# Synthesis, structure, and properties of new phthalocyanines

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**ABSTRACT:** Many low symmetry and/or deformed phthalocyanines (Pcs) have been synthesized, separated, and their spectroscopic and electrochemical properties elucidated in the last decade, mainly because of improvement in separation techniques of reaction mixtures and development of instruments and computers. In this overview, some advances in the chemistry of Pcs are surveyed. In recent years, many types of alkynyl Pcs, various isomers of low symmetry Pcs, severely sterically deformed Pcs, and chiral Pcs have been prepared and some of their properties are reproduced by quantum mechanical calculations, which have not been achieved previously. Also, in the field of Pc sandwich complexes, properties of hetero double- and triple-decker complexes can be compared, since many types of compounds are now available. Some hetrodinuclear planar dimers have also been reported in the last decade.

**KEYWORDS:** phthalocyanine, symmetry, deformation, spectroscopy, electrochemistry.

The first phthalocyanine (Pc) was synthesized accidentally in 1907 when *o*-cyanobenzamide was heated at high temperature [1]. In 1934, the structure of this metal-free Pc was elucidated by Linstead [2-4] so that the year 2004 is the 70th year after the confirmation of the structure of Pcs. Since then, monomeric Pcs have been used in many practical fields, and they are now called "the compounds of the 21st century" with this expectation, since they have a great diversity of possibilities [5].

The chemistry of low symmetry Pcs were elucidated some time ago. For example, tribenzo tetraazaporphyrin was reported as early as 1955 by Elvidge and Linstead [6], and tetrabenzotriazaporphyrin was synthesized in the late 1930s [7, 8]. Although not many researchers were engaged in the chemistry of low symmetry Pcs [9-11], this field underwent a revival by many Pc chemists when Luk'yanets [12], Leznoff [13], and Kobayashi [14, 15] independently reported the synthesis and intriguing spectroscopic properties of several low symmetry Pc derivatives around 1990. Since then, many papers have reported on the synthesis and properties of Pc analogues [9-11, 16]. Some representative examples are mentioned below. 1) Makarova *et al.* prepared opposite and adjacent diazatetrabenzporphyrin [12] and this is still the one and only paper which reports a clear separation of the two isomers. Although the former $D_{2h}$ type derivatives showed a well-split Q band, the latter $C_{2v}$ type species does not show a split Q band, and this has been explained theoretically [17]. 2) Leznoff and McKeown reported synthetic details leading to tetrabenzotriazaporphyrins [13] and these compounds showed electrochemical [18] and spectroscopic [19] properties closer to Pcs than to tetrabenzoporphyrins. 3) A ZnPc having $D_{2h}$ symmetry was reported in 1992 [15], and it showed a four-peak Q band different from the two-peak Q band of normal metal Pcs with $D_{4h}$ symmetry. 4) Pc analogues in which one benzene ring of the Pc is substituted with other aromatic rings or substituted benzenes are obtained by ring-expansion of what were first called subPcs in 1990 [14]; Since then more than a hundred papers have appeared on subPcs and low symmetry Pcs derived by this method [20, 21]. The resulting $C_{2v}$ type compounds generally show a split

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Q band due to lowering of the molecular symmetry, and the position of the Q band can be finely adjusted by the type and kind of introduced aromatic rings. 5) By comparing the electrochemical data and the results of molecular orbital calculations of a series of Pc compounds having different $\pi$ size, a solution was given to a long-standing question as to why the HOMO destabilizes, while the LUMO remains at essentially the same level upon ring expansion. That is, the coefficient of carbons of the HOMO is substantially large even on the fused benzene carbons while that of the LUMO is small. In other words, the HOMO spreads outward while the LUMO does not enlarge even if aromatic rings are fused to the periphery of the tetraazaporphyrins [22]. 6) The splitting and the shift of the Q band of Pc-like compounds synthesized from phthalonitrile and 2,3-naphthalonitrile can be explained by symmetry-adapted perturbation theory, but the NMR data of these compounds cannot be explained by a simple model [23, 24]. This idea also holds when two types of phthalonitriles are condensed to form low symmetry Pc derivatives [25]. 7) The chemistry of triazolephthalocyanines has been developed by Torres and coworkers [26]. Because of the lowering of molecular symmetry and the presence of the triazole ring, they show peculiar absorption spectra; the Q band lies at shorter wavelength and weak but the Soret band appears at longer wavelength than the corresponding Pcs. Furthermore, Torres and coworkers reported $D_{2h}$ type, expanded triazole compounds which can accommodate two transition metal ions in their cavity [27]. Since these type of compounds are 28 $\pi$ systems, it might be interesting to pursue their spectroscopic properties. 8) New Pc derivatives that have metal coordination sites on the Pc periphery, one of which is called gemini porphyrazine [28] have been designed by the group of Hoffman and Barrett. By coordination of metals to these sites, the absorption spectra change markedly (generally broadens), indicating that the perturbation by coordination of metal is quite significant. 9) The group of Hoffman and Barrett also succeeded in synthesizing what we call seco-porphyrazine [29], where a pyrrole ring of tetraazaporphyrin is opened. Although the $\pi$ system is one of the smallest among the porphyrin family, their Q band shifts to ca 700 nm when amino groups were linked to the opened ring. 10) Leznoff developed a novel route leading to unsymmetrical Pcs, which is now called "the polymer support method" [30]. This is a very clean system so long as a phthalonitrile unit can be linked to a polymer, since symmetrical Pcs produced in the reaction can be eluted out from the polymer resin. The chemistry of low symmetry Pcs have thus been extensively developed, and it appears more difficult to obtain new systems. However, it should be stressed that it is now possible to separate all compounds shown in Fig. 1 by use of high quality TLC plates

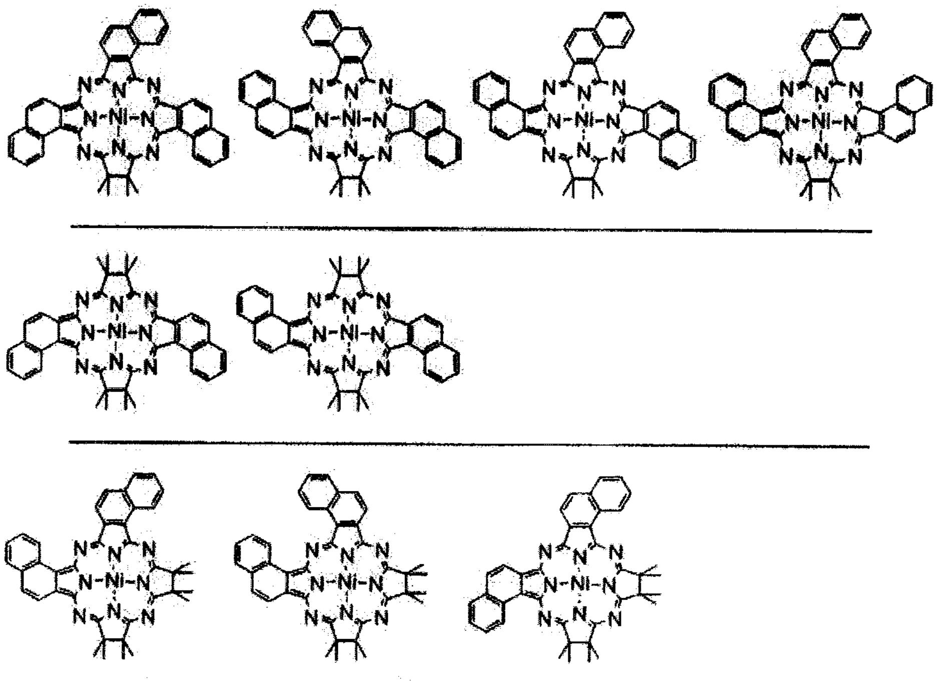

Fig. 1. Low symmetrical tetraazaporphyrins prepared from condensation between 2,3-dicyanonaphthalene and tetramethylsuccinonitrile

and HPLC [31]. New low symmetry Pcs, such as structurally distorted Pcs, have been reported in the past few years. These are attained by linking eight large or long substituent groups at the benzene ring closest to the Pc core. Cook's group was the first who reported these kinds of Pcs [32]. In particular, when eight alkylthio groups were used, the Pc became red in color because of the emergence of a band at ca. 500 nm [33]. In a similar manner, the use of phenyl groups also helps to severely distort the Pc plane [34]. When iron was inserted into its center and isocyanide groups were coordinated as axial ligands to form $D_{2d}$ FePc, it showed a charge-transfer band beyond the Q band, since the CT band which is forbidden in $D_{4h}$ symmetry became allowed [35]. Optically active Pcs are also becoming popular [36]. Representative examples include long alkyl chain- [37], small chiral ring- [38], helicene- [39], and binaphthyl-substituted Pcs [40, 41]. In addition, vibrational CD spectra of synthetic Pc derivatives were reported recently as the first example of VCD spectra for synthetic porphyrins and Pcs (Fig. 2) [42]. Chiral Pc enantiomers having rigid, non-aromatic small molecules give strong VCD signals. The introduction of linear triple bonds opened new fields in Pc chemistry. For example, Pcs containing eight triple bonds at the benzene ring furthest from the Pc core show red-shifted Q bands [43, 44], and triple bonds helped in synthesizing dimers and oligomers of Pcs [16, 45] in which the mutual positions of the constituting monomer unit are fixed. Planar homodinuclear Pcs were reported as early as 1986 [46]. Since then, several types of heterodinuclear Pc dimers have been synthesized [47]. Representative examples include Torres's hemiporphrazine ring-fused Pc [48] and Kobayashi's pyrazinoporphyrazine-fused Pc [49]. Both of these compounds show spectra different from the superimposition of the spectra of constituting monomers. In the field of heterodinuclear lanthanide sandwich Pc complexes, Jiang's group contributed considerably in the past several years. To date, they have succeeded in preparing heterodimers consisting of octaethylporphyrin (OEP), tetraphenylporphyrin (TPP) and its derivatives, Pc and naphthalocyanine (Nc) [50, 51]. It is particularly important to prepare a series of compounds to prevent mistakes, for example, in assigning

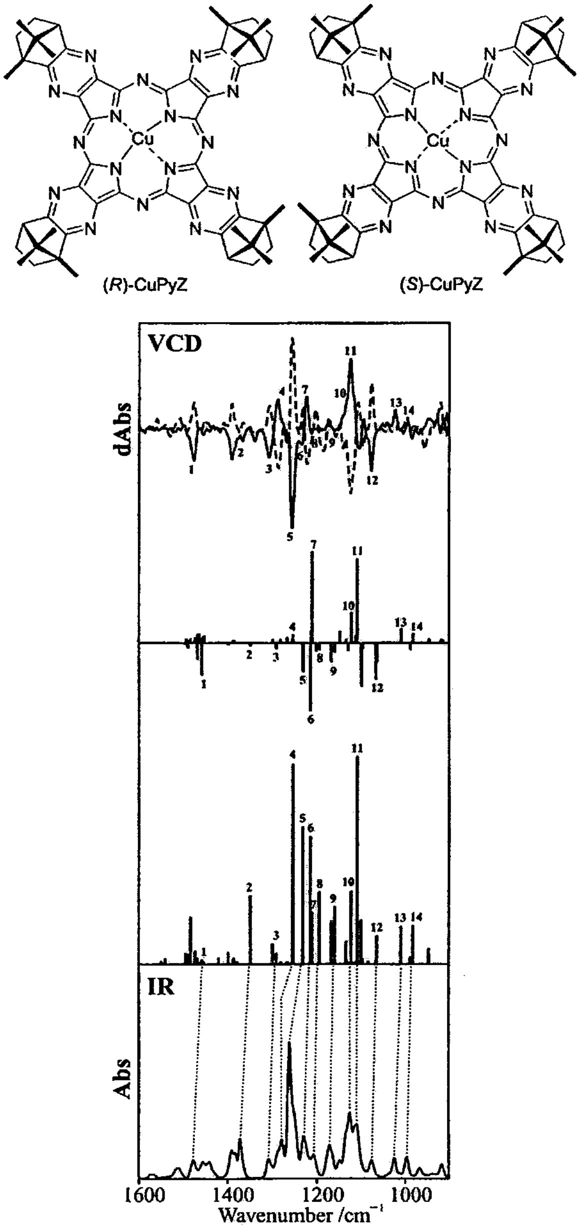

**Fig. 2.** Structures of (*R*)-(-)- and (*S*)-(+)-camphor-substituted tetrapyrazino-porphyrazines and their experimental IR (bottom) and vibrational CD (top) spectra (solid and broken lines for the *R* and *S* enantiomers, respectively), and calculated spectra (bars) in the 900 and 1600 cm$^{-1}$ region. For the vibrational CD spectra, calculation was for the R enantiomer. In the experimental and calculated spectra, the peaks and troughs with the same numbers correspond to each other. The calculated vibrational CD peaks 6 and 7 are very intense with opposite signs but these peaks appear as weak peaks in the experimental spectrum, probably due primarily to the cancellation effect resulting from the small energy separation

electronic absorption bands and redox couples, since gradual changes in properties are generally observed by the change of the ionic size of the central metal ion.

Other important areas of phthalocyanine synthesis include soluble polymeric Pcs [52], low temperature Pc synthesis [53], microwave Pc synthesis [54], Pc synthesis using hexadecachloro- [55] and hexadecafluorophthalocyanines [56], hexadecasubstituted Pcs [57], alkylperfluorosubstituted Pcs [58], macroporous Pc polymers [59] and Pc syntheses using hexamethyldisilazane [60] or cerium (III) [61].

Normally, phthalocyanines are simply flat two-dimensional molecules and it is true that conceptually new types of Pcs are getting harder to prepare. However, there are still many properties to be unraveled, if new types of Pcs are produced. Phthalocyanines have long been described in highly esteemed scientific journals. Thus, phthalocyanines have great versatility and are of great interest to many scientists and industrialists. We are hoping that more people become interested in the chemistry of Pcs. They are the compounds of the 21st century!

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