

## *Supporting Information*

### **Structure and Assembly Studies of Two Planar Dy(III) Single Molecule Magnets with Double Relaxation**

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## 1. Experimental

### Materials and Measurements.

All chemical reagents were used as commercially received without further purification. The Fourier transform infrared (FT-IR) data of the two complexes were collected on Perkin-Elmer Spectrum One FT-IR spectrometer using the corresponding KBr Pellets in the wavenumber range of 4000-400  $\text{cm}^{-1}$ . The powder X-ray diffraction (PXRD) measurements were carried out on a Rigaku D/max 2500v/pc diffractometer equipped with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 40 kV and 40 mA, with a step size of  $0.02^\circ$  in  $2\theta$  and a scan speed of  $5^\circ \text{ min}^{-1}$ . Elemental analyses for C, H, and N for the two complexes were performed on an Elementar Micro cube C, H, N elemental analyzer. The TG analyses (30-1000  $^\circ\text{C}$ ) for **1** and **2** were conducted on a PerkinElmer Diamond TG/DTA thermal analyzer in a flowing nitrogen atmosphere with a heating rate of  $5^\circ \text{C min}^{-1}$ . All magnetic data were measured on a Quantum Design MPMS SQUID-XL-7 SQUID magnetometer furnished with a 7 T magnet. The magnetic data of the two complexes were corrected with a consideration of diamagnetic contribution from the sample and the sample holder.

### Single-crystal X-ray crystallography.

Diffraction data for these complexes were collected on a Bruker SMART CCD diffractometer (Mo K $\alpha$  radiation and  $\lambda = 0.71073 \text{ \AA}$ ) in  $\Phi$  and  $\omega$  scan modes. The structures were solved by direct methods, followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques on  $F^2$  using SHELXL. All other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed at calculated positions and isotropically refined using a riding model.

The lattice molecules in **2** couldn't be modelled directly probably due to heavy disorder.

The use of SQUEEZE procedure gave a volume of 1070 Å<sup>3</sup> with 156 electrons in one unit cell, which corresponds to four MeOH, two CH<sub>3</sub>CN and four H<sub>2</sub>O molecules. Table S3 summarizes X-ray crystallographic data and refinement details for the complexes. Full details can be found in the CIF files provided in the Supporting Information. The CCDC reference numbers are 2291880 and 2291881 for **1** and **2**, respectively.

#### **The detection method for intermediates:**

The similar methods and procedures were used to test and track the assembly process for complexes **1** and **2**. Therefore, only that for **1** was presented here in detail as an example. The synthesis of complex **1** was carried out using solvothermal method in sealed. 20 parallel reactions were carried out simultaneously in an oven at 80 °C with all required raw materials sealed in high-temperature resistant Pyrex tubes. When the reaction time reached 5, 15, 25, 40, 60, 90, 130, 180, 240, and 360 minutes, glass tubes were taken out successively, from which 0.2 ml of reaction solution was quickly taken out, diluted with 20 mL of methanol, and then subjected to HR-ESI tests.

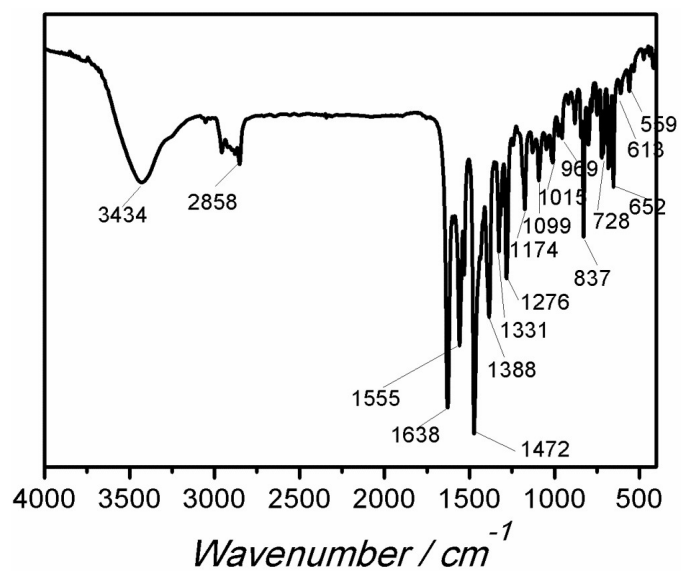
#### **ESI-MS measurement.**

ESI-MS measurements were conducted at a capillary temperature of 275 °C. Aliquots of the solution were injected into the device at 0.3 mL/h. The mass spectrometer used for the measurements was a Thermo Exactive, and the data were collected in positive and negative ion modes. The spectrometer was previously calibrated with the standard tune mix to give a precision of ca. 2 ppm within the region of 200 - 2000 m/z. The capillary voltage was 50 V, the tube lens voltage was 150 V,

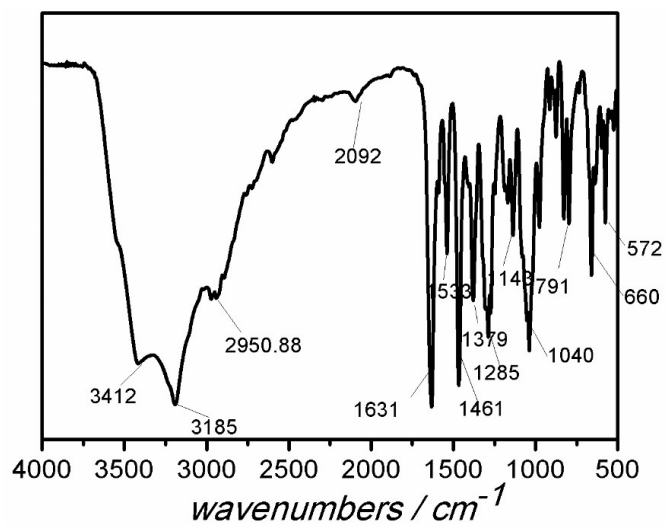
and the skimmer voltage was 25 V. The in-source energy was set within the range of 0-80 eV with a gas flow rate at 10% of the maximum.

## **2. characterization**

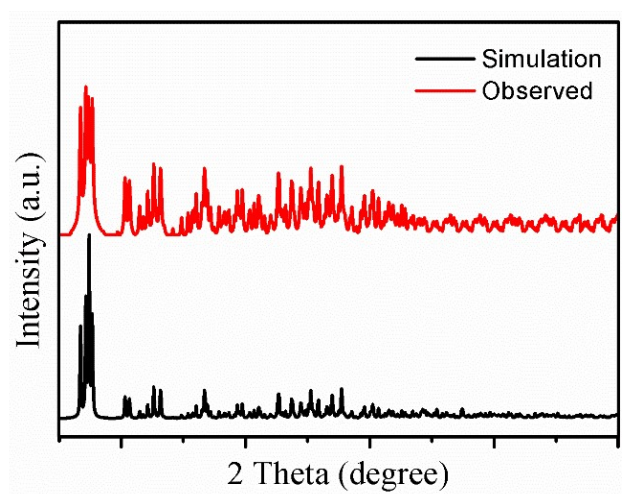
The TG analyses of **1** and **2** are shown in Fig. S5 and S6, respectively. Upon increasing the temperature, **1** underwent a fast weight loss of 6.67% before 80 °C with a subsequent much slower weight loss, which corresponds to the loss of five acetonitrile, (calcd 6.62%) per formular unit of **1**. The followed was a subsequent much slower weight loss at 80 - 347 °C, which corresponds to the loss of the ligands of L'. The followed weight losses were due to the collapse of the Schiff base ligands in **1**, which didn't come to an end even when the temperature reaches 1000 °C. Upon heating, a continuous weight loss was found. It underwent a fast weight loss before 75 °C with a subsequent slower weight loss. The weight loss of 7.24% before 182 °C is due to the loss of free solvent molecules (four H<sub>2</sub>O, four CH<sub>3</sub>OH and two CH<sub>3</sub>CN) per formular unit (calcd 8.45%). Then it keep stable at 182 - 230 °C. Upon heating, the weight losses were due to loss of coordinated Cl and skeleton collapse. The followed weight loss was incomplete even upon being heated at 1000 °C. The purities of the collected bulky crystalline samples of complexes **1** and **2** were confirmed by the nice agreement of the experimental PXRD curves with the simulated ones derived from the corresponding single crystal X-ray diffraction data as shown in Fig. S3 and S4, respectively.



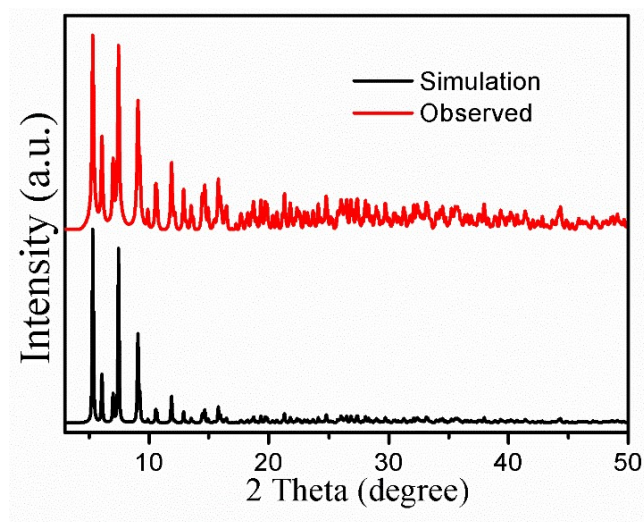
**Fig. S1** FT-IR spectrum of 1.



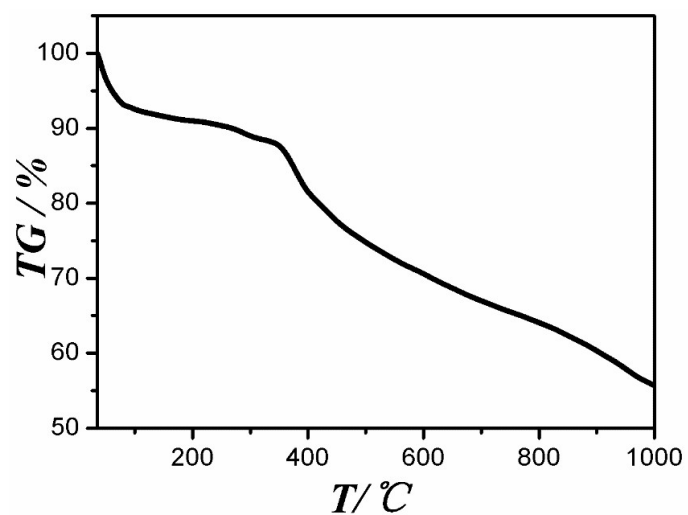
**Fig. S2** FT-IR spectrum of 2.



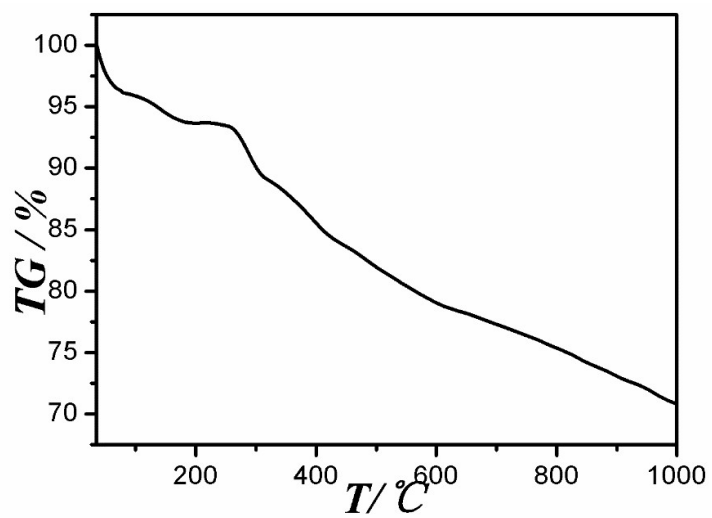
**Fig. S3** PXRD patterns of 1.



**Fig. S4** PXR D patterns of **2**.



**Fig. S5** TG of **1**.



**Fig. S6** TG of **2**.

**Table S1.** Crystallographic data of **1** and **2**.

| Compound   | <b>1</b>   | <b>2</b>  |
|--|--|---|
| Formula  | C <sub>96</sub> H <sub>89</sub> Br <sub>10</sub> Dy <sub>4</sub> N <sub>13</sub> O <sub>14</sub> | C <sub>78</sub> H <sub>116</sub> Br <sub>6</sub> Cl <sub>4</sub> Dy <sub>6</sub> N <sub>8</sub> O <sub>36</sub> |
| fw   | 3097.90  | 3338.00   |
| <i>T</i> / K                                       | 100(2)   | 100(2)  |
| $\lambda$ / Å                                      | 0.71073  | 1.54184   |
| crystal system                                     | Triclinic  | Triclinic   |
| space group  | <i>P</i> $\bar{1}$   | <i>P</i> $\bar{1}$  |
| <i>a</i> / Å                                       | 14.4150 (2)  | 11.8746 (4)   |
| <i>b</i> / Å                                       | 14.6798 (3)  | 15.0586 (6)   |
| <i>c</i> / Å                                       | 15.0212 (2)  | 17.1270 (6)   |
| $\alpha$ / °                                       | 108.858 (2)  | 75.517 (3)  |
| $\beta$ / °  | 103.154 (1)  | 88.043 (3)  |
| $\gamma$ / °                                       | 110.262 (2)  | 86.203 (3)  |
| <i>V</i> / Å <sup>3</sup>                          | 2607.36 (9)  | 2958.24 (19)  |
| <i>Z</i>   | 1  | 1   |
| <i>D</i> <sub>c</sub> / g·cm <sup>-3</sup>         | 1.973  | 1.715   |
| $\mu$ / mm <sup>-1</sup>                           | 6.73   | 23.59   |
| $2\theta$ / °                                      | 3.200 to 49.000  | 5.200 to 157.600  |
| <i>F</i> (000)                                     | 1482   | 1446.0  |
| reflns collected                                   | 11732  | 34598   |
| reflns unique                                      | 8981   | 18744   |
| <i>R</i> <sub>int</sub>                            | 0.050  | 0.081   |
| GOF on <i>F</i> <sup>2</sup>                       | 1.086  | 1.051   |
| <i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> )) | 0.0423   | 0.0670  |
| $\omega R_2$ ( <i>I</i> > 2σ( <i>I</i> ))          | 0.1045   | 0.1799  |
| <i>R</i> <sub>1</sub> (all data)                   | 0.0627   | 0.0727  |
| $\omega R_2$ (all data)                            | 0.1112   | 0.1844  |

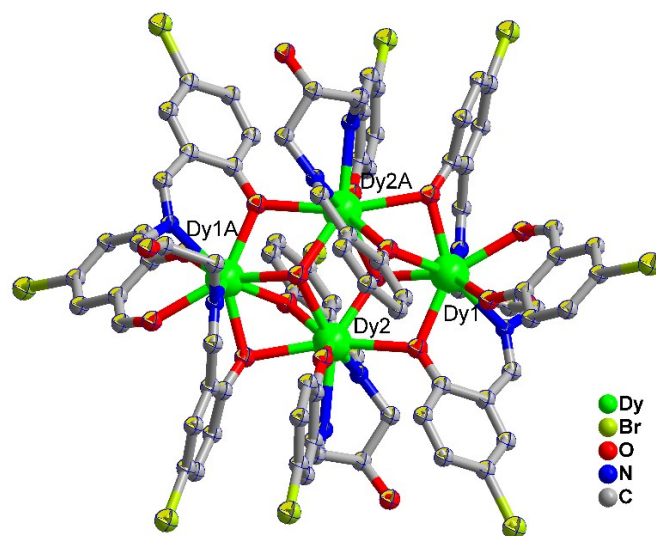
**Table S2.** Selected bond lengths / Å and bond angles / ° for **1**.

|            |             |            |             |             |             |
|------------|-------------|------------|-------------|-------------|-------------|
| Dy1-O1     | 2.326 (4)   | Dy2-O1     | 2.364 (3)   | O1-Dy1-O3   | 69.25 (12)  |
| Dy1-O2     | 2.321 (4)   | Dy2-O1A    | 2.362 (3)   | O1-Dy1-N1   | 72.97 (14)  |
| Dy1-O3     | 2.340 (4)   | Dy2-O2A    | 2.538 (4)   | O1-Dy1-N2   | 109.67 (15) |
| Dy1-N1     | 2.526 (5)   | Dy2-O3     | 2.503 (4)   | O1-Dy1-O5   | 146.43 (14) |
| Dy1-N2     | 2.519 (5)   | Dy2-N3     | 2.474 (5)   | O1-Dy1-O6A  | 69.61 (12)  |
| Dy1-O4     | 2.240 (4)   | Dy2-N4     | 2.522 (5)   | O2-Dy1-O1   | 78.71 (13)  |
| Dy1-O5     | 2.413 (5)   | Dy2-O6     | 2.392 (4)   | O2-Dy1-O3   | 142.61 (13) |
| Dy1-O6A    | 2.487 (4)   | Dy2-O7     | 2.212 (4)   | O2-Dy1-N1   | 73.54 (14)  |
| O3-Dy1-N1  | 112.97 (14) | N2-Dy1-N1  | 69.66 (16)  | O2-Dy1-N2   | 137.23 (14) |
| O3-Dy1-N2  | 73.91 (14)  | O4-Dy1-O1  | 141.17 (14) | O2-Dy1-O5   | 74.37 (15)  |
| O3-Dy1-O5  | 142.04 (15) | O4-Dy1-O2  | 119.38 (15) | O2-Dy1-O6A  | 65.99 (12)  |
| O3-Dy1-O6A | 84.69 (12)  | O4-Dy1-O3  | 78.94 (15)  | O6A-Dy1-N1  | 128.84 (14) |
| O5-Dy1-N1  | 80.40 (17)  | O4-Dy1-N1  | 142.52 (15) | O6A-Dy1-N2  | 156.78 (14) |
| O5-Dy1-N2  | 78.67 (17)  | O4-Dy1-N2  | 80.99 (17)  | O1A-Dy2-O1  | 72.58 (13)  |
| O5-Dy1-O6A | 115.35 (15) | O4-Dy1-O5  | 71.18 (16)  | O1A-Dy2-O2A | 73.85 (12)  |
| O3-Dy2-O2A | 160.87 (12) | O4-Dy1-O6A | 86.21 (14)  | O1-Dy2-O2A  | 132.03 (12) |
| O3-Dy2-N4  | 90.72 (14)  | O1A-Dy2-O6 | 70.69 (12)  | O1A-Dy2-O3  | 111.88 (12) |
| N3-Dy2-O2A | 105.78 (14) | O1-Dy2-O6  | 72.90 (12)  | O1-Dy2-O3   | 65.95 (12)  |
| N3-Dy2-O3  | 81.25 (14)  | O6-Dy2-O2A | 64.18 (12)  | O1-Dy2-N3   | 81.71 (13)  |
| N3-Dy2-N4  | 73.34 (14)  | O6-Dy2-O3  | 134.80 (12) | O1A-Dy2-N3  | 141.75 (13) |
| O7-Dy2-O1  | 121.93 (13) | O6-Dy2-N3  | 75.00 (13)  | O1A-Dy2-N4  | 138.55 (13) |
| O7-Dy2-O1A | 74.45 (12)  | O6-Dy2-N4  | 117.51 (15) | O1-Dy2-N4   | 148.27 (14) |
| O7-Dy2-O2A | 79.46 (13)  | O7-Dy2-N3  | 143.78 (13) | O7-Dy2-N4   | 73.71 (14)  |
| O7-Dy2-O3  | 84.54 (13)  | O7-Dy2-O6  | 134.96 (13) | O26-Dy2-O8  | 80.4 (4)    |

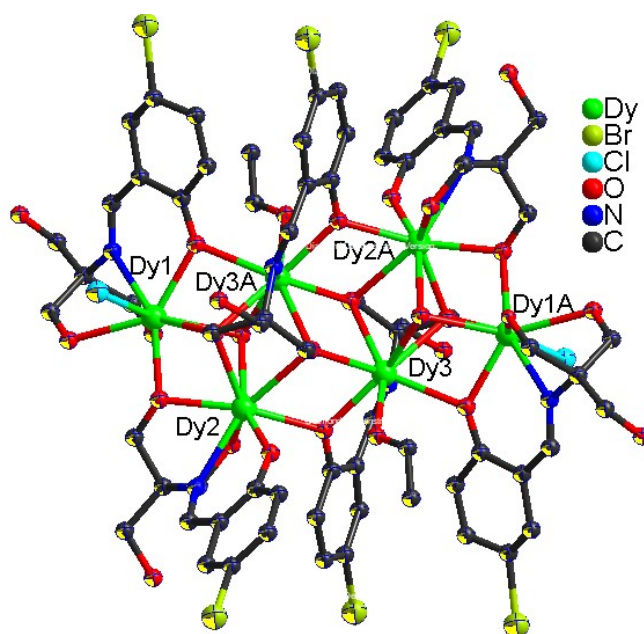


**Table S3.** Selected bond lengths / Å and bond angles / ° for **2**.

|             |             |             |             |             |             |
|-------------|-------------|-------------|-------------|-------------|-------------|
| Dy1-O1      | 2.293 (5)   | Dy2-O1      | 2.394 (6)   | Dy3-O1      | 2.465 (5)   |
| Dy1-O2      | 2.448 (5)   | Dy2-O2      | 2.368 (5)   | Dy3-O2      | 2.366 (5)   |
| Dy1-O3      | 2.385 (6)   | Dy2-O3      | 2.603 (5)   | Dy3-O6      | 2.222 (6)   |
| Dy1-O3A     | 2.338 (6)   | Dy2-O5A     | 2.338 (6)   | Dy3-O10     | 2.459 (6)   |
| Dy1-N1      | 2.460 (7)   | Dy2-O6      | 2.336 (6)   | Dy3-O11     | 2.423 (6)   |
| Dy1-O5      | 2.308 (5)   | Dy2-O7      | 2.400 (6)   | Dy3-N3      | 2.490 (8)   |
| Dy1-O13     | 2.397 (6)   | Dy2-N2      | 2.479 (7)   | Dy3-O13     | 2.287 (6)   |
| Dy1-O14     | 2.405 (6)   | Dy2-O9      | 2.237 (6)   | Dy3-Cl1     | 2.692 (2)   |
| O1-Dy1-O2   | 61.79 (18)  | O3A-Dy1-O2  | 127.73 (18) | O5-Dy1-O2   | 140.11 (19) |
| O1-Dy1-O3   | 83.20 (19)  | O3-Dy1-O2   | 66.44 (18)  | O5-Dy1-O3A  | 74.3 (2)    |
| O1-Dy1-O3A  | 83.71 (19)  | O3A-Dy1-O3  | 71.9 (2)    | O5-Dy1-O3   | 97.86 (19)  |
| O1-Dy1-N1   | 130.7 (2)   | O3-Dy1-N1   | 70.5 (2)    | O5-Dy1-N1   | 70.6 (2)    |
| O1-Dy1-O5   | 156.33 (19) | O3A-Dy1-N1  | 123.2 (2)   | O5-Dy1-O13  | 116.3 (2)   |
| O1-Dy1-O13  | 76.5 (2)    | O3A-Dy1-O13 | 142.2 (2)   | O5-Dy1-O14  | 72.2 (2)    |
| O1-Dy1-O14  | 94.4 (2)    | O3-Dy1-O13  | 135.48 (19) | O13-Dy1-O2  | 69.04 (18)  |
| O2-Dy1-N1   | 69.5 (2)    | O3-Dy1-O14  | 148.1 (2)   | O13-Dy1-N1  | 93.8 (2)    |
| O14-Dy1-O2  | 139.17 (19) | O3A-Dy1-O14 | 76.3 (2)    | O13-Dy1-O14 | 73.5 (2)    |
| O14-Dy1-N1  | 129.5 (2)   | O1-Dy2-O3   | 76.75 (17)  | O1-Dy2-O7   | 78.32 (19)  |
| O2-Dy2-O1   | 61.60 (19)  | O5A-Dy2-O1  | 92.24 (19)  | O1-Dy2-N2   | 134.0 (2)   |
| O2-Dy2-O3   | 64.19 (17)  | O5A-Dy2-O2  | 130.11 (19) | O5A-Dy2-O7  | 74.4 (2)    |
| O2-Dy2-O7   | 131.1 (2)   | O5A-Dy2-O3  | 68.97 (19)  | O5A-Dy2-N2  | 106.2 (2)   |
| O2-Dy2-N2   | 122.8 (2)   | O6-Dy2-O7   | 74.3 (2)    | O7-Dy2-O3   | 134.24 (18) |
| O6-Dy2-O1   | 76.82 (19)  | O6-Dy2-N2   | 65.3 (2)    | N2-Dy2-O3   | 149.2 (2)   |
| O6-Dy2-O2   | 70.47 (19)  | O9-Dy2-O1   | 154.04 (19) | O9-Dy2-O7   | 122.5 (2)   |
| O6-Dy2-O3   | 134.24 (19) | O9-Dy2-O2   | 104.6 (2)   | O9-Dy2-N2   | 71.8 (2)    |
| O6-Dy2-O5A  | 148.3 (2)   | O9-Dy2-O3   | 77.37 (19)  | O1-Dy3-N3   | 115.2 (2)   |
| O2-Dy3-O1   | 60.58 (18)  | O9-Dy2-O5A  | 80.4 (2)    | O1-Dy3-Cl1  | 141.97 (13) |
| O2-Dy3-O10  | 143.9 (2)   | O9-Dy2-O6   | 121.3 (2)   | O10-Dy3-O1  | 136.5 (2)   |
| O2-Dy3-O11  | 131.9 (2)   | O6-Dy3-O1   | 77.5 (2)    | O10-Dy3-N3  | 66.0 (2)    |
| O2-Dy3-N3   | 144.6 (2)   | O6-Dy3-O2   | 72.45 (19)  | O10-Dy3-Cl1 | 78.93 (16)  |
| O2-Dy3-Cl1  | 82.39 (14)  | O6-Dy3-O10  | 81.0 (2)    | O11-Dy3-O1  | 72.6 (2)    |
| O13-Dy3-O1  | 75.3 (2)    | O6-Dy3-O11  | 88.0 (2)    | O11-Dy3-O10 | 69.3 (2)    |
| O13-Dy3-O2  | 72.33 (19)  | O6-Dy3-N3   | 143.0 (2)   | O11-Dy3-N3  | 65.6 (2)    |
| O13-Dy3-O10 | 135.9 (2)   | O6-Dy3-O13  | 142.8 (2)   | O11-Dy3-Cl1 | 145.36 (16) |
| O13-Dy3-O11 | 107.1 (2)   | O6-Dy3-Cl1  | 100.65 (17) | N3-Dy3-Cl1  | 89.37 (19)  |
| O13-Dy3-N3  | 72.8 (2)    | O13-Dy3-Cl1 | 86.06 (16)  |             |             |



**Fig. S7** The structure of **1** with 30% probability ellipsoid and selected atoms labelled. Hydrogen atoms are omitted for clarity. Symmetry code: A)  $-x + 1, -y + 1, -Z + 1$ .



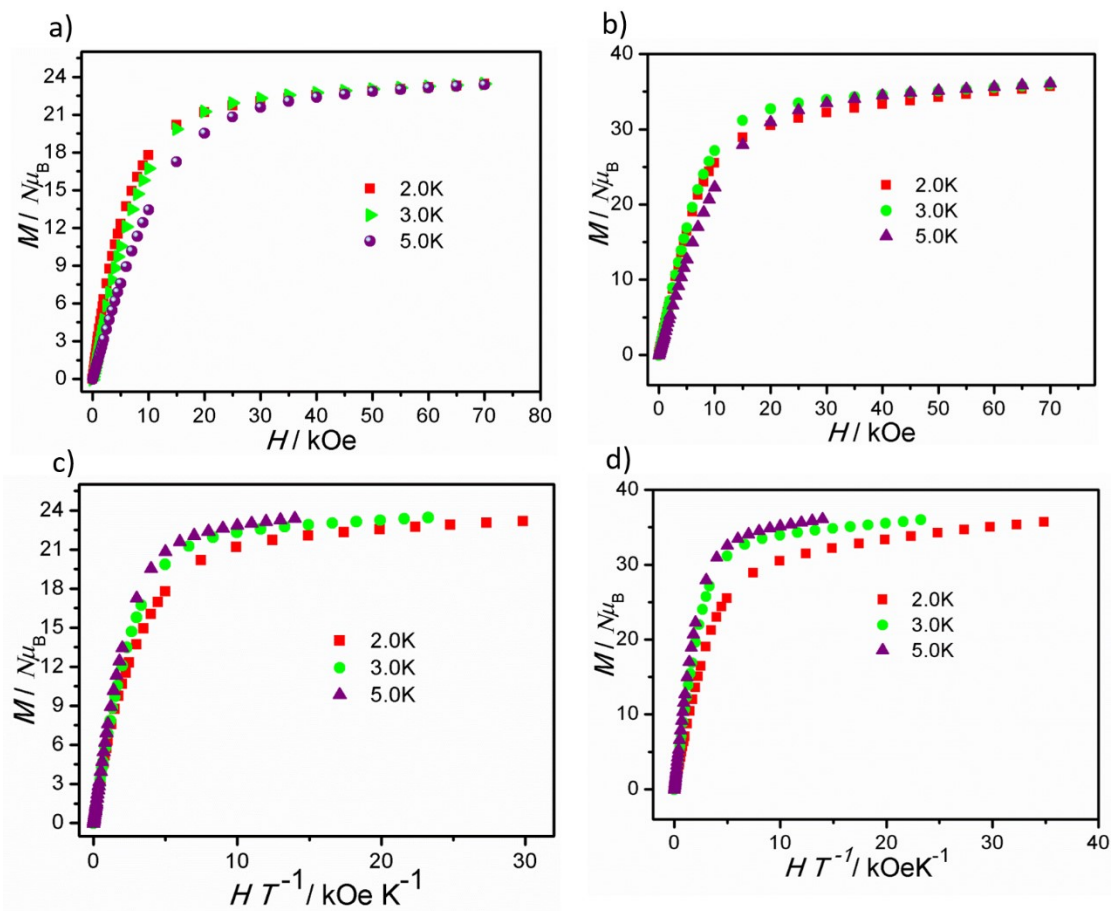
**Fig. S8** The structure of **2** with 30% probability ellipsoid and selected atoms labelled. Hydrogen atoms are omitted for clarity. Symmetry code: A)  $-x + 1, -y + 1, -Z + 1$ .

**Table S4.** SHAPE analysis of Dy1 and Dy2 in **1**

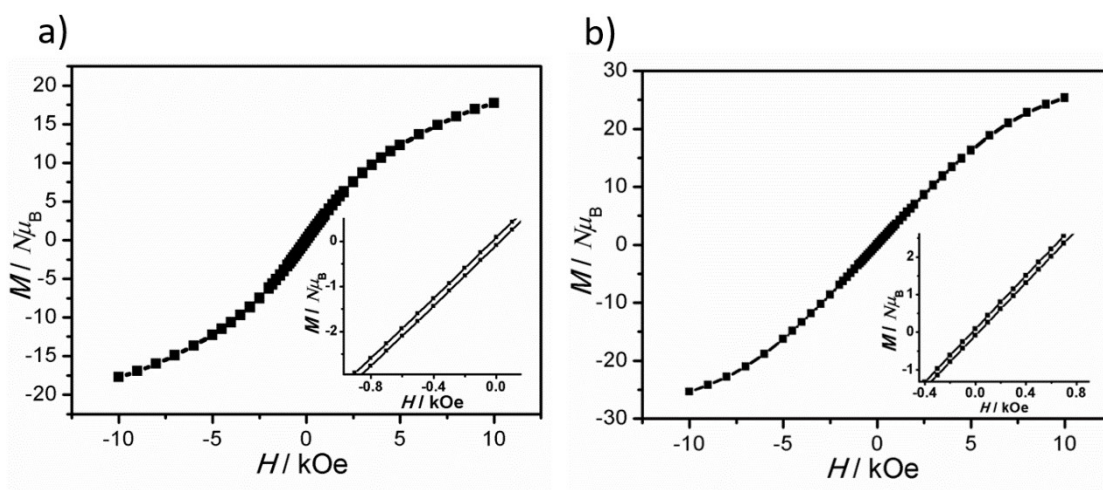
| Configuration   | ABOXIY(Dy1)  | ABOXIY(Dy2)  |
|---|--------------|--------------|
| Octagon ( $D_{8h}$ )                                    | 29.832       | 30.059       |
| Heptagonal pyramid ( $C_{7v}$ )                         | 21.038       | 22.189       |
| Hexagonal bipyramid ( $D_{6h}$ )                        | 15.226       | 14.981       |
| Cube ( $O_h$ )  | 8.282        | 8.848        |
| <b>Square antiprism (<math>D_{4d}</math>)</b>           | <b>0.829</b> | <b>1.173</b> |
| Triangular dodecahedron ( $D_{2d}$ )                    | 2.582        | 2.884        |
| Johnson gyrobifastigium J26 ( $D_{2d}$ )                | 15.593       | 14.951       |
| Johnson elongated triangular bipyramid J14 ( $D_{3H}$ ) | 26.498       | 27.063       |
| Biaugmented trigonal prism J50 ( $C_{2v}$ )             | 3.222        | 3.205        |
| Biaugmented trigonal prism ( $C_{2v}$ )                 | 2.656        | 2.629        |
| Snub diphenoid J84 ( $D_{2d}$ )                         | 5.328        | 5.555        |
| Triakis tetrahedron ( $T_d$ )                           | 8.722        | 9.520        |
| Elongated trigonal bipyramid ( $D_{3h}$ )               | 23.403       | 23.756       |

**Table S5.** SHAPE analysis of Dy1, Dy2 and Dy3 in **2**

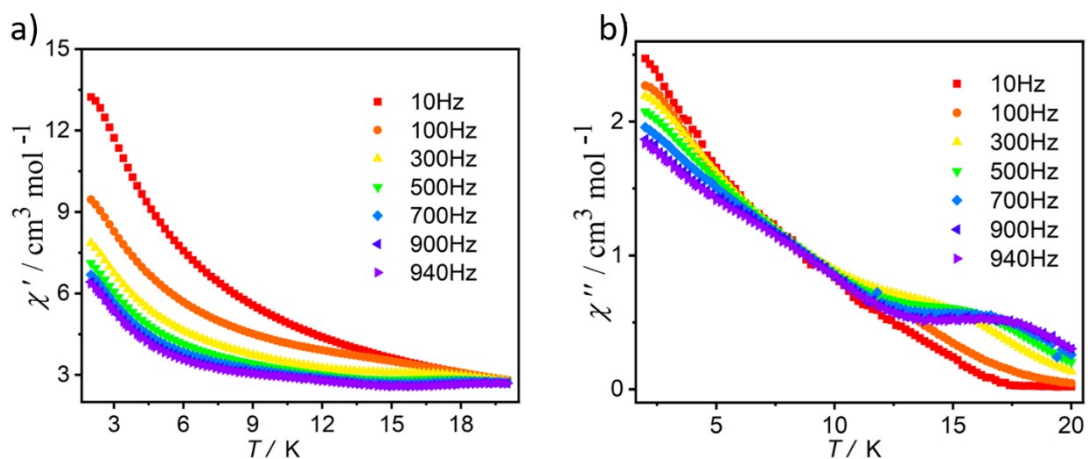
| Configuration   | ABOXIY(Dy1)  | Dy2          | Dy3          |
|---|--------------|--------------|--------------|
| Octagon ( $D_{8h}$ )                                    | 28.969       | 28.677       | 31.584       |
| Heptagonal pyramid ( $C_{7v}$ )                         | 23.494       | 20.055       | 20.249       |
| Hexagonal bipyramid ( $D_{6h}$ )                        | 15.748       | 12.228       | 15.923       |
| Cube ( $O_h$ )  | 11.819       | 11.574       | 12.388       |
| Square antiprism ( $D_{4d}$ )                           | 2.445        | 4.580        | 3.690        |
| Triangular dodecahedron ( $D_{2d}$ )                    | 2.477        | 4.085        | 2.371        |
| Johnson gyrobifastigium J26 ( $D_{2d}$ )                | 13.687       | 8.422        | 12.202       |
| Johnson elongated triangular bipyramid J14 ( $D_{3H}$ ) | 28.202       | 24.262       | 25.646       |
| Biaugmented trigonal prism J50 ( $C_{2v}$ )             | 2.777        | 3.731        | 2.741        |
| <b>Biaugmented trigonal prism (<math>C_{2v}</math>)</b> | <b>2.067</b> | <b>3.482</b> | <b>1.863</b> |
| Snub diphenoid J84 ( $D_{2d}$ )                         | 4.233        | 5.781        | 4.062        |
| Triakis tetrahedron ( $T_d$ )                           | 12.266       | 12.203       | 12.769       |
| Elongated trigonal bipyramid ( $D_{3h}$ )               | 24.183       | 19.895       | 22.526       |



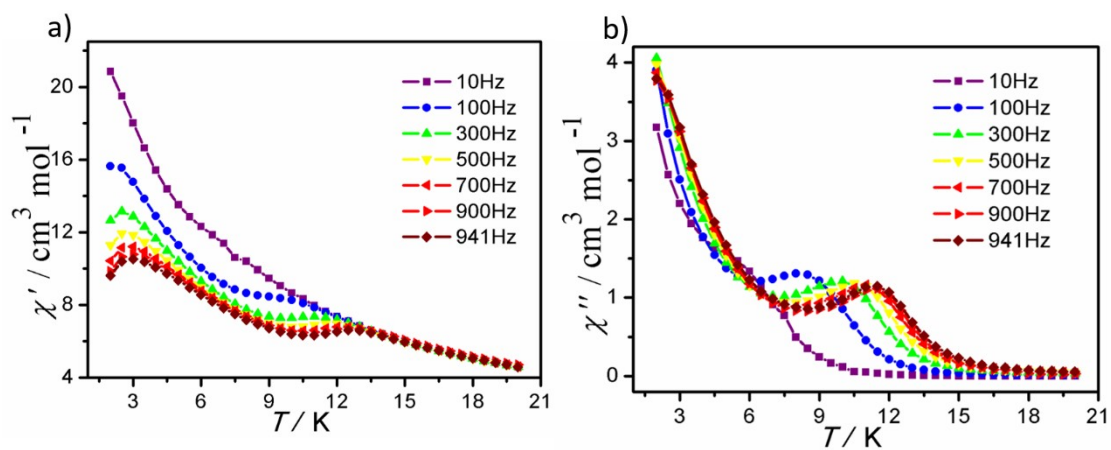
**Fig. S9** Plots of  $M$  vs.  $H$  and  $HT^{-1}$  for **1** (a and c) and **2** (b and d) measured at 2.0, 3.0 and 5.0 K.



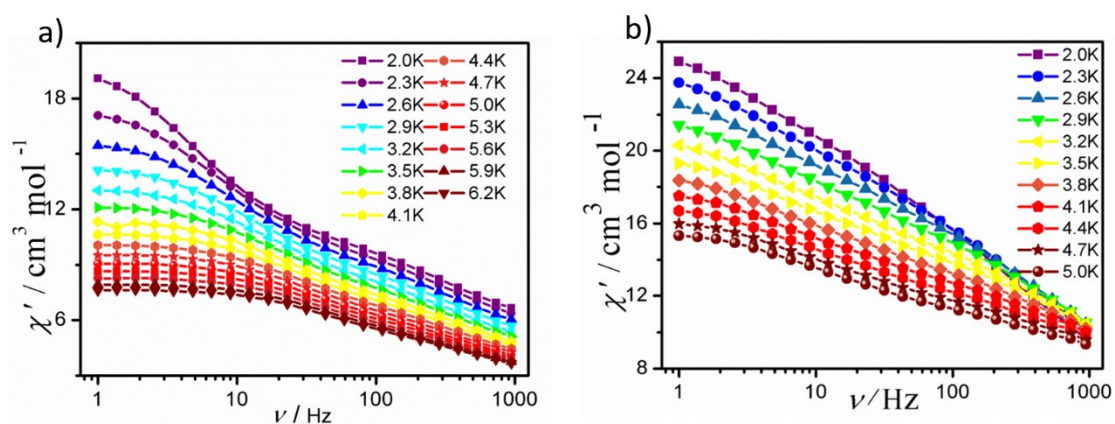
**Fig. S10** Plots of Magnetic hysteresis loops for **1** (a) and **2** (b).



**Fig. S11** Temperature-dependent (a)  $\chi'$  and (b)  $\chi''$  ac susceptibilities under zero dc field for **1**.



**Fig. S12** Temperature-dependent (a)  $\chi'$  and (b)  $\chi''$  ac susceptibilities under zero dc field for **2**.



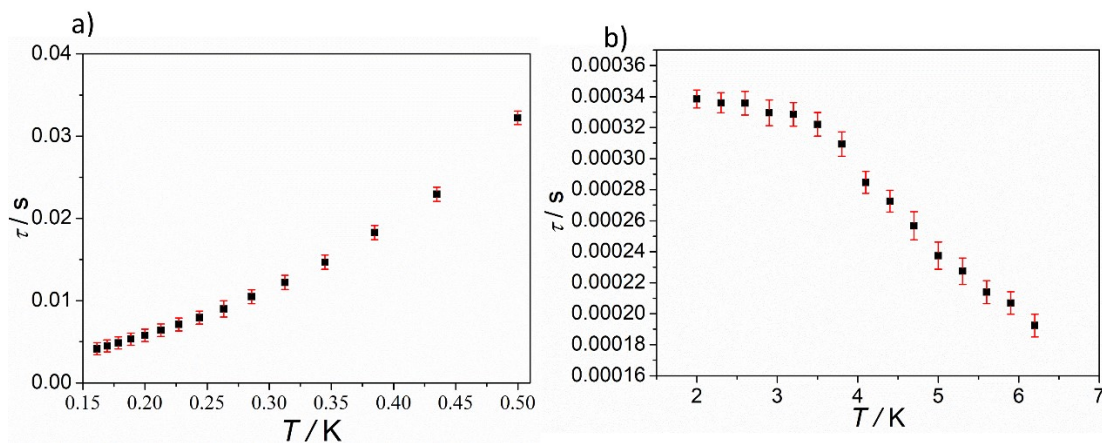
**Fig. S13** Plots of  $\chi'$  vs  $\nu$  (a) at 2.0-6.2 K and 2.0-5.0 K under a dc field of 0 Oe for **1** and **2**.

**Table S6.** Relaxation time ( $\tau$  / s) with the error for complex **1**.

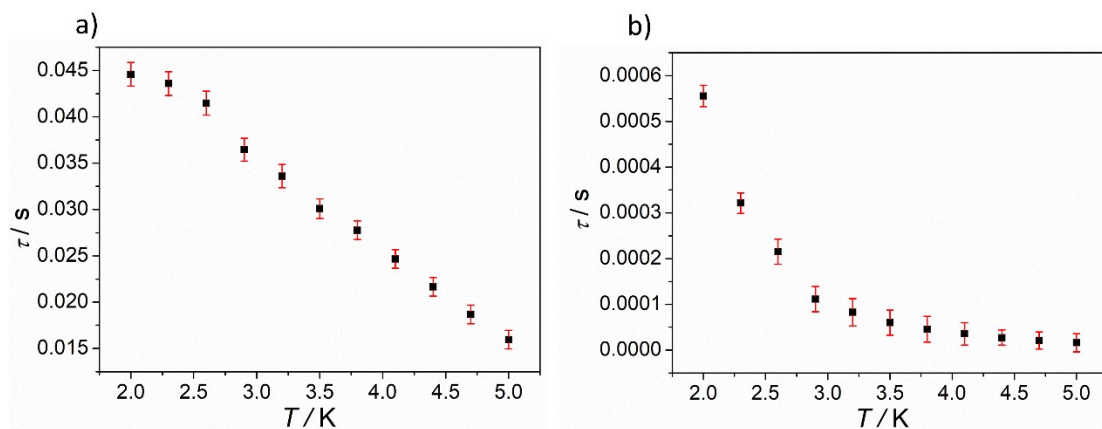
| T   | <b>1 (FR)</b> |            | <b>1 (SR)</b> |            |
|-----|---------------|------------|---------------|------------|
|     | tau           | tau_err    | tau           | tau_err    |
| 2.0 | 3.38462E-4    | 5.77126E-6 | 0.03278       | 8.21785E-4 |
| 2.3 | 3.36021E-4    | 6.56162E-6 | 0.02357       | 8.58735E-4 |
| 2.6 | 3.35801E-4    | 7.66749E-6 | 0.01815       | 8.61034E-4 |
| 2.9 | 3.29588E-4    | 8.28903E-6 | 0.01464       | 8.74872E-4 |
| 3.2 | 3.28574E-4    | 7.60533E-6 | 0.01217       | 8.60597E-4 |
| 3.5 | 3.22099E-4    | 7.66717E-6 | 0.01038       | 8.37678E-4 |
| 3.8 | 3.09327E-4    | 7.85395E-6 | 0.009         | 9.85016E-4 |
| 4.1 | 2.84613E-4    | 7.08028E-6 | 0.00798       | 7.9962E-4  |
| 4.4 | 2.72456E-4    | 7.02313E-6 | 0.0071        | 7.86438E-4 |
| 4.7 | 2.56648E-4    | 9.03056E-6 | 0.0064        | 7.60782E-4 |
| 5.0 | 2.37442E-4    | 8.79552E-6 | 0.0058        | 7.59708E-4 |
| 5.3 | 2.27402E-4    | 8.58745E-6 | 0.00532       | 7.40514E-4 |
| 5.6 | 2.13909E-4    | 7.34948E-6 | 0.00487       | 7.32866E-4 |
| 5.9 | 2.06923E-4    | 7.29622E-6 | 0.00448       | 7.28102E-4 |
| 6.2 | 1.92343E-4    | 7.35153E-6 | 0.00414       | 7.38579E-4 |

**Table S7.** Relaxation time ( $\tau$  / s) with the error for complex **2**.

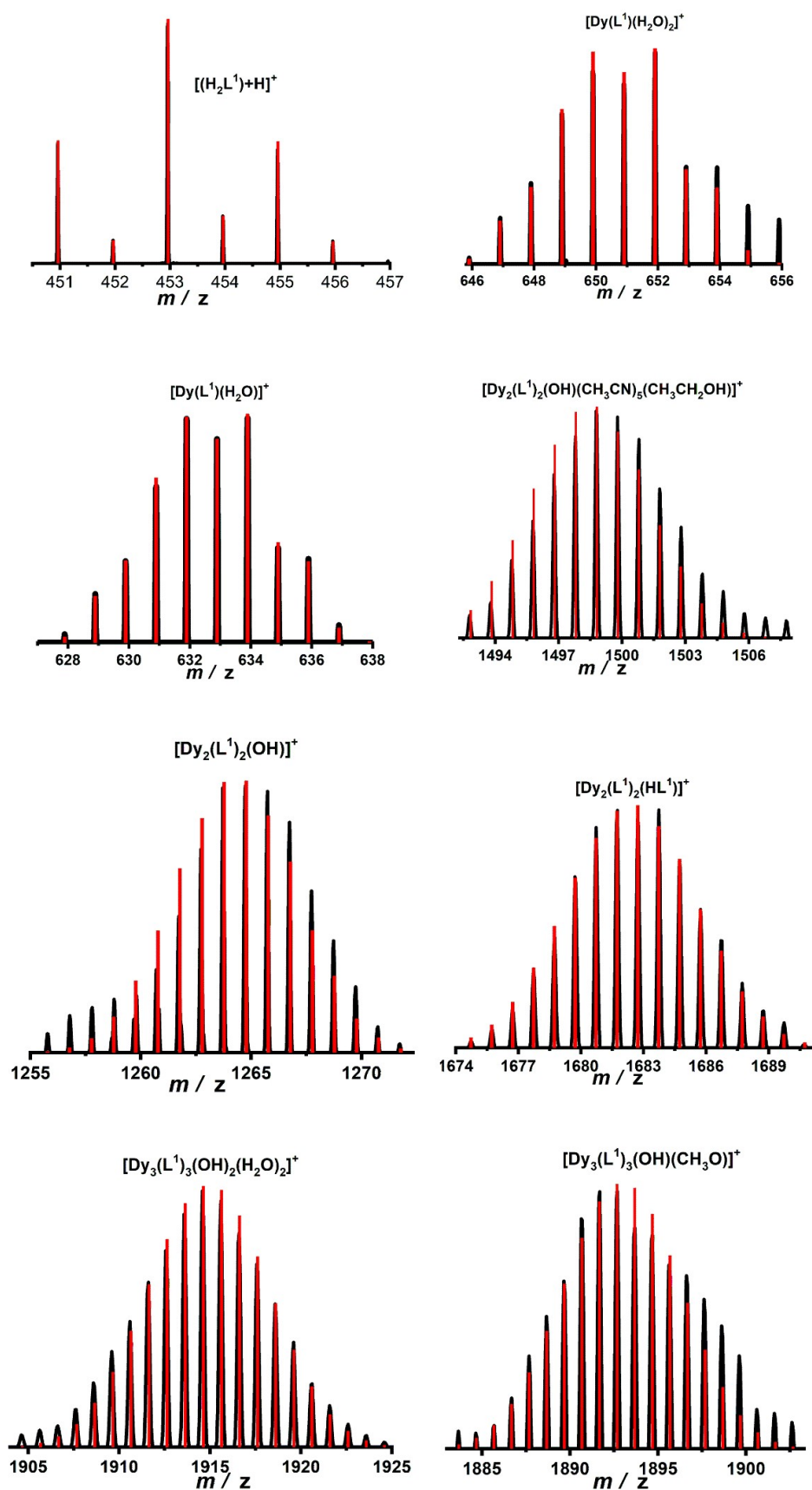
| T   | <b>2 (FR)</b> |            | <b>2 (SR)</b> |         |
|-----|---------------|------------|---------------|---------|
|     | tau           | tau_err    | tau           | tau_err |
| 2.0 | 5.55525E-4    | 2.34323E-5 | 0.04459       | 0.00228 |
| 2.3 | 3.21269E-4    | 2.23459E-5 | 0.0436        | 0.00178 |
| 2.6 | 2.15459E-4    | 2.75539E-5 | 0.04149       | 0.00119 |
| 2.9 | 1.11379E-4    | 2.76643E-5 | 0.03644       | 0.0019  |
| 3.2 | 8.24647E-5    | 2.98877E-6 | 0.03359       | 0.00189 |
| 3.5 | 5.98953E-5    | 2.75657E-6 | 0.03009       | 0.00166 |
| 3.8 | 4.56117E-5    | 2.85016E-6 | 0.02776       | 0.00161 |
| 4.1 | 3.53631E-5    | 2.4545E-6  | 0.02466       | 0.00152 |
| 4.4 | 2.73197E-5    | 1.65646E-6 | 0.02165       | 0.00138 |
| 4.7 | 2.07832E-5    | 1.87586E-6 | 0.01868       | 0.00156 |
| 5.0 | 1.5922E-5     | 1.97755E-6 | 0.01595       | 0.00113 |



**Fig. S14** Plots of  $\tau$  vs  $T$  with the error for complexes 1.

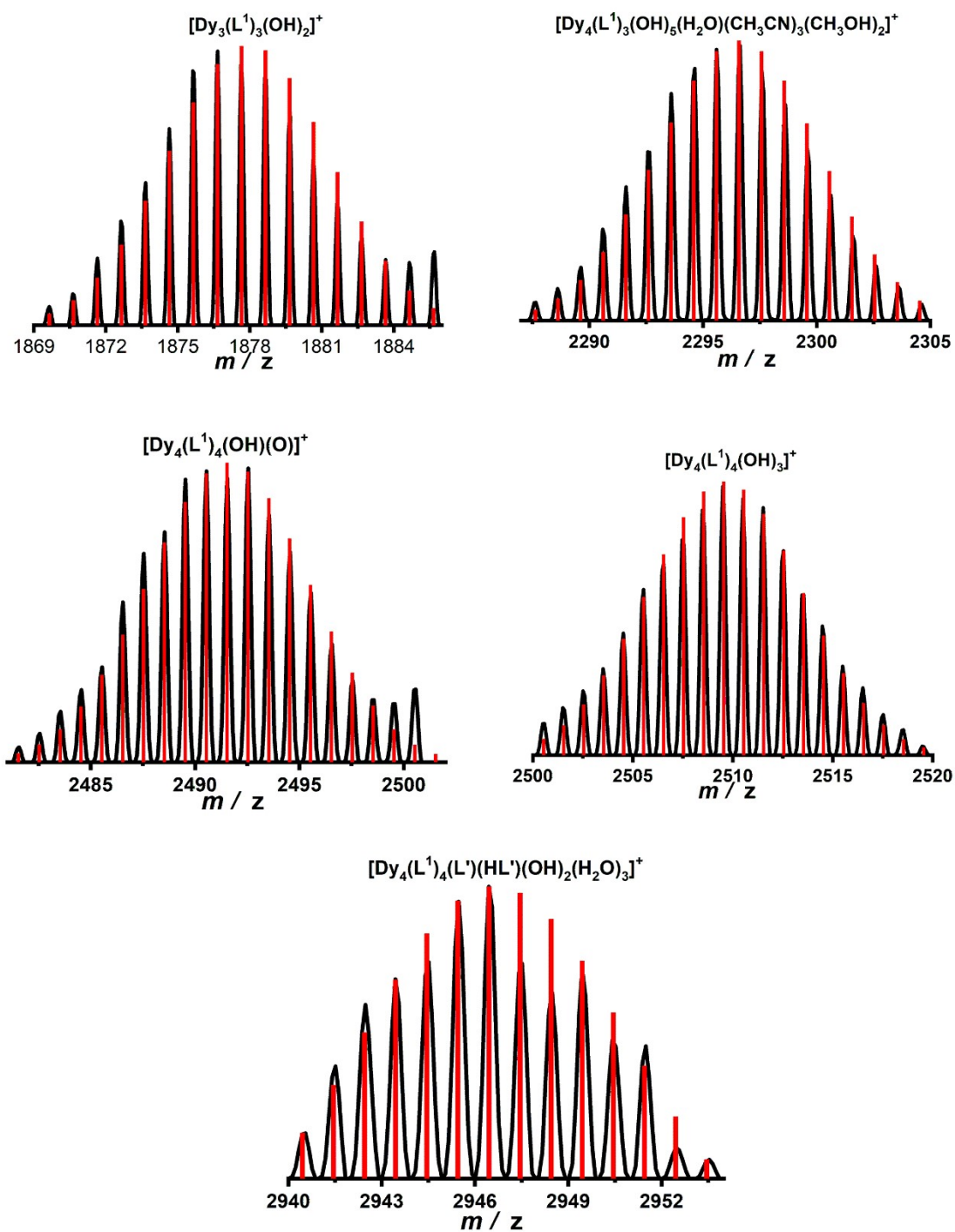


**Fig. S15** Plots of  $\tau$  vs  $T$  with the error for complexes 2.

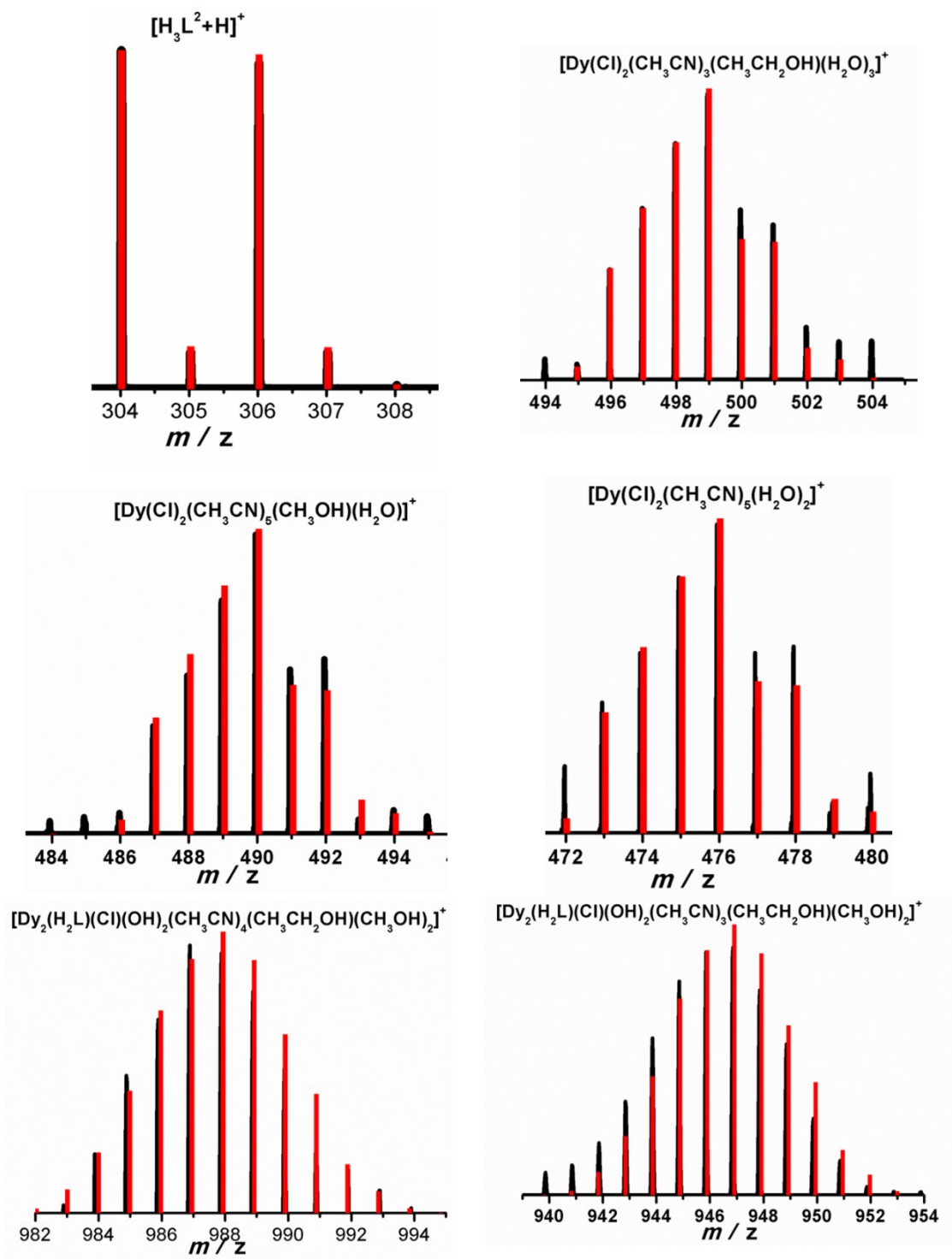


**Fig. S16.** The superposed simulated and observed spectra of several species for **1** (In-Source CID 0 eV).

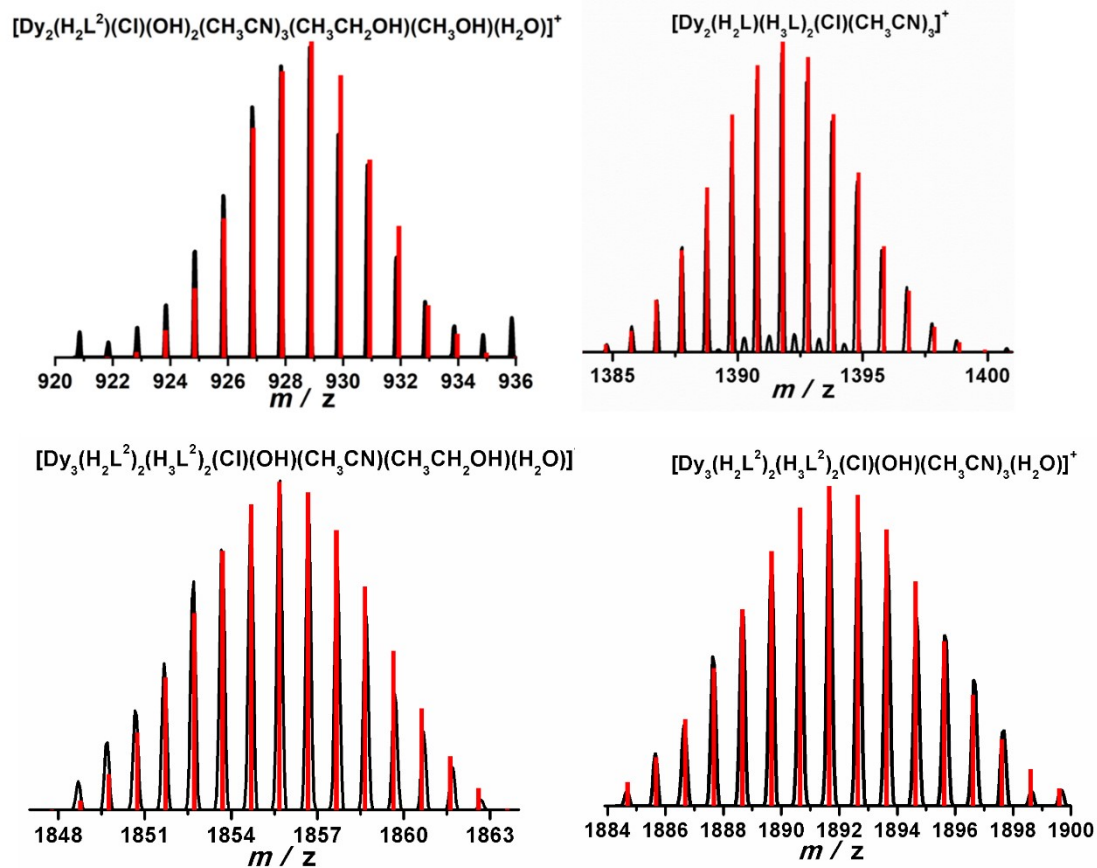




**Fig. S17.** The superposed simulated and observed spectra of several species for **1** (In-Source CID 0 eV).



**Fig. S18.** The superposed simulated and observed spectra of several species for **2** (In-Source CID 0 eV).



**Fig. S19.** The superposed simulated and observed spectra of several species for **2** (In-Source CID 0 eV).

**Table S8.** Major species assigned in the HRESI-MS of **1** in positive mode

| Fragment  | Relative Intensity |        |        |        |        |        |         |         |         |         |
|---|--------------------|--------|--------|--------|--------|--------|---------|---------|---------|---------|
|   | 5 min              | 15 min | 25 min | 40 min | 60 min | 90 min | 130 min | 180 min | 240 min | 360 min |
| L <sup>1</sup>  | 0.90               | 0.12   | 0.05   | 0      | 0      | 0      | 0       | 0       | 0       | 0       |
| DyL <sup>1</sup>  | 0.10               | 0.30   | 0.40   | 0.50   | 0.70   | 0.19   | 0.1     | 0       | 0       | 0       |
| Dy <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub>                                | 0.05               | 0.20   | 0.30   | 0.40   | 0.50   | 0.70   | 0.60    | 0.50    | 0.40    | 0.10    |
| Dy <sub>2</sub> (L <sup>1</sup> ) <sub>3</sub>                                | 0.03               | 0.05   | 0.10   | 0.11   | 0.18   | 0.28   | 0.55    | 0.56    | 0.35    | 0.32    |
| Dy <sub>3</sub> (L <sup>1</sup> ) <sub>3</sub>                                | 0                  | 0.15   | 0.20   | 0.30   | 0.71   | 0.72   | 0.85    | 0.75    | 0.62    | 0.54    |
| Dy <sub>4</sub> (L <sup>1</sup> ) <sub>3</sub>                                | 0                  | 0.30   | 0.45   | 0.40   | 0.50   | 0.60   | 0.85    | 0.76    | 0.67    | 0.60    |
| Dy <sub>4</sub> (L <sup>1</sup> ) <sub>4</sub>                                | 0                  | 0      | 0.08   | 0.14   | 0.20   | 0.22   | 0.31    | 0.48    | 0.65    | 0.51    |
| Dy <sub>4</sub> (L <sup>1</sup> ) <sub>4</sub> (L <sup>1</sup> ) <sub>2</sub> | 0                  | 0      | 0      | 0      | 0      | 0      | 0.10    | 0.21    | 0.30    | 0.80    |

**Table S9.** Major species assigned in the HRESI-MS of **2** in positive mode

| Fragment                                       | Relative Intensity |        |        |        |        |         |         |         |         |         |
|--|--------------------|--------|--------|--------|--------|---------|---------|---------|---------|---------|
|  | 5 min              | 10 min | 20 min | 40 min | 60 min | 120 min | 240 min | 360 min | 480 min | 600 min |
| L <sup>2</sup>                                 | 0.90               | 0.82   | 0.85   | 0.71   | 0.70   | 0.65    | 0.23    | 0.20    | 0.10    | 0.10    |
| Dy   | 0.10               | 0.12   | 0.20   | 0.28   | 0.40   | 0.60    | 0.56    | 0.60    | 0.56    | 0.60    |
| Dy <sub>2</sub> (L <sup>2</sup> )              | 0                  | 0      | 0      | 0.06   | 0.11   | 0.14    | 0.56    | 0.50    | 0.52    | 0.35    |
| Dy <sub>2</sub> (L <sup>2</sup> ) <sub>3</sub> | 0                  | 0      | 0      | 0      | 0.02   | 0.07    | 0.66    | 0.75    | 0.69    | 0.30    |
| Dy <sub>3</sub> (L <sup>2</sup> ) <sub>4</sub> | 0                  | 0      | 0      | 0      | 0.02   | 0.06    | 0.13    | 0.58    | 0.55    | 0.54    |
| Dy <sub>6</sub> (L <sup>2</sup> ) <sub>6</sub> | 0                  | 0      | 0      | 0      | 0      | 0       | 0.10    | 0.20    | 0.30    | 0.80    |