±1⟩, |±6⟩, |±5⟩, |±8⟩, |0⟩
107	|±6⟩, |±7⟩, |±5⟩, |±4⟩, |±8⟩, |±3⟩, |±2⟩, |±1⟩
107	|±6⟩, |±5⟩, |±7⟩, |±4⟩, |±8⟩, |±3⟩, |±2⟩
130	|±3⟩, |±7⟩, |±8⟩, |±2⟩, |±4⟩, |±1⟩, |0⟩, |±5⟩, |±6⟩
130	|±2⟩, |±4⟩, |±7⟩, |±8⟩, |±3⟩, |±1⟩, |±6⟩, |0⟩, |±5⟩
146	|0⟩, |±6⟩, |±3⟩, |±2⟩, |±7⟩, |±4⟩, |±5⟩, |±8⟩
182	|±1⟩, |±5⟩, |±4⟩, |±6⟩, |±3⟩, |±7⟩, |±2⟩, |±8⟩
185	|±6⟩, |±5⟩, |±1⟩, |±4⟩, |±3⟩, |±7⟩, |±8⟩
204	|±5⟩, |0⟩, |±2⟩, |±6⟩, |±4⟩, |±7⟩, |±3⟩, |±8⟩

Table S18. Composition of wave functions for $[Ho(TPP)(cyclen)]^+$ as extracted from CASSCF/RASSI/Single_Aniso calculations with basis set 2.

M_J	Wave Functions and Energies					
	1		2		3	
	0.00 cm^{-1}		1.90 cm^{-1}		5.24 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−8	0.403427-0.053455i	**0.406953**	0.453274-0.059311i	**0.457138**	-0.146653+0.049116i	0.154659
−7	0.213395-0.178748i	0.278367	0.205133-0.145943i	0.251752	0.067851-0.021742i	0.071249
−6	-0.014076+0.236542i	0.236960	0.003611+0.291761i	0.291783	-0.011873-0.203637i	0.203983
−5	0.145251+0.173471i	0.226252	0.069253+0.119019i	0.137701	0.124482+0.145095i	0.191176
−4	-0.169483-0.042815i	0.174807	-0.196579-0.119616i	0.230111	0.185551+0.04429i	0.190764
−3	0.048481+0.125665i	0.134693	0.069789-0.010979i	0.070647	-0.092158+0.026652i	0.095934
−2	0.281873-0.070541i	0.290566	0.110107-0.042415i	0.117994	0.32735-0.092667i	0.340213
−1	0.054725+0.090396i	0.105671	0.013999+0.160333i	0.160943	0.211401-0.414083i	**0.464925**
0	0.102405-0.006755i	0.102628	-0.014761-0.226582i	0.227062	0.172942-0.028191i	0.175225
1	-0.042377+0.096801i	0.105670	-0.006921-0.160794i	0.160943	-0.33196-0.325511i	**0.464925**
2	0.288697+0.032905i	0.290566	-0.11468-0.027771i	0.117995	0.339833-0.016089i	0.340214
3	-0.031555+0.130944i	0.134692	0.070624+0.001832i	0.070648	0.095851-0.003995i	0.095934
4	-0.162391+0.064707i	0.174808	0.179398-0.14411i	0.230112	0.16188-0.100925i	0.190764
5	-0.121206+0.191047i	0.226252	0.053226-0.126998i	0.137701	-0.071959+0.177117i	0.191177
6	-0.045025-0.232643i	0.236960	0.034274+0.289764i	0.291784	0.053412+0.196866i	0.203983
7	-0.235025-0.149169i	0.278367	0.222335+0.118094i	0.251752	-0.071243+0.000932i	0.071249
8	0.406953	**0.406953**	-0.457138	**0.457138**	-0.15466	0.154660

M_J	4		5		6	
	7.71 cm^{-1}		45.2 cm^{-1}		50.5 cm^{-1}	
	c	|c|	c	|c|	c	|c|

–8	0.103834+0.054282i	0.117167	0.027353-0.096774i	0.100565	-0.007465+0.080601i	0.080946
–7	0.118745+0.1321i	0.177625	-0.228925-0.218452i	0.316430	0.251952+0.118563i	0.278455
–6	0.076465+0.057468i	0.095653	-0.182753+0.027748i	0.184848	0.133804-0.094729i	0.163942
–5	-0.180947+0.062136i	0.191318	0.169237-0.248834i	0.300931	-0.139592+0.156355i	0.209602
–4	0.035486-0.080153i	0.087657	-0.020893-0.339419i	**0.340061**	0.001188-0.027034i	0.027060
–3	0.205049-0.313901i	0.374939	-0.005653-0.037888i	0.038307	-0.259227-0.411287i	**0.486164**
–2	0.114449-0.115416i	0.162541	-0.249671-0.058806i	0.256503	-0.210216-0.166476i	0.268151
–1	-0.094933-0.269629i	0.285853	-0.275999-0.029709i	0.277593	-0.018196+0.143392i	0.144542
0	-0.536459-0.131765i	**0.552404**	0.080296-0.060747i	0.100686	-0.117526-0.128914i	0.174445
1	0.209047-0.194965i	0.285853	0.04648-0.273675i	0.277594	-0.144459+0.004894i	0.144542
2	0.047954+0.155305i	0.162540	-0.011319+0.256253i	0.256503	-0.14638-0.224674i	0.268152
3	-0.036289-0.373178i	0.374938	-0.034922-0.015745i	0.038307	0.385627+0.296053i	**0.486164**
4	-0.005686+0.087473i	0.087658	0.320941+0.112424i	**0.340062**	-0.027028-0.00131i	0.027060
5	0.131569+0.138896i	0.191318	-0.285484+0.095177i	0.300932	-0.168562+0.124578i	0.209602
6	0.094388-0.015503i	0.095653	-0.076409+0.168316i	0.184848	-0.106665+0.124498i	0.163943
7	-0.166434+0.062054i	0.177626	-0.147951-0.279711i	0.316430	-0.094822-0.261812i	0.278454
8	0.117167	0.117167	0.100565	0.100565	0.080946	0.080946

M_J	7		8		9	
	55.5 cm^{-1}		57.7 cm^{-1}		102 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–8	0.012776+0.363407i	0.363632	-0.066527-0.366012i	0.372009	0.153318+0.064558i	0.166355
–7	-0.151218+0.038815i	0.156120	0.126574+0.008545i	0.126862	0.017257-0.260336i	0.260907
–6	-0.136244+0.07596i	0.155988	0.136255-0.054314i	0.146681	-0.060222-0.178568i	0.188450
–5	0.129539-0.117189i	0.174681	-0.187981+0.120164i	0.223106	0.103824-0.14496i	0.178305
–4	-0.182696+0.152559i	0.238017	0.099924-0.104358i	0.144483	0.364277-0.158311i	**0.397190**
–3	0.048596+0.081485i	0.094876	0.010588-0.034369i	0.035963	0.055262-0.291249i	0.296445
–2	-0.084612-0.307874i	0.319289	0.142684+0.199995i	0.245676	-0.2094+0.094308i	0.229657
–1	0.140839+0.083731i	0.163849	-0.421908-0.05953i	**0.426087**	0.169502+0.085215i	0.189717
0	-0.301332+0.312112i	**0.433837**	0.109376+0.091288i	0.142466	0.014199-0.070311i	0.071730
1	0.088627+0.13781i	0.163849	0.134022+0.404461i	**0.426088**	0.189287-0.012758i	0.189716
2	0.310657+0.073743i	0.319290	0.222288+0.104618i	0.245676	0.156391+0.168179i	0.229657
3	0.083142+0.045703i	0.094875	0.031921-0.016564i	0.035963	-0.062095+0.289869i	0.296445
4	-0.146045+0.187943i	0.238016	-0.084806+0.116976i	0.144483	-0.274292-0.28727i	**0.397190**
5	-0.112565+0.133576i	0.174681	-0.08461+0.20644i	0.223106	0.039432+0.173891i	0.178306
6	-0.071126+0.138828i	0.155988	-0.029072+0.143771i	0.146681	0.124799-0.141203i	0.188449
7	0.033478-0.152488i	0.156120	-0.031043-0.123005i	0.126862	-0.085125+0.246631i	0.260908
8	-0.363631	0.363631	-0.372009	0.372009	-0.166356	0.166356

M_J	10		11		12	
	107 cm^{-1}		107 cm^{-1}		130 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–8	0.142519+0.14418i	0.202730	0.118096+0.163798i	0.201932	0.105488-0.261305i	0.281794
–7	-0.324292-0.05935i	0.329678	-0.298382-0.07728i	0.308227	-0.028385+0.326094i	0.327327
–6	0.323203-0.17152i	**0.365895**	0.350658-0.141721i	**0.378214**	-0.096706-0.022759i	0.099348
–5	-0.136547+0.293684i	0.323876	-0.154676+0.306082i	0.342944	-0.100878-0.025142i	0.103964
–4	-0.020371-0.259792i	0.260589	-0.010855-0.218199i	0.218469	0.216187-0.131934i	0.253265
–3	0.11764+0.130827i	0.175940	0.104811+0.168404i	0.198356	-0.178596+0.280491i	**0.332523**
–2	-0.076387-0.058645i	0.096303	-0.105326-0.048424i	0.115924	0.061145-0.264741i	0.271710
–1	0.02941-0.043512i	0.052519	0.036323+0.021073i	0.041993	0.139479+0.138726i	0.196721
0	-0.012707+0.030427i	0.032974	0.045159+0.023114i	0.050731	-0.058817-0.087174i	0.105161
1	-0.01027+0.051505i	0.052519	-0.038337-0.01714i	0.041994	-0.076425-0.181269i	0.196721
2	0.095408+0.013099i	0.096303	-0.100877-0.057116i	0.115924	-0.268381-0.042405i	0.271710
3	0.175744-0.008306i	0.175940	-0.197899+0.01347i	0.198357	-0.326953+0.06061i	**0.332523**
4	0.199083-0.168145i	0.260589	-0.183342+0.118804i	0.218469	-0.203269+0.151079i	0.253265

5	0.112873-0.30357i	0.323875	-0.157821+0.304472i	0.342944	-0.014449+0.102955i	0.103964
6	-0.105227-0.350438i	**0.365895**	0.090118+0.367321i	**0.378214**	0.015097-0.098194i	0.099348
7	-0.270186-0.188911i	0.329678	0.237189+0.196839i	0.308228	-0.31301-0.09575i	0.327328
8	-0.20273	0.202730	0.201932	0.201932	-0.281794	0.281794

M_J	13		14		15	
	130 cm^{-1}		146 cm^{-1}		182 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–8	-0.167379+0.223507i	0.279233	0.010693-0.1238i	0.124261	-0.051637-0.041103i	0.065999
–7	0.015696-0.28833i	0.288757	-0.148449-0.176172i	0.230377	-0.145818+0.029538i	0.148780
–6	0.064851+0.115855i	0.132771	-0.319362+0.005842i	0.319415	-0.125665+0.235322i	0.266774
–5	0.088046+0.068361i	0.111469	-0.081656+0.120913i	0.145903	-0.034602+0.310887i	0.312807
–4	-0.28872+0.080631i	0.299768	0.191616+0.024516i	0.193178	-0.108805+0.245252i	0.268304
–3	0.146464-0.221728i	0.265735	0.28559+0.081383i	0.296959	-0.203523+0.153231i	0.254757
–2	-0.02567+0.32153i	**0.322553**	0.207173+0.189829i	0.280991	-0.105266-0.09048i	0.138808
–1	-0.006308-0.193112i	0.193215	-0.03045-0.007718i	0.031413	-0.1984-0.32965i	**0.384749**
0	0.10388-0.051987i	0.116162	-0.334015+0.306409i	**0.453269**	-0.023318-0.008148i	0.024701
1	-0.150792-0.120805i	0.193215	-0.005069-0.031001i	0.031413	0.360528-0.134357i	**0.384750**
2	-0.272749-0.172187i	**0.322553**	-0.171298-0.22274i	0.280991	-0.138709+0.005233i	0.138808
3	-0.265272-0.015675i	0.265735	0.056505+0.291533i	0.296958	0.063806+0.246638i	0.254758
4	-0.237605+0.182768i	0.299767	-0.007936-0.193015i	0.193178	0.06761-0.259646i	0.268304
5	0.001941+0.111452i	0.111469	0.127491-0.070948i	0.145903	-0.166542+0.264786i	0.312806
6	-0.053861-0.121355i	0.132771	-0.033302+0.317675i	0.319416	0.048234-0.262377i	0.266774
7	-0.240197-0.160269i	0.288757	-0.162744-0.163058i	0.230377	0.095692+0.113923i	0.148780
8	-0.279233	0.279233	0.124261	0.124261	-0.065998	0.065998

M_J	16		17	
	185 cm^{-1}		204 cm^{-1}	
	c	|c|	c	|c|
–8	0.051444-0.081543i	0.096414	0.004516+0.066637i	0.066790
–7	-0.094967-0.187107i	0.209828	0.124718+0.085401i	0.151155
–6	-0.312209-0.109576i	**0.330880**	0.26772-0.082303i	0.280085
–5	-0.245623+0.178979i	0.303915	0.215316-0.326377i	**0.391002**
–4	0.157585+0.225078i	0.274760	0.006672-0.257435i	0.257521
–3	0.266888-0.06218i	0.274036	0.05514+0.091528i	0.106854
–2	-0.041213-0.012317i	0.043014	0.275112+0.174358i	0.325710
–1	-0.070602+0.294765i	0.303102	0.004697+0.035494i	0.035803
0	-0.015584-0.028257i	0.032269	-0.229026+0.245072i	0.335430
1	-0.28697-0.097566i	0.303102	0.035731+0.002286i	0.035804
2	0.011573-0.041428i	0.043014	-0.19256-0.262694i	0.325711
3	0.194992-0.192545i	0.274036	0.095047+0.048826i	0.106855
4	0.106279+0.253374i	0.274761	0.256395-0.024062i	0.257522
5	-0.28243+0.112239i	0.303915	-0.311073+0.23689i	**0.391003**
6	0.073911-0.322519i	**0.330880**	0.064014-0.272672i	0.280085
7	0.107575+0.180154i	0.209828	0.093638+0.118658i	0.151155
8	-0.096414	0.096414	-0.06679	0.066790

Table S19. CASSCF/RASSI calculated energies and wave functions of the [Ho(Por)(cyclen)]$^+$ with an absolute coefficient larger than 0.05.

Basis set 2	
Energy (cm^{-1})	Wave Function
0.00	$\|\pm4\rangle, \|0\rangle, \|\pm8\rangle$
4.66	$\|\pm4\rangle, \|\pm8\rangle$
5.73	$\|\pm5\rangle, \|\pm1\rangle, \|\pm3\rangle$

5.73	$\|\pm5\rangle, \|\pm1\rangle, \|\pm3\rangle$
50.4	$\|\pm3\rangle, \|\pm7\rangle, \|\pm1\rangle, \|\pm5\rangle$
50.4	$\|\pm3\rangle, \|\pm7\rangle, \|\pm1\rangle, \|\pm5\rangle$
66.5	$\|\pm6\rangle, \|\pm2\rangle$
68.5	$\|\pm6\rangle, \|\pm2\rangle$
106	$\|\pm2\rangle, \|\pm6\rangle$
117	$\|\pm8\rangle, \|\pm4\rangle, \|0\rangle$
117	$\|\pm8\rangle, \|\pm4\rangle$
149	$\|\pm7\rangle, \|\pm1\rangle, \|\pm3\rangle$
149	$\|\pm7\rangle, \|\pm1\rangle, \|\pm3\rangle$
160	$\|\pm2\rangle, \|\pm6\rangle$
201	$\|\pm1\rangle, \|\pm3\rangle, \|\pm7\rangle, \|\pm5\rangle$
201	$\|\pm1\rangle, \|\pm3\rangle, \|\pm7\rangle, \|\pm5\rangle$
224	$\|0\rangle, \|\pm4\rangle$

Table S20. Composition of wave functions for $[Ho(Por)(cyclen)]^+$ as extracted from CASSCF/RASSI/Single_Aniso calculations with basis set 2.

M_J	Wave Functions and Energies					
	1		2		3	
	0.00 cm^{-1}		4.66 cm^{-1}		5.73 cm^{-1}	
	C	|c|	c	|c|	c	|c|
–8	-0.039958-0.009062i	0.040973	-0.042115-0.009106i	0.043088	0	0.000000
–7	0	0.000000	0	0.000000	0.001895+0.001334i	0.002317
–6	0	0.000000	0	0.000000	0	0.000000
–5	0	0.000000	-0.000001	0.000001	0.21366+0.670302i	**0.703531**
–4	-0.368729-0.594484i	**0.699552**	-0.374996-0.597931i	**0.705793**	0	0.000000
–3	0	0.000000	0	0.000000	0.020016+0.030874i	0.036795
–2	0	0.000000	0	0.000000	0	0.000000
–1	0	0.000000	0	0.000000	0.049529+0.035093i	0.060701
0	-0.132945-0.014886i	0.133776	-0.000038+0.000354i	0.000356	0	0.000000
1	0	0.000000	0	0.000000	0.060632-0.002896i	0.060701
2	0	0.000000	0	0.000000	0	0.000000
3	0	0.000000	0	0.000000	0.033493-0.015234i	0.036795
4	-0.49108+0.498211i	**0.699553**	0.492888-0.505178i	**0.705793**	0	0.000000
5	0	0.000000	0	0.000000	0.541018-0.449728i	**0.703531**
6	0	0.000000	0	0.000000	0	0.000000
7	0	0.000000	0	0.000000	0.002315-0.000103i	0.002317
8	-0.040973	0.040973	0.043088	0.043088	0	0.000000

M_J	4		5		6	
	5.73 cm^{-1}		50.4 cm^{-1}		50.4 cm^{-1}	
	C	|c|	c	|c|	c	|c|
–8	0	0.000000	0	0.000000	0	0.000000
–7	-0.000908-0.002132i	0.002317	0.035565-0.051324i	0.062442	-0.029265+0.055159i	0.062442
–6	0	0.000000	0	0.000000	0	0.000000
–5	-0.171781+0.682237i	**0.703531**	-0.045706+0.009944i	0.046775	-0.044214+0.015263i	0.046774
–4	0.000001	0.000001	0	0.000000	0	0.000000
–3	-0.000734-0.036787i	0.036794	0.594375-0.355288i	**0.692468**	-0.548334+0.422896i	**0.692467**
–2	0	0.000000	0	0.000000	0	0.000000
–1	0.02359+0.05593i	0.060701	0.077142-0.09193i	0.120008	0.065764-0.100385i	0.120009

0	0	0.000000	0	0.000000	0	0.000000
1	-0.05305-0.029501i	0.060701	0.000562-0.120007i	0.120008	0.013592+0.119236i	0.120008
2	0	0.000000	-0.000001	0.000001	0	0.000000
3	0.036491+0.004709i	0.036794	-0.223858-0.655285i	**0.692467**	-0.299564-0.624318i	**0.692468**
4	0.000001i	0.000001	0	0.000000	0	0.000000
5	-0.696816+0.096975i	**0.703532**	0.028447+0.037131i	0.046776	-0.032626-0.033517i	0.046774
6	0	0.000000	0	0.000000	0	0.000000
7	0.002022+0.001133i	0.002318	0.006039-0.062149i	0.062442	-0.001332-0.062428i	0.062442
8	0	0.000000	0	0.000000	0	0.000000

M_J	7		8		9	
	66.5 cm^{-1}		68.5 cm^{-1}		106 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–8	0	0.000000	0	0.000000	0	0.000000
–7	0	0.000000	0	0.000000	0	0.000000
–6	-0.433148+0.521527i	**0.677944**	0.383462-0.588788i	**0.702648**	-0.074445-0.186675i	0.200972
–5	0	0.000000	0	0.000000	0	0.000000
–4	0	0.000000	0	0.000000	0	0.000000
–3	0	0.000000	0	0.000000	0	0.000000
–2	-0.100436+0.174085i	0.200980	0.033673-0.071779i	0.079285	0.355091+0.577513i	**0.677946**
–1	0	0.000000	0	0.000000	0	0.000000
0	0	0.000000	0	0.000000	0	0.000000
1	0	0.000000	0	0.000000	-0.000001i	0.000001
2	0.110405+0.167939i	0.200980	0.052667+0.059264i	0.079285	0.677442-0.026126i	**0.677946**
3	0	0.000000	0	0.000000	-0.000001i	0.000001
4	0	0.000000	0	0.000000	0	0.000000
5	0	0.000000	0	0.000000	0	0.000000
6	0.462789+0.495413i	**0.677944**	0.534856+0.455679i	**0.702648**	-0.196541+0.041964i	0.200971
7	0	0.000000	0	0.000000	0	0.000000
8	0	0.000000	0	0.000000	0	0.000000

M_J	10		11		12	
	117 cm^{-1}		117 cm^{-1}		149 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–8	0.704764-0.03982i	**0.705888**	-0.704665+0.039876i	**0.705792**	0	0.000000
–7	0	0.000000	0	0.000000	0.495178-0.500493i	**0.704056**
–6	0	0.000000	0	0.000000	0	0.000000
–5	0	0.000000	0	0.000000	0.003144-0.001138i	0.003344
–4	-0.029631-0.026506i	0.039756	0.031784+0.029092i	0.043088	0	0.000000
–3	0	0.000000	0	0.000000	-0.053963+0.021376i	0.058043
–2	0	0.000000	0	0.000000	0	0.000000
–1	0	0.000000	0	0.000000	-0.016279+0.02569i	0.030414
0	-0.016817+0.000475i	0.016824	0.000007+0.000263i	0.000263	0	0.000000
1	0	0.000000	0	0.000000	-0.009302+0.028956i	0.030413
2	0	0.000000	0	0.000000	0	0.000000
3	0	0.000000	0	0.000000	0.018148+0.055132i	0.058042
4	-0.028089+0.028135i	0.039756	-0.03009+0.030841i	0.043088	0	0.000000
5	0	0.000000	0	0.000000	-0.00114-0.003144i	0.003344
6	0	0.000000	0	0.000000	0	0.000000
7	0	0.000000	0	0.000000	0.067186-0.700843i	**0.704056**
8	0.705888	**0.705888**	0.705793	**0.705793**	0	0.000000

M_J	13		14		15	
	149 cm^{-1}		160 cm^{-1}		201 cm^{-1}	
	c	|c|	c	|c|	c	|c|

–8	0	0.000000	0	0.000000	0	0.000000
–7	-0.494166+0.501493i	**0.704056**	0	0.000000	-0.004072+0.0196i	0.020019
–6	0	0.000000	-0.038801-0.069166i	0.079306	0	0.000000
–5	0.003142-0.001144i	0.003344	0	0.000000	0.035242-0.040035i	0.053337
–4	0	0.000000	0	0.000000	0	0.000000
–3	0.05392-0.021485i	0.058043	0	0.000000	0.092954-0.084414i	0.125563
–2	0	0.000000	0.422407+0.561501i	**0.702646**	0	0.000000
–1	-0.016227+0.025723i	0.030414	0	0.000000	-0.054021+0.691426i	**0.693533**
0	0	0.000000	0	0.000000	0.000001	0.000001
1	0.009243-0.028974i	0.030413	0.000001i	0.000001	0.131881+0.680879i	**0.693534**
2	0	0.000000	-0.696281+0.094357i	**0.702645**	0	0.000000
3	0.01826+0.055095i	0.058042	0.000001i	0.000001	-0.101905-0.073358i	0.125563
4	0	0.000000	0	0.000000	0	0.000000
5	0.001146+0.003141i	0.003344	0	0.000000	-0.039544-0.035792i	0.053337
6	0	0.000000	0.076466-0.021033i	0.079306	0	0.000000
7	0.065769-0.700977i	**0.704056**	0	0.000000	0.006262+0.019013i	0.020018
8	0	0.000000	0	0.000000	0	0.000000

M_J	16		17	
	201 cm^{-1}		224 cm^{-1}	
	c	|c|	c	|c|
–8	0	0.000000	0.006176-0.002277i	0.006582
–7	0.014781-0.013499i	0.020018	0	0.000000
–6	0	0.000000	0	0.000000
–5	0.052015-0.011801i	0.053337	0	0.000000
–4	0	0.000000	-0.070936-0.06336i	0.095113
–3	-0.124784+0.01396i	0.125562	0	0.000000
–2	0	0.000000	0	0.000000
–1	-0.448823+0.528721i	**0.693533**	-0.000001i	0.000001
0	0	0.000000	0.97546-0.174064i	**0.990869**
1	0.291979-0.629076i	**0.693533**	-0.000001i	0.000001
2	-0.000001	0.000001	0	0.000000
3	-0.039616-0.11915i	0.125563	0	0.000000
4	0	0.000000	-0.044643+0.083984i	0.095112
5	0.011082+0.052173i	0.053337	0	0.000000
6	0	0.000000	0	0.000000
7	-0.006063+0.019078i	0.020018	0	0.000000
8	0	0.000000	0.006582	0.006582

Table S21. Ab initio ligand-field parameters B_n^m (in cm^{-1}) of the [Er(TPP)(cyclen)]$^+$

n	m	Experimental Geometry		Symmetrized-C_4 Geometry	
		Real part	Imaginary part	Real part	Imaginary part
2	0	**71.89**	**0.00**	**110.05**	**0.00**
	1	7.84	7.84	0.18	0.18
	2	-17.38	-0.67	-0.32	0.11
4	0	**-113.16**	**0.00**	**-115.15**	**0.00**
	1	-0.21	0.79	0.00	0.03
	2	1.59	1.59	-0.02	-0.02
	3	6.02	0.70	-0.01	0.00
	4	**-1.60**	**-67.79**	**-32.38**	**-67.85**
6	0	**20.71**	**0.00**	**18.18**	**0.00**
	1	-0.71	-0.75	0.00	0.00
	2	0.00	-0.23	0.00	0.00
	3	2.24	2.24	0.00	0.00

	4	**-5.55**	**-0.67**	**-6.27**	**0.97**
	5	-0.38	1.50	-0.01	0.01
	6	0.49	1.16	0.00	0.00

Table S22. CASSCF/RASSI calculated energies and wave functions of the [Er(TPP)(cyclen)]$^+$ with an absolute coefficient larger than 0.05.

Basis set 2	
Energy (cm^{-1})	Wave Function
0.00	$\|+1/2\rangle, \|-1/2\rangle, \|-7/2\rangle, \|+9/2\rangle$
0.00	$\|-1/2\rangle, \|+1/2\rangle, \|+7/2\rangle, \|-9/2\rangle$
43.0	$\|-3/2\rangle, \|+3/2\rangle, \|+5/2\rangle, \|-5/2\rangle, \|+13/2\rangle, \|-11/2\rangle, \|+11/2\rangle, \|-13/2\rangle$
43.0	$\|+3/2\rangle, \|-3/2\rangle, \|-5/2\rangle, \|+5/2\rangle, \|-13/2\rangle, \|+11/2\rangle, \|-11/2\rangle, \|+13/2\rangle$
83.2	$\|+13/2\rangle, \|+5/2\rangle, \|-3/2\rangle, \|+15/2\rangle, \|-13/2\rangle$
83.2	$\|-13/2\rangle, \|-5/2\rangle, \|+3/2\rangle, \|-15/2\rangle, \|+13/2\rangle$
91.9	$\|-15/2\rangle, \|-13/2\rangle, \|-7/2\rangle$
91.9	$\|+15/2\rangle, \|+13/2\rangle, \|+7/2\rangle$
139	$\|-5/2\rangle, \|+5/2\rangle, \|-13/2\rangle, \|+3/2\rangle, \|+11/2\rangle, \|+13/2\rangle, \|-3/2\rangle$
139	$\|+5/2\rangle, \|-5/2\rangle, \|+13/2\rangle, \|-3/2\rangle, \|-11/2\rangle, \|-13/2\rangle, \|+3/2\rangle$
169	$\|-11/2\rangle, \|-3/2\rangle, \|+11/2\rangle, \|+5/2\rangle, \|-9/2\rangle$
169	$\|+11/2\rangle, \|+3/2\rangle, \|-11/2\rangle, \|-5/2\rangle, \|+9/2\rangle$
199	$\|+7/2\rangle, \|-9/2\rangle, \|-1/2\rangle, \|+9/2\rangle, \|+15/2\rangle, \|-7/2\rangle$
199	$\|-7/2\rangle, \|+9/2\rangle, \|+1/2\rangle, \|-9/2\rangle, \|-15/2\rangle, \|+7/2\rangle$
216	$\|-9/2\rangle, \|+9/2\rangle, \|+7/2\rangle, \|-1/2\rangle, \|-7/2\rangle, \|-11/2\rangle$
216	$\|+9/2\rangle, \|-9/2\rangle, \|-7/2\rangle, \|+1/2\rangle, \|+7/2\rangle, \|+11/2\rangle$

Table S23. Composition of wavefunctions for [Er(TPP)(cyclen)]$^+$ as extracted from CASSCF/RASSI/Single_Aniso calculations with basis set 2.

M_J	Wave Functions and Energies					
	1		2		3	
	0.00 cm^{-1}		0.00 cm^{-1}		43.0 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–15/2	0.005677-0.014404i	0.015482	0	0.000000	0.000388-0.000113i	0.000404
–13/2	-0.001174+0.002634i	0.002884	-0.011147+0.004822i	0.012145	0.027938-0.058361i	0.064703
–11/2	-0.003526-0.006563i	0.007450	-0.005384+0.013914i	0.014919	0.018123+0.098085i	0.099745
–9/2	-0.027447+0.028966i	0.039904	0.052702-0.066975i	0.085224	-0.003262-0.008331i	0.008947
–7/2	0.100608-0.041417i	0.108800	0.040104-0.010595i	0.041480	-0.011742+0.001336i	0.011818
–5/2	-0.002517+0.007309i	0.007730	0.010926+0.00479i	0.011930	0.171533+0.078176i	0.188507
–3/2	0.004215+0.030623i	0.030912	0.008348+0.014986i	0.017154	-0.576555+0.392956i	**0.697732**
–1/2	-0.260842-0.179866i	0.316844	0.770837+0.529983i	**0.935453**	0.016743-0.022411i	0.027975
1/2	0.210413+0.911481i	**0.935452**	0.071691+0.308627i	0.316844	0.015317-0.008848i	0.017689
3/2	-0.010881-0.013262i	0.017154	0.026945+0.015151i	0.030913	-0.414139+0.473369i	**0.628959**
5/2	0.00045+0.011922i	0.011930	-0.007722-0.000338i	0.007729	-0.075412-0.20354i	0.217061
7/2	0.024562-0.033426i	0.041480	-0.075424+0.078413i	0.108800	-0.00155-0.002565i	0.002997
9/2	-0.081635+0.024472i	0.085224	-0.037013+0.014913i	0.039904	0.007166+0.004811i	0.008631
11/2	-0.014919-0.000093i	0.014919	-0.004813-0.005687i	0.007450	-0.088474-0.035066i	0.095170
13/2	0.008574-0.008602i	0.012145	-0.002881+0.000127i	0.002884	0.023403-0.097849i	0.100609
15/2	0	0.000000	-0.015483	0.015483	0.01473	0.014730

M_J	4	5	6

	43.0 cm^{-1}		83.2 cm^{-1}		83.2 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	0.014144-0.004114i	0.014730	0.003971-0.005601i	0.006866	-0.06114+0.08624i	0.105714
−13/2	-0.049802-0.087418i	0.100609	-0.068027+0.05601i	0.088118	0.819673+0.470032i	**0.944878**
−11/2	-0.075159+0.058382i	0.095170	-0.019683-0.025634i	0.032319	0.001587-0.030226i	0.030268
−9/2	-0.005537+0.006621i	0.008631	-0.001796-0.000724i	0.001936	0.000336+0.010982i	0.010987
−7/2	-0.000772+0.002896i	0.002997	0.009329-0.004251i	0.010252	-0.038625-0.017535i	0.042419
−5/2	0.015559-0.216502i	0.217060	-0.032936-0.030491i	0.044883	0.036749+0.219672i	0.222725
−3/2	-0.529874-0.338854i	**0.628958**	0.078648-0.155084i	0.173887	-0.028093+0.038274i	0.047478
−1/2	-0.017178-0.004217i	0.017688	0.007791-0.001175i	0.007879	-0.001353+0.007324i	0.007448
1/2	0.022337+0.016843i	0.027975	-0.006757-0.003133i	0.007448	-0.005465+0.005676i	0.007879
3/2	0.663366+0.216276i	**0.697732**	0.047471-0.000782i	0.047477	0.172002+0.025532i	0.173887
5/2	0.14287-0.122976i	0.188507	-0.157952-0.157027i	0.222725	-0.005826-0.044503i	0.044883
7/2	0.011648-0.001997i	0.011818	0.008034-0.041652i	0.042420	0.008863-0.005152i	0.010252
9/2	-0.000805+0.008911i	0.008947	-0.008765-0.006625i	0.010987	0.000448-0.001884i	0.001937
11/2	0.009995+0.099243i	0.099745	-0.025576-0.016187i	0.030268	0.009528+0.030883i	0.032319
13/2	0.043127+0.048235i	0.064704	0.090612-0.940523i	**0.944878**	0.085036-0.023102i	0.088118
15/2	-0.000404	0.000404	0.105714	0.105714	0.006865	0.006865

M_J	7		8		9	
	91.9 cm^{-1}		91.9 cm^{-1}		139 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	-0.157142+0.975388i	**0.987965**	0.001071-0.00665i	0.006736	-0.016302+0.018993i	0.025030
−13/2	-0.110261+0.001765i	0.110275	0.000488-0.008991i	0.009004	0.250086-0.022428i	0.251090
−11/2	-0.018372+0.004675i	0.018957	0.001603+0.000225i	0.001619	0.033327-0.017069i	0.037444
−9/2	0.011487-0.041852i	0.043400	0.002696-0.00233i	0.003563	-0.007793-0.015466i	0.017318
−7/2	-0.065778+0.062838i	0.090969	0.00246-0.000198i	0.002468	-0.006236-0.007289i	0.009593
−5/2	0.00473-0.014444i	0.015199	0.001507+0.003446i	0.003761	-0.596611-0.653251i	**0.884693**
−3/2	-0.005249+0.002093i	0.005651	0.006641+0.008199i	0.010551	0.056989-0.029553i	0.064196
−1/2	-0.008349-0.003897i	0.009214	0.019061+0.016139i	0.024976	0.003062+0.005594i	0.006377
1/2	0.012902+0.021386i	0.024976	0.002519+0.008863i	0.009214	0.004138+0.009908i	0.010737
3/2	-0.007038-0.00786i	0.010550	0.002902-0.00485i	0.005652	-0.198033+0.101383i	0.222476
5/2	0.003163+0.002036i	0.003762	0.015013-0.002373i	0.015199	-0.065606-0.249981i	0.258447
7/2	0.000586-0.002397i	0.002468	0.0725-0.054946i	0.090969	-0.026258+0.043799i	0.051067
9/2	-0.002729+0.002291i	0.003563	0.043147-0.004684i	0.043401	-0.010415-0.001617i	0.010540
11/2	0.000033-0.001619i	0.001619	0.007537-0.017394i	0.018957	-0.106997-0.100376i	0.146710
13/2	-0.008954-0.000948i	0.009004	-0.01928+0.108577i	0.110275	-0.041408+0.072987i	0.083915
15/2	0.006736	0.006736	0.987966	**0.987966**	-0.000927	0.000927

M_J	10		11		12	
	139 cm^{-1}		169 cm^{-1}		169 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	-0.000604+0.000703i	0.000927	0.013906+0.012668i	0.018811	-0.000484-0.000441i	0.000655
−13/2	0.082353+0.016116i	0.083915	-0.016747-0.016524i	0.023527	0.003314+0.016951i	0.017272
−11/2	0.006479+0.146566i	0.146709	0.315012-0.91138i	**0.964285**	-0.004833-0.143643i	0.143724
−9/2	0.005556-0.008956i	0.010539	-0.061758+0.009914i	0.062549	0.004112-0.002054i	0.004596
−7/2	-0.050337-0.008602i	0.051067	0.01506-0.020058i	0.025082	0.012647+0.006177i	0.014075
−5/2	-0.14696-0.212597i	0.258447	0.014654-0.034208i	0.037215	0.057692-0.094704i	0.110893
−3/2	-0.205911+0.084239i	0.222476	-0.170347+0.008816i	0.170575	-0.01205+0.009367i	0.015262
−1/2	0.004823+0.009593i	0.010737	0.01402+0.013707i	0.019607	0.004971+0.010505i	0.011622
1/2	-0.002251-0.005967i	0.006377	0.010749-0.004418i	0.011622	-0.019595+0.000692i	0.019607
3/2	-0.059543+0.023996i	0.064196	0.0026+0.01504i	0.015263	-0.119992-0.121235i	0.170576
5/2	0.107121+0.878183i	**0.884692**	-0.021128+0.108862i	0.110893	0.012204-0.035157i	0.037215
7/2	-0.00147-0.009479i	0.009592	-0.013509-0.003951i	0.014075	-0.002375+0.02497i	0.025083
9/2	0.006661+0.015987i	0.017319	0.001657+0.004287i	0.004596	0.038978+0.048918i	0.062548

11/2	-0.034659+0.014172i	0.037445	0.100307-0.102933i	0.143724	-0.380881+0.885876i	**0.964286**
13/2	0.179901-0.175162i	0.251090	0.013865-0.0103i	0.017272	0.023508-0.000937i	0.023527
15/2	0.025029	0.025029	0.000655	0.000655	0.018811	0.018811

M_J	13		14		15	
	199 cm^{-1}		199 cm^{-1}		216 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–15/2	-0.003263+0.001737i	0.003697	-0.086988+0.046305i	0.098545	-0.019474+0.033226i	0.038512
–13/2	0.010165+0.001215i	0.010237	0.039588+0.00222i	0.039650	-0.00453-0.008678i	0.009789
–11/2	-0.005988-0.016217i	0.017287	-0.021313+0.018001i	0.027898	0.015749+0.058039i	0.060138
–9/2	0.084055-0.076766i	0.113834	-0.046498+0.087622i	0.099195	-0.689897+0.680022i	**0.968704**
–7/2	0.091522-0.003703i	0.091597	0.947572+0.213913i	**0.971417**	-0.062263-0.05263i	0.081527
–5/2	-0.017063-0.0371i	0.040836	-0.008158+0.000591i	0.008179	0.007944-0.016924i	0.018696
–3/2	0.005156+0.007194i	0.008851	-0.015651+0.00304i	0.015944	0.008977-0.001392i	0.009084
–1/2	0.077274+0.06777i	0.102782	-0.003312-0.006304i	0.007121	0.079187+0.067331i	0.103943
1/2	-0.000038-0.007121i	0.007121	0.036368-0.096132i	0.102781	-0.015486-0.016831i	0.022871
3/2	-0.015244+0.004671i	0.015944	-0.001171+0.008773i	0.008851	-0.01699-0.006933i	0.018350
5/2	0.007479-0.003311i	0.008179	0.002371+0.040767i	0.040836	0.004284-0.004663i	0.006332
7/2	0.735934-0.634076i	**0.971417**	-0.082529+0.039736i	0.091597	0.081578-0.085072i	0.117865
9/2	0.082217+0.055498i	0.099195	0.110269+0.028267i	0.113834	-0.145113+0.048799i	0.153098
11/2	-0.027272-0.005875i	0.027898	-0.002334-0.017129i	0.017287	0.002943+0.016184i	0.016449
13/2	-0.033902+0.020561i	0.039650	0.008402-0.005849i	0.010237	-0.002955+0.003712i	0.004745
15/2	-0.098545	0.098545	0.003697	0.003697	-0.003091	0.003091

M_J	16	
	216 cm^{-1}	
	c	|c|
–15/2	-0.001563+0.002667i	0.003091
–13/2	0.004697-0.000672i	0.004745
–11/2	-0.012475-0.010723i	0.016450
–9/2	0.115478-0.100518i	0.153098
–7/2	0.114645-0.027363i	0.117865
–5/2	-0.006189+0.001338i	0.006332
–3/2	-0.00261+0.018164i	0.018351
–1/2	-0.00669-0.021871i	0.022871
1/2	-0.018047-0.102364i	0.103943
3/2	-0.00574+0.00704i	0.009083
5/2	0.018618+0.001704i	0.018696
7/2	-0.013922-0.080329i	0.081527
9/2	-0.93553+0.25134i	**0.968704**
11/2	0.042109+0.042936i	0.060139
13/2	0.005196+0.008296i	0.009789
15/2	0.038512	0.038512

Table S24. CASSCF/RASSI calculated energies and wave functions of the [Er(Por)(cyclen)]$^+$ with an absolute coefficient larger than 0.05.

Basis set 2	
Energy (cm^{-1})	Wave Function
0.00	$\|-1/2\rangle, \|+7/2\rangle, \|-9/2\rangle$
0.00	$\|+1/2\rangle, \|-7/2\rangle, \|+9/2\rangle$
39.6	$\|-3/2\rangle, \|+13/2\rangle, \|+5/2\rangle, \|-11/2\rangle$
39.6	$\|+3/2\rangle, \|-13/2\rangle, \|-5/2\rangle, \|+11/2\rangle$

96.8	|−13/2⟩, |+3/2⟩, |+13/2⟩, |−3/2⟩, |+11/2⟩, |−11/2⟩
96.8	|+13/2⟩, |−3/2⟩, |−13/2⟩, |+3/2⟩, |−11/2⟩, |+11/2⟩
98.1	|−15/2⟩, |−7/2⟩, |+1/2⟩
98.1	|+15/2⟩, |+7/2⟩, |−1/2⟩
140	|−5/2⟩, |+11/2⟩, |+3/2⟩, |−13/2⟩
140	|+5/2⟩, |−11/2⟩, |−3/2⟩, |+13/2⟩
179	|−11/2⟩, |+5/2⟩, |+13/2⟩
179	|+11/2⟩, |−5/2⟩, |−13/2⟩
194	|−7/2⟩, |+9/2⟩, |−15/2⟩, |+7/2⟩, |−9/2⟩, |+1/2⟩
194	|+7/2⟩, |−9/2⟩, |+15/2⟩, |−7/2⟩, |+9/2⟩, |−1/2⟩
214	|+9/2⟩, |−7/2⟩, |+1/2⟩, |−9/2⟩, |−15/2⟩
214	|−9/2⟩, |+7/2⟩, |−1/2⟩, |+9/2⟩, |+15/2⟩

Table S25. Composition of wavefunctions for $[Er(Por)(cyclen)]^+$ as extracted from CASSCF/RASSI/Single_Aniso calculations with basis set 2.

M_J	Wave Functions and Energies					
	1		2		3	
	0.00 cm^{-1}		0.00 cm^{-1}		39.6 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	0.014448+0.009611i	0.017353	-0.000043-0.000029i	0.000052	0.000086-0.000068i	0.000110
−13/2	0.000003+0.000001i	0.000003	-0.000083-0.000023i	0.000086	-0.045268-0.049346i	0.066964
−11/2	0.000022+0.00011i	0.000112	0.00005-0.000078i	0.000093	0.055353-0.074964i	0.093186
−9/2	-0.000336-0.000075i	0.000344	-0.099585-0.032382i	0.104718	-0.000023+0.000024i	0.000033
−7/2	0.065603+0.111495i	0.129363	-0.000158-0.000299i	0.000338	0.000126+0.000104i	0.000163
−5/2	0.000005-0.000018i	0.000019	-0.000129-0.000241i	0.000273	-0.041159-0.230735i	0.234377
−3/2	-0.000504+0.000485i	0.000699	-0.000068-0.00001i	0.000069	0.604975-0.08757i	0.611280
−1/2	-0.000563-0.002557i	0.002618	-0.179568-0.969405i	**0.985896**	-0.000507+0.000199i	0.000545
1/2	-0.68642+0.707685i	**0.985896**	0.001885-0.001817i	0.002618	-0.00046-0.00004i	0.000462
3/2	0.000063+0.000029i	0.000069	-0.000151-0.000683i	0.000699	0.671309-0.227344i	**0.708760**
5/2	-0.000242+0.000129i	0.000274	0.000006-0.000017i	0.000018	0.058531+0.193448i	0.202109
7/2	0.000297-0.000161i	0.000338	0.116374-0.056498i	0.129364	0.000048-0.000117i	0.000126
9/2	-0.100851-0.028194i	0.104718	0.000322+0.000123i	0.000345	-0.000003-0.000009i	0.000009
11/2	0.000002-0.000093i	0.000093	0.000079-0.000079i	0.000112	0.096603+0.048411i	0.108054
13/2	-0.000082-0.000026i	0.000086	-0.000003-0.000001i	0.000003	-0.015631+0.05592i	0.058064
15/2	0.000052	0.000052	0.017352	0.017352	0.000016	0.000016

M_J	4		5		6	
	39.6 cm^{-1}		96.8 cm^{-1}		96.8 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	-0.000013+0.00001i	0.000016	-0.000483+0.000426i	0.000644	-0.010411+0.009175i	0.013877
−13/2	-0.046867-0.034276i	0.058063	-0.051164-0.047898i	0.070085	0.780312+0.432393i	**0.892105**
−11/2	-0.045974+0.097786i	0.108054	-0.035338+0.038864i	0.052528	-0.002105+0.003442i	0.004035
−9/2	0.000003+0.000008i	0.000009	-0.000079-0.000051i	0.000094	0.00015+0.000161i	0.000220
−7/2	-0.00011-0.000062i	0.000126	-0.000162-0.000006i	0.000162	-0.001541+0.000623i	0.001662
−5/2	-0.073643-0.188215i	0.202109	-0.008661-0.029246i	0.030501	0.198589+0.336648i	0.390857
−3/2	-0.668132+0.236518i	**0.708760**	-0.205376+0.010968i	0.205669	-0.015578+0.004856i	0.016317
−1/2	-0.000337+0.000316i	0.000462	-0.000047-0.000436i	0.000439	-0.000122-0.000085i	0.000149
1/2	0.000522-0.000157i	0.000545	0.000035-0.000144i	0.000148	0.000253+0.000358i	0.000438
3/2	0.529562-0.305332i	0.611280	-0.014898+0.006657i	0.016318	0.16133-0.127563i	0.205669
5/2	-0.110354-0.206771i	0.234376	0.073598+0.383865i	0.390857	0.012839+0.027667i	0.030501
7/2	0.000035-0.00016i	0.000164	-0.001568+0.000552i	0.001662	0.000118-0.000112i	0.000163
9/2	0.000033+0.000004i	0.000033	-0.000006+0.00022i	0.000220	-0.000026+0.00009i	0.000094

11/2	0.089859+0.024675i	0.093185	-0.003855-0.001191i	0.004035	0.052208+0.005793i	0.052528
13/2	0.005055-0.066774i	0.066965	-0.29952+0.84032i	**0.892104**	-0.006715+0.069763i	0.070085
15/2	0.00011	0.000110	-0.013877	0.013877	0.000644	0.000644

M_J	7		8		9	
	98.1 cm^{-1}		98.1 cm^{-1}		140 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	-0.000194-0.000168i	0.000257	0.749825+0.648718i	**0.991500**	0.000002+0.000003i	0.000004
−13/2	-0.001244-0.000975i	0.001581	-0.004545+0.01155i	0.012412	-0.211127-0.170257i	0.271223
−11/2	-0.000505+0.000536i	0.000736	0.000128+0.000192i	0.000231	-0.094067-0.020841i	0.096348
−9/2	0.005797+0.002259i	0.006222	0.000035+0.000021i	0.000041	-0.000098+0.000139i	0.000170
−7/2	-0.000019-0.000031i	0.000036	0.061135+0.108895i	0.124882	0.000021-0.00023i	0.000231
−5/2	-0.000222-0.000544i	0.000588	-0.004264+0.003507i	0.005521	0.187231+0.501502i	0.535313
−3/2	-0.002806+0.0001i	0.002808	-0.000151-0.000469i	0.000493	-0.097298-0.147095i	0.176363
−1/2	0.004359+0.032841i	0.033129	0.000003-0.000002i	0.000004	-0.000094-0.000089i	0.000129
1/2	-0.000001-0.000004i	0.000004	0.024784-0.021984i	0.033129	0.00011-0.000014i	0.000111
3/2	-0.000421+0.000256i	0.000493	0.002057+0.001911i	0.002808	0.121937-0.068179i	0.139703
5/2	0.00093+0.005442i	0.005521	-0.000524+0.000266i	0.000588	-0.499811+0.454989i	**0.675889**
7/2	0.117481-0.042352i	0.124882	0.000035-0.000011i	0.000037	-0.000032+0.000072i	0.000079
9/2	-0.000041-0.000007i	0.000042	0.005862+0.002084i	0.006221	0.000074+0.000207i	0.000220
11/2	0.000222-0.000061i	0.000230	0.000031+0.000736i	0.000737	0.074196+0.019171i	0.076633
13/2	-0.00412+0.011709i	0.012413	-0.001579-0.000076i	0.001581	0.335328-0.069505i	0.342456
15/2	0.9915	**0.991500**	0.000256	0.000256	-0.000162	0.000162

M_J	10		11		12	
	140 cm^{-1}		179 cm^{-1}		179 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	-0.000076-0.000143i	0.000162	-0.000009+0.000028i	0.000029	0.000139-0.000429i	0.000451
−13/2	-0.095135-0.328976i	0.342456	-0.0195-0.000934i	0.019522	-0.00222+0.000737i	0.002339
−11/2	0.051601+0.056656i	0.076633	0.085972-0.062819i	0.106477	-0.642569+0.733126i	**0.974869**
−9/2	-0.000218+0.000031i	0.000220	-0.000131+0.000013i	0.000132	0.000513-0.000425i	0.000666
−7/2	0.000048-0.000062i	0.000078	-0.000112-0.000129i	0.000171	-0.000106+0.001281i	0.001285
−5/2	-0.168921+0.65444i	**0.675889**	0.071006+0.044447i	0.083770	0.008802+0.002915i	0.009272
−3/2	-0.003345+0.139663i	0.139703	-0.01884-0.00299i	0.019076	0.174095-0.011307i	0.174462
−1/2	-0.000039-0.000104i	0.000111	0.000046-0.000129i	0.000137	-0.000055-0.000134i	0.000145
1/2	-0.000122-0.000042i	0.000129	-0.000111-0.000094i	0.000145	0.000137-0.000004i	0.000137
3/2	0.175508+0.017344i	0.176363	0.064377-0.162149i	0.174461	0.002958-0.018845i	0.019076
5/2	0.530894-0.068636i	0.535312	0.000062+0.009272i	0.009272	-0.020417-0.081244i	0.083770
7/2	0.000194-0.000126i	0.000231	-0.001252-0.000293i	0.001286	-0.000088-0.000146i	0.000170
9/2	0.000078-0.000151i	0.000170	-0.000563+0.000358i	0.000667	-0.000053+0.000121i	0.000132
11/2	0.062357+0.073447i	0.096348	-0.895394+0.385537i	**0.974869**	-0.086244+0.062445i	0.106477
13/2	-0.249146-0.107183i	0.271223	0.001385-0.001885i	0.002339	-0.005117+0.01884i	0.019523
15/2	-0.000004	0.000004	0.000451	0.000451	0.000029	0.000029

M_J	13		14		15	
	194 cm^{-1}		194 cm^{-1}		214 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−15/2	-0.000178+0.000218i	0.000281	-0.080704+0.098935i	0.127676	0.007302-0.006062i	0.009490
−13/2	0.000046-0.000004i	0.000046	-0.000083+0.000072i	0.000110	0.00009+0.000081i	0.000121
−11/2	-0.000217-0.000007i	0.000217	-0.001294-0.000064i	0.001296	-0.000302-0.000067i	0.000309
−9/2	-0.110983-0.052829i	0.122915	-0.000497+0.000424i	0.000653	-0.507108-0.244936i	0.563163
−7/2	0.001898-0.001061i	0.002174	0.8393-0.501388i	**0.977658**	-0.083856+0.031924i	0.089727
−5/2	-0.000116+0.000058i	0.000130	0.000088-0.000167i	0.000189	0.000171-0.000031i	0.000174
−3/2	-0.00004+0.000041i	0.000057	0.00004+0.000336i	0.000338	0.000042-0.000021i	0.000047
−1/2	-0.009049-0.112634i	0.112997	0.000109+0.000302i	0.000321	0.003438+0.067678i	0.067765

1/2	-0.000165-0.000275i	0.000321	-0.081559-0.078207i	0.112996	0.059996+0.077099i	0.097692
3/2	0.000235+0.000243i	0.000338	-0.000057+0.000005i	0.000057	-0.000049-0.00011i	0.000120
5/2	0.000185+0.000037i	0.000189	0.000118-0.000054i	0.000130	-0.000206+0.000089i	0.000224
7/2	-0.919039+0.333439i	**0.977658**	0.002022-0.0008i	0.002175	0.058104-0.020445i	0.061596
9/2	-0.000643+0.000117i	0.000654	0.029216-0.119393i	0.122916	0.322105-0.743628i	**0.810391**
11/2	0.000768-0.001044i	0.001296	-0.000132+0.000173i	0.000218	-0.000311+0.000494i	0.000584
13/2	-0.000108+0.000019i	0.000110	-0.000032+0.000033i	0.000046	-0.000014+0.00017i	0.000171
15/2	0.127677	0.127677	-0.000281	0.000281	-0.006486	0.006486

M_J	16	
	214 cm^{-1}	
	c	|c|
−15/2	-0.00499+0.004143i	0.006486
−13/2	0.000119+0.000122i	0.000170
−11/2	-0.000555-0.000181i	0.000584
−9/2	-0.722827-0.36641i	**0.810392**
−7/2	0.057765-0.021383i	0.061596
−5/2	0.000215-0.000063i	0.000224
−3/2	0.000032+0.000116i	0.000120
−1/2	0.003085+0.097644i	0.097693
1/2	-0.040584-0.054268i	0.067765
3/2	-0.000046+0.000011i	0.000047
5/2	0.000152-0.000085i	0.000174
7/2	0.084912-0.029001i	0.089728
9/2	-0.23372+0.512374i	0.563163
11/2	0.000189-0.000244i	0.000309
13/2	0.000017-0.000119i	0.000120
15/2	-0.009491	0.009491

Table S26. Ab initio ligand-field parameters B_n^m (in cm^{-1}) of the [Tm(TPP)(cyclen)]$^+$

n	m	Experimental Geometry		Symmetrized-C_4 Geometry	
		Real part	Imaginary part	Real part	Imaginary part
2	0	**-37.35**	**0.00**	**26.86**	**0.00**
	1	**10.86**	**10.86**	-0.01	-0.01
	2	**-51.85**	**14.76**	0.00	0.00
4	0	**3.54**	**0.00**	**-84.59**	**0.00**
	1	**28.10**	**71.41**	0.01	-0.01
	2	**38.72**	**38.72**	-0.02	-0.02
	3	**51.57**	**31.23**	0.00	0.00
	4	**-0.34**	**76.47**	**-4.74**	**41.19**
6	0	**6.12**	**0.00**	**18.72**	**0.00**
	1	**1.57**	**0.94**	0.00	0.00
	2	**10.81**	**-7.27**	0.00	0.00
	3	**5.01**	**5.01**	0.00	0.00
	4	**0.46**	**-11.46**	**-4.80**	**-3.80**
	5	**15.71**	**-7.06**	0.00	0.00
	6	**3.68**	**8.93**	0.00	0.00

Table S27. CASSCF/RASSI calculated energies and wave functions of the [Tm(TPP)(cyclen)]$^+$ with an absolute coefficient larger than 0.05.

Basis set 2	
Energy (cm^{-1})	Wave Function
0.00	|±6⟩, |±2⟩, |±4⟩, |±5⟩, |±3⟩, |±1⟩

7.40	|±6⟩, |±4⟩, |±5⟩, |±3⟩, |±1⟩, |±2⟩
11.2	|±5⟩, |±3⟩, |±1⟩, |±2⟩, |±4⟩, |0⟩, |±6⟩
16.7	|±5⟩, |±2⟩, |±1⟩, |±6⟩, |±3⟩, |0⟩
24.7	|±1⟩, |±3⟩, |0⟩, |±2⟩, |±4⟩, |±5⟩, |±6⟩
28.0	|0⟩, |±4⟩, |±3⟩, |±2⟩, |±1⟩, |±5⟩, |±6⟩
76.9	|±4⟩, |±6⟩, |±3⟩, |±1⟩, |±2⟩, |±5⟩
99.1	|±4⟩, |±6⟩, |±3⟩, |0⟩, |±5⟩, |±2⟩, |±1⟩
105	|±3⟩, |±2⟩, |±5⟩, |±6⟩, |±1⟩, |±4⟩
167	|±2⟩, |±5⟩, |±6⟩, |±1⟩, |0⟩, |±3⟩
173	|±3⟩, |±5⟩, |±1⟩, |±6⟩, |0⟩, |±4⟩, |±2⟩
212	|±1⟩, |±5⟩, |±4⟩, |±6⟩, |±2⟩, |±3⟩
213	|0⟩, |±2⟩, |±4⟩, |±5⟩, |±3⟩, |±6⟩, |±1⟩

Table S28. Composition of wave functions for $[Tm(TPP)(cyclen)]^+$ as extracted from CASSCF/RASSI/Single_Aniso calculations with basis set 2.

M_J	Wave Functions and Energies					
	1		2		3	
	0.00 cm^{-1}		7.40 cm^{-1}		11.2 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	0.031671-0.456952i	**0.458048**	0.047655-0.521094i	**0.523269**	-0.093659+0.012863i	0.094538
–5	-0.168763+0.003709i	0.168804	-0.274746+0.05922i	0.281056	0.381619+0.139798i	**0.406419**
–4	0.240553+0.155707i	0.286549	0.227647+0.18372i	0.292534	0.07419+0.119315i	0.140500
–3	-0.076736+0.141513i	0.160979	-0.117742+0.118918i	0.167346	-0.296222+0.268763i	0.399976
–2	-0.374779+0.032526i	0.376188	-0.124524+0.03452i	0.129220	-0.171761-0.178005i	0.247361
–1	-0.083914-0.071252i	0.110084	-0.090205-0.093221i	0.129719	0.121814-0.247546i	0.275894
0	-0.006271+0.005851i	0.008577	0.009173+0.01005i	0.013607	-0.009077-0.132801i	0.133111
1	-0.06528-0.08864i	0.110084	0.084618+0.09832i	0.129719	0.154364+0.22867i	0.275895
2	-0.058362+0.371634i	0.376189	0.045717-0.120862i	0.129219	0.145944-0.19972i	0.247362
3	0.14648-0.066767i	0.160979	-0.129146+0.106423i	0.167346	-0.330037-0.225958i	0.399977
4	-0.138702-0.250743i	0.286549	0.162225+0.243432i	0.292534	-0.057266+0.1283i	0.140500
5	0.015369-0.168103i	0.168804	-0.083995+0.268211i	0.281056	0.359048-0.190423i	**0.406419**
6	0.458048	**0.458048**	-0.523268	**0.523268**	0.094538	0.094538

M_J	4		5		6	
	16.7 cm^{-1}		24.7 cm^{-1}		28.0 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	-0.093782+0.216502i	0.235941	-0.028474-0.045304i	0.053509	-0.066672-0.015147i	0.068371
–5	0.485746-0.049532i	**0.488265**	0.018443+0.053869i	0.056939	0.038506+0.114305i	0.120617
–4	0.032537+0.016333i	0.036406	0.196108+0.019972i	0.197122	-0.31574-0.032016i	0.317359
–3	-0.061739+0.135041i	0.148485	0.017074-0.331145i	0.331585	-0.183365-0.252059i	0.311699
–2	-0.340519-0.092003i	0.352729	0.191493-0.068443i	0.203357	-0.209259+0.122564i	0.242510
–1	-0.044512-0.233395i	0.237602	-0.340278-0.396383i	**0.522407**	-0.107081-0.110016i	0.153525
0	0.048512-0.031854i	0.058035	0.120096-0.217327i	0.248302	-0.07059+0.629334i	**0.633281**
1	-0.196473-0.133615i	0.237602	-0.516674-0.077173i	**0.522406**	-0.128794+0.083559i	0.153525
2	-0.050928+0.349033i	0.352729	-0.043951-0.198551i	0.203357	0.176906+0.165879i	0.242511
3	0.148455-0.002976i	0.148485	-0.271282+0.190668i	0.331584	-0.234651+0.205172i	0.311700
4	-0.002055-0.036348i	0.036406	-0.121264-0.15541i	0.197122	0.314987+0.03873i	0.317359
5	-0.238527+0.426037i	**0.488265**	0.055423-0.01305i	0.056939	0.062873-0.102934i	0.120617
6	-0.235941	0.235941	0.053509	0.053509	0.068371	0.068371

M_J	7		8		9	
	76.9 cm^{-1}		99.1 cm^{-1}		105 cm^{-1}	
	c	|c|	c	|c|	c	|c|

–6	0.06796+0.265467i	0.274028	-0.061278-0.378723i	0.383648	0.013145+0.196199i	0.196639
–5	0.018366+0.064907i	0.067455	0.134431-0.124438i	0.183184	-0.216918+0.063282i	0.225960
–4	0.516602+0.222381i	**0.562433**	-0.41273-0.170825i	**0.446685**	0.028442+0.124108i	0.127325
–3	-0.019638-0.235829i	0.236645	0.077889+0.202425i	0.216893	-0.094011+0.487525i	**0.496506**
–2	0.141573+0.044037i	0.148264	0.138848-0.10056i	0.171438	0.32508-0.073295i	0.333240
–1	-0.098496-0.126386i	0.160234	-0.041463-0.143024i	0.148913	0.016836+0.188717i	0.189467
0	0.021465+0.016662i	0.027173	0.133222-0.15651i	0.205532	-0.025253-0.023618i	0.034576
1	0.146865+0.064075i	0.160234	-0.14781-0.018086i	0.148912	-0.189421-0.004183i	0.189467
2	0.077772+0.126228i	0.148263	0.077092-0.153127i	0.171438	-0.0514+0.329253i	0.333241
3	0.233332-0.039462i	0.236645	0.212267+0.044557i	0.216893	-0.48015+0.126391i	**0.496507**
4	0.343552+0.445312i	**0.562433**	0.234555+0.380147i	**0.446685**	0.125731+0.020082i	0.127325
5	-0.067434-0.001695i	0.067455	-0.101368+0.152581i	0.183184	-0.04864+0.220663i	0.225960
6	0.274028	0.274028	0.383648	0.383648	0.196639	0.196639

M_J	10		11		12	
	167 cm^{-1}		173 cm^{-1}		212 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	0.104928+0.278417i	0.297533	-0.095896-0.234707i	0.253542	-0.103351-0.06415i	0.121641
–5	-0.240958+0.230878i	0.333715	0.276218-0.243043i	0.367922	0.10087-0.264967i	0.283518
–4	0.010364-0.015096i	0.018311	0.108201-0.001651i	0.108214	0.248304+0.017375i	0.248911
–3	-0.089121+0.042362i	0.098677	0.022603-0.404101i	**0.404733**	-0.073478+0.00716i	0.073826
–2	-0.489217+0.167012i	**0.516939**	-0.01112+0.080928i	0.081688	-0.093737+0.0385i	0.101335
–1	0.102868+0.081305i	0.131120	0.261655+0.20596i	0.332991	0.489324+0.294579i	**0.571152**
0	-0.08717-0.060303i	0.105996	0.067258-0.100136i	0.120627	0.041484+0.011828i	0.043137
1	-0.112359-0.067586i	0.131120	0.289625+0.164317i	0.332991	-0.571099-0.007769i	**0.571152**
2	-0.016245-0.516684i	**0.516939**	-0.07071+0.040903i	0.081688	-0.059338-0.082145i	0.101335
3	-0.008211+0.098335i	0.098677	-0.365533+0.173766i	**0.404733**	0.058654+0.044834i	0.073827
4	-0.010471+0.015022i	0.018311	-0.039396-0.100787i	0.108213	0.220131+0.116186i	0.248911
5	-0.131068+0.306898i	0.333714	-0.120515+0.347624i	0.367922	0.054032-0.278321i	0.283517
6	0.297533	0.297533	0.253542	0.253542	-0.121641	0.121641

M_J	13	
	213 cm^{-1}	
	c	|c|
–6	0.111273+0.057509i	0.125256
–5	-0.067254+0.224372i	0.234235
–4	-0.252016-0.04571i	0.256128
–3	-0.035381-0.164733i	0.168490
–2	-0.219169+0.247764i	0.330790
–1	0.024684+0.057944i	0.062983
0	0.157448-0.647566i	**0.666432**
1	0.048532-0.040142i	0.062982
2	0.080946+0.320734i	0.330791
3	-0.107066+0.130098i	0.168489
4	0.244869+0.075102i	0.256127
5	0.043271-0.230203i	0.234234
6	-0.125255	0.125255

Table S29. CASSCF/RASSI calculated energies and wave functions of the [Tm(Por)(cyclen)]$^+$ with an absolute coefficient larger than 0.05.

Basis set 2	
Energy (cm^{-1})	Wave Function
0.00	$\|\pm6\rangle, \|\pm2\rangle$

3.31	$\|\pm6\rangle, \|\pm2\rangle$
30.8	$\|\pm1\rangle, \|\pm3\rangle, \|\pm5\rangle$
30.8	$\|\pm1\rangle, \|\pm3\rangle, \|\pm5\rangle$
31.7	$\|0\rangle, \|\pm4\rangle$
37.2	$\|\pm2\rangle, \|\pm6\rangle$
77.1	$\|\pm2\rangle, \|\pm6\rangle$
100	$\|\pm3\rangle, \|\pm1\rangle, \|\pm5\rangle$
100	$\|\pm3\rangle, \|\pm1\rangle, \|\pm5\rangle$
162	$\|\pm4\rangle$
168	$\|\pm4\rangle, \|0\rangle,$
197	$\|\pm5\rangle, \|\pm1\rangle, \|\pm3\rangle$
197	$\|\pm5\rangle, \|\pm1\rangle, \|\pm3\rangle$

Table S30. Composition of wave functions for $[Tm(Por)(cyclen)]^+$ as extracted from CASSCF/RASSI/Single_Aniso calculations with basis set 2.

M_J	Wave Functions and Energies					
	1		2		3	
	0.00 cm^{-1}		3.31 cm^{-1}		30.8 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	-0.251907+0.600185i	**0.650906**	-0.269315+0.641441i	**0.695685**	-0.000037+0.000037i	0.000052
–5	-0.000003-0.000009i	0.000009	-0.000003-0.00001i	0.000010	0.010692-0.071001i	0.071802
–4	0.000013+0.000038i	0.000040	0.000015+0.00005i	0.000052	-0.000059-0.000105i	0.000120
–3	0.000011+0.000009i	0.000014	0.000008+0.000005i	0.000009	0.189816+0.116022i	0.222466
–2	0.276161+0.007517i	0.276263	0.126536+0.003352i	0.126580	-0.000111-0.000059i	**0.000126**
–1	0.000005-0.000005i	0.000007	0.000006-0.000005i	0.000008	-0.667069+0.019283i	0.667348
0	-0.000063+0.000042i	0.000076	0.000013+0.000019i	0.000023	-0.000828+0.00034i	0.000895
1	-0.000006+0.000002i	0.000006	0.000007-0.000003i	0.000008	0.487915-0.455293i	0.667348
2	0.099945-0.257551i	0.276263	-0.045894+0.117967i	0.126580	-0.000037+0.00012i	**0.000126**
3	0.000004+0.000013i	0.000014	-0.000002-0.000009i	0.000009	-0.053407+0.215961i	0.222467
4	-0.00003-0.000027i	0.000040	0.00004+0.000033i	0.000052	0.000032+0.000116i	0.000120
5	-0.000007-0.000006i	0.000009	0.000008+0.000006i	0.000010	-0.057523-0.042972i	0.071802
6	-0.650906	**0.650906**	0.695685	**0.695685**	-0.000052	0.000052

M_J	4		5		6	
	30.8 cm^{-1}		31.7 cm^{-1}		37.2 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	-0.000021	0.000021	0.000231-0.000432i	0.000490	0.107274-0.254585i	0.276263
–5	0.037086-0.061512i	0.071827	-0.000003+0.000063i	0.000063	-0.000002-0.000009i	0.000009
–4	-0.000009-0.000008i	0.000012	-0.083509-0.118755i	0.145177	0.00016+0.000182i	0.000242
–3	-0.130895-0.179925i	0.222501	-0.000204-0.000056i	0.000212	0.000072+0.000065i	0.000097
–2	-0.000026-0.000048i	0.000055	0.001036+0.00009i	0.001040	0.650639+0.018625i	0.650906
–1	-0.623529-0.237794i	**0.667334**	0.000603-0.000066i	**0.000607**	-0.000103+0.00004i	0.000110
0	0.000069i	0.000069	-0.839434+0.503184i	0.978695	0.001323-0.000878i	**0.001588**
1	-0.625122+0.233574i	**0.667334**	-0.000342+0.000501i	**0.000607**	0.000077-0.00008i	0.000111
2	0.000026-0.000048i	0.000055	0.000409-0.000956i	0.001040	0.235482-0.606816i	0.650905
3	-0.132108+0.179036i	0.222500	0.000047-0.000206i	0.000211	0.000032+0.000091i	0.000096
4	0.000009-0.000008i	0.000012	0.065377+0.129624i	0.145178	-0.000105-0.000218i	0.000242
5	0.036669+0.061761i	0.071826	0.000057+0.000026i	0.000063	-0.000007-0.000005i	0.000009
6	0.000021	0.000021	0.00049	0.000490	0.276263	0.276263

M_J	7		8		9	
	77.1 cm^{-1}		100 cm^{-1}		100 cm^{-1}	
	c	|c|	c	|c|	c	|c|

–6	0.049336-0.116569i	0.126580	-0.000011-0.000004i	0.000012	0.000006+0.000012i	0.000013
–5	-0.000009-0.000011i	0.000014	-0.032176-0.022129i	0.039051	-0.021468-0.032468i	0.038924
–4	0.000034+0.00001i	0.000035	-0.000055-0.000032i	0.000064	0.000048+0.000051i	0.000070
–3	0.000062+0.000071i	0.000094	-0.620623+0.255193i	**0.671041**	0.671016-0.004826i	**0.671033**
–2	0.695385+0.020414i	**0.695685**	0.000002-0.000073i	0.000073	-0.000089+0.000066i	0.000111
–1	-0.000067+0.000067i	0.000095	-0.09209+0.199244i	0.219497	-0.159902+0.150435i	0.219543
0	-0.00001-0.000014i	0.000017	0.000004-0.000026i	0.000026	-0.000022-0.000013i	0.000026
1	-0.000088+0.000036i	0.000095	-0.026038-0.217947i	0.219497	-0.057285+0.211938i	0.219543
2	-0.252235+0.648348i	**0.695685**	0.00002-0.00007i	0.000073	0.000016-0.000109i	0.000110
3	-0.000041-0.000084i	0.000093	-0.511437-0.434428i	**0.671041**	-0.312086-0.594044i	**0.671033**
4	-0.000004+0.000035i	0.000035	0.000062-0.000014i	0.000064	0.000067+0.000019i	0.000070
5	0.000007+0.000012i	0.000014	-0.037438+0.011107i	0.039051	0.038754+0.003626i	0.038923
6	-0.12658	0.126580	0.000012	0.000012	0.000014	0.000014

M_J	10		11		12	
	162 cm^{-1}		168 cm^{-1}		197 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–6	-0.00002-0.000042i	0.000047	0.000019+0.000041i	0.000045	0.000002-0.00001i	0.000010
–5	0.000015+0.0001i	0.000101	-0.000016-0.000104i	0.000105	-0.292427-0.638602i	**0.702372**
–4	0.626591+0.32769i	**0.707105**	-0.613939-0.319384i	**0.692046**	0.0001+0.000017i	0.000101
–3	-0.000063+0.000027i	0.000069	0.000063-0.000027i	0.000069	-0.012249-0.007631i	0.014432
–2	-0.000037+0.000006i	0.000037	0.000028+0.000004i	0.000028	-0.000003-0.000001i	0.000003
–1	0.000001-0.000003i	0.000003	0.000021-0.000004i	0.000021	0.06607-0.04583i	0.080409
0	0.002234+0.001424i	0.002649	0.110049-0.173307i	0.205295	0.00001+0.000013i	0.000016
1	0.000003-0.000002i	0.000004	0.000005+0.000021i	0.000022	0.06028-0.053216i	0.080409
2	-0.000011-0.000036i	0.000038	-0.000016-0.000024i	0.000029	-0.000003i	0.000003
3	0.000002+0.000069i	0.000069	0.000002+0.000068i	0.000068	0.004486+0.013716i	0.014431
4	0.561686+0.42954i	**0.707104**	0.550166+0.419815i	**0.692046**	-0.000008+0.000101i	0.000101
5	-0.000097+0.000028i	0.000101	-0.000101+0.00003i	0.000105	0.550308+0.436449i	**0.702372**
6	-0.000046	0.000046	-0.000045	0.000045	-0.00001	0.000010

M_J	13	
	197 cm^{-1}	
	c	|c|
–6	-0.000003+0.00001i	0.000010
–5	0.2908+0.639339i	**0.702367**
–4	-0.000101-0.000025i	0.000104
–3	-0.012355-0.007728i	0.014573
–2	0.000003+0.000001i	0.000003
–1	-0.066198+0.045672i	0.080425
0	0.000018-0.000014i	0.000023
1	0.060428-0.053072i	0.080425
2	-0.000003i	0.000003
3	-0.004484-0.013865i	0.014572
4	-0.000001+0.000104i	0.000104
5	0.549192+0.437844i	**0.702367**
6	-0.00001	0.000010

Table S31. Ab initio ligand-field parameters B_n^m (in cm^{-1}) of the [Yb(TPP)(cyclen)]$^+$

n	m	Experimental Geometry		Symmetrized-C_4 Geometry	
		Real part	Imaginary part	Real part	Imaginary part
2	0	**32.44**	**0.00**	**46.11**	**0.00**
	1	21.19	21.19	-0.03	-0.03

	2	10.99	1.91	0.03	0.01
4	0	**-84.24**	**0.00**	**-88.89**	**0.00**
	1	-23.24	-3.95	0.05	-0.01
	2	-3.85	-3.85	-0.01	-0.01
	3	2.69	0.73	-0.01	-0.01
	4	**40.73**	**-34.38**	**-43.15**	**-24.47**
6	0	**16.92**	**0.00**	**18.58**	**0.00**
	1	7.72	0.54	-0.01	0.00
	2	0.74	0.63	0.00	0.00
	3	1.96	1.96	0.00	0.00
	4	**-2.08**	**-4.22**	**2.55**	**-2.91**
	5	-1.98	-0.94	0.00	0.00
	6	0.77	-0.36	0.00	0.00

Table S32. CASSCF/RASSI calculated energies and wave functions of the $[Yb(TPP)(cyclen)]^+$ with an absolute coefficient larger than 0.05.

Basis set 2	
Energy (cm^{-1})	Wave Function
0.00	$\|-5/2\rangle, \|+3/2\rangle, \|+5/2\rangle, \|-3/2\rangle, \|-7/2\rangle$
0.00	$\|+5/2\rangle, \|-3/2\rangle, \|-5/2\rangle, \|+3/2\rangle, \|+7/2\rangle$
146.9	$\|+3/2\rangle, \|-3/2\rangle, \|-5/2\rangle, \|+5/2\rangle, \|+7/2\rangle, \|+1/2\rangle$
146.9	$\|-3/2\rangle, \|+3/2\rangle, \|+5/2\rangle, \|-5/2\rangle, \|-7/2\rangle, \|-1/2\rangle$
176.5	$\|+1/2\rangle, \|-7/2\rangle, \|-3/2\rangle, \|-1/2\rangle, \|+7/2\rangle$
176.5	$\|-1/2\rangle, \|+7/2\rangle, \|+3/2\rangle, \|+1/2\rangle, \|-7/2\rangle$
244.2	$\|-7/2\rangle, \|+1/2\rangle, \|-5/2\rangle, \|+3/2\rangle$
244.2	$\|+7/2\rangle, \|-1/2\rangle, \|+5/2\rangle, \|-3/2\rangle$

Table S33. Composition of wave functions for $[Yb(TPP)(cyclen)]^+$ as extracted from CASSCF/RASSI/Single_Aniso calculations with basis set 2.

M_J	Wave Functions and Energies					
	1		2		3	
	0.00 cm^{-1}		0.00 cm^{-1}		146.9 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−7/2	-0.078977-0.055558i	0.096561	0	0.000000	0.003073+0.042351i	0.042462
−5/2	0.702978+0.627906i	**0.942573**	-0.09666-0.068744i	0.118612	-0.047363-0.239204i	0.243848
−3/2	0.068527+0.077001i	0.103078	0.220475+0.168959i	0.277770	0.505816+0.077572i	0.511730
−1/2	-0.013494-0.004644i	0.014271	0.000625+0.01335i	0.013365	-0.041499-0.00485i	0.041781
1/2	-0.008192+0.010559i	0.013364	-0.013709-0.003966i	0.014271	-0.064021-0.046816i	0.079312
3/2	0.277539-0.011337i	0.277770	-0.100351+0.02355i	0.103077	0.580203+0.547295i	**0.797601**
5/2	0.11861-0.00061i	0.118612	0.936239-0.109091i	**0.942573**	-0.083488+0.133779i	0.157693
7/2	0	0.000000	0.096562	0.096562	-0.088306	0.088306

M_J	4		5		6	
	146.9 cm^{-1}		176.5 cm^{-1}		176.5 cm^{-1}	
	c	|c|	c	|c|	c	|c|
−7/2	-0.006391-0.088075i	0.088307	0.319412+0.296713i	0.435962	-0.039239-0.036451i	0.053557
−5/2	-0.127386+0.092951i	0.157693	0.014528+0.043169i	0.045548	-0.019293+0.009361i	0.021444
−3/2	0.587849+0.539074i	**0.797601**	0.091804-0.011813i	0.092561	0.007196+0.004147i	0.008305
−1/2	0.051327+0.060465i	0.079313	-0.078512-0.025536i	0.082560	-0.756493-0.465619i	**0.888303**
1/2	-0.00784-0.041039i	0.041781	0.87115+0.173724i	**0.888303**	-0.074902-0.034726i	0.082560
3/2	-0.113974-0.498876i	0.511730	0.008095+0.001859i	0.008306	-0.059222-0.071136i	0.092561

5/2	-0.242004-0.029927i	0.243847	0.007765+0.019989i	0.021444	0.040025-0.021741i	0.045549
7/2	-0.042463	0.042463	-0.053557	0.053557	-0.435961	0.435961

M_J	7		8	
	244.2 cm^{-1}		244.2 cm^{-1}	
	c	|c|	c	|c|
–7/2	-0.744514-0.483545i	**0.887759**	0.004318+0.002805i	0.005149
–5/2	-0.077474-0.067327i	0.102641	-0.008439-0.004279i	0.009462
–3/2	-0.024927-0.024447i	0.034914	0.063667+0.016589i	0.065793
–1/2	-0.000321+0.015102i	0.015105	-0.377974-0.229327i	0.442103
1/2	0.441895+0.013552i	0.442103	0.007957-0.01284i	0.015106
3/2	0.06243+0.020766i	0.065793	0.034221-0.006926i	0.034915
5/2	0.009408+0.001008i	0.009462	-0.101645+0.014265i	0.102641
7/2	0.005149	0.005149	0.88776	**0.887760**

Table S34. CASSCF/RASSI calculated energies and wave functions of the [Yb(Por)(cyclen)]$^+$ with an absolute coefficient larger than 0.05.

Basis set 2	
Energy (cm^{-1})	Wave Function
0.00	$\|-5/2\rangle, \|+3/2\rangle, \|+5/2\rangle, \|-3/2\rangle$
0.00	$\|+5/2\rangle, \|-3/2\rangle, \|-5/2\rangle, \|+3/2\rangle$
143.7	$\|-3/2\rangle, \|+3/2\rangle, \|+5/2\rangle, \|-5/2\rangle$
143.7	$\|+3/2\rangle, \|-3/2\rangle, \|-5/2\rangle, \|+5/2\rangle$
176.4	$\|-1/2\rangle, \|+7/2\rangle$
176.4	$\|+1/2\rangle, \|-7/2\rangle$
252.7	$\|-7/2\rangle, \|+1/2\rangle$
252.7	$\|+7/2\rangle, \|-1/2\rangle$

Table S35. Composition of wave functions for [Yb(Por)(cyclen)]$^+$ as extracted from CASSCF/RASSI/Single_Aniso calculations with basis set 2.

M_J	Wave Functions and Energies					
	1		2		3	
	0.00 cm^{-1}		0.00 cm^{-1}		143.7 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–7/2	0	0.000000	0.000166+0.000079i	0.000184	0.00001+0.000023i	0.000025
–5/2	0.084038-0.012304i	0.084934	0.946456+0.160992i	**0.960051**	-0.17296+0.021727i	0.174319
–3/2	0.253571-0.078947i	0.265577	-0.023637-0.000267i	0.023639	-0.728966+0.030391i	**0.729599**
–1/2	-0.000056+0.000033i	0.000065	-0.000028-0.000024i	0.000037	0.00022-0.000091i	0.000238
1/2	0.000036-0.000009i	0.000037	-0.000036-0.000053i	0.000064	-0.000044+0.000033i	0.000055
3/2	-0.021455-0.009922i	0.023638	-0.194987-0.180308i	0.265577	-0.566339-0.275418i	0.629758
5/2	-0.923717-0.261616i	**0.960050**	0.070582+0.047243i	0.084934	-0.173422-0.103089i	0.201749
7/2	0.000184	0.000184	0	0.000000	0.000119	0.000119

M_J	4		5		6	
	143.7 cm^{-1}		176.4 cm^{-1}		176.4 cm^{-1}	
	c	|c|	c	|c|	c	|c|
–7/2	0.000048+0.000109i	0.000119	0	0.000000	0.351291+0.126352i	0.373323
–5/2	0.164052+0.117429i	0.201749	0.00006-0.000021i	0.000064	-0.000083+0.000002i	0.000083

–3/2	-0.479656-0.408075i	0.629758	0.000169-0.00004i	0.000174	-0.000088+0.000049i	0.000101
–1/2	-0.000013+0.000054i	0.000056	0.858477-0.351634i	**0.927701**	-0.000115-0.000183i	0.000216
1/2	0.000005+0.000238i	0.000238	-0.000171+0.000134i	0.000217	-0.688802-0.621434i	**0.927701**
3/2	0.264891+0.679815i	**0.729600**	0.000066+0.000076i	0.000101	0.000145+0.000095i	0.000173
5/2	-0.049555-0.167127i	0.174319	-0.000077-0.00003i	0.000083	-0.000049-0.00004i	0.000063
7/2	-0.000025	0.000025	-0.373323	0.373323	0	0.000000

M_J	7		8	
	252.7 cm^{-1}		252.7 cm^{-1}	
	c	|c|	c	|c|
–7/2	0	0.000000	-0.704799-0.603231i	**0.927701**
–5/2	0.000034-0.000006i	0.000035	0.000163+0.000076i	0.000180
–3/2	0.000098-0.000015i	0.000099	-0.00014-0.000007i	0.000140
–1/2	0.345466-0.141504i	0.373323	-0.000017-0.000085i	0.000087
1/2	-0.000069+0.000054i	0.000088	-0.170448-0.332141i	0.373323
3/2	0.00011+0.000086i	0.000140	0.000064+0.000075i	0.000099
5/2	0.000173+0.000049i	0.000180	-0.000022-0.000026i	0.000034
7/2	0.927701	**0.927701**	0	0.000000