# Electronic Supplementary Information for

# Heterometallic $Cu^{II}/Dy^{III}$ 1D chiral polymer: Chirogenesis and Exchange Coupling of Toroidal Moments in trinuclear $Dy_3$ Single Molecule Magnets

**Ghenadie Novitchi[a], Guillaume Pilet[a], Liviu Ungur[b,c], Victor V. Moshchalkov[d], Wolfgang Wernsdorfer[e], Liviu F. Chibotaru[b]*, Dominique Luneau[a]*, Annie K. Powell[f,g]***

Infrared spectra were recorded on a NICOLET spectrophotometer with solid samples on a Golden Gate diamond ATR accessory. The circular dichroism (CD) spectra were recorded on a Chirascan spectropolarimeter using Chirascan software (Applied Biophysics Ltd., Leatherhead, UK). All starting materials and solvents were purchased from Aldrich and were used without further purification.

Synthesis of **L-2**($\{CuDy_3\}_n$)**:**

The 0.15g (1mmol) *o-vanillin,* 0.12g (1mmol) *L-valine* and 0.23g (1mmol) $Cu(NO_3)_2 2.5H_2O$ were dissolved in 10 ml of methanol and stirred for 10 min. A solution of $Dy(NO_3)_3 6H_2O$ 0.70g (1.53mmol) in 7 ml of methanol was added. Upon formation of a green solution the 0.4-0.5 ml of *triethylamine* were added dropwise. The intense green solution was filtered and covered. After two days of slow evaporation 0.085g of blue well-formed crystal were isolated by filtration and dried in air. *Anal*. Found, %: C, 27.01; H, 2.92; N, 5.12. Calc. for $C_{69}H_{85}Cu_2Dy_6N_{11}O_{54}$(3034.57 g/mol): C, 27.31; H, 2.82; N, 5.08.

The compounds **L-1**($\{CuY_3\}_n$), **D-2**($\{CuDy_3\}_n$), and **D-3**($\{CuGd_3\}_n$), were obtained in similar ways.
**L-1** *Anal*. Found, %: C, 32.05; H, 3.23; N, 6.10. Calc. for $C_{69}H_{85}Cu_2Y_6N_{11}O_{54}$(2592.98): C, 31.96; H, 3.30; N, 5.95%. **D-2** *Anal*. Found, %: C, 27.03; H, 2.96; N, 5.09. Calc. for $C_{69}H_{85}Cu_2Dy_6N_{11}O_{54}$(3034.57 g/mol): C, 27.31; H, 2.82; N, 5.08. **D-3** *Anal*. Found, %: C, 27.10; H, 2.91; N, 5.17. Calc. for $C_{69}H_{85}Cu_2Gd_6N_{11}O_{54}$(2568.6): C, 27.60; H, 2.85; N, 5.13%.

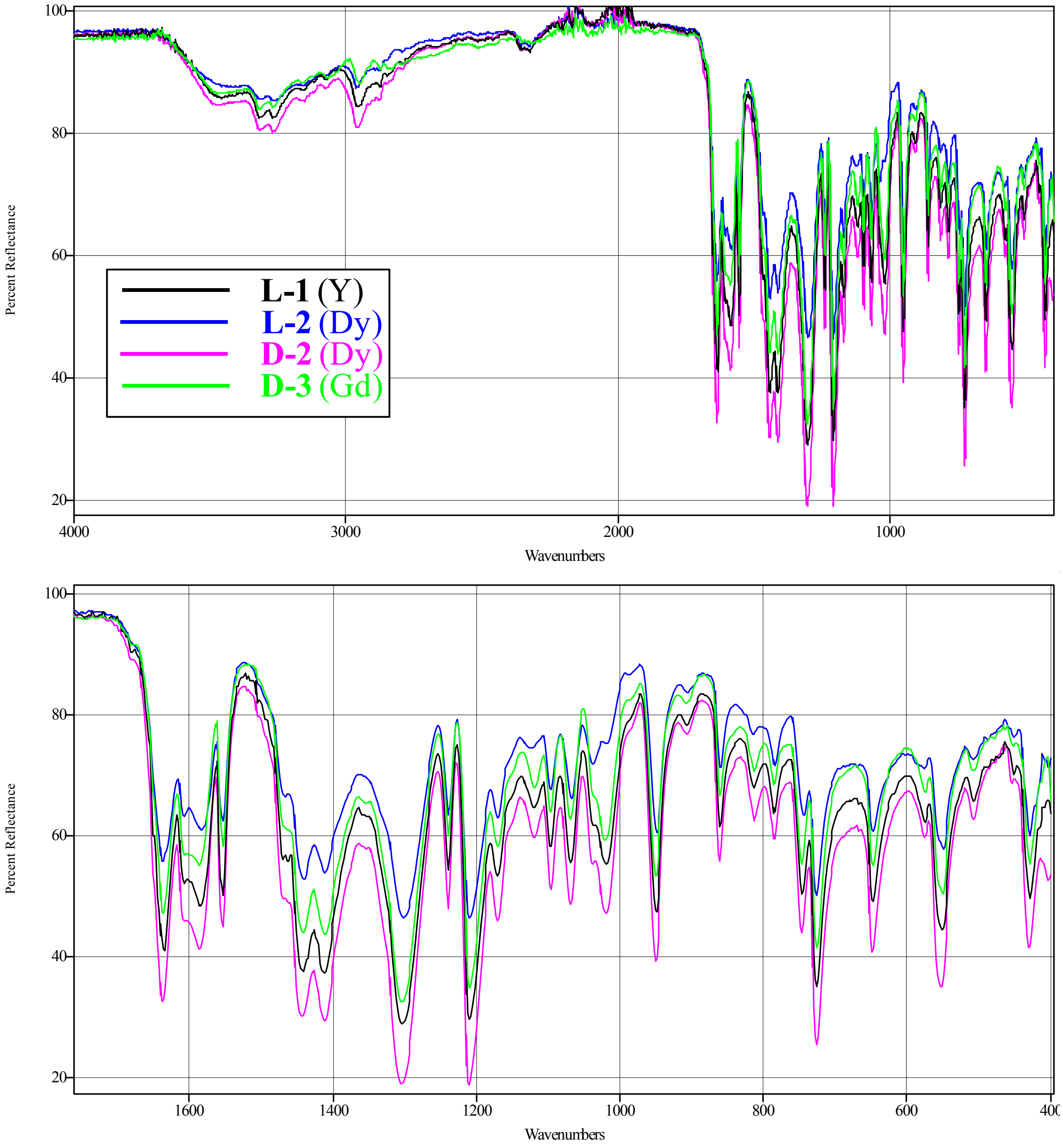

***Figure S1*** IR spectra of **1-3** compounds.

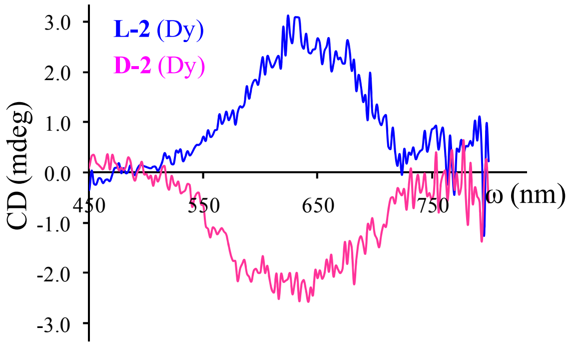

***Figure S2***. The CD spectra of **L-2** and **D-2** in KBr

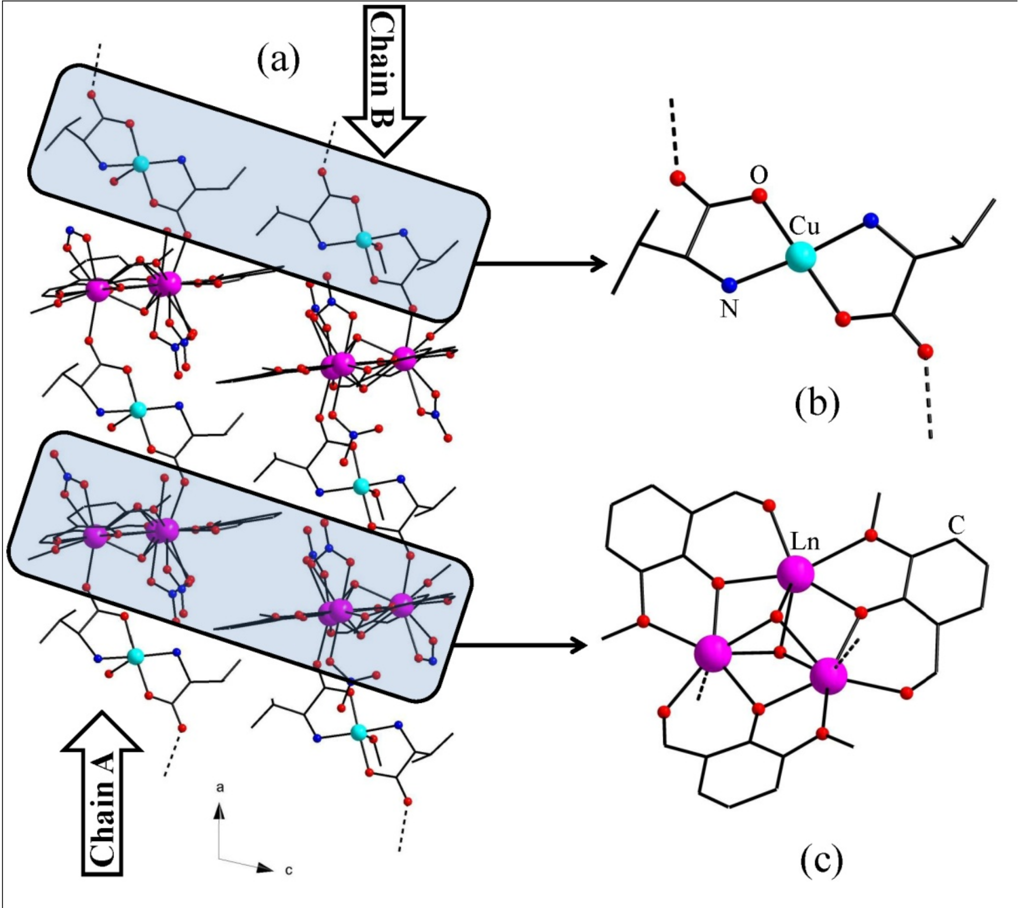

***Figure S3.***(a) chains A and B running along the *a*-axis of the unit-cell; (b) copper(II) complex bridging two $Ln_3$ units. For clarity, the fifth coordination position ($H_2O$ or MeOH) has been removed; (c) $Ln_3$ cluster. Axial ligands ($NO_3$ and $H_2O$) have been removed for clarity; hydrogen atoms have been removed for clarity.

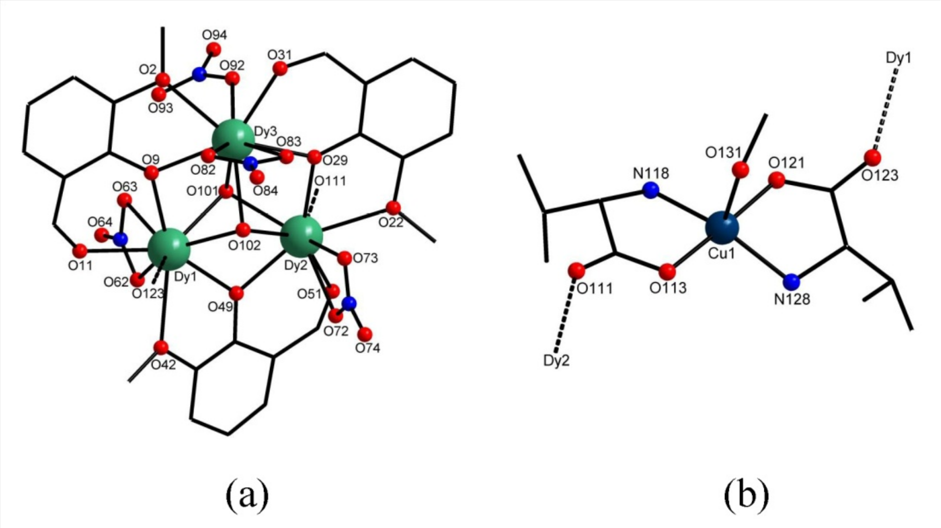

***Figure S4:***$Ln_3$ units (a) and Cu complex (b) with labelling

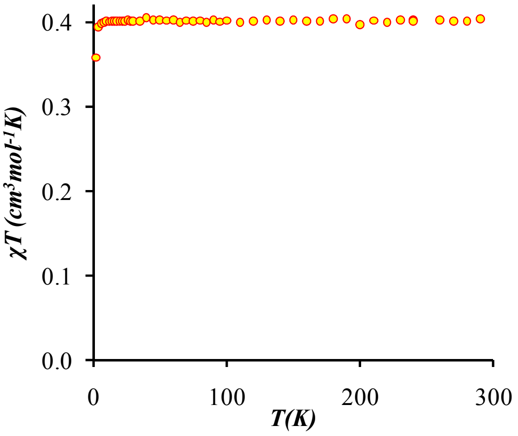

***Figure S5*** Thermal dependence of the $\chi T$ products per $CuY_3$ units at 0.1T for **L-1.**

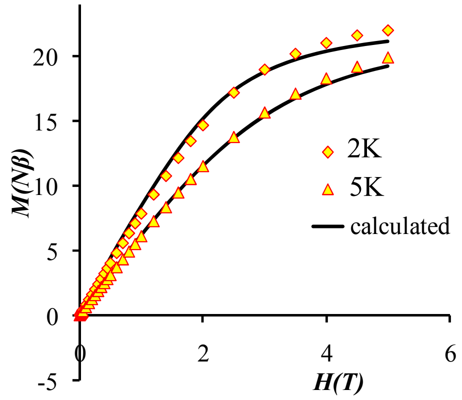

***Figure S6*** Magnetisation M vs applied field H at 2K and 5K, for **D-3**, The solid lines correspond to the best simulated data corresponding to coupled $Cu^{II}$ and $Gd^{III}$ ions see main text for details.

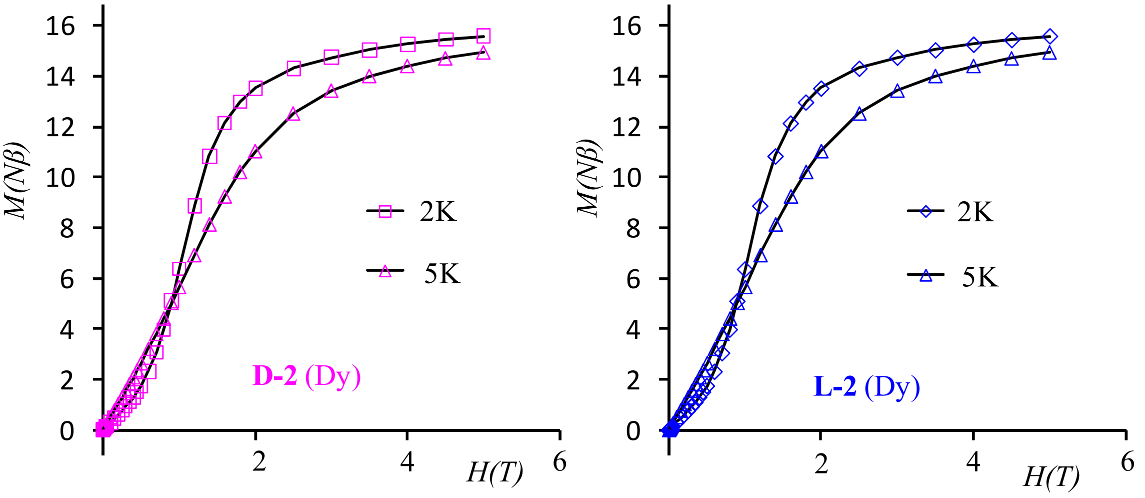

***Figure S7.*** Magnetisation M vs applied field H at 2K and 5K, for **D-2** (left), **L-2**(*right*), The solid lines are just to guide the eyes.

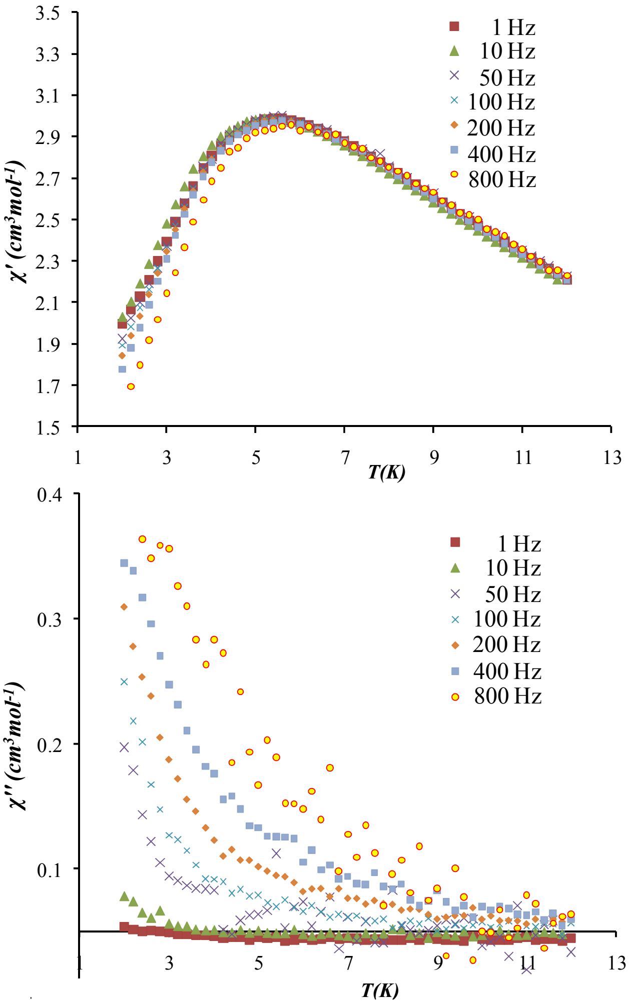

***Figure S8*** Temperature dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility component at different frequencies for **D-2**

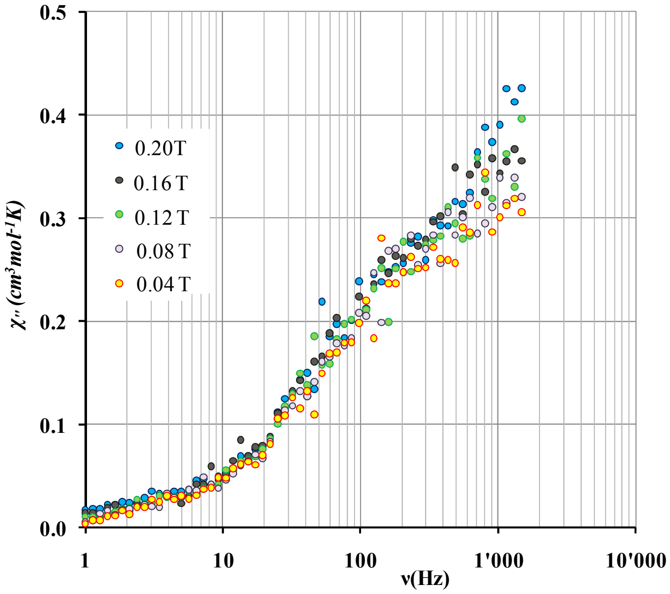

***Figure S9*** Frequency dependence of the out-of-phase (χ'') ac susceptibility component at different field for **L-2** at 2K

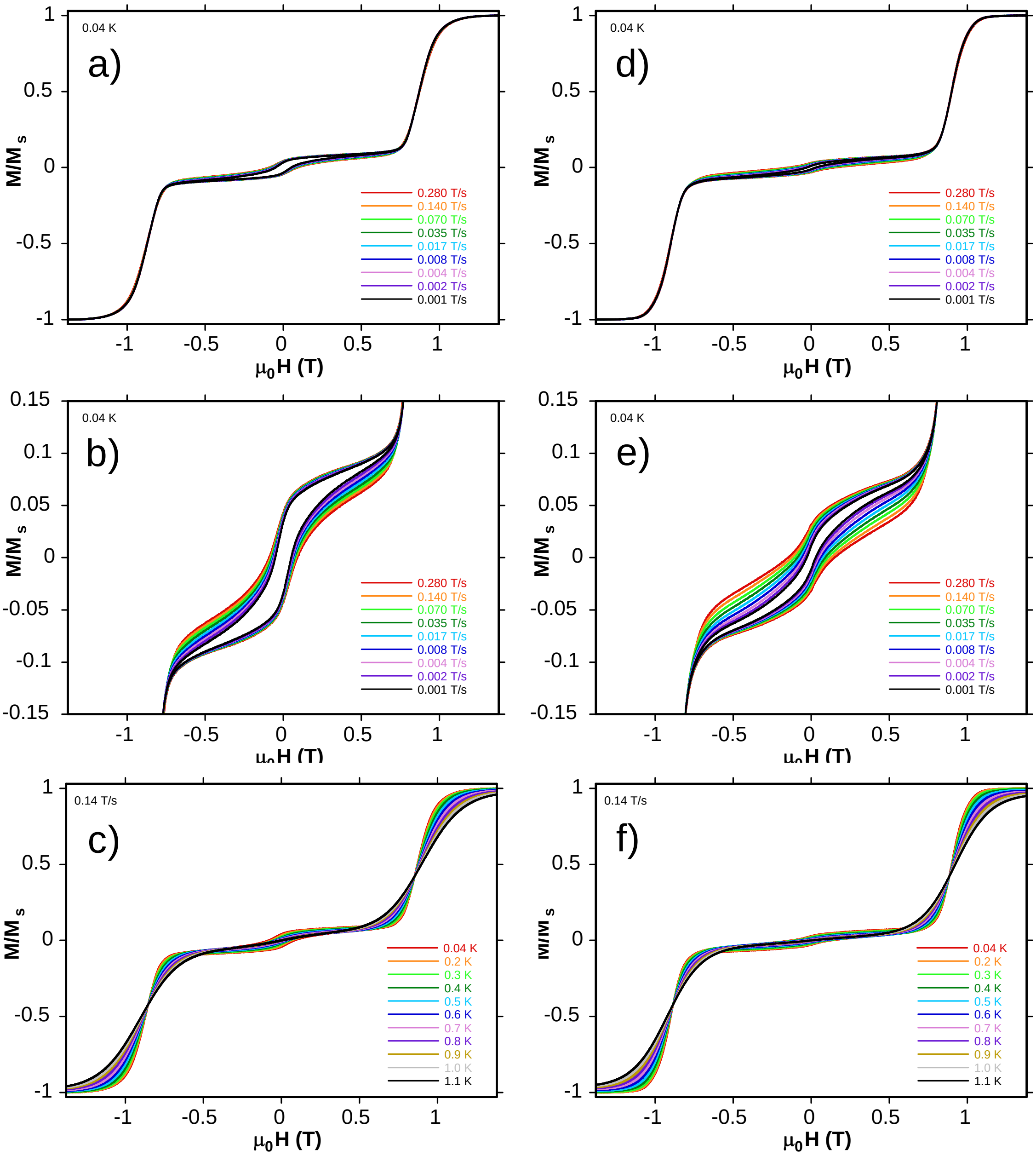

***Figure S10*** Single-crystal magnetization (M) vs. applied field measurements for complex **L-2** (left) **D-2** (right) . a) and d) with different field sweep rates at 0.04 K; c) and f) at constant field sweep rate (0.14T/s) at different temperatures. b) and e) is zoom of a ) and d). M is normalised to its saturation value at 1.4 T.

**Table S1. Important bond lengths (in Å) for L-2, D-2 and D-3 compounds**

| | | **D-2** | **L-2** | **D-3** |
|---|---|---|---|---|
| **Chain B** | Ln1 - O123 | 2.34(1) | 2.33(1) | 2.37(1) |
| | Ln1 - O9 | 2.30(1) | 2.30(1) | 2.32(1) |
| | Ln1 - O11 | 2.36(1) | 2.38(1) | 2.38(1) |
| | Ln1 - O42 | 2.63(1) | 2.61(1) | 2.61(2) |
| | Ln1 - O49 | 2.33(1) | 2.32(1) | 2.37(1) |
| | Ln1 - O62 | 2.46(1) | 2.48(1) | 2.54(1) |
| | Ln1 - O63 | 2.594(9) | 2.59(1) | 2.62(1) |
| | Ln1 - O101 | 2.301(8) | 2.297(8) | 2.354(9) |
| | Ln1 - O102 | 2.345(8) | 2.351(8) | 2.397(8) |
| | Ln2 - O22 | 2.51(1) | 2.53(1) | 2.54(2) |
| | Ln2 - O29 | 2.31(1) | 2.30(1) | 2.33(1) |
| | Ln2 - O49 | 2.32(1) | 2.32(1) | 2.35(1) |
| | Ln2 - O51 | 2.38(2) | 2.42(1) | 2.38(2) |
| | Ln2 - O72 | 2.44(1) | 2.46(1) | 2.48(1) |
| | Ln2 - O73 | 2.72(1) | 2.72(1) | 2.70(1) |
| | Ln2 - O101 | 2.330(8) | 2.335(8) | 2.367(9) |
| | Ln2 - O102 | 2.34(1) | 2.327(9) | 2.384(8) |
| | Ln2 - O111 | 2.351(9) | 2.335(9) | 2.41(1) |
| | Ln3 - O2 | 2.61(1) | 2.54(1) | 2.61(2) |
| | Ln3 - O9 | 2.312(9) | 2.324(9) | 2.391(9) |
| | Ln3 - O29 | 2.29(1) | 2.29(1) | 2.33(1) |
| | Ln3 - O31 | 2.34(1) | 2.33(1) | 2.36(1) |
| | Ln3 - O82 | 2.46(1) | 2.461(9) | 2.51(1) |
| | Ln3 - O83 | 2.54(1) | 2.50(1) | 2.54(1) |
| | Ln3 - O92 | 2.40(1) | 2.41(1) | 2.46(1) |
| | Ln3 - O101 | 2.370(9) | 2.359(9) | 2.386(9) |
| | Ln3 - O102 | 2.35(1) | 2.379(8) | 2.358(9) |
| | Cu1 - O113 | 1.930(8) | 1.934(9) | 1.956(9) |
| | Cu1 - N118 | 1.95(1) | 1.97(1) | 1.96(1) |
| | Cu1 - O121 | 1.928(8) | 1.93(1) | 1.935(8) |
| | Cu1 - N128 | 2.01(1) | 2.02(2) | 2.03(2) |
| | Cu1 - O131 | 2.38(1) | 2.32(1) | 2.34(1) |
| **Chain A** | Ln11 - O323 | 2.34(1) | 2.35(1) | 2.37(1) |
| | Ln11 - O209 | 2.32(2) | 2.34(1) | 2.33(2) |
| | Ln11 - O211 | 2.37(1) | 2.36(1) | 2.41(1) |
| | Ln11 - O242 | 2.58(2) | 2.51(1) | 2.57(2) |
| | Ln11 - O249 | 2.32(1) | 2.316(9) | 2.37(1) |
| | Ln11 - O262 | 2.60(1) | 2.66(1) | 2.62(1) |
| | Ln11 - O263 | 2.49(2) | 2.50(1) | 2.52(2) |
| | Ln11 - O301 | 2.31(1) | 2.34(1) | 2.35(1) |
| | Ln11 - O302 | 2.38(1) | 2.39(1) | 2.42(1) |
| | Ln12 - O222 | 2.53(2) | 2.52(1) | 2.53(2) |
| | Ln12 - O229 | 2.33(1) | 2.33(1) | 2.35(1) |
| | Ln12 - O249 | 2.31(1) | 2.33(1) | 2.32(1) |
| | Ln12 - O251 | 2.35(1) | 2.35(1) | 2.39(1) |
| | Ln12 - O272 | 2.47(1) | 2.47(1) | 2.52(1) |
| | Ln12 - O273 | 2.68(1) | 2.67(1) | 2.69(1) |
| | Ln12 - O301 | 2.320(9) | 2.349(9) | 2.362(9) |
| | Ln12 - O302 | 2.34(1) | 2.334(8) | 2.39(1) |
| | Ln12 - O311 | 2.36(1) | 2.33(1) | 2.41(1) |
| | Ln13 - O202 | 2.53(2) | 2.57(1) | 2.58(2) |
| | Ln13 - O209 | 2.29(2) | 2.29(1) | 2.35(2) |
| | Ln13 - O229 | 2.30(1) | 2.29(1) | 2.35(1) |
| | Ln13 - O231 | 2.33(2) | 2.36(2) | 2.31(2) |
| | Ln13 - O282 | 2.47(2) | 2.49(2) | 2.54(2) |
| | Ln13 - O283 | 2.62(2) | 2.59(2) | 2.70(2) |
| | Ln13 - O291 | 2.44(2) | 2.40(2) | 2.52(2) |
| | Ln13 - O301 | 2.37(1) | 2.37(1) | 2.41(1) |
| | Ln13 - O302 | 2.36(1) | 2.356(9) | 2.35(1) |
| | Cu11 - O313 | 1.96(1) | 1.95(1) | 1.96(1) |
| | Cu11 - N318 | 1.94(2) | 1.94(1) | 1.92(1) |
| | Cu11 - O321 | 1.97(2) | 1.95(1) | 2.00(2) |
| | Cu11 - N328 | 1.95(2) | 2.00(2) | 1.96(2) |
| | Cu11 - O331 | 2.51(2) | 2.71(2) | 2.87(2) |

**Table S2. Important angles (in deg.) for L-2, D-2 and D-3 compounds**

| | | **D-2** | **L-2** | **D-3** |
|---|---|---|---|---|
| **Chain B** | Ln1 - O101 - Ln2 | 99.4(3) | 99.8(3) | 99.1(3) |
| | Ln1 - O49 - Ln2 | 99.0(4) | 99.5(4) | 99.2(5) |
| | Ln1 - O102 - Ln2 | 97.9(3) | 98.4(3) | 97.5(3) |
| | Ln1 - O9 - Ln3 | 99.0(4) | 98.9(4) | 98.2(3) |
| | Ln1 - O101 - Ln3 | 97.3(3) | 97.9(3) | 97.3(3) |
| | Ln1 - O102 - Ln3 | 96.7(3) | 95.8(3) | 96.9(3) |
| | Ln2 - O29 - Ln3 | 99.5(3) | 99.4(3) | 99.1(3) |
| | Ln2 - O101 - Ln3 | 96.7(3) | 96.5(3) | 96.4(3) |
| | Ln2 - O102 - Ln3 | 97.1(3) | 96.1(3) | 96.7(3) |
| **Chain A** | Ln11 - O249 - Ln12 | 98.8(5) | 98.7(4) | 99.6(4) |
| | Ln11 - O301 - Ln12 | 99.0(4) | 97.5(3) | 98.8(3) |
| | Ln11 - O302 - Ln12 | 96.4(4) | 96.6(3) | 96.1(4) |
| | Ln11 - O209 - Ln13 | 99.1(4) | 98.7(4) | 98.2(4) |
| | Ln11 - O301 - Ln13 | 97.1(3) | 96.4(3) | 96.1(3) |
| | Ln11 - O302 - Ln13 | 95.2(3) | 95.5(3) | 95.8(4) |
| | Ln12 - O229 - Ln13 | 99.8(5) | 100.2(4) | 99.8(5) |
| | Ln12 - O301 - Ln13 | 98.2(4) | 97.2(4) | 97.7(4) |
| | Ln12 - O302 - Ln13 | 97.8(3) | 97.9(3) | 98.4(4) |

# *Ab initio* results for D-$Dy_3Cu$ chain

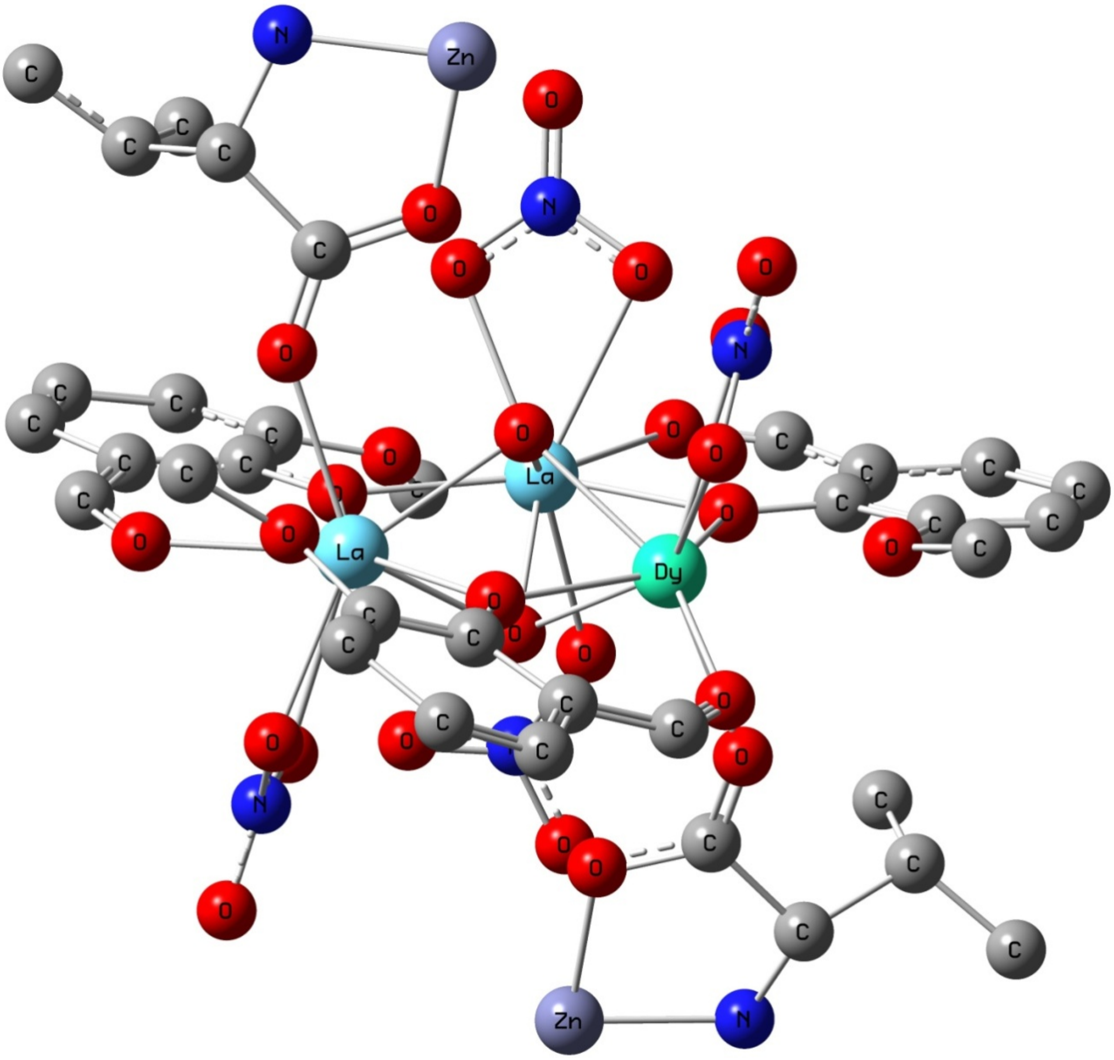

**Figure S11.** Structure of the calculated Dy1 fragment of the D-$Dy_3Cu$ complex. Model fragments for Dy2 and Dy3 are similar. Hydrogen atoms are not shown for clarity.

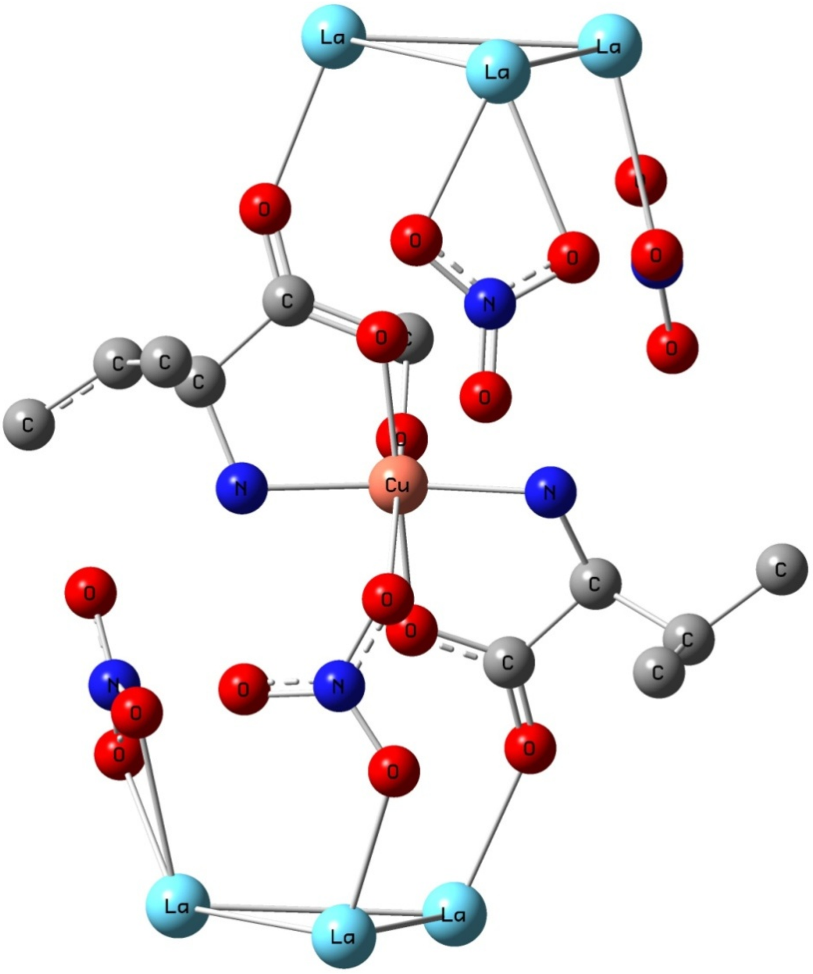

**Figure S12.** Structure of the calculated Cu fragment of the D-$Dy_3Cu$ complex. Hydrogen atoms are not shown for clarity.

**Computational details:**

**Basis Sets:** All employed basis sets were taken from the standard ANO-RCC basis set library from MOLCAS. The following contractions were used for the atoms:

Dy – 8s7p5d4f2g1h
La –.7s6p4d3f1g.
Zn – Zn.ECP.Lopez-Moraza.0s.0s.0e-AIMP-KZnF3.
N, O – 4s3p2d. (only for the first coordinated atoms, which make a bond with Dy)
C – 4s3p2d.(only for the atoms which are directly bonded to the first coordination sphere of O and N)
N,O, C – 3s2p. (for distant atoms)
H – 3s1p. (only for the atoms which are directly bonded to the first coordination sphere of O and N)
H – 2s. (for distant atoms)

**Active space** of the CASSCF method included 9 electrons in 7 orbitals. It includes the 4f shell of the $Dy^{3+}$ ion. The **spin orbit interaction** was computed by mixing of 21 sextets, 128 quartets and 32 doublet spin free states.

**Table S3.** CASSCF energies of the lowest spin-free states ($cm^{-1}$) on magnetic sites.

| Spin multiplicity | | Spin free energies | | | |
|---|---|---|---|---|---|
| | | **Dy1** | **Dy2** | **Dy3** | **Cu** |
| 6 | H | 0.000 | 0.000 | 0.000 | --- |
| | | 58.547 | 37.708 | 42.769 | |
| | | 114.738 | 122.597 | 164.704 | |
| | | 192.204 | 181.795 | 233.910 | |
| | | 221.912 | 284.944 | 300.483 | |

| | | | | | |
|---|---|---|---|---|---|
| | | 282.877 | 314.131 | 340.609 | |
| | | 302.631 | 367.924 | 379.556 | |
| | | 421.734 | 430.904 | 458.440 | |
| | | 441.565 | 464.930 | 483.917 | |
| | | 565.586 | 678.246 | 537.146 | |
| | | 578.746 | 689.955 | 560.746 | |
| | F | 7637.184 | 7668.929 | 7677.012 | --- |
| | | 7669.328 | 7686.831 | 7704.940 | |
| | | 7704.903 | 7747.301 | 7748.476 | |
| | | 7763.935 | 7794.063 | 7782.296 | |
| | | 7797.614 | 7833.875 | 7809.627 | |
| | | 7806.572 | 7874.712 | 7835.987 | |
| | | 7849.228 | 7895.155 | 7871.694 | |
| | P | 34863.266 | 34811.224 | 34842.200 | --- |
| | | 34976.271 | 35101.538 | 35095.198 | |
| | | 35149.086 | 35194.005 | 35142.731 | |
| 4 | | 24921.338 | 24935.248 | 24950.297 | --- |
| | | 24932.571 | 24941.165 | 24955.975 | |
| | | 24971.905 | 24985.656 | 25031.445 | |
| | | 24972.482 | 25004.350 | 25039.293 | |
| | | 24997.838 | 25015.956 | 25053.241 | |
| | | 25013.514 | 25035.701 | 25060.538 | |
| | | 25034.771 | 25070.681 | 25074.027 | |
| | | 25059.803 | 25083.984 | 25082.517 | |
| | | 25066.513 | 25094.751 | 25101.128 | |
| | | 25085.484 | 25100.519 | 25109.640 | |
| | | 25088.979 | 25133.752 | 25118.739 | |
| | | 25114.661 | 25170.122 | 25161.065 | |
| | | 25129.636 | 25178.985 | 25179.714 | |
| | | 25205.112 | 25245.370 | 25251.573 | |
| | | 25274.500 | 25288.708 | 25290.019 | |
| | | 25286.552 | 25323.901 | 25334.903 | |
| | | 25313.357 | 25325.601 | 25355.237 | |
| | | 25336.014 | 25344.771 | 25373.237 | |
| | | 25340.959 | 25368.331 | 25384.941 | |
| | | 25344.690 | 25389.946 | 25388.548 | |
| | | … | … | … | |
| 2 | | 37354.086 | 37371.424 | 37386.579 | 0.000 |
| | | 37365.103 | 37376.730 | 37390.437 | 16791.038 |
| | | 37373.495 | 37389.643 | 37428.001 | 17955.770 |
| | | 37382.668 | 37394.561 | 37434.720 | 18613.942 |
| | | 37399.086 | 37430.764 | 37436.525 | 19278.372 |
| | | 37420.832 | 37448.663 | 37481.421 | 22898.133 |
| | | 37470.519 | 37509.928 | 37512.880 | 39717.705 |
| | | 37486.726 | 37520.625 | 37526.860 | 40890.507 |
| | | 37505.008 | 37554.523 | 37529.926 | 41567.112 |
| | | 37560.492 | 37588.057 | 37569.176 | 42230.478 |
| | | 37577.797 | 37617.094 | 37575.014 | |
| | | 37588.154 | 37617.726 | 37594.714 | |
| | | 37601.318 | 37645.417 | 37632.357 | |
| | | 37633.091 | 37668.563 | 37653.810 | |
| | | 37641.610 | 37668.617 | 37658.583 | |
| | | 37649.880 | 37694.565 | 37667.426 | |
| | | 37663.999 | 37713.147 | 37682.429 | |
| | | 39033.593 | 39055.683 | 39070.861 | |
| | | 39046.601 | 39066.455 | 39075.776 | |
| | | 39084.498 | 39111.077 | 39132.158 | |
| | | … | … | … | |

**Table S4.** Energies of the lowest spin-orbit states (cm$^{-1}$).

| **Spin orbit energies (RASSI)** | | | |
|---:|---:|---:|---:|
| **Dy1** | **Dy2** | **Dy3** | **Cu** |
| 0.000 | 0.000 | 0.000 | 0.000 |
| 89.773 | 94.571 | 118.074 | 16627.750 |
| 118.022 | 176.540 | 182.822 | 17580.246 |
| 164.407 | 227.134 | 229.912 | 18725.574 |
| 208.756 | 282.757 | 297.322 | 19989.554 |
| 307.808 | 338.063 | 343.775 | 22948.429 |
| 336.295 | 400.718 | 383.366 | 39752.866 |
| 423.123 | 560.323 | 430.332 | 40853.364 |
| 3551.928 | 3546.645 | 3560.904 | 41677.107 |
| 3620.905 | 3659.036 | 3674.445 | 42356.186 |
| 3669.121 | 3713.725 | 3730.757 | |
| 3724.763 | 3776.179 | 3760.973 | |
| 3751.344 | 3825.827 | 3798.209 | |
| 3776.087 | 3863.476 | 3833.829 | |
| 3843.512 | 3931.708 | 3872.628 | |
| 6114.084 | 6113.740 | 6134.979 | |
| 6173.736 | 6209.531 | 6216.301 | |
| 6212.571 | 6273.561 | 6256.435 | |
| 6252.427 | 6326.127 | 6305.842 | |
| 6283.432 | 6369.102 | 6359.751 | |
| 6373.973 | 6441.745 | 6389.779 | |
| 8068.298 | 8083.296 | 8105.473 | |
| 8124.199 | 8170.589 | 8166.007 | |
| 8185.385 | 8244.191 | 8224.562 | |
| 8224.474 | 8307.926 | 8293.394 | |
| 8312.462 | 8377.693 | 8338.530 | |
| 9587.747 | 9615.002 | 9632.561 | |
| 9694.531 | 9732.668 | 9734.192 | |
| 9749.728 | 9829.804 | 9798.893 | |
| 9827.277 | 9895.367 | 9866.874 | |
| … | … | … | |

**Table S5.** Main values of the *g* tensors for the lowest Kramers doublet on Cu (II) calculated in different computational approximations:

| | **A** | **B** | **C** |
|---|---|---|---|
| $g_x$ | 2.0879 | 2.0561 | 2.0757 |
| $g_y$ | 2.1174 | 2.0896 | 2.0994 |
| $g_z$ | 2.5098 | 2.3357 | 2.4137 |

**A** – CAS (9 in 10), RASSI – mixing of 5 ligand field (LF) states;
**B** – CAS (11 in 11),RASSI – mixing of 5 LF states + 5 charge transfer (CT) states;
**C** – CAS (11 in 11),CASPT2, RASSI – mixing of 5 LF states + 5 CT states.

The exchange couplings between all interacting magnetic sites were found antiferromagnetic. The values of the best Lines exchange parameters, obtained from the fitting of $\chi T(T)$ and *M(H)* for **D-2** are **$J_1$(Dy-Dy)=-0.47 cm$^{-1}$** and **$J_2$(Dy-Cu) = -0.64 cm$^{-1}$**. Figures 5 (from the main text) and S3-S5 show the comparison between measured and calculated magnetic properties.

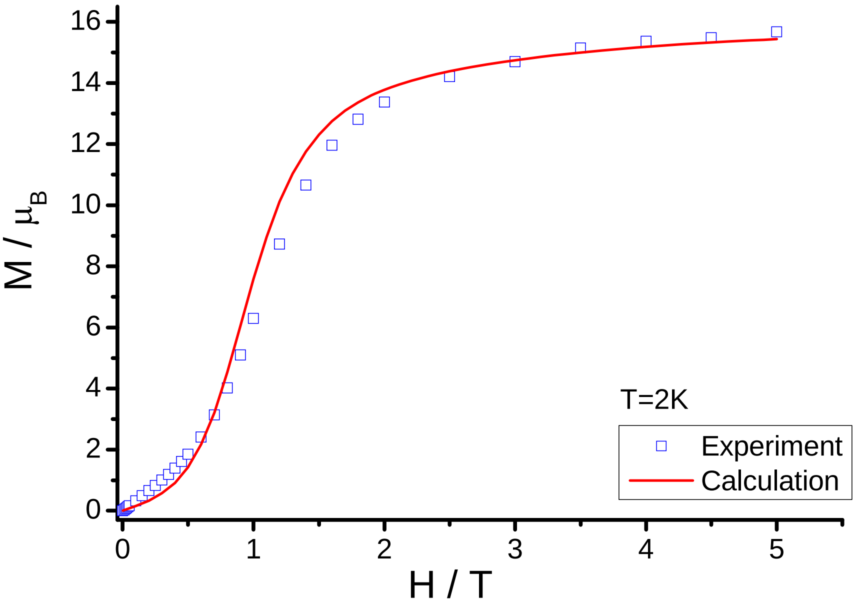

**Figure S13.** A comparison between measured (empty squares) and calculated (red line) molar magnetization at 2.0 K for the D-$Dy_3Cu$ chain.

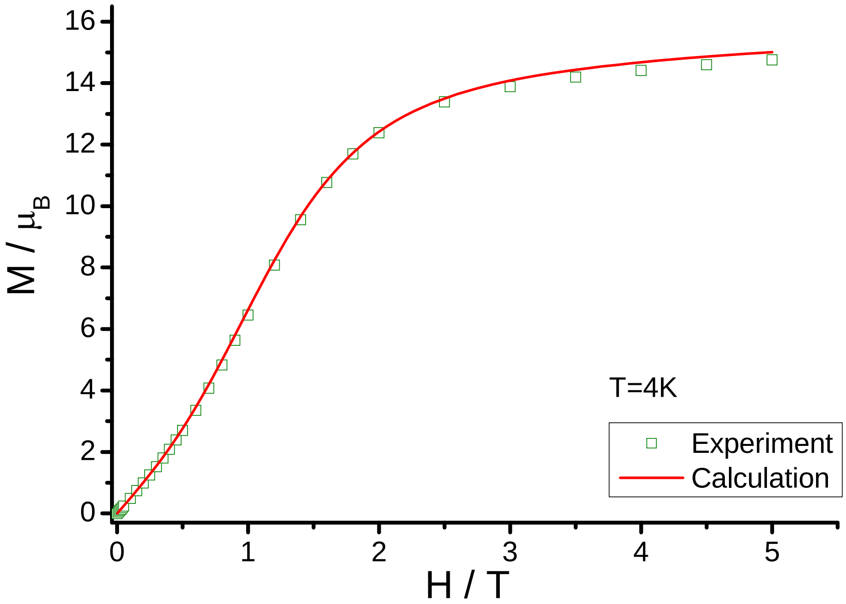

**Figure S14.** A comparison between measured (empty squares) and calculated (red line) molar magnetization at 4.0 K for the D-$Dy_3Cu$ chain.

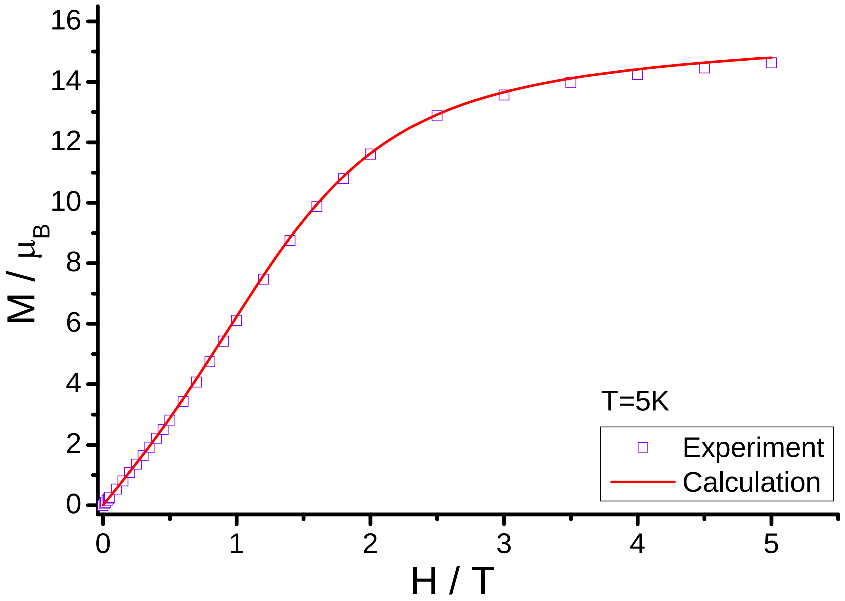

**Figure S15.** A comparison between measured (empty squares) and calculated (red line) molar magnetization at 5.0 K for the **D-2** chain.