

Probing Nanotribological and Electrical Properties of Organic Molecular Films with Atomic Force Microscopy

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Summary: Structural aspects of organic molecular films, such as disordering, packing density, molecular bending or tilts, and phase separation, influence electrical properties as well as friction and adhesion. This indicates a correlation between nanomechanical and charge transport properties of molecular films at the molecular scale. In this review, we highlight the recent studies on correlations between charge transport and nanomechanical properties probed with atomic force microscopy. We discuss the key issues that determine charge transport and nanomechanical properties on several organic molecular films, including self-assembled monolayers formed by saturated hydrocarbon molecules conjugated molecules, and hybrid molecules as well as polymer and polymer blend films. We address the role of molecular deformation and bending in friction and conductance measurements. SCANNING 31: 1–8, 2010. © 2010 Wiley Periodicals, Inc.

Key words: self-assembled monolayer, friction, charge transport, polymer films, atomic force microscopy

Introduction

The charge transport mechanisms in organic molecular films have drawn much interest due to potential applications in organic electronics. Organic molecular films can be in the form of self-assembled monolayers (SAMs; thickness—a few nanometers) or bulk films (e.g., polymer films; thickness—tens to hundreds of nanometers). The electronic structures of SAMs have been extensively studied with various techniques, such as conductance atomic force microscopy (AFM) (Kelley *et al.* 1999; Song *et al.* 2007), break junction experiments (Reed *et al.* 1997; Reddy *et al.* 2007; Xu and Tao 2003), or hanging mercury-drop electrode measurements (Slowinski *et al.* 1997). For example, octadecyltrichlorosilane has been proposed and used as a gate insulator in organic electronics (Fontaine *et al.* 1993). Earlier studies indicate that the charge transport properties of SAMs are greatly influenced by molecular deformation that result in structural variation of molecules, such as tilting or disordering (Qi *et al.* 2008; Slowinski *et al.* 1997). Passivating surfaces with SAMs or hydrocarbon molecules is one of the strategies used for minimizing stiction and reducing adhesion and friction in micro- and nanoelectromechanical systems (Bhushan and Liu 2001; Kim *et al.* 2001; Liu and Bhushan 2002). The strong influence of structural aspects of SAMs on mechanical properties indicates an atomic or molecular scale correlation between charge transport and mechanical properties of SAMs. Similar effects were also observed for rather thick organic films.

Structural aspects that influence the mechanical and electrical properties of organic molecular films include packing density, lattice order, orientation configuration, load-induced disorder, grain boundaries, annealing-induced morphological evolution,

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and phase separation/segregation. Figure 1 depicts the structural factors that influence charge transport and friction properties. For example, the tight packing of SAMs due to van der Waals attractive forces prevents, at moderate loads, low energy excitations (molecular bending or tilt, gauche defects, etc.), which are major contributors to energy dissipation processes during friction (Salmeron 2001), implying a strong correlation between tribological properties and molecular conformation in the SAMs.

Experimental Approach

The organic molecular films on various types of substrates (conducting, semiconducting, or insulating substrates) have been prepared with techniques, such as the Langmuir-Blodgett technique, dipping the substrates into solution with molecules, drop casting, or spin-coating (Barrena *et al.* 2000; Bocking *et al.* 2007; Flater *et al.* 2007; Xiao *et al.* 1996; Zhang *et al.* 2002). The friction and conductance measurements were performed with a conductive-probe AFM (CP-AFM) system. The normal force exerted by the cantilever was kept constant during AFM imaging, while the current and friction force between tip and sample were recorded simultaneously (Park *et al.* 2006; Qi *et al.* 2008). To determine these forces, the cantilever spring constant was calibrated by using the resonance-damping method of Sader *et al.* (1995), whereas the lateral force was calibrated with the wedge method of Ogletree *et al.* (1996). The spring constant of the cantilever used for the study varies between 0.1 and 10 N/m, while the cantilever is coated with a metallic layer for the conductance measurements. It is crucial to carry out the experiment in the low-load regime so that there was no damage to the surface. This can be confirmed by inspection of the images with Ångstrom depth sensitivity as well as by the reproducibility of the friction and

adhesion measurements. If the measured friction force did not change at constant load and did not show time-dependent behavior in the elastic regime, we can assume that the tip experiences minimal changes during subsequent contact measurements.

Figure 2(A) shows this experimental approach involving the formation of SAM islands with the size of 100–200 nm. The heights of islands (molecular deformation) can be obtained from topographical AFM images, while nanotribological and charge transport properties of alkylsilane SAMs on silicon surface are measured using AFM with a conducting tip (Park *et al.* 2009). In this manner, we can vary the load applied to the tip-sample contact while simultaneously measuring the frictional responses and electric conductance. Figures 2(B–D) show the topographic, friction, and current images, respectively, that were acquired simultaneously on hexadecylsilane islands on silicon (111) surface. The hexadecylsilane islands are 100–200 nm in diameter and have a height of 1.6 nm at the applied load of 0 nN (or effective total load of 20 nN). Friction on the island is approximately 30% of that on the surrounding bare silicon, consistent with the low friction of the lubricating alkylsilane layer. It is also clear that the current measured on the alkylsilane island is much smaller than that measured on the silicon surface due to the insulating nature of alkylsilane molecules.

Alkylthiol and Alkylsilane SAMs

For insulating SAMs, such as alkylthiol or alkylsilane, molecular tilt induced by the pressure applied by the tip is one major factor that leads to increased film conductivity. When insulating SAMs are placed between electrodes, the junction resistance changes exponentially: $R = R_0 \exp(\beta s)$, with electrode separations, where R_0 is the contact resistance and β is a decay parameter (Wang *et al.* 2005). By measuring the

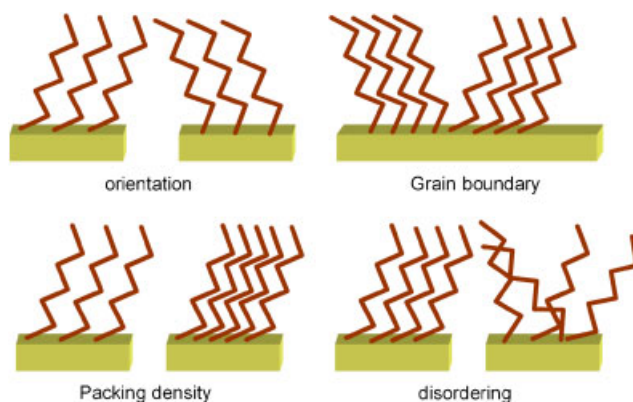


Fig 1. Structural aspects that influence the mechanical and electrical properties of self-assembled monolayers: orientation configuration, packing density, lattice order, and grain boundaries.

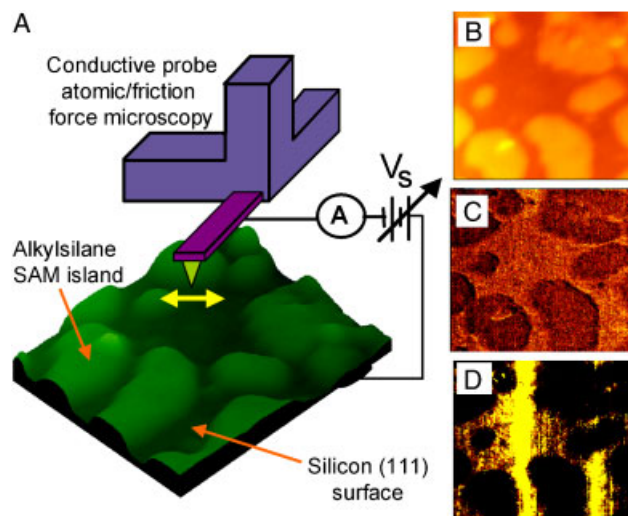


Fig 2. (A) Schematic of AFM measurement of current and friction on SAM organic molecules/Si (111) surface. $500 \times 500 \text{ nm}^2$ images of (B) topography, (C) friction, and (D) current taken in contact AFM mode on hexadecylsilane molecules/Si (111) surface that were measured at the effective load of 20 nN and $V = -2 \text{ V}$ (Reprinted figure with permission from (Park *et al.* 2009)).

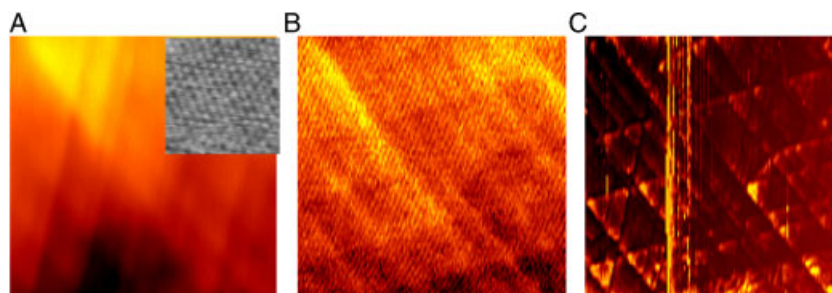


Fig 3. (A) $200 \text{ nm} \times 200 \text{ nm}$ topographic image (load = 48 nN) of a C16 monolayer on Au(111). Inset is a high-resolution image ($2.5 \times 2.5 \text{ nm}$) showing the $(\sqrt{3} \times \sqrt{3})R30^\circ$ molecular periodicity. (B) Friction force image. (C) Current image (sample bias 1.5 V) (Reprinted figure with permission from (Qi *et al.* 2008)).

current between the conductive AFM tip and SAMs as a function of the height of the molecules, the decay parameter (β) can be obtained.

Figures 3(A–C) shows topography, friction, and current images obtained simultaneously for a full monolayer of C16 alkythiol SAMs (Qi *et al.* 2008). The topographic image reveals the commonly found structure of the gold film substrate, composed of triangular-shaped terraces separated by atomic steps. The current is low and uniform except at the step edges, presumably because the alkythiol molecules are not well organized at these locations; thus, the tip can get closer to the Au surface. Lattice-resolved images of the film (inset in Fig. 3(A)) reveal a $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity of the molecules relative to the gold substrate.

Current–voltage (I–V) characteristics were measured on the C16 alkythiol sample for loads varying between -20 and 120 nN . Figure 4(A) shows a semilog plot of the current at a bias of 1 V as a function of applied load. The current changes in a stepwise manner, and the plateaus are associated

with the discrete tilt angle of the molecules (Qi *et al.* 2008). A stepwise response of the SAM film to pressure has been observed previously in other properties, such as film height and friction of alkyldisilanes on mica and alkythiols on gold (Barrena *et al.* 1999; Salmeron 2001).

These changes were shown to correspond to the molecules adopting specific values of their tilt angle relative to the surface, and explained as the result of methylene groups interlocking with neighboring alkyl chains. The results for both islands (triangles) and complete monolayers (square) are shown in the semilog plot of junction resistance (R) per unit area vs. film thickness of Figure 4(B). In the case of complete monolayers, the data in Figure 4(A) were converted to current vs. electrode separation by assigning each step in the current to a specific molecular tilt angle, following the sequence established in previous experiments. As can be seen, $\ln(R)$ increases approximately linearly with tip–surface separation, with an average slope of $\beta = 0.57$ (± 0.03) \AA^{-1} . The solid line shows a linear fit to the

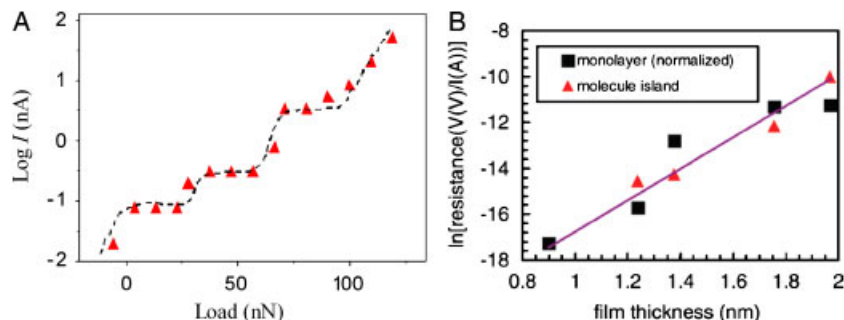


Fig 4. (A) Semilog plot of the current at 1 V bias as a function of applied load measured on C16 monolayer on Au(111). (B) Semilog plot of the junction resistance per unit area vs. distance between electrodes. Square symbols are experimental data for complete monolayers after the normalization by the contact area. Triangle symbols are experimental data on the C16 island sample. The line is a linear fit to the data with β of 0.57 \AA^{-1} (Reprinted figure with permission from (Qi *et al.* 2008)).

data with a fitting parameter of $\beta = 0.57 \text{ \AA}^{-1}$. Similar measurement of the decay parameter on the molecular tilts was carried out with a scanning tunneling microscope and simultaneous sensing of forces (Park *et al.* 2008). By measuring the current as a function of applied load, a tunneling decay constant $\beta = 0.53 (\pm 0.02) \text{ \AA}^{-1}$ was obtained.

The correlation between molecular conductivity and mechanical properties (molecular deformation and frictional responses) of hexadecylsilane SAMs was studied with CP-AFM and friction force microscopy (Park *et al.* 2009). By measuring the tunneling current change due to the change of height of the molecular islands by tilting the molecules under pressure from the tip, an effective conductance decay constant β of 0.52 \AA^{-1} for hexadecylsilane SAMs was obtained.

Conducting Organic Molecules

Conjugated Molecules and Hybrid Molecules

In the previous section, saturated hydrocarbon chains have been discussed. In this section, we will focus on conjugated and hybrid molecules, which have shown many applications in organic electronic devices (e.g., organic thin-film transistors) as well as organic optoelectronic devices (e.g., organic light emitting diode and organic photovoltaic device). Note that “hybrid” molecules are defined rather broadly in this article to be any molecule that contains both conjugated groups and saturated hydrocarbon chains.

Similar to saturated hydrocarbon chains, packing density, lattice ordering, and orientation configuration of conjugated/hybrid molecules show profound influences on their charge transport and nanotribological properties. Trans-stilbene (TSB) is such a conjugated molecule. When connected to a sufficiently long hydrocarbon chain with a thiol group as the head group, these molecules can be

self-assembled onto Au. In such TSB-based SAMs, salient changes take place after the sample is heated for 1 h at 120°C (Qi *et al.* 2010). One such change is that the formation of ultra-flat and crystalline molecular islands on which the molecular lattice resolution can be easily obtained. These islands also correspond to lower friction, consistent with higher lattice ordering and better packing. Under the same load, the current level on these crystalline islands is more than two orders of magnitude higher than that of the SAM before heating. The heating promotes crystallinity in these islands, resulting in reduced friction and higher conductivity. Scanned with high-load-induced disorder destroys the high crystallinity, leading to the observed current level reduction based on the conductance AFM measurements.

The second example is the friction anisotropy due to the orientational configuration of penta-thiophene-based molecules (C14-5TBA) in the SAM (Chen *et al.* 2006; Ratera *et al.* 2005). The central part of the molecule C14-5TBA (Fig. 5(A)) is a penta-thiophene unit exhibiting good electronic properties. The top of C14-5TBA is a 14-carbon alkyl chain for better solubility, and a surface-active carboxylic acid group is used as the anchor group to aid in self-assembly. C14-5TBA in the fully extended conformation is 4.1 nm in length. Molecular islands of C14-5TBA form via drop casting, allowing precise measurements of the molecular height. The molecular conformation can be inferred from the molecular height by assuming that the penta-thiophene unit adopts upright orientation in the SAM. The smaller diameter of the alkyl chain (0.46 nm) than that of penta-thiophene unit (0.65 nm) allows the alkyl chains to tilt, with the height changing from 4.1 to 3.2 nm and eventually to 2.6 nm (Fig. 5(B)). It is worth noting that a decrease in the height is accompanied by a simultaneous increase in the friction force (Fig. 5(B)). The better molecular packing introduced by the long alkyl chains enables high-resolution imaging. Two lattice parameters (0.45 and 0.65 nm) are identified in the lattice-resolved AFM

images. The friction is anisotropic with respect to scanning directions. A factor of 1.6 is observed between the friction values when scanning at an angle of 78° relative to the compact molecular rows that are at 49° . The friction anisotropy is originated from the anisotropic sizes of the penta-thiophene unit along two in-plane directions.

Although saturated hydrocarbon chains mainly interact with each other via weak van der Waals forces, much stronger intermolecular π - π interactions can be present in organic films comprising conjugated/hybrid molecules. This will affect nanotribological properties, and even more dramatically influence charge transport. In a conductance AFM study of two SAM systems, Fang *et al.* revealed the role of π - π stacking on charge transport and nanotribological properties of SAM consisting of aromatic molecules (Fang *et al.* 2007). The two model molecules chosen in this study are (4-mercaptophenyl) anthrylacetylene (MPAA, Fig. 6(A)) and (4-mercaptophenyl)-phenylacetylene (MPPA, Fig. 6(B)). While in MPPA the end group is a single benzene ring, in MPAA it is changed to a three fused benzene ring structure. This structural difference induces different degrees of lattice ordering in these two molecular SAM systems. Lattice

resolution is readily achieved in the MPAA SAM, but it is not possible for the MPPA SAM under the same imaging conditions, indicating the MPAA is lacking long-range order. Correspondingly, the friction force is substantially lower in the MPPA SAM than that in the MPAA SAM, a common feature of well-packed molecular films. However, it is important to note that even without long-range order, the stronger intermolecular π - π stacking in the MPAA SAM greatly facilitates charge transport, resulting in approximately one order of magnitude higher conductivity than in the MPPA SAM (Fig. 6(C)). It is also reported in this article that the nanotribological properties, in particular the friction force on the two types of SAMs, can be well described by the Johnson-Kendall-Roberts model (Fig. 6(D); Johnson *et al.* 1971).

Polymers and Polymer Blends

In polymer films, grain boundaries are commonly observed on a 100-nm length scale. A recent scanning Kelvin probe microscopy (SKPM) study has revealed that these boundaries between crystalline

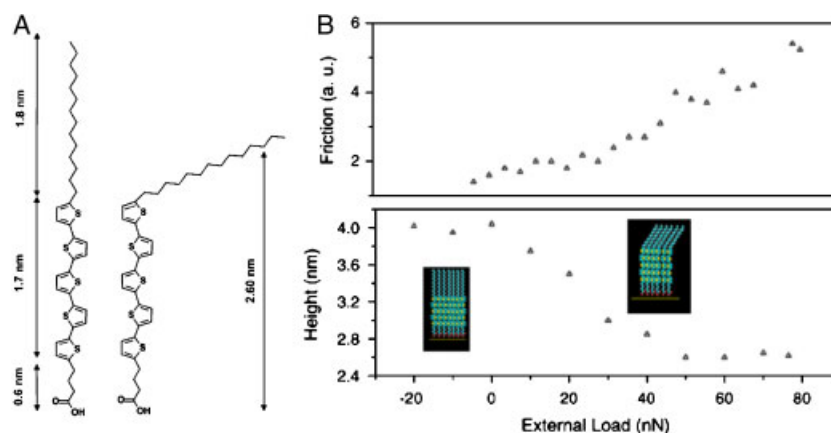


Fig 5. (A) Schematic representation of the structure of C14-STBA. (B) Plots of friction and molecular island height as a function of external load (Reprinted figure with permission from (Chen *et al.* 2006)).

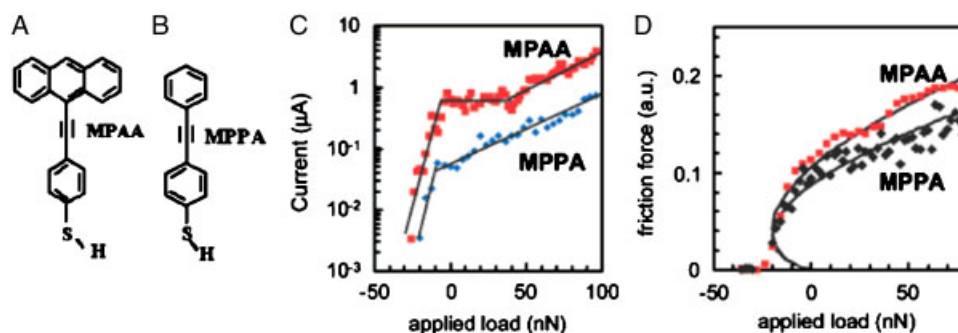


Fig 6. Schematic representation of MPAA (A) and MPPA (B). Plots of current (C) and friction (D) as a function of applied load acquired on the MPAA (square) and MPPA (diamond) SAMs (Reprinted figure with permission from (Fang *et al.* 2007)).

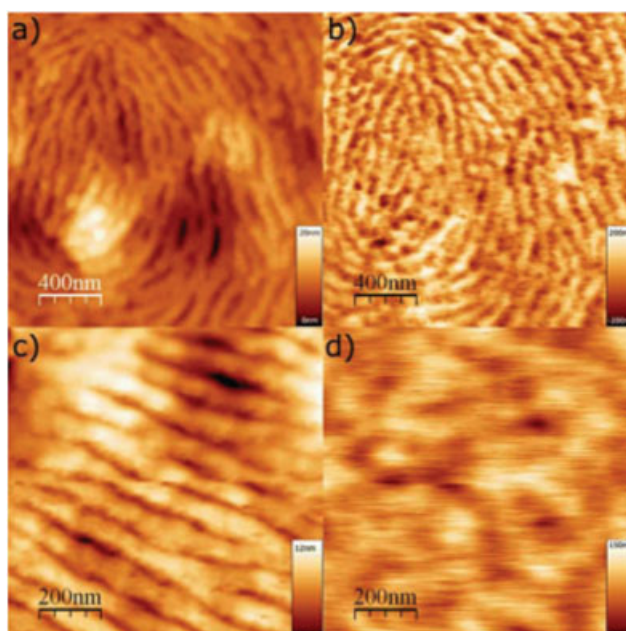


Fig 7. AFM topographic (A) and surface potential (B) images of an 80-nm thick ribbon phase pBTTT film. AFM topographic (C) and surface potential (D) images of the same area of the film taken after 1 h stress at $V_g = -80$ V (Reprinted figure with permission from (Hallam *et al.* 2009)).

domains constitute preferential charge trapping sites and lead to variations of the carrier concentration (Hallam *et al.* 2009). The formation and population of charge traps, especially the long-lifetime ones, has a pronounced effect on the long-term performance and stability of OFET, e.g., threshold voltage shift. With a single-walled carbon nanotube attached to the metal-coated tip, a resolution better than 50 nm can be achieved, which enables the observation of fine details of the ribbon mesophase (See Fig. 7(A) for the topographic image of the ribbon phase) of poly[2,5-bis(3-alkylthiophen-2-yl)thieno(3,2-b)thiophene] (pBTTT). When a gate voltage is applied, the SKPM surface potential image (Fig. 7(B)) reveals that charges are preferentially trapped in the transition regions between the chain-extended crystalline ribbons (Hallam *et al.* 2009). The remarkable similarity between Figures 7(A) and (B) is in clear contrast to the unrelated features in topographic and surface potential images (Fig. 7(C) and (D)) when no gate bias is applied. This emphasizes the heterogeneous microstructure, which cannot be explicitly extracted from the traditional FET device performance measurements. In this study, once again, the power of high-resolution AFM techniques is demonstrated, because it is very difficult to identify and investigate the effects of heterogeneity on a 100-nm scale with traditional electrical measurements over a length scale of several micrometers using FET structures.

With the presence of more than one component in a film, e.g., small molecules:polymer blend films,

phase separation and annealing-induced morphological changes can be crucial for charge transport properties of such films. One of the most widely studied small molecule:polymer blend systems is PCBM:P3HT. In a spin-coated PCBM:P3HT film (blend ratio 1:1 by weight), drastic morphological evolution and increase of the surface roughness after annealing is observed using AFM (Campoy-Quiles *et al.* 2008). The increase of surface roughness is caused by PCBM molecules diffusing out of the blend film toward the air surface on annealing and the subsequent formation of larger aggregates of PCBM (Campoy-Quiles *et al.* 2008). It is demonstrated via the conductance AFM study by Pingree *et al.* that such morphological changes and phase separation tremendously influence charge transport properties of such blends (Pingree *et al.* 2009). It was found that both hole mobility and dark current strongly depend on annealing time. Therefore, the annealing-induced disordering is one crucial molecular factor that influences charge transport properties.

Summary and Outlook

In this study, we review recent progress on charge transport and nanotribological studies of organic molecular films formed by saturated hydrocarbon molecules, conjugated molecules, or hybrid molecules as well as polymers or polymer blends. A number of influencing factors are discussed,

including packing density, lattice ordering, molecular deformation, grain boundaries, annealing-induced morphological evolution, and phase separation. We show that AFM operated using various modes serves as a suitable and powerful tool for tackling these challenging issues.

Although substantial advances in the understanding of various aspects of organic films in particular and organic electronics in general have been achieved, there are still many fundamental and practical issues awaiting exploration. As emphasized in this review, high resolution offered by using scanning probe microscopy (SPM) is key in identifying and studying microstructures (e.g., molecular tilt, lattice ordering, defects, vacancies, and grain boundaries) in organic films and their effects on electronic and mechanical properties. Parallel with the growth of organic electronics, researchers also devote tremendous efforts in developing new SPM techniques with even higher resolution. Nanoelectrodes, in combination with AFM, are one of the most promising venues to explore the correlation between microstructures and electronic properties of organic films. Because AFM can apply a force to a precise local position with an accurate magnitude, it is possible for inducing lattice disorder/defects in a controlled fashion. Therefore, much more can be learned from such AFM measurements.

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