

Single Molecule Spectroscopic Investigation on Energy Migration Processes of Various Porphyrin Arrays

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Various synthetic strategies have been developed to devise a variety of covalently linked and self-assembled cyclic porphyrin arrays as artificial light-harvesting system for applications in molecular photonics because of their similarities in architecture and subunit structures to the natural photosynthetic LH1 and LH2 complexes. The covalent linkage between porphyrin units in cyclic form can provide an increased rigidity as well as a precise control in overall structures. In this regard, we have prepared two wheel-like structures such as dodecameric **C12Z** and tetracosameric porphyrin wheels **C24ZA** that are respectively composed of six meso-meso linked diporphyrin **Z2** and tetraporphyrin **Z4** subunits bridged by 1,3-phenylene linkers. The energy migration processes in **C12Z** and **C24ZA** have been comparatively investigated by single molecule spectroscopy (SMS) with a particular focus on energy migration efficiency using fluorescence intensity trajectory and coincidence measurements, and wide-field defocused images. Since the spectroscopic investigation on the single molecule level eliminates the averaging effect inherent in ensemble measurements, SMS can provide information on individual molecular behaviors hidden in ensemble measurements that is indispensable for future application of such molecular systems on the single molecule level in solid state. As other types of porphyrin cyclic arrays, the directly linked cyclic tetramer (**CZ4**), hexamer (**CZ6**), and octamer (**CZ8**) were prepared. Based on our single molecule spectroscopic measurements including fluorescence intensity trajectories, fluorescence lifetime distributions, and photobleaching behaviors we are able to unveil the conformational heterogeneities under local environments, otherwise hidden in ensemble measurements. As porphyrin based photonic and electronic wires, the porphyrin arrays should have the very regular pigment arrangements which allow a facile light energy or charge flow along the arrays but do not result in the alteration of individual properties of the constituent pigments leading to formation of so-called energy or charge sink. In these respects, the directly coupled (orthogonal and fused) porphyrin arrays without any linkers are ideal, since the conformational heterogeneity mainly arising from a dihedral angle distribution between the neighboring porphyrin moieties should be minimized. In addition, the electronic effect of the linker can be disregarded in design strategy of molecular photonic devices, because the linker can also be considered as a transmission

element in electronic communication. Considering these features, these types (orthogonal vs. fused) of porphyrin arrays would be one of the most suitable synthetic molecular modules for the realization of molecular photonic and electronic devices. Thus, single molecule spectroscopic measurements on directly linked porphyrin orthogonal arrays as photonic wires were done to have detailed information on the energy migration behavior on single molecule level. We've also investigated the electric conduction behaviors between orthogonal and fused porphyrin arrays on single molecule level to gain further insight into electronic coupling between the neighboring porphyrins in the transport phenomena of charges.

References

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