**Supporting Information**

# Regulating the magnetic properties of seven-coordinated Dy(III) single-ion magnets through the effect of positional isomers on axial crystal-field

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**X-ray crystallographic data**

**Table S1a.** Crystallographic data and structure refinement parameters for **1**, **3** and **5**.

| Complex | **1** | **3** | **5** |
|---|---|---|---|
| Formula | $C_{30}H_{32}ClDyN_4O_4$ | $C_{30}H_{32}ClDyN_4O_4$ | $C_{30}H_{32}ClDyN_4O_4$ |
| Formula weight | 710.54 | 710.54 | 710.54 |
| Temperature / K | 296 | 296 | 296 |
| Crystal system | Orthorhombic | Monoclinic | Orthorhombic |
| Space group | $P2_12_12_1$ | $C2/c$ | $P$bcn |
| $a$ / Å | 8.6071 (13) | 21.062 (2) | 8.6217 (12) |
| $b$ / Å | 17.845 (3) | 9.5266 (10) | 17.052 (2) |
| $c$ / Å | 18.836 (3) | 15.5658 (14) | 19.783 (3) |
| $\alpha$/ ° | 90 | 90 | 90 |
| $\beta$/ ° | 90 | 114.012 (4) | 90 |
| $\gamma$ / ° | 90 | 90 | 90 |
| $V$ /Å$^3$ | 2893.1 (8) | 2853.0 (5) | 2908.5 (7) |
| $Z$ | 4 | 4 | 4 |
| $F$(000) | 1420 | 1420 | 1420 |
| $D_{calc}$ /Mg m$^{-3}$ | 1.631 | 1.654 | 1.623 |
| Mo Kα /Å | 0.71073 | 0.71073 | 0.71073 |
| $R_1$ [$I>2\sigma(I)$] | 0.0154 | 0.0232 | 0.0279 |
| $wR_2$ [$I>2\sigma(I)$] | 0.0368 | 0.0470 | 0.0559 |
| *$R_1$, (all data)* | 0.0162 | 0.0263 | 0.0431 |
| *$wR_2$, (all data)* | 0.0371 | 0.0485 | 0.0641 |
| $\mu$ / mm$^{-1}$ | 2.72 | 2.76 | 2.70 |
| $R_{int}$ | 0.021 | 0.040 | 0.030 |
| Collected reflections | 22377 | 23382 | 24106 |
| Unique reflections | 5894 | 4398 | 3528 |
| Goodness-of-fit on $F^2$ | 1.14 | 1.06 | 1.26 |

**Table S1b.** Crystal data and structure refinement parameters for **2**, **4** and **6**.

| Complex | **2** | **4** | **6** |
|---|---|---|---|
| Formula | $C_{30}H_{32}BrDyN_4O_4$ | $C_{30}H_{32}BrDyN_4O_4$ | $C_{30}H_{32}ClDyN_4O_4$ |
| Formula weight | 755.00 | 755.00 | 710.54 |
| Temperature / K | 296 | 296 | 296 |
| Crystal system | Orthorhombic | Monoclinic | Orthorhombic |
| Space group | $P2_12_12_1$ | $C2/c$ | $P$bcn |
| $a$ / Å | 8.5766 (7) | 20.971 (2) | 8.6618 (8) |
| $b$ / Å | 18.0373 (14) | 9.7062 (11) | 17.2729 (16) |
| $c$ / Å | 18.8912 (15) | 15.6099 (17) | 19.7054 (18) |
| $\alpha$/ ° | 90 | 90 | 90 |
| $\beta$/ ° | 90 | 113.913 | 90 |
| $\gamma$ / ° | 90 | 90 | 90 |
| $V$ /Å$^3$ | 2922.4 (4) | 2904.7 (6) | 2948.2 (5) |
| $Z$ | 4 | 4 | 4 |
| $F$(000) | 1492 | 1492 | 1492 |
| $D_{calc}$ /Mg m$^{-3}$ | 1.716 | 1.726 | 1.701 |
| Mo Kα /Å | 0.71073 | 0.71073 | 0.71073 |
| $R_1$ [$I>2\sigma(I)$] | 0.0220 | 0.0182 | 0.0292 |
| $wR_2$ [$I>2\sigma(I)$] | 0.0463 | 0.0472 | 0.0583 |
| $R_1$, *(all data)* | 0.0261 | 0.0208 | 0.0417 |
| $wR_2$, *(all data)* | 0.0475 | 0.0486 | 0.0650 |
| $\mu$ / mm$^{-1}$ | 3.97 | 3.99 | 3.93 |
| $R_{int}$ | 0.030 | 0.026 | 0.033 |
| Collected reflections | 20494 | 12319 | 43412 |
| Unique reflections | 5169 | 3476 | 3028 |
| Goodness-of-fit on $F^2$ | 1.07 | 1.12 | 1.17 |

**Table S2.** Selected bond distances (Å) and bond angles (°) for **1–6**.

| Bond distances (Å) | | | |
|---|---|---|---|
| Complex **1** | | Complex **2** | |
| Dy(1)-Cl(1) | 2.6647 (8) | Dy(1)-Br(1) | 2.8412 (5) |
| Dy(1)-O(1) | 2.156 (2) | Dy(1)-O(1) | 2.135 (3) |
| Dy(1)-O(2) | 2.153 (2) | Dy(1)-O(2) | 2.150 (3) |
| Dy(1)-N(1) | 2.558 (3) | Dy(1)-N(1) | 2.563 (4) |
| Dy(1)-N(2) | 2.603 (2) | Dy(1)-N(2) | 2.599 (4) |
| Dy(1)-N(3) | 2.596 (2) | Dy(1)-N(3) | 2.588 (4) |
| Dy(1)-N(4) | 2.571 (3) | Dy(1)-N(4) | 2.599 (4) |
| Complex **3** | | Complex **4** | |
| Dy(1)-Cl(1) | 2.6294 (7) | Dy(1)-Br(1) | 2.7892 (4) |
| Dy(1)-O(1) | 2.1697 (14) | Dy(1)-O(1) | 2.1666 (17) |
| Dy(1)-N(1) | 2.5440 (17) | Dy(1)-N(1) | 2.5610 (18) |
| Dy(1)-N(2) | 2.5854 (16) | Dy(1)-N(2) | 2.5770 (17) |
| Complex **5** | | Complex **6** | |
| Dy(1)-Cl(1) | 2.6641 (11) | Dy(1)-Br(1) | 2.8228 (6) |
| Dy(1)-O(1) | 2.165 (2) | Dy(1)-O(1) | 2.155 (3) |
| Dy(1)-N(1) | 2.586 (3) | Dy(1)-N(1) | 2.595 (4) |
| Dy(1)-N(2) | 2.579 (3) | Dy(1)-N(2) | 2.570 (3) |

| Bond angles (°) | | | |
|---|---|---|---|
| Complex **1** | | Complex **2** | |
| O1-Dy1-O2 | 157.02 (9) | O1-Dy1-O2 | 157.79 (13) |
| O1-Dy1-Cl1 | 99.48 (6) | O1-Dy1-Br1 | 104.28 (9) |
| O1-Dy1-N1 | 89.72 (9) | O1-Dy1-N1 | 92.37 (14) |
| O1-Dy1-N2 | 84.23 (8) | O1-Dy1-N2 | 76.99 (13) |
| O2-Dy1-Cl1 | 103.49 (6) | O2-Dy1-Br1 | 97.89 (9) |
| O2-Dy1-N1 | 93.19 (9) | O2-Dy1-N1 | 89.78 (14) |
| O2-Dy1-N2 | 76.41 (8) | O2-Dy1-N2 | 83.97 (13) |
| O2-Dy1-N3 | 85.05 (8) | O2-Dy1-N3 | 76.62 (12) |
| O2-Dy1-N4 | 88.09 (9) | O2-Dy1-N4 | 97.05 (14) |

| | | | |
|---|---|---|---|
| N1-Dy1-Cl1 | 80.76 (7) | N1-Dy1-Br1 | 80.72 (10) |
| N1-Dy1-N3 | 132.81 (9) | N1-Dy1-N3 | 132.91 (14) |
| N1-Dy1-N4 | 161.59 (10) | N1-Dy1-N4 | 161.68 (15) |
| N2-Dy1-Cl1 | 145.74 (6) | N2-Dy1-Br1 | 145.64 (9) |
| N3-Dy1-Cl1 | 145.44 (6) | N3-Dy1-Br1 | 145.11 (9) |
| N4-Dy1-Cl1 | 81.08 (7) | N4-Dy1-Br1 | 81.50 (10) |
| N4-Dy1-N2 | 132.69 (9) | N4-Dy1-N2 | 132.54 (13) |
| Complex **3** | | Complex **4** | |
| O1-Dy1-O1A | 170.65 (7) | O1-Dy1-O1A | 171.58 (8) |
| O1-Dy1-Cl1 | 94.68 (4) | O1-Dy1-Br1 | 94.21 (4) |
| O1-Dy1-N1 | 101.98 (6) | O1-Dy1-N1 | 101.73 (7) |
| O1-Dy1-N2 | 74.17 (5) | O1-Dy1-N2 | 74.40 (6) |
| O1A-Dy1-N2 | 97.97 (6) | O1A-Dy1-N2 | 98.52 (6) |
| N1-Dy1-Cl1 | 85.23 (4) | N1-Dy1-Br1 | 85.24 (4) |
| N1-Dy1-N1A | 170.45 (7) | N1-Dy1-N1A | 170.47 (8) |
| N2-Dy1-Cl1 | 145.41 (4) | N2-Dy1-Br1 | 145.31 (4) |
| Complex **5** | | Complex **6** | |
| O1-Dy1-O1A | 157.44 (12) | O1-Dy1-O1A | 158.29 (14) |
| O1-Dy1-Cl1 | 101.28 (6) | O1-Dy1-Br1 | 100.86 (7) |
| O1-Dy1-N1 | 97.04 (10) | O1-Dy1-N1 | 96.60 (11) |
| O1-Dy1-N2 | 77.51 (9) | O1-Dy1-N2 | 77.82 (10) |
| O1A-Dy1-N2 | 84.00 (9) | O1A-Dy1-N2 | 84.39 (10) |
| N1-Dy1-Cl1 | 80.59 (6) | N1-Dy1-Br1 | 80.63 (7) |
| N1-Dy1-N1A | 161.17 (13) | N1-Dy1-N1A | 161.25 (14) |
| N2-Dy1-Cl1 | 145.08 (6) | N2-Dy1-Br1 | 145.03 (7) |

## X-ray powder diffraction and IR spectra

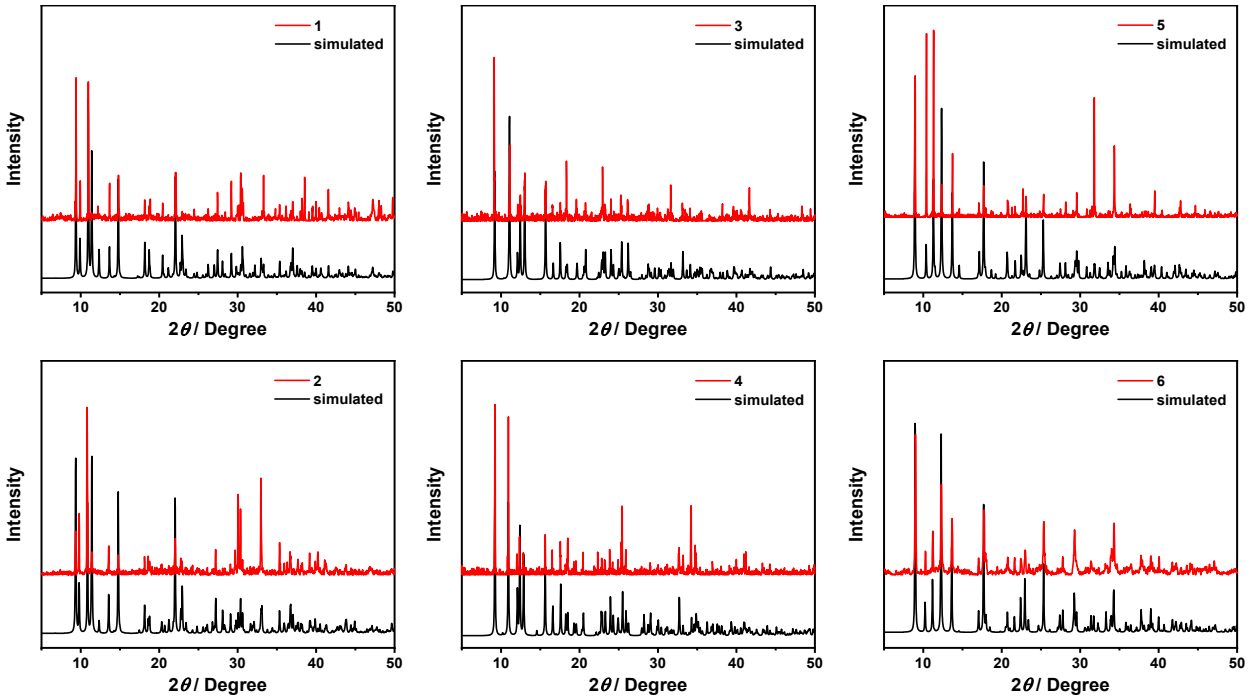



**Figure S1.** PXRD patterns of complexes **1–6**.

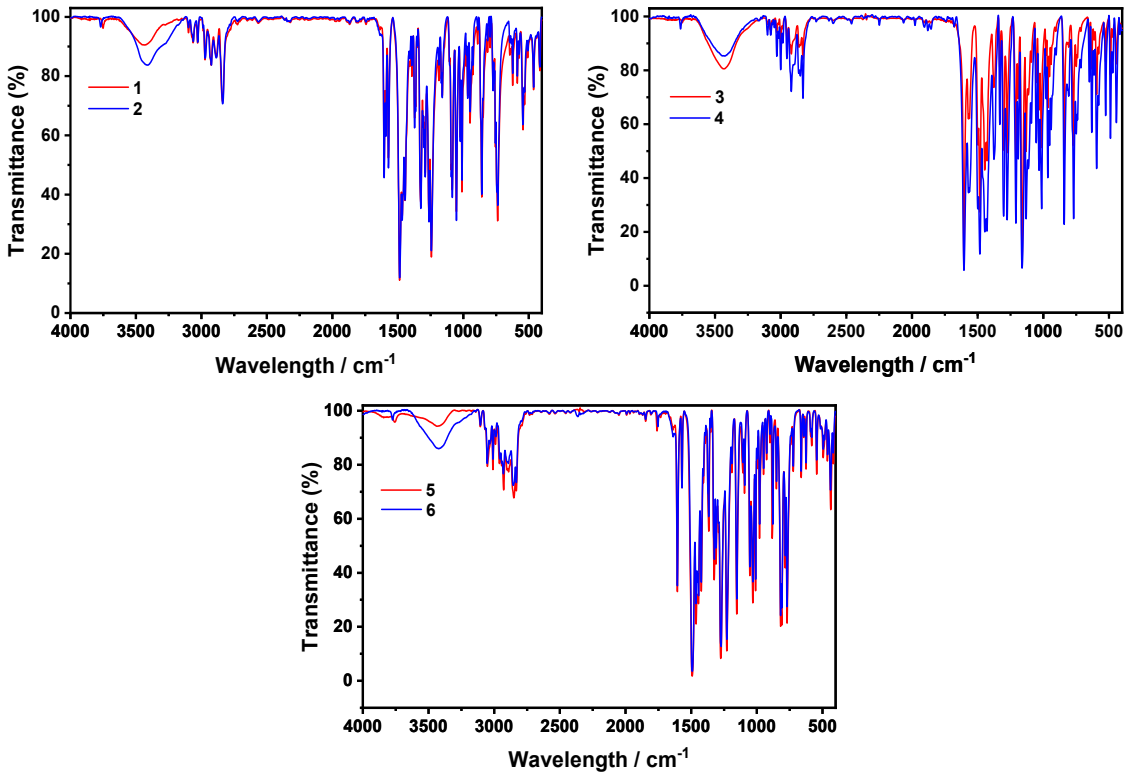



**Figure S2.** Infrared spectra of complexes**1–6**.

## Crystal structures

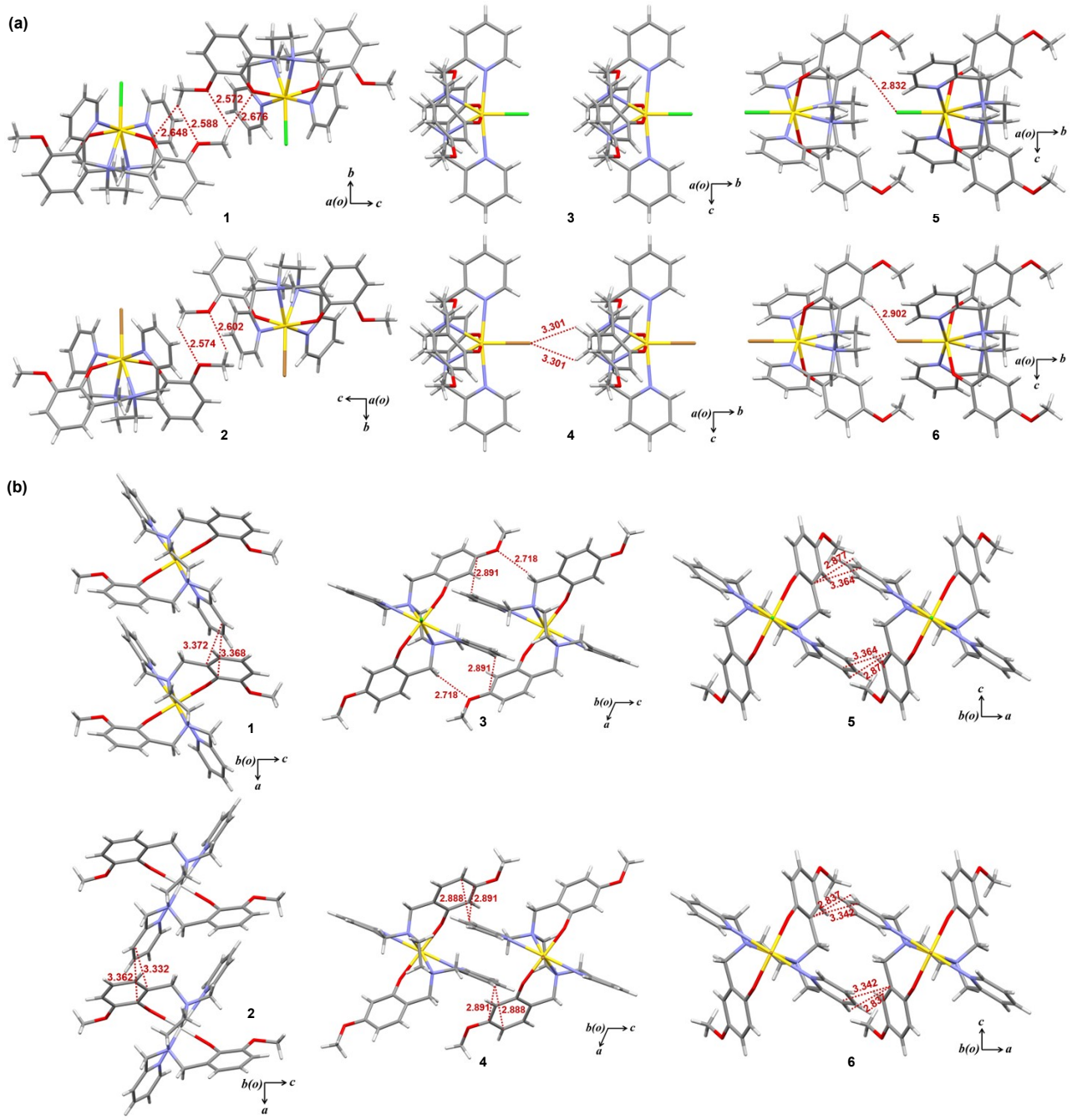



**Figure S3.** The crystal packing modes of **1–6** ((a) along *a* axis direction, (b) along *b* axis direction), where weak intermolecular interactions (red dashed lines) are included.

**Table S3.** The calculated results for $Dy^{III}$ ions configuration of complexes **1–6** by SHAPE 2.0 Software.

| Configuration | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Heptagon ($D_{7h}$) | 33.903 | 34.091 | 34.687 | 34.749 | 33.762 | 34.007 |
| Hexagonal pyramid ($C_{6v}$) | 23.303 | 23.516 | 21.419 | 21.812 | 23.181 | 23.361 |
| Pentagonal bipyramid ($D_{5h}$) | **1.895** | **2.277** | 4.032 | 4.327 | **1.866** | **2.152** |
| Capped octahedron ($C_{3v}$) | 7.607 | 8.001 | 4.339 | 4.617 | 8.493 | 8.849 |
| Capped trigonal prism ($C_{2v}$) | 6.189 | 6.546 | **3.491** | **3.768** | 6.709 | 7.010 |
| Johnson pentagonal bipyramid J13 ($D_{5h}$) | 2.267 | 2.331 | 5.154 | 5.222 | 2.281 | 2.332 |
| Johnson elongated triangular pyramid J7 ($C_{3v}$) | 21.998 | 22.54 | 21.294 | 21.783 | 21.154 | 21.752 |

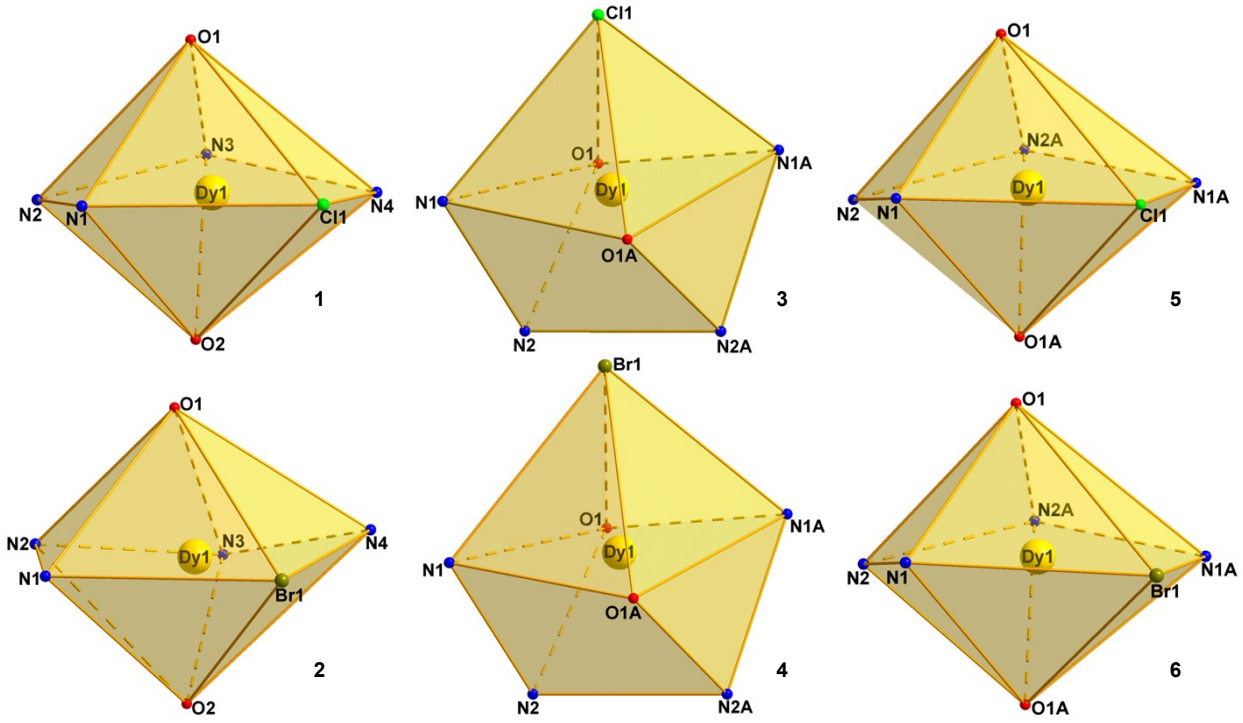



**Figure S4.** Polyhedrons around $Dy^{III}$ ion for complexes **1–6**.

## Magnetic measurements

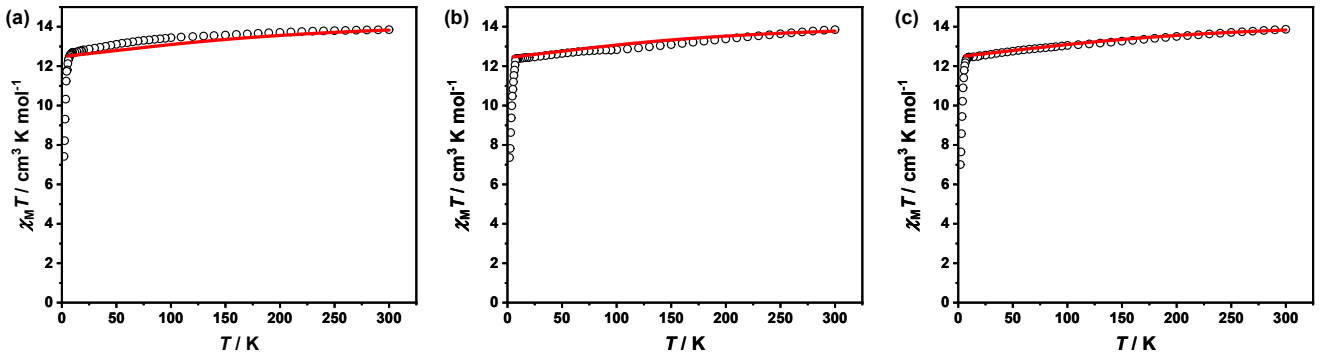



**Figure S5.** The variable-temperature magnetic susceptibilities of **1**, **3** and **5**. Solid lines correspond to the *ab initio* calculation results.

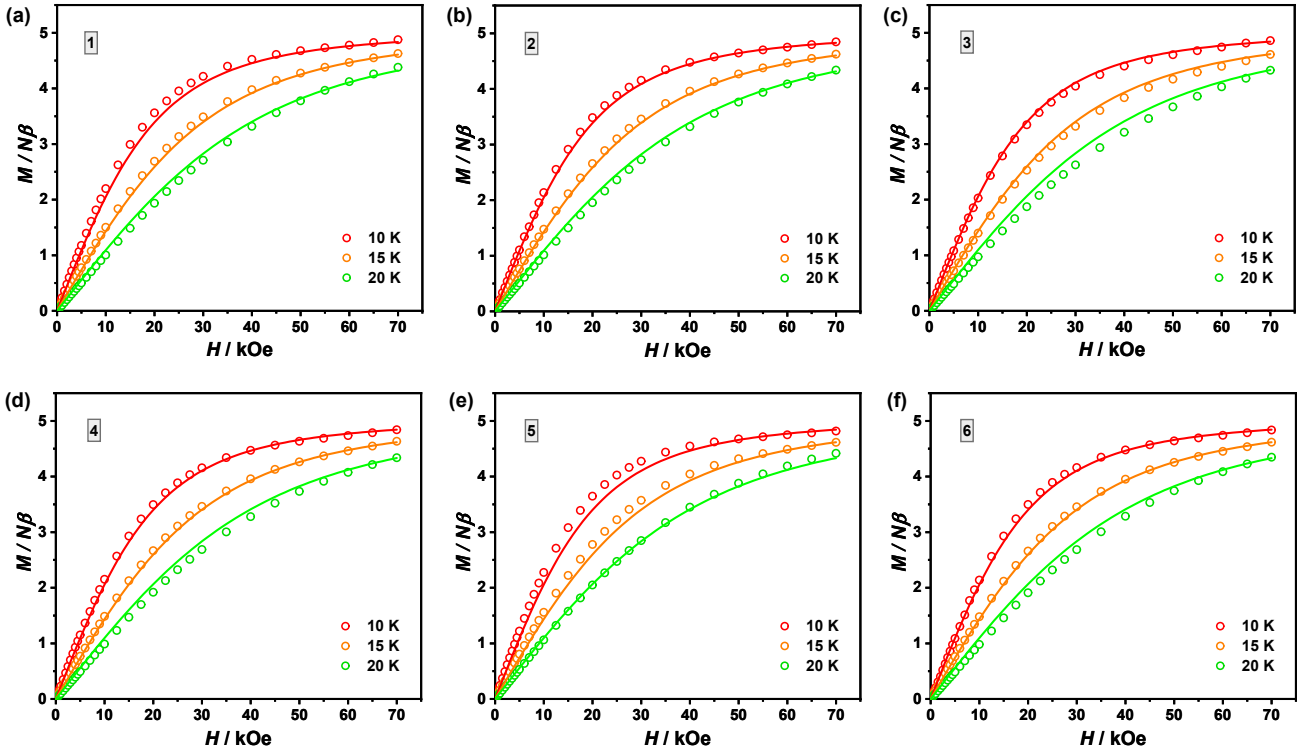
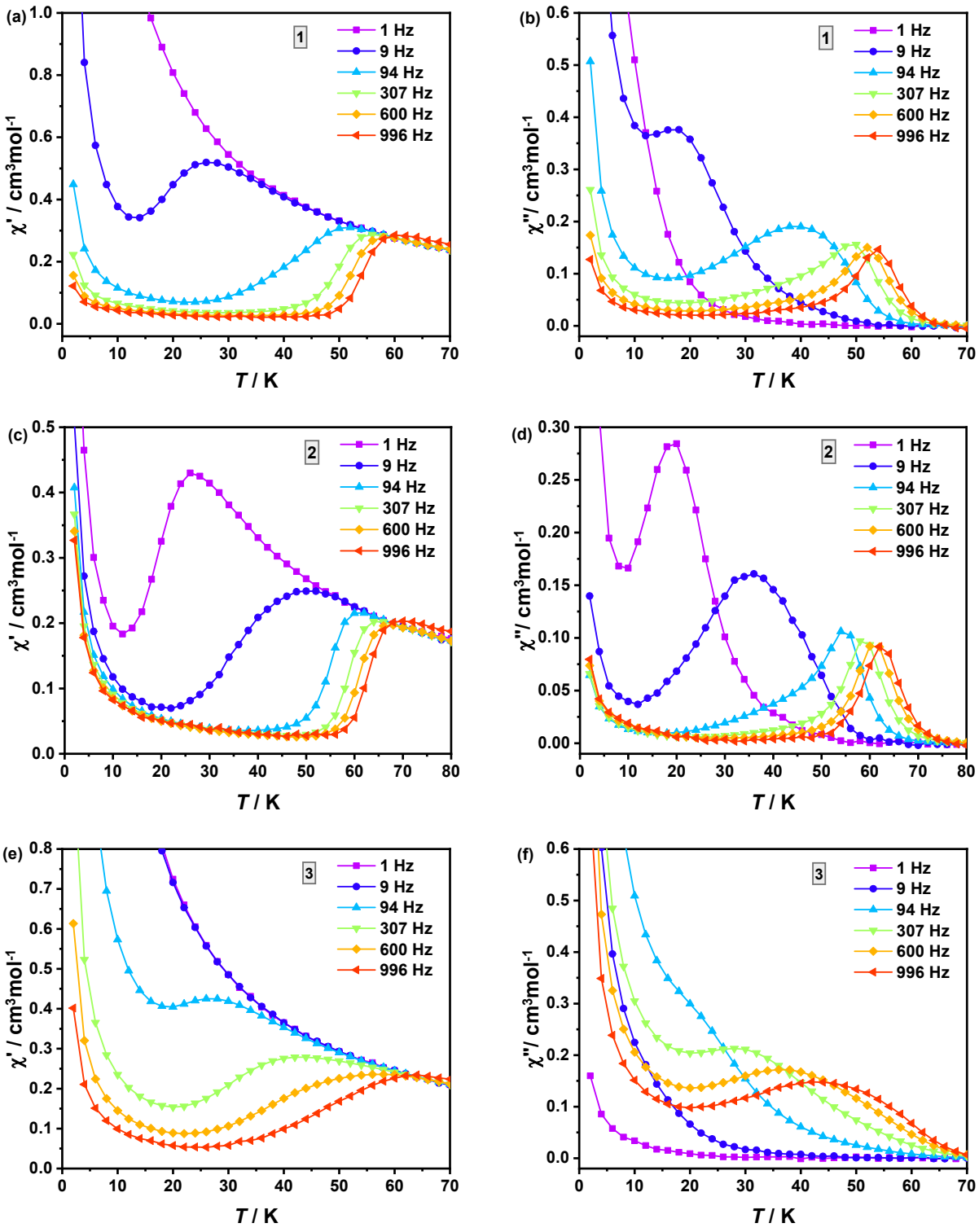



**Figure S6.** Field dependent magnetization data for complexes **1–6** at 2 K. Data were collected from 0 to 70 kOe in steady fields. Solid lines correspond to the *ab initio* calculation results.


(a)
1
1 Hz
9 Hz
94 Hz
307 Hz
600 Hz
996 Hz
χ' / cm³mol⁻¹
T / K
(b)
1
χ'' / cm³mol⁻¹
(c)
2
(d)
(e)
3
(f)

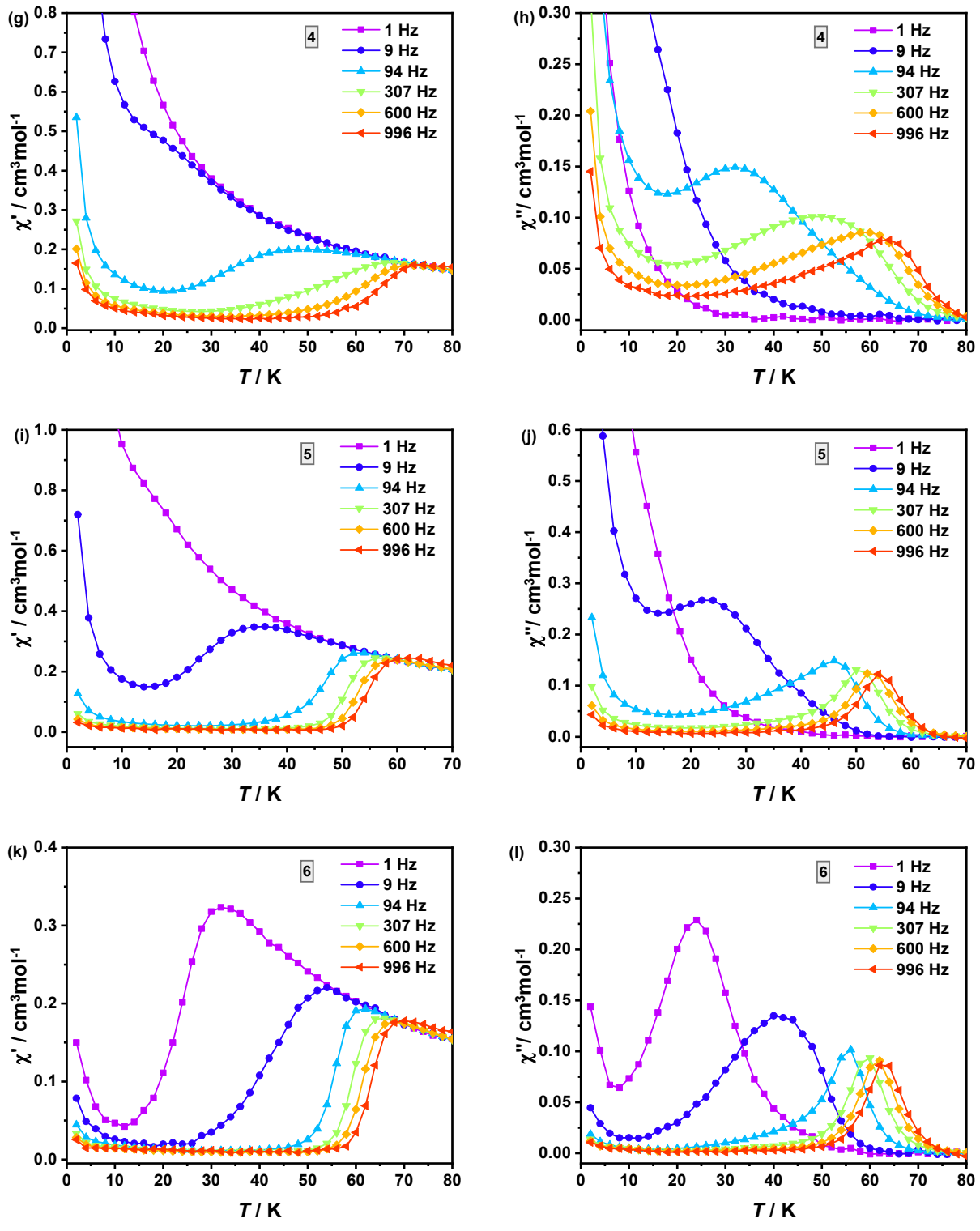
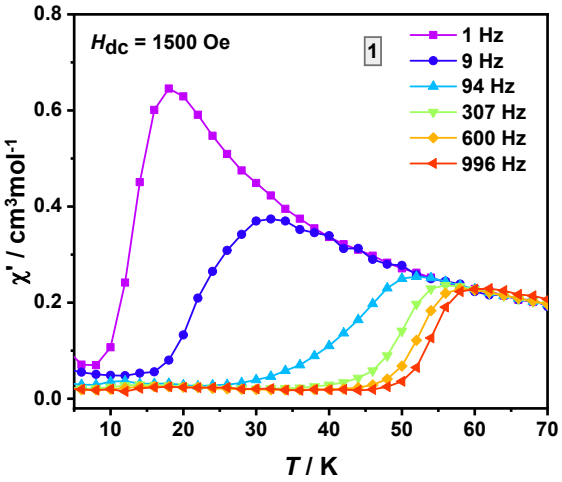
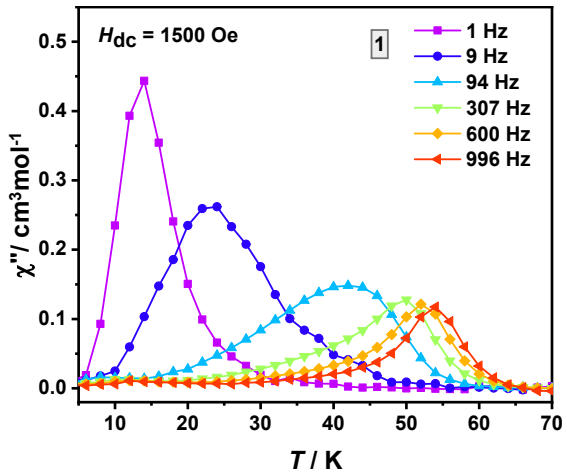
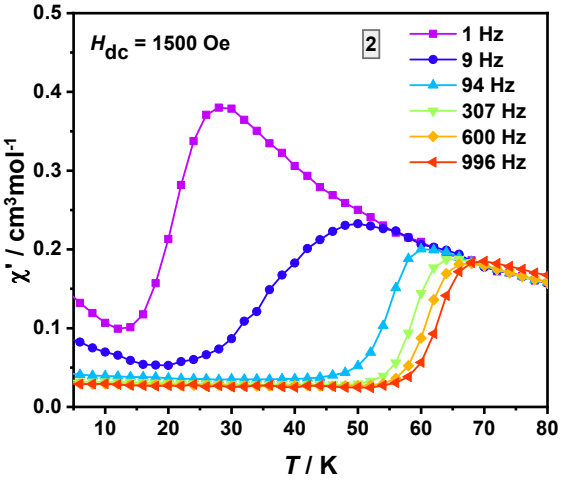
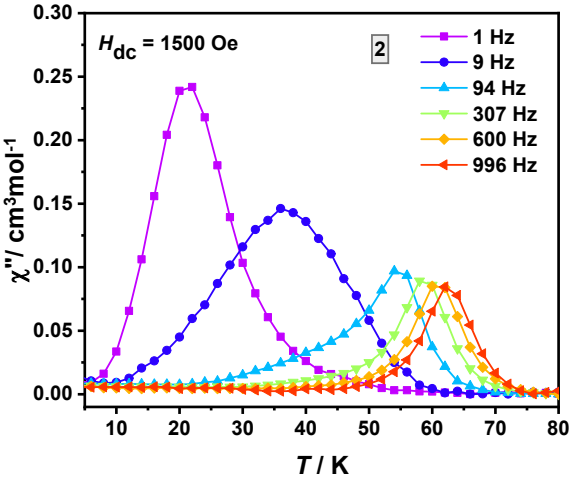


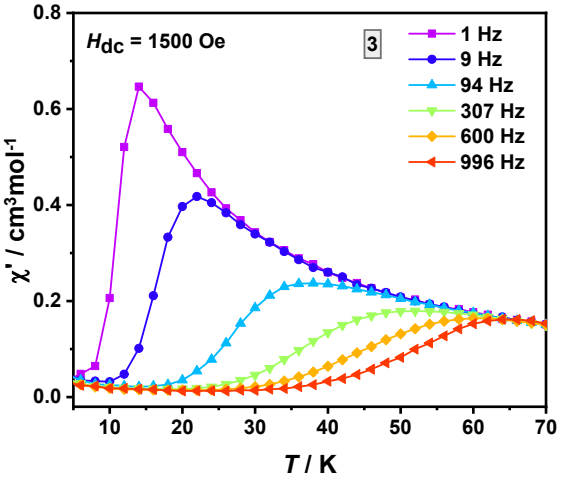

**Figure S7.** Temperature-dependence of in-phase ($\chi'$) and out-of-phase ($\chi''$) ac susceptibility of **1–6** in zero dc field.

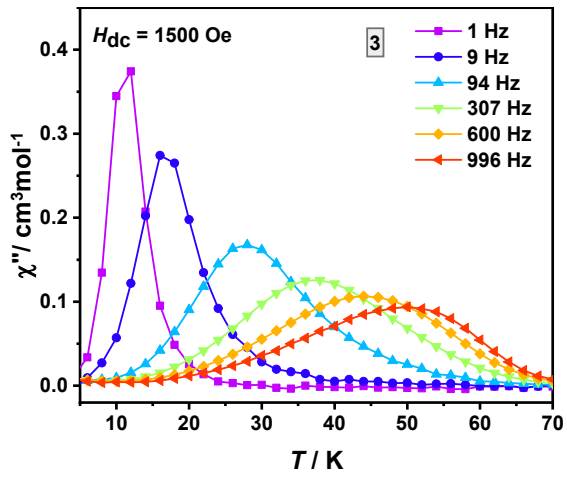

$H_{dc}$ = 1500 Oe
1
1 Hz
9 Hz
94 Hz
307 Hz
600 Hz
996 Hz
χ' / cm³mol⁻¹
T / K


$H_{dc}$ = 1500 Oe
1
1 Hz
9 Hz
94 Hz
307 Hz
600 Hz
996 Hz
χ''/ cm³mol⁻¹
T / K


$H_{dc}$ = 1500 Oe
2
1 Hz
9 Hz
94 Hz
307 Hz
600 Hz
996 Hz
χ' / cm³mol⁻¹
T / K


$H_{dc}$ = 1500 Oe
2
1 Hz
9 Hz
94 Hz
307 Hz
600 Hz
996 Hz
χ''/ cm³mol⁻¹
T / K


$H_{dc}$ = 1500 Oe
3
1 Hz
9 Hz
94 Hz
307 Hz
600 Hz
996 Hz
χ' / cm³mol⁻¹
T / K


$H_{dc}$ = 1500 Oe
3
1 Hz
9 Hz
94 Hz
307 Hz
600 Hz
996 Hz
χ''/ cm³mol⁻¹
T / K

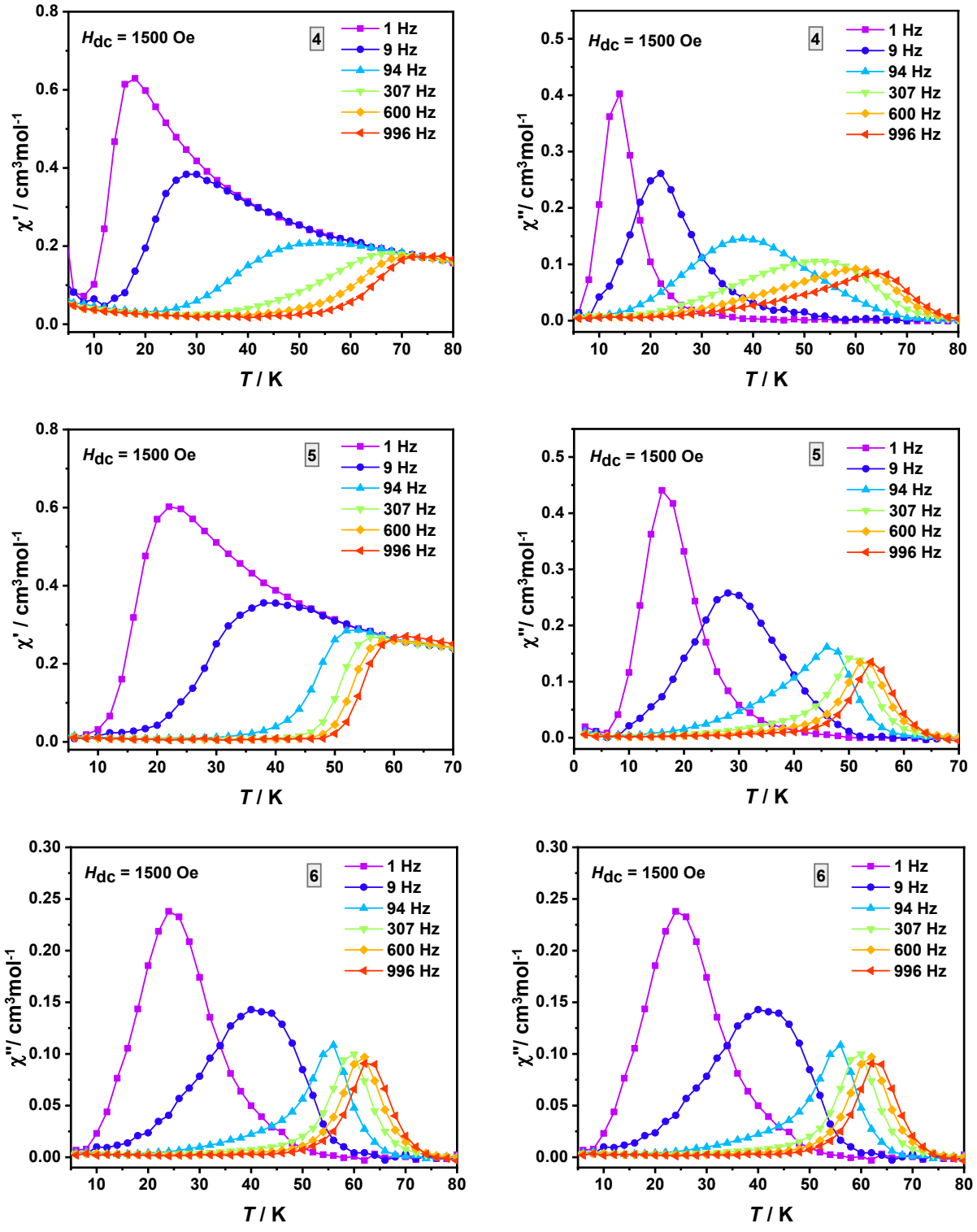
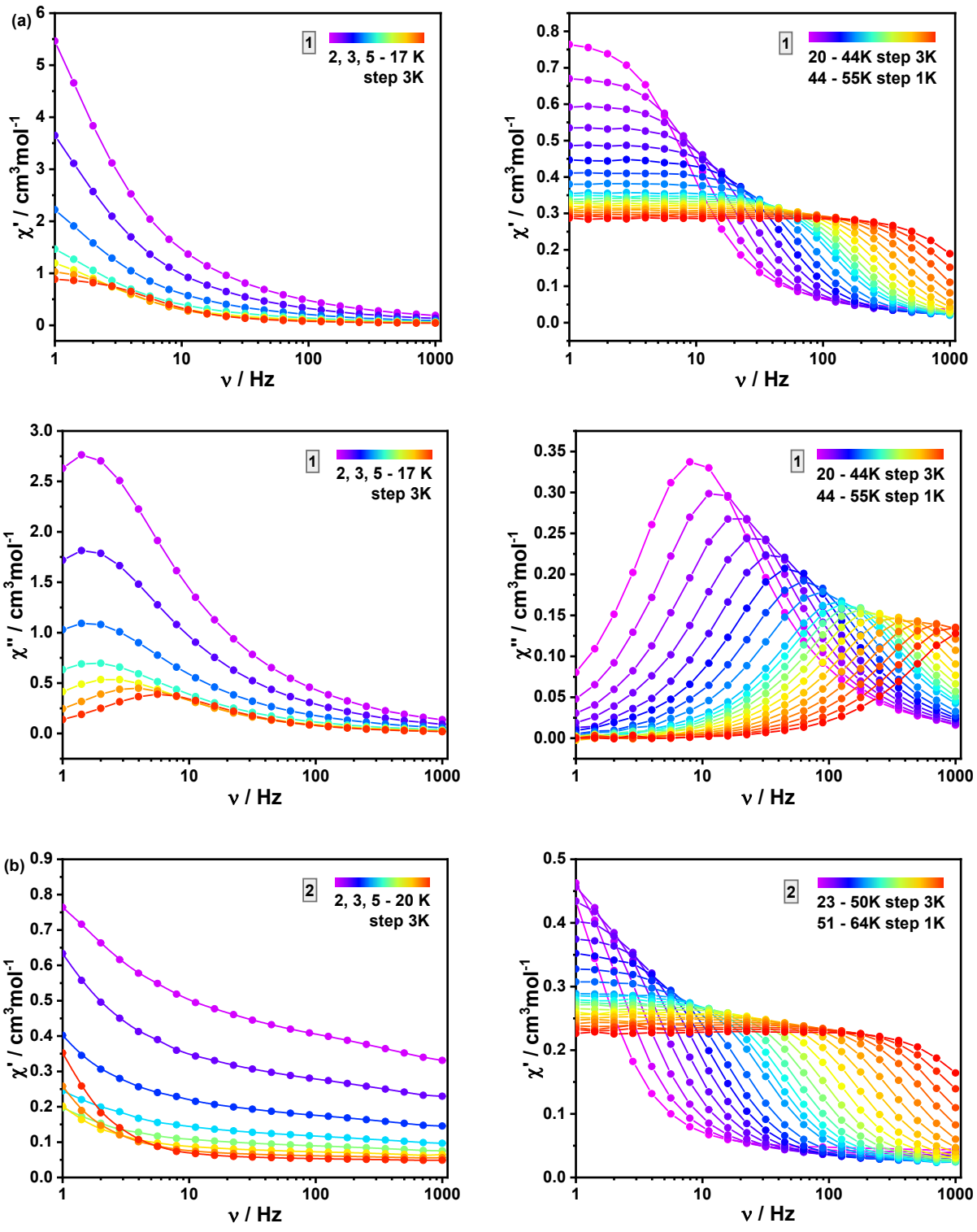
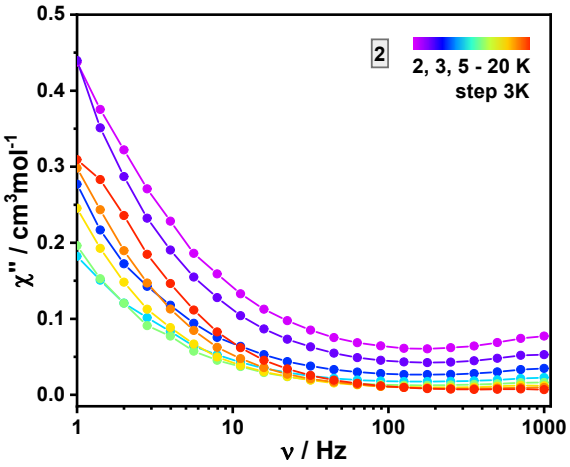
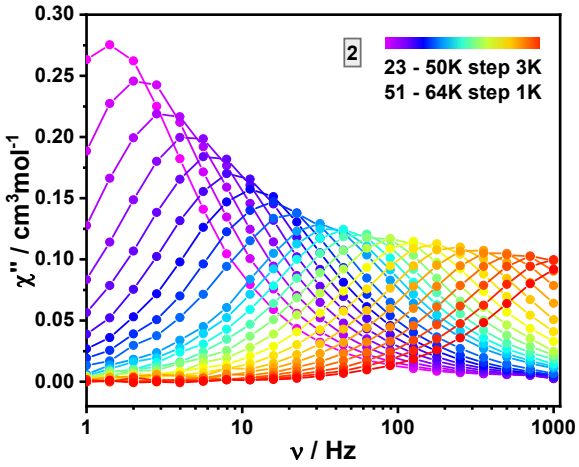


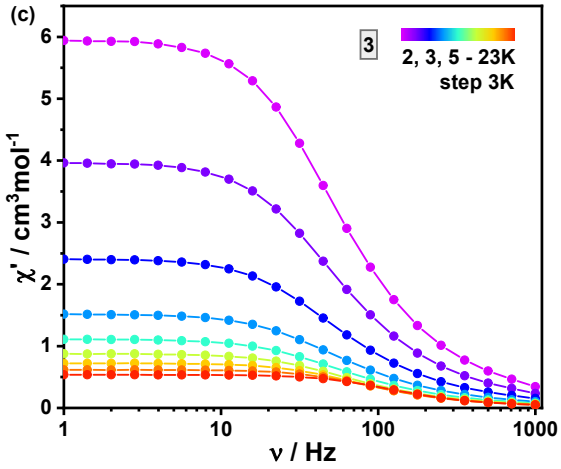

**Figure S8.** Temperature-dependence of in-phase ($\chi'$) and out-of-phase ($\chi''$) ac susceptibility of **1–6** under 1500 Oe applied dc field.

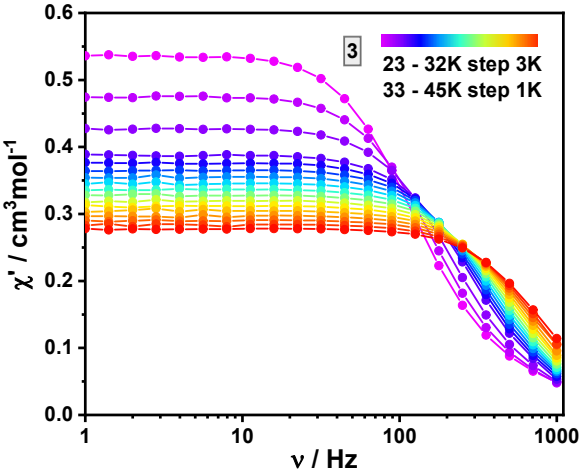

(a)
1
2, 3, 5 - 17 K
step 3K
χ' / cm3mol-1
ν / Hz
1
20 - 44K step 3K
44 - 55K step 1K
χ' / cm3mol-1
ν / Hz
1
2, 3, 5 - 17 K
step 3K
χ'' / cm3mol-1
ν / Hz
1
20 - 44K step 3K
44 - 55K step 1K
χ'' / cm3mol-1
ν / Hz
(b)
2
2, 3, 5 - 20 K
step 3K
χ' / cm3mol-1
ν / Hz
2
23 - 50K step 3K
51 - 64K step 1K
χ' / cm3mol-1
ν / Hz

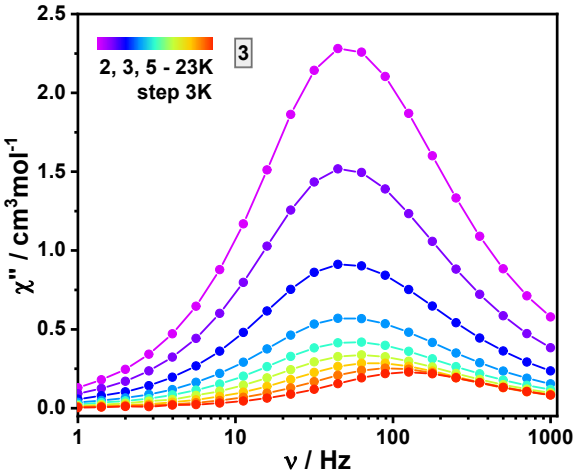

2
2, 3, 5 - 20 K
step 3K
χ'' / cm3mol-1
ν / Hz

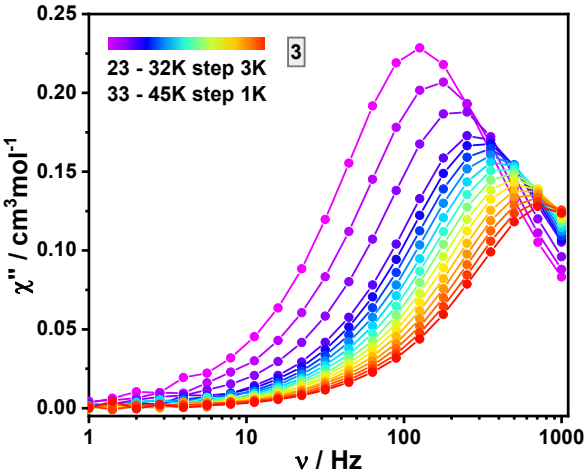

2
23 - 50K step 3K
51 - 64K step 1K
χ'' / cm3mol-1
ν / Hz

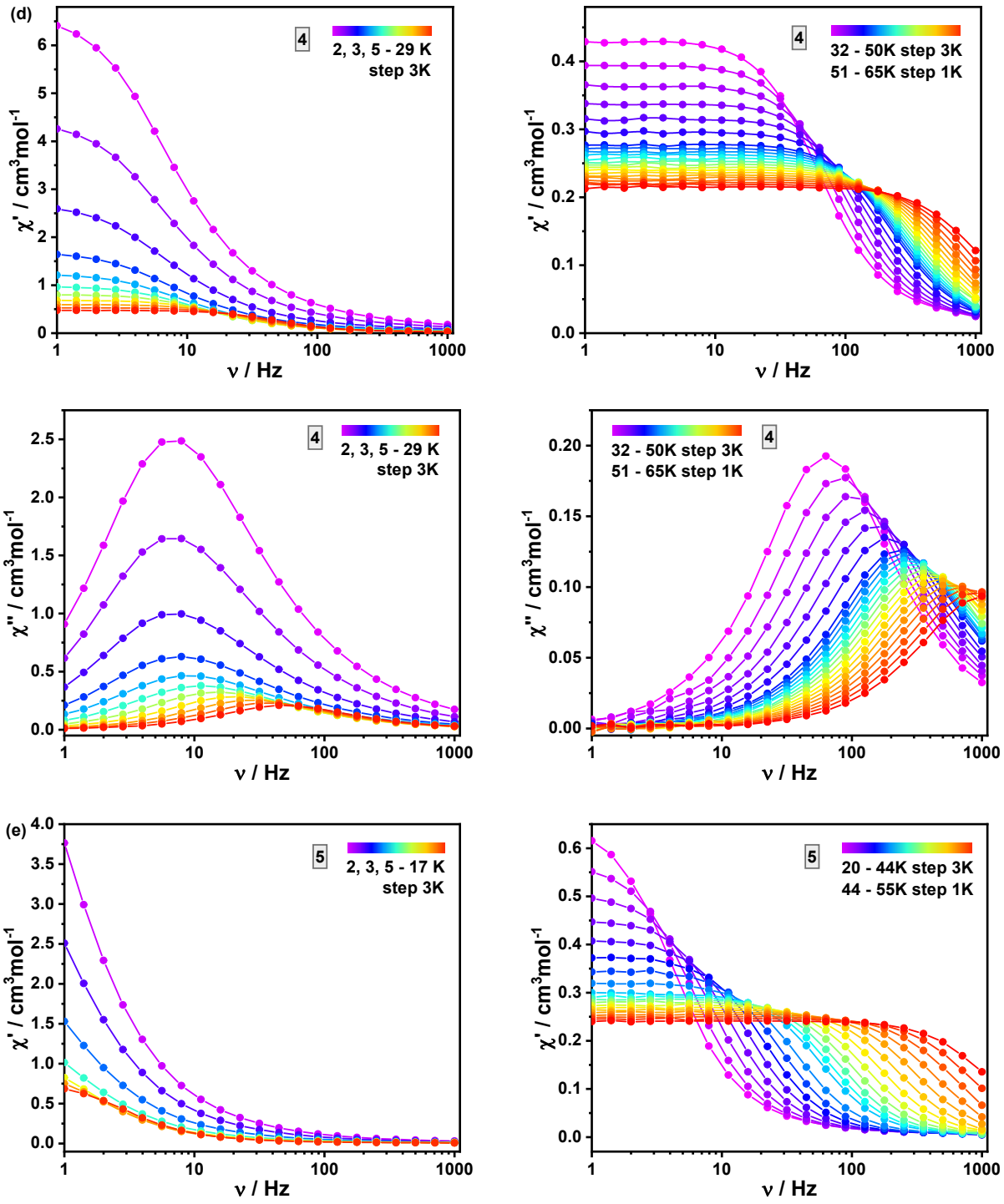
(c)


3
2, 3, 5 - 23K
step 3K
χ' / cm3mol-1
ν / Hz


3
23 - 32K step 3K
33 - 45K step 1K
χ' / cm3mol-1
ν / Hz


3
2, 3, 5 - 23K
step 3K
χ'' / cm3mol-1
ν / Hz


3
23 - 32K step 3K
33 - 45K step 1K
χ'' / cm3mol-1
ν / Hz


(d)
4
2, 3, 5 - 29 K
step 3K
χ' / cm3mol-1
ν / Hz
4
32 - 50K step 3K
51 - 65K step 1K
χ' / cm3mol-1
ν / Hz
4
2, 3, 5 - 29 K
step 3K
χ'' / cm3mol-1
ν / Hz
4
32 - 50K step 3K
51 - 65K step 1K
χ'' / cm3mol-1
ν / Hz
(e)
5
2, 3, 5 - 17 K
step 3K
χ' / cm3mol-1
ν / Hz
5
20 - 44K step 3K
44 - 55K step 1K
χ' / cm3mol-1
ν / Hz

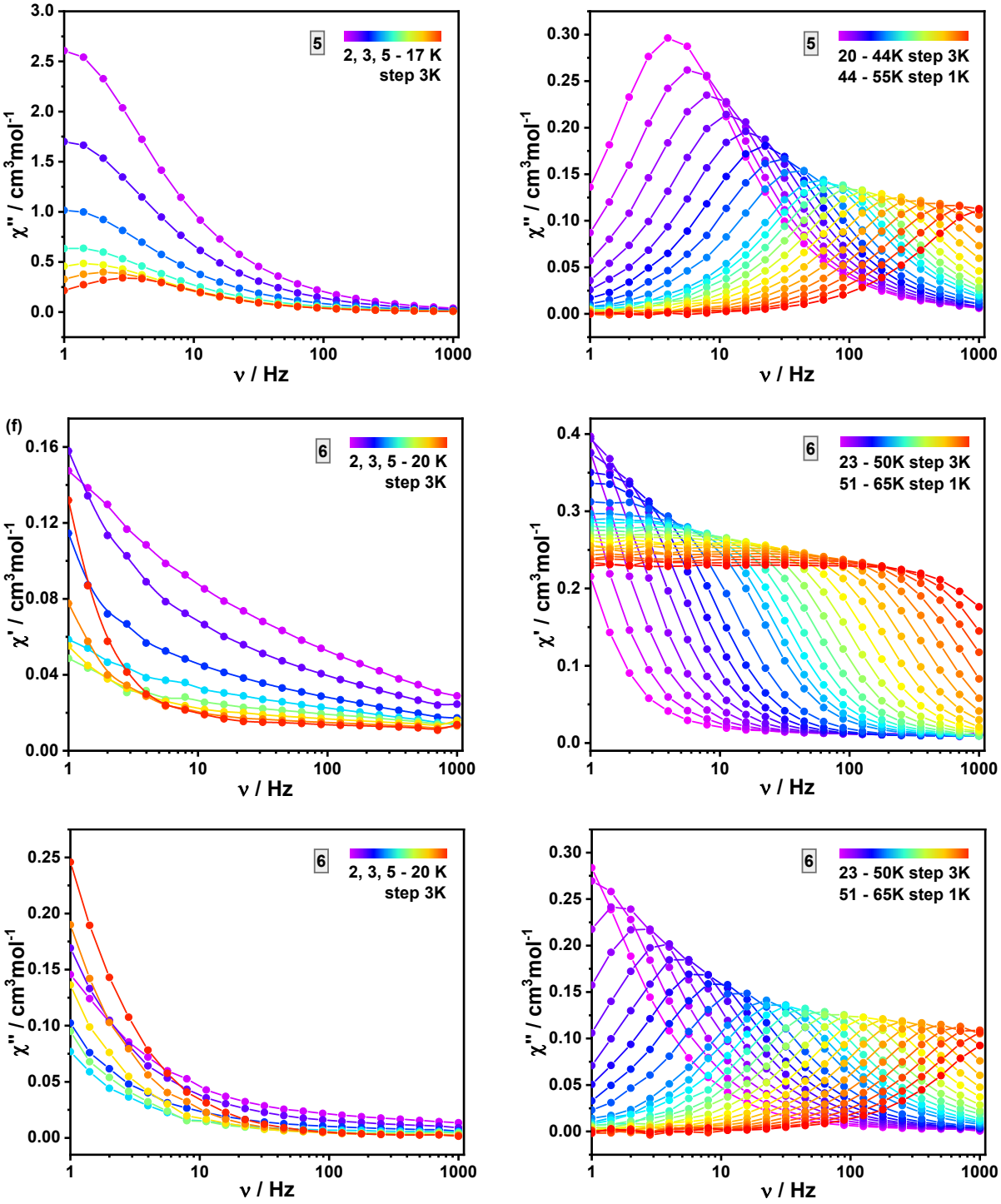
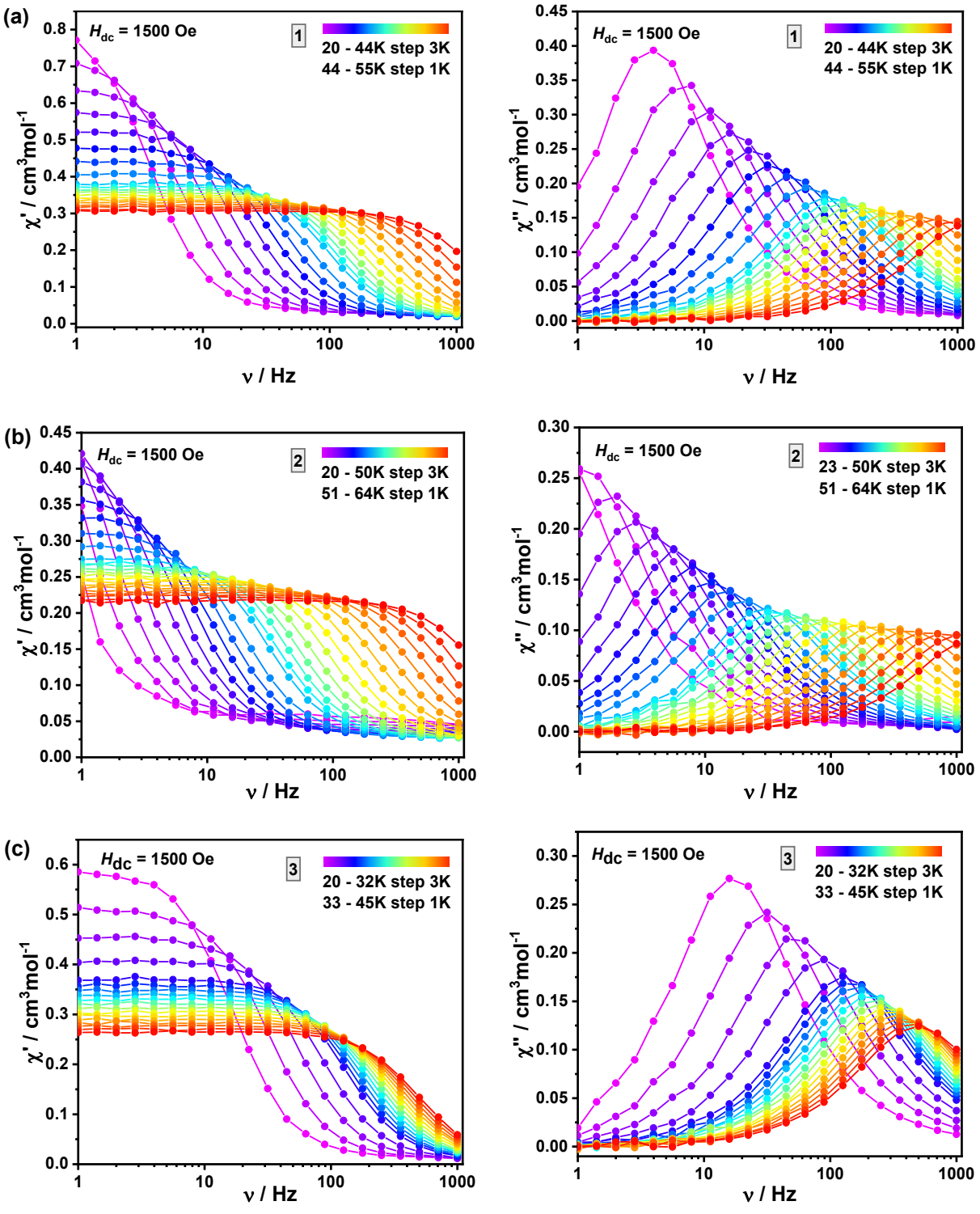



**Figure S9.** Frequency dependence of the in-phase ($\chi'$) and out-of-phase ($\chi''$) ac susceptibility of complexes **1**–**6** in zero dc field.


(a)
$H_{dc}$ = 1500 Oe
1
20 - 44K step 3K
44 - 55K step 1K
χ' / cm³mol⁻¹
χ'' / cm³mol⁻¹
ν / Hz
(b)
$H_{dc}$ = 1500 Oe
2
20 - 50K step 3K
51 - 64K step 1K
23 - 50K step 3K
51 - 64K step 1K
(c)
$H_{dc}$ = 1500 Oe
3
20 - 32K step 3K
33 - 45K step 1K

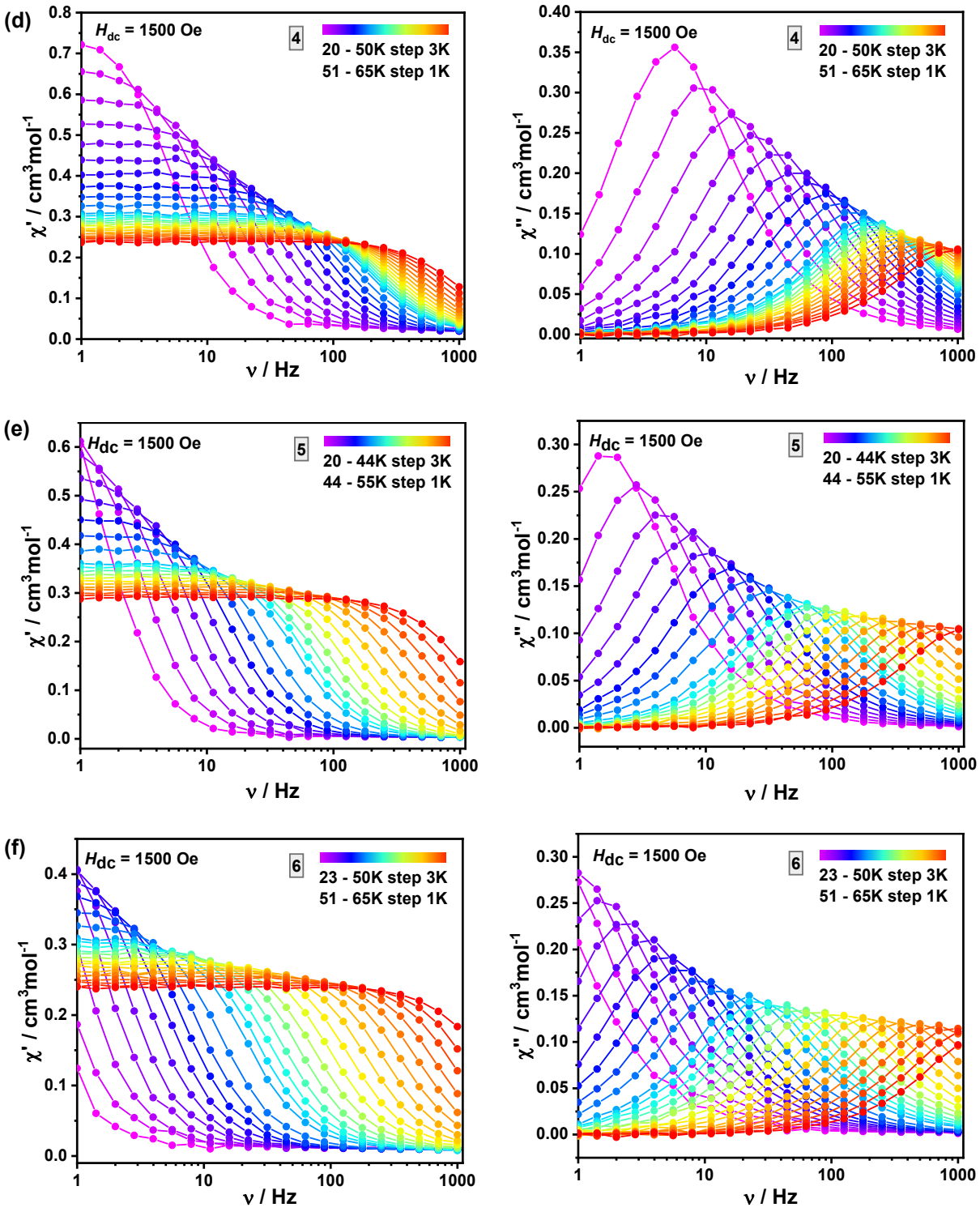



**Figure S10.** Frequency dependence of the in-phase ($\chi'$) and out-of-phase ($\chi''$) ac susceptibility of complexes **1**–**6** under 1500 Oe applied dc field.

**Fitting for the complexes**

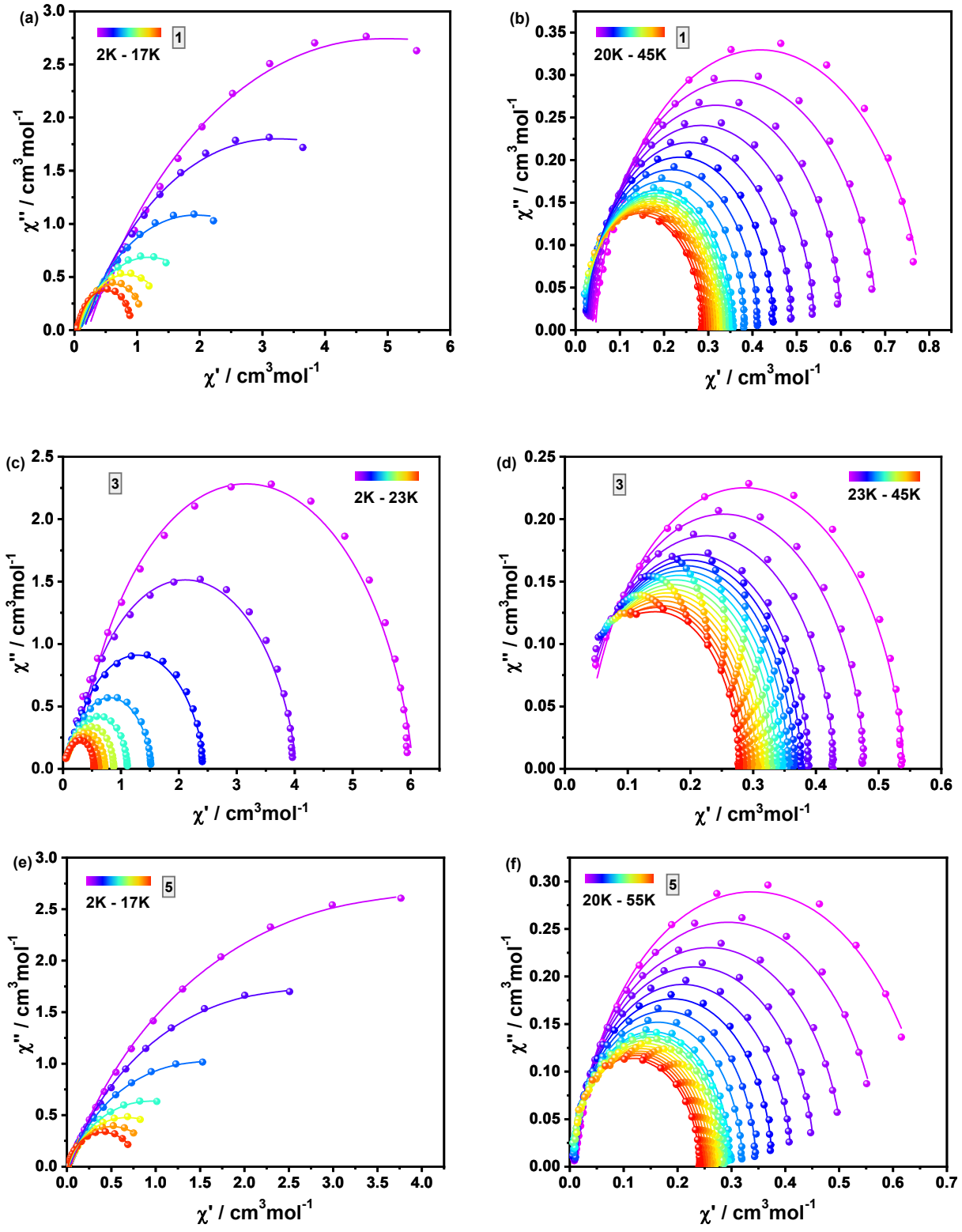



**Figure S11.** Cole-Cole plots for complexes **1**, **3** and **5**. The solid lines are the best fits for the generalized Debye model ($0 < \alpha < 0.32$).

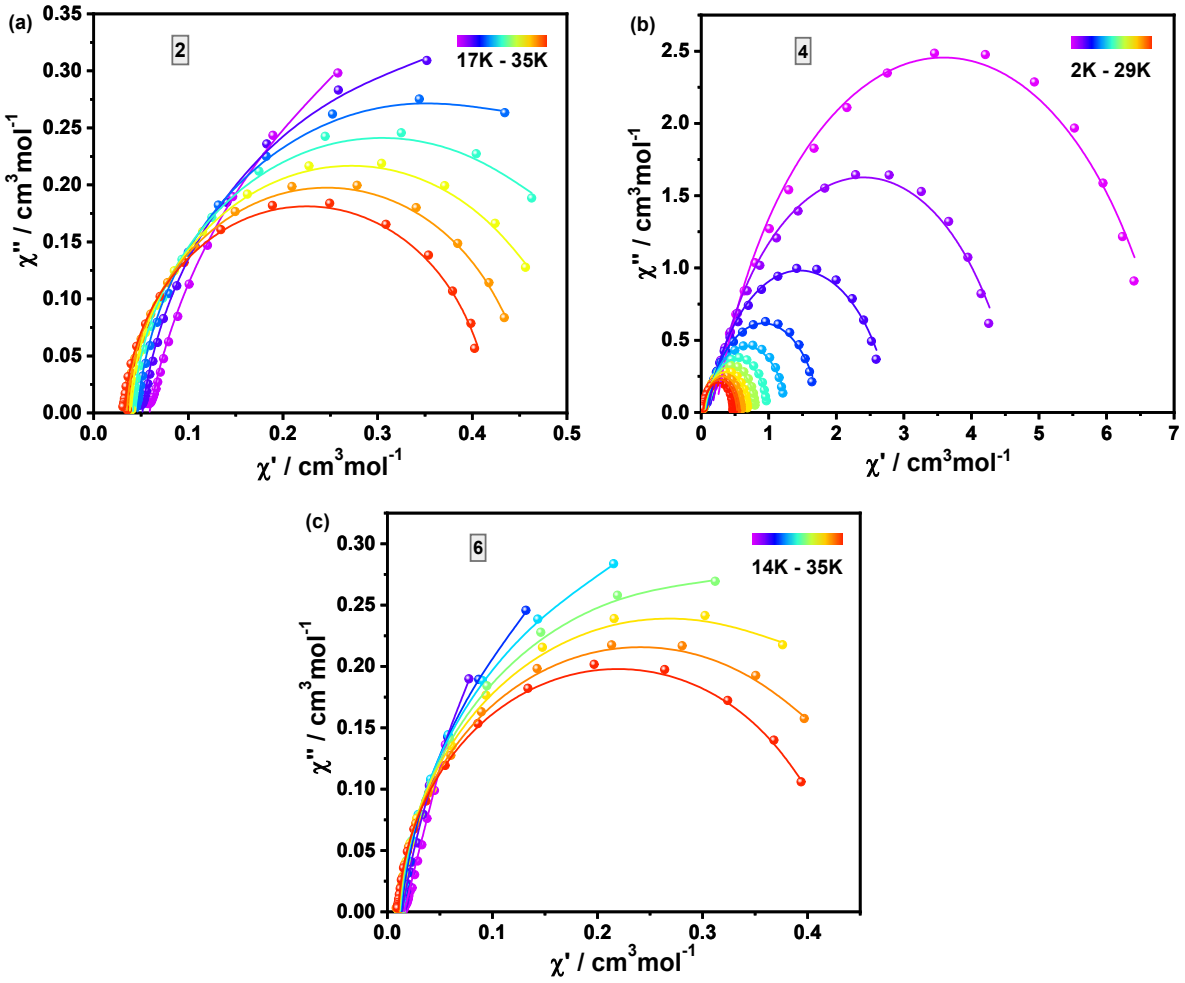



**Figure S12.** Cole-Cole plots of complexes **2**, **4** and **6** measured at low temperature (below 35 K). The solid lines are the best fits for the generalized Debye model ($0 < \alpha < 0.19$).

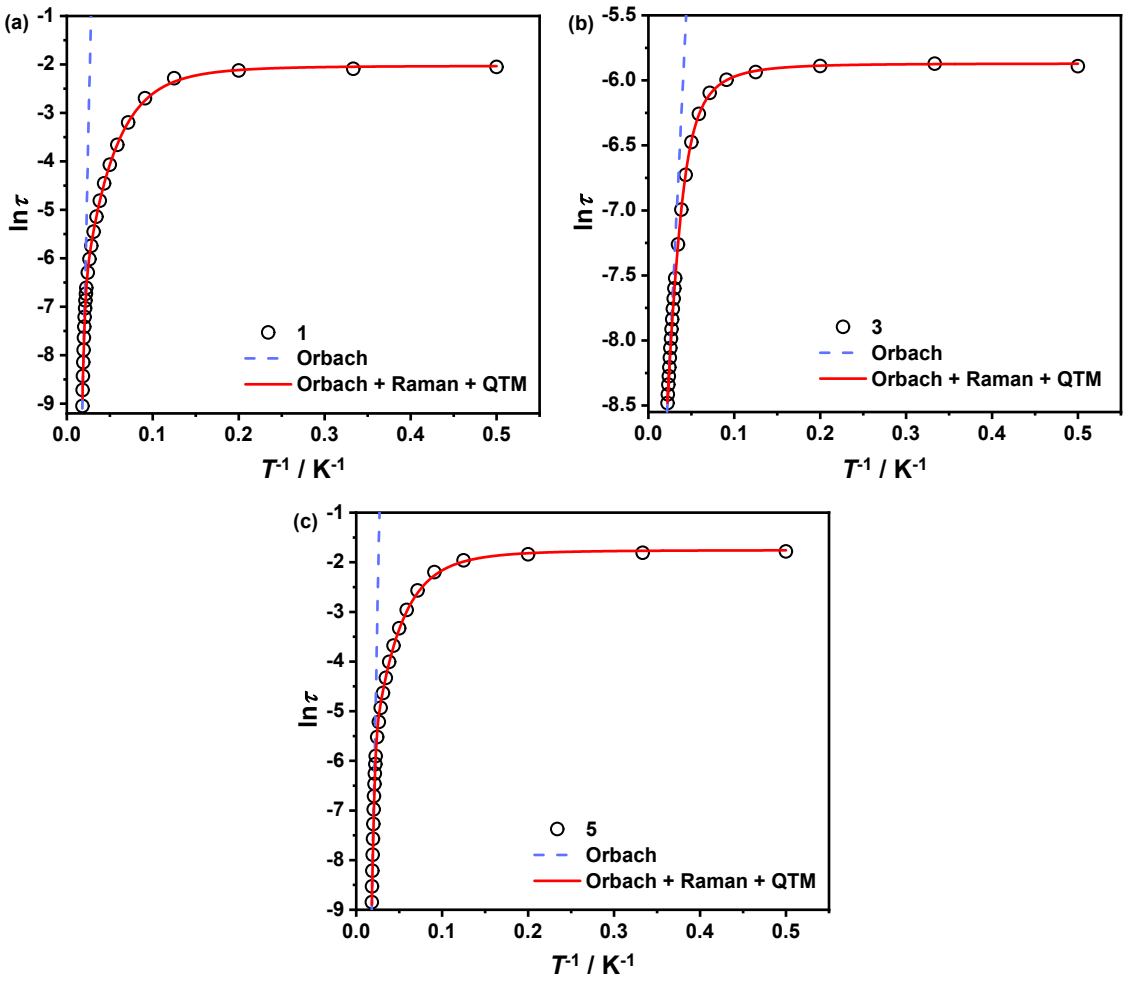



**Figure S13.** Temperature dependence of the magnetic relaxation time ($\tau$) under zero dc field are shown as ln($\tau$) versus $T^{-1}$ for **1**, **3**, and **5**. The blue dashed line and red solid line represent part of the Orbach process and the best fitting based on Arrhenius law, respectively.

## Magnetization hysteresis

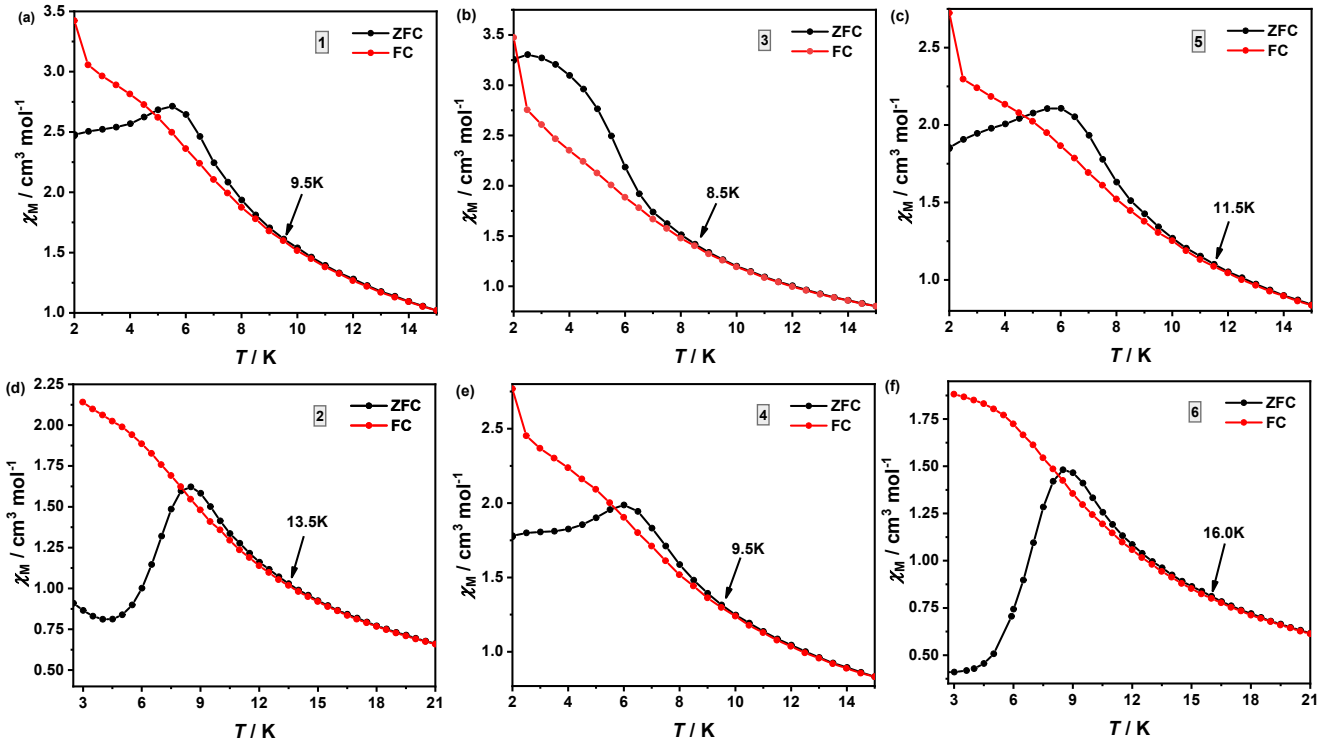



**Figure S14.** FC and ZFC measurements for **1**–**6** under 2 kOe applied dc field.

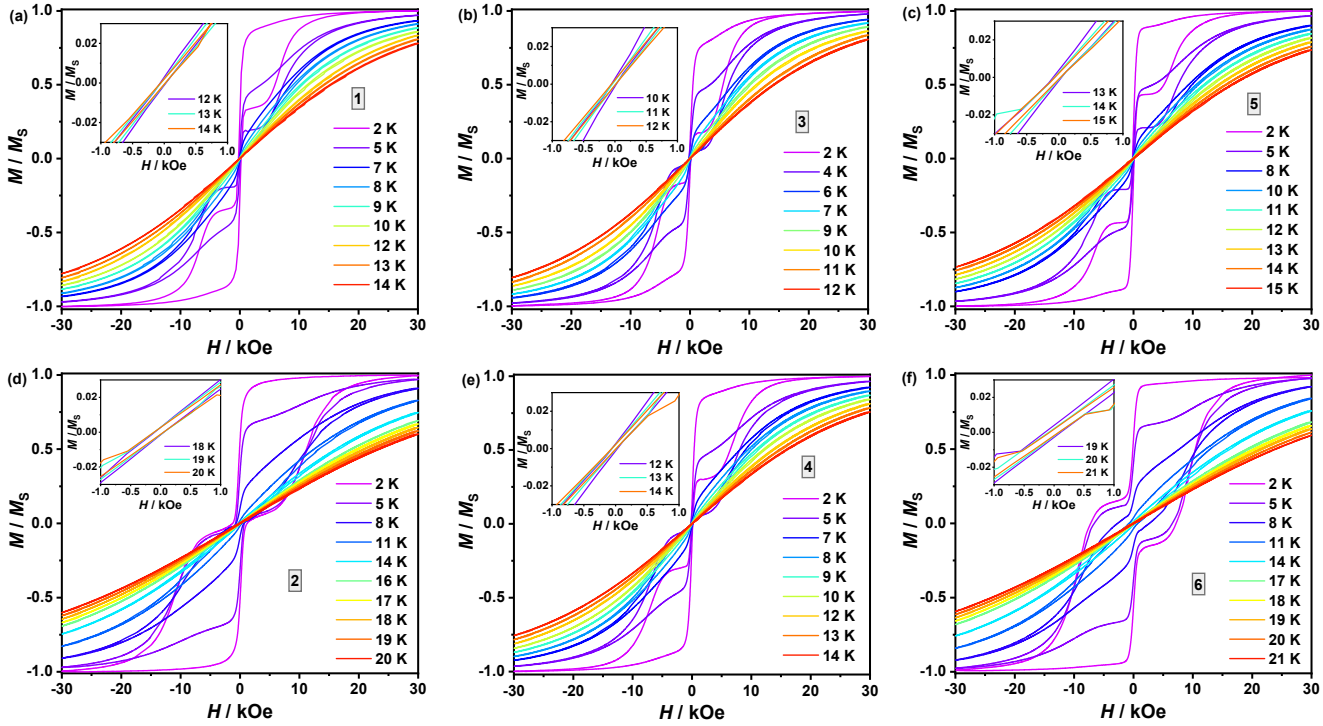



**Figure S15.** Magnetic hysteresis loops were measured at a sweep rate of 0.02 T $s^{-1}$ of complexes **1**–**6**.

**Fitting parameters**

**Table S4.** Best fit parameters of the generalized Debye model at temperature ranging from 2 to 55 K under a 0 Oe DC field for **1**.

| T / K | $\chi_S$ / $cm^3mol^{-1}K$ | $\chi_T$ / $cm^3mol^{-1}K$ | τ / s | α |
|---|---|---|---|---|
| 2 | 0.21573 | 9.51054 | 0.128640 | 0.31819 |
| 3 | 0.14973 | 6.23459 | 0.123530 | 0.31627 |
| 5 | 0.09934 | 3.75124 | 0.119610 | 0.31528 |
| 8 | 0.07411 | 2.30463 | 0.101900 | 0.29434 |
| 11 | 0.06661 | 1.58686 | 0.067400 | 0.22944 |
| 14 | 0.06019 | 1.18132 | 0.040840 | 0.15476 |
| 17 | 0.05233 | 0.94462 | 0.025780 | 0.10181 |
| 20 | 0.04476 | 0.79064 | 0.017070 | 0.06888 |
| 23 | 0.03762 | 0.6831 | 0.011630 | 0.04992 |
| 26 | 0.03322 | 0.60196 | 0.008140 | 0.035 |
| 29 | 0.02904 | 0.54026 | 0.005850 | 0.02676 |
| 32 | 0.02602 | 0.48948 | 0.004290 | 0.01963 |
| 35 | 0.02343 | 0.44781 | 0.003210 | 0.01514 |
| 38 | 0.02246 | 0.41218 | 0.002430 | 0.00871 |
| 41 | 0.02045 | 0.38206 | 0.001840 | 0.00672 |
| 44 | 0.01766 | 0.35667 | 0.001340 | 0.00657 |
| 45 | 0.01871 | 0.34844 | 0.001190 | 0.0028 |
| 46 | 0.01785 | 0.34132 | 0.001040 | 0.00433 |
| 47 | 0.01774 | 0.3342 | 0.000885 | 0.00357 |
| 48 | 0.01625 | 0.32741 | 0.000738 | 0.00506 |
| 49 | 0.01601 | 0.32091 | 0.000603 | 0.00439 |
| 50 | 0.01466 | 0.31453 | 0.000481 | 0.00518 |
| 51 | 0.0123 | 0.30875 | 0.000375 | 0.00873 |
| 52 | 0.01432 | 0.30275 | 0.000290 | 0.00584 |
| 53 | 0.01361 | 0.29709 | 0.000219 | 0.00616 |
| 54 | 0.01626 | 0.29174 | 0.000164 | 0.00704 |
| 55 | 0.0102 | 0.28666 | 0.000118 | 0.01408 |

**Table S5.** Best fit parameters of the generalized Debye model at temperature ranging from 17 to 64 K under a 0 Oe DC field for **2**.

| T / K | $\chi_S$ / $cm^3mol^{-1}K$ | $\chi_T$ / $cm^3mol^{-1}K$ | τ / s | α |
|---|---|---|---|---|
| 17 | 0.0588584 | 1.05779 | 0.448384 | 0.145317 |
| 20 | 0.0513882 | 0.783125 | 0.203405 | 0.0921734 |
| 23 | 0.0461892 | 0.654362 | 0.116269 | 0.0623435 |
| 26 | 0.0414993 | 0.568407 | 0.0728741 | 0.0456349 |
| 29 | 0.0381685 | 0.505894 | 0.0488129 | 0.0376772 |
| 32 | 0.0350577 | 0.457169 | 0.0337935 | 0.0310743 |
| 35 | 0.032783 | 0.417399 | 0.0243553 | 0.026734 |
| 38 | 0.0305499 | 0.383597 | 0.0178845 | 0.0238394 |
| 41 | 0.0281754 | 0.354938 | 0.0133699 | 0.0240602 |
| 44 | 0.0276068 | 0.330133 | 0.010086 | 0.0182577 |
| 47 | 0.0260556 | 0.310496 | 0.00747244 | 0.023527 |
| 50 | 0.025213 | 0.290988 | 0.00495633 | 0.0210496 |
| 51 | 0.0251768 | 0.287005 | 0.00420339 | 0.0254486 |
| 52 | 0.0252969 | 0.280379 | 0.00344103 | 0.0201953 |
| 53 | 0.0255142 | 0.275296 | 0.00276712 | 0.0200261 |
| 54 | 0.0258332 | 0.271225 | 0.00217648 | 0.023181 |
| 55 | 0.0268594 | 0.265314 | 0.00167874 | 0.0138113 |
| 56 | 0.0259721 | 0.260015 | 0.00125498 | 0.0147009 |
| 57 | 0.0258266 | 0.256733 | 0.000941912 | 0.0166888 |
| 58 | 0.0263898 | 0.252126 | 0.000696406 | 0.0135946 |
| 59 | 0.0255876 | 0.247925 | 0.000513543 | 0.0142742 |
| 60 | 0.0260131 | 0.243281 | 0.000376531 | 0.00999408 |
| 61 | 0.0275882 | 0.23968 | 0.000279303 | 0.0108217 |
| 62 | 0.0283449 | 0.235847 | 0.000205959 | 0.00862397 |
| 63 | 0.0225348 | 0.232689 | 0.000146052 | 0.0235729 |
| 64 | 0.0229242 | 0.228224 | 0.000108188 | 0.0145579 |

**Table S6.** Best fit parameters of the generalized Debye model at temperature ranging from 2 to 45 K under a 0 Oe DC field for **3**.

| T / K | $\chi_S$ / $cm^3mol^{-1}K$ | $\chi_T$ / $cm^3mol^{-1}K$ | τ / s | α |
|---|---|---|---|---|
| 2 | 0.27645 | 6.05126 | 0.002760 | 0.14098 |
| 3 | 0.18636 | 4.03826 | 0.002820 | 0.14501 |
| 5 | 0.11639 | 2.45356 | 0.002770 | 0.15025 |
| 8 | 0.07507 | 1.54392 | 0.002640 | 0.15333 |
| 11 | 0.05543 | 1.12978 | 0.002490 | 0.15239 |
| 14 | 0.04654 | 0.8897 | 0.002250 | 0.13819 |
| 17 | 0.04174 | 0.73228 | 0.001920 | 0.11373 |
| 20 | 0.03612 | 0.62249 | 0.001540 | 0.09004 |
| 23 | 0.03232 | 0.54033 | 0.001200 | 0.06698 |
| 26 | 0.02751 | 0.47783 | 0.000917 | 0.05252 |
| 29 | 0.02288 | 0.42891 | 0.000702 | 0.04272 |
| 32 | 0.01856 | 0.3888 | 0.000542 | 0.03643 |
| 33 | 0.019 | 0.37699 | 0.000500 | 0.03271 |
| 34 | 0.01888 | 0.36591 | 0.000462 | 0.02993 |
| 35 | 0.01779 | 0.35591 | 0.000427 | 0.02951 |
| 36 | 0.0165 | 0.34615 | 0.000395 | 0.02823 |
| 37 | 0.01555 | 0.33689 | 0.000366 | 0.02657 |
| 38 | 0.01542 | 0.32838 | 0.000340 | 0.02626 |
| 39 | 0.0153 | 0.3197 | 0.000316 | 0.02367 |
| 40 | 0.01371 | 0.31219 | 0.000294 | 0.02554 |
| 41 | 0.01207 | 0.30515 | 0.000273 | 0.0275 |
| 42 | 0.01344 | 0.29718 | 0.000255 | 0.02199 |
| 43 | 0.01522 | 0.29054 | 0.000239 | 0.02092 |
| 44 | 0.01236 | 0.28399 | 0.000222 | 0.02019 |
| 45 | 0.01348 | 0.27788 | 0.000207 | 0.02031 |

**Table S7.** Best fit parameters of the generalized Debye model at temperature ranging from 2 to 65 K under a 0 Oe DC field for **4**.

| T / K | $\chi_S$ / $cm^3mol^{-1}K$ | $\chi_T$ / $cm^3mol^{-1}K$ | τ / s | α |
|---|---|---|---|---|
| 2 | 0.21447 | 6.9676 | 0.020540 | 0.19331 |
| 3 | 0.15271 | 4.64842 | 0.020910 | 0.19667 |
| 5 | 0.09829 | 2.82291 | 0.020370 | 0.19889 |
| 8 | 0.06771 | 1.77403 | 0.018180 | 0.19722 |
| 11 | 0.05681 | 1.29042 | 0.015440 | 0.18204 |
| 14 | 0.05101 | 1.00874 | 0.012400 | 0.15301 |
| 17 | 0.04483 | 0.82494 | 0.009520 | 0.1208 |
| 20 | 0.03947 | 0.69822 | 0.007200 | 0.09419 |
| 23 | 0.03625 | 0.6031 | 0.005400 | 0.06812 |
| 26 | 0.03088 | 0.53339 | 0.004080 | 0.05556 |
| 29 | 0.02829 | 0.47796 | 0.003120 | 0.04293 |
| 32 | 0.02628 | 0.43197 | 0.002420 | 0.03275 |
| 35 | 0.02255 | 0.39611 | 0.001900 | 0.03138 |
| 38 | 0.02126 | 0.36525 | 0.001520 | 0.02598 |
| 41 | 0.02001 | 0.33831 | 0.001230 | 0.02129 |
| 44 | 0.01825 | 0.31582 | 0.001000 | 0.02064 |
| 47 | 0.01848 | 0.29621 | 0.000830 | 0.01797 |
| 50 | 0.01656 | 0.27779 | 0.000677 | 0.01752 |
| 51 | 0.01653 | 0.2727 | 0.000635 | 0.01763 |
| 52 | 0.0164 | 0.26744 | 0.000592 | 0.01701 |
| 53 | 0.01713 | 0.26313 | 0.000556 | 0.01796 |
| 54 | 0.01551 | 0.25765 | 0.000513 | 0.01729 |
| 55 | 0.0151 | 0.25296 | 0.000475 | 0.01685 |
| 56 | 0.01798 | 0.24872 | 0.000444 | 0.01366 |
| 57 | 0.01561 | 0.24443 | 0.000404 | 0.01832 |
| 58 | 0.01532 | 0.24051 | 0.000368 | 0.01982 |
| 59 | 0.01859 | 0.23649 | 0.000339 | 0.01661 |
| 60 | 0.01817 | 0.23247 | 0.000304 | 0.01722 |
| 61 | 0.01782 | 0.22871 | 0.000272 | 0.01564 |
| 62 | 0.01802 | 0.22514 | 0.000239 | 0.01834 |
| 63 | 0.01779 | 0.22127 | 0.000209 | 0.01467 |
| 64 | 0.01812 | 0.21886 | 0.000181 | 0.02334 |
| 65 | 0.01951 | 0.21534 | 0.000155 | 0.02441 |

**Table S8.** Best fit parameters of the generalized Debye model at temperature ranging from 2 to 55 K under a 0 Oe DC field for **5**.

| T / K | $\chi_S$ / $cm^3mol^{-1}K$ | $\chi_T$ / $cm^3mol^{-1}K$ | τ / s | α |
|---|---|---|---|---|
| 2 | 0.03678 | 7.61596 | 0.168200 | 0.22986 |
| 3 | 0.0262 | 5.00147 | 0.163780 | 0.23383 |
| 5 | 0.01826 | 2.99042 | 0.158570 | 0.2347 |
| 8 | 0.0147 | 1.85555 | 0.140680 | 0.22628 |
| 11 | 0.01419 | 1.32824 | 0.110970 | 0.19559 |
| 14 | 0.01402 | 1.00677 | 0.076560 | 0.14669 |
| 17 | 0.01323 | 0.80335 | 0.051780 | 0.10215 |
| 20 | 0.01226 | 0.66811 | 0.035770 | 0.07025 |
| 23 | 0.01072 | 0.57593 | 0.025280 | 0.04967 |
| 26 | 0.00926 | 0.50836 | 0.018170 | 0.04013 |
| 29 | 0.00886 | 0.45478 | 0.013170 | 0.02655 |
| 32 | 0.00821 | 0.41132 | 0.009730 | 0.02068 |
| 35 | 0.00686 | 0.3757 | 0.007220 | 0.01627 |
| 38 | 0.00757 | 0.34579 | 0.005430 | 0.00919 |
| 41 | 0.00666 | 0.32039 | 0.004000 | 0.00843 |
| 44 | 0.00643 | 0.29928 | 0.002720 | 0.00811 |
| 45 | 0.0063 | 0.29289 | 0.002320 | 0.00768 |
| 46 | 0.00516 | 0.28714 | 0.001920 | 0.01014 |
| 47 | 0.00602 | 0.28137 | 0.001550 | 0.01017 |
| 48 | 0.00595 | 0.27514 | 0.001220 | 0.01243 |
| 49 | 0.00521 | 0.26954 | 0.000931 | 0.01545 |
| 50 | 0.00296 | 0.26464 | 0.000694 | 0.02247 |
| 51 | 0.00371 | 0.25979 | 0.000515 | 0.02302 |
| 52 | 0.00246 | 0.2546 | 0.000374 | 0.02564 |
| 53 | 0.00162 | 0.24988 | 0.000271 | 0.02645 |
| 54 | 0.00359 | 0.24565 | 0.000198 | 0.02929 |
| 55 | 0.00555 | 0.24129 | 0.000144 | 0.02912 |

**Table S9.** Best fit parameters of the generalized Debye model at temperature ranging from 17 to 65 K under a 0 Oe DC field for **6**.

| T / K | $\chi_S$ / $cm^3mol^{-1}K$ | $\chi_T$ / $cm^3mol^{-1}K$ | τ / s | α |
|---|---|---|---|---|
| 17 | 0.01416 | 1.37147 | 1.340440 | 0.11442 |
| 20 | 0.01323 | 0.82233 | 0.464970 | 0.07125 |
| 23 | 0.01226 | 0.69349 | 0.261810 | 0.05616 |
| 26 | 0.01182 | 0.59005 | 0.154530 | 0.04323 |
| 29 | 0.01117 | 0.52463 | 0.098120 | 0.03449 |
| 32 | 0.01076 | 0.47171 | 0.065260 | 0.03135 |
| 35 | 0.01058 | 0.428 | 0.044520 | 0.0227 |
| 38 | 0.01051 | 0.39213 | 0.031590 | 0.01778 |
| 41 | 0.00987 | 0.36375 | 0.022880 | 0.02032 |
| 44 | 0.00983 | 0.34093 | 0.016660 | 0.0211 |
| 47 | 0.00988 | 0.31757 | 0.011540 | 0.01773 |
| 50 | 0.0105 | 0.29833 | 0.007160 | 0.01633 |
| 51 | 0.01058 | 0.29159 | 0.005830 | 0.01489 |
| 52 | 0.01094 | 0.28702 | 0.004670 | 0.01735 |
| 53 | 0.01156 | 0.28074 | 0.003620 | 0.0111 |
| 54 | 0.01103 | 0.27597 | 0.002760 | 0.01414 |
| 55 | 0.01227 | 0.27063 | 0.002080 | 0.01011 |
| 56 | 0.01241 | 0.26624 | 0.001540 | 0.00888 |
| 57 | 0.0124 | 0.26116 | 0.001130 | 0.00743 |
| 58 | 0.01239 | 0.25695 | 0.000825 | 0.00589 |
| 59 | 0.01278 | 0.25333 | 0.000605 | 0.0071 |
| 60 | 0.01311 | 0.2486 | 0.000441 | 0.00389 |
| 61 | 0.01257 | 0.24468 | 0.000323 | 0.00354 |
| 62 | 0.01326 | 0.24044 | 0.000237 | 0.00113 |
| 63 | 0.01388 | 0.23718 | 0.000174 | 0.0074 |
| 64 | 0.01564 | 0.23328 | 0.000131 | $4.31 \times 10^{-14}$ |
| 65 | 0.01598 | 0.22984 | 0.000096 | $6.61 \times 10^{-14}$ |

**Theoretical analysis**

**Table S10.** Decomposition of the wavefunctions of lowest-lying KDs in terms of the components of the ground $^6H_{15/2}$ multiplet of $Dy^{III}$, the key diagonal crystal field parameter (CFP) B(2,0) and non-diagonal CFP B(2,2).

| | $KD_0$ | $KD_1$ | $KD_2$ | B(2,0) | B(2,2) | ESP ratio |
|---|---|---|---|---|---|---|
| **1** | \|±15/2>, 99.90% | \|±13/2>, 98.54% | \|±11/2>, 78.32% | -4.340 | 1.187 | 1.180 |
| **2** | \|±15/2>, 99.94% | \|±13/2>, 99.34% | \|±11/2>, 93.93% | -4.962 | 0.533 | 1.261 |
| **3** | \|±15/2>, 99.54% | \|±13/2>, 97.98% | \|±11/2>, 86.27% | -5.308 | 0.960 | 1.153 |
| **4** | \|±15/2>, 99.62% | \|±13/2>, 98.49% | \|±11/2>, 92.81% | -5.654 | 0.352 | 1.205 |
| **5** | \|±15/2>, 99.91% | \|±13/2>, 98.91% | \|±11/2>, 80.07% | -4.361 | 1.391 | 1.196 |
| **6** | \|±15/2>, 99.94% | \|±13/2>, 99.46% | \|±11/2>, 94.15% | -4.819 | 0.803 | 1.262 |

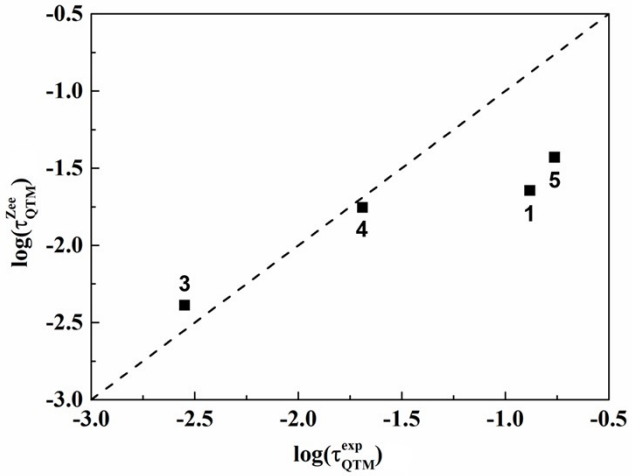



**Figure S16** Direct comparison between experimental and theoretical $\tau_{QTM}$ of **1** and **3 – 5**.

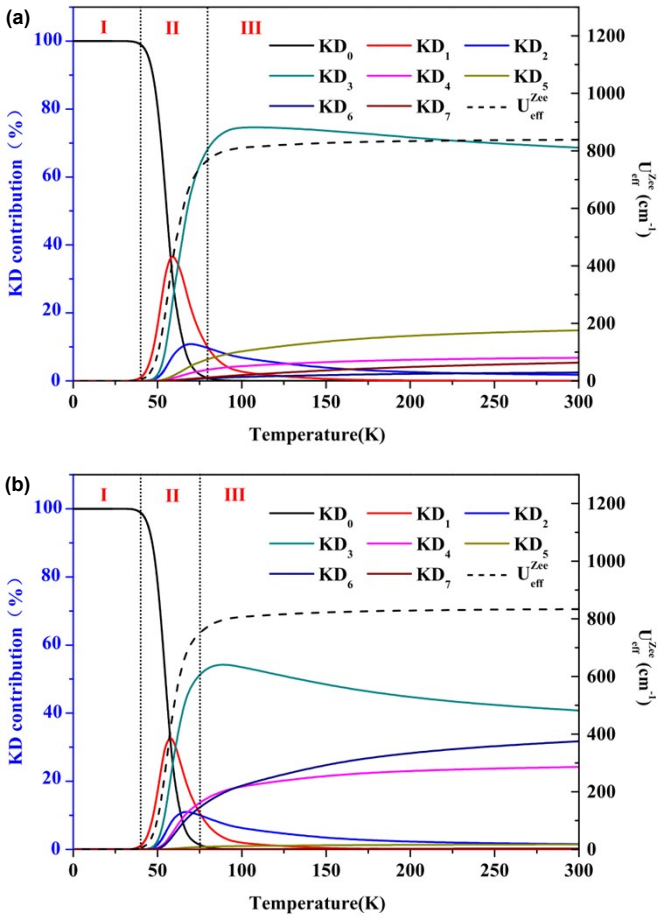



**Figure S17** Quantitative results of $U_{eff}^{Zee}$ within the framework of TA-QTM of **2** (a) and **6** (b).

**The $^{1}$H NMR and $^{13}$C spectra of n-OMe-$H_2$bbpen**

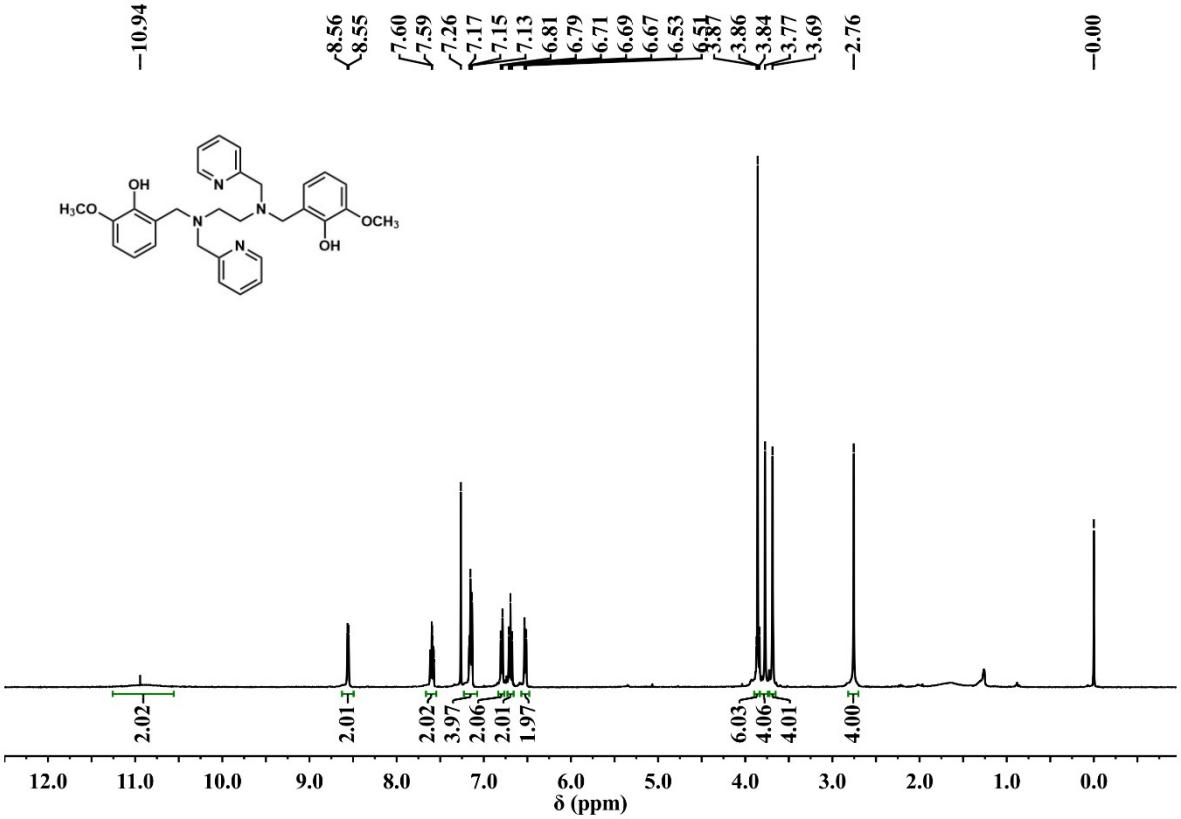



**Figure S18** $^{1}$H NMR spectra of **3-OMe-$H_2$bbpen** in $CDCl_3$ at room temperature.

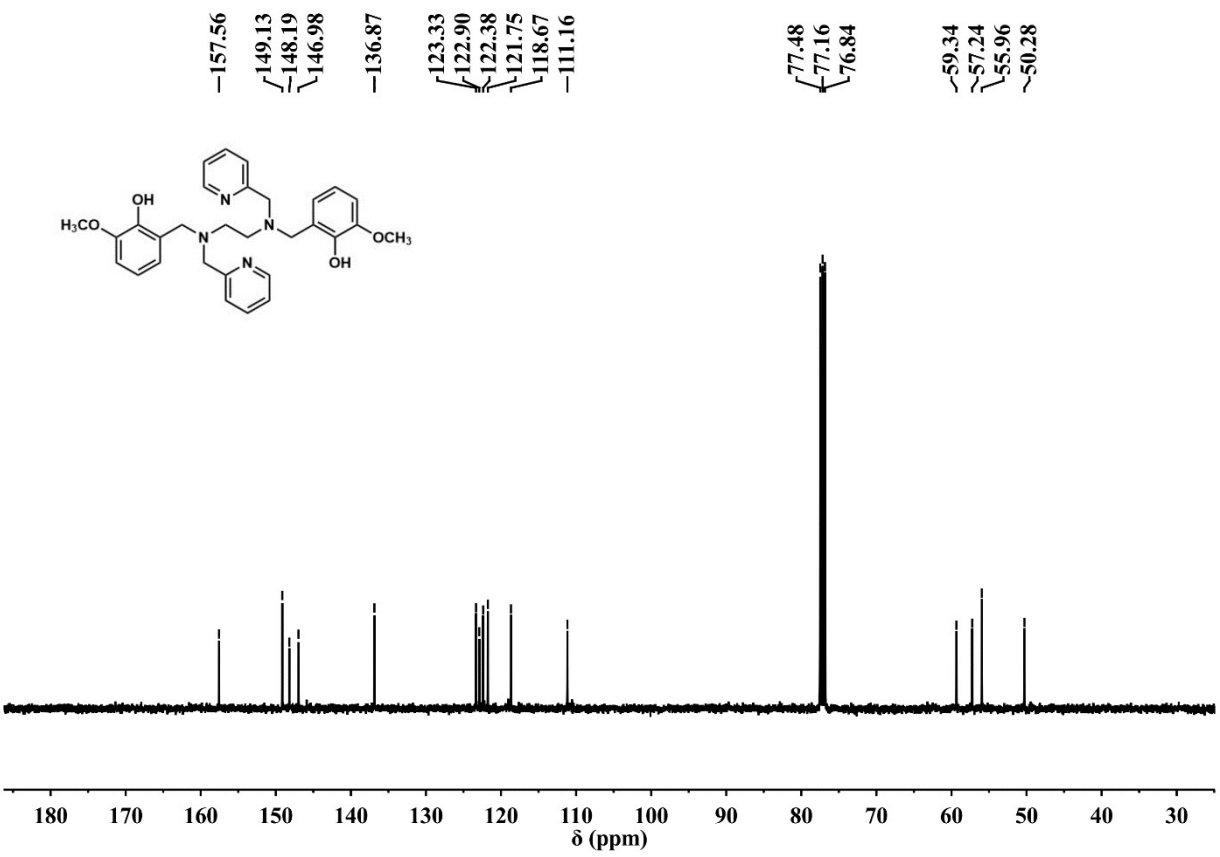



**Figure S19** $^{13}C$ NMR spectra of **3-OMe-$H_2$bbpen** in $CDCl_3$ at room temperature.

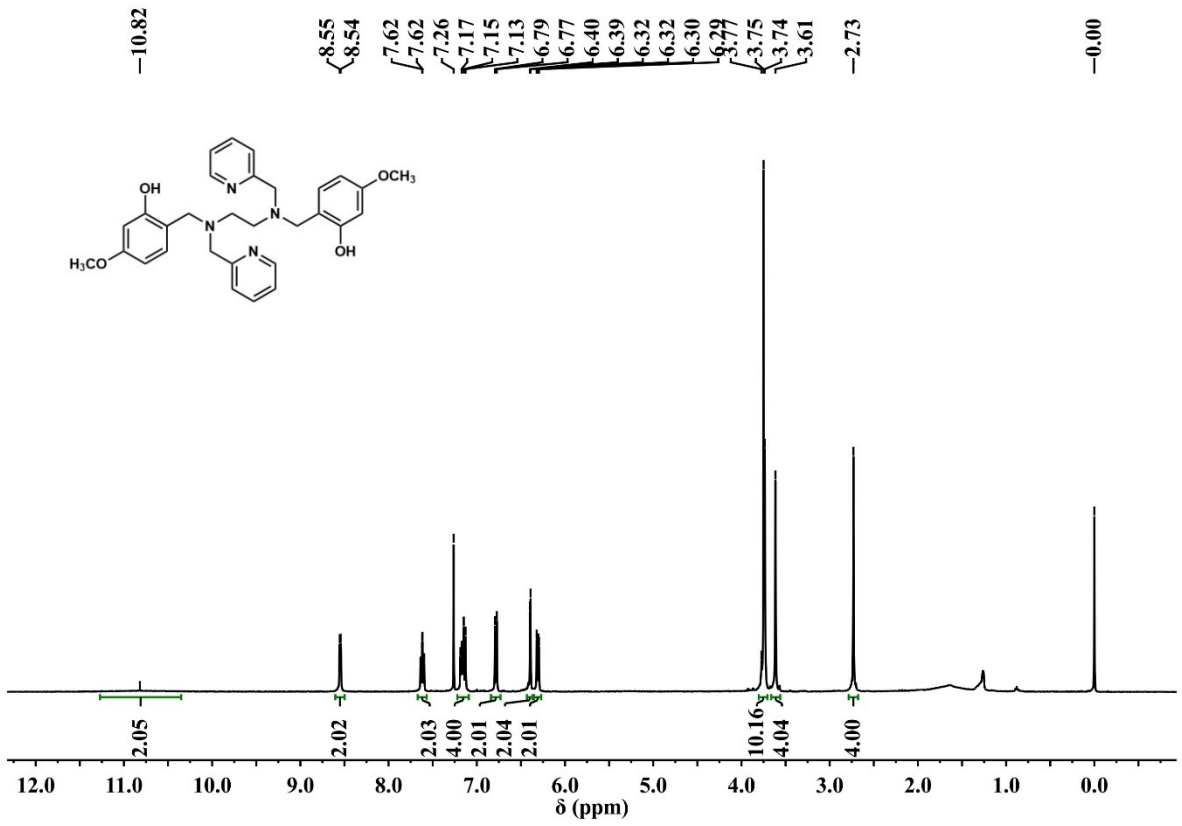



**Figure S20** $^{1}$H NMR spectra of **4-OMe-$H_2$bbpen** in $CDCl_3$ at room temperature.

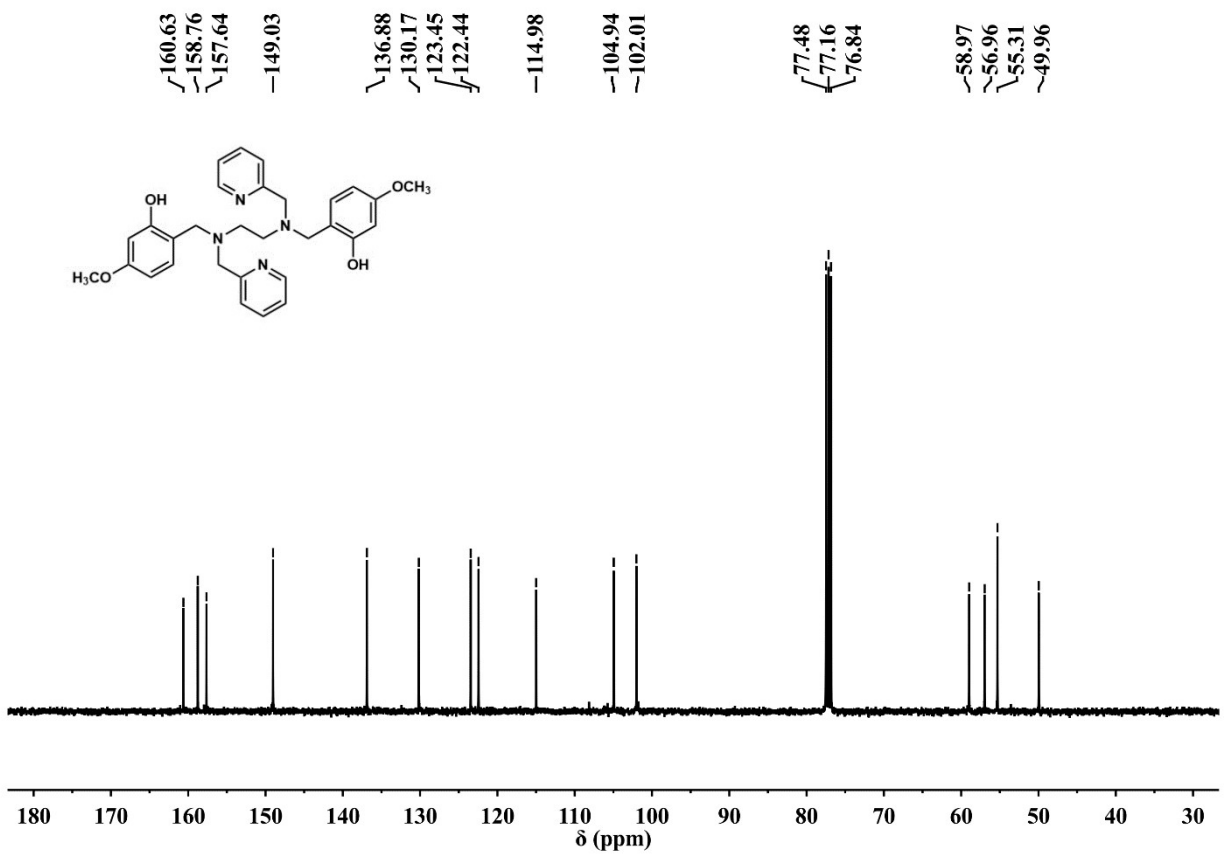



**Figure S21** $^{13}C$ NMR spectra of **4-OMe-$H_2$bbpen** in $CDCl_3$ at room temperature.

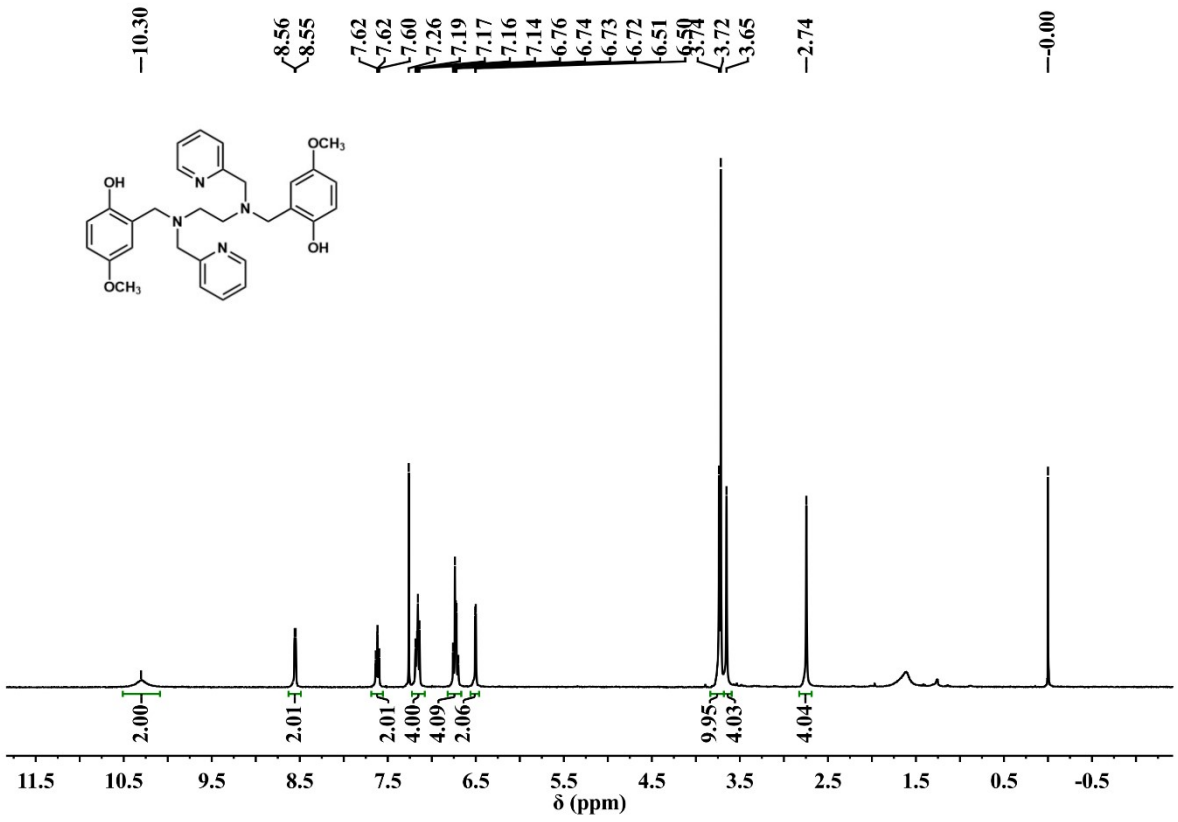



**Figure S22** $^{1}$H NMR spectra of **5-OMe-$H_2$bbpen** in $CDCl_3$ at room temperature.

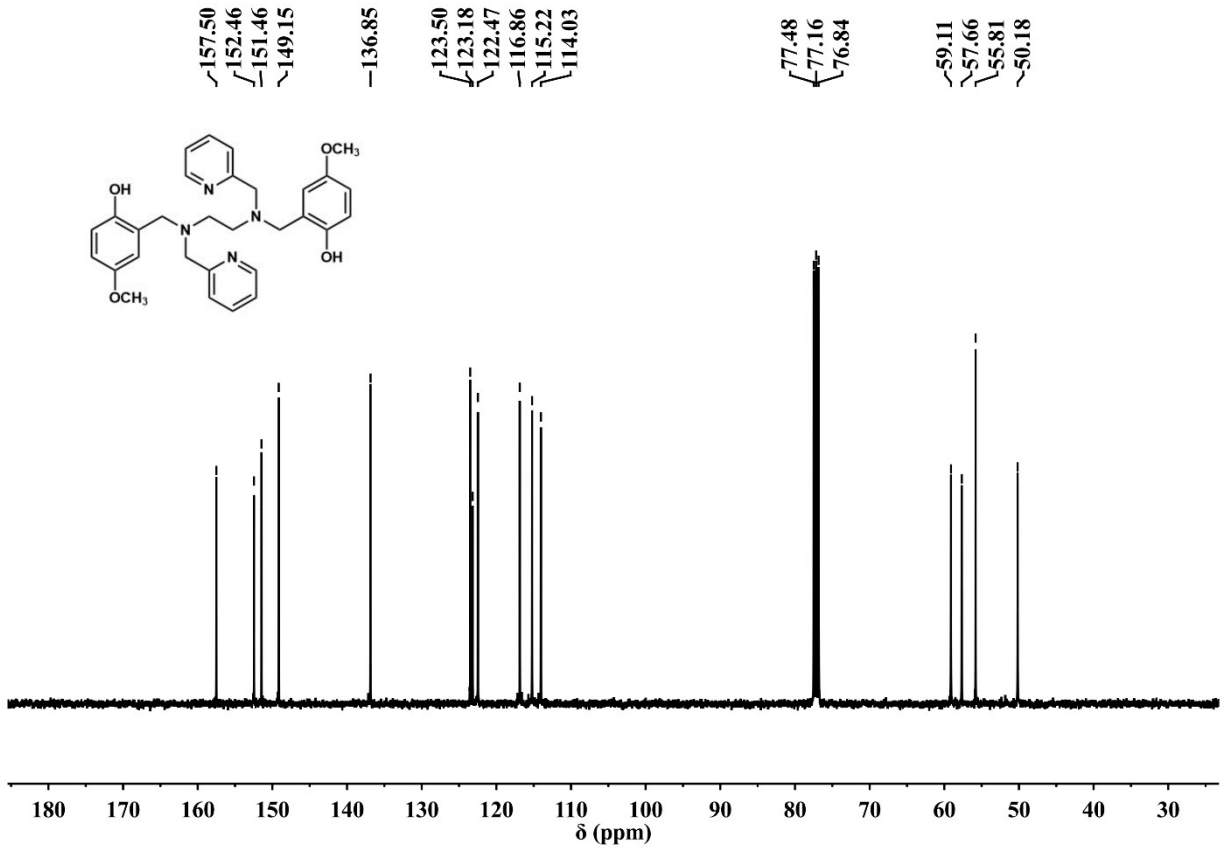



**Figure S23** $^{13}C$ NMR spectra of **5-OMe-$H_2$bbpen** in $CDCl_3$ at room temperature.