Intrinsic Charge Transport on the Surface of Organic Semiconductors

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The air-gap field-effect technique enabled realization of the intrinsic (not limited by static disorder) polaronic transport on the surface of rubrene (C_{42}H_{28}) crystals over a wide temperature range. The signatures of this intrinsic transport are the anisotropy of the carrier mobility, \( \mu \), and the growth of \( \mu \) with cooling. Anisotropy of \( \mu \) vanishes in the activation regime at low temperatures, where the transport is dominated by shallow traps. The deep traps, introduced by x-ray radiation, increase the field-effect threshold without affecting \( \mu \), an indication that the filled traps do not scatter polarons.

One of the problems of experiments with organic semiconductors is realization of the intrinsic, not limited by static disorder charge transport. The difficulty of its demonstration is related to the polaronic nature of the charge carriers in organic molecular crystals (see, e.g., [1]): small polarons can be trapped by numerous types of crystal defects. The benchmark in the study of the intrinsic transport has been established in time-of-flight (TOF) experiments [2], which probe the charge transport in the bulk ultrapure organic crystals at small carrier densities. The intrinsic transport in TOF experiments is characterized by an increase of the carrier mobility, \( \mu \), with cooling and a pronounced anisotropy of \( \mu \). Theoretical treatment of these results was based on the Holstein concept of small polarons (see, e.g., [1,3]).

Until recently, the experimental tool used to probe the intrinsic charge transport on the surface of organic semiconductors was unavailable: the current flow in the organic thin-film transistors (TFTs) is typically dominated by disorder [4]. Fabrication of the single-crystal organic field-effect transistors (OFETs) (see, e.g., [5,6]) provides an opportunity to study the charge transport on the organic surface with significantly reduced disorder. It also offers a possibility to explore the regime of high charge densities, many orders of magnitude greater than in the TOF experiments, which may lead to observation of new electronic phases. However, despite recent technological advances, realization of the intrinsic transport on the organic surface remains a challenge because the concentration of defects at the surface is typically higher than in the bulk.

In this Letter, we report on the observation of the intrinsic transport of field-induced charges on the surface of single crystals of rubrene (C_{42}H_{28}). Application of a novel experimental technique based on the “air-gap” transistor stamps [7] allowed realization of a high mobility of \( p \)-type carriers, \( \mu(300 \text{ K}) \approx 20 \text{ cm}^2/\text{V}s \). Two signatures of the intrinsic transport—the mobility increase with decreasing temperature and the mobility anisotropy—have been observed in the temperature range \( \sim 150–300 \text{ K} \). At lower temperatures, where the charge transport is dominated by shallow traps, \( \mu \) decreases exponentially with cooling and its anisotropy vanishes.

The single crystals of rubrene have been grown from the vapor phase [5]. We have used the transistor stamps based on elastomeric polydimethylsiloxane (PDMS) substrates with a surface relief pattern (see the inset of Fig. 1) [7]. The continuous metal film, deposited on the stamp by thermal evaporation of gold, breaks at the vertical walls of the pattern imprinted on the PDMS surface: this produces the electrically isolated source, drain, and gate electrodes. The gate is recessed from the level of the source and drain pads by 3 to 5 \( \mu \)m. Fabrication of the field-effect structures is completed after the organic crystal is laminated against the surface of the stamp [8].

FIG. 1 (color online). The surface conductivity, \( \sigma_{\parallel} \), as a function of the gate voltage, \( V_g \), measured with the 4-probe air-gap transistor stamp along the \( b \) axis of rubrene (the source-drain voltage \( V_{SD} = 5 \text{ V} \), the drain is grounded). The inset schematically shows the transistor stamp: \( L = 0.75 \text{ mm} \), \( D = 0.25 \text{ mm} \), \( W = 1.25 \text{ mm} \), \( t = 5 \mu \text{m} \); \( C_i = 0.2 \text{ nF/cm}^2 \).
The charge carriers are injected in OFETs through the Schottky barriers at the metal/organic interface [10]. In order to exclude the contact effects, we have used the 4-probe configuration [5]. Figure 1 shows the dependence of the sheet conductance $\sigma_{SD} = (D/W)(I_{SD}/V)$ on the gate voltage $V_g$ measured at a constant source-drain voltage $V_{SD}$ ($I_{SD}$ is the source-drain current, $V$ is the voltage difference between the voltage probes separated by a distance $D$, and $W$ is the channel width). At large $V_g$, the dependences $\sigma_{SD}(V_g)$ are linear: this regime corresponds to the $V_g$-independent mobility of carriers $\mu = \sigma_{SD}/en$ ($n$ is the two-dimensional density of mobile field-induced carriers). The carrier mobility in the linear regime is proportional to the slope of $\sigma_{SD}(V_g)$ dependences, $\mu = (1/C_i)(d\sigma/dV_g)$ [11], where $C_i$ is the specific capacitance between the gate and the channel (the gate dielectric is air or vacuum, depending on the experimental conditions). For the estimate of $\mu$, we have used the capacitance 0.2 nF/cm$^2$ calculated from the device geometry; this value is consistent with the direct measurements of $C_i$ in the test structures formed by lamination of the stamp against a metallic surface [7]. This definition of $\mu$ assumes that all carriers with the density $n = [C_i(V_g - V_{th})]/e$, induced by the transverse electric field above the threshold, are mobile and their energies are within the highest occupied molecular orbital (HOMO) band. A weak dependence $\mu(V_g)$ observed for our field-effect structures justifies this assumption. For comparison, the mobility in organic TFTs [12] and amorphous silicon ($\alpha$-Si:H) FETs [13] are strongly $V_g$ dependent; in the latter case, the density of localized states is so high that the Fermi level at the surface remains below the bottom of the conduction band even at largest $V_g$, and the conduction is governed by the multiple trap and release (MTR) mechanism.

Figure 1 shows the evolution of the $\sigma_{SD}(V_g)$ dependences measured along the $b$ axis of rubrene with decreasing temperature. The mobility, proportional to the slope $d\sigma_{SD}/dV_g$, initially increases, reaches a maximum at $T \approx 150$ K, and decreases rapidly with further cooling (see also Fig. 2). The mobility measured along the $a$ axis is found to be systematically lower by a factor of 2.5–3 at 300 K, in line with our recent study [14]; this anisotropy is due to a stronger $\pi-\pi$ overlap in the $b$ direction in rubrene crystals (the molecular packing is shown in the inset of Fig. 3). The mobility anisotropy persists with cooling down to $T \approx 150$ K. The increase of the field-effect threshold with decreasing temperature (Figs. 1 and 2) precludes measurements of $\mu$ below 100 K [15].

On the basis of our results, we can qualitatively reconstruct the energy diagram of the electronic states near the HOMO level in the studied rubrene crystals (see the inset of Fig. 2). Within the HOMO-LUMO (lowest unoccupied molecular orbital) gap, there are localized electronic states (traps) associated with the crystal defects, such as chemical impurities, structural disorder, and surface states. Injection of $p$-type carriers results in filling the traps and shifting the Fermi energy at the organic surface, $E_F$, towards the HOMO level. Below the field-effect threshold ($|V_g| < |V_{th}|$), the injected charge is trapped in the localized states with energies separated by more than a few $k_BT$ from the HOMO level (the deep traps). When the Fermi level reaches the traps with energies within a few $k_BT$ from the HOMO level (the shallow traps), the surface conductivity increases dramatically by many orders of magnitude, owing to the thermal excitation of the carriers from the shallow traps to the HOMO level.

With cooling, the borderline between deep and shallow traps shifts towards HOMO. The concentration of deep traps with energies $\geq$ few $k_BT$ above the HOMO level, $N_{tr} = (C_iV_{th})/e$, increases from $0.7 \times 10^{10}$ cm$^{-2}$ at 300 K to $2 \times 10^{10}$ cm$^{-2}$ at 150 K. Interestingly, the quasilinear
anisotropy of 15 not unique: the values of naphthalene and anthracene [2]. This high mobility is
20 cm$^2$/V s in rubrene exceeds by a factor of 10 $\mu$ (300 K) observed in the TOF experiments with
naphthalene and anthracene [2]. This high mobility is not unique: the values of $\mu$ for most of the studied
crystals were within the interval 15–20 cm$^2$/V s. Note that the electric field along the conduction channel in
our experiment (~50 V/cm) is by several orders of magnitude smaller than that in the TOF measurements.
Therefore, detrapping due to the large drag fields can be neglected.

Two transport regimes are clearly seen in Fig. 2: (i) at high temperatures (150–300 K), the mobility is strongly
anisotropic and increases with cooling; (ii) at $T < 150$ K, the mobility rapidly decreases with cooling, and the
anisotropy of $\mu$ vanishes. The low-temperature drop of the mobility can be fitted by an Arrhenius dependence
$\mu(T) = \mu_0 \exp(-E_a/k_B T)$ with the activation energy $E_a = 70$ meV, which is the same for both
crystallographic directions (see also the inset of Fig. 4). We argue that the former regime corresponds to the intrinsic
electronic transport, whereas at low temperatures the transport is dominated by the multiple trapping and re-
leasings of carriers by shallow traps [12]. Typically, the increase of $\mu$ with cooling is observed for the devices
with $\mu^b(300 \text{ K}) \geq 10 \text{ cm}^2$/V s. For the devices with $\mu^b(300 \text{ K}) < 10 \text{ cm}^2$/V s (which constitute a
small fraction of all studied devices), $\mu$ is almost $T$ independent at high $T$, and exponentially decreases at lower $T$
with $T_0$ similar to that for the higher-$\mu$ devices (Fig. 4).

Observation of the intrinsic transport at high $T$ does not imply that the trapping is completely eliminated. On
the contrary, the higher the temperature, the higher the total number of shallow traps involved in the trap-and-
release processes. However, at high enough $T$, the time that a polaron spends within a shallow trap with energy
$E_a$, $\tau_u = \exp(E_a/k_B T)$, can be much smaller than the time it propagates between the traps, $\tau$. In this case ($\tau_a <\tau$),
the effective drift mobility in the MTR model [16], $\mu_{eff} = \mu_0(\tau/\tau + \tau_u)$, is reduced to the intrinsic (trap-
free) mobility $\mu_0$. In the opposite limit ($\tau_a \gg \tau$), the charge transport is dominated by trapping and $\mu_{eff} = \mu_0(\tau/\tau_u) = \exp(-E_a/k_B T)$. This regime is observed for
the studied OFETs at $T < 150$ K. Note that the crossover from the intrinsic to the thermally activated transport in
the bulk has been observed in the TOF measurements of organic crystals [17] with ppm impurity concentrations
that are close to the trap density in the studied rubrene crystals.

Our experiments show that the mobility anisotropy vanishes in the trap-dominated regime (Fig. 2). This observation is consistent with the MTR model. Indeed, the time of propagation of the carrier between the traps, $\tau$, is inversely proportional to the intrinsic mobility in the direction of propagation (e.g., $\tau^b \propto 1/\mu^b$). Thus, for an isotropic distribution of traps in the crystal, one might expect vanishing of the anisotropy of $\mu_{\text{eff}}$ in the regime $\tau_0 \gg \tau$.

In order to better understand charge trapping, we deliberately introduced defects in the rubrene crystals by exposing them to the x-ray radiation [18]. The ionizing radiation breaks the molecules and produces new chemical species that act as local defects in the crystal structure [19]. The trans-conductance characteristics of the rubrene OFET measured along the $a$ and $b$ axes before and after the x-ray exposure are shown in Fig. 3; the corresponding $\mu(T)$ and $V_{\text{th}}(T)$, measured by the 4-probe technique, are shown in Fig. 4. The x-ray treatment significantly increases $V_{\text{th}}$ and thus the density of deep traps, without affecting $\mu(T)$. This indicates that (i) the x-ray does not create traps within $\sim 0.1$ eV from the HOMO level (shallow traps) and (ii) the deep traps, being filled above the threshold, do not affect the motion of mobile polaronic carriers.

To summarize, we have studied the transport of $p$-type polaronic carriers on the surface of single crystals of rubrene by the air-gap field-effect transistor stamps. This technique allowed us to minimize the density of surface defects/traps and to realize the intrinsic polaronic transport on the surface of organic semiconductors. Two transport regimes have been identified: (i) the intrinsic regime observed at high temperatures, where the mobility is anisotropic and increases with decreasing temperature, and (ii) the shallow-trap-dominated regime, where the mobility decreases rapidly with cooling and the anisotropy of mobility vanishes. Our experiments with x-ray irradiation of organic crystals show that the filled deep traps do not contribute to the scattering of polarons.

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[8] Assembling of the rubrene FETs was performed in air; no degradation of the device performance was noticed after prolonged storage of the crystals in air and in the dark.


[15] The field-effect threshold $V_{\text{th}}$ is determined as the voltage of the interception of linear interpolation of $\sigma(V_{g})$ curve and $V_{g}$ axis.


