Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary material

Eight coordinated mononuclear dysprosium complexes of heptadentate aminophenol ligands: the influence of the phenol substituents and the ancillary donors on the magnetic relaxation

Matilde Fondo,[a,*] Julio Corredoira-Vázquez,[a] Ana M. García-Deibe,[a] Jesús Sanmartín-Matalobos,[a] Daniel Reta,[b] and Enrique Colacio[c]

[a] Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, Campus Vida, 15782 Santiago de Compostela, Spain.
[b] Departament de Química Inorgànica i Orgànica, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain
[c] Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, Avda Fuentenueva s/n, 18071 Granada, Spain

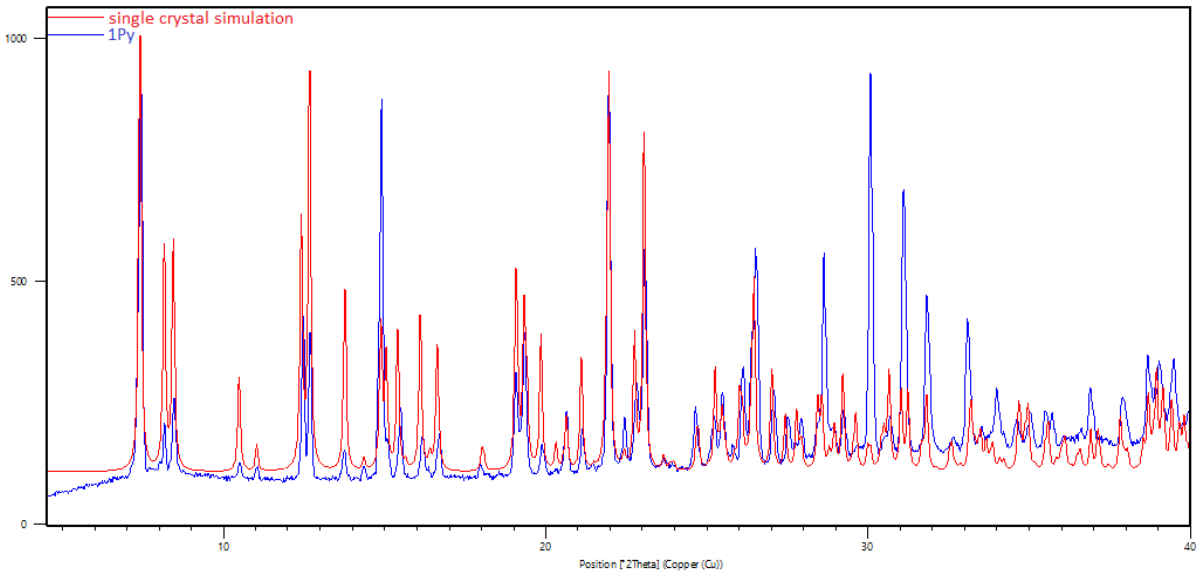


Fig. S1 Comparison of X-powder diffractogram for the crystalline sample of **1Py** (blue line) with the simulated one from single X-ray data (red line).

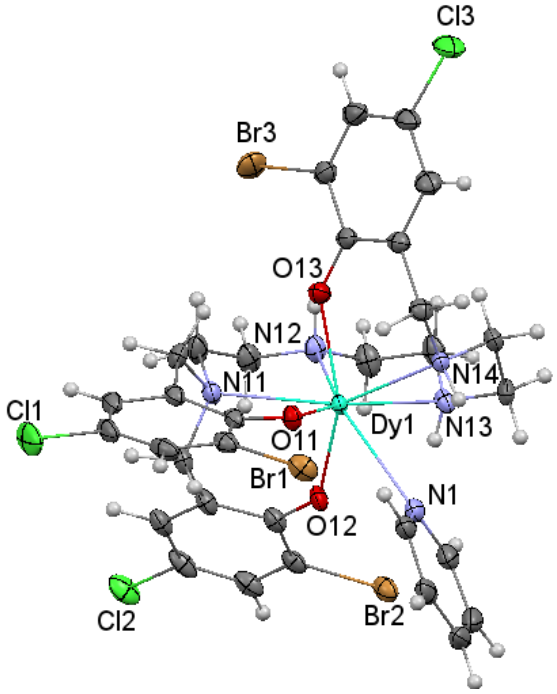


Fig. S2 Ellipsoid (50% probability) diagram for **1Py**.

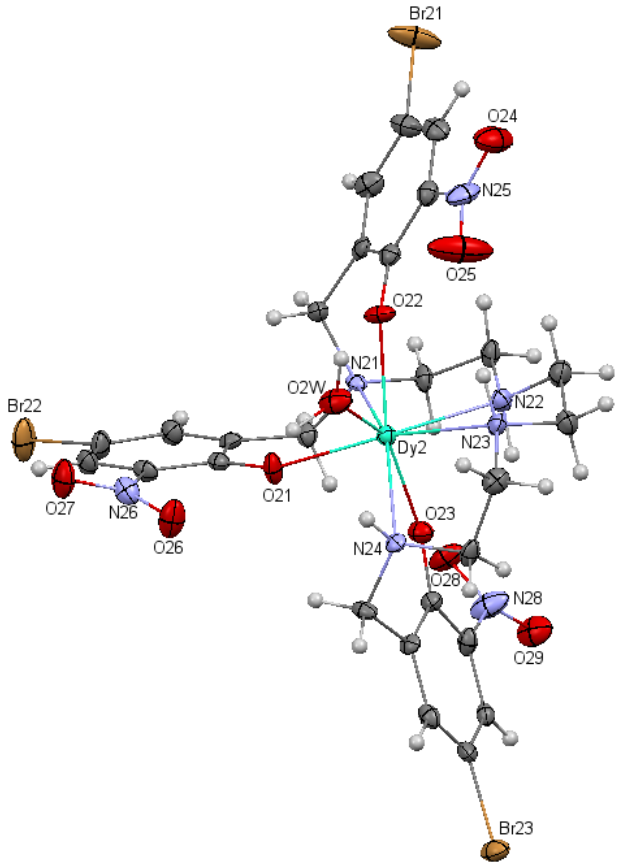


Fig. S3 Ellipsoid (50% probability) diagram for **2W**.2**.**

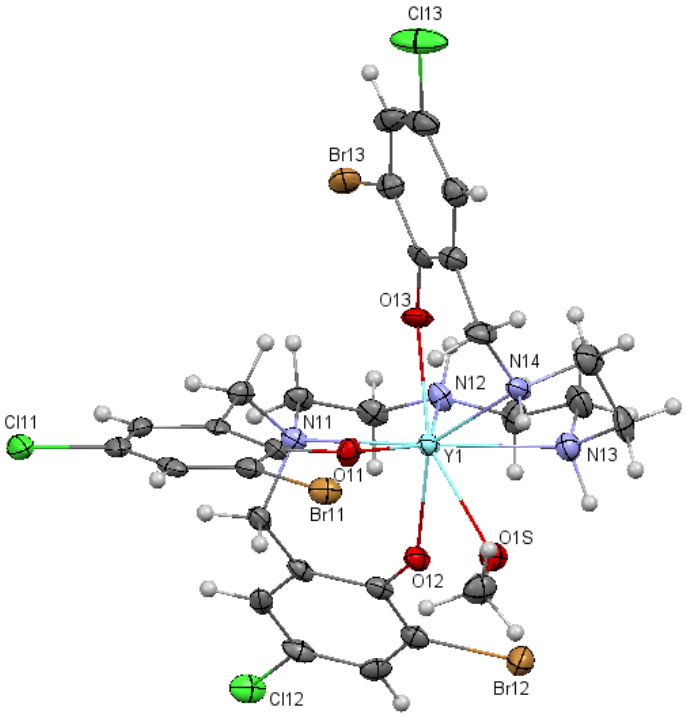


Fig. S4 Ellipsoid (50% probability) diagram for **3M**.1**.**

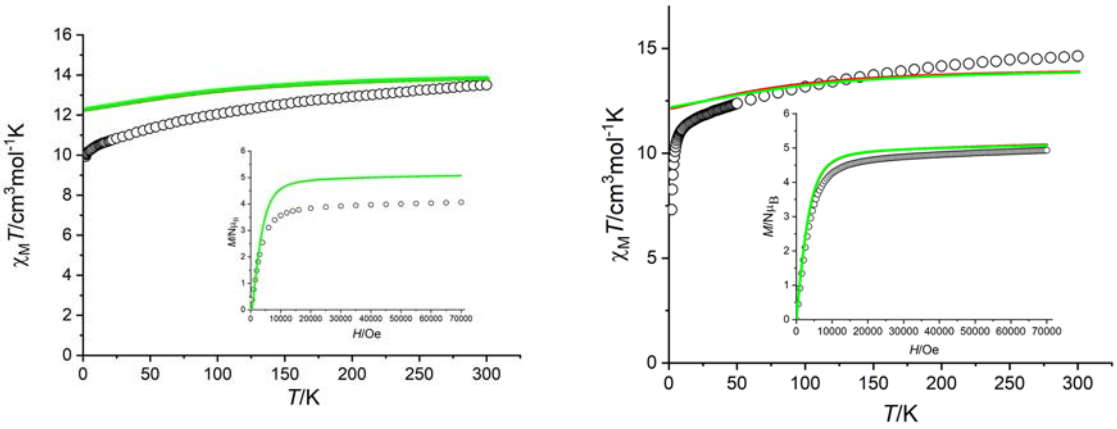


Fig. S5 $\chi_M T$ *vs* T for **1W**·0.25MeOH (left) and **2W** (right). Insets: $M/N\mu_B$ *vs* H at 2 K. The solid red and green lines (that nearly superimpose) represent the theoretical data obtained from *ab initio* calculations (with CASSF-SO methodology) for **1W**.1 and **1W**.2 or **2W**.1 and **2W**.2, respectively.

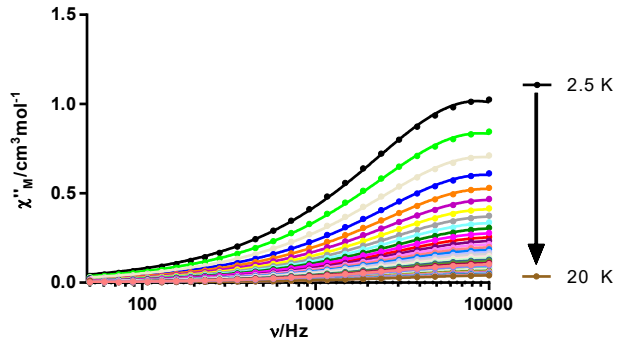


Fig. S6 Frequency dependence of χ''_M at different temperatures in H_{dc} = 0 for **2W**.

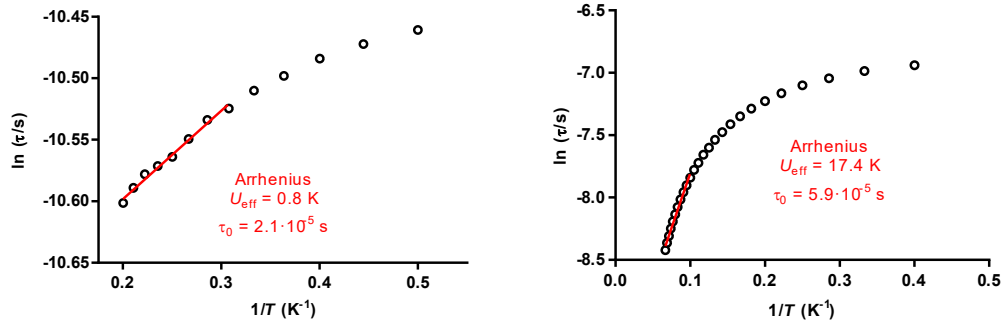


Fig. S7 Arrhenius plot in H_{dc} = 0 for**1W**·0.25MeOH(left) and**1Py** (right). The red solid lines account for the best fit considering only Orbach relaxation (red) in the linear region.

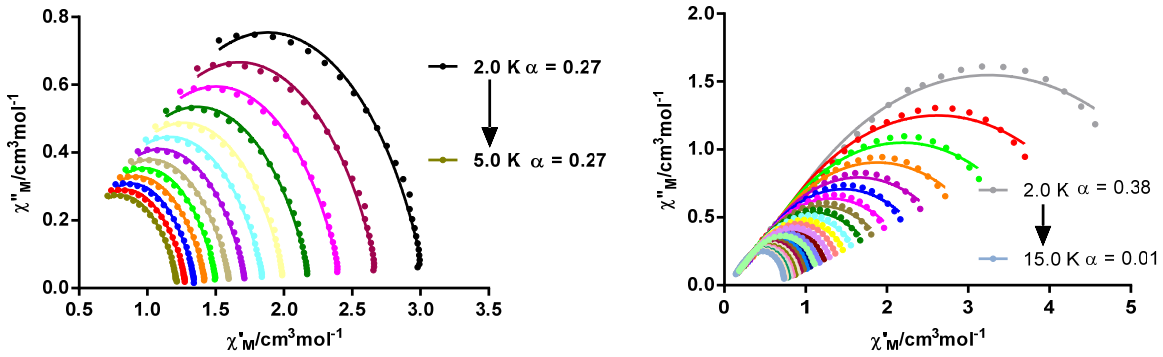


Fig. S8 Cole–Cole plot for **1W**·0.25MeOH (left) and **1Py** (right) in zero field.

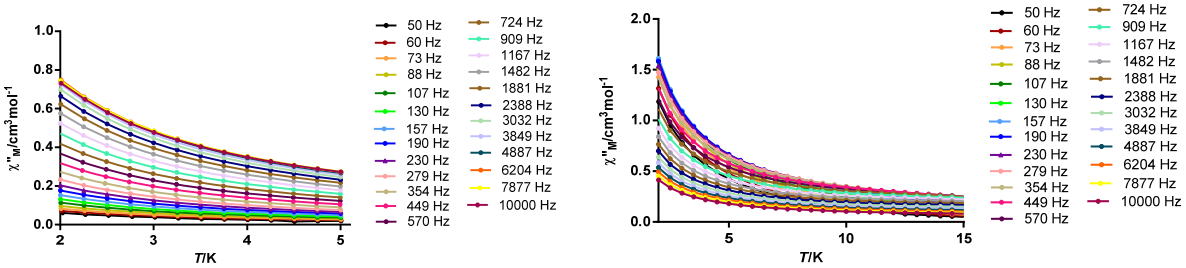


Fig. S9 Temperature dependence of χ''_M at different frequencies in H_{dc} = 0 Oe for **1W**·0.25MeOH (left) and **1Py** (right).

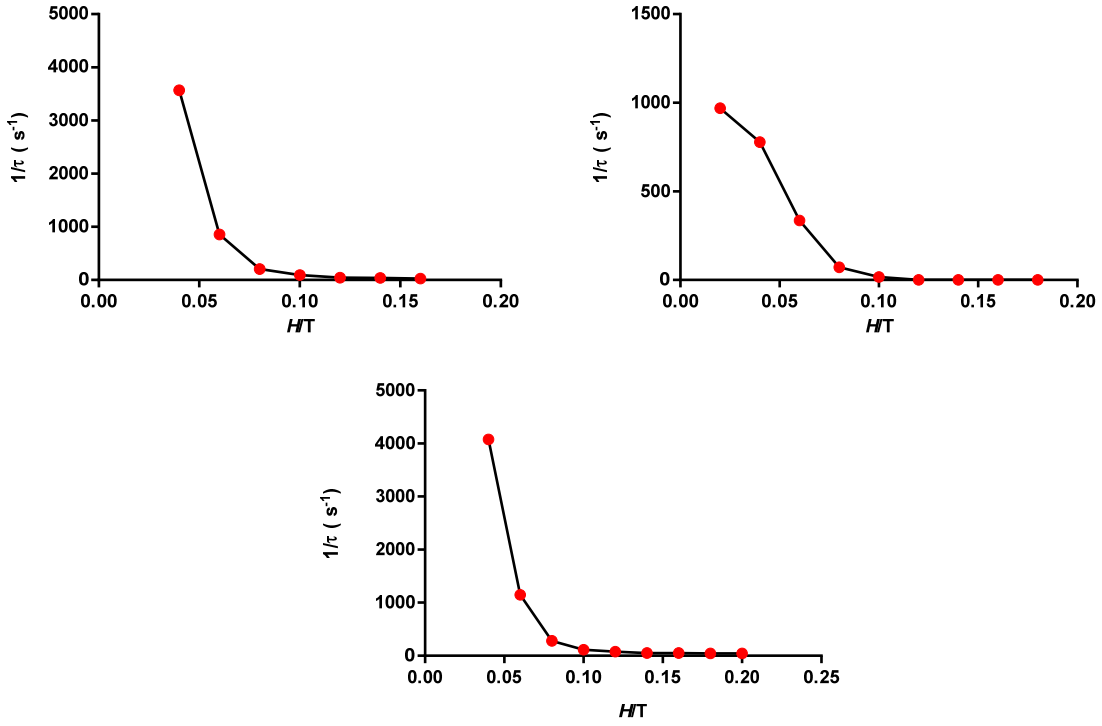


Fig. S10 Field dependence of the magnetic relaxation time at 2.5 K for **1W**·0.25MeOH (left up), **1Py** (right up) and **2W** (middle botton).

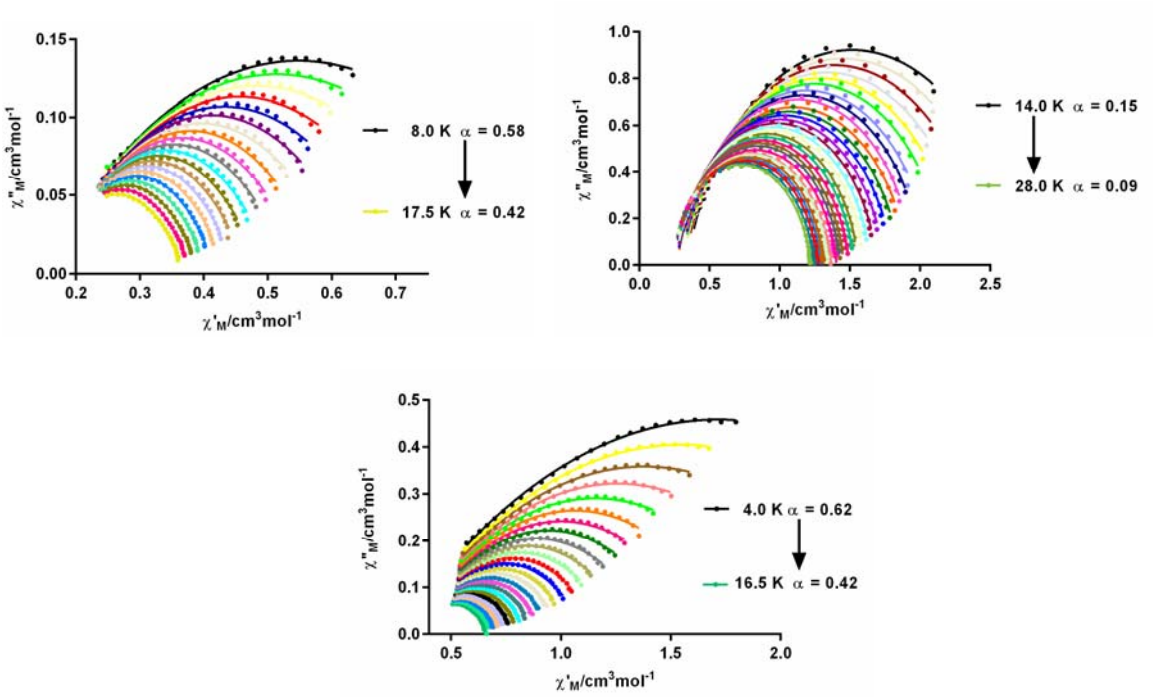


Fig. S11 Cole–Cole plot at 1000 Oe dc field for **1W**·0.25MeOH (left up), **1Py** (right up) and **2W** (middle bottom).

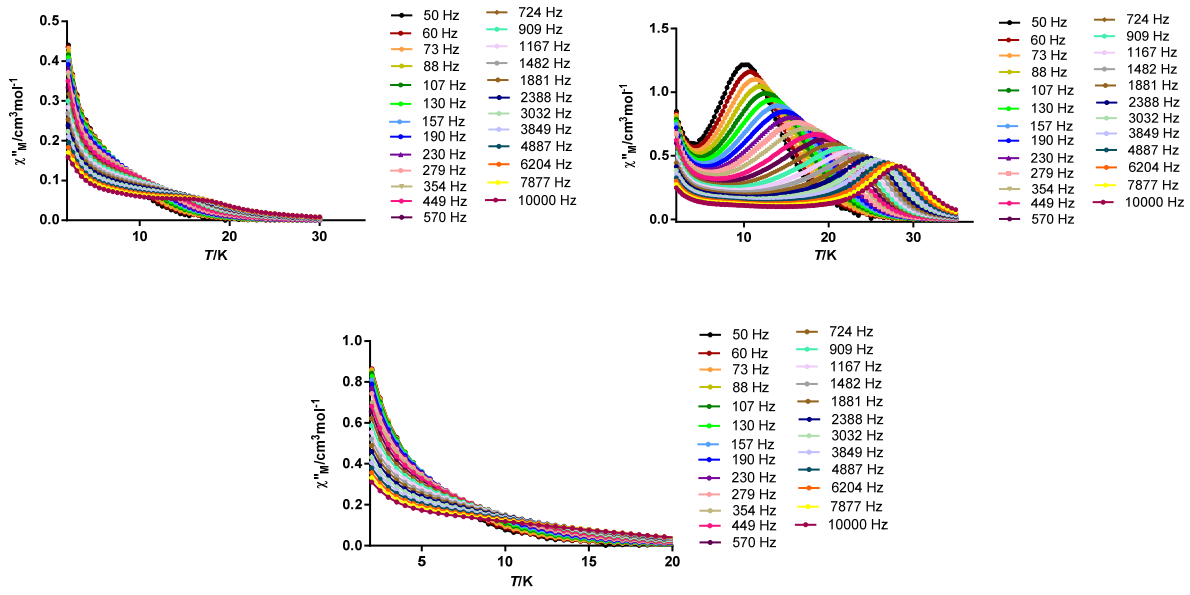


Fig. S12 Temperature dependence of χ''_M at different frequencies in H_{dc} = 1000 Oe for **1W**·0.25MeOH (left up), **1Py**·(right up) and **2W** (middle bottom).

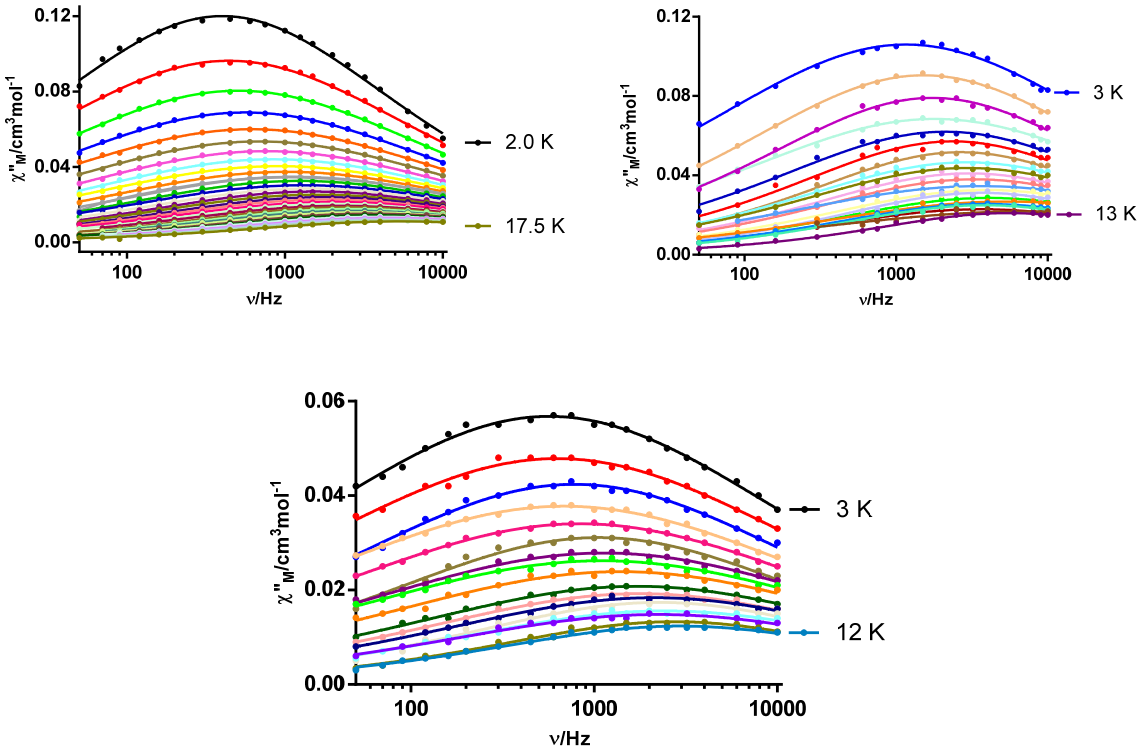


Fig.S13 Frequency dependence of χ''_M at different temperatures in zero dc field for: **1W@Y** (left up), **1Py@Y** (right up) and **2W@Y** (middle bottom).

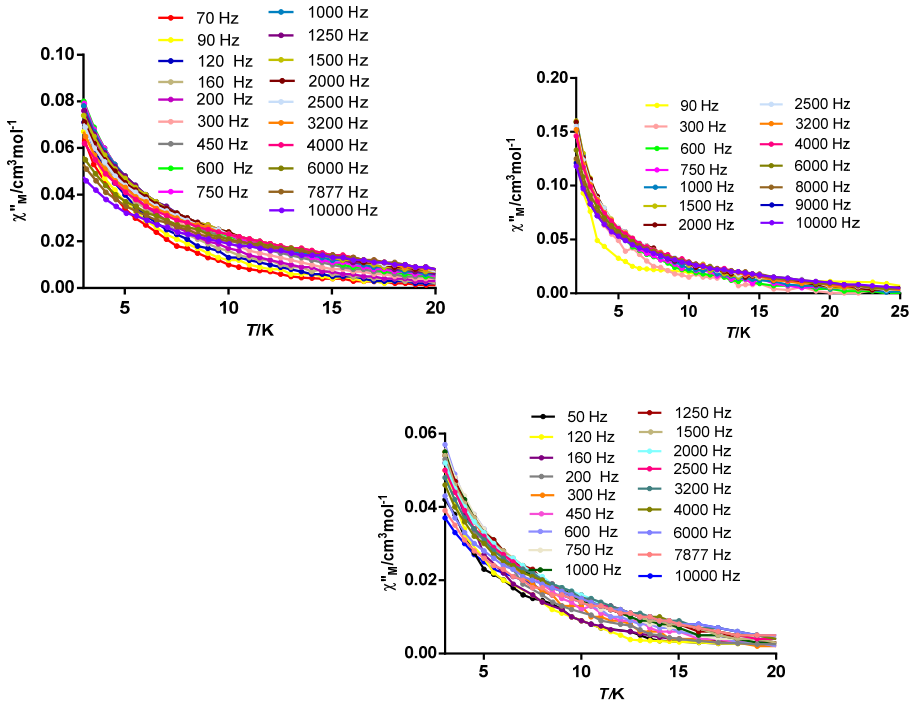


Fig. S14 Temperature dependence of χ''_M at different frequencies in H_{dc} = 0 Oe for **1W@Y** (left up), **1Py@Y** (right up) and **2W@Y** (middle bottom).

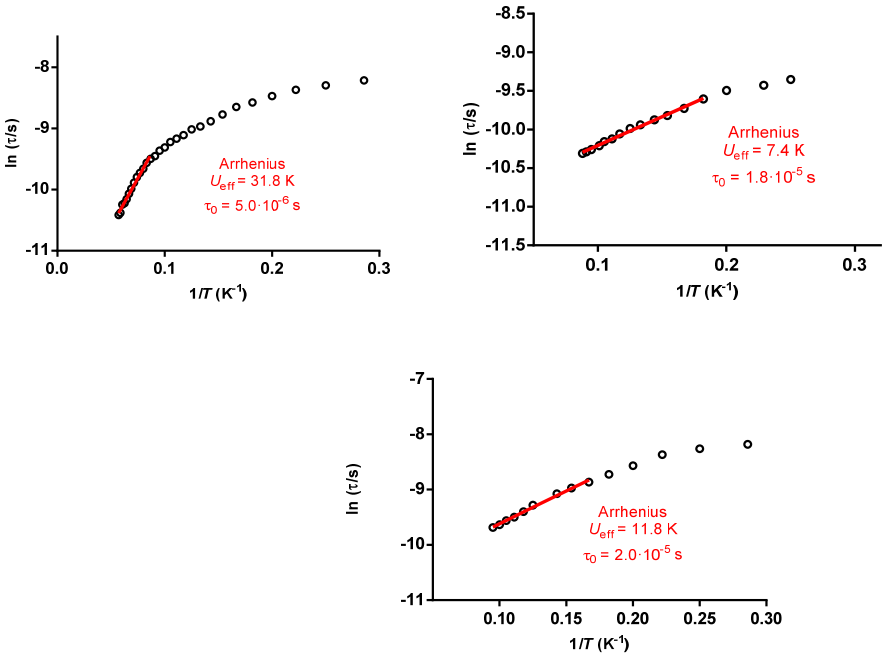
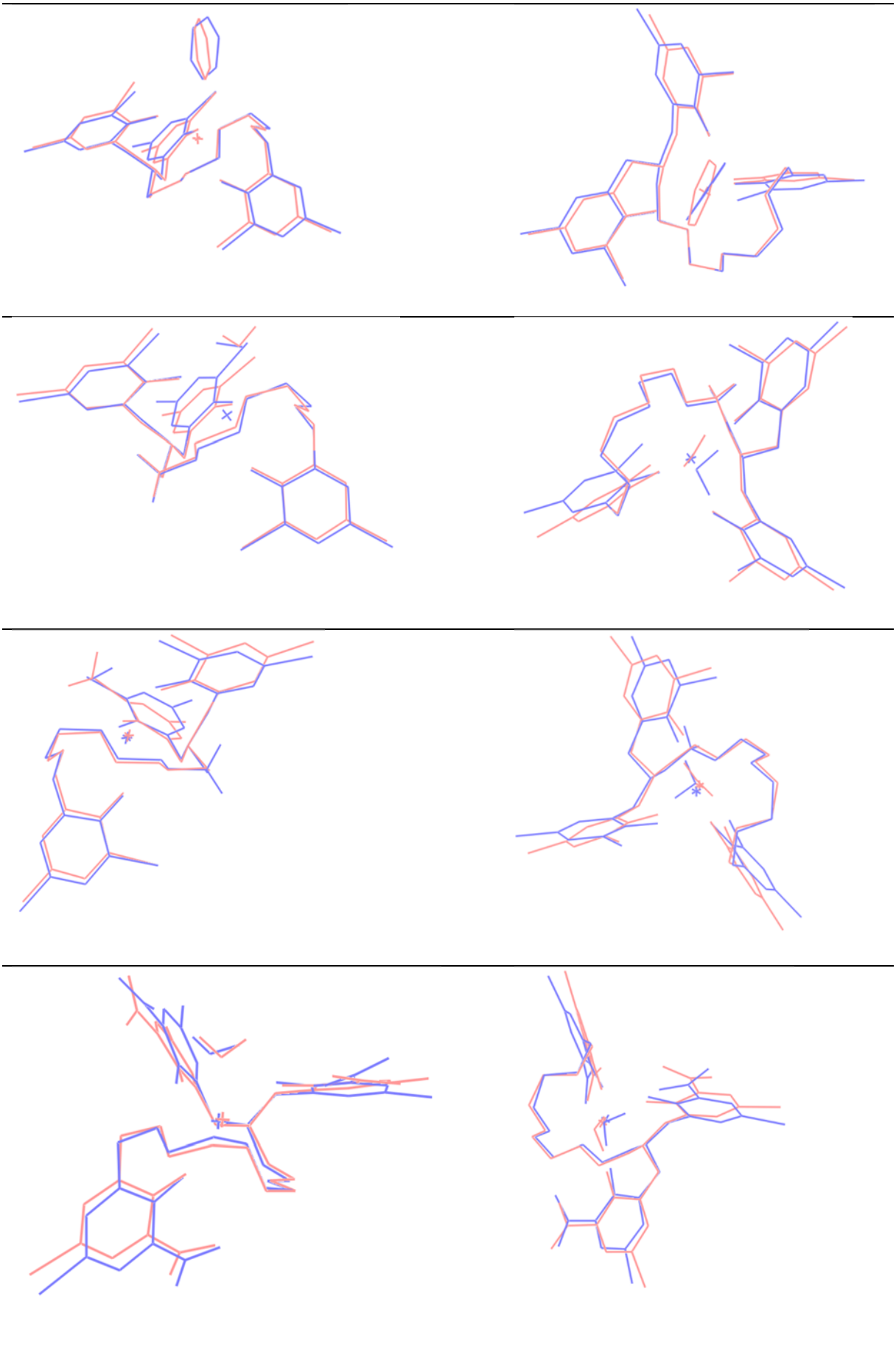


Fig. S15 T Arrhenius plot in H_{dc} = 0 Oe for **1W@Y** (left up), **1Py@Y** (right up) and **2W@Y** (middle bottom).



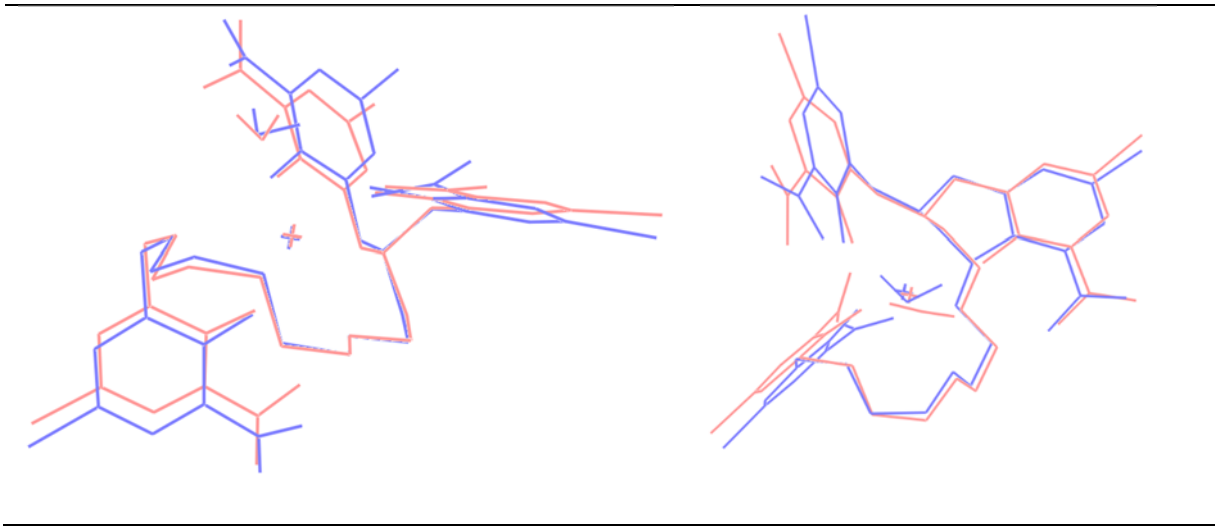


Fig. S16. Comparison of crystal (red) and optimized (blue) structures viewed from the side (left) and top (right). **1Py**, **1W.1**, **1W.2**, **2W.1** and **2W.2** are shown in top, middle and bottom panels, respectively.

Table S1. Crystal data and structure refinement for **1W**·0.25MeOH, **1Py**, **2W**·$2CH_3C_6H_5$ and **3M**·$CH_3C_6H_5$

	1W·0.25MeOH	**1Py**	**2W**·$2CH_3C_6H_5$	**3M**·$CH_3C_6H_5$
Empirical formula	$C_{27.5}H_{30}Br_3Cl_3DyN_4O_{4.25}$	$C_{32}H_{32}Br_3Cl_3DyN_5O_3$	$C_{41}H_{45}Br_3DyN_7O_{10}$	$C_{35}H_{39}Br_3Cl_3N_4O_4Y$
Molecular weight	990.13	1043.20	1198.07	1014.69
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	$Pna2_1$	Pbca	$P2_12_12_1$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal size (mm^3)	0.178 x 0.087 x 0.022	0.190 x 0.150 x 0.090	0.080x 0.040 x 0.020	0.100x 0.050 x 0.030
Color, shape	Needle, colorless	Prism, yellow	Prism, yellow	Needle, yellow
T (K)	100(2)	100(2)	100(2)	100(2)
a (Å)	21.7630(9)	11.824(2)	27.713(4)	12.5375(4)
b (Å)	13.3167(5)	21.450(4)	19.006(3)	23.5583(8)
c (Å)	23.8177(10)	13.054(3)	33.722(4)	26.0114(9)
α (º)	90	90	90	90
β (º)	93.015(2)	90	90	90
γ (º)	90	90	90	90
Volume ($Å^3$)	6893.1(5)	3310.6(12)	17762(4)	7682.8(4)
Z	4	4	16	8
Absorpt. coef. (mm^{-1})	5.918	6.164	4.447	4.891
Reflections collected	30844	65964	278418	108840
Independent reflections	30844	10782 [R_{int} = 0.0380]	18171 [R_{int} = 0.1632]	19076 [R_{int} = 0.1003]
Data / restraints / param.	30844 / 0 / 786	10782 / 1 / 424	18171 / 701 / 1203	19076 / 0 / 909
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0855 wR_2 = 0.1775	R_1 = 0.0246 wR_2 = 0.0482	R_1 = 0.0454 wR_2 = 0.0759	R_1 = 0.0455 wR_2 = 0.0835
R indices (all data)	R_1 = 0.1550 wR_2 = 0.2129	R_1 = 0.0307 wR_2 = 0.0504	R_1 = 0.0966 wR_2 = 0.0931	R_1 = 0.0743 wR_2 = 0.0934

Table S2. Main distances (Å) and angles (º) for **1W**·0.25MeOH, **1Py** and **2W**·$2CH_3C_6H_5$

	1W		**1Py**	**2W**	
	1W.1 (X = 1)	**1W**.2 (X = 2)	(X = 1)	**2W**.1 (X = 1)	**2W**.2 (X = 2)
DyX-OX1	2.224(10)	2.219(12)	2.223(3)	2.201(4)	2.196(4)
DyX-OX2	2.217(11)	2.218(11)	2.166(3)	2.245(4)	2.247(4)
DyX-OX3	2.248(10)	2.237(10)	2.194(3)	2.252(4)	2.263(4)
DyX-NX1	2.559(11)	2.599(12)	2.512(4)	2.603(5)	2.601(5)
DyX-NX2	2.508(11)	2.544(13)	2.563(3)	2.537(5)	2.538(5)
DyX-NX3	2.534(11)	2.582(13)	2.531(4)	2.558(5)	2.573(5)
DyX-NX4	2.534(11)	2.524(13)	2.445(3)	2.511(5)	2.517(5)
Dy1-N1 DyX-OXw	 2.592(12)	 2.54(2)	2.651(4)	 2.460(4)	 2.456(4)
OX1-DyX-NX3	145.8(4)	149.0(4	150.80(11)	149.91(16)	150.27(16)
OX2-DyX-OX3	149.5(4)	150.8(4)	148.65(11)	148.96(15)	149.11(15)
NX4-DyX-NX1	147.1(4)	151.8(4)	147.99(11)	148.97(17)	149.87(16)
NX2-DyX-NX3/	69.3(4)	67.3(4)	66.27(12)	67.79(16)	67.76(16)
OX1-DyX-OXw	68.2(4)	85.2(6)		82.11(16)	81.82(17)
OX2-DyX-OXw	71.5(5)	63.7(6)		67.40(15)	67.66(16)

Table S3. SHAPE v2.1. Continuous Shape Measures calculation (c) 2013 Electronic Structure Group, Universitat de Barcelona.

Geometries Coordination number 8

ETBPY-8	13 D3h	Elongated trigonal bipyramid
TT-8	12 Td	Triakis tetrahedron
JSD-8	11 D2d	Snub diphenoid J84
BTPR-8	10 C2v	Biaugmented trigonal prism
JBTPR-8	9 C2v	Biaugmented trigonal prism J50
JETBPY-8	8 D3h	Johnson elongated triangular bipyramid J14
JGBF-8	7 D2d	Johnson gyrobifastigium J26
TDD-8	6 D2d	Triangular dodecahedron
SAPR-8	5 D4d	Square antiprism
CU-8	4 Oh	Cube
HBPY-8	3 D6h	Hexagonal bipyramid
HPY-8	2 C7v	Heptagonal pyramid
OP-8	1 D8h	Octagon

[Dy(3Br,5Cl-$H_3L^{1,1,4}$)(H_2O)]·0.25MeOH (**1W**·0.25MeOH)

1W.1

Structure [ML8] ETBPY-8 TT-8 JSD-8 BTPR-8 **JBTPR-8** JETBPY-8
24.915, 10.098, 2.568, 2.094, **1.731**, 26.883,
JGBF-8 **TDD-8** **SAPR-8** CU-8 HBPY-8 HPY-8 OP-8
11.869, **1.906**, **1.677**, 9.645, 13.967, 22.765, 32.306

1W.2

Structure [ML8] ETBPY-8 TT-8 JSD-8 BTPR-8 **JBTPR-8** JETBPY-8
23.956, 11.400, 2.715, 2.112, **1.855**, 26.310,
JGBF-8 **TDD-8** **SAPR-8** CU-8 HBPY-8 HPY-8 OP-8
11.691, **1.961**, **1.914**, 10.729, 14.726, 22.521, 31.063

[Dy(3Br,5Cl-$H_3L^{1,1,4}$)(Py)] (**1Py**)

Structure [ML8]	ETBPY-8	TT-8	JSD-8	BTPR-8	**JBTPR-8**	JETBPY-8
	23.785,	10.518,	2.459,	2.290,	**1.723**,	26.850,
JGBF-8	**TDD-8**	**SAPR-8**	CU-8	HBPY-8	HPY-8	OP-8
12.033,	**2.156**,	**1.652**,	9.954,	14.853,	23.528,	29.721

[Dy(3NO_2,5Br-$H_3L^{1,1,4}$)(H_2O)]·2$CH_3C_6H_5$ (**2W**·2$CH_3C_6H_5$)

2W.1

Structure [ML8]	ETBPY-8	TT-8	JSD-8	BTPR-8	**JBTPR-8**	JETBPY-8
	24.200,	10.972,	2.495,	2.158,	**1.941**,	26.212,
JGBF-8	**TDD-8**	**SAPR-8**	CU-8	HBPY-8	HPY-8	OP-8
11.959,	**1.661**,	**1.738**,	10.292,	14.661,	23.358,	31.544

2W.2

Structure [ML8]	ETBPY-8	TT-8	JSD-8	BTPR-8	**JBTPR-8**	JETBPY-8
	24.214,	10.561,	2.677,	2.053,	**1.870**,	26.117,
JGBF-8	**TDD-8**	**SAPR-8**	CU-8	HBPY-8	HPY-8	OP-8
12.234,	**1.826**,	**1.620**,	9.901,	14.590,	23.301,	31.318

[Y(3Br,5Cl-$H_3L^{1,1,4}$)(CH_3OH)]·2$CH_3C_6H_5$ (**3M**·$CH_3C_6H_5$)

3M.1

Structure [ML8]	ETBPY-8	TT-8	JSD-8	BTPR-8	JBTPR-8	JETBPY-8
	23.971,	12.104,	2.182,	2.241,	2.223,	26.466,
JGBF-8	**TDD-8**	**SAPR-8**	CU-8	HBPY-8	HPY-8	OP-8
11.320,	**1.495**,	**2.035**,	11.378,	14.871,	23.005,	31.795

3M.2

Structure [ML8]	ETBPY-8	TT-8	JSD-8	BTPR-8	**JBTPR-8**	JETBPY-8
	24.984,	9.980,	2.914,	1.836,	**1.564**,	27.483,
JGBF-8	TDD-8	**SAPR-8**	CU-8	HBPY-8	HPY-8	OP-8
12.522,	2.216,	**1.600**,	9.418,	14.089,	22.591,	31.749

Table S4. Main distances (Å) and angles (º) for **3M**·2$CH_3C_6H_5$.

3M.1		**3M.**2	
Y1-O11	2.165(5)	Y2-O21	2.201(5)
Y1-O12	2.245(5)	Y2-O22	2.229(5)
Y1-O13	2.205(5)	Y2-O23	2.233(5)
Y1-O1S	2.501(6)	Y2-O2S	2.529(5)
Y1-N11	2.597(6)	Y2-N21	2.558(5)
Y1-N12	2.522(6)	Y2-N22	2.508(5)
Y1-N13	2.544(6)	Y2-N23	2.535(6)
Y1-N14	2.544(6)	Y2-N24	2.550(5)
O13-Y1-O12	149.15(18)	O22-Y2-O23	149.24(16)
O12-Y1-O1S	64.70(19)	O2S-Y2-N24	68.73(17)

Table S5. Generalised Debye model fitting parameters for **1W**·0.25MeOH-**2W** and **1W@Y-2W@Y**

Compounds	*T*/K	χ_S /(cm^{3}mol^{-1})	χ_T/(cm^{3}mol^{-1})	τ/(10^{-4}s)	α
1W·0.25MeOH (H_{dc} = 0 Oe)	2.00	0.72	3.04	0.286	0.27
	2.25	0.64	2.70	0.283	0.27
	2.50	0.58	2.53	0.280	0.27
	2.75	0.53	2.20	0.276	0.27
	3.00	0.52	2.01	0.273	0.26
	3.25	0.47	1.86	0.269	0.27
	3.50	0.46	1.73	0.266	0.27
	3.75	0.43	1.23	0.262	0.27
	4.0	0.44	1.51	0.258	0.27
	4.25	0.41	1.43	0.256	0.27
	4.50	0.40	1.36	0.255	0.27
	4.75	0.39	1.29	0.252	0.27
	5.00	0.38	1.23	0.249	0.27
1Py (H_{dc} = 0 Oe)	2	0.32	6.19	11.56	0.38
	2.5	0.27	4.97	10.64	0.38
	3	0.24	4.15	10.61	0.37
	3.5	0.22	3.55	9.68	0.37
	4	0.20	3.09	9.30	0.36
	4.5	0.19	2.74	8.25	0.36
	5	0.18	2.45	7.67	0.35
	5.5	0.17	2.22	6.84	0.34
	6	0.16	2.02	6.43	0.33
	6.5	0.16	1.86	6.03	0.33
	7	0.15	1.71	5.66	0.32
	8	0.15	1.48	5.00	0.30
	8.5	0.14	1.39	4.72	0.29
	9	0.14	1.31	4.43	0.28
	9.5	0.14	1.23	4.18	0.27
	10	0.13	1.17	3.94	0.23
	10.5	0.13	1.11	3.70	0.25
	11	0.13	1.06	3.50	0.24
	11.5	0.13	1.01	3.30	0.23
	12	0.13	0.96	3.10	0.22
	12.5	0.13	0.92	2.93	0.21
	13	0.12	0.88	2.77	0.20
	13.5	0.12	0.85	2.61	0.19
	14	0.12	0.82	2.46	0.18
	14.5	0.12	0.79	2.33	0.17
	15	0.12	0.76	2.20	0.16
1W·0.25MeOH (H_{dc} = 1000 Oe)	8	0.95	1.15	9.94	0.58
	8.5	0.88	1.15	7.76	0.57
	9	0.81	1.16	5.94	0.55
	9.5	0.75	1.16	4.83	0.53
	10	0.70	1.16	4.16	0.52
	10.5	0.65	1.17	3.38	0.50
	11	0.62	1.17	2.80	0.49
	11.5	0.59	1.17	2.36	0.48
	12	0.56	1.17	2.00	0.47
	12.5	0.54	1.17	1.70	0.46
	13	0.51	1.17	1.43	0.45
	13.5	0.49	1.17	1.22	0.43

	14	0.47	1.17	1.02	0.42
	14.5	0.45	1.17	0.87	0.41
	15	0.43	1.17	0.72	0.41
	15.5	0.42	1.17	0.61	0.40
	16	0.40	1.17	0.49	0.41
	16.5	0.39	1.17	0.405	0.41
	17	0.38	1.16	0.33	0.42
	17.5	0.37	1.16	0.28	0.42
1Py (H_{dc} = 1000 Oe)	14	0.34	2.69	15.19	0.15
	14.25	0.28	2.79	14.02	0.21
	14.5	0.32	2.58	12.86	0.15
	14.75	0.28	2.63	11.99	0.20
	15	0.32	2.46	11.11	0.14
	15.25	0.28	2.50	10.36	0.19
	15.5	0.31	2.36	9.67	0.14
	15.75	0.28	2.38	9.07	0.17
	16	0.31	2.27	8.51	0.13
	16.25	0.27	2.27	7.97	0.16
	16.5	0.31	2.18	7.50	0.13
	16.75	0.27	2.18	7.07	0.16
	17	0.30	2.08	6.62	0.11
	17.25	0.27	2.09	6.26	0.15
	17.5	0.30	2.02	5.90	0.10
	17.75	0.27	2.01	5.56	0.14
	18	0.30	1.96	5.23	0.10
	18.25	0.27	1.96	4.93	0.13
	18.5	0.27	1.92	4.65	0.12
	18.75	0.27	1.90	4.39	0.12
	19	0.27	1.86	4.14	0.12
	19.25	0.27	1.83	3.89	0.11
	19.5	0.26	1.81	3.67	0.11
	19.75	0.26	1.77	3.45	0.11
	20	0.26	1.75	3.24	0.11
	20.25	0.26	1.73	3.06	0.11
	20.5	0.26	1.69	2.86	0.10
	20.75	0.26	1.67	2.69	0.10
	21	0.26	1.65	2.51	0.10
	21.25	0.26	1.62	2.35	0.10
	21.5	0.26	1.61	2.19	0.10
	21.75	0.26	1.58	2.04	0.09
	22	0.25	1.56	1.89	0.09
	22.5	0.25	1.53	1.63	0.09
	23	0.25	1.49	1.39	0.09
	23.5	0.25	1.45	1.18	0.08
	24	0.25	1.43	0.99	0.09
	24.5	0.25	1.40	0.83	0.10
	25	0.24	1.37	0.69	0.10
	25.5	0.25	1.34	0.60	0.09
	26	0.25	1.31	0.47	0.08
	26.5	0.24	1.29	0.39	0.09
	27	0.25	1.27	0.32	0.08
	27.5	0.23	1.25	0.26	0.09
	28	0.23	1.22	0.22	0.09
	28.5	0.23	1.53	0.18	0.09

2W (H_{dc} = 1000 Oe)	4	0.25	3.19	26.18	0.62
	4.5	0.26	2.84	20.68	0.61
	5	0.27	2.48	14.28	0.60
	5.5	0.29	2.23	10.66	0.59
	6	0.30	2.02	8.07	0.58
	6.5	0.31	1.81	5.81	0.57
	7	0.31	1.69	4.79	0.57
	7.5	0.32	1.56	3.78	0.56
	8	0.33	1.45	3.02	0.56
	8.5	0.34	1.35	2.47	0.54
	9	0.34	1.27	2.02	0.54
	9.5	0.35	1.19	1.67	0.53
	10	0.36	1.11	1.40	0.52
	10.5	0.36	1.06	1.19	0.51
	11	0.36	1.07	1.01	0.51
	11.5	0.36	0.97	0.86	0.51
	12	0.36	0.92	0.74	0.50
	12.5	0.37	0.88	0.66	0.49
	13	0.38	0.85	0.58	0.48
	13.5	0.38	0.82	0.51	0.48
	14	0.38	0.79	0.45	0.47
	14.5	0.37	0.76	0.40	0.48
	15	0.38	0.73	0.36	0.46
	15.5	0.38	0.71	0.32	0.45
	16	0.39	0.68	0.30	0.44
	16.5	0.39	0.66	0.27	0.42
1W@Y (H_{dc} = 0 Oe)	2	0.02	0.65	3.97	0.54
	2.5	0.02	0.53	3.61	0.55
	3	0.02	0.46	3.15	0.55
	3.5	0.02	0.40	2.84	0.56
	4	0.02	0.35	2.59	0.55
	4.5	0.02	0.32	2.32	0.55
	5	0.03	0.29	2.09	0.55
	5.5	0.03	0.26	1.89	0.55
	6	0.03	0.24	1.72	0.55
	6.5	0.03	0.22	1.55	0.54
	7	0.03	0.21	1.38	0.54
	7.5	0.03	0.20	1.27	0.53
	8	0.03	0.19	1.21	0.53
	8.5	0.03	0.17	1.10	0.52
	9	0.03	0.16	1.04	0.50
	9.5	0.03	0.16	0.99	0.50
	10	0.04	0.15	0.90	0.49
	10.5	0.04	0.14	0.86	0.49
	11	0.04	0.14	0.78	0.49
	11.5	0.04	0.13	0.75	0.47
	12.0	0.04	0.13	0.70	0.49
	12.5	0.04	0.12	0.64	0.46
	13	0.04	0.12	0.60	0.47
	13.5	0.04	0.11	0.56	0.47
	14	0.04	0.11	0.51	0.48
	14.5	0.04	0.10	0.46	0.46
	15	0.04	0.09	0.42	0.48

	15.5	0.04	0.09	0.39	0.47
	16	0.04	0.09	0.36	0.47
	16.5	0.04	0.09	0.34	0.45
1Py@Y **(H_{dc} = 0 Oe)**	3	0.02	0.58	1.37	0.54
	3.5	0.02	0.50	1.05	0.54
	4	0.02	0.45	0.92	0.56
	4.5	0.02	0.40	0.84	0.56
	5	0.03	0.34	0.75	0.52
	5.5	0.03	0.32	0.67	0.53
	6	0.05	0.27	0.60	0.46
	6.5	0.05	0.22	0.54	0.49
	7	0.04	0.25	0.51	0.50
	7.5	0.03	0.22	0.48	0.54
	8	0.03	0.23	0.46	0.53
	8.5	0.02	0.23	0.43	0.58
	9	0.04	0.20	0.40	0.49
	9.5	0.05	0.18	0.39	0.43
	10	0.04	0.19	0.37	0.54
	10.5	0.05	0.16	0.35	0.43
	11	0.04	0.16	0.34	0.48
	11.5	0.05	0.16	0.33	0.42
2W@Y **(H_{dc} = 0 Oe)**	3.5	0.02	0.29	2.80	0.56
	4	0.03	0.25	2.58	0.54
	4.5	0.02	0.24	2.32	0.58
	5	0.02	0.21	1.90	0.56
	5.5	0.03	0.19	1.62	0.53
	6	0.03	0.18	1.41	0.54
	6.5	0.03	0.18	1.27	0.55
	7	0.03	0.16	1.14	0.53
	8	0.03	0.19	0.93	0.53
	8.5	0.03	0.17	0.83	0.53
	9	0.03	0.16	0.75	0.50
	9.5	0.03	0.16	0.70	0.50
	10	0.03	0.15	0.65	0.50
	10.5	0.04	0.14	0.62	0.49
	11.5	0.04	0.13	0.56	0.47
	12.0	0.04	0.12	0.54	0.47

Table S6. Electronic structure of **1W** complexes calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet. Last column reports the CASSCF-SO energies.

Energy (cm^{-1})	Energy (K)	g1	g2	g3	Angle	Wavefunction	<Jz>	Energy^{CAS} (cm^{-1})
				1W.1				
0.00	0.00	0.00	0.00	19.80	--	$99\%\|\pm 15/2\rangle$	$\pm$ 7.5	0.00
202.30	291.06	0.71	1.62	16.83	47.1	$46\%\|\pm 13/2\rangle$ + $12\%\|\pm 11/2\rangle$ + $9\%\|\pm 7/2\rangle$ + $9\%\|\pm 3/2\rangle$ + $5\%\|\pm 9/2\rangle$ + $5\%\|\pm 5/2\rangle$ + $5\%\|\pm 1/2\rangle$ + $5\%\|\mp 1/2\rangle$	$\pm$ 4.4	202.42
264.15	380.05	0.18	1.81	13.21	40.7	$47\%\|\pm 13/2\rangle$ + $10\%\|\pm 5/2\rangle$ + $8\%\|\mp 1/2\rangle$ + $9\%\|\pm 1/2\rangle$ + $8\%\|\pm 3/2\rangle$ + $7\%\|\pm 9/2\rangle$	$\pm$ 3.7	261.71
399.85	575.29	2.65	4.95	11.16	45.8	$48\%\|\pm 11/2\rangle$ + $13\%\|\pm 9/2\rangle$ + $10\%\|\mp 3/2\rangle$ + $7\%\|\mp 1/2\rangle$ + $6\%\|\pm 3/2\rangle$ + $5\%\|\pm 1/2\rangle$	$\pm$ 3.2	396.76
492.64	708.79	0.28	6.65	8.44	79.1	$22\%\|\pm 11/2\rangle$ + $19\%\|\pm 7/2\rangle$ + $17\%\|\mp 5/2\rangle$ + $11\%\|\mp 1/2\rangle$ + $8\%\|\mp 3/2\rangle$ + $6\%\|\mp 9/2\rangle$	$\pm$ 1.2	489.54
558.17	803.07	2.39	3.57	10.60	68.5	$38\%\|\pm 9/2\rangle$ + $11\%\|\mp 7/2\rangle$ + $15\%\|\mp 5/2\rangle$ + $11\%\|\pm 11/2\rangle$	$\pm$ 1.8	558.62
620.26	892.41	0.96	2.26	15.53	81.5	$22\%\|\pm 7/2\rangle$ + $18\%\|\pm 9/2\rangle$ + $14\%\|\mp 1/2\rangle$ + $14\%\|\mp 3/2\rangle$ + $13\%\|\mp 5/2\rangle$ + $8\%\|\pm 1/2\rangle$	$\pm$ 1.1	619.68

748.16	1076.43	0.05	0.12	19.46	74.8	$24\%\|\pm 3/2\rangle$ + $26\%\|\pm 5/2\rangle$ + $18\%\|\pm 7/2\rangle$ + $16\%\|\pm 1/2\rangle$ + $7\%\|\mp 1/2\rangle$	$\pm$ 1.9	748.14
				1W.2				
0.00	0.00	0.01	0.02	19.81	--	$99\%\|\pm 15/2\rangle$	$\pm$ 7.5	0.00
187.72	270.09	0.89	1.84	17.54	59.3	$29\%\|\pm 13/2\rangle$ + $12\%\|\pm 7/2\rangle$ + $13\%\|\pm 3/2\rangle$ + $9\%\|\pm 5/2\rangle$ + $10\%\|\pm 11/2\rangle$	$\pm$ 3.5	186.84
251.38	361.68	0.21	2.51	13.19	26.7	$63\%\|\pm 13/2\rangle$ + $8\%\|\pm 5/2\rangle$ + $6\%\|\pm 3/2\rangle$ + $6\%\|\pm 1/2\rangle$ + $6\%\|\mp 1/2\rangle$	$\pm$ 4.4	249.83
376.64	541.90	3.11	5.93	10.62	45.5	$45\%\|\pm 11/2\rangle$ + $14\%\|\pm 9/2\rangle$ + $9\%\|\mp 3/2\rangle$ + $7\%\|\pm 1/2\rangle$ + $5\%\|\pm 3/2\rangle$ + $1\%\|\mp 1/2\rangle$	$\pm$ 3.1	373.85
475.09	683.54	0.50	6.31	9.92	79.5	$25\%\|\pm 11/2\rangle$ + $18\%\|\pm 7/2\rangle$ + $12\%\|\mp 1/2\rangle$ + $11\%\|\mp 3/2\rangle$ + $11\%\|\pm 5/2\rangle$	$\pm$ 1.7	471.67
552.06	794.28	2.54	4.18	9.60	69.0	$30\%\|\pm 9/2\rangle$ + $13\%\|\pm 11/2\rangle$ + $12\%\|\pm 3/2\rangle$ + $11\%\|\pm 1/2\rangle$ + $12\%\|\mp 5/2\rangle$ + $7\%\|\mp 3/2\rangle$	$\pm$ 1.9	550.96
587.37	845.09	1.90	6.92	12.66	75.6	$31\%\|\pm 7/2\rangle$ + $19\%\|\pm 9/2\rangle$ + $10\%\|\mp 5/2\rangle$ + $8\%\|\pm 5/2\rangle$ + $10\%\|\pm 1/2\rangle$	$\pm$ 1.8	588.40
716.55	1030.95	0.05	0.12	19.62	75.4	$24\%\|\pm 3/2\rangle$ + $20\%\|\pm 5/2\rangle$ + $19\%\|\pm 1/2\rangle$ + $12\%\|\mp 1/2\rangle$ + $6\%\|\mp 3/2\rangle$ + $10\%\|\pm 7/2\rangle$	$\pm$ 1.9	716.03

Table S7. Electronic structure of **1W** complex calculated with the crystal field parameters obtained from CASSCF-SO at the DFT-optimised structure. Each row corresponds to a Kramers doublet. Last column reports the CASSCF-SO energies.

Energy (cm^{-1})	Energy (K)	g1	g2	g3	Angle	Wavefunction	<Jz>	$Energy^{CAS}$ (cm^{-1})
0.00	0.00	0.03	0.05	19.72	--	$99\%\|\pm 15/2\rangle$	7.4	0.00
106.54	153.28	0.45	0.57	19.23	81.5	$8\%\|\mp 3/2\rangle$ + $4\%\|\pm 11/2\rangle$ + $9\%\|\pm 7/2\rangle$ + $18\%\|\pm 3/2\rangle$ + $5\%\|\pm 9/2\rangle$ + $10\%\|\pm 5/2\rangle$ + $14\%\|\pm 1/2\rangle$ + $19\%\|\mp 1/2\rangle$	1.1	106.46
213.06	306.54	1.64	2.26	14.83	8.2	$86\%\|\pm 13/2\rangle$ + $4\%\|\mp 1/2\rangle$	5.6	212.69
318.82	458.70	1.99	5.40	11.06	71.4	$27\%\|\pm 11/2\rangle$ + $14\%\|\pm 9/2\rangle$ + $16\%\|\mp 3/2\rangle$ + $8\%\|\mp 5/2\rangle$ + $7\%\|\mp 3/2\rangle$ + $8\%\|\pm 5/2\rangle$	1.7	315.62
397.25	571.55	0.54	7.06	8.53	51.3	$49\%\|\pm 11/2\rangle$ + $14\%\|\pm 5/2\rangle$ + $9\%\|\mp 7/2\rangle$ + $7\%\|\pm 3/2\rangle$ + $7\%\|\mp 3/2\rangle$	2.8	397.08
442.20	636.22	2.72	6.00	10.63	66.2	$38\%\|\pm 9/2\rangle$ + $17\%\|\pm 7/2\rangle$ + $12\%\|\mp 7/2\rangle$ + $8\%\|\mp 1/2\rangle$	1.9	441.42
478.70	688.74	1.40	2.25	16.85	84.2	$22\%\|\pm 3/2\rangle$ + $14\%\|\pm 9/2\rangle$ + $25\%\|\mp 1/2\rangle$ + $14\%\|\mp 3/2\rangle$ + $9\%\|\mp 7/2\rangle$ + $12\%\|\pm 5/2\rangle$	0.8	478.12
625.07	899.33	0.05	0.07	19.52	69.6	$20\%\|\pm 3/2\rangle$ + $27\%\|\pm 5/2\rangle$ + $24\%\|\pm 7/2\rangle$ + $13\%\|\pm 9/2\rangle$ + $9\%\|\pm 1/2\rangle$	2.5	625.82

Table S8. Electronic structure of **1Py** complex calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet. Last column reports the CASSCF-SO energies.

Energy (cm^{-1})	Energy (K)	g1	g2	g3	Angle	Wavefunction	<Jz>	Energy^{CAS} (cm^{-1})
0.00	0.00	0.01	0.01	19.80	--	$99\%\|\pm 15/2\rangle$	$\pm$7.5	0.00
224.80	323.43	0.29	0.41	16.98	15.7	$87\%\|\pm 13/2\rangle$ + $8\%\|\pm 11/2\rangle$	$\pm$6.2	226.04
342.89	493.34	1.05	1.39	15.39	53.6	$24\%\|\pm 9/2\rangle$ + $21\%\|\pm 11/2\rangle$ + $11\%\|\pm 5/2\rangle$ + $9\%\|\pm 1/2\rangle$ + $9\%\|\pm 7/2\rangle$	$\pm$3.4	339.23
437.51	629.48	1.46	4.16	11.22	39.3	$46\%\|\pm 11/2\rangle$ + $13\%\|\pm 7/2\rangle$ + $10\%\|\pm 5/2\rangle$ + $9\%\|\pm 3/2\rangle$ + $5\%\|\pm 1/2\rangle$	$\pm$3.4	435.75
508.90	732.19	2.83	6.01	12.87	76.5	$22\%\|\pm 3/2\rangle$ + $16\%\|\pm 7/2\rangle$ + $15\%\|\pm 9/2\rangle$ + $13\%\|\pm 5/2\rangle$ + $7\%\|\mp 1/2\rangle$ + $9\%\|\pm 1/2\rangle$ + $6\%\|\pm 11/2\rangle$	$\pm$1.9	507.41
576.68	829.71	0.94	2.05	13.58	80.1	$30\%\|\pm 1/2\rangle$ + $16\%\|\mp 1/2\rangle$ + $11\%\|\pm 9/2\rangle$ + $11\%\|\pm 5/2\rangle$ + $9\%\|\mp 3/2\rangle$ + $6\%\|\pm 7/2\rangle$	$\pm$1.0	574.12
647.30	931.32	0.02	0.48	15.69	69.8	$32\%\|\pm 3/2\rangle$ + $20\%\|\pm 5/2\rangle$ + $17\%\|\pm 9/2\rangle$ + $10\%\|\pm 1/2\rangle$ + $9\%\|\pm 7/2\rangle$	$\pm$2.1	646.89
724.61	1042.54	0.15	0.59	18.33	59.5	$38\%\|\pm 7/2\rangle$ + $23\%\|\pm 9/2\rangle$ + $21\%\|\pm 5/2\rangle$ + $9\%\|\pm 11/2\rangle$	$\pm$3.5	726.59

Table S9. Electronic structure of **1Py** complex calculated with the crystal field parameters obtained from CASSCF-SO at the DFT-optimised structure. Each row corresponds to a Kramers doublet. Last column reports the CASSCF-SO energies.

Energy (cm^{-1})	Energy (K)	g1	g2	g3	Angle	Wavefunction	<Jz>	$Energy^{CAS}$ (cm^{-1})
0.00	0.00	0.02	0.03	19.79	--	$99\%\|\pm 15/2\rangle$	$\pm$ 7.5	0.00
145.75	209.70	0.61	1.02	17.82	54.1	$32\%\|\pm 13/2\rangle$ + $13\%\|\pm 11/2\rangle$ + $10\%\|\pm 9/2\rangle$ + $13\%\|\pm 7/2\rangle$ + $9\%\|\pm 5/2\rangle$ + $10\%\|\pm 3/2\rangle$	$\pm$ 4.0	145.73
225.92	325.05	1.04	2.18	13.26	27.6	$60\%\|\pm 13/2\rangle$ $9\%\|\pm 5/2\rangle$ + $6\%\|\pm 1/2\rangle$ + $6\%\|\pm 3/2\rangle$	$\pm$ 4.4	225.51
342.00	492.06	2.96	5.61	10.18	42.5	$48\%\|\pm 11/2\rangle$ + $8\%\|\pm 9/2\rangle$ + $6\%\|\pm 3/2\rangle$ $8\%\|\mp 3/2\rangle$ + $8\%\|\pm 1/2\rangle$	$\pm$ 3.0	340.20
438.66	631.13	0.89	6.30	9.35	79.0	$22\%\|\pm 11/2\rangle$ + $15\%\|\pm 7/2\rangle$ + $13\%\|\pm 9/2\rangle$ + $11\%\|\mp 3/2\rangle$ + $11\%\|\mp 1/2\rangle$ + $10\%\|\pm 5/2\rangle$	$\pm$ 1.9	437.37
504.83	726.33	0.20	3.96	11.02	77.9	$26\%\|\pm 9/2\rangle$ + $16\%\|\pm 3/2\rangle$ + $15\%\|\pm 1/2\rangle$ + $9\%\|\mp 1/2\rangle$ + $8\%\|\mp 3/2\rangle$ + $8\%\|\mp 5/2\rangle$	$\pm$ 1.3	504.72
539.11	775.66	1.26	3.83	15.32	61.6	$35\%\|\pm 7/2\rangle$ + $20\%\|\pm 5/2\rangle$ + $19\%\|\pm 9/2\rangle$ + $5\%\|\pm 1/2\rangle$ + $5\%\|\pm 3/2\rangle$	$\pm$ 2.7	540.11
612.67	881.48	0.08	0.16	19.56	74.7	$24\%\|\pm 5/2\rangle$ + $22\%\|\pm 3/2\rangle$ + $19\%\|\pm 7/2\rangle$ + $8\%\|\pm 9/2\rangle$	$\pm$ 1.9	612.70

Table S10. Electronic structure of **2W** complexes calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet. Last column reports the CASSCF-SO energies.

Energy (cm^{-1})	Energy (K)	g1	g2	g3	Angle	Wavefunction	<Jz>	Energy^{CAS} (cm^{-1})
				2W.1				
0.00	0.00	0.02	0.03	19.68	--	$97\%\|\pm 15/2\rangle$ + $3\%\|\pm 11/2\rangle$	$\pm$ 7.4	0.00
82.42	118.59	0.20	0.24	19.52	79.6	$18\%\|\pm 3/2\rangle$ + $16\%\|\mp 1/2\rangle$ + $17\%\|\pm 1/2\rangle$ + $13\%\|\pm 5/2\rangle$ + $8\%\|\mp 3/2\rangle$ + $10\%\|\pm 7/2\rangle$ + $6\%\|\pm 9/2\rangle$ +	$\pm$ 1.3	82.12
180.99	260.40	1.27	2.00	15.40	9.1	$83\%\|\pm 13/2\rangle$ + $5\%\|\pm 11/2\rangle$ + $2\%\|\pm 9/2\rangle$ + $2\%\|\pm 5/2\rangle$	$\pm$ 5.8	180.46
256.19	368.59	3.28	6.03	11.33	73.1	$26\%\|\pm 11/2\rangle$ + $19\%\|\pm 9/2\rangle$ + $16\%\|\mp 3/2\rangle$ + $10\%\|\pm 5/2\rangle$	$\pm$ 1.9	255.60
330.45	475.44	0.55	4.99	11.87	77.2	$28\%\|\pm 11/2\rangle$ + $17\%\|\pm 7/2\rangle$ + $11\%\|\mp 7/2\rangle$ + $9\%\|\pm 9/2\rangle$ + $8\%\|\mp 5/2\rangle$ + $5\%\|\mp 9/2\rangle$ + $5\%\|\pm 1/2\rangle$	$\pm$ 1.7	329.38
383.06	551.13	0.64	2.16	14.99	84.2	$18\%\|\pm 1/2\rangle$ + $16\%\|\pm 7/2\rangle$ + $15\%\|\pm 3/2\rangle$ + $14\%\|\mp 5/2\rangle$ + $9\%\|\pm 5/2\rangle$ + $9\%\|\pm 9/2\rangle$	$\pm$ 0.8	381.91
434.97	625.82	0.22	1.16	16.62	52.8	$37\%\|\pm 9/2\rangle$ + $21\%\|\pm 11/2\rangle$ + $13\%\|\pm 7/2\rangle$ + $7\%\|\mp 1/2\rangle$ + $6\%\|\pm 13/2\rangle$	$\pm$ 3.8	434.91
492.62	708.77	0.25	0.63	18.92	74.1	$25\%\|\pm 5/2\rangle$ + $23\%\|\pm 3/2\rangle$ +	$\pm$ 1.9	493.13

						$21\%\|\pm 7/2\rangle$ + $13\%\|\pm 1/2\rangle$ + $7\%\|\pm 9/2\rangle$		
2W.2								
0.00	0.00	0.00	0.00	19.74	--	$98\%\|\pm 15/2\rangle$ + $2\%\|\pm 11/2\rangle$	7.2	0.00
168.74	242.77	0.77	1.51	18.30	73.8	$17\%\|\pm 3/2\rangle$ + $16\%\|\mp 1/2\rangle$ + $11\%\|\pm 1/2\rangle$ + $9\%\|\pm 5/2\rangle$ + $5\%\|\mp 3/2\rangle$ + $11\%\|\pm 7/2\rangle$ + $13\%\|\pm 13/2\rangle$ +	1.9	168.41
217.38	312.76	0.16	2.13	14.14	12.8	$77\%\|\pm 13/2\rangle$ + $5\%\|\mp 1/2\rangle$ + $4\%\|\pm 9/2\rangle$ + $4\%\|\pm 5/2\rangle$	2.7	217.32
321.68	462.82	4.11	5.97	10.96	71.2	$35\%\|\pm 11/2\rangle$ + $14\%\|\pm 9/2\rangle$ + $14\%\|\mp 3/2\rangle$ + $8\%\|\pm 5/2\rangle$ + $6\%\|\mp 7/2\rangle$	2.0	321.61
401.16	577.17	0.32	3.61	10.22	87.4	$32\%\|\pm 11/2\rangle$ + $6\%\|\pm 7/2\rangle$ + $17\%\|\mp 7/2\rangle$ + $9\%\|\mp 5/2\rangle$ + $11\%\|\mp 9/2\rangle$ + $8\%\|\pm 1/2\rangle$	0.6	399.90
479.94	690.52	1.50	2.19	12.40	68.2	$34\%\|\pm 9/2\rangle$ + $17\%\|\pm 11/2\rangle$ + $16\%\|\mp 7/2\rangle$ + $11\%\|\mp 5/2\rangle$	1.8	478.54
546.41	786.15	0.60	1.13	15.82	81.9	$19\%\|\pm 9/2\rangle$ + $17\%\|\pm 7/2\rangle$ + $15\%\|\mp 3/2\rangle$ + $12\%\|\mp 5/2\rangle$ + $12\%\|\mp 1/2\rangle$ + $7\%\|\mp 7/2\rangle$	0.9	546.72
623.75	897.43	0.08	0.18	19.16	77.8	$25\%\|\pm 3/2\rangle$ + $24\%\|\pm 5/2\rangle$ + $14\%\|\pm 7/2\rangle$ + $18\%\|\pm 1/2\rangle$ + $10\%\|\mp 1/2\rangle$	0.4	624.29

2W.1 with solvent

0.00	0.00	0.02	0.03	19.68	--	$97\%\|\pm 15/2\rangle$ + $2\%\|\pm 11/2\rangle$	7.4	0.00
72.43	104.21	0.17	0.21	19.55	79.8	$18\%\|\pm 3/2\rangle$ + $16\%\|\mp 1/2\rangle$ + $17\%\|\pm 1/2\rangle$ + $13\%\|\pm 5/2\rangle$ + $9\%\|\mp 3/2\rangle$ + $10\%\|\pm 7/2\rangle$ + $6\%\|\pm 9/2\rangle$ +	1.3	72.10
178.26	256.48	1.42	2.15	15.34	9.5	$83\%\|\pm 13/2\rangle$ + $5\%\|\pm 11/2\rangle$ + $2\%\|\pm 9/2\rangle$ + $2\%\|\pm 5/2\rangle$	5.8	177.74
249.31	358.70	3.05	6.03	11.29	74.1	$24\%\|\pm 11/2\rangle$ + $19\%\|\pm 9/2\rangle$ + $16\%\|\mp 3/2\rangle$ + $10\%\|\pm 5/2\rangle$ + $7\%\|\mp 7/2\rangle$	1.8	248.74
324.81	467.33	0.67	5.11	11.83	76.8	$28\%\|\pm 11/2\rangle$ + $16\%\|\pm 7/2\rangle$ + $10\%\|\mp 7/2\rangle$ + $9\%\|\pm 9/2\rangle$ + $8\%\|\mp 5/2\rangle$ + $5\%\|\mp 9/2\rangle$ + $5\%\|\pm 1/2\rangle$	1.7	323.70
377.18	542.67	0.64	2.13	15.06	83.9	$18\%\|\pm 1/2\rangle$ + $16\%\|\pm 7/2\rangle$ + $15\%\|\pm 3/2\rangle$ + $14\%\|\mp 5/2\rangle$ + $9\%\|\pm 5/2\rangle$ + $9\%\|\pm 9/2\rangle$	0.8	376.02
429.93	618.56	0.22	1.15	16.65	52.5	$37\%\|\pm 9/2\rangle$ + $21\%\|\pm 11/2\rangle$ + $13\%\|\pm 7/2\rangle$ + $7\%\|\mp 1/2\rangle$ + $6\%\|\pm 13/2\rangle$	3.8	429.88
487.61	701.56	0.25	0.63	18.93	74.1	$25\%\|\pm 5/2\rangle$ + $23\%\|\pm 3/2\rangle$ + $21\%\|\pm 7/2\rangle$ + $13\%\|\pm 1/2\rangle$ + $7\%\|\pm 9/2\rangle$	1.9	488.10

Table S11. Electronic structure of **2W** complex calculated with the crystal field parameters obtained from CASSCF-SO at the DFT-optimised structure. Each row corresponds to a Kramers doublet. Last column reports the CASSCF-SO energies.

Energy (cm^{-1})	Energy (K)	g1	g2	g3	Angle	Wavefunction	<Jz>	Energy^{CAS} (cm^{-1})
0.00	0.00	0.04	0.07	19.63	--	$96\%\|\pm 15/2\rangle$ + $3\%\|\pm 11/2\rangle$	7.4	0.00
66.30	95.39	0.31	0.35	19.38	80.7	$18\%\|\pm 3/2\rangle$ + $18\%\|\mp 1/2\rangle$ + $17\%\|\pm 1/2\rangle$ + $11\%\|\pm 5/2\rangle$ + $8\%\|\mp 3/2\rangle$ + $9\%\|\pm 7/2\rangle$ + $5\%\|\pm 9/2\rangle$ +	1.2	65.85
173.50	249.63	2.28	2.67	14.54	10.3	$80\%\|\pm 13/2\rangle$ + $5\%\|\pm 11/2\rangle$ + $4\%\|\mp 1/2\rangle$ + $3\%\|\pm 7/2\rangle$	5.5	171.94
249.07	358.36	2.38	6.91	10.13	74.1	$20\%\|\pm 11/2\rangle$ + $18\%\|\pm 9/2\rangle$ + $21\%\|\mp 3/2\rangle$ + $13\%\|\pm 5/2\rangle$	1.6	245.84
317.86	457.32	0.56	4.03	14.25	73.1	$22\%\|\pm 11/2\rangle$ + $12\%\|\pm 7/2\rangle$ + $6\%\|\mp 7/2\rangle$ + $10\%\|\pm 9/2\rangle$ + $6\%\|\pm 1/2\rangle$ + $11\%\|\pm 5/2\rangle$ + $11\%\|\pm 3/2\rangle$ + $8\%\|\mp 1/2\rangle$ + $7\%\|\mp 3/2\rangle$	2.0	316.38
338.89	487.59	1.46	2.80	15.78	81.2	$28\%\|\pm 1/2\rangle$ + $15\%\|\pm 7/2\rangle$ + $9\%\|\pm 3/2\rangle$ + $6\%\|\mp 3/2\rangle$ + $17\%\|\pm 5/2\rangle$ + $8\%\|\pm 11/2\rangle$	1.0	337.73
419.55	603.63	0.16	0.91	17.60	48.8	$34\%\|\pm 9/2\rangle$ + $29\%\|\pm 11/2\rangle$ + $16\%\|\pm 7/2\rangle$ + $8\%\|\pm 13/2\rangle$	4.4	419.74
472.79	680.23	0.27	0.96	18.82	69.4	$23\%\|\pm 7/2\rangle$ + $23\%\|\pm 5/2\rangle$ + $19\%\|\pm 9/2\rangle$ + $16\%\|\pm 3/2\rangle$ + $7\%\|\pm 1/2\rangle$	2.5	472.73

Table S12. Root mean squared deviation values* in Angstroms between pairs of crystal and optimized coordinates.

1Py	**1W.1**	**1W.2**	**2W.1**	**2W.2**
0.33	0.46	0.47	0.41	0.48
* calculated following Kabsch algorithm[1] as implemented by Charnley[2].				

Given the observed dependency of the electronic structure of compounds **1W** and **2W** we have performed gas-phase molecular geometry optimizations on all compounds with Gaussian09d[3] suite of programs using the PBE[4,5] exchange-correlation functional with cc-pVTZ[6] basis set for all coordinating atoms, cc-pVDZ[6] for the rest of non-metal atoms, the Stuttgart RSC 1997[7] effective core potential (ECP) for the 28 core electrons of yttrium and the corresponding valence basis set for the remaining valence electrons, and Grimme's dispersion corrections.[8-10] To facilitate convergence, dysprosium is substituted by yttrium (where the isotopic mass is set to 162.5, that of the naturally abundant dysprosium), which is justified by their similar ionic radii and the fact that these derivatives are widely found to be structural analogues. Calculation of normal modes was performed by explicit calculation of the Hessian at the optimized geometry, making sure that the forces and displacements are zero and that all frequencies are positive.

[1] W. Kabsch, *Acta Crystallog*., 1976, **A32**, 922-923

[2] http://github.com/charnley/rmsd

[3] M. J. Frisch, et al. Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2016

[4] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.,* 1996, **77**, 3865–3868.

[5] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.,* 1997, **78**, 1396–1396.

[6] T. H. Dunning, *J. Chem. Phys.,* 1989, **90**, 1007–1024.

[7] J. M. L. Martin and A. Sundermann, *J. Chem. Phys.,* 2001, **114**, 3408–3420.

[8] S. Grimme, *J.* Comput*. Chem.,* 2004, **25**, 1463–1473.

[9] S. Grimme, *J. Comput. Chem.,* 2006, **27**, 1787–1799.

[10] S. Grimme, *Wiley Interdiscip. Rev. Comput. Mol. Sci.,* 2011, **1**, 211–228.