Supplementary Information

Exchange-biased Quantum Tunneling of Magnetization in a [Mn₃]₂ Dimer of Single-Molecule Magnets with Rare Ferromagnetic Inter-Mn₃ Coupling

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Experimental Section:

Synthesis of 1,3-ppmdH₂: Freshly synthesized 1,3-phenylenebis(pyridine-2-ylmethanone) (1.0 g, 3.5 mmol) was dissolved in methanol (20 ml), the solution was treated with a solution of NH₂OH·HCl (1.3 g, 18.7 mmol) in water (5 ml) and with pyridine (1.7 ml, 21.1 mmol), refluxed for 2 hours and then concentrated. The product, precipitated with water, was recrystallized from methanol. Yield was 85%. ¹H NMR (500 MHz, DMSO-d₆) δ (ppm): 11.72 (s, 2H), 8.82 (dt, *J* = 7.24 Hz, 3.22 Hz, 1H), 8.78 (dd, *J* = 8.24 Hz, 2.35 Hz, 2H), 8.31 (dd, *J* = 6.93 Hz, 4.19 Hz, 2H), 8.12 (dd, *J* = 5.87 Hz, 3.52 Hz, 2H), 7.87 (ddd, *J* = 12.89 Hz, 8.56 Hz, 6.22 Hz, 2H), 7.53 (t, *J* = 7.69 Hz, 1H), 7.46 (ddd, *J* = 11.48 Hz, 7.34 Hz, 3.45 Hz, 2H). ¹³C (125 MHz, DMSO-d₆) δ (ppm): 155.07, 155.01, 148.77, 136.75, 131.94, 130.45, 129.65, 126.95, 123.63 and 121.86. HRMS (ESI): [M+H]⁺, found 319.1194, C₁₈H₁₅N₄O₂ requires 319.1190. Elemental analysis: found C, 67.84; H, 4.51; N, 17.54; C₁₈H₁₄N₄O₂ requires C, 67.91; H, 4.43; N, 17.60. Selected IR data (cm⁻¹): 3151 (br), 1588 (s), 1565 (m), 1472 (s), 1431 (s), 1312 (m), 1286 (m), 1152 (s), 1095 (m), 1000 (s), 946 (s), 791 (s), 749 (s), 705 (s), 625 (m).

	Mn ^{II}	Mn ^{III}	Mn ^{IV}	Assignment		BVS	Assignment
Mn1	3.27	3.06	3.10	Mn ^{III}	01	1.98	O ²⁻

Table S1. BVS calculations for the Mn^a and selected O^b atoms of complex 3

^a The bold value is the one closest to the charge for which it was calculated. The oxidation state of a particular atom is the nearest to the value in bold. ^b The O atom is not protonated if the BVS is ~ 1.8 - 2.2, mono-protonated if the BVS is ~ 1.0 - 1.2, and doubly-protonated if the BVS is ~ 0.2 - 0.4.



Figure S1. (top) ¹H NMR (500 MHz, DMSO-d₆) spectrum of 1,3-ppmdH₂. **(bottom)** ¹³C NMR (125 MHz, DMSO-d₆) spectrum of 1,3-ppmdH₂.



Figure S2. (top) Complete cation of **3** also including the three pyridine solvent molecules π -stacking between 1,3-ppmd²⁻ pyridyl rings on neighboring Mn₃ molecules, viewed (left) along the C_3 axis, and (right) from a side viewpoint that emphasizes one π -stacked column of three aromatic rings. (bottom) Packing diagram of **3** viewed (left) along the *a* axis, and (right) along the *b* axis, showing that all Mn₃ planes and all molecular C_3 axes are aligned parallel.

VAN VLECK EQUATIONS USED FOR FITTING XMT vs. T DATA

Fitting Procedure: $\chi_{[Mn3]2} = 2\chi_{Mn3} + TIP$

(A) Equilateral triangle (e.g. Mn⁽¹⁾-Mn⁽²⁾-Mn⁽³⁾):

The data for $3.6H_2O$ and $3.3pyH_2O$ were fit to the theoretical expression for two independent equilateral triangles, assuming that the interaction between Mn₃ triangles is very weak compared to the interaction between Mn ions within each triangle.

$$\hat{S}_{\rm T} = \hat{S}_1 + \hat{S}_2 + \hat{S}_3$$

 $\hat{H} = -2J[\hat{s}_1 \cdot \hat{s}_2 + \hat{s}_1 \cdot \hat{s}_3 + \hat{s}_2 \cdot \hat{s}_3]$

 $\mathbf{E}(S_{\mathrm{T}}) = -J[S_{\mathrm{T}}(S_{\mathrm{T}}+1)]$

VAN VLECK EQUATION



 $\chi_{Mn3} = (Ng^2\mu_B^2/3kT)[+150.0000 \times \exp(6.0000 \times m) + 18.0000 \times \exp(2.0000 \times m) + 336.0000 \times \exp(12.0000 \times m) + 0.0000 \times \exp(0.0000 \times m) + 540.0000 \times \exp(20.0000 \times m) + 660.0000 \times \exp(30.0000 \times m) + 546.0000 \times \exp(30.0000 \times m)] /$

$$[+25.0000 \times \exp(6.0000 \times m) + 9.0000 \times \exp(2.0000 \times m) + 28.0000 \times \exp(12.0000 \times m) + 1.0000 \times \exp(0.0000 \times m) + 27.0000 \times \exp(20.0000 \times m) + 22.0000 \times \exp(30.0000 \times m) + 13.0000 \times \exp(42.0000 \times m)]$$

Where m = J/kT

 $TIP = 600 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$

Constraints g > 1.85 and g < 2.2

(B) Isosceles triangle

The data were also fit to the theoretical expression for two independent isosceles triangles, assuming that the interaction between Mn₃ triangles is very weak compared to the interaction between Mn ions in each triangle.

$$\begin{split} \hat{S}_{A} &= \hat{s}_{2} + \hat{s}_{3} \\ \hat{S}_{T} &= \hat{S}_{A} + \hat{s}_{1} \\ \hat{H} &= -2J[\hat{s}_{1}\cdot\hat{s}_{2} + \hat{s}_{1}\cdot\hat{s}_{3}] - 2J' [\hat{s}_{2}\cdot\hat{s}_{3}] \\ \hat{H} &= -J(\hat{S}_{T}^{2} - \hat{S}_{A}^{2} - \hat{s}_{1}^{2}) - J'(\hat{S}_{A}^{2} - \hat{s}_{2}^{2} - \hat{s}_{3}^{2}) \\ E(S_{T}) &= -J[S_{T}(S_{T} + 1) - S_{A}(S_{A} + 1)] - J'[S_{A}(S_{A} + 1)] \end{split}$$



VAN VLECK EQUATION

 $\chi_{Mn3} = (Ng^2\mu_B^2/3kT)[+30.0000 \times \exp(6.0000 \times m + 0.0000 \times n) + 6.0000 \times \exp(0.0000 \times m + 2.0000 \times n) + 30.0000 \times \exp(4.0000 \times m + 2.0000 \times n) + 84.0000 \times \exp(10.0000 \times m + 2.0000 \times n) + 0.0000 \times \exp(-6.0000 \times m + 6.0000 \times n) + 6.0000 \times \exp(-4.0000 \times m + 6.0000 \times n) + 30.0000 \times \exp(0.0000 \times m + 6.0000 \times n) + 84.0000 \times \exp(6.0000 \times m + 6.0000 \times n) + 180.0000 \times \exp(14.0000 \times m + 6.0000 \times n) + 6.0000 \times \exp(-10.0000 \times m + 12.0000 \times n) + 30.0000 \times \exp(-6.0000 \times m + 12.0000 \times n) + 84.0000 \times \exp(-10.0000 \times m + 12.0000 \times n) + 180.0000 \times \exp(-6.0000 \times m + 12.0000 \times n) + 330.0000 \times \exp(18.0000 \times m + 12.0000 \times n) + 30.0000 \times \exp(-14.0000 \times m + 20.0000 \times n) + 84.0000 \times \exp(-8.0000 \times m + 20.0000 \times n) + 180.0000 \times \exp(-14.0000 \times m + 20.0000 \times n) + 330.0000 \times \exp(-8.0000 \times m + 20.0000 \times n) + 180.0000 \times \exp(-14.0000 \times m + 20.0000 \times n) + 330.0000 \times \exp(-8.0000 \times m + 20.0000 \times n) + 180.0000 \times \exp(-2.0000 \times m + 20.0000 \times n) + 330.0000 \times \exp(-8.0000 \times m + 20.0000 \times n) + 180.0000 \times \exp(-2.0000 \times m + 20.0000 \times n) + 330.0000 \times \exp(-8.0000 \times m + 20.0000 \times n) + 180.0000 \times \exp(-2.0000 \times m + 20.0000 \times n) + 330.0000 \times \exp(-8.0000 \times m + 20.0000 \times n) + 330.0000 \times \exp(-8.0000 \times m + 20.0000 \times n) + 546.0000 \times \exp(-2.0000 \times m + 20.0000 \times n)]$

$$[+ 5.0000 \times \exp(6.0000 \times m + 0.0000 \times n) + 3.0000 \times \exp(0.0000 \times m + 2.0000 \times n) + 5.0000 \times \exp(4.0000 \times m + 2.0000 \times n) + 7.0000 \times \exp(10.0000 \times m + 2.0000 \times n) + 1.0000 \times \exp(-6.0000 \times m + 6.0000 \times n) + 3.0000 \times \exp(-4.0000 \times m + 6.0000 \times n) + 5.0000 \times \exp(0.0000 \times m + 6.0000 \times n) + 7.0000 \times \exp(-10.0000 \times m + 12.0000 \times n) + 9.0000 \times \exp(-6.0000 \times m + 12.0000 \times n) + 7.0000 \times \exp(-10.0000 \times m + 12.0000 \times n) + 9.0000 \times \exp(-6.0000 \times m + 12.0000 \times n) + 11.0000 \times \exp(18.0000 \times m + 12.0000 \times n) + 5.0000 \times \exp(-14.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(18.0000 \times m + 12.0000 \times n) + 7.0000 \times \exp(-14.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(-14.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(-8.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(10.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times n) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times m + 20.0000 \times m) + 11.0000 \times \exp(22.0000 \times m + 20.0000 \times$$



Figure S3. Two-dimensional contour plot of the r.m.s. error vs. J and J' for the fit of $\chi_M T$ vs. T data for 3.6H₂O. The asterisks are the global minima, where two fits of comparable quality are located.



Figure S4. $\chi_M T$ per [Mn₃]₂ dimer *vs. T* for air-dried **3**·3py·H₂O in a 0.1 T dc field. The solid lines are the fits of the 25-300 K data to an equilateral triangle model (one exchange coupling, *J*) and an isosceles model (two couplings, *J* and *J'*). See the text for the fit parameters.



Figure S5. S_T spin state energies for air-dried $3 \cdot 3py \cdot H_2O$ in a 0.1 T dc field calculated using the J and J/J' fit parameters from the fits of $\chi_M T$ per [Mn₃]₂ dimer vs T data to equilateral and isosceles models, respectively. See the text for the fit parameters.



Figure S6. Inclusion of single-ion ZFS to assess its effect on the fits of dc magnetic susceptibility data. Comparison of fits of $\chi_M T$ per [Mn3]₂ dimer *vs. T* data in the 25-300 K range (blue line) and 5-300 K range (red line) for air-dried **3**·3py·H₂O in a 0.1 T dc field using (**top**) an equilateral model and including a single-ion zfs of d = -1.1 cm⁻¹ for each Mn^{III}, and (**bottom**) an isosceles model including a single-ion zfs of d = -1.1 cm⁻¹. The fit parameters are given in the figure. The employed value of *d* is considerably smaller than the -4 to -5 cm⁻¹ typically found for JT distorted Mn^{III} ions

in similar coordination environments because of the significant tilting ($\theta \approx 46.5^{\circ}$) of the JT axes relative to the molecular C₃ axis. This introduces a geometric reduction factor of $\frac{1}{2}(3\cos^2\theta - 1)$ into the equation that projects the single-ion ZFS onto the molecular spin ground state which, for three ferromagnetically coupled s = 2 spins, is $D_{S=6} = 3d(3\cos^2\theta - 1)/22$. In the absence of a precise knowledge of the single-ion *d* parameter, we simply assumed parallel tensors and inverted this expression to set d = 11D/3 in our analysis of the susceptibility data, using the molecular *D* value obtained from EPR. This ensures that employed *d* value is consistent with molecular ZFS deduced from all the other measurements reported in the main text. It can be seen that the obtained average *J* values are identical, or nearly so, to within the experimental uncertainties.



Figure S7. Two-dimensional contour plot of the r.m.s. error *vs. D* and *g* for the $M/N\mu_B vs. H/T$ fit for **3**·6H₂O. The asterisk is the global minimum corresponding to the fit parameters given in the text.



Figure S8. Plot of the in-phase (χ'_{M} , as $\chi'_{M}T$) ac susceptibility data *vs T* for [Mn₃]₂dpd (4) in a 3.5 G field at the indicated oscillation frequencies.



Figure S9. Structural comparison of complexes **3** and $[Mn_3]_2dpd$ (**4**). (a) Side-view of **3**; (b) structure 1,3-ppmd²⁻; (c) Side-view of **4**; and d) dpd²⁻. Emphasised in red in (b) and (d) are the number of σ -bonds separating the two oximate groups of the linkers. Colour code: Mn(III), green; O, red; N, blue; C, gray. See text for further discussion.



Figure S10. Optically modulated ultra-high field EPR spectrum of a constrained powder of **3** at 650 GHz and 4.2 K recorded in water-cooled resistive magnet at the US National High Magnetic Field Laboratory. Microwaves were generated using a Backward-Wave Oscillator (BWO). Unlike the field-modulated spectra seen in the Fig. 10 of the main text, the transmitted signal is recorded, with dips in transmission corresponding to EPR absorption intensity (*I*). In the high field limit, the simulations become less sensitive to the weak ferromagnetic interaction between the Mn₃ subunits of **3** discussed in the main text. This allows a tight constraint on the *g* values of 1.98(1) used to simulate the data at lower frequencies (Table 4), particularly the g_{xy} (= $g_x = g_y$) values that dictate the position of the sharp dip in transmission just below 25 T.

COMPARISON BETWEEN HYSTERESIS AND HFEPR SPIN HAMILTONIANS

We briefly compare the Hamiltonians of eqs. 6 and 12, showing that the associated parameter sets are fully compatible. Ignoring off-diagonal terms, the 4th order spin Hamiltonian of eq. 12 for the isolated Mn₃ SMMs can be simplified as follows in order to give the eigenvalues, $E(m_S)$, allowing comparisons with eq. 9:

$$E(m_{\rm S}) = D'm_{\rm S}^2 + Bm_{\rm S}^4 + \gamma m_{\rm S} \times \mu_0 H \tag{S1}$$

Where D' is a modified 2^{nd} order axial ZFS parameter that combines the D parameter in Table 4 with the quadratic contribution to the 4^{th} order axial interaction, i.e.,

$$D' = D - 1235B_4^0 \tag{S2}$$

Meanwhile, B parameterizes the purely quartic axial ZFS interaction, i.e.,

$$B = 35B_4^0$$
 (S3)

Finally, the last term in eq. S1 represents the Zeeman interaction, with γ denoting the gyromagnetic ratio in appropriate units ($\approx 28 \text{ GHz/T}$ or 0.934 cm⁻¹/T). For an isolated SMM, the first quantum tunneling resonance ($m_s = +6 \rightarrow -6$) occurs at exactly zero magnetic field. The next resonance occurs between the states $m_s = +6$ and -5. Therefore, finding the field at which these levels cross is equivalent to evaluating the magnetic field spacing between the first two resonances. Doing so yields the following expression that can be compared directly with eq. 9 in the main text:

$$\mu_0 \Delta H = \frac{D' + 61B}{\gamma} = \frac{-0.35 \text{ cm}^{-1}}{\gamma}$$
(S4)

As can be seen, the numerator of eq. S4 simplifies to the value of *D* determined from the hysteresis measurements when substituting the EPR values for *D*' and *B* from eqs. S2 and S3 along with the parameters given in Table 4 of the main text, while the obtained spacing, $\mu_0 \Delta H = 0.37$ T, is in perfect agreement with the hysteresis experiments.