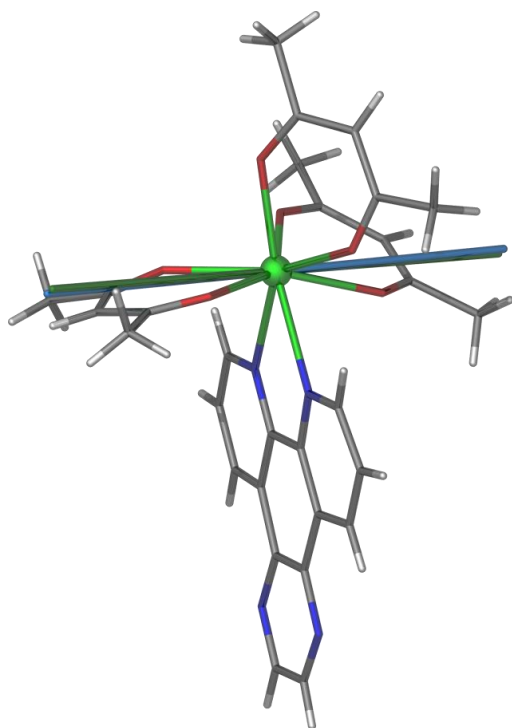
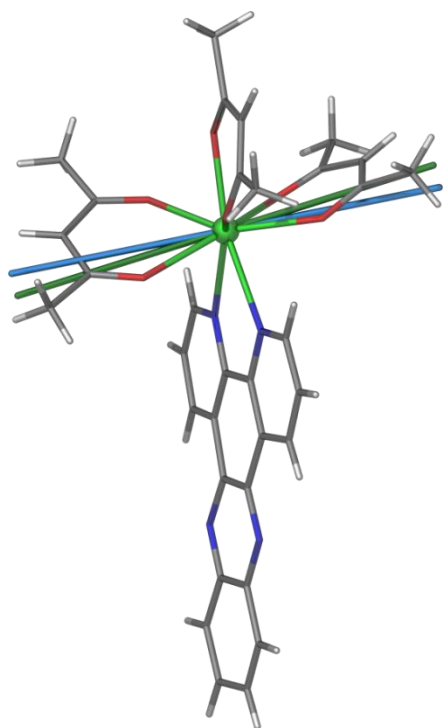


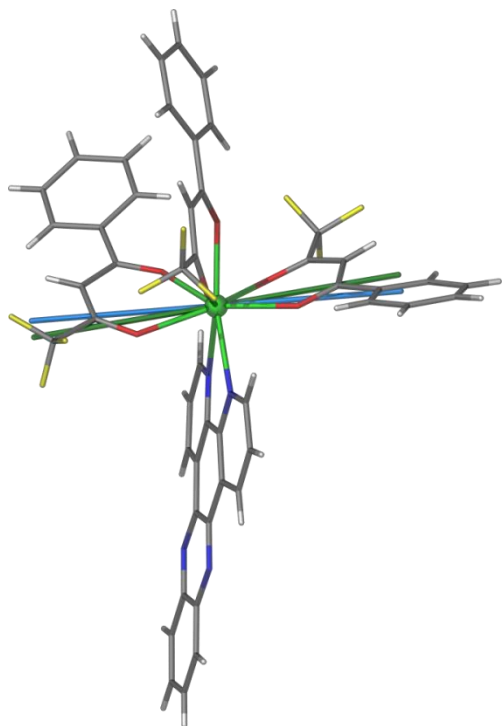
Supplementary Figure S1 – Comparison of the *ab initio* (blue rod) and electrostatic (green rod) anisotropy directions for the ground Kramers doublet in **2**. Dy = green, O = red, N = blue, C = grey and H = white.



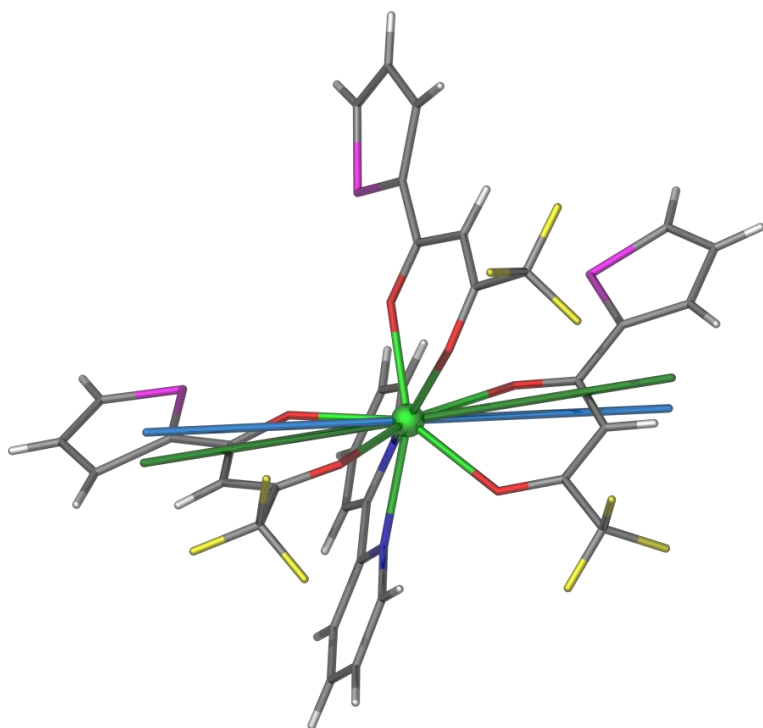
Supplementary Figure S2 – Comparison of the *ab initio* (blue rod) and electrostatic (green rod) anisotropy directions for the ground Kramers doublet in **3**. Dy = green, O = red, N = blue, C = grey and H = white.



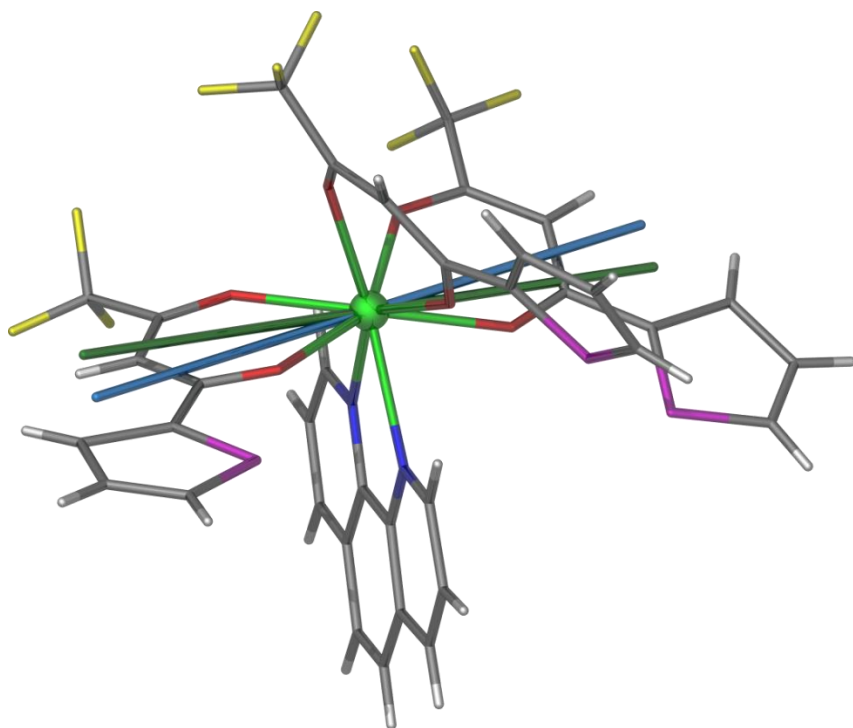
Supplementary Figure S3 – Comparison of the *ab initio* (blue rod) and electrostatic (green rod) anisotropy directions for the ground Kramers doublet in **4**. Dy = green, O = red, N = blue, C = grey and H = white.



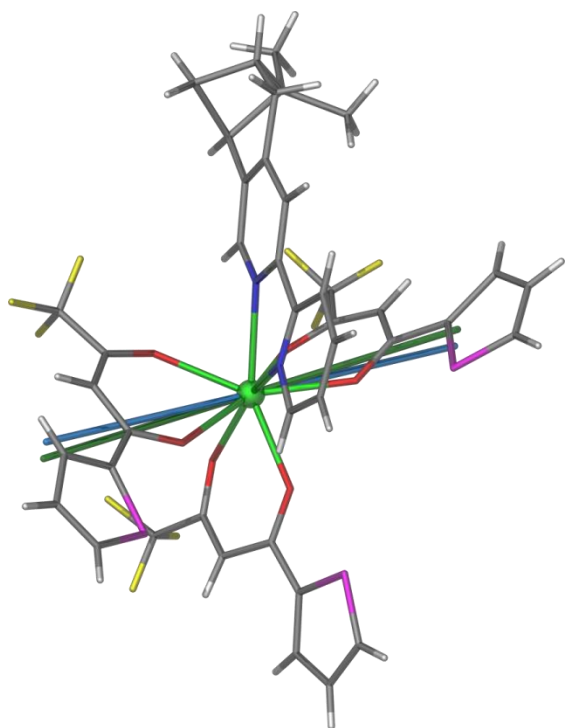
Supplementary Figure S4 – Comparison of the *ab initio* (blue rod) and electrostatic (green rod) anisotropy directions for the ground Kramers doublet in **5**. Dy = green, F = yellow, O = red, N = blue, C = grey and H = white.



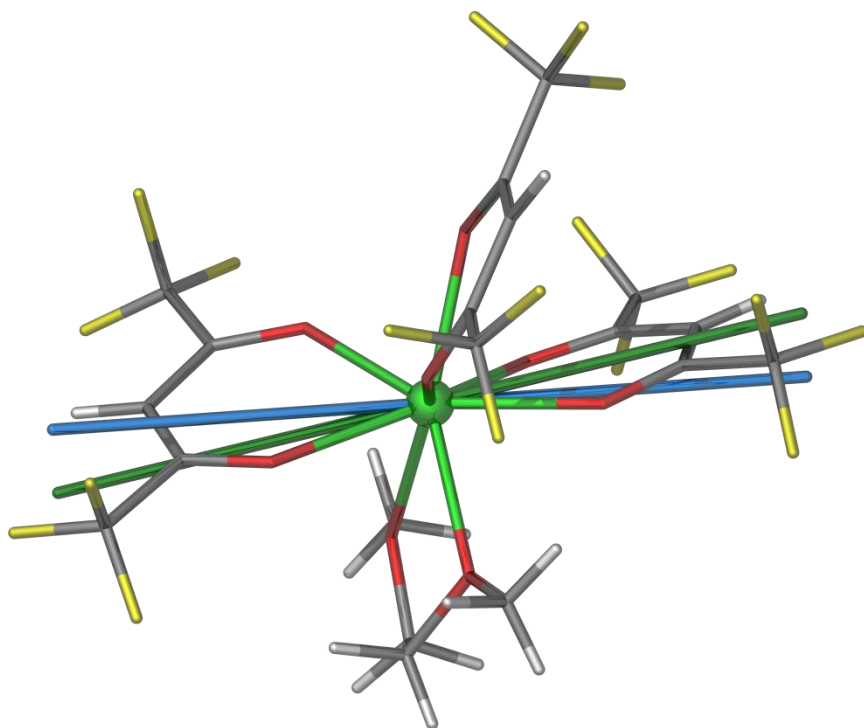
Supplementary Figure S5 – Comparison of the *ab initio* (blue rod) and electrostatic (green rod) anisotropy directions for the ground Kramers doublet in **6**. Dy = green, S = purple, F = yellow, O = red, N = blue, C = grey and H = white.



Supplementary Figure 6 – Comparison of the *ab initio* (blue rod) and electrostatic (green rod) anisotropy directions for the ground Kramers doublet in **7**. Dy = green, S = purple, F = yellow, O = red, N = blue, C = grey and H = white.

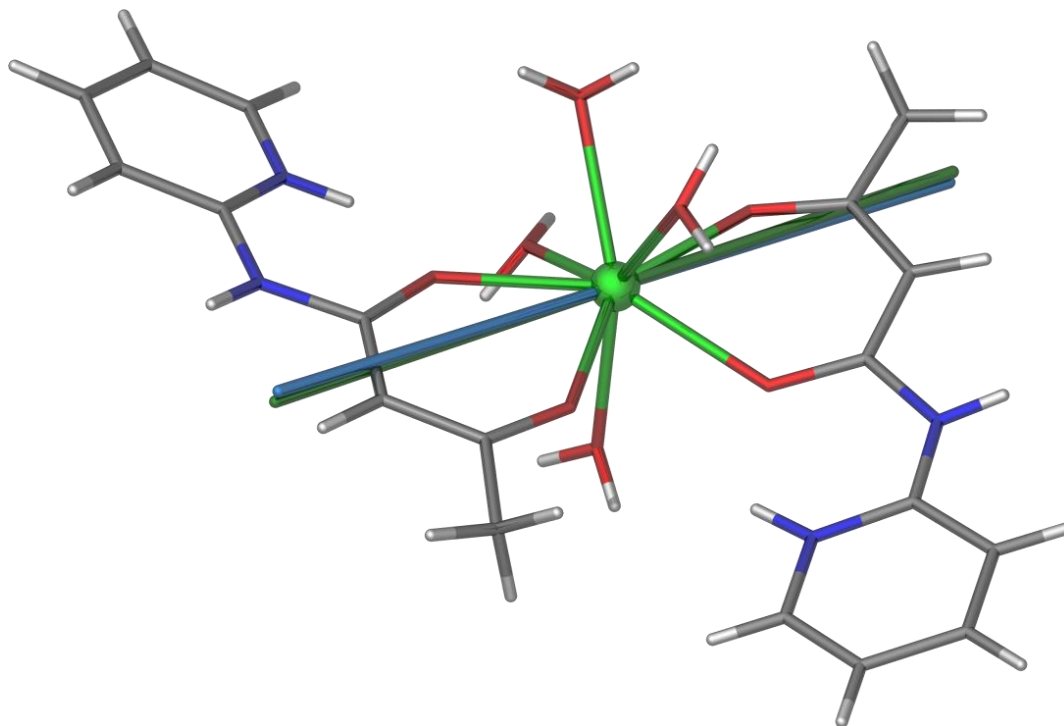


Supplementary Figure S7 – Comparison of the *ab initio* (blue rod) and electrostatic (green rod) anisotropy directions for the ground Kramers doublet in **8**. Dy = green, S = purple, F = yellow, O = red, N = blue, C = grey and H = white.

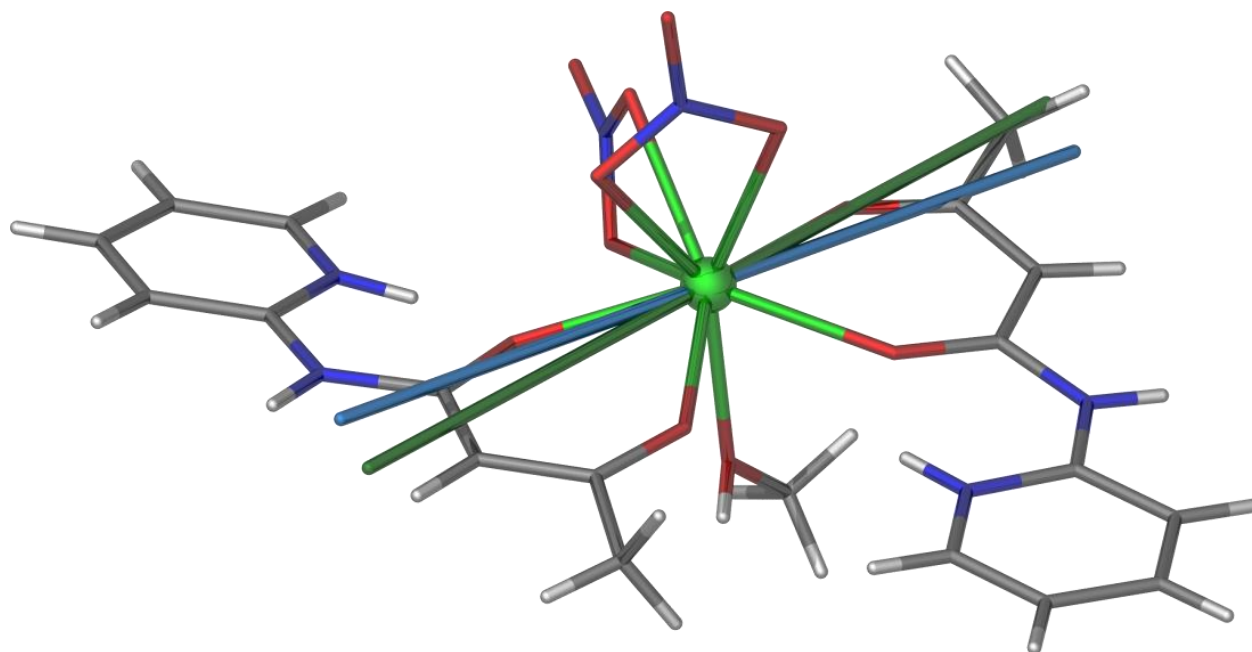


Supplementary Figure S8 – Comparison of the *ab initio* (blue rod) and electrostatic (green rod) anisotropy directions for the ground Kramers doublet in **9**. Dy = green, S = purple, F = yellow, O = red, N = blue, C = grey and H = white.

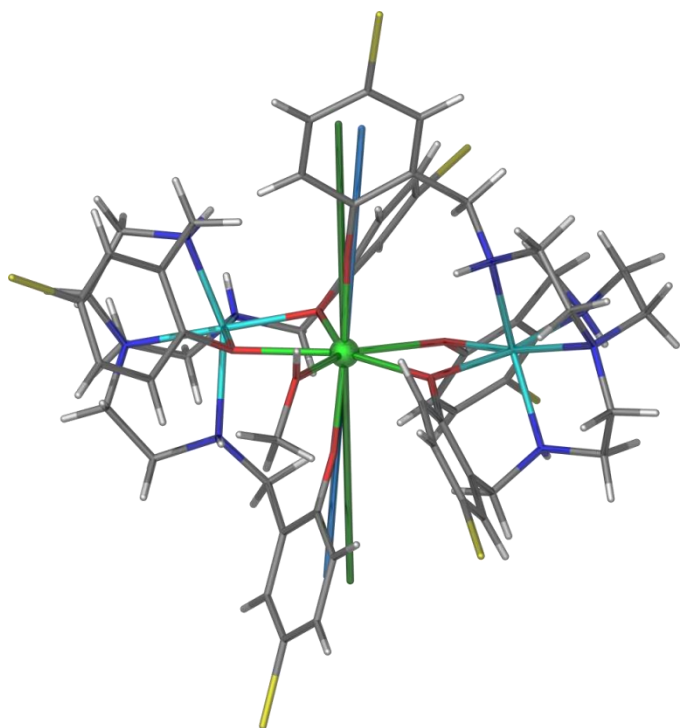




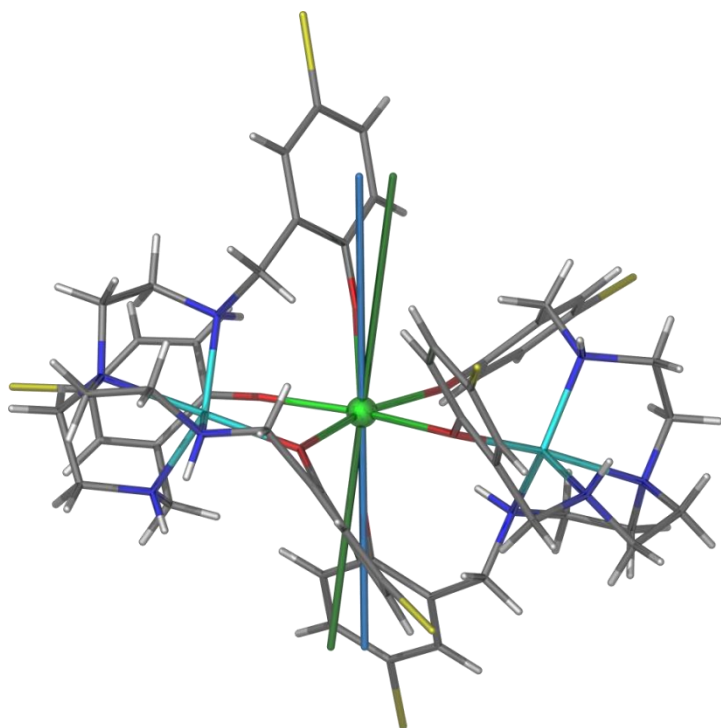
Supplementary Figure S9 – Comparison of the *ab initio* (blue rod) and electrostatic (green rod) anisotropy directions for the ground Kramers doublet in **10**. Dy = green, O = red, N = blue, C = grey and H = white.



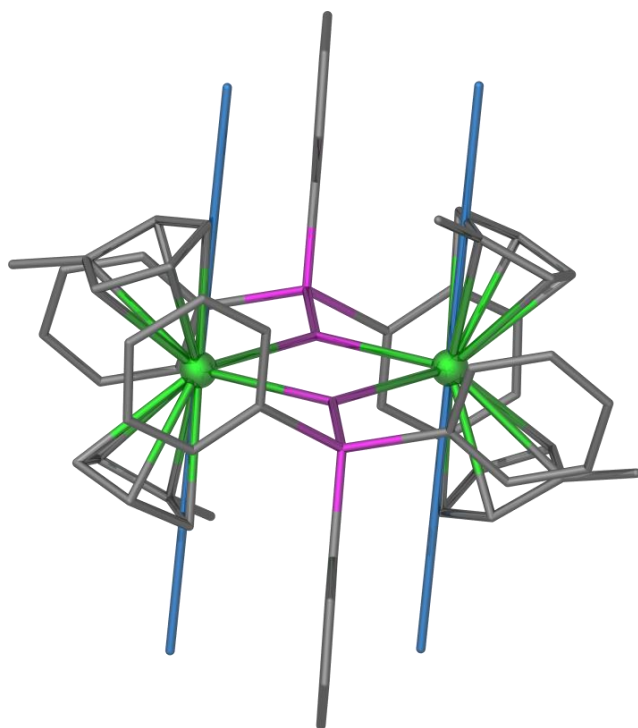
Supplementary Figure S10 – Comparison of the *ab initio* (blue rod) and electrostatic (green rod) anisotropy directions for the ground Kramers doublet in **11**.  $D_y$  = green, O = red, N = blue, C = grey and H = white.



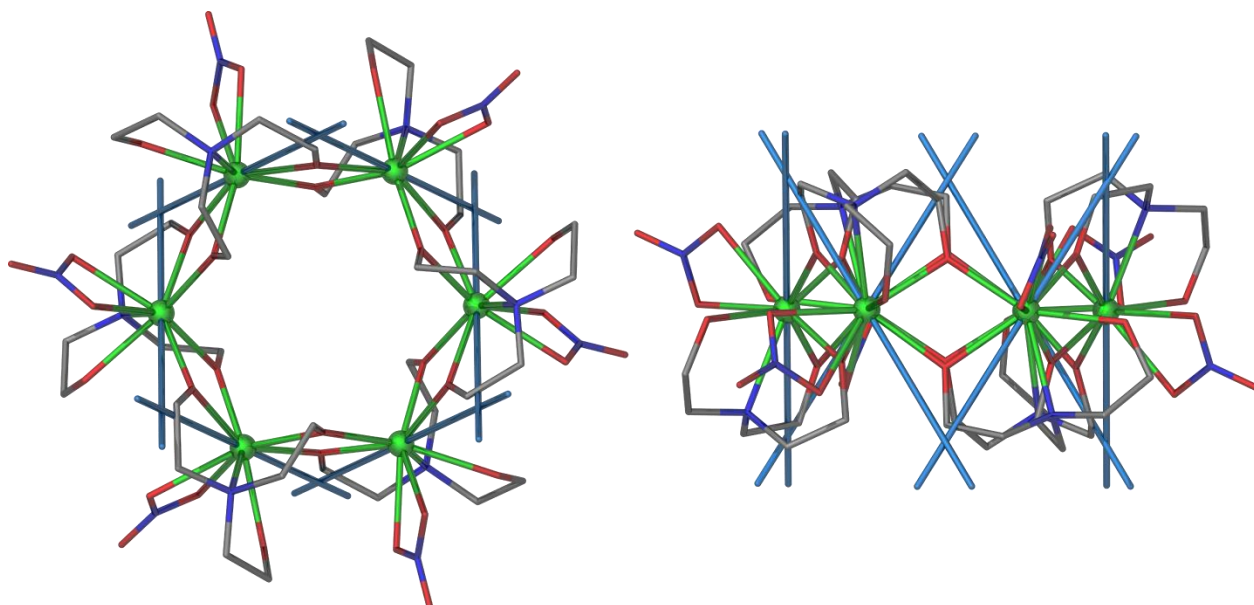
Supplementary Figure S11 – Comparison of the *ab initio* (blue rod) and electrostatic (green rod) anisotropy directions for the ground Kramers doublet in **12**. Dy = green, Br = yellow, Zn = teal, O = red, N = blue, C = grey and H = white.



Supplementary Figure S12 – Comparison of the *ab initio* (blue rod) and electrostatic (green rod) anisotropy directions for the ground Kramers doublet in **13**. Dy = green, Br = yellow, Zn = teal, O = red, N = blue, C = grey and H = white.



Supplementary Figure S13 – The ground state anisotropy directions (blue rods) for the Dy<sup>III</sup> ions in **15**, calculated with the electrostatic model. Dy = green, S = purple and C = grey; H atoms not shown for clarity.



Supplementary Figure S14 – The ground state anisotropy directions (blue rods) for the Dy<sup>III</sup> ions in **16**, calculated with the electrostatic model. Dy = green, O = red, N = blue and C = grey; H atoms not shown for clarity.

Supplementary Table S1 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 1. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy (cm <sup>-1</sup> )	$g_x$	$g_y$	$g_z$	Angle (°)
1	0.0	0.00	0.01	19.62	-
2	167.4	0.17	0.27	15.89	7.1
3	252.7	1.81	2.43	11.75	11.7
4	309.7	1.40	2.00	7.56	14.5
5	338.3	2.65	7.73	11.63	89.5
6	431.3	0.01	0.28	15.29	86.3
7	475.9	0.09	0.22	17.69	70.7
8	549.3	0.02	0.04	19.11	60.2

Supplementary Table S2 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 2. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy (cm <sup>-1</sup> )	$g_x$	$g_y$	$g_z$	Angle (°)
1	0.0	0.00	0.01	19.55	-
2	142.2	0.16	0.24	15.84	16.4
3	211.0	1.20	1.59	12.42	17.8
4	262.3	3.82	5.37	8.44	14.0
5	310.5	2.25	4.03	9.68	73.6
6	350.2	1.12	2.37	16.52	72.3
7	457.2	0.01	0.06	17.61	85.0
8	530.1	0.01	0.03	18.90	57.0

Supplementary Table S3 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 3. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^\circ$ )
1	0.0	0.01	0.02	19.42	-
2	133.3	0.37	0.52	15.90	7.1
3	202.5	2.67	4.75	11.17	25.0
4	240.6	2.07	5.78	7.32	89.4
5	284.0	0.52	3.30	10.05	67.1
6	313.1	1.05	3.05	15.36	76.6
7	444.4	0.00	0.02	19.21	84.2
8	545.1	0.00	0.02	19.71	52.9

Supplementary Table S4 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 4. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^\circ$ )
1	0.0	0.00	0.01	19.57	-
2	159.8	0.17	0.26	15.72	1.8
3	239.0	1.95	2.96	11.54	12.4
4	276.4	1.95	5.75	10.95	72.4
5	321.3	1.11	4.26	9.42	69.4
6	365.1	1.56	3.38	15.85	67.3
7	448.3	0.05	0.29	18.81	89.7
8	519.1	0.04	0.09	19.47	52.0



Supplementary Table S5 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 5. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^\circ$ )
1	0.0	0.01	0.02	19.48	-
2	134.1	0.61	1.60	14.88	6.9
3	163.9	0.65	2.15	16.66	89.3
4	211.7	1.02	4.42	9.70	9.5
5	243.8	3.58	4.60	11.42	51.8
6	273.7	0.63	1.76	16.46	84.0
7	336.8	0.02	0.04	19.67	89.5
8	476.2	0.00	0.01	19.86	49.6

Supplementary Table S6 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 6. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^\circ$ )
1	0.0	0.00	0.01	19.76	-
2	142.4	0.09	0.65	16.50	63.7
3	161.7	1.67	2.00	13.63	22.9
4	201.1	3.28	4.62	12.42	44.7
5	234.2	2.47	3.73	12.04	67.1
6	305.9	0.74	1.07	16.12	79.9
7	415.0	0.02	0.21	17.53	80.5
8	470.6	0.05	0.20	18.57	51.5

Supplementary Table S7 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 7. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^{\circ}$ )
1	0.0	0.01	0.01	19.66	-
2	134.2	0.72	0.91	15.79	11.2
3	181.3	3.34	4.90	10.68	25.9
4	216.5	1.38	5.99	6.78	38.7
5	243.8	1.81	2.78	12.29	56.3
6	298.8	0.77	1.23	16.03	79.1
7	411.6	0.05	0.14	18.56	85.7
8	516.5	0.02	0.04	19.49	53.0

Supplementary Table S8 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 8. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^{\circ}$ )
1	0.0	0.00	0.01	19.81	-
2	94.3	0.12	0.41	18.84	78.6
3	159.6	2.12	2.41	13.99	18.7
4	185.9	3.65	5.75	11.39	36.1
5	215.1	2.24	2.80	13.55	63.1
6	281.8	0.51	0.78	16.44	84.8
7	409.1	0.07	0.08	19.17	49.0
8	472.0	0.02	0.15	19.49	89.1

Supplementary Table S9 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 9. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^{\circ}$ )
1	0.0	0.01	0.01	19.65	-
2	118.5	0.58	0.96	15.96	12.8
3	164.9	3.85	5.73	10.06	51.8
4	196.4	3.70	5.05	7.46	48.8
5	228.6	4.02	4.93	10.95	53.8
6	273.2	1.31	2.27	16.04	85.9
7	344.8	0.10	0.23	19.11	89.1
8	457.1	0.01	0.02	19.70	51.0

Supplementary Table S10 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 10. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^{\circ}$ )
1	0.0	0.00	0.00	19.78	-
2	250.5	0.05	0.07	16.40	2.0
3	408.4	1.18	1.90	12.50	1.5
4	508.3	5.35	5.95	6.92	3.5
5	600.3	2.07	2.19	10.39	89.4
6	689.8	0.36	0.56	14.89	88.0
7	774.5	0.01	0.03	19.30	67.9
8	817.8	0.01	0.02	19.48	72.8

Supplementary Table S11 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 11. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^{\circ}$ )
1	0.0	0.01	0.02	19.68	-
2	113.6	0.23	0.44	16.56	7.9
3	194.9	3.43	4.14	11.47	25.5
4	249.7	3.57	4.19	10.01	79.9
5	307.3	0.59	0.89	15.47	80.2
6	338.5	0.22	1.77	15.54	83.8
7	394.3	0.77	1.51	17.04	83.6
8	432.4	0.08	1.68	17.65	81.0

Supplementary Table S12 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 12. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^{\circ}$ )
1	0.0	0.00	0.00	19.98	-
2	270.0	0.46	0.55	18.61	84.8
3	294.6	0.14	0.25	16.58	4.6
4	346.8	1.34	1.84	14.28	84.0
5	410.8	4.57	5.92	8.84	59.0
6	447.3	1.53	2.01	12.25	26.7
7	484.8	0.41	0.50	16.21	49.2
8	526.3	0.02	0.10	17.57	50.3

Supplementary Table S13 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 13. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^{\circ}$ )
1	0.0	0.01	0.02	19.90	-
2	287.8	2.38	6.82	11.77	56.2
3	324.0	3.02	5.50	8.40	42.5
4	406.6	0.37	2.38	14.22	76.5
5	481.0	2.03	7.31	9.69	46.8
6	559.0	2.19	2.44	15.59	57.6
7	697.9	0.43	0.74	16.48	82.7
8	816.8	0.09	0.20	19.09	82.5

Supplementary Table S14 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 14,  $H_2O$  rotation A. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^{\circ}$ )
1	0.0	0.07	0.14	19.67	-
2	94.3	1.10	1.43	17.67	77.3
3	167.2	3.03	3.94	11.18	20.7
4	241.4	0.99	6.74	8.78	85.3
5	311.4	2.85	4.35	10.50	77.1
6	374.0	0.55	1.79	13.55	85.6
7	449.5	0.68	0.82	16.44	85.2
8	621.6	0.01	0.03	19.64	86.9

Supplementary Table S15 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 14,  $H_2O$  rotation B. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^\circ$ )
1	0.0	0.14	0.29	19.51	-
2	72.5	0.96	1.11	17.97	78.1
3	156.7	4.05	4.30	11.18	23.9
4	228.4	0.01	7.23	7.90	84.9
5	299.7	2.28	5.38	10.50	73.8
6	361.5	0.95	2.29	13.32	90.0
7	441.9	0.77	1.01	16.50	82.3
8	611.3	0.02	0.06	19.63	87.5

Supplementary Table S16 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of  $Dy^{III}$  for compound 14,  $H_2O$  rotation C. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy ( $cm^{-1}$ )	$g_x$	$g_y$	$g_z$	Angle ( $^\circ$ )
1	0.0	0.30	0.83	18.93	-
2	45.8	0.23	1.14	17.61	80.8
3	144.6	4.27	6.46	9.82	40.2
4	209.8	1.92	5.75	7.81	70.8
5	284.1	3.18	4.93	10.47	74.0
6	346.5	0.34	1.59	13.55	85.5
7	424.3	0.78	0.85	16.55	83.1
8	595.7	0.01	0.04	19.65	87.2

Supplementary Table S17 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of Dy<sup>III</sup> for compound 14, H<sub>2</sub>O rotation D. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy (cm <sup>-1</sup> )	$g_x$	$g_y$	$g_z$	Angle (°)
1	0.0	0.05	0.08	19.75	-
2	117.8	1.30	2.39	16.58	67.3
3	178.9	1.26	3.79	10.96	28.4
4	265.0	2.37	6.69	8.99	85.2
5	329.8	1.35	4.65	10.55	74.8
6	391.0	1.31	2.71	13.26	88.0
7	466.7	0.66	0.87	16.47	84.3
8	637.4	0.03	0.05	19.63	87.1

Supplementary Table S18 – Energies and  $g$ -tensors for the Kramers doublets of the ground multiplet of Dy<sup>III</sup> for compound 14, average of the four H<sub>2</sub>O rotations A – D. The angles between the principal axis of each doublet and the ground state are also given.

Doublet	Energy (cm <sup>-1</sup> )	$g_x$	$g_y$	$g_z$	Angle (°)
1	0.0	0.1(1)	0.3(3)	19.5(4)	-
2	83(31)	0.9(5)	1.5(6)	17.5(6)	74.9
3	162(15)	3(1)	5(1)	10.8(7)	27.3
4	236(23)	1(1)	6.6(6)	8.4(6)	79.8
5	306(19)	2.4(8)	4.8(4)	10.50(4)	74.8
6	368(19)	0.8(4)	2.1(5)	13.4(2)	87.5
7	446(18)	0.72(6)	0.89(8)	16.49(4)	84.0
8	616(18)	0.02(1)	0.05(1)	19.637(7)	86.9

Supplementary Table S19 – Angles between anisotropy axes and terminal <sup>1</sup>PrO<sup>-</sup>-Dy bond for dysprosium(III) sites in complex 17.

Method	Dy1 (°)	Dy2 (°)	Dy3 (°)	Dy4 (°)	Dy5 (°)
<i>Ab initio</i>	5.8	4.1	2.7	4.7	5.2
Electrostatic	4.6	1.9	5.0	4.0	4.0