Laboratory of Supramolecular Photochemistry and Biochemistry

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Supramolecular and Biomolecular Photochirogenesis

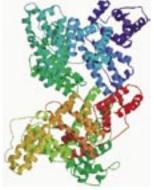
Light is the most abundant clean source of energy in our environment, thus making photochemistry an inherently environmentally benign method for converting molecules. Of the various targets of photochemical studies, molecular chirality is our particular interest. Asymmetric synthesis is one of the most crucial topics in current chemistry, and hence a variety of catalytic and enzymatic asymmetric reactions have been developed in the last three decades.



In sharp contrast to these successful thermal asymmetric syntheses, the photochemical counterpart does not appear to have been investigated extensively or intensively, at least until recently. However, the photochemical approach to asymmetric synthesis, or "photochirogenesis," has several unique, inherent advantages over the thermal approach, since photochemical reaction proceeds through the electronically excited state and often provides strained and/or thermally difficult-to-access products with unique structures in a single step. Furthermore, photochemical

reactions are in principle free from the fetters of activation energy and of ground-state thermodynamics and therefore can be performed over a wide range of temperatures without any accompanying retardation of reaction rate at lower temperatures or side reactions at elevated temperatures. Utilizing these advantages, we are working on photochirogenesis in chiral molecular, supramolecular, and biomolecular environments (e.g., human serum albumin HSA).

Focusing our interest on reaction control based on molecular recognition phenomena in both ground and electronically excited states, we are pursuing mechanistic and synthetic studies on chiral molecular, supramolecular, and biomolecular chemistry and photochemistry. Thus, our group's studies are not restricted to (1) supramolecular and biomolecular photochirogeneses, but also extend to (2) entropy control of rates and equilibria and (3) active control of biomolecular functions with artificial nucleic acids.



HSA

Entropy-Driven Chemistry, Photochemistry, and Biochemistry

The control of reaction rates and equilibria is central to modern chemical science. To realize this, a wide variety of sophisticated reagents, catalysts and methodologies have been developed in the last century. However, in developing these tools and in discussing the factors governing rates and equilibria, the enthalpic contribution has traditionally been more, or over-, emphasized as far as the "strong interactions" making covalent or ionic bonds are concerned, while the entropic contribution has generally not been explicitly or extensively considered to play a crucial role. In contrast, living organisms employ a smarter strategy, controlling biological reactions and equilibria not by enthalpy, but through the entropy factor.

In our recent studies of (1) asymmetric photosensitization with chiral sensitizers, (2) supramolecular asymmetric photochemistry using natural and synthetic chiral host molecules such as modified zeolite, cyclodextrin, protein, and DNA, and (3) the relevant thermodynamic work on supramolecular systems, we have demonstrated for the first time that the entropy-related factors, such as temperature, pressure, and solvation, do indeed play decisive roles particularly in chiral photochemistry and molecular recognition, where several weak forces (<5 kcal/mol), including hydrogen bonding, dipole-dipole, van der Waals, and hydrophobic interactions, simultaneously operate in a concerted manner. Such intriguing findings prompted us to widely explore the possibility and feasibility of general reaction/equilibrium control by entropy factors.

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