

(Macro)molecular Assemblies by Underexplored Directional Interactions

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Abstract: Precise organization of synthetic polymers into well-defined nanostructures are relevant for various applications in pharmaceuticals, organic electronics, catalysis and many others. Nature displays examples of biopolymers that utilize directional interactions such as hydrogen (H)-bonding as the primary tool for adopting well-defined conformation, which is essential for their incredible complex functions. To emulate the structural elegance and functional diversity of biological system, the influence of H-bonded supramolecular entities on macromolecular assemblies have been studied with great interest. However, these systems have limited scopes in water due to competing solvent interactions. Concurrently, multicomponent systems that are constituted of several distinct supramolecular interactions operating simultaneously and orthogonally are prerequisite for creating more complex supramolecular architectures with advanced properties.

Recently, halogen (X)-bonding has emerged as a powerful tool for molecular recognition, particularly in the field of crystal engineering. However, their influence in dictating supramolecular assembly in solution phase is still at its infancy. Due to its complementary nature, directionality and wide-range of tailorable association constants, X-bonding offers a powerful arsenal for precise molecular organization, similar to H-bonding. Additionally, its hydrophobicity makes X-bonding an attractive substitute for H-bonding in water. We envisaged that orthogonal utilization of X-bonding with other directional non-covalent interactions can be an interesting combination for introducing structural complexity in multicomponent polymeric systems. Our group has extensively investigated the role of X-bonding in dictating (macro)molecular assemblies in aqueous milieu to construct bioinspired self-assembled systems. Towards this end, we have demonstrated a novel molecular design utilizing orthogonal H-bonding and X-bonding for multicomponent surface-decorated supramolecular polymers of different π -systems in water with unprecedented stability and stimuli responsive properties. Under similar conditions, H-bonding strategy was non-operational due to competition from the bulk water, making the X-bonding approach a superior one for noncovalent functionalization in water. This design principle has been successfully implemented in organic solvents as well.

Crystallization-driven self-assembly (CDSA) of semicrystalline block copolymers (BCPs) has recently emerged as a powerful technique for fabrication of diverse hierarchical anisotropic structures, including two-dimensional (2D) architectures in solutions with precision of single crystals. In this area, our group has made an important contribution. We have utilized the known crystallization property of a biodegradable and biocompatible polymer, namely, poly(L-lactide) (PLLA) for controlled 2D-assemblies of distinct π -conjugated chromophores with exciting photoluminescent properties. PLLAs end-functionalized with dipolar chromophores such as merocyanine (MC) or NMI and nonpolar pyrene (PY) or benzene (Bn) could be crystallized into precise diamond-shaped platelets in isopropanol, which enabled the terminally-attached chromophores to assemble on the 2D-surface by either dipolar-interactions (for NMI and MC) or π -stacking (for PY and Bn). Further, by co-assembly between NMI- and PY-functionalized PLLAs, we could successfully achieve two-component co-platelets of similar shape and structural precision with highly efficient (~80%) Förster Resonance Energy Transfer (FRET) from the donor (PY) to the acceptor (NMI). By “living” CDSA, we have also demonstrated fabrication of hierarchical segmented block co-platelets with sequence-controlled compartmentalized self-assembly of chromophores (PY and NMI) on the 2D-surface. The approached has opened up new possibilities for construction of functional crystalline 2D-architectures from a commercially important

renewable polymer source. Various design aspects of halogen bonding driven supramolecular polymers and crystallization-driven macromolecular assemblies will be discussed in this presentation.

References

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