

# Electronic Supplementary Information for

## **A new air- and moisture-stable pentagonal-bipyramidal Dy<sup>III</sup> single-ion magnet based on HMPA ligand**

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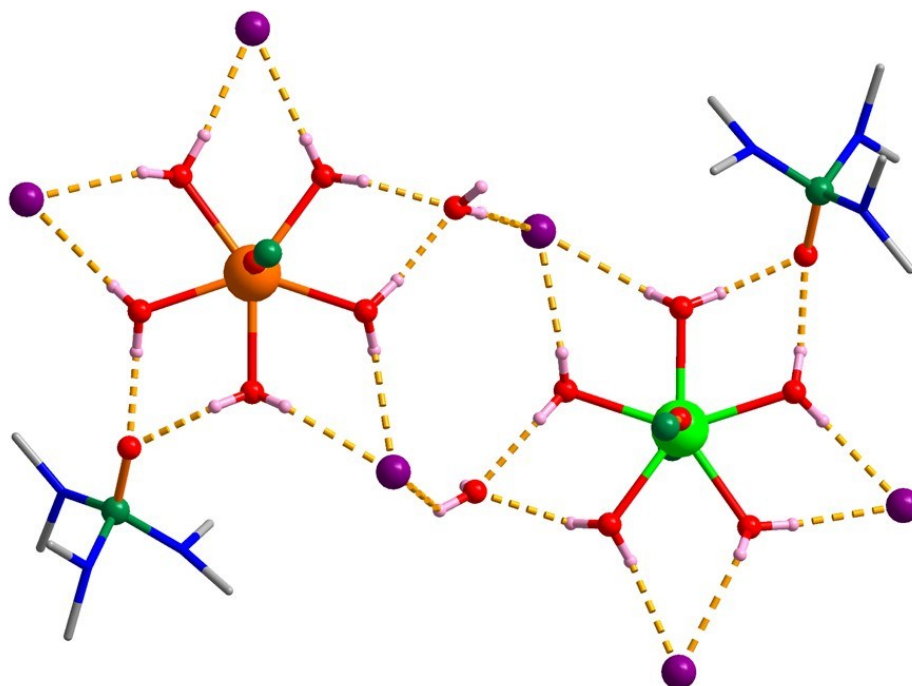
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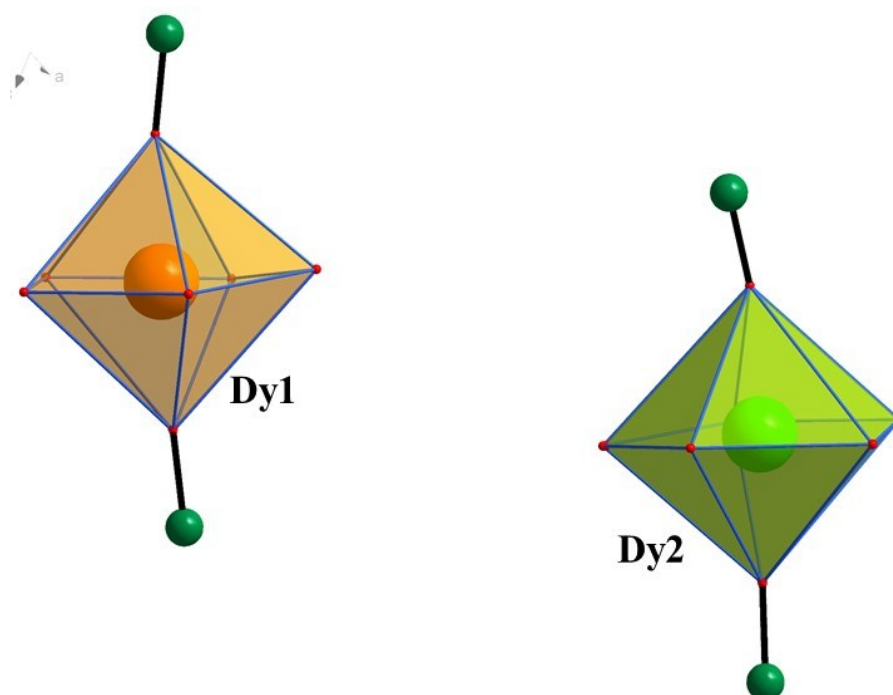
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## 1. Crystal data and structure



**Fig S1.** The hydrogen bonds between coordinated H<sub>2</sub>O molecules and free solvents, free ligands and Br<sup>-</sup> ions. Color codes: O red, H pink, N blue, C gray, P green, Br violet



**Fig S2.** Coordination polyhedrons of Dy<sup>III</sup> centers. Colour codes: O red, P green.

**Table S1.** Selected bonds and angles for complex **1**

| <b>1</b>     |           |              |          |
|--------------|-----------|--------------|----------|
| Bonds/Angles | Å/°       | Bonds/Angles | Å/°      |
| Dy1-O6       | 2.195(8)  | O17-Dy1-O13  | 143.8(3) |
| Dy1-O7       | 2.228(9)  | O17-Dy1-O19  | 143.5(3) |
| Dy1-O12      | 2.347(8)  | O17-Dy1-O20  | 71.2(3)  |
| Dy1-O13      | 2.383(8)  | O19-Dy1-O13  | 72.5(3)  |
| Dy1-O17      | 2.334(8)  | O20-Dy1-O12  | 142.4(3) |
| Dy1-O19      | 2.371(9)  | O20-Dy1-O13  | 144.6(3) |
| Dy1-O20      | 2.337(8)  | O20-Dy1-O19  | 72.3(3)  |
| Dy2-O5       | 2.218(8)  | O5-Dy2-O9    | 176.9(3) |
| Dy2-O9       | 2.224(9)  | O5-Dy2-O11   | 89.0(3)  |
| Dy2-O11      | 2.368(8)  | O5-Dy2-O14   | 89.9(4)  |
| Dy2-O14      | 2.362(10) | O5-Dy2-O15   | 90.7(3)  |
| Dy2-O15      | 2.346(8)  | O5-Dy2-O16   | 86.0(3)  |
| Dy2-O16      | 2.368(9)  | O5-Dy2-O1    | 91.8(3)  |
| Dy2-O1       | 2.351(8)  | O9-Dy2-O11   | 89.1(3)  |
| O6-Dy1-O7    | 177.8(3)  | O9-Dy2-O14   | 93.1(4)  |
| O6-Dy1-O12   | 87.4(3)   | O9-Dy2-O15   | 89.4(3)  |
| O6-Dy1-O13   | 92.7(3)   | O9-Dy2-O16   | 91.1(3)  |
| O6-Dy1-O17   | 92.0(3)   | O9-Dy2-O1    | 89.9(3)  |
| O6-Dy1-O19   | 88.8(4)   | O11-Dy2-O16  | 72.1(3)  |
| O6-Dy1-O20   | 90.3(3)   | O14-Dy2-O11  | 144.2(3) |
| O7-Dy1-O12   | 90.5(3)   | O14-Dy2-O16  | 143.4(3) |
| O7-Dy1-O13   | 86.1(3)   | O15-Dy2-O11  | 144.4(3) |
| O7-Dy1-O17   | 88.0(3)   | O15-Dy2-O14  | 71.4(3)  |
| O7-Dy1-O19   | 92.5(4)   | O15-Dy2-O16  | 72.3(3)  |
| O7-Dy1-O20   | 91.8(3)   | O15-Dy2-O1   | 144.0(3) |
| O12-Dy1-O13  | 73.0(3)   | O1-Dy2-O11   | 71.5(3)  |
| O12-Dy1-O19  | 145.0(3)  | O1-Dy2-O14   | 72.7(3)  |
| O17-Dy1-O12  | 71.4(3)   | O1-Dy2-O16   | 143.6(3) |

**Table S2.** Continuous Shape Measures (CshM)<sup>[1]</sup> calculation for complex 1

| Structure | HP-7   | HPY-7  | PBPY-7 | COC-7 | CTPR-7 | JPBY-7 | JETPY-7 |
|-----------|--------|--------|--------|-------|--------|--------|---------|
| Dy1       | 34.232 | 25.269 | 0.196  | 7.568 | 5.785  | 2.789  | 23.472  |
| Dy2       | 34.314 | 24.936 | 0.114  | 7.923 | 6.046  | 2.701  | 24.612  |

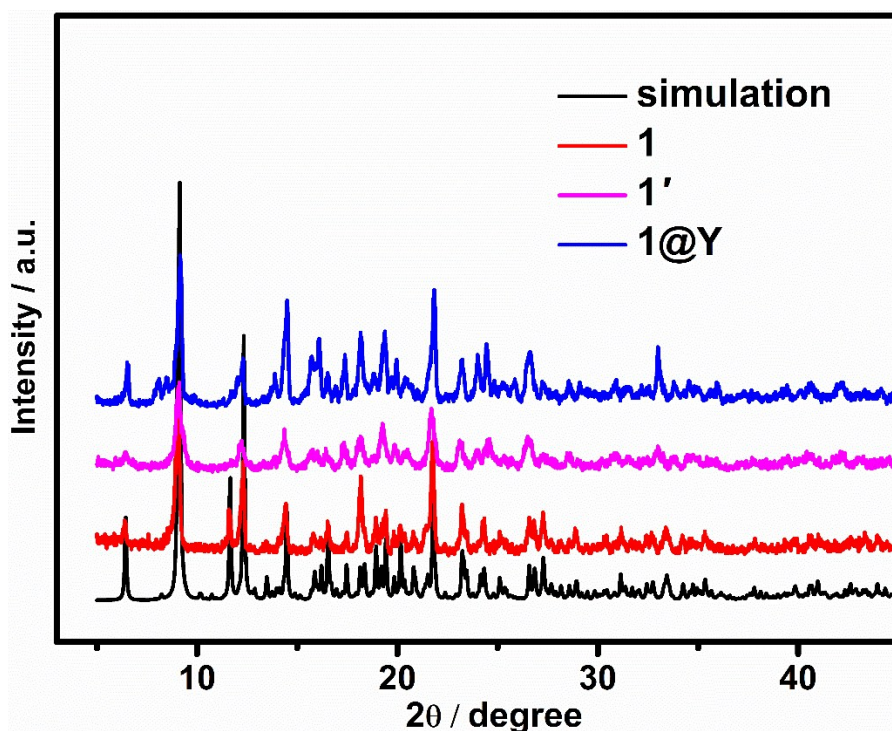
HP-7 = Heptagon ( $D_{7h}$ ); HPY-7 = Hexagonal pyramid ( $C_{6v}$ ); PBPY-7 = Pentagonal bipyramid ( $D_{5h}$ ); COC-7 = Capped octahedron ( $C_{3v}$ ); CTPR-7 = Capped trigonal prism ( $C_{2v}$ ); JPBY-7 = Johnson pentagonal bipyramid J13 ( $D_{5h}$ ); JETPY-7 = Johnson elongated triangular pyramid J7 ( $C_{3v}$ ).

**Table S3.** Comparison of selected crystallography parameters of 1 with other phosphine oxide based SIMs

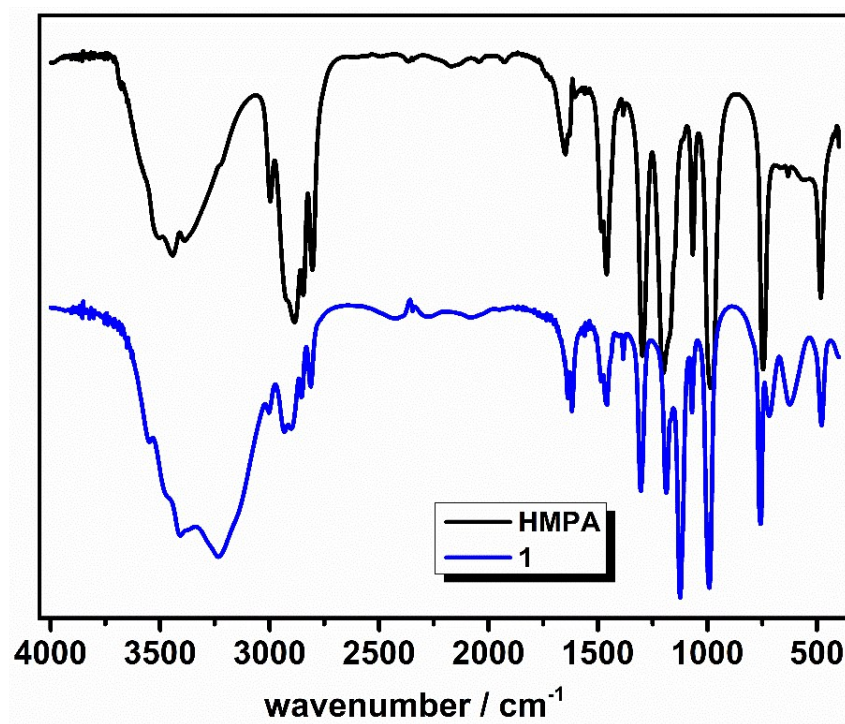
| complex                                                                                                                                                                                                        | Average axial Dy-O | Average equatorial Dy-Ow | Angle of axial | Deviation from ideal $D_{5h}$ | $U_{\text{eff}}$ (diulted |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------|--------------------------|----------------|-------------------------------|---------------------------|
|                                                                                                                                                                                                                | bond length (Å)    | bond length (Å)          | O-Dy-O (°)     | symmetry                      | sample) (K)               |
| [Dy(Cy <sub>3</sub> PO) <sub>2</sub> (H <sub>2</sub> O) <sub>5</sub> ]Br <sub>3</sub> ·2(Cy <sub>3</sub> PO)·2H <sub>2</sub> O·2EtOH <sup>[2]</sup>                                                            | 2.200              | 2.352                    | 179.04         | 0.142                         | 543(-) <sup>a</sup>       |
| [Dy(Cy <sub>3</sub> PO) <sub>2</sub> (H <sub>2</sub> O) <sub>5</sub> ]Cl <sub>3</sub> ·(Cy <sub>3</sub> PO)·H <sub>2</sub> O·EtOH <sup>[2]</sup>                                                               | 2.219              | 2.359                    | 175.79         | 0.239                         | 472(-) <sup>a</sup>       |
| [Dy( <sup>t</sup> BuPO(NH <sup>t</sup> Pr <sub>2</sub> )) <sub>2</sub> (H <sub>2</sub> O) <sub>5</sub> ]I <sub>3</sub> ·( <sup>t</sup> BuPO(NH <sup>t</sup> Pr <sub>2</sub> ))·H <sub>2</sub> O <sup>[3]</sup> | 2.206              | 2.364                    | 175.14         | 0.224                         | 651(735.4)                |
| [Dy(CyPh <sub>2</sub> PO) <sub>2</sub> (H <sub>2</sub> O) <sub>5</sub> ]Br <sub>3</sub> ·2(Cy <sub>3</sub> PO)·3H <sub>2</sub> O·EtOH <sup>[4]</sup>                                                           | 2.217              | 2.364                    | 174.2          | 0.174                         | 508(467)                  |
| [Dy(HMPA) <sub>2</sub> (H <sub>2</sub> O) <sub>5</sub> ]Cl <sub>3</sub> ·HMPA·H <sub>2</sub> O <sup>[5]</sup>                                                                                                  | Dy1                | 2.219                    | 175.6          | 0.154                         | 460(-)                    |
|                                                                                                                                                                                                                | Dy2                | 2.219                    | 176.7          | 0.284                         |                           |
| [Dy(HMPA) <sub>2</sub> (H <sub>2</sub> O) <sub>5</sub> ]I <sub>3</sub> ·2HMPA <sup>[5]</sup>                                                                                                                   | 2.205              | 2.360                    | 178.0          | 0.131                         | 600(-)                    |
| 1-Dy1                                                                                                                                                                                                          | 2.212              | 2.354                    | 177.8          | 0.196                         | 556(550)                  |
| 1-Dy2                                                                                                                                                                                                          | 2.221              | 2.359                    | 176.9          | 0.114                         |                           |

<sup>a</sup> The author stated the dilution sample had similar ac susceptibility pattern with the pure sample.

## 2. PXRD patterns and IR spectrum

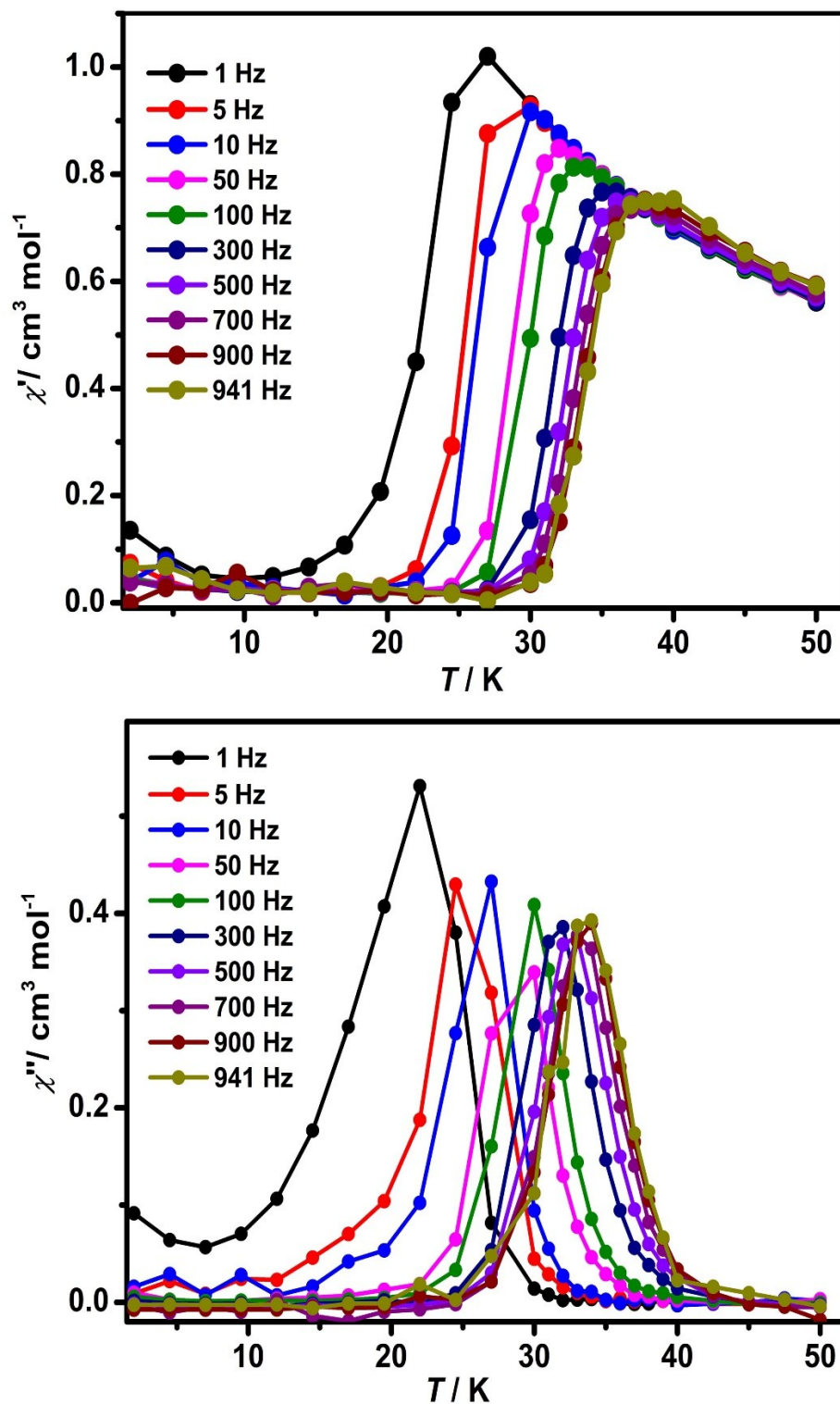


**Fig S3.** Comparison of the experimental PXRD pattern of **1**, **1'** and **1@Y** with the simulated one from the single crystal data of **1**. **1'** was tested after kept in a glass vial at ordinary condition for *ca.* seven months without inert-gas protection or any special measures.



**Fig S4.** The IR spectrum of **1** and HM

### 3. Other magnetic data

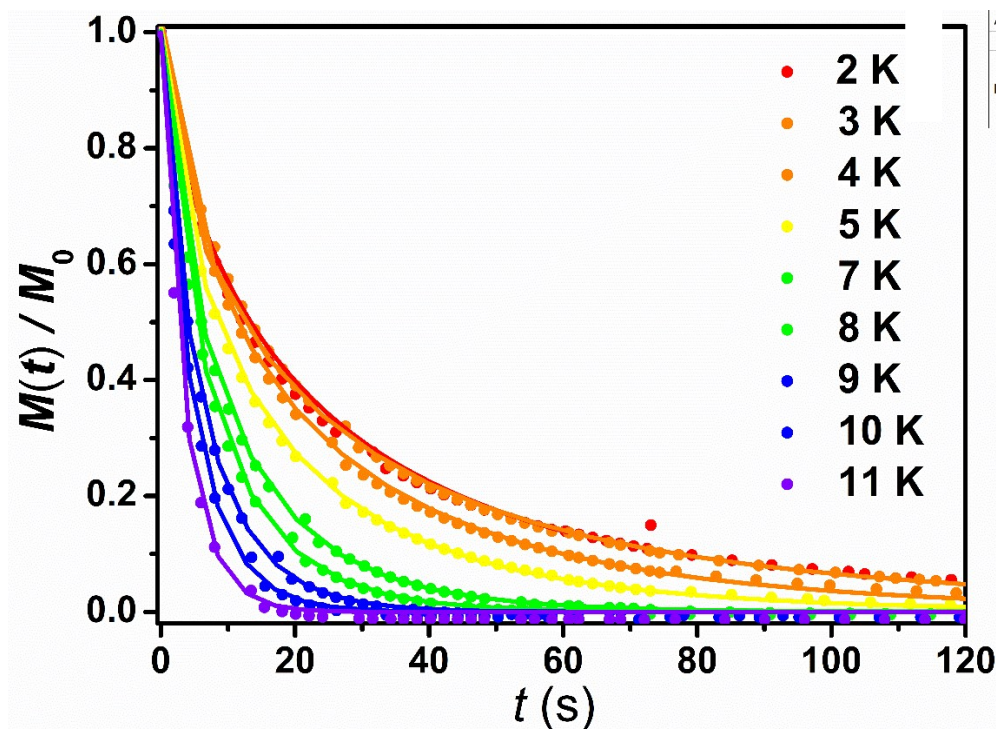


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**Fig S5.** In-phase (top) and put-of-phase (bottom) components of variable-temperature ac susceptibility of **1** under zero dc field. The solid lines are guides for eyes.

**Table S4.** The best fitting parameters for Cole-Cole plots of **1** under zero applied dc field.

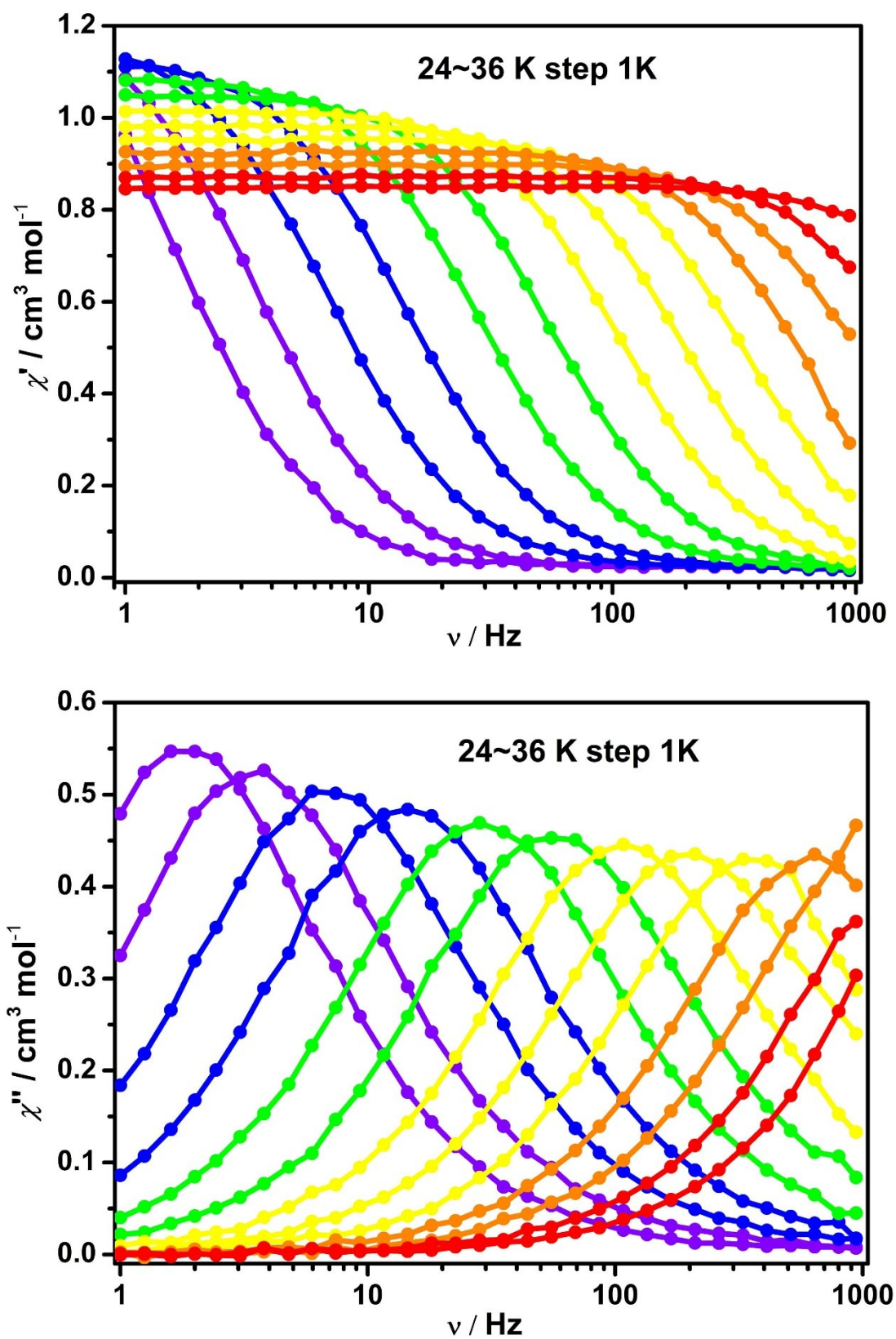
| $T$ (K) | $\chi_s$    | $\chi_t$ | $\tau$ (s) | $\alpha$    |
|---------|-------------|----------|------------|-------------|
| 20      | 0.0180813   | 1.12818  | 0.309932   | 0.0136141   |
| 21      | 0.0175817   | 1.31656  | 0.302864   | 0.0418059   |
| 22      | 0.017144    | 1.2751   | 0.215238   | 0.0429817   |
| 23      | 0.016392    | 1.24585  | 0.14129    | 0.052536    |
| 24      | 0.0138342   | 1.2216   | 0.0833704  | 0.0706592   |
| 25      | 0.0126073   | 1.1853   | 0.0440235  | 0.0828304   |
| 26      | 0.0122267   | 1.14254  | 0.0219444  | 0.084406    |
| 27      | 0.011026    | 1.10025  | 0.0107135  | 0.0853662   |
| 28      | 0.00949227  | 1.05991  | 0.00531943 | 0.0839113   |
| 29      | 0.00939185  | 1.02249  | 0.00270571 | 0.0816184   |
| 30      | 0.00360095  | 0.987629 | 0.0014146  | 0.0789837   |
| 31      | 9.84069E-16 | 0.956308 | 7.64871E-4 | 0.0745778   |
| 32      | 2.18111E-15 | 0.925174 | 4.30026E-4 | 0.0638014   |
| 33      | 6.89439E-16 | 0.895847 | 2.50864E-4 | 0.0434504   |
| 34      | 4.61974E-32 | 0.875001 | 1.51793E-4 | 0.0563724   |
| 35      | 7.09848E-32 | 0.846085 | 9.78859E-5 | 4.32305E-10 |
| 36      | 1.03409E-31 | 0.826617 | 6.37915E-5 | 4.52927E-10 |



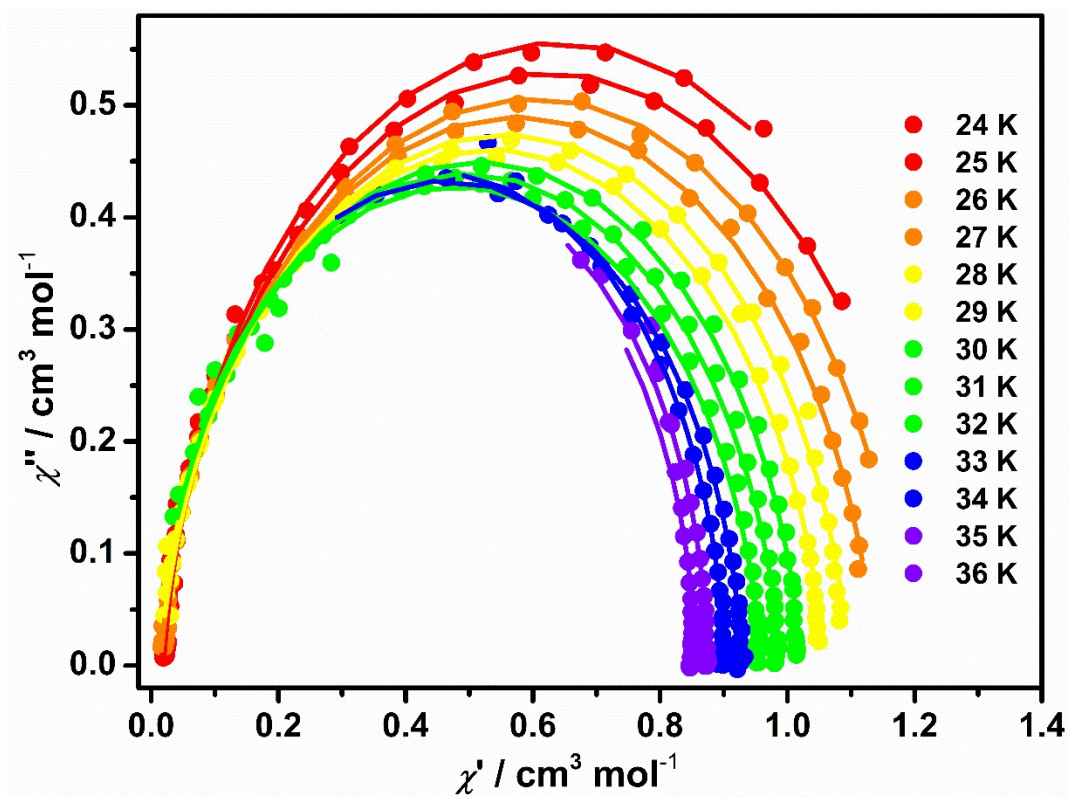
**Fig S6.** Normalized dc magnetic relaxation data for **1** under the final zero dc field. The solid lines are fits using  $M(t) = M_f + (M_f - M_0) \exp[-(t/\tau)^\beta]$  ( $\tau$ , relaxation time;  $M(t)$ , magnetization at time  $t$ ;  $M_f$ , the final magnetization at  $t = \infty$ ;  $M_0$ , magnetization at  $t = 0$ ;  $\beta$ , a free variable).

**Table S5.** The best fitting results for dc magnetic relaxation data for **1** under zero applied dc field.

| $T$ (K) | $M_0/M_0$ | $M_{\text{f}}/M_0$ | $\tau$ (s) | $\beta$ |
|---------|-----------|--------------------|------------|---------|
| 2       | 1.02473   | 0.00421            | 20.3535    | 0.64684 |
| 3       | 1.02762   | 0.00397            | 21.45572   | 0.68495 |
| 4       | 1.02137   | 0.00032695         | 18.20233   | 0.70888 |
| 5       | 1.01075   | 6.81356E-23        | 13.89797   | 0.72386 |
| 7       | 1.0028    | 1.13724E-32        | 9.58285    | 0.81689 |
| 8       | 1.00026   | 1.22968E-22        | 7.8238     | 0.85959 |
| 9       | 0.99986   | 1.48445E-23        | 6.10766    | 0.88554 |
| 10      | 0.99971   | 3.96581E-25        | 4.77086    | 0.92493 |
| 11      | 0.99932   | 1.21215e-24        | 3.46552    | 0.94468 |



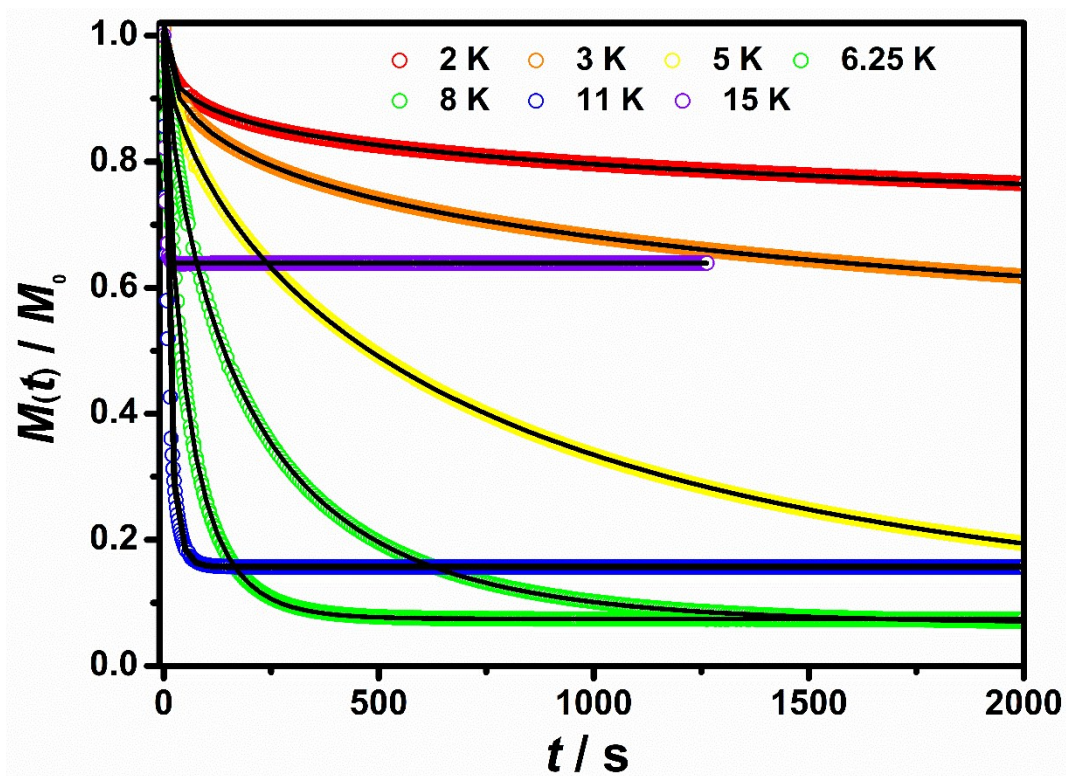
**Fig S7.** In-phase (top) and put-of-phase (bottom) components of variable-frequency ac susceptibility of **1** under 1200 Oe dc field.



**Fig S8.** Cole-Cole plots for **1** under 1200 Oe dc field. The solid lines represent the best fitting results using Debye mode.

**Table S6.** The best fitting parameters for Cole-Cole plots of **1** under 1200 Oe applied dc field

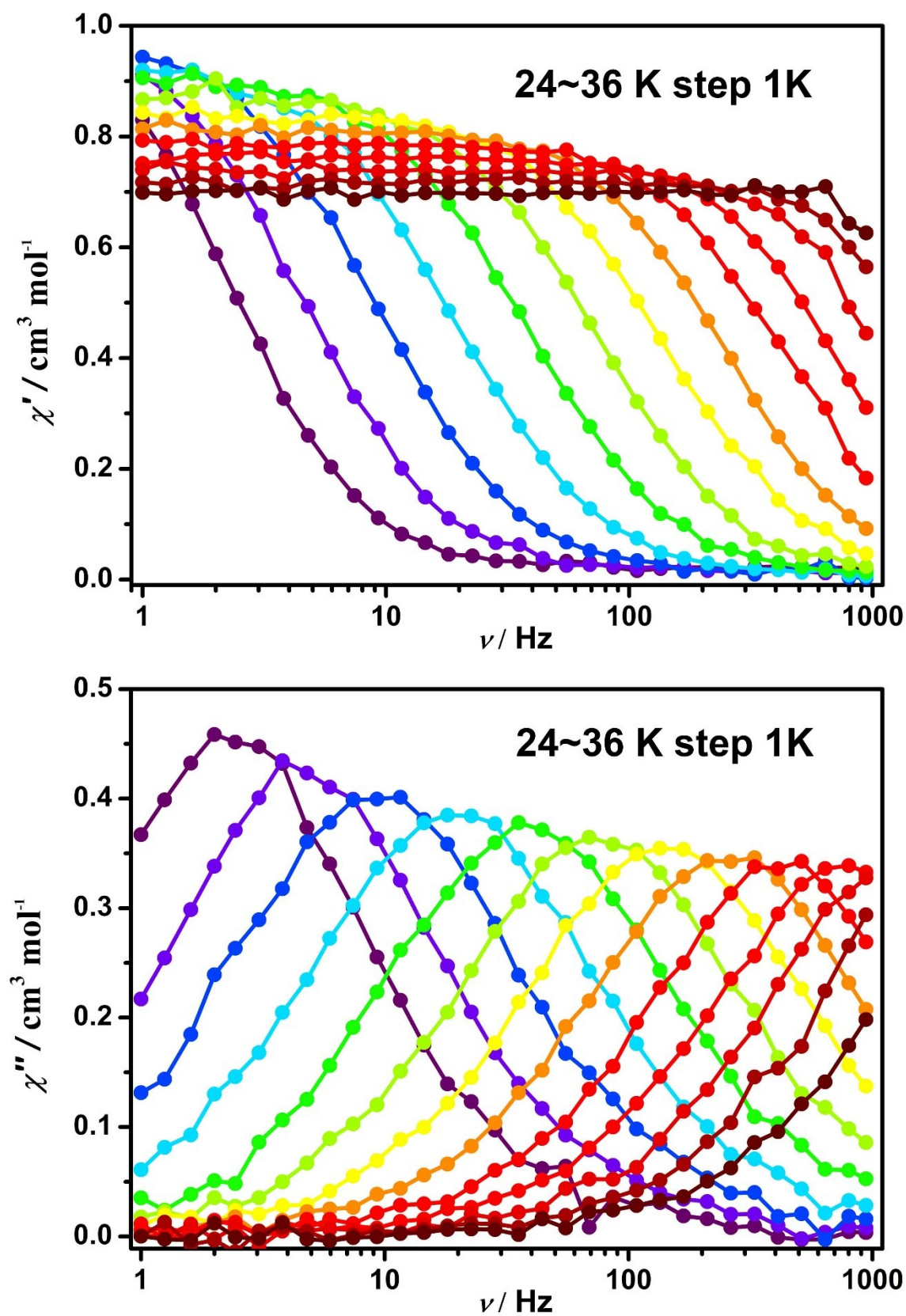
| $T$ (K) | $\chi_s$    | $\chi_t$ | $\tau$ (s) | $\alpha$    |
|---------|-------------|----------|------------|-------------|
| 24      | 0.0191384   | 1.2626   | 0.0847527  | 0.071032    |
| 25      | 0.015884    | 1.22945  | 0.0455386  | 0.0867322   |
| 26      | 0.0135576   | 1.18861  | 0.0226638  | 0.0943448   |
| 27      | 0.0135171   | 1.13865  | 0.0110128  | 0.0877455   |
| 28      | 0.0131759   | 1.0968   | 0.00544843 | 0.0843537   |
| 29      | 0.00887373  | 1.05778  | 0.0027657  | 0.0817149   |
| 30      | 0.00660415  | 1.02166  | 0.00145054 | 0.0767424   |
| 31      | 1.43263E-16 | 0.988882 | 7.79334E-4 | 0.0752084   |
| 32      | 1.34492E-16 | 0.959081 | 4.42432E-4 | 0.0721931   |
| 33      | 2.30371E-17 | 0.927856 | 2.61368E-4 | 0.0441084   |
| 34      | 6.29411E-18 | 0.899305 | 1.53519E-4 | 0.0149175   |
| 35      | 1.255E-17   | 0.873192 | 9.70537E-5 | 0.00426391  |
| 36      | 4.46166E-17 | 0.853373 | 6.38201E-5 | 1.89805E-11 |



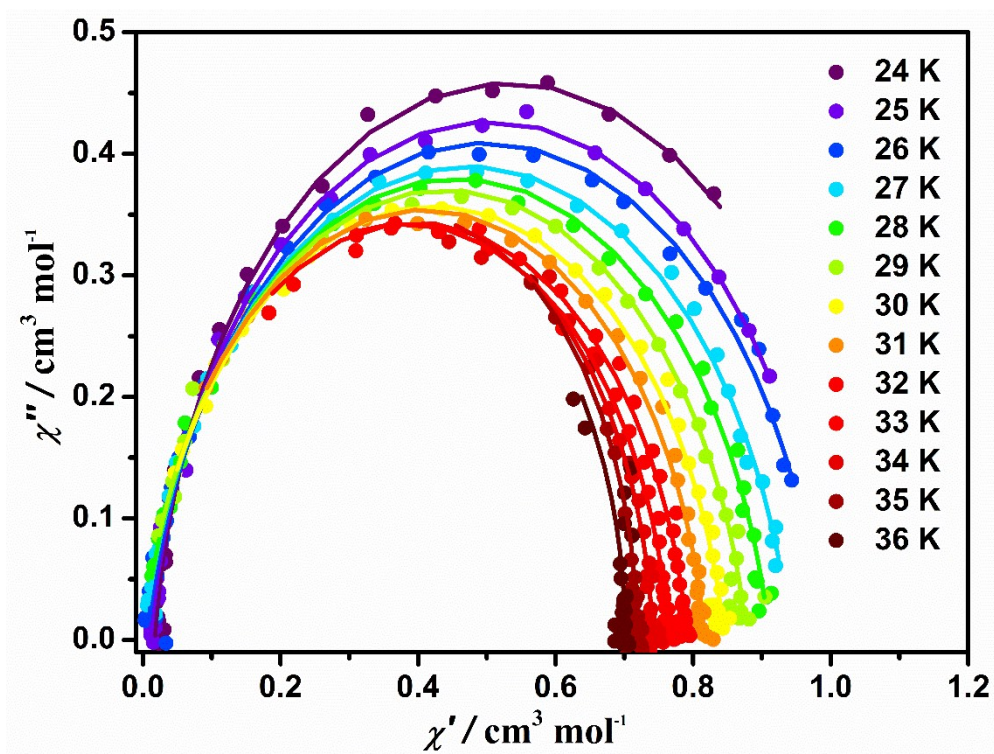
**Fig S9.** Normalized dc magnetic relaxation data for **1** under the final 1200 Oe dc field. The solid lines are fits using  $M(t) = M_f + (M_i - M_0) \exp[-(t/\tau)^\beta]$  ( $\tau$ , relaxation time;  $M(t)$ , magnetization at time  $t$ ;  $M_f$ , the final magnetization at  $t = \infty$ ;  $M_0$ , magnetization at  $t = 0$ ;  $\beta$ , a free variable).

**Table S7.** The best fitting results for dc magnetic relaxation data for **1** under 1200 Oe applied dc field.

| $T$ (K) | $M_0/M_0$ | $M_f/M_0$ | $\tau$ (s) | $\beta$ |
|---------|-----------|-----------|------------|---------|
| 2       | 1.02108   | 0.61588   | 2002.67819 | 0.30643 |
| 3       | 1.01020   | 0.41325   | 1701.440   | 0.41520 |
| 5       | 0.97970   | 0.06081   | 753.07138  | 0.67376 |
| 6.25    | 1.00584   | 0.06703   | 198.10346  | 0.73986 |
| 8       | 1.01760   | 0.07434   | 54.2002    | 0.79894 |
| 11      | 1.00421   | 0.15698   | 12.25133   | 0.87192 |
| 15      | 1.00008   | 0.63899   | 3.01431    | 0.86666 |



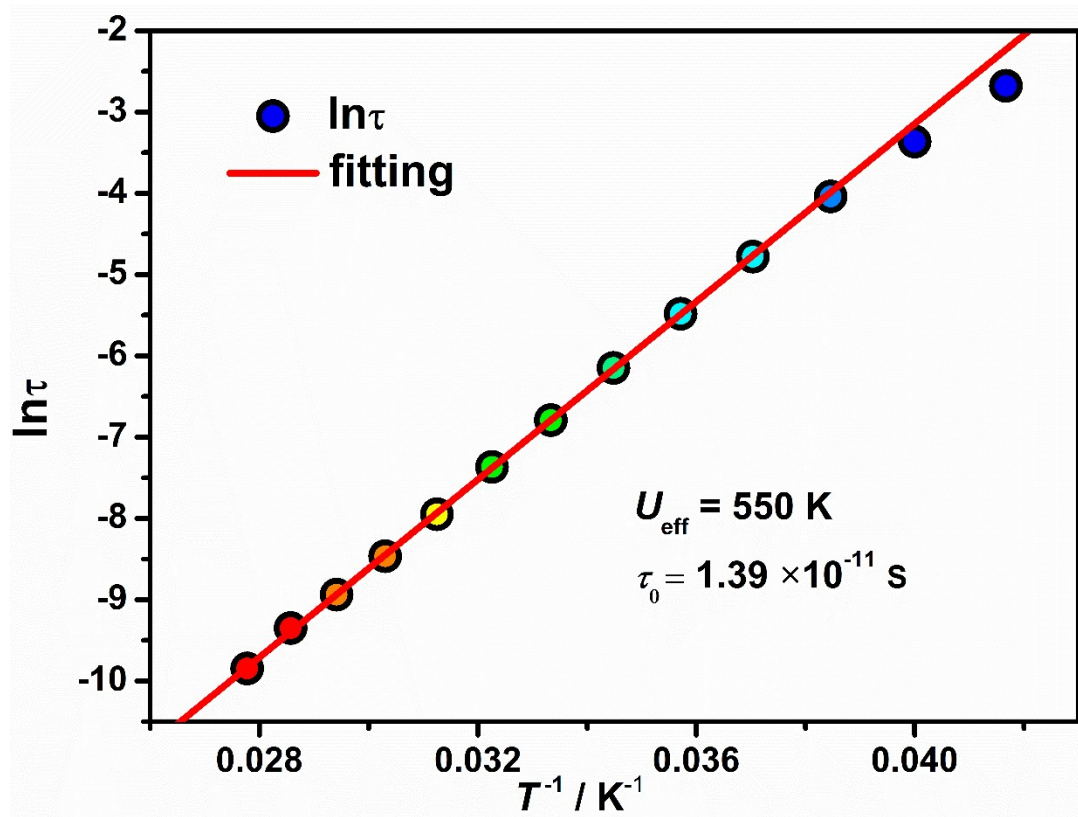
**Fig S10.** In-phase (top) and put-of-phase (bottom) components of variable-frequency ac susceptibility of **1@Y** under zero dc field.



**Fig S11.** Cole-Cole plots for **1@Y** under zero dc field. The solid lines represent the best fitting results using Debye mode.

**Table S8.** The best fitting parameters for Cole-Cole plots of **1@Y** under zero applied dc field

| $T$ (K) | $\chi_s$   | $\chi_t$ | $\tau$ (s) | $\alpha$    |
|---------|------------|----------|------------|-------------|
| 24      | 0.0174151  | 1.04432  | 0.0687094  | 0.0723027   |
| 25      | 0.0109649  | 0.997467 | 0.0346205  | 0.0921045   |
| 26      | 0.00521581 | 0.98864  | 0.0175952  | 0.116606    |
| 27      | 0.00115185 | 0.942075 | 0.00839536 | 0.118721    |
| 28      | 4.9165E-4  | 0.911204 | 0.00416077 | 0.114785    |
| 29      | 9.61294E-9 | 0.878219 | 0.0021356  | 0.107779    |
| 30      | 1.82644E-8 | 0.845336 | 0.00112449 | 0.106629    |
| 31      | 1.61992E-8 | 0.816794 | 6.31646E-4 | 0.0905478   |
| 32      | 3.04684E-8 | 0.791316 | 3.53297E-4 | 0.0897982   |
| 33      | 4.56221E-9 | 0.764765 | 2.1081E-4  | 0.0695049   |
| 34      | 7.78275E-9 | 0.741249 | 1.31219E-4 | 0.0349722   |
| 35      | 1.55545E-8 | 0.71838  | 8.70765E-5 | 2.2123E-16  |
| 36      | 2.42841E-8 | 0.701336 | 5.3029E-5  | 2.26028E-16 |



**Fig S12.** Plot of  $\ln\tau$  versus  $T^{-1}$  of **1@Y** under zero dc field. The solid lines represent the best fitting results using Arrhenius law.

## 4. References

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