# Two-Dimensional Conjugated Polymers: From Dream to Reality

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Two-dimensional (2D) conjugated polymers have been a highly sought-after class of polymeric materials in the synthetic polymer and organic electronics communities. The extensive conjugation in two dimensions can, in principle, offer the possibility to confront the major challenges faced by linear polymer semiconductors. The sheet-like network can be regarded as n-strand ladder chains, where charge carriers can travel through the different chains, and therefore, bypass the possible defects and grain boundaries with the hopping mechanism that is commonly present in linear conjugated polymers. The unique structural features and electronic band structures would render 2D conjugated polymers highly promising candidates for next-generation electronic, optoelectronic, and spintronic devices.

However, synthetic chemistry methodologies to achieve extensive 2D conjugation and efficient 2D polymerization have yet to be developed. Classical dynamic covalent chemistry commonly used in covalent organic frameworks, and topochemical polymerization strategies, fail to provide 2D conjugated polymers with required structural features, let alone access to their unique properties. In this lecture, we will present our recent efforts towards the design and synthesis of crystalline 2D conjugated polymers. In the first part, we will focus on solution-based 2D polymerization, including the Knoevenagel reaction, HWE reaction, and Wittig reaction, to synthesize 2D polyarylenevinylenes (2D PAVs) in a robust manner. The C=C conjugation linkage provides excellent conjugation pathways for 2D PAVs, as evidenced by the decreased optoelectronic bandgaps, and reasonable charge carrier transport properties through the studies using THz spectroscopy methods, etc. Additionally, we will demonstrate the development of 2D PAVs for high-performance photoelectrochemical water splitting. In the second part, theoretical design is utilized to guide the synthesis of 2D conjugated polymers with extensive conjugation. We will demonstrate the synthesis of 2D benzimidazobenzophenanthroline (BBL)-type ladder-type conjugated polymers, which exhibit enhanced band-dispersion and outstanding charge carrier mobilities (~1000 $cm^2V^{-1}s^{-1}$ at room temperature). In the final part, we will discuss the on-water surface chemistry to synthesize 2D conjugated polymer crystals, ranging from monolayer to a few layers. In particular, we will highlight the synthesis of unprecedented 2D polyaniline crystals. The unique anisotropic metallic state of 2D polyaniline crystals will also be demonstrated.

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