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Tip-induced C–H activation and oligomerization of thienoanthracenes

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The tip of a scanning tunneling microscope (STM) can be used to dehydrogenate freely-diffusing tetrathienoanthracene (TTA) molecules on Cu(111), trapping the molecules into metal-coordinated oligomeric structures. The process proceeds at bias voltages above ~3 V and produces organometallic structures identical to those resulting from the thermally-activated cross-coupling of a halogenated analogue. The process appears to be substrate dependent: no oligomerization was observed on Ag(111) or HOPG. This approach demonstrates the possibility of controlled synthesis and nanoscale patterning of 2D oligomer structures on selected surfaces.

The demand for smaller electronic devices has fuelled the pursuit of methodologies for spatially controlled chemical reactions to fabricate electronic materials with nanoscale precision. Devices based on organic materials are an appealing alternative to traditional inorganic semiconductor devices, since they can be built from the bottom up by using building blocks only a few atoms in width.[1] Scanning probe microscopy offers the possibility to image,[2] manipulate,[3] and induce chemical reactions with nanoscale spatial resolution,[4, 5, 6, 7] making it an ideal instrument both for creating and characterizing molecular materials. Recent examples of STM-induced phenomena include localized atomic reactions on silicon,[8] tip-induced polymerization of diboronic acids,[9] tip-induced polymerization of diacetylenes,[10, 11] and tip-induced S–S bond dissociation and recombination in dimethyldisulfides.[12] In these systems, the STM tip is typically used to induce a reaction that propagates without additional input until it is terminated by a defect,[4, 11, 13] or until all available monomers are consumed.[9]

Herein we report a new concept in STM-initiated reactions: starting from a surface-confined ensemble of diffusing molecular monomers, we demonstrate that the STM tip can be used to activate surface-mediated dehydrogenation of molecular precursors, leading to the formation of oligomers on a copper surface. Cross-dehydrogenative C–C coupling is one of the fastest growing fields of synthetic organic chemistry.[14] Unlike previous tip-induced surface polymerization reactions,[9-13] this reaction is initiated from surface

confined diffusing molecules, and is not self-perpetuating. The area patterned with molecules is defined by the scanned region, allowing for precise spatial control over the polymerized region.

The monomer we used is trithieno[2',3':5,6:3',2':3,4:3',2':7,8]anthra[1,2-b]thiophene (2TTA – schematically represented in the inset of Figure 1(a)).[15] Polythiophenes are widely used as organic semiconductors, due to their useful electro-optical properties.[16] We previously reported the formation of disordered polymers through the surface-catalyzed polymerization of a brominated analogue of 2TTA (TB2TTA) on Cu and Ag surfaces.[17, 18]
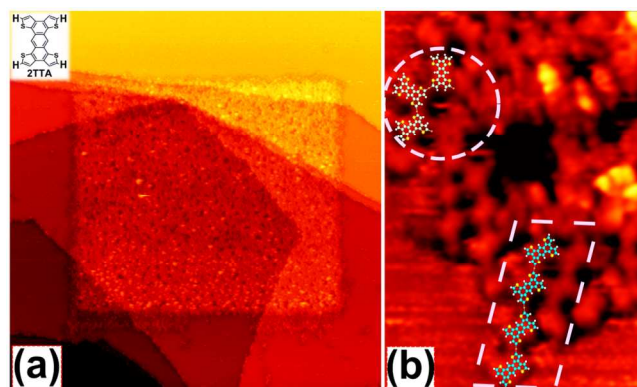

Figure 1. STM images of 2TTA on Cu(111) surface. (a) A rectangular region (100×90 nm^2) of patterned aggregates from 2TTA, at patterning bias $U_{bias,pattern} \sim 5$ V. (b) The lower left corner of the patterned region from (a). Dashed regions highlight oblique (inside the rectangle, Figure S1(a)) and hexameric structures (inside the circle, structure "**1**" from Figure S1(c), ESI†). The inset in (a) shows the molecular structure of 2TTA. Image/scanning parameters: 150×150 nm^2, tunneling current $I_t = -0.41$ nA, bias voltage $U_b = -831$ mV for (a); and 8.5×12 nm^2, $I_t = 0.40$ nA, $U_b = 374$ mV for (b).

After sublimation on Cu(111) it is not possible to image submonolayer coverage of 2TTA at room temperature, due to its

high mobility (see methods, ESI†). Instead, STM images acquired at imaging biases below 1 V show an indistinct, flat surface overlaid with streaks along the fast-scan direction, as is typically observed in the presence of freely diffusing molecules.[19] However, after scanning the surface at a bias $U_{bias,pattern} \sim 5$ V, subsequent imaging over a larger area reveals a patterned region (Figure 1(a); Figure S2-S3, ESI†). This region is "wear resistant" to scanning biases as low as 0.02 V and tunneling currents up to 4 nA. At its center, the patterned region comprises dense molecular aggregates, whereas distinct interconnected molecular geometries can be identified at the periphery (Figure 1(b); Figure S4, ESI†).
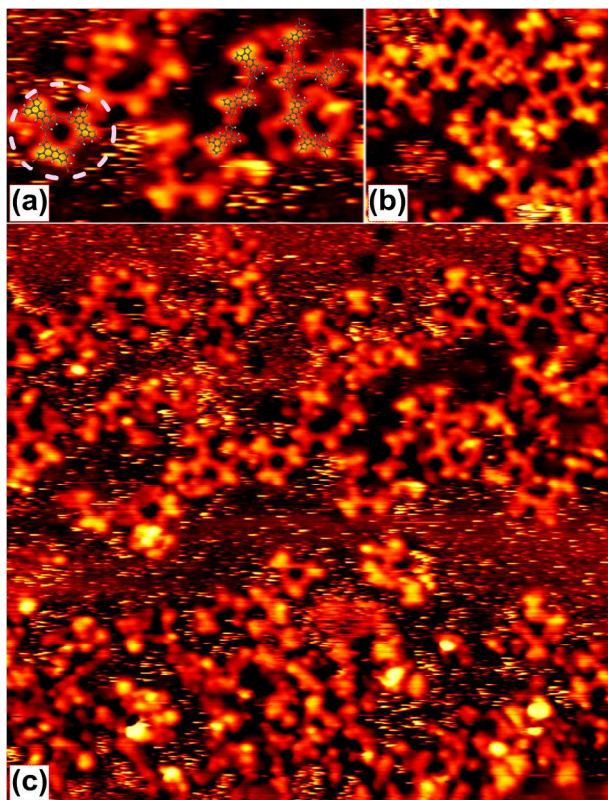

Figure 2. Oligomer motifs created by $U_{bias,pattern} \sim 3.5$ V. Image sizes: 5.3×3.0 nm^2 in (a), 8.4×7.3 nm^2 in (b), and 20×20 nm^2 in (c). Scanning parameters: (a-c) $I_t = 0.12$ nA, $U_b = 116.58$ mV. The molecular coverage on the surface in this particular set of images was estimated at ~1% of a monolayer, based on molecular counting on a surface cooled to -160 °C (Figure S5, ESI†). Dashed (circle) is highlighted in (a) another type of organometallic oligomer – a trimer (structure "**2**", as part of a Kagome lattice in Figure S1(c), ESI†).

It is possible to pattern regions with dimensions of the order of tens of nanometers,[20] at $U_{bias,pattern}$ as low as 3 V (Figure 2). The dimension of the patterned area corresponds approximately to the scan size, with the area of the patterned region slightly exceeding the scanned area (detailed measurements are presented in Figure S2 and Figure S3(b), ESI†). The slight spillover effect that we observe is spatially confined and is likely due to the finite radius of the tip. At lower patterning voltages near 3 V, the molecular density within the patterned region is reduced. In particular, the dense molecular aggregates are largely avoided (center of Figure 1(a)), and lower-density well-defined oligomers dominate the patterned region (Figure 2).

The structures observed in Figure 1(b) and Figure 2 are similar to the organometallic networks formed through the surface-catalyzed

dehalogenation of TB2TTA on the (111) surfaces of Cu and Ag.[17, 18] In the present experiments we measured an average length of 1.43 ± 0.06 nm between the centers of mass of any two neighboring connected molecules in the oblique structure (Figure S1(a), ESI†). Based on these bond-length measurements we also identify the products of the tip-induced process as organometallics.[18]

The geometry of the structures indicates that oligomerization occurs following dehydrogenation at the α-carbons in the 2TTA thiophene rings, likely due to tunneling electron induced molecular activation. A similar STM tip-induced dehydrogenation of benzene has been demonstrated previously on Cu(110)[7] and Cu(001).[6] In both cases, the geometry of the benzene molecule switches from planar to upright adsorption with the activated bond(s) coordinated into the surface after dehydrogenation, and no cross-coupling was observed.[21] In the tip-induced dehydrogenation and oligomerization we observe, two key factors could work together to favor intermolecular bonding over coordination of the activated bond into the Cu surface: (1) the TTA molecule is much larger and therefore more strongly adsorbed to the surface than benzene, and (2) at room temperature we can assume the presence of freely diffusing Cu adatoms on the surface,[22] which would facilitate the coordination of activated bonds to Cu adatoms rather than substrate atoms. At room temperature the liberated hydrogen is not retained on Cu(111),[23] avoiding one of the challenges encountered in on-surface Ullmann coupling of halogenated monomers, where an accumulation of reaction byproducts occupies surface sites on the substrate.[24]

A limited number of tunnelling electron related processes can induce bond-breaking. The primary mechanisms are vibrational heating and electronic excitation.[25] While vibrational heating occurs through a multi-electron process and is generally initiated at relatively low bias voltages (on the order of hundreds of mV),[25, 26] in the case of electronic excitation, the injection of electrons occurs via the lowest unoccupied molecular orbital (LUMO).[7, 27] We interpret the dehydrogenation we observe as being due to electronic excitation following electron injection into the LUMO of 2TTA (see Figure S6, ESI†).

Whereas on HOPG no observable change was produced by the high-bias scanning (even after extensive scanning at 5-6 V), on Ag(111) the process produced pits in the surface and, depending on the molecular coverage, small domains of adsorbed molecules in the regions around and between these pits (**Error! Reference source not found.**). As in the case of tip-induced immobilization of copper phthalocyanine (CuPc) on Cu(111),[28] the mechanism for the immobilization of 2TTA/Ag(111) is not immediately apparent, although the molecules seem to preferentially adsorb around pits etched in the substrate, suggesting that the undercoordinated atoms at the edges of these pits may help anchor the molecules.
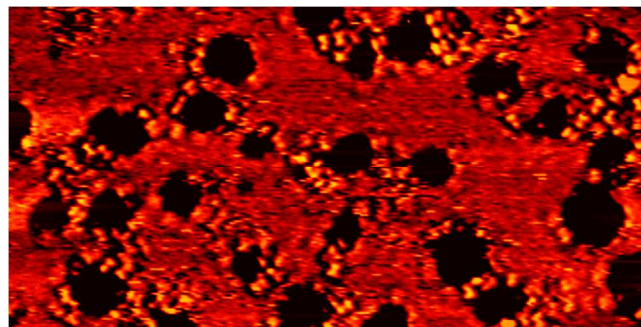

Figure 3. 34×17 nm^2 STM image of a patterning attempt of 2TTA on Ag(111), with aggregation of molecules around the formed pits on the surface ($U_{bias,ppattern} \sim 5$ V). Scanning parameters: $I_t = 0.55$ nA, $U_b = 968.93$ mV.

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The negative results on Ag(111) and HOPG could result from lower reactivity of silver in the C–H insertion reaction as well as the increased molecular diffusion rate on these surfaces, which leads to decreased exposure to tunneling electrons. Electronic excitation can also involve a bonding configuration change,[6,7] as observed theoretically in dehydrogenation of small aromatics, where the hydrogen must be oriented into a preferred surface site.[29] The energetics of the transition states associated with this process are substrate dependent,[29] which is consistent with our finding that the reaction progresses on Cu(111) but not on Ag(111) or HOPG.

This work demonstrates that molecular patterns comprising 2D oligomers can be 'drawn' onto Cu(111) with nanoscale precision using an STM tip. The tip-induced reaction manifests through the formation of oligomers and amorphous molecular aggregates in regions scanned at 3-5 V. Similar oligomers were previously produced without spatial control using a brominated derivative of the 2TTA molecule on the Cu(111) surface via Ullmann dehalogenation. Comparatively, the present method allows for precise spatial control and at the same time avoids the creation of reaction byproducts that remain adsorbed on the surface.[18] Geometric considerations indicate that in this tip-induced process, the creation of free bonds is due to C-H bond activation. Experiments performed in an identical manner on HOPG or Ag(111) did not produce any oligomers, illustrating that the surface plays an important role in the reaction.

In future experiments we plan to optimize the process to increase the yield and density of the oligomer. We will also investigate whether other electron sources can be used to initiate the reaction. In addition, a detailed theoretical study could elucidate the mechanism for dehydrogenation in this large molecular system.

Notes and references

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