Supramolecular Polymers and the Subtleties of Molecular Recognition
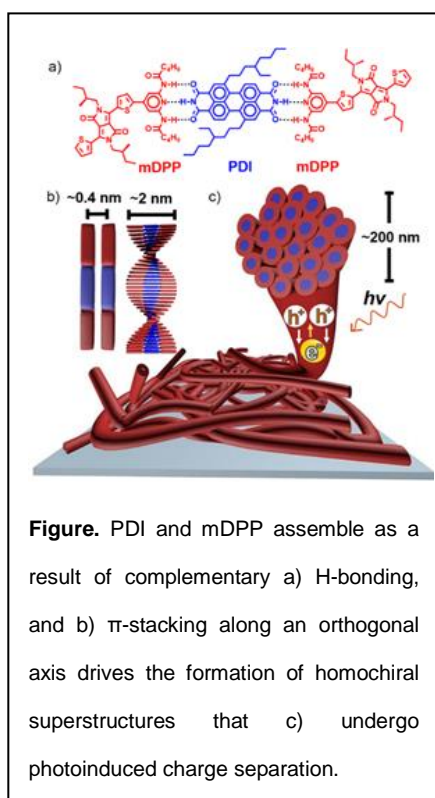
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Developing synthetic materials that emulate the architectural and functional sophistication of biomaterials involves creating supramolecular systems where multiple noncovalent interactions operate in concert. To this end, we have developed a system composed of an electron rich dikettopyrrolopyrrole (DPP) donor and an electron poor perylene bisdiimide (PDI) acceptor that aggregate into homochiral superstructures as a result of cooperative assembly driven by orthogonal H-bonding and π••π interactions, and the resulting superstructures undergo photoinduced charge separation (**Figure**).[1-3] The question arises as to whether we can redesign the individual components to finely tune assembly, structure, and function of these superstructures. In this lecture, we report a systematic study on the homo- and hetero-aggregation of a series of mDPPs and PDIs to determine quantitatively how structure affects ΔG, ΔH, and ΔS by fitting spectroscopic changes in variable-temperature UV-Vis titrations to isodesmic or cooperative binding models. These efforts reveal that changes in the molecular components often result in unanticipated binding effects, and that attempts to design rationally even the simplest supramolecular assembly can overlook the subtle interrelationships between structure, bond-strength, and solvation that contribute to architecture and stability.

Figure. PDI and mDPP assemble as a result of complementary a) H-bonding, and b) π-stacking along an orthogonal axis drives the formation of homochiral superstructures that c) undergo photoinduced charge separation.

[1] Guzman, C. X. *et al. J. Phys. Chem. C.* **2015**, DOI: 10.1021/acs.jpcc.5b03713

[2] Ley, D. *et al. J. Am. Chem. Soc.* **2014**, *136*, 7809 – 7812.

[3] Rieth, *et al. J. Phys. Chem. C.* **2013**, *117*, 11347-11356