Responsive Membranes and Materials

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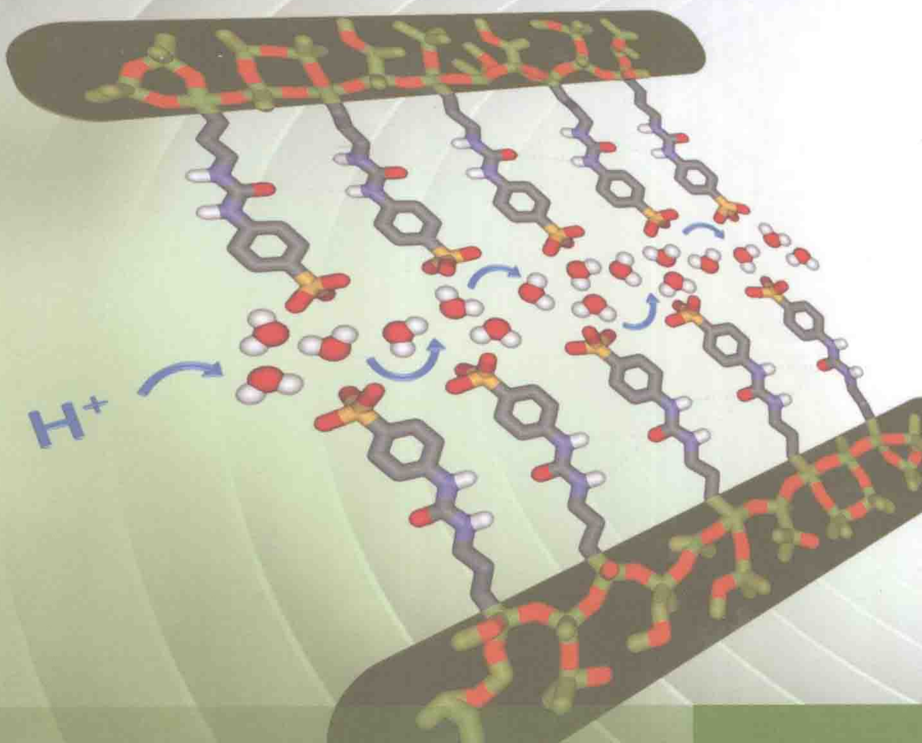

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Responsive Membranes and Materials

D. Bhattacharyya: To Gale, my wife, for her encouragement and understanding; To my graduate and undergraduate students, for making academic life very stimulating; To my grandchildren, Nathan, Madeline, Lila, and Zoe for bringing additional joy in my life.

Thomas Schäfer: With gratitude to Belén, Maria, Monika, and Rainer for constant company. In memory of Conny.

S. R. Wickramasinghe: To my parents, for their encouragement; Xianghong, for her support and optimism; and Aroshe, for reminding me of the excitement each day holds.

Sylvia Daunert: I would like to dedicate this book to my students, colleagues, and mentors who constantly inspire and challenge me to be a creative scientist. Also, many thanks to all whom supported me and contributed throughout the writing and editing processes; it has been a pleasure working with all of you!

Preface: Overview of the Book Highlighting Responsive Behaviour

D. Bhattacharyya, T. Schäfer, S. Daunert, and S. R. Wickramasinghe

The integration of knowledge from the life sciences field with synthetic membranes and materials to create stimuli-responsive behaviour is an important area of science and engineering. Martien, *et al.* (*Nature Materials*, 2010) wrote: "Responsive polymer materials can adapt to surrounding environments, regulate transport of ions and molecules, change wettability and adhesion of different species on external stimuli, or convert chemical and biochemical signals into optical, electrical, thermal and mechanical signals, and vice versa". Touchscreens, light-emitting diodes, etc. are everyday devices that rely on stimuli-responsive materials. However, the response to stimuli can also be explored at the molecular scale for controlling mass transport or creating motion. The fabrication of membranes and materials which can respond to pH, temperature, light, biochemicals, and so on is an important aspect of this book. While reading this text, a multitude of stimuli and responses are taking place in the reader's body, be it for exchanging information through the dendrites and axons of neurons, or for the homeostatic control of the trillions of cells in the hosts. Our health and function entirely relies on the fine-tuned interplay of varied kinds of stimuli-triggered responses at the molecular level, which create a cascade of concerted actions that result in our body working as a perfectly fine-tuned machine. We are far from being able to reproduce the complexity of natural stimuli responsive systems, but in recent years a growing scientific community has been concerned with creating responsive systems that allow us, at the molecular level, to control global release, separation, or actuation as a response to an external stimulus. Similar to the architecture of high-rise buildings or the evolution of living systems, the underlying idea is to use a bottom-up approach for assembling individually characterized elements, molecules, or molecular constructs, which together execute a controllable function. The beauty of such systems emerges when molecular building blocks of very diverse responses are rationally designed and subsequently assembled in order to yield a fine-tuned global system response – that emulates the beauty which Nature in its mastery accomplishes incessantly.

This book is about such constructs, with a particular focus on responsive membranes and materials. It comprises contributions which range from the synthesis of stimuli-responsive membranes and colloids to their applications at very different scales; from self-assembled systems with molecular recognition capabilities within nanopores, to the combination of

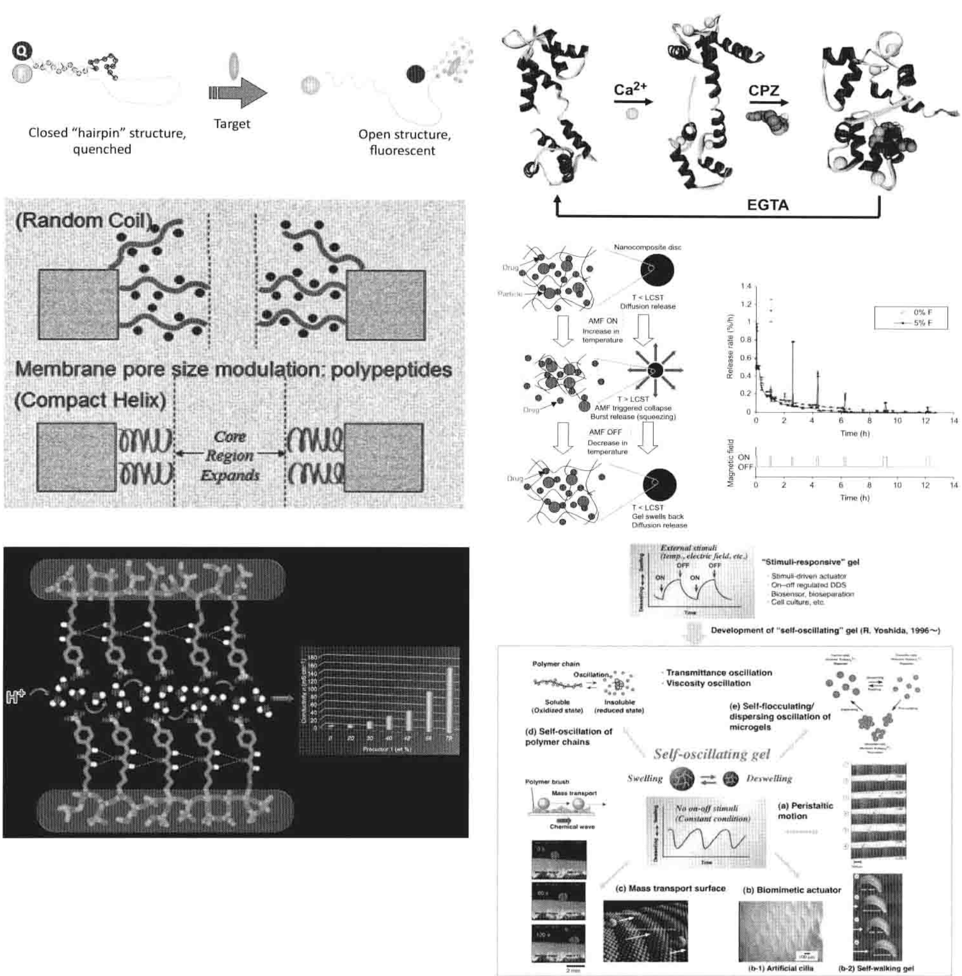

Figure 1 *Examples of some stimuli-responsive systems for tuning the permeability to selectivity of nanopores to self-organization and drug release.*

bulk materials that alter either the effective pore diameter or restrict entrance into pores. Some examples are summarized in Figure 1. Whatever their concept or final use, stimuli-responsive membranes and materials cannot be understood without bearing in mind that their response upon interaction with a stimulus results in a more favourable energetic state, translated as a decrease of the Gibbs energy. This is the basis for understanding under what conditions a system may undergo alterations, or elicit a "response", in order to release energy. The reader's attention is drawn to the role of the total chemical potential. It is the sum of the internal chemical potential – comprising parameters such as density or activity – and the external chemical potential – referring to an external force field such as an electrostatic, magnetic, luminescent, or gravitational field.

In this context, responses to stimuli are the result of driving forces that can have very different origins. As a consequence, on the one hand this provides a large degree of freedom for fine-tuning responses through the creation of subtle interplay between different kinds of forces. On the other hand, this also means that responses must not be designed or interpreted without accounting for *all* possible variable parameters, as otherwise a responsive system might naturally fail. For example, DNA-aptamers can selectively bind to target molecules, the stimulus, and thereby undergo conformational changes as a specific response. This can be explored for gating mechanisms in nanopores (Chapter 1). However, a significant increase in temperature can result in similar conformational changes as an unspecific response in which case, the DNA-aptamer loses its function. Proteins embedded in hydrogels can bind to specific ions resulting in an overall swelling of the hydrogel; however, external pressure through shear forces might strongly counteract this response (Chapter 11) and partially frustrate the responsive function. Conversely, opposing forces or interactions might also be systematically exploited for designing stimulus-responsive materials such as Janus particles (Chapter 12) or self-oscillating polymer gels (Chapter 13). These examples demonstrate that a thorough understanding of the underlying phenomena is indispensable as it provides a vast playground for creatively designing responsive membranes and materials.

Figure 2 gives an overview of the chapters of this book and their main emphasis and is intended as a quick reference. The book starts with three chapters (1 to 3) dealing with the formation of responsive hybrid materials through modification of suitable support structures. The aim is to mimic molecular transport across cell membranes, rather than relying on bulk responses. Chapter 1 explores the capacity of existing building blocks, DNA-aptamers, to undergo conformational changes upon specific binding to a target molecule. If embedded within a fine-tuned nanoporous support structure, it is shown how these receptors can trigger the release or permeation of compounds depending on the presence of a target

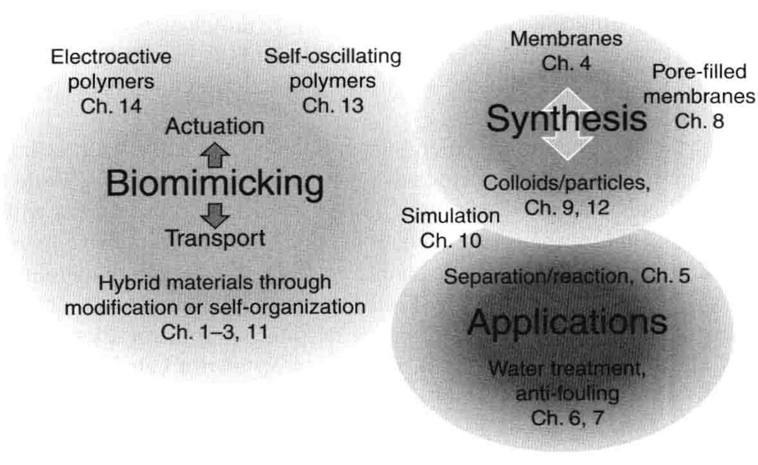

Figure 2 *Overview of the chapters of this book and a rough division by their main emphasis. Naturally, all chapters overlap in one aspect or another given that the common theme is the formation or investigation of responsive materials.*

molecule. The chapter also gives a glimpse of the analytical tools employed for verifying the dimensional changes that DNA-aptamers undergo during this process. Chapter 2 describes a methodology to create self-organized supramolecular structures in which simple building blocks are allowed to self-assemble under the influence of an external stimulus in order to achieve hybrid materials of desired selectivity, for example for selective ion-transport. Here, the concept of evolution is employed in order to upregulate the function of a membrane through adaptive adjustment in the presence of a target solute. Chapter 3 focuses on the modification of the front tip of carbon nanotubes with functional molecules to serve as "gatekeepers" and function as ideal transport channels. The proposed system benefits from the fast fluid flow through the cores of the nanotubes combined with a high density of selective receptors at their tips, mimicking molecular transport across biological membrane transporter proteins.

Modification of materials requires knowledge of the tools and methods needed to achieve the desired properties in the materials, and Chapter 4 discusses routes to surface modifications for producing responsive membranes. Different grafting methods are presented such as photo-initiated polymerization, atom transfer radical polymerization (ATRP, and reversible addition-fragmentation chain transfer polymerization RAFT), which will also be explored in subsequent chapters (5–7). Chapter 5 spans the gap from the synthesis of responsive polymers to their final application, introducing in this way the engineering component of such systems. After an overview of membrane modification techniques, it describes applications (including layer by layer assembly) concerning tunability of water flux and separation of salts (compare to Chapter 2). The chapter then goes well beyond these more obvious applications by introducing responsive (temperature and pH) membranes and hydrogels for nanoparticle synthesis and degradation of contaminants in aqueous solutions. Chapters 6 and 7 further focus on responsive membranes in water treatment, given its global importance and the fact that fouling phenomena strongly affect otherwise economic membrane separations. Linking with Chapter 4, common synthesis strategies for membrane modification as well as magnetically driven micromixers are presented in Chapter 6 and their effect on water filtration is discussed. Chapter 7 further elaborates on fouling control of the membrane surface and feed spacers, while introducing other membrane surface treatments such as ultraviolet, plasma, or surface irradiation by ion beams and chemically induced free radical polymerization.

In addition to the aforementioned emerging applications, controlled release has traditionally been the predominant field for responsive membranes and materials. While the related physico-chemical phenomena are the same, important differences can exist with regard to particular requirements for the final applications. For example, responsive membranes for water treatment must be easily available on a large scale, thus requiring membrane fabrication to be as straightforward as possible. Furthermore, the membranes should be relatively robust and maintain their level of performance despite possible variations in the composition of the (aqueous) feed solutions. In contrast, materials for controlled release mainly find their application in relatively stable physiological conditions and on an individually small scale where biocompatibility is vital. Comparing the various chapters of this book will allow the reader to become aware of one crucial aspect of responsive membranes and materials, which is often ignored at the early stage of technology developments, and that is the engineering requirements of the final application. Chapter 8 deals with pore-filled hybrid membranes capable of responding to changes in pH, and elaborates on methods to estimate the resulting pore sizes. The membranes are intended for drug release applications. The use of a magnetic field as an external stimulus is described in Chapter 9 with a focus on magnetic nanoparticles that are incorporated into a polymeric host matrix. It is shown how a magnetic field can generate responses in various ways depending on whether it is used in a static or alternating mode.

A highly important research effort is currently being made in simulating the physico-chemical behaviour of bulk materials such as polymers by molecular dynamics (MD) simulation. Although still far from substituting experimental evidence, increasingly refined MD models accompanied by enhanced computational capacities will enable experiments made *in silico*, paving the way to systematic and automated screening algorithms for the optimization of material properties and, as a consequence, diminishing considerably the need for material and time-intensive experimental trial and error approaches. Chapter 10 provides such an example for the state-of-the-art of MD simulations by describing the interaction of salt ions with a thermo-responsive polymer.

Chapter 11 extends the biomimicking concepts outlined in previous chapters to the use of hybrid bulk materials which have biological recognition moieties incorporated in their polymeric structure. The chapter describes protein-hydrogel systems which can act as sensors or valves upon interaction with targets. It draws attention to the mechanical characterization of such hydrogels which is of utmost importance for practical applications. From the previous chapters it can be seen that responsive systems can be fabricated in various forms, be it as surfaces on membranes or particles, or inside pores. The final application determines which is the most efficient or appropriate overall strategy. Chapter 12 gives an extensive overview on the fabrication of responsive polymer colloids and how their topology can be controlled depending on the final application. It also presents particular opportunities in colloidal responsive systems such as Janus and patchy particles. The use of polymer gels as self-oscillating systems is described in Chapter 13. Using the Belousov–Zhabotinsky reaction as a stimulus, its oscillation is converted into a continuous swelling–deswelling of a polymer gel and it is shown how under defined experimental conditions this can be explored by allowing the gel to “walk” autonomously. Finally, Chapter 14 introduces electroactive polymers which deform in an electrical field. The chapter gives extensive examples of such dielectric elastomers together with their characterization and a theoretical description of the underlying thermodynamic phenomena.

The book closes with Chapter 15, summarizing the developments and research needs in the predominant fields of application of responsive materials, and providing an outlook onto the vast opportunities which lie ahead for this fascinating multi-disciplinary field of materials research.

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Contents