Polymer Synthesis Enabled by Interfaces: Towards a world of organic 2D materials

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Interface has been playing a key role in most “bottom-up” synthesis methods and is advantageous for directing the orientation of the molecules or precursors. By looking back at the history, the interfacial synthesis has been largely developed for the controlled polymer synthesis, which can be dated back to 1930s by Gee et al who achieved polymer monolayers at an air-water interface. Typically, the reactions at the interfaces between air-water (or gas-liquid), liquid-liquid, liquid-solid and gas-solid (or vacuum-solid) have been explored to offer paramount control over the morphology and the structure of polymers. While the synthetic linear polymers and cross-linked polymers are the main resultant structures in the historic interfacial polymer synthesis, it turns out only in recent years that a controlled 2D covalent reaction can take place if a finely designed interface is provided. A subsequent consequence of adsorption, nucleation, arrangement and polymerization of suitably designed precursors or intermediates, guided by a confined 2D geometry of interface, can yield a structurally well-defined, periodic organic 2D material such as 2D polymer.

In this lecture, we will present our recent efforts on the bottom-up synthetic approaches towards novel organic 2D materials with structural control at the atomic/molecular-level or at the meso-scale. First, we will introduce the latest development on the synthetic 2D conjugated polymers including 2D Schiff-base type covalent polymers and 2D metal-dithienene/diamine coordination polymers at the air-water or liquid-liquid interfaces. The resulting 2D conjugated polymers exhibit single- to multi-layer feature, good local structural ordering and with a large size. The functional exploration of such 2D conjugated (coordination) polymers for the electrical, magnetic and mechanical properties, as well as serving as efficient electrocatalytic water splitting catalysts will be demonstrated. Next, we will introduce the self-assembly of a host-guest enhanced donor-acceptor interaction, consisting of a tris(methoxynaphthyl)-substituted truxene spacer, and a naphthalene diimide substituted with N-methyl viologenyl moieties as donor and acceptor monomers, respectively, in combination with cucurbit[8]uril as host monomer toward monolayers of 2D supramolecular polymers at liquid-liquid interface. Third, we will present the supramolecular approaches to synergistically control the multi-component assembly, which results into 2D conducting polymers, such as polypyrrole and polyaniline nanosheets featuring 2D structures and with adjustable mesopores with/without on various functional free-standing surfaces. The unique structure with adjustable pore sizes (5–20 nm) and thickness (35–45 nm), enlarged specific surface area as well as high electrical conductivity make 2D conducting polymers promising for a number of applications. Finally, we will present a controlled synthesis of few-layer 2D polymer crystals on the water surface assisted by soft templates; we achieved micrometer-sized either horizontally or vertically grown 2D polyamide crystals by tailoring templating layers. The future perspective and outlook regarding the goal towards highly crystalline organic 2D materials will be also provided.