Electronic functions of solid-to-liquid interfaces of organic semiconductor crystals and ionic liquid

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Abstract. The environment of surface electrons at “solid-to-liquid” interfaces is somewhat extreme, subjected to intense local electric fields or harsh chemical pressures that high-density ionic charge or polarization of mobile molecules create. In this proceedings, we argue functions of electronic carriers generated at the surface of organic semiconductor crystals in response to the local electric fields in the very vicinity of the interface to ionic liquid. The ionic liquids (ILs), or room temperature molten salts, are gaining considerable interest in the recent decade at the prospect of nonvolatile “green solvents”, with the development of chemically stable and nontoxic compounds. Moreover, such materials are also applied to electrolytes for lithium ion batteries and electric double-layer (EDL) capacitors. Our present solid-to-liquid interfaces of rubrene single crystals and ionic liquids work as fast-switching organic field-effect transistors (OFETs) with the highest transconductance, i.e. the most efficient response of the output current to the input voltage, among the OFETs ever built.

1. Introduction
Room-temperature ionic liquids (RTILs) is gaining considerable interest at the prospect of nonvolatile “green solvents”, with the development of chemically stable and nontoxic compounds in the recent decade [1]. Such materials have been attractive not only for technologies to produce chemicals without volatilizing organic solvents both in industry and chemistry laboratories, but also for applications to energy conversion and energy storage devices, making use of their fast ionic diffusion [2]. They are indeed being applied to electrolytes for lithium ion batteries and electric double-layer (EDL) capacitors. However, the use of the RTILs for electronic devices is not as developed as the above areas. In this letter, we disclose a new class of organic semiconductor devices functionalized by the fast ionic motion in the room temperature molten salts. Solid-to-liquid interfaces are formed between organic semiconductor single crystals and ionic liquids, so that the structures work as fast-switching organic field-effect transistors (OFETs) with the highest transconductance, i.e. the most efficient response of the output current to the input voltage, among the OFETs ever built.

2. Organic field-effect transistors with electric double layers
OFETs are candidate for next generation low-cost devices producible by simple fabrication processes. Fabricating a layered strucure of organic semiconductor and an electronically insulating film, carrier density $Q$ in the organic semiconductor is controlled by gate electric field $E_g$ applied to the insulating

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layer, as \( Q = \varepsilon E_G \). Carrier density of organic semiconductor layer is modified by the application of gate voltage \( V_G \) to the insulating layer, so that current is controlled from zero to finite values, giving rise to the on-off switching function. The OFETs most commonly consist of organic polycrystalline thin films and dielectric insulators such as silicon dioxide. With typical thickness of the gate dielectric insulators of a few hundred nanometers, tens of volts are needed to apply sufficient \( E_G \) to accumulate enough \( Q \), so that practical current amplification is achieved. Though the use of gate dielectrics with minimum thickness enables low-power operation with small \( V_G \), leakage current through the thin insulator becomes more serious for such devices, causing additional energy loss. Current enhancement ratio in response to \( V_G \) defines transconductance, which parameterizes the performance of the transistor devices and is proportional to mobility \( \mu \) of the carriers.

Not like the conventional thin-film OFETs, we use RTILs for the gate insulating layer and organic single crystals for the semiconductor layer. When \( V_G \) is applied to the ionic liquid layer, the EDLs are formed as the result of the ionic motion. Noting that gate electric field is confined only to the double layers with the thickness of 1 nm, only a fraction of volt is necessary to get the same \( E_G \) and therefore \( Q \) as compared to the above described devices with more than two orders thicker gate dielectrics. If the mobility is similar to that in the dielectric/semiconductor interface, the same current can be achieved with such a small gate voltages. Moreover, since organic single crystal transistors have much higher carrier mobility than polycrystalline thin films, as shown in previous experiments [3,4], the transistor performance is further idealized.

3. Experimental

So far, there have been reports on the use of such polymer electrolytes as LiClO\(_4\) dissolved in poly(ethylene oxide) or ionic liquid sustained in a polymer gel [5,6]. However, these devices suffer from either poorer mobility or slow response to the \( V_G \) application, because of relatively slow ionic diffusion in the polymer platforms. Among them, the ionic-liquid gel device exhibits the best performance among the electrolyte OFETs [6]; their maximum response frequency of 5 kHz and the mobility up to 1 cm\(^2\)V\(^{-1}\)s\(^{-1}\). In order to make the best use of the ionic conduction in the RTILs, we developed a well structure to hold the poorly viscous liquid underneath organic single crystals by the capillary force; the well structure is shaped with polydimethylsiloxan (PDMS) elastomer on which rubrene single crystal is electrostatically attached as shown in Fig. 1(a). The gap height was typically 25 \( \mu \)m and the channel length \( L \) and width \( W \) were 180 \( \mu \)m and 250 \( \mu \)m, respectively.

Using pure ionic liquid of \( 1\)-ethyl-3-methylimidazorium bis(trifluoromethylsulfonyl)imid [emimTFSI] [Fig. 1(b)], whose ionic conductivity is as high as 10\(^{-2}\) Scm\(^{-1}\), the maximum cut-off frequency can reach MHz order with the well height of 20 \( \mu \)m. The ionic liquid was inserted into the gap space underneath the rubrene crystal so that the liquid-to-solid interface was formed to operate as an organic field effect transistor. Electrical measurements were performed with a Keithley Model 4200-SCS Semiconductor Characterization System to characterize the performances of the ionic-liquid gated transistor in comparison with air-gap gated one. Solartron 1260 and 1296 impedance analyzers were used to obtain capacitance of the ionic liquid over the frequency range from 0.1 Hz to 1 MHz with the application of AC voltage amplitude of 10 mV. The high mobility of the rubrene single crystals and the high capacitance of the EDL capacitor lead to the best transconductance in the devices.

Figure 1. (a) Structure of organic crystal / ionic liquid transistors. (b) \( 1\)-ethyl-3-methylimidazorium bis(trifluoromethyl-sulfonyl)imid [emimTFSI].
4. Results and discussion

The EDL capacitance $C_{\text{EDL}}$ of emimTFSI is measured using a test device consisting of the same PDMS structure, where the top electrode is composed of gold thin films as shown in Fig. 2(a). Solartron 1260 and 1296 impedance analyzers are used to obtain the frequency profiles over the range from 0.1 Hz to 1 MHz with the application of AC voltage amplitude of 10 mV. As shown in Fig. 2(b), the values of the capacitance increase with decreasing frequency to reach $4 \, \mu\text{Fcm}^{-2}$ at 10 Hz. If we assume the thickness of the EDLs to be typical length scales of the ionic molecules, the relative dielectric constant $\varepsilon$ would be $\sim 5$ for this frequency. Though the reason of the frequency dependence in the range of 0.1-10 Hz has not been elucidated yet, it is suspected that rotational rearrangement of the ionic molecules is responsible for the observation of the slow relaxation. As a consequence of such high values for the EDL of emimTFSI, application of the gate voltage of 0.5 V accumulates the carrier density as high as $1.0 \times 10^{13} \, \text{cm}^{-2}$, which is comparable to the maximum carrier density that the usual SiO$_2$ devices can reach. It is to be emphasized that the EDL capacitance of the RTILs remains in the same order even at 1 MHz, demonstrating the fast ionic diffusion in response to the voltage application. Therefore, the EDL OFETs incorporating the RTILs allow switching operation at such a high frequency, which none of the previously reported devices with polymer electrolytes do.

![Figure 2](image2.png)

**Figure 2.** Capacitance of the electric double layers of emimTFSI the thickness of the liquid layer is approximately 25 $\mu$m. The inset shows the structure of the sample to measure capacitance of the ionic liquid.

![Figure 3](image3.png)

**Figure 3.** (a) Transfer and (b) output characteristics of the air-gap rubrene single-crystal transistor before filling the ionic liquid. Inset of (a) optical view of the device.
Before we introduce the RTIL, the rubrene single crystals are characterized by measuring transistor performance with the application of $V_G$ to the 25-µm air-gap layer, whose capacitance $C_{air}$ is 35 pF cm$^{-2}$ per area. Channel length $L$ and width $W$ are 180 µm and 250 µm, respectively. Figure 3(a) shows transfer characteristics of the air-gap transistor. Using the standard equation of 

$$
\mu = \frac{L}{W C_{air} V_D} \frac{dI_D}{dV_G},
$$

$\mu$ is estimated to be $\approx 11$ cm$^2$ V$^{-1}$ s$^{-1}$, which is comparable to the best value for the rubrene air-gap OFETs in literature.\[4\] The output characteristics show fairly good saturation behavior as shown in Fig. 3(b). We note that saturation mobility is evaluated to be almost the same value using the standard formula of

$$
\mu = 2L/W \left( \frac{d\sqrt{I_D}}{dV_G} \right)^2.
$$

After introducing proper amount of RTIL, the liquid filled in the gap is sustained stably by the capillary force. Figure 4(a) shows transfer characteristics of the device measured with the sweeping rate of 0.2 V s$^{-1}$. As the simultaneously measured gate leakage current $I_G$ through the electrolytes is plotted together, $I_G$ is negligibly small as compared to the drain current $I_D$ as long as $V_G$ is less than +/-0.5 V. The sweeping rate is translated to 10 Hz to change 10 mV, which is the amplitude of the capacitance measurement shown in Fig. 2. Assuming the value of $C_{EDL}$ as that of 10 Hz, mobility $\mu$ is estimated to be 5 cm$^2$ V$^{-1}$ s$^{-1}$, which is only half of the value of the air-gap OFET. Therefore, we conclude that the surface of the rubrene crystal is not seriously damaged by forming the solid-to-liquid interface.

![Figure 4](image_url)

**Figure 4.** (a) Transfer and (b) output characteristics of the ionic liquid / rubrene single-crystal transistor. Inset of (a) optical view of the device.

The sheet transconductance $\sigma'$, defined by $L/W \frac{dI_D}{dV_G}$, measures the rate of the current amplification for OFET devices and therefore directly determines the transistor performance. Since it is the product of mobility and capacitance of the device, both parameters should be large to have the best sheet transconductance. $\sigma'$ turned out to be as high as 20 µS when $V_D$ = -1 V, which is the best among all the reported OFETs; as long as usual dielectric insulators are used, the value is only 30 nS for the best pentacene thin-film transistors [7], and 250 nS for the best organic single crystal transistors [3]. Replacing the dielectrics with self-assembled monolayers, the value becomes 0.5 µS [8]. Even with the best devices electrolytes reported so far, it is evaluated as $\approx 4$ µS [6]. It is to be emphasized that $\sigma'$ of the present device of rubrene single crystals / RTIL sold-to-liquid interface demonstrates one order higher value than others. Moreover, the high-speed response can be guaranteed by the capacitance measurement given in Fig. 2, suggesting that the RTIL device works with high frequency up to $\approx 1$ MHz.
Figure 4(b) shows output characteristics of the device, exhibiting a typical saturating behavior of field-effect transistors. Therefore, the EDLs are well-formed as intended with the $V_G$ application. It is again noticeable that rather large current in the order of $\mu$A is generated with the application of less than 1 V for both $V_G$ and $V_D$, demonstrating the very low-power operation of the organic transistors due to the highly efficient carrier accumulation at the RTIL / rubrene liquid-to-solid interfaces.

5. Conclusion
We introduce a high-performance organic field-effect transistor making use of the rubrene single crystal / room temperature ionic liquid interface. Owing to high mobility of rubrene single crystals and high capacitance of electric double layers in the electrolyte, the device realizes the highest transconductance ever achieved for organic transistors. The fast ionic diffusion of the present electrolyte material emimTFSI favors high-speed switching, which had been a drawback of former electrolyte-gated organic transistors.

6. References
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