

Self-Organization of Phenyleneethynylene into Wire-Like Molecular Materials on Surfaces

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A model phenyleneethynylene, which does not possess any functional groups, self-organizes into wire-like structures on 2D surfaces. High-resolution STM imaging revealed that the molecules are arranged in a skewed 1D fashion. Analysis of various domains indicated the existence of two types of molecular packing arising from different modes of alkyl $\text{CH}\cdots\pi$ interaction, which was further supported by theoretical calculations.

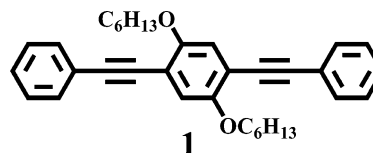
Introduction

Organization of photo- or electroactive molecules on two-dimensional surfaces, with atomic-level precision, provides excellent possibilities for designing nanoscale optoelectronic devices.¹ Various noncovalent interactions between the molecules and with surfaces play a decisive role in their organization.² An in-depth understanding of these interactions is essential for device fabrication, and scanning tunneling microscopy (STM) is an excellent tool for probing these aspects with atomic-scale resolution.^{3–7} Among the various molecular building blocks, π -conjugated molecular systems such as oligo(phenyleneethynylene)s (OPE) have been suggested as elements in optoelectronic devices because of their fascinating structural and optical properties.^{7–11} The unique properties of OPEs include (i) the rigid structure that does not involve any possibility of isomerization and (ii) the cylindrical symmetry of the acetylene unit, which maintains the π -electron conjugation at any degree of rotation. Recent photophysical and theoretical investigations from our group⁸ and others^{9–11} have revealed that OPE-based systems possess excellent luminescent properties. Interchromophoric interactions of such molecules in assemblies can alter their optoelectronic properties, hence the way in which OPEs organize on surfaces is very crucial for device applications. Herein we report the self-organization of a model OPE molecule, which does not possess any functional groups, (Chart 1) on a highly oriented pyrolytic graphite (HOPG) surface at ambient conditions and investigate the various modes of interactions.

Experimental Section

Synthesis of compound **1** has been reported elsewhere.^{8b,11a} Samples for STM investigations were prepared by drop casting 0.1 mM solution of **1** in 1,2-dichlorobenzene on to a freshly cleaved HOPG surface, dried in air for ~ 12 h. The STM images were acquired in the constant-height mode under ambient conditions on a multimode scanning probe microscope (Nano-

CHART 1. Structure of Phenyleneethynylene 1



scope IV controller, digital instruments). Electrochemically etched Pt/Ir wire (80:20) was used as the STM tip.

Results and Discussion

STM images of phenyleneethynylene **1** showed well-organized domains at various locations on the HOPG surface. When imaged at larger scan sizes (for example, 45×45 nm²; Figure 1A), parallel arrangements of wire-like structures running over several nanometers were observed. An end-to-end arrangement of molecules was observed when the scan size was reduced to 18×18 nm² (inset of Figure 1A). It may be interesting to note that **1** does not possess any functional groups and then an obvious question arises: What are the forces that drive the molecules into a wire-like arrangement? To address this issue, we recorded high-resolution images at a smaller scan size of 6×6 nm² (Figure 1B). Bright rod-like structures arranged as 1D rows in a tilted fashion, each of them having an average length of 1.8 ± 0.1 nm, were observed throughout. In the STM images presented here, the bright and dark areas correspond to regions possessing high and low tunneling current, respectively. The aromatic phenyleneethynylene core can be distinguished easily in STM images as bright rod-like structures. In contrast, the alkyl chains appeared as dark because of the large energy difference between the electronic states of the aliphatic chain and the Fermi level of the substrate.^{4–6} The observed length of each bright region is in good agreement with the molecular length of the phenyleneethynylene core (1.844 nm), calculated from the X-ray crystal structure of **1** reported by West and co-workers.^{11a}

On further analysis of various domains, two types of images having very close resemblance with slightly dissimilar molecular packings were observed (Figure 1C and D). Each domain extends over an area of ~ 150 – 200 nm². A typical STM image

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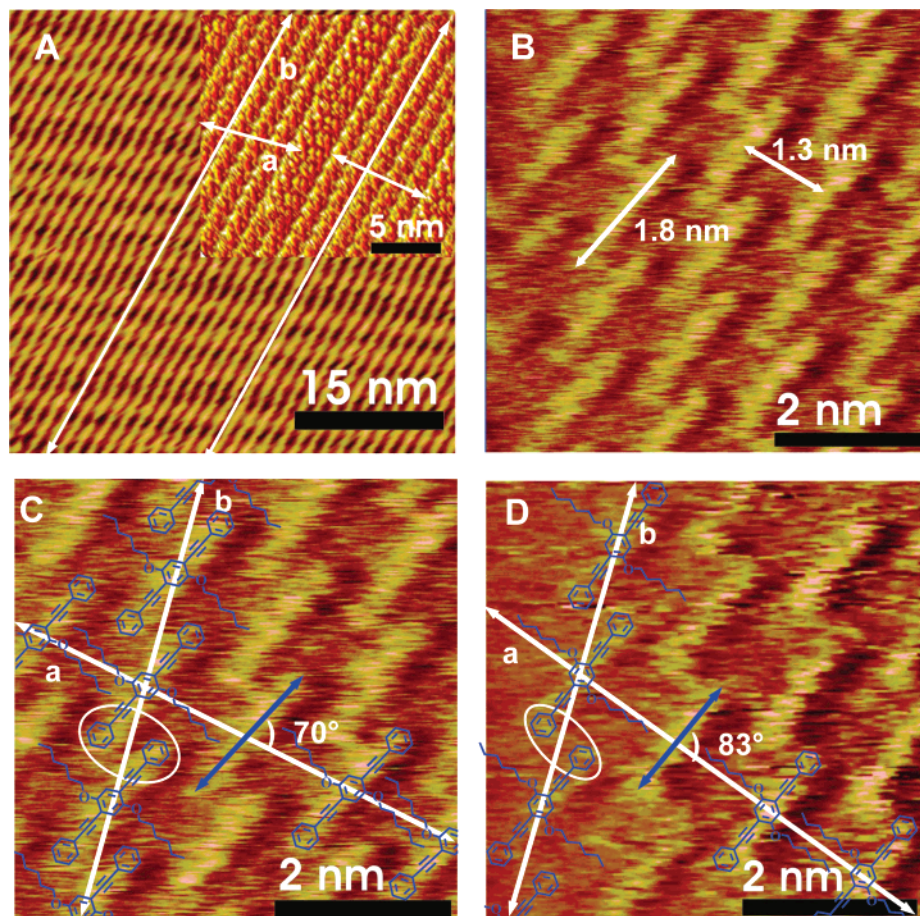


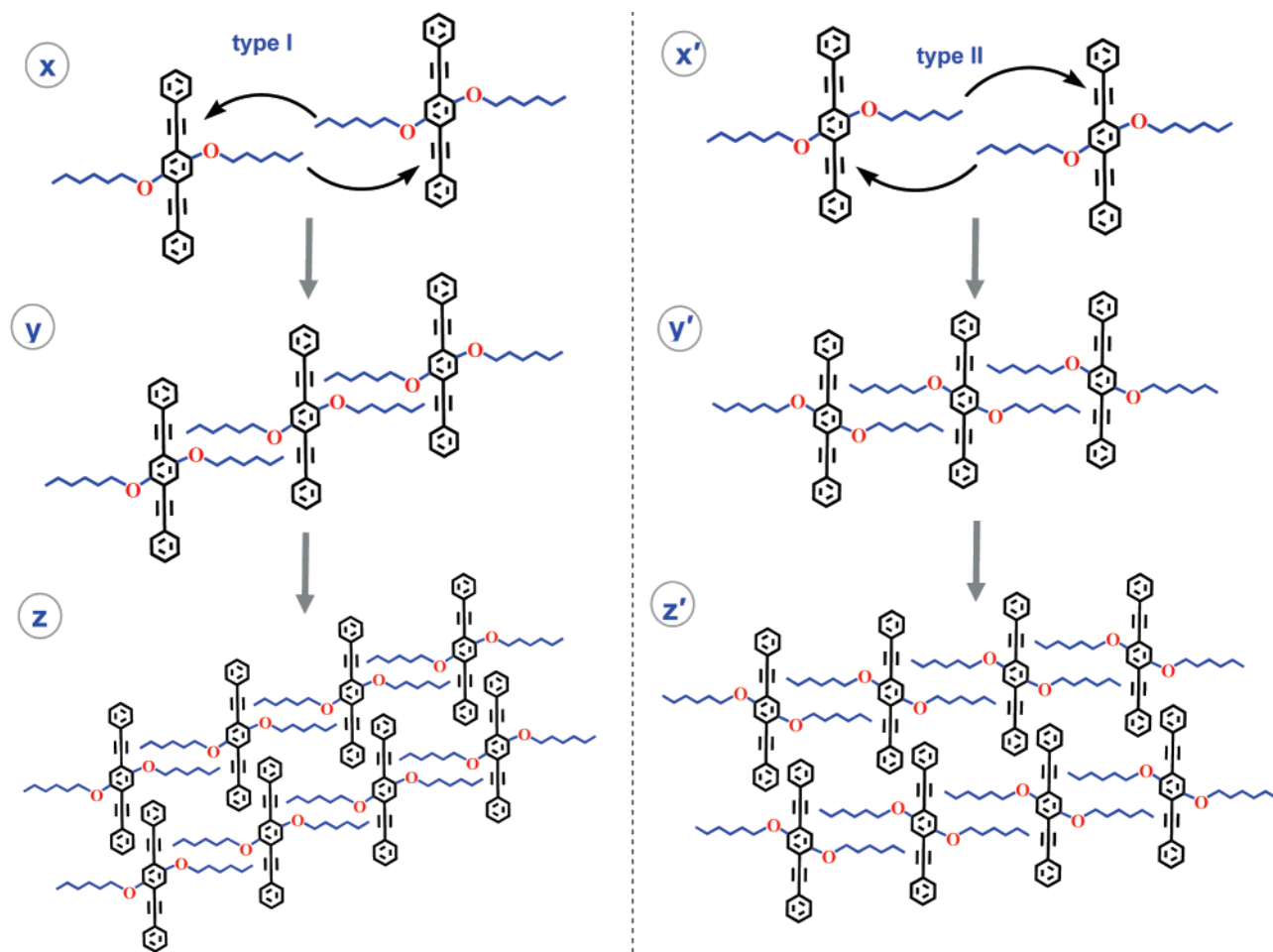
Figure 1. STM current images of **1** on HOPG (A) scan size of $45 \times 45 \text{ nm}^2$; $V_{\text{bias}} = 700 \text{ mV}$; $I_t = 700 \text{ pA}$, and the inset shows the real time zoomed image over a scan area of $18 \times 18 \text{ nm}^2$; $V_{\text{bias}} = -969 \text{ mV}$; $I_t = 118 \text{ pA}$. (B) High-resolution image showing the skewed 1D organization of **1**; scan size $6 \times 6 \text{ nm}^2$; $V_{\text{bias}} = -1072 \text{ mV}$; $I_t = 400 \text{ pA}$. (C and D) $5 \times 5 \text{ nm}^2$ scan-size images showing the two types of molecular packing observed at different locations; $V_{\text{bias}} = -1602 \text{ mV}$; $I_t = 324 \text{ pA}$.

showing the two types of packing and the domain boundary is presented in the inset of Figure 1A. It is interesting that these molecular packings have several similarities: both possess a parallel strip-like arrangement along the “a” axis (“a-strip”) and a skewed 1D arrangement along the “b” axis (“b-strip”). In both cases, the average distance between identical points on adjacent molecules along the *a*-strip is $1.3 \pm 0.1 \text{ nm}$ (averaged over 10 images), suggesting that there is enough room between two adjacent molecules for accommodating the hexyloxy groups because its length is $\sim 0.89 \text{ nm}$ in the extended conformation. The major difference between the two arrangements is the extent to which the molecules on adjacent *a*-strips overlap; the aromatic moieties are more interlocked in Figure 1C compared to those in Figure 1D (encircled portions). This raises another interesting question about how two types of organizations are formed from the same molecule. These aspects were analyzed further using computational methods.

Since the molecule is devoid of any strong hydrogen-bonding moieties, the self-organization of the system can be explained only on the basis of weak noncovalent interactions¹² (e.g., $\text{CH}\cdots\pi$ and $\text{CH}\cdots\text{O}$). Interestingly, the crystal structure of **1** is rich in such noncovalent interactions.^{11a} This includes (i) acetylenic π -alkyl CH, (ii) acetylenic π -aromatic CH, and (iii) alkoxy oxygen-aromatic CH interactions (Supporting Information). Furthermore, within a crystallographic plane, a constant distance of 1.37 nm is maintained between the two molecules through the interdigitation of the hexyloxy groups and the acetylenic π -alkyl CH interactions (from the terminal

$-\text{CH}_3$ of the hexyloxy moiety). Interestingly, this value and the intermolecular distances observed along the a axis of the STM images have close resemblance ($1.3 \pm 0.1 \text{ nm}$), indicating that the interdigitation and $\text{CH}\cdots\pi$ interactions assist the organization of molecules as strips. Alkyl chains can also play a major role in the self-assembly of molecules on 2D surfaces, and these aspects have been investigated by various groups.¹³

To explain the two types of molecular assemblies, we analyzed various possibilities of acetylenic π -alkyl CH interactions, between two molecules (Scheme 1 and Supporting Information). It can be seen that with respect to the hexyloxy groups the alkyl chain of the adjacent molecules can interact with the acetylenic moiety, either from the *ortho* or *meta* position, leading to a type-I or type-II interaction, respectively (*x* and *x'* in Scheme 1). The extension of such structures can lead to the formation of 1D organization (*y* and *y'* in Scheme 1) similar to that observed as *a*-strips in the STM images. The interlocking of such strips can result in the formation of 2D molecular assemblies (*z* and *z'* in Scheme 1). However, the extent to which they interlock differ because of the steric restrictions imposed by the hexyloxy group. This can be understood easily because the interdigitation of hexyloxy chains occupies more space in the case of type-II interaction due to their *meta* arrangement. In contrast, the *ortho* arrangement of type-I interactions result in the close packing of hexyloxy groups, leaving enough space for interlocking of adjacent *a*-strips.

SCHEME 1: Two Possible Modes of Interactions Leading to the Formation of a-Strips and Their Interdigitation to 2D Structures


Furthermore, the interlocked 1D strips of type-I and -II molecular assemblies (z and z' in Scheme 1), each having a pack of six molecules, were optimized at the AM1 level of the semiempirical method. For mimicking the 2D surface, constraints were applied during the geometry optimization in order to keep the carbon atoms along the molecular axis of two adjacent molecules in the same plane by fixing appropriate dihedral angles (Supporting Information). However, this restriction will allow the free rotation of the phenyl rings and the movement of the alkyl chains. The type-I assembly showed close packing of the hexyloxy chains with $\text{CH}\cdots\pi$ interactions and relatively strong alkyl $\text{CH}\cdots\text{O}$ interactions (Figure 2A). Alternatively, the type-II assembly possesses only alkyl $\text{CH}\cdots\pi$ interactions on the acetylenic π bond (Figure 2B). Model calculations clearly indicate that the way in which the hexyloxy chains interdigitate plays a decisive role on the extent to which the adjacent strip inserts. For example, in the optimized structure of the type-I assembly (Figure 2A), the aromatic moiety of one strip is inserted up to the acetylenic region of the previous strip.

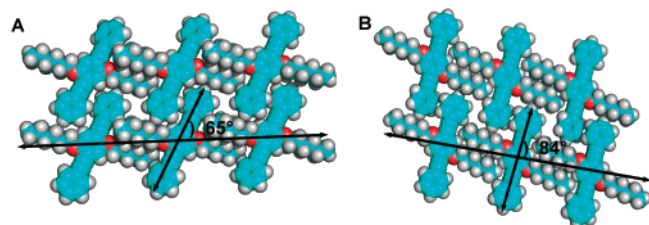


Figure 2. AM1 level optimized structures of 2D molecular packing.

This molecular packing closely resembles the STM image presented in Figure 1C. From the molecular calculations, it can also be seen that the 2D organization is stabilized further through $\text{CH}\cdots\pi$ interactions between the aromatic CH and acetylenic π bond. In contrast, type-II assembly has a lesser extent of insertion of the two strips and the optimized 2D assembly is stabilized by aromatic $\text{CH}\cdots$ aromatic π interactions. The optimized molecular packing (Figure 2B) resembles the STM image shown in Figure 1D. Moreover, the orientation of molecules along the a-axis and the measured distances between the identical points along the b strip in the STM images (70° and 1.2 nm in Figure 1C; 83° and 1.5 nm in Figure 1D) are in good agreement with the calculated values presented in Figure 2.

In conclusion, the model phenyleneethynylene **1**, the basic building block of many molecular systems, forms well-organized assemblies on surfaces through weak intermolecular interactions. The organization of these systems can be modulated further by varying the length of the alkoxy group and introducing proper functional moieties. Understanding the optoelectronic properties of these well-organized molecular assemblies may pave way in the design of next-generation photonic devices.

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Supporting Information Available: Details of the molecular modeling, the coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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