A systematic study of influence of ligand substitutions on the electronic structure and magnetic properties of Mn_4 single-molecule magnets

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Abstract: We present a density-functional theory study of the influence of ligand substitutions on the geometric structure, electronic structure, and magnetic properties of Mn_4 single-molecule magnets (SMMs), in order to investigate the role of ligands in controlling these features, as well as in developing new SMMs and single-chain magnets (SCMs). Our results show that the peripheral ligands play an important role in controlling the magnetic ground-state of Mn_4 SMMs. A new model is proposed to explain the spin state of manganese ions in Mn_4 molecules. This model shows that the saving energy from distortion, which can be controlled by peripheral-ligand substitutions, plays a crucial role in determining the spin state of manganese ions in Mn_4 molecules. The mechanism of strong exchange couplings between manganese ions in Mn_4 SMMs is revealed. The strength of exchange-couplings between manganese ions in Mn_4 SMMs as a function of their charge and spin state can be also controlled by substituting peripheral-ligands. The results demonstrate the possibilities of developing new Mn_4-based SMMs. In addition, strong spin polarizations on peripheral ligands containing sp^2-hybridized carbon sites show that using ligands containing sp^2-hybridized carbon sites can enhance exchange couplings between Mn_4 building blocks to develop new SMMs and SCMs which operate at high temperatures. ?? the Owner Societies.

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