Supporting Information for:
Syntheses, Structures, and Magnetic Properties of a Family of End-On Azido-Bridged Cu^{II}-Ln^{III} Complexes

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Table S1. Crystallographic Data and Structure Refinement Parameters for $\mathbf{2}_{\mathbf{CuCe}}$-$\mathbf{4}_{\mathbf{CuNd}}$.

Complex	$\mathbf{2}_{CuCe}$	$\mathbf{3}_{CuPr}$	$\mathbf{4}_{CuNd}$
Formula	$Cu_2Ce_2C_{43}H_{52}N_{22}O_9$	$Cu_2Pr_2C_{43}H_{52}N_{22}O_9$	$Cu_2Nd_2C_{43}H_{52}N_{22}O_9$
Mr ($gmol^{-1}$)	1428.39	1429.97	1436.63
CCDC number	1060761	1060762	1060763
Crystal size(mm^3)	0.16×0.12×0.04	0.24×0.10 ×0.04	0.12×0.10×0.08
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.254(2)	12.2038(16)	12.179(2)
b (Å)	12.594(2)	12.5702(16)	12.571(2)
c (Å)	19.666(4)	19.689(3)	19.723(3)
α (˚)	76.546(3)	76.538(2)	76.538(2)
β (˚)	87.219(3)	87.325(2)	87.492(2)
γ (˚)	64.860(3)	65.045(2)	65.094(2)
V ($Å^3$)	2667.7(9)	2658.6(6)	2658.3(8)
Z	2	2	2
T , K	293(2)	293(2)	293(2)
ρ_{calcd}(g cm^{-3})	1.778	1.786	1.795
μ(Mo–Kα) (mm^{-1})	2.535	2.664	2.785
F (000)	1420	1424	1428
θ range (˚)	1.07 – 27.62	1.07 – 27.68	1.06 – 27.74
Refl.collected/unique	34309 / 12236	34437 / 12309	34487 / 12393
R(int)	0.0662	0.0419	0.0382
T_{max}/T_{min}	0.9054 / 0.6872	0.9009 / 0.5673	0.8968 / 0.4022
Data/restraints/parameters	12236 / 0 / 682	12309 / 0 / 682	12393 / 0 / 682
$R_1{}^a/wR_2{}^b$ ($I > 2\sigma(I)$)	0.0463 / 0.0897	0.0361 / 0.0791	0.0333 / 0.0787
R_1/wR_2 (all data)	0.0737 / 0.1002	0.0498 / 0.0853	0.0416 / 0.0834
GOF on F^2	0.992	1.020	1.031
Max/min (e $Å^{-3}$)	1.161 / -1.061	1.514 / -1.201	1.573 / -1.129

Table S2. Crystallographic Data and Structure Refinement Parameters for $\mathbf{6_{CuEu}}$, $\mathbf{9_{CuDy}}$ and $\mathbf{10_{CuHo}}$.

Complex	$\mathbf{6_{CuEu}}$	$\mathbf{9_{CuDy}}$	$\mathbf{10_{CuHo}}$
Formula	$Cu_2Eu_2C_{43}H_{52}N_{22}O_9$	$Cu_2Dy_2C_{44}H_{56}N_{22}O_{10}$	$Cu_2Ho_2C_{43}H_{52}N_{22}O_9$
Mr ($gmol^{-1}$)	1452.07	1505.19	1478.01
CCDC number	1060765	1540634	1060769
Crystal size(mm^3)	0.24×0.16×0.14	0.18×0.14×0.05	0.36×0.24×0.22
Crystal system	monoclinic	triclinic	monoclinic
Space group	*C2/c*	*P* ī	*C2/c*
a (Å)	22.254(3)	9.900(3)	22.205(6)
b (Å)	9.6647(11)	10.778(3)	9.666(2)
c (Å)	26.110(3)	13.432(4)	25.926(7)
α (˚)	90	99.895(8)	90
β (˚)	109.7290(10)	91.177(7)	109.841(3)
γ (˚)	90	100.921(7)	90
V ($Å^3$)	5285.9(10)	1384.2(8)	5234(2)
Z	4	1	4
T , K	293(2)	293(2)	293(2)
ρ_{calcd}($g\ cm^{-3}$)	1.825	1.806	1.895
μ(Mo–*K*α) (mm^{-1})	3.209	3.501	3.869
F (000)	2880	744	2912
θ range (˚)	1.66 – 27.60	1.54 – 27.91	1.67 – 27.76
Refl.collected/unique	32930 / 6115	30861 / 6541	32654 / 6092
R(int)	0.0340	0.0474	0.0324
T_{max}/T_{min}	0.6621 / 0.5129	0.8444 / 0.5714	0.4832 / 0.3365
Data/restraints/parameters	6115 / 20 / 361	6541 / 2 / 364	6092 / 20 / 361
$R_1{}^a/wR_2{}^b$ ($I > 2\sigma(I)$)	0.0263 / 0.0591	0.0259 / 0.0618	0.0271 / 0.0644
R_1/wR_2 (all data)	0.0300 / 0.0606	0.0370 / 0.0643	0.0304 / 0.0657
GOF on F^2	1.109	1.032	1.172
Max/min (e $Å^{-3}$)	0.804 / -0.355	1.086 / -0.916	0.824 / -0.570

Table S3. Crystallographic Data and Structure Refinement Parameters for **11$_{CuEr}$** to **14$_{CuLu}$**.

Complex	**11$_{CuEr}$**	**12$_{CuTm}$**	**13$_{CuYb}$**	**14$_{CuLu}$**
Formula	$Cu_2Er_2C_{43}H_{52}N_{22}O_9$	$Cu_2Tm_2C_{43}H_{52}N_{22}O_9$	$Cu_2Yb_2C_{44}H_{56}N_{22}O_{10}$	$Cu_2Lu_2C_{44}H_{56}N_{22}O_{10}$
Mr ($gmol^{-1}$)	1482.67	1486.01	1526.27	1530.13
CCDC number	1060770	1060771	1060772	1060773
Crystal size(mm^3)	0.22×0.10×0.04	0.36×0.24×0.18	0.35×0.20 ×0.08	0.26×0.19×0.06
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	*C*2/*c*	*C*2/*c*	*P* $\bar{1}$	*P* $\bar{1}$
a (Å)	22.177(6)	22.168(4)	9.986(4)	9.993(11)
b (Å)	9.669(2)	9.6653(16)	10.816(4)	10.791(11)
c (Å)	25.894(7)	25.841(4)	13.393(5)	13.421(15)
α (˚)	90	90	100.436(6)	100.423(16)
β (˚)	109.798(3)	109.811(2)	91.137(6)	91.737(16)
γ (˚)	90	90	100.644(6)	100.596(15)
V ($Å^3$)	5224(2)	5209.1(15)	1395.9(10)	1396(3)
Z	4	4	1	1
T , K	293(2)	293(2)	293(2)	293(2)
ρ_{calcd}($g\ cm^{-3}$)	1.885	1.895	1.816	1.820
μ(Mo–*K*α) (mm^{-1})	4.059	4.255	4.145	4.331
F (000)	2920	2928	752	754
θ range (˚)	1.67 – 27.62	1.68 – 27.60	1.55 – 27.00	1.55 – 26.00
Refl. collected / unique	32568 / 6050	32402 / 6029	9079 / 6031	8148 / 5473
R(int)	0.0413	0.0295	0.0191	0.0258
T_{max}/T_{min}	0.8545 / 0.4687	0.5147 / 0.3096	0.7327 / 0.3248	0.7811 / 0.3989
Data/restraints/parameters	6050 / 20 / 361	6029 / 20 / 361	6031 / 69 / 384	5473 / 82 / 384
R_1[a]/wR_2[b] ($I > 2\sigma(I)$)	0.0297 / 0.0680	0.0308 / 0.0757	0.0323 / 0.0859	0.0397 / 0.0945
R_1/wR_2 (all data)	0.0356 / 0.0703	0.0333 / 0.0768	0.0383 / 0.0888	0.0539 / 0.1007
GOF on F^2	1.131	1.191	1.040	1.021
Max/min ($e\ Å^{-3}$)	0.800 / -0.540	0.836 / -0.731	1.074 / -0.984	1.776 / -0.955

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^1$

Table S4 Selected Bond Distances (Å) for $\mathbf{2}_{CuCe}$–$\mathbf{4}_{CuNd}$

	$\mathbf{2}_{CuCe}$	$\mathbf{3}_{CuPr}$	$\mathbf{4}_{CuNd}$
Ln1-O1	2.516(3)	2.492(2)	2.482(2)
Ln1-O2	2.471(3)	2.456(2)	2.442(2)
Ln1-O3	2.742(3)	2.723(3)	2.710(3)
Ln1-O4	2.686(4)	2.664(3)	2.642(3)
Ln1-N5	2.677(4)	2.659(3)	2.638(3)
Ln1-N8	2.598(5)	2.587(3)	2.581(3)
Ln1-N11	2.592(5)	2.575(4)	2.568(4)
Ln1-N14	2.433(5)	2.418(4)	2.486(3)
Ln1-N22#1	2.556(4)	2.542(3)	2.532(3)
Ln2-O5	2.491(3)	2.475(2)	2.461(2)
Ln2-O6	2.468(3)	2.451(2)	2.438(2)
Ln2-O7	2.630(3)	2.617(3)	2.613(2)
Ln2-O8	2.655(3)	2.643(3)	2.635(2)
Ln2-O9	2.559(3)	2.537(3)	2.518(2)
Ln2-N5	2.565(4)	2.556(3)	2.545(3)
Ln2-N8	2.654(4)	2.626(3)	2.608(3)
Ln2-N11	2.585(5)	2.574(4)	2.561(4)
Ln2-N17	2.469(5)	2.448(4)	2.435(3)
Cu1-O1	1.920(3)	1.919(3)	1.916(2)
Cu1-O2	1.911(3)	1.913(2)	1.913(2)
Cu1-N1	1.931(4)	1.929(3)	1.927(3)
Cu1-N2	1.943(4)	1.938(3)	1.938(3)
Cu1-N7	2.653(5)	2.647(5)	2.646(3)
Cu2-N3	1.964(4)	1.966(3)	1.973(3)
Cu2-N4	1.956(4)	1.960(3)	1.958(3)
Cu2-O5	1.959(3)	1.958(2)	1.961(2)
Cu2-O6	1.955(3)	1.956(2)	1.958(2)
Cu2-N13	2.814(5)	2.804(5)	2.802(4)
Cu2-N20	2.448(5)	2.453(4)	2.454(3)
Ln1···Cu1	3.5651(9)	3.5518(6)	3.5423(7)
Ln2···Cu2	3.5691(8)	3.5515(5)	3.5415(6)
Ln1···Ln2	4.0444(8)	4.0166(6)	3.9966(7)

Symmetry transformations used to generate equivalent atoms: #1 x+1, y, z

Table S5 Selected Bond Distances (Å) for $\mathbf{8}_{CuTb}$, $\mathbf{9}_{CuDy}$, $\mathbf{13}_{CuYb}$ and $\mathbf{14}_{CuLu}$

	$\mathbf{8}_{CuTb}$	$\mathbf{9}_{CuDy}$	$\mathbf{13}_{CuYb}$	$\mathbf{14}_{CuLu}$
Ln1-O1	2.343(4)	2.311(2)	2.287(3)	2.278(4)
Ln1-O2	2.360(4)	2.340(2)	2.304(3)	2.287(4)
Ln 1-N11#1	2.403(5)	2.370(3)	2.325(4)	2.313(5)
Ln1-N3	2.407(6)	2.395(3)	2.345(5)	2.353(7)
Ln1-N6	2.446(4)	2.456(3)	2.383(4)	2.374(6)
Ln1-N6#1	2.482(5)	2.401(3)	2.323(4)	2.337(5)

Ln1-O3	2.532(4)	2.513(2)	2.494(3)	2.481(5)
Ln1-O4	2.553(4)	2.532(2)	2.530(3)	2.517(5)
Cu1-O2	1.973(4)	1.962(2)	1.971(3)	1.968(4)
Cu1-O1	1.974(4)	1.967(2)	1.971(3)	1.956(4)
Cu1-N1	1.985(5)	1.970(3)	1.989(4)	1.978(6)
Cu1-N2	1.998(5)	1.980(3)	1.987(4)	1.979(6)
Cu1-N9	2.474(6)	2.468(3)	2.492(4)	2.510(7)
Ln1 ··Cu1	3.4901(10)	3.4579(9)	3.4363(11)	3.4224(27)
Ln1 ··Ln1#1	4.1154(11)	4.0572(10)	3.9467(13)	3.9622(37)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z.

Table S6 Selected Bond Distances (Å) for **6**$_{CuEu}$, **7**$_{CuGd}$, **10**$_{CuHo}$, **11**$_{CuEr}$ and **12**$_{CuTm}$

	6$_{CuEu}$	**7**$_{CuGd}$	**10**$_{CuHo}$	**11**$_{CuEr}$	**12**$_{CuTm}$
Ln1-O1	2.361(2)	2.352(2)	2.316(2)	2.303(2)	2.298(3)
Ln1-O2	2.353(2)	2.345(2)	2.306(2)	2.295(2)	2.287(3)
Ln1-O3	2.556(2)	2.547(2)	2.537(2)	2.532(3)	2.532(3)
Ln1-O4	2.520(2)	2.511(2)	2.494(2)	2.486(3)	2.489(3)
Ln1-N3	2.375(3)	2.371(3)	2.330(3)	2.321(4)	2.305(4)
Ln1-N6	2.455(3)	2.443(3)	2.369(3)	2.360(3)	2.330(4)
Ln1-N6#1	2.529(2)	2.511(2)	2.445(3)	2.440(3)	2.412(3)
Ln1-N11#1	2.407(3)	2.399(3)	2.360(3)	2.336(3)	2.328(4)
Cu1-O1	1.963(2)	1.964(2)	1.958(2)	1.957(2)	1.954(3)
Cu1-O2	1.969(2)	1.968(2)	1.967(2)	1.963(2)	1.963(3)
Cu1-N1	1.977(3)	1.976(3)	1.978(3)	1.974(3)	1.981(3)
Cu1-N2	1.979(3)	1.977(3)	1.982(3)	1.980(3)	1.980(3)
Cu1-N9	2.370(3)	2.368(3)	2.376(3)	2.378(4)	2.377(4)
Ln1 ··Cu1	3.4961(5)	3.4880(8)	3.4577(9)	3.4453(9)	3.4378(7)
Ln1 ··Ln1#1	4.1748(5)	4.1437(8)	4.0351(9)	4.0308(9)	3.9759(5)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2, -y+1/2, -z.

Table S7 The geometry analysis of **1**$_{CuLa}$ **-4**$_{CuNd}$ by SHAPE Software

Complex	Cu1 (SPY-5)	Cu2 (Oc-6)	Ln1 (CSAPR-9)	Ln1 (TCTPR-9)	Ln2 (MFF-9)	Ln2 (CSAPR-9)	Ln2 (TCTPR-9)
1$_{CuLa}$	1.978	2.323	**1.799**	1.816	**0.999**	1.113	1.819
2$_{CuCe}$	2.003	2.355	**1.776**	1.782	1.104	**1.067**	1.751
3$_{CuPr}$	1.982	2.327	1.720	**1.692**	**0.995**	1.024	1.698
4$_{CuNd}$	1.949	2.305	1.673	**1.612**	**0.981**	0.983	1.660

SPY-5: Spherical square pyramid (C_{4v}); OC-6: Octahedron (O_h); CSAPR-9: Spherical capped square antiprism (C_{4v}); TCTPR-9: Spherical tricapped trigonal prism (D_{3h}); MFF-9: Muffin (*C*s)

Table S8 The geometry analysis of **5**$_{CuSm}$ by SHAPE software

Complex	Cu1 (Oc-6)	Cu2 (SPY-5)	Ln1 (MFF-9)	Ln1 (CSAPR-9)	Ln2 (CSAPR-9)	Ln2 (TCTPR-9)
5$_{CuSm}$	2.972	1.111	**0.956**	1.197	**1.368**	1.378

Table S9 The geometry analysis of $\mathbf{6}_{CuEu}$-$\mathbf{14}_{CuLu}$ by SHAPE software

Complex	Cu1(SPY-5)	Ln1(TDD-8)	Ln1(BTPR-8)
$\mathbf{6}_{CuEu}$	0.942	**2.345**	2.481
$\mathbf{7}_{CuGd}$	0.939	**2.261**	2.422
$\mathbf{8}_{CuTb}$	1.183	2.189	**2.089**
$\mathbf{9}_{CuDy}$	1.218	2.182	**2.016**
$\mathbf{10}_{CuHo}$	0.982	**2.155**	2.309
$\mathbf{11}_{CuEr}$	0.977	**2.104**	2.285
$\mathbf{12}_{CuTm}$	0.986	**2.089**	2.218
$\mathbf{13}_{CuYb}$	1.281	2.114	**1.904**
$\mathbf{14}_{CuLu}$	1.315	2.109	**1.873**

SPY-5: Spherical square pyramid(C_{4v}); TDD-8: Triangular dodecahedron (D_{2d}); BTPR-8: Biaugmented trigonal prism (C_{2v}).

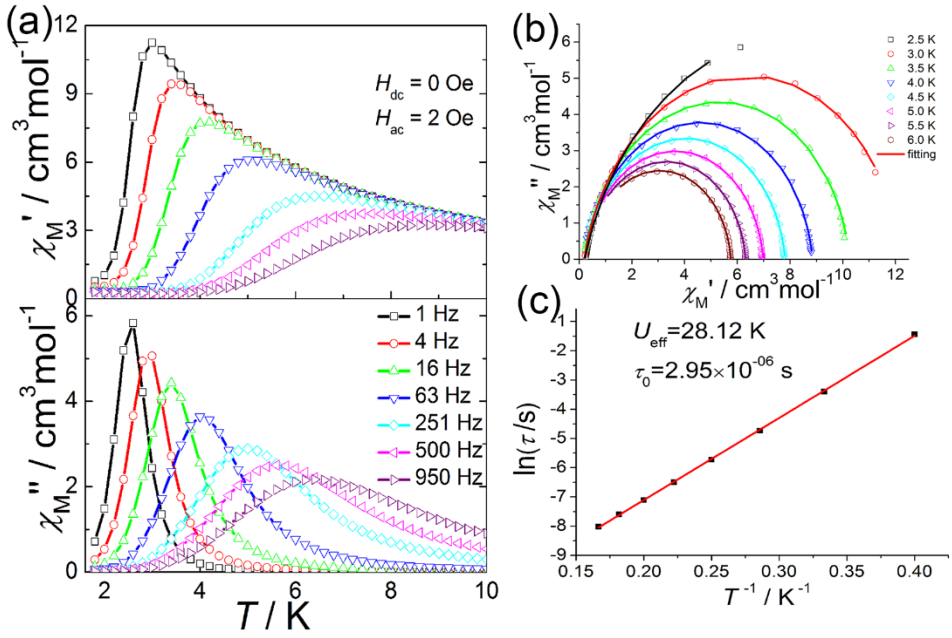

Fig. S1 (a) Temperature dependence of the in-phase (χ_M') and out-of phase (χ_M'') ac susceptibilities for $\mathbf{8}_{CuTb}$ under zero-dc field. **(b)** Cole-Cole plots of 8_{CuTb} measured under zero dc field from 3.0 to 6.0 K. The solid lines correspond to the best fit obtained with a generalized Debye model. **(c)** Relaxation time of the magnetization ln(τ) vs T^{-1} (Arrhenius plot) for $\mathbf{8}_{CuTb}$. The red line corresponds to the fit.

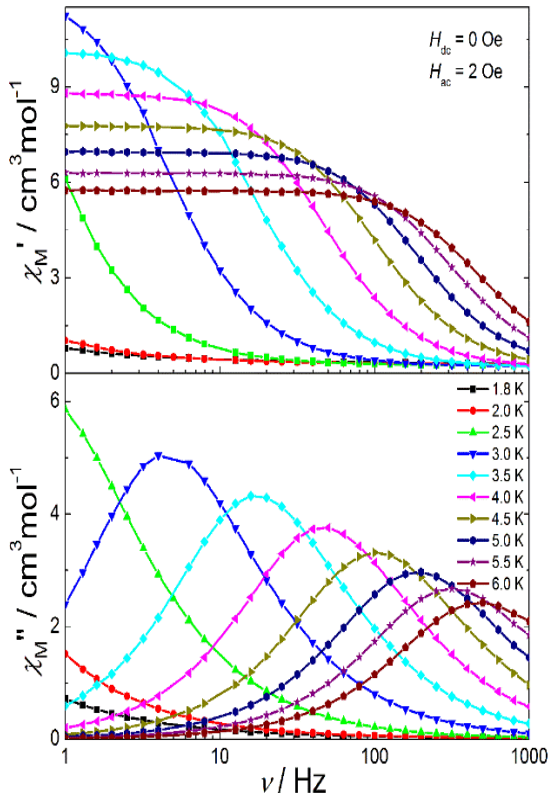

Fig. S2 Frequency dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibilities for $\mathbf{8}_{\mathbf{CuTb}}$. The data were measured under a 2 Oe *ac* field and a zero *dc* field.

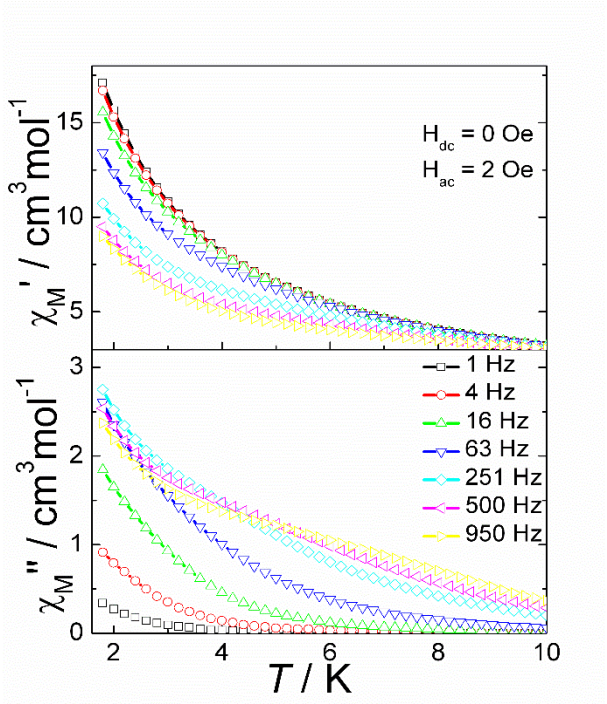

Fig. S3 Frequency dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibilities for $\mathbf{9}_{\mathrm{CuDy}}$. The data were measured under a 2 Oe *ac* field and a zero *dc* field.

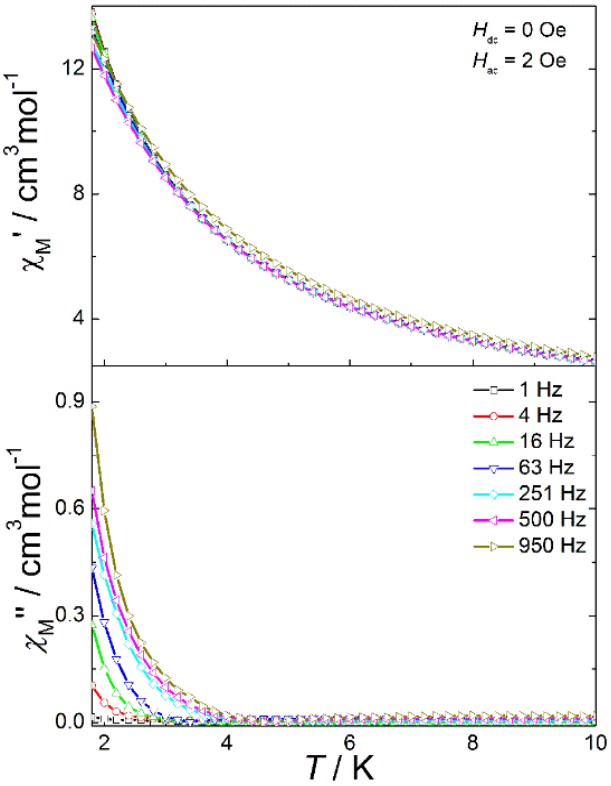

Fig. S4 Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibilities for $\mathbf{10}_{CuHo}$. The data were measured under a 2 Oe *ac* field and a zero *dc* field.

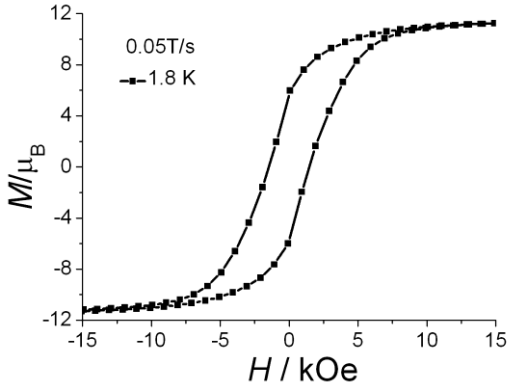

Fig. S5 The hysteresis loops of $\mathbf{8}_{CuTb}$ measured on the powder samples on a conventional SQUID VSM at 1.8 K and field sweep-rate of 0.05 T/s.

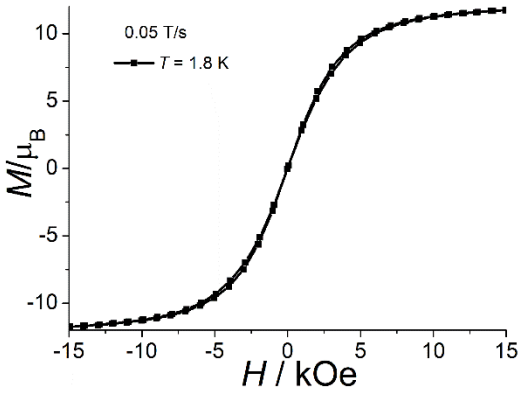

Fig. S6 The hysteresis loops of $\mathbf{9}_{CuDy}$ measured on the powder samples on a conventional SQUID VSM at 1.8 K and field sweep-rate of 0.05 T/s.

Table S10 Relaxation Fitting Parameters from the Least-Square Fitting of the Cole-Cole plots of $\mathbf{8}_{CuTb}$ according to the Generalized Debye Model

Temperature / K	χ_S / $cm^3mol^{-1}K$	χ_T / $cm^3mol^{-1}K$	τ / s	α
3.0	0.19984	12.19104	0.03346	0.10598
3.5	0.19031	10.2464	0.00883	0.09245
4.0	0.17688	8.84795	0.00325	0.08718
4.5	0.17887	7.81119	0.0015	0.08471
5.0	0.19836	6.98283	8.2E-4	0.08046
5.5	0.22775	6.30991	5E-4	0.076
6.0	0.29686	5.75563	3.3E-4	0.06909

Table S11 Relaxation Fitting Parameters from the Least-Square Fitting of the Cole-Cole plots of $\mathbf{9}_{CuDy}$ according to the Generalized Debye Model

Temperature / K	χ_S / $cm^3mol^{-1}K$	χ_T / $cm^3mol^{-1}K$	τ / s	α
1.8	4.89922	17.59408	0.00101	0.46291
2.0	4.59992	15.95	9.5E-4	0.45141
2.5	3.99988	12.99984	8.3E-4	0.42557
3.0	3.54686	10.97092	7E-4	0.40085
3.5	3.19989	9.39988	5.6E-4	0.36313
4.0	3.04974	8.19993	4.6E-4	0.32036
4.5	2.85	7.3	3.8E-4	0.29389
5.0	2.67487	6.57912	3.1E-4	0.27778
5.5	2.55	5.94997	2.6E-4	0.25594
6.0	2.2929	5.47005	2.1E-4	0.2663