

Isotropic transport in an oligothiophene derivative for single-crystal field-effect transistor applications

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(Received 1 March 2009; accepted 13 April 2009; published online 18 May 2009)

Single-crystal organic semiconductors have proven invaluable tools in the exploration of charge transport in molecular materials. We employ the elastomeric, photolithographically patterned single-crystal field-effect transistor in the study of an α -substituted oligothiophene. The terminal units specify a symmetric layered motif, while allowing the oligothiophene cores to pack closely. Angle-resolved measurements of the field-effect mobility reflect the symmetric edge/face interactions and isotropic mobility. These measurements are supported by electronic structure calculations that show nearly equivalent intermolecular interactions along cell diagonals. These results reveal that the transport is diffusive and a minimum of fourfold symmetry is required for in-plane mobility isotropy. © 2009 American Institute of Physics. [DOI: 10.1063/1.3129162]

The single crystal has emerged as a powerful tool for the exploration of charge transport phenomena in organic materials, paramount to their rational design.^{1,2} Its long-range order facilitates the study of microscopic properties such as molecular identity and supramolecular arrangement via macroscopic optical and electronic properties. Furthermore, they offer the highest performance of any solid-state organic materials, and typically outperform their polycrystalline counterparts.

Recently, we reported a technique for the selective vapor deposition of single-crystalline semiconductors on patterned substrates containing a prefabricated transistor architecture.³ This technique eliminates the need for masked deposition of the active semiconductor layer, minimizing the postprocessing of the sensitive organic material. It also replaced the tedious technique of hand-selecting and placing crystals traditionally required in the fabrication of single-crystal transistors. The isotropic nature of the patterned surface, however, results in randomly oriented crystals. As documented extensively in literature,^{4–6} the frequently anisotropic crystal structures of organic semiconductors result in anisotropic electronic transport, with field-effect mobilities differing by as much as three to four times from maxima to minima. Randomly oriented crystals may therefore exhibit characteristics that vary unpredictably, complicating circuit and device design. Accurate prediction and/or characterization of any anisotropy in the field-effect mobility are therefore keys for active-layer materials, particularly for single crystals. Recently, we reported a technique for the highly resolved angular characterization of single-crystal field-effect mobility.⁶ Building upon the pioneering work of Sundar *et al.*,⁴ our method employs lithography atop an elastomer dielectric to allow multifaceted analysis of a single organic crystal, eliminating the need for its removal and replacement. Ideally, however, this level of characterization should be unnecessary, with the anisotropy of optoelectronic properties predictable via electronic structure calculations.

Here, we apply our experimental technique to an α -substituted oligothiophene, trimethyl-[2,2';5',2'';5'',2'''] quaterthiophen-5-yl-silane (4TTMS) (cf. Fig. 1), whose asymmetric, building-block structure specifies a symmetric planar motif through steric interactions, yet allows the electronically active cores to pack closely. Furthermore, we carry out electronic structure calculations in order to correlate microscopic intermolecular interactions to macroscopic electronic properties, and employ these results to evaluate both the utility of the 4TTMS crystal and develop a general design rule for organic crystalline semiconductors based on symmetry considerations.

The molecular semiconductor 4TTMS was synthesized and characterized as previously reported.⁷ Single crystals were grown from the vapor phase by the physical vapor transport technique⁸ in a two-zone furnace⁹ in semiconductor-grade argon, using resublimed synthesis product; no decomposition was apparent. In four to eight hours with a source temperature of 225C, two-dimensional yellow plate crystals were formed almost exclusively, with very little (<15 mg) material required to form large numbers of thin (several hundred nm) crystals, relatively monodisperse in size. Lateral dimensions varied from hundreds of micrometers to several millimeters, depending on growth time. Crystals were relatively irregularly shaped platelets, showing no obvious faceting that would indicate crystal orientation. Shown in Fig. 1 are the molecular and single-crystal structures of 4TTMS, as determined by x-ray diffraction (see Ref. 9 for crystal growth and analysis details). The substituted oligothiophene packs in plane-by-plane herringbone fashion typical of rod-shaped molecules, with the *bc*-plane comprising the faces of the plate-shaped crystals. The bulky TMS group is arranged so that all edge-face adjacent molecules (on the unit cell diagonals) alternate up and down, grouping between *bc*-planes of the aromatic thiophene cores. The result is alternating columns/rows of TMS-up and TMS-down molecules in the orthorhombic unit cell. The cell axes are within 20% in length, and the planes of the edge/face-oriented oligothiophene units are all at 56° relative to one another along cell diagonals.

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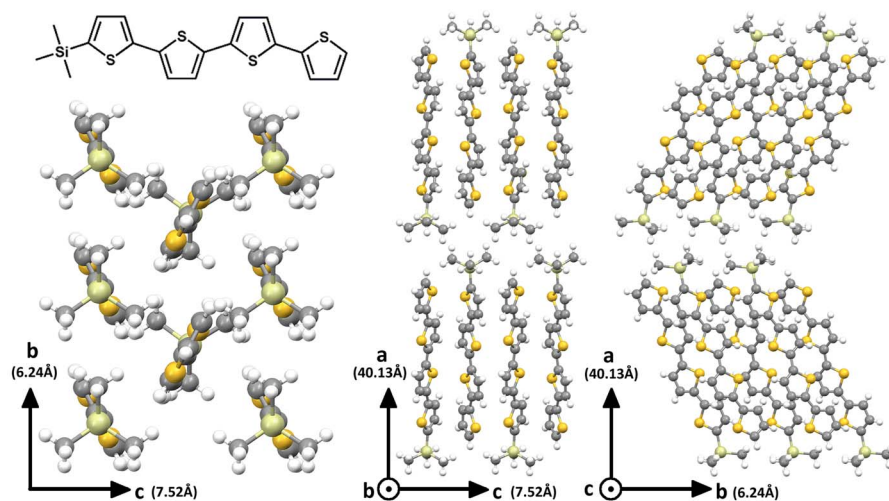


FIG. 1. (Color online) Molecular and crystal structure of the vapor-grown 4TTMS single crystal, with primary crystallographic axes as indicated, as determined by x-ray diffraction. The crystal structure is orthorhombic; all crystal axes are perpendicular.

Single-crystal field-effect transistors (SCFETs) were fabricated as reported previously,¹⁰ with freshly grown crystals placed atop the anisotropic device structure, allowing determination of field-effect mobility at 15° intervals. The crystals were characterized with devices of various dimensions, all showing remarkably similar transistor characteristics. Shown in Fig. 2 are the saturation-regime mobilities as a function of angular orientation for a typical SCFET structure with channel width/length of 600/30 μm . Mobility is remarkably consistent, $0.12 \pm 0.01 \text{ cm}^2/\text{V s}$ for the set of devices shown, with errors distributed symmetrically about the mean. Analysis of device characteristics (see Ref. 10) suggests contact effects are negligible. Furthermore, deviations are clearly within experimental error, and show no clear correlation with orientation. Therefore, at the resolution of this technique, 4TTMS demonstrates isotropic field-effect mobility within the bc -plane of the crystal. As noted, the fourfold bc -plane symmetry of the 4TTMS single crystal suggests upon inspection that its electronic properties should share this symmetry. As documented extensively, however, the parameters governing charge transport in organic materials are extremely sensitive to proximity and orientation. Because the molecular units in an organic solid are weakly bound by van der Waals interactions, the wave function overlap is exponentially dependent on distance, as well as being affected critically by the nodes of the molecular orbital wave functions. The strength of interactions is therefore a nontrivial assessment that cannot be made by a superficial analysis of the crystal structure. For this reason, electronic calculations are essential for a meaningful evaluation of the true electronic isotropy. The transfer integral, t , is the most commonly employed metric of orbital wave function overlap, the facilitator of intermolecular charge transport. Although there is much debate in

literature over the exact correlation between the absolute value of t and observed field-effect mobilities,^{11–13} its importance in carrier transport is without question. Here, we seek solely to demonstrate the symmetry of electronic interactions within the 4TTMS crystal. While recent work seeks to correlate ground-state polarization with the true polaronic transfer integral,¹¹ we avoid this confusion by working within the framework of a symmetric system and operating comparatively within only the 4TTMS crystal structure. Listed in Table I are the transfer integrals calculated using the B3LYP density functional and the 6-311G* basis set. For hole transport, the highest occupied molecular orbital (HOMO) overlap is critical, here indicated by the magnitude of t_{HOMO} . For the 4TTMS dimers, HOMO transfer integrals in $\langle \frac{1}{2}, \frac{1}{2} \rangle$ and $\langle \frac{1}{2}, -\frac{1}{2} \rangle$ crystallographic directions are within 5%, mirroring the experimental isotropy of mobility along the primary crystallographic axes.

Combined with the previously reported results for rubrene,⁶ these data reveal a key detail about charge transport in molecular materials: fourfold rotational symmetry of molecular interactions gives completely symmetric transport

TABLE I. Transfer integrals for the 4TTMS single crystal calculated at the B3LYP/6-311G* level, indexed by crystallographic orientation, in units of meV

	Crystallographic direction $\langle b, c \rangle$			
	$\langle 1, 0 \rangle$	$\langle 0, 1 \rangle$	$\langle \frac{1}{2}, \frac{1}{2} \rangle$	$\langle \frac{1}{2}, -\frac{1}{2} \rangle$
t_{HOMO}	5	3	147	136
t_{LUMO}	91	7	155	143

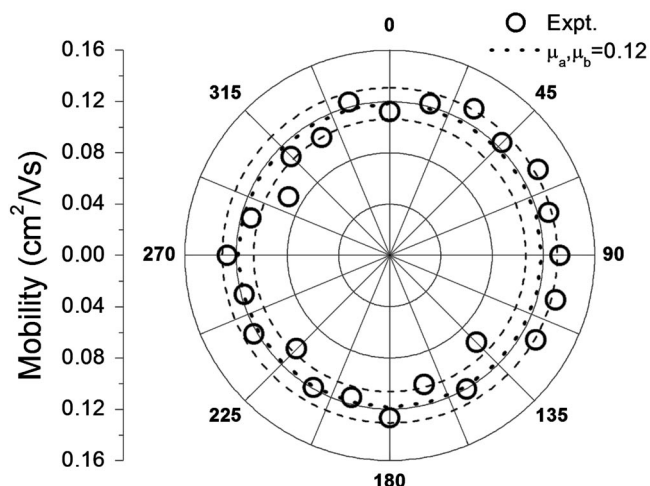


FIG. 2. Field-effect mobility (circles) as a function of orientation relative to the first measurement made at zero degrees, as measured in the saturation regime. Black dotted and gray dashed lines are averaged mobility and error intervals corresponding to the standard deviation of the entire data set. Devices are elastomeric SCFETs with channel width/length of 600/30 μm .

within the *bc*-plane, while twofold yields twofold symmetric anisotropic transport. This is a nontrivial conclusion that further confirms the model invoked previously,⁶ where the measured field-effect mobility is determined by $\mu_{\text{FET}} = u_i n_{ij} u_j$, where $n_i = n_j$ is the direction of applied field and normal vector to the plane of carrier collection, and indices are summed in accordance with Einstein notation. This conclusion is key for the design of molecular materials, especially for those used in circuits where crystal orientation cannot easily be specified. In order to guarantee consistent material performance, fourfold symmetry must be achieved. This symmetry, along with ease and quality of crystal formation and relatively good performance, make 4TTMS a good candidate for these applications. Furthermore, the correlation between experimentally observed anisotropy of field-effect mobility with the symmetry of electronic interactions—as estimated using quantum chemical calculations—suggests that the *a priori* prediction of orientation-dependent properties is indeed possible.

C.R. acknowledges support from the AFCEA graduate fellowship. M.E.R. acknowledges support from the NASA GSRP fellowship. Z.B. acknowledges the financial support from NSF-CPIMA, Sloan Research Fellowship, Air Force Office of Scientific Research, and NSF DMR Solid State

Chemistry (Award No. DMR-0705687). Work was performed in part at the Stanford Nanofabrication Facility of NNIN supported by the National Science Foundation under Grant No. ECS-9731293.

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