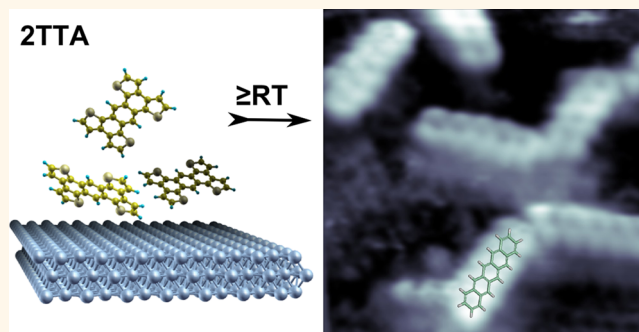


Unprecedented Transformation of Tetrathienoanthracene into Pentacene on Ni(111)

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ABSTRACT The imaging and characterization of single-molecule reaction events is essential to both extending our basic understanding of chemistry and applying this understanding to challenges at the frontiers of technology, for example, in nanoelectronics. Specifically, understanding the behavior of individual molecules can elucidate processes critical to the controlled synthesis of materials for applications in multiple nanoscale technologies. Here, we report the synthesis of an important semiconducting organic molecule through an unprecedented reaction observed with submolecular resolution by scanning tunneling microscopy (STM) under ultrahigh vacuum (UHV) conditions. Our images reveal a sulfur abstraction and cyclization reaction that converts tetrathienoanthracene precursors into pentacene on the Ni(111) surface. The identity of the final reaction product was confirmed by time-of-flight secondary ion mass spectrometry (TOF-SIMS). This reaction has no known literature analogue, and highlights the power of local-probe techniques for exploring new chemical pathways.



KEYWORDS: STM · SIMS · thiophene · desulfurization · pentacene · Ni(111)

The ability to probe the properties of individual molecules is important for understanding basic chemical, physical, and biological processes,^{1–3} as single molecular species often exhibit behavior that is radically different from that of molecular aggregates and films. The characterization of discrete molecules requires highly sensitive measurement techniques, including optical tweezers,⁴ surface-enhanced Raman scattering,⁵ and fluorescence spectroscopy.⁶ Among these, scanning probe techniques have emerged as unique tools for high resolution imaging of molecules supported on a surface.^{7,8} Scanning tunneling microscopy (STM) had a revolutionary impact in surface chemistry, for example, for allowing the observation^{9,10} and induction¹¹ of chemical reactions in individual molecules at surfaces.^{12–14} Extending surface-confined reactions from a single molecule to an ensemble of molecules can significantly broaden the experimental focus and scope from

fundamental chemistry to materials synthesis and nanotechnology.¹⁵ Studies from the emerging field of surface-confined reactions identify opportunities for synthesizing new organic materials with the aid of one- or two-dimensional spatial constraints.¹⁶ The chemistry employed in surface reactions so far has largely been based on mimicking known reactions: diacetylene 1,4-addition,^{17–19} electrooxidative^{20,21} and Ullmann coupling,^{22–25} Schiff-base²⁶ and boronic acid^{27–29} polycondensations. There are a few cases where a new type of reaction was suggested, for instance, in the polymerization of tetrakis(*p*-tolyl)porphyrine *via* dehydrogenative C–C coupling³⁰ or in the addition polymerization of tetrazapyrene *via* its tautomeric carbene intermediates.³¹ However, the products of these latter reactions were solely investigated by STM, and their structure was not unambiguously established due to the lack of chemical sensitivity of this technique.

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Polythiophenes are one of the cornerstone materials in organic semiconductors,³² and therefore a considerable effort has been expended toward the synthesis of conjugated polymers in the surface-confined reaction of thiophene monomers.^{20–22} However, in addition to conferring useful electronic properties, the presence of the thiophene groups introduces a literal weak link into the monomer. Thiophene degradation on transition metal surfaces, including the (111) facet of nickel,³³ has been reported.³⁴ This reactivity of thiophene and other organosulfur compounds with transition metals is also exploited in large-scale applications such as desulfurization of petroleum or spirits distillery, where copper stills are used to remove foul-tasting sulfur compounds.³⁵ Hydrodesulfurization of benzothiophene derivatives has been used in the total synthesis of natural products although the reaction did not increase the molecular complexity of the product (see for example ref 36 or ref 37 and references therein).

Here we report an application of sulfur abstraction from a thiophene derivative to create preconditions for new intramolecular C–C bonds. Following the deposition of 2,5,9,12-tetrabromoanthra[1,2-b:4,3-b':5,6-b'':8,7-b''']-tetrathiophene (TB2TTA) onto the (111) surface of nickel,

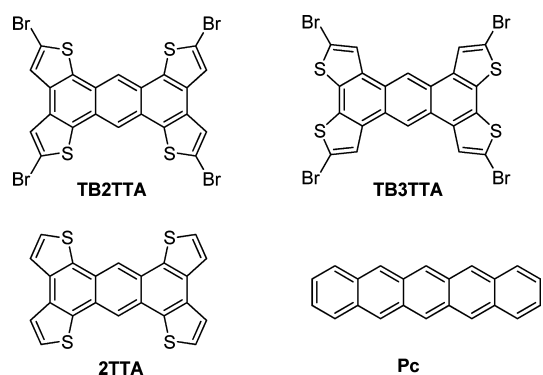


Figure 1. Molecular structures of TB2TTA, TB3TTA, 2TTA, and pentacene (Pc).

we observed an unanticipated five-ring linear product that was identified as pentacene—the most popular organic semiconductor.³⁸ This reaction demonstrates the possibility for the controlled and well-defined formation of useful, known or potentially new polycyclic products following sulfur abstraction, and highlights the ability of local probe techniques for revealing novel and unexpected chemical mechanisms.

RESULTS AND DISCUSSION

Following the deposition of TB2TTA (Figure 1) onto Ni(111) at room temperature (Figure 2a) and after annealing (Figure 2b,c, and Supporting Information, Figure S1b,c), STM images reveal a distinctly different molecular morphology than is observed under solution on graphite,^{39,40} where the appearance of TB2TTA resembles its gas-phase structure, with molecular contrast arising from both the anthracene core and from the four outward-extending thiophene moieties.

Figure 2b displays a representative image obtained from a Ni(111) surface deposited with TB2TTA (~1 ML) and subsequently annealed at 100 °C for 15 min: instead of the “usual” morphology with the four expected protrusions corresponding to the thiophene groups the images only reveal elongated linear features without any lateral protrusions. These molecular features do not exhibit long-range order in their packing, but lie with their long axes aligned along one of the $\langle 1-10 \rangle$ crystalline directions, which correspond to the close packing directions of the (111) substrate. They have an average length of 1.24 ± 0.05 nm and an average width of 0.44 ± 0.05 nm.

We also observe atomically reconstructed surface regions that coexist with the molecular domains, which we attribute to heteroatoms extracted from the TB2TTA molecules. The reconstructions include a $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase (Figure 2b and Supporting Information, Figure S1b) as well as a rectangular phase that is identical to the known $c(9 \times 5\sqrt{3})$ -rectangular reconstruction of sulfur

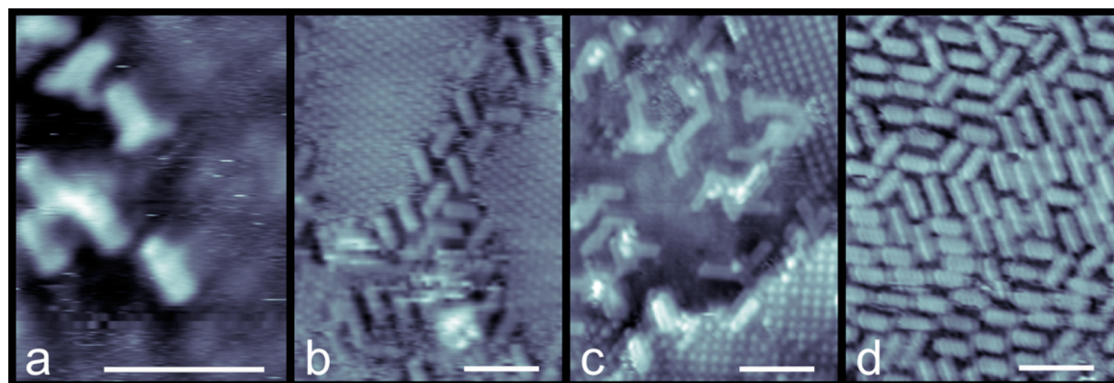


Figure 2. Representative STM images of the products of TB2TTA on the Ni(111) surface after different thermal treatments: (a) no annealing; (b) after annealing at 100 °C, the molecular products coexist with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase; (c) after annealing to 200 °C, the branched molecular features coexist with a $c(9 \times 5\sqrt{3})$ -rectangular reconstruction; (d) pentacene, as-deposited directly onto the Ni(111) surface. STM image parameters: (a) $V_b = -78.120$ mV, (b) $V_b = 156$ mV, (c) $V_b = 1680$ mV, (d) $V_b = 10$ mV. The scale bars in the bottom right are 3 nm in all images.

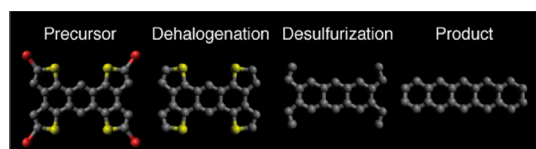


Figure 3. Proposed reaction scheme for conversion of TB2TTA to pentacene. The optimized shapes of precursor molecular structures, result from gas phase density functional theory (DFT) calculations using Gaussian 09 at the B3LYP/6-31G(d) level.⁴⁸ Avogadro, an open-source molecular builder and visualization tool, was used for producing basic molecular models and for molecular mechanics calculations (UFF force field, steepest descent).⁴⁹

adsorbed on Ni(111) (Figure 2c).⁴¹ We ascribe the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase to bromine,⁴² which forms the same phase on other (111)-terminated fcc metal surfaces.^{43–45}

These results strongly suggest the following reactions between TB2TTA and Ni(111): after deposition onto the Ni surface, the molecule undergoes dehalogenation, ring-opening, and desulfurization, extracting both Br and S heteroatoms, which subsequently form reconstructed domains on the surface. The undercoordinated carbon atoms at each end of the molecule then bond to one another, terminating each end of the anthracene core of the TB2TTA with a new benzene ring. Accompanying this process, the molecule may undergo at least partial dehydrogenation, as has been observed for both cyclohexanethiol and benzenethiol at similar temperatures on the Ni(111) surface.^{46,47} This rebonding scheme, shown in Figure 3 (see also Supporting Information, Figure S2a), describes the formation of the carbon backbone of a pentacene molecule that lies flat or nearly flat on the Ni(111) surface. The product formed from the reaction of TB2TTA at room temperature appears nearly identical to pentacene deposited directly onto the Ni(111) surface (Figure 2d), which has an average apparent length of 1.22 ± 0.05 nm.

Although the scheme shown in Figure 3 depicts only intramolecular rebonding, the formation of intermolecular C–C bonds is also possible, particularly in regions covered by a high density of precursor molecules. As shown in Figure 2c (and Supporting Information, Figure S1c), on surfaces annealed to 200 °C, we observed the formation of branched aggregates that comprise pentacene-like subunits.

To test the proposed mechanism, we deposited TB3TTA (Figure 1), an isomer of TB2TTA, onto Ni(111). In this case, the undercoordinated carbon atoms produced by dehalogenation and desulfurization cannot rebond with one another; the reaction with Ni(111) is therefore expected to yield a product with a much different geometry than the pentacene-like product of TB2TTA. Figure 4 shows a typical molecular product (see also Supporting Information, Figure S2b), formed without annealing, along with a proposed reaction scheme. The features are H-shaped on the surface (see also Supporting Information, Figures S3 and S4a), with

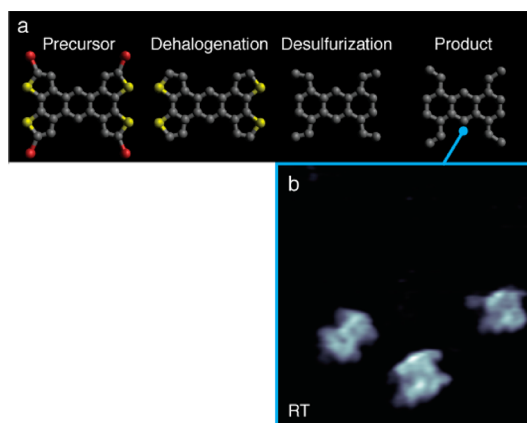


Figure 4. Reaction scheme (a) and representative STM image (b) of products for TB3TTA on the Ni(111) surface. STM image parameters: 6.7×6.7 nm², 1.780 nA, 3.052 mV.

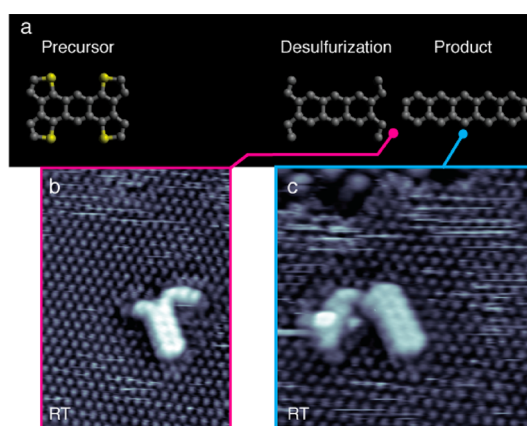


Figure 5. Reaction scheme (a) and representative STM images of products for 2TTA on the Ni(111) surface, (b) frequently observed partially rebonded product of 2TTA, (c) the final product. Image parameters: 4.4×6.2 nm², 0.110 nA, -6.104 mV (b), and 4.8×4.8 nm², 0.080 nA, -6.104 mV (c).

dimensions of 0.73 ± 0.05 nm for the core, consistent with anthracene, and 0.55 ± 0.05 nm for the distance between the two adjacent branches. As expected, no pentacene-like products were observed on the surface. Further annealing to 100 °C produces both isolated and coalesced molecular features with indistinct structures.

To investigate if the halogen plays any role in the formation of the new rings, we conducted identical experiments using 2TTA (Figure 1), a nonhalogenated analogue of TB2TTA. In this case, desulfurization and ring-opening are the only major reaction steps prior to product formation (see the model in Figure 5a). Figure 5b,c and Figure 6a (see also Supporting Information, Figures S2c,d), show STM images of the typical molecular products formed without annealing.

In the experiments with 2TTA, we frequently observed structures exhibiting the expected geometry for a molecule rebonded only at one end (see Supporting Information, Figure S2d), as well as interconnected molecular aggregates that formed without annealing (see Supporting Information, Figures S4b and S5). The detailed measurement

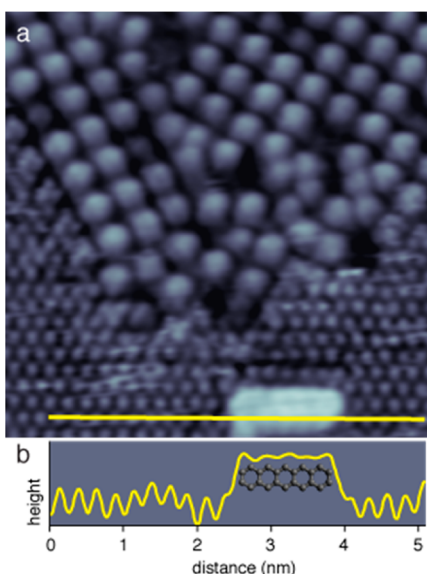


Figure 6. (a) A molecular product formed from 2TTA, on a region with Ni(111) atomic resolution and a neighboring rectangular sulfur phase. The yellow line indicates the location of the line profile shown in panel b; it illustrates the similarity between the molecular structure and pentacene.

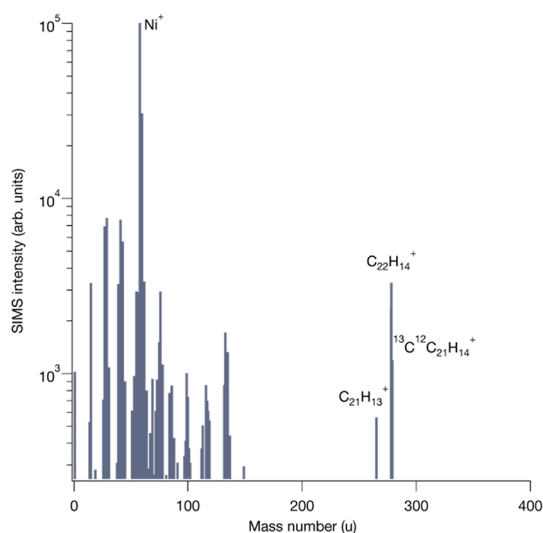


Figure 7. TOF-SIMS showing the positive ions formed from surface species on a 2TTA/Ni(111) sample. The peaks corresponding to nickel and pentacene ($C_{22}H_{14}$) have been labeled.

of a fully rebonded 2TTA product is shown in Figure 6b; the product is identical to that formed from TB2TTA and has dimensions in agreement with pentacene.

Although the STM experiments support the formation of pentacene from 2TTA and TB2TTA, the

identification of the products through measurements of their structure in STM images is not unequivocal. To confirm the identity of the molecular products formed from 2TTA, we performed *ex situ* time-of-flight secondary ion mass spectrometry (TOF-SIMS). The mass spectrum of the positive ions with weights up to 400 amu is shown in Figure 7. The peak at $m/z = 278.12$ amu corresponding to pentacene ($C_{22}H_{14}$, $m = 278.11$ amu) is the dominant peak above 100 amu, with the M+1 peak ($^{13}C^{12}C_{21}H_{14}$, $m = 279.11$ amu) appearing with the expected intensity of $\sim 25\%$ of the main isotope peak.⁵⁰ Also observed is a weak peak corresponding to $C_{21}H_{13}$, which we can tentatively ascribe to the removal of one C–H group from the incompletely rebonded molecular structure shown in Supporting Information, Figure S2d. The peak corresponding to 2TTA has a negligible intensity (see Supporting Information, Figure S6).

CONCLUSIONS

We identified a new reaction involving the abstraction of sulfur from thiophene, with subsequent intramolecular cyclization to produce a well-defined polycyclic aromatic product, by STM imaging. The product was independently verified using TOF-SIMS.

Although thiophene degradation is a known phenomenon, its use in organic synthesis has been limited to hydrodesulfurization ($C-S \rightarrow C-H$). In the case of the reactions observed for TB2TTA and 2TTA, the adsorption of the precursor on the Ni surface not only cleaves the C–S bonds but also stabilizes the reactive intermediates, allowing for the intramolecular rebonding to form a new benzene ring. Owing to the versatile chemistry of thiophene, this reaction could be a useful pathway for the surface-confined synthesis of new polyaromatic molecules. Surface-confined reaction of the isomer TB3TTA does not result in this cyclization product.

These results highlight the ability of STM to reveal the details of molecular reactions. The extremely high spatial resolution of local probe methods provides unique opportunities to study chemical reactions at the single-molecule level, allowing the identification of minority products and intermediates. However, as STM yields limited structural information and chemical contrast, it must be complemented with an additional analysis technique for unambiguous identification of products (in our case TOF-SIMS). As this study demonstrates, planar polycyclic molecules are excellent candidates for discovering new reactions through STM.

METHODS

STM experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of 10^{-10} mbar. The Ni(111) substrate was cleaned by repeated cycles of sputtering with 1 keV Ar^+ for 30 min followed by annealing at 850 °C for 30 min.

TB2TTA,⁵¹ TB3TTA,⁴⁰ and 2TTA⁵¹ were synthesized as described elsewhere and were purified by vacuum sublimation (10^{-1} mbar; 300 °C). The molecules were deposited on the Ni(111) substrate *via* sublimation from a pyrolytic boron nitride (PBN) crucible in a Knudsen-type effusion cell at temperatures of approximately 210 °C for TB2TTA and TB3TTA, and 180 °C for

2TTA. In separate experiments, pentacene (98% Acros Organics) was sublimated from an effusion cell at 200 °C. During deposition the substrate was held at room temperature (RT). After deposition and characterization at room temperature, the samples were annealed at specific temperatures for 15 min.

STM characterization was performed at RT using a commercial variable-temperature instrument (Aarhus 150, SPECS GmbH) equipped with cut Pt/Ir tips. Bias voltages are reported with respect to the STM tip. To compensate for instrumental drift and creep, the STM images were corrected to reflect lattice parameters of known structures wherever possible using WSxM software.⁵² Flattening, smoothing, and Fourier filtering were applied as needed to the images.

TOF-SIMS was carried out using an ION-TOF SIMS IV with a base pressure of 10^{-10} mbar. A 15 keV Bi_1^+ beam was used to sample an area of approximately $50 \times 50 \mu\text{m}^2$. Both positive and negative SIMS were carried out at three different locations on the surface. The results were consistent in all three locations; normalized peak intensities for pentacene and 2TTA from the positive SIMS performed at each of the three locations are reported in the Supporting Information (Figure S6).

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Additional STM images of TB2TTA, TB3TTA, and 2TTA on the Ni(111) surface at room temperature and at different stages of annealing, normalized positive SIMS data for pentacene and TTA in different three locations, full reference for Gaussian 09. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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