Synthesis of π-conjugated two-dimensional polymers and their electronic properties

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Two-dimensional covalent organic frameworks (2D COFs) are crystalline 2D polymer networks whose monomers are organized predictably using directional bonding principles. Although various examples have been reported so far in this class of materials, their electronic conductivities are very limited, which is unlike their natural 2D polymer counterparts, such as graphene/graphite. Here we studied 2D polymers consisting of benzotrithiophene (BTT) derivative monomers. BTT has two structural isomers depending on the direction of three thiophenes in their fused structures: **BTT**$_{C3sym}$ has the same direction for three thiophenes in it, while **BTT**$_{Asym}$ has one thiophene directing oppositely from the other two (Fig. 1). By employing with DFT calculation methods, we found the 2D polymers made from those two different BTTs exhibit very different band structures and **BTT**$_{Asym}$ can construct a 2D polymer with a highly distorted band structure.[1]

For synthesizing the 2D polymer structure composed of **BTT**$_{Asym}$, tribrominated **BTT**$_{Asym}$ monomer, **BTT**$_{Asym}$**Br**$_3$, was synthesized and heated on metal surfaces to conduct Ullmann coupling reaction, affording π-conjugated 2D polymers under ultra-high vacuum conditions. By carefully selecting metal surfaces to use, we successfully obtained a 2D polymer composed of **BTT**$_{Asym}$, which is visualized by STM imaging (Fig 2).[2] The detailed synthetic conditions and features of obtained 2D polymer structures will be discussed in this talk.

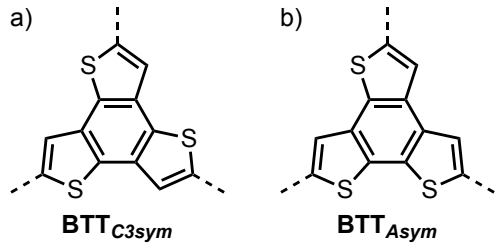

Fig. 1 Chemical structures of (a) **BTT**$_{C3sym}$ and (b) **BTT**$_{Asym}$

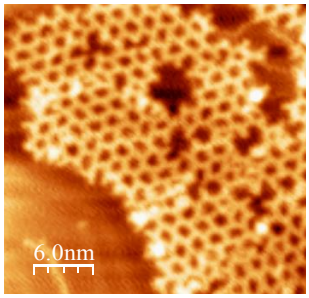

Fig. 2 STM topography of **BTT**$_{Asym}$**Br**$_3$ polymerized on Au(111).

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