Fe(III) Spin Crossover thin films and nanoparticles

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Abstract

Spin crossover (SCO) compounds represent a highly promising class of switchable materials for molecular devices. To access the materials level behaviour of Fe(III) SCO compounds, the magnetic studies of SCO thin films and nonaparticles have been investigated.

The Langmuir-Blodgett technique was used to prepare monolayer and multilayer films for new Fe(III) SCO with long chain alkyl substituent, $[Fe(qsal\text{-}OR)_2]NO_3$ (R = $C_{12}H_{25}$, $C_{16}H_{33}$ and $C_{22}H_{45}$). The results show that the longer alkyl chain ligands and complexes form stable films. In addition, X-ray crystallographic studies of Hqsal-$OC_{12}H_{25}$ shows extensive π-π and alkyl interactions. The single crystal structure of $[Fe(qsal\text{-}OC_{12}H_{25})_2]NO_3$ also shows strong organization in the structure. The magnetic properties were studied by variable temperature NMR spectroscopic studies using the Evan's method revealing that $[Fe(qsal\text{-}OC_{12}H_{25})_2]NO_3$ undergoes a 50% SCO to a HS-LS state. $[Fe(qsal\text{-}OC_{16}H_{33})_2]NO_3$ also shows a spin transition while $[Fe(qsal\text{-}OC_{22}H_{45})_2]NO_3$ forms a gel at lower temperatures.

Fe(III) SCO nanoparticles have been prepared using the reverse micelle method with NaAOT as a surfactant. The amount of surfactant, reaction time and the solvent used in the preparation have been explored in $[Fe(qsal)_2]NO_3$. Ideal conditions produce parallelogram shaped materials with length × width × thickness of 1-2 μm × 300-600 nm × 90-110 nm on average. The SQUID profile of the bulk $[Fe(qsal)_2]NO_3$ and the nanomaterials are almost identical. Similar nanosizing of $[Fe(qsal\text{-}I)_2]OTf$ and $[Fe(qsal\text{-}I)_2]NTf_2$ also yield nanomaterials with an average size of 510 ± 27 nm and 709 ± 193 nm, respectively. The $[Fe(qsal\text{-}I)_2]NTf_2$ nanomaterials have a particularly strong nanorod morphology while $[Fe(qsal\text{-}I)_2]OTf$ resembles plate like aggregates. The magnetic profile of $[Fe(qsal\text{-}I)_2]OTf$ shows a reduced hysteresis and 19% of Fe(III) centres that remain HS even at low temperature. In contrast, the $[Fe(qsal\text{-}I)_2]NTf_2$ nanomaterials exhibit the same magnetic profile as the bulk material strongly suggesting that provided that the hysteresis in the bulk sufficiently large nanosizing results in little change. This makes $[Fe(qsal\text{-}I)_2]NTf_2$ an extremely promising material for future device development.

Keywords: Iron(III), Spin crossover, nanoparticles, thin films