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Creative Chemical Sensor Systems

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Creative Chemical Sensor Systems

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Preface

Since several excellent books have appeared on the issue of chemical and biochemical sensing, this compendium concentrates on recent creative new approaches using *chemical means* for the detection and quantification of important analytes. These are presented either from a technical viewpoint or from the perspective of selective molecular recognition with artificial receptor molecules. Consequently, the entire book is subdivided into two categories, i.e., natural targets and detection techniques.

In the first part, the challenging task of sensing peptides and proteins as well as saccharides is addressed from several perspectives: Small libraries with maximum diversity are efficiently used to reach high affinity and selectivity of artificial hosts for short peptide sequences. Preorganized aromatic vessels are tailored for certain protein epitopes and shown to selectively address the prion protein, and a new conjugation technique operating at physiological conditions on helix-loop-helix motifs, leads to protein binders of exquisite affinity. Finally, elegant sensor systems for multifunctional carbohydrates in their natural form, which use the principle of photo-induced electron transfer for fluorescence detection, are presented.

The second part of this book is devoted to creative detection techniques employing chemical processes: Liposomes with integral self-assembled diacetylene lipid areas show an intense blue color, which gradually changes to red if biological analytes of various sizes specifically interact with embedded hosts. Principal component analysis and artificial neuronal networks are novel methods to quantitatively analyze complex mixtures. An alternative approach uses artificial peptidic pores, which are able to release self-quenched fluorophores that are substituted by tighter binding analytes. The last two chapters of this book highlight new promising areas of combinatorial chemistry: A fluorescence signal indicates that among thousands of candidates a certain organocatalyst has performed a successful asymmetric aldol reaction. Adding equilibrating conditions to combinatorial screening paves the way to generating self-optimized receptors and sensors, with a minimum need for design.

All chapters are written by leading experts in their fields and demonstrate that the fascinating topic of sensing, although often inspired by nature, goes far beyond biological principles and even today opens new doors to interdisciplinary research. Some of these areas are so new that technical applications have

not yet evolved. However, according to the editor, it can only be a question of time before chemical noses and dynamic combinatorial libraries are integrated into commercial sensor systems, to pick just two prominent examples.

I am indebted to the authors of this timely compilation, who presented their very latest research in an easy-to-read fashion. Their cutting edge contributions are intended to stimulate further research in other groups and to provide the advanced reader with latest sensing concepts and techniques originating from the realm of chemistry. Many thanks are also due to Dr. Marion Hertel and Birgit Kollmar-Thoni for their encouragement and professional support throughout the entire process of putting the book together.

Essen, March 2007 Thomas Schrader

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Part I
Creative Sensing of Natural Targets

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The Development of Artificial Receptors for Small Peptides Using Combinatorial Approaches

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Abstract In this article we describe some examples how combinatorial libraries are applied in supramolecular chemistry e.g. to identify artificial receptors for peptide binding in aqueous solvent. Whereas in the classical combinatorial approach mainly large but completely random libraries are used, nowadays also the use of small but focused libraries is coming into focus. We discuss the pros and cons of these two different approaches, using examples from literature work and our own studies in this field.

Keywords Combinatorial libraries · Peptides · Receptors · Supramolecular chemistry

Abbreviations

Ac	Acetyl
Bn	Benzyl
Boc	*tert*-Butoxycarbonyl
CBS	Carboxylate binding site
dansyl	(Dimethylamino)naphthalene-1-sulfonyl
Fmoc	9-Fluorenylmethoxycarbonyl
Ph	Phenyl
Suc	Succinic acid

1 Introduction

1.1 Combinatorial Methods

The use of combinatorial chemistry has fundamentally changed the pace and scope of scientific research in some areas. The introduction of synthetic peptide libraries has proven that combinatorial chemistry is a powerful tool for the generation of libraries with immense molecular diversity. But the hype as a new tool mainly in the pharmaceutical industry at the beginning of the 1990s has slowed down in recent years. The original hope that the screening of large libraries that contain millions of compounds would produce many new drug candidates has not been fulfilled with complete satisfaction. Nevertheless, combinatorial chemistry has established itself as a powerful tool—among others—in chemistry, even though it is not the magic bullet initially anticipated by some. However, combinatorial chemistry is currently changing once more and is coming again into the focus of scientists. Besides the large but random libraries initially employed, small but focused libraries are also increasingly used to address specific problems in various fields of research. The progress in the development of dynamic combinatorial libraries is also a promising development. This article will describe first some general aspects of combinatorial chemistry and then give a summary of different approaches in artificial receptor finding for biologically relevant small peptides over the years, with a focus on the advantages of small and focused libraries as used in our own research.

1.2 Supramolecular Chemistry

Combinatorial chemistry was initially mainly considered as a versatile tool for drug discovery, but has evolved in recent years into broad fields of applications as diverse as materials science [1–3], catalyst development [4–7], and biochemistry to identify the substrates of novel enzymes [8–10]. It also opens the way in the widespread area of supramolecular chemistry. We use combinatorial methods in this context to find new receptors that are capable of binding to a given target peptide, even in aqueous solvents. This can help us to increase our knowledge of molecular recognition in general and to design biosensors for the targeting of cellular processes or for the discovery of new therapeutics. But what should a peptide receptor look like? In principle there are two distinct paths one can follow [11]. One can try to rationally design a complete receptor de novo with the help of theoretical calculations [12]. However, the larger the substrate, the more difficult this gets as theoretical methods such as force field calculations are not yet

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