Anomalous Cooling-Rate-Dependent Charge Transport in Electrolyte-Gated Rubrene Crystals

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Supporting Information

ABSTRACT: Although electrolyte gating has been demonstrated to enable control of electronic phase transitions in many materials, long sought-after gate-induced insulator–metal transitions in organic semiconductors remain elusive. To better understand limiting factors in this regard, here we report detailed wide-range resistance–temperature (R–T) measurements at multiple gate voltages on ionic-liquid-gated rubrene single crystals. Focusing on the previously observed high-bias regime where conductance anomalously decreases with increasing bias magnitude, we uncover two surprising (and related) features. First, distinctly cooling-rate-dependent transport is detected for the first time. Second, power law R–T is observed over a significant T window, which is highly unusual in an insulator. These features are discussed in terms of electronic disorder at the rubrene/ionic liquid interface influenced by (i) cooling-rate-dependent structural order in the ionic liquid and (ii) the intriguing possibility of a gate-induced glassy short-range charge-ordered state in rubrene. These results expose new physics at the gated rubrene surface, pointing to exciting new directions in the field.

Electrolyte gating in the field-effect transistor (FET) geometry has emerged as an effective technique to induce very high charge carrier densities \((10^{13}–10^{15} \:\text{cm}^{-2})\) at surfaces. Accumulation of such charge densities has led to a series of breakthroughs in electrical control of ground states, including gate-induced insulator–metal transitions, superconductivity, and ferromagnetism. These achievements have been largely limited to electrolyte-gated transistors (EGTs) based on inorganic materials, however, such as oxides and two-dimensional (2D) materials. Although tuning transitions among electronic ground states in organic conductors has been an active area since the 1970s, the techniques used to control charge density (e.g., chemical doping, charge-transfer interactions, etc.) are discrete and irreversible. Notably, gate-tuned electronic phase transitions such as insulator–metal transitions, or even superconducting transitions, remain elusive in organic semiconductor EGTs.

Driven by the above, several recent studies have reported EGTs based on single crystals of the benchmark organic semiconductor rubrene, which exhibits high hole mobility \((>10 \:\text{cm}^2 \:\text{V}^{-1} \:\text{s}^{-1})\) and bandlike transport in air-gap transistors. High hole densities (of order \(10^{13} \:\text{cm}^{-2}\)) have been induced on the surface of rubrene crystals using ionic liquid (IL) electrolytes, but, critically, without an insulator–metal transition. Rather, poorly understood conductance peaks have been observed versus gate voltage \((V_G)\), where the conductance decreases at the highest \(V_G\) magnitudes. Temperature \((T)\)-dependent measurements reveal conventional (activated or hopping-based) insulating transport at low \(|V_G|\), near-metallic behavior at the conductance peak, but then reentrance of anomalous, strongly localized transport at the highest \(|V_G|\).

Remarkably, near the conductance peak, the resistance decreases on cooling to as low as 120 K, reaching within a factor of 2 of \(\hbar/\varepsilon^2\). This is tantalizingly close to a 2D insulator–metal transition, and it is thus imperative to understand the reentrance of strongly insulating behavior at high \(|V_G|\).

While the origin of the unusual transport at the highest hole densities in rubrene is unclear, previous results suggest a key role for the rubrene/IL interface. Intrinsic electrostatic doping (without gate bias) and free carrier saturation have been observed at the rubrene/IL interface by charge modulation spectroscopy, for example, which are not present in rubrene FETs with conventional dielectrics. It has also been observed that the sizes of the ions in ILs impact device performance and peak mobility in rubrene EGTs, indicating that the Coulomb corrugation potential experienced by holes at the rubrene surface could be a limiting factor (unpublished results). Several studies have in fact suggested a role for interfacial electrostatic disorder at high bias in rubrene EGTs. Better understanding of the ion–hole interaction at the IL/rubrene interface would thus provide vital insight, both for device optimization and realization of metallicity on the rubrene surface.

In this work we have performed systematic wide \(T\) range resistance–temperature \((R–T)\) measurements on IL-gated rubrene crystals at multiple \(V_G\)s and cooling rates. Consistent with earlier observations, with increasing \(|V_G|\) the transport...
mechanism is found to crossover from thermally activated to a highly unusual power law $T$ dependence. More surprisingly, in the anomalous power law regime, devices are found to exhibit distinctly cooling-rate-dependent $R-T$. Specifically, significantly smaller resistances are achieved at low $T$ (e.g., 50 K) when cooled from high $T$ (e.g., 240 K) at faster cooling rates. These observations are discussed in terms of likely differences in structural order on the IL side of the IL/rubrene interface at different cooling rates, thereby influencing interfacial electrostatic disorder. Inspired by recent observations in related organic conductors,29 the fascinating possibility of glassy behavior due to geometrically frustrated short-range charge order at fractional filling is also discussed.

Rubrene EGTs were fabricated on polydimethylsiloxane (PDMS) stamps by first fabricating air-gap transistors and then filling the gap with IL (Figure 1a). The IL [1-butyl-1-methylpyrrolidinium][tris(pentafluoroethyl)trifluorophosphate] ([P14][FAP], Figure 1b) was chosen here as it provides a large $V_G$ stability window.24 Because of the mechanical rigidity of the frozen IL, such rubrene EGTs can survive to much lower temperatures than air-gap transistors by overcoming the thermal expansion mismatch between PDMS and rubrene. All electronic transport measurements were performed in a standard cryostat (a Quantum Design Physical Property Measurement System) with 4-terminal methods. $R-T$ data were taken both on cooling and warming, after cooling at the rates specified. More details on device fabrication and measurements are given in Experimental Methods.

The $R-V_G$ relationship at 200 K in a typical rubrene EGT is shown in Figure 1c. Note that these data were not acquired by sweeping $V_G$ because of the freezing point of the IL. Instead, $V_G$ was applied at 240 K, above the freezing point, and then the temperature was lowered to 200 K to record each $R$ value. (For a typical 300 K EGT transfer curve, see Figure S1 in the Supporting Information). Clearly, from Figure 1c, $R-V_G$ is nonmonotonic. As $V_G$ is driven from zero to $-1.5$ V, the resistance decreases, as expected, but then at $V_G < -1.5$ V an anomalous resistance increase sets in. As discussed above, such conductance peaks are common in EGTs based on organic crystals and polymers, arising because of a poorly understood mobility maximum.24,25,27,31 As in our prior work on rubrene, the minimum resistance here is within a factor of 2 of $h/e^2$, indicating proximity to a 2D metallic phase. Corresponding $R-T$ characteristics at a cooling rate of 1 K/min are shown in Figure 1d, where the nonmonotonic $R-V_G$ is apparent. $R-T$ is relatively weak at small $|V_G|$ (< 1.5

Figure 1. (a) Cross-sectional device structure of a rubrene EGT. (b) Molecular structures of rubrene (left) and [P14][FAP] (right). (c) $V_G$-dependent sheet resistance of a rubrene EGT at 200 K. (d) $T$ dependence of the sheet resistance (log scale) at each $V_G$ shown in panel c, at a 1 K/min cooling rate. (e) Arrhenius plots (log $R$ vs $1/T$) for $V_G = -0.5$, -1, and -1.5 V. Extracted activation energies are shown. (f) Log-log plot of $R-T$ for $V_G = -2$, -2.5, and -3 V. Shown are the onset temperatures of power law behavior and the extracted exponents. Data shown in panels e and f are the same as shown in panel d. All $R-T$ data are taken on warming.
V), but at $V_G \leq -2$ V, the resistance is first flat down to some $T$ before increasing rapidly at lower $T$. As shown in Figure 2e, at $-0.5$, $-1$, and $-1.5$ V, $R-T$ at low $T$ can be well fit by an Arrhenius function, $R \propto \exp(-E_A/k_B T)$, with $E_A$ as low as 8.2 meV at $-1$ V. At $-2$, $-2.5$, and $-3$ V, however, the log $R$--log $T$ plot in Figure 1f illustrates highly unusual power law $T$-dependence, i.e., $R \propto T^{-n}$, with $n$ consistently around 6. Note that the power law $R-T$ turns on abruptly below some fairly well-defined ($V_G$-dependent) $T \approx 100-160$ K and that it is obeyed over substantial $T$ and $V_G$ windows. Zabrodskii plots\(^{32}\) (Supporting Information Figure S2) confirm the crossover from thermally activated to power law behavior, consistent with our previous publication.\(^{25}\) This behavior is thus reproducible across devices.

In addition to these relatively slow cooling rate (1 K/min) $R-T$ measurements, data were also acquired on the same device (Figure 2) at order-of-magnitude faster cooling rates (10 K/min). The cooling rate is seen to have negligible impact for $V_G = -1$ and $-1.5$ V (Figure 2a,b). For $V_G = -2$ and $-2.5$ V, however, in the anomalous high-bias regime, substantially smaller low-$T$ resistance is found after fast cooling (Figure 2c,d). Significantly, this provides clear evidence of a kinetic effect in charge transport at large $|V_G|$ in rubrene EGTs, which was apparently overlooked in prior work. At high cooling rates such as 10 K/min, the rubrene surface at low $T$ is somehow kinetically trapped in a different electronic state than when it is cooled more slowly. Importantly, in the “fast-cooled” state, the resistance at low $T$ is smaller than at slow cooling rates, i.e., fast cooling is beneficial for charge transport.

It should be emphasized that cooling-rate-dependence is observed only in the anomalous high-bias regime, coincident with power law $R-T$. The starting temperature $T_s$ is 240 K here. (b) Influence of $T_s$ on $R_{\text{slow}}/R_{\text{fast}}$ (50 K). Note that these data were taken from a device other than those shown in Figures 1 and 2. A critical temperature is expected (dashed line) between 210 and 220 K. Here the device was first slowly cooled from 240 K to $T_s$ then fast-cooled to 50 K.

Figure 2. Cooling-rate-dependent $R-T$ curves (log scale), from the same device shown in Figure 1, at different gate voltages: (a) $-1$ V, (b) $-1.5$ V, (c) $-2$ V, and (d) $-2.5$ V. All data are shown at cooling rates of 1 and 10 K/min. Note the clear cooling rate dependence in panels c and d. All data are taken on both cooling and warming.

Figure 3. (a) Summary of the cooling rate dependence of the resistance at different gate voltages for 6 different devices. $R_{\text{slow}}/R_{\text{fast}}$ (50 K), i.e., the ratio of 50 K resistances at 1 and 10 K/min cooling rates, is plotted vs the magnitude of $V_G-V^*$. $V^*$ is defined in the text. Note the simultaneous onset of cooling rate dependence in all devices, coinciding with power law $R-T$. The starting temperature $T_s$ is 240 K here. (b) Influence of $T_s$ on $R_{\text{slow}}/R_{\text{fast}}$ (50 K). Note that these data were taken from a device other than those shown in Figures 1 and 2. A critical temperature is expected (dashed line) between 210 and 220 K. Here the device was first slowly cooled from 240 K to $T_s$ then fast-cooled to 50 K.

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parameter is $V^\circ$, the $V_G$ at which power law $T$-dependence is first detected. This latter parameter is introduced to enable facile comparison between devices, which tend to have slightly different onsets of power-law $R-T$. Figure 3a plots $R_{\text{slow}}/R_{\text{fast}}$ versus $[V_G] - [V^\circ]$, vividly illustrating that cooling-rate-dependent $R-T$ turns on simultaneously with the crossover from thermally activated to power-law $R-T$; the vertical dashed line marks the transition between these two regimes.

Additional information was obtained by varying the starting temperature ($T_0$) for fast-cooling. To do this, devices were first slowly cooled at 1 K/min from 240 K to some temperature $T_{\text{std}}$ below which they were fast-cooled at 10 K/min. $R_{\text{slow}}/R_{\text{fast}}$ at $T = 50$ K is then plotted as a function of $T_{\text{std}}$ in Figure 3b. Significantly, a critical $T_{\text{std}}$ between 210 and 220 K (vertical dashed line) is discovered, below which $R_{\text{slow}}/R_{\text{fast}}$ is very close to 1, i.e., there is no cooling rate dependence. This critical temperature coincides remarkably with the freezing point of the IL, [P14][FAP]. As shown in Supporting Information Figures S3 and S4, differential scanning calorimetry (DSC) and transport measurements indicate that the freezing point of [P14][FAP] is $\sim 215$ K. It is thus the cooling rate across the freezing point of the IL that affects transport in IL-gated rubrene EGTs. Fast cooling from temperatures below this has no influence on the electronic state, whereas fast cooling from above this does. Complementary to the above, we also performed experiments where fast cooling (at 10 K/min) was done from 240 to 200 K, followed by slow cooling to 50 at 1 K/min. $R-T$ under these conditions is identical to that obtained when the device is simply cooled to 50 at 10 K/min (Figure S4b in the Supporting Information). The dynamics of freezing of the IL are thus clearly important.

A final observation is provided in Figure 4, which plots $R_{\text{slow}}/R_{\text{fast}}(T)$, comparing 1 and 10 K/min cooling rates at $V_G = -2$ V. A clear onset temperature, $T^\circ$, is uncovered, below which cooling rate dependence kicks in. Although the device studied here is not identical to Figure 1, note that $T^\circ$ is quite similar to the point at which the resistance dramatically increases on cooling, following the anomalous power law $R-T$. Intriguingly, this $T^\circ$ is far beneath the IL freezing point. This indicates that although it is cooling across the IL freezing point that plays such an important role (Figure 3b), the cooling-rate-dependent $R-T$ does not develop until much lower $T$.

In terms of discussion of the above observations, we first note that it is known that the low-$T$ solid-state structure of ILs can be influenced by cooling conditions. To demonstrate this in our [P14][FAP], DSC measurements were performed at different cooling rates (Figure S3, Supporting Information). A freezing peak was clearly observed at 1 K/min but was suppressed at 10 K/min. The solid phase of [P14][FAP] thus exhibits stronger crystalline order when slow-cooled at 1 K/min but is more glassy (amorphous) when fast-cooled at 10 K/min. We propose that this provides a viable explanation for cooling-rate-dependent $R-T$ in rubrene/IL EGTs. Specifically, the electrostatic disorder experienced by holes at the rubrene surface due to the arrangement of ions in the IL is very likely influenced by the (cooling-rate-dependent) degree of ionic ordering. Interfacial electrostatic disorder in rubrene/IL devices has been discussed in terms of Coulomb-mediated trapping of holes at clusters of anions. These anion clusters emerge at negative $V_G$ from the anion/cation checkerboard anticipated on the IL side of the interface at $V_G = 0$. Hole conduction on the rubrene side of the interface is then percolative, occurring through a network of trap-free sites.

In this picture, or related ones, reduced crystalline order in the IL at fast cooling rates could result in a less ordered arrangement of traps. This IL configuration, as opposed to a more rigid crystalline one, could then be beneficial for percolative hole transport, thus explaining lower resistance after fast cooling. Within this picture, electrostatic disorder at the rubrene/IL interface is also likely responsible for the power law $R-T$, and we hope that this work will stimulate further theory in this context. Multiphonon hopping is one mechanism for power law $T$-dependence in insulators, but it is usually observed only in highly disordered systems, such as amorphous semiconductors, very different than single-crystal rubrene.

We also discuss another class of phenomena that could potentially explain our results: charge ordering. Recently, a number of organic conductors, such as BEDT-TTF-based compounds (bis(ethylenedithio)tetrathiafulvalene) have been found to display charge ordering. In these materials, an equilateral triangular structural motif leads to geometric frustration of charge ordering at fractional (1/4) filling. This leads to a short-range charge-ordered cluster glass, with strongly cooling-rate-dependent $R-T$, strikingly similar to our data on rubrene in some cases. Highly significant in this context is that the molecular arrangement in the close-packing plane of rubrene is essentially identical to that of the conducting plane of BEDT-TTF compounds. Both have herringbone motifs, the rubrene lattice in fact being even closer to an ideal equilateral triangle. Strong geometric frustration of charge order could thus be anticipated in rubrene. Moreover, the hole densities accumulated at the rubrene surface in EGTs are in the mid-$10^{13}$ cm$^{-2}$ range (Supporting Information Figure S1 and ref 25), corresponding to 1/3 to 1/4 filling, as in the reported charge cluster glasses.

A short-range charge-ordered cluster glass analogous to that seen in the BEDT-TTF compounds could potentially provide qualitative explanations for many aspects of our data. First, the sharp onset temperatures for strongly insulating behavior in Figure 1f could correspond to $V_G$-dependent charge-ordering temperatures, thus explaining the overall increase in resistance at high $[V_G]$ (Figure 1c) as fractional filling (e.g., 1/4) is approached. The cooling-rate-dependent $R-T$ of Figure 2c,d would then be natural, arising from the glassy short-range charge-ordered state, i.e., kinetic avoidance of charge order at high cooling rate. This would also qualitatively explain the data of Figure 4, where $R_{\text{slow}}/R_{\text{fast}}$ turns on sharply, reminiscent of a phase transition, at a temperature $T^\circ$. Importantly, in certain
charge-ordered systems, such as $\text{La}_{1-\delta}\text{Sr}_{\delta}\text{FeO}_3$, the unusual power law $R-T$ we report here has also been observed. While this is not well-understood, it nevertheless points to an important additional parallel with charge-ordered systems. While challenging, we note that in operando synchrotron X-ray scattering on rubrene EGTs at high bias could potentially provide a test for charge cluster glass behavior.

Finally, we note that one aspect of our data is difficult to understand within either of the pictures advanced. Specifically, it is difficult to reconcile that the onset of power law $R-T$ and strong cooling-rate dependence occurs below $\approx 160$ K (Figures 1f, 2c,d, and 4), while the temperature important for cooling rate dependence is $210-220$ K, i.e., the freezing point of the IL (Figure 3b). Within the picture of cooling-dependent structural ordering in the IL, it is difficult to understand why cooling rate dependence in $R-T$ emerges only far below the $215$ K freezing point. Similarly, within the charge cluster glass picture, it is difficult to understand why the IL freezing point is so important. In fact, additional experiments show that changing the cooling rate across the putative charge ordering temperature $T^*$ has no impact on $R-T$ (Figure S5, Supporting Information). One possible resolution involves interplay, across the interface, between rubrene charge ordering and IL structural ordering. Unlike the BEDT-TTF systems, the rubrene here is electrostatically doped via electric double layers. Because the electric double layer configuration will be different at different cooling rates, different charge-ordered states in the rubrene could be anticipated, and these may be frozen in below $215$ K.

In summary, we have reported extensive $V_G$- and cooling-rate-dependent $R-T$ measurements on a benchmark organic semiconductor/electrolyte interface: rubrene/[P14][FAP]. The anomalous high gate bias regime was studied, where a reentrant strongly insulating state prevents a 2D insulator–metal transition. In this regime we find a crossover from thermally activated to power-law $T$-dependence, as well as significant cooling-rate dependence, apparently overlooked in prior work. These results have been thoroughly discussed in terms of cooling-rate-dependent structural ordering in the ionic liquid, as well as possible short-range frustrated charge ordering near fractional filling. This work thus not only uncovers new physics at the rubrene/IL interface but also points to a clear need for additional experimental and theoretical work.

■ EXPERIMENTAL METHODS

Rubrene and [P14][FAP] ILS were purchased from Sigma-Aldrich. Rubrene crystals were grown by physical vapor transport, and device fabrication was based on previously established methods. First, a four-terminal rubrene-air-gap transistor was fabricated on a patterned PDMS (Dow Sylgard184) substrate by laminating a rubrene crystal across the channel so that the $bc$ crystal plane of rubrene (space group Cmca) is gated. The metal electrodes were formed by e-beam evaporation of Cr/Au (3/20 nm) prior to crystal lamination. Devices dimensions are channel length ($L = 150 \mu m$) and distance between 2 voltage-sensing probes ($\Delta L = 70 \mu m$). Channel width $W$ is determined by the width of the rubrene crystal, which is in the range of 200–600 $\mu m$. Next, a droplet of IL was dragged by a probe tip to fill the air-gap by capillarity, thus completing the fabrication process. For electrical characterization, devices were loaded into a Quantum Design Physical Property Measurement System and cooled to $240$ K to apply $V_G$. To measure $R-T$ characteristics, $V_G$ was held constant while the device was cooled to $50$ K at desired cooling rates. A Keithley 2612B source-measure unit and a Keithley 2022 multimeter were used to measure DC resistance between 50 and $240$ K at a constant drain voltage of $0.1$ V.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b01751.

Transfer curves for rubrene EGTs; additional analysis of temperature-dependent transport; DSC on [P14][FAP]; transport determination of the freezing point of [P14][FAP] and fast quenching data; additional cooling-rate-dependent transport data (PDF)

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Notes

The authors declare no competing financial interest.

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