On-Surface Growth of Covalent Organic Frameworks using Functionalized Aromatic Amines

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Aromatic amine precursors have been studied to form polymers displaying effective transport layers suitable for various application. In particular, triphenylamine (TPA) is a simple, aromatic amine consisting of three phenyl rings arround a nitrogen atom. TPAs are typically used as molecular precursors to build polymeric structures via wet-chemistry techniques [1,2]. Moreover, the design of TPAs makes them possible precursors to synthesize 2D covalent organic frameworks (COFs) in a similar manner as 1,3,5-triphenylbenzene derivatives [3]. However, we are not aware of any previous studies of the controlled elaboration of COFs from these TPA molecules by using this approach.

In this study, we report preliminary results on COFs growth based on to TPA derivatives. The formation of molecular domains and COFs has been investigated under ultra-high vacuum (UHV) conditions RT-STM by evaporating molecules on Au(111) and Ag(111) surfaces held at either room (RT) or elevated temperatures to induce their self-assembly or several possible reactions (i.e. cyclotrimerization, Ullmann and Glaser couplings).

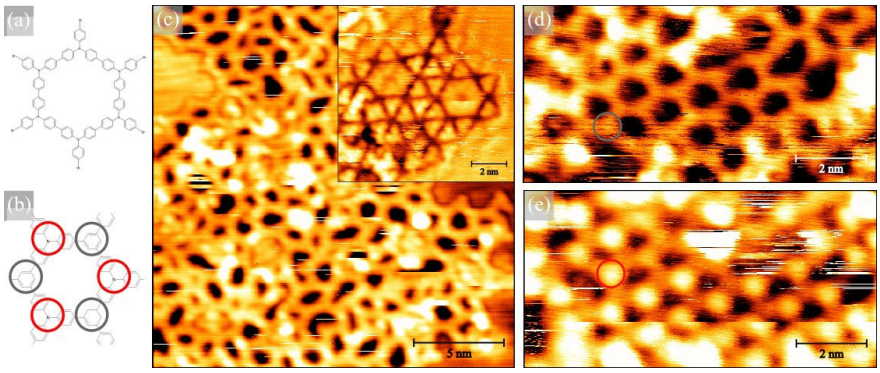

Figure 1. (a,b) Anticipated on-surface reactions of BrTPa and Ethyl-TPA on Au(111), respectively. (c) STM images of reacted BrTPA (V_b= 1 V, I_t = 10 pA, 20 x 20 nm²) and (inset) of small metal-organic molecular domains (V_b= 1 V, I_t = 5 pA, 7.5 x7.5 nm²) on Au(111). (d,e) STM images of Ethyl-TPA at positive and negative bias (V_b= +1V and -2V, I_t = 15 pA, 10 x 5 nm²) on Au(111) , respectively.

For BrTPA precursors, two distinct self-assembled molecular patterns were obtained on Au and Ag substrates held at RT [4]. Upon annealing, debromination of the BrTPA molecules is triggered, leading to Ullman Coupling and the formations of similar reacted molecular domains on both substrates (Fig. 1c) co-existing with a few intermediate metal-organic domains (Fig. 1c inset). Surprisingly, not only structures made of six molecules (Fig. 1a), which is the most favourable regarding the substrates symmetry, were found but also structures made of two up to eight molecules.

For Ethyl-TPA building blocks, no self-assembled molecular domains were observed on either substrate. Only molecular diffusion is observed on Ag(111) when the substrate is held at room temperature, but subsequent annealing induces the formation of ordered covalent fragments.

In contrast, Ethyl-TPA on Au(111), appears to form ordered COFs even when deposited onto room-temperature substrates. This polymeric structure is grown through cyclotrimerization coupling, in which the three ethyl groups react to form a benzene-like ring between the molecules (Fig. 1b). The resulting porous hexagonal structure would exhibit half of the vertices with N atoms and the other half with these new carbon rings. The presence of alternating vertices of SCOFs formed on Au(111) is confirmed with STM images recorded at positive and negative sample bias (Fig. 1d,e).

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