

Enhanced Charge Transport in Printed Small Organic Semiconductor Thin Films due to Strained Molecular Packing

It is a well-known fact that the exact arrangement of small organic semiconductor molecules in thin films is one of the main factors governing the intrinsic charge carrier mobility and consequently the electrical performance of organic thin-film devices such as organic thin film transistors and plastic solar cells. For inorganic semiconductors, a general method of increasing charge carrier mobility is to introduce strain within the crystal lattice (e.g., Si/Ge). Up until now, however, there have been no reports of a similar electrical conductivity enhancement due to stabilized strain formation in small molecule organic materials.

A new printing technique was recently developed for organic semiconductor deposition (Figure 1a) in the research group of Zhenan Bao (Stanford University).¹ This technique is scalable, mimics important aspects of industrial printing tools and works by shearing the organic ink used to deposit the films on a solid (rigid or flexible) substrate. Through careful tuning of the printing conditions, a team of researchers from Bao's group led by graduate student Gaurav Giri was able to increase the charge carrier mobilities in the printed films substantially in comparison to conventionally solution-processed films. For small aromatic organic semiconductors

6,13-bis(triisopropylsilyl)ethynyl pentacene (TIPS-pentacene, inset in Figure 1a), the electrical performance improved by as much as a factor of about six when the film was prepared at a printing speed of 2.8 mm/s. In order to determine the physical cause for this improvement, the researchers performed hard X-ray diffraction experiments at SSRL Beam Lines 7-2 and 11-3. The results revealed an unexpected gradual distortion and strain in the thin film unit cell that grows in magnitude with the printing speed (Figure 2a). SSRL staff scientists Stefan Mannsfeld and Mike Toney, applied a unique computational refinement method to the X-ray data that they had recently developed to extract precise information on the molecular packing from X-ray diffraction data of weakly scattering thin films.²

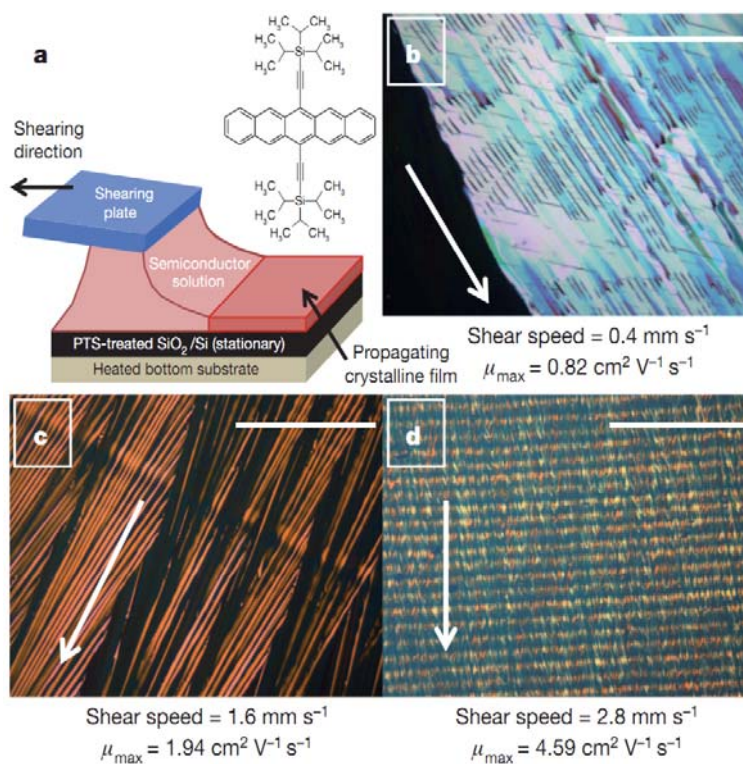


Figure 1. **a**, Schematic of the "solution-shearing" printing method (inset shows chemical structure of TIPS-pentacene). **b–d**, Optical micrographs (cross-polarized) of solution-sheared TIPS-pentacene thin films, fabricated at different printing speeds. The printing speed and the electrical performance of the films in thin film transistor devices are listed below each of the images. Copyright Nature Publishing Group 2011.

These calculations revealed that the packing of the TIPS-molecules in the distorted unit cell differs significantly from that in the unstrained state in vacuum-deposited or slowly printed films (Figure 2). Specifically, the distance between the π -electron rich aromatic backbones of the TIPS-pentacene molecules was reduced from 3.33 Å to 3.08 Å in the most strained films printed at a speed of 8.0 mm/s (see Figure 2b). Such a small π - π stacking distance had not been observed before in any van der Waals-packed organic semiconductor material. The positive charge carrier mobility in corresponding thin film transistors devices in which the printed films served as active layers increased from $0.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for unstrained films to a record value of $4.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ —much higher than other literature values for this material. The research team suspected that it was this reduction in the stacking distance between the aromatic planes that was mainly responsible for the measured increase in electrical performance. With the packing of the TIPS-pentacene molecules accurately determined for both the strained and unstrained film states, Alan Aspuru-Guzik's group (Harvard University) was able to corroborate this hypothesis by performing quantum-chemical transport calculations on the two molecular packing motifs. Their calculations predict an improvement in the charge carrier mobility in the strained packing motif close to the one the Stanford researchers had measured experimentally.

The importance of this study lies in two aspects. First, the successful stabilization of strain in a crystalline organic thin film is a novel route to improve the electrical performance of these materials. In fact, a combined Stanford/SLAC research team is actively developing this technique and they have already found more material systems that they can grow with strained lattices. Second, the performance improvement was achieved by using printing which most researchers in the field consider the most promising film deposition technique for large-area mass-production of inexpensive plastic circuitry.

Primary Citation

Gaurav Giri, Eric Verploegen, Stefan C. B. Mannsfeld, Sule Atahan-Evrenk, Do Hwan Kim, Sang Yoon Lee, Hector A. Becerril, Ala'n Aspuru-Guzik, Michael F. Toney, Zhenan Bao, Tuning charge transport in solution-sheared organic semiconductors using lattice strain. *Nature* **480**, 504–508 (2011)

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