Mechanism of Magnetization Relaxation in $\{M^{III}_2Dy^{III}_2\}$ (M = Cr, Mn, Fe, Al) "Butterfly" Complexes: How Important Are the Transition Metal Ions Here?

Yan Peng,[ab] Mukesh Kumar Singh,[c] Valeriu Mereacre,[a] Christopher E. Anson,[a] Gopalan Rajaraman,*[c] Annie K. Powell,*[ab]

Supporting Information

Table S1. Crystal data and structure refinement for compounds **1**, **2**, **3**, **4** and **8**

Compound	**1**	**2**	**3**	**4**	**8**
Formula	$Cr_2Dy_2C_{72}H_{78}N_6O_{18}$	$Cr_2Y_2C_{72}H_{78}N_6O_{18}$	$Mn_2Dy_2C_{74}H_{82}N_6O_{20}$	$Mn_2Y_2C_{74}H_{82}N_6O_{20}$	$Al_2Dy_{0.18}Y_{1.82}C_{72}H_{78}N_6O_{18}$
Mr [g mol^{-1}]	1744.40	1597.22	1878.46	1731.27	1560.43
Colour	green	green	brown	brown	white
Crystal System	monoclinic	monoclnic	triclinic	triclinic	monoclinic
Space Group	*C2/c*	*C2/c*	*P-1*	*P-1*	*C2/c*
T [K]	150 (2)	200	150 (2)	293	150 (2)
a [Å]	28.044 (3)	28.1143(3)	11.1952 (2)	11.20	27.5982(3)
b [Å]	10.4184 (9)	10.5198(2)	13.2472 (3)	13.27	10.6800 (2)
c [Å]	24.335 (3)	24.3898(3)	14.6071(3)	14.73	24.4179 (2)
[°]	90	90	111.771 (2)	111.68	90
[°]	94.793 (9)	94.7940(10)	93.386 (2)	93.55	94.202 (1)
[°]	90	90	110.092 (2)	110.12	90
V [Å]	7085.30 (13)	7188.21(18)	1845.67 (7)	1854.20	7177.80 (17)
Z	4	4	1		4
D_{xcalc} [g·cm^{-3}]	1.635	1.476	1.595		1.444
μ(Mo-Ka) [mm^{-1}]	2.46	5.13	13.98		3.81
F(000)	3504	3288	892		3219
Reflns collected	28433	23208	26827		20216
Unique data	6736	6828	7030		6811
Rint	0.0912	0.017	0.035		0.032
Data with I> 2σ(I)	4031	6110	6602		6259
parameters/restraints	459/1	474/1	198/19		460/1
S on F^2	0.875	1.06	1.04		1.04
R_1 [I> 2σ(I)]	0.0432	0.027	0.026		0.029
wR_2 (all data)	0.0886	0.073	0.065		0.074
Largest diff. peak/hole [e Å^{-3}]	+0.59/-0.93	+0.39/-0.31	+0.64/-0.69		+0.35/-0.54
CCDC	1880458	1902469	1880459		1880460

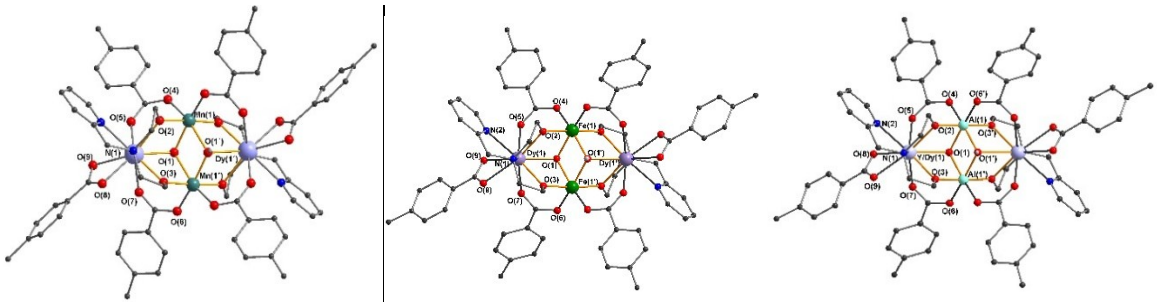

Fig S1. Structures of compound **3** $\{Mn_2Dy_2\}$, **5** $\{Fe_2Dy_2\}$ and **8** $\{Al_2Dy_{0.18}Y_{1.82}\}$, from left to right.

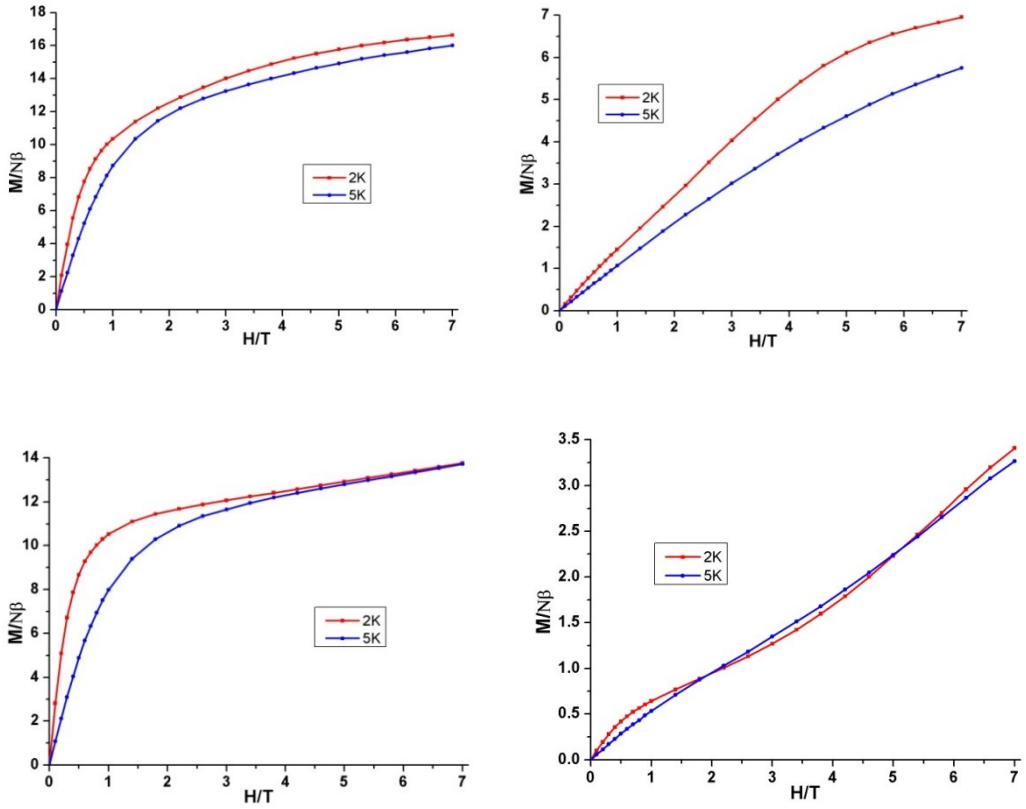

Fig S2. M vs H plots for **1** $\{Cr_2Dy_2\}$ upper left, **2** $\{Cr_2Y_2\}$ upper right, **3** $\{Mn_2Dy_2\}$ lower left and **4** $\{Mn_2Y_2\}$ lower right at 2 and 5 K

Table S2. Magnetic data of compounds **1**-**8** summarized from the dc measurement

Compound	Ground state of Ln^{III} ion	χT expected for non-interacting ions per complex (cm^3 K mol^{-1})	χT measured at 300 K per complex (cm^3 K mol^{-1})	χT measured at 2 K per complex (cm^3 K mol^{-1})	Magnetization at 2 K and 7 T (Nβ)
Cr_2Dy_2 (**1**)	$^6H_{15/2}$	32.09	27.70	23.00	16.64
Cr_2Y_2 (**2**)	0	3.75	3.73	1.44	6.95
Mn_2Dy_2 (**3**)	$^6H_{15/2}$	34.34	33.16	31.75	13.77
Mn_2Y_2 (**4**)	0	6	5.38	1.10	3.41
Fe_2Dy_2 (**5**)	$^6H_{15/2}$	37.09	36.60	25.77	11.97
Fe_2Y_2 (**6**)	0	8.75	6.61	0	0.005
Al_2Dy_2 (**7**)	$^6H_{15/2}$	28.34	28.73	26.85	11.09
$Al_2Dy_{0.18}Y_{1.82}$ (**8**)	$^6H_{15/2}$	2.55	2.56	2.25	1.46

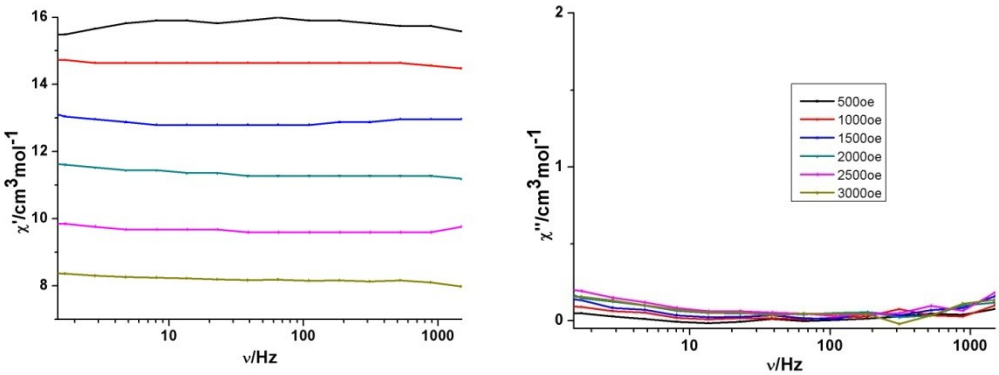

Fig S3. Frequency dependence of the in-phase, (χ', left), and out-of-phase, (χ'', right) for **1** $\{Cr_2Dy_2\}$ in different dc applied field at 2 K

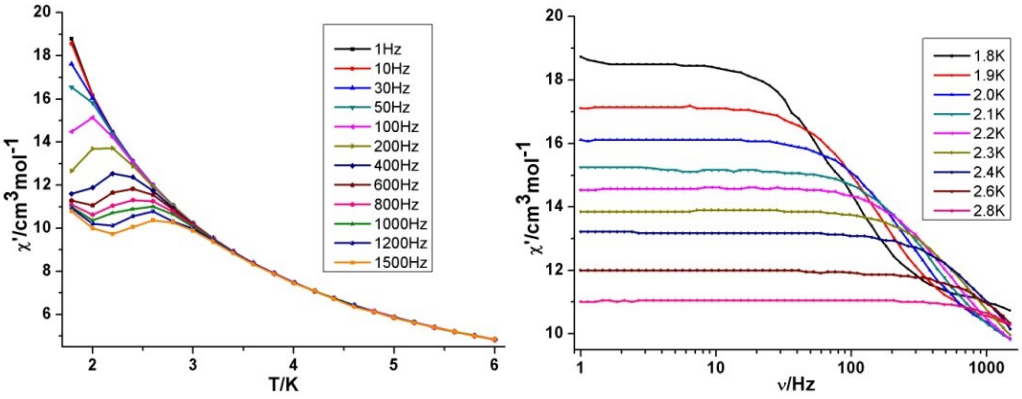

Fig S4. Temperature (left) and frequency (right) dependence under zero dc field of the in-phase (χ') for compound **3** $\{Mn_2Dy_2\}$

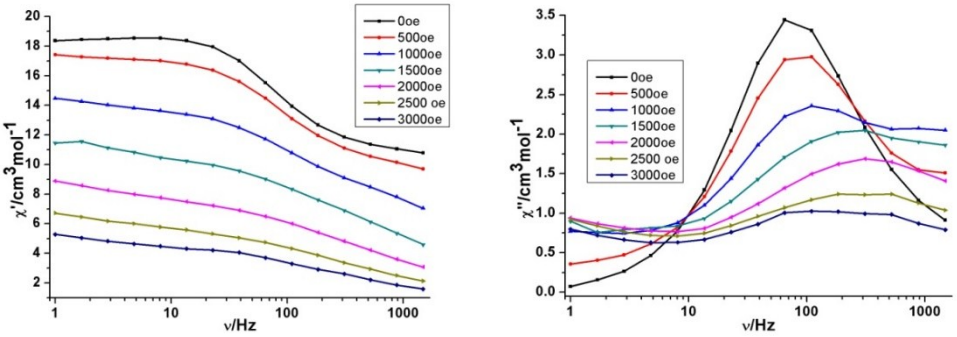

Fig S5. Frequency dependence of the in-phase, (χ', left), and out-of-phase, (χ'', right) for **3** $\{Mn_2Dy_2\}$ in different dc applied field at 2 K

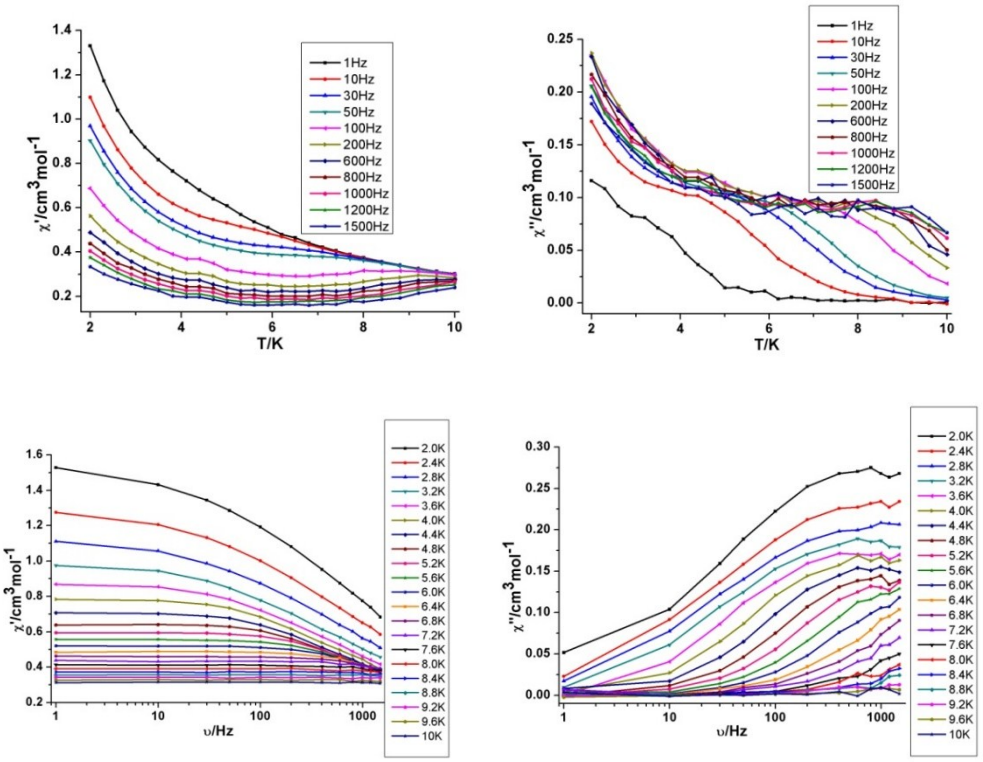

Fig S6. Temperature (upper) and frequency (lower) dependence under zero dc field of the in-phase (χ', left) and the out-of-phase (χ'', right) for compound **8** $\{Al_2Dy_{0.18}Y_{1.82}\}$.

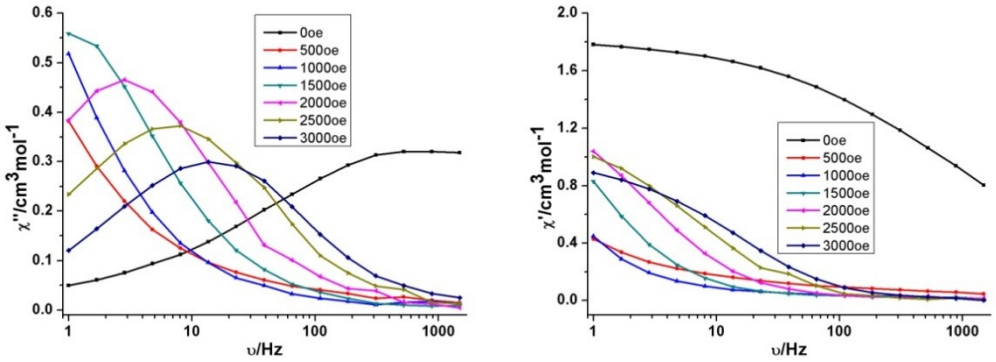

Fig S7. Frequency dependence of the in-phase, (χ', left), and out-of-phase,(χ", right) for **8** $\{Al_2Dy_{0.18}Y_{1.82}\}$ in different dc applied field at 2 K.

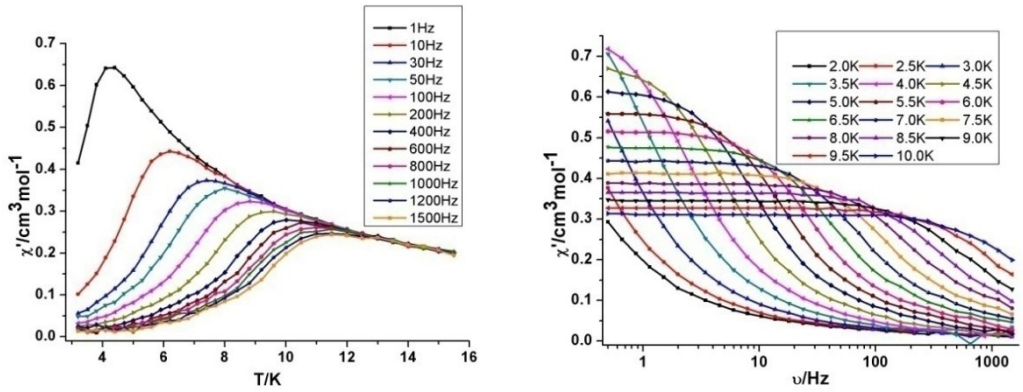

Fig S8. Temperature (left) and frequency (right) dependence under 1000 Oe dc field of the in-phase (χ') for **8** $\{Al_2Dy_{0.18}Y_{1.82}\}$.

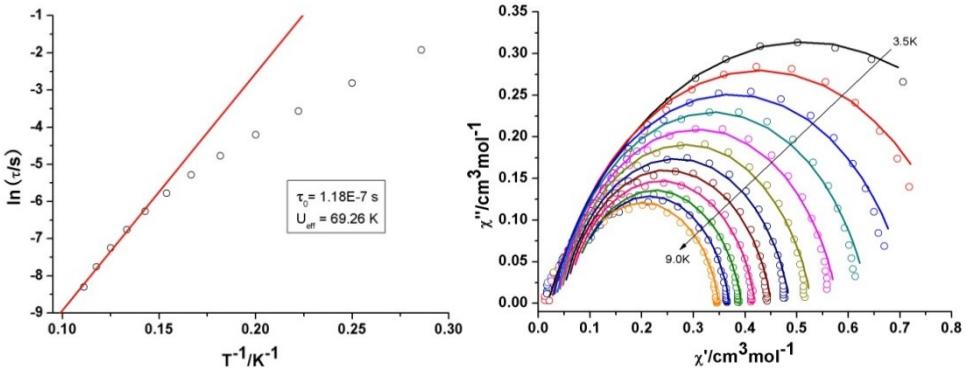

Fig S9. τ vs T^{-1} plot in 1000 Oe dc field (left)) and Cole-Cole plots at indicated temperature (right) for **8** $\{Al_2Dy_{0.18}Y_{1.82}\}$ under 1000 Oe dc field.

CC-Fit results for **3** $\{Mn_2Dy_2\}$

```
##################################################
#########          CC-FIT          #########
#########                          #########
#########         (C) 2014         #########
#########     NICHOLAS F CHILTON    #########
#########                          #########
#########    nfchilton@gmail.com    #########
##################################################
Number of relaxation processes: 1
Number of temperatures:  7
Number of frequencies:  60

ChiS         ChiT         Tau          Alpha        Residual
0.107216E+02  0.186312E+02  0.174093E-02  0.934268E-01  0.107496E+01
  0.100344E+02  0.172184E+02  0.931198E-03  0.903989E-01  0.445438E+00
  0.950108E+01  0.161609E+02  0.571458E-03  0.827729E-01  0.223243E+00
  0.903574E+01  0.152250E+02  0.373962E-03  0.826088E-01  0.189436E+00
  0.880901E+01  0.146193E+02  0.281169E-03  0.668418E-01  0.184881E+00
  0.842699E+01  0.138960E+02  0.193295E-03  0.676645E-01  0.108447E+00
  0.806101E+01  0.132001E+02  0.133901E-03  0.713518E-01  0.466416E-01
```

CC-Fit results for **8** $\{Al_2Dy_{0.18}Y_{1.82}\}$

```
##################################################
#########          CC-FIT          #########
#########                          #########
#########         (C) 2014         #########
#########     NICHOLAS F CHILTON    #########
#########                          #########
#########    nfchilton@gmail.com    #########
##################################################
Number of relaxation processes: 1
Number of temperatures: 17
Number of frequencies:  30

ChiS         ChiT         Tau          Alpha        Residual
  0.137259E-01  0.185012E+01  0.359401E+01  0.412251E+00  0.415399E-03
  0.162190E-01  0.155148E+01  0.148373E+01  0.379562E+00  0.374572E-03
  0.161577E-01  0.123017E+01  0.447231E+00  0.336044E+00  0.685720E-03
  0.187810E-01  0.100887E+01  0.146498E+00  0.286646E+00  0.348529E-02
  0.244279E-01  0.831419E+00  0.600243E-01  0.235533E+00  0.430114E-02
  0.267668E-01  0.719509E+00  0.281982E-01  0.209957E+00  0.512967E-02
  0.326300E-01  0.638829E+00  0.147587E-01  0.185053E+00  0.589465E-02
  0.366325E-01  0.577515E+00  0.844365E-02  0.174194E+00  0.507749E-02
  0.409173E-01  0.526689E+00  0.505776E-02  0.164395E+00  0.429966E-02
  0.451417E-01  0.484839E+00  0.308612E-02  0.161713E+00  0.314975E-02
  0.496245E-01  0.448845E+00  0.190498E-02  0.154199E+00  0.226735E-02
  0.541091E-01  0.417665E+00  0.116453E-02  0.149515E+00  0.134646E-02
  0.587139E-01  0.390639E+00  0.704651E-03  0.145857E+00  0.955193E-03
  0.610797E-01  0.366848E+00  0.424532E-03  0.129336E+00  0.344414E-03
  0.538812E-01  0.346708E+00  0.246788E-03  0.140537E+00  0.223625E-03
  0.646365E-01  0.328133E+00  0.155656E-03  0.126125E+00  0.112848E-03
  0.730838E-01  0.311723E+00  0.101946E-03  0.111941E+00  0.166666E-03
```

Table S3. *Ab Initio* computed ground state *g*-tensors, D, E values along with their respective energy for all paramagnetic metal centers in complexes **1** $\{Cr_2Dy_2\}$, **3** $\{Mn_2Dy_2\}$, **5** $\{Fe_2Dy_2\}$ and **7**$\{Al_2Dy_2\}$.

	Dy1/Dy2				Cr1/Cr2				
	E	g_{xx}	g_{yy}	g_{zz}	g_{xx}	g_{yy}	g_{zz}	D cm^{-1}	E cm^{-1}
KD1	0.0/0.0	0.28/0.18	0.47/0.30	18.14/18.67	1.96	1.96	1.96	-0.14	-0.03
KD2	27.0/33.9	0.22/0.10	0.45/0.26	18.10/17.90					
KD3	78.3/92.0	1.97/1.93	3.42/3.22	13.06/12.98					
KD4	140.9/161.6	7.49/3.97	5.79/5.67	3.81/7.48					
KD5	223.0/246.5	2.42/0.94	3.66/3.39	8.57/9.41					
KD6	255.5/291.1	1.42/1.34	5.04/3.64	13.10/13.66					
KD7	317.9/368.3	0.17/0.11	0.59/0.35	18.46/18.74					
KD8	418.0/449.8	0.04/0.03	0.09/0.08	19.57/19.56					

	Dy1/Dy2				Mn1/Mn2				
	E	g_{xx}	g_{yy}	g_{zz}	g_{xx}	g_{yy}	g_{zz}	D cm^{-1}	E cm^{-1}
KD1	0.0/0.0	0.13/0.13	0.36/0.36	19.35/19.34	1.99	1.99	1.97	-3.35	0.73
KD2	50.2/50.2	1.78/1.78	5.93/5.92	12.16/12.16					
KD3	79.7/79.7	2.89/2.88	4.80/4.80	7.91/7.90					
KD4	112.2/112.2	1.30/1.30	3.29/3.28	11.80/11.79					
KD5	178.6/178.6	1.67/1.66	3.24/3.24	11.95/11.94					
KD6	223.3/223.3	1.98/1.97	2.49/2.49	15.60/15.59					
KD7	283.5/283.5	0.23/0.23	0.38/0.38	19.08/19.05					
KD8	344.5/344.5	0.00/0.00	0.08/0.08	19.40/19.38					

	Dy1/Dy2				Fe1/Fe2				
	E	g_{xx}	g_{yy}	g_{zz}	g_{xx}	g_{yy}	g_{zz}	D cm^{-1}	E cm^{-1}
KD1	0.0/0.0	0.25/0.18	0.47/0.35	18.01/18.09	2.00	2.00	2.00	-0.10	-0.02
KD2	39.9/44.0	1.26/0.88	1.40/0.97	15.18/15.79					
KD3	88.6/96.0	0.25/0.82	2.94/3.08	14.14/14.14					
KD4	126.6/142.3	4.29/4.39	5.34/5.23	8.92/8.60					
KD5	192.1/212.0	1.48/0.84	2.63/2.65	10.67/10.29					
KD6	218.5/247.5	1.25/1.17	3.77/3.11	14.34/14.39					
KD7	291.2/330.3	0.09/0.05	0.21/0.13	18.92/19.17					
KD8	391.8/407.0	0.02/0.02	0.04/0.04	19.67/19.64					

	Dy1/Dy2			
	E	g_{xx}	g_{yy}	g_{zz}
KD1	0.0/0.0	0.17/0.14	0.19/0.16	19.05/19.00
KD2	47.0/43.5	1.02/0.70	1.62/0.98	16.56/16.98
KD3	87.9/93.0	0.75/1.14	3.18/3.15	13.87/13.60
KD4	133.1/146.4	4.36/4.64	5.53/5.42	8.02/8.02
KD5	212.3/229.2	1.19/0.63	2.31/2.37	9.54/9.52
KD6	251.6/275.9	1.04/1.01	2.82/2.48	14.11/14.00
KD7	322.0/358.9	0.06/0.04	0.16/0.14	19.13/19.13
KD8	430.8/445.4	0.02/0.02	0.03/0.04	19.67/19.62

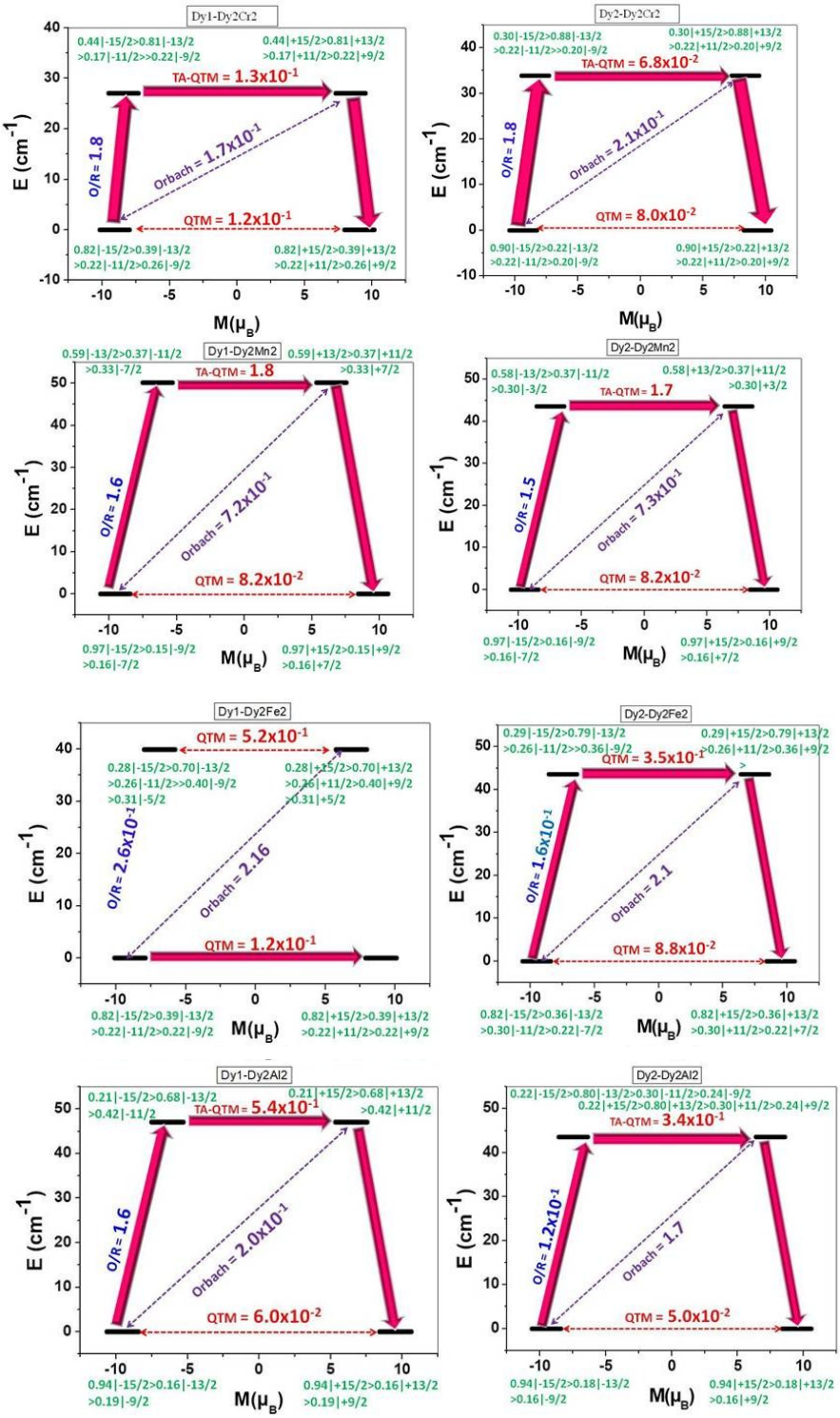

Fig S10. The *ab initio* computed magnetization blocking barrier for Dy1 and Dy2 ions of complexes **1** $\{Cr_2Dy_2\}$, **3** $\{Mn_2Dy_2\}$, **5** $\{Fe_2Dy_2\}$ and **7**$\{Al_2Dy_2\}$. The x-axis indicates the magnetic moment of each state along main magnetic axis of Dy ions, while y-axis denotes the energy of the respective states. The thick black lines indicate the Kramer's doublets as a function of computed magnetic moment. The indigo arrows show the possible pathway via Orbach/Raman relaxation. The dotted red lines represent the presence of QTM/TA-QTM between the connecting pairs. The numbers provided at each arrow are the mean absolute value for the corresponding matrix element of transition magnetic moment. The numbers given in green color correspond to wave function analysis of the m_J levels.

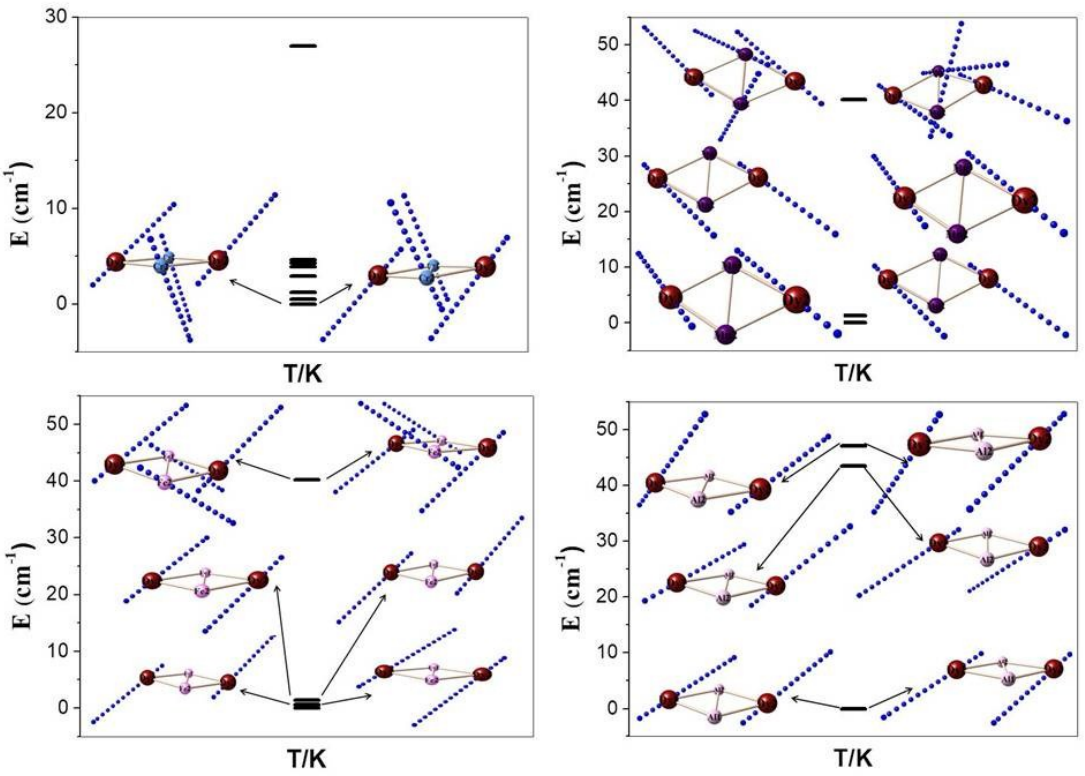

Fig S11. POLY_ANISO computed low-lying exchange spectrum for complexes **1** {Cr_2Dy_2}, **3** {Mn_2Dy_2}, **5** {Fe_2Dy_2} and **7**{Al_2Dy_2}.

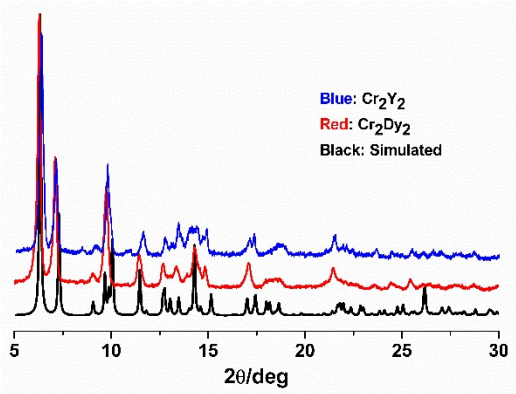

Fig S12. The powder diffraction of compounds **1** {Cr_2Dy_2} and **2** {Cr_2Y_2}

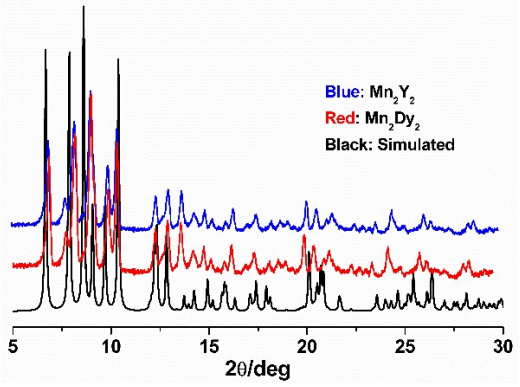

Fig S13. The powder diffraction of compounds **3** {Mn_2Dy_2} and **4** {Mn_2Y_2}