Porphyrin Assemblies in Solution and on Surface

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We are exploring chemistry on porphyrin assemblies because their rich photonic and electronic properties hold promise for potential applications to molecule-based devices. Intermolecular interactions are key to direct the component entities into desired supramolecular architectures. Interaction sites introduced into the peripheral positions are used to make lateral assemblies, while axial coordination to the central metal ion in the porphyrin macrocycle is a straightforward interaction to make vertical assemblies. The intermolecular linkage sometimes play a more active role in electronic processes than as a mere structural element. We found that the amidinium–carboxylate salt bridge mediates "through-bond" energy transfer even though the bond is noncovalent [1]. Distinct assembles formed in solution are useful for disclosing the assembling behaviors and photophysical processes, because advanced spectroscopic techniques are available to reveal intricate mechanisms in the assemblies in great detail. However, in view of the potential device applications, assemblies on a solid surface may be more attractive. Graphite is the substrate of choice because it provides a unique opportunity that one can observe surface immobilized molecules on an individual molecule basis at ambient conditions. Thus, we can learn how molecules assemble themselves on the surface at the molecular level. The knowledge obtained can then be used to design molecules to be made into a specific supramolecular structure. Peripheral substitution [2] and axial coordination [3] can be exploited to assemble porphyrins on surface as well.

Various porphyrin assemblies both in solution and on surface will be presented and discussed in terms of their structural, electronic, and dynamic properties, with potential applications to molecular devices in mind.

References

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