

# Controllable Synthesis of *cis*-Enediyne Trimer, Graphdiyne and Graphyne Nanowires on a Ag(111) Surface

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How to steer an on-surface reaction with complex and multi-pathways remains a great challenge. Herein, we report the successful control of the reaction of 1,1'-biphenyl,4-bromo-4'-ethynyl (BPBE) on a Ag(111) surface. The pathways of the formation of *cis*-enediyne trimer,[1] graphdiyne and graphyne nanowires are picked out respectively by different annealing procedures (See Figure 1). Firstly, highly active *cis*-enediyne type trimer are formed with a yield up to 90 % when BPBE molecules are deposited onto Ag(111) held at 420 K. The high-selectivity originates from the Br...H intermolecular hydrogen bonds, which aggregates the generated *cis*-enediynes into well-ordered close-packed islands, thus protecting them from further reactions. Secondly, when depositing BPBE molecules on Ag(111) held at a lower temperature of 360 K, only Glaser coupling can be activated, leading to the formation of conjugated diyne type dimer. These conjugated diynes typically connect with each other via C-Ag-C bonds, forming organometallic graphdiyne chains. Further annealing the sample to 460 K gives rise to the ejection of interstitial Ag adatoms and the generation of covalent graphdiyne nanowires. Thirdly, Sonogashira coupling occupies the dominant position when BPBE molecules are deposited on a hot Ag(111) surface of 670 K and covalent graphyne nanowires can be formed. The competition between molecular reaction, diffusion and desorption results in the high-selectivity of the high-barrier Sonogashira reaction. Specifically, because of the strong desorption of molecules at high temperature on Ag(111), only the occasionally formed molecular chains can stay on the surface. Glaser coupling is still the lowest-barrier pathway and easiest to occur, however, once a conjugated diyne is formed, Sonogashira coupling becomes dominating in the following reaction process due to its lower energy barrier than that of Ullman coupling. Scanning tunnelling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations are interplayed to confirm the successful control of the multiple reaction pathways and corroborate the mechanisms proposed above. This work provides a great guidance for the selection of reaction pathway with low-priority in energy barrier and protection of highly active products.

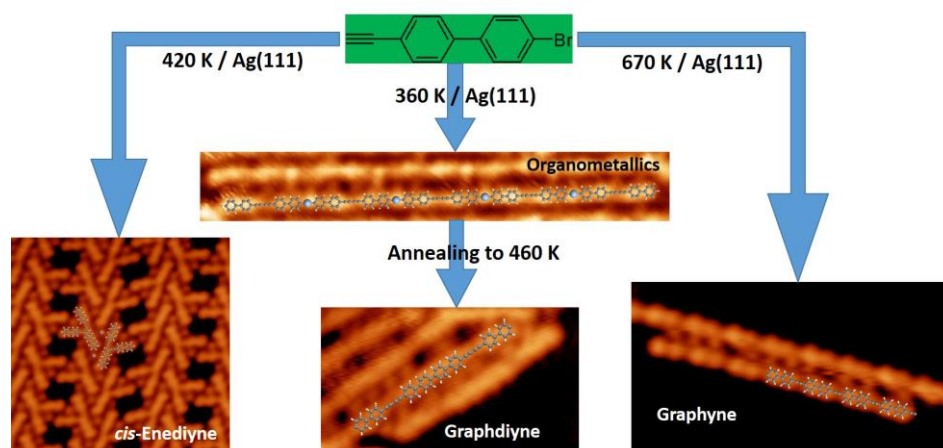


Figure 1. The reaction pathways of BPBE on Ag(111) by distinct thermal stimuli strategies.

## References:

[1] T. Wang, H. Lv, Q. Fan, L. Feng, X. Wu, J. Zhu, *Angew. Chem. Int. Ed.* **56**, 4762 (2017).