Foreword

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Foreword

That you can read the title of this book "Molecular Photoswitches" and do not get lost during a fascinating journey through it is due to the billions of tiny molecular switches working frantically in your eyes. Arguably vision is one of the most magnificent results of biological evolution, and it is intriguing that the fundamental process behind it is in fact a *Z–E* photoisomerization of an alkene unit in the cis-retinal photoswitch triggered by visible light. But it is more than this as the photoswitch does not operate on its own. To exert its function, the switch is integrated within a dynamic multicomponent system that interfaces it with the complex machinery of life. This duality is reflected in several of current research objectives in the field of artificial molecular photoswitches.

Unsurprisingly, beyond tuning the well-known classes of switches for specific functions, the design of novel molecular photoswitches, and elucidating the fundamental mechanisms of the photochemical event itself, major future challenges are associated with the exploration of these trigger elements in complex dynamic systems ranging from responsive materials all the way to the control of biological function in cells. Drawing inspiration from Nature, numerous chemists have contributed over the last decades to the blooming field of artificial molecular photoswitches, which is testimony to its prominent role in the transition from molecules to dynamic molecular systems in contemporary chemical sciences.

In this timely volume the "Molecular Photoswitch Community" has joined forces to provide an in-depth and balanced account of the progress as well as challenges and perspectives in this flourishing and highly dynamic field under the editorship of Zbigniew Pianowski.

The study of the interplay of light and matter, i.e. photoresponsive molecules, continues to offer remarkable new insights not in the least due to the advances in transient spectroscopies and computational methods. These developments guide the design of novel photoswitches toward specific applications. It is amazing how "revisiting" more classical photochromic compounds, such as azobenzenes, stilbenes, and spiropyrans, is stimulated by the quest for visible light switching, enhanced bistability or compatibility with the molecular systems or materials in which they are to exert their function. It has initiated many unforeseen opportunities. The introduction of new classes of switches such as overcrowded alkenes, arylhydrazones, diazocines, indigoids, and Stenhouse adducts has significantly enlarged our playground for instance toward multistate or multicomponent orthogonal switching systems.

The discussion of adaptive materials based on molecular photoswitches in Section II again illustrates a vibrant research field. Introducing switching functions in liquid crystal polymers, a variety of soft materials, and supramolecular systems enables the amplification of the molecular triggering event along the length scales to macroscopic function, ranging from responsive surfaces to mechanical muscle-type movement. In addition, the confinement of photoswitches on nanoparticles or in 2D and 3D assemblies, including porous frameworks, addresses issues of functioning at interfaces and cooperative action, and brings entirely new dimensions to the field.

Among the most spectacular developments over the past decade is the use of molecular switches for the photomodulation of biological systems. It is evident that the rapidly emerging area of photopharmacology has its roots in the field of photoswitches, in particular azobenzenes which were reported by Mitscherlich as early as 1834. The control of the activity of a drug by light with high spatiotemporal precision holds promise for precision therapy, smart pharmaceuticals, and imaging techniques. In addition, Section III illustrates how photochromic systems can be applied in a much broader perspective, including control of peptides, oligonucleotides, saccharides, and ion channels. Photoregulation of specific pathways in complex biochemical networks, cellular communication, transcription, or membrane transport are fascinating examples of the opportunities that emerge. It is also evident that the photoswitch community has to tackle many challenges entering the realm of biology – not least in how to make these molecular switches biocompatible, operate in the aqueous environment of the cells, be compatible with multi-chromophore functional systems, and switchable with visible or NIR light. Answering these questions will ultimately allow the application of molecular photoswitches in vivo.

Arguably the question as to how to use molecular switches and achieve controlled movement at the nanoscale has been essential in the discoveries leading toward molecular machines. With the expected key role of chemistry in future complex systems, molecular information science, and soft robotics, taking advantage of the solid basis in molecular photoswitches as presented here will likely become increasingly important. Indeed, this book showcases many novel approaches and opportunities in this vibrant field and without doubt will guide molecular explorers in their odyssey in the world of responsive molecular systems.

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