Self-assembled Building Blocks for Artificial Photosynthesis: Correlating SAXS/WAXS Structures Obtained in Solution with Photo-driven Charge Transport

Michael R. Wasielewski

Department of Chemistry and Argonne-Northwestern Solar Energy Research (ANSER) Center, Northwestern University, Evanston, IL 60208-3113

In studies of supramolecular assemblies in solution, it is important to establish direct relationships between structure and observed function. It has been recently demonstrated that small- and wide-angle x-ray scattering (SAXS/WAXS) from monodisperse non-covalent aggregates using a synchrotron source is a powerful tool for the elucidation of their solution-phase structures. We have used the Advanced Photon Source at Argonne National Laboratory to determine the *solution* structures of supramolecular assemblies for artificial photosynthesis and organic photovoltaics at concentrations typical of optical and EPR spectroscopic measurements used to characterize their function. Guinier analysis of the scattering data provides at a minimum the radius of gyration of the complex, R_g, an estimate of its molecular weight (provided appropriate standards are available), and more importantly, a gauge of the polydispersity of the aggregates. In favorable cases, if the assemblies are nearly monodisperse, further analysis of the SAXS/WAXS data using atomic pair distance distribution functions (PDFs) and simulated annealing procedures can be performed to obtain structures in solution with a resolution approaching 3-4 Å for molecular weights up to about 50 kD. For example, using these techniques we have previously obtained structures of complex oligomeric arylene diimide assemblies having molecular weights up to 28 kD. New computational approaches allow SAXS/WAXS data to be interpreted in terms of coordinate models and molecular dynamics simulations, and can be used to refine the structures of self-assembled systems.