On-Surface Formation of One-Dimensional Polyphenylene through Bergman Cyclization

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S *Supporting Information*

ABSTRACT: On-surface fabrication of covalently interlinked conjugated nanostructures has attracted significant attention, mainly because of the high stability and efficient electron transport ability of these structures. Here, from the interplay of scanning tunneling microscopy imaging and density functional theory calculations, we report for the first time on-surface formation of one-dimensional polyphenylene chains through Bergman cyclization followed by radical polymerization on Cu(110). The formed surface nanostructures were further corroborated by the results for the ex situ-synthesized molecular product after Bergman cyclization. These findings are of particular interest and importance for the construction of molecular electronic nanodevices on surfaces.

Fabrication of on-surface molecular electronic devices remains one of the most fascinating goals within the rapidly developing field of nanotechnology.[1,2] Key challenges lie in controllable construction of nanostructures with molecular precision, efficient electron transport ability, and high stability. Recently, the synthesis of covalently interlinked nanostructures from individual molecular building blocks through various kinds of well-known chemical reactions (e.g., Ullmann reaction, imine coupling, alkyne homocoupling, and dehydrogenation) on single-crystal metal surfaces under ultrahigh vacuum (UHV) conditions has been achieved.[3−11] This strategy has stimulated intense attention in surface chemistry since it (1) allows the formation of nanostructures with high thermal and chemical stability in comparison with non-covalent self-assembled nanostructures, (2) prohibits the risk of solvents and other contaminants, and (3) facilitates in situ characterization by, for example, scanning tunneling microscopy (STM).[2,12−16] The Bergman reaction, an intramolecular cyclization of enediyne compounds, has been widely investigated in pharmaceutics and materials science.[17−20] This reaction should be especially interesting for on-surface fabrication of molecular nanostructures because it is a simple, byproduct-free synthetic route involving one component with no strict requirement of a catalyst. Here we demonstrate what is to our knowledge the first example showing how the Bergman cyclization reaction can be employed on a surface to explore the feasibility of forming covalently linked conjugated carbon nanostructures.

In this work, we designed the compound 1,6-di-2-naphthylhex-3-ene-1,5-diyne (DNHD), which has an enediyne moiety and two naphthyl groups (Scheme 1). According to

Scheme 1. Mechanism of Bergman Cyclization and Radical Polymerization of DNHD
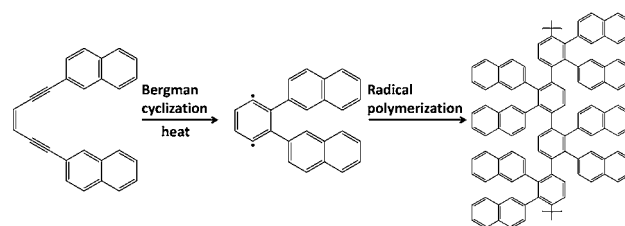
previous studies of the Bergman reaction,[19,21] the intramolecular cyclization takes place upon stimulation by heat, forming the diradical intermediate, which then grows into a linear polyphenylene through radical polymerization (Scheme 1). The Cu(110) surface was chosen as the substrate because of its well-known one-dimensional (1D) templating effect to facilitate the formation of unidirectional linear structures.[22−24] Using the interplay of high-resolution UHV-STM imaging and density functional theory (DFT) calculations, we demonstrated that the on-surface formation of 1D polyphenylene through Bergman cyclization of the enediyne precursor was successfully achieved. The result was also validated by comparison with the STM image of the product of Bergman cyclization of DNHD via ex situ synthesis. The findings demonstrate that Bergman cyclization could be a promising approach for constructing molecular nanostructures containing conjugated backbones with submolecular precision, which would shed light on the design of molecular nanodevices with engineered chemical and electronic properties.

The STM experiments were performed in a UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable-temperature "Aarhus-type" scanning tunneling microscope purchased from SPECS,[25,26] a molecular evaporator, and standard facilities for sample preparation. After the system was thoroughly degassed, the molecules were deposited by thermal sublimation onto the Cu(110) substrate. The sample

was thereafter transferred within the UHV chamber to the microscope, where measurements were carried out at ~100 K. All of the calculations were carried out in the framework of DFT by using the Vienna Ab Initio Simulation Package (VASP).[27,28] The projector augmented wave method was used to describe the interaction between ions and electrons.[29,30] We employed the Perdew−Burke−Ernzerhof generalized gradient approximation exchange−correlation functional,[31] and van der Waals (vdW) interactions were included using the dispersion-corrected DFT-D2 method of Grimme.[32] The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in VASP until the forces on all unconstrained atoms were ≤0.03 eV/Å. The simulated STM image was obtained using the Tersoff−Hamann method, in which the local density of states (LDOS) is used to approximate the tunneling current.[33]

We first deposited the DNHD molecules on Cu(110) held at ~170 K. As illustrated in Figure 1a, some heart-shaped
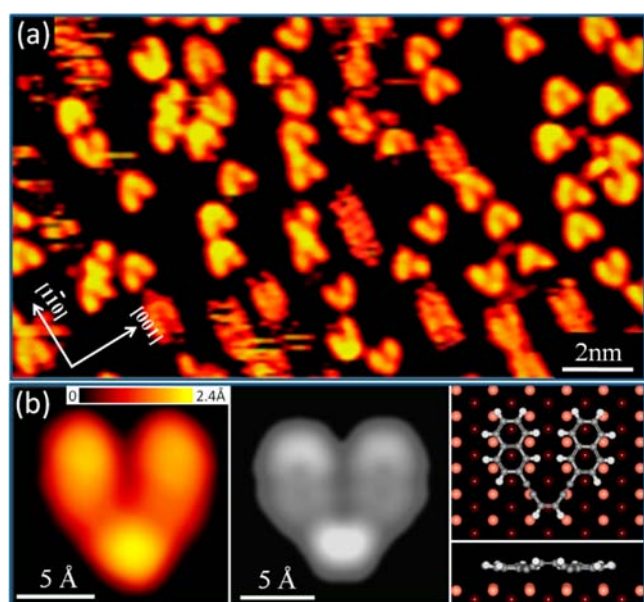

Figure 1. (a) STM image after deposition of DNHD molecules on Cu(110) held at 170 K. The lattice direction of the substrate is indicated. Scanning conditions: I_t = 0.65 nA, V_t = −2500 mV. (b) (left) high-resolution STM image of a single DNHD molecule; (middle) simulated STM image of a single DNHD molecule on Cu(110) obtained using the Tersoff−Hamann method at a bias voltage of −2500 mV; (right) top and side views of the DFT-optimized geometry of a DNHD molecule adsorbed on Cu(110).

molecules with two elliptical lobes and one round protrusion were distributed in an isolated way on the substrate, mainly with their symmetry axes aligned along the $[1\bar{1}0]$ direction of the substrate. The simulated STM image of DNHD on Cu(110) obtained with the same bias voltage of −2500 mV as used in the STM experiments (Figure 1b, middle panel) exhibits a heart-shaped profile rather similar to the experimental STM image (Figure 1b, left panel). Moreover, the DFT-optimized model of DNHD on Cu(110) clearly shows that the molecule tends to adopt a flat-lying adsorption geometry on Cu(110) (Figure 1b, right panel). Thus, we could convincingly attribute the heart-shaped motif to a single DNHD molecule adsorbed on Cu(110) and assign the elliptical lobes to the two naphthyl groups and the round protrusion to the vinyl group. It

should be noted that even at ~100 K the DNHD molecules were still highly mobile on the surface, as reflected by the blurred shapes in the STM image. The fuzzy trajectories indicate that the speed of the molecular motion along the $[1\bar{1}0]$ direction of the substrate was higher than the STM scanning speed.

Interestingly, after the sample was annealed to ~400 K, we found that the heart-shaped motifs had disappeared and dispersed one-dimensional chains growing along the $[1\bar{1}0]$ direction of the substrate had formed (Figure 2a). The high-
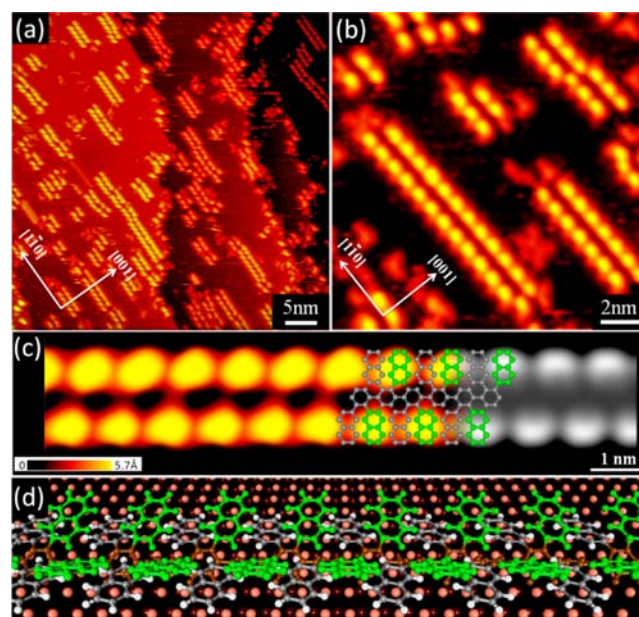

Figure 2. (a) Large-scale and (b) close-up STM images showing the formation of one-dimensional molecular chain structures along the $[1\bar{1}0]$ direction of the substrate after the sample with adsorbed molecules was annealed at 400 K. Scanning conditions: I_t = 0.65 nA, V_t = −2500 mV. (c) High-resolution close-up STM image of the molecular chain and a DFT-based STM simulation (black-and-white part). An equivalently scaled model of the polyphenylene structure is superimposed. (d) Perspective view of the structural model showing the tilted naphthyl groups (shown in green).

resolution STM image presented in Figure 2b clearly shows that the molecular chains consisted of two columns of protrusions along the growing direction that exhibited a staggered arrangement. Superimposing the equivalently scaled chemical structure of the polyphenylene chain on the close-up STM image demonstrates the good agreement in the periodicities and widths (Figure S1 in the Supporting Information). Moreover, comparison of the experimental STM image with the simulated one shows that both the dimension and the molecular appearance correspond well (Figure 2c). Comparison of the STM image with the perspective view of the model (Figure 2d) shows that each of the staggered bright protrusions corresponds to a naphthyl group of a molecular constituent that is lifted as a result of steric hindrance within the formed structure (shown in green), while the other naphthyl group (shown in gray) is not clearly resolved. The apparent heights of the DNHD molecule (Figure 1b) and the molecular chain (Figure 2c) were found to be different. The robustness of the molecular chain was demonstrated by lateral STM manipulation (data not shown). On the basis of the above analyses, it is plausible to deduce that

the molecular chains were formed by Bergman cyclization of DNHD molecules with subsequent free diradical polymerization. Copper adatoms in the molecular chain can be excluded because of the discrepancy in periodicity along the chain (Figure S2). It should be noted that in addition to the majority of molecular chain structures, there were also some randomly distributed species on the surface (Figure S3), which could be attributed to byproducts of Bergman cyclization or free radical polymerization.

To verify our findings further, we prepared the molecular product of DNHD after Bergman cyclization (denoted as DNYB) ex situ and conducted a control experiment in which the DNYB molecules were deposited onto the surface to compare the single-molecule appearance of DNYB with the appearance of the molecular constituents inside the polymer chain formed by in situ Bergman cyclization. As shown in Figure 3a, after deposition of DNYB on Cu(110) held at ~170
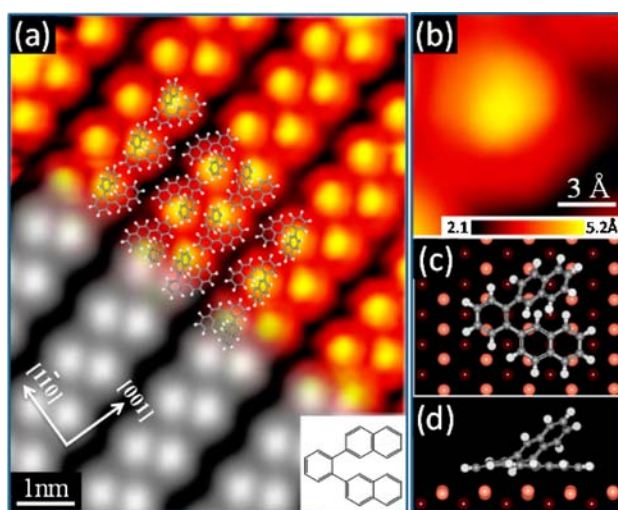

Figure 3. (a) STM image and DFT-based STM simulation (black-and-white part) showing the formation of an ordered nanostructure after deposition of the DNYB molecules on Cu(110). The DFT-optimized model of the self-assembled nanostructure is overlaid on the STM image. Scanning conditions: I_t = 0.65 nA, V_t = −2500 mV. The chemical structure of DNYB is shown in the inset at the lower right. (b) Close-up STM image of a DNYB molecule in the structure. (c) Top and (d) side views of the adsorption geometry of DNYB extracted from the optimized model of the self-assembled nanostructure on Cu(110).

K, the molecules self-assembled into two-dimensional enantiomerically pure nanostructures with both chiralities (cf. Figure S6). To unravel the molecular adsorption geometry and intermolecular interactions in the self-assembled nanostructure, we performed DFT calculations on the formed nanostructures involving Cu(110) substrate and vdW interactions (Figure S7) as well as a DFT-based STM simulation of the nanostructure (Figure 3a). From the comparison of experimental STM image with the simulated one, we could clearly identify that one DNYB molecule was imaged as a bright protrusion with some shadows (Figure 3b), which resembles the molecular constituent in the polymer chain very much. In addition, the molecular adsorption geometry of DNYB on Cu(110) (cf. Figure 3c,d) shows that one of its naphthyl groups lifts upward, which also exhibits a similar configuration to that of the molecular constituent in the polymer chain. Note that

disordered short molecular chains are formed after annealing the surface at 400K as shown in Figure S9.

From the above analysis, the scenario for the formation of quasi-straight unidirectional polyphenylene chains on Cu(110) is considered to be the following: (1) the intramolecular Bergman cyclization induces the formation of diradical intermediates in the first step; (2) the subsequent radical polymerization results in the formation of polyphenylene chains; and (3) in addition, the 1D templating effect of the Cu(110) surface is responsible for governing the unidirectional growth. It should be noted that to get a high yield and extended polyphenylene chains, the lifetime, diffusion barrier, and proper arrangement of the radicals with respect to the substrate lattice are considered to be the limitations. Because of the chemically active nature of the diradical intermediates, the diradicals must be immediately linked together before they are quenched. In our case, heat served not only to initiate the Bergman cyclization but also to facilitate the formation of molecular chains through radical polymerization.

In conclusion, by combining high-resolution UHV-STM imaging and DFT calculations, we have for the first time reported that Bergman cyclization can occur on a Cu(110) surface and that 1D polyphenylene chains are formed along the [1$\bar{1}$0] direction of Cu(110) via subsequent radical polymerization. The investigations have widened our vision of the on-surface synthesis of covalently linked molecular nanostructures and further demonstrated the fascinating potential of surface chemistry. Moreover, the controllable growth of conjugated nanostructures with molecular precision and different functional groups would be of particular interest and importance for the construction of molecular electronic nanodevices. Further work to fabricate more complicated and advanced surface nanostructures by Bergman cyclization is underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental and theoretical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Heath, J. R. *Annu. Rev. Mater. Res.* **2009**, *39*, 1.

(2) Franc, G.; Gourdon, A. *Phys. Chem. Chem. Phys.* **2011**, *13*, 14283.

(3) Otero, G.; Biddau, G.; Sanchez-Sanchez, C.; Caillard, R.; Lopez, M. F.; Rogero, C.; Palomares, F. J.; Cabello, N.; Basanta, M. A.; Ortega, J.; Mendez, J.; Echavarren, A. M.; Perez, R.; Gomez-Lor, B.; Martin-Gago, J. A. *Nature* **2008**, *454*, 865.

(4) Grill, L.; Dyer, M.; Lafferentz, L.; Persson, M.; Peters, M. V.; Hecht, S. *Nat. Nanotechnol.* **2007**, *2*, 687.

(5) Cai, J.; Ruffieux, P.; Jaafar, R.; Bieri, M.; Braun, T.; Blankenburg, S.; Muoth, M.; Seitsonen, A. P.; Saleh, M.; Feng, X.; Müllen, K.; Fasel, R. *Nature* **2010**, *466*, 470.

(6) Deshpande, A.; Sham, C. H.; Alaboson, J. M. P.; Mullin, J. M.; Schatz, G. C.; Hersam, M. C. *J. Am. Chem. Soc.* **2012**, *134*, 16759.

(7) Bebensee, F.; Bombis, C.; Vadapoo, S. R.; Cramer, J. R.; Besenbacher, F.; Gothelf, K. V.; Linderoth, T. R. *J. Am. Chem. Soc.* **2013**, *135*, 2136.

(8) Zhang, Y. Q.; Kepcija, N.; Kleinschrodt, M.; Diller, K.; Fischer, S.; Papageorgiou, A. C.; Allegretti, F.; Bjork, J.; Klyatskaya, S.; Klappenberger, F.; Ruben, M.; Barth, J. V. *Nat. Commun.* **2012**, *3*, 1286.

(9) Treier, M.; Richardson, N. V.; Fasel, R. *J. Am. Chem. Soc.* **2008**, *130*, 14054.

(10) Zhong, D.; Franke, J. H.; Podiyanachari, S. K.; Blömker, T.; Zhang, H.; Kehr, G.; Erker, G.; Fuchs, H.; Chi, L. *Science* **2011**, *334*, 213.

(11) Wang, W.; Shi, X.; Wang, S.; Van Hove, M. A.; Lin, N. *J. Am. Chem. Soc.* **2011**, *133*, 13264.

(12) Schlogl, S.; Sirtl, T.; Eichhorn, J.; Heckl, W. M.; Lackinger, M. *Chem. Commun.* **2011**, *47*, 12355.

(13) Bieri, M.; Blankenburg, S.; Kivala, M.; Pignedoli, C. A.; Ruffieux, P.; Müllen, K.; Fasel, R. *Chem. Commun.* **2011**, *47*, 10239.

(14) Mendez, J.; Lopez, M. F.; Martin-Gago, J. A. *Chem. Soc. Rev.* **2011**, *40*, 4578.

(15) Gourdon, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 6950.

(16) Garah, M. E.; MacLeod, J. M.; Rosei, F. *Surf. Sci.* **2013**, *613*, 6.

(17) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660.

(18) Kar, M.; Basak, A. *Chem. Rev.* **2007**, *107*, 2861.

(19) Xiao, Y.; Hu, A. *Macromol. Rapid Commun.* **2011**, *32*, 1688.

(20) Li, Z.; Song, D.; Zhi, J.; Hu, A. *J. Phys. Chem. C* **2011**, *115*, 15829.

(21) Chen, X.; Tolbert, L. M.; Hess, D. W.; Henderson, C. *Macromolecules* **2001**, *34*, 4104.

(22) Dong, L.; Sun, Q.; Zhang, C.; Li, Z.; Sheng, K.; Kong, H.; Tan, Q.; Pan, Y.; Hu, A.; Xu, W. *Chem. Commun.* **2013**, *49*, 1735.

(23) Oehzelt, M.; Grill, L.; Berkebile, S.; Koller, G.; Netzer, F. P.; Ramsey, M. G. *ChemPhysChem* **2007**, *8*, 1707.

(24) Forster, M.; Raval, R.; Carrasco, J.; Michaelides, A.; Hodgson, A. *Chem. Sci.* **2012**, *3*, 93.

(25) Besenbacher, F. *Rep. Prog. Phys.* **1996**, *59*, 1737.

(26) Laegsgaard, E.; Österlund, L.; Thostrup, P.; Rasmussen, P. B.; Stensgaard, I.; Besenbacher, F. *Rev. Sci. Instrum.* **2001**, *72*, 3537.

(27) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *48*, 13115.

(28) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.

(29) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.

(30) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.

(31) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(32) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787.

(33) Tersoff, J.; Hamann, D. R. *Phys. Rev. B* **1985**, *41*, 805.

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