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Conducting polymers as substrates for surface-mounted molecular devices

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Abstract

Thin films of poly(3,4-diethoxythiophene), PEDOT, were prepared by vacuum sublimation/polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene onto freshly cleaved mica. AFM studies show that the films are exceptionally smooth and contain both highly crystalline and amorphous regions. Exposure of the film to polar solvents for one hour causes an increase in the surface roughness, while exposure to non-polar solvents or thermal annealing decreases surface roughness. Aryl thiols linked to diazo dye labels can be covalently bound to the films by simple exposure in dilute methylene chloride solutions. This provides a convenient way to functionalize PEDOT surfaces with molecular devices.

Keywords: sublimation, polymerization, atomic force microscopy. self-assembly using surface chemistry, special purpose functionalized conjugated polymers

1. Introduction

1.1 Self-assemby on Conducting Polymer Surfaces

Investigations of self-assembled monolayers (SAMs) have progressed from fundamental studies of surface phenomena to serious attempts to fabricate functional optical and electronic structures. The vast majority of these studies have focused on metal or metal oxide substrates, since these are well characterized and can feature atomically smooth domains. The concepts developed in these studies, however, also offer important ideas for the surface modification of other materials, such as polymers. Such surfaces are typically very rough in the nanometer size regime and the formation of densely packed, highly organized SAMs such as those formed on polycrystalline gold may not be possible. We have found, however, that the treatment of electronically conducting polymers with thiols leads to surfaces that display many of the physical and electronic characteristics of the well-studied SAMs. Thus, treatment of polyaniline and polypyrrole films with alkane- or perfluoroalkane thiols results in very hydrophobic surfaces similar to those of SAMs on inorganic surfaces. [1] Treatment of polypyrrole with thiols tethered to ferrocene [2] has also shown that the packing density of the electroactive moiety can be on the same order of magnitude as that on gold. Other species, such as porphyrins can also be linked to the surface by coupling reactions with prepositioned surface “anchors”; thiols containing terminal groups suitable for coupling reactions. [3]

1.2 PEDOT Surfaces

Poly(3,4-ethylenedioxythiophene), commonly known as PEDOT, is one of the most commercially successful of the conducting polymers. [4] It has many advantageous features, including high stability and conductivity. Interestingly, it is also nearly transparent when in its oxidized, conducting state, unlike most other conducting polymers that are intensely absorbing in the visible region. PEDOT films are prepared by three major routes, including chemical oxidation, electrochemical oxidation and catalytic coupling of 2,5-disubstituted derivatives. Chemical oxidative polymerization is the most widely used method. The development of a water-soluble derivative using polystyrene sulfonate (PEDOT/PSS, sold commercially as Baytron P by Bayer AG) has proven to be particularly popular for industrial applications. Relatively smooth films can be obtained by the spin-coating of this material onto various substrates. Electrochemical polymerization has also been widely used and can controllably give films that range from very dense and amorphous to highly porous and crystalline, depending upon reaction conditions. Transition-metal mediated coupling generally gives oligomeric materials. [4]

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Very recently, Wudl and co-workers have described a unique solid-state polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT). [5] This reaction can occur in single crystals or during the sublimation of the monomer. [6] Polymerization of single crystals resulted in amorphous materials that retain the general shape of the monomeric crystal. However, the surface was found to be damaged during the reaction, probably due to both changes in the crystal packing and to migration of Br_2 from the solid. The sublimation/polymerization process produces thin films that can be deposited onto a variety of substrates, including plastics. This technique could prove valuable in the construction of all organic electronic and optical devices. [6] A critical parameter of such devices is the surface morphology of the thin films. Here we look at the surfaces of PEDOT films deposited onto mica and the changes induced by exposure to solvents and heat. We also demonstrate the surface modification of the films with diazo dye-linked thiols.

2. Experimental

2.1 General

All reagents were purchased from commercial houses and used as received. Solvents were dried on a solid-state purification system under argon. Compound 4 was prepared as previously described. [7] PEDOT films were prepared by vacuum sublimation-polymerization onto freshly cleaved mica substrates as previously described. [6] AFM/STM images were obtained with a Veeco MultiMode Scanning Probe Microscope with a Nanoscope IIIa controller operated in tapping mode with TESPA tips. All compounds were characterized by standard spectroscopic methods.

2.2 Synthesis of Dyes 3

The appropriate amine 1a (4.34 g, 0.02 mol), 1b (5.24 g. 0.02 mol) was made into a slurry with sodium nitrite (1.66 g, 0.024 mol) in a small quantity of water and added portion-wise to cold concentrated sulfuric acid (23.52 g, 0.24 mol), maintaining the temperature below –5 °C. After stirring for 15 min, acetic acid (5 mL) was added and stirring was continued until diazotization was complete.

In a separate flask, a solution of 2 (4.47 g, 0.030 mol) in acetic acid (15 mL) was added to an ice-water mixture (200 g) in a beaker equipped with a mechanical stirrer and pH meter. The diazonium salt liquor 1 was then added at 5 °C over 30 minutes. The mixture was further stirred for at least 3 hours at ambient temperature. During the addition and stirring period, the pH was adjusted from 1.5 to 2.0 by dropwise addition of aqueous sodium hydroxide (20% w/v) to the mixture. The pH was finally raised to 4.0-4.5 by dropwise addition of the sodium hydroxide solution. After completion of the coupling reaction, the precipitated dye was filtered, washed with warm water and dried. The product was purified by column chromatography using hexane and ethyl acetate as eluents. [8]

2.3 Synthesis of Protected Thiols 5

To a solution of 3a or 3b (0.0024 mole) in THF (30 mL) was added bis(triphenylphosphine)palladium(II) chloride (0.108 g, 0.000154 mol), copper iodide (0.030 g, 0.00016 mol) and triethylamine (7.26 g, 0.0711 mole). The solution was stirred under argon for 1 hour. Compound 4 (0.45 g, 0.0026 mol) was added and the reaction was allowed to stir at room temperature for 2 d. The reaction was quenched with water, extracted with ethyl acetate and dried over sodium sulfate. The solvent was removed, and the residue purified by silica gel flash chromatography to give 5a or 5b. [9]

2.4 Synthesis of Thiols 6.

Compounds 5 (0.000719 mole) were dissolved in a mixture of 25 mL of dry methanol and 10 mL of dry dichloromethane and degassed with argon for 10 minutes. To this solution was added anhydrous potassium carbonate (0.60 g, 0.0043 mole) under positive pressure of argon and stirred overnight. The solution was filtered and the solvent removed. The residue was purified on neutral alumina to give compounds 6a and 6b. [10]

3. Results and Discussion

3.1 Synthesis of Chromophores for Surface Derivatization

For this study, two probe molecules were prepared. (Fig. 1) Each consisted of an aryl thiol "anchor" for surface attachment and an intensely absorbing diazo dye that could be used to monitor surface attachment using UV-vis spectroscopy. Diazotization of bromoanilines 1 was followed by coupling to the substituted aniline 2 to give diazo dyes 3 in good yields. This was then coupled to the protected surface anchor 4 (prepared by the method of Tour [7]) by a palladium-catalyzed cross-coupling reaction. After removal of the acetate protecting group, thiols 6 were isolated.

3.2 Surface Morphology of PEDOT Films

The surface and bulk properties of PEDOT vary significantly, depending on the method of preparation. In addition, exposure to either solvent or elevated temperature has been found to substantially change the physical and electronic properties of various PEDOT films. [11, 12] We are interested in preparing ultra-smooth films that are stable to organic solvents in order to construct and characterize surface-mounted molecular devices. [1-3]