Electronic Supplementary Material (ESI) for Dalton Transactions

ELECTRONIC SUPPORTING INFORMATION

for

"A family of 13 tetranuclear zinc(II)-lanthanide(III) complexes of a [3+3] Schiff-base macrocycle derived from 1,4-diformyl-2,3-dihydroxybenzene"

Humphrey L. C. Feltham, Frederik Klöwer, Scott A. Cameron, David S. Larsen, Yanhua Lan, Manuel Tropiano, Stephen L. Faulkner, Annie K. Powell and Sally Brooker**

A note on disorder modeling in $[Zn_3Pr(\mathbf{L}^{Pr})(NO_3)_2(DMF)_3](NO_3)\cdot 0.45DMF$: Two of the three aliphatic propylene linkages are disordered. In one linkage, the central carbon is disordered over two sites labelled C21 and C81 with 0.75 and 0.25 occupancy, respectively. Carbon atoms C20 and C22 are not disordered but the hydrogens on these atoms are partitioned so as to avoid using EADP/EXYZ commands. In the other propylene linkage, two of the carbon atoms are disordered; one atom is split into C32 and C82 (0.6 and 0.4 occupancy, respectively) and the second disordered atom is split into C33 and C83 (0.6 and 0.4 occupancy, respectively). Carbon atom C31 is not disordered but the attached hydrogen atoms are again partitioned to avoid EADP/EXYZ. The non-coordinated solvent DMF molecule is disordered two over intertwinned two positions that do not share a common atom. The positions have 0.4 and 0.5 occupancies given an average occupancy of 0.45.

NMR Data

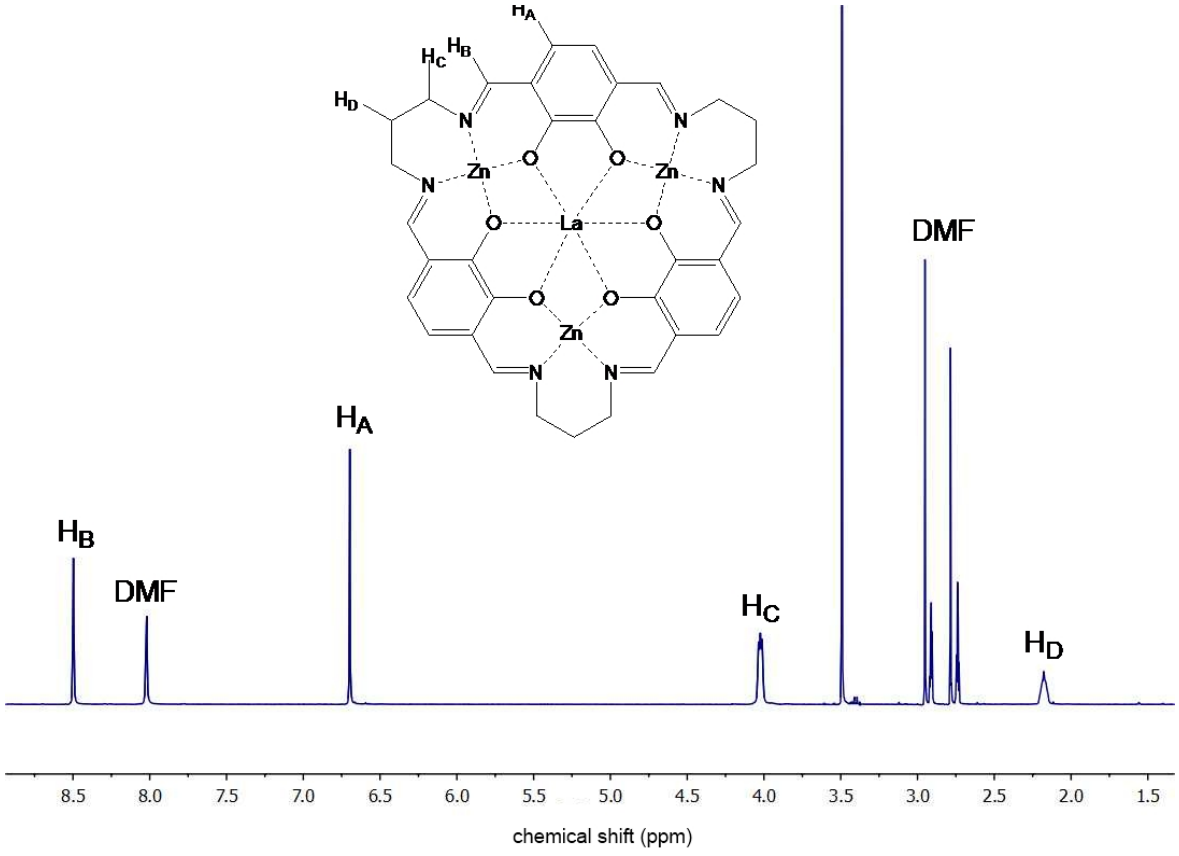

Figure S1. ^{1}H NMR spectrum of $Zn_3La(\mathbf{L}^{Pr})(NO_3)_2(MeOH)_3(NO_3)\cdot MeOH\cdot H_2O$ (dired under vacuum prior to measurement) in DMF-d_7.

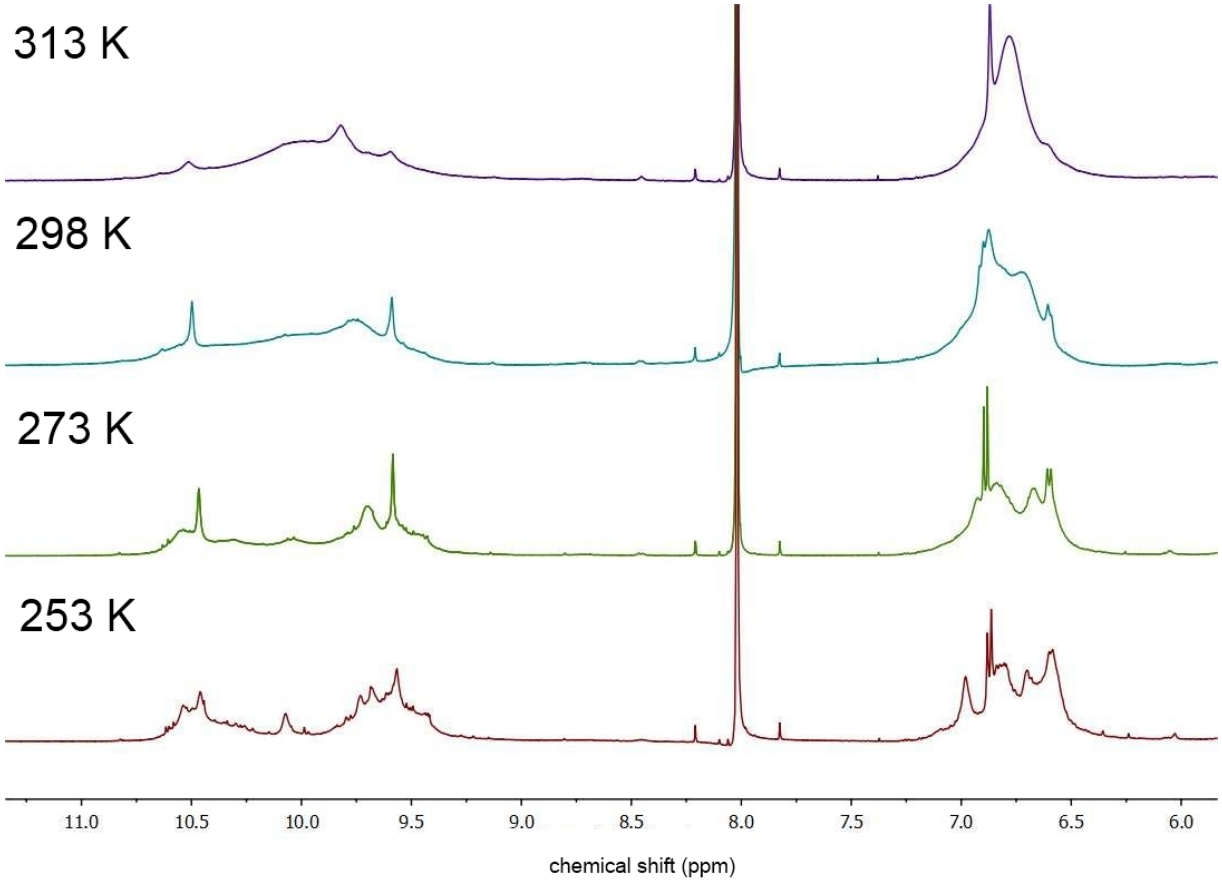

Figure S2. ^{1}H NMR spectrum of $[Zn_5(\mathbf{L^1})_5(H_2O)_6]\cdot 3H_2O$ (dired under vacuum prior to measurement) in DMF-d_7 at the temperatures indicated.

Magnetic data

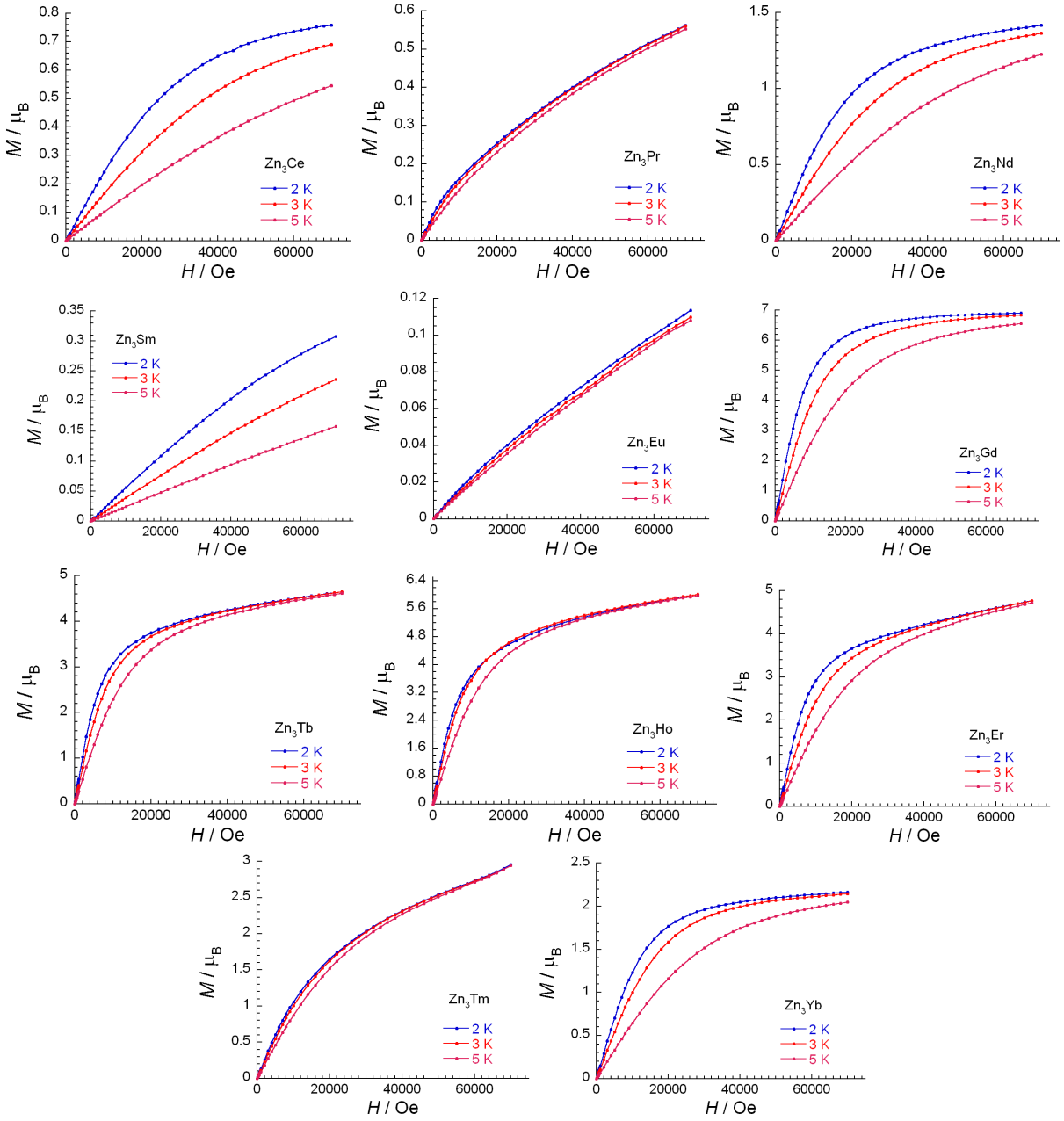

Figure S3. Field dependence of magnetization for $Zn_3Ln(\mathbf{L}^{Pr})(NO_3)_3 \cdot x$solvents complexes.

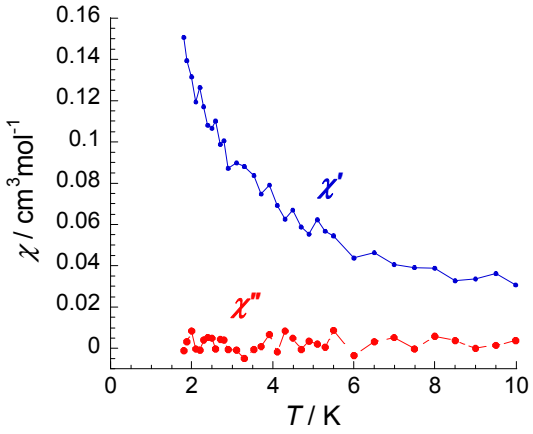

Figure S4. The in-phase (χ') and out-of-phase (χ'') components of the ac susceptibility of $Zn_3Gd(\mathbf{L}^{Pr})(NO_3)_3\cdot 3MeOH$ in a 1000 Hz field, illustrative of the dynamic behavior of the $Zn_3Ln(\mathbf{L}^{Pr})(NO_3)_3\cdot x$solvents complexes (Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Tm or Yb) in zero dc field.

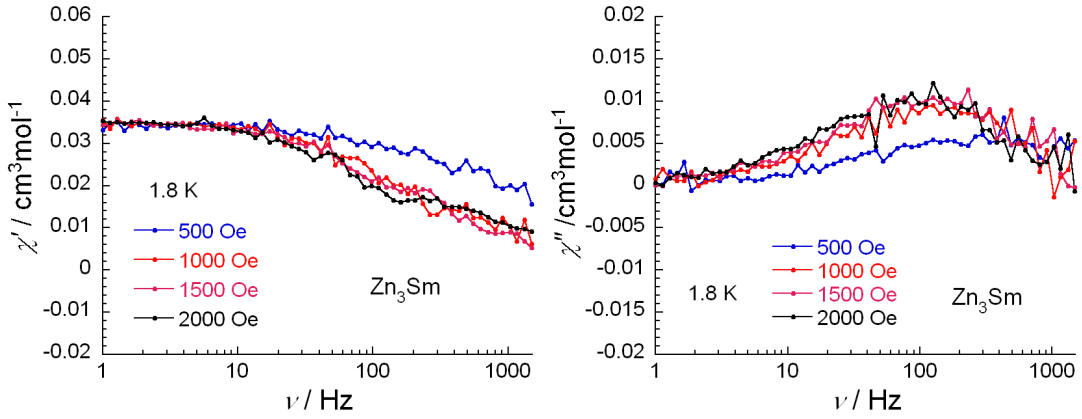

Figure S5. (Left) Frequency dependence of the in-phase component of ac susceptibility of $Zn_3Sm(\mathbf{L}^{Pr})(NO_3)_3\cdot 3MeOH\cdot 3H_2O$ with the external dc fields indicated. (Right) Frequency dependence of the out-of-phase component

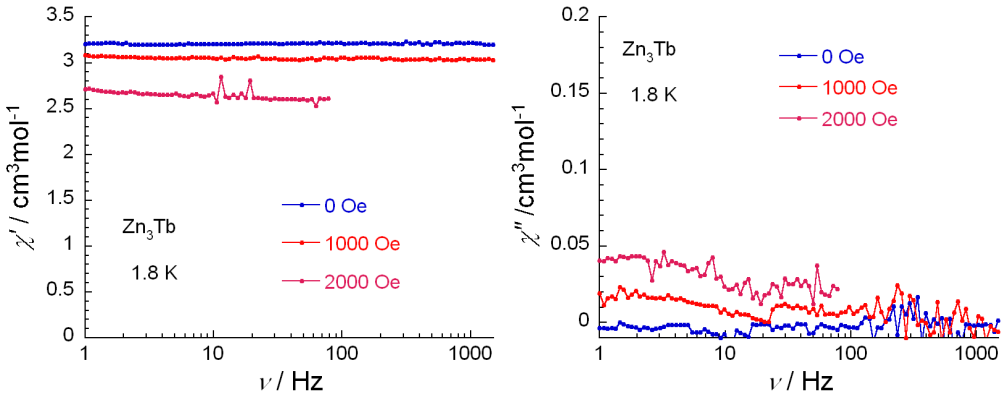

Figure S6. (Left) Frequency dependence of the in-phase component of ac susceptibility of $Zn_3Tb(\mathbf{L}^{Pr})(NO_3)_3\cdot 3MeOH\cdot H_2O$ with the external dc fields indicated. (Right) Frequency dependence of the out-of-phase component

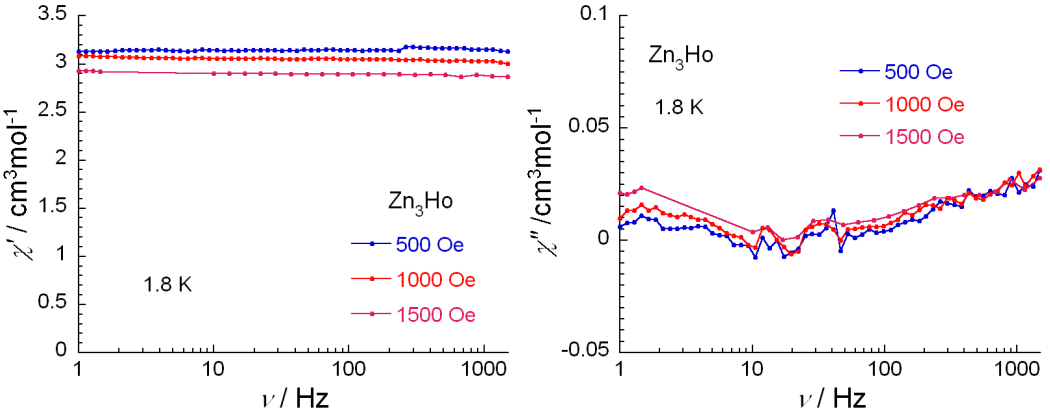

Figure S7. (Left) Frequency dependence of the in-phase component of ac susceptibility of $Zn_3Ho(\mathbf{L}^{Pr})(NO_3)_3{\cdot}2MeOH{\cdot}4H_2O$ with the external dc fields indicated. (Right) Frequency dependence of the out-of-phase component

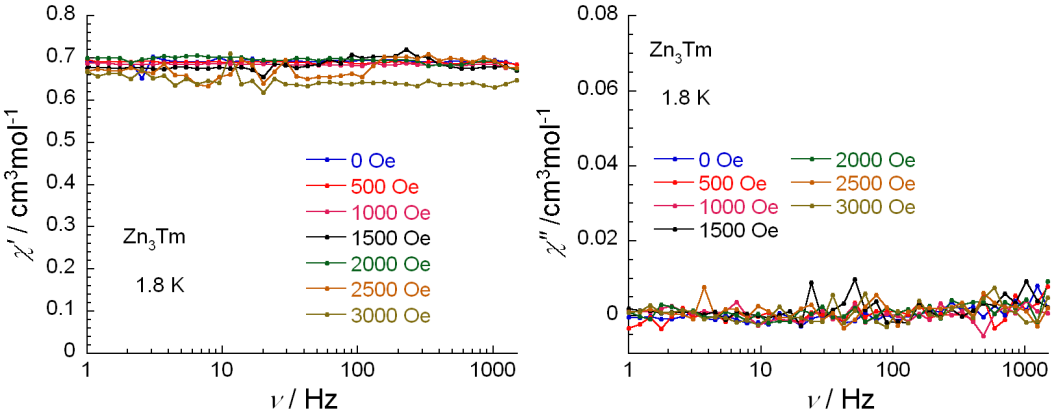

Figure S8. (Left) Frequency dependence of the in-phase component of ac susceptibility of $Zn_3Tm(\mathbf{L}^{Pr})(NO_3)_3{\cdot}3MeOH$ with the external dc fields indicated. (Right) Frequency dependence of the out-of-phase component

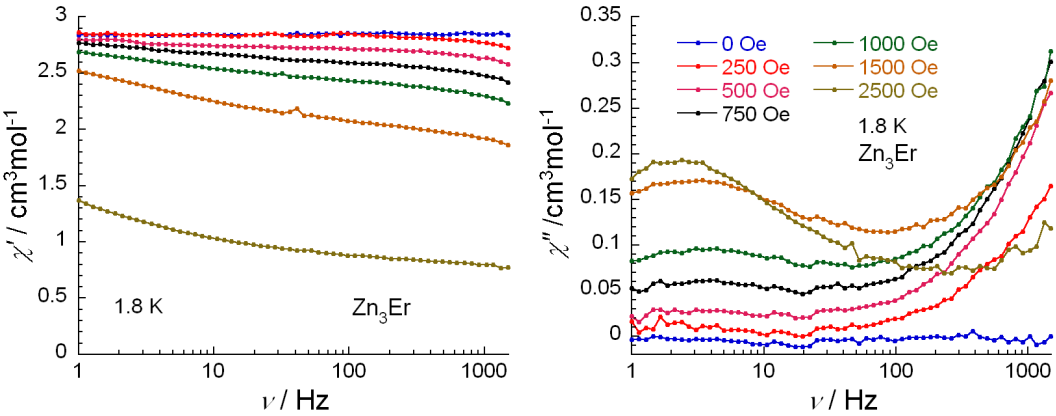

Figure S9. (Left) Frequency dependence of the in-phase component of ac susceptibility of $Zn_3Er(\mathbf{L}^{Pr})(NO_3)_3{\cdot}2MeOH{\cdot}5H_2O$ with the external dc fields indicated. (Right) Frequency dependence of the out-of-phase component

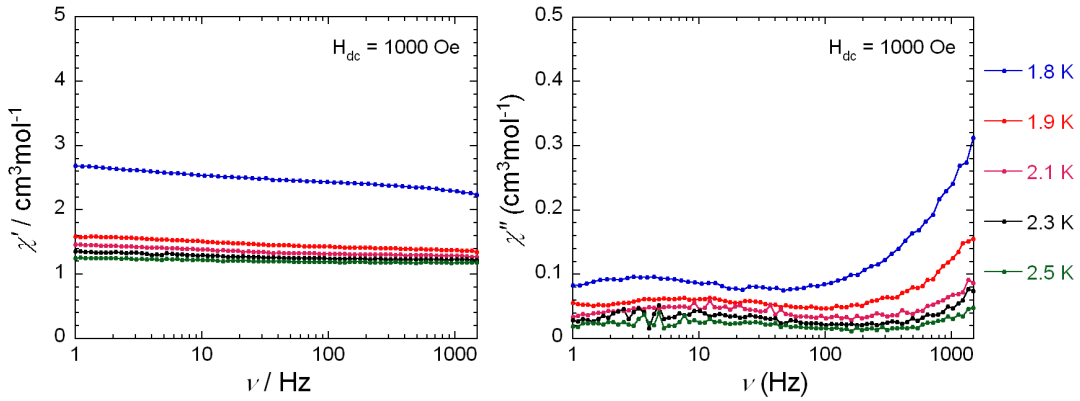

Figure S10. (Left) Frequency dependence of the in-phase component of ac susceptibility of $Zn_3Er(\mathbf{L}^{Pr})(NO_3)_3{\cdot}2MeOH{\cdot}5H_2O$ with a 1000 Oe external dc field at the temperatures indicated. (Right) Frequency dependence of the out-of-phase component

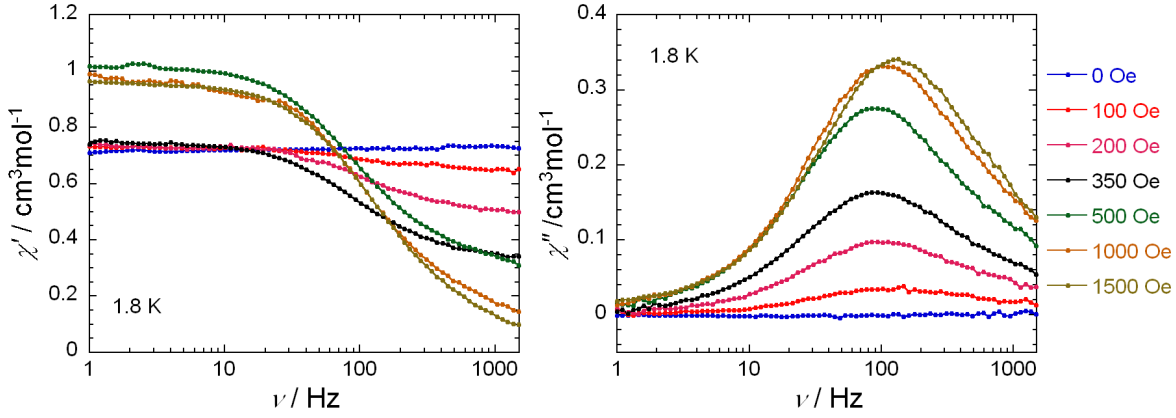

Figure S11. (Left) Frequency dependence of the in-phase component of ac susceptibility of $Zn_3Yb(\mathbf{L}^{Pr})(NO_3)_3{\cdot}4MeOH$ with the external dc fields indicated. (Right) Frequency dependence of the out-of-phase component

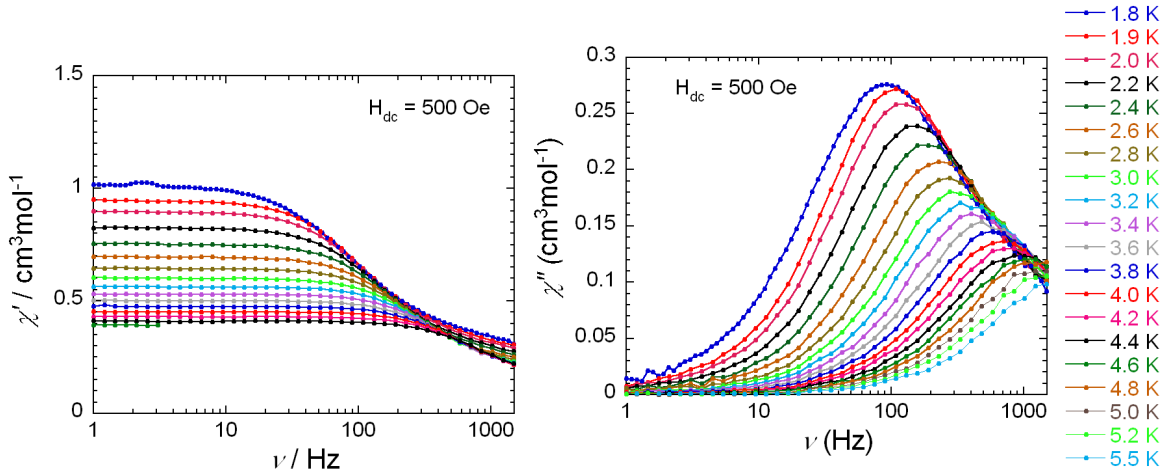

Figure S12. (Left) The frequency dependence of the in-phase component of the ac susceptibility of $Zn_3Yb(\mathbf{L}^{Pr})(NO_3)_3{\cdot}4MeOH$ under a 500 Oe dc field at the temperatures indicated. (Right) Frequency dependence of the out-of-phase component

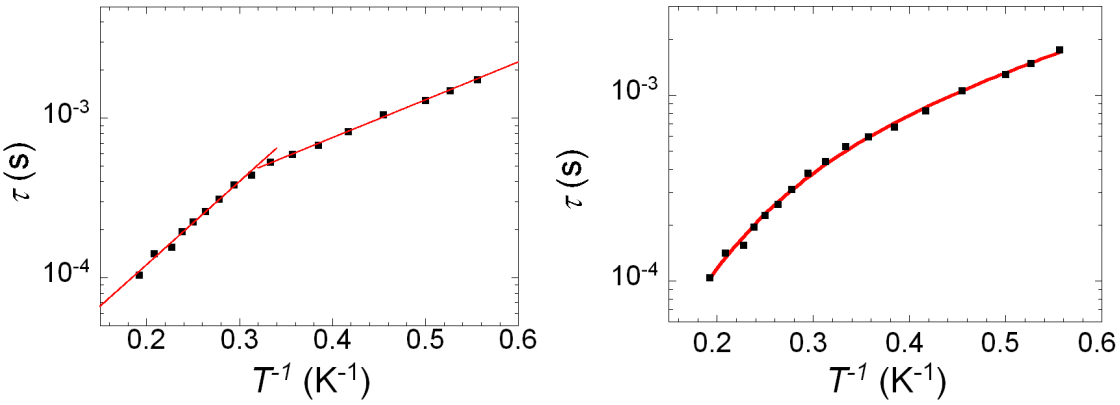

Figure S13. The relaxation time of $Zn_3Yb(\mathbf{L}^{Pr})(NO_3)_3 \cdot 4MeOH$ as a function of temperature. The relaxation plot is described by two Arrhenius laws in different temperature regimes (left) and a nonlinear Arrhenius plot (right). The red solid lines are the fittings. See the text for more detailed information.

Luminescence data

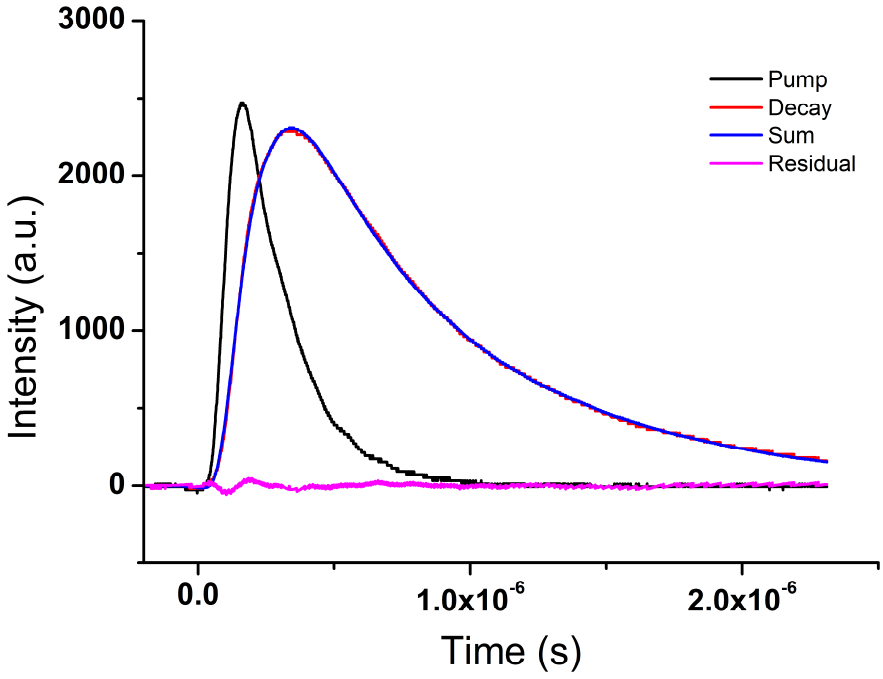

Figure S14. Luminescence decay of $Zn_3Nd(\mathbf{L}^{Pr})(NO_3)_3{\cdot}3MeOH{\cdot}H_2O$ measured at 1055 nm in the solid state.

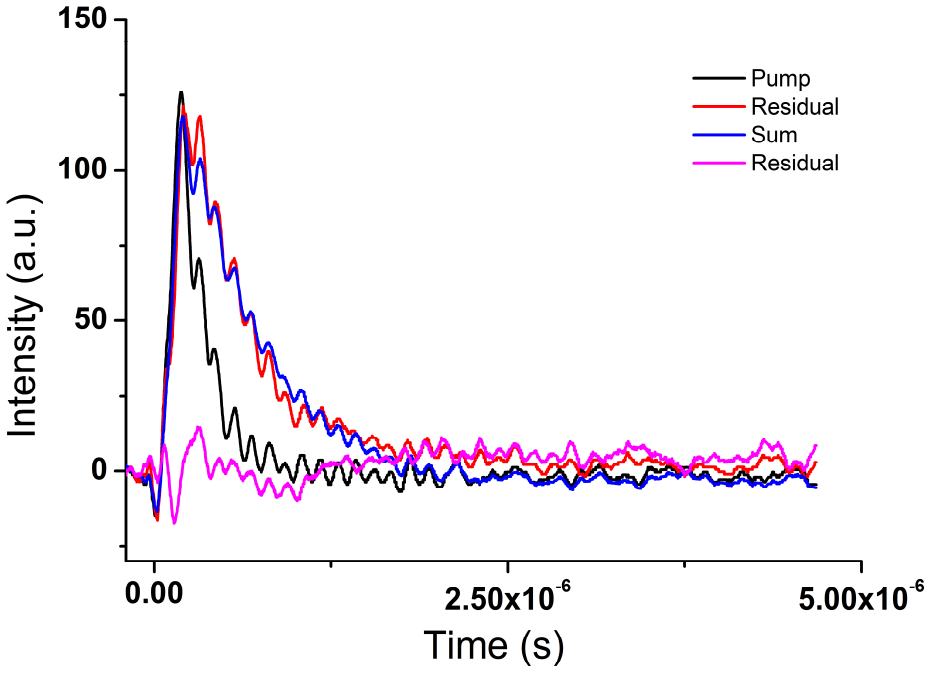

Figure S15. Luminescence decay of $Zn_3Er(\mathbf{L}^{Pr})(NO_3)_3{\cdot}3MeOH{\cdot}H_2O$ measured at 1560 nm in the solid state.

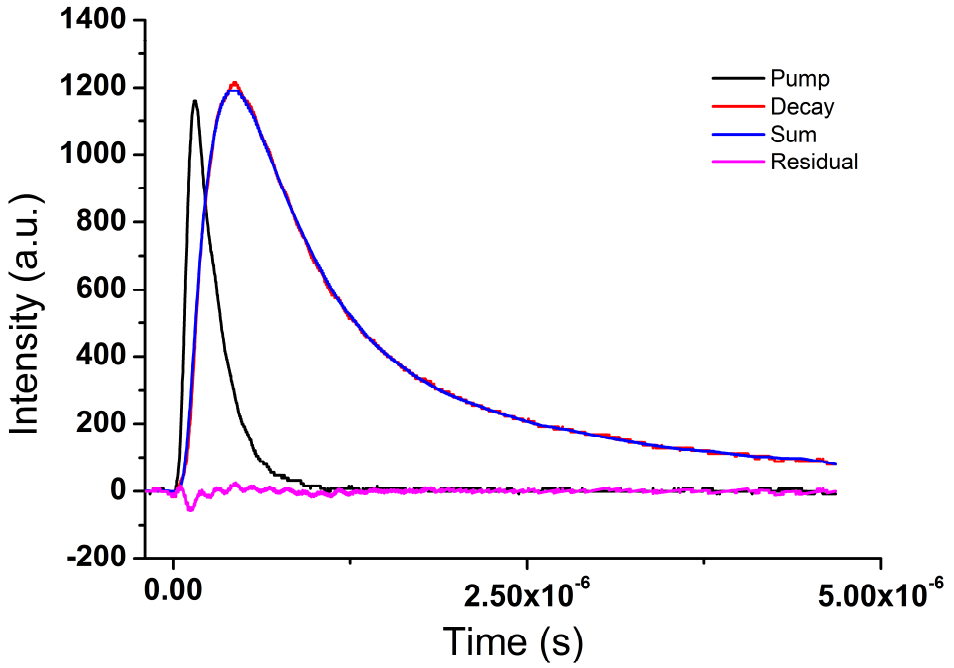

Figure S16. Luminescence decay of $Zn_3Yb(\mathbf{L}^{Pr})(NO_3)_3{\cdot}3MeOH{\cdot}H_2O$ measured at 980 nm in the solid state.

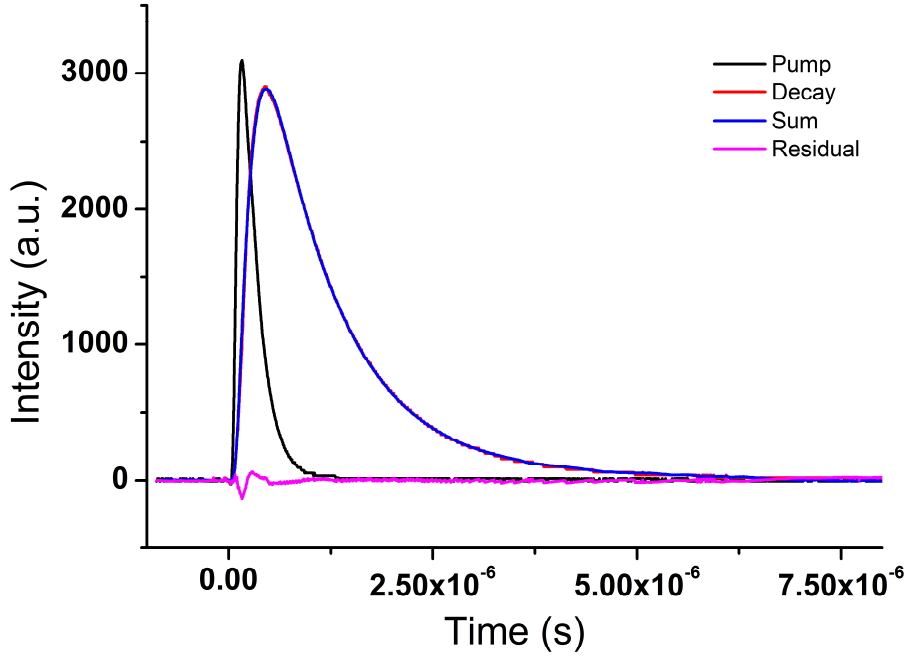

Figure S17. Luminescence decay of $Zn_3Nd(\mathbf{L}^{Pr})(NO_3)_3{\cdot}3MeOH{\cdot}H_2O$ measured at 1055 nm in solution.

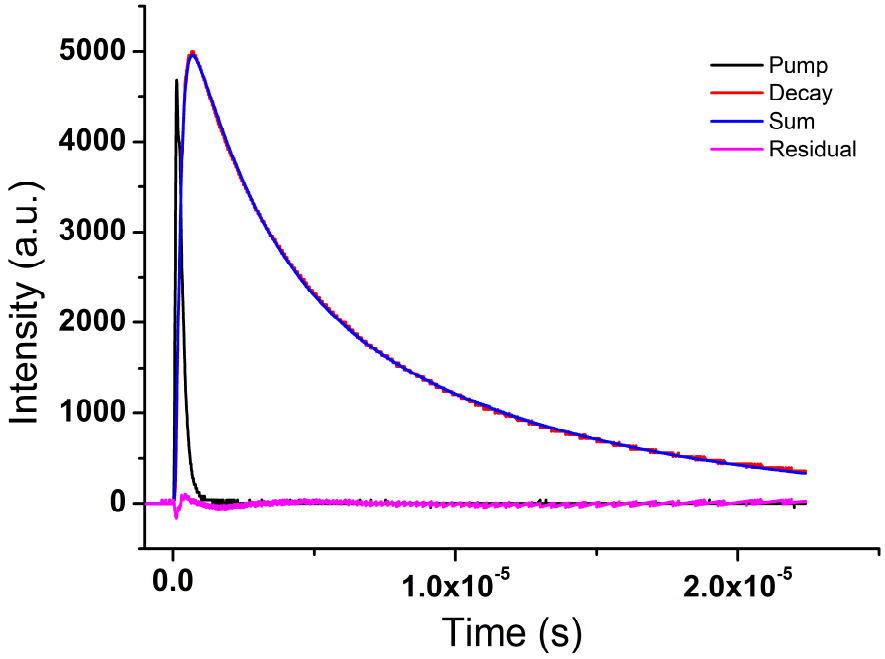

Figure S18. Luminescence decay of $Zn_3Yb(\mathbf{L}^{Pr})(NO_3)_3{\cdot}3MeOH{\cdot}H_2O$ measured at 980 nm in solution.

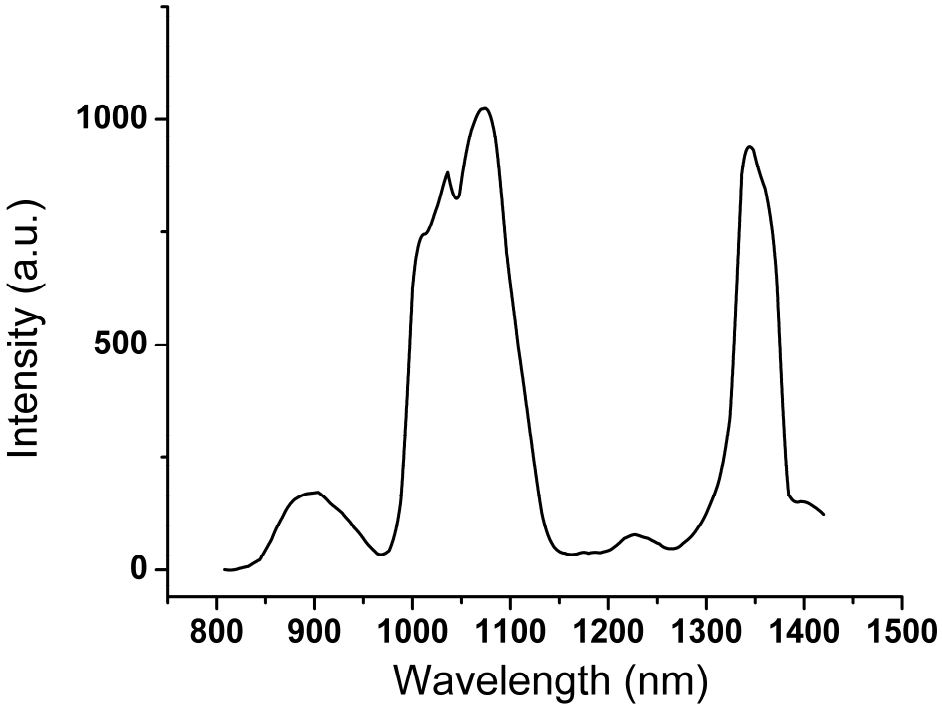

Figure S19. Luminescence emission spectrum of $Zn_3Nd(\mathbf{L}^{Pr})(NO_3)_3{\cdot}3MeOH{\cdot}H_2O$ upon 337 nm excitation in the solid state.

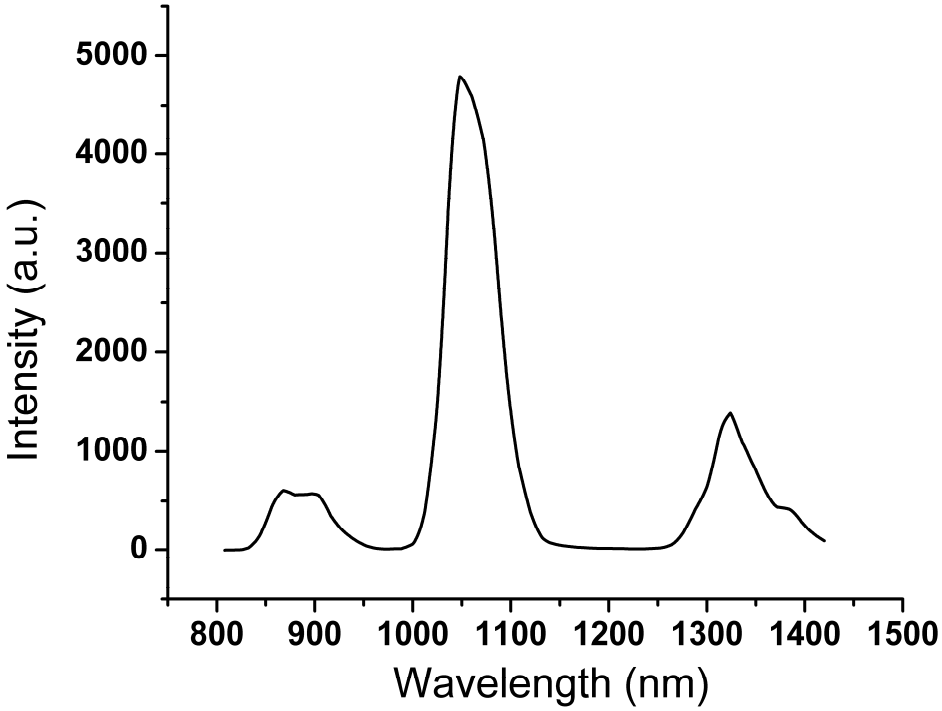

Figure S20. Luminescence emission spectrum of $Zn_3Nd(\mathbf{L}^{Pr})(NO_3)_3{\cdot}3MeOH{\cdot}H_2O$ upon 337 nm excitation in solution.

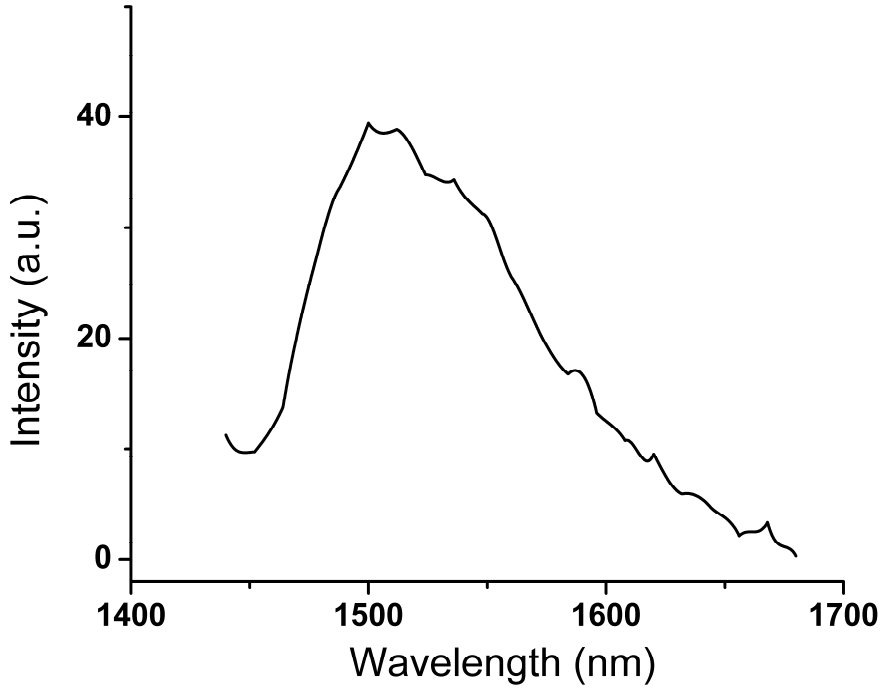

Figure S21. Luminescence emission spectrum of $Zn_3Er(\mathbf{L}^{Pr})(NO_3)_3{\cdot}3MeOH{\cdot}H_2O$ upon 337 nm excitation in the solid state.

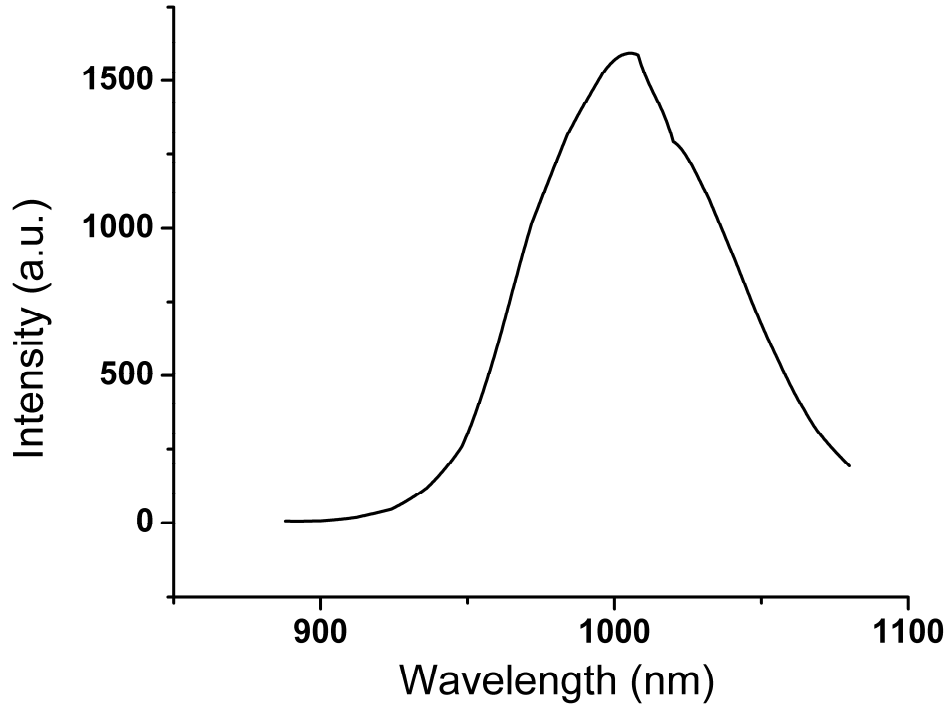

Figure S22. Luminescence emission spectrum of $Zn_3Yb(\mathbf{L}^{Pr})(NO_3)_3{\cdot}3MeOH{\cdot}H_2O$ upon 337 nm excitation in solution.

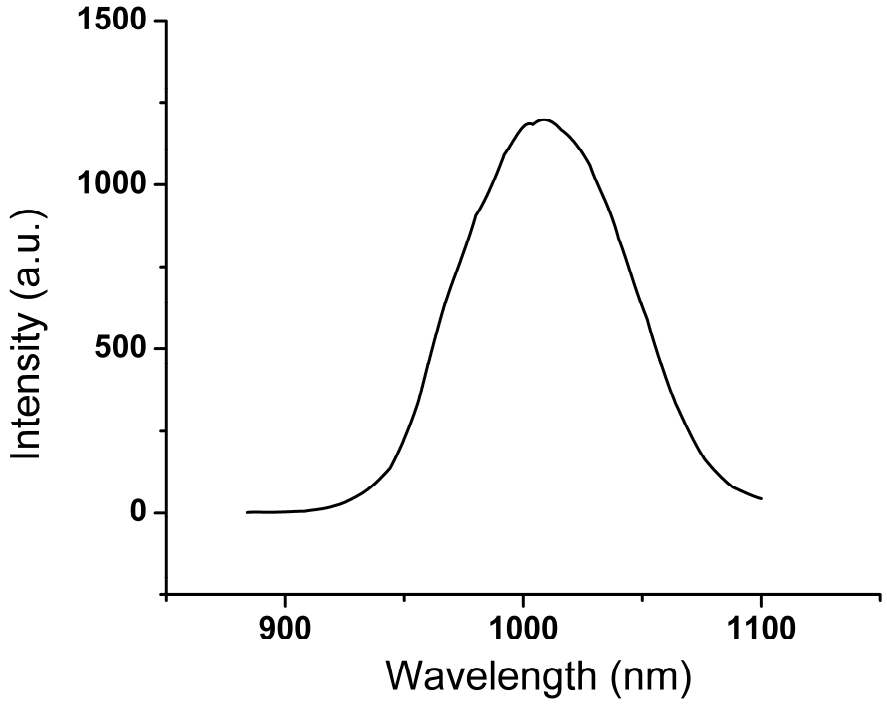

Figure S23. Luminescence emission spectrum of $Zn_3Yb(\mathbf{L}^{Pr})(NO_3)_3{\cdot}3MeOH{\cdot}H_2O$ upon 337 nm excitation in the solid state.

checkCIF/PLATON report (basic structural check)

Datablock: fdk99_0

Bond precision: C-C = 0.0030 A Wavelength=0.71073

Cell: a=13.2518(17) b=15.4056(19) c=18.836(2)
alpha=82.352(7) beta=70.545(6) gamma=87.186(7)

Temperature: 93 K

	Calculated	Reported
Volume	3593.6(8)	3593.6(8)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C58 H62 N6 O26 Zn5, 2(C3 H7 N O)	?
Sum formula	C64 H76 N8 O28 Zn5	C64 H76 N8 O28 Zn5
Mr	1732.28	1732.18
Dx,g cm-3	1.601	1.601
Z	2	2
Mu (mm-1)	1.734	1.734
F000	1780.0	1780.0
F000'	1783.64	
h,k,lmax	16,19,23	16,19,23
Nref	15158	14935
Tmin,Tmax	0.680,0.812	0.631,0.819
Tmin'	0.631	

Correction method= MULTI-SCAN

Data completeness= 0.985 Theta(max)= 26.670

R(reflections)= 0.0249(13088) wR2(reflections)= 0.0637(14935)

S = 1.037 Npar= 962

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT230_ALERT_2_B Hirshfeld Test Diff for N5 -- C53 .. 12.76 su

Alert level C

PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ... 3.42 Ratio
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Zn4 -- O25 .. 8.12 su
PLAT048_ALERT_1_C MoietyFormula Not Given ..... ?
PLAT125_ALERT_4_C No '_symmetry_space_group_name_Hall' Given ..... ?
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 2 C3 H7 N O

Alert level G

PLAT432_ALERT_2_G Short Inter X...Y Contact O20 .. C48 .. 3.01 Ang.
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 1

O13 -ZN5 -O1 -C1 -69.00 0.70 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 6
O13 -ZN5 -O1 -ZN3 113.50 0.70 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #
61
O9 -ZN1 -O5 -C9 -83.10 0.70 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #
66
O9 -ZN1 -O5 -ZN3 110.30 0.60 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #
101
O5 -ZN1 -O9 -C17 -21.00 0.70 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #
131
O1 -ZN5 -O13 -C25 -27.80 0.70 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #
207
O23 -ZN2 -O22 -C44 164.00 0.50 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #
215
O22 -ZN2 -O23 -C47 116.00 0.50 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #
217
O25 -ZN4 -O24 -C50 169.70 0.50 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #
224
O24 -ZN4 -O25 -C53 103.80 0.50 1.555 1.555 1.555 1.555
PLAT794_ALERT_5_G Note: Tentative Bond Valency for Zn1 ..... 2.13
PLAT794_ALERT_5_G Note: Tentative Bond Valency for Zn2 ..... 2.14
PLAT794_ALERT_5_G Note: Tentative Bond Valency for Zn3 ..... 2.17
PLAT794_ALERT_5_G Note: Tentative Bond Valency for Zn4 ..... 2.12
PLAT794_ALERT_5_G Note: Tentative Bond Valency for Zn5 ..... 2.11

checkCIF/PLATON report (basic structural check)

Datablock: fdk122

Bond precision: C-C = 0.0045 A Wavelength=0.71073
Cell: a=12.6867(14) b=14.9480(18) c=15.631(2)

alpha=67.354(6) beta=89.080(6) gamma=76.787(5)

Temperature: 92 K

	Calculated	Reported
Volume	2654.8(6)	2654.8(6)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	2(C42 H50 N11 O15 Pr Zn3), 0.4(C6 H14 N2 O2), C3 H7 N O, 2(N O	?
Sum formula	C89.40 H112.60 N25.80 O37.80 Pr2 Zn6	C44.70 H56.30 N12.90 O18.90 Pr Zn3
Mr	2827.62	1413.75
Dx,g cm-3	1.769	1.769
Z	1	2
Mu (mm-1)	2.328	2.328
F000	1430.0	1430.0
F000'	1431.83	
h,k,lmax	15,18,19	15,18,19
Nref	11079	10889
Tmin,Tmax	0.756,0.911	0.542,0.913
Tmin'	0.497	

Correction method= MULTI-SCAN

Data completeness= 0.983 Theta(max)= 26.570

R(reflections)= 0.0321(9753) wR2(reflections)= 0.0729(10889)

S = 1.049 Npar= 749

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT220_ALERT_2_A Large Non-Solvent C Ueq(max)/Ueq(min) ... 5.39 Ratio

PLAT430_ALERT_2_A Short Inter D...A Contact O70 .. O75 .. 0.23 Ang.

PLAT430_ALERT_2_A Short Inter D...A Contact O70 .. N75 .. 2.31 Ang.

PLAT430_ALERT_2_A Short Inter D...A Contact N70 .. N75 .. 0.44 Ang.

PLAT430_ALERT_2_A Short Inter D...A Contact N70 .. O75 .. 2.27 Ang.

Alert level B

PLAT242_ALERT_2_B Check Low Ueq as Compared to Neighbors for N75

Alert level C

PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uso(min) ... 4.76 Ratio

PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for N1

PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for N60

PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C33

PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C82

PLAT411_ALERT_2_C Short Inter H...H Contact H18 .. H32B .. 2.06 Ang.

PLAT413_ALERT_2_C Short Inter XH3 .. XHn H62B .. H62B .. 2.12 Ang.
PLAT041_ALERT_1_C Calc. and Reported SumFormula Strings Differ ?
PLAT045_ALERT_1_C Calculated and Reported Z Differ by ..... 0.50 Ratio
PLAT048_ALERT_1_C MoietyFormula Not Given ..... ?
PLAT125_ALERT_4_C No '_symmetry_space_group_name_Hall' Given ..... ?
PLAT234_ALERT_4_C Large Hirshfeld Difference C20 -- C81 .. 0.18 Ang.
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of N30
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 4 N O3

Alert level G

PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 5.56
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 8.00 Perc.
PLAT343_ALERT_2_G Check sp? Angle Range in Main Residue for .. C19
PLAT432_ALERT_2_G Short Inter X...Y Contact O70 .. C75 .. 1.26 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact O70 .. C77 .. 2.82 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact N70 .. C75 .. 1.22 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact N70 .. C76 .. 1.42 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact N70 .. C77 .. 1.75 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C2 .. C8 .. 3.19 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C70 .. C75 .. 0.24 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C70 .. O75 .. 1.13 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C70 .. N75 .. 1.36 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C70 .. C77 .. 2.35 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C70 .. C76 .. 2.53 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C71 .. C76 .. 0.31 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C71 .. N75 .. 1.45 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C71 .. C75 .. 2.36 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C71 .. C77 .. 2.52 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C72 .. N75 .. 1.63 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C72 .. C77 .. 1.87 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C72 .. C75 .. 2.25 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C72 .. C76 .. 2.30 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C72 .. O75 .. 2.87 Ang.
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 55
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 28.00 Perc.
PLAT380_ALERT_4_G Check Incorrectly? Oriented X(sp2)-Methyl Moiety C41

PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #
12
O4 -PR1 -O1 -C3 134.70 1.40 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #
21
O4 -PR1 -O1 -ZN2 -53.80 1.50 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #
91
O1 -PR1 -O4 -C15 -151.60 1.40 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #
100
O1 -PR1 -O4 -ZN3 21.30 1.50 1.555 1.555 1.555 1.555
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 96
C33 -N1 -C83 1.555 1.555 1.555 29.80 Deg.