High Charge Carrier Mobility in Conjugated Organometallic Polymer Networks

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Scheme 1. Synthesis of EHO–OPPE–Pt0 Networks

The charge carrier mobility of conjugated polymers is usually limited by disorder effects, which prevent efficient interchain coupling and lead to one-dimensional electronic properties.1 Rapid charge transport, however, is important for the exploitation of these materials in electronic devices.2 Enhanced interchain interactions, which concur with improved charge carrier mobility, are observed in highly ordered structures,3 but their fabrication is usually intricate. We show here that rapid charge transport can also be achieved by introducing conjugated cross-links between conjugated macromolecules. Examples of such materials are rare and were often obtained accidentally.4–7 We have recently shown that organometallic networks can readily be prepared by ligand-exchange reactions8 and now adopt this framework for the introduction of conjugated cross-links between conjugated polymers.

The conjugated polymer employed here was EHO–OPPE,9 a common poly(p-phenylene ethynylene) (PPE) derivative,10 which comprises ethynylene groups that may act as ligand sites (Scheme 1). Pt0 was chosen as cross-linker, since it forms stable bis-(ethynylene) complexes,11 which due to π-back-bonding allow for electronic conjugation.12 A styrene solution of Pt(styrene)3 served as the Pt0 source.13 Since styrene is volatile, the ligands can be removed from the product after exchange with the PPE. In a model reaction with diphenylacetylene (DPA) and using in situ195 Pt NMR spectroscopy, we confirmed that even in the presence of a ~150-fold excess of styrene the ligands of Pt(styrene)3 are quantitatively replaced by DPA, and the only product formed is Pt(DPA)2. The analogous reaction between EHO–OPPE and Pt(styrene)3 was accomplished by combining styrene solutions of these reactants (Scheme 1). The ratio of the molar concentrations of Pt0 and phenylene ethynylene (PE) moieties, [Pt0]/[PE], was varied between 0.016 and 0.34. The reaction mixtures gelled in seconds, consistent with the formation of cross-linked structures (Scheme 1). Homogeneous, amorphous films could be produced by spin and solution casting before gelation. Consistent with their cross-linked structure, the films were insoluble in solvents for EHO–OPPE. On the other hand, styrene was found to readily dissolve EHO–OPPE–Pt0, demonstrating that the ligand exchange is reversible. Raman spectra of EHO–OPPE–Pt0 showed a broad signal at 1842 cm−1, which was also observed for Pt(DPA)2 (1882 and 1864 cm−1) but not the neat EHO–OPPE, and indicates the formation of the target Pt0–ethynylene complex.11,12 The insolvency of the cross-linked EHO–OPPE–Pt0 samples prevented further structural analysis. Thus, the data ultimately do not allow a discrimination between conjugated cross-links and EHO–OPPE–Pt0– styrene complexes, which may also be present (Scheme 1).

The complexation of the PPE with Pt0 causes a blueshift of the absorption (Figure 1) and a reduction of the extinction coefficient, suggesting that the effective conjugation length is reduced. This is consistent with the fact that the phenyl rings bend away from the platinum (the phenyl–C=C angle in Pt(DPA)2 is 153°).11 The changes in the absorption spectra correlate with the Pt content but appear to level off at [Pt0]/[PE] ~ 0.17. The complexation also leads to a substantial reduction of the photoluminescence intensity, consistent with exciton migration to the complexation sites, which appear to provide pathways for nonemissive relaxation processes. The remaining emission is similar to that of the parent PPE, suggesting that the same singlet excited states are involved.

The carrier mobilities of EHO–OPPE–Pt0 and an EHO–OPPE reference were determined by time-of-flight (TOF) measurements on indium–tin oxide/polymer/gold samples.14 In this technique, a short light pulse incident on the polymer–electrode interface creates a thin sheet of charge carriers, and, depending on the polarity of the applied electric field F (with respect to the illuminated electrode), holes or electrons are driven across the sample. The mobility of these carriers, μ = LτF, can be obtained from the sample thickness L (which is large compared to the optical absorption depth) and the transit time τ of the charge carriers.14 The shape of the photocurrent transients of EHO–OPPE and EHO–OPPE–Pt0 ([Pt0]/[PE] = 0.17), shown in Figure 2, is representative for all transients observed here and is characteristic of dispersive transport.15–18 This mechanism is typical for materials with a high degree of spatial and/or energetic disorder and is concomitant with a wide variation of local transport rates.19

TOF measurements were performed as functions of carrier type (by changing the bias), electric field, and Pt0 content. It was confirmed for EHO–OPPE and EHO–OPPE–Pt0 with [Pt0]/[PE] = 0.25 that the drift mobility scales with L, which demonstrates that the photocurrents are not range-limited. Further, no photocurrent was observed in a reference film (L = 2 μm) of PMMA comprising 50% w/w Pt(DPA)2, confirming that the current was not caused by a Pt0–ethynylene complex per se. High electron (1.9 × 10−3 cm2 V−1 s−1) and hole (1.6 × 10−3 cm2 V−2 s−1) mobilities were found at low F (3.8 × 104 V cm−1) for the neat EHO–OPPE. These data compare favorably with the highest values yet observed for

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an ambipolar conjugated polymer. The mobility depends on the electric field. The negative field dependence was also predicted for the hole mobilities of ordered materials (\(10^{-1} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}\)).

In conclusion, we demonstrated that organometallic conjugated polymer networks can be synthesized and processed by ligand exchange between a linear conjugated polymer and a labile metal complex. The introduction of conjugated cross-links between the conjugated macromolecules leads to a substantial increase of the charge carrier mobility. The charge carrier mobilities of the present EHO–OPPE–Pt\({}^0\) networks represent the highest mobilities yet observed in disordered conjugated polymers and also compare well to the hole mobilities of ordered materials (\(10^{-1} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}\)).

The ease of processing and the ambipolar characteristics of the new materials are particularly intriguing and may lead to a new generation of higher-performance semiconducting devices.

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Supporting Information Available: Experimental details for synthesis of EHO–OPPE–Pt\({}^0\) and TOF measurements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References