

Supporting Information

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

Xinglong Ren, C. Daniel Frisbie, and Chris Leighton**

Department of Chemical Engineering and Materials Science, University of Minnesota,

Minneapolis, MN 55455, USA

1. Typical transfer curve and induced charge density in a rubrene EGT

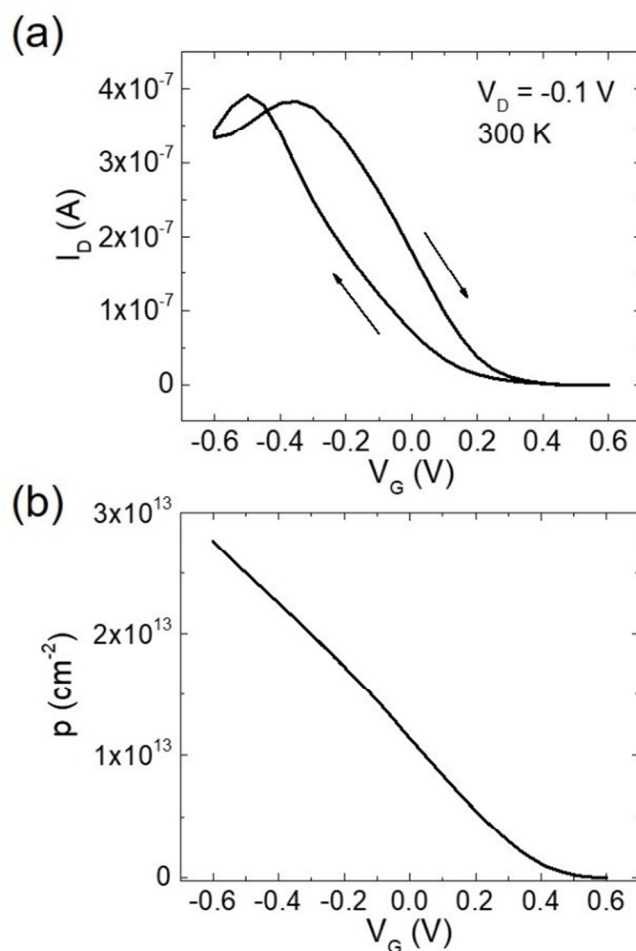


Figure S1. (a) Typical 300 K transfer curve for a rubrene EGT at a sweep rate of 50 mV/s. Device dimensions: $L = 300 \mu\text{m}$, $W = 340 \mu\text{m}$. (b) V_G -dependent hole density for the same device, as determined from gate displacement current measurements.

2. Verification of temperature dependence from Zabdorskii plots

To describe R - T characteristics, a reduced activation energy (W) as a logarithmic derivative of $R(T)$ can be defined as:

$$W = -\frac{d(\ln R)}{d(\ln T)}$$

If $R(T)$ follows a thermally-activated T -dependence of the form $R \propto \exp(T_0/T)^n$, the reduced activation energy then becomes:

$$\ln W = A - n \ln T$$

where A is a constant. The values of n are then determined from the slopes of Zabdorskii plots, *i.e.*, plots of $\ln W$ - $\ln T$.

If $R(T)$ follows a power law T dependence, on the other hand, of the form $R \propto T^{-m}$, then W becomes a constant ($W = m$), such that $\ln W$ - $\ln T$ plots should have zero slope.

In the context of the above, consider the data shown in Figure S2 below. For $V_G = -0.5$ V, -1 V, and -1.5 V, reasonable adherence to thermally-activated behavior is observed, *i.e.*, the $\ln W$ - $\ln T$ plots are reasonably close to straight lines with clearly negative slopes in the low T limit. For the other 3 curves, however, at $V_G = -2$ V, -2.5 V and -3 V, zero slope is observed over a significant T range, evidencing power-law behavior. These conclusions are supported by Arrhenius fitting and log-log fitting as in Figure 1 in the main article. Note that at higher temperatures, negative values of $\ln W$ are obtained in Figure S2, evidencing non-exponential, weak temperature dependence, with positive temperature coefficient of resistance.

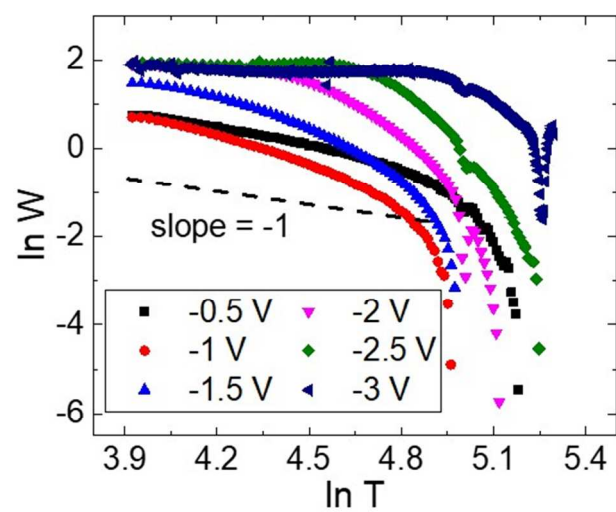


Figure S2. $\ln W$ - $\ln T$ plots for the data shown in Figure 1d.

3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were carried out using a TA Instruments Q1000 DSC with liquid nitrogen cooling capability. A sample of 5–10 mg was contained in a hermetically sealed aluminum pan. Data were acquired during cooling, on the first cooling and heating cycle performed, at 1 K/min and 10 K/min.

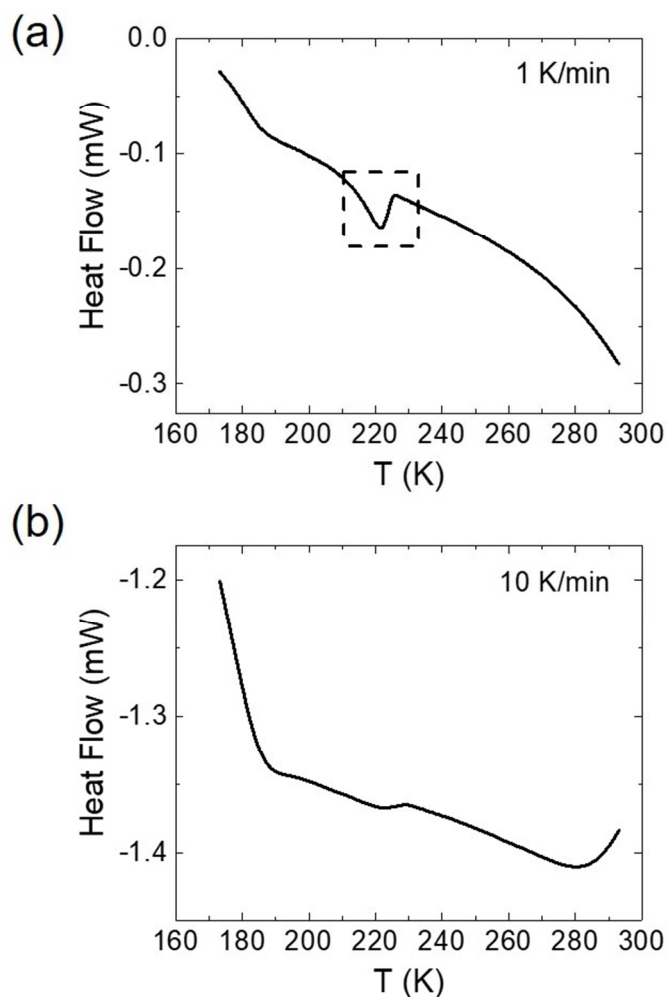


Figure S3. DSC data on [P14][FAP] taken during cooling at different cooling rates: (a) 1 K/min and (b) 10 K/min. A crystallization peak is observed at 1 K/min, but it does not show up at 10 K/min.

4. Freezing point of [P14][FAP] and fast quenching across the freezing point

The following transport experiment was also used to determine the freezing point of [P14][FAP]. A negative V_G (-2.5 V) was first applied at 240 K, then a device was cooled to 200 K and V_G was changed to 0 at 200 K. No change in resistance was observed after changing V_G since the IL was frozen and the charge carriers were “locked” in the channel by frozen ions. Next, the device was slowly warmed up at 1 K/min, and R - T was monitored (Figure S4a). A sharp increase in resistance was observed at ~ 215 K, suggesting that the IL ions became mobile (*i.e.*, the IL melted) and the charge density in the channel was significantly reduced (Figure S4a).

An additional R - T curve was also obtained by fast quenching across the freezing point followed by slow cooling (Figure S4b). After collecting R - T data at cooling rates of 1 K/min (line A) and 10 K/min (line B), we quenched the device from 240 K to 200 K at 10 K/min, and then changed the cooling rate to 1 K/min (line C). Clearly, line B and line C overlap, demonstrating that changing the cooling rate does not make a difference when the ions in the IL are no longer mobile.

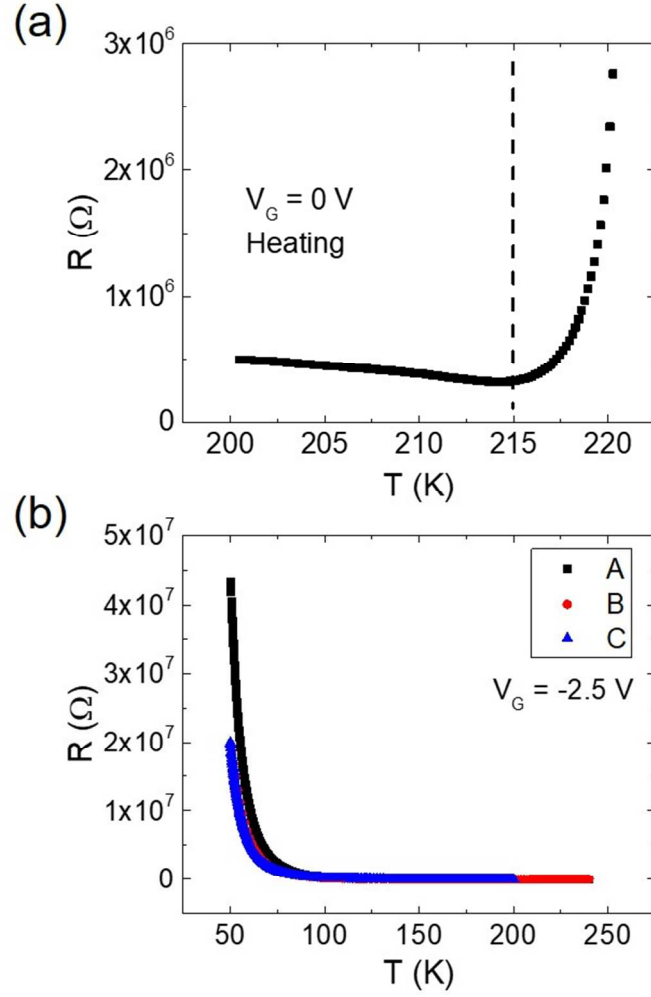


Figure S4. (a) R - T data taken during heating (1 K/min) after changing V_G from -2.5 V to 0 V at 200 K. An increase in resistance upon heating across ~ 215 K represents the melting of IL. (b) R - T data of the same device taken at different cooling conditions: 1 K/min from 240 K to 50 K (A), 10 K/min from 240 K to 50 K (B), 10 K/min from 240 K to 200 K and then 1 K/min to 50 K (C). Line B and line C match very well.

5. Changing the cooling rate across T^*

First, R - T data at 1 K/min and 10 K/min were collected and the ratio $R_{\text{slow}}/R_{\text{fast}}$ was plotted as a function of T (Figure 4 in the main article). Based on such data, the temperature T^* is defined. The following measurements were then performed at $T \leq 200$ K, *i.e.*, with the IL in the solid state. The device was first quenched from 200 K to a desired temperature (180 K, 120 K, or 70 K) at 10 K/min, and then the cooling rate was changed to 1 K/min while the R - T relationship was recorded (Figure S5). The 3 curves in Figure S5 overlap with each other, indicating that, once cooled below the IL freezing point, cooling rate across T^* has little influence on R - T .

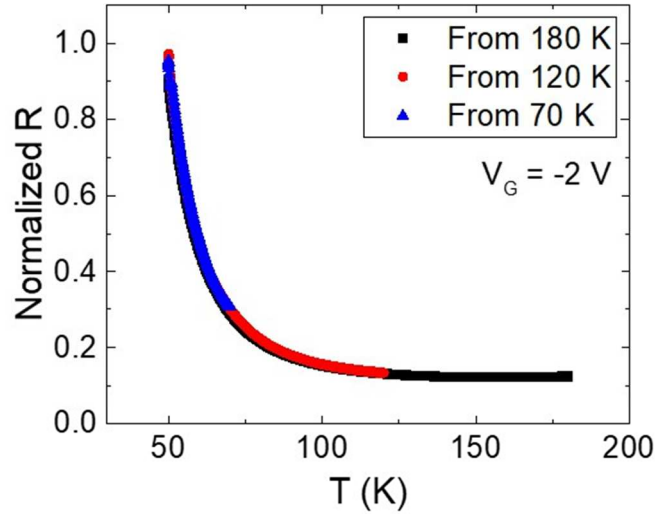


Figure S5. Slow-cooling resistance normalized by R_{fast} (50 K) for the same device in Figure 4 after quenching from 200 K to different start temperatures: 180 K, 120 K, and 70 K. The 3 curves overlap very well.