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Formation and Manipulation of Protopolymer Chains

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Abstract: We define "protopolymer" to mean that the monomer units of a polymer are together and aligned, but are not yet reacted to their final form, the polymer. We have created, observed, and manipulated this new chemical state in linear chains of phenylene on Cu{111} at low temperature. We demonstrate that protopolyphenylene forms by manipulating individual monomer units out of the chains using a scanning tunneling microscope. Both the bare and the phenylene-covered Cu{111} surface can serve as an extended catalytic active site to bring together and to align the monomer phenylene units formed from the dissociative chemisorption of *p*-diiodobenzene. When short segments of protopolymer chains are moved on the phenylene-covered surface, the intermolecular interactions are sufficiently strong to realign the chains in new locations. The alignment due to these interactions may be used in the controlled growth and assembly, as well as for the simplified manipulation of complex, hierarchical structures.

Introduction

Adsorbed atoms and molecules modify their local electronic environment, thereby creating preferential adsorption sites for other molecules, aligning reactants and intermediates, and stabilizing both local and extended surface structures.[1-9] The scanning tunneling microscope (STM) allows direct visualization of these atomic-scale electronic perturbations, simultaneously collecting topographic and electronic information.[2-7] Here, we use the STM to explore the interactions between intermediates in the formation of polyphenylene and find these interactions to be surprisingly strong, thereby leading to robust, extended intermediate structures.

As known from the reactions of haloaromatics to form coupled aromatic rings, iodobenzene dissociates upon adsorption to Cu{111} at temperatures above 175 K into an iodine atom and a phenyl.[6-12] The phenyl intermediates interact and are then available for coupling reactions.[6-8] Surface features such as steps, defects, and I adatoms were found to promote the catalytic reaction by stabilizing one phenyl and through surface-mediated interactions stabilize the two proximal phenyl complexes

properly aligned for reaction. In an elegant series of experiments, Rieder and co-workers employed a low-temperature STM tip to dissociate, to position, and to couple fragments from iodobenzene molecules adsorbed adjacent to a Cu{111} atomic step;[13,14] each step of the chemical reaction that ultimately forms biphenyl from iodobenzene was controlled with the probe tip. In the work presented here, intermolecular interactions alone align and stabilize phenylene intermediates (from the dissociative chemisorption of *p*-diiodobenzene) into "protopolymer" on the surface, as described below. The surface serves as an extended active catalytic site in holding the monomers in place in the proper alignment for subsequent reaction.

Materials and Methods

Low-Temperature Scanning Tunneling Microscope. Experiments were carried out in a low-temperature STM described in detail elsewhere.[15] Briefly, this custom instrument is comprised of two attached stainless steel ultrahigh vacuum (UHV) chambers mounted on an optical table. Suspended from these vacuum chambers and encompassed by a liquid helium dewar, the STM hangs from the optical table vibration isolated from the rest of the instrument. This configuration allows samples to be transferred under UHV conditions from sample preparation and dosing stages to the low-temperature STM, while maintaining an STM chamber that is well insulated from environmental noise and thermally stable at 77 K (liquid nitrogen) and 4 K (liquid helium). This experimental configuration has proven to be very stable and capable of collecting extremely high-resolution images.

Sample Preparation. The Cu{111} sample was electrochemically polished and then transferred into the UHV chamber. In vacuum, the Cu{111} substrate was prepared by repeated cycles of Ar ion bombardment and annealing. The *p*-diiodobenzene was used as received.

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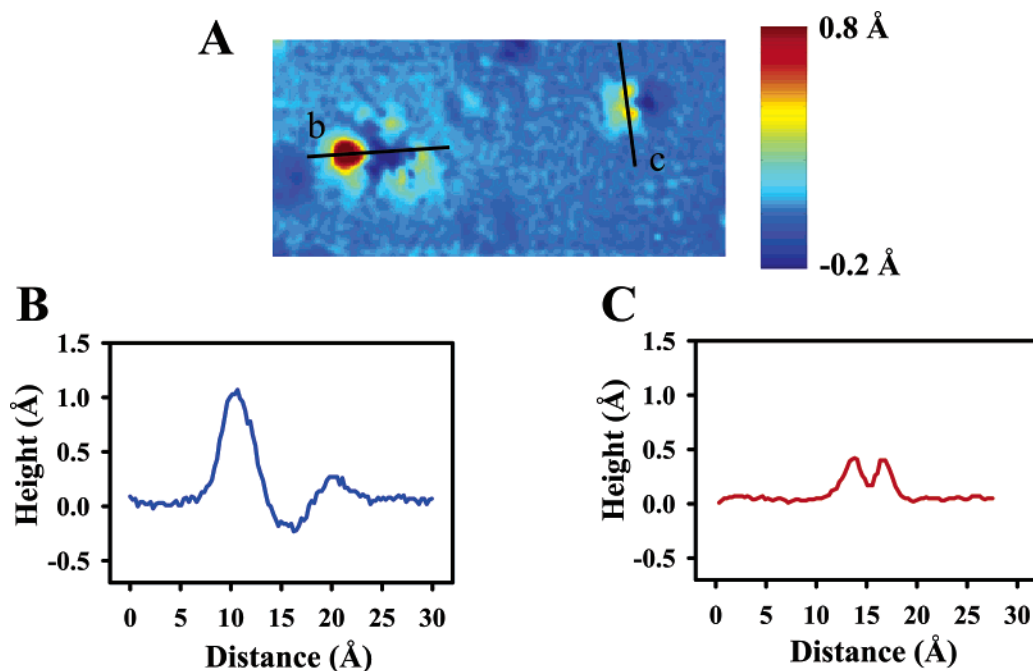
Figure 1. STM image (A) of Cu{111} after exposure to ~1 Langmuir of *p*-diiodobenzene and two profiles (B,C) extracted from the STM image at the positions labeled b,c. (A) The STM image shows the resulting surface species after the dissociative chemisorption of *p*-diiodobenzene on Cu{111}, phenylene intermediates, and I atoms. The image area is 75 Å × 40 Å and was acquired with a sample bias of 200 mV and a tunneling current of 40 pA at 77 K. I atoms appear in pairs and are immobile, presumably decorating the site of dissociation. (B,C) Profiles of the apparent topography as collected by STM of the adsorbed (B) phenylene intermediate and (C) I atoms. Note that the electronic structure due to the I atom pairs interacts to give the structure shown in (A) and (C); isolated I adatoms yield a cylindrically symmetric feature in STM images on Cu{111}.

To enable precise control of sample dosing, the *p*-diiodobenzene was introduced into the vacuum system through a sapphire leak valve.

Sample Analysis. The Cu{111} surface was exposed to small quantities of *p*-diiodobenzene in UHV at room temperature. After allowing the system time to equilibrate, the sample was transferred for study to a low-temperature STM, where any additional reaction or motion of the adsorbates was limited. All images were acquired at 77 K in UHV. Experiments were performed at sequentially increasing coverages to identify the adsorbed species, to observe their interactions, and then to follow the assemblies that resulted.

Results and Discussion

Identification of Surface Species. To identify the primary compounds involved in the reactions, we first dosed the surface to very low coverage by exposure to ~1 Langmuir (1×10^{-6} Torr s) of *p*-diiodobenzene.[16] Figure 1A shows a STM image of a portion of a Cu{111} atomic terrace after dosing, with several surface species, including phenylene sectioned by line b and two adsorbed iodine atoms sectioned by line c (shown in cross section in Figure 1B and C, respectively). Located adjacent to both the iodine atoms and the phenylene intermediates are atomic-scale defects, appearing as dark-blue depressions in the images. These are vacancies or substitutional defects in the Cu{111} lattice resulting from the surface preparation.

As shown in Figure 1, *p*-diiodobenzene dissociatively chemisorbs on Cu{111} into a surface-stabilized phenylene intermediate and two adsorbed iodine atoms,[16] analogous to the dissociation of iodobenzene.[10–12] At room temperature, the phenylene intermediates are mobile on the surface. Initially, the phenylene intermediates adsorb to surface defects (as shown in Figure 1A) and atomic steps (not shown). No stationary individual phenylene species were imaged on the perfect regions of Cu{111}

terraces; presumably they remain mobile in these areas at 77 K, as previously reported for phenyl on Cu{111}.[7,8,17]

"Protopolymer" Chains on Cu{111}. We are able to observe interacting phenylene intermediates at higher coverage after additional exposure to *p*-diiodobenzene. Figure 2 shows a STM image of Cu{111} after exposure to ~5 Langmuirs of *p*-diiodobenzene. Monatomic substrate steps propagate through the area imaged (as marked). Extended phenylene structures have self-assembled on the surface through substrate-mediated and intermolecular interactions (likewise marked). Surprisingly, such features continue even across the monatomic substrate steps. While interactions between molecules can cross step edges,[16] the electronic perturbations due to the substrate steps are typically the strongest on the surface, and thus can disrupt the continuity of such organized molecular assemblies.[7,14,18] The effects of electronic perturbations due to adsorbates crossing step edges have previously been observed, however, to align molecules within parallel rows lined up on adjacent terraces (across monatomic steps) for benzene on Cu{111}.[19]

The phenylene monomers in the molecular chains on Cu{111} are not moved under the typical imaging conditions used. Phenylene species that are not in such chains, even those adsorbed adjacent to atomic steps, remain mobile. All phenylene species observed in the low coverage experiments that had similar dosing conditions were individual entities; no short chains were observed. Additionally, using molecular manipulation, we tested whether the molecules in the chains were chemically attached to one another. Phenylene molecules were extracted from the molecular chains by applying several 2.5 V pulses to the STM tip (Figure 2C), suggesting that the chains

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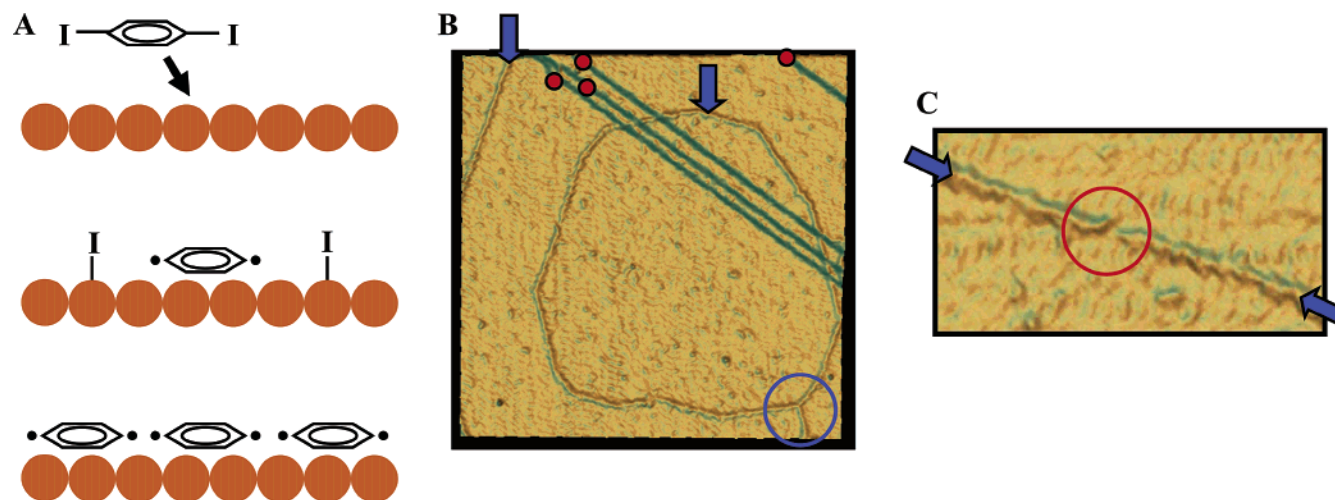
Figure 2. (A) Paradiiodobenzene dosed on the Cu{111} surface (top) dissociatively chemisorbs (center) giving the structures shown in Figure 1. The phenylene species then assemble into protopolymer (bottom) as shown in the STM images in B, C. (B) STM image of Cu{111} exposed to ∼5 Langmuirs of *p*-diiodobenzene. Phenylene assembles into molecular rows (blue arrows) that are not covalently linked. The image area is 270 Å × 270 Å and was acquired with a sample bias of 1.0 V and a tunneling current of 200 pA at 77 K. Four monatomic substrate steps (marked by red dots) propagate through the area imaged. Two blue arrows mark extended phenylene structures that have self-assembled on the surface through substrate-mediated and intermolecular interactions. (C) A molecular row (blue arrows) of phenylene that is not covalently linked spans the Cu terrace. A single phenylene (red circle) has been removed from the molecular row by a voltage pulse from the probe tip. The image area is 90 Å × 45 Å and was acquired with a sample bias of 1.0 V and a tunneling current of 200 pA at 77 K.
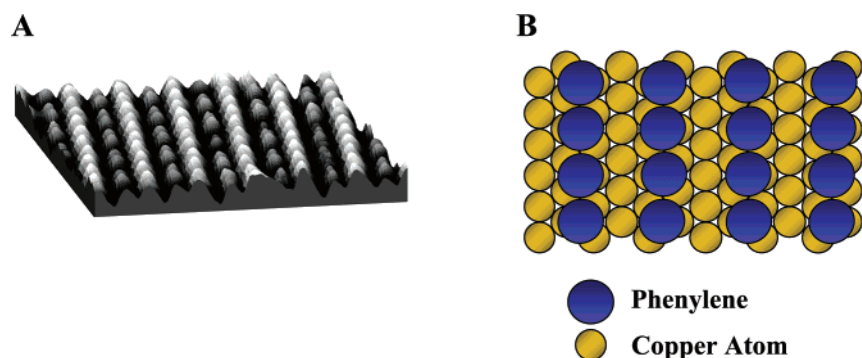

Figure 3. (A) STM image of a Cu{111} surface exposed to ∼20 Langmuirs of *p*-diiodobenzene, showing alternating rows of phenylene and Cu. The image area is 60 Å × 60 Å with an apparent height variation of 0.0−0.6 Å for the black to white shading and was acquired with a sample bias of 100 mV and a tunneling current of 60 pA at 77 K. (B) Schematic of the alternating row structure shown in (A). The less protruding rows are assigned as close-packed rows of Cu atoms of the substrate. The more protruding rows are assigned as phenylene intermediates adsorbed at three-fold hollow sites spaced by ∼3.9 Å.

are not covalently bound together, but rather are held by molecule−molecule and surface-mediated interactions. These observations are in accord with previous studies on the formation of biphenyl from phenyl intermediates that show that aryl coupling does not occur on the substrate terraces at or below room temperature,[11] and that if the rings are covalently coupled, the (two-ringed) molecule will be moved intact.[14] As noted above, we refer to these aligned chains that are not yet chemically bound as "protopolymer".

In the lower right-hand corner of Figure 2B, a blue circle highlights the position of a species that we tentatively assign as 1,3,5-phenylyne (C_6H_3 − a tri-radical if not attached to the surface, with three possible binding sites) in the molecular chain. The phenylyne species is most likely the result of an impurity in the diiodobenzene or hydrogen abstraction on the Cu surface.[14] Three molecular chains radiate from this molecule. At other joints in the phenylene protopolymer chains, 120° turns highlight *m*-phenylene, the result of either hydrogen migration or *m*-diiodobenzene impurities in our starting material. Further investigations with depositions of dihalo- and trihaloaryl precursors to these molecules are underway to determine if we can

select the structures formed by controlling the ratios of "angle joints" to straight monomer segments in the protopolymer chains.

Overlayer of Phenylene on Cu{111}. Increasing surface coverage enables us to determine the behavior of overlayers of phenylene. A Cu{111} terrace after exposure to ∼20 Langmuirs of *p*-diiodobenzene is shown in Figure 3 and is characterized by a structure of rows alternating in apparent height with a periodicity of 7.8 Å. The lower rows have three apparent protrusions per period, with a feature spacing of 2.6 Å; the higher rows have two protrusions per period, with a feature spacing of 3.9 Å. From lower row to lower row, the peak-to-peak spacing is 6.7 Å. The Cu{111} nearest-neighbor spacing (along the ⟨101⟩ direction) is 2.56 Å, or a distance of 7.68 Å for three Cu atoms along the nearest-neighbor direction. The feature and row spacing for the lower rows in the alternating row structure match those for the Cu atoms in every third ⟨101⟩ directed row of the Cu{111} substrate. We attribute the features in the higher rows to phenylene, because the feature spacing, 3.9 Å, is close to the 3.8 Å fwhm length observed for phenylene (and iodine is known to form a $(\sqrt{3} \times \sqrt{3})R30°$ overlayer) on
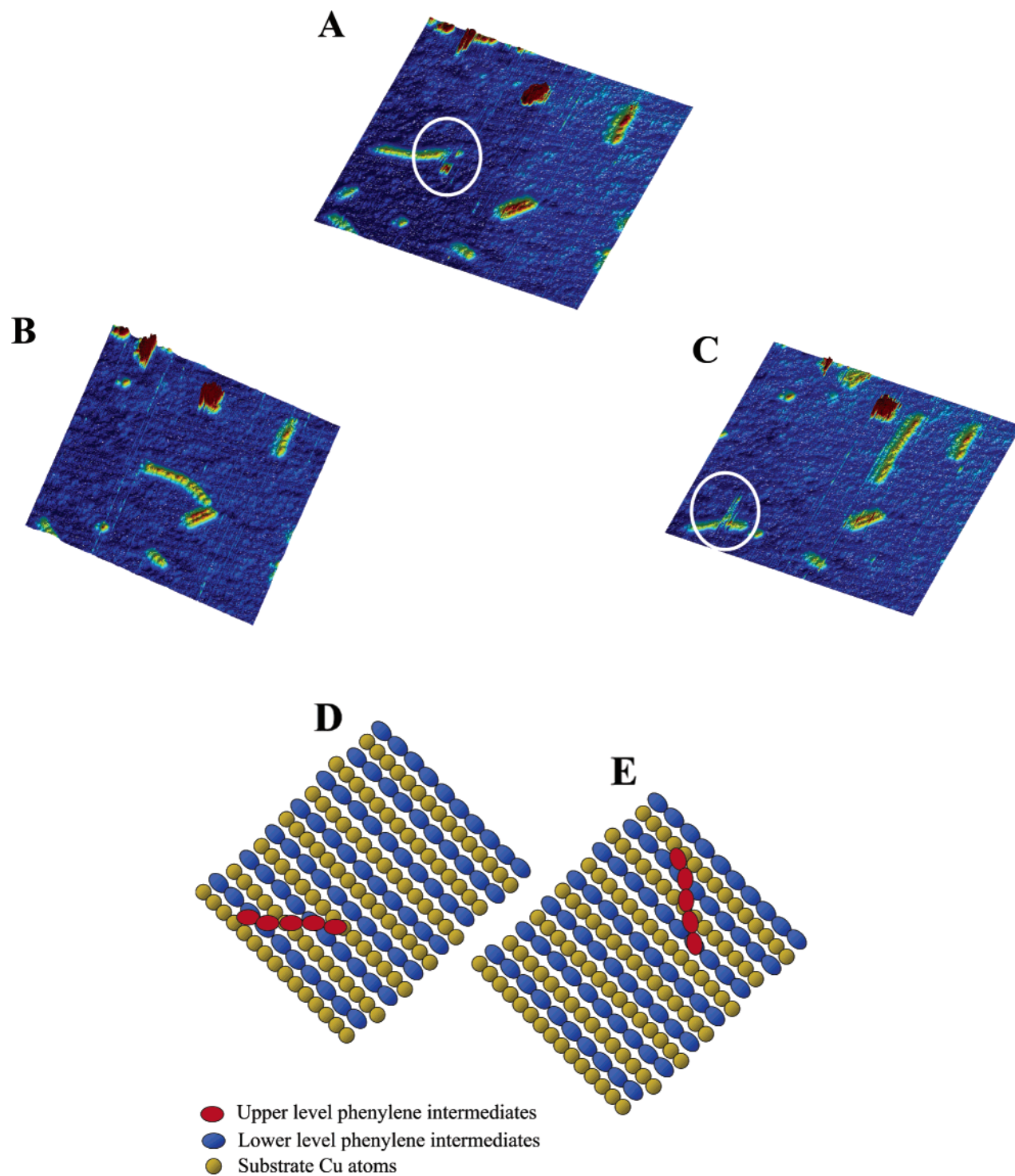
Figure 4. (A−C) STM images collected sequentially of Cu{111} exposed to ∼20 langmuirs of *p*-diiodobenzene. The images were collected 5 min apart, of the same area with the same tunneling conditions. Short molecular chains of phenylene intermediates can be manipulated on the alternating row structure. The image size is 120 Å × 120 Å with an apparent height variation of 0.0−2.2 Å for the blue to red coloring and was collected with a sample bias of −200 mV and a tunneling current of 100 pA at 77 K. (D,E) Schematic illustrating the motion of the short molecular protopolymer phenylene chain in images A and B, respectively.

Cu{111}.[20] A schematic of the proposed phenylene overlayer structure on Cu{111} is shown in Figure 3B. The spacings of the phenylene and the Cu atoms in this schematic are consistent with those recorded experimentally, with the Cu{111} nearest-neighbor spacing of 2.56 Å and the apparent phenylene length

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of 3.8 Å. Previous studies of *p*-diiodobenzene on Cu{111} at low temperature have shown preferential adsorption at three-fold hollow sites.[14] Similar behavior is observed for the phenylene in the molecular chains; they are positioned at alternating face-centered cubic and then next-nearest hexagonal close-packed sites, each at a separation of ∼3.9 Å. This configuration is consistent with the experimentally observed

structure (Figure 3A). As with the individual molecular rows reported above, no motion of the phenylene species in the rows was observed in these experiments.

"Protopolymer" Chains on an Overlayer of Phenylene. For this series of experiments, the Cu substrate was dosed with ~20 Langmuirs of *p*-diiodobenzene at room temperature. The system was allowed to equilibrate and then transferred to the 77 K STM chamber for study. Regions of phenylene-covered Cu{111} are found separated from regions of I-covered Cu{111}, the latter identified through its characteristic ($\sqrt{3} \times \sqrt{3}$)*R*30° overlayer structure.[20] At this higher coverage, some protopolyphenylene chains could be found as an overlayer on the phenylene-Cu structure, as shown in Figure 4. We anticipated that spacing the adsorbed species from the substrate would reduce the interactions through the substrate, and thus might reduce the tendency of the molecules to form chains. Indeed, only short-chain segments were observed. Unlike the phenylene chains on the bare copper substrate that showed no tip-induced motion during imaging, the short phenylene chains on the phenylene-Cu structure were mobile during imaging. Each of the images in Figure 4 is of approximately the same area and was recorded with the same tunneling conditions. The images were collected sequentially, with 5 min intervals between each measurement. A short molecular chain of approximately eight phenylene units is moved from the left side of the image, Figure 4A, to a defect in the center of the image, Figure 4B, and then moved toward the top of image, Figure 4C. The white circles in Figure 4A and C mark positions where phenylenes have been moved several Å by the STM probe tip during the collection of the image. By the next image, the molecular chain returned to its original length by recruiting the molecules of the chain into new positions. During imaging, the probe tip moved phenylene monomers without destroying the protopolymer. Figure 4D,E shows schematics of the motion of the protopolyphenylene chain on the alternating row structure. In Figure 4, the substrate−molecule interactions have indeed been reduced, as is evident from our ability to manipulate the protopolymer on the surface, as compared to the linear structures adsorbed directly on Cu-{111}, but the intermolecular interactions are nonetheless sufficient to hold the chains together.

In this work, linear structures formed by exposing Cu{111} to *p*-diiodobenzene were studied. Protopolymer chains of phenylene were observed to be stationary on Cu{111}, whereas short protopolymer chains on phenylene-covered Cu{111} could be moved with the STM tip, while retaining their constituent monomers. This demonstrates the strength of intermolecular interactions in aligning and stabilizing the protopolymer. These results suggest that such interactions could be used to form and to manipulate stable surface structures without the need to move each individual component into its precise position; intermolecular interactions can be used to "snap together" components through the effective choice of both assembly units and substrate.

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