Electronic Supplementary Information (ESI) for

Enhancement of magnetic relaxation properties with 3d diamagnetic cations in [$Zn^{II}Ln^{III}$] and [$Ni^{II}Ln^{III}$], Ln^{III} = Kramers lanthanides.

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Table S1. Crystallographic collection data for complexes **1*RR*** and **1*SS***.

Parameter	**1*RR***	**1*SS***
Formula	$C_{30}H_{26}EuN_5NiO_{13}$	$C_{30}H_{26}EuN_5NiO_{13}$
FW / g mol^{-1}	875.23	875.23
Crystal system	Monoclinic	Monoclinic
Space group	*C*2	*C*2
a / Å	19.125(1)	19.098(1)
b / Å	15.5700(8)	15.5383(7)
c / Å	22.084(1)	22.039(1)
α / °	90	90
β / °	99.096(2)	99.059(2)
γ / °	90	90
V / Å^3	6493.4(6)	6458.5(6)
Z	8	8
T / K	100.0(2)	100.0(2)
ρ_{calc} / g cm^{-3}	1.791	1.800
μ / mm^{-1}	2.569	2.583
θ range / °	2.016 - 30.603	2.160 - 26.448
Index ranges	$-27 \leq h \leq 27$	$-23 \leq h \leq 23$
	$-22 \leq k \leq 22$	$-19 \leq k \leq 18$
	$-31 \leq l \leq 31$	$-27 \leq l \leq 27$
Collected reflections	98906	40759
Independent reflections	19717 (R_{int} = 0.0700)	13171 (R_{int} = 0.0422)
Flack parameter	0.13(2)	0.01(2)
Final $R^{b,c}$ indices [I>2σ(I)]	$R1$ = 0.0387	$R1$ = 0.0313
	w$R2$ = 0.0991	w$R2$ = 0.0714
$(\Delta\rho)_{max,min}$ / e Å^{-3}	1.956, -1.203	1.038, -0.959

Table S2. Crystallographic collection data for **2*RR***, **2*SS***, **2*SS-b*** and **2*SS-c***.

Parameter	**2*RR***	**2*SS***	**2*SS*-b**	**2*SS*-c**
Formula	$C_{32}H_{34}EuN_5O_{15}Zn$	$C_{32}H_{34}EuN_5O_{15}Zn$	$C_{63}H_{64}Eu_2N_{10}O_{29}Zn_2$	$C_{30}H_{30}EuN_5O_{15}Zn$
FW / g mol^{-1}	945.97	945.97	1859.90	917.92
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P21*	*P21*	*P21*	*P21*
a / Å	9.2811(4)	9.2850(6)	9.209(1)	9.062(1)
b / Å	16.2336(8)	16.239(1)	16.418(3)	17.159(2)
c / Å	23.407(1)	23.453(2)	23.140(4)	22.414(2)
α / º	90	90	90	90
β / º	95.232(2)	95.284(2)	95.496(6)	97.001(4)
γ / º	90	90	90	90
V / Å^3	3512.0(3)	3521.2(4)	3482	3459.1(6)
Z	4	4	2	4
T / K	100.0(2)	100.0(2)	100(2)	100.0(2)
ρ_{calc} / g cm^{-3}	1.789	1.784	1.774	1.763
μ / mm^{-1}	2.532	2.526	2.551	2.568
θ range / °	2.151 - 30.592	2.148 - 30.558	2.160-25.943	2.544-30.539
Index ranges	$-13 \leq h \leq 12$	$-11 \leq h \leq 13$	$-10 \leq h \leq 11$	$-12 \leq h \leq 10$
	$-23 \leq k \leq 23$	$-23 \leq k \leq 23$	$-20 \leq k \leq 20$	$-24 \leq k \leq 23$
	$-33 \leq l \leq 33$	$-33 \leq l \leq 33$	$-28 \leq l \leq 27$	$-31 \leq l \leq 31$
Coll. Reflections	149772	117630	31197	42189
Indep. Reflections	21530	21475	12529	18446
	(R_{int} = 0.0682)	(R_{int} = 0.0308)	(R_{int} = 0.0956)	(R_{int} = 0.0592)
Flack parameter	0.015(5)	0.017(9)	0.29(4)	0.14(2)
Final $R^{b,c}$ indices	$R1$ = 0.0359	$R1$ = 0.0281	$R1$ = 0.0737	$R1$ = 0.0435
[I>2σ(I)]	w$R2$ = 0.0667	w$R2$ = 0.0662	w$R2$ = 0.1773	w$R2$ = 0.0996
$(\Delta\rho)_{max,min}$ / e Å^{-3}	0.991, -1.374	0.968, -2.201	3.731, -2.214	2.672, -2.547

Table S3. SHAPE CShM parameters for the A-molecule of complexes **1*RR*** and **2*SS*-c**. The topology for both complexes is intermediate to JSPC-10, SDD-10 and TD-10

			1*RR*	**2*SS*c**
DP-10	D10h	Decagon	36.370	36.223
EPY-10	C9v	Enneagonal pyramid	23.701	25.930
OBPY-10	D8h	Octagonal bipyramid	16.198	15.675
PPR-10	D5h	Pentagonal prism	8.931	11.193
PAPR-10	D5d	Pentagonal antiprism	9.812	12.382
JBCCU-10	D4h	Bicapped cube J15	9.216	10.237
JBCSAPR-10	D4d	Bicapped square antiprism J17	5.134	4.682
JMBIC-10	C2v	Metabidiminished icosahedron J62	6.146	7.348
JATDI-10	C3v	Augmented tridiminished icosahedron J64	17.626	19.313
JSPC-10	C2v	Sphenocorona J87	***3.241***	***3.360***
SDD-10	D2	Staggered Dodecahedron (2:6:2)	***4.578***	***3.438***
TD-10	C2v	Tetradecahedron (2:6:2)	***4.219***	***2.782***
HD-10	D4h	Hexadecahedron (2:6:2) or (1:4:4:1)	6.119	6.986

Table S4. Selected bond parameters for the A-molecule of **2*SS*-b**.

Eu(1)-O(1)	2.60(2)	Zn(1)-N(1)	2.10(2)
Eu(1)-O(2)	2.41(1)	Zn(1)-N(2)	2.02(2)
Eu(1)-O(3)	2.34(1)	Zn(1)-O(2)	1.96(1)
Eu(1)-O(4)	2.69(2)	Zn(1)-O(3)	2.08(1)
Eu(1)-O(5)	2.48(2)	Zn(1)-O(14)	2.06(2)
Eu(1)-O(6)	2.41(2)	Zn(1)-O(2)-Eu(1)	106.9(6)
Eu(1)-O(8)	2.57(2)	Zn(1)-O(3)-Eu(1)	105.7(6)
Eu(1)-O(9)	2.41(1)	Zn(1)···Eu(1)	3.519(3)
Eu(1)-O(11)	2.52(2)		
Eu(1)-O(12)	2.49(2)		

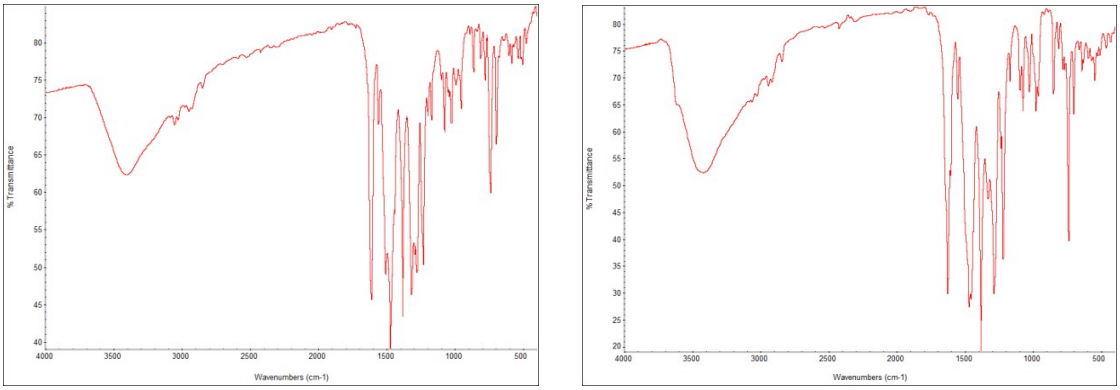


Fig. S1 IR spectra for the for the representative [$Ni^{II}Eu^{III}$] complexes **1** (left) and [$Zn^{II}Eu^{III}$] **2** (rigth). The spectra are similar but not identical due to the different conformation of the phenyl rings of the ligands.

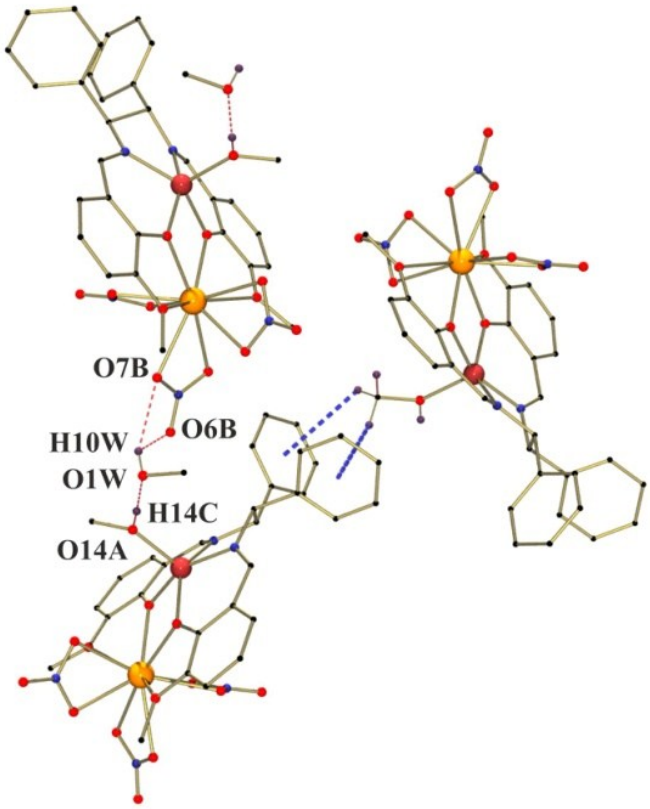


Fig. S2 Intermolecular interactions for complex **2*SS***: 1-D arrangement of H-bonds and interchain CH-π(ring) contacts.

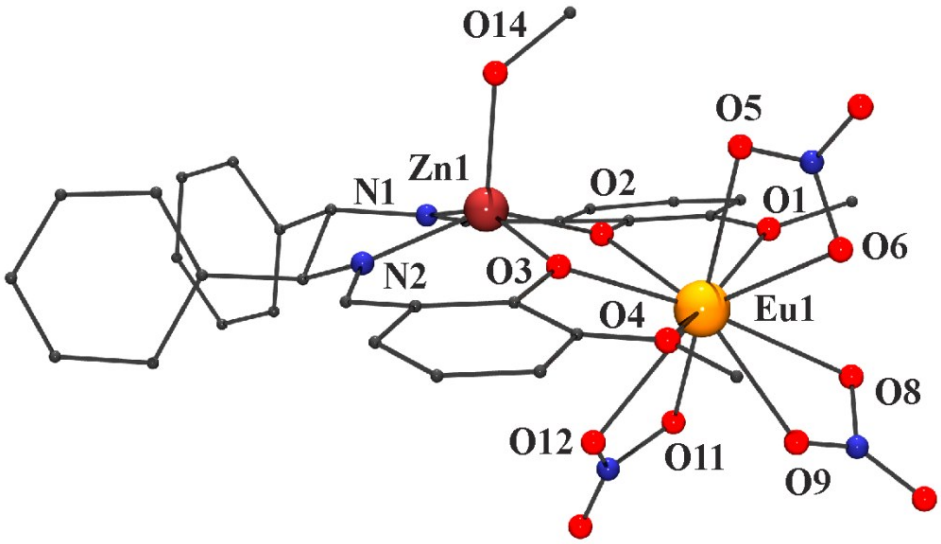


Fig. S3 Labelled view of the A-molecule of structure **2*SS*b**. At molecular level is practically identical to the structure of the fresh crystal **2*SS***. The main differences are found in the intermolecular interactions.

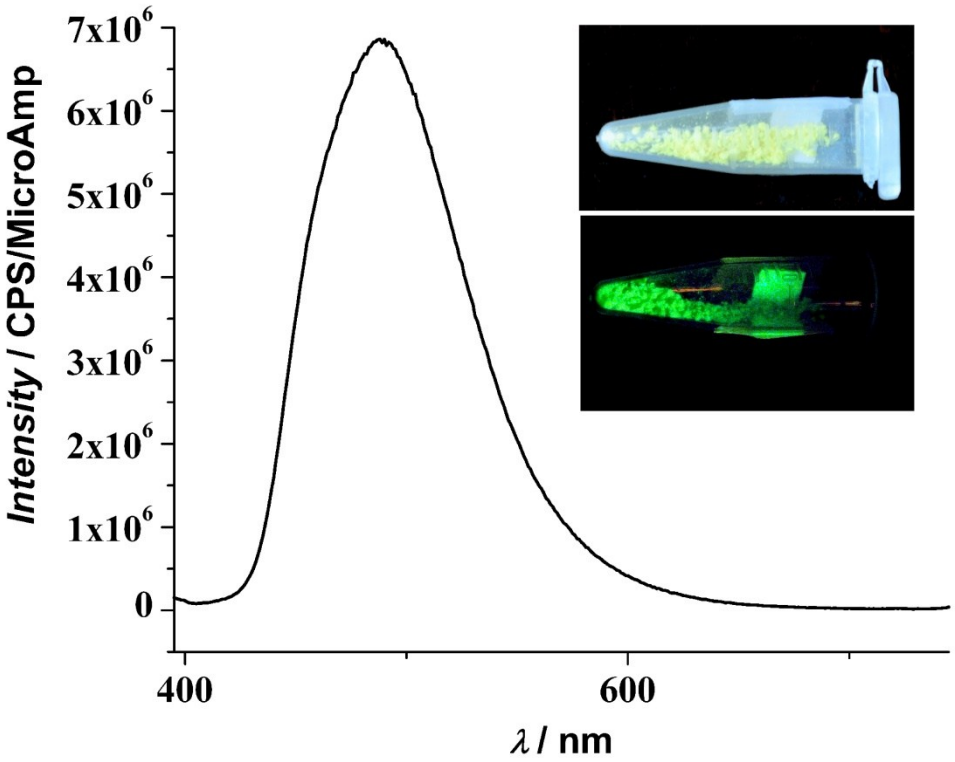


Fig. S4 Emission spectrum for the mononuclear precursor [$Zn^{II}L$]. Inset, the sample under white and UV (400 nm) lamp.

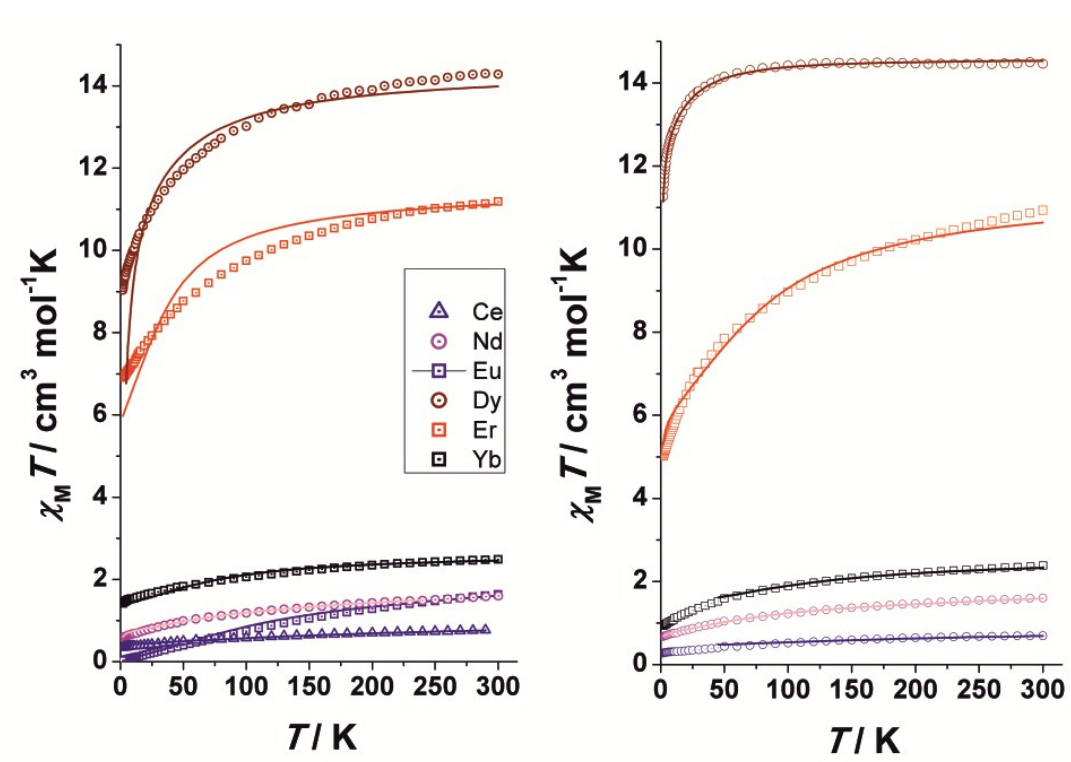


Fig. S5 $\chi_M T$ product vs. Temperature for the [Ni^{II}Ln^{III}] (left) and [Zn^{II}Ln^{III}] compounds (right). Solid lines show the best simulation.

In our opinion the absolute fit values must be assumed with large caution, but allowed us to give a reliable indication about the sign of Δ, profiting that different Δ sign gives clearly different shaped $\chi_M T$ vs temperature curves, Fig. S5.[27]

$\Delta > 0$ means that the smallest value of M_J corresponds to the lowest energy state, and so, the lowest spin-orbit $\pm M_J$ states (±1/2 for Kramers ions) will be the ground one, while the opposite for $\Delta < 0$. Reasonable fits of the experimental data were reproduced for negative Δ values for Dy^{III} complexes and positive ones for Ce^{III}, Nd^{III}, Er^{III} and Yb^{III}. Although in low symmetry environment, different M_J values can be mixed, and this is probably the reason why the lanthanide Kramers cations with a large number of M_J mixed states have more discrepancies with the fitting Hamiltonian (Dy^{III} and Er^{III}). The method seems to provide a simple alternative to approach the lowest M_J state.

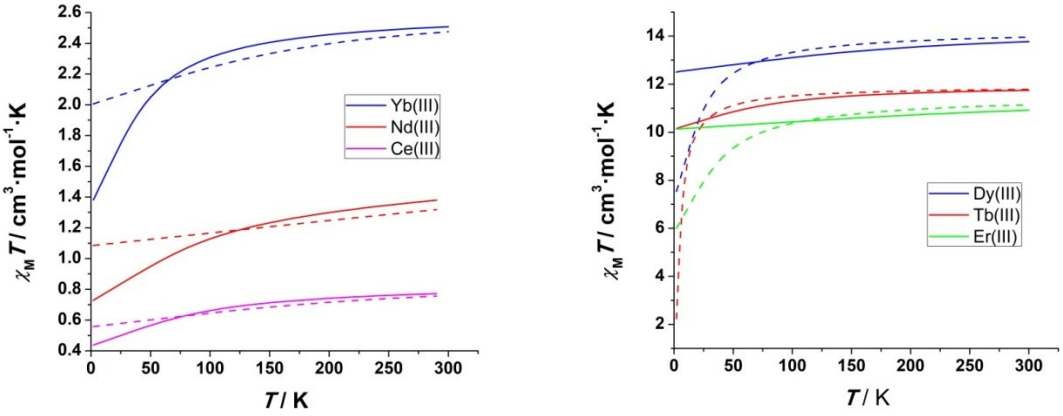


Fig. S6 Simulated $\chi_M T$ plots for a mononuclear Ln^{III} for Δ = +25 cm^{-1} (solid lines) and Δ = -25 cm^{-1} (dotted lines).

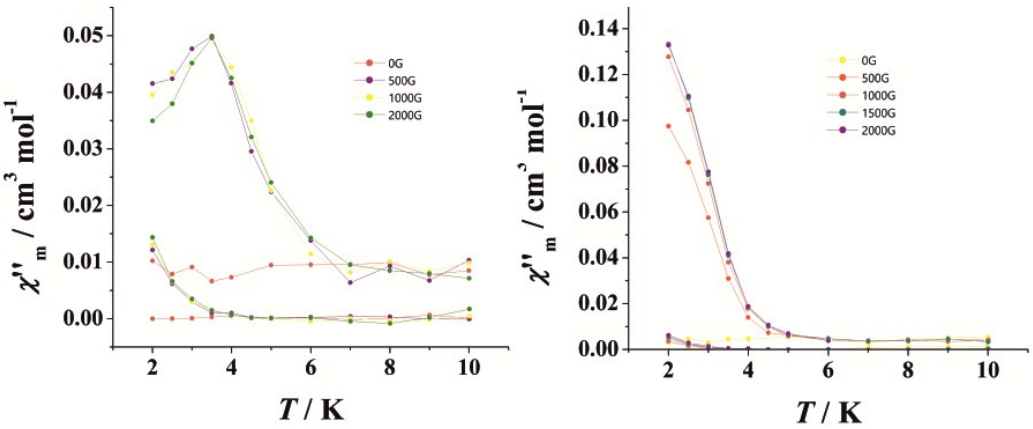
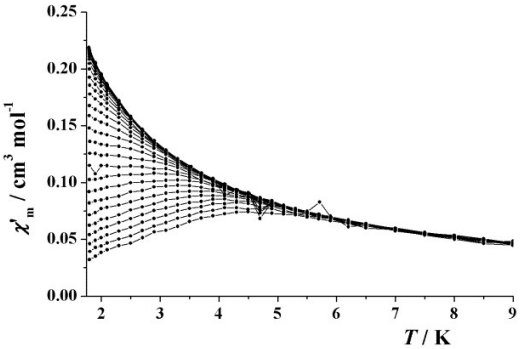
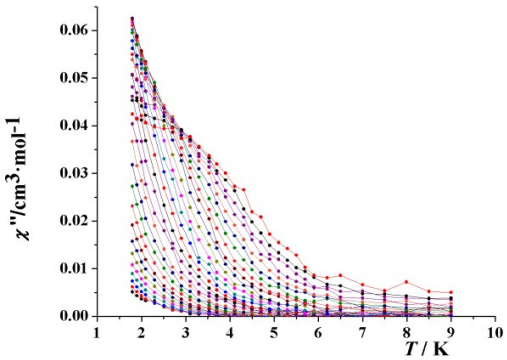


Fig. S7 AC measurements for the [ZnCe] complex **8** (left) and the [NiNd] complex **4** (right) at variable field. The field that gives the maximum dependence of the ac signal was selected in all cases to perform the complete measurements.

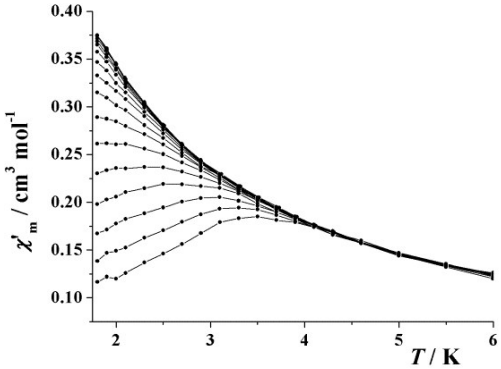
χ'_M *vs. T*	χ''_M *vs. T*

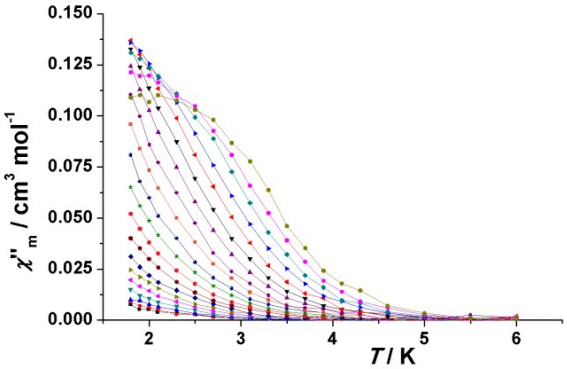
[$Ni^{II}Ce^{III}$] (**3*RR***)



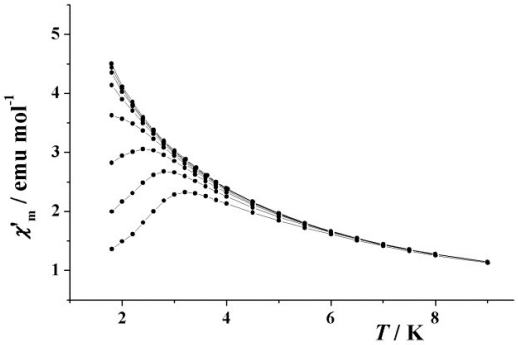


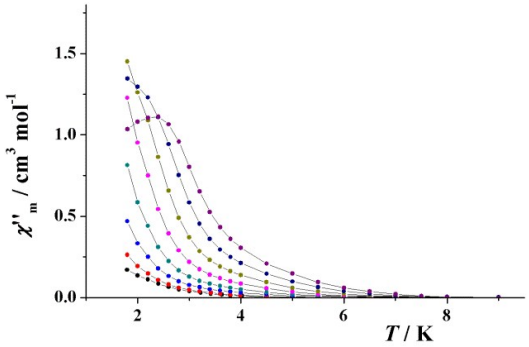
[$Ni^{II}Nd^{III}$] (**4*RR***)



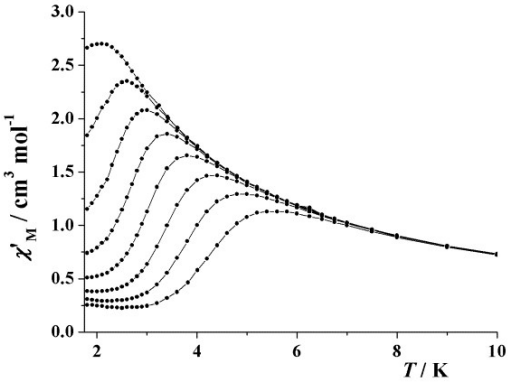


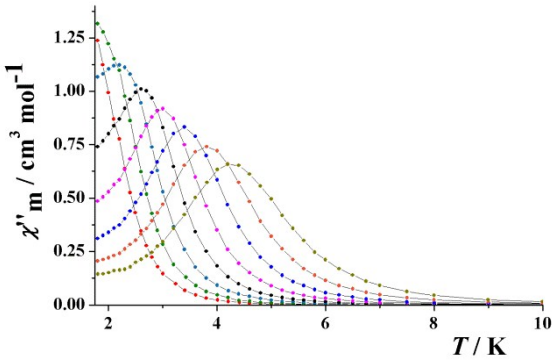
[$Ni^{II}Dy^{III}$] (**5*RR***)





[$Ni^{II}Er^{III}$] (**6*SS***)





[$Ni^{II}Yb^{III}$] (**7*SS***)

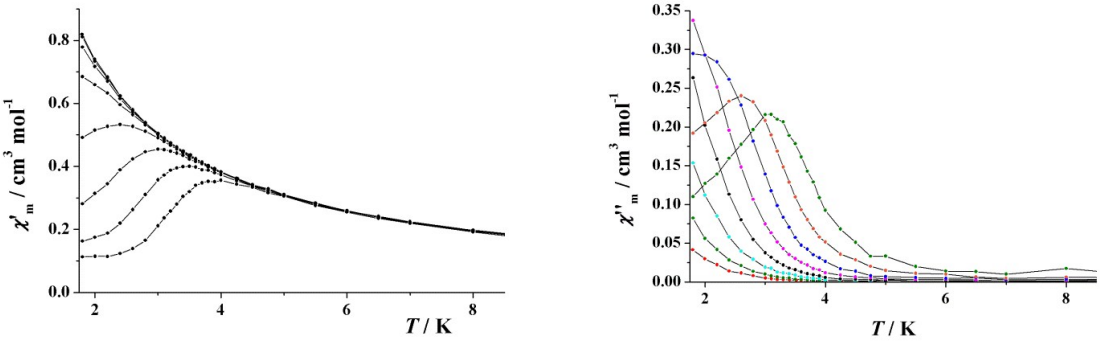


Fig. S8 χ_M' and χ_M" vs. *T* plots for the [$Ni^{II}Ln^{III}$] complexes **3** -**7**.

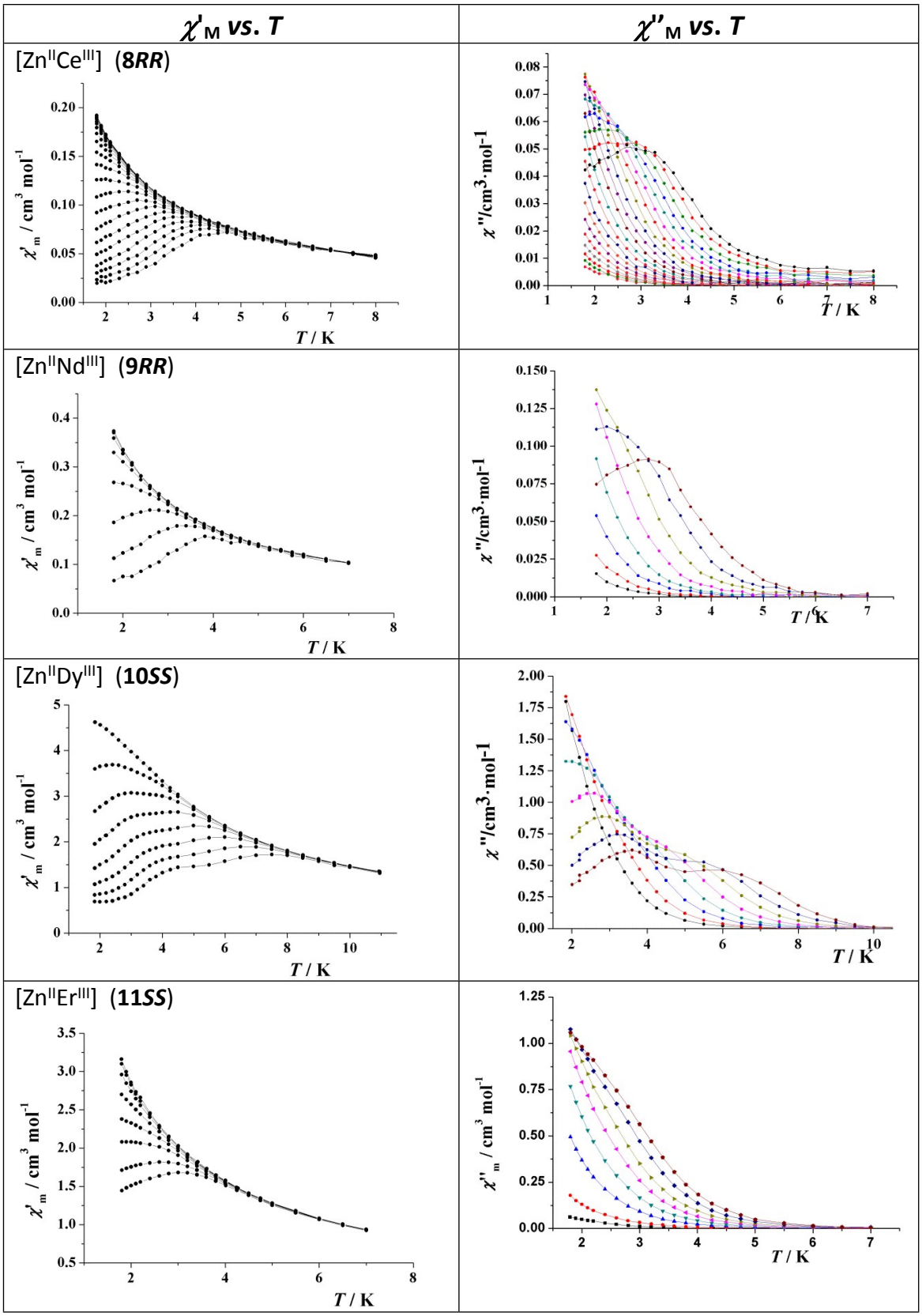


Fig. S9 χ_M' and χ_M" vs. *T* plots for the [$Zn^{II}Ln^{III}$] complexes **8** -**11**. Complex [$Zn^{II}Yb^{III}$] (**12**) do not shows ac response.

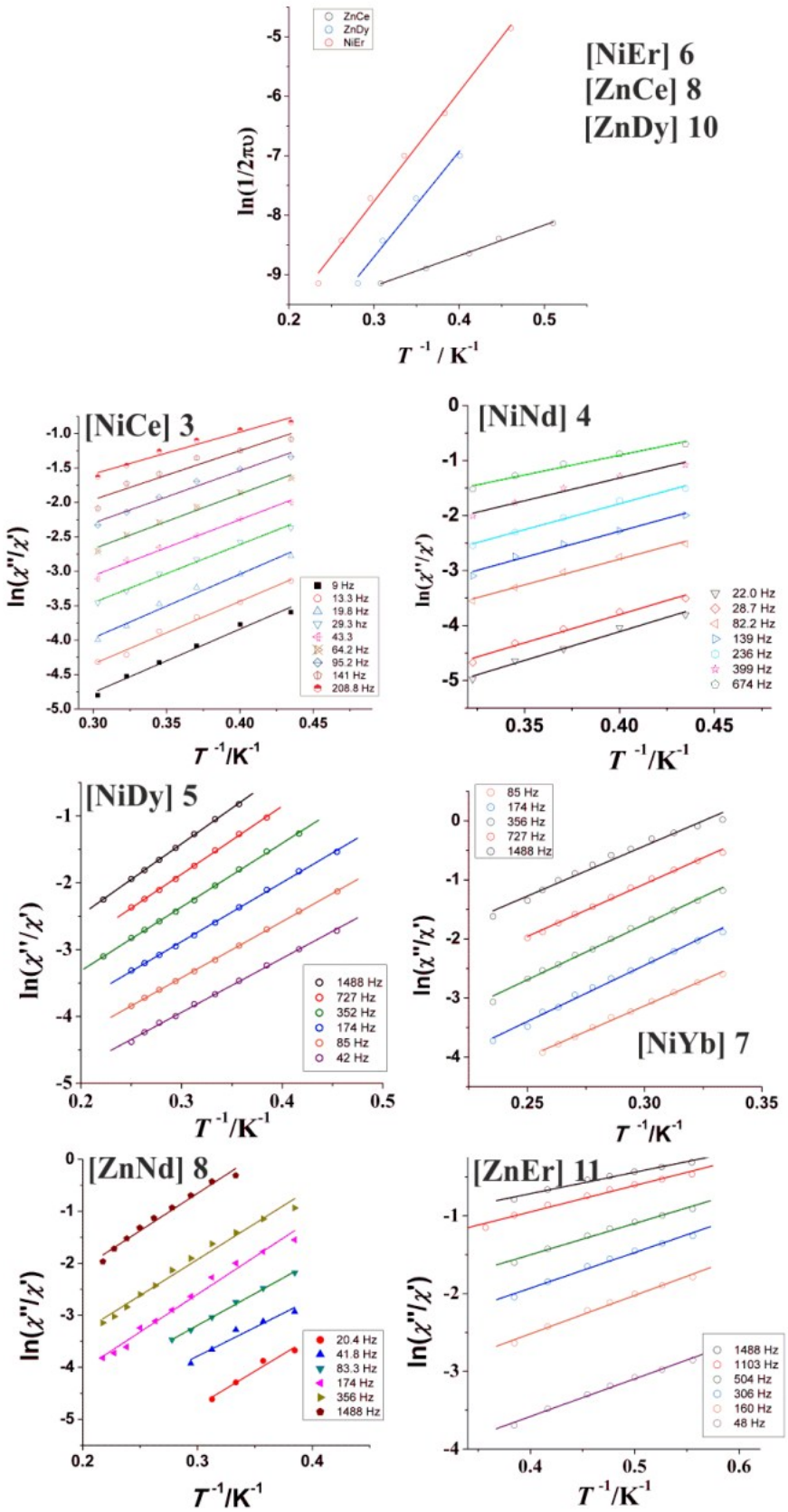


Fig. S10 Fit of the ac data for complexes **6**, **8** and **10** ($\ln(1/(2\pi\omega) = \ln(1/\tau_0) - U_{eff}/(k_B T)$) and for **3**, **4**, **5**, **8** and **11** ($\ln(\chi_M''/\chi_M') = \ln(\omega\tau_0) - U_{eff}/(k_B T)$).

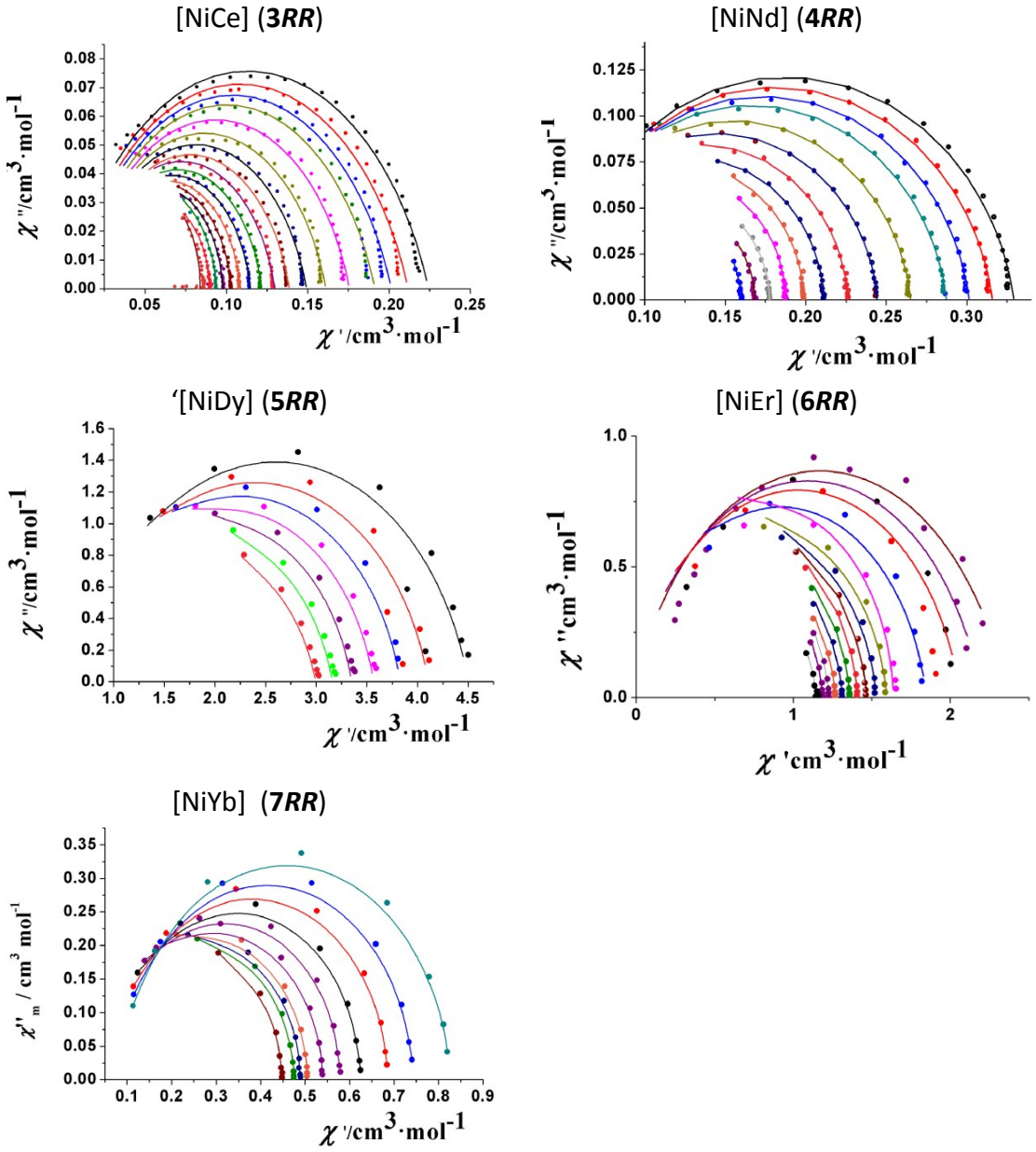


Fig. S11 Cole-Cole plots for the [$Ni^{II}Ln^{III}$] complexes **3** -**7** measured in the temperature range 1.8-4.5K. The solid lines represent the best fit.

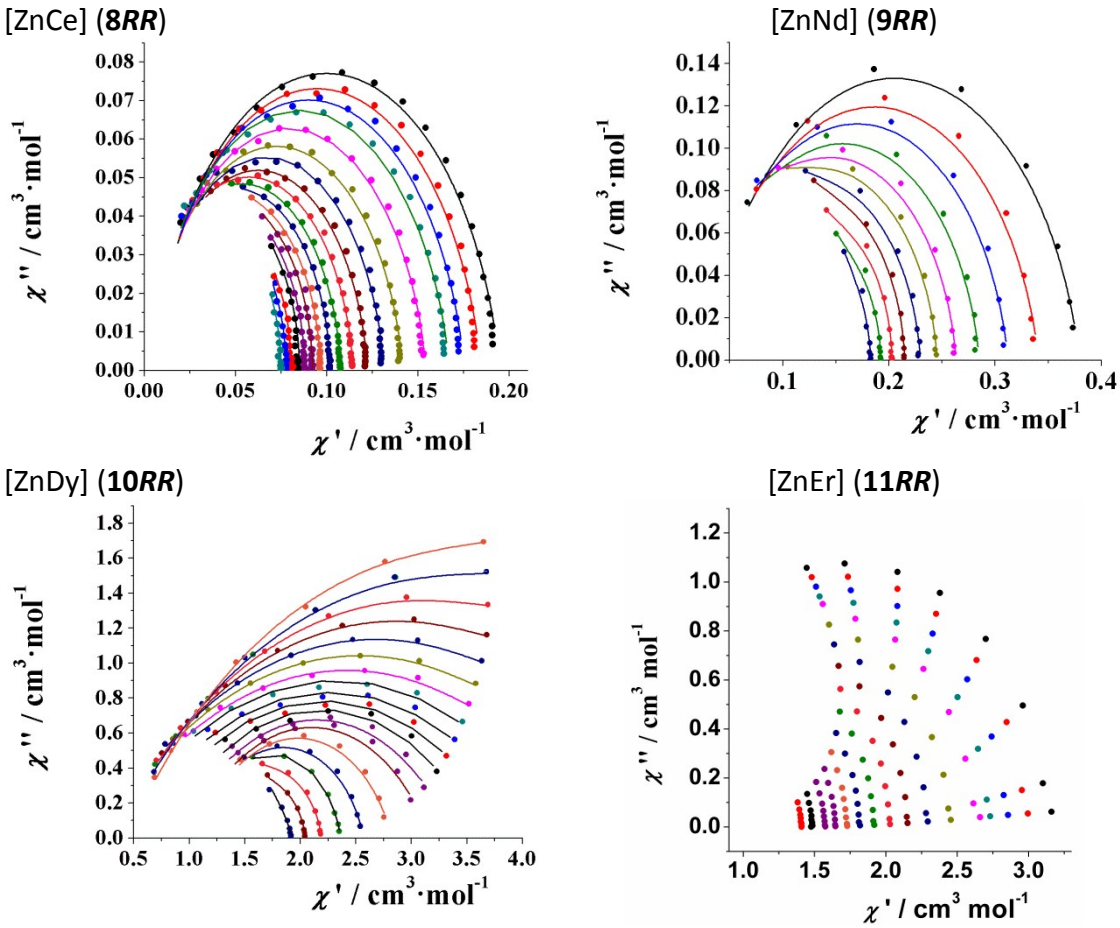


Fig. S12. Cole-Cole plots for the [$Zn^{II}Ln^{III}$] complexes **8 -11.** measured in the temperature range 1.8-4.5K. The solid lines represent the best fit except for **10** that are eye guide. Data for complex [$Zn^{II}Er^{III}$] (**11**) is not enough to fit the data and complex [$Zn^{II}Yb^{III}$] (**12**) do not shows ac response.

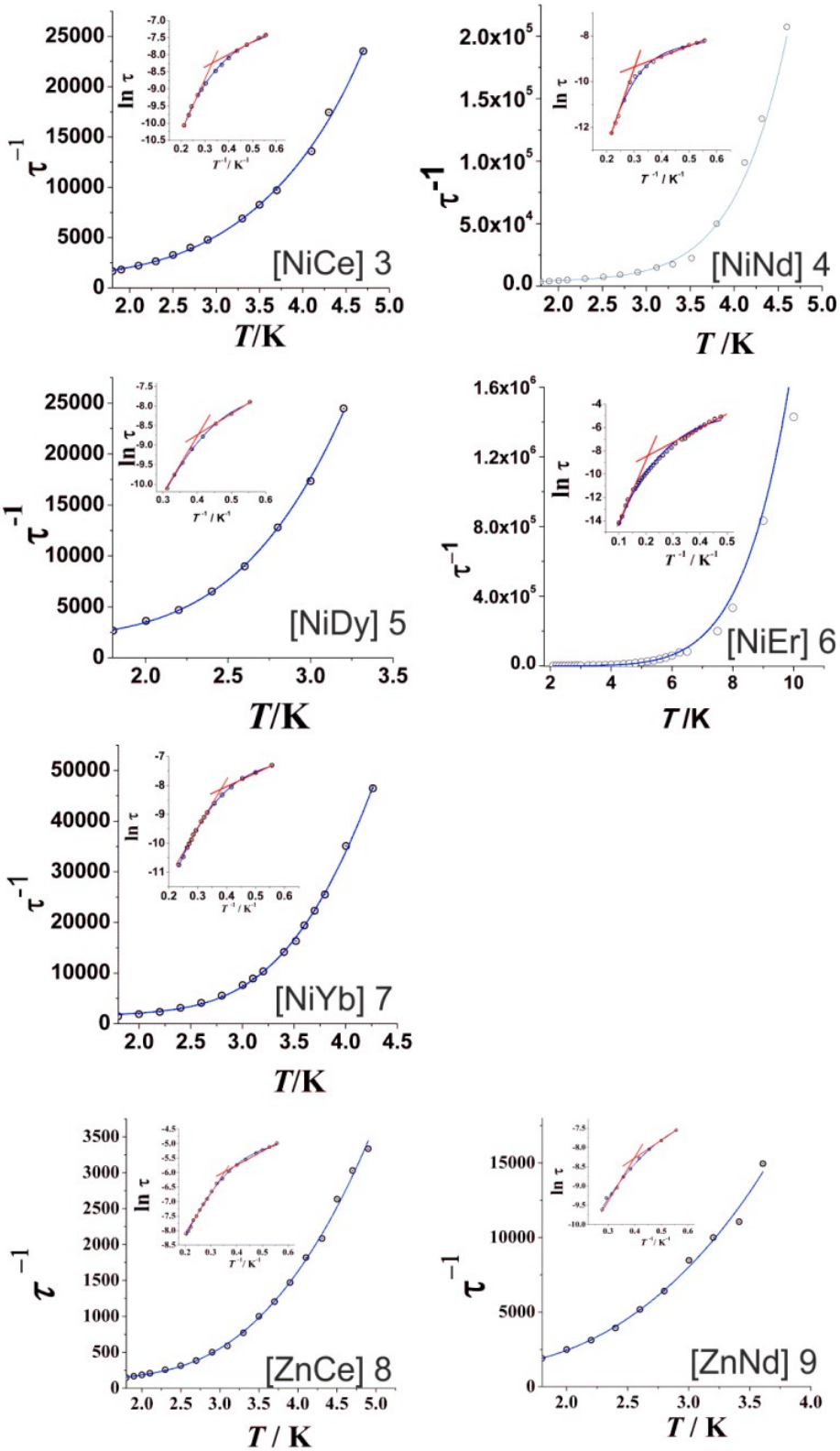


Fig. S13 Dependency of the spin-lattice relaxation temperature obtained from Cole-Cole plots under static dc field as τ-1 vs. T or ln(τ) vs T^{-1} (inset). The n values for the term BT^n lies between 6.5-9.1 for all complexes and in agreement with the calculated values by Arrhenius or Debye methods, τ_0 are comprised between 10^{-5}-10^{-7}.