Supporting Information

Exploiting Miraculous Atmospheric CO_2 Fixation in the Design of Dysprosium Single-molecule Magnets

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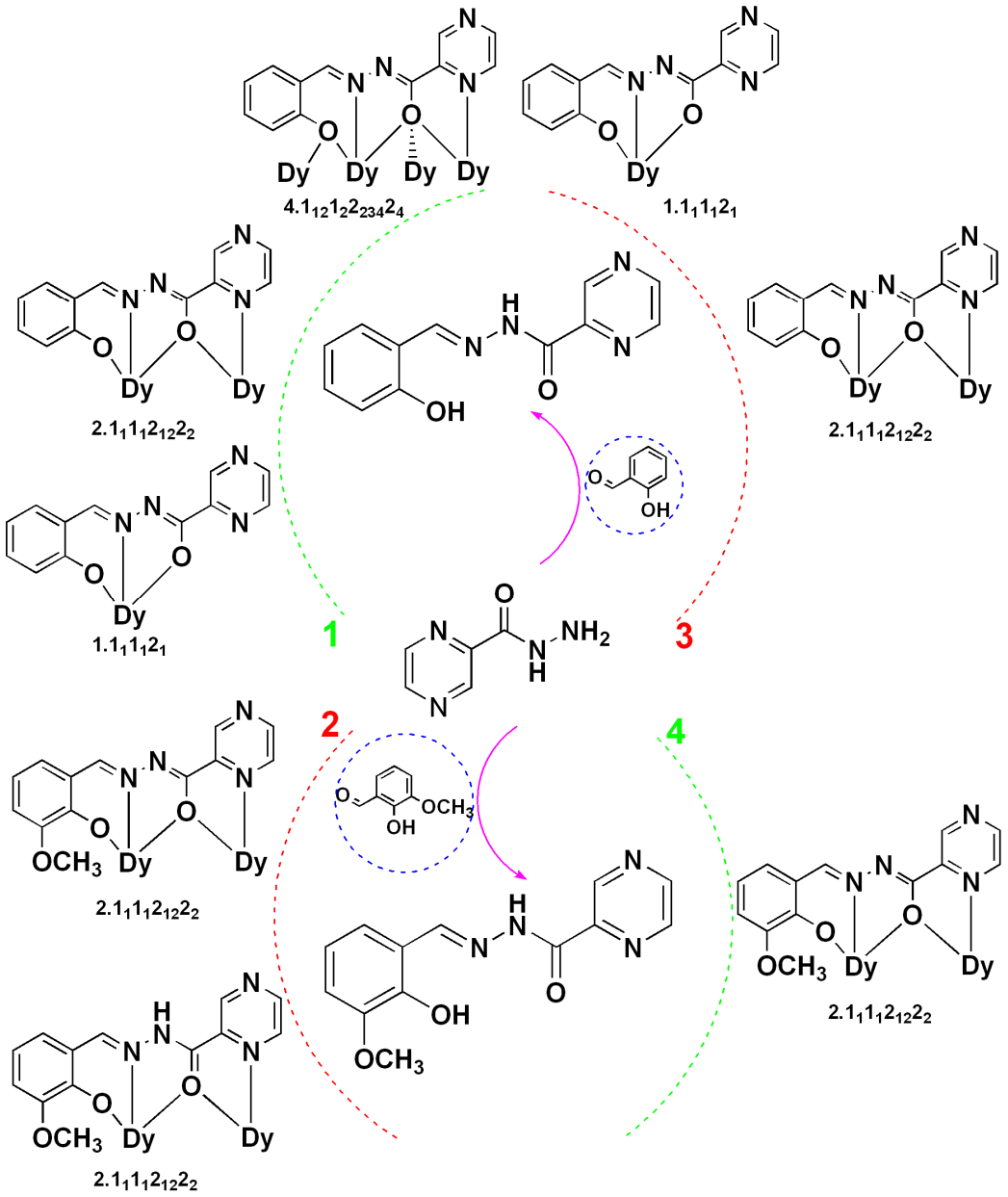
Table S1. Summary of structural data of **1**, **2**, **3** and **4**.

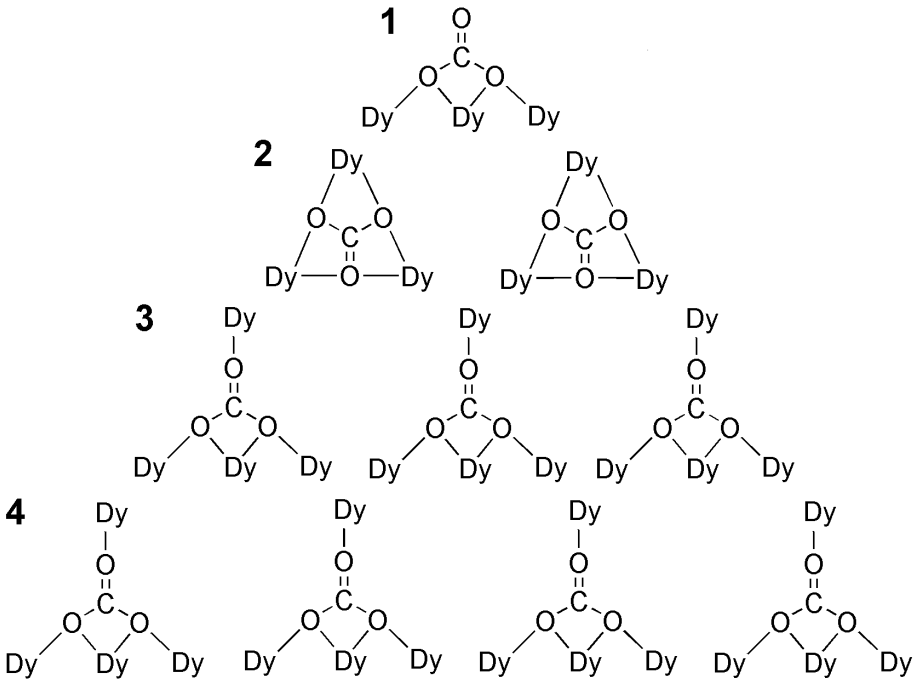
Complexes	**1**	**2**	**3**	**4**
formula	$C_{157}H_{144}Dy_{12}N_{48}O_{53}$	$C_{183}H_{190}Dy_{12}N_{48}O_{74}$	$C_{93}H_{140}Dy_{6}N_{24}O_{52}$	$C_{118}H_{140}Dy_{8}N_{32}O_{56}$
M_r	2528.68	6169.83	3401.29	4202.62
cryst size	0.25 × 0.18 × 0.20	0.20 × 0.25 × 0.15	0.25 × 0.23 × 0.18	0.28 × 0.23 × 0.17
T [K]	191(2)	191(2)	191(2)	296(2)
crystal syst	Triclinic	Monoclinic	trigonal	monoclinic
space group	*P*-1	$P2_1/c$	*R-3*	$C2/c$
a [Å]	23.0307(12)	33.272(3)	24.8206(11)	31.0303(14)
b [Å]	24.2955(13)	25.317(2)	24.8206(11)	18.2012(8)
c [Å]	24.9328(13)	27.923(2)	38.4236(18)	28.6372(13)
α [deg]	68.2260(10)	90	90	90
β [deg]	63.3280(10)	106.009(2)	90	117.4650(10)
γ [deg]	81.2220(10)	90	120	90
V [Å^3]	11575(2)	22609(3)	20500(2)	14351(1)
Z	2	4	6	4
ρ[g cm^{-3}]	1.579	1.820	1.653	1.945
GOF	1.034	1.043	1.116	1.077
R_{int}	0.0500	0.0621	0.0333	0.0659
$R1$ [$I > 2\sigma(I)$]	0.0691	0.0681	0.0465	0.0535
w$R2$ (all data)	0.2009	0.2105	0.1103	0.1285
CCDC number	826831	830076	945883	844333

Table S2. Selected bond lengths (Å) and angles (º) between the dysprosium(III) centers and the CO_3^{2-} ligands for complexes **1**-**4**.

NO.	**1**	**NO.**	**2**
Dy2 - O19	2.3906(106)	Dy1 - O59	2.4432(1)
Dy4 - O19	2.3336(111)	Dy1 - O61	2.4664(2)
Dy4 - O21	2.4532(146)	Dy2 - O60	2.4551(2)
Dy6 - O21	2.4028(110)	Dy2 - O61	2.4705(2)
Dy4 ⋯ C77	2.8390(207)	Dy3 - O59	2.4827(2)
Dy2 – O19 – Dy4	112.831(453)	Dy3 - O61	2.4064(2)
Dy4 – O21 – Dy6	111.124(498)	Dy4 - O62	2.4441(1)
NO.	**3**	Dy4 - O64	2.4203(2)
Dy1 - O6	2.3562(40)	Dy5 - O63	2.4892(2)
Dy1 - O7	2.4642(38)	Dy5 - O64	2.4605(2)
Dy1 - O6B	2.4683(43)	Dy6 - O62	2.4315(1)
Dy2 - O5	2.3388(52)	Dy6 - O63	2.4573(2)
Dy2 - O7	2.3150(41)	Dy1 ⋯ C164	2.8364(2)
Dy1 ⋯ C27B	2.9014(62)	Dy2 ⋯ C164	2.8184(2)
Dy1 – O7 – Dy2	112.544(157)	Dy3 ⋯ C164	2.8274(2)
Dy1 – O6 – Dy1A	113.338(160)	Dy4 ⋯ C163	2.8236(2)
NO.	**4**	Dy5 ⋯ C163	2.8387(2)
Dy1 - O16	2.3221(89)	Dy6 ⋯ C163	2.8120(2)
Dy1 - O22A	2.3160(83)	Dy1 – O61 – Dy2	168.180(9)
Dy2 - O15	2.3759(102)	Dy1 – O59 – Dy3	163.916(5)
Dy2 - O16	2.5086(57)	Dy2 – O60 – Dy3	167.265(5)
Dy2 - O18	2.3736(68)	Dy4 – O64 – Dy5	167.761(9)
Dy3 - O15	2.3166(90)	Dy4 – O62 – Dy6	166.517(5)
Dy3 - O17	2.3346(81)	Dy5 – O63 – Dy6	164.513(5)
Dy4 - O14	2.3564(106)	**NO.**	**4**
Dy4 - O17	2.5077(73)	Dy2 – O15 – Dy3	116.440(351)
Dy4 - O22	2.3525(68)	Dy3 – O17 – Dy4	111.225(296)
Dy1 – O16 – Dy2	109.986(224)	Dy2 ⋯ C65	2.8823(112)
Dy1 – O22 – Dy4	116.981(367)	Dy4 ⋯ C53A	2.8707(90)



Scheme S1. Binding modes of the H_2spch and H_2opch ligands observed in compounds **1-4**.



Scheme S2. Binding modes of all the CO_3^{2-} ligands observed in compounds **1-4**.

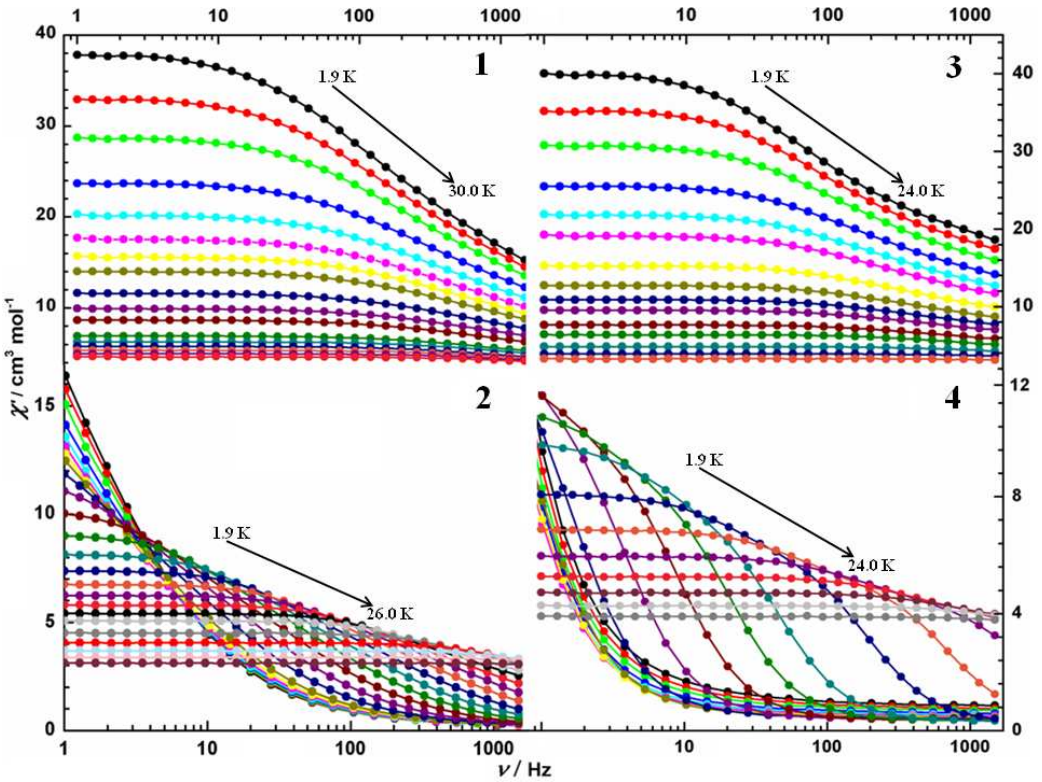


Figure S1. Frequency dependence of the in-phase ac susceptibility of compounds **1-4** under zero-dc field.

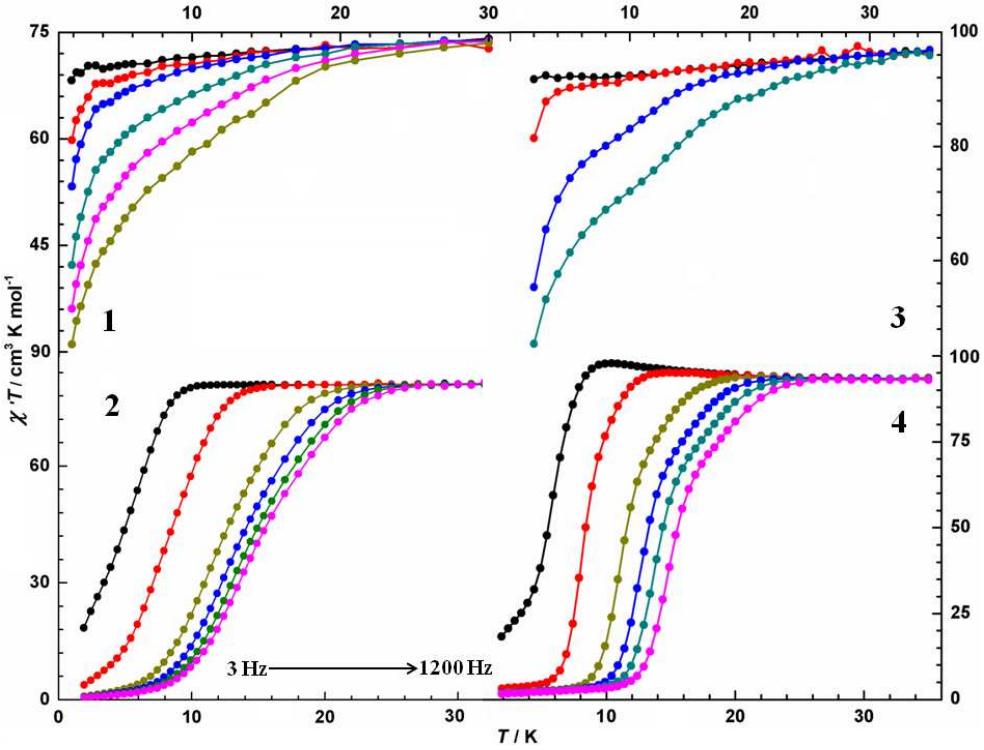


Figure S2. Temperature dependence of the $\chi'T$ product *ac* susceptibility under zero-dc field for compounds **1-4**.

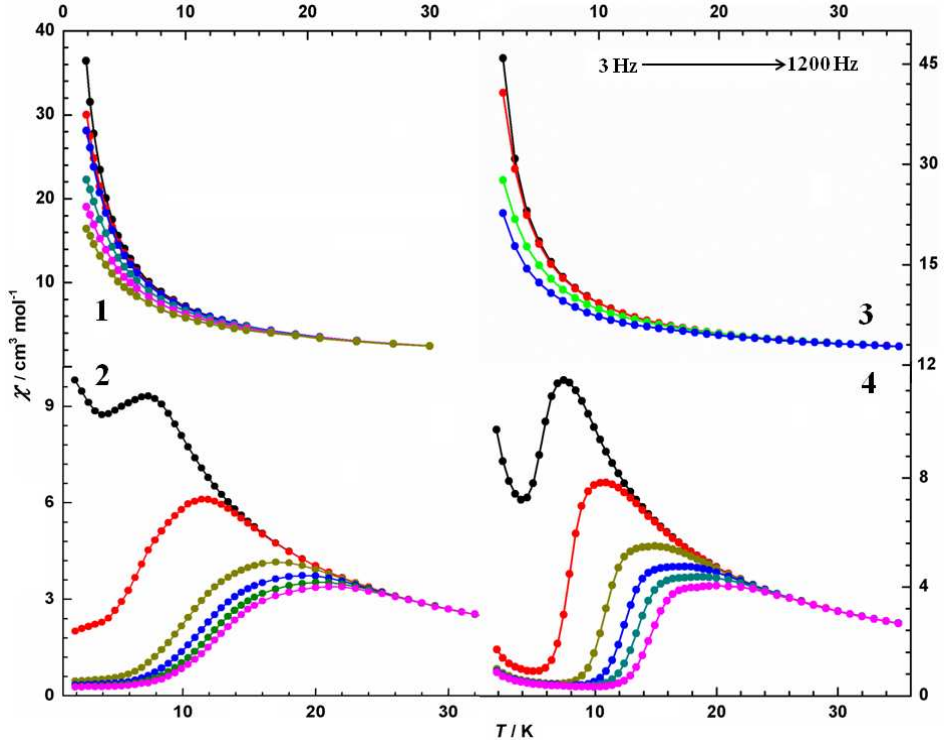


Figure S3. Temperature dependence of the in-phase *ac* susceptibility under zero-dc field for compounds **1-4**.

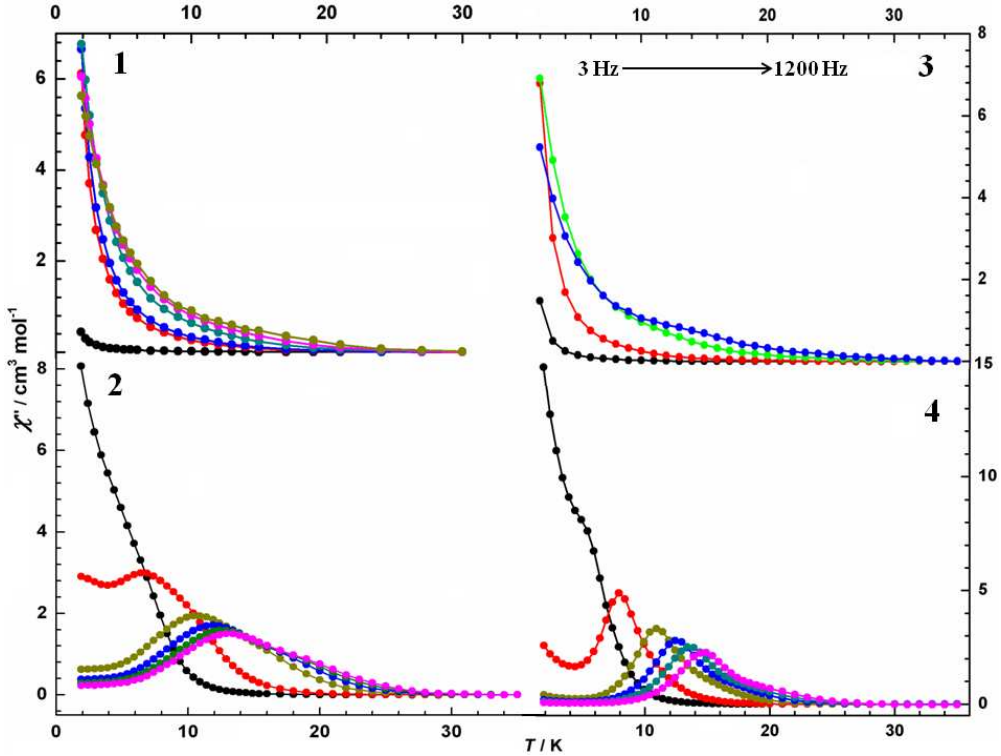


Figure S4. Temperature dependence of the out-of-phase *ac* susceptibility under zero-dc field for compounds **1-4**.