

Abstract

Nonconjugated radical polymers and small molecules are employed as electrically conducting materials in multiple organic electronic devices, including electrolyte-supported devices and solid-state electronic devices, because of their charge transport and redox-active properties. In fact, macromolecules with nonconjugated backbones and stable radical pendent groups can have impressive charge transport capabilities (i.e., thin-film conductivities of $\sim 20 \text{ S m}^{-1}$) if proper molecular design principles are employed.

In the first part of this work, a polysiloxane-based polymer bearing galvinoxyl radical groups has been synthesized. Density functional theory (DFT) calculations predicted that the spin delocalization behavior of the galvinoxyl group would result in a higher charge transfer rate compared with nitroxide radical systems. It is determined that the flexible backbone endowed the polymer with a glass transition temperature around $0 \text{ }^\circ\text{C}$, and this feature allowed the radical moieties to pack into conductive domains after thermal annealing. Furthermore, the conductivity of this radical polymer was quantified to be $\sim 10^{-1} \text{ S m}^{-1}$ after being cast into a thin film. Thus, these studies provide a strategy to direct molecular packing and facilitate charge transport in radical polymers with delocalized open-shell sites, which can aid in deciphering the charge transport mechanism in radical polymer thin films.

In the second part of this work, the charge transport and the magnetic properties of several nitroxide radical-based small molecules have been studied because 1) despite the success of nonconjugated radical polymers as solid-state charge conductors, the charge transport properties of nonconjugated open-shell small molecules have received less attention despite the fact that studying small molecule systems can facilitate the development of macromolecular radical conductors; 2) the unpaired electrons on these materials provide a means by which to respond to magnetic fields, making these materials promising candidates for organic magnets. Motivated by the need to develop open-shell small molecule materials, we quantify the electrical conductivity and magnetic properties in organic radical single crystals. Through proper molecular engineering of functional groups, we synthesized and crystallized a nitroxide radical-based material that has a single-crystal electrical conductivity of $\sim 3 \text{ S m}^{-1}$, which is the highest values over $1 \text{ }\mu\text{m}$ -scale for nonconjugated organic materials reported to date. Furthermore, we manipulate the molecular packing of the nitroxide radical molecules in the single crystals by introducing alkyl chains to the molecular structures. As a result, a strong antiferromagnetic ordering is obtained in the crystals

with a Néel temperature of 40 K. In conclusion, new open-shell materials are developed with excellent charge transport capabilities and strong magnetic properties. This effort provides clear insights into designing the next-generation organic radical electrical conductors and magnetic materials.