Electronic Supplementary Information for Dalton Transactions

Supporting Information

Title: Formation of Monometallic Single-molecule Magnets with a *S* value of 3/2 in Diluted Frozen Solution

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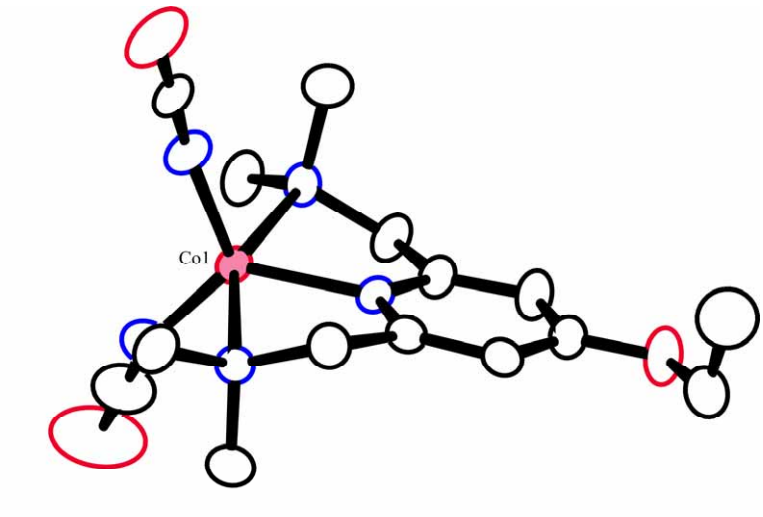

Figure S1. ORTEP drawing of the molecular structure of [**Co(EBAMP)(NCO)$_2$**] (50 % probability)

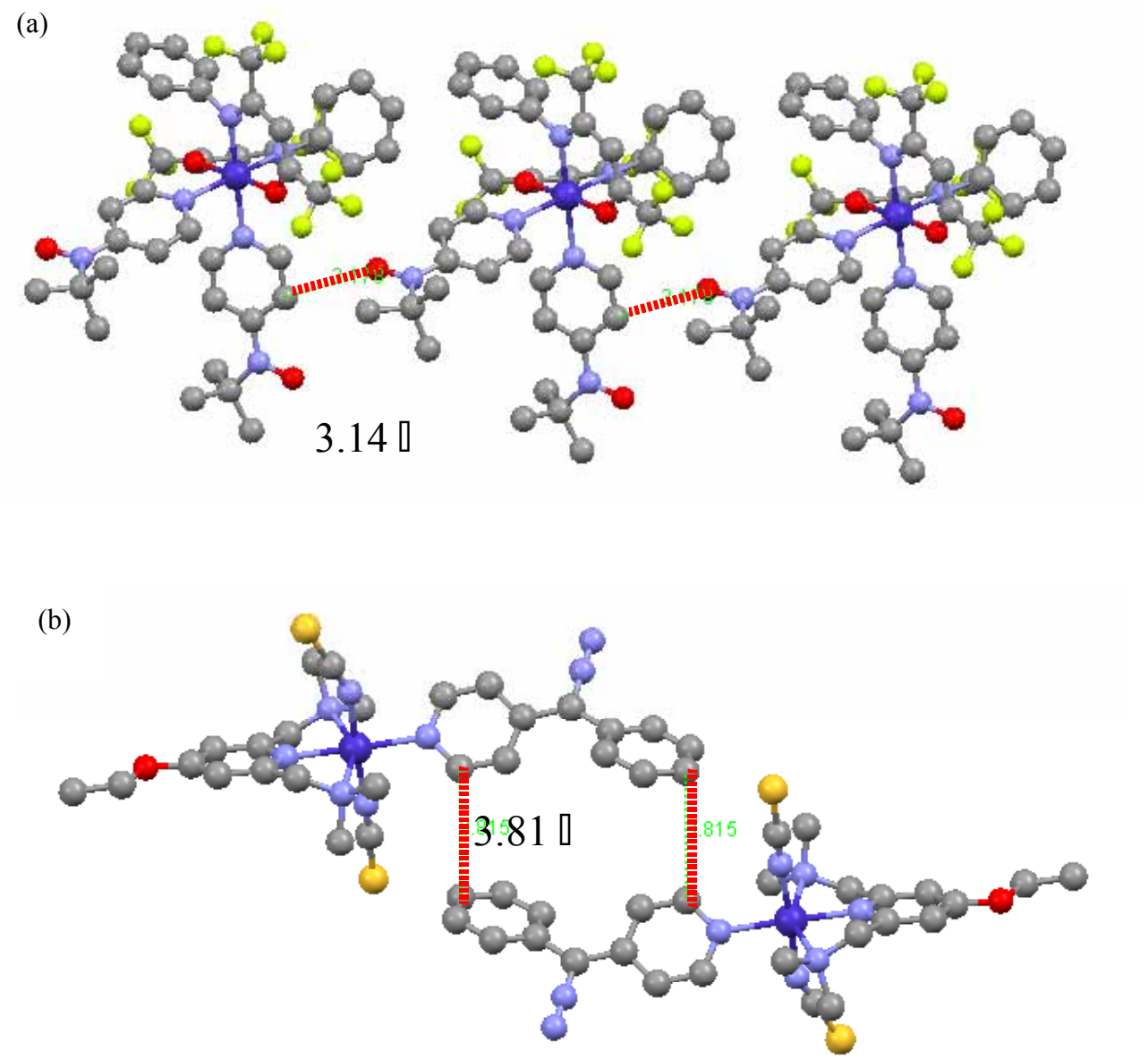

Fig S2 Crystal packing with a ball-stick model (Color Code: C, gray; N, right blue; O, red; S, tan; F, right green; and Co, navy blue) of (a) **1** and (b) **2'**.

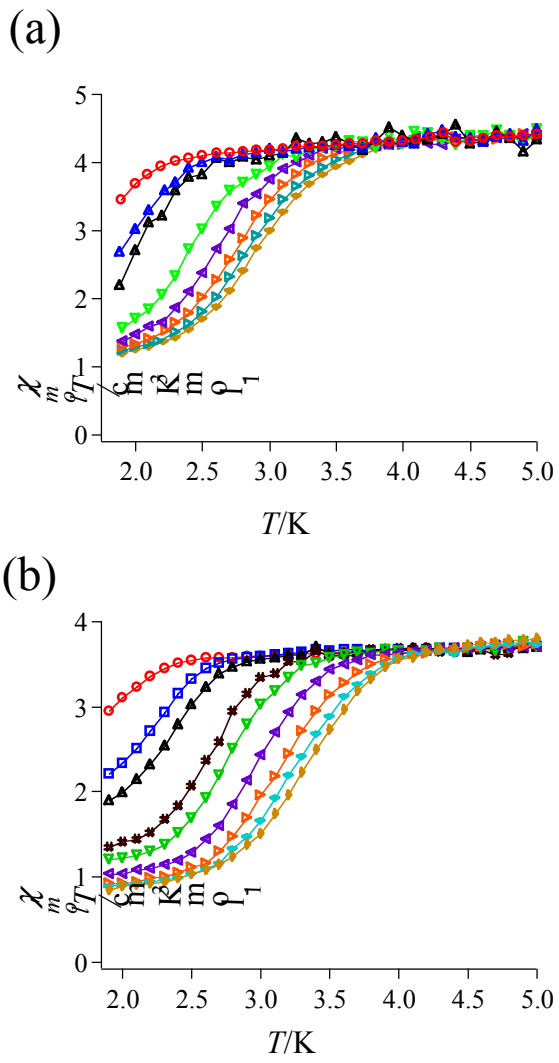

Figure S3. Plots of $\chi'T$ vs. T for (a) **1** and (b) **2c** in MTHF solution with a 3.9 Oe ac field oscillating at 1000 (tan) - 1(red) Hz. The solid lines are visual guides.

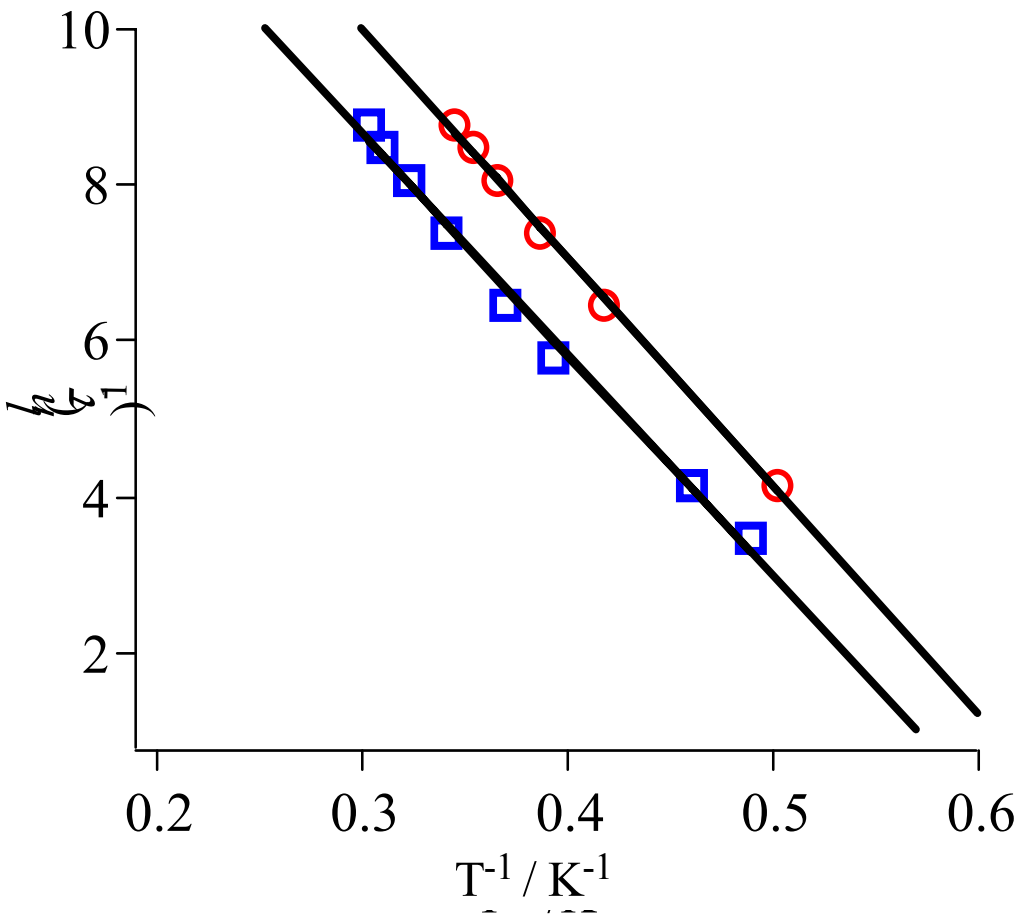

Figure S4. Arrhenius plots of **1**(red) and **2c**(blue)

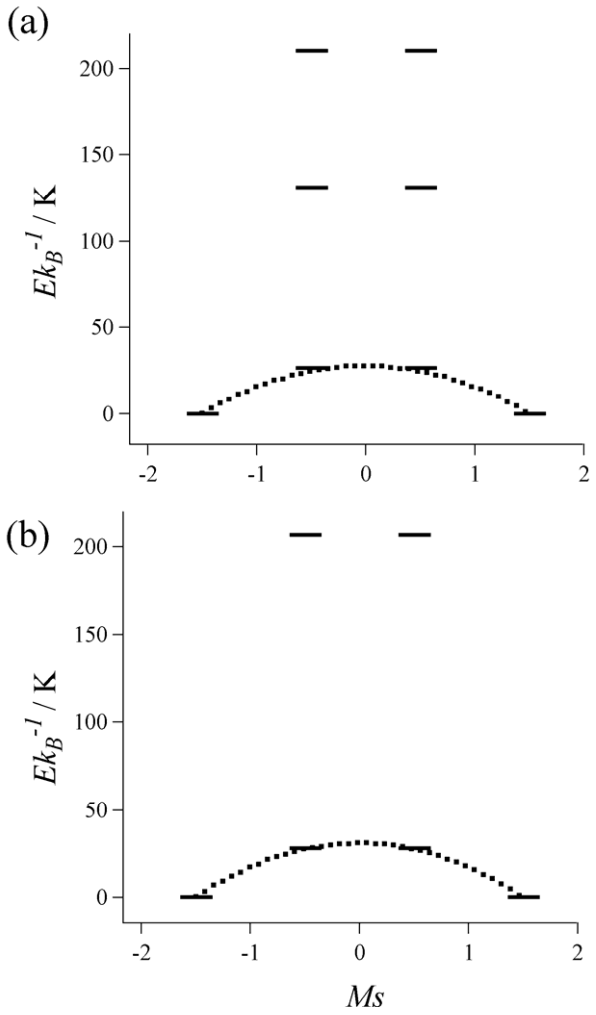

Figure S5. E/k_B vs. Ms diagrams for (a) **1** and (b) **2c** obtained from the optimized parameters.

$$\hat{H} = \Delta \bullet (\hat{L}_z^2 - \frac{1}{3}\hat{L}^2) - \frac{3}{2}k\lambda \hat{L} \cdot \hat{S}_0 - 2J\sum_{i=1}^{n} \hat{S}_0 \cdot \hat{S}_i + \mu_B \left(\frac{3}{2}k\hat{L} + g_e \sum_{i=0}^{n} \hat{S}_i \right) \cdot B$$

where Δ and $\hat{L}$ are the energy splitting between $^4A_{2g}$ and ^4E_g states and an effective angular momentum with its magnitude of $L = 1$, respectively, $\hat{S}_0$ and $\hat{S}_i$ are spin operators of the Co(II) ion ($S_0 = 3/2$) and two radicals ($S_i = 1/2$, $n = 2$) or one carbene($S_i = 1$, $n = 1$), μ_B and g_e are the Bohr magneton and the Landé g factor for free electron, and parameters k, λ, and J stand for the Stevens orbital reduction factor of Co(II), the spin-orbit coupling of Co(II), and the superexchange interaction between Co(II) and each radical, respectively.

The optimized parameters for **1**; Δ/k_B = -300 K, λ/k_B = -150 K(fixed), k = 0.8(fixed), and J/k_B =50.1 K

The optimized parameters for **2c**; Δ/k_B = -330 K, λ/k_B = -150 K(fixed), k = 0.8(fixed),

and J/k_B = 51.2 K

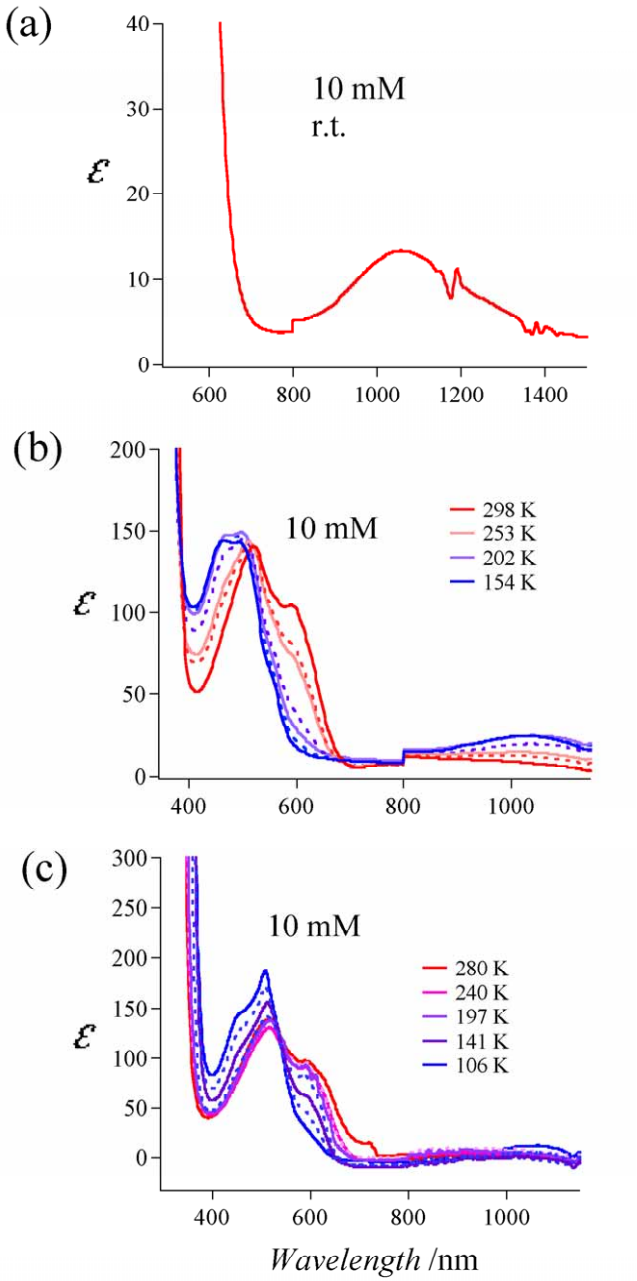

Figure S6. Visible spectra change of (a) **1** at r.t., (b) **2** in the temperature range of 298 (red) – 154 (blue) K, and (c) **2'** in the temperature range of 280 (red) – 106 (blue) K in MTHF.