Supporting Information

Linear Trinuclear Cobalt(II) Single-Molecule Magnets

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Fig. S1 NMR spectra of HPymp in CDCl₃.
Fig. S2 Experimental and simulated powder x-ray diffraction patterns of 1.

The powder X-ray diffraction (PXRD) data of ground fine powder was collected on a Rigaku Multiplex powder X-ray diffractometer with Cu Kα radiation (40 kV, 40 mA) between 5.0 and 35° (2θ) at ambient temperature.(Fig. S1) The PXRD data at room temperature on the sample 1 well matched with the calculated one from single crystal data.
**Fig. S3.** Ball-and-stick view of X-ray structure of 2. All anions and hydrogen atoms are eliminated for clarity.

**Fig. S4** Packing view of 1 showing a 3D structure, where the linear [CoI₃]²⁺ cations are well isolated by the large counter anions of [BPh₄]⁻.
**Fig. S5.** $M$ vs. $H$ plot at 1.8 K for 2. Inset: Reduced magnetization data in applied fields (30, 50 and 70 kOe) at temperatures between 1.8 and 3.0 K; the solid lines represent the best fitting via ANISOFIT\textsuperscript{2.0} with $D = -2.3$ cm\textsuperscript{-1}, $E = 0.016$ cm\textsuperscript{-1}, and $g = 2.05$ for a $S_T = 9/2$ spin model.

**Fig. S6.** Magnetic hysteresis loop at 1.9 K for 1. Solid line is guide for eyes.
Fig. S7 In-phase ($\chi_m'$) and out-of-phase ($\chi_m''$) ac susceptibilities under zero applied $dc$ field and an $ac$ field of 3 Oe at different frequencies for 1.

Fig. S8 Variable-frequency out-of-phase ($\chi_m''$) components of the ac magnetic susceptibility data for 1, collected at temperatures of 1.80 K with an ac filed of 3 Oe and 0-1500 Oe dc applied fields.
**Fig. S9.** (left) Cole-Cole diagrams of 1 at 1.80 K with applied dc fields of 0-1500 Oe and ac field of 3 Oe. The solid lines are least-square fittings of the data to a distribution of single relaxation processes with a generalized Debye model. (right) the plot of the pre-exponential time (τ) vs. applied dc fields.


**Table S1.** Fittings of Cole-Cole plots of the variable-frequency ac data, collected at 1.8 K under different dc fields (0-1500 Oe), based on a generalized Debye model.

<table>
<thead>
<tr>
<th>$H$ / Oe</th>
<th>$\chi_s$ (cm$^3$ mol$^{-1}$)</th>
<th>$\chi_t$ (cm$^3$ mol$^{-1}$)</th>
<th>$\tau$ (S)</th>
<th>$\alpha$</th>
<th>R</th>
</tr>
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<tbody>
<tr>
<td>300</td>
<td>1.72426</td>
<td>8.34446</td>
<td>0.00118</td>
<td>0.14442</td>
<td>$4.32 \times 10^{-4}$</td>
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<tr>
<td>600</td>
<td>0.49137</td>
<td>8.20729</td>
<td>0.00251</td>
<td>0.17532</td>
<td>$2.72 \times 10^{-4}$</td>
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<tr>
<td>900</td>
<td>0.34342</td>
<td>7.63448</td>
<td>0.00271</td>
<td>0.17051</td>
<td>$1.65 \times 10^{-4}$</td>
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<tr>
<td>1200</td>
<td>0.30042</td>
<td>6.86897</td>
<td>0.00187</td>
<td>0.17673</td>
<td>$3.86 \times 10^{-4}$</td>
</tr>
<tr>
<td>1500</td>
<td>0.30021</td>
<td>6.08291</td>
<td>0.00130</td>
<td>0.19045</td>
<td>$1.12 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Fig. S10 Cole-Cole diagrams of 1 at 1.80 to 2.60 K with an applied dc field of 500 Oe and ac field of 3 Oe. The solid lines are least-square fittings of the data to a distribution of single relaxation processes with a generalized Debye model.

<table>
<thead>
<tr>
<th>T / K</th>
<th>$\chi_s$ (cm$^3$ mol$^{-1}$)</th>
<th>$\chi_i$ (cm$^3$ mol$^{-1}$)</th>
<th>$\tau$ (S)</th>
<th>$\alpha$</th>
<th>R</th>
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<tbody>
<tr>
<td>1.80</td>
<td>0.60296</td>
<td>8.38488</td>
<td>0.00218</td>
<td>0.18453</td>
<td>3.43 x 10^{-4}</td>
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<td>1.95</td>
<td>0.60761</td>
<td>7.70748</td>
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<td>0.14832</td>
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<td>2.10</td>
<td>0.59273</td>
<td>7.13226</td>
<td>0.00067</td>
<td>0.11995</td>
<td>1.19 x 10^{-4}</td>
</tr>
<tr>
<td>2.20</td>
<td>0.57666</td>
<td>6.89795</td>
<td>0.00049</td>
<td>0.11111</td>
<td>8.62 x 10^{-5}</td>
</tr>
<tr>
<td>2.30</td>
<td>0.56791</td>
<td>6.58369</td>
<td>0.00030</td>
<td>0.10246</td>
<td>4.79 x 10^{-5}</td>
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<td>2.40</td>
<td>0.60278</td>
<td>6.31127</td>
<td>0.00019</td>
<td>0.09268</td>
<td>3.21 x 10^{-5}</td>
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<td>2.50</td>
<td>0.63322</td>
<td>6.06312</td>
<td>0.00013</td>
<td>0.08485</td>
<td>1.93 x 10^{-5}</td>
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<td>2.60</td>
<td>0.69169</td>
<td>5.83851</td>
<td>0.00009</td>
<td>0.07783</td>
<td>1.56 x 10^{-5}</td>
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</table>
Fig. S11 In-phase ($\chi'_m$) and out-of-phase ($\chi''_m$) ac susceptibilities in zero (left) and 1 kOe (right) applied dc field and an ac field of 3 Oe at different frequencies for 2.

Fig. S12 Estimations of the $U_{\text{eff}}$ and $\tau_0$ for both 1 and 2 by fitting the experimental data at 4111 Hz based on a relative expression: $\ln(\chi''/\chi') = \ln(\omega\tau_0) + \Delta E/K_B T$ gave: (left) for 1, $U_{\text{eff}}$ (zero) = 11.7(2) K and $\tau_0$(zero) = $1.7 \times 10^{-7}$ S; (Right) for 2, $U_{\text{eff}}$ (1kOe) = 11.4(1) K and $\tau_0$(1kOe) = $8.5 \times 10^{-8}$ S.