Abstract

In this work, the magnetic properties of a series of poly(alkylthiophene)s (PAT)s featuring different chain topologies and morphologies are investigated.

First, the investigated materials are tailored by a systematic integration of ill-coupled bithiophene (defect) units. By means of UV-vis, the effect of the engineered conjugation length L_C on the optical band gap is revealed. Differential scanning calorimetry (DSC) methods are subsequently employed to accurately distinguish between amorphous and semi-crystalline samples. Moreover, diverse morphologies featuring a constant number of topological defects are prepared by thermal treatment, providing a measure to deconvolute the influence of topology and morphology in the magnetic properties of PATs. To facilitate such endeavor, PATs are classified into amorphous and semi-crystalline.

Secondly, field- and temperature-dependent SQUID magnetization experiments demonstrate that the magnetic susceptibility of all samples is composed of up to four different contributions. A relatively constant diamagnetic susceptibility contribution for all samples is identified, and many of the samples show a complex temperature-dependent susceptibility similar to the *Curie-Weiss* behavior of antiferromagnetic solids. The density of spins contributing to this phenomenon is approximated. For amorphous samples. It is found that the antiferromagnetic coupling weakens with increasing L_C, to the point of vanishing for an amorphous sample with large L_C (low density of defects).

Finally, an *ab initio* π-based four-level molecular magnetism model is employed to simulate the temperature-dependent magnetization curves. Originally developed by *Van Vleck* in 1932, the approach provides access to the susceptibility caused by spins in triplet states. According to the model, the isotropic interaction constant J is negative for the investigated polymers. For most semi-crystalline PATs, beside the temperature-dependent susceptibility, an additional temperature-independent, but field-dependent paramagnetic contribution is observed. This contribution is related to a singlet-triplet mixing as consequence of the magnetic field, as covered by the *ab initio* description. The singlet-triplet mixing is found to be field dependent.

In summary, amorphous poly(alkylthiophene) samples show temperature-dependent magnetic response, arising from a density of spins proportional to the density of topological chain defects. For semi-crystalline systems an antiferromagnetic-like behavior, experimental evidence for temperature-independent, field-dependent, positive susceptibility is shown. Considering the high purity and magnetic behavior of the investigated materials, the possibility of foreign dopants per topological chain defect is excluded. Altogether this work provides evidence for a new class of tailored magnetic polymers with potential applications in magnetic storage devices and emerging organic-based technologies.