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# Hole mobility in thieno[3,2-*b*]thiophene oligomers

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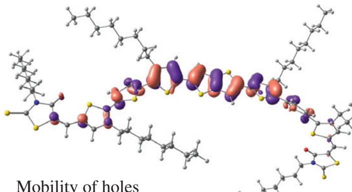
**A study of transient and steady state electrical currents in the solution-processed thin films of thieno[3,2-*b*]thiophene oligomers has demonstrated charge carrier mobility of about $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$. Thieno[3,2-*b*]thiophene moieties serve as reasonable charge transport sites providing the high mobility. Varying end alkyl chains in such oligomers is suggested as a viable tool to tune the mobility.**



Mobility of holes
~0.01 cm$^2$ V$^{-1}$ s$^{-1}$

The large-scale production of lightweight electronic devices in a cost-effective way has stimulated unprecedented interest in organic semiconductor materials in the last decade.[1] A key requirement imposed on organic semiconductors is the ability to form thin layers exhibiting high charge carrier mobility. The enhanced charge carrier transport determines the applicability of such materials to devices such as solar cells, photodiodes, light emitting diodes, and thin-film transistors.[2–5] Due to the facile formation of homogeneous films from solution, which enable the use of conventional printing techniques, conjugated polymers are most promising for large-scale production.[6,7] However, conjugated oligomers have gained interest due to the relatively easy synthesis, well-defined structures and higher possibility for molecular engineering over their polymer counterparts.[8–10] Recently, for oligothiophenes comprising terminal electron-donating triphenylamine and electron-withdrawing phenyldicyanovinyl groups, the tunability of photophysical and electrochemical properties has been demonstrated.[11]

A conjugated oligomer having an *N*-ethylrhodanine end group and a thieno[3,2-*b*]thiophene core connected through an alkylated terthiophene π-linker is a promising organic semiconductor in view of its expected high mobility.[12] Here, we report the results of studies on charge carrier mobility in thin solid films of thieno[3,2-*b*]thiophene oligomers **1** and **2**.

Synthesis of the oligomers is described in Online Supplementary Materials. Electric currents in oligomer thin films were measured in a linearly increasing voltage (CELIV) mode[13] for the extraction of preliminary injected charge carriers (MIS-CELIV)[14–16] and at a constant voltage for approaching the space-charge limited current (SCLC) regime.[17] The former measures the signals of transient currents whereas the latter measures steady state currents. The setups used for CELIV and SCLC measurements were described previously.[18–21] In a typical CELIV signal (Figure 1), $j(0)$ is the displacement current and $\Delta j$ is the maximum drift current at the time $t_{\max}$. The hole mobility is calculated as[15]

$$\mu = \frac{2d^2}{At_{\max}^2}, \tag{1}$$

where $d$ is the oligomer film thickness, and $A$ is the applied voltage ramp rate. Figure 1 shows that $\Delta j < j_0$; thus, the charge of mobile holes does not disturb the applied electric field in the bulk.[16] Moreover, the hole mobility remains constant with varying

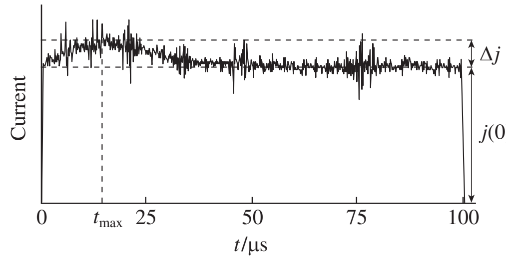
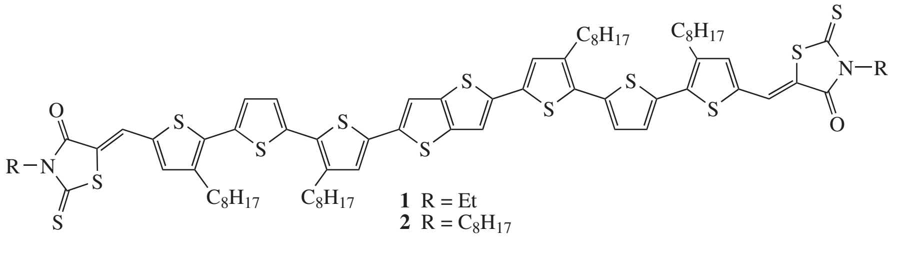


**Figure 1** MIS-CELIV transient current for oligomer **2** ($t_{\max} \approx 1.4\times10^{-5}$ s, $A = 1.2\times10^4$ V s$^{-1}$).



**1** R = Et
**2** R = $C_8H_{17}$

**Table 1** Hole mobility in the oligomers at room temperature.

| Oligomer | $t_{\max}$/s | $A$/V s$^{-1}$ | Mobility/cm$^2$ V$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| **1** | $1.54\times10^{-5}$ | $4.8\times10^{4}$ | $(1.9\pm0.7)\times10^{-2}$ |
| | $4.4\times10^{-5}$ | $6.0\times10^{5}$ | $(1.9\pm0.7)\times10^{-2}$ |
| **2** | $1.4\times10^{-5}$ | $1.2\times10^{4}$ | $(3.1\pm0.2)\times10^{-2}$ |
| | $1.0\times10^{-5}$ | $2.4\times10^{4}$ | $(3.0\pm0.2)\times10^{-2}$ |

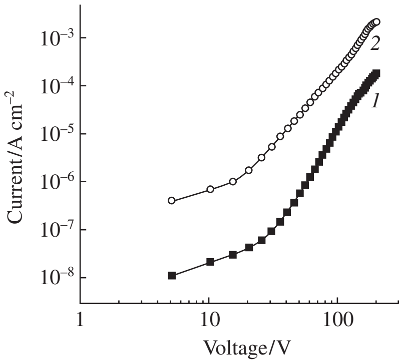


**Figure 2** *j–V* curves of ITO/oligomer/Au devices with the oligomer (*1*) **1** and (*2*) **2** layers 4.1 and 3.6 μm in thickness, respectively.

the ramp $A$ within the measurement error (*i.e.*, $At_{\max}^2$ = const) (Table 1). This suggests that the extraction of small charge in the CELIV signals related to the transport of equilibrium charge carriers.

Measuring *j–V* curves of steady state currents (Figure 2) did not exhibit the trap free SCLC regime given by Mott's law:

$$j_{\mathrm{SCLC}} = 9\varepsilon\varepsilon_0\mu V^2/8d^3, \tag{2}$$

where $j_{\mathrm{SCLC}}$ is the electric current density, $\varepsilon$ is the relative dielectric constant of the charge transport medium, and $\varepsilon_0$ is the permittivity of free space. In consequence, no mobility values can be calculated correctly from the *j–V* curves. Nevertheless, a comparison of the *j–V* curves clearly indicated that steady state currents in oligomer **2** are larger than those in oligomer **1** in the entire range of applied voltages. Therefore, it is believed that the SCLC mobility [equation (2)] in oligomer **2** is also larger than that in oligomer **1**.

The high mobility of about $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ evidently resulted from the strong intermolecular π–π stacking of the oligomers. The formation of stacks was shown earlier for similar thiophene oligomers.[12] It is important that the hole mobility and electric currents in oligomer **2** are larger than those in oligomer **1**. The oligomers differ only in the lengths of alkyl tails in the terminal groups. The hopping transport of holes occurs by electron transfer over highest occupied molecular orbital (HOMO) levels. To reveal the spatial distribution of electrons at HOMO levels, the GAMESS program was used for computing parameters of the oligomers. Apparently (Figure S2, Online Supplementary Materials), the electron density of HOMO level is distributed on the thieno[3,2-*b*]thiophene core moieties of both oligomers, and the electronic states of alkyl moieties cannot serve as a hole transporting site. Thus, the increased hole mobility of oligomer **2** can originate from additional supramolecular interaction (van der Waals force) provided by the alkyl chain improving both intermolecular π–π stacking and electronic communication between the domains of molecules **2**. In poly{2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene}, which has a similar thieno[3,2-*b*]thiophene moiety, a large free volume between alkyl chains facilitates the interdigitation and formation of closely packed lamellar structures.[22] Analogous results on the importance of long alkyl chains in benzobisthiazole–naphthobisthiadiazole polymers for inducing intermolecular stacking have been reported recently.[23]

The varying of alkyl chains in semiconducting thieno[3,2-*b*]thiophene gives a route for tuning charge mobility in thin films. To reveal the exact influence of alkyl chains on the charge mobility, a correlation between alkyl chains and intermolecular interactions in conjugated molecules should be studied. In terms of applied research, long alkyl chains are known to exclude moisture and oxygen from the ambient air.[24] In this regard, the oligomers are expected to be promising organic semiconductors for devices with improved stability.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.03.035.

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