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Supramolecular Dye Chemistry

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Volume Editor: Frank Würthner

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258
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Preface

Dye chemistry was one of the initial topics of chemical research in the academic as well as industrial field. At the early stage of dye research, in the last decades of the 19th and the beginning of the 20th century, the focus was on the elucidation of structures of natural dyes aiming at the development of their chemical syntheses and to establish theoretical concepts for the understanding of the color–constitution relationship as a prerequisite for the design of new artificial colorants. The major outcome of these pioneering efforts for mankind was that color is no more a privilege of nature and, hence, multi-colored paints entered our everyday life and textiles of any desirable shade became accessible.

Nowadays most colorants have the purpose to satisfy our aesthetical needs and, thus, thousands of dyes and pigments are produced on industrial scales. Nevertheless, nearly periodically new demands arise for so-called "functional dyes" whose π-conjugated systems exhibit novel functionalities beyond aesthetical purposes. Optical brighteners or near-infrared absorbers are examples where even transparency in the visible spectrum is desired and dyes for non-linear optics, holographic optical data storage and two photon absorption are further examples where the color properties of "dyes" are insignificantly related to the functional demands.

Whereas most of these applications can still be addressed by appropriate design of the molecular properties of the π-conjugated backbone, i.e. the chromophore, nature has developed other types of functional dyes which obtain their functionality only by proper organization of dye molecules in space, typically within a protein matrix. Moreover, in most cases not a particular dye, rather a multichromophoric entity imparts the desired functionality. For example, regulation of oxygen transport requires oligomeric protein assemblies containing iron porphyrins (hemoglobin) and the photoinduced electron transfer cascade in the reaction center of photosynthesis needs a set of functional dyes arranged across the photosynthetic membrane in proper geometry. Most intriguing, to enable highly efficient conversion of sunlight into chemical energy, nature has developed light-harvesting systems which incorporate hundreds of dye molecules in well-defined spatial proximity to efficiently feed the reaction centers of photosynthesis with excitation energy.

Exploration of the structure–function relationship of such complex natural assemblies with the aim to develop efficient artificial photoactive devices constitutes, indeed, a major goal of current interdisciplinary research in the field of functional dye systems. Supramolecular chemistry contributes to this field by offering the toolbox for the synthesis of the desired architectures and their structural characterization. Time resolved spectroscopic characterization of photophysical properties of these structures allows to compare their functionality with those of the natural counterparts and to evaluate the prospects for various technical applications. It is very encouraging in this respect that in the last few years rationally designed dye assemblies proved to be successful in the fields of organic electronics and photonics where dye-dye interactions in the bulk state and at interfaces are of crucial importance for the desired functionalities of charge and energy transport.

This monograph is intended to provide coverage of a selection of different aspects of supramolecular dye chemistry with special emphasis on the elaboration of concepts for the realization of defined multichromophoric architectures in solution and at interfaces. We regret that some interesting topics, e.g. photoswitches and sensor materials, of this very rapidly growing research field could not be considered and, even not all classes of dye assemblies are covered by the given chapters. For example, the oldest class of dye assemblies, i.e. cyanine dye aggregates, is not included because our principle of organization is based on the respective noncovalent forces and not on the classes of dyes. Only in the first chapter by *T. S. Balaban*, *H. Tamiaki* and *A. R. Holzwarth* insight is provided into the structural and functional peculiarities of a special dye system, namely the chlorins, which combine hydrogen-bonding, metal-ligand coordination and π-π stacking in the most beneficial way to accomplish nature's most successful light-harvesting machinery. The following two chapters are organized from the supramolecular point of view with a comprehensive review on metal-directed self-assembly by *C.-C. You*, *R. Dobrawa*, *C. R. Saha-Möller* and *F. Würthner* (here porphyrins and perylene bisimides constitute the most important classes of dyes) and an article dealing with hydrogen-bond directed self-assembly by *A. Ajayaghosh*, *S. J. George* and *A. P. H.J. Schenning*. Combining these noncovalent interactions (hydrogen-bonding and metal-ligand coordination) with π-π stacking is the method of choice to create more complex materials like organogels which is the topic of the fourth chapter by *T. Ishi-i* and *S. Shinkai*.

The concept behind the other three chapters is the interaction of dye molecules with macromolecular scaffolds or surfaces. Thus, in chapter five *H. Ihmels* and *D. Otto* highlight the field of dye-based DNA intercalators. Although this field is traditionally not considered as a central topic of supramolecular chemistry, it provides a bridge towards biomedicinal applications of concepts emerging from supramolecular research. Likewise the last two chapters by *S. De Feyter* and *F. De Schryver* and by *V. Kriegisch* and *C. Lambert* constitute the interface to physics and nanotechnology covering important aspects of dye organization at surfaces.

The selection of subjects presented here is not aimed to offer a balanced compilation of "hot topics" of supramolecular dye chemistry, rather it attempts to identify concepts which hold promise for successful development of this field with tremendous prospects. I cordially thank the authors of the chapters for their efforts to provide high standard manuscripts and the publishers for giving me the opportunity to edit this volume.

Würzburg, June 2005 Frank Würthner

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Contents

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Chlorins Programmed for Self-Assembly

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Abstract The supramolecular chemistry of chlorins which are the most abundant photosynthetic pigments is reviewed. In chlorophyll-protein complexes, ligation of the central magnesium atom can occur in two diastereomeric configurations. Light-harvesting complexes of purple bacteria are formed by the self-assembly of short polypeptides which bind bacteriochlorophylls into circular structures. The light-harvesting organelle of green photosynthetic bacteria, the so-called "chlorosome", is the most efficient natural antenna system and is formed by self-assembly of bacteriochlorophylls *c*, *d* or *e* without the help of a protein scaffold. Semisynthetic and fully synthetic mimics of these self-assembling bacteriochlorophylls have been prepared and their self-assemblies have been studied in detail in view of artificial light-harvesting systems. From a single crystal X-ray diffraction analysis, one could put into evidence hierarchic supramolecular interactions within such self-assembling systems. Interestingly, hydrogen bonding which all present models of bacteriochlorophyll self-assemblies contain as one of the important supramolecular interactions is absent in the fully synthetic mimics.

Keywords Self-assembly, chlorophyll, bacteriochlorophyll, antenna complex, chlorosome, biomimetic models, porphyrinoids.

1
Introduction

1.1
Chlorins as the Most Abundant Natural Photosynthetic Chromophores

Nature uses tetrapyrroles such as chlorophylls and bacteriochlorophylls as the main chromophores for light-harvesting in photosynthetic organisms. While porphyrins have a fully conjugated 26 π electron system, in chlorins one of the pyrrolic double bonds is reduced and in bacteriochlorins two such double bonds are reduced (Fig. 1). In bacteriochlorins, the basic tetrapyrrole of the chlorophyllous ancestors, the single bonds are in opposite and not adjacent pyrrole rings. Corroles lack the 20-*meso* carbon atom while phthalocyanines are very robust fully synthetic pigments which have benzo-annulated pyrrole rings and nitrogen bridges instead of the four *meso*-methine units.

Chlorophylls (Chls) are chlorins which carry an additional five-membered ring having thus a phorbin skeleton and are usually encountered in cyanobac-

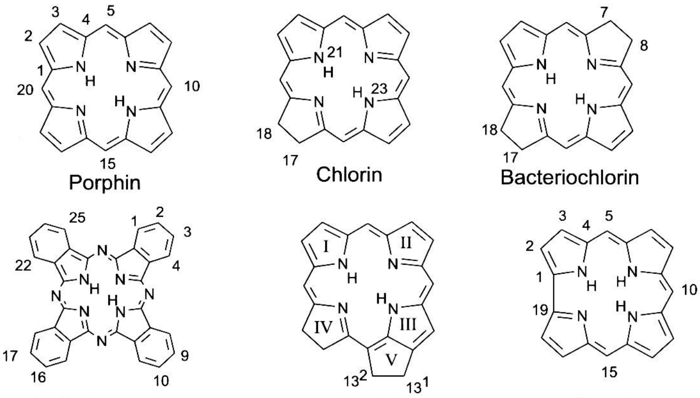
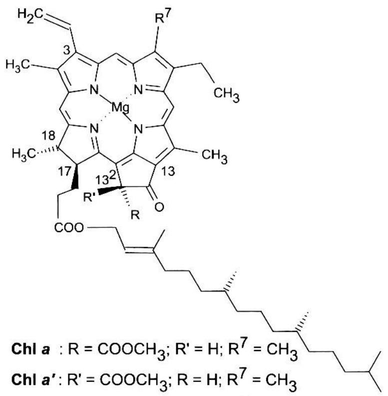


Fig. 1 Basic cyclic tetrapyrroles shown here with the usual numbering system

teria, red algae, green algae, and higher plants. Bacteriochlorophylls (BChls) occur in photosynthetic bacteria and also possess the annulated five-membered ring. While BChls typically derive from the bacteriochlorin structure (such as BChl *a*, Fig. 2) some "bacteriochlorophylls" actually have a chlorin chemical and electronic structure (c.f. Fig. 2). These chlorin-based "bacteriochlorophylls"—due to the fact that they are present in some photosynthetic bacteria—received their trivial name before their actual chemical structure was known. This chapter focuses on the properties of special (bacterio)-chlorins which have been endowed for supramolecular self-organization. Supramolecular chemistry or the "chemistry beyond the molecule" [1] is effected via non-covalent interactions such as metal-ligation, hydrogen bonding, π-stacking and hydrophobic or dispersive interactions. All these can come into play with chlorins and often their combinations act cooperatively.

In a supramolecular system the non-covalently bound assemblies have properties that are often drastically different from those of their monomeric constituents. Thus, ensemble characteristics are dominant and novel functions emerge. Since a chlorin molecule with its peripheral substituents is a little over 1 nm in diameter, the term *functional nanostructure* is appropriate for their supramolecular assemblies.

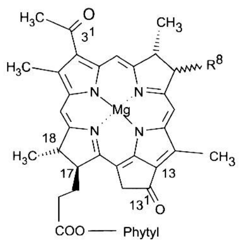
Chls and BChls are typically found as light-harvesting pigments in the membrane-bound antenna systems of photosynthetic organisms [2]. Besides these cyclic tetrapyrroles, carotenoids are also encountered in most antenna systems. Some special photosynthetic organisms contain, however, also extra-membraneous antenna systems which make use of different chromophores. These are the phycobilisomes of cyanobacteria and red algae which contain open chain tetrapyrroles as pigments, the so-called phycobilins which are covalently bound to proteins. The other notable exception are the so-called "chlorosomes" of the green bacteria, which are extra-membraneous antenna systems containing BChls *c*, *d*, or *e*. The photosynthetic antenna systems have been optimized by evolution during the past 2.6 billion years, after cyanobacteria and eucaryotes evolved from the archaebacteria [3]. Cyanobacteria were the first organisms capable of oxygenic photosynthesis and they evolved into the photosynthetic eukaryotes, a process which eventually led to the development of the higher plant kingdom. Light and oxygen can be extremely noxious to cells if the long-lived triplet excited states of chromophores are allowed to generate singlet oxygen ($O_2\ \Delta_g^1$). This problem was solved during evolution by the incorporation of carotenoids which are able to efficiently quench both B(Chl) triplet states as well as singlet oxygen by thermal deactivation. The association of carotenoids with Chls is also beneficial for light-harvesting since carotenoids absorb well between 450 and 550 nm, in the so-called Chl absorption gap (c.f. spectra in Fig. 3). A third role of carotenoids is probably structural: due to their extended and rigid conformation they help in the assembly of chlorophyll-protein complexes (CP)



Chl *a* : R = $COOCH_3$; R' = H; R^7 = CH_3

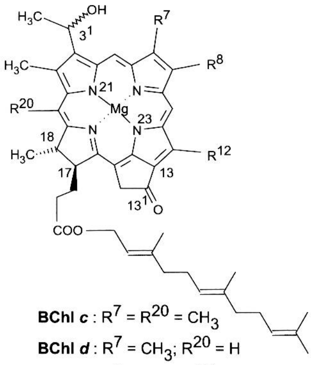
Chl *a'* : R' = $COOCH_3$; R = H; R^7 = CH_3

Chl b : R = $COOCH_3$; R' = H; R^7 = CHO



BChl *a* : R^8 = ◄CH_2CH_3

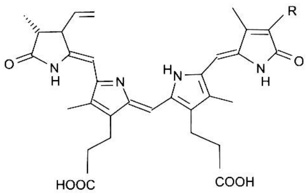
BChl *b* : R^8 = =CH-CH_3



BChl *c* : $R^7 = R^{20} = CH_3$

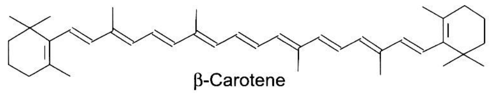
BChl *d* : $R^7 = CH_3$; R^{20} = H

BChl *e* : R^7 = CHO; $R^{20} = CH_3$

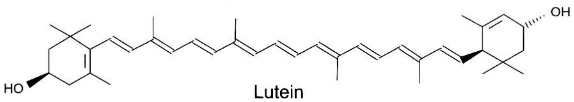


Phycocyanobilin: R = CH_2CH_3

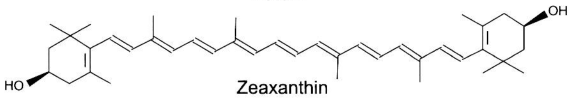
Phytochromobilin: R = CH=CH_2



β-Carotene



Lutein



Zeaxanthin