

Aligned Conjugated Polymers Standing Upright

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Conjugated polymers have enormous potential as novel electronic materials that combine the electrical properties of semiconductors with the good mechanical strength and processing advantages of plastics.^[1,2] Perhaps nowhere is this more evident than in the synthesis of conjugated heterocyclic polymers based on thiophene units or monomers.^[3] Owing to their facile preparation, relatively high conductivity, and good long-term stability under ambient conditions, these polymers have been the focus of intense study for use in devices such as plastic photovoltaics, light-emitting diodes, transistors, and flexible displays.^[4–6] The ability to change color, due to twisting of the polymer backbone in response to changes in solvent, temperature, applied potential, and binding to other molecules, also makes the polythiophenes attractive as optical sensors.^[7] Despite the phenomenal growth in diverse synthetic methodologies that allow the fabrication of the polythiophenes with desired chain length and structure, however, the deposition and patterning of these molecules on a substrate has remained challenging.

Conventional techniques for depositing films of conjugated polymers include solution casting, dip coating, and spin coating of the polymer from solutions. However, for many conductive polymers, these approaches are often limited by the insolubility of the polymers, which form aggregates without extended molecular ordering upon deposition. Another common route to deposit conjugated polymers is through an electrochemical polymerization process on an electrode substrate that involves monomer oxidation, dimerization, and the growth of oligomers and polymers of the oxidized monomer.^[8] Because of localized deposition of polymers at the electrode surface, this approach can be used to prepare patterned arrays of conjugated polymers on pre-patterned electrodes.

The standard procedures to create large-area conjugated-polymer-array patterns generally involve sequential polymer deposition, photolithography, and a subsequent etching step to remove dissolved polymers by appropriate solvents. However, the ultraviolet light, typically used in the process of photolithographic patterning, may cause degradation of the conjugated polymers. In addition, many types of etching solvents can also dissolve and swell the conjugated polymer

films, resulting in unreproducible optical and electronic measurements.

Soft lithographic techniques, such as microcontact printing, have also been widely used to generate polymer arrays.^[9] While useful for many applications, these methods do not allow one to control structures in a site-specific manner and therefore do not enable the fabrication of complex multicomponent polymer arrays on nano- to microscopic length scales. To this end, inkjet printing and atomic force microscopy (AFM) have been developed to pattern multicomponent polymer arrays with controlled feature sizes and shapes.^[10–13] The capability to directly deliver monomers through an inkjet nozzle or AFM microcantilever allows one to generate small but diverse libraries of polymer structures.^[12]

The patterning of 1- or 2D conjugated molecular networks of single or several molecular layers thick presents a substantial challenge.^[14–19] Very recently, Griff et al. have shown that 2D poly(tetrakisphenylporphyrin) networks can be achieved by annealing tetrakis(bromophenyl)porphyrin on a gold substrate.^[20,21] By controlling the chemical structure of the constituent monomer units, they have demonstrated topology tuning of the 2D networks. Important steps to the design of the aligned 1D conjugated polythiophenes were taken by Sakaguchi and co-workers.^[22,23] Using electropolymerization of thiophene monomers on an iodine-covered single-crystalline gold substrate, they fabricated highly aligned conjugated copolymers.^[23] However, extended long-range order is not preserved because of the presence of occasional *cis*-conformations in the polythiophene framework.^[22] To increase the charge-carrier mobility of the polymers, it is essential to prepare ordered structures that have well-defined spatial conformations.

Writing in the *Proceedings of the National Academy of Sciences*, Lipton-Duffin et al. demonstrated an elegant method that enables just that, by using a copper substrate simultaneously as both template and catalyst for the polymerization of thiophene derivatives.^[24] The importance of their work rests on the controlled fabrication of industrially relevant conjugated polymers, poly(3,4-ethylenedioxythiophene) (PEDOT),^[25] in a unique structure alignment previously inaccessible by conventional approaches. In stark contrast to the previous attempts that afford *anti*-PEDOT conformation structures lacking molecular order,^[26,27] Lipton-Duffin et al. were able to achieve all-*cis* isomers, as confirmed by high-resolution scanning tunneling microscopy (STM) measurements under ultrahigh-vacuum conditions.

In their experiment, Lipton-Duffin et al. exploit the Ullmann coupling^[28] reaction of 2,5-diiodo-3,4-ethylenedioxythiophene (DIEDOT) to fabricate an ordered assembly of PEDOT on an atomically flat Cu(110) substrate. The anisotropy of the

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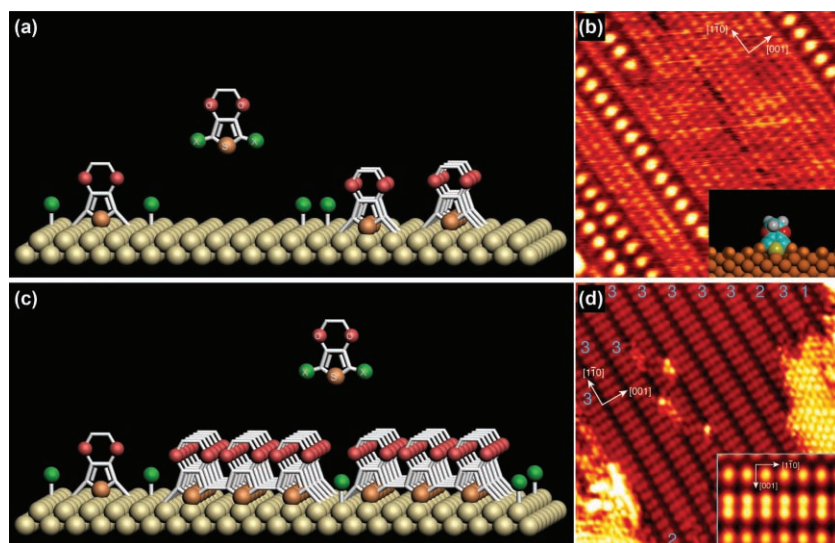


Figure 1. a) Schematic diagram of Cu-mediated Ullmann coupling at a low coverage of EDOT molecules. b) STM image showing stacks of EDOT molecules on Cu(110) after a 5-min DIEDOT exposure. Inset: the front view of the molecule in the stack as calculated by density functional theory (DFT) shows the upright topology of the molecule. c) Schematic diagram of the Cu-mediated Ullmann coupling at a high coverage of EDOT molecules. d) Corresponding STM image of a high surface coverage showing a well-organized oligomer array. Inset: high-resolution STM data for dimer arrays. Figure 1b,d are adapted with permission.^[24] Copyright 2010, National Academy of Sciences, USA.

Cu(110) facet was utilized to orient the polymer growth in a single direction. Interestingly, upon deposition of DIEDOT in small quantities at 200 °C, they discovered ordered surface structures of adsorbates in the form of dotted lines (**Figure 1a,b**). As the spacing (calculated to be 5.12 Å) between the dots is significantly larger than the internal spacing (calculated to be 3.963 Å)^[29] for PEDOT, the dot arrays were attributed as individual molecules bonded to the substrate. The dehalogenation of the molecules was further confirmed by an X-ray photoelectron spectroscopy study. The ordered alignment of the dot arrays clearly reveals oriented epitaxial growth of the molecules with respect to the underlying Cu lattice.

To verify the topology of the adsorbed molecules, Lipton-Duffin et al. performed density functional theory (DFT) calculations. Their results show that the molecules stand upright on the substrate plane with a slight tilt of 18° from the surface normal. Normally, oligothiophenes lie essentially flat on less-reactive substrates, such as Ag and Au, because this conformation enables maximum molecule–metal contact.^[30,31] Thus far, the vertical orientation has rarely been reported as this extreme conformation generates substantially high adsorption energies. However, this would be the case if a strong binding interaction existed between the molecule and the substrate. Very clearly, in their experiment, the two C–Cu bonds and strong S–Cu interactions, along with weak repulsive adsorbate–adsorbate interactions, are the primary cause of the observed virtually upright conformations.

Remarkably, when the authors increase DIEDOT deposition, the resulting adjacent lines start to bond together,

leading to the formation of an all-*cis* conformation in which the sulphur atoms point toward the surface (**Figure 1c**). By contrast, the EDOT dimers and polymers in previous studies always adopt the *anticonformation*.^[29] A typical STM image of the oligomer arrays shows highly ordered structures of dimers and trimers (**Figure 1d**). By correlating the STM data with DFT calculations, the authors identified the energy gain resulting from molecular bonding as being pivotal to the highly ordered structures. A further increase in surface coverage of monomers leads to surface-confined arrays of thiophene oligomers up to 14-units long. The chain length is limited by the formation of iodine atoms on the Cu substrate. The authors also performed their experiments on the Pd(110) substrate but no evidence was found for dimer or oligomer formation.

The work reported by Lipton-Duffin et al. to control the alignment and orientation of polythiophenes through use of a Pd(110) substrate should open up entirely new opportunities in molecular elec-

tronics. Although the extension of their technique to other metal substrates remains an important challenge, being able to achieve such high degrees of molecular ordering for conjugated polymers provides a powerful platform for investigations of fundamental science. There is no doubt that this work will deepen our knowledge of surface-confined reactions and improve our control of the material properties.

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