Design of the electronic structure of poly-MTO
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Abstract
Polymeric methyltrioxorhenium (poly-MTO) is the first member of a new class of organometallic hybrids which adopts the structural motives and physical properties of classical perowskites in two dimensions. In this study we demonstrate how the electronic structure of poly-MTO can be tailored by intercalation of organic donor molecules such as tetrathiafulvalene (TTF). With increasing donor intercalation the metallic behavior of the parent compound, (CH$_3$)$_{0.92}$ReO$_3$·x% TTF (x = 0) becomes suppressed leading to an insulator at donor concentrations x larger than 50. Specific heat, electric resistance and magnetic susceptibility studies indicate that an increasing amount of TTF causes the itinerant electrons of the poly-MTO matrix to localize.

Key words: organometallic hybrids, highly correlated electrons

Polymeric methyltrioxorhenium (poly-MTO), (CH$_3$)$_{0.92}$ReO$_3$, represents the first example of a conductive organometallic polymeric oxide. From analytical studies it is known that ≈10% of the methyl groups are missing in comparison with the monomer. The Re d$^3$ centers which are formed during demethylation are supposed to provide the itinerant electrons of the conduction band, leading to metallic behavior [1,2]. Since its discovery by Herrmann, Fischer and Scherer in 1992 [3] several attempts have been undertaken to use its unique chemical properties to design new materials by manipulating its chemical composition. Here we present for the first time successful approaches to manipulate the electronic and magnetic structure of poly-MTO by controlled intercalation employing the organic donor species tetrathiafulvalene (TTF) attempting to increase the electronic conductivity.

For the synthesis of poly-MTO, two methods have been established. One consists in dissolving MTO (CH$_3$ReO$_3$) in water under stirring at 80°C for two days. However, this is not applicable for the intercalation of TTF. Another method has been established

which is based on auto-polymerization of MTO in the flux. In the same way finely ground mixtures of MTO are used to intercalate TTF in a sealed ampoule at 120°C during two days. The intercalated samples (poly-MTO + x% TTF) prepared by this way form bronze-colored solids for low TTF concentrations (x < 40) and almost black powders for higher intercalation ratios.

X-ray powder diffraction measurements clearly show that two-dimensional ordering of the {ReO$_2$}$_\infty$ framework is preserved in all samples. Hence poly-MTO (Fig. 1) displays a layered structure without significant interlayer ordering. Intercalated TTF is assumed to settle in between the layers to cause a decrease in crystallinity, which is indicated by the powder diffraction studies.

This two-dimensional character is also seen in the temperature dependent phonon contribution calculated from specific heat measurements (Fig. 2). For the pure poly-MTO sample the specific heat increases considerably below 3 K giving rise to a nuclear electric Schottky effect, but also disorder cannot be ruled out at present. This significant upturn seems to be suppressed with increasing TTF intercalation above T = 2 K (insert Fig. 2). An estimated γ ≈ 7 ± 2 mJ/molK$^2$
is in agreement with typical values displayed by d band metals. Measurements of the resistance (Fig. 3A) display a decrease of the metallic behavior with increasing amount of TTF. Furthermore the temperature dependency of the resistance becomes reduced. This may be caused by increasing amount of defects induced in the conducting layers, in accord with our X-ray diffraction studies. Below 20 K an logarithmic temperature dependency as it is known from Kondo-impurity systems is observed. These results are opposite to the common assumption that TTF as a donor acts as a source of itinerant electrons.

To explain this unexpected behavior of the intercalated samples, magnetic susceptibility studies have been performed (Fig. 3B). Below 50 K $\chi(T)$ is well accounted for by a simple modified Curie-Weiss type behavior, $\chi(T) = C/(T - \Theta) + \chi_0$, yielding $\chi_0 \leq 0.1$ mmu/mol and $\Theta \approx 0$ K indicating no correlations of the residual localized d$^1$ electrons at Re positions. The effective paramagnetic moment $\mu_{eff}$ obtained from the Curie constant $C$ corresponds to 0.05% Re atoms carrying d$^1$ moments in the case of pure poly-MTO and 2% for samples with Re to TTF ratios of one. Calculations from magnetization measurements (Fig. 3C) lead to the same amount of localized d$^1$ centers. On the other hand an observed decrease of $\chi_0$ with TTF content exhibits a reduction of the itinerant electron density which corroborates nicely the conductivity data. In addition the Wilson-ratio $R = \pi^2 k_B \chi_0 / 2 \mu_0 \mu_B \gamma \approx 1$ as it is expected for non-magnetic metals.

Summarizing, an organic compound has been intercalated in a polymeric organometallic oxide for the first time. TTF intercalation in poly-MTO leads to a crossover from metallic to insulating behavior.
[3] W. A. Herrmann, R. W. Fischer, W. Scherer, Adv. Mater. 4, 653, (1992)