Organic semiconductor materials have been extensively studied as the most promising candidates for flexible and large-area electronic products. The electrical behaviors and charge transport mechanisms of organic semiconductors have been attracting much interest these years.\cite{14-17} Carrier transport processes in organic semiconductors, contrary to their inorganic counterparts, cannot solely be accurately described by the conventional energy band theory. The electronic coupling energy between molecules, which are bonded by a much weaker van der Waals interaction, is usually in the order of 0.1 eV, much smaller than that of inorganic materials bonded via a covalent interaction. In addition, the softness of organic materials leads to strong couplings between carriers and molecular vibration modes, also known as local electron–phonon interaction. These characteristics lead to formation of polaronic carriers and remarkably influence charge transport processes.\cite{18,21-28}

Organic single crystals (OSCs), as highly ordered systems, can probe the intrinsic charge transport experimentally.\cite{14-17} Space-charge-limited current (SCLC) is an adequate technique employed to study the intrinsic bulk charge transport properties of a semiconductive single crystal.\cite{18} The pioneering work by Karl and co-workers\cite{19,20} had aroused the extensive investigations of the bulk charge transport in OSCs,\cite{21-28} which elucidated the physical understanding of the motion of carriers in organic molecular semiconducting materials. In a number of studies characterizing the electrical properties along the vertical direction out of the $ab$-planes,\cite{21} thermal activation transport through the vertical direction has been observed. Traditional theories developed in inorganic semiconductors like trap-limited transport or mobility edge model were employed to depict the transport mechanism.\cite{21,24} However, the polaronic effect induced carriers’ localization was seldom taken into consideration, which has significant influence on or even dominates the charge transport when the intermolecular electronic coupling is weak. Reorganization energy $\lambda$ usually quantitatively used to depict the polaronic effect, is related to electron–vibration interaction between an added charge and its residual molecule. In recent years, newly emerging organic small molecular semiconducting materials, such as 6,13-bis(triisopropylsilyl-ethynyl)pentacene, $\text{C}_n\text{BTBT}$, and $\text{F}_4\text{BDOPV}$,\cite{29,30} usually have various side chains for the enhancement of their solubility, which will inevitably lead to much stronger electron–vibration interaction and thus show a pronounced polaronic effect. Values of $\lambda$ of newly emerging small molecules mentioned above are often larger than 200 meV or even 300 meV,\cite{31,32} whereas those of...
conventional acene materials like penta-
cene are no more than 100 meV,[31] thus
produce difference in transport character-
istics. In this paper, we designed a method
to study the vertical charge transport
mechanism in organic lamellar single crys-
tals based on TIPS-pentacene molecules
by considering a strong polaron effect.
Current–voltage ($I-V$) characterization is
a desirable approach to directly probe the
vertical charge transport process of bulk
crystal. This process determines the elec-
trical properties by analyzing the SCLCs.
We adopted a modified drop casting tech-
nique for single crystal growth to fabri-
cate a sandwich-like two-terminal device.
Temperature-dependent current–voltage ($I-V$) data were analyzed with a small
polaron hopping modified SCLCs model.
Values of the parameters containing hop-
ping distance $a$, reorganization energy $\lambda$,
and transfer integral $t$, were extracted.
The results show that the small polaron
hopping model provides a rational way
to describe the charge transport in the
vertical direction of the TIPS-pentacene
single crystal.

To obtain high quality TIPS-pentacene lamellar single
crystal with large size, toluene solution of TIPS-pentacene
(Aldrich Co. Purity ≥99%) was dropped to coat the Au-
coated substrate, the solvent was evaporated in a sealed
space full of toluene solvent vapor to slow down the growth
rate of crystal. The reabsorption of the ambient solvent vapor
molecules would slow down the effective evaporation rate of
the liquid solvent and postpone crystallization to approach
the quasistatic process (Figure 1a). Large lamellar single
crystals of TIPS-pentacene with widths of hundreds of micro-
meters and lengths of millimeters were obtained (Figure 1b).
Single crystalline phase crystals were verified with selected
area electron diffraction using a transmission electron micro-
scope (Figure 1c), indexed with lattice constant obtained
from powder diffraction data.[33] Lattice structure along
the $b$-axis is illustrated in Figure 1d, with acene parts sepa-
rated with each other along the $c$-axis. As similar technique
employed by Xu et al.[34] we characterized the vertical axis
of the lamellar crystal with powder and single crystal X-ray
diffraction (XRD), as illustrated in Figure S1 of the Sup-
porting Information, the XRD of single crystal shows prefer-
ential orientation of (00l) compared with that of powder,
with 1.63 nm interplanar separation. As Figure 2a shows,
we adopted a pair of unsymmetrical electrodes to minimize
the injection and extraction barriers of the holes. The 3 nm
molybdenum trioxide film and decanethiol monolayer[19]
acted as buffer layers to minimize the contact resistance, the
optimization of the single crystal and device contact could be
found in Figure S2 (Supporting Information).

The $I-V$ curves of different temperatures are displayed
in Figure 2b. The currents with low voltage bias (<1 V) were
clearly dominated with intrinsic thermal carriers, showing
Ohmic character. By contrast, the injected holes soon became
dominant at higher voltage, accompanied by a transition from
Ohmic to SCLC regime. The current monotonically increased

Figure 1. a) Illustration of the 6,13-bis(triisopropylsilyl-ethynyl)pentacene (TIPS-pentacene)
single crystal grown under toluene vapor. b) An optical image of the ultralarge TIPS-pentacene
single crystal. c) Selected area electron diffraction image of the TIPS-pentacene single crystal.
d) View of the lattice structure of TIPS-pentacene single crystal from $b$-axis.

Figure 2. a) Illustration of the structure of the two-terminal device and sketches of energy level and the charge transfer process. b) Current–voltage curves at temperatures from 240 to 300 K, with linear (right) and logarithm (left) scales.
with temperature at different voltages, indicating a thermal activation process during the transport of charge carriers. The Arrhenius plots of the currents’ natural logarithm are shown in Figure 3a. Figure 3b shows the thermal activation energy \( E_1 \) (the position of Fermi level relative to mobility edge) at different applied voltage, \( E_a \) varied from 120 to 20 meV at injected voltage \( U = 0.1 \) and 120 V, respectively. We note that the smooth variation of \( E_1 \) at low voltage, indicating that the metal–semiconductor interface is ideal enough for the holes’ injection,[21] i.e., the transport is limited by the bulk resistance rather than the injection.

Thermal-assisted hopping process of polaronic charge transport was assumed in our samples. According to Holstein,[6] to realize a transfer of a carrier from the cation to another neutral molecule in a system with weak intermolecule electronic coupling but strong electron–vibration coupling, the carrier needs to overcome a barrier with a height \( E_a \), also called polaron activation energy. \( E_a \) is normally equal to one quarter of the reorganization energy \( \lambda \) of the molecules without considering the transfer integral \( t \), as shown in Figure S3 of the Supporting Information. This value is directly related to the coupling between carriers and molecular vibration modes, whereas \( t \) could lower the barrier height to \( E_a' \).

In our study, we could treat \( E_a' \) to be approximately equal to \( E_a \), because of the infinitesimal transfer integral and strong electron–vibration interactions. This phenomenon offers an experimental approach to extract the reorganization energy with electrical characterization. By contrast, \( \lambda \) was always obtained by theoretical calculation[31] or some optical measurements.[33,38]

We employed the Marcus hopping rate, frequently used in a system with strong polaronic effect to depict the thermal activation hopping process in our samples.[8] The rate of a polaron hopping from sites \( i \) to site \( j \) can be written as follows:

\[
W_{i,j} = \frac{W_0}{\sqrt{T}} \exp\left(-\frac{E_a}{k_B T}\right) \exp\left(\frac{\varepsilon_i - \varepsilon_j}{2k_B T} + O(\varepsilon_i - \varepsilon_j)\right)
\]

where the prefactor \( W_0 = \frac{e^2}{4\pi \epsilon_0 \epsilon_r \hbar} \), \( t \) is intermolecular transfer integral, \( E_a \) is the polaron activation energy, and \( \varepsilon_{ij} \) stands for the site energy of \( ij \). For the single crystal has highly ordered molecular packing, we neglected the energy disorder and assumed that the dynamic disorder[21] is small enough compared with \( E_a \), i.e., the energy difference between sites \( i \) and \( j \) is zero, \( \varepsilon_i - \varepsilon_j \to 0 \). Considering the influence of the applied electric field \( F \), \( \Delta E_a = qaF/2 \), the hopping rate between sites \( i \) and \( j \) is written as follows:

\[
W_{i,j/ij} = \frac{W_0}{\sqrt{T}} \exp\left(-\frac{E_a}{k_B T} + \frac{qaF}{2k_B T}\right)
\]

where \( q \) is the elementary charge, \( a \) is the effective hopping distance, and \( F \) is the electric field strength. The random distribution of energy sites was not considered when the effective mobility along the electric field was calculated as follows:

\[
\mu_{Marcus}(F) = \frac{a(W_{i,j} - W_{j/i})}{F} = \frac{\mu_0 \sinh \left(\frac{qaF}{2k_B T}\right)}{F}
\]

We obtained \( \lim_{F \to 0} \mu_{Marcus}(F) = qa^2 W_0/(2\pi^2) \cdot \exp(-E_a/k_B T) \) when the electric field strength decreases close to zero. This value corresponds with the result derived from Einstein relationship in the diffusion limit.[36]

Instead of a conventional \( J \propto V^2 \) relationship usually appeared in previous literature, an analytical model for SCLC with considering small polaron hopping mobility was developed to quantitatively study the system (illustrated in Figure S4 of the Supporting Information). Numerical method was used to simulate the experimental \( I-V \) data. The small polaron hopping modified SCLC developed as mentioned above could fit well the experimental data (Figure 4a). Moreover, \( \mu_0 \) exhibited poor values no more than \( 10^{-3} \) cm² V⁻¹ s⁻¹ as anticipated, much smaller than those of the crystal’s \( ab \)-plane, which were reported to be \( \approx 10 \) cm² V⁻¹ s⁻¹. An Arrhenius activation relationship between \( \mu_0 T^{3/2} \) and \( T^{-1} \) was obtained from 320 to 240 K as shown in Figure 4b. We extracted the activation energy \( E_a = 65 \) meV accordingly, and obtained the relevant reorganization energy \( \lambda = 260 \) meV, which are reasonable compared with the theoretically predicted data by Griffith et al.[37] The small deviation might origin from unavoidable disorder existing in the interface or caused by the dislocations in the crystal.

The best fitting values of hopping distance \( a \) along vertical direction were \( \approx 1.4–1.9 \) nm as indicated in Figure 4c, which is consistent with the lattice constant in \( c \)-axis previously reported.[33,38] Meanwhile, this result presents a scenario that hopping transport in our samples takes place from one molecule to its nearest neighbor along the \( c \)-axis, i.e.,
every molecule acts as a charge trapping center (Figure 4d). Ultrasmall transfer integral \( t \approx 0.49 \) meV was obtained by extracting the prefactor in Equation (1), revealing the weak intermolecular electronic coupling. Paramonov et al.\[^{39}\] showed that two pentacene molecules adsorbed on graphite have an edge-to-edge transfer integral of approximately only 3 meV. The much smaller value of \( t \) in our samples could be attributed to the influence of the side chains located between the edges of two molecules, which further separate the \( \pi \)-electron conjugated parts. The effective mass \( m^* \) of the bare charge carrier could be estimated by the expression \( m^* = \hbar^2/(2a^2) \). A very large \( m^* \) of \( \approx 26 \) electron masses was obtained.

We experimentally obtained an evident distinct transport feature in the weakest molecular overlapping direction with low hole mobility of \( \approx 10^{-4} \)–\( 10^{-3} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\). Charge carriers with large effective masses are localized within single molecular scale, and charge transfer occurs by thermal activation or field assistance. These features are remarkably different from those observed in the \( ab \)-plane of organic crystals. Vertical charge transport may play an especially important role in devices, such as in organic light emitting diodes and organic field effect transistors (OFET). For example, the injection process of OFETs in the carriers may play a role in deciding the performance of the device because of its high resistance, as shown in Figure S5 of the Supporting Information.

It is noted, although the molecules are arranged in a highly ordered manner in OSCs, unintentional doping, lattice defect, and interface states could result in energetic disorders in the system, which would lead to the trapping of charges and thermal activated transport. An additional electrical characterization revealed band-like transport behavior within the \( ab \)-plane of the single crystal fabricated under same condition (Figure S6, Supporting Information). The distinct behavior between the temperature dependence in transport properties in \( ab \)-plane and the vertical direction suggested that the origin of the thermal activation process in vertical charge transport should not be attributed to the energetic disorders in the crystal. It is the formation of small polaron induced by strong electron–vibration coupling that leads to the hopping transport along the vertical direction of the crystal. Especially, when the intermolecular electronic coupling is weak compared with the electron–vibration interaction, the polaron effect should play vital roles, as the situation in the charge transport through the out-plane of the TIPS-pentacene lamellar single crystal.

In summary, a modified solution casting technique with very slow solvent evaporation process is employed, to grow lamellar TIPS-pentacene single crystal with ultralarge size. This enabled the fabrication of sandwich-like two terminal devices, and the holes transport mechanism was investigated by analyzing the \( I-V \) data of the system. A small polaron hopping modified space charge limited current model was developed and employed to successfully simulate the experimental data. Values of effective hopping distance \( a \), transfer integral \( t \), and reorganization energy \( \lambda \) were extracted and fully discussed reasonably, which present a scenario that hopping transport takes place from one molecule to its nearest neighbor along the \( c \)-axis, i.e., every molecule acts as a charge trapping center. This study may deepen the understanding of the charge transport in well-ordered but strong localized system of organic molecular crystal and help optimize the design of devices based on organic semiconductor.
Experimental Section

In the fabrication of the device, gold (Au, 30 nm thick) was vacuum evaporated on 300 nm silicon dioxide-coated silicon wafer basics at a rate of 0.1 A s⁻¹, followed by deposition of decanethiol monolayer. Toluene solution of TIPS-pentacene (5 mg in 0.55 mL toluene) was dropped onto the substrate, after which, the substrate was placed in a sealed crystalline dish with toluene gas. The crystals were annealed at 80 °C in a vacuum oven to remove the residual solvent, followed by the vacuum deposition of 3 nm thick molybdenum oxide and 30 nm thick platinum through shadow-mask on the top face of the crystals. The size of the top electrodes was 0.04 mm². Vacuum evaporation was performed with AUTO 306 physical vapor deposition system (Edwards Co.) under pressure of 3 × 10⁻⁷ mbar.

Optical microscope images of TIPS-pentacene single crystal were obtained using a Leica DML6000 optical microscope, and their thickness was characterized with a step profiler. Electric properties were measured in a commercial probe station (Lakeshore Co.) with a cat whisker probe to prevent damage to the crystal samples. The platinum electrode was positively biased with gold electrode with a cat whisker probe to prevent damage to the crystal samples. The temperature of the sample ranged from 320 to 240 K. A sufficiently long interrupt was needed before every I–V test for the thermal equilibrium of the devices at every temperature point. The temperature increase again. We measured the I–V curves twice to exclude the possible damage to the crystals under the low temperature.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.


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