On-surface Molecular Frameworks – Synthesis, Properties and Function

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Crystalline and porous molecular framework materials with specific encoded properties hold promise as a novel, highly tunable, functional platform.[1] Through the principles of reticular chemistry, numerous two- and three-dimensional molecular frameworks with diverse structural, optical, and electrical properties are now accessible. On-surface deposition of molecular framework coatings is crucial for their utilization as active layers in advanced device-based applications, including separation, sensing, and optoelectronics. In addition to the variable backbone properties, achieving precise control over the molecular framework film characteristics is of critical importance for achieving the intended functionality.[2]

In my presentation, I will first provide an overview of the synthesis of 2D molecular frameworks. In particular, I will discuss new insights into and crystallization process of covalent organic frameworks (COFs).[3] Following this, the on-surface synthesis of COFs as films and deposits will be presented. The *in-situ* thin film synthesis approach will be discussed and highlighted as a reliable and well-established methodology for the synthesis of COF thin films. Here, the synthesis of novel layered thiophene-extended benzotrithiophene-based (BTT) COFs as highly oriented and crystalline thin films and their respective directional electrical conductivity will be illustrated.[4] In addition, thienothiophene (TT) isomer alloying of a COF scaffold will be introduced as an efficient tool for band-gap engineering of ordered organic solids in both bulk and film forms.[5] Furthermore, a three-component synthesis using pyrene-dione, 2,3,6,7,10,11-hexahydroxytriphenylene, and diamines as building blocks in a one-pot reaction to form pyrene-fused azaacene COFs, —termed Aza-COFs—will be discussed. This three-component synthesis achieves a quantitative conversion of the pyrene-dione moiety into its respective azaacene building block, alongside the formation of an Aza COF. The resulting crystalline and porous framework series features a systematic elongation of the π-system. By employing the three-component synthesis, highly oriented and crystalline Aza-COF films are in reach.[6]

References

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