

RESOLVING STRUCTURE AND STRUCTURAL DYNAMICS OF DESIGNED PHOTOSYNTHETIC ARCHITECTURES

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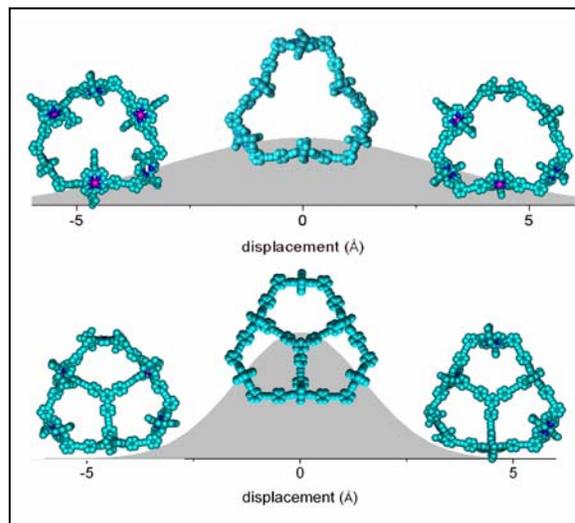
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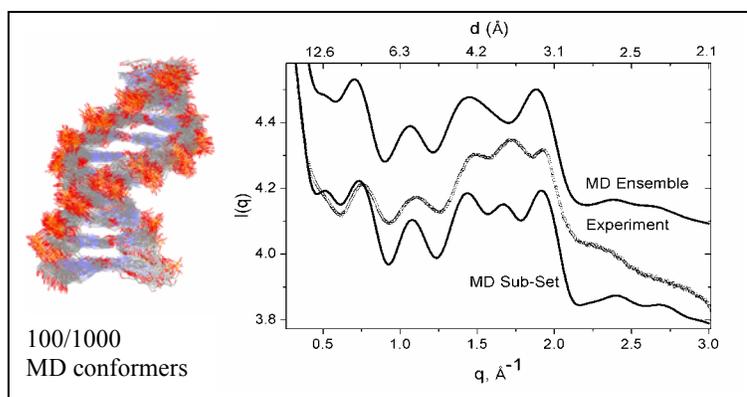
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One of the major challenges for resolving fundamental mechanisms for solar energy conversion in natural and artificial photosynthesis lies in obtaining direct structural resolution of atomic reorganization events and structural dynamics linked light-induced electron transfer. This talk will present results on our development of synchrotron high angle scattering techniques for the resolution of structure and dynamics of molecular systems in liquids and other photochemically relevant non-crystalline media. Results will be presented on the analyses of designed, artificial photosynthetic architectures and opportunities will be discussed for extending these methods for time-resolved applications in both natural and artificial photosynthesis.

Macrocyclic multiporphyrin architectures based on covalent connectivity. Precisely-designed, modular supramolecular architectures are being developed by the Lindsey group to accomplish a variety of photosynthetic functions. We have characterized structures of a hexameric, diphenylethyne-linked porphyrin macrocyclic array and the corresponding host-guest complex formed by inclusion of a tripyridyl guest molecule in solution using high-angle X-ray scattering. Scattering measurements made to 6 Å resolution coupled with pair distance function (PDF) analyses demonstrated that (1) the porphyrin architectures are not rigid but are distributed across a conformational ensemble with a mean diameter that is 1.4 Å shorter than the diameter of a symmetric, energy-minimized model structure, (2) the conformational envelope has limits of 3 Å positional dispersion and full rotational freedom for all six porphyrin groups, and (3) insertion of the tripyridyl guest molecule expands the diameter of the host conformer by 0.6 Å and decreases the configurational dispersion by two. These results validate the molecular design, provide a new measure of conformational ensembles in solution that can not be obtained by other techniques, and establish a structural basis for understanding the photophysical and guest-hosting functions of the hexameric porphyrin architectures in liquids.



DNA molecular-wire, π -stacked architectures. Duplex DNA sequences are widely explored as model architectures for long-range electron transfer through aromatic face-to-face, π -stacked spacers. The Lewis group is investigating fundamental sequence and distance dependent electron transfer processes in DNA. Measurements of DNA conformation in liquids are critical for interpreting mechanisms for electron transfer. Scattering patterns measured for a series of DNA sequences to 2 Å resolution were found to resolve both nearest-neighbor and longer range base-pair distance correlations. Sequence and temperature dependent measurements combined with molecular modeling studies show that scattering peak positions are strongly correlated to DNA conformation, while configurational dynamics are reflected in peak broadening and angle-dependent attenuation of scattering patterns. High angle scattering measurements are found to resolve discrepancies between crystallographic and NMR structures, and provide a new approach for quantitatively checking molecular dynamics (MD) simulations. Currently available MD simulations yield ensembles of DNA conformers with composite calculated scattering patterns that fall far from agreement with experimental data. However, experimental scattering is found to be in good agreement with scattering calculated from conformational sub-sets of the MD ensembles. These results suggest the opportunity of using scattering measurements for optimizing molecular force-fields for the solution state.



Functional supramolecular assemblies based on coordination chemistry. Metal/ligand directed-assembly techniques are widely utilized for obtaining discrete, high-symmetry supramolecular entities. The Hupp group is devising novel architectures for photochemical energy conversion based on rhenium coordination chemistry. Key features of these designs include multiporphyrin host macrocyclics capable of chiral guest discrimination, induced-fit transition states, and tunable nanoscale chemical environments that mimic molecular recognition and site-specific tuning of cofactors in natural photosynthesis. These architectures comprised of high-Z atoms held in fixed, nanoscale geometries are found to be almost ideal molecular samples for x-ray scattering. In favorable cases, well-defined x-ray scattering patterns are measured beyond 1 Å spatial resolution. These measurements permit accurate calibration of the scattering technique and resolution of details of solvent-solute interactions that are critical for understanding light-induced charge-transfer reactions.

Outlook. High-angle SXD scattering patterns are found to contain unique information on structures and configurational dispersions for macromolecules in solutions that can be combined with pulsed EPR and x-ray spectroscopies to obtain both global and local structural information. Synchrotron scattering techniques can be extended to 100 ps time-resolution for measurement of structural dynamics correlated to photochemistry in natural and artificial photosynthesis.