



Top left: A fragment of the cross section of a "grid-electrode" organic FET. The organic material in this study is poly(3-hexylthiophene) and the insulator is a high-dielectric-constant material, TiO_2 . Bottom: A photograph of an

actual device with dimensions $10 \times 14 \text{ mm}^2$. Inset: Closeup of the area to be studied.

Arguably, one of the main challenges in achieving these goals is finding a means of investigating the

polymer chains that make up plastics, the "holes" left behind could act as positive charge carriers, increasing the conductivity of the material by a factor of up to ten million. The prospect of electronic devices incorporating lightweight, moldable, relatively cheap plastic has since stimulated intensive research and development toward a wide variety of applications, including largearea flat-screen displays, chemical and biological sensors, and environmentally friendly solar cells. Semiconducting organic polymers can also be used in field-effect transistors (FETs), solid-state electronic devices used to amplify wireless and other weak electromagnetic signals. But the ability to do this depends upon the density of the charge carriers that can be introduced into the transistor's conducting channel. This channel is confined to a nanometer-thick layer at the interface between the device's semiconducting and insulating layers, thus its intrinsic properties are very difficult to interrogate experimentally. Li et al. take a novel approach to probing the electronic characteristics of organic FETs, using infrared light to map the density of charge

intrinsic electronic properties of the charge carriers in organic FETs without the need for metallic contacts that could interfere with the

carriers under various conditions.

properties under study. In FETs, the charge carriers are confined to a nanometer-thick layer at the semiconductor-insulator interface, buried under several layers of the device. This makes it difficult to experimentally study injected charge carriers using some of the most informative experimental techniques in the arsenal of physicists and chemsists, including scanning tunneling microscopy, photoemission spectroscopy, and inelastic x-ray and neutron scattering.

In this research, the scientists instead employed infrared light to study the electronic processes in organic FETs that are based on poly(3-hexylthiophene), a semiconducting polymer featuring exceptionally high charge-carrier mobility. In such materials, charge carriers can induce infrared vibrations of the polymer chain. In addition, when these charges are displaced under the influence of an electric field, they drag the local polarization cloud of the molecular chains with them, forming so-called polarons. The scientists have been able to employ infrared spectroscopy to directly probe the vibrational modes and polarons in a functional organic FET device. This information is difficult or impossible to obtain using other experimental techniques.



The voltage-induced infrared absorption spectra ($\Delta \alpha d$) of the device. Employing infrared spectroscopy, the researchers were able to directly probe the electronic excitations associated with the injected carriers in a functional organic FET device: infrared active vibrational modes of the polymer chain (sharp resonances in the 1,000–1,500 cm⁻¹ range) and polarons (broad absorption band centered at 3,500 cm⁻¹).

Furthermore, infrared spectromicroscopy can also be used to explore the distribution of charges in the conducting channel of the FETs with high spatial resolution, made possible by the exceptionally high brightness and small focal-spot size of the infrared beams at the ALS. Using the infrared Beamline 1.4.3, the researchers were able to acquire infrared spectra from individual spots less than 10 microns in diameter. By scanning the beam over the conducting channel of the device and measuring the infrared spectra in different areas, they were able to map out the density of the charge carriers in different regions and examine its evolution as the applied voltage is increased. Comparisons were made between FETs having insulating layers of either SiO₂ or TiO₂. The latter, having a high dielectric constant, are much desired in FETs because they allow for a much higher density of charge carriers in their channels than SiO₂-based FETs.



The variation of carrier density away from the injection contacts in the area shown by the blue square in the figure at top, obtained by spatially monitoring the spectroscopic fingerprints of the injected charges using infrared microspectroscopy.

However, the measurements revealed severe restrictions of the charge-carrier channel length for TiO₂-based devices, a significant departure from the behavior expected for an "ideal" FET, in which the charge density increases linearly with voltage and is uniform in the channel. This is particularly important if one wants to use these insulators in chemical or biological sensors. In general, these experiments indicate that infrared spectroscopy and spectromicroscopy offer researchers unique tools to explore physical phenomena at the nanoscale occurring at the semiconductor-insulator interface in organic FETs. The team hopes to employ the same techniques in the study of other materials in FET devices, including polymers, organic molecular crystals, and transition-metal oxides.

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