SUPRAMOLECULAR ASSEMBLIES OF STILBENES, AZOBENZENES AND RELATED AROMATICS: STRUCTURE, PHOTOPHYSICS AND PHOTOREACTIVITY

David G. Whitten

Department of Chemistry and NSF Center for Photoinduced Charge Transfer, University of Rochester, Rochester, New York 14627, USA

Amphiphilic molecules (fatty acids, sulfonates, phospholipids) containing rodlike aromatic or dye chromophores have been found to exhibit strong aggregation upon self-assembly into structures such as micelles, bilayer vesicles or Langmuir-Blodgett Films. [1-3] Although it was originally suspected that the aggregation occurred as a consequence of the self-assembly process, recent work has demonstrated that aggregation occurs as a result of strong noncovalent interactions and that aggregation may frequently occur even where the molecules are not tightly organized as in "gas phase" films at the air-water interface. [3] In several cases the "unit aggregate" is a relatively small chiral "pinwheel" structure stabilized by edge-face interactions between the aromatic chromophores; extended aggregates may be regarded as a mosaic of these unit aggregates into a glide or herringbone lattice. [4] The presence of these relatively "stiff" aggregates hae large effects on the macroscopic properties of the structures of assemblies of these amphiphiles. For example, bilayer assemblies of the pure stilbene or azobenzene phospholipids in water are not small unilamellar vesicles capable of entrapping reagents but rather much larger, sheet-like structures. [5] Closed mixed vesicles can be formed using the azobenzene or stilbene phospholipids with staturated or unsaturated natural phospholipids and these can entrap reagents such as the fluorescent dye carboxyfluorescein. Irradiation of the azobenzene phospholipids results in photoisomerization while the stilbene phospholipids are unreactive towards photoisomerization when incorporated into the assemblies. [1] For the azobenzene phospholipid containing vesicles, photoisomerization results in destruction of the vesicle and release of entrapped reagents, only when the azobenzene is in the aggregate state. Reagent release upon irradiation has been observed for other systems; the mechanisms for photoinduced vesicle leakage with several different aromatic systems is currently under investigation and will be discussed.

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References

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