Supporting Information For:

Record High Single-Ion Magnetic Moments through $4f^n5d^1$ Electron Configurations in the Divalent Lanthanide Complexes $[(C_5H_4SiMe_3)_3Ln]^-$

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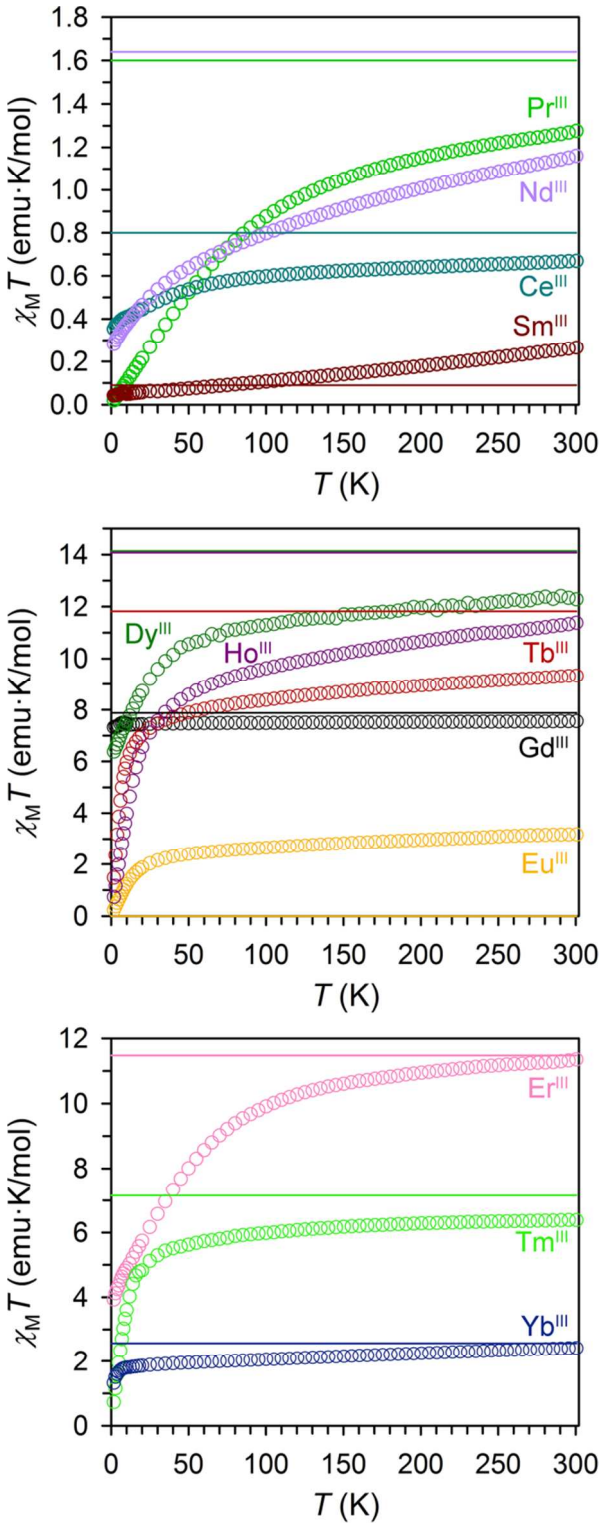

Figure S1. Plot of the magnetic susceptibility times temperature ($\chi_M T$) versus temperature for the stable trivalent lanthanides, cerium through ytterbium. Colored circles correspond to experimental data and colored lines represent the theoretical room temperature $\chi_M T$ value for each of the free trivalent lanthanides.

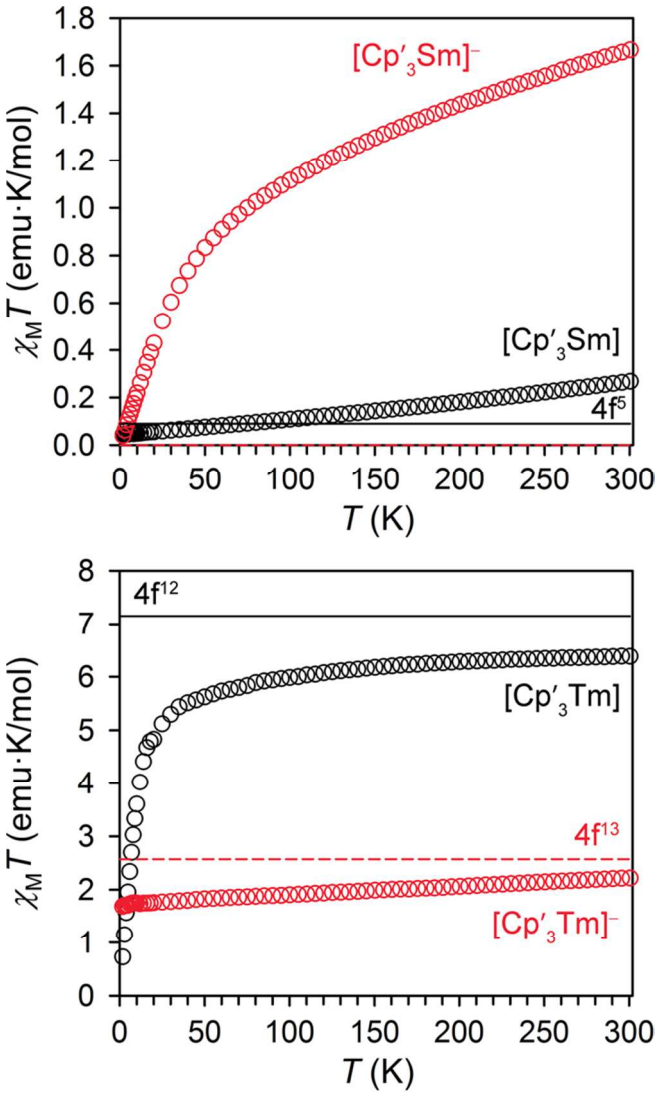

Figure S2. (Top) Plot of the magnetic susceptibility times temperature ($\chi_M T$) versus temperature for Cp′$_3$Sm (black circles) and [K(crypt-222)][Cp′$_3$Sm] (red circles) under an applied field of 0.1 T. Solid black and dashed pink lines represent the theoretical room temperature values for free Sm^{III} ($4f^5$) and Sm^{II} ($4f^7$), respectively. For [K(crypt-222)][Cp′$_3$Sm] at T = 300 K, $\chi_M T$ is 1.66 emu·K/mol, larger than the theoretical value of 0 emu·K/mol, assuming only the ground state (S = 3, L = 3, J = 0) is populated. However, the energy separation between ground and excited J for Sm^{II} and isoelectronic Eu^{III} is ~300 cm^{-1}, thus due to population of excited J states, the room temperature moment is often larger than the theoretical prediction. (Bottom) Plot of the magnetic susceptibility times temperature ($\chi_M T$) versus temperature for Cp′$_3$Tm (black circles) and [K(crypt-222)][Cp′$_3$Tm] (red circles) under an applied field of 0.1 T. Solid black and dashed pink lines represent the theoretical room temperature values for free Tm^{III} ($4f^{12}$) and Tm^{II} ($4f^{13}$), respectively. The experimental room temperature $\chi_M T$ values of 6.38 emu·K/mol and 2.22 emu·K/mol both closely approach the predicted values for free Tm^{III} (7.15 emu·K/mol) and Tm^{II} (2.57 emu·K/mol).

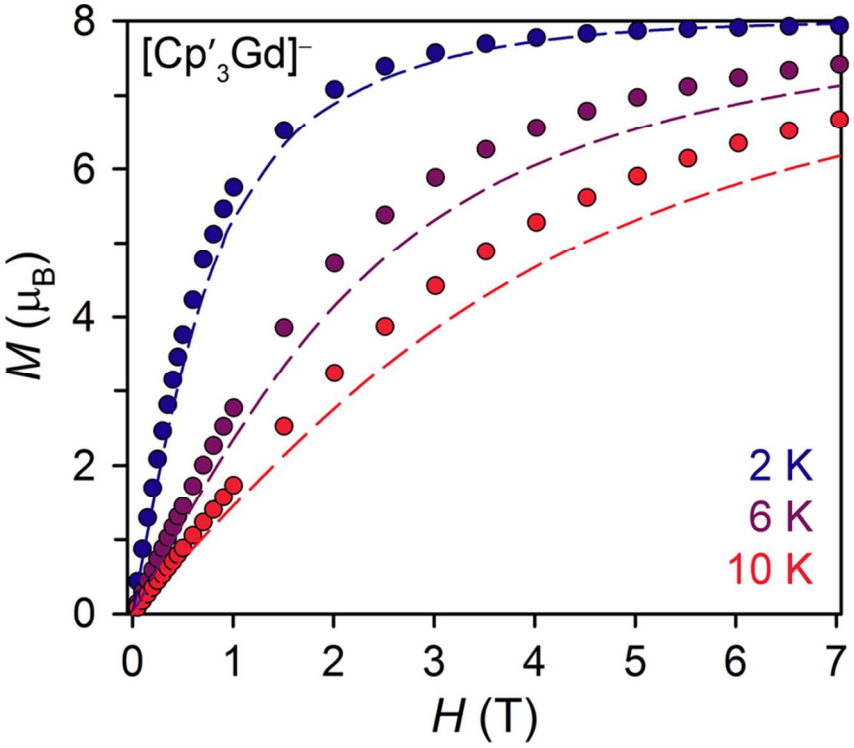

Figure S3. Variable temperature $M(H)$ curves for [K(2.2.2-cryptand)][Cp′$_3$Gd] collected from zero to 7 T. Data points are given by colored spheres and dashed lines represent the corresponding sum of an $S = ½$ and $S = {}^7/_2$ Brillouin function.

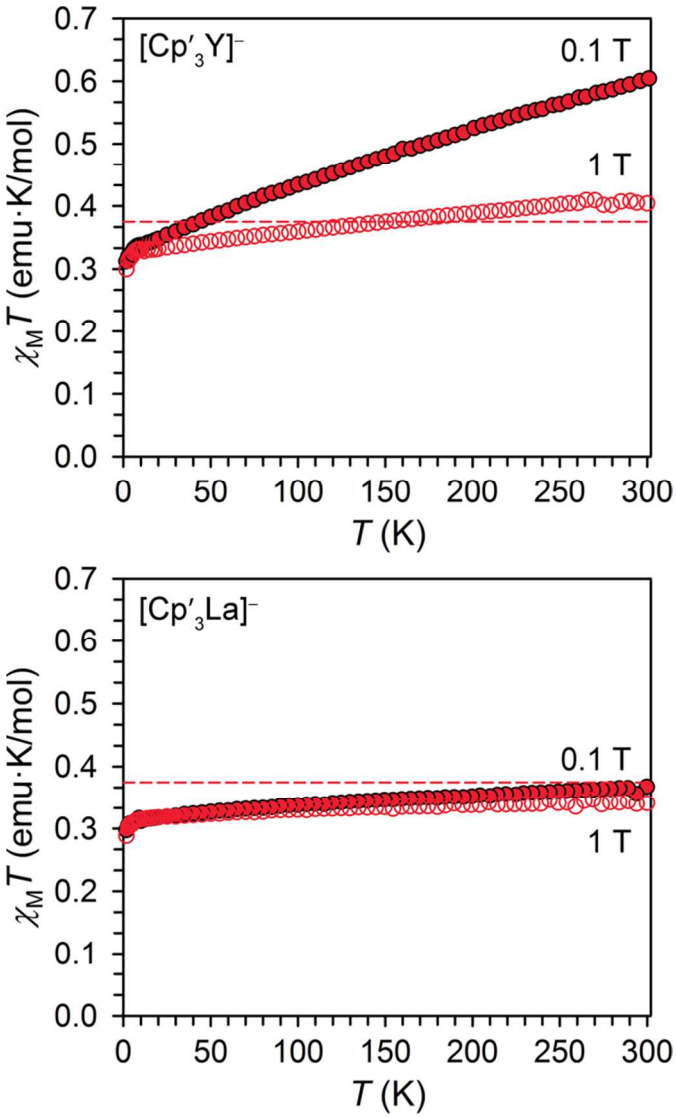

Figure S4. Plot of the magnetic susceptibility times temperature ($\chi_M T$) versus temperature for [K(crypt-222)][Cp′$_3$Y] (top) and [K(crypt-222)][Cp′$_3$La] (bottom) under applied fields of 0.1 T (filled circles) and 1 T (empty circles). Solid dashed pink lines represent the theoretical room temperature $\chi_M T$ values = 0.375 emu·K/mol for S = ½. The large slope and linear increase with temperature in the case of [K(crypt-222)][Cp′$_3$Y] is indicative of temperature independent paramagnetism.

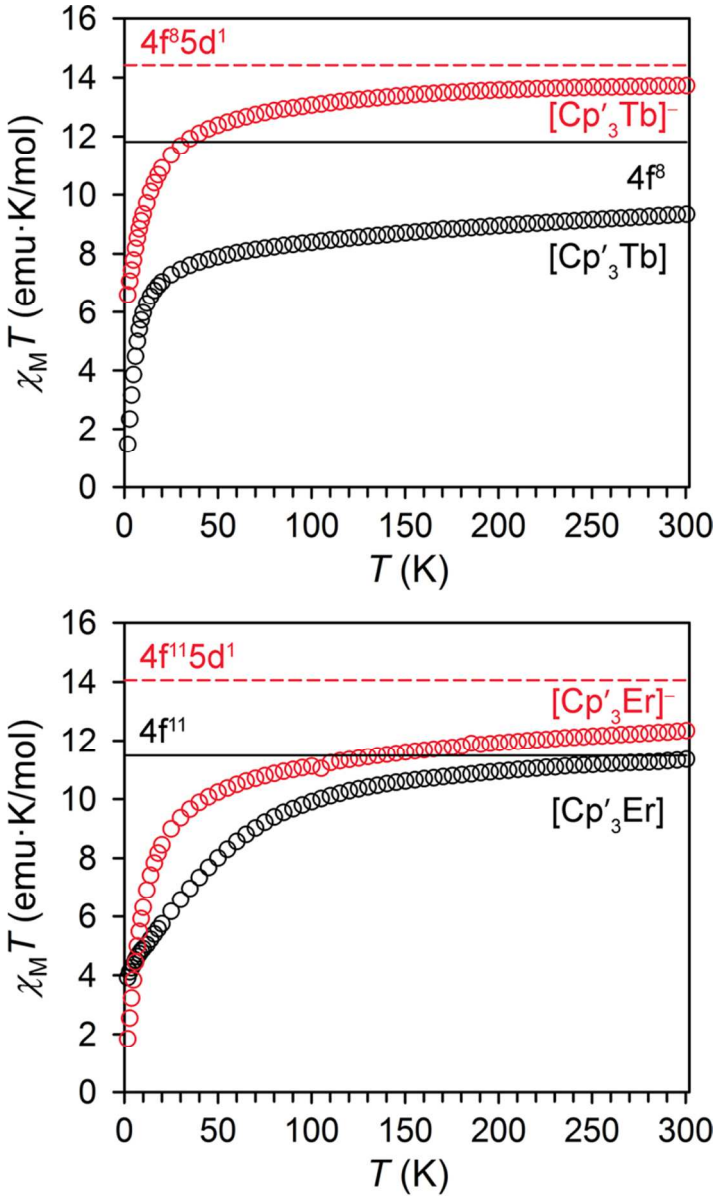

Figure S5. (Top) Plot of the static magnetic susceptibility times temperature ($\chi_M T$) versus T collected at 0.1 T for Cp'_3Tb (black circles) and [K(2.2.2-cryptand)][Cp'_3Tb] (red circles), with room temperature $\chi_M T$ values of 13.73 emu·K/mol and 9.34 emu·K/mol, respectively. Dashed pink line and solid black line represent the theoretical $\chi_M T$ values at 300 K for free Tb^{II} (14.42 emu·K/mol, coupled $4f^8 5d^1$) and free Tb^{III} (11.82 emu·K/mol). (Bottom) Plot of the static magnetic susceptibility times temperature ($\chi_M T$) versus T collected at 0.1 T for Cp'_3Er (black circles) and [K(2.2.2-cryptand)][Cp'_3Er] (red circles), with room temperature $\chi_M T$ values of 12.35 emu·K/mol and 11.35 emu·K/mol, respectively. Dashed pink line and solid black line represent the theoretical $\chi_M T$ values at 300 K for free Er^{II} (14.06 emu·K/mol, coupled $4f^{11} 5d^1$) and free Er^{III} (11.48 emu·K/mol).

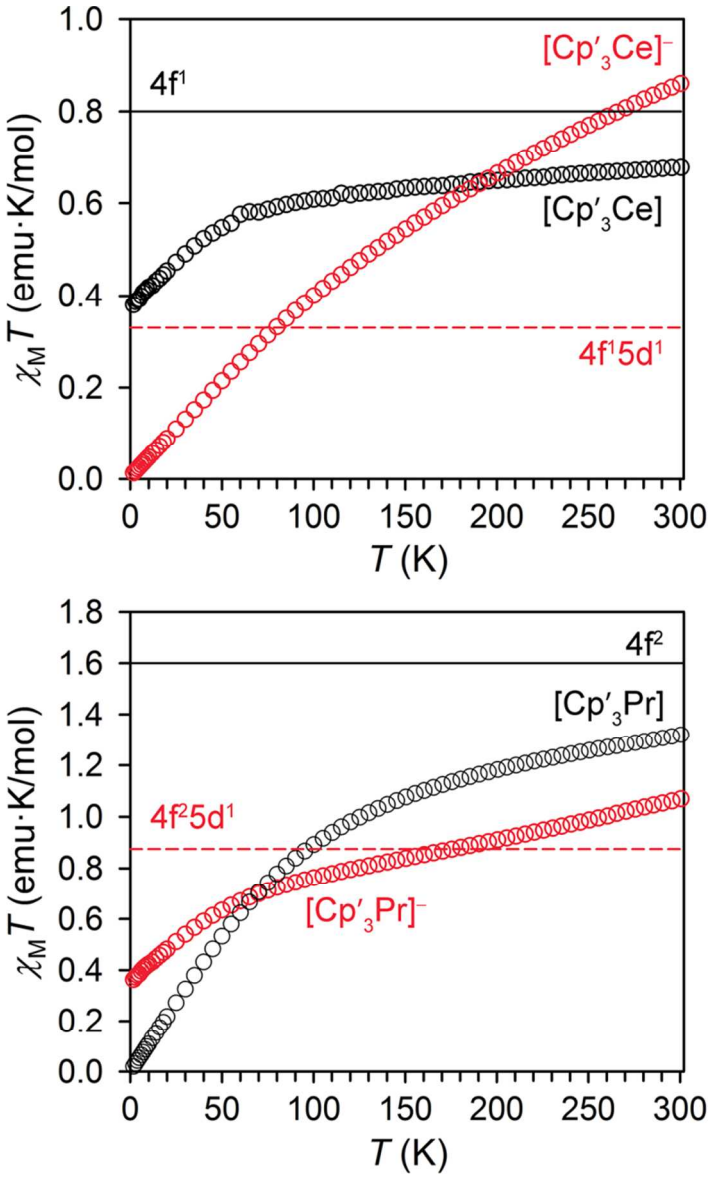

Figure S6. (Top) Plot of the magnetic susceptibility times temperature ($\chi_M T$) versus temperature for Cp′$_3$Ce (black circles) and [K(crypt-222)][Cp′$_3$Ce] (red circles) under an applied field of 0.1 T. Solid black and dashed pink lines represent the theoretical room temperature values for free Ce^{III} ($4f^1$) and Ce^{II} (assuming $4f^15d^1$), respectively. For [K(crypt-222)][Cp′$_3$Ce] at T = 300 K, $\chi_M T$ is 0.86 emu·K/mol, larger than the theoretical value for the coupled $4f^15d^1$ configuration (0.33 emu·K/mol), though smaller than the theoretical value for the $4f^2$ and uncoupled $4f^15d^1$ configurations (1.6 emu·K/mol and 1.18 emu·K/mol, respectively). (Bottom) Plot of the magnetic susceptibility times temperature ($\chi_M T$) versus temperature for Cp′$_3$Pr (black circles) and [K(crypt-222)][Cp′$_3$Pr] (red circles) under an applied field of 0.1 T. Solid black and dashed pink lines represent the theoretical room temperature values for free Pr^{III} ($4f^2$) and Pr^{II} ($4f^25d^1$ coupled), respectively. The room temperature $\chi_M T$ value of 1.07 emu·K/mol for [K(crypt-222)][Cp′$_3$Pr] falls in between the values for the $4f^2$ and $4f^25d^1$ configurations, similar to Ce^{II} and Nd^{II} as discussed in the main text.

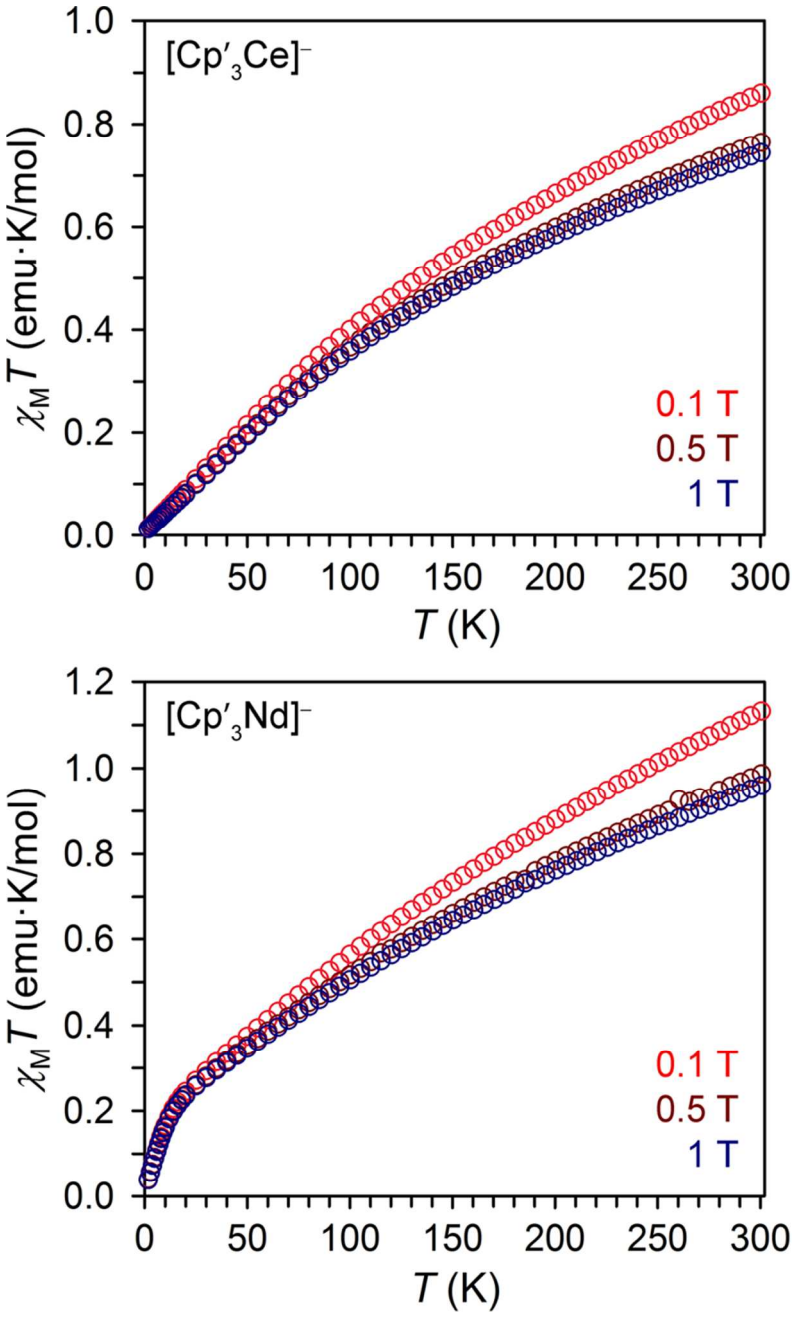

Figure S7. Plot of the magnetic susceptibility times temperature ($\chi_M T$) versus temperature for [K(crypt-222)][Cp′$_3$Ce] (top) and [K(crypt-222)][Cp′$_3$Nd] (bottom) collected at fields of 0.1 T, 0.5 T, and 1 T (red, dark red, and dark blue circles, respectively).