

Self-Assembly of Porphyrins and Energy Transfer Therein

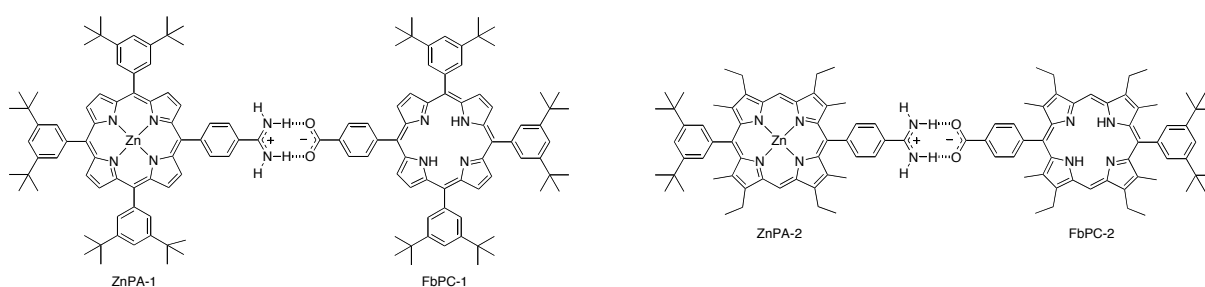
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Self-assembled organization of porphyrins are of interest as a basis for their development into molecule-based nanomaterials due to their rich electronic, optical, and catalytic properties. Porphyrin organizations may be assembled either in solution or on surface. As for the former, we have examined various porphyrin assemblies, particularly in terms of electron/energy transfer properties therein [1]. An example is the set of zinc-porphyrin/free base porphyrin dyads, structures shown below, which were prepared to examine energy transfer processes through intermolecular bonds. We have previously found that the energy transfer rate in dyad ZnPA-1/FbPC-1, which is connected through an amidinium-carboxylate salt bridge, is nearly an order of magnitude larger than expected for the Förster-type energy transfer mechanism [2]. Recently, we have compared the rate with that in ZnPA-2/FbPC-2 and found that the rate is substantially smaller in the latter [3]. These results indicate that the orbital symmetry plays an important role in the energy transfer process, which points to the involvement of a Dexter-type through-bond mechanism. Thus, hydrogen bonded interface may effectively mediate electronic communication in these assemblies.

As for porphyrin assemblies on surface, the surface of highly oriented pyrolytic graphite is particularly appealing as a substrate as it allows us to observe molecular assemblies on an individual molecule basis by means of scanning tunneling microscopy under ambient conditions. Alkyl chains are often introduced into molecules to be assembled to enhance the adsorptivity onto the surface. Due to the affinity of the alkyl chains and the substrate and favorable alkyl-alkyl interactions, close-packed monolayers are normally observed. To construct yet new patterned architectures of porphyrins distinctly different from conventional close-packed structures, we have been examining several strategies that include:

- Introducing directional interaction sites, such as hydrogen bonds [4] and coordination interaction sites.
- Introducing a perturbation into the part of alkyl chains. Highly ordered porphyrin columns have been obtained with this strategy, which are of particular interest for their exciton/charge migration properties.
- Axial ligation to metal-porphyrin complexes [5].



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