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Frequency-Dependent Electrical Transport Properties of 4, 4', 4''-Tri(*N*-carbazolyl)-Triphenylamine Investigated by Impedance Spectroscopy *

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Frequency-dependent electrical transport properties of 4, 4', 4''-tri(*N*-carbazolyl)-triphenylamine (TCTA) are analyzed by impedance spectroscopy (IS) as functions of bias and temperature. The Cole-Cole plot shows a single semicircle which indicates that the equivalent circuit can be designed as a single parallel resistor R_p and capacitor C_p network with a series resistance R_s . The bulk capacitance C_p remains unchanged while the resistance R_p decreases along with bias voltage. Conduction mechanism matches well with the space-charge-limited current (SCLC) model with exponential trap charge distributions. The temperature-dependent impedance studies reveal the activation energy of 0.246 eV with no phase change in the temperature range 220–320 K. These results indicate that the IS method is applicable for organic semiconductors having a wide band gap.

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There has been increasing interest in organic semiconductors for next generation optoelectronic device applications, such as organic light emitting diodes (OLEDs)^[1,2] and organic solar cells (OSCs)^[3,4]. In contrast to the rapid progress made in the device performance, the research on the basic mechanisms governing the devices is lacking, which is mainly due to the complexity of disorder nature in the organic semiconductors.^[5] The charge transport inside organic semiconductors is one of the most crucial elements to determine the performance of OLED devices. Therefore it is desirable for us to further understand the underlying transport properties of organic semiconductors.

In this Letter, we investigate the charge transport properties of 4, 4', 4''-tri(*N*-carbazolyl)-triphenylamine (TCTA) by impedance spectroscopy (IS). TCTA with large highest occupied molecular orbital (HOMO) level of 5.9 eV has been widely used as the hole transport layer and the host in phosphorescent OLEDs.^[6–8] There are some earlier attempts to understand the charge transport properties of TCTA by time-of-flight (TOF) technique and current density-voltage (J - V) characteristics.^[9,10] However, the impedance analysis of TCTA as a wide band gap material has never been reported. As we know, IS is a powerful tool in investigating the charge injection, the charge transport, the behavior of organic/electrode interface and the charge relaxation processes in organic devices.^[11–22] We study the effect of frequency at different bias voltages and temperatures on the conduction mechanism in TCTA. From the equivalent circuit analysis, the dielectric behavior

and the conduction mechanism are revealed, which is correlated with J - V characteristics.

The devices used in this study were prepared in the sandwiched structure ITO/MoO₃ (5 nm)/TCTA (200 nm)/MoO₃(5 nm)/Al, where ITO is indium-tin-oxide used as anode and MoO₃ is molybdenum oxide. MoO₃ was used to facilitate hole injection from ITO and suppress electron injection from Al.^[18] The glass substrates precoated with ITO were cleaned thoroughly using isopropyl alcohol, de-ionized water and acetone in an ultrasonic bath followed by drying with nitrogen gas. The devices were prepared by thermal evaporation in a high-vacuum system with pressure less than 5×10^{-4} Pa. The active area was 16 mm².

The thickness was controlled *in situ* by a quarter crystal monitor and calibrated by Dektak 6M Profiler (Veeco). The J - V characteristics were performed with a computer controlled Keithley 2400 sourcemeter. The IS measurements were carried out on an Agilent E4980A precision LCR meter in the frequency range of 20 Hz–2 MHz with the oscillation amplitude of the ac voltage kept at 100 mV. Temperature-dependent IS is measured by a vacuum cryostat (Optistat DN-V, Oxford Instruments) in the temperature range of 220–320 K.

Figures 1(a) and 1(b) show the frequency dependence of the real part ($\text{Re}Z$) and imaginary part ($\text{Im}Z$) of the hole-only device based on TCTA as a function of frequency at different bias voltages in semi-logarithmic plots, respectively. It is observed that the magnitude of $\text{Re}Z$ remains constant up to a certain frequency range depending on applied bias and then decreases rapidly with further increase in frequency.

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Its magnitude also shows a decrease with the increase of bias voltage. This should indicate the single charge relaxation process in the TCTA film. It can be seen from Fig. 1(b) that the $-\text{Im}Z$ initially increases with increasing frequency, then reaches a maximum peak and finally decreases with further increases in frequency, which also indicates the single relaxation process in the system. It is shown that the peak frequency shifts towards higher frequency with increasing bias, indicating the decrease of the bulk resistance with applied bias. At higher frequency, the $-\text{Im}Z$ curves at different bias voltages merge together, indicating that the device behaves like a pure capacitor showing the characteristics of a disordered insulator.^[16]

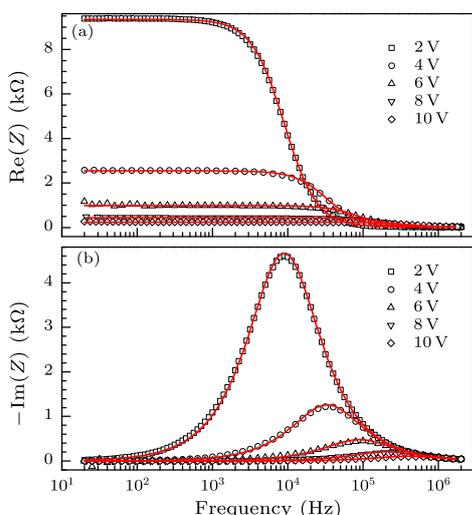


Fig. 1. Frequency-dependent (a) real and (b) imaginary parts of the complex impedance of the hole only device at different bias voltages. The solid lines are the fitting results according to Eq. (1).

Figure 2 shows the variation of the $\text{Re}Z$ and $-\text{Im}Z$ of the impedance (Cole-Cole plot) at frequency between 20 Hz and 2 MHz at different bias voltages. In this plot the implicit variation is the frequency which increases from right to left. The impedance shows a single semicircle at bias voltages above 2 V and the size of the semicircle decreases abruptly with increasing bias voltage. The minimum $\text{Re}Z$ represents the existence of a series resistance with the capacitor. The maximum $\text{Re}Z$ value represents the summation of the series resistance and the parallel resistance with the capacitor. Therefore the equivalent circuit for the TCTA-based device can be considered as a single parallel resistor R_p and capacitor C_p network with a series resistance R_s , as shown in the inset of Fig. 2. The impedance spectra can be fitted by^[23]

$$Z = R_s + \frac{R_p}{1 + i\omega R_p C_p}. \quad (1)$$

The semicircle of the Cole-Cole plot can be defined as.^[24]

$$\left[\text{Re}Z - \left(R_s + \frac{R_p}{2} \right) \right]^2 + (-\text{Im}Z)^2 = \left(\frac{R_p}{2} \right)^2. \quad (2)$$

This means that the circle centers at $(R_s + R_p/2, 0)$ with radius $R_p/2$.

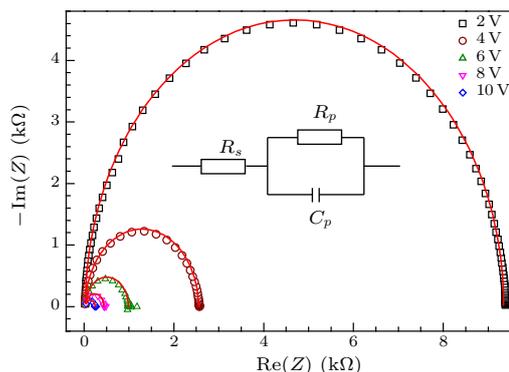


Fig. 2. Cole-Cole plot of the device at different bias voltages. The inset shows an equivalent circuit to describe the impedance spectroscopy. The solid lines are the fitting results according to Eq. (2).

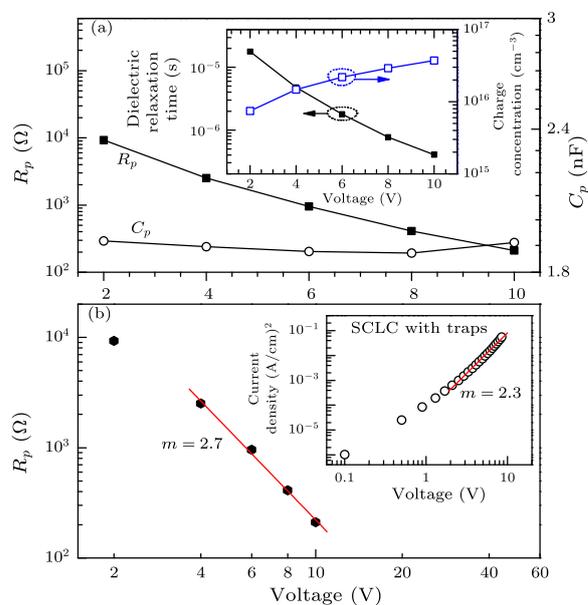


Fig. 3. (a) The fitting parameters capacitance C_p and resistance R_p with bias voltage. The inset shows the variations of the dielectric relaxation time and charge concentration with bias voltage. (b) The variations of the parallel resistance R_p with bias voltage. The inset shows the J - V characteristic.

The variations of the fitting parameters for the TCTA-based device at different bias voltages are shown in Fig. 3(a). The value of R_s is about 30 Ω and varies slightly with bias voltage, which may originate from electrode contact. The bulk resistance R_p decreases rapidly with increasing the bias voltage while the bulk capacitor C_p is almost independent of the bias. This behavior can be understood as follows. As the bias is increased, a large number of charge carriers are injected into the device resulting in a decrease in the dielectric relaxation time and hence the bulk resistance decreases.^[13] Also it can be seen that the peak frequency ω_p of the Cole-Cole plot shifts to

the higher frequency when the bias is increased from 2 V to 10 V. The peak frequency satisfies the relation $\omega_p \tau = 1$, where τ is the dielectric relaxation time. On basis of space-charge-limited current (SCLC) with an exponential trap distribution theory, the voltage-dependent current for one-carrier dominated transport, hole in this case, is given by^[25]

$$J = K \frac{V^{m+1}}{d^{2m+1}}, \quad (3)$$

where K and d are the proportional constant and the thickness of the film, respectively. Therefore, the voltage dependence of R_p is given by^[26]

$$R_p \propto \frac{V}{J} \propto V^{-m}. \quad (4)$$

The plot of $\log R_p$ vs $\log V$ is shown in Fig. 3(b). Here m of about 2.7 is obtained by the linear fitting of the data, which is in reasonable agreement with the value obtained from the J - V characteristics of $m = 2.3$. The linear dependence of $\log R_p$ vs $\log V$ implies that the conductance of the hole in TCTA follows the SCLC with exponential trap distribution. The traps may be the chemical impurities or structural defects.^[13] The invariance of C_p with applied bias is exactly the behavior expected for the SCLC conditions, where the total charge in the device is equal to $C_p V$, as shown in the inset of Fig. 3(a).

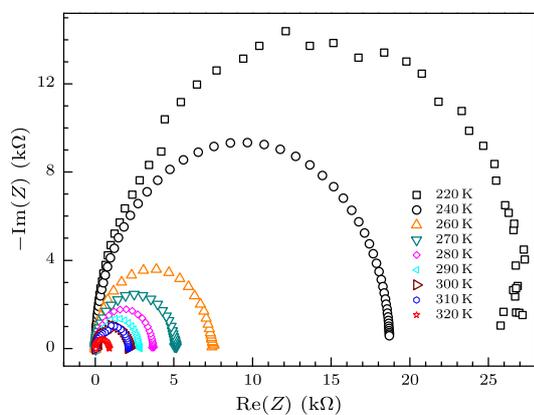


Fig. 4. The Cole-Cole plot of the device at different temperatures.

Figure 4 shows the Cole-Cole plot of the TCTA-based device under a constant voltage of 5 V at different temperatures. This plot is characterized by a closed and single semicircle-like curve for each temperature. It can be clearly seen that the size of the semicircle increases as the temperature decreases, suggesting a temperature-dependent relaxation mechanism. R_p can be directly obtained from the intercept of the semicircle on the $\text{Re}Z$ -axis. It is observed that R_p decreases with increasing temperature, which can be associated with the increase in conductivity of the bulk as the temperature grows (Fig. 5(a)). The frequency-dependent conductivity shows two distinct

regimes: the low-frequency plateau regime and the high-frequency dispersion regime.^[20,22] In general, the ac conductivity in such disordered materials follows the power law, as predicted for the conducting materials by Jonscher,^[27]

$$\sigma_{ac} = \sigma_{dc} + A\omega^s, \quad (5)$$

where σ_{dc} is the frequency-independent conductivity, ω is the angular frequency, A and s are the material and doping-dependent constants, respectively. The activation energy can be estimated from the variation of σ_{dc} as a function of temperature $1000/T$ as follows:^[20]

$$\sigma_{dc} = \sigma_o \exp \left[-\frac{E_a}{kT} \right], \quad (6)$$

where k is the Boltzman constant, E_a is the activation energy and T is the absolute temperature. As shown in Fig. 5(b), the plot gives a straight line which indicates that the activation energy is 0.246 eV. This value is consistent with the result obtained from the temperature-dependent current density.^[28] ($E_a = 0.242$ eV). Unlike the results of 4, 4', 4''-tris(*N*-3-methylphenyl-*N*-phenylamine)triphenylamine (*m*-MTDATA) obtained by Chauhan *et al.*^[14] there is no phase change of TCTA molecules in the temperature range 220–320 K. Here σ_{dc} is correlated with the conductivity σ_H for the hopping between the localized states in the temperature range investigated.^[28,29]

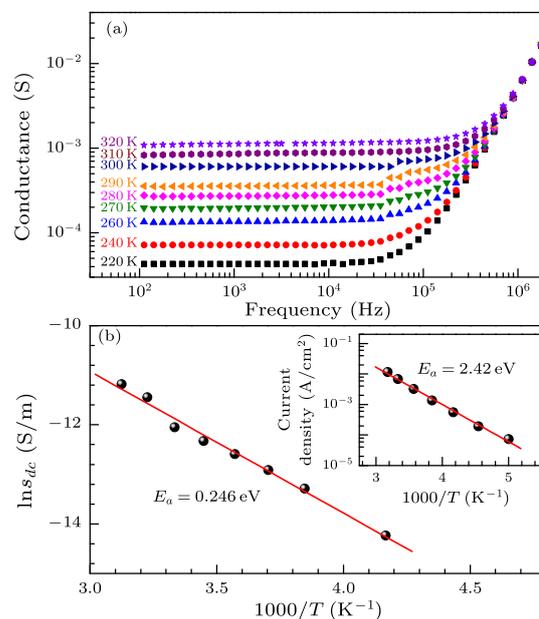


Fig. 5. (a) The ac conductivity versus temperature. (b) The dc conductivity with $1000/T$. The solid line is the fitting result according to Eq. (6). The inset shows the variations of the current density with $1000/T$.

We have investigated the transport properties of TCTA by using impedance spectroscopy. The device can be modeled by an equivalent parallel RC network with a contact resistance R_s in series, in which the bulk capacitance remains unchanged and the bulk re-

sistance decreases with the bias. The result is correlated with J - V characteristics. Impedance spectroscopy appears to be a valuable tool in evaluating the frequency-dependent electrical transport properties in organic semiconductors even with deep HOMO levels. We hope that the present analysis can be a guideline for the device design and performance analysis.

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