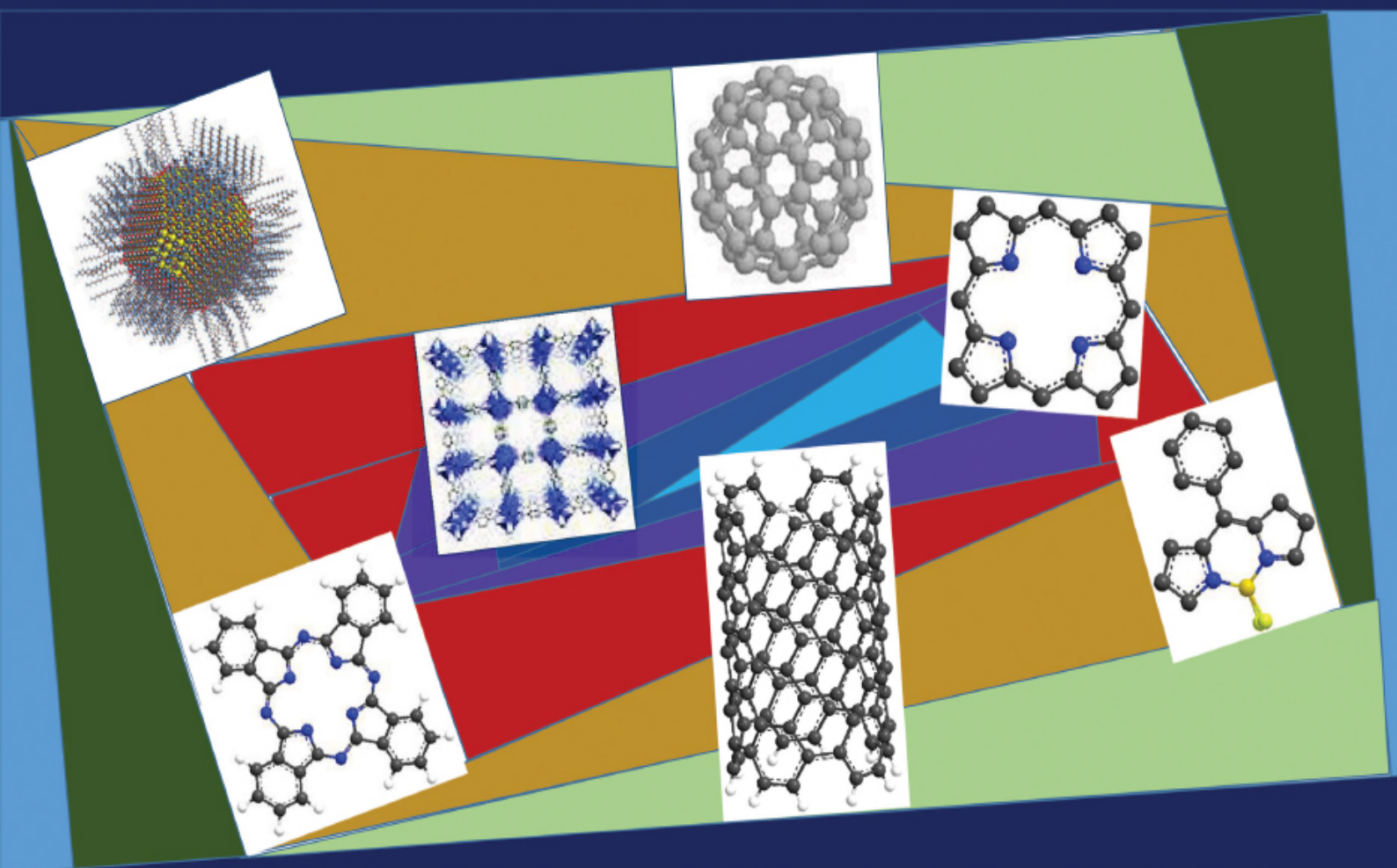


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FUTURE TRENDS FOR TOP MATERIALS



Mário J. F. Calvete

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FUTURE TRENDS FOR TOP MATERIALS

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CONTENTS

FOREWORD	i
PREFACE	ii
CONFLICT OF INTEREST	ii
ACKNOWLEDGEMENTS	iii
BIOGRAPHY	iv
CHAPTER 1 PHTHALOCYANINES AS TOP MATERIALS	3
INTRODUCTION	3
SYNTHESIS OF PHTHALOCYANINE DERIVATIVES	6
APPLICATIONS OF PHTHALOCYANINES	13
Applications in Catalysis	14
Applications as Langmuir-Blodgett Films	15
Applications as Fluorogenic Chemical Sensors	19
Applications as Semiconductors	21
Applications as Liquid Crystals	21
Applications as Light-harvesting Modules for Organic Photovoltaics and Dye-sensitized Solar Cells	22
Applications in Nonlinear Optics	27
Applications as Photosensitizers for Photodynamic Cancer Therapy	32
Applications as Antibacterial Composites	33
Applications in Molecular Imaging	35
EXPERIMENTAL SECTION	37
Synthesis of Water Soluble Tetrasulfonated Phthalocyanine (Scheme 4)	37
Synthesis of (2,3)-type Octa-alkoxy Substituted Phthalocyanines (Scheme 5)	37
Synthesis of (1,4)-type Octa-alkoxy Substituted Phthalocyanines (Scheme 6)	38
Synthesis of Sulfonamide Substituted Phthalocyanines (Scheme 7)	38
Synthesis of Tetra Substituted Glucopyranosyl Phthalocyanines (Scheme 8)	39
Synthesis of Unsymmetrically Substituted (AAAB) Phthalocyanines (Scheme 9)	39
Synthesis of Subphthalocyanines (Scheme 10)	40
Synthesis of (AABB) Substituted Phthalocyanines (Scheme 11)	40
Synthesis of (ABAB) Substituted Phthalocyanines (Scheme 12)	41
Synthesis of an Octa-substituted Naphthalocyanine (Scheme 13)	41
CONCLUDING REMARKS	42
REFERENCES	42
CHAPTER 2 POLYMETHINES AS TOP MATERIALS	78
INTRODUCTION	78
SYNTHESIS OF CYANINE DERIVATIVES	79
APPLICATIONS OF POLYMETHINE DYES	83
Applications as Photoactive Materials	84
Applications in Nonlinear Optics	88
Applications in Biomedicine	89
EXPERIMENTAL SECTION	96
Synthesis of Monomethine Dyes (Scheme 7)	96
Synthesis of Trimethine and Pentamethine Dyes (Scheme 8)	96
Synthesis of Heptamethine Cyanine Dyes by the N,N'-diphenylformamidine Method (Scheme 9)	97
Functionalization of Heptamethine Dyes with Amines (Scheme 10)	98

CONCLUDING REMARKS	98
REFERENCES	98
CHAPTER 3 PORPHYRINS AS TOP MATERIALS	113
INTRODUCTION	113
SYNTHESIS OF PORPHYRIN DERIVATIVES	116
Porphyrin Functionalization	123
APPLICATIONS OF PORPHYRINS	133
Applications in Catalysis	133
Applications as Chemical Sensors	138
Applications as Nonlinear Optical Materials	143
Applications in Solar Cells	146
Applications as Polymer Based Porphyrinic Materials	149
Applications in Antimicrobial Photodynamic Inactivation	154
Applications in Photodynamic Therapy	157
Applications in Disease Diagnostics	160
EXPERIMENTAL SECTION	165
Synthesis of 2,3,7,8,12,13,17,18-octaethylporphyrin (Scheme 21)	165
Synthesis of 5-phenyldipyrromethane (Scheme 22)	165
Synthesis of 5,15-diphenylporphyrin (Scheme 23)	166
Synthesis of Unsymmetric Meso-substituted Porphyrins via Suzuki Coupling Reaction (Scheme 24)	166
Synthesis of [5-(4-carboxyphenyl)-10,15,20-tris(4-pyridyl)porphyrin] (Scheme 25)	167
Synthesis of Meso-substituted Halogenated Bacteriochlorins (Scheme 26)	167
Synthesis of beta-substituted Bacteriochlorins (Scheme 27)	168
CONCLUDING REMARKS	168
REFERENCES	169
CHAPTER 4 BODIPY DYES AS TOP MATERIALS	212
INTRODUCTION	212
SYNTHESIS OF BODIPY DERIVATIVES	213
Functionalization of BODIPYs	216
APPLICATIONS OF BODIPY DYES	218
Applications in Biolabeling	218
Applications in Cell Imaging	219
Applications as Sensors	222
Application in Nonlinear Optics	224
Application in Dye Sensitized Solar Cells	225
EXPERIMENTAL SECTION	228
Synthesis of a BODIPY-triazine-based Tripod Fluorescent System (Scheme 12)	228
Synthesis of an Extended BODIPY Sensor (Scheme 13)	228
Synthesis of Extended BODIPY Dyes with Restricted Bond Rotation (Schemes 14 and 15)	229
Synthesis of BF ₂ -azadipyrromethenes (Scheme 16)	229
CONCLUDING REMARKS	230
REFERENCES	230
CHAPTER 5 DENDRIMERS AS TOP MATERIALS	245
INTRODUCTION	245
SYNTHESIS OF DENDRIMER DERIVATIVES	249
APPLICATIONS OF DENDRIMERS	253
Applications in Catalysis	254
Applications as Liquid Crystals	255

Applications in Light Harvesting	256
Applications in Guest-host Interactions	259
Applications as Sensors	259
Applications in Drug Delivery	260
Applications in Therapeutics	262
Applications in Disease Diagnostics	263
EXPERIMENTAL SECTION	265
Synthesis of Poly(Propylene Imine) Dendrimer (PPI) (Scheme 5)	265
Synthesis of Melamine (Triazine) Dendrimers (Scheme 6)	265
CONCLUDING REMARKS	266
REFERENCES	266
CHAPTER 6 CARBON ALLOTROPES AS TOP MATERIALS	291
INTRODUCTION	291
SYNTHESIS OF CARBON BASED MATERIALS	295
Functionalization of Carbon Materials	296
APPLICATIONS OF FULLERENES	308
Applications in Catalysis	308
Applications as Electroactive Materials	309
Applications in Organo-photovoltaics	311
Applications in Thin Films	312
Applications in Nonlinear Optics	314
Applications in Biomedicine	316
APPLICATIONS OF CARBON NANOTUBES	318
Applications in Energy Storage	318
Applications in Fuel Cells	319
Applications as Capacitors	320
Applications in Catalysis	321
Applications as Sensors	321
Applications in Solar Cells	322
Applications in Biomedicine	323
APPLICATIONS OF GRAPHENE	326
Applications in Catalysis	326
Applications in Energy Storage	328
Applications as Sensors	329
Applications in Solar Cells	331
Applications in Biomedicine	332
EXPERIMENTAL SECTION	335
Synthesis of N-methylpyrrolidine-C60 (Scheme 6)	335
Preparation of N-benzyl-2-carbomethoxy Pyrrolidine-C60 (Scheme 7)	335
Preparation of Methano-PC61BM (Scheme 8)	336
Synthesis of N-substituted Single-wall Carbon Nanotubes (Scheme 9)	336
Synthesis of Amine Functionalized Carbon Nanotubes (Scheme 10)	337
Functionalization of Carbon Nanotubes with Pyrene Derivatives (Scheme 11)	337
CONCLUDING REMARKS	338
REFERENCES	338
CHAPTER 7 ORGANIC FRAMEWORKS AS TOP MATERIALS	402
INTRODUCTION	402
SYNTHESIS OF ORGANIC FRAMEWORKS	405
APPLICATIONS OF ORGANIC FRAMEWORKS	408

Applications in Gas Purification/separation	408
Applications in Catalysis	411
Applications in Sensing	413
Applications as Conducting Materials	414
EXPERIMENTAL SECTION	415
Synthesis of HKUST-1 MOF	415
Synthesis of UMCM-2 MOF	415
Microwave Synthesis of IRMOF2 MOF	416
Synthesis of IRMOF3 MOF	416
Microwave Synthesis of MOF-5	416
Synthesis of MIL-101 COF	416
Synthesis of COF-1	416
Synthesis of COF-6	416
Synthesis of COF-8	416
Synthesis of COF-202	416
CONCLUDING REMARKS	416
REFERENCES	417
CHAPTER 8 NANOPARTICLES AS TOP MATERIALS	444
INTRODUCTION	444
SYNTHESIS OF NANOPARTICLES	446
Metal Nanoparticles	446
Magnetic Nanoparticles	450
Quantum Dots	452
APPLICATIONS OF METAL NANOPARTICLES	454
Applications in Energy Storage	455
Applications in Water Purification	457
Applications as Sensors	458
Applications in Solar Cells	461
Applications in Biomedicine	463
APPLICATIONS OF MAGNETIC NANOPARTICLES	469
Biological Applications	469
Applications in Catalysis	472
Applications in Environmental Remediation	474
APPLICATIONS OF QUANTUM DOTS	475
Applications in Biomedicine	475
Applications in Optoelectronics	478
Applications in Solar Cells	479
EXPERIMENTAL SECTION	481
Synthesis of Functionalized Au Nanoparticles with Doxorubicin (Scheme 4)	481
Synthesis of Self-assembled Porphyrin Monolayers (Scheme 5)	481
Synthesis of Iron Based Magnetic Nanoparticles (Scheme 6)	482
Synthesis of Hydrophilic Iron Magnetic Nanoparticles (Scheme 7)	482
Synthesis of cRGD-peptide Conjugated Near-infrared CdTe/ZnSe Core-shell Quantum Dots (Scheme 8)	
.....	483
Synthesis of Peptide Conjugated Quantum Dots (Scheme 9)	483
CONCLUDING REMARKS	484
REFERENCES	484
CHAPTER 9 FUTURE PROSPECTS	538
CATALYSIS APPLICATIONS	539

SENSING APPLICATIONS	540
ORGANIC PHOTOVOLTAIC APPLICATIONS	541
PHOTOTHERAPY APPLICATIONS	543
MOLECULAR IMAGING APPLICATIONS	544
DRUG DELIVERY APPLICATIONS	545
ENERGY STORAGE APPLICATIONS	545
HYBRID MATERIALS	546
REFERENCES	557
SUBJECT INDEX	560

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.

ACKNOWLEDGEMENTS

Declared none.

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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.

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 iminoisoindoline 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.

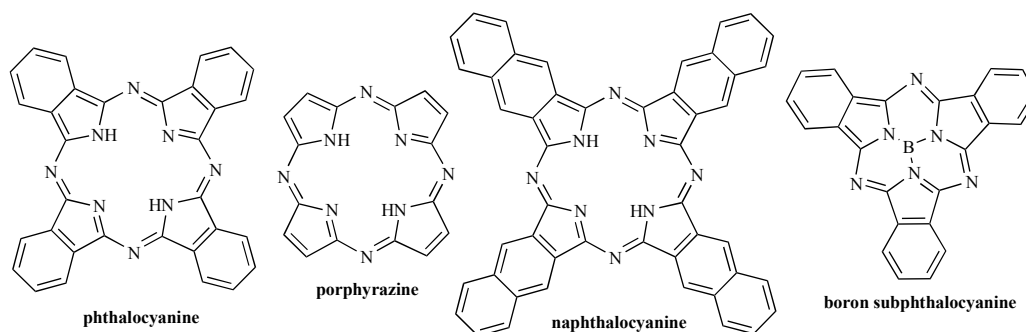


Fig. (1). Phthalocyanine derivatives.

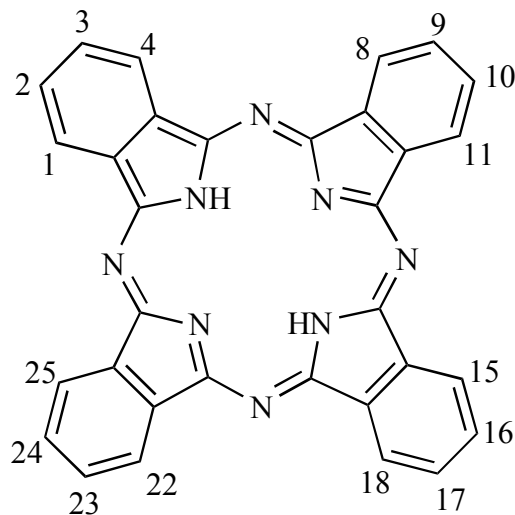


Fig. (2). Phthalocyanine ring numbering.

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 revealed 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 hastened 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

Polymethines as Top Materials

Abstract: Polymethines are planar, conjugated compounds made up from an odd number of methine groups (CH) linked together by alternating single and double bonds, also known as cyanines. These highly conjugated compounds can absorb light at wide range of wavelengths, ranging from ultraviolet to infra red, just depending on the number of alternating double bonds present in their structure. Herein is presented a conspectus on the field of cyanines, where emphasis is set on their preparation and functionalization methods, along with more detailed examples on several promising applications with 165 references provided. Some synthetic details on the preparation of state-of-the-art compounds are given as well.

Keywords: Biolabeling, Cyanines, Infrared dyes, Near infrared dyes, Polymethines, Ultra violet dyes.

INTRODUCTION

Polymethines are planar, conjugated compounds made up from an odd number of methine groups (CH) linked together by alternating single and double bonds [1, 2]. These compounds differ from related polyenes, which are compounds made up from an even number of methine groups. This family of compounds is also known as cyanines, a non-systematic name of this synthetic dye family.

The word cyanine derives from the English word “cyan”, meaning blue-green, being derived from the Greek “kyanos” which means a rather different color: “dark blue”.

Cyanines are cationic compounds possessing a +1 charge, being classified in three types: i) hemicyanines, ii) open chain cyanines and iii) closed chain cyanines (Fig. 1). Inside that classification they can also be symmetric or unsymmetric, depending on the nature of each of the open or closed chain groups at the extremities of the compounds. Each nitrogen is an independent part of a heteroaromatic moiety, such as imidazole, pyrrole, pyridine, thiazole, indole,

benzothiazole, quinoline, *etc* [3 - 5] and, depending on their structure, their absorption spectra can cover the spectrum from UV to IR.

In 1856, Williams reported the first carbocyanine [6]. Not much importance was given to this type of compounds, as it was an extremely light sensitive type of molecules. The great value of carbocyanine dyes was not discovered until almost 20 years later when Vogel used them to increase sensitivity of a photographic plate [7]. Cyanine dyes were also recognized as natural products dyes [8 - 11], as observed by Wyler [8, 9] and Musso [10] (Fig. 2).

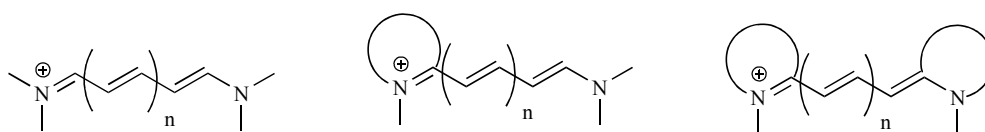


Fig. (1). General cyanine structures.

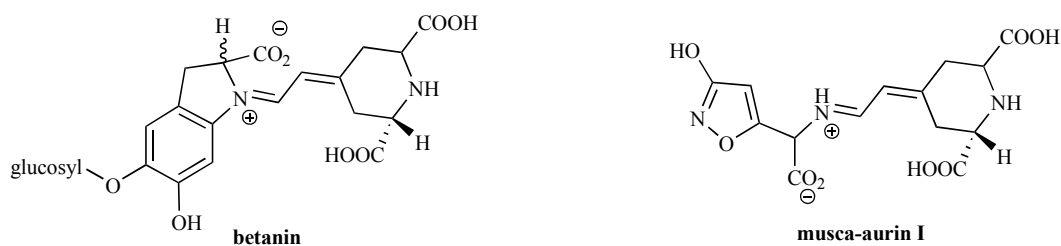


Fig. (2). Natural carbocyanine dyes.

Since then, several synthetic methods for the preparation of polymethine dyes with varied molecular structures have been reported [11 - 20], including monomethines [21 - 27], dimethines [28 - 32], trimethines [33 - 36], tetramethines [37, 38], pentamethines [39 - 43], heptamethines [44 - 48] and various other cyanine dyes [49 - 51].

SYNTHESIS OF CYANINE DERIVATIVES

The synthesis of polymethine cyanine derivatives is typically accomplished through a condensation reaction between a polyene-chain precursor and two nucleophilic *aza*-heterocycles bearing an activated methyl group.

In general, in the synthesis of most methine dyes, a counterpart contains a methylene group activated by a quaternized nitrogen atom and another component has a reactive group with an auxochrome (Fig. 3).

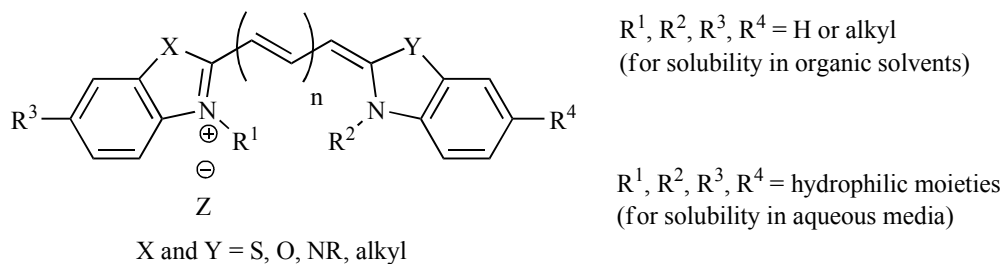
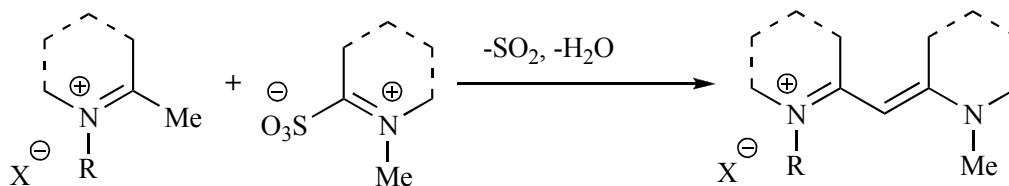


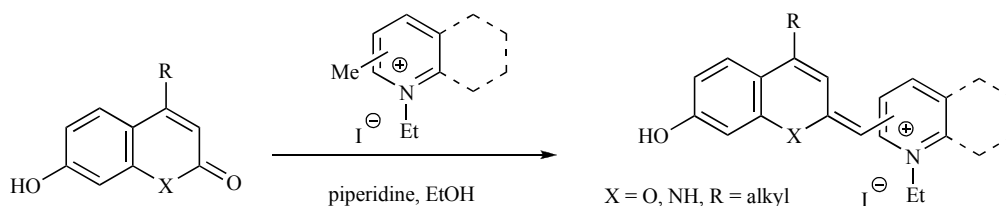
Fig. (3). General cyanine structure.

For instance, monomethine cyanine dyes can be synthesized by heating a quaternary salt of heterocyclic compounds and sulfobetaines under basic conditions (Scheme 1) [52, 53].



Scheme (1). Methine dyes.

Other approach regards the reaction of coumarins and 2- or 4-methyl quaternary salts, in the presence of piperidine (Scheme 2) [54].



Scheme (2). Monomethine cyanine dyes.

Porphyrins as Top Materials

Abstract: Porphyrins are colored aromatic macrocycles, composed of four pyrrole units, linked by four methine bridges, giving origin to a highly conjugated macrocycle, known for its remarkable stability. Their remarkable features have given them a wide fame, and continue to pave the way for multiple purposes nowadays. Herein is presented a conspectus on the field of porphyrins, where emphasis is set on their preparation and functionalization methods, along with more detailed examples on several promising applications with 508 references provided. Some synthetic details on the preparation of state-of-the-art compounds are given as well.

Keywords: Energy conversion, Photocatalysis, Photodynamic therapy, Photosynthesis, Porphyrins, Porphyrinoids, Photodynamic therapy.

INTRODUCTION

Porphyryns and their related compounds are colored aromatic macrocycles, composed of four pyrrole units, linked by four methylenic bridges, giving a highly conjugated macrocycle known for its remarkable stability. Porphyrins contain a total of 22 π -electrons, with 18 π -electrons participating in the delocalization pathway each time, which can create up to six different 18 π -electron delocalization pathways (Fig. 1).

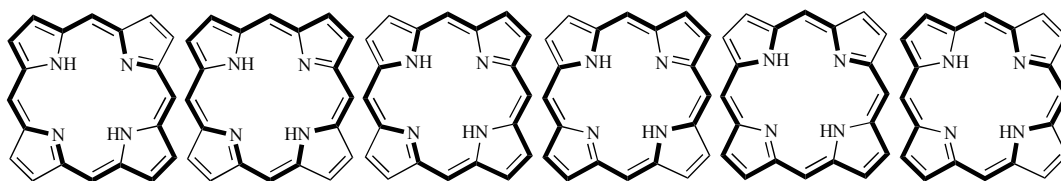


Fig. (1). 18 π -electron delocalization pathways.

Porphyryns follow Huckel's $[4n + 2]$ rule for aromaticity ($n = 4$), meaning that their two peripheral double bonds can suffer additional reactions without delocalization pathway interfering. Other porphyrin related macrocycles include

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benzoporphyrins (similar to porphyrins, but with β -fused benzene rings) [1 - 5], corroles (constituted by four pyrrole units intercalated with 3 methine bridges, having two of the pyrrole units directly connected) [6 - 10] and subporphyrins (the lower porphyrin homologues, constituted by three pyrrole units interconnected by three methine bridges) [11 - 14].

Nomenclature of porphyrins is an evolving issue. The first system of nomenclature was developed by Fischer in 1934 [15]. Here, substitution can occur at two positions along the periphery of the macrocycle in the β -carbons of the pyrrole fragments or at the four *meso*-positions which are the methine bridges between the α -carbons of the pyrrole fragments (Fig. 2).

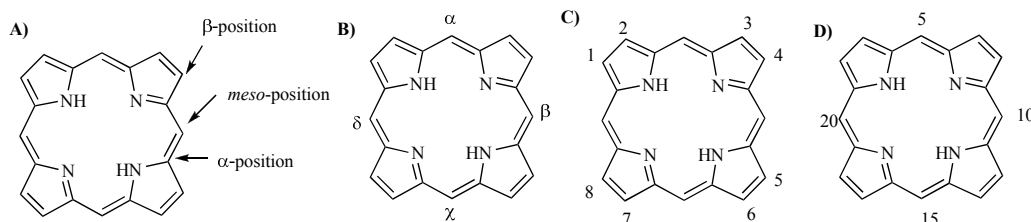


Fig. (2). Porphyrin nomenclature developed by Fischer. **A)** porphyrin positions; **B)** notation for meso-positions; **C)** numbering for β -positions; **D)** numbering for meso-positions.

This nomenclature is still used today; however, a more appropriate system had to be developed, to name more complicated structures, where Fischer's nomenclature failed. The International Union of Pure and Applied Chemistry (IUPAC) nomenclature was adopted in early 1970's [16]. This nomenclature differs from Fischer's in that all the carbons and nitrogens in the porphyrin macrocycle are given a number. Looking at the basic porphyrin system (porphine) the β -positions then become 2,3,7,8,12,13,17,18 instead of 1-8. The *meso*-positions are numbered 5,10,15,20, in place of the Greek letters Fischer previously assigned (Fig. 2).

Porphyrins are naturally occurring compounds (Fig. 3). Bottom-line, one can even say that these pigments are so important that life would simply not be possible without them. Photosynthesis and respiration are at the heart of what makes life possible and in both phenomena, porphyrinoids are omnipresent. In remote times,

when the atmosphere in our planet was void of free oxygen, the evolution of oxygenic photosynthesis by chlorophyll (the process involves the oxidation of water forming molecular oxygen releasing it into the atmosphere) caused the change of Earth atmosphere from anaerobic to aerobic leading to a dramatic increase in biodiversity.

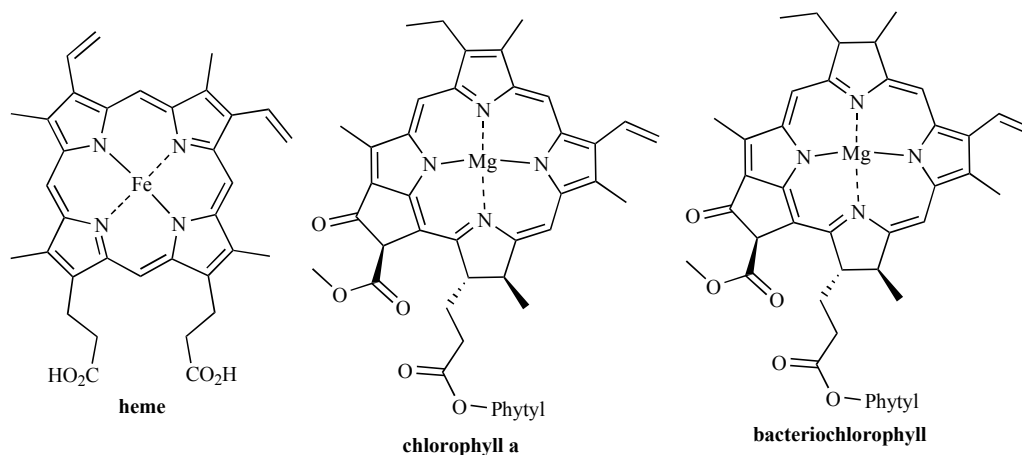


Fig. (3). Naturally occurring porphyrin derivatives.

Life has evolved using oxygen leading to organisms and plants containing chloroplasts for photosynthesis and eventually hemoglobin in the red blood cells for the respiration of vertebrates.

Understanding events related to these compounds became the life goal of several scientists, whose findings are well documented [17]. For instance, iron in human blood was first reported in 1747, when Menghini burned human blood to ash separating particles of iron with a magnet. Later, the experiments by Joseph Priestly in 1774 proved that the oxygen consumed by fire and breathing animals could be restored to the air by plants. This ignited interest in understanding the role of oxygen in respiration. In 1864, Hoppe-Seyler was able to isolate the red blood cell iron-containing metalloprotein responsible for oxygen-transport, naming it hemoglobin. Later, in 1871, Hoppe-Seyler isolated porphyrins from blood and demonstrated they were pyrrole derivatives, being later credited to reporting similarities between chlorophyll and heme, in 1879. Only in 1912 the correct structure for porphyrins was proposed by Kuester, though not accepted at

BODIPY Dyes as Top Materials

Abstract: BODIPY dyes are structures based on two pyrrolic units linked through a methine bridge, complexated with boron(III) fluoride. These dyes possess usually a strong fluorescence, absorbing light in the visible range, and are known for their remarkable photophysical properties, gaining recognition as one of the highly versatile fluorophores with increasing popularity. Herein is presented a conspectus on the field of BODIPY dyes, where emphasis is set on their preparation and functionalization methods, along with more detailed examples on several promising applications with 165 references provided. Some synthetic details on the preparation of state-of-the-art compounds are given as well.

Keywords: Biolabeling, Bodipy, Boron dipyrromethene, Dyes, Fluorescence, Methine bridge, Pyrrole, Sensors, Solar cells.

INTRODUCTION

The 4,4'-difluoro-4-bora-3a,4a-diaza-*s*-indacene dyes, or BORON DIPYRROMETHENES, *aka* BODIPY dyes, are structures based on two pyrrolic units linked through a methine bridge, complexated with boron(III) fluoride, possessing π -electron conjugation. This structure can be illustrated as a boradiazaindacene, being considered as an indacene family member, with similar number assignments for any substituents, according to IUPAC rules.

The numbering of the related dipyrromethane and dipyrromethene systems is depicted in Fig. (1). While for a dipyrromethane and dipyrromethene these are identical, the boron complex is different, in analogy with indacene. In all three cases, the central carbon is considered the *meso*-position, arising from porphyrin nomenclature. Also, the positions adjacent to the nitrogen atoms are called α -positions, while the others are β -positions.

These compounds are dyes that generally absorb light in the visible range, and are often highly fluorescent [1, 2], having no charge. Their complexes are very stable,

only decomposing in strong acidic and basic conditions [3], possessing also low toxicity [4].

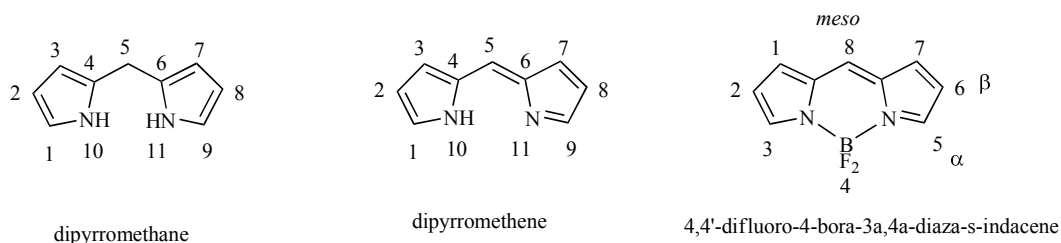
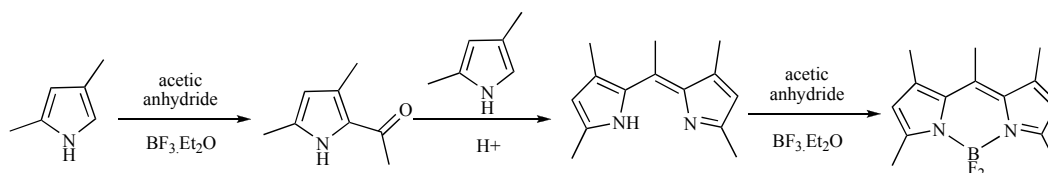


Fig. (1). Dipyrromethene system numbering.

SYNTHESIS OF BODIPY DERIVATIVES

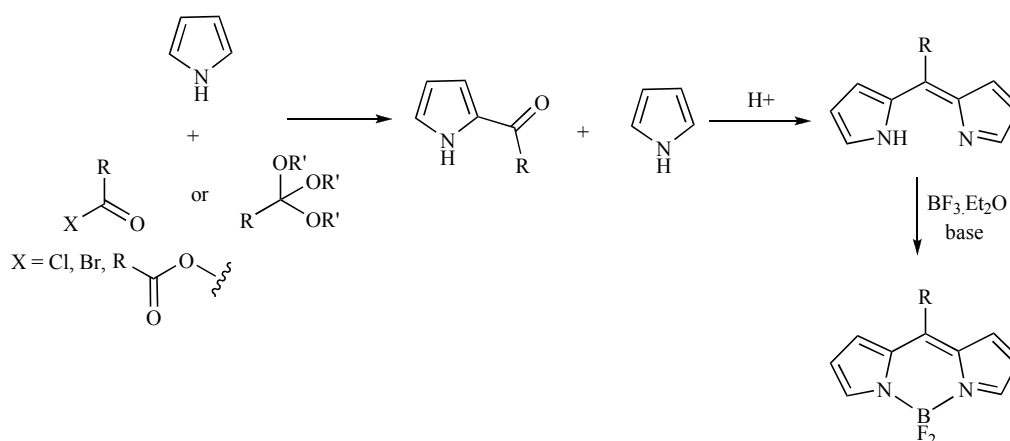
In 1968, Treibs and Kreuzer [5] tried to perform the acylation of 2,4-dimethylpyrrole with acetic anhydride, using boron trifluoride as Lewis acid, instead they obtained a highly fluorescent compound (Scheme 1). These findings however did not cause much interest at that time, and it was only in the end of the 70's-80's that this chemistry flourished [6 - 8]. When the biological labeling potential of these dyes was acknowledged [9, 10], various new BODIPY-type dyes were then designed and even commercialized [11].



Scheme (1). Synthesis of boron difluoride dipyrromethene.

There are two distinct synthetic approaches to prepare BODIPYs [12 - 14]. One is based on the reaction of pyrrole with an acylium equivalent, which can be an acid halide [15, 16], anhydride [17] or an orthoester [18] (Scheme 2). The intermediate acylpyrrole is frequently used further without isolation, reacting with an excess of pyrrole under acidic conditions to form the dipyrromethene. This approach allows the synthesis of asymmetric dipyrromethenes and, as an isolated acylpyrrole can be conjugated with a structurally different pyrrole unit under acidic condensation, which leads to the formation of the corresponding BODIPY dye, using an excess

of base and boron trifluoride etherate.



Scheme (2). Synthetic approaches to prepare BODIPYs.

Burgess [19] discovered, in 2008, that the second pyrrole equivalent is sometimes unnecessary for the dipyrromethene formation. He postulated a mechanism for the reaction, in which phosphorus oxychloride could substitute the aldehyde's oxygen, yielding a chlorinated azafulvene, which could be further reacted with the second pyrrolic aldehyde. Dipyrromethene could be obtained after chloride anion nucleophilic attack. This mechanism is only plausible in the case of 2-substituted pyrrole aldehydes, but the yields are exceptionally high, due to the fact the reaction is a one pot procedure and requires less purification procedures.

The other route, mostly followed by researchers, lies in the synthesis of the starting dipyrromethene unit by pyrrole condensation reaction, originated from the well-known porphyrin chemistry. In this case a carbonyl compound possessing high electrophilicity (aldehyde, acyl chloride or anhydride) leads to the formation of a methine bridge between two commonly substituted pyrrole units at 2- (or 5-) positions, to prevent polymerization. If a naked dipyrromethene is intended, an excess of pyrrole is needed to obtain satisfactory yields [20, 21]. Complexation of BF₃·Et₂O using a base, *e.g.* amine [15, 22], originates the symmetric F-BODIPY dyes (Scheme 3). 8-Substituted BODIPY's (substituted at the *meso*-position) are relatively easy to synthesize *via* this type of condensation of pyrroles with acyl chlorides [15, 16].

Dendrimers as Top Materials

Abstract: Dendrimers are monodispersed macromolecules, also known as cascade molecules, arborols or starburst polymers. The term dendrimers derives from the Greek language (*dendron* = tree, *meros* = part) and exploits two qualities that are frequently observed in many naturally occurring systems: globular structure and polyvalence. Herein is presented a conspectus on the field of dendrimers, including preparation and functionalization methods, as well as detailed examples on several promising applications with 291 references provided. Some synthetic details on the preparation of state-of-the-art compounds are given as well.

Keywords: Dendrimers, Drug delivery, Nanocarriers, Nanocatalysts, Starburst polymers.

INTRODUCTION

Dendrimers are also known as cascade molecules, arborols or starburst polymers. The term dendrimer (Greek: *dendron* = tree, *meros* = part) describes the architecture of this type of molecules. Dendrimers exploit two qualities that are frequently observed in many naturally occurring systems: globular structure and polyvalence [1 - 3].

Branched polymers have been known for many years, however, the control of their branching has always been considered an issue in polymer synthesis. Their are a class of polymers intermediate between linear and network polymers. In the early 1940's, observations of what appeared to be three-dimensional macromolecules were described theoretically and experimentally by Flory [4, 5], who received the Nobel Prize for Chemistry, due to his work on the design of linear and non-linear polymer chemistry in 1974.

The synthesis of polymers containing a controlled number and position of branches is a more recent phenomenon. The synthesis of both star and comb polymers have been reported during the last few decades [6]. Star polymers

possess a single focal point from which emanates a number of arms [7, 8], while comb polymers are produced when the arms are attached to a polymer backbone (Fig. 1) [9, 10].

The exponential evolution of synthetic dendritic polymers has resulted in the creation of two classes of branched macromolecules, specifically dendrimers and hyperbranched polymers [11, 12]. The later class encompasses irregularly branched structures that have varying degrees of branching and are polydisperse in size and structure [13]. On the other hand, dendrimers are usually defined as perfectly branched, monodisperse macromolecules [1]. Dendrimers are normally synthesized using a repetitive sequence of several reactions, frequently coupled with purification actions. A dendrimer encompasses three distinctive regions: the core, the interior branching units and the terminal or end groups (Fig. 2). The number of layers within a dendrimer is usually described as the generation (G) of the structure.

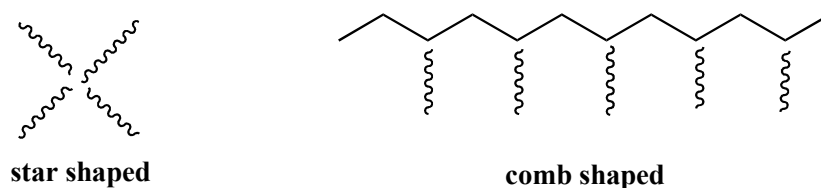


Fig. (1). Star and comb polymers.

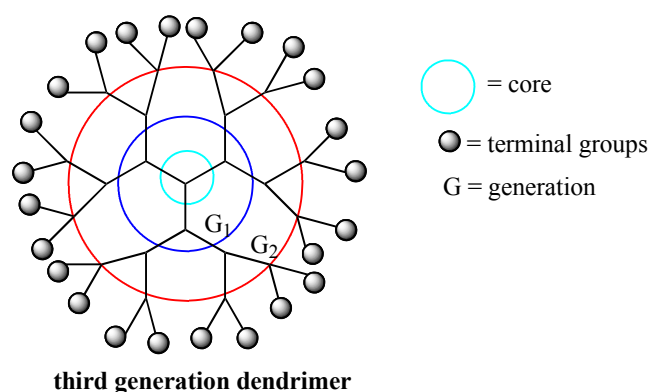


Fig. (2). Dendrimer schematics.

Dendrimers were first reported in 1978, named as “cascade molecules”, by Vögtle [14], who acknowledged the analogy with a waterfall, as a cascade (poly(propylene imine) dendrimer) (Fig. 3) [15]. The methodology for preparing these cascade molecules [16 - 18] consisted of two steps; i) Michael addition in which a diamine becomes a tetranitrile and ii) nitrile reduction to primary amines. This sequence of reactions could be taken repetitively to obtain regularly branched molecules bearing several arms. Regardless of the novelty, the growth on research on this type of molecules was hampered by synthetic and subsequent purification difficulties.

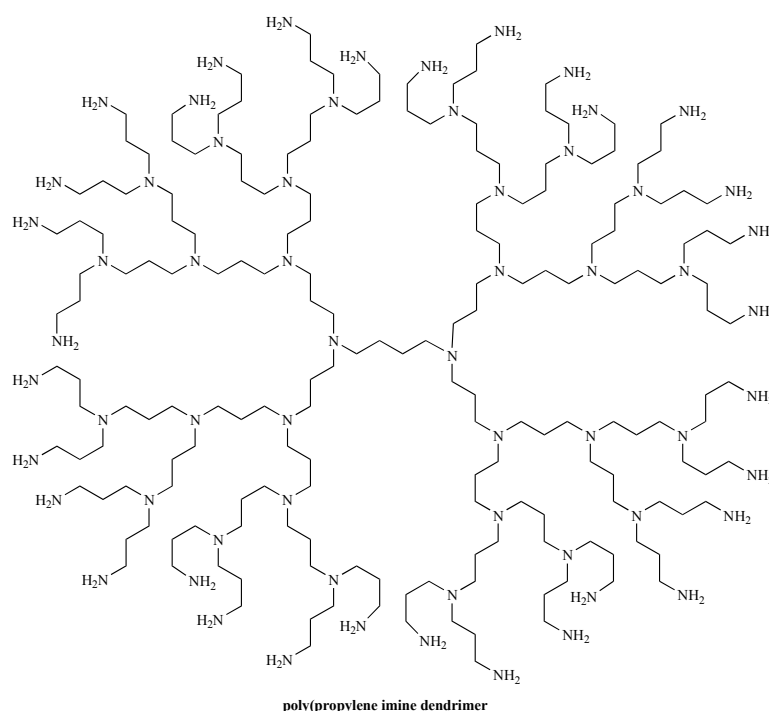


Fig. (3). Poly(propylene imine) dendrimer (PPI).

Later, in the 80's, progress continued with Denkewalter (polylysine [19]) and Maciejewski (dense cascade-like polymers [20]). It was not until 1985 that Tomalia synthesized the first branched “starburst” polyamidoamine (PAMAM) molecule (Fig. 4) [21] and coined the name *dendrimers* [21 - 23], which were also the first commercially available ones (Starburst™ polymers) [24]. In the same year, Newkome [25] synthesized the so-called “arborols”; hydroxyl-terminated

Carbon Allotropes as Top Materials

Abstract: Carbon is the basic element of organic materials. Depending on how the carbon atoms are bonded, carbon-based systems can be divided into groups with different physical and chemical properties. As both the widely diamond and graphite carbon allotropes are of natural sources, the main interest here discussed will be regarding the other main existing forms of carbon arising from laboratory practice, which are the fullerenes, carbon nanotubes and graphene. Herein is presented a conspectus on the field of the above mentioned synthetic carbon allotropes, where emphasis is set on their preparation and functionalization methods, along with more detailed examples on several promising applications with 770 references provided. Some synthetic details on the preparation of state-of-the-art compounds are given as well.

Keywords: Capacitors, Carbon allotropes, Carbon nanotubes, Fullerenes, Functionalization of carbon nanotubes, Functionalization of fullerenes, Functionalization of graphene, Graphene, Graphene oxide, Fuel cells, Sensors, Solar cells.

INTRODUCTION

Carbon is the basic element of organic materials. The great interest in carbon materials fundamentally originates from a variety of chemical bonding styles, which has never been seen in other elements [1, 2]. Each carbon atom possesses six electrons occupying $1s^2$, $2s^2$, and $2p^2$ atomic orbitals. As a result, a carbon atom may assume three different bonding configurations, sp , sp^2 , and sp^3 [3]. Depending on how the carbon atoms are bonded, carbon-based systems can be divided into groups with different physical and chemical properties.

The specific carbon hybridization and its binding to surrounding atoms determine the type of allotrope assumed. sp^3 hybridized carbon possesses tetrahedral lattice (diamond), while sp^2 hybridized carbon may produce buckminsterfullerene, carbon nanotubes or graphite, depending on the conditions in which it is formed.

Graphite and diamond are known since primeval times, but it was only in the nineteenth century that the structural difference between diamond and graphite was clarified [4], while buckminsterfullerene and carbon nanotubes have only been discovered within the last twenty years, and are just beginning to be understood. Although the theoretical calculations about graphene properties existed for many decades and graphite thin film has been grown by all types of methods over decades, interest in this material was ignited by two independent reports, published in 2004. de Heer [5] demonstrated that ultrathin epitaxial graphite films grown on SiC with 2D electron gas behavior could be patterned *via* conventional lithographic techniques.

Each of the graphitic materials possesses different dimensionality (Fig 1). The two-dimensional graphene can be considered as the "mother" of all other dimensionalities, *i.e.* fullerenes (0-dimension), carbon nanotubes (1-dimension) and graphite (3-dimensions) [6].

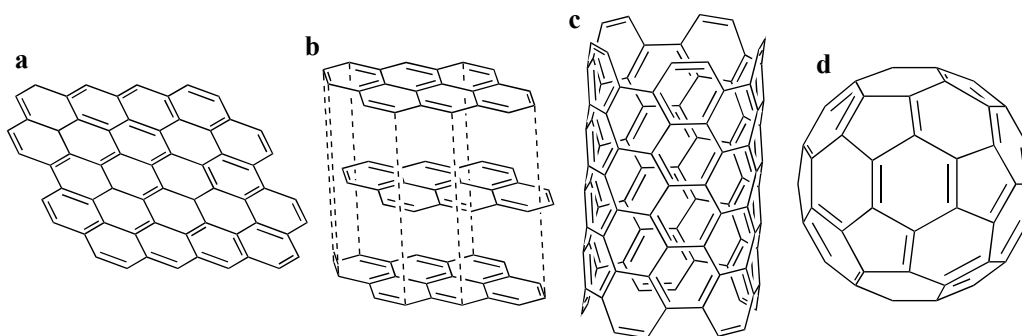


Fig. (1). (a) graphene; (b) graphite; (c) carbon nanotube; (d) fullerene.

As both diamond and graphite carbon allotropes are of natural sources, the main interest here discussed will be regarding the other main existing forms of carbon, which arise from laboratory practice, fullerenes, carbon nanotubes and graphene.

Buckminsterfullerene, C_{60} , was named after Buckminster Fuller, inventor of the geodesic dome), was discovered by Smalley, Kroto and Curl in 1985 [7], being awarded with the Nobel Prize in Chemistry in 1996 for those discoveries [8]. However, C_{60} has a pre-history. In 1970 Osawa, a Japanese chemist reported about

a molecule that would be consisted of 60 carbon atoms [9]. It would be, he guessed, a spherical, stable molecule with soccer ball shape, later discussing its probable theoretical aromatic properties in more detail [10]. Also in theory, Gal'pern and Bochvar published a study in 1973 bringing up these structures [11].

About a decade later, Orville L. Chapman initiated its intents to synthesize C_{60} [12]. While Chapman and his colleagues were working on attempted syntheses of C_{60} , Smalley and his group were busy with a completely distinct subject, the study of atomic clusters. They used a self-made device in which laser energy was used for vaporization of an element sample, having no interest in carbon until a visitor, Kroto, suggested the use of their device to direct light on some carbon clusters detected by Smalley. When performing the experiment, the researchers observed an atypical concentration of carbon clusters, spontaneously self-assembled from hot nucleating carbon plasma [7].

After this acclaimed disclosure, the unambiguous proof of the soccer ball structure still remained opened. Several groups made crucial contributions [13 - 15], including theoreticians [16, 17], but the ultimate thrust was given by Krätschmer's group, who succeeded in the first extraction of macroscopic quantities of C_{60} [18 - 20], igniting the explosive expansion of Fullerene Science [21 - 25]. In their milestone work, they produced carbon soot by carbon evaporation in He gas atmosphere and found macroscopic quantities of C_{60} in the soot. They also found that fullerenes are soluble in aromatic solvents (*e.g.* benzene and toluene) and C_{60} crystals, named fullerite, could be grown from the solution as the solvent evaporated. These properties were used to separate C_{60} , C_{70} and other molecules from the other non-soluble forms of carbon products, using chromatography [26]. At last, nuclear magnetic resonance (NMR) study using the mass-produced C_{60} clearly demonstrated that the C_{60} actually has the soccer ball structure [27]. Later, in 1991, Haddon reported the first evidence that the fullerene solids could be doped by the alkali metals [28]. They grown thin films of C_{60} after first attaching electrical leads to the glass substrate and when exposing the film to a flux of alkali metal atoms, they found that the resistivity dropped with exposure time, reached a minimum, then increased and ultimately saturated. Among the properties of the doped fullerene solids, named fullerides, the most attention from the physics community was the appearance of superconductivity. For $Rb_1Cs_2C_{60}$, a rather high

Organic Frameworks as Top Materials

Abstract: Organic frameworks are interconnected networks of channels, created in order to obtain stable rigid one-, two-, or three-dimensional pore structures, having well-ordered structures and uniform pore sizes. Hence, herein is presented a conspectus on the field of organic frameworks, namely covalent-organic frameworks (COF) and metal-organic frameworks (MOF), including their preparation, as well as detailed examples on several promising applications with 300 references provided. Some synthetic details on the preparation of some state-of-the-art compounds are given as well.

Keywords: COF, Covalent organic framework, Energy storage, Gas adsorption, Metal organic framework, MOF, Separation technologies, Porous catalysts.

INTRODUCTION

Porous solids are classified as microporous, mesoporous and macroporous, according to the size of the pores [1]. Solids with a pore size of 2 nm or below are known as microporous [2]. The mesoporous solids are in the range of 2 nm – 50 nm and above 50 nm are known as macroporous [3, 4]. For instance, zeolites, which are crystalline aluminosilicates, are the main example of microporous materials [5, 6]. Usually zeolites occur as natural minerals, but a considerable number of synthetic zeolites might also be synthesized and are used in various applications [7 - 10]. Regardless of their widespread use, zeolites have several potential drawbacks that hamper their utility as porous solids. Those drawbacks include syntheses that can be difficult to control, a limited number of structural and channel architectures that are available, and crystalline structures based on covalently-bonded networks of atoms that cannot be modified easily to vary the structures, topologies or properties of channels without altering the structure of the zeolite. The micropore presence ($d < 2$ nm) leads to quite high surface areas (>1000 m²/g). Gas adsorption (usually nitrogen at 77 K) is commonly used to measure the surface areas in polymer networks and are determined using

Brunauer–Emmett–Teller (BET) [11] or Langmuir [12] theories, the most frequently used approach the BET theory [13].

In order to obtain an accessible stable pore structure, an interconnected channels network should be formed, using rigid building blocks to avoid collapsing the networks, being reported years ago [14]. Rigidity is frequently ascribed to aromatic monomers, either linked by other rigid groups or directly linked together [15, 16]. Porous polymer networks can be of two types: crystalline and amorphous networks. Amorphous networks can possess a broad pore size distribution and a structure statistically disordered, while crystalline networks possess structures that are well-ordered and pore sizes that are uniform [17]. This chapter will be dealing with examples of the latter category, which for instance include covalent organic frameworks (COFs) or metal-organic frameworks (MOFs). MOFs can be seen as inorganic zeolites' organic analogs, where oxygen atoms are swapped by metal ion linking rigid organic ligands. The resulting crystalline solids are comprised of rigid frameworks of molecules coordinated to metal ions in one, two and three dimensional open networks (Fig. 1), providing high porosity for the crystalline structure. MOFs modulation depends on the ligand's chemical structure and the properties of the connecting metals [18].

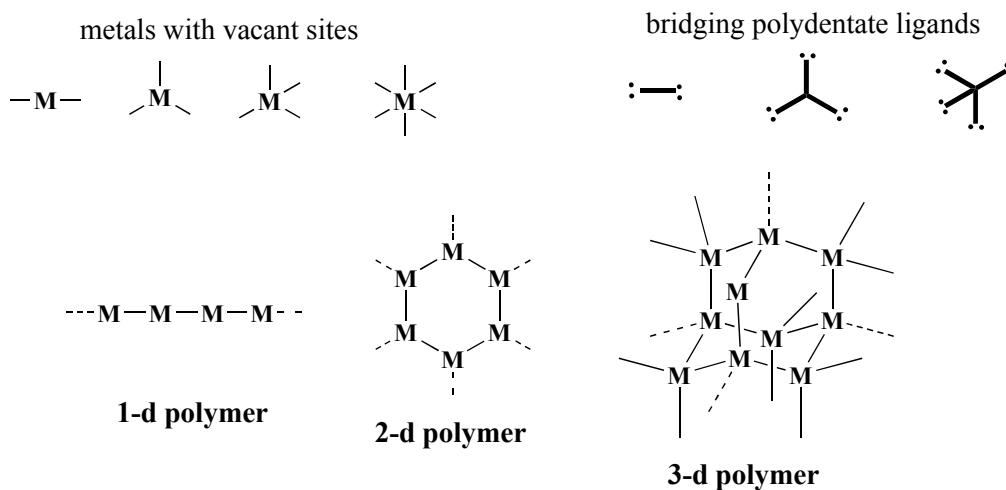


Fig. (1). Modular principle for the formation of coordination polymers.

In a large amount of cases, MOFs also exhibit permanent porosity and high thermal stability to above 300 °C, high dimensions and possess tunable properties (*e.g.*, hydrophobicity, exposed functionality, reactivity), channels can be controlled by synthetic modification of the ligand either before or after the MOF preparation [19 - 25].

In literature we can find several derived acronyms: IRMOF (IsoReticular MOF), MMOF (Microporous MOF), ZIF (Zeolitic Imidazole Framework), PCP (Porous Coordination Polymers), MOP (Metal Organic Polyhedra), CP (Coordination Polymers) and PMOF (Porous Metal Organic Framework) [26 - 31]. To organize and describe MOFs structures, a nomenclature system has been created and can be found at the Reticular Chemistry Structure Resource [32, 33].

The name coordination polymer was used for the first time in 1916 [34], but it was impossible to demonstrate the veracity of the structure at that time. Later in 1936, the well-known Prussian Blue compounds, based on Fe-CN-Fe linkages, were introduced in literature, however without assuming their three-dimensional coordination framework [35], which was not known at that time. Only in the end of the 1980's-early 1990's, new reports were made by Robson [36 - 38]. Immediately after, materials with polymeric structures based on organic bridging ligands and metal ions have been reported by Moore [39, 40], Yaghi [41] and Zawarotko [42].

The first sanctioned "MOF", denoted as MOF-5, was synthesized by the group of Yaghi in 1999 [22]. MOF-5 consists of Zn_4O tetrahedra clusters connected with each other by 1,4- benzenedicarboxylate organic linkers. Since then, this seminal paper triggered the field of organic frameworks, and a large number of reports appeared in the literature [27, 43 - 52]. Among the several remarkable structures have been reported, MOF-177 [52] and MIL-101 [51] are exemplary, having surface areas of 5640 m²/g and 5900 m²/g respectively. Nowadays, many other mesoporous MOFs with very high surface areas have been reported [51, 53 - 56].

Most MOFs are constructed from metal carboxylates bearing divalent (*e.g.* Cu^{2+} , Zn^{2+}) or trivalent (*e.g.* Cr^{3+} , Al^{3+}) cations, interlinked by different organic fragments. The rigid building block assembly process is called reticular synthesis

Nanoparticles as Top Materials

Abstract: Nanoparticles are particles more than one dimension smaller than 1 micron. Theoretically, any metal is a candidate to produce metal nanoparticles. However, certain metals are more prone and advantageous for metal nanoparticle synthesis. Hence, herein is presented a conspectus on the field of metal nanoparticles, including the preparation and functionalization of the most representative types of metal nanoparticles, as well as detailed examples on several promising applications with 646 references provided. Some synthetic details on the preparation of some state-of-the-art compounds are given as well.

Keywords: Biomedical applications, Drug delivery, Gold nanoparticles, Magnetic nanoparticles, Metal nanoparticles, Nanocatalysts, Quantum dots.

INTRODUCTION

Nanomaterials generally refer to materials on the nanometer scale, usually in the 1-100 nm range, which exhibit superior properties compared to their bulk counterparts. This aspect of nanotechnology is closely related to all science disciplines, particularly in the field of chemistry. In nanochemistry, chemists use a chemical approach and the tool of synthetic chemistry to assemble individual atoms or molecules into nanomaterials in a size and shape - controlled manner [1 - 5]. With the knowledge of coordination chemistry, the surface properties of nanomaterials can be modified to suit the applications in various fields. Of particular interest is utilizing the large active surface area provided by nanoparticles in organic transformation reaction and organic synthesis [1, 6 - 9]. Nanoparticles are particles as small as ~0.2 nm possessing high surface energy, spatial confinement and reduced imperfections and large fraction of surface atoms.

Faraday reported, for the first time, the optical properties of nanometer-scale metals in 1857 [10], where he described a method for preparing aqueous gold colloids by electrical discharge. Maxwell-Garnett attempted to theoretically

describe the colors of metal nanoparticles in 1904, using the theory of Lorenz and Rayleigh [11]. Later, Mie performed a thorough theoretical study on the optical properties of metal particles [12], applicable to spheres of any size.

In 1960, the famous talk of Richard Feynman [13] allured scientists for the nanotechnology field, with his premonitory words “*there is plenty of room at the bottom*” and then, in the 1970s, the term *nanotechnology* was created [14] and remarkable progress and new discoveries in the “nanoworld” followed – often resulting in a Nobel Prizes for the respective scientists. Since late 1970’s and early 1980’s, several groups became interested in “the neglected dimension between atoms or molecules and bulk materials” [15 - 18], followed by some convergence of perspectives in the 1990’s. The use of nanoparticles in the preparation of bigger structures is yet in its early years. Pileni established the metal nanoparticles ability in producing ordered lattices [19], while Schiffrin reported the synthesis of highly ordered lattices with two dimensions [20].

Theoretically, any metal is a candidate to produce metal nanoparticles. However, certain metals are more prone and advantageous for the synthesis of metal nanoparticles. Among them, gold nanoparticles have been highly studied [21]. Other metal nanoparticles include the ones based on silver, iron, copper, cobalt, nickel, platinum, palladium, rhodium and aluminum [22 - 32]. Also various nanometric metal oxides have been prepared, the most common ones, being titanium dioxide, zinc oxide and silica. Other metal oxides are also produced, including iron, cerium, zirconium, copper, nickel, aluminium, yttrium, barium, manganese, antimony and oxides [22 - 24].

One of the most studied types of nanoparticles is the magnetic nanoparticle type. Superparamagnetic nanoparticles are small (typically 5-500 nanometers) iron, cobalt or nickel based crystals, characterized by possessing a large magnetic momentum in the presence of a static external magnetic field [33 - 36].

Last but definitely not least, quantum dots have emerged, during the past years, as an exciting field of research, commonly being combinations of periodic table Group II and IV or Group III and V elements and are nanometer-sized semiconductor nanocrystals or crystals of inorganic semiconductor. Quantum dots

possess exclusive electronic and optical properties with 1-10 nm of diameter. They can, for instance, absorb ultraviolet or white light, with emission at a precise wavelength a few nanoseconds later [37].

For instance, there is a significant fluorescence dependence of the wavelength on the material composition and nanocrystal dimensions, which is consequence from using materials with different band gaps: CdSe (blue), InP (green) and InAs (red). The fluorescence emission fine-tuning is also controlled by the quantum dots size.

Quantum dots exist since more than 2000 years ago, when the Greeks and Romans used these materials as cosmetics [38]. In the beginning of the 20th century, red-yellow colors could be obtained by inclusion of CdSe and CdS into silicates [39]. In 1982, Efros [40] postulated that by changing CdS_xSe_{1-x} stoichiometry or size, the effect of quantum size could control the glass color.

Later, Brus [41] discussed the color change in semiconductor colloidal solutions. This booming research field has flourished, with theoretical and experimental research [42 - 50], also paying attention to commercialization efforts [51, 52].

Nanoparticles can be classified by their morphology, composition, dimensionality, agglomeration and uniformity [53]. It is useful to classify nanoparticles based on their number of dimensions: i) 1D nanomaterials have one dimension and are characteristically surface coatings or thin films (monolayers); ii) 2D nanomaterials are two-dimensional nanomaterials.

These include nanopore filters used for small particle separation and filtration or 2D nanostructured films, with nanostructures firmly attached to a substrate; iii) 3D nanomaterials have three dimensions, including free nanoparticles and colloids.

SYNTHESIS OF NANOPARTICLES

Metal Nanoparticles

Nanoparticles may be produced by various methods (Fig. 1). Some of them are bottom-up methods (chemical methods), *i.e.* construction from smaller synthons, and involve precursor decomposition for atom formation, followed by atomic

Future Prospects

Abstract: A property vs application analysis is herein carried out, using the materials focused in this book, recapitulating: phthalocyanines, polymethines, porphyrins, BODIPYs, dendrimers, carbon allotropes, organic frameworks and nanoparticles. Their own unique characteristics can be scrutinized, in order to, at least from a prospect point to view, anticipate the best property-application associations, with basis on their structure-property relationships for the most important applications.

Keywords: BODIPYs, Carbon allotropes, Dendrimers, Nanoparticles, Organic frameworks, Phthalocyanines, Polymethines, Porphyrins, Structure-property.

The establishment of highly accurate structure-property relationships is the one of the most important aspects when designing any new materials for any applications. Each application should, in an ideal model, match the best material, *i.e.*, one should predict, to the best possible approximation, which materials should chosen for any envisaged application.

This structure-property relationship can be perfected by several approaches, such as computational modeling, empirically, or by molecule screening. The computational modeling approach trusts the outcome of software for property prediction, usually based on existing or purposely created databases, relying on theoretical aspects of the structure, reactivity and properties. On the other hand, the empirical approach uses the observation outcome of experiences carried out on determining any property, related to a given application. Finally, the screening approach relies on the initial preparation of a set of molecules, closely related to each other, followed by application testing to obtain a certain number of “proof of concept molecules”.

Nonetheless, the best approach is the one that manages to comprise parts of each of the above mentioned in a single approach. This way a researcher can extract the best outcomes, in a selective manner, where the theoretical knowledge can

symbiotically function with empiricism and screening. The best way is to flag a property or a set of properties for a certain application that requires them, in order to be distinguished as a useful application.

In the next paragraphs, a property *vs* application analysis will be carried out, using the materials focused in this book, recapitulating: phthalocyanines, polymethines, porphyrins, BODIPYs, dendrimers, carbon allotropes, organic frameworks and nanoparticles. Their own unique characteristics can be scrutinized, in order to, at least from a prospect point to view, anticipate the best property-application associations, with basis on their structure-property relationships for the most important applications.

CATALYSIS APPLICATIONS

For instance, application in catalysis requires compounds which fulfill certain requirements, such as inertness during application, structural features that allow effective reaction acceleration and recyclability. Moreover, the typically used homogeneous catalysis has turned into a more environmentally concerned heterogeneous catalysis, which is nowadays of paramount importance for a variety of research areas, from chemistry to energy, always thinking in an industrial prospect, as well. Thus, added to the aforementioned requirements, the best catalysts for any given catalytic application should also be easily recoverable.

Aiming on these premises, catalysts that are easier to immobilize onto/into any type of supports are the most promising ones. There are many possible supports, from organic, such as polymeric ones, or inorganic, such as based on silicates, among others, as well as several ways to immobilize the catalysts, from adsorption, covalent linkage or encapsulation.

Tetrapyrrolic macrocycles (porphyrin and phthalocyanine derivatives) are appealing molecules to be used in catalysis, since they can be straightforwardly fine-tuned. Both types of compound have already proven their worth in homogenous catalysis, but there is yet much to be established, regarding their use in heterogeneous catalysis. This means, as well, that there are plenty of possibilities ahead. For instance, they are very suitable from hosting metals in their cavities, which opens the possibility to use them in direct and asymmetric

transition metal catalysis. Another possibility deals with their photosensitizing abilities, which makes them good candidates to be used in photocatalysis, mostly in oxidation reactions.

These macrocycles are also capable to be properly modulated to be linked to several supports, allowing a facilitated posterior separation from catalytic reaction mixture. As stated above, many supports are possible to be used. The main rule is that these supports stand inert during the course of reaction. The polymeric supports are quite useful, but since they are mostly from organic origin, one must prevent their reactivity, hence their stability during reaction. More stable, carbon allotropes are also quite promising supports for several types of reactions, provided that their functionalization process does not interfere afterwards with the catalytic reactivity, hence their inertness. On the other hand, supports of inorganic nature are more stable against harsh conditions, ensuring their inertness. As possible candidates, we can find double layered hydroxides, silicas, metal oxides, aluminium-silicate mesoporous materials, and nanoparticles, particularly magnetic nanoparticles. The last ones, without a doubt are probably the most promising, for their superior ease of recovery, specially the magnetic nanoparticles, which can easily be recovered by simple application of an external magnet.

Dendrimers are also good candidates as catalysts, since they mostly keep the advantages of homogeneous catalysts, when properly modulated to encapsulate appropriate catalyst synthons inside their branches or the branch endings. Their size makes them suitable for heterogeneous catalysis in the sense that, due to the simplicity in recovering the catalyst by ultra-filtration, after precipitation. Similarly, organic frameworks (metal or organic) are also pivotal candidates, both due to their size and ability to hold a variety of suitable metals for acting as catalysts, displaying the same straightforwardness in recovery and reuse. Finally, metal nanoparticles, as its name points, are of extreme use as catalysts, having features such as very large surfaces of contact, and chemical stability, two key properties in heterogeneous catalysis.

SENSING APPLICATIONS

Another important application is in sensing of any specific analytes. Since most of

SUBJECT INDEX

B

Biolabeling 78, 212, 218, 235
Biomedical applications 42, 444
Biomedicine dyes 3
Bodipy i, 474, 530, 547, 550, 554,
556-559
Boron dipyrromethene i, 212, 235, 238,
240, 243

C

Capacitors 291, 318, 320, 374, 375, 382,
383, 395
Carbon allotropes i, ii, 291, 292, 296, 297,
338, 343, 351, 538-542
Carbon nanotubes i, 47, 58, 194, 291, 292,
294, 297, 300, 326, 329, 363, 400, 401,
541
COF 402, 405, 407, 416, 434, 443
Cyanines 78, 82, 86, 108

D

Dendrimers i, ii, 149, 150, 153, 207, 307,
351, 362, 451, 454, 542, 544, 545, 550,
552, 553, 558
Drug delivery 201, 245, 253, 260, 261,
266, 268, 324, 325, 332, 389, 394, 423,
444, 455, 465, 466, 471, 545

E

Energy conversion i, 25, 58, 113, 340,
364, 373, 374, 461, 501, 505, 521, 548,
557
Energy materials 3, 378, 390

F

Fluorescence 19, 35, 36, 74, 76, 100, 104,
105, 107, 145, 153, 160, 161, 163, 164,

211, 212, 231, 260, 264, 288, 325, 331,
333, 334, 387, 393, 400, 413, 414, 441,
446, 475, 477, 500, 518, 541, 544, 547,
552

Fullerenes i, 300, 308, 311, 312, 314, 316,
317, 322, 348, 349, 351, 505, 542

Functionalization of fullerenes 291, 349

G

Gas adsorption 402, 410, 437, 439
Gold nanoparticles 72, 412, 429, 434, 444,
445, 449, 481, 486, 491, 492, 502, 555,
557, 559

Graphene i, 291, 292, 299, 338, 377, 378,
381, 387, 458, 502, 515, 542, 545, 548,
556, 557, 559

Guel cells 291

I

Infrared dyes 78, 99, 104, 107, 243, 244

M

Magnetic nanoparticles 393, 444, 474,
482, 486, 493, 496, 497, 530, 540, 558

Metal organic framework 402, 404, 418,
425, 428, 437, 438

Methine bridge 212, 214

N

Nanocarriers 245, 260, 283, 286, 506, 558

Nanocatalysts 245, 270, 429, 444, 457,
472, 489, 491, 496, 529

Near infrared dyes 78, 107

P

Photocatalysis 47, 106, 113, 197, 321,
514, 536, 540

Photodynamic therapy 32, 33, 73, 74, 113,

Subject Index

129, 133, 154, 157, 184, 186, 187, 242,
285, 286, 316, 317, 334, 366, 367, 372,
373, 401, 507, 543, 559
Photosynthesis 195, 206, 309, 363, 505
Phthalocyanines i, ii, 88, 143, 169, 174,
175, 177, 184, 186, 187, 200, 208, 210,
224, 302, 306, 538, 539, 541, 542, 544,
546, 548, 557
Polymethines i, ii, 78, 85, 96, 97, 538, 539
Porous catalysts 402
Porphyrinoids i, 73, 113, 114, 179
Porphyrins i, ii, 3, 46, 47, 57, 59, 141,
143, 153, 155, 166, 210, 211, 256, 257,
275, 280, 286, 302, 309, 352, 418, 481,
505, 541, 542, 544, 552, 553, 555, 556,
558, 559
Pyrrole i, 78, 117, 118, 120, 122, 131,
158, 170, 171, 176, 328, 396

Q
Quantum dots i, 325, 394, 400, 483, 487,
543, 551

Future Trends for Top Materials 561

S
Sensors 13, 19, 20, 49, 50, 66, 110, 133,
138, 139, 142, 143, 191, 204, 205, 212,
218, 222, 237, 238, 243, 253, 259, 260,
278, 279, 291, 318, 321, 326, 329, 330,
376, 377, 384, 385, 391, 397, 398, 413,
414, 436, 455, 458, 460, 500, 504, 505,
516, 518, 530, 541
Separation technologies 402
Solar cells 14, 22, 24, 57, 58, 69, 70, 106,
110, 133, 150, 180, 181, 194, 195, 206,
207, 212, 218, 240, 241, 244, 257, 275,
276, 291, 308, 312, 318, 322, 323, 326,
331, 338, 364, 365, 369, 370, 378, 392,
393, 399, 401, 455, 461, 475, 479, 501,
505, 506, 520, 531, 532, 536, 537, 541,
542, 553, 559
Starburst polymers 245
Subphthalocyanines 3, 5, 21, 40, 45, 59,
67, 76, 169

U
Ultra violet dyes 78