Ferrocene–Tetrathiafulvalene Hybrids: Coexistence of Fe 3d and π Spins and Substituent-Dependent Spin Density Distribution

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Redox active compounds are promising components of molecule-based functional materials, because the removal or addition of electrons (i.e., oxidation or reduction) enables fine control of the compounds’ structures and their electronic and spin states.¹⁻³ For example, ferrocene (Fc) forms a localized 3d spin upon oxidation, and tetrathiafulvalene (TTF) forms a delocalized π spin. The former behaves as a magnetic center¹ and the latter exhibits electrical (super)-conductivity in the solid state.² A combination of these two molecular systems, Fc–TTF, is expected to achieve novel magneto-conducting properties by multiple oxidation, which would lead to unusual electronic and spin states, such as the coexistence of 3d spins and π-conducting electrons in the same molecule.

We report on the successful isolation of the dicationic, monocationic, and neutral forms of new Fc–TTF hybrids Fc₄TTF(R)₂ (R = CF₃ and SMe; Figure 1). Structural and spectroscopic investigations showed that the molecular structure of each oxidation state reflects its spin-density distribution. Chemical modification on R significantly altered the spin-density distribution in the monocation, yielding localized 3d spin for R = CF₃ and delocalized π spin for R = SMe. The dication showed the coexistence of localized 3d and delocalized π spins with antiferromagnetic spin–spin interaction.⁴

Figure 1. (a) Chemical structure of Fc₄TTF(R)₂ and (b) the spin states upon oxidation.

References