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Metallic conductivity at low temperatures in poly(3,4-ethylenedioxythiophene) doped with PF_6

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The temperature dependences of the conductivity and magnetoconductivity of poly(3,4-ethylenedioxythiophene) doped with PF_6 (room-temperature conductivity of 200–300 S/cm) have been studied; $\sigma(T)$ is weakly temperature dependent with the characteristic resistivity ratio $\rho_r=\rho(1.4\ \mathrm{K})/\rho(291\ \mathrm{K})=1.5$–$2.8$. The sign of the temperature coefficient of resistivity (TCR) changes below 10 K from negative to positive for metallic samples with $\rho_r<2.1$; the temperature of the resistivity maximum, T_m, decreases with increasing ρ_r. High magnetic fields induce the transition from positive to negative TCR for all samples with $\rho_r<2.1$ and decrease the low-temperature conductivity (negative magnetoconductance) for samples with $\rho_r>2.1$. The conductivity at low temperatures is well described by a $T^{1/2}$ dependence in both cases (negative and positive TCR) in a magnetic field and with the magnetic field equal to zero. The magnetoconductance is negative, isotropic, and exhibits an H^2 dependence at low magnetic fields and an $H^{1/2}$ dependence at high magnetic fields. These results are successfully explained as resulting from the influence of electron-electron interactions on the low-temperature conductivity. [S0163-1829(97)00532-8]

I. INTRODUCTION

The synthesis of stable metallic materials has been an important research goal in the field of conducting polymers. In parallel with the development of stable conducting polymers, charge-carrier transport in the metallic state in such polymers has been the subject of intensive research.[1] Measurements of the temperature dependence of the conductivity, thermopower, magnetic susceptibility, and magnetoconductance of heavily doped conjugated polymers such as polyacetylene $[(CH)_x]$, polyaniline (PANI), polypyrrole (PPy), and poly(pherylene vinylene) (PPV) have demonstrated properties that are characteristic of disordered metals near the metal-insulator transition.[1] Although relatively high values of the room-temperature conductivity have been observed in heavily doped $(CH)_x$ and in heavily doped PPV, the negative temperature coefficient of resistivity (TCR) found in such polymers indicates that disorder plays an important role in limiting the metallic transport. Only recently has a positive TCR been found in heavily doped conjugated polymers: for $FeCl_3$-$(CH)_x$ in the temperature range 220–300 K (Refs. 2 and 3) and for PANI-CSA (comphorsulfonic acid) from room temperature down to 160 K.[4] A crossover from negative to positive TCR below 20 K has been reported for several polymers: PPy-PF_6,[1,5,6] PPV-AsF_6,[7] PPV-H_2SO_4,[8] K-$(CH)_x$,[9] ion-implanted PANI,[10] and PF_6 doped poly(3-methylthiophene) (PMeT-PF_6).[11] This low-temperature crossover in TCR was interpreted in terms of a competition between disorder and screening in the presence of electron-electron interactions in the regime of weak localization.[1] However, the physical origin of the TCR crossover at low temperatures in conducting polymers is not yet clearly understood.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a conjugated polymer which has a maximum in the optical absorption at around 2 eV, in the middle of the visible spectrum. After doping, PEDOT becomes highly conducting with electrical conductivities up to 200 S/cm; PEDOT shows good stability.[12–14] The details of charge-carrier transport in doped PEDOT films have not previously been thoroughly studied.

We present the results of transport studies of PEDOT films doped with PF_6 (PEDOT-PF_6) with room-temperature conductivities of 200–300 S/cm. The temperature dependence $\sigma(T)$ of PEDOT- PF_6 films is very weak with characteristic resistivity $(\rho=1/\sigma)$ ratio $\rho_r=\rho(1.4\mathrm{K})/\rho(291\ \mathrm{K})=1.5$–$2.8$. We conclude, therefore, that the PEDOT-PF_6 films are on the metallic side of the metal-insulator transition. The temperature coefficient of resistivity is negative for all samples down to 10 K, but becomes positive below 10 K for samples with $\rho_r<2.1$. As ρ_r becomes smaller, the resistivity maximum shifts to higher temperatures. Application of a high magnetic field induces the transition from positive to negative TCR for samples with $\rho_r<2.1$ and increases the low-temperature resistivity (negative magnetoconductance) for samples with $\rho_r>2.1$. The low-temperature conductivity is well described by $\sigma(T)$ proportional to $T^{1/2}$ in both cases (negative and positive TCR), both in a magnetic field and with the magnetic field equal to zero. The resistivity increases as H^2 at low magnetic fields, saturating to an $H^{1/2}$ dependence at high magnetic fields. The results are explained in terms of the influence of electron-electron interactions in the disordered metallic regime which characterizes the transport of PEDOT-PF_6 films.

II. EXPERIMENT

PEDOT-PF_6 films were prepared by anodic oxidation of 3,4-ethylenedioxythiophene (EDOT). An electrochemical

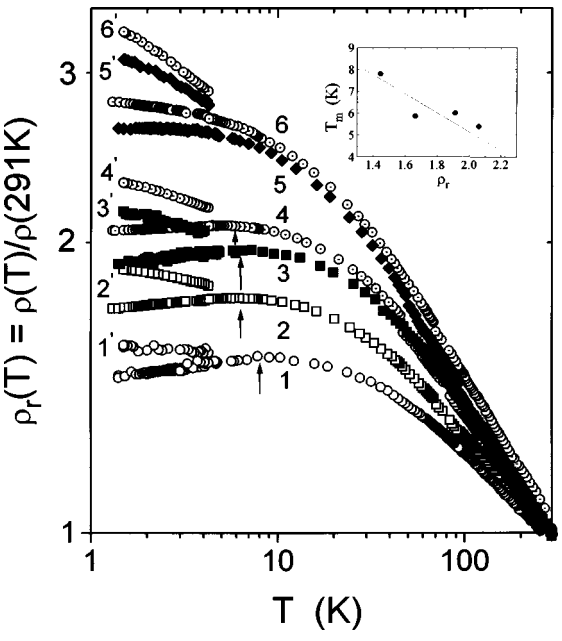


FIG. 1. Temperature dependence of the resistivity, $\rho_r(T) = \rho(T)/\rho(291\ \mathrm{K})$ for metallic PEDOT-PF_6 samples. The numbers on the curves refer to different samples with different $\rho_r(0)$ as listed in Table I. The data indicated with $1'$, $2'$, etc. indicate $\rho_r(T,H)$ a dependences for the corresponding samples at 8 T. The inset shows T_m as function of ρ_r.

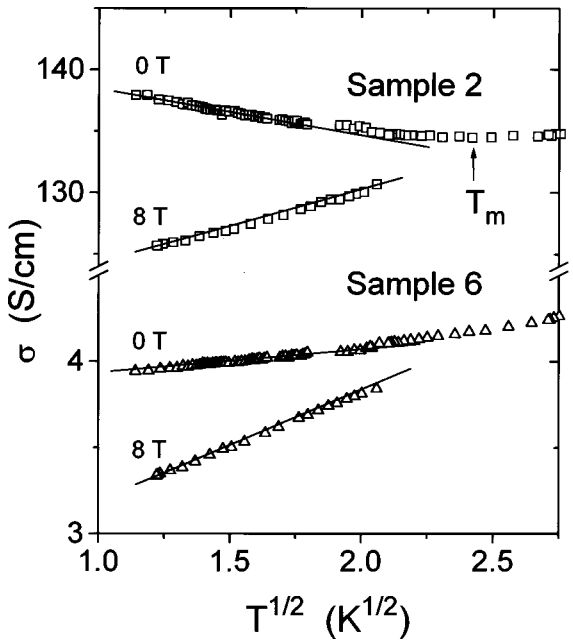


FIG. 2. Conductivity vs $T^{1/2}$ at low temperatures for metallic PEDOT- PF_6; sample 2 ($\rho_r = 1.67$) and sample 6 ($\rho_r = 2.76$) at zero field and 8 T.

cell containing a solution of 0.06 *M* of EDOT, and 0.06 *M* of tetrabutylammonium hexafluorophosphate in propylene carbonate (PC), was thoroughly purged with dry argon prior to use. PC and EDOT were freshly distilled prior to using. Tetrabutylammonium hexafluorophosphate was crystallized from ethanol and dried under vacuum at boiling toluene temperature for 3 days. A glassy carbon electrode and platinum foil were used for the working and counter electrodes, respectively. A constant current was applied (0.01–0.06 mA/cm^2) and the polymerization temperature maintained at −30 °C. Black, lustrous films with thicknesses from 10 to 300 μm were peeled from the electrode, washed twice in acetonitrile, and dried *in vacuum* for 72 h at room temperature.

The four-probe method was used for the conductivity measurements. Electrical contacts were made in planar geometry with conductive graphite adhesive. A computer-controlled measuring system, including a helium cryostat with a superconducting magnet (8 T), was used to obtain the dc conductivity data. To avoid any sample heating, the power dissipated in the samples at low temperatures was less than 1 μW. The temperature was measured with a calibrated Cernox™ resistor ($T = 300 - 1.3$ K). Magnetoconductance measurements were carried out with the magnetic fields both parallel and perpendicular to the film surface and current direction.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the normalized resistivity $\rho_r(T) = \rho(T)/\rho(291\ \mathrm{K})$ for typical PEDOT-PF_6 samples of various thicknesses with ρ_r less than 3, prepared under different polymerization conditions. For all samples with $\rho_r < 3$, $\rho_r(T)$ exhibited a negative TCR in the temperature range 290–10 K, as in disordered metals. For more highly conducting samples with $\rho_r < 2.1$, the TCR changed sign from negative to positive below 10 K, whereas for samples with $\rho_r > 2.1$ the sign of the TCR remains negative over the entire temperature range. For samples with $\rho_r < 2.1$, the temperature of the maximum in $\rho_r(T)$, T_m, shifts to higher temperatures (from 5.8 to 7.8 K) as ρ_r decreases (see inset to Fig. 1). The observed increase in conductivity below T_m was about 2–3 % of the room-temperature conductivity. Such ''metallic'' positive TCR is observed only for PEDOT-PF_6 samples with room-temperature conductivity $\sigma_{291\ \mathrm{K}} = 130 - 300$ S/cm and with $\rho_r < 2.1$. These features are similar to those observed earlier in films of PPy-PF_6 (Refs. 1, 5, and 6) and PMeT-PF_6.[11]

Figure 2 shows that the low-temperature conductivity of PEDOT-PF_6 films is well described by a $T^{1/2}$ law in both cases: positive and negative TCR. The application of magnetic fields up to 8 T leads to crossover from positive to negative TCR in the samples with $\rho_r < 2.1$; for samples with $\rho_r > 2.1$, the TCR becomes more negative at high magnetic fields, independent of the direction of the field with respect to the current direction.

The transport properties of PEDOT-PF_6 films can be summarized as follows: (i) the resistivity ratios are small ($\rho_r < 3$), (ii) the conductivity remains finite (and relatively high) as $T \to 0$, (iii) a positive TCR is found for the most highly conducting samples below 10 K, and (iv) the magnetoresistance is isotropic. These features, typical for doped crystalline semiconductors and for highly conducting polymers,[1] suggest that the three-dimensional (3D) localization-interaction model for disordered metallic systems near the metal-insulator transition[15,16] can be used for an explanation of low-temperature metallic transport in PEDOT-PF_6 films.

According to this model, the conductivity of disordered metallic systems is generally fitted by the form[15,16]

TABLE I. Properties of PEDOT-PF_6. $\rho_r=\rho(1.4\ \mathrm{K})/\rho(291\ \mathrm{K})$.

Sample	$\sigma_{291\ \mathrm{K}}$ (S/cm)	ρ_r	σ_0 (S/cm)	m	σ_0(H) (S/cm) at 8 T	m_H at 8 T	MR % at 8 T
1	131	1.45	93.67	−2.90	82.30	1.5	7.65
2	230	1.67	141.53	−3.10	118.50	5.77	9.60
3	205	1.92	110.24	−3.02	85.65	7.03	13.25
4	300	2.06	123.30	−1.37	98.52	8.24	8.31
5	100	2.64	29.40	0.34	21.15	3.44	17.73
6	11	2.78	3.76	0.15	2.58	0.61	18.38

$$\sigma(T)=\sigma_0+mT^{1/2}+BT^{p/2}, \tag{1}$$

where the second term on the right side results from electron-electron interactions and the third term is the correction to σ_0 resulting from localization effects. The value of p is determined by the temperature dependence of the scattering rate $\tau^{-1}\sim T^p$ of the dominant dephasing mechanism. This model predicts that in disordered metals electron-electron interactions play an important role in the low-temperature transport, whereas weak localization effects are dominant at higher temperatures.

The electron-electron interaction contribution to the low-temperature conductivity $\sigma_I(T)$ is given by[16]

$$\sigma_I(T)=\sigma_0+mT^{1/2}, \tag{2}$$

$$m=\alpha[\tfrac{4}{3}-(3\gamma F_\sigma/2)], \tag{3}$$

$$\alpha=(e^2/\hbar)(1.3/4\pi^2)(k_B/2\hbar D)^{1/2}, \tag{4}$$

$$F_\sigma=32[(1+F/2)^{3/2}-(1+3F/4)]/3F, \tag{5}$$

where the Hartree factor F is the screened interaction averaged over the Fermi surface, α is a parameter depending on the diffusion coefficient D, and γF_σ is the interaction parameter where the value of γ depends on the details of the scattering. The sign of m is negative when the Hartree term in Eq. (3) dominates; i.e., $\gamma F_\sigma>\frac{8}{9}$. In the presence of a magnetic field, when the field exceeds the limit for Zeeman splitting, $g\mu_B H>k_B T$, m_H is given by[16]

$$m_H=\alpha[\tfrac{4}{3}-(\gamma F_\sigma/2)]. \tag{6}$$

As can be seen from Fig. 2, below 4.2 K, $\sigma(T)$ is well described by the $T^{1/2}$ dependence for both negative and positive TCR, in a magnetic field and in zero field. The parameters σ_0 and m are magnetic-field dependent; the magnetic field decreases σ_0 and suppresses the positive TCR at low temperatures, in good agreement with theoretical predictions for disordered systems on the metallic side of the metal-insulator transition in which the electron-electron interaction contribution is dominant at low temperatures. The fitting parameters m, m_H, σ_0, $\sigma_0(H)$ obtained from $T^{1/2}$ plots of the conductivity below 4.2 K are summarized in Table I. The negative sign of m found for the more metallic samples (with $\rho_r<2.1$ and positive TCR) implies that $\gamma F_\sigma>\frac{8}{9}$ in Eq. (3); thus, the Hartree term dominates below 4.2 K. Following the same approach as Refs. 1, 6, and 16, the parameters α and γF_σ have been estimated from the temperature dependences of the conductivity at 0 and 8 T. Since $\alpha=3/8(3m_H-m)$ and $\gamma F_\sigma=(m_H-m)/\alpha$, the corresponding values for α and γF_σ are 7.66 and 1.56, respectively, for sample 2 with positive TCR and 3.74 and 0.83, respectively, for sample 5 with negative TCR. These results are comparable to those found for PPy-PF_6 films[1,6] and doped semiconductors at doping levels near the metal-insulator transition.[16]

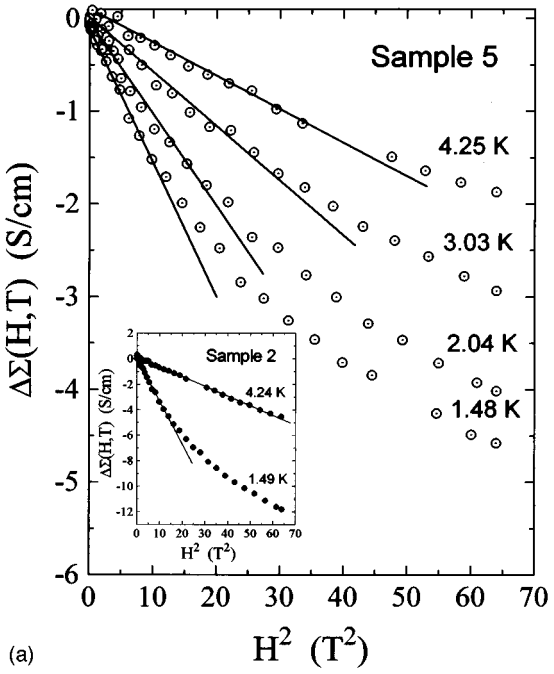
In the metallic regime, the magnetoconductance (MC) of PEDOT-PF_6 is negative (magnetoresistance is positive) and as can seen from Table I, increases as ρ_r increases. Figures 3(a) and 3(b) show that for both negative and positive TCR, the MC fits rather well to H^2 and $H^{1/2}$ dependences at low and high magnetic fields, respectively. The slopes of the $H^{1/2}$ lines are parallel at high fields for the various temperatures. Similar results were obtained for magnetic fields both parallel and perpendicular to the sample surface and current direction. This MC behavior is in agreement with the 3D localization-interaction model for disordered metallic systems and confirms that the electron-electron interaction contributions dominant at low temperatures (i.e., in comparison with the weak localization contribution).

The MC actually involves a competition between two contributions: weak localization and electron-electron interaction effects. Weak localization leads to positive MC in the absence of strong spin-orbit effects, while the electron-electron interaction gives only negative MC. Since only negative MC has been found in PEDOT-PF_6 films within temperature range 4.2–1.4 K, the dominant contribution to MC must result from the electron-electron interaction. The contribution to the MC in this case can be written as $\Delta\Sigma(H,T)=\sigma(H,T)-\sigma(0,T)$:[15,16]

$$\Delta\Sigma_I(H,T)=-0.041(g\mu_B/k_B)\alpha\gamma F_\sigma T^{-3/2}H^2,\quad g\mu_B H\ll k_B T, \tag{7}$$

$$\Delta\Sigma_I(H,T)=\alpha\gamma F_\sigma T^{1/2}-0.77\alpha(g\mu_B/k_B)^{1/2}\times\gamma F_\sigma H^{1/2},\quad g\mu_B H\gg k_B T. \tag{8}$$

Thus at low and high fields, $\Delta\Sigma_I(H,T)$ is proportional to H^2 and $H^{1/2}$, respectively, in agreement with the low-temperature behavior in metallic PEDOT- PF_6 films. As can be seen from Fig. 3(a), the slopes of the H^2 dependences increase when the temperature is decreased from 4.2 down to 1.48 K. At the same time, the upper limit of the field for the H^2 dependences is decreased, consistent with the temperature dependence of the electron-electron interaction contribution to the MC that results from Zeeman splitting of the



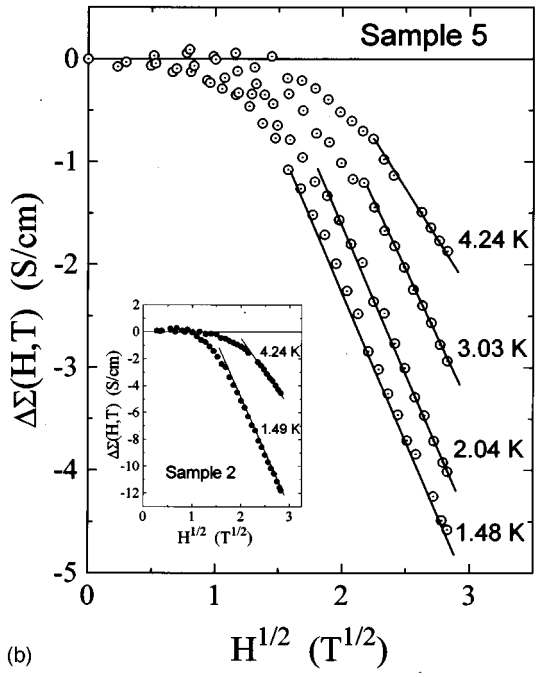


FIG. 3. (a) Magnetoconductance vs H^2 for metallic PEDOT-PF_6 sample 5 ($\rho_r=2.64$) at various temperatures. The inset shows similar data for sample 2 ($\rho_r=1.67$). (b) Magnetoconductance vs $H^{1/2}$ for metallic PEDOT- PF_6 sample 5 ($\rho_r=2.64$) at various temperatures. The inset shows similar data for sample 2 ($\rho_r=1.67$).

spin-up and spin-down bands. The MC of PEDOT-PF_6 films in high magnetic fields follows an $H^{1/2}$ dependence. Using Eq. (8) to determine the parameter γF_σ from the slope of the high-field dependence [Fig. 3(b)], the values for γF_σ are 1.18 for sample 2 and 0.86 for sample 5, closely consistent with those obtained from the temperature dependence of the conductivity. The good agreement once again implies that the MC at high fields arises from the electron-electron interaction.

The importance of the electron-electron interaction was

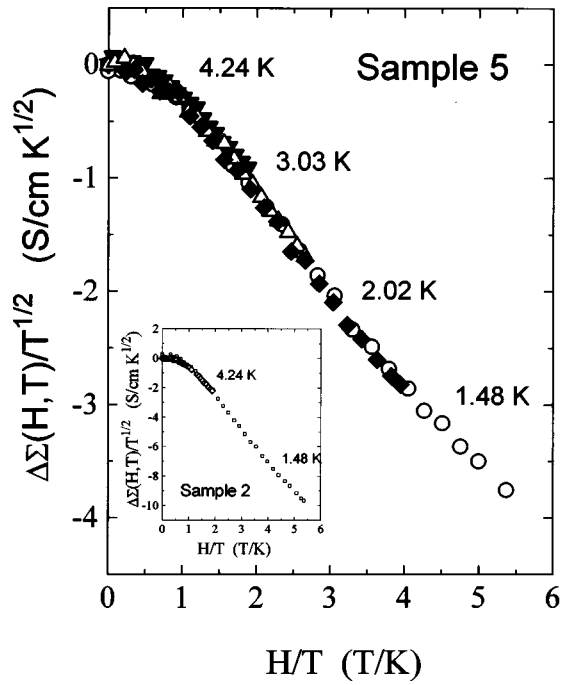


FIG. 4. $\Delta\Sigma(H,T)/T^{1/2}$ vs (H/T) plots for PEDOT- PF_6 sample 5 ($\rho_r=2.64$) at various temperatures. The inset shows similar data for sample 2 ($\rho_r=1.67$).

confirmed by the universal scaling behavior of the MC in metallic PEDOT-PF_6 films. According to this method,[17] the electron-electron interaction contribution to the MC follows a universal scaling law given by $\Delta\Sigma(H,T)=\sigma(H,T)-\sigma(0,T)\propto T^{1/2}f(H/T)$, where $f(H/T)$is determined by the interaction theory.[15] Figure 4 shows the plot of $[\Delta\Sigma(H,T)/T^{1/2}]$ versus (H/T) for PEDOT-PF_6 samples at various temperatures. The results are in excellent agreement with universal scaling behavior expected when the electron-electron interaction contribution is dominant.

IV. CONCLUSIONS

We have studied the temperature dependence of the dc conductivity and the magnetoconductivity of free standing PEDOT films prepared by anodic oxidation and doped with PF_6; the room-temperature conductivities are 200–300 S/cm. The principal results and conclusion are the following.

(a) The temperature dependence of the conductivity was very weak, with characteristic resistivity ratio $\rho_r=\rho(1.4\ \mathrm{K})/\rho(291\ \mathrm{K})=1.5$–$2.8$. We conclude, therefore, that these films are on the metallic side of the metal-insulator transition.

(b) The sign of temperature coefficient of resistivity changes at low temperatures (below 10 K) from negative to positive for metallic samples with $\rho_r<2.1$, and the temperature of the conductivity minimum, T_m, decreases from 5.8 to 7.8 K with increasing ρ_r.

(c) High magnetic fields induce a transition from positive to negative TCR for all samples with $\rho_r<2.1$ and decrease the low-temperature conductivity for samples with $\rho_r>2.1$.

(d) At low temperatures, the conductivity is well described by a $T^{1/2}$ dependence for samples with either negative or positive TCR, with and without a magnetic field.

(e) The magnetoconductance is negative, isotropic, and

follows H^2 and $H^{1/2}$ dependences at low and high magnetic fields, respectively, for samples with either negative or positive TCR.

The results indicate that the localization-interaction model is satisfactory for explaining both $\sigma(T)$ and MC for both positive and negative TCR and that the electron-electron interaction contribution to the low-temperature transport is dominant in PEDOT-PF_6.

The transition from negative to positive TCR at low temperatures, and the dominance of the electron-electron interaction contributions to $\sigma(T)$ and to the MC have now been observed in a number of conducting polymers, including PPy-PF_6.[1,5,6] PMeT-PF_6,[11] and PEDOT-PF_6, a well as in PEDOT doped with BF_4 and CF_3SO_3.[18] We conclude, therefore, that the transition from negative to positive TCR at low temperatures, with dominant contributions from the electron-electron interaction to $\sigma(T)$and to the MC, is not a feature specific to these systems, but a general phenomenon in highly conducting conjugated polymers. Given this apparent generality, extension of the conductivity and magnetoconductivity measurements of metallic polymers with positive TCR to temperatures below 1.3 K should be carried out to probe this phenomenon more completely.

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