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Review

Application of phthalocyanines in flow- and sequential-injection analysis and microfluidics systems: A review



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ABSTRACT

Phthalocyanines and metallophthalocyanines play a very important role in the metabolism of living organisms through biological pigments or biochromes and are therefore also employed in numerous applications in analytical chemistry. In flow-, and sequential-injection analysis and microfluidic systems the role of phthalocyanines and metallophthalocyanines is centered as either that of analyte or that of a reagent or modifier in the determination of other species. This paper covers the attributes of phthalocyanines and metallophthalocyanines complexes as enhancements in chemical analysis in flow- and sequential injection analysis and microfluidic systems and points out the advantages and disadvantages in the implementation thereof.

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1. Introduction

Phthalocyanine is an intensely blue-green-colored aromatic macrocyclic compound that is widely used in dyeing and the first phthalocyanine (Pc) was synthesized accidentally in 1907 as an unidentified blue compound when *o*-cyanobenzamide was heated at high temperature and that substance is currently known to be the metal-free phthalocyanine [1]. Furthermore copper phthalocyanine was also accidentally synthesized in 1927 [2] and in the same year, copper phthalocyanine was also discovered at Scottish Dyes, Ltd., Grangemouth, Scotland (later ICI). This was followed with the synthesis of the parent compound, phthalocyanine (Pc) by Linstead in 1934 [3] and the structure of the metal-free Pc elucidated experimentally by Linstead and co-workers in a series of publications in the same year [4–6]. The term phthalocyanine finds its origin in the Greek word ‘naphtha’ that means rock oil and ‘cyanine’ (that means dark blue). It was first used to describe this class of macrocyclic compounds by Sir Reginald Linstead in 1934 during his pioneering work on the subject [4–6]. Phthalocyanines (Pcs, Fig. 1) and metallophthalocyanines (MPcs) [7–9] play a very important role in human life since their discovery in the early nineteenth century and besides their role as colorful dye stuffs also have a wide variety of applications due to their diverse chemical, structural, electronic, and optical properties. Phthalocyanines and metallophthalocyanines are not only very useful in several innovative and emerging high technological applications like dyes, thermal writing displays, dye-sensitized photovoltaic solar cells, oxidation-, reduction- and photo-catalysis, membrane catalytic reactors, nonlinear optics and photonics, semiconductor materials, gas sensors and biosensors [10–23], but they also perform a very important role in photodynamic therapy (PDT) [7,24–35] a novel cancer treatment that is receiving increased attention and where the group of Tobello Nyokong [7,31–35] is very actively involved as a major role player. Phthalocyanines and metallophthalocyanines are also among the families of photosensitizers that are currently being scrutinized for antimicrobial photodynamic therapy applications [31–41] and a variety of photosensitizers from different groups including porphyrins, chlorophyll derivatives, phthalocyanines and azines have been effective in the photokilling of many Gram-positive and Gram-negative bacteria pathogens in addition to parasites, fungi, and viruses [37].

The phthalocyanines are basically structurally related to some other macrocyclic pigments, especially the porphyrins (Fig. 2) [42–44]. The common feature of these macrocycles is a basic structure consisting of 4 pyrrole-like subunits, which are linked in a circular manner by methine or azamethine bridges to form a 16-membered ring. The pyrrole-like rings within conjugated base of phthalocyanines (H_2Pc) are closely related to isoindole that are the building blocks of phthalocyanines. The spectral properties of phthalocyanines (Pcs) are central to their chemical and electronic properties and are governed by the

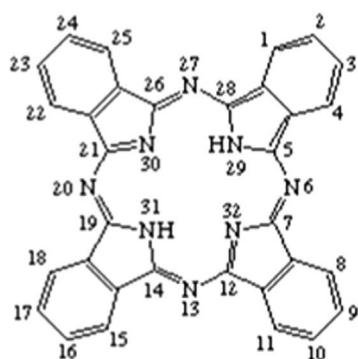


Fig. 1. Structure of basic phthalocyanine with IUPAC nomenclature. Reproduced from Ref. [9].

18π system of the most inner 16-membered ring. The intense blue-green color of phthalocyanines is due to the electronic delocalization of their 18π electrons making them very useful to be utilizing industrially as dyes and pigments, catalysts and photoconductors in various fields [7,20,21,31–33,42–48]. Dedicated specificity in many applications of phthalocyanines can be obtained by modification of the phthalocyanine ring or by changes in the central metal or axial ligands. Phthalocyanines furthermore also function as planar tetradentate dianionic ligands that bind metals through four inwardly projecting nitrogen centers [7,32,42,44].

The UV–vis absorption spectrum of metal-free phthalocyanines (Pcs), governed by the 18π system of the inner 16-membered ring, consists of an intense and energetic absorption band in the visible region near 670 nm, the so-called Q-band and a generally weaker band near 340 nm, the so-called Soret or B-band. Charge transfer bands between the central metal and the ring are also observed for some phthalocyanine complexes. The color of the phthalocyanine molecules is in general determined by the Q-band. The positions of the absorption bands in phthalocyanines, particularly the Q band, are affected to a varying degree by the central metal, axial ligation, solvents, peripheral and non-peripheral substitution, and aggregation and by extension of the conjugation. A change in the shape of the Q band occurs with a change in symmetry. However for highly red-shifted metallophthalocyanine complexes, the Q-band no longer determines the color [7,31]. It is well established that increasing expansion of the π -conjugation in phthalocyanines shifts the Q-band to the red [7,49]. Extension of the conjugation system is accompanied by change in color from blue/green to colors including brown, red, or purple. Kobayashi and co-workers [7,31,49] have performed extensive calculations on the molecular orbitals of the phthalocyanines and related molecules and have shown that red-shifting resulting from ring expansion is due to destabilization of the highest occupied molecular orbital (HOMO) [49]. Destabilization of the HOMO increases with addition of benzene units to the phthalocyanine ring in a linear fashion [49]. A π deficiency due to the presence of a thiodiazole, instead of benzene ring of the phthalocyanine unit, results in a blue shifting of the Q band. The lowering of the highest occupied molecular orbital (HOMO) is larger than that of the lowest unoccupied molecular orbital (LUMO), resulting in a larger HOMO–LUMO gap [50].

The importance of phthalocyanines and metallophthalocyanines is not limited to their valuable contribution as photosensitizers to photodynamic therapy and antimicrobial photodynamic therapy applications in health sciences and activities in dyes, dye-sensitized photovoltaic solar cells, electro- and photo-catalytic activities and

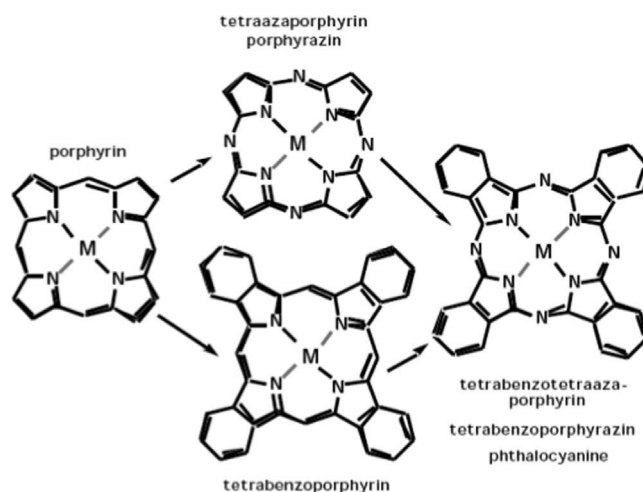


Fig. 2. Structural relationships between porphyrins, tetrabenzoporphyrazins, porphyrazines and phthalocyanines. Reproduced from Ref. [42].

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