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Magnetic properties of novel dendrimeric spin crossover iron(III) complex

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ABSTRACT

The synthesis and magnetic properties of novel dendrimeric spin crossover Fe(III) complex of formula $[\text{Fe}(\text{L})_2]^+\text{PF}_6^-$, where $\text{L} = 3,5\text{-di}(3,4,5\text{-tris}(\text{tetradecyloxy})\text{benzoyloxy})\text{benzoyl-4-oxy-salicylidene-}N'\text{-ethyl-}N\text{-ethylenediamine}$ have been studied for the first time by magnetic susceptibility, Electron Paramagnetic Resonance (EPR) and Mössbauer spectroscopy in the wide (2–300 K) temperature range. EPR showed that the compound is magnetically inhomogeneous, consists of two magnetic sub-lattices, displays a partial spin crossover ($S = 5/2 \rightleftharpoons 1/2$) of ~25% of the Fe(III) molecules above 160 K and undergoes the antiferromagnetic (AF) ordering below 10 K. High-spin (HS, $S = 5/2$) Fe(III) centers with weakly distorted octahedral environment most probably form chains in layers. The dimeric molecules, formed from low-spin (LS, $S = 1/2$) centers and HS centers with strongly distorted octahedral environment are likely located between the layers and are involved in the spin crossover. EPR has shown the presence of AF dynamical spin clusters in the high temperature (70–300 K) range, which are visible in the short time scale (10^{-10} s) and could not be registered in the static magnetic measurements. Mössbauer spectra demonstrated in a paramagnetic state of the compound a quadrupole doublet with average isomer shift of 0.35 mm/s and splitting 0.72 mm/s corresponding to HS Fe(III) centers. Below 60 K, the spectra displayed the appearance of magnetic hyperfine structure, whose relaxation nature testifies the collective spin flips of small clusters in the material. Mössbauer spectroscopy confirmed the existence of AF ordering in the Fe(III) dendrimeric complex at 5 K.

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1. Introduction

Designing magnetic materials with two or more potential functions arising from different physical properties has become a strong topic in chemical and materials science [1,2]. A wide choice of constituent molecules could allow the appearance in the same compound of unusual combination of physical properties. A suitable approach to obtain such a multifunctional material is the hybrid approach in which the material structure is constructed through self-assembly of two different molecular fragments having distinct properties. An interesting example is the multifunctional material that exhibits spin-crossover behavior with other physical properties [3–5]. Such synergic approach makes possible the production of systems in which one property may be controlled

by another. In this context, cationic spin-crossover (SCO) iron(III) complexes are suitable for this purpose. Iron(III) centers can adopt two different spin states, that is, low-spin (LS) and high-spin (HS) states that are interconvertible under an external stimulus such as temperature, pressure, light irradiation or solvents [6]. Considerable research efforts are focused to utilize the SCO phenomenon together with the non-linear optical properties [4], chirality [7], electrical conductivity [8] or long-range order [9].

The motivation for this work came from our desire to create a novel multifunctional material, in which spin-crossover phenomena and magnetic ordering coexist. This strategy may open a way to design switching magnets in which the magnetic ordering of the system could be tuned, thus taking advantage of the possibility to induce the SCO phenomenon by applying the external stimuli such as light or pressure. However, this challenging goal requires first the preparation of such a material which is able to display the coexistence of spin crossover and magnetic ordering.

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