A Series of Tetrathiafulvalene-Based Lanthanide Complexes Displaying Either Single Molecule Magnet or Luminescence-Direct Magnetic and Photo-Physical Correlations in the Ytterbium Analogue

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Résumé en anglais	The reaction between (4,5-bis(2-pyridyl-N-oxidemethylthio)-4,5)-ethylenedithiotetrathiafulvene (L-1) or -methyldithiotetrathiafulvene (L-2) ligands and Ln(hfac)(3)center dot nH(2)O precursors (Ln(III) = Pr, Tb, Dy, Er, and Yb) leads to the formation of seven dinudear complexes of formula [Ln(2)(hfac)(6)(H2O)(x)(L-y)(2)] (x = 2 and y = 1 for L-III = Pr (1); x = 0 and y = 1 for Ln(III) = Tb (2), Dy (3), Er (4) and Yb (5); x = 0 and y = 2 for Ln(III) = Tb (6) and Dy (7)). Their X-ray structures reveal that the coordination environment of each Ln(III) center is filled by two N-oxide groups coming from two different ligands L-y. UV-visible absorption properties have been experimentally measured and rationalized by TD-DFT calculations. The temperature dependences of static magnetic measurements have been fitted. The ground state corresponds to the almost pure vertical bar M-J = +/- 13/2 while the first excited state (+/- 0.77 vertical bar +/- 11/2 +/- 0.50 vertical bar +/- 3/2 +/- 0.39 vertical bar +/- 5/2) is located at 19 cm(-1) and 26.9 cm(-1) respectively for 3 and 7. Upon irradiation at 77 K and at room temperature, in the range 25 000-20 835 cm(-1), both compounds 4 and 5 display a metal-centered luminescence attributed to I-4(13/2) -I-4(15/2) (6660 cm(-1)) and F-2(5/2) -E-2(7/2) (9972 cm(-1)) transitions, respectively. Emission spectroscopy provides a direct probe of the vertical bar +/- 5/2 ground state multiplet splitting, which has been confronted to magnetic data. The energy separation of 225 cm(-1) between the ground state and the first excited level (M-J = +/- 3/2) fits exactly the second emission line (234 cm(-1)). While no out-phase-signal is detected for 3, the change of ligand L-1 - L-2 induces a change of coordination sphere symmetry around the Dy-III increasing the energy splitting between the ground and first excited states, and 7 displays a single molecule magnet behavior.
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