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Creating and Seeing the First Pure Carbon Ring

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The synthesis, isolation, and characterizations of sp-hybridized carbon materials remain challenging due to their high reactivities. Recently in *Science*, Kaiser et al. synthesized the first pure carbon ring, cyclo[18]carbon, and demonstrated its bonding structure of alternating single and triple bonds.

Carbon, as one of the most abundant elements in the universe, plays a key role for all the known forms of life. Several carbon allotropes can be formed via the hybridization of s and p orbitals. Diamond is the representative of sp^3-hybridized carbon materials, while fullerene, carbon nanotube, and graphene are composed of sp^2-hybridized carbon though they possess 0D, 1D, and 2D network structures, respectively.[1–3] However, the synthesis and confirmation of sp-hybridized carbon materials are still of a great challenge.

Carbyne, as an infinite sp-hybridized carbon chain, has attracted great attentions while the as-synthesized materials remained ill defined in most cases. The production of polyyne addressed this issue, whereas its end-capping groups would unavoidably introduce non-carbon species into the material. Instead, cyclocarbon, where carbon atoms arrange in the shape of a ring, is saturated and thus free from impurities. However, the preparation of cyclocarbons only succeeded in the gas phase, without being able to isolate and characterize the as-synthesized materials due to their high reactivities.[4] Thus, no direct evidence could be provided for the way sp-hybridized carbon atoms are bonded, namely, via double bonds (cumulenic structure) or alternating single and triple bonds (polyynic structure).

In 2018, Gawel, Anderson, Gross, and their coworkers successfully induced the skeletal rearrangement toward the generation of linear carbon segments with end-capping phenyl rings via atom manipulation.[5] Very recently, using a similar technique, this group accomplished the synthesis and imaging of the first sp-hybridized pure carbon ring, cyclo[18]carbon, and this great work was published in *Science*.[6] Initially, researchers prepared the triangular-shaped $C_{24}O_6$ as the precursor of cyclo[18]carbon. As shown in Figures 1A–1E, $C_{24}O_6$ contains three carbon squares off the 18-carbon-atom ring with two C = O groups on each square, contributing to the enhancement of molecular stability. Then $C_{24}O_6$ was sublimed onto a cold Cu substrate, which was partially covered by inert bilayer NaCl islands. The atom manipulation and imaging were carried out in a STM-AFM system operated at an ultrahigh vacuum condition of 10^{-10} mbar and an ultralow temperature of 5 K. By placing the AFM tip a few nanometers away from the molecule and then applying voltage pulses, pairs of C = O groups could be removed from the precursor, leading to the formation of longer polyynic segments. The major products were $C_{22}O_4$, $C_{20}O_2$, and C_{18} (namely, cyclo[18]carbon) (Figure 1). Cyclo[18]carbon could be formed via either one step or multiple steps, while its total yield was just 13%. In AFM images of the as-synthesized cyclo[18]carbon, it was observed that with the decrease of the tip height, a circle arranged by nine bright lobes (Figure 1Q) gradually transited into a nonagon with evident corners (Figure 1R). The lobes and corresponding corners were attributed to the triple bonds, as the evidence for the polyynic structure of cyclo[18]carbon. Furthermore, the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional theory calculations revealed the similar bond-length alternation for $C_{24}O_6$, $C_{22}O_4$, $C_{20}O_2$, and C_{18} rings. For cyclo[18]carbon, HSE calculations converged to a polyynic structure with alternating shorter (1.195 Å) and longer (1.343 Å) bonds. Using the results derived from HSE calculations, the simulated AFM images of $C_{24}O_6$, $C_{22}O_4$, $C_{20}O_2$, and C_{18} rings were obtained, in good agreement with the experimental observations (Figure 1). This indicated that the HSE hybrid functional can provide a reliable structure prediction for sp carbon materials.

This is truly a breakthrough in synthetic carbon allotropes and even the whole field of materials. Rather than the widely used bottom-up strategies toward the synthesis of carbon chains or rings, this group employed the pick-off method realized via atom manipulation, successfully creating and seeing the sp-hybridized pure carbon material for the first time. This provided a hint for the preparation of advanced materials; namely, to break a substance can be easier than to build one. More importantly, this work gave the direct evidence of the polyynic structure with alternating triple and single bonds, indicating that carbon rings can act as semiconductors with great application potentials in molecular-sized electronics.[7] Furthermore, the high chemical reactivity of sp-hybridized carbon rings suggested the possibilities of forming larger carbon-rich

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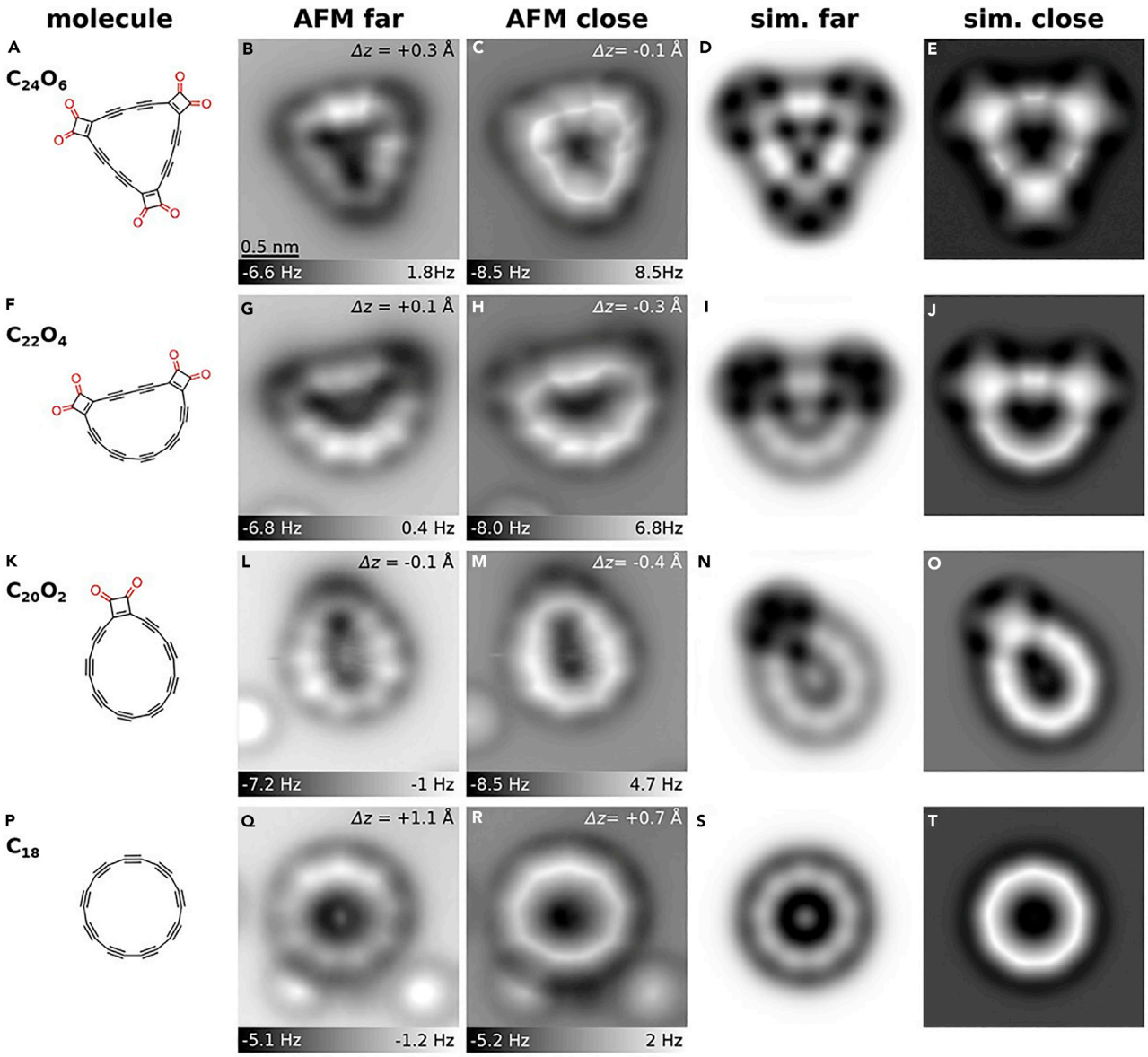

Figure 1. Precursor and Products Generated by Tip-Induced Decarbonylation

Structures (1st column), AFM images (2nd and 3rd columns), and simulated AFM images (4th and 5th columns). From Kaiser et al.[6] and reprinted with permission from AAAS.

molecules (large rings, multiple rings, long chains, etc.) and also implied their broad applications in the field of chemistry, which make them distinct from the sp^2- and sp^3-hybridized carbon materials.

Great challenges remain despite the impressive achievement the researchers have made. The first challenge is the production efficiency. Namely, only one molecule could be synthesized at a time due to the precise atom manipulation by a tip. A large amount of byproducts even made the matter worse, leaving the yield of cyclo[18]carbon as low as 13%. The second challenge is the stability of the as-synthesized material. Cyclo[18] carbon seemed unable to survive in the ambient atmosphere and at the room temperature due to its high reactivity, making it hard to conduct comprehensive characterizations to know more about its properties and to further put it into practical applications. Except for STM-AFM, HRTEM and the more advanced S-TEM can be promising approaches to visualize the structures of sp-hybridized materials as indicated by our image simulations,[8] and other characterizations such as Raman, IR, and UV-Vis spectroscopies need to be done as well.

The successful synthesis and imaging of cyclo[18]carbon provide a glimpse into the fascinating group of sp-hybridized carbon materials, which marks a new era of materials. A great number of efforts into this field are strongly needed, both in theoretical calculations on the relations between structures and properties[9] and in the experimental investigations to obtain samples with higher amounts and stabilities.

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