

With their great variety of opt-electronic functions, conjugated polymers have a vital role in modern life and technology. One of the most important keys to influence the functions of conjugated polymers is their assembly structures. However, assemblies of conjugated polymers have still remained difficult to rationally design and control. Metal–organic frameworks (MOFs) or porous coordination polymers are constituted by the self-assembly of metal nodes and organic linkers that form a nanoporous crystalline framework. The characteristic features of MOFs are highly regular channel structures, controllable channel sizes, and designable surface functionality. Here, I proposed a new strategy to regulate the assembly structures of conjugated polymers at the molecular level using MOFs, allowing for eliciting potentially useful yet unexplored properties as well as fabrication of synergistic electronic nanohybrids.

1. Unraveling physicochemical properties of conjugated polymers in MOFs

Understanding the properties of a few polymer chain assemblies is important because of their potential applications for molecule-based devices. However, in many cases, polymer chains are randomly entangled and amorphous in the bulk state. Thus, exploited properties result from the averaged behaviors of multiple disordered chains. By using MOFs, control of the number of polymer chains was achieved for the first time, which enabled us to reveal the relationship between the chain number and physicochemical properties, such as conductivity, luminescence, and chirality (*J. Am. Chem. Soc.*, 2015; *Angew. Chem. Int. Ed.*, 2016; *J. Am. Chem. Soc.*, 2019; *Angew. Chem. Int. Ed.*, 2021).

2. Functional synergistic nanohybrids between MOFs and conjugated polymers

I reported a new category of hybrid system using electroactive MOFs, such as an electron acceptor MOF, $[\text{Ti}_6\text{O}_5(\text{mdip})]_n$ (mdip = methylenediisophthalate). This MOF represents infinite $(\text{Ti}_6\text{O}_9)_n$ chains arranged in a hexagonal packing, that line the side walls of 1-D nanochannels. Positioning a donor polythiophene in the pores of acceptor $[\text{Ti}_6\text{O}_5(\text{mdip})]_n$ created a perfectly alternating donor/acceptor heterojunction at the molecular level. Strikingly, the composites exhibited an extremely long charge carrier lifetime ($\tau_{1/2} = 1$ ms) that is among the longest observed for solid-state dye-sensitized TiO systems ever reported. This finding revealed that the confinement of donor polymers in acceptor MOFs provides an ideal architecture for the charge separation, which appears therefore as a promising model system for the understanding of charge carrier dynamics and further development of efficient photoenergy conversion devices (*Nat. Commun.*, 2018).

3. Precise and scalable synthesis of graphene nanoribbons templated by MOFs (to be presented in the 102nd CSJ meeting)

Graphene nanoribbons (GNRs), defined as nanometer-wide stripes of graphene, have attracted significant attention as candidates for next-generation semiconductor materials. The structural perfection of GNRs is an essential issue because their physicochemical properties are critically dependent on nanoribbon's width and edge geometry. The widespread implementation of GNRs into the various devices has yet to be realized, as methods for the synthesis of GNRs in precise and scalable fashion are currently lacking. I disclosed a new method for the bulk synthesis of atomically precise GNRs utilizing the MOFs as a template (*J. Am. Chem. Soc.*, 2020; *Chem. Sci.*, 2020), paving the way for their widespread use in both the scientific and industrial fields.