

Low Symmetry Phthalocyanines and Their Analogues

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1. Introduction

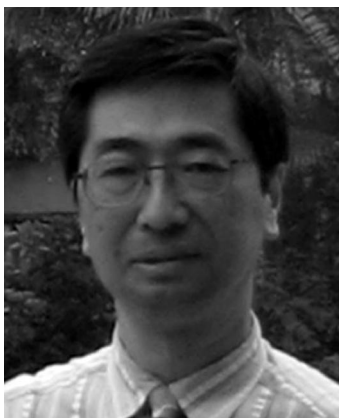
Phthalocyanines (Pc's)^{1–3} have been the focus of intense research interest ever since their initial characterization in the 1930s by Linstead and Robertson^{4,5} after the accidental formation of Fe^{II}Pc at a dye factory in Scotland during the industrial production of phthalimide from phthalic anhydride. Their high thermal stability, and low reactivity and solubility quickly led to extensive use in dyestuffs and as pigments in the textile, printing, and paint industries.⁶ In more recent times, there has been renewed interest in the use of Pc's in many high technology fields,⁷ including low-dimensional metals and semiconductors,^{8–14} photovoltaic and solar cells,^{15–17} electrophotography,^{18,19} molecular electronics and photonics,^{20–26} electrochromism in display devices,²⁷ gas sensors,^{14,28,29} liquid crystals,^{30–33} nonlinear optics,^{34,35} photodynamic therapy (PDT),³⁶ and electrocatalysis.³⁷

Pc synthesis has traditionally been based^{38–44} on cyclotetramerization reactions, primarily of phthalonitriles (1,2-dicyanobenzenes), but also of a variety of other precursors, such as phthalic anhydrides, phthalimides, 1,3-diiminoisoindolines, and phthalamides (Figure 1). The initial focus of Pc research was, therefore, primarily on radially symmetric compounds and on the effect of changes to the peripheral substituents at the α - and/or β -positions (Figure 2).⁴⁵ Modification of the number of peripheral fused benzene rings in the precursor resulted in a series of analogues including the porphyrazines (Pz's) (also commonly referred to as tetraazaporphyrins),⁴⁶ 1,2-⁴⁷ and 2,3-naphthalocyanines (2,3-Nc's),⁴⁸ and 2,3-anthracocyanines (2,3-Ac's)⁴⁹ (Figure 3). Pz's have been the focus of considerable research interest in recent decades,^{50–52} but Nc and Ac complexes⁵³ have received considerably less attention, since the presence of additional fused benzene rings makes the ligand more vulnerable to oxidative attack.⁵⁴ Radially symmetric analogues, such as fluoranthocyanine,⁵⁵ triphenylcyanine,⁵⁶ perylenophthalocyanine,⁵⁷ and phenanthrocyanine,⁵⁸ have also been formed by replacing the peripheral fused benzene rings with other types of fused ring systems, with some, such as the tetrapyrrodo-,⁵⁹ tetrapyrzino-,⁵⁹ thiopheno-,⁶⁰ and

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John Mack, born in Edinburgh, Scotland (1966), received his Bachelor's degree from the University of Aberdeen and his Doctor's degree from the University of Western Ontario, under the direction of Professor Martin J. Stillman. His graduate research focused on the MCD spectroscopy of phthalocyanine anion radical species. He carried out postdoctoral research in the laboratories of Martin J. Stillman and James R. Bolton at the University of Western Ontario and of Nagao Kobayashi at Tohoku University in Japan. He was an Assistant Professor and currently holds a research position at Tohoku University. His research interests are focused on studying trends in the electronic structure and optical spectroscopy of porphyrinoids.



Nagao Kobayashi, born in Nagano, Japan (1950), received his Dr. of Science degree from Tohoku University based on a study of the MCD spectroscopy of peroxidase and catalase. He later obtained a Dr. of Pharmacy degree based on a study of the electrocatalytic reduction of oxygen by water-soluble porphyrins and phthalocyanines. He was appointed as a research associate at the Chemical Research Institute of Non-Aqueous Solutions and, subsequently, at the Pharmaceutical Institute of Tohoku University in 1983 and 1985, respectively, and he held visiting Professor positions in the laboratories of Prof. A. B. P. Lever at York University, Toronto, and Prof. J. Simon at ESPCI, Paris. Since 1995, he has been a Professor at Tohoku University. His research interests cover many different areas of phthalocyanine and porphyrin chemistry, with a strong focus on synthesis, electrochemistry, and optical spectroscopy. The MCD and CD spectroscopy of porphyrinoids is a key area of expertise.

dithioleporphyrazines,⁶¹ also containing peripheral heteroatoms. The properties of these compounds have not been investigated in depth, however.⁶²

Since radially symmetric Pc's and their analogues do not always provide the optimal set of properties required for many of the more recent high technology applications, there has been increasing interest over the last 20 years in the synthesis of low symmetry Pc's and Pc analogues with the aim being to fine-tune the molecular properties. For the purposes of this review, a low symmetry Pc or Pc analogue is defined as being a structure in which the main 4-fold proper rotation axis is removed through a modification of

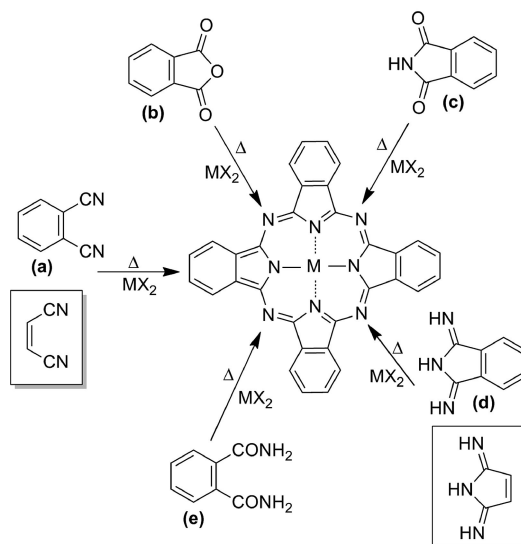


Figure 1. Phthalocyanine precursors include (a) phthalonitriles, (b) phthalic anhydrides, (c) phthalimides, (d) 1,3-diiminoisoindolines, and (e) phthalamides. The equivalents for (a) and (d) in porphyrazine synthesis (INSET) are maleonitriles and 2,5-diimino pyrroles, respectively.

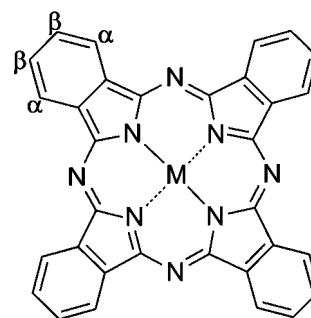


Figure 2. α - and β -positions of phthalocyanine.

the peripheral substituents and/or the nature of the π -conjugation system. It should be noted, however, that free base compounds and alkali metal complexes of otherwise radially symmetric compounds are not generally regarded as low symmetry Pc's despite their D_{2h} symmetry. Although this definition of low symmetry normally entails the complete loss of a 4-fold axis, the presence of sterically hindered substituents at the α -positions (Figures 2 and 3) can result in a special class of low symmetry Pc's in which the C_4 axis is replaced by an S_4 axis, resulting in saddled D_{2d} symmetries.^{63,64} Since low symmetry Pc's and their analogues were reviewed in a comprehensive manner about a decade ago,^{38,50,51} emphasis is placed on the comprehensive coverage of research from 2002 onward, with the focus being primarily on key breakthrough papers prior to that. This review focuses almost exclusively on monomeric tetrapyrrole porphyrinoid structures. Although ring contracted tripyrrole and ring expanded pentapyrrole structures with a C_3 or C_5 , rather than a C_4 , major axis of symmetry, such as the subporphyrazines,^{65,66} subphthalocyanines (subPc's),^{66,67} subnaphthalocyanines,^{65,66} and superphthalocyanines,^{68–70} have also been reported, their low symmetry compounds have only been studied to a limited extent, primarily in the context of subPc's.^{67,71–75} The formation of dimers, trimers, and polymers is also not covered in depth,^{76–136} with the sole exception being directly fused coplanar Pc dimers and trimers, which have a peripheral fused ring shared by two adjacent Pc or Pz

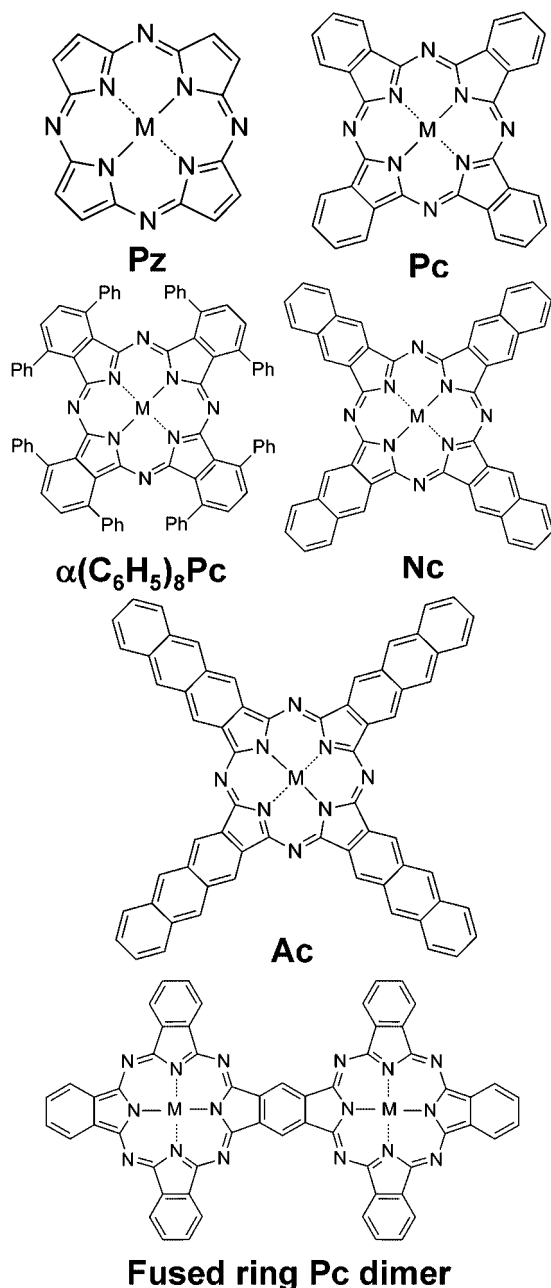


Figure 3. Molecular structures of the metal complexes of porphyrazine (Pz), phthalocyanine (Pc), octa- α -phenylphthalocyanine ($\alpha(\text{C}_6\text{H}_5)_8\text{Pc}$), 2,3-naphthalocyanine (Nc), anthracocyanine (Ac), and a fused ring Pc dimer.

π -systems (Figure 3).^{125–141} This topic was reviewed relatively recently in the context of radially symmetric complexes.¹⁴² Many of the approaches described can be readily applied to low symmetry Pc's and Pz's.^{76–142}

The most common approach to the synthesis of low symmetry Pc's and their analogues involves modifications to the precursors such as phthalonitriles and 1,3-diiminoisoindolines in the case of Pc's (Figure 1) or the corresponding maleonitriles and 2,5-diiminopyrrolines in the case of Pz's.^{50,51} Three other approaches have also been explored. First, the links between the isoindoline or pyrrole moieties can be modified. The aza-nitrogens linking the pyrrole and isoindoline moieties of Pz's and Pc's can be replaced by *meso*-carbons to form ligands such as tetrabenzotriazaporphyrins (TBTrAPs).^{143,144} Although porphyrins and tetrabenzoporphyrins (TBPs) could be viewed as Pc analogues on

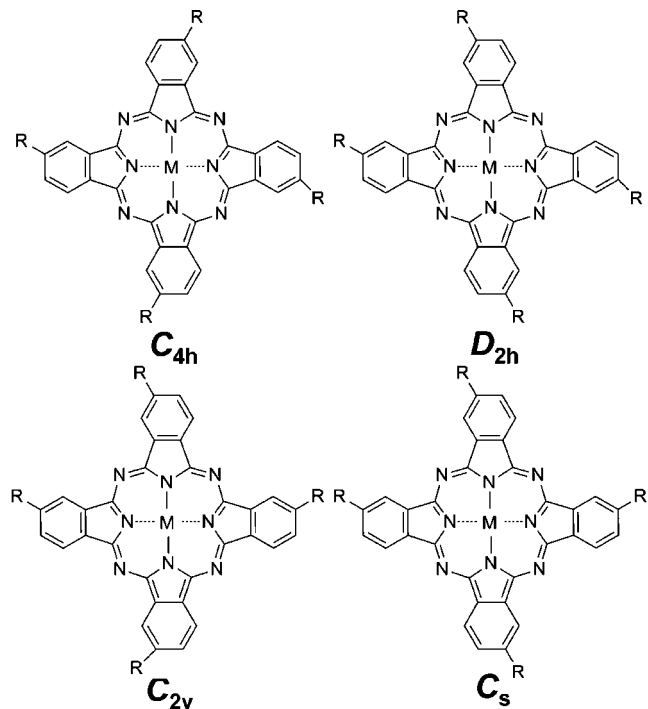


Figure 4. Four constitutional isomers of 2,9(or 10),16(or 17),23(or 24)-tetrasubstituted phthalocyanines.

this basis, they will not be considered, since porphyrin chemistry has been extensively reviewed elsewhere¹⁴⁵ and has traditionally been regarded as a separate field of research. Only ligands with at least one aza-nitrogen are typically regarded as being Pc analogues. At elevated temperatures, in the presence of a high valent central metal, an aza-nitrogen can be removed, resulting in the formation of corrolazines (Cz's)^{146,147} and tetrabenzocorrolazines (TBCz's)¹⁴⁸ with a direct C–C bond linking two neighboring pyrrole moieties. Second, the pyrrole and isoindoline moieties can be partially replaced by other ring systems to form hemiporphyrazines (HPz's)^{38,149,150} and three-quarters-phthalocyanines.^{38,151,152} The third type of structural modification involves the modification of peripheral bonds of the π -system. Partial reduction of the Pz π -system results in the formation of the tetraaza-analogues of the chlorins (TACs), bacteriochlorins (TABs), and isobacteriochlorins (TAiBs),^{153–164} while partial oxidation results in the formation of *seco*-porphyrazines (*seco*Pz's).^{165,166} The synthesis and properties of each of these types of low symmetry Pc and Pc analogue will be described in depth.

2. Peripheral Substitution and Fused Ring Modification

2.1. Synthesis

Ever since the initial research by Linstead and co-workers^{167,168} in the 1930s, MPc complexes and their analogues³⁸ have usually been formed via condensation reactions of precursors such as phthalonitriles, 1,3-diiminoisoindolines, phthalic anhydrides, phthalimides, or phthalamides (Figure 1). The reactions required to prepare these precursors have been reviewed extensively elsewhere.^{40,41} Free base Pc's are often prepared via demetalation of alkali metal complexes,⁴² but they can sometimes also be prepared directly from the precursors, especially in the case of 1,3-diiminoisoindolines. It should be noted that when peripheral

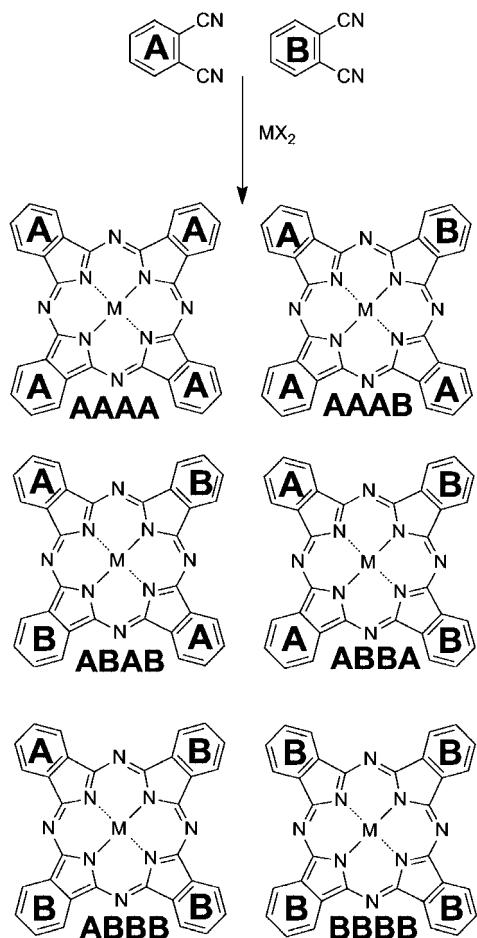


Figure 5. The products anticipated for a mixed condensation of two phthalonitriles A and B.

substituents are taken into consideration, a condensation reaction of a single precursor need not necessarily result in a Pc with a C_4 symmetry axis. Chiral Pc's^{169–171} can be formed, and when phthalonitriles with non- C_{2v} -symmetry are used, the substituents on each fused benzene ring can be oriented in two directions with respect to the rest of the ligand, resulting in four constitutional isomers with C_{4h} , C_{2v} , C_s , and D_{2h} symmetry^{34,38,169–172} (Figure 4). Although the separation of these isomers through chromatography is technically feasible,^{170,173–179} it tends to be an extremely arduous task. Industrial patents based on this sort of synthetic methodology usually involve mixtures of isomers.

2.1.1. Mixed and Cross-condensations

The most common strategy for the formation of low symmetry Pc's based on peripheral substitution and/or fused ring modification is to carry out condensation reactions with two different precursors to form compounds with AAAA, AAAB, AAB, ABAB, ABBA, and BBBB structures (Figure 5). In this review we adopt the terminology of Leznoff,⁴² who reserved the term mixed condensation for reactions between the same type of precursor (Figure 1) and used the term cross-condensation for reactions involving different types of precursor. Even when bulky *t*-C₄H₉- groups are incorporated to enhance the solubility,¹⁸⁰ the complete separation of the different structures formed can be extremely challenging.^{93,181–196} The formation of the AAAB type structures can be optimized in statistical terms by adjusting the ratio of the precursors, and its chromatographic separation from the other

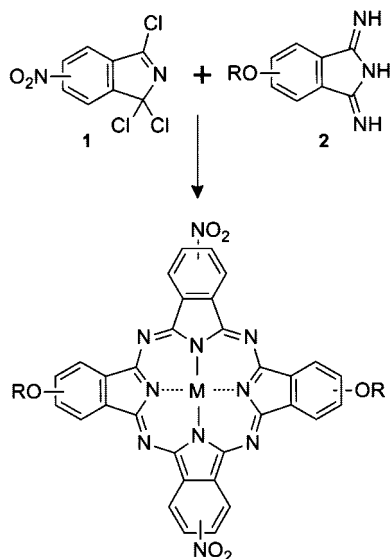
products is usually relatively straightforward. The separation of AAB and ABAB structures is inherently problematic, however, since these isomers have identical molecular weights and usually have similar molecular properties. There are some examples of the complete resolution and characterization of the four products for both peripheral substitution^{87,192,195,197–200} and fused ring modification,^{93,181,182,184,187–191,201} but most recent low symmetry Pc studies have focused on the relatively easily separated AAAB products formed through partial peripheral substitution of Pz,^{100,202–212} Nc,²¹³ unsubstituted Pc,^{213–231} α -substituted Pc,^{112,232–245} β -substituted tetrapyrzoporphyrazine,²⁴⁶ β -substituted Pc,^{84–86,88–92,95–99,101,105,106,109–111,113–121,123,193,195,213,226,231–233,243,245,247–325} and α,β -substituted Pc^{117,195,326,327} AAAA parent compounds and through the partial fused ring modification of Pz,^{124,203,204,209,210,328–340} Nc,^{219,263} unsubstituted Pc,^{122,214,215,230,341–343} α -substituted Pc,^{57,344–346} β -substituted Pc,^{104,105,111,248,285,294,296,312,318,344,347–350} and α,β -substituted Pc³²⁷ AAAA parent compounds. Fused ring dimers have also been formed based on mixed and cross-condensations with precursors such as 1,2,4,5-tetracyanobenzene^{125–135,142} and naphthalene-2,3,6,7-tetracarbonitrile,¹³⁶ while heterodimers^{137–140} and bimetallic fused Pc dimers¹⁴¹ can be formed by isolating a Pc with two adjacent -CN groups at the β -positions and then using this compound as a precursor in a second mixed or cross-condensation.

2.1.2. Selective Synthesis

Since the late 1980s, a number of breakthrough methodologies have been developed for the selective synthesis of specific low symmetry Pc structure types.^{66,351} In 1990, Kobayashi et al.^{285,296} reported the selective formation of low symmetry free base AAAB complexes based on the insertion of a series of 1,3-diiminoisoindolines into a B^{III}subPc (Scheme 1). This approach has subsequently only been adopted to a limited extent, however.^{106,122,213,219,229,230,247,282,283,285,294,296,327,343,352–354} Unfortunately, AAAB products can only be formed with a reasonable level of selectivity (i.e., the side products are reduced to trace levels) when a 1,2-diiminoisoindoline containing electron donating substituents is reacted with either an unsubstituted B^{III}subPc or a B^{III}subPc with electron withdrawing substituents.^{352–354} When the B^{III}subPc contains electron donating substituents, a mixture of compounds with significant yields is obtained because the tetrapyrrole structure formed upon initial ring-opening of the B^{III}subPc does not remain intact and can recombine to form other structures.

Leznoff³⁵⁵ developed a selective polymer-based method for “fishing out” AAAB isomers during condensation syntheses based on the use of a 1% cross-linked divinylbenzene–styrene polymer support which reacts preferentially with the B precursor via a reaction of the peripheral substituents. The polymer supported precursor can then be reacted to selectively form an AAAB structure, which can be isolated and characterized after treatment with acid. Although this method has subsequently been used to a limited extent by Hoffman and Barrett,^{205,206} the range of Pc's and their analogues that can be synthesized in this manner is restricted by the need for the B unit to react with the hydrophobic polystyrene resin. Another key drawback is that the Soxhlet extraction purification steps, first to remove the AAAA product and then to remove the AAAB product upon acid cleavage, are time-consuming and not always fully successful.³⁵⁶ Recently, Hammer and co-workers³⁵⁷ have reported a new solid phase approach for selectively deriving AAAB structures by using a hydrophilic poly(ethylene glycol)-based support with a Wang-type linker, which makes the separation of the AAAA

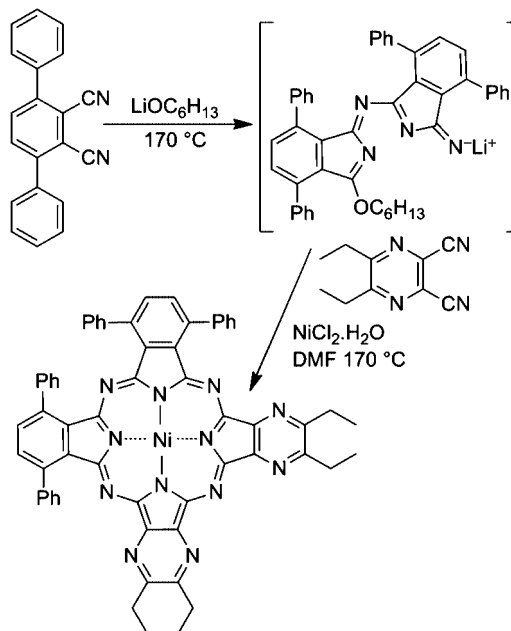
Scheme 2. Selective Formation of an ABAB Structure from a Cross-condensation Reaction of 1,3,3-Cl-6-NO₂-Isoindolenine (1) and a 1,3-Isoindole-diimine (2)³⁶¹



and AAAB products much more straightforward than was the case previously. The possibility of AABB products forming due to reactions occurring prior to the addition of the second precursor is a potential issue, but the authors have outlined the steps required to prevent it, such as the addition of a divalent metal ion. They also postulated that it may be possible to adjust the reaction conditions in the future to selectively or predominantly form AABB products.

The selective synthesis of ABAB^{186,195,343,358–372} and AABB^{63,124,186,373–376} isomers has proven to be every bit as challenging as that of their AAAB counterparts. One of the most interesting approaches used to form ABAB structures is a cross-condensation between two types of precursor in which six of the eight nitrogens on the inner perimeter of the product can only be provided by one type of precursor (Scheme 2). This methodology was originally reported as a patent in 1978 by Idelson³⁶² on behalf of the Polaroid Corporation. A reaction between aminoimino- and trihalo-substituted pyrrole in the presence of an acid acceptor and a hydrogen donor was reported to result in the preferential formation of ABAB Pz structures. Lever and Leznoff³⁶³ and Shirai and co-workers³⁶⁴ were the first to use this type of reaction in an academic setting. In 1990, Young and Onyebuagu³⁶¹ reported a cross-condensation reaction involving 1,3,3-trichloro-6-nitroisoindolenine and 1,3-diiminoisoindoles to form ABAB Pc's in high yields ranging from 17 to 72% (Scheme 2). Stihler et al.³⁶⁵ subsequently pointed out, however, that while the ABAB structure is the predominant product, a trace of AAAB product is also found, which has to be separated through chromatography. Idelson's approach has only rarely been utilized by Pc researchers in recent years,^{343,358–360} but a recent report of ABAC compounds being synthesized on this basis by Dumoulin and Ahsen³⁶⁶ may point the way to the selective synthesis of a great number of previously unreported Pc analogues given the problematic nature of attempting a mixed condensation reaction with three precursors. The Kobayashi group^{186,367,368,372} and others^{369–371} have also occasionally used the incorporation of bulky substituents at the α -positions to selectively form ABAB rather than AABB compounds. This approach does not always work, however. For example, a significant yield of the AABB isomer was obtained during a mixed

Scheme 3. Use of the Lithium Method To Selectively Form AABB Structures³⁸¹



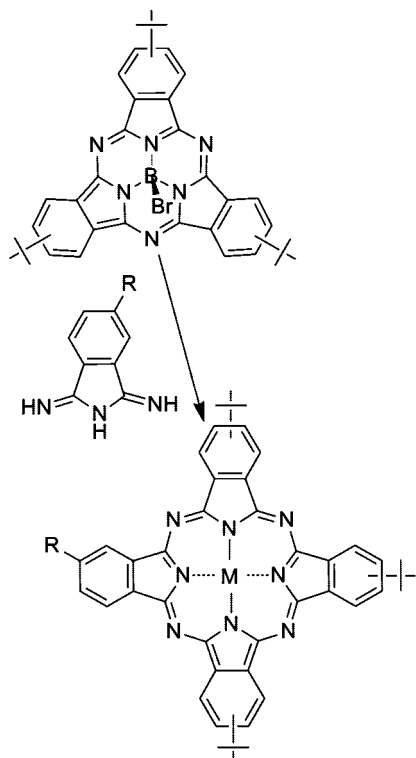
condensation of tetraphenylphthalonitrile and 4-phenylthiophthalonitrile in the presence of CuCl₂ at 260 °C,¹⁹⁵ probably due to the high temperature and the use of Cu(II) ion as a template, which favors a square planar environment.

Two methods have been developed to selectively obtain AABB structures. Unfortunately, neither is generally applicable. The first approach involves the use of bisphthalonitriles. Research by the Kobayashi group^{124,186,373,374} in this regard has focused on the synthesis of optically active Pc's using 2,2'-dioxy-1,1'-binaphthyl bisphthalonitriles as a precursor. Optically active structures^{169,170,373} and dimers¹⁴² can also be formed when these precursors combine to form tetrapyrrole compounds. The second approach is sometimes referred to as the "lithium method"^{377–380} (Scheme 3). Reaction of a phthalonitrile containing bulky groups at the α -positions with lithium hexyl oxide at *ca.* 150 °C results in the formation of a half-phthalocyanine, since tetramerization is disfavored by the steric hindrance between neighboring peripheral substituents.^{63,188,193,375,381,382} Subsequent reaction with a second type of precursor results in the selective formation of the AABB compound.

2.1.3. Synthesis Based on Derivatization of Substituents and Fused Rings

Many recent studies of low symmetry AAAB structures have involved a mixed or cross-condensation to form a Pz or Pc compound with a reactive substituent which can be further modified to form more complex structures such as dimers, dyads, and bimetallic monomeric complexes. This work was recently reviewed in detail.³⁹ The major focus in recent years has been on AAAB structures with an iodine atom substituent at one of the eight β -positions.^{84,86,87,91,93,95,108,113,114,116–118,249,263,264,271,272,275,277,284,287,307,308,316,326,383–385} Sonogashira coupling reactions³⁸⁶ can then be used to form ethynyl groups,^{84,86,87,95,108,113,114,116–118,249,257,263,264,269,275,287,305,306,321,326,384,385} which can in turn be modified to form dyads,^{87,113,116–118,257,269,275,287,305,306} dimers,^{87,95,108,113,114,117,264,385} and phosphonium salts.^{95,260} Heck coupling reactions³⁸⁷ have also been used to form vinyl groups, which have been further reacted to form dyads,^{111,277,281,284,287,383} while the use of Suzuki coupling reactions with organoboranes has also been reported.^{307,308,384} Dimers or dyads and

Scheme 1. Mechanism for the Formation of AAAB Structures from B^{III} subPc's^a



^a The reaction is usually carried out at 80–90 °C in a mixture of *N,N*-dimethyl sulfoxide and either chlorobenzene, *o*-dichlorobenzene, 1-chloronaphthalene, or 2-chloronaphthalene (2:1 to 1:1 v/v) for 5–27 h.²⁸⁵

their related structures have also been formed via the further modification of $-\text{NO}_2$,^{101,105,240,311,316} $-\text{NH}_2$,^{98,109,271,272,309} $-\text{ROH}$,^{120,242,278,279,289,310,320,322,388} $-\text{CHO}$,^{113,245,319} and $-\text{CN}$ ⁹⁴ substituents. In an unconventional approach to Pc synthesis, two recent papers have reported the use of electrophilic substitution reactions of unsubstituted D_{4h} symmetry metal phthalocyanines to enhance the solubility properties by introducing peripheral substituents.^{389,390} There has also been a recent report of a phthalocyanine–cyclodextrin dyad being formed based on the nucleophilic substitution of zinc hexadecafluorophthalocyanine.³⁹¹

The reactivity of peripheral fused rings can also be exploited. For example, Barrett, Hoffman, and co-workers have formed diaminoporphyrazines via a reaction of a peripheral selenodiazole fused ring with H_2S in pyridine,^{203,204,207,209–211,334,336,392} due to low reactivity of diaminomaleonitrile in mixed condensations. The $-\text{NH}_2$ substituents can be further modified to form peripherally appended Schiff base metal chelates,^{203,204,392} picalinomido chelates,^{207,210,211} and peripheral pyrazine rings.²⁵⁶ Selenodiazole fused porphyrinoids were originally reported by Ercolani and Stuzhin.^{393–395} More recently, Hanack has reported the formation of novel AAAB structures by using a triazole ring fused to a Pc^{396,397} or benzoporphyrine³⁹⁷ to form dehydro- compounds with a peripheral triple bond, which can be further modified via Diels–Alder reactions,²⁹⁴ reactions with solvents,³⁹⁷ and through ring-opening reactions to form azo-dye moieties.³⁹⁸ It should be noted that Grignard reagents can also be used to form the corresponding dehydrobenzoporphyrine from 2,3-dihalobenzoporphyrines,³²⁷ but this approach proved impossible in the case of Pc's.

2.2. Spectroscopic and Redox Properties

2.2.1. Optical Spectroscopy

Many of the present day and future applications for Pc's and their analogues are based ultimately on properties arising from the heteroaromatic nature of the π -system, such as the intense $\pi \rightarrow \pi^*$ bands observed in the visible region. Optical spectroscopy can be used to validate molecular orbital (MO) descriptions of the electronic structure derived from both semiempirical approaches and density functional theory (DFT).^{399,400} Absorption of an incident photon results in a circular rearrangement of charge within the π -system and, therefore, induces a strong magnetic dipole moment. Magnetic circular dichroism (MCD) spectroscopy has, therefore, featured prominently in Pc research.^{399,400} When a magnetic field is applied parallel to the axis of light propagation, there is a complete lifting of the orbital and spin degeneracies of the ground and excited states. Key state symmetry and band polarization information can be derived from this based on an analysis of the Faraday A_1 , B_0 , and C_0 terms, which arise, respectively, from the Zeeman splitting of the absorption bands for left and right circularly polarized light into an orbitally degenerate excited state, the field-induced mixing of zero-field states, and Zeeman splittings associated with the population

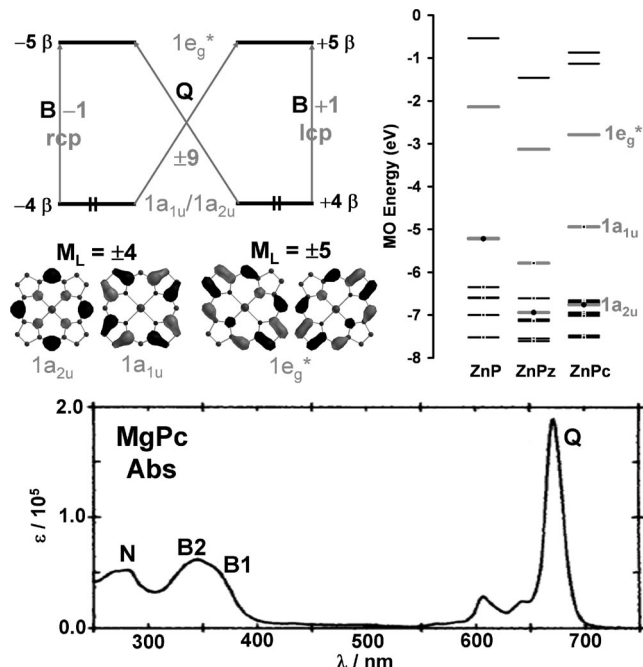


Figure 6. Origin of the Q and B bands in Gouterman's 4-orbital model (top left).⁴⁰³ The four frontier π -MO's of ZnPz (center left) and the $\text{C}_{16}\text{H}_{16}^{2-}$ parent perimeter (Figure 8) exhibit $M_L = \pm 4, \pm 5$ nodal patterns in INDO/s calculations at an isosurface value for electrostatic potential of 0.04 au. This results in a forbidden Q band with " $\Delta M_L = \pm 9$ " β properties and an allowed B band with " $\Delta M_L = \pm 1$ " β properties. In the case of MPz and MPc, but not metal porphyrin (MP), complexes, a marked lifting of the degeneracy of the HOMO's is predicted in DFT calculations (top right).⁴⁵² The MO's derived from the four frontier π -MO's of the hydrocarbon perimeter are highlighted in light gray. Small squares and large circles are used to denote occupied MO's and the $1a_{2u}$ MO's, respectively. The $1a_{2u}$ MO is markedly stabilized by the presence of aza-nitrogens. The Q band gains significant intensity in the UV-visible absorption spectrum of MgPc in CH_2Cl_2 due to the lifting of the degeneracy of $1a_{1u}$ and $1a_{2u}$ HOMO's (bottom). The Q, B, and N band terminology was originally developed by Gouterman⁴⁰⁸ and later modified by Stillman and co-workers to include the B1 and B2 bands in the 300–400 nm region.⁴⁰⁹ Reproduced with permission from ref 409. Copyright 1988 American Chemical Society.

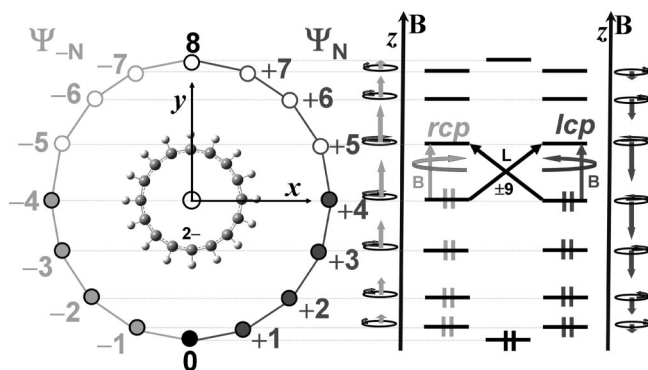


Figure 7. Michl's perimeter model (left).^{404,405} The circle is a diagrammatic representation of the clockwise and counterclockwise motion of π -system electrons on the $C_{16}H_{16}^{2-}$ parent perimeter of metal porphyrinoid complexes based on the 16 $2p_z$ atomic orbitals. The extent of the circular motion generates the M_L value for each complex wave function MO. The perspective is toward the light source. The alignment of the magnetic moments in each MO either with or against the applied field (right) can be predicted based on Ampere's rule (right-hand rule) for conventional current flow in a solenoid. The magnitudes are diagrammatic based on the result of INDO calculations.^{404,405} Upon absorption of a photon of lcp or rcp, the excited electron retains the left or right handed motion of charge associated with the M_L quantum number so that the total angular momentum within the system is conserved. There is an electronically allowed B transition ($\Delta M_L = \pm 1$) and an electronically forbidden L transition ($\Delta M_L = \pm 9$).

adjustment for an orbitally degenerate ground state.^{399,400} MCD spectra have been reported for a wide range of low symmetry Pc's.^{98,105,106,111,123,124,127,130,137,140,169,186–191,195,201,247,248,295,296,311,367,368,372,373,375,399–402} In the absence of a 4-fold axis of symmetry, these spectra are usually dominated by coupled pairs of oppositely signed Gaussian-shaped \mathcal{B}_0 terms rather than first derivative-shaped \mathcal{A}_1 terms due to the lifting of excited state degeneracies.^{399,400}

The optical spectra of Pc's and their analogues are usually described in terms of Gouterman's 4-orbital model⁴⁰³ (Figure 6) and Michl's perimeter model^{404,405} (Figure 7). The spectroscopy of metal porphyrinoids can be understood conceptually in terms of a free electron model for a 16 atom 18 π -electron system on the inner ligand perimeter with MO's arranged in ascending energy with $M_L = 0, \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6, \pm 7$, and 8 properties based on the magnetic quantum number. The HOMO ($M_L = \pm 4$) and LUMO ($M_L = \pm 5$) are linked by an allowed $\Delta M_L = \pm 1$ and a forbidden $\Delta M_L = \pm 9$ transition, since an incident photon can only provide a maximum of one quantum of angular momentum. MCD spectroscopy has been used to confirm the relative magnitudes of the magnetic moments associated with the Q and B excited states based on $\mathcal{A}_1/\mathcal{D}_0$ ratios, since the intensity of Faraday \mathcal{A}_1 terms is based on both the magnetic dipole moment of the excited state and the dipole strength (\mathcal{D}_0) of the corresponding band in the UV–visible absorption band.^{406,407} When the D_{4h} symmetry of radially symmetric metal porphyrinoids is considered, the degeneracy of the even numbered $M_L = \pm n$ MO's is lifted while that of the odd numbered MO's is retained, resulting in a $1e_g^*$ LUMO and $1a_{1u}$ and $1a_{2u}$ HOMO's (Figures 6 and 8). The HOMO's of metal porphyrins are accidentally degenerate despite the D_{4h} symmetry, resulting in a forbidden Q band in the visible region and an allowed B (or Soret) band at ca. 400 nm. In the case of Pz's and Pc's, however, the introduction of the aza-nitrogens substantially stabilizes the $1a_{2u}$ HOMO and there is a marked energy separation between the $1a_{1u}$ and $1a_{2u}$ HOMO's (a large Δ HOMO value in terms of Michl's

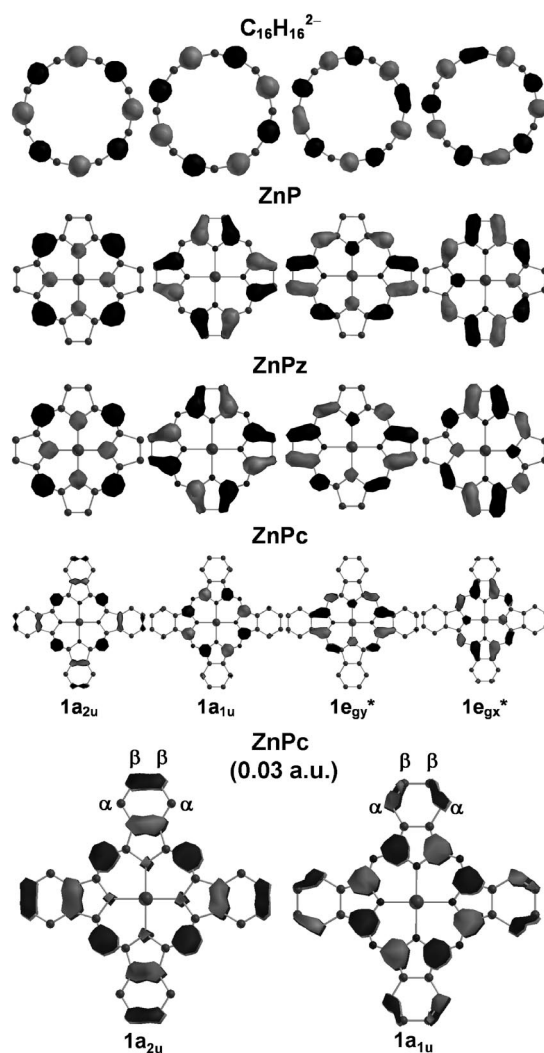


Figure 8. Frontier π -system MO's for $C_{16}H_{16}^{2-}$, ZnP, ZnPz, and ZnPc predicted by B3LYP geometry optimizations at an isosurface value of 0.04 au (top) and the $1a_{1u}$ and $1a_{2u}$ MO's of ZnPc at an isosurface value of 0.03 au (bottom).

terminology^{404,405}). As a result, there is a mixing of the allowed and forbidden character of the B and Q transitions and the Q band gains significant intensity. Since the degree of configurational interaction between the Q and B excited states is markedly reduced, the $1a_{1u} \rightarrow 1e_g^*$ one-electron transition is typically the predominant contribution to the Q band, while the $1a_{2u} \rightarrow 1e_g^*$ one-electron transition is the key factor with the B band. The introduction of fused benzene rings, in the case of Pc, results in the presence of a number of additional higher energy $\pi\pi^*$ states, which interact with the B excited state through configurational interaction. Several broad $\pi \rightarrow \pi^*$ bands overlap in the 200–400 nm region to form broad envelopes of absorption intensity. In the case of complexes of main group and close shell d^{10} metals, these bands are usually referred to as the B1 (ca. 370 nm), B2 (ca. 330 nm), N (ca. 275 nm), L (ca. 245 nm), and C (ca. 210 nm) bands (Figure 6), based on terminology originally developed by Gouterman⁴⁰⁸ and later modified by Stillman and co-workers⁴⁰⁹ on the basis of spectral band deconvolution analyses of UV–visible absorption and MCD spectral data. The spectra of transition metal complexes are considerably more complex due to the presence of ligand to metal and metal to ligand charge transfer bands (LMCT, MLCT).⁴¹⁰ An in depth analysis of the optical spectroscopy

Table 1. UV–Visible Absorption Bands Reported for AAAB (A = β -*t*-C₄H₉) ZnPc Complexes

B ^a	(solvent): λ_{max} (log ϵ)	ref
1 β -OCH ₂ -norbornene	(CHCl ₃): 673 (5.15), 610 (4.39), 352 (4.7)	99
1 β -NHC(O)-2,2'Bipy Pc	(THF): 676 (5.30), 611 (4.53), 350 (4.86), 289 (4.60), 212 (4.93)	257
1 β -OCH ₂ CH ₂ NH ₂	(DMF): 677 (5.33), 610 (4.59), 350 (4.89)	299
1 β -CH ₂ OH	(CHCl ₃): 678 (5.13), 616 (4.18), 349 (4.71)	388
1 β -CH ₂ CH ₂ CHO	(CHCl ₃): 678 (5.11), 612 (4.48), 350 (4.81)	287
1 β -I Pc	(CHCl ₃): 679 (5.1), 612 (4.3), 351 (4.7)	87
1 β -CH ₂ CH ₂ - <i>N</i> -methyl-3,4-fulleropyrrolidine dyad	(CHCl ₃): 679 (5.22), 613 (4.45), 346 (4.91), 256 (5.10)	287
1 β -O-2,4-Br-3-ORPh Pc	(CHCl ₃): 680 (5.14), 610 (4.39), 350 (4.80)	290
1 β -O-2,4-CH=CH ₂ -3-ORPh Pc	(CHCl ₃): 680 (5.13), 612 (4.36), 350 (4.79)	290
1 β -O-2,4-CHO-3-ORPh Pc	(CHCl ₃): 680 (5.13), 610 (4.40), 351 (4.76)	290
1 β -OC ₂ H ₄ [18]aneO ₄ N ₂ C ₂ H ₄ OH	(CHCl ₃): 680 (5.13), 614 (4.39), 351 (4.75)	251
1 β -OC ₂ H ₄ [18]aneO ₄ N ₂ C ₂ H ₄ O-1-(3-COC ₃ H ₇)-1-Ph-[6,6]-C ₆₁	(CHCl ₃): 680 (4.1), 614 (3.35), 469 (3.32), 430 (sh), 344 (3.8)	251
1 β -HC=CH-Ferrocene	(CHCl ₃): 681 (5.18), 615 (4.60), 331 (4.97), 289 (4.86)	88
1 β -bis(⁶⁰ fullerene)-phthalocyanine triad	(CHCl ₃): 682 (5.13), 336 (5.01), 255 (5.27)	290
1 β -NH ₂ -Pc	(CHCl ₃): 682 (5.01), 617 (4.24), 351 (4.71)	257
1 β -C ⁺ C ⁻ -C(CH ₃) ₂ OH Pc	(CHCl ₃): 684 (5.1), 613 (4.5), 351 (4.9)	87
1 β -2-C ⁺ C ⁻ -H Pc	(CHCl ₃): 684 (5.4), 612 (4.7), 350 (5.1)	87
1 β -C ⁺ C ⁻ CCH ₂ OH	(CHCl ₃): 684 (5.02), 614 (4.28), 352 (4.73)	287
1 β -C ⁺ C ⁻ - <i>N</i> -methyl-3,4-fulleropyrrolidine dyad	(CHCl ₃): 686 (5.17), 617 (4.51), 350 (4.94), 257 (5.12)	287
1 β -C ⁺ C ⁻ -2,2'Bipy Pc	(THF): 687 (5.15), 671 (5.06), 633 (4.35), 610 (sh), 352 (4.89)	257
2 β -I Pc	(CH ₂ Cl ₂): 688 (4.9), 674 (4.8), 611 (4.2), 352 (4.6)	84
1 β -C ⁺ C ⁻ -2,2'Bipy Pc	(THF): 688 (5.28), 677 (5.23), 613 (4.52), 352 (5.00), 225 (4.68)	257
1 β -C ⁺ C ⁻ - <i>N</i> -methyl-3,4-fulleropyrrolidine dyad	(CHCl ₃): 689 (5.14), 678 (5.12), 615 (4.51), 351 (4.96), 255 (5.11)	287
1 β -CN	(CHCl ₃): 692 (5.05), 669 (5.04), 636 (4.45), 611 (4.31), 352 (4.68)	94
2 β -C ⁺ C ⁻ -H Pc	(CH ₂ Cl ₂): 696 (5.3), 672 (5.2), 612 (4.6), 353 (5.1)	84
1 β -CHO	(CHCl ₃): 698 (5.03), 670 (5.03), 639 (4.42), 610 (4.33), 353 (4.82)	94
2 β -C ⁺ C ⁻ -TMS Pc	(CH ₂ Cl ₂): 699 (4.4), 674 (4.3), 614 (3.6), 353 (4.3)	84
1 β -C ⁺ C ⁻ CCHO	(CHCl ₃): 700 (5.08), 672 (5.04), 641 (4.54), 612 (4.40), 354 (4.86)	287
1 β -C ⁺ C ⁻ CCHO	(CHCl ₃): 702 (5.10), 675 (5.05), 642 (4.56), 353 (4.86)	287

^a Number and position of substituents.

of these complexes is beyond the scope of this review. The topic has already been reviewed elsewhere, however, in the context of high symmetry Pc's,⁴¹⁰ and many of the band assignments outlined could be readily applied in the context of low symmetry compounds. In the context of free base tetraazaporphyrinoids, the protonation of the two pyrrole nitrogens along the y -axis results in a slight lifting of the degeneracy of the $1e_g^*$ LUMO (or a small Δ LUMO value in terms of Michl's terminology^{404,405}) and a significant splitting of the x - and y -polarized components of the Q band. Although similar band splittings occur in the UV region, the effect is less obvious due to the presence of many broad overlapping bands arising from the B and higher energy $\pi \rightarrow \pi^*$ transitions.

The Kobayashi and Luk'yanets groups have recently studied the effect of peripheral substituents in the context of radially symmetric Pc's.⁴⁵ It has long been known that substitution with electron donating and withdrawing substituents at the α - and β -positions has differing effects on the optical spectroscopy of Pc's.^{42,411} When strongly electron-donating substituents, such as alkoxy and thioalkyl groups, are bound to four α -positions (Figure 2), the Q bands shift to the red by up to 40 nm.⁴⁵ When the same electron-donating groups are introduced at the other four α -positions, the red shifts of the Q bands are magnified by a factor of between 1.6 and 2.0. Although clear trends are not consistently observed,⁴¹² when strongly electron-donating alkoxy and thioalkyl groups are introduced at the β -positions, the Q band shifts slightly to the blue. The shifts observed when strongly electron-withdrawing nitro- and phenylsulfonyl groups are introduced at the α - and β -positions are the reverse of those observed with alkoxy and thioalkyl groups.⁴⁵ These effects can be readily explained by considering the size of the atomic orbital coefficients in MO calculations (Figure 8). The coefficients at the α -carbons in the $1a_{1u}$ HOMO are larger than those at the β -carbons, so the extent of destabilization of this orbital is larger when electron-donating groups are

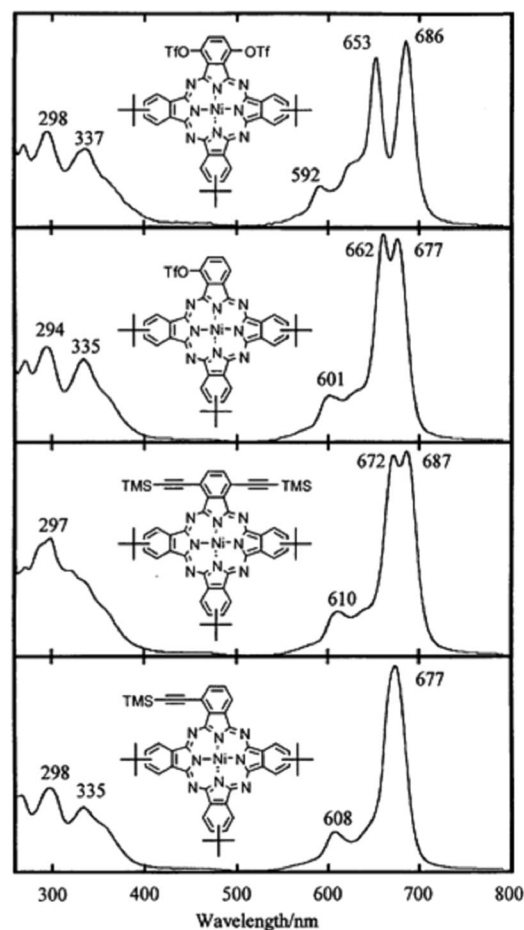


Figure 9. UV–visible absorption spectra of tri- β -*tert*-butyl-substituted Ni^{II}2 α -trifluorosulfonylPc, Ni^{II}1 α -trifluorosulfonylPc, Ni^{II}2 α -trimethylsilylethynylPc and Ni^{II}1 α -trimethylsilylethynylPc complexes. Reproduced with permission from ref 248. Copyright 2007 Society of Porphyrins and Phthalocyanines.

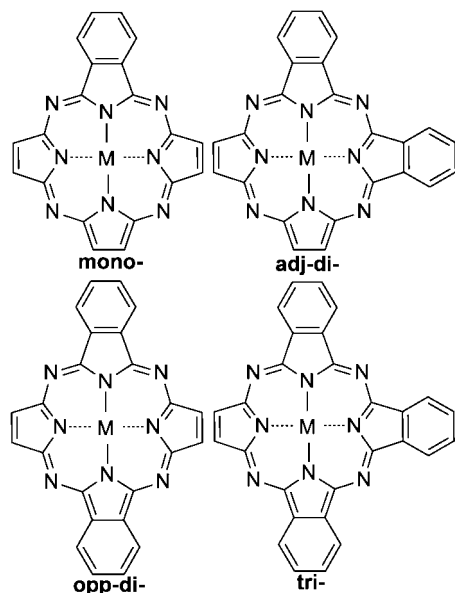


Figure 10. Molecular structures of the low-symmetry benzo-fused derivatives of Pz.

introduced at the α -positions. As a result, the HOMO–LUMO gap becomes smaller and the Q band, which arises primarily from the $1a_{1u} \rightarrow 1e_g^*$ transition, shifts to longer wavelength. The effect of asymmetrical peripheral substitution on MPc complexes with AAAB structures (where B denotes an isoindole moiety with electron donating or withdrawing groups at the α - or β -positions) is usually relatively minor, with the Q band often showing no apparent splitting (Table 1). Although the presence or absence of a marked splitting of the Q band is sometimes used to monitor the progress of metal insertion reactions, this is potentially problematic. For example, Kobayashi and co-workers²⁴⁸ have recently reported spectra of Ni^{II} Pc complexes partially substituted at the α -positions (Figure 2), with strongly electron withdrawing trifluorsulfonyl substituents in which the splitting of the Q band is comparable to that observed in the spectrum of H_2Pc , since the y-polarized component shifts to lower energy (Figure 9).

The effect of lowering the symmetry is more pronounced, in the case of partial peripheral fused ring substitution (Figure 10). Extension of the π -system with peripheral fused rings tends to destabilize the $1a_{1u}$ MO (Figure 11), since there are large MO coefficients on the peripheral carbon atoms of the pyrrole moieties (Figure 8). This results in a marked red shift of the Q band (Figures 12 and 13). In contrast, the largest MO coefficients of the $1a_{2u}$ MO lie on the eight nitrogen atoms of the inner perimeter, so fused ring substitution has significantly less effect. The magnitude of the Δ LUMO values and the splitting of the Q00 bands depend on the substitution pattern (Figures 14 and 15).^{124,186–189,375} The splitting of the x- and y-polarized bands tends to be most marked in the case of D_{2h} symmetry opp-disubstituted compounds, while the spectra of C_{2v} symmetry adj-disubstituted structures are typically very similar to those observed for D_{4h} symmetry MPz and MPc complexes (Figures 12, 13, and 15).^{124,186–189} This can be readily explained by the fact that the structural perturbation is the same along both the x- and y-axes in the adj-disubstituted isomer but differs markedly in the opp-disubstituted isomer. There is typically a pronounced splitting of the Q bands of C_{2v} symmetry mono-³⁷⁵ and tri-^{187–189} benzo-substituted MPz complexes, since the perturbation to the structure differs along the x- and

y-axes (Figure 12), while only a slight Q band splitting is observed in the spectra of the corresponding MPc complexes (Figure 13). Fused ring expansion of Pz compounds (Figure 12) tend to result in more marked spectral changes than those observed for Pc and Nc compounds (Figure 13), since most of the electron density in the frontier π -MOs is located on the inner ligand perimeter (Figure 8).^{186–189}

The longer wavelength Q00 bands of low symmetry Pz compounds typically become weaker and shift markedly to the red as the π -system is further enlarged (Figure 16), while the shorter wavelength Q00 bands remain at a similar wavelength to the x/y-polarized Q00 band of the parent MPz complex.³⁷⁵ These trends can be readily accounted for based on the size of the MO coefficients at the peripheral β -position pyrrole carbons (Figure 16). The energies of the $1e_{gx}^*$ and $1e_{gy}^*$ MOs of MPz complexes are identical due to the D_{4h} symmetry. When a fused benzene ring is added along the y-axis, the $1e_{gx}^*$ MO is destabilized, since it has large coefficients at the β -position carbons while the $1e_{gy}^*$ MO is unaffected, since the coefficients are near zero. The energies of the Q bands can be readily accounted for based on the splitting of the energies of the LUMO and LUMO+1. The longer wavelength Q00 band arising primarily from the $1a_{1u} \rightarrow 1e_{gx}^*$ transition is steadily red-shifted, as the π -system is expanded along the y-axis and the $1e_{gx}^*$ MO is further destabilized. The destabilization of the $1e_{gx}^*$ MO also accounts for the lower intensities observed for the shorter wavelength Q00 bands (Figure 16), since the overlap between the $1a_{1u}$ and the $1e_{gx}^*$ MO's is reduced (Figure 8), while that of the $1a_{1u}$ and the $1e_{gy}^*$ MO's is not significantly affected.

The optical spectra of directly fused Pc dimers contain a complex set of bands in the Q band region, with the most intense band red-shifted relative to that of the monomer (Figure 17), due to the effect of exciton coupling.^{125–141} As is the case with radially symmetric phthalocyanines, significant issues can be faced with aggregation when the symmetry is lowered, which can make key spectroscopic measurements including the optical and NMR spectra extremely challenging.⁴¹³ Careful selection of peripheral substituents can help to alleviate this problem.

2.2.2. Redox Properties

As is the case with optical spectroscopy, the redox properties of Pc's and their analogues are best rationalized on the basis of the heteroaromatic nature of the π -system. In the case of main group metal and closed shell d^{10} complexes where the central metal remains divalent, up to four electrons can be added to the $1e_g^*$ LUMO and up to two can be removed from the $1a_{1u}$ HOMO, so four reduction and two oxidation steps are typically observed.⁴¹⁴ MPc radical anions are usually highly oxygen sensitive and have only been studied to a limited extent,^{410,415,416} while the radical cations are air stable and have been studied extensively.^{410,417} A limited range of spectroelectrochemical data have been reported for low symmetry Pc's,^{124,127,136,186,310,320,323,367,372,375} The few recent examples have often tended to focus primarily on the redox properties of the central metal.^{124,186,375} Data have been obtained for the redox couples of a wide range of Pc's and their analogues based on the use of cyclic and differential pulse voltammetry (CV and DPV)^{53,62,86,98,122,124,127,128,131,133,135,136,140,183,186,189,192,195,201–203,205,209,219,219,245,261,267,268,273,274,277,278,284,298,305,306,310,316,318,329,350,367,375,381,401,402,418} and Osteryoung square-wave voltammetry.^{96,111,112,219,251,277,305,306,383} In the absence of an open shell central metal, the trends in

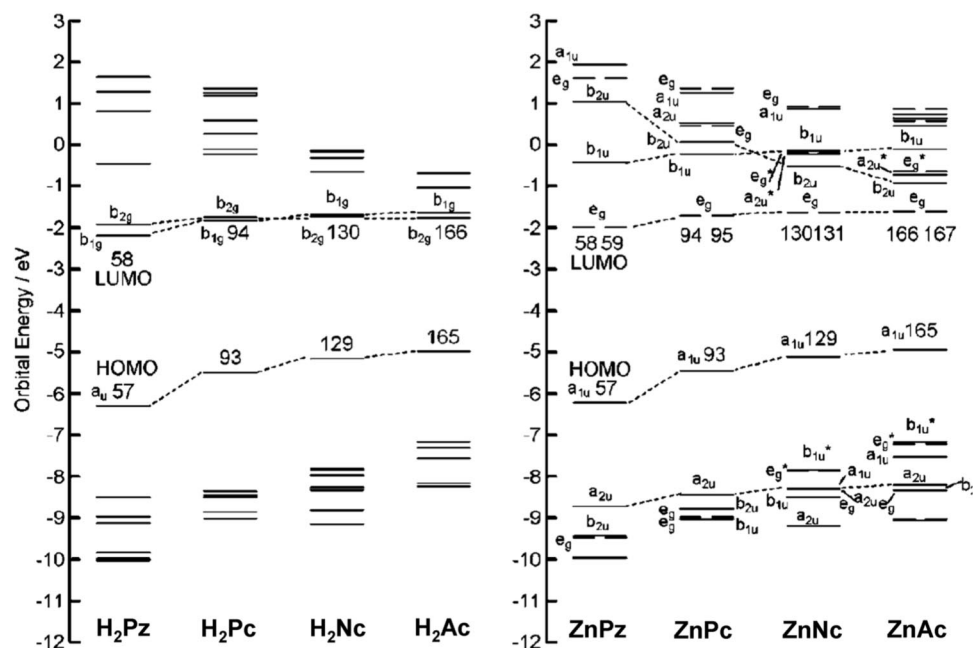


Figure 11. Partial MO energy diagrams for the H_2 (left) and $Zn(II)$ (right) derivatives of Pz, Pc, 2,3-Nc, and Ac, with the trends observed for the frontier π -MO's highlighted. An asterisk is used to denote naphthalene- and anthracene-centered MO's. The numbers indicate the orbital number in INDO/s calculations. Reproduced with permission from ref 54. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA.

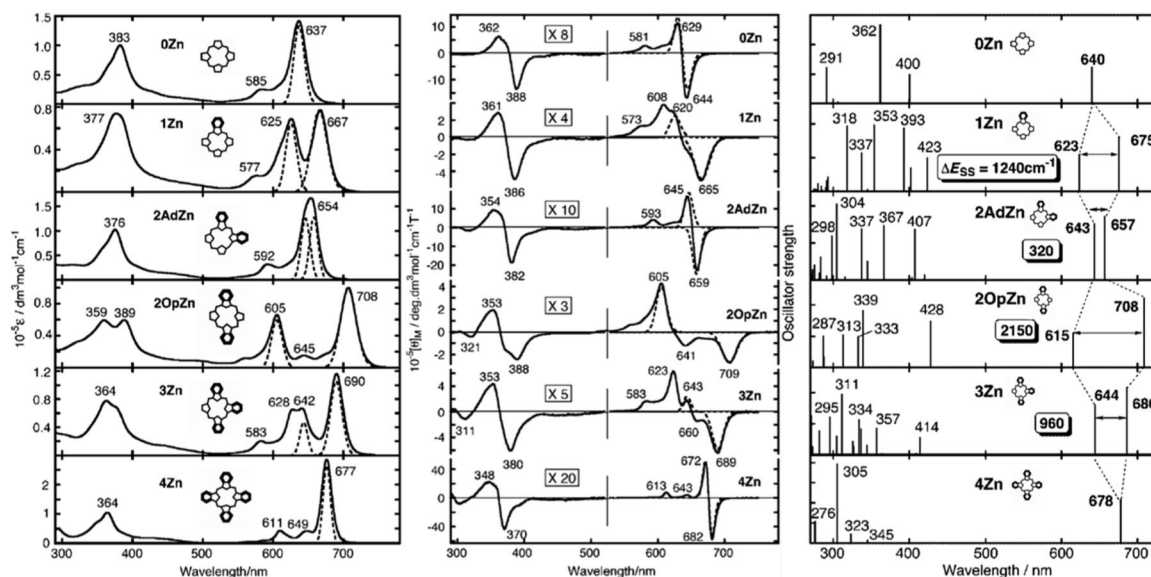


Figure 12. Electronic absorption (left) and MCD (center) spectra of a series of partially benzo-fused $ZnPz$ compounds in toluene solutions containing 1×10^{-2} M pyridine. Q_x and Q_y bands evaluated by spectral band deconvolution analysis are highlighted with dashed lines. Absorption wavelengths and oscillator strengths derived from semiempirical configuration interaction calculations (right). Reproduced with permission from ref 188. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA.

the optical and redox properties tend to mirror each other and often provide similar information. Typically, when there is a red shift of the Q band based on a destabilization of the HOMO, there will also be a decrease in the first oxidation potential, since it is easier to remove an electron. Conversely, a stabilization of the LUMO makes it easier to add an electron and, hence, leads to a decrease in the first reduction potential.

These trends are illustrated in the cyclic voltammograms of benzo-substituted $ZnPz$ 's¹⁸⁸ (Figure 18). Since the central $Zn(II)$ is redox inactive, the trends in the reduction and oxidation couples are related primarily to changes in the energies of the frontier π -MOs (Figure 15). The first oxidation potential decreases in the following order: **0Zn**

(0.65 V) > **1Zn** (0.50 V) > **2AdZn** (0.36 V) \approx **2OpZn** (0.34 V) > **3Zn** (0.19 V) > **4Zn** (0.08 V) (where the nomenclature is based on the number and arrangement of fused benzene rings; Figure 14), since the $1a_{1u}$ HOMO is steadily destabilized upon the addition of each successive fused benzene ring. The first reduction potential shifts to negative values in a different order: **0Zn** (−1.28 V) \approx **1Zn** (−1.29 V) \approx **2OpZn** (−1.29 V) > **2AdZn** (−1.46 V) \approx **3Zn** (−1.47 V) > **4Zn** (−1.65 V). Thus, at first glance, the LUMO energy appears to have no relationship to the number of fused benzene rings. The key parameter to consider is the energy gap between the first reduction and oxidation potentials (ΔE_{o-r}), however, since this is usually very close in energy to the Q band.¹⁸⁸ The ΔE_{o-r} values decrease in the following order:

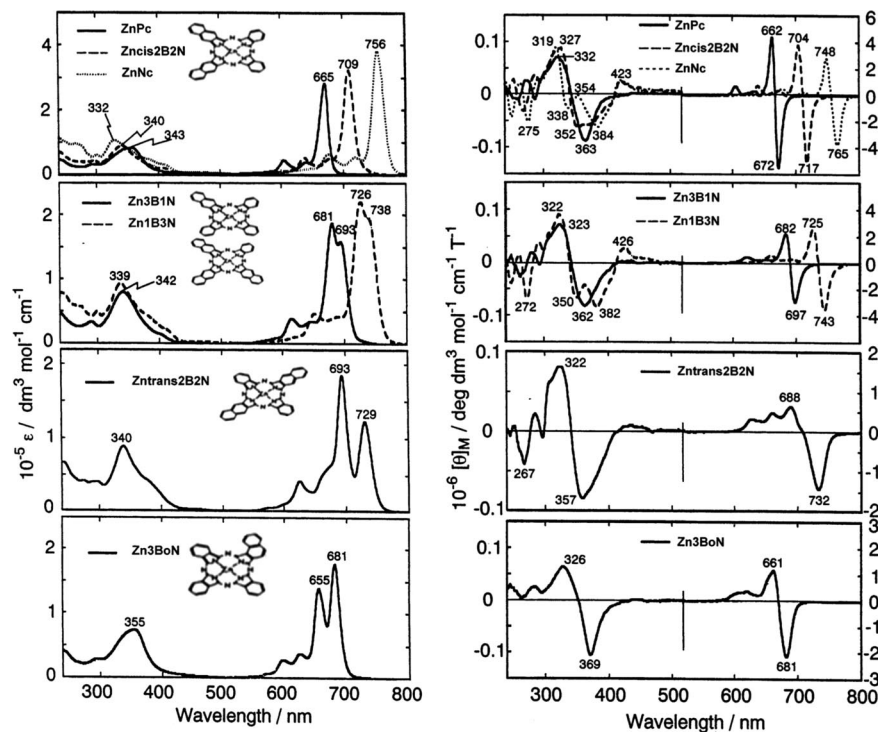


Figure 13. Electronic absorption (left) and MCD (right) spectra of ZnPc, Zn3B1N, Zn_{cis}2B2N, Zn_{trans}2B2N, Zn1B3N, ZnNc, and Zn3BoN in THF, where 3B1N, *cis*2B2N, *trans*2B2N, and 1B3N refer to fused-ring substitution of a pyrrole moiety, with B and N denoting the differing numbers of peripheral benzene and 2,3-fused naphthalene rings (left). 3BoN refers to substitution with three benzene rings and a 1,2-fused naphthalene moiety. Reproduced with permission from ref 187. Copyright 2002 American Chemical Society.

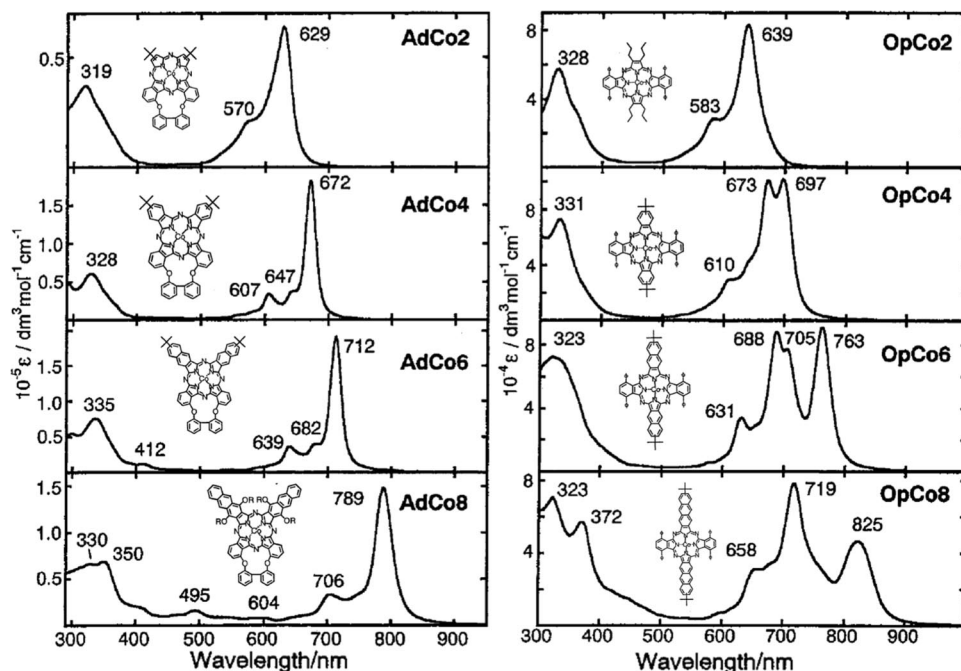


Figure 14. Electronic absorption spectra of *o*-dichlorobenzene solutions of Co^{II}Pz compounds partially substituted with peripheral fused benzene, naphthalene, and anthracene rings in an adj-di- (left) and an opp-di- (right) substitution pattern. Reproduced with permission from ref 186. Copyright 2002 American Chemical Society.

0Zn (1.93 V) > **2AdZn** (1.82 V) > **1Zn** (1.79 V) > **4Zn** (1.73 V) > **3Zn** (1.66 V) > **2OpZn** (1.63 V). The Q band energies closely mirror this trend: **0Zn** (1.95 eV) > **2AdZn** (1.90 eV) > **1Zn** (1.87 eV) > **4Zn** (1.84 eV) > **3Zn** (1.80 eV) > **2OpZn** (1.76 eV).¹⁸⁸ The trends observed in the first reduction potentials and the calculated LUMO energies are very similar (Figure 15) and can be readily explained based on a consideration of the size of the MO coefficients at the

β -position pyrrole carbons (Figure 16). In contrast with the $1a_{1u}$ HOMO, the nodal patterns of the LUMO are not radially symmetric (Figure 8), so the position of substitution determines the magnitude of the destabilization of this MO when a fused benzene ring is added to the ligand periphery. Jiang, Ng, and co-workers have recently investigated the effect of electron donating and withdrawing substituents on the redox properties of Pz, Pc, and Nc complexes.⁴¹²

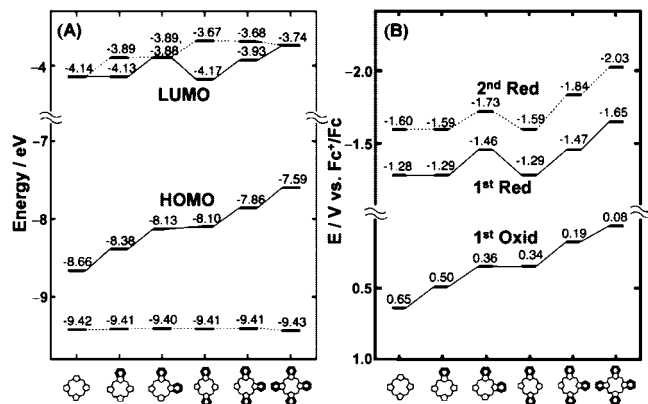


Figure 15. Calculated energies of the four key frontier π -MO's of a series of partially benzo-fused ZnPc compounds based on INDO/s calculations (left) and electrochemical data (right), recorded at a scan rate of 50 mV s⁻¹ in *o*-dichlorobenzene solutions containing 2.5×10^{-2} M pyridine and 0.1 M tetrabutylammonium perchlorate. Reproduced with permission from ref 188. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA.

2.2.3. Other Characterization Methods

A variety of other techniques have been used to analyze the properties of low symmetry Pc's and their analogues. One of the most important from the standpoint of characterization is NMR spectroscopy. In the absence of a paramagnetic central metal, the ¹H NMR spectroscopy of Pc's and their analogues is largely determined by the ring current associated with the heteroaromatic π -system. The signals of the two inner protons on the pyrrole nitrogens of the free base compounds lie at *ca.* -2 ppm, while the α - and β -proton signals typically lie at *ca.* 7 and 6 ppm, respectively, due to the shielding and deshielding effects associated with the ring current generated on the inner ligand perimeter.⁴¹⁹ Analysis of the NMR spectra of Pc's and Pc analogues is based on the assumption that the ¹H NMR signals shift to lower field when there is a stronger ring current and the protons are more strongly deshielded.^{420–424} For example, the ¹H signals of the inner pyrrole protons of tetra-*tert*-butylated H₂Pz, H₂Pc, H₂Nc, and H₂Ac are observed at -2.47, -2.17, -1.64, and -0.73 ppm, respectively, in CDCl₃ because expansion of the π -system reduces the strength of the ring current and decreases the shielding effect.^{54,62}

The spectra of partially benzo-substituted ZnPc complexes provide a good example of the trends typically observed for low symmetry fused ring modified tetraazaporphyrinoids (Figure 19). In order to interpret the NMR spectroscopy of low symmetry Pc derivatives on a qualitative level, the ring currents associated with the inner ligand perimeter and the benzene and naphthalene ring systems have to be taken into consideration. When the molecular symmetry is lowered from *D*_{4h} to either *C*_{2v} or *D*_{2h} through the partial addition of peripheral fused benzene rings, the strength of the ring current on the inner perimeter decreases. The anticipated shift to higher field due to the weaker deshielding effect can be observed for protons **a** and **b** on moving from the ¹H NMR spectra of ZnPc to those of Zn3B1N, Zn3B2N, and Zn3B3N and for protons **c**, **d**, and **e** on moving from the spectrum of ZnNc to that of Zn1B3N (where the nomenclature is based on the number and arrangement of fused benzene rings) (Figure 19). The signal for proton **k** of Zn3B3N lies at significantly lower field, however, due to the close proximity to one of the aza-nitrogens on the inner

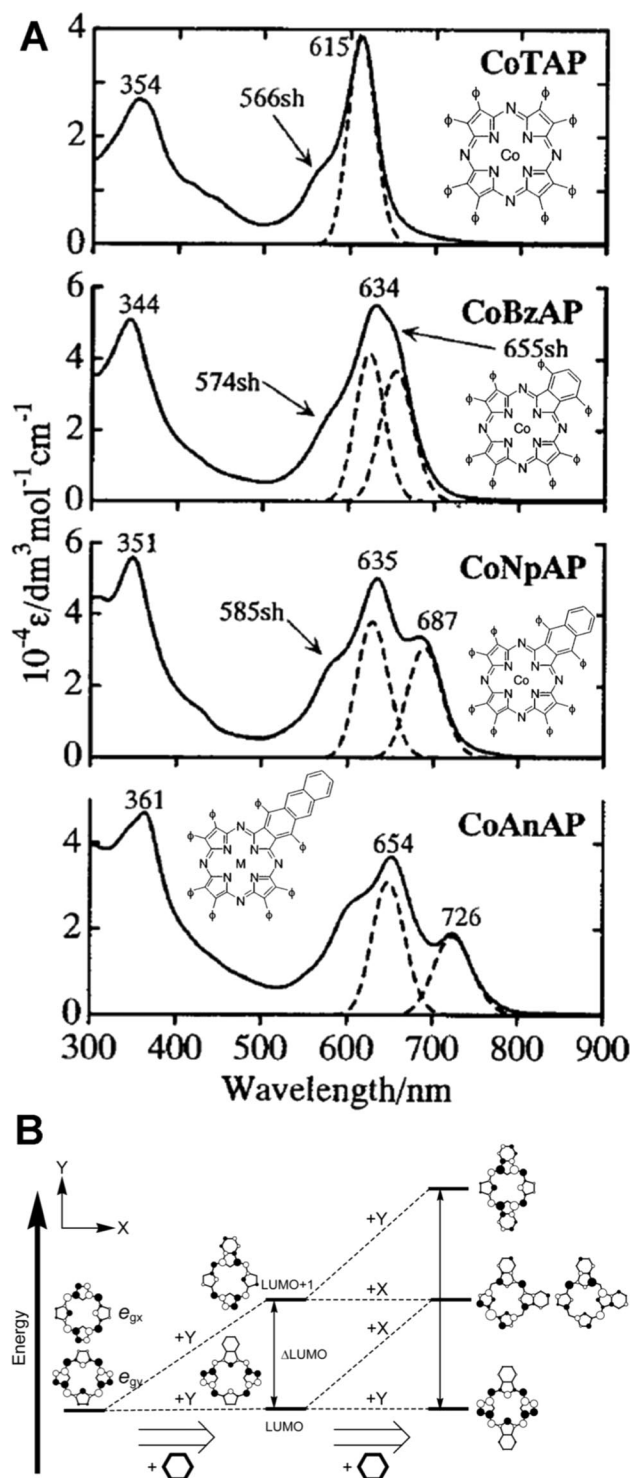


Figure 16. (A) Electronic absorption spectra in toluene of CoPz (CoTAP) and monosubstituted CoPz compounds with peripheral fused benzene (CoBzAP), naphthalene (CoNpAP), and anthracene (CoAnAP) ring systems. The Gaussian-shaped lines denote the Q0 bands identified by spectral band deconvolution analysis. Reproduced with permission from ref 375. Copyright 2004 American Chemical Society. (B) Effects of fused benzene rings on the energies of the LUMO and LUMO+1 of partially benzo-fused ZnPz's.¹⁸⁸ The Δ LUMO value can be expressed approximately as $1500(N_y - N_x)$ cm⁻¹, where N_y and N_x denote the number of fused benzo rings on the y- and x-axes. The Δ LUMO values were evaluated as 3000, 1500, and 1500 cm⁻¹ for the opp-di-, mono-, and tri-fused compounds, respectively, while the LUMO's are degenerate or near degenerate in the case of the Pz, Pc, and adj-di-fused compounds. Reproduced with permission from ref 188. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA.

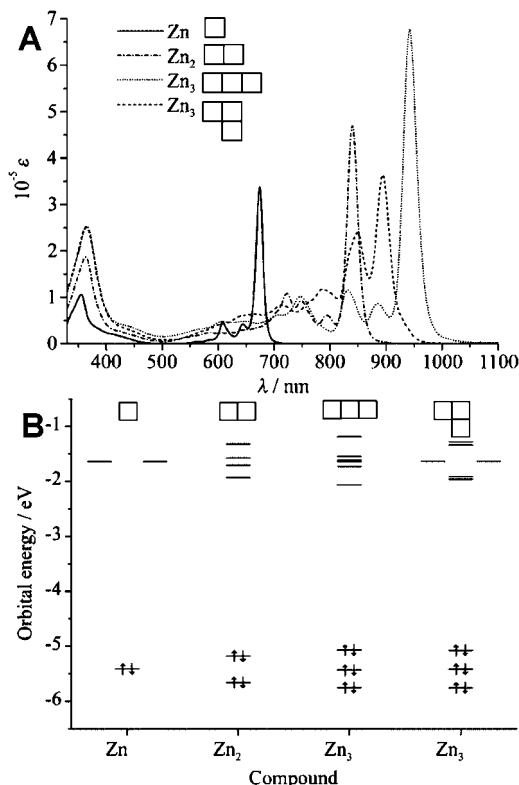


Figure 17. Electronic absorption spectra of ZnPc and the directly fused dimer and trimers in tetrahydrofuran (A). The MO's arising from the $1a_{1u}$ HOMO and $1e_g^*$ LUMO of the directly fused dimer and trimers in ZINDO/s calculations. The fused ring substitution patterns are denoted with sets of squares. Reproduced with permission from ref 134. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.

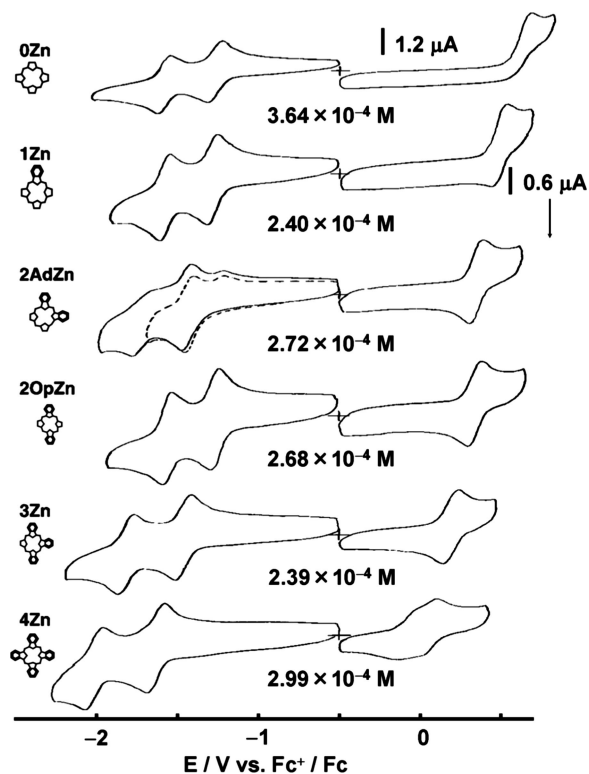


Figure 18. Cyclic voltammograms of benzo-substituted ZnPz complexes (named according to the number and arrangement of the benzo groups) obtained at a scan rate of 50 mV s^{-1} in *o*-dichlorobenzene solutions containing $2.5 \times 10^{-2} M$ pyridine and $0.1 M$ tetrabutylammonium perchlorate. Reproduced with permission from ref 188. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA.

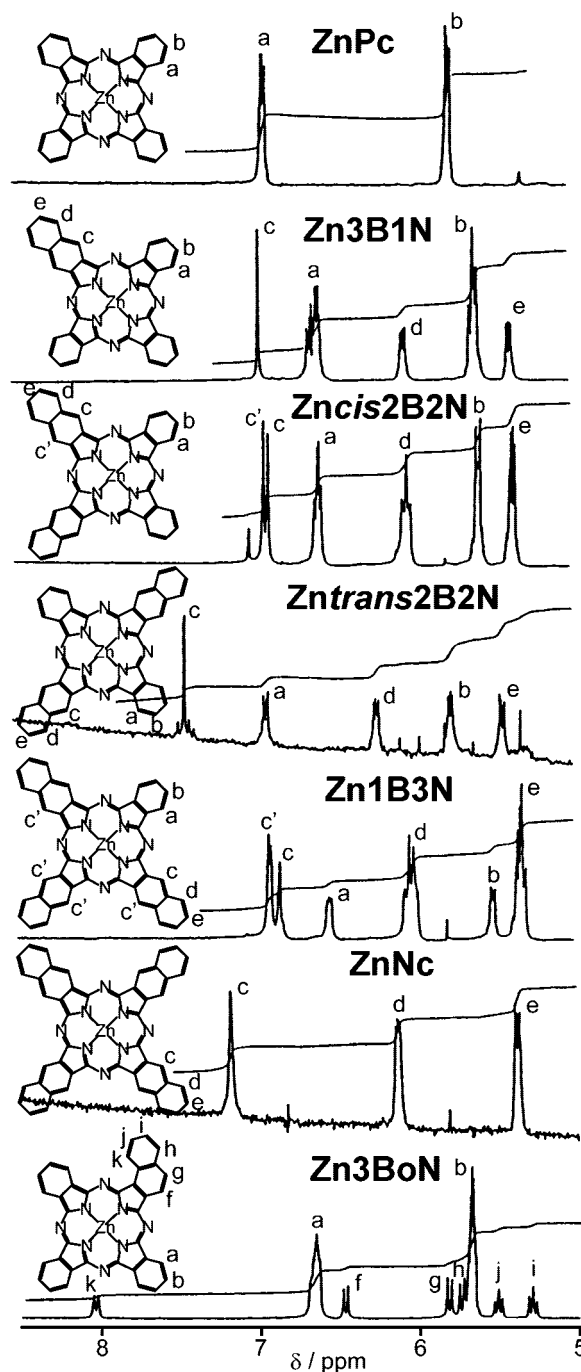


Figure 19. 1H NMR spectra and molecular structures of ZnPc, Zn₃B1N, Zncis2B2N, Zntrans2B2N, Zn1B3N, ZnNc, and Zn₃BoN, where 3B1N, cis2B2N, trans2B2N, and 1B3N refer to fused-ring substitution of a pyrrole moiety with benzenes (B) and 2,3-fused Nc's (N) and 3BoN refers to substitution with three benzenes and a 1,2-fused Nc ring. The letters a–k are used to denote the carbon atoms associated with the protons responsible for each NMR signal. Reproduced with permission from refs 187 and 401. Copyright 2002 American Chemical Society and 2009 Chemistry Society of Japan.

cyclic perimeter. An abrupt shift to lower field is observed for the **c**, **d**, and **e** proton signals of Zntrans2B2N relative to the spectrum of ZnNc, but no such shift is observed for the **a** and **b** proton signals in the spectra of Zntrans2B2N and ZnPc. The fact that the proton **c** peaks for Zn1B3N, Zn3B1N, and ZnNc lie at lower field than the proton **a** peaks of Zn3B1N and ZnPc, despite the weaker ring current on

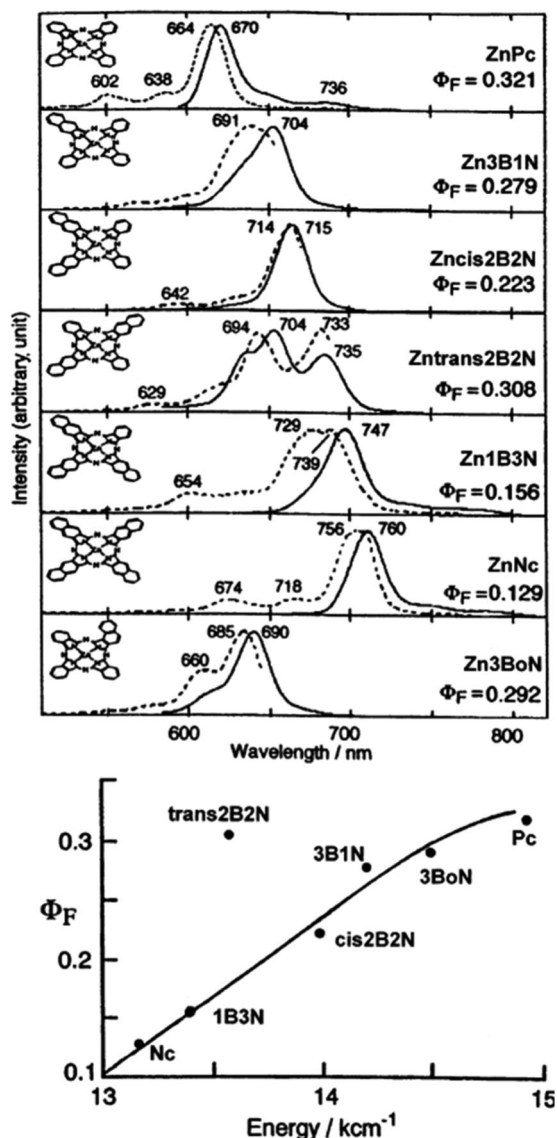


Figure 20. Fluorescence emission and excitation spectra (top) and fluorescence quantum yields (bottom) of ZnPc, Zn3B1N, Zncis2B2N, Zntrans2B2N, Zn1B3N, ZnNc, and Zn3BoN in deaerated CHCl_3 , where 3B1N, cis2B2N, trans2B2N, and 1B3N refer to fused-ring substitution of a pyrrole moiety with benzenes (B) and 2,3-fused Nc's (N) and 3BoN refers to substitution with three benzenes and a 1,2-fused Nc ring. Reproduced with permission from ref 187. Copyright 2002 American Chemical Society.

the inner ligand perimeter, is strong evidence that significant deshielding can also occur due to ring currents associated with the peripheral benzene and naphthalene moieties. It has recently been demonstrated that DFT calculations broadly reproduce the experimental data for this series of compounds.⁴²⁵ The characterization of the NMR spectra of low symmetry Pc's and their analogues can, therefore, be readily accomplished based on an understanding of the broad anticipated trends, integrated intensity and symmetry considerations, and a comparison with calculated spectra.

In addition to UV–visible absorption, NMR and IR spectroscopy, and mass spectrometry (MS), which are now used almost universally to characterize newly synthesized porphyrinoids, and the more specialized techniques of MCD spectroscopy and cyclic voltammetry, research has also been carried out based on a wide range of other characterization techniques. Several single-crystal X-ray structures have been reported.^{63,92,176,185,194,203,204,207,209–211,237,240,}

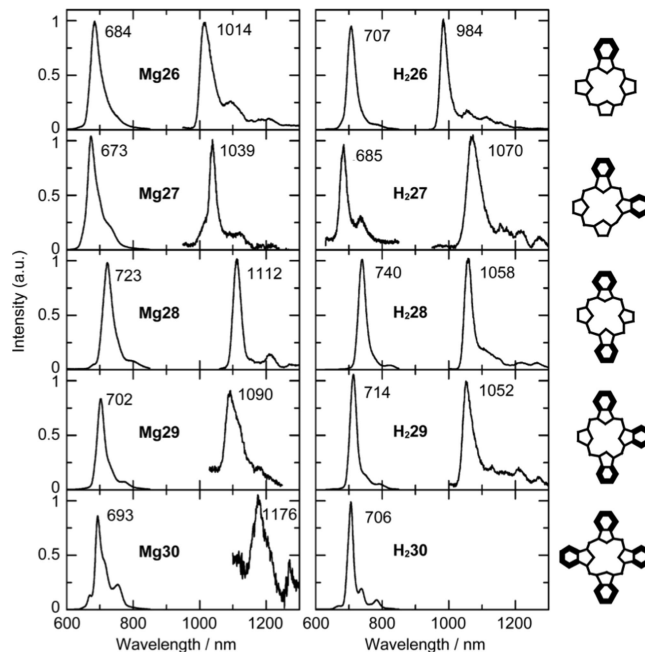


Figure 21. Luminescence spectra of the Mg(II) complexes (left) and metal-free (right) compounds of a series of benzo-fused Pz's. The fluorescence and phosphorescence spectra were measured at ambient temperature and 77 K, respectively. Reproduced with permission from ref 190. Copyright 2005 American Chemical Society.

Table 2. Fluorescence Lifetimes (τ_F) and Singlet Oxygen Yields (Φ_Δ)¹⁹⁰ for Benzo-Substituted Pz Compounds (Figure 10)

	τ_F (ns)	Φ_Δ^a	$\Phi_\Delta/\tau_F (\times 10^{-8} \text{ s})$
1H ₂	1.7	0.23	1.4
2AdH ₂	0.081	0.01	1.3
2OpH ₂	2.4	0.5	2.0
3H ₂	4.2	0.27	0.64
4H ₂	6.1	0.14	0.24

^a Φ_Δ measurements were carried out at various different laser powers, and the average Φ_Δ value obtained is reported. The experimental errors were within 15%.

260,262,321,330,334,335,337–339,360,392,402 Work by Barrett and Hoffman^{203,204,207,209–211,334,335,337–339,392} on Pz compounds has been particularly prominent in this regard, in recent years. There has been a growing focus on excited state properties over the past decade.⁴²⁶ Fluorescence excitation and emission spectra,^{94,96,99,100,109–111,123,127,132,134,136,137,185,188–190,192,202,205,208,209,214,218222,227,229,236,242,244,246,255,257,269–272,277,284,287,290,296,305,307,310,313,315,317,319,320,323,325,326,334,337,338,343,347,350,367,369,372,374,388,427} excited state lifetimes and decay curves,^{96,98,99,109,111,123,127,132,134,137,184,190,192,205,217,218,236,251,255,267,271,272,277–279,284,287,290,296,313,316,323,326,347,372,388} fluorescence quantum yields,^{94,96,99,109–111,123,127,132,134,136,137,187,192,205,208,209,215–217,227,244,246,266,271,272,277,284,287,294,296,310,313,315,318,326,337,347,350,367,372} and transient absorption spectra^{96,99,109,111,114,218,255,257,267,271,272,277–279,284,287,288,290,305,306,310,313,347,350} are increasingly being reported, since low symmetry Pz and Pc compounds are the focus of interest due to their possible use as photosensitizers in photodynamic therapy^{36,96,132,184,190,192,209,215–217,231,236,246,282,283,291,310,313,315,317,318,323,325,327,336–339,347,350,427,428} and as dyads in artificial photosynthesis research.^{39,89,94,111,218,257,278,279,284,287–290,310,316,319–321,323} The fluorescence and phosphorescence properties of partially benzo-fused ZnPz and ZnPc complexes have been studied in depth (Figures 20 and 21). The fluorescence quantum yields generally decrease as the molecular size increases or the

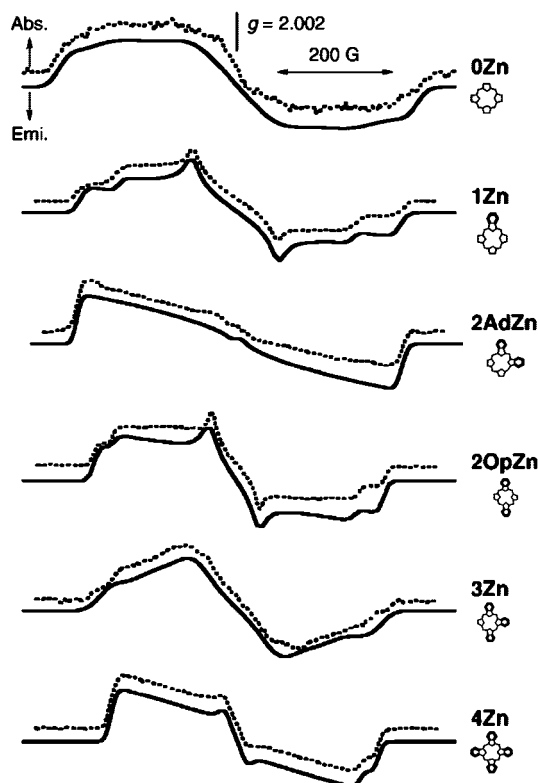


Figure 22. TREPR spectra (dotted lines) of partially benzo-fused ZnPz complexes in cyclohexanol plotted along with simulated spectra (solid lines). A toluene solution containing 0.1 M pyridine was used for ZnPc (**4Zn**). The spectra were recorded at 20 K, 1 ms after laser excitation. Reproduced with permission from ref 188. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA.

Table 3. Observed EPR Parameters¹⁸⁸ D_{obs} , E_{obs} , and g_{zz} with Sublevel Population Ratios $P_y:P_x:P_z$ for Benzo-Substituted ZnPz Compounds (Figure 10)

	D_{obs}^a	$ E _{\text{obs}}^a$	g_{zz}	$P_y:P_x:P_z$
0Zn	29	5.33	1.999	0.1:0:0.9
1Zn	26	4.00	1.999	0.2:0:0.8
2AdZn	26.8	8.54	1.998	0:0.4:0.6
2OpZn	23.5	5.17	1.999	0.2:0:0.8
3Zn	22.8	2.92	1.999	0.2:0:0.8
4Zn	21.8	6.09	1.995	0:0.0:0.1

^a The units are 10^{-3} cm^{-1} .

molecular symmetry is lowered, while those of ABAB compounds are significantly larger than those of their AABB isomers.^{187–189} ABAB compounds are therefore usually the best candidates for obtaining high singlet oxygen quantum yields (Φ_{Δ}) (Table 2). Singlet oxygen is produced from triplet oxygen by energy transfer from the triplet excited state of a porphyrinoid chromophore generated by intersystem crossing.¹⁹⁰

EPR spectroscopy^{53,62,115,123,128,134,135,188,190,204,210,211,334,340,392,429} and magnetic susceptibility measurements^{98,133,203,204,207,262,392} are also often made when a paramagnetic metal forms a complex either in the ligand cavity or with peripheral substituents. Over the past decade, time-resolved electron paramagnetic resonance (TREPR)^{123,129,188,189,296,401} data have occasionally been reported. In the case of partially benzo-fused ZnPz and PdPz complexes (Figure 22), the zero-field splitting parameter, D , which reflects the anisotropic interaction between unpaired electrons toward the out-of-plane z -axis, has been found to be related to the size of the π -system (Table 3). No such structural relationship has been

observed in the other zero-field splitting parameter, E , which reflects the anisotropic interaction between unpaired electrons toward the in-plane x - and y -axes. Figure 23 shows the splitting energy of the singlet excited (ΔE_{SS}) and triplet excited states (ΔE_{TT}) of partially benzo-fused MgPz, ZnPc, and H₂Pz compounds. As would be anticipated, the trends observed in the ΔE_{SS} and ΔE_{TT} values closely mirror trends in the calculated ΔLUMO values. Other more rarely used techniques include the use of circular dichroism spectroscopy to study compounds with optically active substituents,^{97,169,170,373,374,401} X-ray diffraction,^{106,128,179,265,276,374} thermogravimetric analysis,^{107,309,323} direct current conductivity,^{102,103} X-ray photoelectron spectroscopy,^{292,338} vapor pressure osmometric measurements,²⁶⁵ and polarized light,¹²⁸ transmission electron,^{236,289,388,309,322} scanning electron,^{292,309,322} and atomic force microscopy.^{100,279,309} Research has also focused on the formation of Langmuir–Blodgett films,¹²⁷ and on nonlinear optical,^{92,113,293,309,330,335,385} photovoltaic,^{243,245,254,261,298,302,430} optical limiting,^{264,321} liquid crystal,^{300,333–340} catalysis,³⁴⁰ antimicrobial photodynamic activity,²¹⁷ and HIV infection prevention⁴³¹ properties.

3. D_{2d} Symmetry Phthalocyanines

3.1. Synthesis

The symmetry of radially symmetric phthalocyanines with AAAA structures can be lowered by introducing structural modifications, which result in a folding of the π -system of the ligand. For example, slight deviations from planarity are often observed in X-ray structures of metal complexes when the central metal ion does not fit into the central cavity.⁴³² Doming of the ligand is most pronounced in the case of lanthanide ions,⁴³³ but since a C_4 axis is usually retained, complexes of this type lie outside the definition of low symmetry adopted in this review. Another potential source of nonplanarity is steric hindrance between peripheral substituents at the α - and β -positions (Figure 2). In marked contrast with porphyrins, where aryl and other bulky substituents are often present at the *meso*-carbons,¹⁴⁵ there is no substituent on the *aza*-nitrogen. Planarity is often retained, therefore, even in the case of hexadecasubstituted Pc's. For example, Gorun and co-workers^{434–436} have reported a planar perfluorinated Pc ligand with bulky $-i\text{-C}_3\text{F}_7$ groups at the β -positions but relatively small $-\text{F}$ atoms at the α -positions. When a phthalonitrile introduces very bulky substituents at the α -positions, however, cyclotetramerization reactions can result in the formation of MPc complexes with an S_4 rather than a C_4 axis of symmetry,^{45,63,64,195,239,376,382,402,411,437–451} since saddling of the isoindole moieties above and below the plane formed by the four *aza*-nitrogens relieves the steric crowding. In the year 2000, Cook and co-workers⁶⁴ reported an X-ray structure for α -octaisopentylphthalocyanine with a dihedral angle of 32.0° between the planes formed by the saddled isoindole moieties. The following year, Kobayashi and co-workers⁶³ reported that α -octaphenylphthalocyanine has dihedral angles of 46.0 and 41.9° due to a slight deviation from D_{2d} symmetry (Figure 24). In both cases, the “lithium method” described above in the context of the selective synthesis of AABB compounds was initially used to synthesize a free base compound, prior to metal insertion reactions.

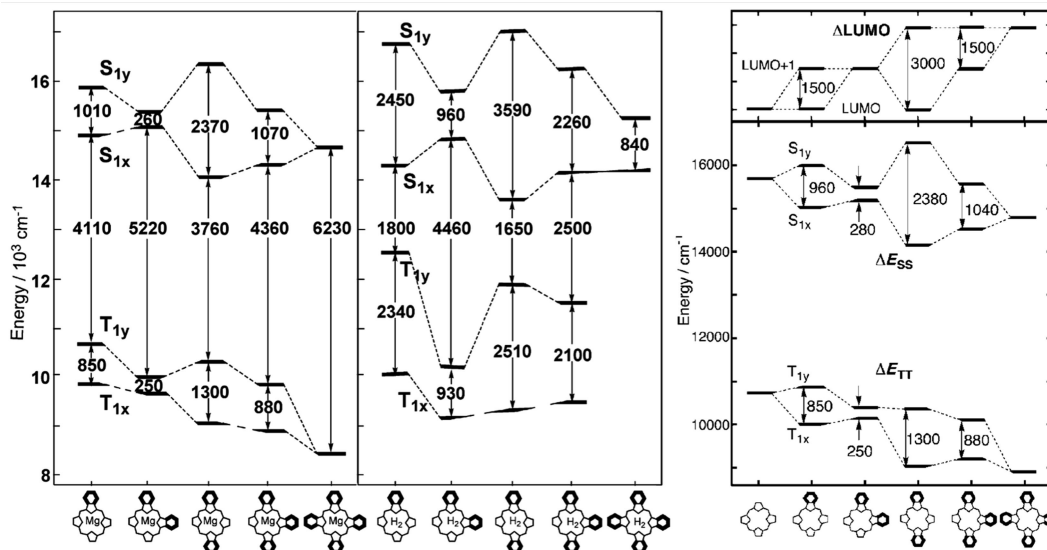


Figure 23. Summary of the ΔLUMO , ΔE_{SS} , and ΔE_{TT} values of low symmetry benzo-fused ZnPz compounds (right)¹⁸⁸ and of the ΔE_{SS} and ΔE_{TT} values of the corresponding Mg (left) and metal-free (center) compounds.¹⁹⁰ The splittings of the metal-free derivatives are largest. Reproduced with permission from refs 188 and 190. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA and 2005 American Chemical Society.

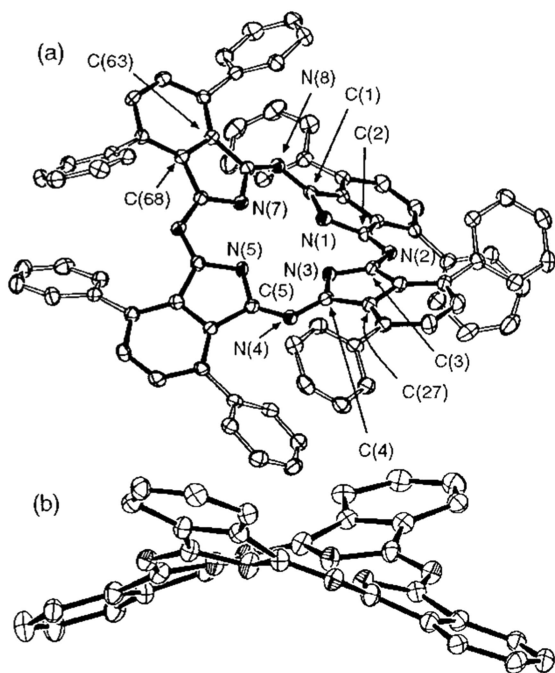


Figure 24. Molecular structure of $\text{H}_2\alpha(\text{C}_6\text{H}_5)_8\text{Pc}$: (a) top view and (b) side view. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms (in both parts a and b) and phenyl groups (in part b) are omitted for clarity. Reproduced with permission from ref 63. Copyright 2001 American Chemical Society.

3.2. Spectroscopic and Redox Properties

3.2.1. Optical Spectroscopy

The optical properties of radially symmetric Pc's can be modified significantly when there is a folding of the ligand, due primarily to the changes in the energies of the key frontier π -MO's. The effects of the minor deviations from planarity introduced by the coordination of a large central metal are typically limited, however. The small changes in the relative energies of the frontier π -MO's have only a minor impact on the relative intensities of the Q and B1

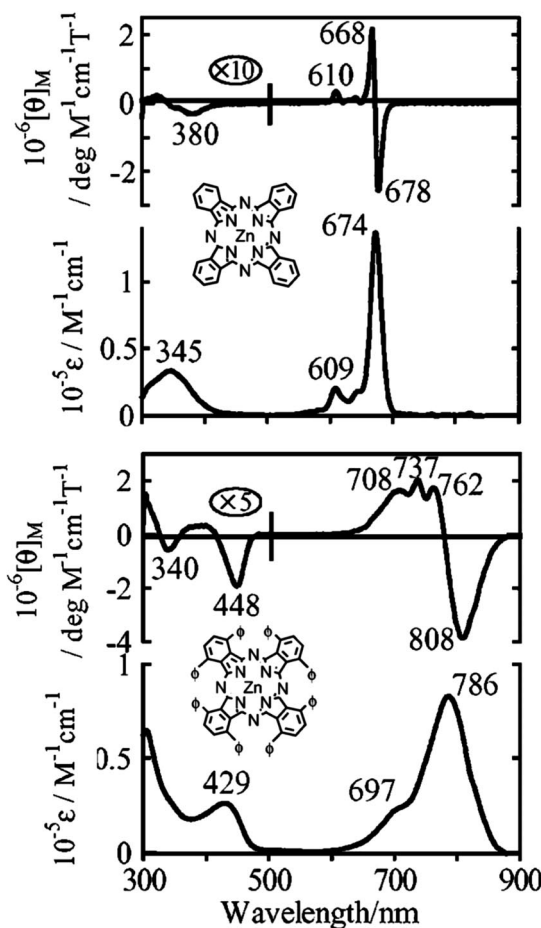


Figure 25. Absorption and MCD spectra of ZnPc (top) and $\text{Zn}\alpha(\text{C}_6\text{H}_5)_8\text{Pc}$ in pyridine (bottom). Reproduced with permission from ref 402. Copyright 2005 Wiley-VCH Verlag GmbH & Co. KGaA.

bands, since tetraazaporphyrinoids have large ΔHOMO values and very intense Q00 bands. In contrast, minor structural modifications can have a much larger effect on the Q band region of the optical spectra of porphyrins, since

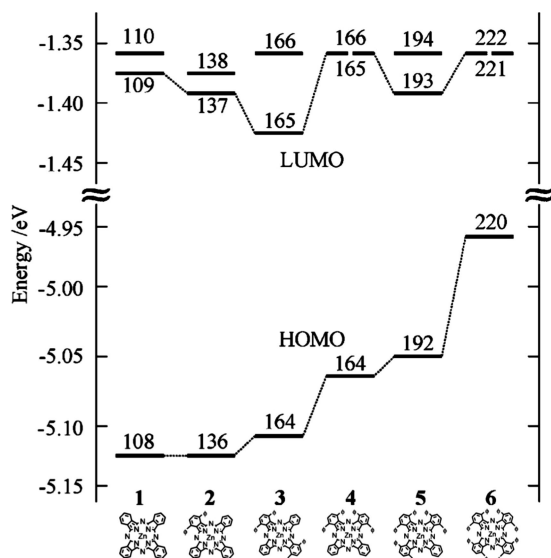


Figure 26. Frontier MO energy diagram for ZnPc (1), Zn α (C₆H₅)₂Pc (2), oppZn α (C₆H₅)₄Pc (3), adjZn α (C₆H₅)₄Pc (4), Zn α (C₆H₅)₆Pc (5), and Zn α (C₆H₅)₈Pc (6) based on B3LYP geometry optimizations with 6-31G(d) basis sets. Reproduced with permission from ref 402. Copyright 2005 Wiley-VCH Verlag GmbH & Co. KGaA.

there are small Δ HOMO values and vibrational borrowing from the allowed B band tends to be the major intensity mechanism due to the forbidden nature of the Q00 bands.⁴⁰³

Significant spectral changes are observed when steric hindrance between bulky substituents at the α -positions results in a deep saddling of the phthalocyanine π -system based on an S₄ axis of symmetry. The 1e_g* LUMO remains orbitally degenerate, so no splitting is observed in the Q00 band and the MCD spectra are dominated by Faraday \mathcal{A}_1 terms. A marked red shift of the Q band into the near IR region is usually observed (Figure 25) due to a destabilization of the 1a_{1u} HOMO⁴⁰² (Figure 26) but, unlike with severely saddled porphyrins,⁴⁵² not for the B1 and B2 bands. The OAM properties of D_{2d} symmetry MPc complexes are markedly different from those of the C₁₆H₁₆²⁻ parent perimeter, since there is a very large Δ HOMO value. This leads to extensive configurational interaction between the B1 and higher energy $\pi\pi^*$ states. Additional effects related to ligand saddling can sometimes be observed in the spectra of transition metal complexes. For example, while the Q00 band is the lowest energy band observed in the spectra of low spin Fe(II)Pc complexes,⁴⁵³ the corresponding α -octaphenylphthalocyanine spectrum contains a broad absorption band envelope to the red of the Q00 band, which extends out to 1000 nm (Figure 27).⁴⁴⁰ Spectral deconvolution analysis provides strong evidence for the presence of two MLCT transitions in the near IR region. A detailed analysis of a wide range of different D_{2d} symmetry transition metal complexes, based on the measurement of MCD spectra at both room and cryogenic temperatures, will be required to definitively assign these bands, however.

3.2.2. Redox Properties

Some spectroelectrochemical data have been reported for α -substituted Pc complexes,^{382,445} and CV data have been reported for complexes with phenyl^{402,440,441} and alkoxy^{382,445} substituents at the α -positions. The electrochemical data provide direct evidence that nonplanarity causes a significant destabilization of the HOMO energy and that this in turn

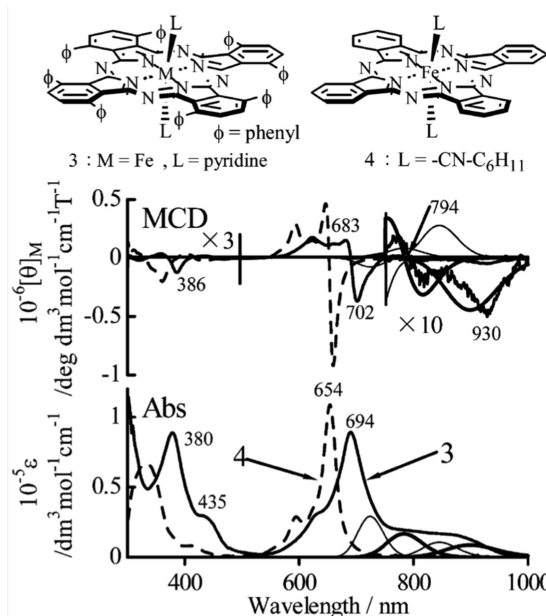


Figure 27. MCD (top) and absorption (bottom) spectra of Fe^{II} α (C₆H₅)₈Pc (3) (solid lines) and Fe^{II}Pc (4) (dashed lines) in pyridine, respectively. Deconvoluted Gaussian-shaped bands are overlaid in the spectra. Reproduced with permission from ref 440. Copyright 2003 Royal Society of Chemistry.

leads to the marked red shift of the Q band. The CV data of a series of partially α -phenylated ZnPc complexes⁴⁰² provide a good example of the changes induced by ligand saddling (Figure 28). Trends observed in the redox properties of compounds with increasing numbers of phenyl substituents closely mirror those observed in the Q band energies and ΔE_{o-r} values. The HOMO energies increase as the Q band energies decrease, but the LUMO energies remain relatively stable. The first and second oxidation potentials shift to the negative on going from Zn α (C₆H₅)₂Pc to Zn α (C₆H₅)₈Pc, but the first and second reduction potentials remain relatively constant (Figure 28). A linear trend is maintained only for the planar derivatives. The size of the deviation from this trend is related to the extent of ligand folding. So, for example, the ΔE_{o-r} value of the adj-disubstituted complex is slightly smaller than that of the opp-di-complex as would be anticipated based on the larger red shift of the Q band relative to unsubstituted ZnPc (Figure 28).

3.2.3. Other Characterization Methods

Several other techniques have been used to study D_{2d} symmetry Pc's beyond the standard use of IR and NMR spectroscopy and MS to characterize newly synthesized compounds. X-ray structures have been reported,^{64,402,443,444,449} although it should be noted that the symmetry is lowered somewhat from D_{2d} in each case due to the use of the free base rather than a metal complex^{63,64} and/or due to the influence of axial ligation⁴⁰² and stacking effects.^{444,448} EPR spectroscopy of lithium 5,9,14,18,23,27,32,36-octa-*n*-butoxy-2,3-naphthalocyanine crystals⁴⁴⁶ has been studied as a possible probe for determining the level of trace amounts of NO₂ gas. Fluorescence excitation and emission spectra,^{45,411,439,443} excited state lifetimes and decay curves,^{45,439,443} fluorescence quantum yields,^{45,196,443} and transient absorption spectra^{382,443,444,449} have also been reported. The fluorescence quantum yields of D_{2d} symmetry Pc's tend to be markedly lower than those of planar Pc's.¹⁹⁶

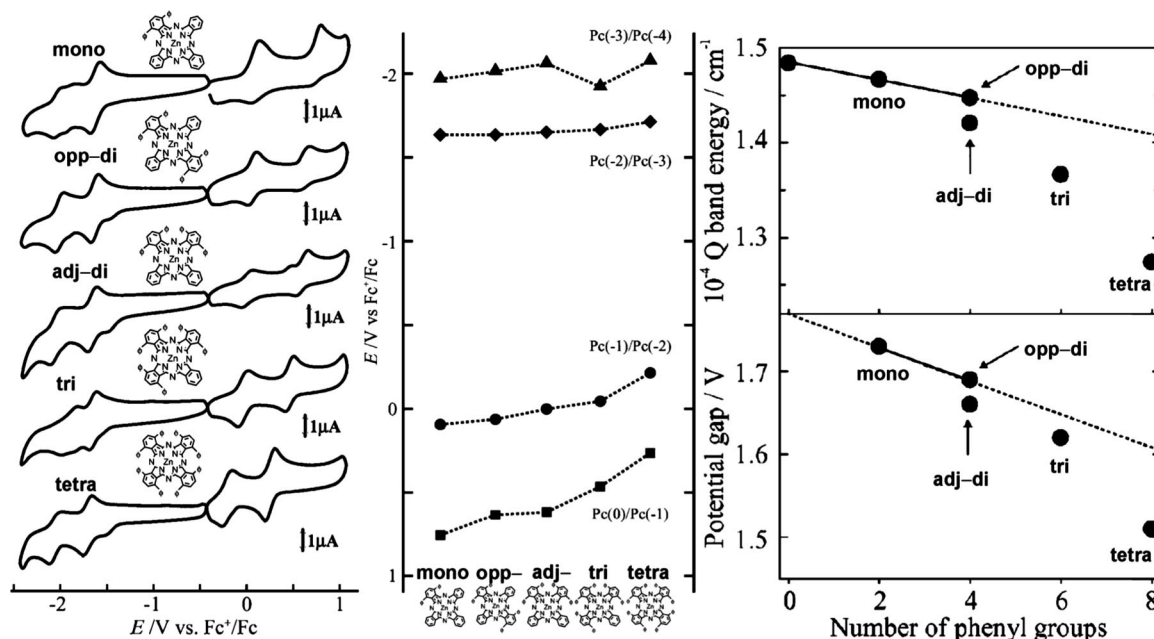


Figure 28. Cyclic voltammograms of $Zn\alpha(C_6H_5)_2Pc$ (mono), $oppZn\alpha(C_6H_5)_4Pc$ (opp-), $adjZn\alpha(C_6H_5)_4Pc$ (adj-), $Zn\alpha(C_6H_5)_6Pc$ (tri), and $Zn\alpha(C_6H_5)_8Pc$ (tetra) in *o*-dichlorobenzene solutions containing 0.1 M tetrabutylammonium perchlorate (left), and a plot of the redox data (center).⁴⁰² Trends observed in the Q band energies and the ΔE_{o-r} values with respect to the number of phenyl substituents (right). The first oxidation potential shifts negatively, while, in contrast, the first reduction potential does not shift appreciably from complex to complex. The first oxidation potentials are +0.10 and -0.20 V (vs Fc^+/Fc) for $Zn\alpha(C_6H_5)_2Pc$ and $Zn\alpha(C_6H_5)_8Pc$, respectively, indicating a destabilization of the HOMO by 0.30 V. In contrast, the first reduction potentials shift to the negative by only 0.08 V on going from $Zn\alpha(C_6H_5)_2Pc$ to $Zn\alpha(C_6H_5)_8Pc$ (center). As a consequence, the ΔE_{o-r} energy gap decreases from +1.73 to +1.51 as would be anticipated given the observed red shift of the Q band (right). On going from $Zn\alpha(C_6H_5)_2Pc$ to $oppZn\alpha(C_6H_5)_4Pc$, the first oxidation potential shifts by 0.04 V, while the first reduction potential remains almost identical (-1.63 V vs Fc^+/Fc). This indicates that the phenyl groups cause a slight destabilization of the HOMO levels. Ring deformation effects are also significant in the case of $adjZn\alpha(C_6H_5)_4Pc$, $Zn\alpha(C_6H_5)_6$, and $Zn\alpha(C_6H_5)_8Pc$ (right), where there is scope for steric hindrance between adjacent phenyl groups. Reproduced with permission from ref 402. Copyright 2005 Wiley-VCH Verlag GmbH & Co. KGaA.

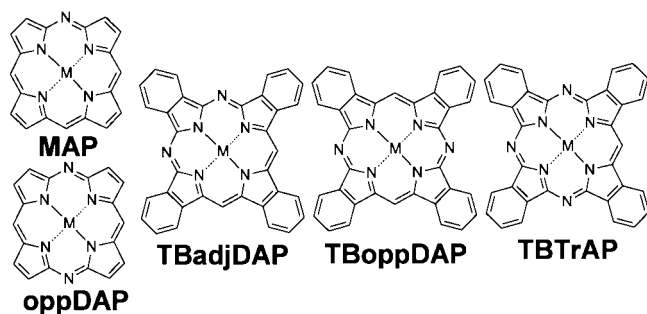


Figure 29. Molecular structures of MAP, oppDAP, TBadjDAP, TBoppDAP, and TBTrAP compounds.

4. Partial Aza-Substitution

4.1. Synthesis

One of the most obvious approaches to lowering the symmetry of porphyrinoids is to modify the four bridging atoms linking the four pyrrole moieties. Pc and Pz analogues have been reported in which the aza-nitrogens are partially replaced by *meso*-carbons (Figure 29).^{50,51,62,143,144,454–481} Two sets of compounds have been studied extensively in this regard: first, monoazaporphyrins (MAPs) and opp-diazaporphyrins (oppDAPs), which arise primarily from synthetic methods associated with porphyrins, and second, adj-diazaporphyrins (adjDAPs) and TBTrAPs, which are usually formed based on Pc chemistry. The synthesis of MAPs^{469–471,473} and oppDAPs^{472,474} was first reported by Fischer and Helberger in the mid-1930s. Fischer

derived the highest yields for MAP⁴⁷³ based on the action of bromine in acetic acid on dipyrromethene-5-urethanes and for oppDAP⁴⁷³ based on the reaction of 5,5'-dibromodipyrromethenes with ammonia in pyridine at high temperature and pressure. The synthesis of MgTBTrAP was reported by Linstead and co-workers a few years later¹⁴³ based on the reaction of MgPc with a stoichiometric amount of Grignard reagent in ether followed by heating of the crude product in a higher boiling solvent. Enhanced synthetic methods for MAPs and oppDAPs have been reported building on Fischer's approach,^{460–464,468,475} while Leznoff and McKeown reinvestigated the synthesis of TBTrAPs in the early 1990s.¹⁴⁴ Cook and co-workers⁴⁵⁶ subsequently reported the serendipitous formation of $\alpha(C_6H_{13})_8TBTrAP$ as the main side product in the preparation of $\alpha(C_6H_{13})_8Pc$ via a cyclotetramerization of 3,6-dihexylphthalonitrile induced by lithium pentyloxide in pentanol, with the carbon atom apparently coming from the solvent. This reaction has recently been used to synthesize the corresponding tetrabenzodiaza- and tetrabenzomonoazaporphyrin compounds.⁴⁵⁷ Luk'yanets and co-workers⁴⁷⁶ have reported the formation of tetrabenzoadj-diazaporphyrin (TBadjDAP) complexes (Figure 29) based on a reaction of dimeric isoindolone with 3-iminothalimide at 280 °C in the presence of zinc acetate in bromonaphthalene. Shaposhnikov and co-workers recently reported the synthesis of the entire series of Zn(II) *meso*-phenyltetrabenzomonoazaporphyrins based on a reaction of a 1,3-diiminoisoindoline with phenylacetic acid in the presence of zinc oxide.^{480,481}

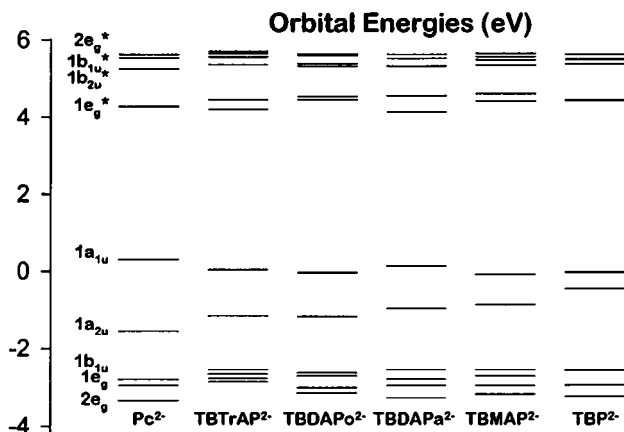


Figure 30. Partial MO energy diagrams based on INDO/1 calculations for deprotonated Pc^{2-} , TBTrAP^{2-} , oppTBDAP^{2-} (TBDAPo^{2-}), adjTBDAP^{2-} (TBDAPa^{2-}), TMAP^{2-} , and TBP^{2-} dianion structures. Reproduced with permission from ref 454. Copyright 1997 American Chemical Society.

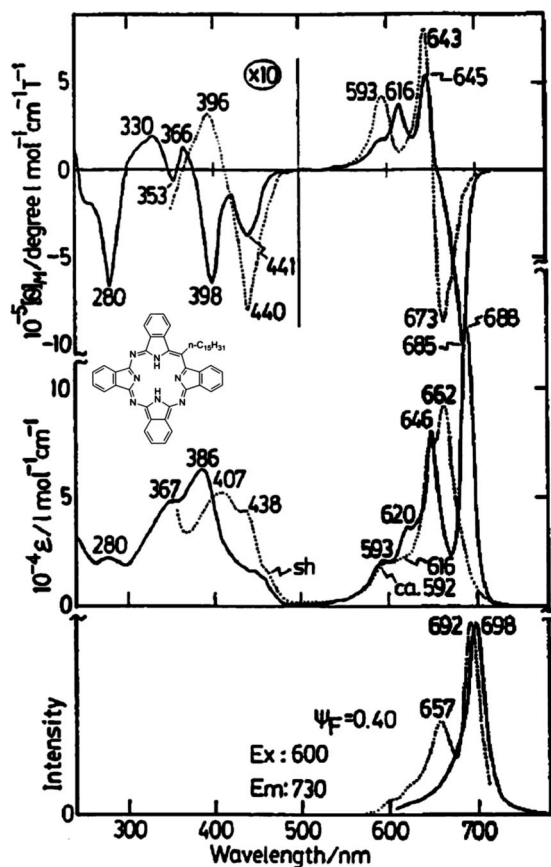


Figure 31. MCD (top), electronic absorption (center), and fluorescence excitation spectra (bottom) of neutral (solid lines) and deprotonated (dotted lines) tetra-*tert*-butyltetraabenz[5,10,15]triazaporphyrin in tetrahydrofuran. Reproduced with permission from ref 454. Copyright 1997 American Chemical Society.

4.2. Spectroscopic and Redox Properties

4.2.1. Optical Spectroscopy

Partial aza-substitution has a relatively minor effect on the optical properties of Pz and Pc analogues. The perturbation to the electronic structure is usually relatively minor, since it is based primarily on the electronegativity difference between *meso*-carbon and aza-nitrogen atoms. The $1a_{2u}$ HOMO-1 of TBP is steadily stabilized with the

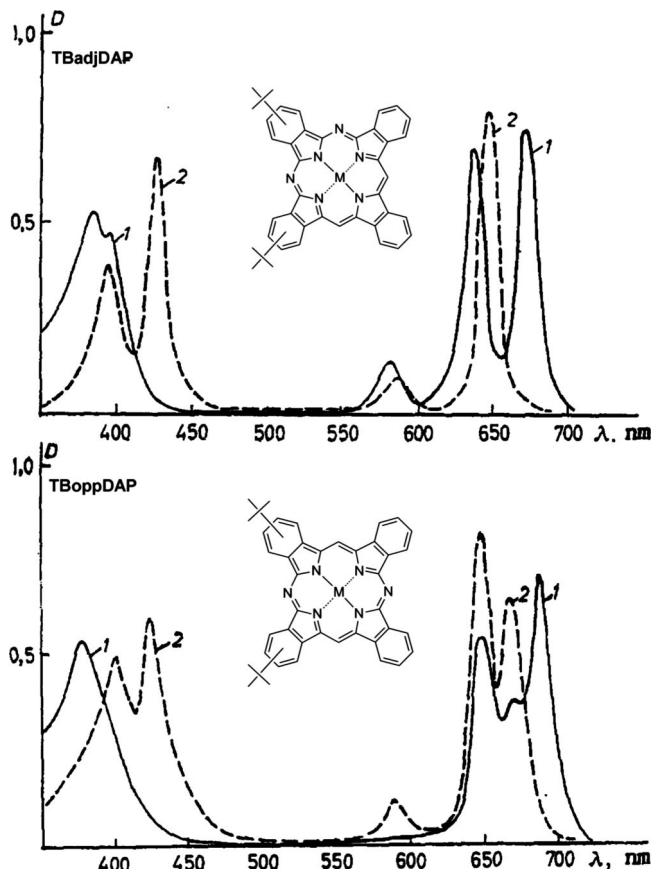


Figure 32. Electronic absorption spectra of $\text{H}_2\text{adjTBDAP}$ (top) and $\text{H}_2\text{oppTBDAP}$ (bottom) in benzene (solid line, 1) and dimethylformamide in the presence of NaOH (dashed line, 2). Reproduced with permission from ref 476. Copyright 1989 Springer.

addition of each successive aza-nitrogen, and the ΔHOMO values become progressively larger⁴⁵⁴ (Figure 30). The UV–visible absorption and MCD spectra of TBTrAP compounds⁴⁵⁴ are, therefore, similar to those of H_2Pc (Figure 31). There is a much larger splitting of the $Q00$ bands of oppTBDAP than there is for adjTBDAP ⁴⁷⁶ (Figure 32), since the aza-substitution perturbation to the structure varies along the *x*- and *y*-axes. As predicted on the basis of the symmetry-adapted perturbation method,⁵⁰ no splitting is observed in the $Q00$ band of the metal complex of the adjTBDAP compound, since the perturbation to the structure is identical along the *x*- and *y*-axes. The degeneracy of the LUMO level is lifted only slightly and the MCD spectrum is dominated by pseudo- \mathcal{A}_1 terms (Figure 31). The spectra of MAP and oppDAP complexes are similar to those of TBP (Figure 33). The B bands are narrower and more intense than those of ZnPz and are shifted to longer wavelength at *ca.* 400 nm.⁴⁵⁵

4.2.2. Redox Properties

Lever, Leznoff, and co-workers⁴⁶⁵ reported some spectro-electrochemical data for TBTrAP compounds in the 1990s. As would be anticipated based on the optical spectroscopy of the neutral complexes, the data are similar to spectra reported previously for the parent D_{4h} symmetry MPc complexes.⁴¹⁵ Some CV and DPV data have also been reported.^{455,459,465,466} Kobayashi, Stuzhin, and co-workers⁴⁵⁵ recorded CV and DPV data for $\text{Cu}^{\text{II}}\text{Pz}$ and $\text{Cu}^{\text{II}}\text{oppDAP}$, together with the cyclic voltammograms of copper octaethylporphyrin ($\text{Cu}^{\text{II}}\text{OEP}$) and $\text{Cu}^{\text{II}}\text{Pz}$ in *o*-dichlorobenzene (Figure 34). As the number of aza-nitrogen atoms increases

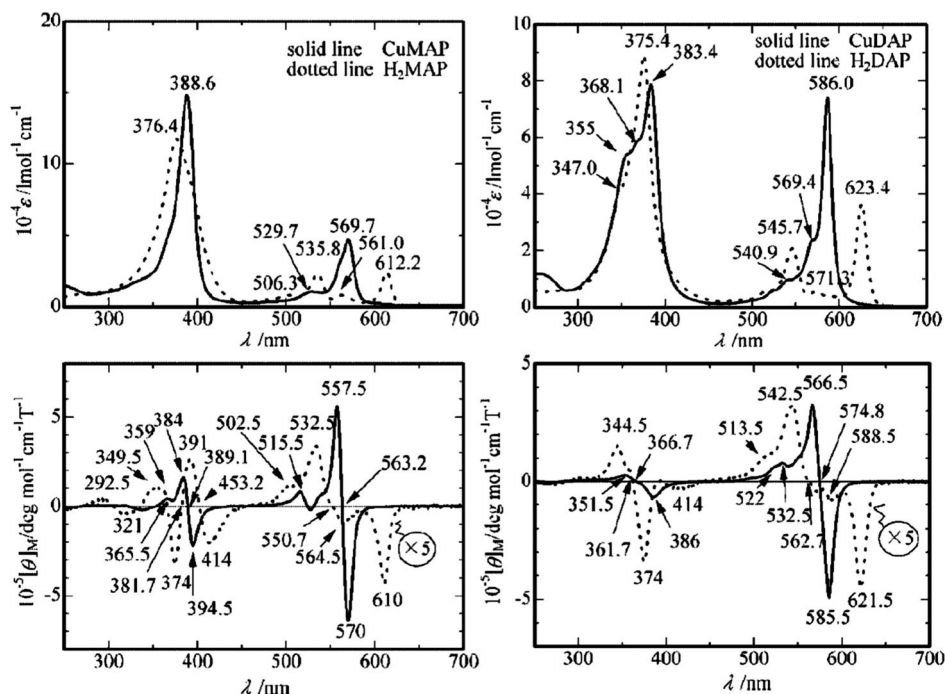


Figure 33. Electronic absorption (top) and MCD (bottom) spectra of Cu^{II}MAP (solid lines) and H₂MAP (dotted lines) (left) and Cu^{II}oppDAP (solid lines) and H₂oppDAP (dotted lines) (right) in CHCl₃; note the encircled magnification factor for the MCD spectra of H₂MAP and H₂oppDAP. Reproduced with permission from ref 455. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA.

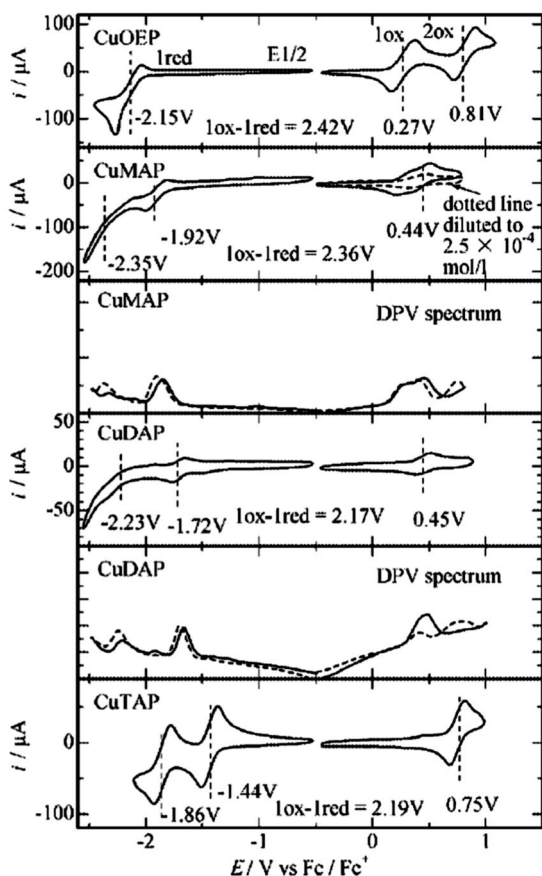


Figure 34. Cyclic and differential pulse voltammograms of Cu^{II}OEP, Cu^{II}MAP, Cu^{II}oppDAP, and Cu^{II}Pz (from top to bottom) in *o*-dichlorobenzene containing 0.1 M tetrabutylammonium perchlorate. Reproduced with permission from ref 455. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA.

in the sequence OEP, MAP, oppDAP, and Pz, the first oxidation and the first and second reduction potentials become

steadily more positive. The $\Delta E_{\text{ox-r}}$ values for Cu^{II}MAP, Cu^{II}oppDAP, and Cu^{II}Pz are 2.36, 2.17, and 2.19 V, respectively, while the corresponding values for OEP derivatives are reported to be $2.25 \pm 0.15 \text{ V}$.⁴⁸² This demonstrates that the presence of the aza-nitrogens has only a minor effect on the magnitude of the HOMO–LUMO band gap as would be anticipated based on their similar Q band wavelengths.

4.2.3. Other Characterization Methods

A limited number of techniques have been used to study partially aza-substituted Pc analogues beyond the standard use of IR and NMR spectroscopy and MS to characterize newly synthesized compounds. Single crystal X-ray structures have been reported for MAP,⁴⁶² DAP,⁴⁷⁸ and TBTrAP complexes.^{456,457} A detailed analysis of the IR spectra has been carried out for MAPs and oppDAPs based on DFT calculations⁴⁵⁵ (Figure 35). The calculated and observed experimental spectra are in reasonably close agreement in terms of both the intensity and the energies of the bands. Fluorescence emission has also been studied to a limited extent.^{458,459} Singlet oxygen quantum yields of up to 0.92 have been reported by Osuka and co-workers for free base and metal DAPs,⁴⁵⁸ while Nakamura and co-workers⁴⁷⁷ used NMR, EPR, and IR spectroscopy to demonstrate that Fe^{II}MAP has an unusual ground-state when isocyanide is present as an axial ligand. Liquid crystal formation⁴⁶⁷ and the polarized absorption and dichroism properties of Langmuir–Blodgett films⁴⁶⁶ have been reported for TBTrAP compounds.

5. Corrolazines and Tetrabenzocorrolazines

5.1. Synthesis

A second type of structural modification that can be made at the aza-linkages is the replacement of an aza-nitrogen with a direct bond between the α -carbons on neighboring pyrrole

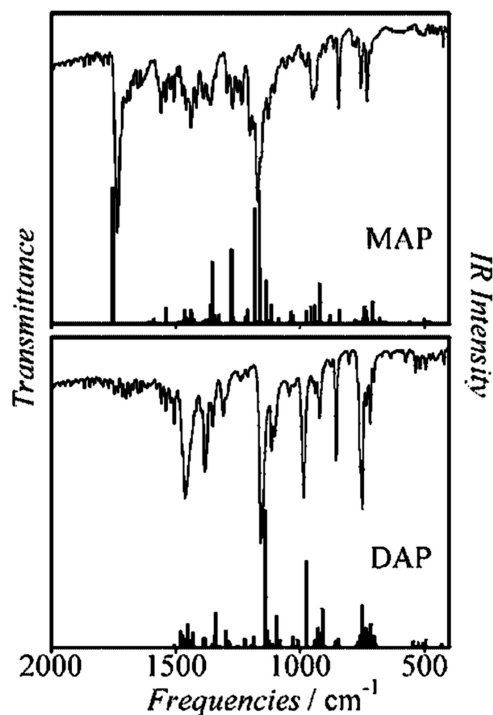


Figure 35. Experimental and calculated (bars) IR spectra of Cu^{II} MAP (top) and Cu^{II} oppDAP (bottom); in the calculation, Cu atoms were replaced by Zn atoms. The in-plane motions of the structure are located at 1136, 973, 922, 917, 740, and 732 cm^{-1} for MAP and at 1340, 1132, 1094, 973, 928, 917, 910, 749, and 734 cm^{-1} for oppDAP. The out-of-plane motions of the hydrogen atoms appear in the energy region below 1000 cm^{-1} . The vibrations associated with the C–H *meso*-groups were assigned to the peaks at 842 and 846 cm^{-1} for MAP and oppDAP, respectively. Reproduced with permission from ref 455. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA.

moieties to form TBCz's and Cz's^{146–148,483–505} (Figure 36). Fujiki et al.¹⁴⁸ reported the first synthesis of a stable TBCz in 1986 after studying anomalous spectra reported by Gouterman for what were believed at the time to be Ge^{II} Pc and P^{III} Pc complexes.⁵⁰⁶ $(\text{Cl}^-)\text{Ge}^{\text{IV}}$ TBCz was found to be formed via a one-step ring-contraction reaction from $(\text{Cl}^-)_2\text{Ge}^{\text{IV}}$ Pc in the presence of reducing agents such as NaBH_4 at 160 °C. In order to maintain a planar heteroaromatic π -system, a trianion is formed to compensate for the loss of the sp^2 hybridized aza-nitrogen. Li et al.⁴⁸⁵ later reported the formation of $(\text{X}^-)\text{Si}^{\text{IV}}$ TBCz (where X^- is an axial ligand) (Figure 37) based on a reaction of Si_2Cl_6 with an alkyl substituted 1,3-diiminoisindoline. Kobayashi et al.,⁴⁸⁴ who had earlier reported the formation of cofacial SiPc dimers based on very similar reaction conditions,^{500,501} subsequently demonstrated that the use of Si_2Cl_6 is not actually required to synthesize monomeric compounds, since HSiCl_3 can also be used. Li et al. demonstrated after reacting H_2Pc with PBr_3 in pyridine at 90–100 °C that the anomalous spectrum reported by Gouterman for P^{III} Pc had been misassigned and is actually due to $(\text{X}^-)\text{PTBCz}$. Goldberg and co-workers¹⁴⁷ subsequently used a similar procedure to form corrolazines from Pz's. In contrast with TBCz complexes, attempts to form free base compounds were successful and metal insertion reactions have subsequently enabled the preparation of a wide range of Cz compounds.¹⁴⁶ The Cz ligand can be used, in a similar manner to the corroles,^{507,508} to stabilize the higher oxidation states of central metals, such as Cr(V), Mn(IV), Fe(IV), Co(IV), and Cu(III), in solution.¹⁴⁷

5.2. Spectroscopic and Redox Properties

5.2.1. Optical Spectroscopy

The removal of an aza-nitrogen results in marked changes in the spectroscopic properties due to the loss of the main C_4 axis of symmetry and changes in the energies of the frontier π -MOs. The four frontier π -MO's of the $\text{C}_{15}\text{H}_{15}^{3-}$ parent perimeter are very similar to those of the porphyrins (Figure 8), so Gouterman's 4-orbital model⁴⁰³ and Michl's perimeter model^{404,405} can still be used to rationalize the optical and redox properties (Figure 38). The ΔLUMO values of Cz and TBCz complexes are relatively small (Figure 39), so only minor splittings of the Q00 and B00 bands are observed in the optical spectra. The $1a_{2u}$ MO from Gouterman's 4-orbital model⁴⁰³ is destabilized due to the large MO coefficients on the aza-nitrogens, so the ΔHOMO values are markedly lower than those of Pz and Pc compounds. As a consequence, the optical spectra of TBCz complexes exhibit similarities to the spectra of TBP complexes, especially in the B band region (Figure 36). For example, the B band of $(\text{OMe}^-)\text{P}^{\text{V}}\alpha(\text{n-BuO})_8\text{TBCz}$ shifts to the red with an intensity maximum at 520 nm. A single pair of intense Faraday \mathcal{B}_0 terms is observed in the B band region of the MCD spectrum.⁵⁰⁵ Since the ΔHOMO and ΔLUMO values are similar and both comparatively low, the OAM properties are closer to those of the parent hydrocarbon perimeter and there is less configurational interaction between the B excited state and higher energy $\pi\pi^*$ states. There is a marked red shift of the Q band of $(\text{OMe}^-)\text{P}^{\text{V}}\alpha(\text{n-BuO})_8\text{TBCz}$ due to substitution of bulky electron-donating substituents at the α -positions.⁵⁰⁵

5.2.2. Redox Properties

No spectroelectrochemical data have been reported to date. A limited range of CV and DPV data has been reported for both Cz^{146,490,493,498} and TBCz^{489,500,501} compounds.

5.2.3. Other Characterization Methods

A variety of techniques have been used to study Cz and TBCz compounds beyond the standard use of IR and NMR spectroscopy and MS to characterize newly synthesized compounds. Single crystal X-ray structures have been reported for several corrolazines^{146,488,493,496,497} and for Si^{IV} TBCz (Figure 37).⁵⁰¹ Resonance Raman spectroscopy has been used to confirm the presence of $\text{V}\equiv\text{O}$ and $\text{Mn}\equiv\text{O}$ bonds,^{487,490} while EPR^{487,494,497,498} and magnetic susceptibility⁴⁹⁷ measurements have been made in instances where the central metal is paramagnetic. Some X-ray absorption near edge structure (XANES)^{498,500,501} and extended X-ray absorption fine structure (EXAFS)⁴⁹⁷ data have also been reported. Catalysis applications of metals stabilized in solution in high oxidation states by the corrolazine ligand have been explored.^{147,495,496,502,503} Recently, Chinese researchers have studied the fluorescence emission, excitation and transient absorption spectra, and the fluorescence emission and singlet oxygen quantum yields of a sulfonated $(\text{OH})_2\text{P}^{\text{V}}$ TBCz to assess the suitability of TBCz compounds for use as photosensitizers in PDT.⁴⁹² A Φ_{Δ} value of 0.88 was obtained, which is higher than what is typically observed for benzo-substituted Pz's (Table 2).

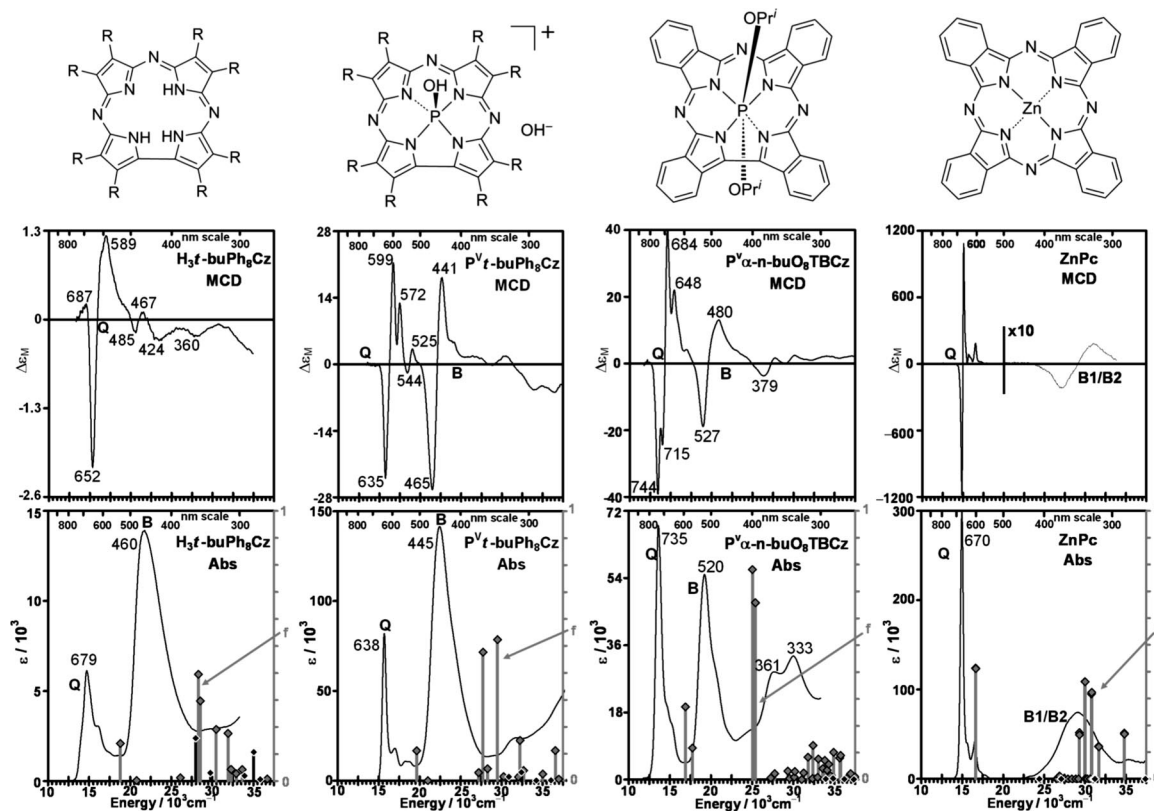


Figure 36. Molecular structures (TOP) and MCD and UV–visible absorption spectra (bottom) of $H_3(p\text{-}t\text{-}BuPh)_8Cz$, $(OH^-)_2P^V(p\text{-}t\text{-}BuPh)_8Cz$, $(OCH_3^-)_2P^V\alpha(n\text{-}BuO)_8TBCz$, and $ZnPc$. The five-coordinate structure of $(OH^-)_2P^V(p\text{-}t\text{-}BuPh)_8Cz$ was determined based on an analysis of ^{31}P NMR data.¹⁴⁶ Calculated TD-DFT absorption spectra for H_3Cz , $(OH^-)_2P^VCz$, and $(OH^-)_2P^VTBCz$ model compounds are plotted against the right-hand axes. Bands arising from transitions to $n\pi^*$ states are denoted by black diamonds. Reproduced with permission from ref 505. Copyright 2008 Japan Institute of Heterocyclic Chemistry.

6. Hemiporphyrazines and Three-Quarters-Phthalocyanines

6.1. Synthesis

Pc and Pz ligands can also be modified through the partial replacement of the four pyrrole or isoindoline moieties.^{50,51,62,149–152,365,509–559} Core modified porphyrin compounds in which one or more of the pyrrole nitrogens is replaced by either a carbon atom or another type of heteroatom have been the focus of considerable research interest.⁵⁶⁰ This type of structural modification is less common in the Pc literature, however, due to the limitations imposed by the cyclotetramerization approach. Most of the research that has been carried out in this area involves the synthesis and characterization of AAAB compounds, typically referred to as three-quarters-phthalocyanines, and ABAB compounds, which are typically referred to as hemiporphyrazines (Figure 40). In 1952, Elvidge and Linstead reported the first example of an HPz based on a cross-condensation of 2,6-diaminopyridine and 1,3-diiminoisoindoline to form an opp-dipyridine structure¹⁴⁹ in which two of the isoindoline moieties of Pc are replaced by pyridines (Scheme 4). Almost simultaneously, Campbell applied for a U.S. Patent.⁵⁵⁶ The synthetic strategy is analogous in concept to Idelson's subsequent patent for the selective formation of ABAB compounds³⁶² (Scheme 2), since the diamine compound can only react with the diiminoisoindoline precursor. The authors subsequently reported the formation of a series of free base macrocycles using 1,3-diaminobenzene, 2,7-diaminonaphthalene, 2,8-diaminoacridine, and 3,5-diaminopyridine⁵¹⁰ (Scheme 5). Elvidge and co-workers also

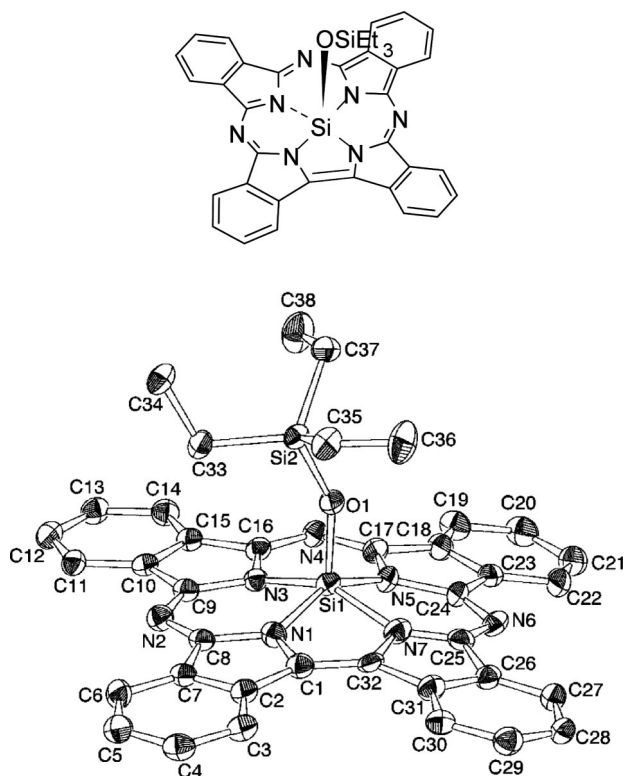


Figure 37. Molecular structure of $(OSiEt_3)Si^{IV}TBCz$ (top) and an ORTEP plot with thermal ellipsoids drawn at the 30% probability level (bottom). Hydrogen atoms are omitted for clarity. Reproduced with permission from ref 501. Copyright 2002 Wiley-VCH Verlag GmbH & Co. KGaA.

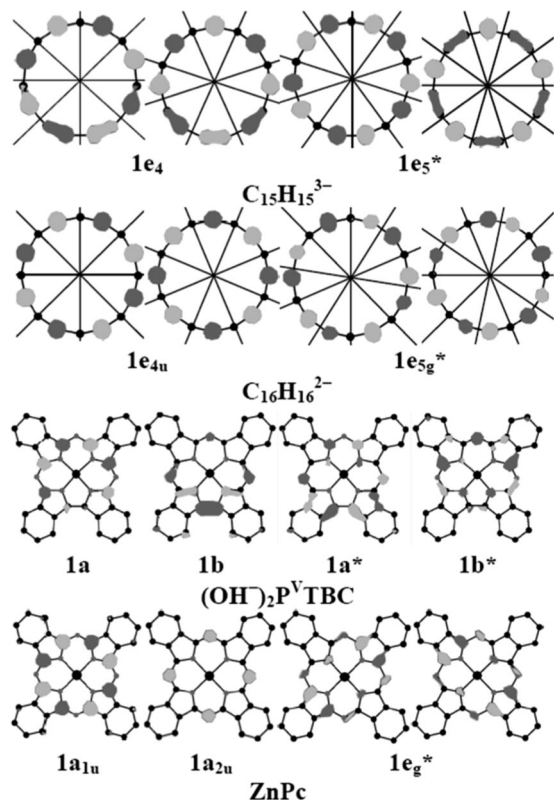


Figure 38. Nodal patterns of the four frontier π -MO's of $C_{15}H_{15}^{3-}$, $C_{16}H_{16}^{2-}$, $(OH)_2P^VTBCz$, and $ZnPc$ at an isosurface value of 0.05 au. The HOMO's and LUMO's display $M_L = \pm 4, \pm 5$ properties in terms of the phase changes on the inner ligand perimeter, as anticipated on the basis of Gouterman's 4-orbital model⁴⁰³ (Figure 6). Reproduced with permission from ref 505. Copyright 2008 Japan Institute of Heterocyclic Chemistry.

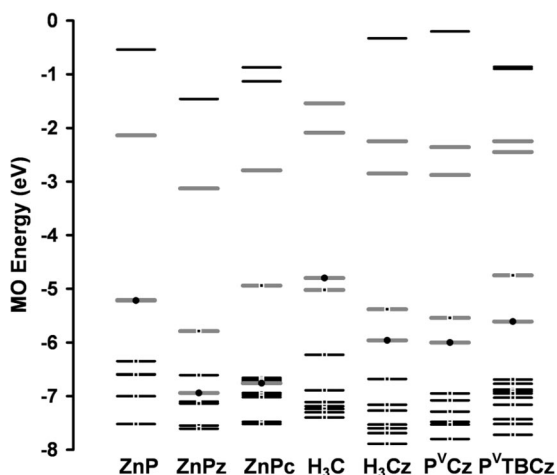


Figure 39. Frontier MO energy diagram for zinc porphyrin (ZnP), ZnPz, ZnPc, free base corrole (H_3C), H_3Cz , P^VCz , and P^VTBCz based on DFT geometry optimizations using the B3LYP functional with 6-31G(d) basis sets.^{452,505} Thicker gray lines are used for the four frontier π -MO's from Gouterman's 4-orbital model.⁴⁰³ The $1a_{2u}$ MO, which has large MO coefficients on the *meso*-carbons and aza-nitrogens (Figure 8) is highlighted with a circle.

studied the synthesis of opp-di-*m*-benzophthalocyanine and explored the formation of metal complexes.^{149,510} Benzophthalocyanines are of particular interest in this regard, since organometallic complexes can be formed (Scheme 6). Russian researchers subsequently reported a wide range of other HPz's based on the reaction of 1,3-diiminoisindolines with 2,4-diamino-6-chloropyrimidine,⁵²³ 2,4-diamino-3-chloro-s-

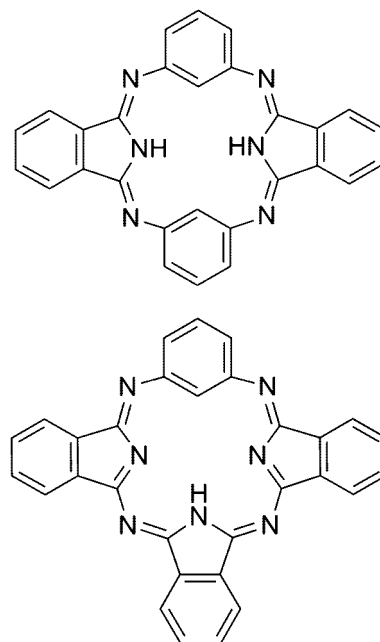
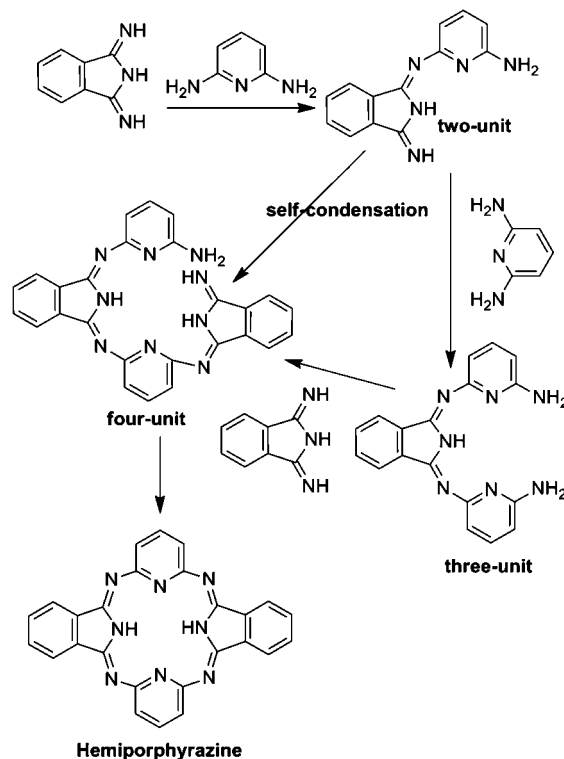


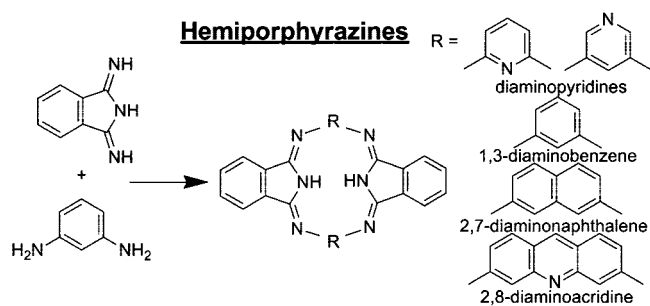
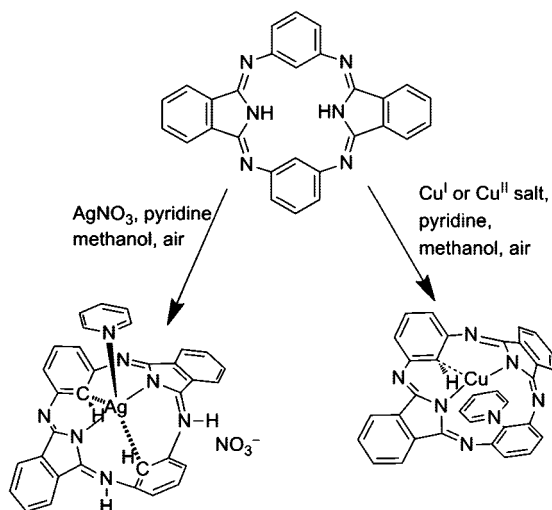
Figure 40. Molecular structures of dicarbahemiporphyrizine (top), an HPz, and *m*-benzophthalocyanine, a three-quarters-phthalocyanine (bottom).

Scheme 4. Formation of Hemiporphyrazines¹⁴⁹

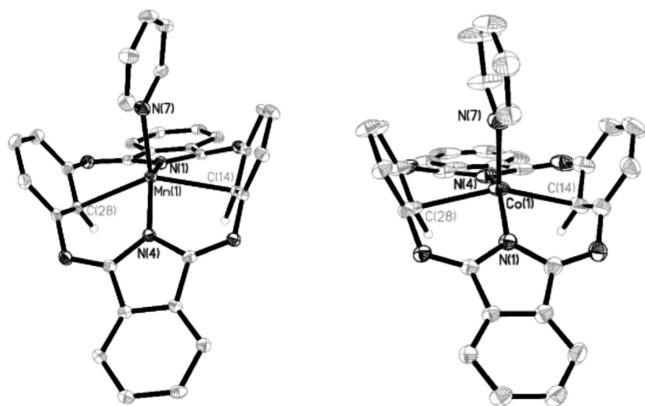
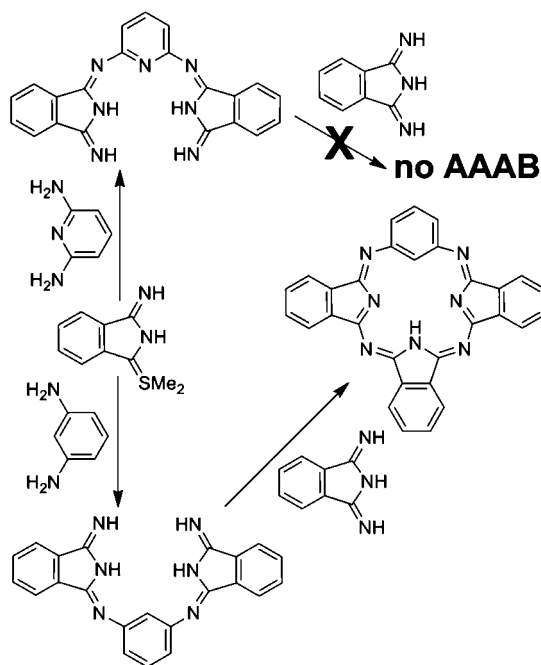


triazine,⁵²⁴ 2,5-diaminotriazole,^{525–527} 2,7-diamino-fluorene,^{527–534} 2,7-diaminophenylene sulfone,⁵¹⁸ and 2,4-diamino-3,4-dicyanothiophene.⁵²⁹ HPz's have recently been the subject of renewed interest by Ziegler and Durfee (Figure 41).^{535–537,557–559}

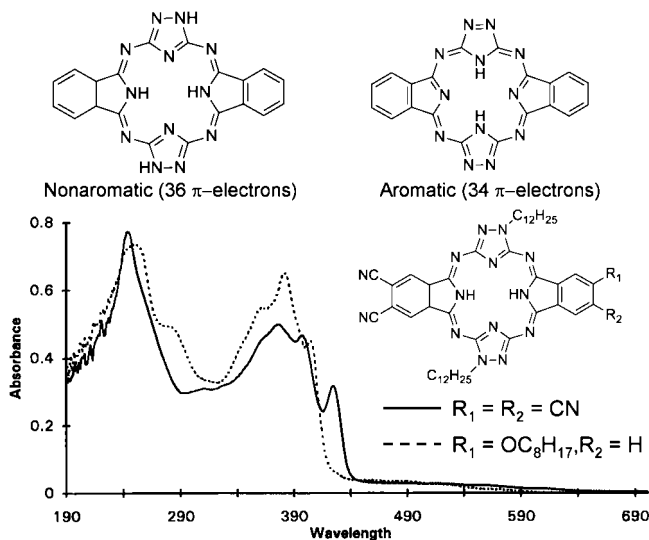
In 1957, Elvidge^{151,512} reported the synthesis of a three-quarters-Pc with a benzene ring (*m*-benzophthalocyanine) based on a cross-condensation of 1,3-diaminobenzene and 1,3-diiminoisindoline and a two step [3 + 1] synthetic strategy. Reaction of the -SCH₃ derivative of 1-imino-3-thioisindoline with 1,3-diaminobenzene or 2,6-diaminopy-

Scheme 5. Synthesis of Hemiporphyrazines from a Series of Diamines**Scheme 6. Synthesis of Dicarbahemiporphyrazine Metal Complexes⁵³⁵**

ridine results in the formation of three unit precursors, containing two isoindoles and one benzene moiety, which can then be reacted with 1,3-diiminoisoindoline (Scheme 7). Attempts to form a three-quarters-Pc compound containing a pyridine ring on this basis failed,¹⁵¹ as did attempts to form ABCB compounds because the three unit precursors split to form two unit compounds which preferentially undergo self-condensation to form symmetrical ABAB HPz products.⁵¹² In the late 1960s, Bamfield reported the first successful formation of a three-quarters-Pc containing a pyridine ring by using the Ni^{II}, Cu^{II}, and Au^{III} complexes of a 2,6-bis(3'-imino-1'-isoindolylidene amino)pyridine three unit.⁵¹³ In

**Figure 41.** ORTEP diagrams of the Mn(II) and Co(II) complexes of dicarbahemiporphyrazine drawn at the 35% probability level. Hydrogen atoms are omitted for clarity except at the internal positions. Reproduced with permission from ref 536. Copyright 2007 American Chemical Society.**Scheme 7. Formation of Three Unit Structures^{512 a}**

^a Further reactions with 1,3-diiminoisoindoline result in *m*-benzophthalocyanine in the case of 2,6-bis(3'-imino-1'-isoindolylideneamino)benzene, but the corresponding three-quarters-phthalocyanine is not formed in the case of 2,6-bis(3'-imino-1'-isoindolylideneamino)pyridine.

**Figure 42.** Nonaromatic and aromatic structures of triazolehemiporphyrazine (top). The nonaromatic structure is more stable due to instability arising from the structure that the triazole rings must adopt to enable aromatization.^{132,426,446} UV-visible absorption spectra of 8,21-didodecyl-2,3,14,15-tetracyanotriazolehemiporphyrazine (continuous line) and 8,21-octoxy-2,3-dicyanotriazolehemiporphyrazine (dashed line) in ca. 9×10^{-6} M CHCl₃ solutions (bottom). Reproduced with permission from refs 150 and 568. Copyright 1996 and 1998 American Chemical Society.

the late 1980s, Torres and co-workers^{152,514,515,538,540} adopted this approach, building on earlier research by Russian researchers,^{516–519} to synthesize a wide range of 1,2,4-triazolephthalocyanines (Figure 42) and 1,2,4-triazoleporphyrazines, including many with ABCB structures.^{38,152,262,539,561–569} Cross-condensation syntheses were often also carried out. Torres and co-workers have reported that three unit precursors can also be combined to form ring expanded analogues with four isoindole and two triazole

moieties.⁵²⁰ In 2001, expanded hemiporphyrazines with ABABAB structures containing three sets of alternating nitrogen and sulfur atoms at the core were reported by the Torres and Kobayashi groups based on a cross-condensation of 1,3-diiminoisindoline and 2,5-diamino-1,3,4-thiadiazole.^{521,522} The ABABAB structure is believed to be energetically favored relative to a conventional ABAB structure due to the angles formed at the bridging nitrogen atoms. In recent years, Berezina and Vorob'ev^{531–533} have used a three unit precursor formed from 1,3-indandione and 2,5-diamino-1,3,4-thiadiazole to form HPz and three-quarters phthalocyanine compounds with sulfur atoms replacing the metal coordinating pyridine nitrogen atoms of the parent HPz compound and carbon atoms replacing the pyrrole nitrogens. Peripheral pyridine and pyrazine rings have also been incorporated into the isindoline moieties.⁵³¹ There is clearly scope for the synthesis of a very wide range of core modified HPz's.

Given recent advances in Pc synthesis, the traditional hemiporphyrazine and three-quarters-phthalocyanine nomenclature for core modified ABAB and AAAB structures may prove to be inadequate. In recent years, Kobayashi and co-workers have reported the use of 1,8-dicyanaphthalene as a precursor in conventional mixed condensations with phthalonitriles to form a series of compounds in which at least one of the five-membered pyrrole moieties of the Pc ligand is replaced by a six-membered ring.^{549,553} ABBB, AABBB, and ABAB structures have been reported where A denotes the presence of a six-membered pyridine ring and B denotes an isindoline moiety. Although AAAB and AAAA structures would normally be expected to form as well during mixed condensations (Figure 5), steric considerations probably prevent it in this context. The AAAB, AABBB, and ABAB compounds are best described as core modified phthalocyanines, since they are formed using the conventional cyclotetramerization approach to phthalocyanine synthesis and the AABBB structure does not fit the existing nomenclature.

6.2. Spectroscopic and Redox Properties

6.2.1. Optical Spectroscopy

Although the structures are superficially similar, the electronic properties of HPz's often differ markedly from those of other Pc analogues with ABAB structures, since they are typically nonaromatic (Figure 42). It is debatable, therefore, whether most HPz's should actually be regarded as Pc analogues, given that most of the key properties of Pc's rest primarily on the heteroaromatic nature of the π -system. HPz's are typically brown-red in color, since absorption occurs only at the high energy end of the visible region (Figure 42).⁵⁶⁸ Three-quarters-Pc's are usually heteroaromatic, however, and have spectra which are broadly similar to those of Pc's (Figure 43), which can be interpreted in qualitative terms using Gouterman's 4-orbital model.⁴⁰³ The electronic structure of 1,2,4-triazolephthalocyanines has been calculated at the semiempirical level.^{540,555} The OAM properties of the four frontier π -MO's (Figure 44) exhibit $M_L = \pm 4, \pm 5$ patterns in the phase changes on the inner ligand perimeter in MO calculations, consistent with what would be expected for a π -system derived from a $C_{16}H_{16}^{2-}$ parent perimeter (Figure 6). Triazolephthalocyanine spectra contain a *Q00* band at *ca.* 625 nm¹⁵² slightly to the blue of the *Q00* band of MPc's and three broad overlapping bands between 450 and 600 nm, which can be assigned to a second

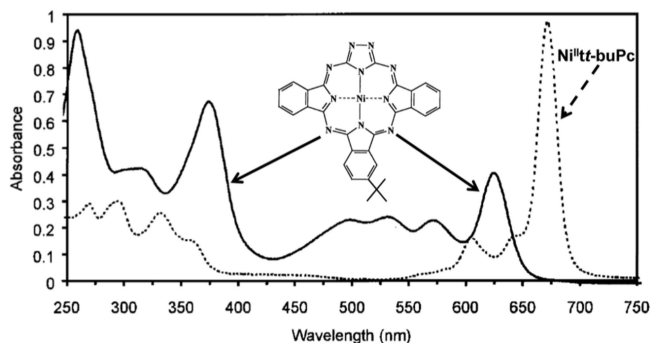


Figure 43. The UV–visible absorption spectra of a 1,2,4-triazolephthalocyanine in $CHCl_3$, $\text{conc} = 2.1 \times 10^{-5}$ M, and nickel tetra-*tert*-butylphthalocyanine (Ni^{II} -*tt*-buPc) in $CHCl_3$, $\text{conc} = 3.4 \times 10^{-6}$ M. Reproduced with permission from ref 566. Copyright 2001 American Chemical Society.

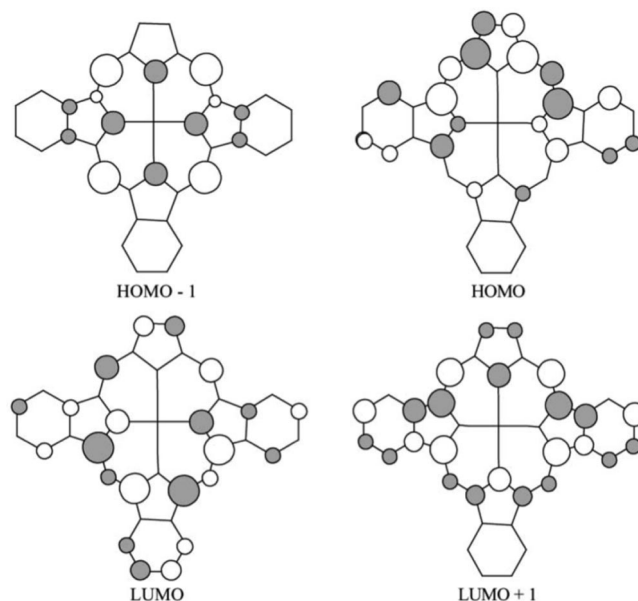


Figure 44. Frontier π -MO's predicted for metal triazolephthalocyanines on the basis of INDO/s calculations. The phase changes on the inner perimeter of the ligand of the HOMO's and LUMO's exhibit $M_L = \pm 4, \pm 5$ OAM properties (Figure 6). Reproduced with permission from ref 555. Copyright 2002 Royal Society of Chemistry.

higher energy *Q00* band and to vibrational bands (Figure 43). There is a broad envelope of absorbance in the UV-region, which can be assigned to the B and higher energy $\pi \rightarrow \pi^*$ transitions. Although the optical spectroscopy of conventional HPz's and three-quarters-Pc's has not been studied by MCD spectroscopy, Kobayashi and co-workers have reported MCD spectra for core modified phthalocyanines^{549,553} derived from conventional mixed condensations and for superhemiporphyrazines.⁵²¹ In marked contrast with nonaromatic HPz's, the core modified phthalocyanines with ABAB and AABBB structures^{549,553} were found to have heteroaromatic π -systems broadly similar to those of conventional Pc's.

6.2.2. Redox Properties

No redox properties have been reported for HPz's or three-quarters-Pc's.

6.2.3. Other Characterization Methods

The study of HPz's and three-quarters-Pc's has tended to focus primarily on the standard use of UV–visible absorption, IR and NMR spectroscopy, and MS to characterize

newly synthesized compounds. In the case of HPz's and three-quarters-Pc's with triazole moieties, the main focus in recent years has been on nonlinear absorption and refraction index properties^{35,262,541,543,544,561} and the formation of liquid crystals.^{564,565} Hanack and Meneghetti have recently studied the two-photon absorption cross-section of a series of HPz metal complexes and have outlined reasons why the InCl HPz complex may find use in optical limiting applications.^{551,552} Infrared linear dichroism and EPR spectroscopy have been used to study Langmuir–Blodgett films,⁵⁵⁰ and some conductivity^{515,542} and fluorescence emission^{549,569} measurements and a limited number of single crystal X-ray structures have also reported.^{150,535,536,557–559}

7. Tetraazachlorins, -bacteriochlorins, and -isobacteriochlorins

7.1. Synthesis

Another approach, which has been adopted to synthesize novel Pc analogues, is to partially reduce the peripheral pyrrole bonds of Pz's to form TACs, TABs, and TAiBs^{50,51,62,153–165,376,570–581} (Figure 45). Nature makes use of the corresponding porphyrin analogues, the chlorins, bacteriochlorins, and isobacteriochlorins, in photosynthesis. Monoazachlorins have also been reported.⁴⁶⁸ The tetraaza-analogues of chlorins were first investigated by Linstead and co-workers^{157–159} in the late 1950s. The compounds were initially synthesized by hydrogenating Pz complexes in pyridine in the presence of palladium black catalyst. Interest in this class of compounds was renewed in 1999, when the Luk'yanets group⁵⁷³ reported the formation of H₂TAC during the synthesis of H₂Pz through the reaction of succinonitrile (similar to maleonitrile (Figure 1) but with a saturated bond) with lithium dimethylaminoethylate in dimethylaminoethanol. Reaction with O₂ converts the peripheral saturated bonds to form H₂TAC and H₂Pz. In the same year, Hoffman and Barrett also reported the formation of a TAC compound based on an OsO₄ mediated dihydroxylation of a low symmetry Pz with an AAAB structure (A and B refer, respectively, to pyrrole moieties with *p*-C₄H₉C₆H₄- and -H substituents) during a study on *seco*Pz's.¹⁶⁵ The Luk'yanets

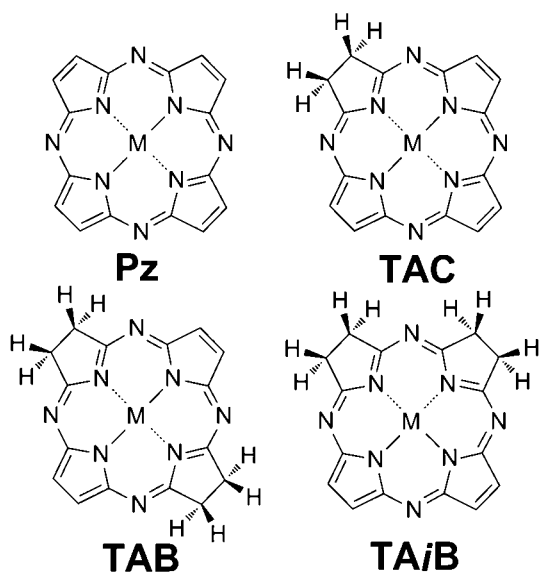
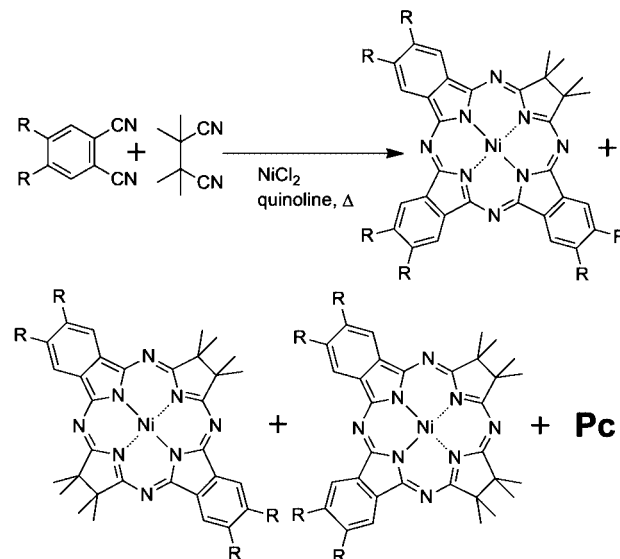
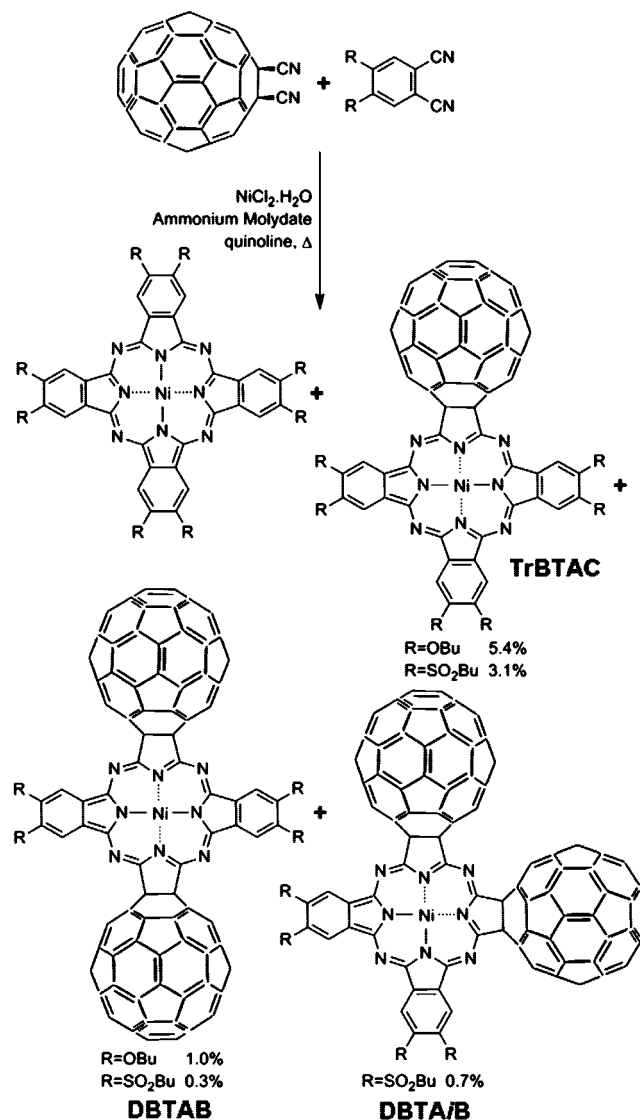


Figure 45. Molecular structures of porphyrazine (top left), tetraazachlorin (top right), tetraazabacteriochlorin (bottom left) and tetraazaisobacteriochlorin (bottom right) complexes.

Scheme 8. Synthesis of Benzo- and 2,3-Naphtho-Fused TACs, TABs, and TAiBs



Scheme 9. Synthesis of C₆₀-Fused Tribenzotetraazachlorin (TrBTAC), Dibenztetraazabacteriochlorin (DBTAB), and Dibenztetraazaisobacteriochlorin (DBTAiB) Compounds²⁰¹



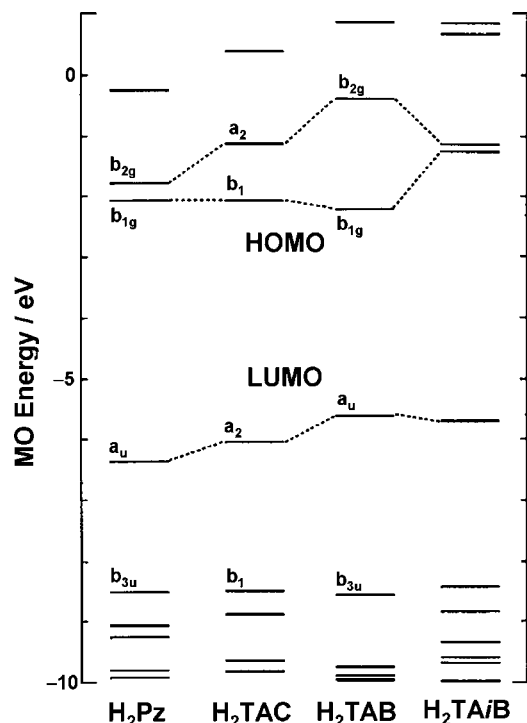


Figure 46. Partial MO energy diagram for H_2Pz , H_2TAC , H_2TAB , and H_2TAiB based on INDO/s calculations. Reproduced with permission from ref 160. Copyright 2002 Wiley-VCH Verlag GmbH & Co. KGaA.

group subsequently prepared substituted TAC, TAB, and TAiB compounds from H_2Pz based on a Diels–Alder reaction with anthracenes and cyclopentadienes and used mixed condensation reactions to obtain tribenzotetraazachlorin (TrBTAC), dibenzotetraazabacteriochlorin (DBTAB), and dibenzotetraazaisobacteriochlorin (DBTAiB) and phenyl-

substituted TAC, TAB, and TAiB compounds.^{153–156} Mixed and cross-condensation reactions between succinonitrile and phthalonitriles, phthalic anhydrides, and phthalimides in boiling quinoline (Scheme 8) were subsequently used to prepare Ni(II) and V(O) complexes of TAC, TAB, and TAiB compounds with fused benzene, 2,3- and 1,2-naphthalene, pyrazine, and 2,3- and 3,4-pyridine rings on the nonreduced pyrroles.^{570,571,576} Free base compounds were also obtained based on mixed condensation reactions carried out under reflux in the presence of an excess of lithium dimethylaminoethylate in dimethylaminoethanol.⁵⁷⁰ In recent years, Kobayashi and co-workers have reported the synthesis of TrBTAC, DBTAB, and DBTAiB compounds directly fused to C_{60} moieties based on the mixed condensation of 1,2-dicyanofullerene and phthalonitrile derivatives (Scheme 9).^{201,574,575}

7.2. Spectroscopic and Redox Properties

7.2.1. Optical Spectroscopy

The Kobayashi and Luk'yanets groups have used optical spectroscopy and theoretical calculations to explore the impact of the partial reduction of peripheral bonds on the electronic structure of the Pz ligand. The $1a_{1u}$ HOMO is destabilized, since there are significant MO coefficients on these atoms in Pz π -systems (Figure 8). H_2TAC and H_2TAB compounds have large ΔLUMO values, since the perturbation to the π -system differs markedly along the x - and y -axes (Figure 46).¹⁶ This results in a splitting of the Q_x and Q_y bands of *ca.* 4500 cm^{-1} for H_2TAC and 9000 cm^{-1} for H_2TAB , relative to the *ca.* 2300 cm^{-1} splitting observed in the case of H_2Pz (Figure 47). While a marked red shift into the near IR region is observed for the Q_x band, due primarily to the lifting of the degeneracy of the LUMO, the definitive identification of the Q_y bands based on the sign sequences

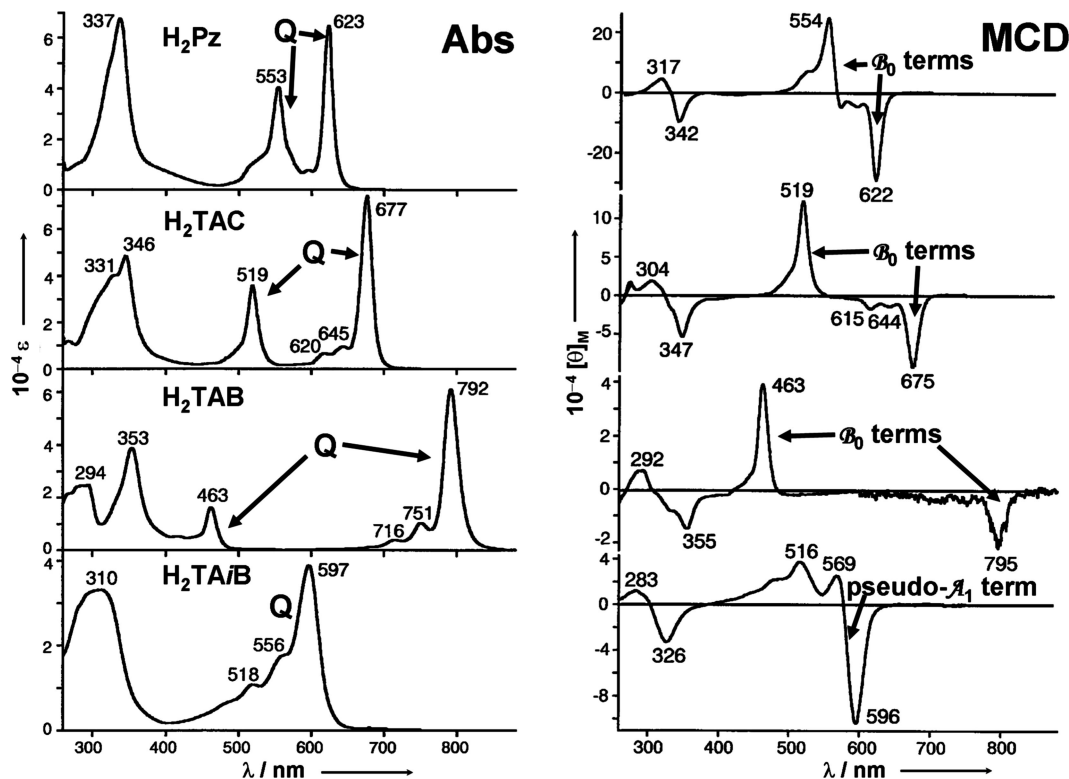


Figure 47. Electronic absorption (left) and MCD (right) spectra of Pz, TAC, TAB, and TAiB in CHCl_3 . The applied magnetic field strength was 1.09 T. Reproduced with permission from ref 160. Copyright 2002 Wiley-VCH Verlag GmbH & Co. KGaA.

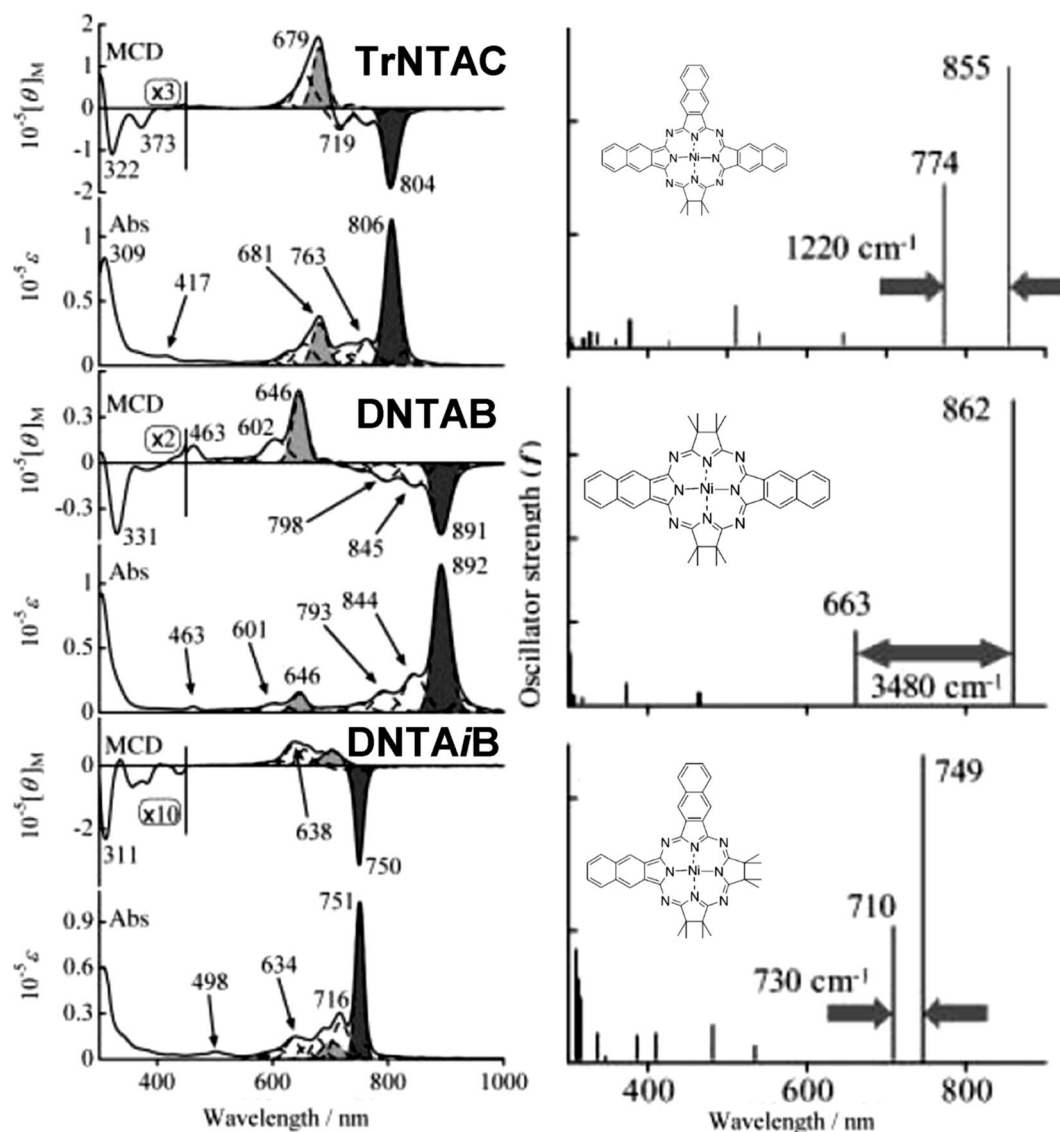


Figure 48. UV–visible absorption and MCD spectra (left) of the Ni(II) complexes of trinaphthotetraazachlorin (TrNTAC), dinaphthotetraazabacteriochlorin (DNTAB), and dinaphthotetraazaisobacteriochlorin (DNTA/B).⁵⁷⁰ The shaded components are the symmetry-split Q00 bands identified by simultaneous band deconvolution of the electronic absorption and MCD spectra. There is a close correspondence between the experimental data and the ZINDO/s calculated spectra (right) in terms of both the splitting energies and relative intensities of the Q00 bands. The intensity of the Q00 band component at longer wavelength is always larger than that at shorter wavelength, and this intensity difference becomes larger as the splitting becomes larger. This trend is observed for all compounds in this section (Figures 47 and 52). Reproduced with permission from ref 570. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA.

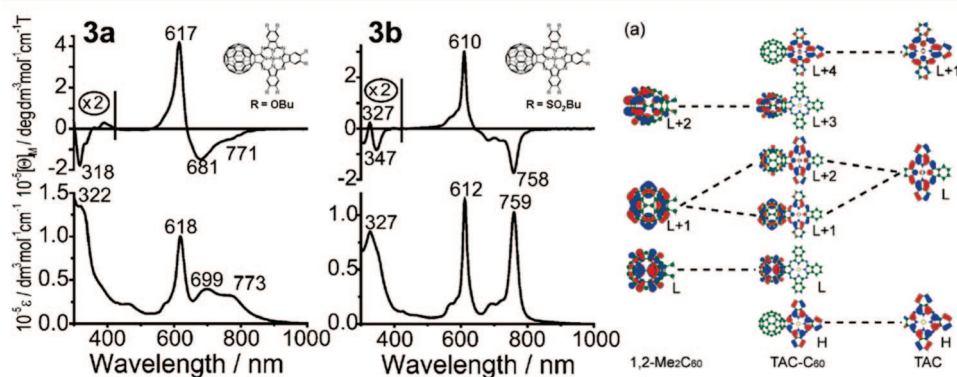


Figure 49. Absorption and MCD spectra of solutions of an electron-donating butyloxy-substituted TAC-C₆₀ conjugate (**3a**) (left) and an electron-withdrawing butylsulfonyl-substituted TAC-C₆₀ conjugate (**3b**) (center) in CHCl₃. The MO's principally associated with the Q bands (right) are derived from TD-DFT calculations in which the B3LYP functional was used with 6-31G(d) basis sets. The HOMO and LUMO are denoted as H and L, respectively. Reproduced with permission from ref 201. Copyright 2007 American Chemical Society.

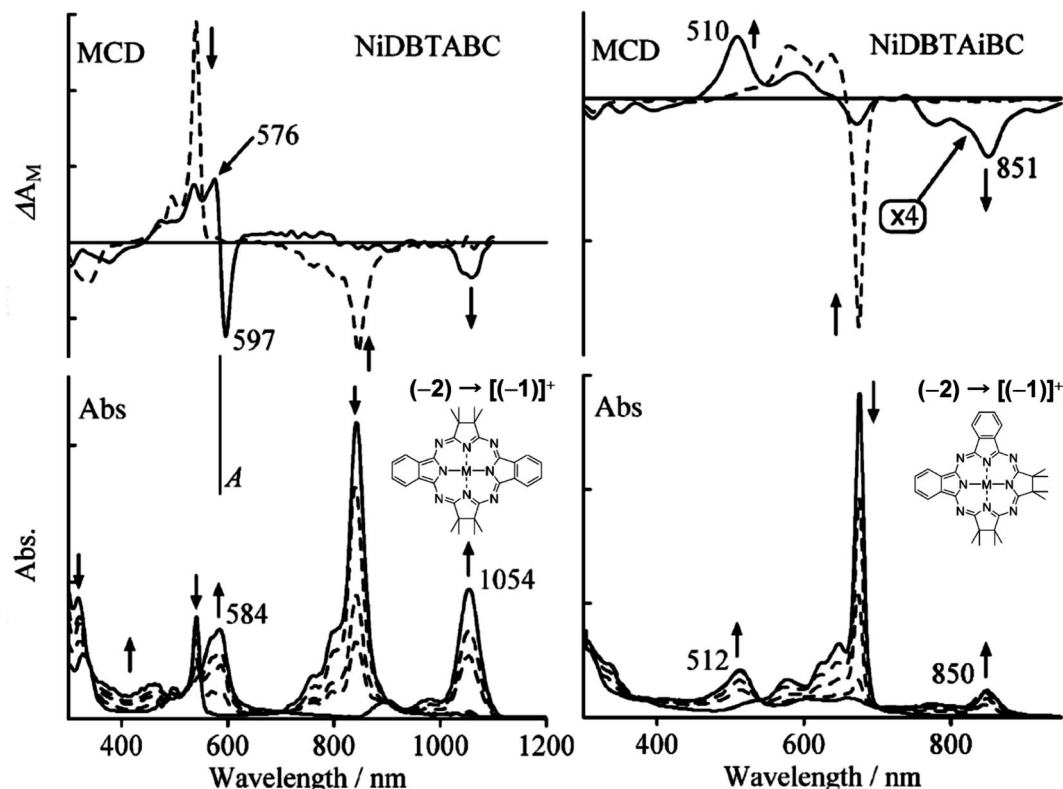


Figure 50. Development of the absorption and MCD spectra during the oxidation of the D_{2h} symmetry dibenzo-fused TAB (left) and the C_{2v} symmetry TAiB (right) at +0.7 V vs Ag/AgCl in *o*-dichlorobenzene (0.3 M tetrabutylammonium perchlorate) to form ring-oxidized cation radicals. The directions of spectroscopic changes are shown by the bold arrows. The MCD spectrum of the starting neutral compound is shown as a broken line, while that of the electrolyzed species is shown as a solid line. Reproduced with permission from ref 570. Copyright 2004 Wiley.

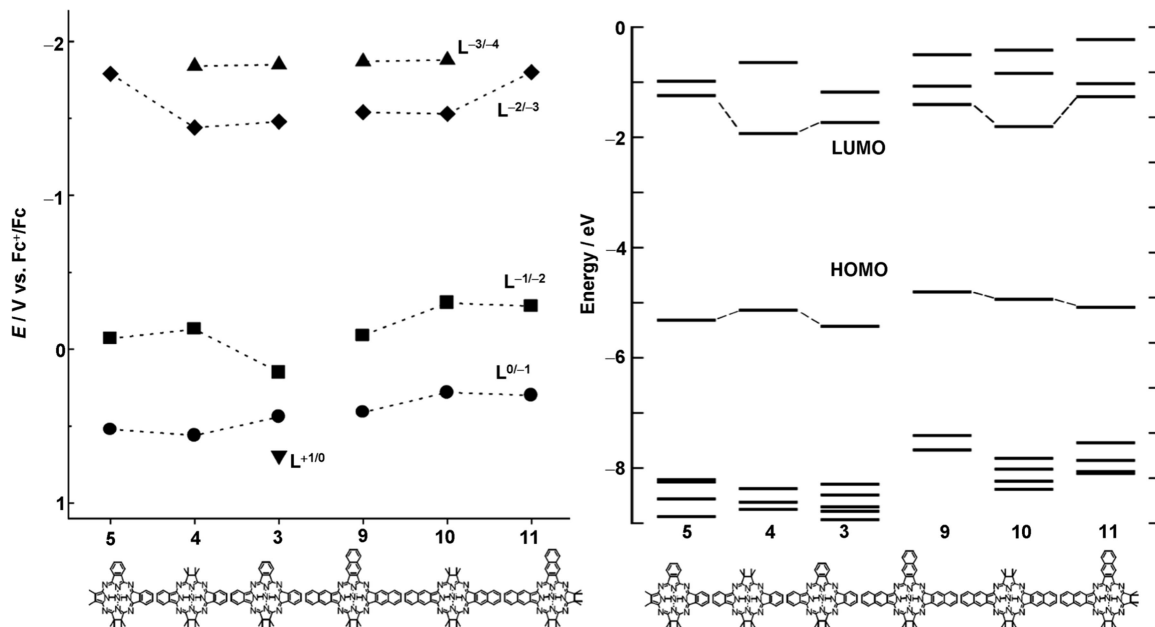


Figure 51. Redox data of benzene- and 2,3-naphthalene-fused Ni(II) TAC, TAB, and TAiB complexes in *o*-dichlorobenzene (left) and the energies of the frontier π -MO's based on DFT calculations using the B3LYP functional.⁵⁷⁰ The oxidation and reduction steps are denoted based on the charge on the ligand. The neutral state is, therefore, a dianion in this context. Trends in the first oxidation and reduction steps broadly reflect the trends in the HOMO and LUMO energies, respectively. Reproduced with permission from ref 570. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA.

of the most intense Faraday \mathcal{B}_0 terms in the MCD spectra makes it clear that the average Q band energy remains almost constant. In the case of H_2TAiB , while there is a marked destabilization of the $1a_{1u}$ MO, the LUMO's are almost degenerate due to the adjacent pattern of the reduced bonds. This results in a smaller splitting of the Q_x and Q_y bands

than is observed even in the case of free base Pz, since the perturbation to the structure is identical along the x - and y -axes. Similar Q band splitting patterns are observed when additional peripheral fused benzene rings are added to TAC and TAB compounds through the mixed condensation of tetramethylsuccinonitrile with phthalonitrile or 2,3-dicyanon-

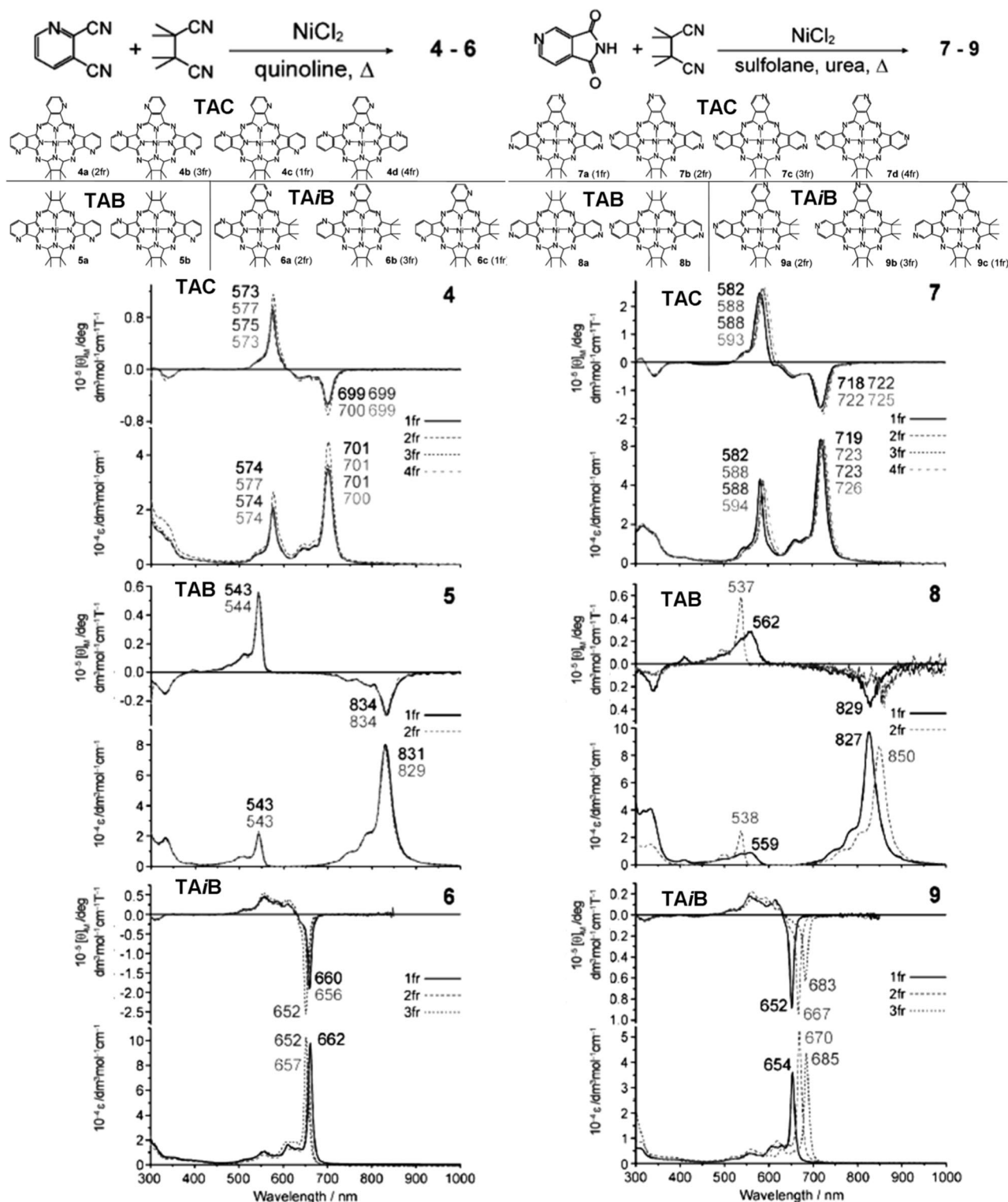


Figure 52. Synthesis of TAC, TAB, and TAiB compounds containing fused peripheral 3-pyridyl and 4-pyridyl rings (top). The wavelength differences observed for the four TAC, two TAB, and three TAiB isomers (bottom) are small for compounds containing peripheral 3-pyridyl fused rings but larger in compounds with 4-pyridyl fused rings, especially in the case of the three TAiB isomers. Reproduced with permission from ref 576. Copyright 2009 American Chemical Society.

aphthalene (Figure 48)⁵⁷⁰ and in the spectra of 2,3-naphthalene, pyrazine, and 2,3- and 3,4-pyridine fused TAC, TAB, and TAiB complexes^{160,570,571,576} and C₆₀ fused TrBTAC, DBTAB, and DBTAiB compounds (Scheme 9).^{201,574,575,580}

The spectroscopic properties of C₆₀-fused TAC compounds differ markedly depending on the nature of the peripheral substituents on the TAC moiety (Figure 49). It has been postulated that key frontier MO's on the C₆₀ and TAC moieties

have the same symmetry and similar energies when electron-donating groups are introduced to the chlorin moiety and interact significantly as a result.

7.2.2. Redox Properties

Spectroelectrochemical data have been reported for the first oxidation step of NiDBTAB and NiDBTAiB (Figure 50).⁵⁷⁰

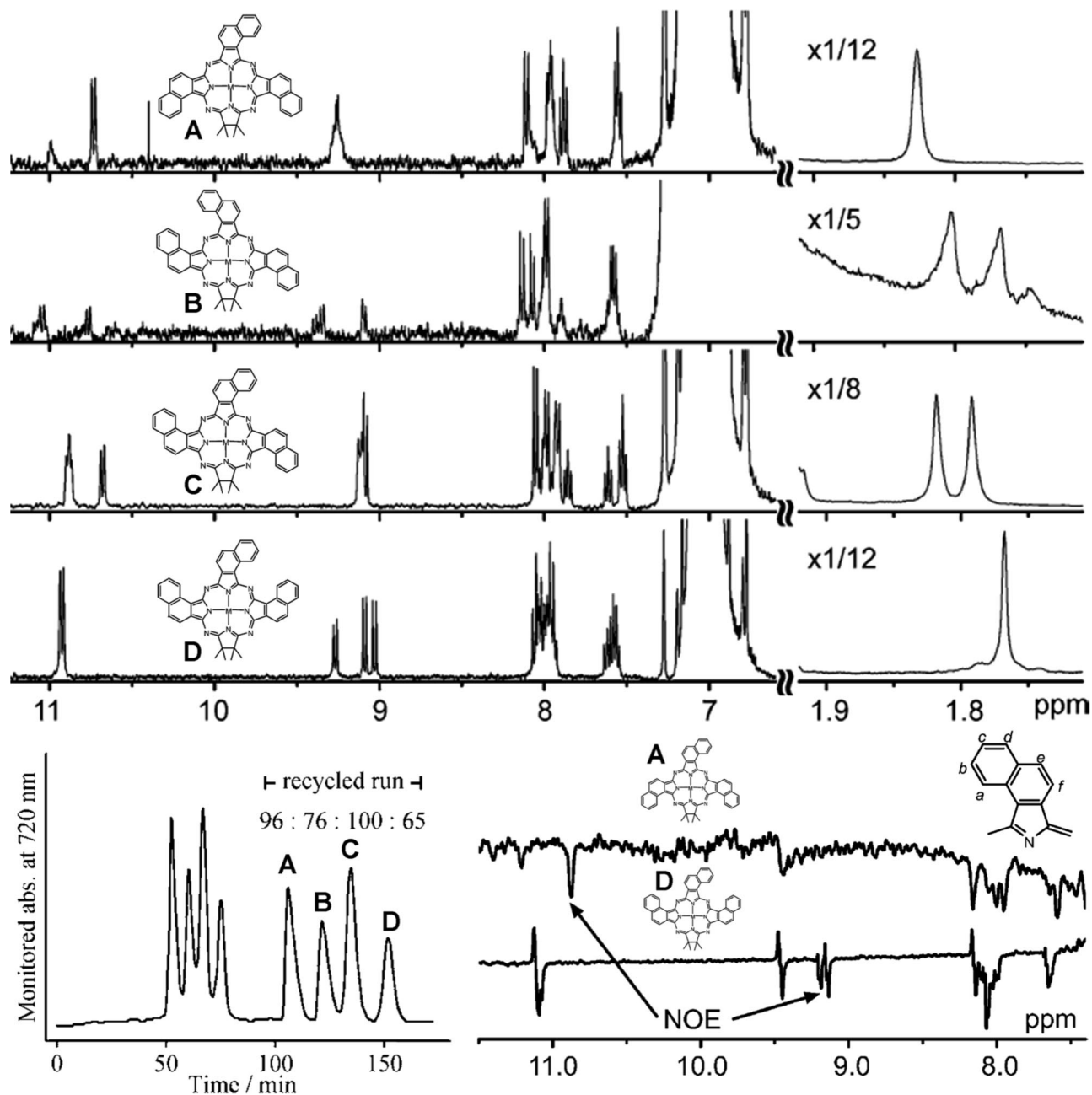


Figure 53. Four TAC isomers containing three fused 1,2-naphthyl units can be readily identified using NMR spectroscopy based on structural considerations and an analysis of the ^1H NMR data (top).⁵⁷¹ The isomeric mixture consists of a 96:76:100:65 ratio in the order of elution from the octadecyl-modified silica gel HPLC column (bottom left). The ^1H NMR spectra of the first and fourth fractions have only one type of methyl signal at *ca.* 1.8 ppm, while the second and third fractions show two separate methyl signals. The first and fourth fractions can, therefore, be assigned to isomers A or D, because the local structure surrounding the methyl groups is symmetric. In contrast, the two types of methyl resonance for the second and third fractions are consistent with the presence of oppositely fused naphthalene rings. NOE experiments (bottom right) determined the molecular structures of the first and fourth fractions. The first fraction shows a detectable NOE for proton **a** (10.9 ppm), which is not observed in the fourth fraction, indicating that proton **a** is located closer to the methyl groups in the first fraction. On the other hand, the fourth fraction exhibits an NOE for proton **f** (9.2 ppm). As a consequence, the structures of the first and fourth fractions can be assigned definitively to isomers A and D, respectively. No NOE signals were observed for the second and third fractions, probably because of the very low solubility of these compounds, so the assignments could only be made tentatively on the basis of the formation ratios (bottom left), since the second and fourth fractions would be expected to have sterically hindered molecular structures. Reproduced with permission from ref 571. Copyright 2005 Wiley-VCH Verlag GmbH & Co. KGaA.

The *x*- and *y*-polarized *Q*00 bands of the D_{2h} symmetry NiDBTAB compound split further upon oxidation at +0.7 V and shift to longer wavelength. In contrast, there is a very small splitting of the *Q*00 bands of the C_{2v} symmetry NiDBTAiB compound, and the resulting spectrum is broadly similar to that of a D_{4h} symmetry MPc cation radical species.⁴⁰⁹ CV and DPV data have been reported for unsubstituted and benzene, 1,2- and 2,3-naphthalene, pyra-

zine, and 2,3- and 3,4-pyridine fused TAC, TAB, and TAiB complexes^{160,570,571,576} and the C_{60} fused TrBTAC, DBTAB, and DBTAiB compounds.^{200,574,575,580} The trends observed in the first oxidation and reduction steps in the CV data for benzo- and 2,3-naphtho-fused TAC, TAB, and TAiB complexes (Figure 51) are consistent with what would be anticipated based on MO calculations and the observed *Q* band energies.⁵⁷¹

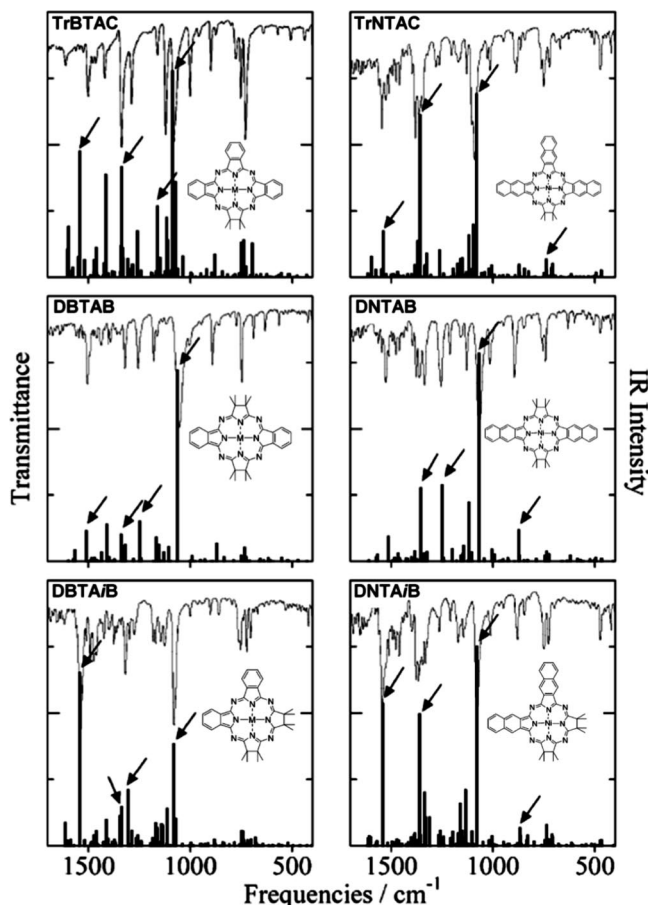


Figure 54. There is very close agreement between the calculated spectra and the experimental IR data for the benzene- (left) and 2,3-naphthalene- (right) fused TAC, TAB, and TAiB complexes in terms of both energy and intensity. Reproduced with permission from ref 570. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA.

7.2.3. Other Characterization Methods

A variety of other techniques have been used to study TAC, TAB, and TAiB compounds.^{578,579} In the case of fused ring expanded TAC, TAB, and TAiB compounds containing pyridine⁵⁷⁰ and 1,2-naphthalene⁵⁷¹ units, there are many isomers formed, which cannot easily be distinguished on the basis of their optical properties (Figure 52). NMR spectroscopy has proven to be particularly useful in this context (Figure 53), when correlation spectroscopy (COSY) and nuclear Overhauser effect (NOE) experiments have been used to analyze the data.^{570,571} Detailed DFT based analyses of the IR spectra have been carried out for TAC, TAB, and TAiB compounds with fused benzene and either 1,2- or 2,3-naphthalene rings attached to the nonreduced pyrrole moieties.^{570,571} Isomers can now be differentiated solely on this basis (Figure 54), since the calculated IR spectra are in excellent agreement with the experimental data. Both of these approaches will probably find much wider utility in the future in identifying low symmetry Pc analogue isomers. Electroabsorption spectroscopy has been used to study the effect of peripheral substitution with strongly electron withdrawing and donating groups on the porphyrinoid fullerene MO interactions of C₆₀ fused TrBTACs.⁵⁸¹ Fluorescence excitation and emission spectra, fluorescence quantum yields, and TREPR spectra have also been reported for H₂Pz, H₂TAC, H₂TAB, H₂TAiB^{160–164} and C₆₀ fused TrBTACs,²²¹ while a

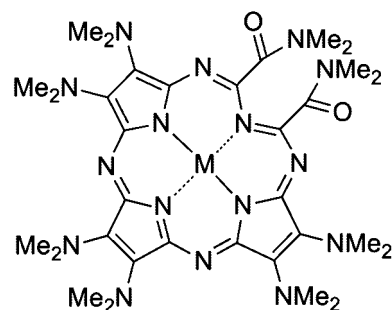


Figure 55. Molecular structure of 2,3,7,8,12,13,17,18-octakis-(dimethylamino)-2-secoPz-2,3-dione.

single crystal X-ray structure was reported for vanadyl dibenzotetraazaisobacteriochlorin.⁵⁷⁰

8. seco-Porphyrazines

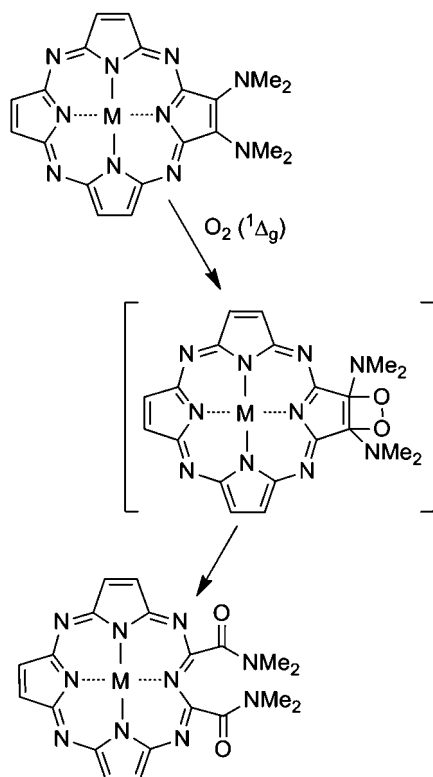
8.1. Synthesis

A second approach, which has been used to modify the π -system of Pz's at the peripheral bonds, involves partial oxidation rather than reduction to form *seco*Pz's.^{165,195,208,396,582–594} A *seco*Pz^{587,588} has been defined as being a Pz compound in which at least one of the outer peripheral pyrrole bonds has been broken and replaced by two acyclic substituents, which usually contain oxygen atoms (Figure 55). In 1999, Barrett and Hoffman and co-workers¹⁶⁵ reported the formation of a free base *seco*Pz, during standard Lindsey condensation reactions⁵⁹⁵ of maleonitrile derivatives (Figure 1) containing two *n*-BuS[−] or -NMe₂ substituents. A side product had earlier been noticed during the formation of star porphyrazines,^{166,585} which contain eight metal ligating S[−] substituents. When this was investigated in depth, it was found to only occur when the reaction was carried out under aerobic conditions. The presence of strongly electron donating substituents such as -NMe₂ results in electron rich double bonds on the ligand periphery, which can readily react with singlet oxygen (Scheme 10). Further studies demonstrated that metal complexes can be prepared and that AAAB, ABAB, and AABC *seco*Pz structures^{192,208,582} can also be formed (where A, C, and B denote substitution of pyrroles with alkyl and -NMe₂ groups and the pyrrole moieties which are disrupted, respectively) based on oxidation of the products from mixed condensations. More recently, Gonca and co-workers have reported the synthesis of *seco*Pz's based on the presence of eight 4-biphenyl,⁵⁹¹ 1-naphthyl,⁵⁹² and *t*-Bu-phenyl⁵⁹³ substituents.

8.2. Spectroscopic and Redox Properties

8.2.1. Optical Spectroscopy

To date, no detailed analyses of the electronic structures of *seco*Pz's have been reported, based on MCD spectroscopy and TD-DFT calculations. Hoffman and Barrett have reported a number of UV–visible absorption spectra, however, and have attempted to assign bands on the basis of Gouterman's 4-orbital model.⁴⁰³ For example, the spectra of H₂(NMe₂)₈Pz and Zn(NMe₂)₈Pz contain a Q band in the 700–750 nm region (Figure 56) and a B band at ca. 330 nm.⁵⁸⁷ An intense peak in the 450–550 nm region was assigned to $n \rightarrow \pi^*$ transitions associated with MO's located primarily on the nitrogen lone pair orbitals of the dimethylamino substituents. Significant red shifts are observed in the Q band wavelengths of H₂(NMe₂)₈*seco*Pz, Zn(NMe₂)₈*seco*Pz, and Zn(NMe₂)₈-

Scheme 10. Mechanism for *seco*-ZnPz Formation⁵⁸²

opdisecoPz relative to the spectra of the corresponding Pz parent compounds. Metalation of nitrogen atoms at the ligand periphery has been found to result in significant spectral changes (Figure 57). The Q band is significantly less broadened, since the $n \rightarrow \pi^*$ states no longer interact with the Q and B excited states to the same extent.

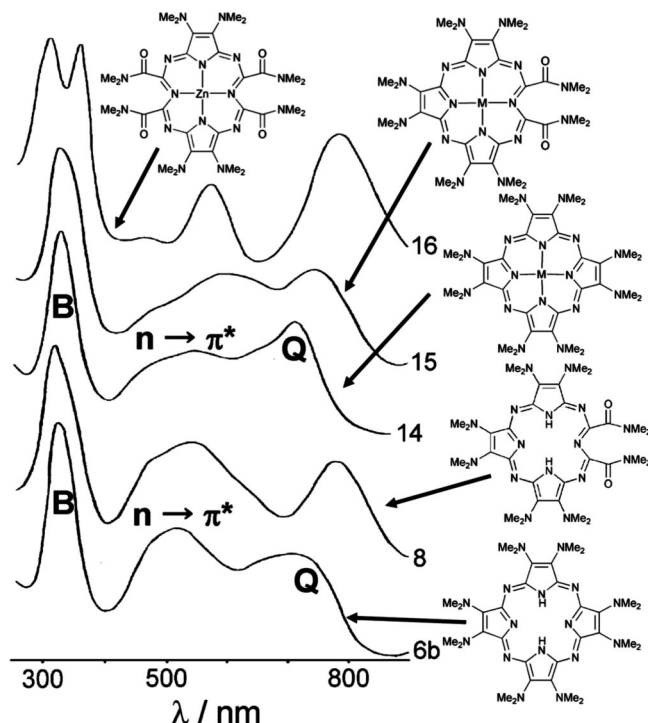


Figure 56. The UV–visible absorption spectra of $\text{H}_2(\text{NMe}_2)_8\text{Pz}$ (6b), $\text{H}_2(\text{NMe}_2)_8\text{secoPz}$ (8), $\text{Zn}(\text{NMe}_2)_8\text{Pz}$ (14), $\text{Zn}(\text{NMe}_2)_8\text{secoPz}$ (15), and $\text{Zn}(\text{NMe}_2)_8\text{trans-di-secoPz}$ (16) in CH_2Cl_2 . Reproduced with permission from ref 587. Copyright 2003 Royal Society of Chemistry.

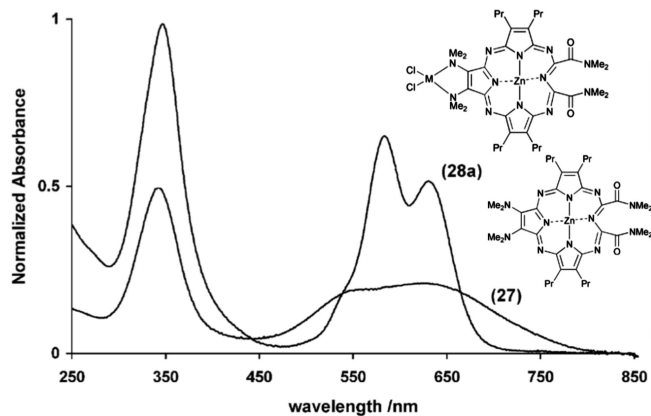


Figure 57. The UV–visible absorption of the Zn(II) complex of 2,3,12,13- C_3H_7 -17,18- $\text{NMe}_2\text{secoPz}$ (27) and its PtCl_2 complex (28a) in CH_2Cl_2 . Reproduced with permission from ref 587. Copyright 2003 Royal Society of Chemistry.

8.2.2. Redox Properties

No redox properties have been reported for *seco*Pz's.

8.2.3. Other Characterization Methods

Several single crystal X-ray structures have been reported.^{165,582,584} Fluorescence excitation and emission spectra,^{192,208,583} fluorescence quantum yield and decay curves,^{192,583} singlet oxygen phosphorescence decays,^{192,208,209,583} and transient absorption spectra^{192,208,583} have also been studied. These studies have demonstrated that *seco*Pz's have considerable potential as photosensitizers for the production of singlet oxygen ($^1\text{O}_2$) at high quantum yields relative to other Pc analogues (Table 2). For example, the Φ_{Δ} value for hexapropyl bis(dimethylamino)Zn*seco*Pz-2,3-dione is 0.54.⁵⁸³ The use of *seco*Pz's as photo-oxygenation catalysts in the synthesis of endoperoxides from the corresponding dienes was found to be more effective than the dyes traditionally used for this purpose.⁵⁸⁹ Barrett and Hoffman and co-workers have recently reported the synthesis and properties of a water-soluble Zn*seco*Pz complex designed for use in PDT.⁵⁸⁶

9. Conclusions

Research on low symmetry Pc's and their analogues is likely to increase in scope in coming decades given the wide range of potential applications for these compounds. The problems associated with product separation during mixed condensation reactions remain a considerable challenge, however. In order for this field of research to reach its full potential, further breakthrough methodologies in selective synthesis are going to be needed. Research into Pc analogues is, perhaps, more promising at this point, since extensive purification by chromatography is often not required. The D_{2d} symmetry Pc's first reported by the Cook and Kobayashi groups could extend the traditional use of Pc's as dyes into the near-IR region. The work by Goldberg and co-workers on corrolazines^{147,499} could facilitate the catalysis chemistry of transition metals in higher valence states using ligands which are considerably more stable than their corrole counterparts. The research by the Luk'yanets and Kobayashi groups on tetraazachlorins may eventually open the way to applications which successfully mimic the role of chlorins in photosynthesis. The three-quarters-phthalocyanines, which have been studied by the Torres group, exhibit considerable promise in the field of nonlinear optics,^{152,515} while Hoffman

and Barrett's work on *seco*-porphyrazines^{587,588} may find application in the field of PDT and in the catalysis of other reactions involving singlet oxygen.

10. Abbreviations

Ac	anthracocyanine
CV	cyclic voltammetry
COSY	correlation spectroscopy
Cz	corrolazine
adjDAP	adj-diazaporphyrin
DBTAB	dibenzotetraazabacteriochlorin
DBTAiB	dibenzotetraazaisobacteriochlorin
DFT	density functional theory
DPV	differential pulse voltammetry
EPR	electron paramagnetic resonance
ΔE_{o-r}	energy gap between the first oxidation and first reduction steps
ΔE_{SS}	energy splitting of the singlet excited state
ΔE_{TT}	energy splitting of the triplet excited state
EXAFS	extended X-ray absorption fine structure
Φ_{Δ}	quantum yield of 1O_2 formation
$\Delta HOMO$	energy separation of the MO's arising from the HOMO of the parent perimeter
HOMO	highest occupied molecular orbital
HPz	hemiporphyrazine
INDO	intermediate neglect of differential overlap
LMCT	ligand to metal charge transfer
$\Delta LUMO$	energy separation of the MO's arising from the LUMO of the parent perimeter
LUMO	lowest unoccupied molecular orbital
MAP	monoazaporphyrin
MCD	magnetic circular dichroism
MO	molecular orbital
M_L	magnetic quantum number
MLCT	metal to ligand charge transfer
MS	mass spectrometry
Nc	naphthalocyanine
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
OAM	orbital angular momentum
OEP	octaethylporphyrin
oppDAP	opp-diazaporphyrin
Pc	phthalocyanine
PDT	photodynamic therapy
Pz	porphyrazine
<i>seco</i> Pz	<i>seco</i> -porphyrazine
subPc	subphthalocyanine
TAB	tetraazabacteriochlorin
TAC	tetraazachlorin
TAiB	tetraazaisobacteriochlorin
TBCz	tetrabenzocorrolazine
TBP	tetrabenzoporphyrin
TBadjDAP	tetrabenzo-adj-diazaporphyrin
TBTrAP	tetrabenzotriazaporphyrin
TrBTAC	tribenzotetraazachlorin
TREPR	time resolved electron paramagnetic resonance
XANES	X-ray absorption near edge structure

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12. References

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