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High Charge Carrier Mobility in Conjugated Organometallic Polymer Networks

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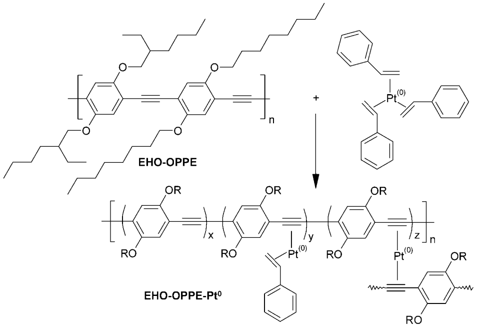
Received May 21, 2002

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 reactions[8] 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). Pt^0 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 Pt^0 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 situ ^{195}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 Pt^0 and phenylene ethynylene (PE) moieties, $[Pt^0]/[PE]$, 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−Pt^0, demonstrating that the ligand exchange is reversible. Raman spectra of EHO−OPPE−Pt^0 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 Pt^0−ethynylene complex.[11,12] The insolubility of the cross-linked EHO−OPPE−Pt^0 samples prevented further structural analysis. Thus, the data ultimately do not allow a discrimination between conjugated cross-links and EHO−OPPE−Pt^0−styrene complexes, which may also be present (Scheme 1).

The complexation of the PPE with Pt^0 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 $[Pt^0]/[PE] \approx 0.17$. 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.

Scheme 1. Synthesis of EHO−OPPE−Pt^0 Networks



The carrier mobilities of EHO−OPPE−Pt^0 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, $\mu = L/t_{tr}F$, can be obtained from the sample thickness L (which is large compared to the optical absorption depth) and the transit time t_{tr} of the charge carriers.[14] The shape of the photocurrent transients of EHO−OPPE and EHO−OPPE−Pt^0 ($[Pt^0]/[PE] = 0.17$), 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 Pt^0 content. It was confirmed for EHO−OPPE and EHO−OPPE−Pt^0 with $[Pt^0]/[PE] = 0.25$ 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 ($L = 2\ \mu m$) of PMMA comprising 50% w/w $Pt(DPA)_2$, confirming that the current was not caused by a Pt^0−ethynylene complex per se. High electron ($1.9 \times 10^{-3}\ cm^2\ V^{-1}\ s^{-1}$) and hole ($1.6 \times 10^{-3}\ cm^2\ V^{-2}\ s^{-1}$) mobilities were found at low F ($3.8 \times 10^4\ V\ cm^{-1}$) for the neat EHO−OPPE. These data compare favorably with the highest values yet observed for

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10.1021/ja026988+ CCC: $22.00 © 2002 American Chemical Society

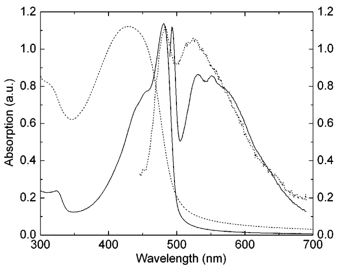

Figure 1. Photoluminescence and UV−vis absorption spectra of films of EHO−OPPE (solid line) and EHO−OPPE−Pt^0 with $[\mathrm{Pt}^0]/[\mathrm{PE}] = 0.17$ (dotted line).

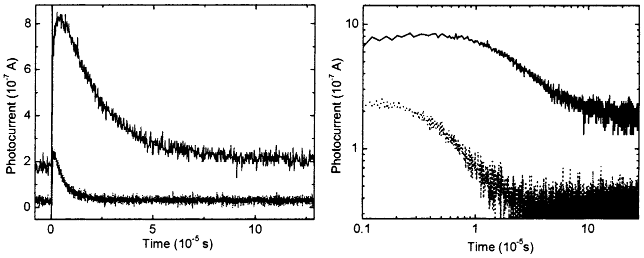

Figure 2. Electron TOF photocurrent transients of EHO−OPPE (top, $L = 8\ \mu$m) and EHO−OPPE−Pt^0 (bottom, $L = 30\ \mu$m, $[\mathrm{Pt}^0]/[\mathrm{PE}] = 0.17$) films in linear and logarithmic plots, measured at 295 K and $F = 1.5 \times 10^5$ V cm^{-1}.

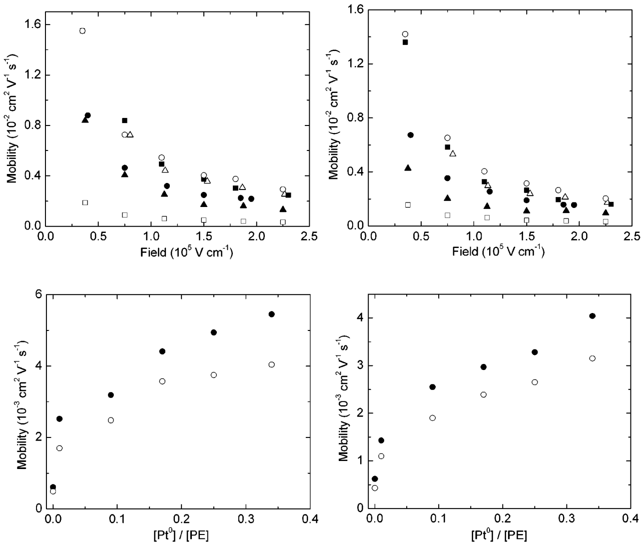

Figure 3. Electron (top left) and hole (top right) mobility of EHO−OPPE−Pt^0 as a function of $[\mathrm{Pt}^0]/[\mathrm{PE}]$ and electric field F ($[\mathrm{Pt}^0]/[\mathrm{PE}]$: □, 0; ▲, 0.016; ●, 0.086; △, 0.17; ■, 0.25; ○, 0.34). Electron (bottom left) and hole (bottom right) mobility at $F = 1.1 \times 10^5$ (●) and 1.5×10^5 Vcm^{-1} (○) as a function of $[\mathrm{Pt}^0]/[\mathrm{PE}]$.

an ambipolar conjugated polymer.[20] The mobility depends on F and decreases with increasing bias (Figure 3). This somewhat unusual behavior was observed previously[16] and is explained by a hopping transport model that accounts for off-diagonal (positional) disorder caused by variations of intersite distances in addition to diagonal (energetic) disorder in the transport manifold.[21] The large off-diagonal disorder results in a negative field dependence of the mobility at low fields, since higher fields favor forward hopping and inhibit faster routes for carriers involving hops transverse to the electric field. The negative field dependence was also predicted for quasi one-dimensional transport in the presence of defects and barriers.[22] The data shown in Figure 3 also show that the carrier mobility strongly increases upon introduction of Pt^0. While a distinct enhancement of the mobility is observed for EHO−OPPE−Pt^0 with small $[\mathrm{Pt}^0]/[\mathrm{PE}]$, the effect levels off at a $[\mathrm{Pt}^0]/[\mathrm{PE}]$ of ~0.17, where mobilities of 1.6×10^{-2} cm^2 V^{-1} s^{-1} (electrons) and 1.4×10^{-2} cm^2 V^{-1} s^{-1} (holes) are reached (at $F = 3.8 \times 10^4$ V cm^{-1}, cf. Figure 3 top). These values are an order of magnitude higher than those of the neat PPE. Higher Pt^0 contents did not further increase μ. Thus, as indicated by the optical data, the cross-link density may have reached a saturation limit, and no further cross-links but complexes of the type EHO−OPPE−Pt^0−styrene are formed (Scheme 1). Further, an excessive complexation may limit the effective conjugation length of the PPE. The EHO−OPPE−Pt^0 networks display the same field dependence as the parent PPE, which suggests that introduction of Pt^0 preserves the large off-diagonal disorder in the network.

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} cm^2 V^{-1} s^{-1}).[3] 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.

Acknowledgment. This work was supported by DuPont, the Goodyear Tire and Rubber Co., the AFOSR Air Force Material Command (F49620-99-1-0018), and the New Energy and Industrial Technology Development Organization of Japan (NEDO). We thank F. Bangerter, W. Caseri, and C. Huber for valuable interactions and help with the NMR study, and Dr. C. Löwe for help with the Raman spectra.

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.

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JA026988+