

Abstract

Molecules of the class of porphyrins and phthalocyanines are used in various fields of research owing to their outstanding properties. Porphyrins occur both naturally, e.g. as blood and leaf dyes and are synthetically produced and researched for a variety of applications. Phthalocyanines, on the other hand, are purely synthetic and used in similar fields to porphyrins due to their analogous structure and properties.

Because of their unique absorption properties in the visible range, these macrocycles have a high potential in developing novel organic optoelectronic applications such as solar cells. In addition to the absorption properties, the arrangement of the molecules also plays a decisive role. By using them in surface-anchored thin films of metal-organic frameworks, the crystallinity promising for effective conversion can be achieved.

This work describes the optimized synthesis of various *trans*-A₂B₂ porphyrins based on previous research. In addition to their absorption properties, they can be used for other research areas, such as post-modification and sensing, due to their functionalizability. Furthermore, novel linear linkers were synthesized from hybrid structures of porphyrins and phthalocyanines like tetrabenzoporphyrins and tetrabenzodiazaporphyrins and investigated for their absorption of red light. To ensure effective absorption, the synthesis of a linear ABAB-functionalized phthalocyanine linker was developed and the absorption properties were investigated. A library of three different ABAB-phthalocyanines was synthesized, and metal exchange was investigated.

In addition, the reactivity of bicyclo[1.1.1]pentanes, commonly known for their application as bioisosteres in medicinal chemistry, was investigated. For this purpose, the synthesis of sulfoxide functionalized derivatives was of interest, as further functional groups such as sulfoximines or sulfones, which are relevant for developing bioactive substances, can be introduced in subsequent reaction steps. The synthesis of sulfoxides was optimized, and a library with ten examples was synthesized. In addition, previously inaccessible derivatives could be synthesized during this work.

During a research stay at Trinity College Dublin, the synthesis of further pyrrole-based macrocycles with bicyclo[1.1.1]pentane units was also developed and optimized. Due to the similarity to calix[4]arenes and calix[4]pyrroles, the novel macrocycles are promising for future application in fields like molecular caging, drug delivery, and as stationary phase in chromatography.

Kurzzusammenfassung

Moleküle der Klasse von Porphyrinen und Phthalocyaninen finden aufgrund ihrer herausragenden Eigenschaften Anwendung in verschiedenen Bereichen der Forschung. Porphyrine kommen sowohl in der Natur als Blut- und Blattfarbstoff vor, als auch als synthetisch hergestellte Bausteine, die für eine Vielzahl an Anwendungen erforscht werden. Phthalocyanine dagegen kommen nur synthetisch vor und werden aufgrund ihrer ähnlichen Struktur und Eigenschaften in verwandten Bereichen wie Porphyrine verwendet.

Durch ihre einzigartigen Absorptionseigenschaften im sichtbaren Bereich weisen die Makrocyclen ein hohes Potential in der Entwicklung neuartiger organischer optoelektronischer Anwendungen wie Solarzellen auf. Dabei spielt neben den Absorptionseigenschaften auch der Aufbau der Moleküle eine entscheidende Rolle. Durch Verwendung in oberflächenverankerten Dünnschichten metallorganischer Gerüste kann die, für eine effektive Umwandlung vielversprechende, Kristallinität erreicht werden.

Diese Arbeit beschreibt die optimierte Synthese verschiedener *trans*-A₂B₂-Porphyrine auf Basis der vorangegangenen Forschung, die neben ihren Absorptionseigenschaften aufgrund ihrer gezielten Funktionalisierbarkeit für andere Forschungsgebiete wie Postmodifikation und Sensorik verwendet werden können. Darüberhinaus wurden neuartige, lineare Linker aus Hybridstrukturen von Porphyrinen und Phthalocyaninen synthetisiert und auf ihre Absorption von rotem Licht untersucht. Um eine effektive Absorption zu gewährleisten, wurde außerdem die Synthese von ABAB-funktionalisierten Phthalocyaninen und deren Absorptionseigenschaften untersucht.

Es wurden außerdem, für ihre Anwendung als Bioisoster in der medizinischen Chemie bekannten, Bicyclo[1.1.1]pentane und ihre Reaktivität untersucht. Dabei war unter anderem die Synthese von Sulfoxid-funktionalisierten Derivaten von verstärktem Interesse, da in nachfolgenden Reaktionsschritten weitere, für die Wirkstoffentwicklung relevanten, funktionelle Gruppen wie Sulfoximine oder Sulfone eingeführt werden können. Im Rahmen dieser Arbeit konnten darüber hinaus bisher unzugängliche Derivate synthetisiert werden.

Während eines Forschungsaufenthaltes am Trinity College Dublin wurde zudem die Synthese weiterer pyrrolbasierten Makrocyclen mit Bicyclo[1.1.1]pentan-Einheiten

entwickelt und optimiert. Durch strukturelle Gemeinsamkeiten zu Calix[4]arenen und Calix[4]pyrrolen können die neuartigen Makrocyclen ebenfalls in ähnlichen Bereichen Anwendung finden.

1 Introduction

More than ever, finding renewable energy sources is one of humanity's greatest challenges. The sun provides a quasi-inexhaustible source of energy, which is already being used in the form of inorganic silicon solar cells. For the development of more efficient organic solar cells,^[1-2] the process of photosynthesis in plants has been taken as a model function. Chlorophyll belongs to the class of porphyrins, which is why they have long been established in organic photovoltaics. However, porphyrins only allow the use of a small range of visible light. Related structures can be used to increase the efficiency of solar cells by broader absorption of light. Since phthalocyanine-based systems enables the absorption of red light, the use of such systems is obvious. Phthalocyanines are a class of macrocyclic molecular organic semiconductors derived from the naturally occurring porphyrin, but do not exist in nature. Nevertheless, phthalocyanines and porphyrins can both be applied in various fields like catalysis,^[3-4] sensing,^[4-5] or photodynamic therapy,^[4, 6] which shows the importance of the development of modified porphyrins and phthalocyanines.

1.1 Porphyrins

Porphyrins are tetrapyrrolic macrocycles and can be found in several different natural processes, acting as prosthetic groups of proteins and enzymes. Beside their role in oxygen transport in blood and muscles, such as in hemoglobin and myoglobin, they can be found in the human body. They are part of type c cytochromes responsible for cellular respiration, cytochromes of the P450 family, that are involved in biosynthesis as well as drug metabolism, and catalases and peroxidases, which help in the detoxification of organisms.^[7-8] Chlorophyll belongs to the class of porphyrins and acts as a photosensitizer absorbing the light and forwarding its energy.^[9]

The structural motif of porphyrins is based on a macrocycle of four π -conjugated pyrrole-units which are bridged by four methine groups. The porphyrin possesses 18 π -electrons along the shortest cyclic path, the [18]annulene, obeying HÜCKEL's $[4n+2]$ rule for aromatic compounds,^[10-13] which is why it was assumed that the aromaticity of porphyrins is based on this [18]annulene (Figure 1).^[14-15] A few years later studies suggested that all 26 π -electrons contribute to the ring current.^[16-17]

Introduction

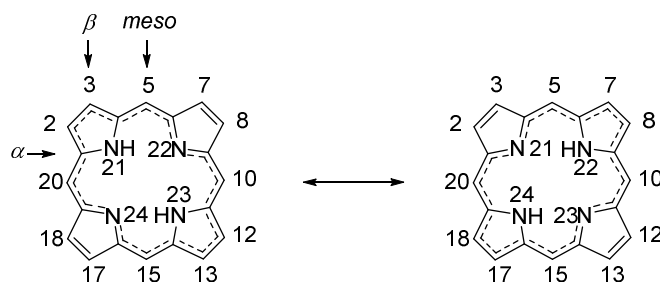


Figure 1: Tautomerism of N-H in the porphyrin core, the shortest π -electron pathway (dashed), the specific numbering, and the α -, β - and the *meso*-positions are shown.

The original numbering, which HANS FISCHER suggested, and also non-scientific names were used for a long time, before in 1986 the *International Union of Pure and Applied Chemistry* (IUPAC) introduced a systematic numbering (Figure 1).^[18] The IUPAC nomenclature does not use the older naming of α - β - and *meso*-positions, but they are still commonly used to describe these positions.

For the classification of *meso*-substituted porphyrins with different substitutions, a method is used in which up to four different residues are named “A”, “B”, “C” and “D”. In the case of two identical substituents, the term “*trans*” is used for a 5,15-substitution and “*cis*” for an 5,10-substitution (Figure 2).

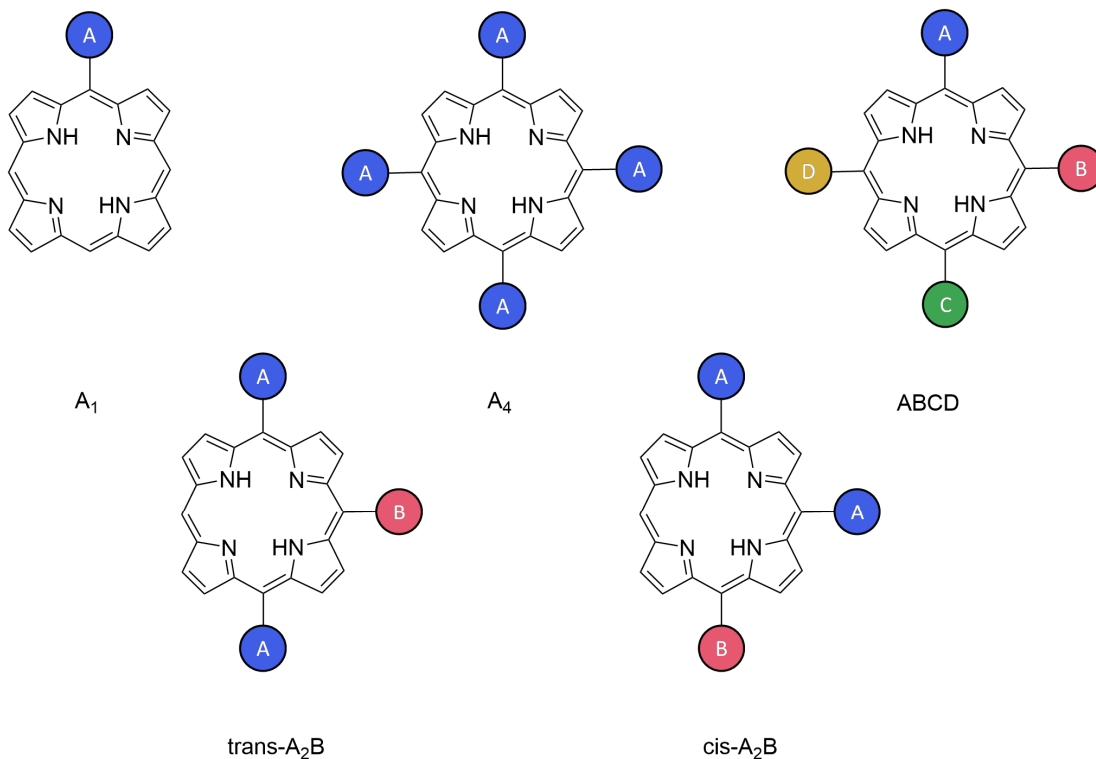


Figure 2: Representation of schematic porphyrins from type A_x to ABCD.