

## **Complex Formation and Electronic Energy Transfer between Oppositely Charged Conjugated Polyelectrolytes**

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There is a pressing need to develop inexpensive, light-weight light-harvesting machinery to convert the energy of sunlight into chemical potential energy. An intriguing route to doing so is to use ionic assembly in aqueous solution. To this end, we are using oppositely charged conjugated polyelectrolyte (CPE) complexes as the foundation for an ionically assembled electronic energy transfer antenna. For the first time, we have shown that CPE complexation proceeds through a free energy barrier that appears to have a substantial enthalpic contribution. We find that upon complex formation, the backbone CPE microstructure is drastically altered in such a way as to qualitatively change the nature of the electronic wavefunction delocalized along the backbone. Using a combination of spectroscopic and structural probes, our recent work shows that the photophysical changes that accompany complexation are highly dependent on the relative polyion charge ratio. As a result, the energy transfer rate depends very strongly on the ionic stoichiometry and thus the physical state of the assembly. Further, we find the complex microstructure and its associated photophysics show substantial dependence on the solution temperature during complexation, which allows us to trap metastable states. Our results point towards a path to using CPEs to construct truly panchromatic light-harvesting systems using ionic self-assembly. Importantly, understanding complexation between polyelectrolytes with very strongly coupled electronic and ionic degrees of freedom allows us to take advantage of spectroscopic probes to shed new light on the physics of polyelectrolyte complex formation.