Electron transfer and magnetism in hybrid molecular magnets based on $\{V_{12}O_{32}\}$ vanadium cage and functionalized with phtalocyaniato lanthanide moieties $(LnPc)_n$ (n=1,2)

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There are many different types of molecular magnets synthesized in the last decades in hope of practical application in quantum computing or molecular electronics. Their properties are determined by the type of magnetic ions and the molecular structure in which they are incorporated. Hybrid molecular magnets comprise at least two different types of magnetic molecules coupled with each other, which should lead to new interesting properties and applications.

In this contribution we present magnetic and electronic properties of a family of hybrids $(PcLn)_n$-$\{V_{12}O_{32}\}$ (n=1,2) consisting of a vanadium core $\{V_{12}O_{32}\}$ coupled covalently to a phtalocyaniato lanthanide moiety (LnPc). By using combined experimental (EPR, DC and AC SQUID) and theoretical (DFT, MD and model Hamiltonian approach) methods it is demonstrated that the proximity of the molecules in solid state and in concentrated solutions induces partial reduction of V^{5+} centers due to the electron transfer from Pc to $\{V_{12}O_{32}\}$. The intramolecular (through Ln) and intermolecular (through counter cations) electron transfers can coexist in different proportions dependent on Ln. As a result an unpaired electron can be found delocalized over $\{V_{12}O_{32}\}$ and/or at Pc. The research is carried out for Ln=Sm^{3+} - Er^{3+} and diamagnetic Lu^{3+} and Y^{3+}, but we focus mainly on molecules with $n = 1$ and Ln=Lu^{3+} or Ln=Dy^{3+} for which all the effects can be clearly demonstrated. The Dy^{3+} based hybrid appears to be also a field induced single molecule magnet with a slow relaxation of order 10^{-3} s. It has been also proven that there is an interaction between a radical electron and Dy^{3+}.

Our results open the way to further investigation of such hybrids, e.g. in electric field, which can pave the way to their application in molecular electronics or spintronics.

References:

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