# Nanoscale Charge Transport in Light Emitting Diode Materials Using Conducting Atomic Force Microscopy

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## INTRODUCTION

Conducting atomic force microscopy (C-AFM) is an important technique in the study of nanoscale charge transport properties of materials, and is of interest in the growing field of energy-related research. Conjugated polyelectrolytes (CPEs) are a particularly interesting class of materials, as they have been used in multiple applications, such as optical components in biosensors in solution,[1] as electron injection layers in conjugated polymer light-emitting diodes (PLEDs),[2] and as active layers in solar cells[3] and light-emitting electrochemical cells.[4] Despite the many potential applications, very little is known about their electronic properties, such as charge transport and energy levels, although these parameters are crucial in determining device performance.

Unfortunately, electronic charge transport studies typically use an applied bias by conventional methods (including diodes and field effect transistors), which does not work in CPE studies due to the interference of ion conduction. Therefore, C-AFM is useful for studying the nanoscale transport of CPE films as a function of counter ion size. The AFM has distinct advantages in this research because it:

1) Enables transport measurements without requiring the processing of a top electrode (thereby preventing shorting/modification of the underlying device), allowing ultra-thin films to be measured.
2) Enables the correlation between surface morphology and charge transport at the size scale of the underlying structure, thereby facilitating correlations to morphology and the computation of mobility.

## CONJUGATED POLYELECTROLYTES

CPEs are materials having a conjugated backbone and ionic charged functional groups (see figure 1). Thus, they are soluble in polar solvents such as polar organic solvents and water, thereby combining the unique properties of conjugated polymers and the processibility of polyelectrolytes. Since the charge transport in conjugated polymer films depends strongly on the interchain interactions, in this study we manipulated the interchain interactions in these CPE systems by counter anion exchange. The strong interchain contacts of PFBT-Br in solution and films were reduced by replacing the smaller $Br^-$ counter anion with the dimensionally larger $BAr^F_4{}^-$ counter anion (PFBT-$BAr^F_4$).[5]

## CONDUCTIVE ATOMIC FORCE MICROSCOPY

In C-AFM the surface topography and local current passing through the sample can be measured simultaneously by rastering a metal-coated tip in contact mode over the surface while a fixed bias is applied between the conductive probe and the substrate. Alternatively, the metal-coated tip can act as a single-point electrode to obtain local I-V curves, from which

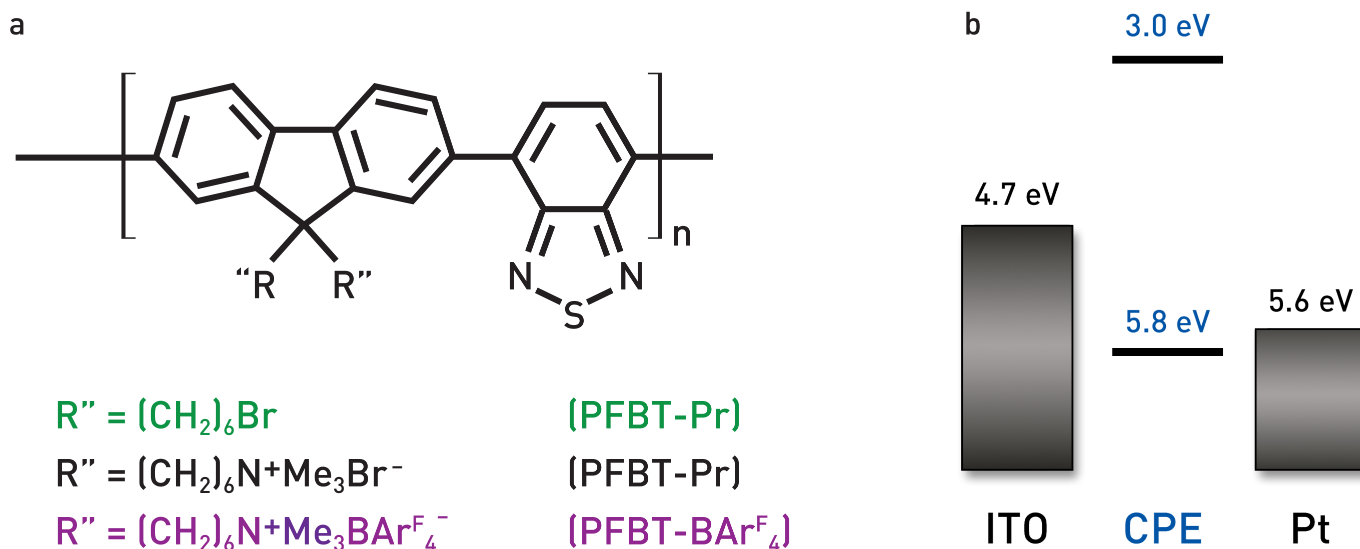


Figure 1. (a) Chemical structures of CPEs used in this study and (b) energy levels of the conducting substrate, metal-coated probe, and CPEs.

carrier mobilities can be extracted. In this application note we describe the application of C-AFM for charge transport measurements of CPE thin films used in PLEDs (see figure 2). This measurement is particularly difficult to perform with conventional electrode evaporated, hole-only diodes because of the thickness restriction in the CPEs.

Several advantages of using C-AFM for charge transport measurements are 1) no separate set of devices is needed because the measurements can be done on the same PLED; 2) correlation between surface morphology and charge transport can be made; 3) thin and soft polymer films can be studied (these are typically difficult to study by conventional diode techniques); 4) distribution of hole mobility can be computed; and 5) C-AFM provides a charge transport measuring technique that by-passes the effects and restrictions caused by thermal evaporation of a top electrode in hole- and electron-only diodes. Often, a high work function metal such as Pt or Au is used and damage to the organic thin film can occur during metal evaporation.

## SAMPLE PREPARATION AND MEASUREMENTS

Thin films of approximately 20 nanometers were spin-coated onto indium tin oxide (ITO) substrates. Silver paste was used to provide electrical contact between the ITO substrate/ sample and the metal puck for bias application.

C-AFM measurements were performed with a Veeco MultiMode® equipped with a C-AFM module. A Pt-coated Si tip with a 0.2 N/m spring constant and ~25 nm tip radius was used. The Pt-coated tip in contact with the CPEs complete the sandwiched hole-only device. Pt and ITO with work functions of 5.6 eV and 4.8 eV ensure a large electron injection barrier when either is negatively biased and allows hole injection when Pt is positively biased (see figure 1b). A contact force of 40 pN was used for all measurements showing no apparent

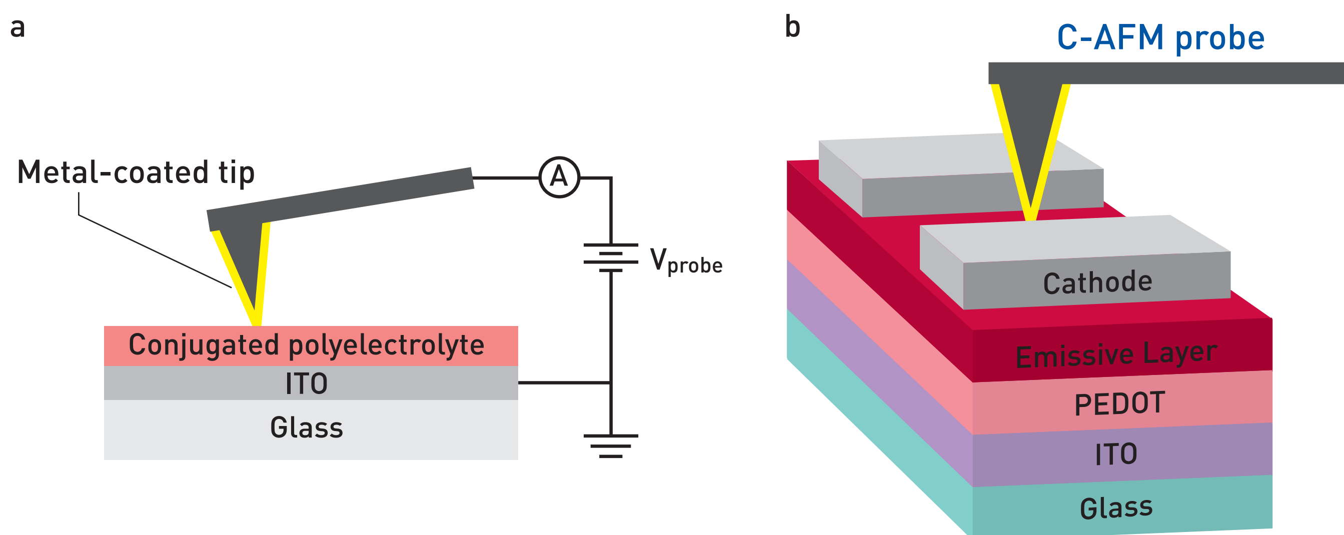


Figure 2. Schematic drawing of C-AFM setup to study (a) thin polymer film or (b) organic light-emitting diode.

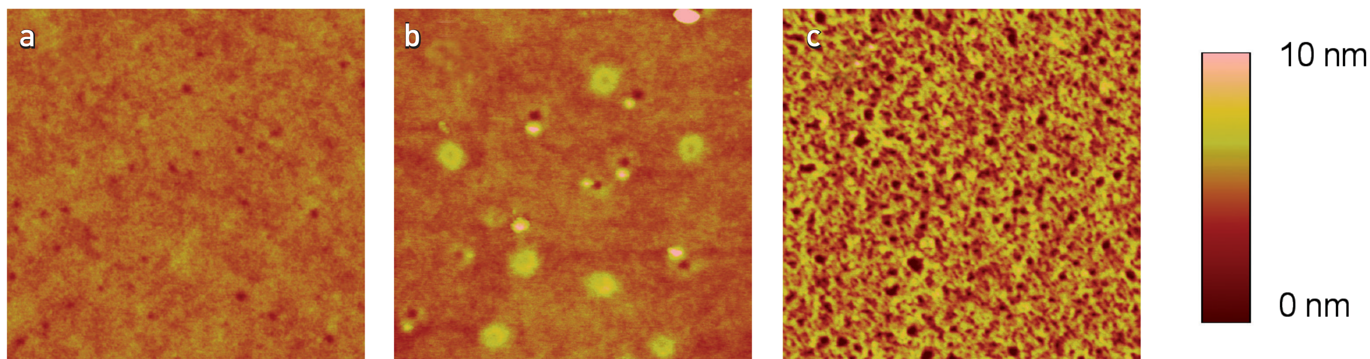


Figure 3. AFM topography images of a) PFBT-Br, b) PFBT-BAr$^F_4$, and c) PFBT-Pr.

variation upon repeated applications. A tip/sample contact area of 84 nm$^2$ was calculated using the Hertz model, where the contact radius, a, is described by: $a = (3FR/4Y^*)^{1/3}$ and $1/Y^* = (1 - \nu^2_1)/Y_1 + (1 - \nu^2_2)/Y_2$, where $F$ the load, $R$ the tip radius, $Y$ the Young's modulus, and $\nu$ the Poisson's ratio. With $F$ = 40 nN, $R$ = 25 nm, $Y_1$ = 168 GPa and $\nu_1$ = 0.38 for Pt, $Y_2$ = 3 GPa and $\nu_2$ = 0.35 for polymer, and $a$ is calculated to be around 6.03 nm.

## SURFACE TOPOGRAPHY BY AFM

The surface topography AFM images of the CPE films along with the film of the neutral precursors are shown in figure 3. The AFM images of the CPEs are similar while that of the neutral precursor is much rougher. Similarities between the CPE films are likely due to identical solution processing; CPEs solutions were spin-coated from methanol while the neutral precursor from toluene.[5]

## NANOSCALE CHARGE TRANSPORT BY C-AFM

I-V measurements at various locations were performed in each sample and averaged manually (see figure 4). As expected, significantly lower currents are observed in PFBT-Pr and PFBT-BAr$^F_4$ films at positive tip bias than negative due to larger hole injection barriers from ITO.

For the PFBT-Br film, a large current is observed at positive tip bias, indicating reduced hole injection barriers from ITO with this CPE. This was not anticipated but is believed to be due to the formation of an interface dipole at the ITO/CPE interface caused by the more exposed ionic charge of the Br- counter anion.[5]

Carrier mobilities were extracted using the space charge limited current model commonly adopted in organic diode charge transport measurements (see figure 4b).[6] Log$J$-logV plots of the films exhibit two regions; space charge transport with shallow traps region ($J \sim V^2$) and a trap limiting regime ($J \sim V^m$, m > 2). Hole mobilities of 3.4 x 10$^{-4}$ cm$^2$/Vs, 1.1 x 10$^{-5}$ cm$^2$/Vs and 6.5 x 10$^{-6}$ cm$^2$/Vs were determine for PFBT-Br, PFBT-BAr$^F_4$ and PFBT-Pr, respectively. One order decrease in hole mobility with exchange of the counter anion from Br- to BAr$^{F-}_4$ was observed supporting our hypothesis that the dimensionally larger BAr$^{F-}_4$ anion act as a spacer that separates polymer chains and hence affects the optical and charge transport properties.[5]

## CONCLUSION

C-AFM can be employed for charge transport measurements of sensitive and soft organic films with little damage. This is in contrast to the irreversible

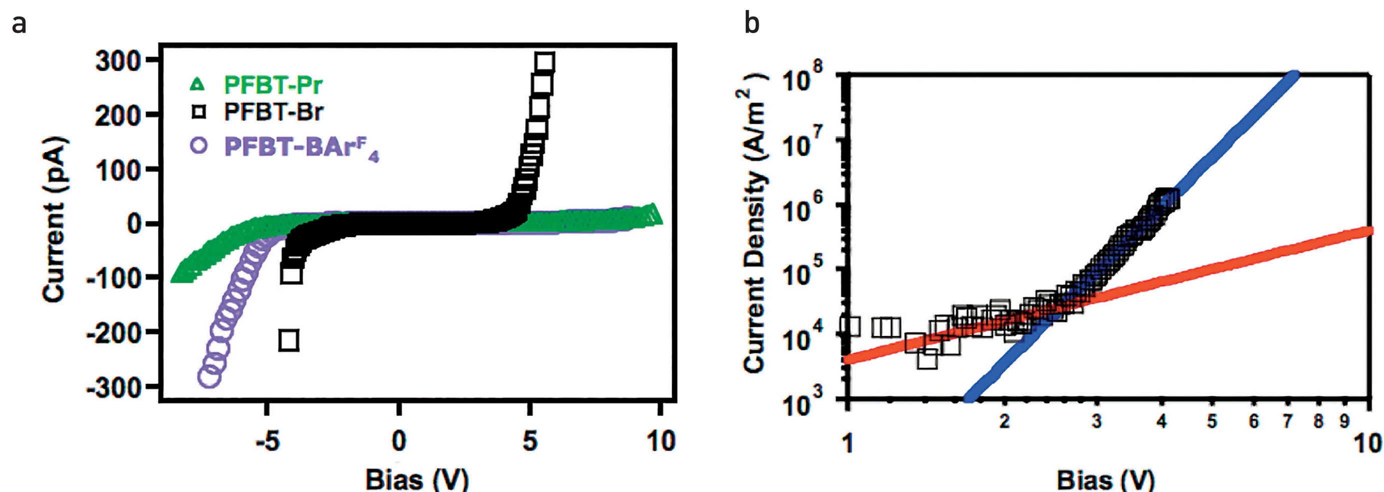


Figure 4. Average I-V curves of a) the three polymer films and b) a representative logJ-logV plot showing general behavior observed in all samples.

damage that can be caused upon the deposition of thermally evaporated electrodes. When using C-AFM, the top electrode is a metal-coated tip in light contact with the surface, so there is little chance of electrically shorting the thin sample during the transport measurements. This proves particularly useful for situations in which thick films are difficult to fabricate and for materials with little availability. Additionally, it is possible to conduct charge transport measurements at selective locations with <100 nm resolution, allowing examination of transport across different domains within a film. To the best of our knowledge, C-AFM is the only technique allowing charge transport measurements on the nanometer scale.

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