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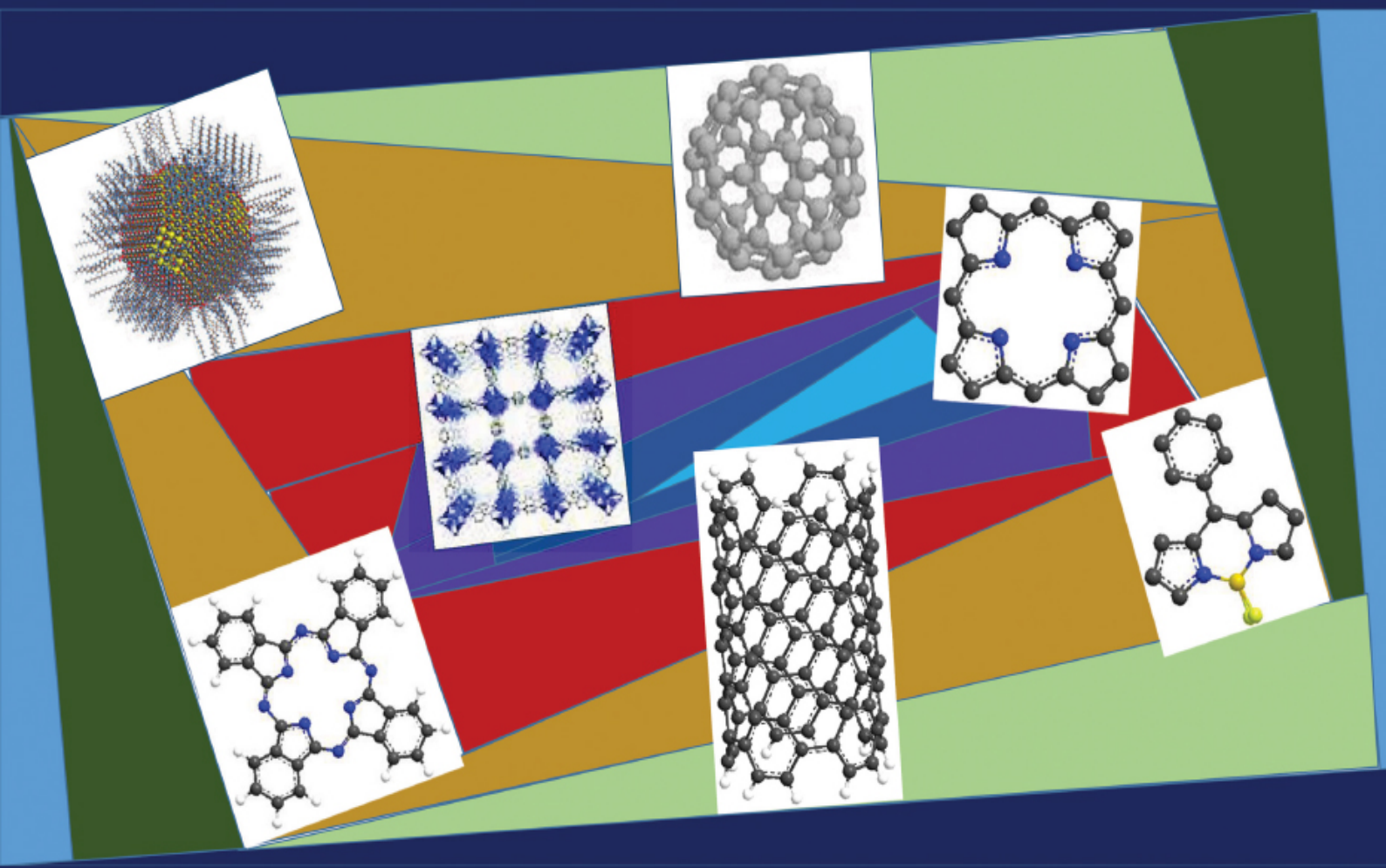
FUTURE TRENDS FOR TOP MATERIALS



Mário J. F. Calvete

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FUTURE TRENDS FOR TOP MATERIALS

Authored By

Mário J. F. Calvete

Department of Chemistry, Faculty of Science and Technology, University of Coimbra
3004-535 Coimbra, Portugal

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FOREWORD

Chemistry is central to science, engineering and medicine, and has been at the forefront of the development of advanced materials for applications ranging from personal electronics, lighting and displays, solar energy conversion, energy storage, through environmental remediation, to clinical diagnosis, and advanced therapies for the treatment of cancer.

In this book, *Future Trends for Top Materials*, my colleague Mário J. F. Calvete presents an extensive review of the chemistry of some of the most important materials for these applications. These include the pyrrole-based systems phthalocyanines, porphyrins, porphyrinoids, boron dipyrromethene (bodipy) dyes, together with polymethine (cyanine) systems, and the carbon allotropes of fullerenes, carbon nanotubes and graphene. Further, from our understanding of mechanisms, stereochemistry and chemical bonding, it is now possible to design molecular architecture with specific materials functions. Dendrimers, metal-organic and covalent- organic frameworks are discussed within this perspective. The author also considers relevant aspects of metal and semiconductor based nanoparticles, including superparamagnetic systems and quantum dots. In the final chapter, he summarizes possible achievements based on relevancy of the most important materials.

All of the systems discussed are treated in terms of their synthesis and functionalization, before discussing their most important applications (real and potential). Examples are given in catalysis, photovoltaics, sensing, imaging, nonlinear optics, optoelectronics, biomedicine… This book provides both a good starting point for those entering the field, and a presentation of the state-of-the-art in for more experienced researchers.

The author is to be commended for both the breadth and depth of the work described, and for the extensive bibliography. This can form the basis for a course in advanced materials chemistry, but also acts as an excellent entry for those starting research in this area.

The author, Mário Calvete, has extensive experience in many of the topics discussed, and is to be commended for this excellent publication.

Hugh D. Burrows
Chemistry Department
University of Coimbra, Portugal

PREFACE

The idea behind this book arose from a necessity typical from Organic Chemists. Exploration of search engines in diverse topics usually leads to isolated results on each certain thematic issue. Hence, a directed and simple approach seemed necessary. After a careful compilation, discussion of synthetic methodology, historical perspective and relevance is provided for each of the families of compounds here described. The most representative and notable examples are mentioned/scrutinized at historical level, either regarding synthetic aspects or applications (which can be across any field, from medical, biological or materials applications, among others).

This contribution focuses on defined compounds (or types of compounds) which are sure candidates to occupy a prominent place in synthesis (and in diverse applications) in the forthcoming years, for a large number of readers, who by any motivation want to explore new compounds for any given application. In this book, general and established synthetic methodologies for several compounds are also given, in an attempted way to provide straightforward approaches for researchers who intend to start new topics, as a hands on reference guide for scientists working in the fields of chemistry, physics, biology, biomedicine, materials science, polymer science, nanotechnology or supramolecular science.

This eBook is divided in 9 chapters, in following order: phthalocyanines, polymethines, porphyrins, BODIPYs, dendrimers, carbon allotropes, organic frameworks, nanoparticles and future prospects. Each chapter covers detailed synthetic aspects of the most established preparation routes for each type of compounds, while giving a historical perspective, with selected information on actual and outstanding applications of each material, unraveling what likely might be the future for each one. I would like to refer to the last chapter, which deals with the synthesis and functionalization of several types of inorganic nanoparticles, but emphasizing the organic functionalization of such inorganic materials.

Bottom-line, it is intended to provide a clear concept on each section as a "*since when/how/why/what's next"* overall idea, targeted for researchers either from industries or universities, who by any motivation want to explore new compounds for any given application, providing general and established synthetic approaches, or to readers who would like to know more in a concise manner, without spending unnecessary efforts on isolated thematic search through available search engines.

CONFLICT OF INTEREST

The author confirms that this eBook content has no conflict of interest.

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Declared none.

Mário J. F. Calvete
Department of Chemistry
University of Coimbra
Coimbra, Portugal
Email: mcalvete@qui.uc.pt

BIOGRAPHY

Mário José Ferreira Calvete is of Portuguese nationality and he was born in Portugal in 1975. He received his Industrial Chemistry diploma from the University of Coimbra in 2000 and his Ph.D. in Natural Sciences – Organic Chemistry in 2004 from the Eberhard Karls University of Tübingen, Germany, under the guidance of Prof. Dr. H. C. Michael Hanack on the synthesis and optical applications of phthalocyanines derivatives.

After a period in University/Industry working on Materials Science field, under the supervision of Prof. Dr. H. C. Michael Hanack, he returned to Portugal in 2007 for a postdoctoral position at the University of Aveiro with Prof. Dr. José Cavaleiro, working on the field on porphyrin-phthalocyanine heteroarrays. In 2010 he was appointed an Auxiliary Researcher at the University of Coimbra, currently being also Auxiliary Professor at the University of Coimbra.

His main research interest focus on the design and photophysics of near infrared absorbing/emitting materials and its conjugation with supports (of organic or inorganic nature) for application/study in homogeneous/heterogeneous catalysis and theranostics.

CHAPTER 1

Phthalocyanines as Top Materials

Abstract: Phthalocyanines are colored aromatic macrocycles, composed of four iminoisoindoline units, giving origin to a highly conjugated planar macrocycle, known for its remarkable stability. Their remarkable features have rendered them wide attention, which continues to live on nowadays. Herein is presented a conspectus on the field of phthalocyanines, where emphasis is set on their preparation methods, along with more detailed examples on several promising applications with 418 references provided. Some synthetic details on the preparation of state-of-the-art compounds are given as well.

Keywords: Biomedicine dyes, Energy materials, Phthalocyanines, Subphthalocyanines.

INTRODUCTION

Phthalocyanines are intensely blue-green colored aromatic macrocyclic compounds, consisted by an 18 π-electron system, composed of four iminoiso indoline units, conferring a remarkable stability for an organic compound. Nevertheless, phthalocyanines offer great structural flexibility, being capable of forming coordination metal complexes with the majority of periodic table elements. Phthalocyanine structures are directly associated to the naturally existing porphyrins, with the differences being the four benzo-subunits and the nitrogen atoms at each of the four *meso* positions, reason why phthalocyanines are occasionally referred to as tetrabenzotetraazaporphyrins.

Other quite known related macrocycles include the tetraazaporphyrins, more known as porphyrazines (without the four benzo-subunits at each of the four *meso* positions) and naphthalocyanines (with additional four benzo-subunits at each of the four *meso* positions) (Fig. **1**).

Less known, but also important are the subphthalocyanines, which are the lower homologues of phthalocyanines (having three *N*-fused iminoisoindoline units

bearing a boron core). These compounds possess delocalized 14 π-electronic system, being considered aromatic compounds, although they possess nonplanar cone-shaped structure.

Nomenclature in phthalocyanines follows adapted IUPAC nomenclature codes. A system of abbreviations is necessary to avoid the long-winded nature of Pc nomenclature demanded by the IUPAC system. Fig. (**2**) shows the accepted numbering system of the Pc ring, where sixteen possible substitution sites in the macrocycle appear.

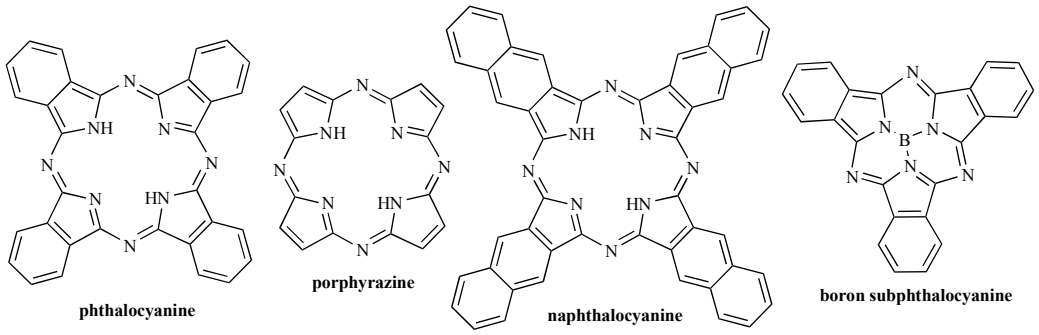

Fig. (1). Phthalocyanine derivatives.

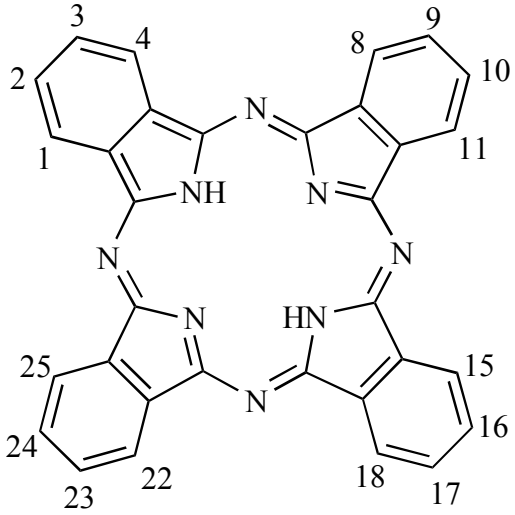

Fig. (2). Phthalocyanine ring numbering.

As many great findings in History, phthalocyanines were discovered fortuitously. Braun and Tcherniac observed a dark, insoluble material during the preparation of 2-cyanobenzamide from phthalimide and acetic acid in 1907 [1]. Nevertheless, less importance was given to such findings at the time. Later, in 1927, a remarkably stable blue material, ascribed as copper phthalocyanine, was synthesized by de Diesbach and von der Wied in 23% yield, as a side reaction of 1,2-dibromobenzene with copper(I) cyanide in pyridine (Rosenmund-von Braun reaction) [2]. Almost coincidentally, the preparation of a blue-green material occurred during the industrial synthesis of phthalimide from phthalic anhydride, at the Grangemouth plant of Scottish Dyes Ltd. in the year 1928. Dandridge and Dunsworth, two laboratory employees analyzed the side-reaction meticulously and discovered that it was prone to occur inside older iron reactors, which could release some iron splinters from reactor cracks during production. Initial studies on these iron containing pigments reveled an outstandingly stable insoluble dye, whose preparation and properties gave rise to a patented, granted in 1929 [3]. One year earlier, Imperial Chemistry Industries (ICI) had acquired Scottish Dyes Ltd., and the curiosity of the new owners provoked a decisive chain of events, by sending some samples to Professor Jocelyn Thorpe and Imperial College, London, who in turn gave the investigation to newly appointed Reginald P. Linstead (later entitled Sir) who, through collaboration with ICI, managed to meticulously explore most aspects of this new substance. Indeed, the term phthalocyanine was the first used by him [4], as a derivatization from the Greek words *phthal* (rock oil) and *cyanine* (blue).

In following years phthalocyanine structure was clarified, along with procedures for the preparation of several metal phthalocyanines and their metal-free complexes [5 - 10]. Research continued until it was interrupted by World War II, including seminal outcomes reporting the first synthesis of naphthalocyanines [11] and accomplishment of two dozen different metals inside phthalocyanine cavities [12]. In the subsequent years after World War II, research hasted and great developments were reported on the family of phthalocyanines. For instance, in 1972, subphthalocyanines were accidentally discovered by Ossko and Meller [13], when attempting to synthesize boron containing phthalocyanines *via* cyclotetramerization reaction of boron trichloride with phthalonitrile in