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Biological Applications—
Supramolecular Chemistry

Masahiko Inouye

9.1. INTRODUCTION

One aspect of supramolecular chemistry is the development and characterization of simple and artificial models for biologically important functions as well as the exploration of their biological applications. (For a recent review, see Ref. 1). The two definitive and essential vital functions are heredity and metabolism. The former results from duplication of DNA, and the latter from catalytic action of enzymes. Both phenomena involve molecular recognition at the initial stage of the process. During the last two decades, artificial models developed in supramolecular chemistry have demonstrated the importance of strict complementarity in size, shape, and functional groups at the molecular level for selective host-guest recognition. (For a recent review, see Refs. 2–4). Recent investigations in the field reveal a shift of attention from static phenomena to dynamic ones, i.e., from simple synthetic hosts to real artificial receptors. (For a recent review, see Refs. 5–13).

A naturally occurring receptor is generally defined as a complex molecule or molecular assembly that, upon recognition of a specific substrate, undergoes a structural change that usually induces a series of functions (allosteric effect, signal transduction), which eventually results in a physiological response. (For a recent review, see Refs. 14–17). Thus, the construction of artificial receptors, in which the molecular recognition process is synchronized with the signal transduction, is of critical importance from the viewpoint not only of creating the next field of supramolecular chemistry, but also of producing devices of practical value such as molecular sensors. Photochromic molecules are suitable for mimicking such signal transduction processes, and, therefore, by combining molecular recognition
with photochromic chemistry, conceptually new photoresponsive systems will be created.

This chapter is devoted to biological applications of photochromic compounds. The relevant works, however, are too numerous to be surveyed within the space available. Thus, our discussion will be focused on the background and principles of an approach to the construction of new photoresponsible systems utilizing spiropyran derivatives (for general reviews on the chemistry of spiropyrans, see Refs. 18–20). The use of other photochromic compounds, such as azoarenes and diarylethenes, is not treated here and has been reviewed elsewhere. 21–23 It is hoped that this chapter includes sufficient key and up-to-date references on biological applications of spiropyran derivatives. The chapter is divided into two main parts. The first part deals with photoregulation of peptide and protein characteristics by the use of spiropyran derivatives. Potential applications of such photoregulated proteins include their use as light-signal amplifiers, information storage devices, and sensing assemblies. The second part is concerned with spiropyran derivatives possessing a molecular recognition site. These spiropyran receptors have been designed to have their binding affinities controlled by irradiation. From the opposite point of view, the receptors are also intended to enable molecular recognition information to be signaled as changes in the optical properties of the spiropyran unit. This type of new photoresponsive receptor is conceptually different from the signaling receptors synthesized thus far, such as crown ether dyes, and is functionally referred to as a self-indicating receptor.

9.2. PHOTOCONTROL OF PEPTIDE AND PROTEIN CHARACTERISTICS BY SPIROPYRANS

9.2.1. Photomodulation of Polypeptide Conformation

Synthetic polymers containing photochromic units can undergo reversible changes of their physical and chemical characteristics. (For recent reviews, see Refs. 24–26). Recent examples involving photochromic compounds other than spiropyrans are reported in Refs. 27–31. Spiropyran-containing polymers such as polyacrylates have also been prepared and were found to show photoinduced variations of their viscosity. 18–20 The change in the viscosity of the polymers partly reflects the polymer conformation. Thus, spiropyran-attached poly(l-tyrosine) and poly(l-lysine) were synthesized by Vandeweyer and Smets at the University of Louvain in 1970. 32,33 No photoresponsiveness was observed, however, for these modified peptides.

On the other hand, in 1989 Ciardelli et al. at the Università di Pisa reported the first photomodulation of the conformation of spiropyran-containing poly-