



On-surface synthesis of Disilabenzene-Bridged Covalent Organic Frameworks

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Since the first systematic on-surface covalent coupling of bromo-substituted porphyrins,^[1] on-surface synthesis has attracted tremendous interest of researchers. In this reaction, small precursor molecules, synthesized in wet chemistry, are usually deposited on noble metal surface under ultrahigh vacuum and subsequently linking each other by annealing. Combining with ultra-high resolution scanning probe microscopy (SPM) with a CO terminated tip,^[2] this field has been rapidly developed.

In this contribution, I will present our recent activity, relating to on-surface silicon chemistry studied with high-resolution SPM operating at low temperature. We synthesized diacetylene linked anthracene oligomers by on-shot homocoupling of trimethylsilyl groups in 9,10-bis(trimethylsilyl)ethynylanthracene on a Cu(111) surface.^[3] This reaction was further extended for chemoselective Sonogashira coupling between (trimethylsilyl)ethynyl and chlorophenyl groups in silylethynyl- and chloro-substituted partially fluorinated phenylene ethynylenes (SiCPFPEs) on a Ag(111) surface.^[4] This head-to-tail reaction leads to a synthesis of PFPE alternating oligomers. We also synthesized one- and two-dimensional covalent organic frameworks whose backbones contain 1,4-disilabenzene linkers (Figure 1).^[5] In this case, we induced the coupling between silicon atoms and the bromo-substituted polyaromatic hydrocarbon on Au(111) by annealing. The structural and electronic properties were characterized by a combination of high-resolution SPM and photoelectron spectroscopy as well as density functional theory calculations. In this way, on-surface synthesis can also contribute to silicon chemistry.

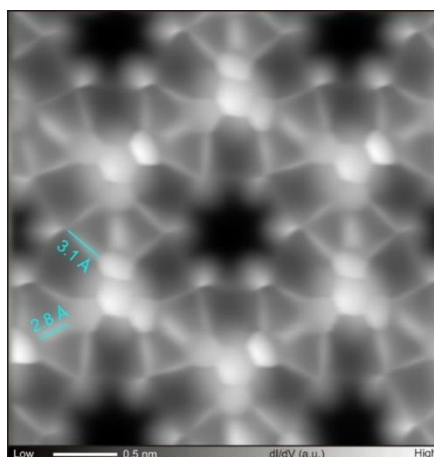


Figure 1. Bond-resolved image of silabenzene incorporated covalent organic frameworks.

References

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