Synthesis of substituted phthalocyanines

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Abstract

This review summarizes the synthetic strategies for substituted phthalonitriles and phthalocyanines. Preparation of alkyl-, aryl-, halo-, nitro-, alkoxy-, aryloxy-, alkylthio-, arylthio-, and amino- substituted phthalocyanines along with the derivatives of phthalocyanine carboxylic- and sulfoacids is overviewed. Influence of the substituents on the position of Q-band in UV-vis spectra of substituted phthalocyanines is also briefly discussed.

Keywords: Phthalocyanines, phthalonitriles, synthesis, structure, electronic spectra

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1. Introduction

The most comprehensive early study of phthalocyanines was conducted by Linstead and co-workers in 1930s.[1] For the first thirty years after their discovery, phthalocyanines were widely used as blue and green light-resistant pigments and dyes in the paper and textile industries because of their high thermal, chemical, and photochemical stabilities.[2] Almost all early phthalocyanine complexes were unsubstituted on the periphery and had a low solubility in most known solvents even in such high-boiling aromatic solvents as 1-chloro- or 1-bromonaphthalene and quinoline, with sulfuric acid was found to be the best solvent for them.

Change of the central atom and/or its axial coordination, change of the *meso*-atoms in the phthalocyanine macrocycle, and its peripheral modification[3] are the major ways of modifying the phthalocyanine structure the last one of which turned out to be the most fruitful. Because the scope and limitations of the first two modification approaches are rather well explored, here we will discuss only the peripheral modification of the phthalocyanine core. We use here term "periphery" for all substituents on the benzene rings of the molecule. The substituents located at positions 1, 4, 8, 11, 15, 18, 22, and 25 of the phthalocyanine ring (α-positions, Figure 1) are named as α–substituents, while those located at positions 2, 3, 9, 10, 16, 17, 23, and 24 (β-positions, Figure 1) are regarded as β-substituents.

Introduction of peripheral substituents can dramatically increase the solubility of the target phthalocyanine in water or common organic solvents and can be used for an accurate tuning of optical and redox properties of phthalocyanines designed for a specific high-tech application. Peripheral substituents can also be used as anchoring or bridging groups for formation of controlled supramolecular assemblies and similar applications (*e.g.* heterogeneous catalysis).[4]

In addition to traditional applications as dyes and pigments,[5] peripherally substituted phthalocyanines are currently widely used as industrial catalytic systems;[6] photosensitizers for photodynamic therapy of cancer;[7] materials for electrophotography, ink-jet printing, semiconductors, chemical sensors, and electrochromic devices; functional polymers and liquid

crystals; nanotechnology;[8] and non-linear optics.[9] The majority of these applications take advantage of the unique optical (specifically low-energy Q-band) and redox properties of phthalocyanines which can be fine-tuned using appropriate peripheral substitutions.[3]

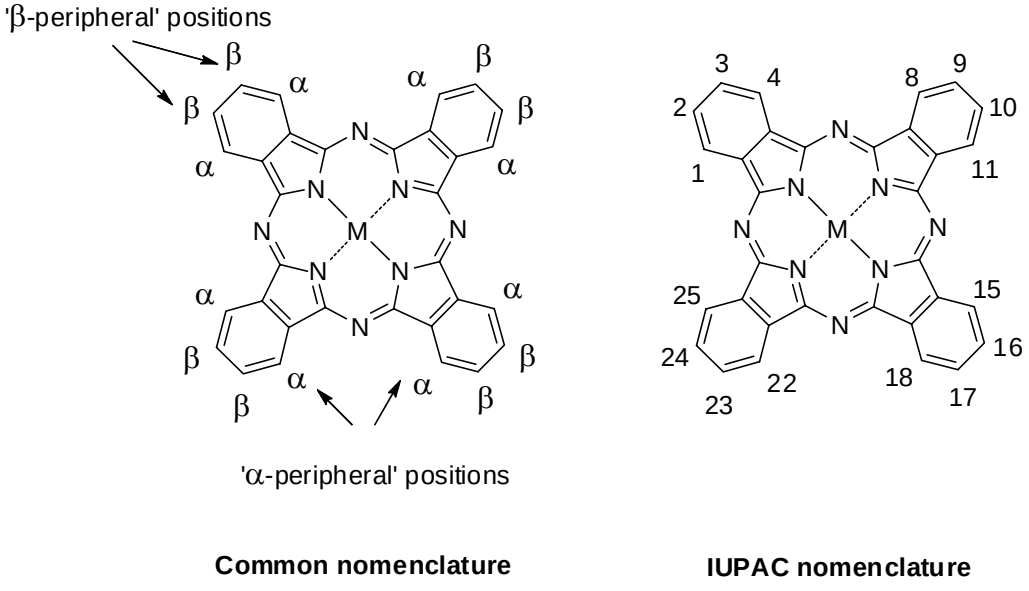
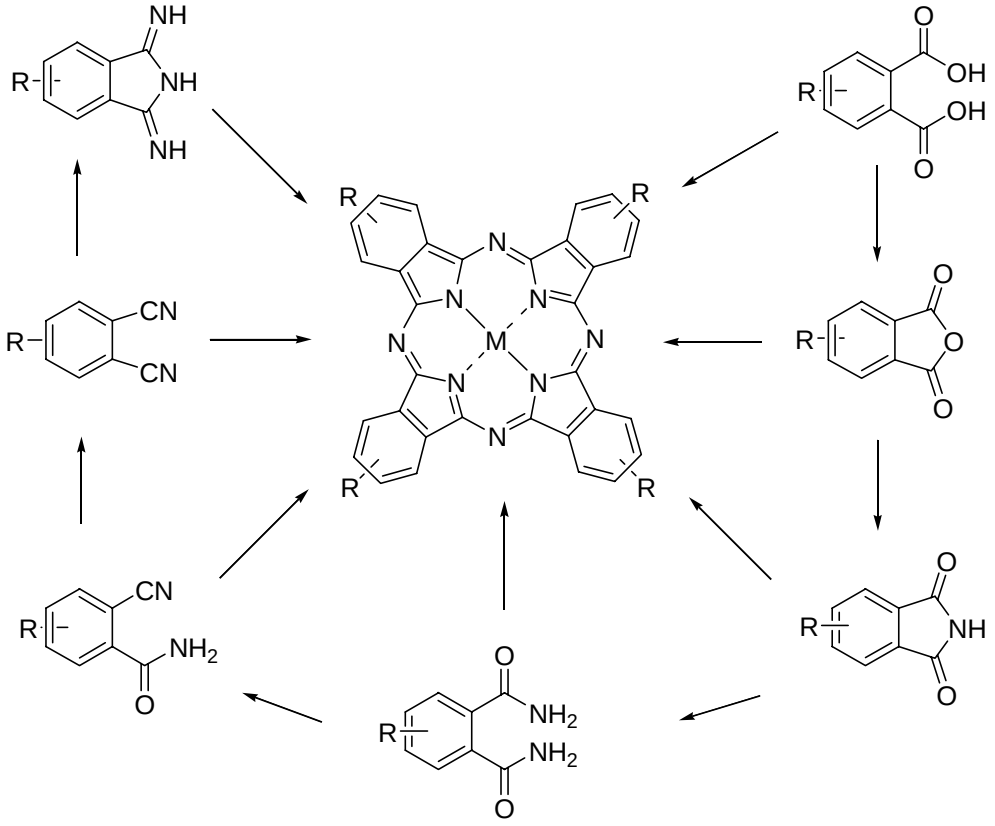


Figure 1. Numbering scheme for the phthalocyanine core.

Peripheral substituents can be introduced into the phthalocyanine core using one of the two basic methods. The first approach involves modification of the already existing phthalocyanine core using aromatic electrophilic substitution reactions as well as cycloaddition reactions.[3,10] The second basic approach involves the tetramerization of already substituted phthalocyanine precursors, which leads to a controlled number of substituents on the target phthalocyanine.[3] The useful precursors for this method include substituted derivatives of *ortho*-phthalic acid (*i.e.* anhydrides, imides, amides, and nitriles) with the nitriles being the most popular choice (Scheme 1).

The two most important synthetic pathways for preparation of the substituted phthalonitriles still include phthalic acid transformation (*i.e.* the 'acidic' route which includes the acid – anhydride – imide – amide – nitrile sequence) and the Rosenmund-von Braun reaction (*i.e.* transformation of *o*-dihalides into dinitriles using CuCN), although Diels-Alder and cross-coupling reactions often provide reliable alternatives. The cyclotetramerization approach (which is in general based on fundamental reactions developed by Linstead in the 1930s) will be primarily discussed here. It should be noted that since several excellent reviews on the preparation and properties of substituted phthalocyanines have already been published[3,11-14] some partial overlap between what is presented in this review and published material is unavoidable; however, we have tried to focus on the introduction of the specific substituents into the phthalocyanine core. Since the introduction of the alkyl-, alkenyl-, alkynyl-, aryl(heteroaryl)-,

and trialkylsilyl- substituents into the phthalocyanine core only slightly affects their optical and redox properties, these peripheral groups will be considered together. Most of the phthalocyanines substituted by substituents of the general formula $(CH_2)_nX$ (in which the influence of electron-withdrawing or electron-donating group X is small) will also be described. Next, phthalocyanines with at least one electron-withdrawing or electron-donating group per isoindole fragment will also be discussed. Finally, phthalocyanines with both electron-donating and electron-withdrawing groups in the same isoindole core will be reviewed.



Scheme 1

2. Phthalocyanines with alkyl-, aryl-, alkenyl-, and alkynyl substituents

2.1 Phthalocyanines with alkyl- and aryl-substituents

2.1.1 1,8(11),15(18),22(25)-Tetrasubstituted compounds. To date, only a very limited number of alkyl-, and aryl-1,8(11),15(18),22(25)-tetra substituted phthalocyanines are known. 3-Substituted derivatives of phthalic acid are the most common precursors for preparation of the 1,8(11),15(18),22(25)-tetra substituted phthalocyanines. As in the case of the other tetrasubstituted phthalocyanines, all four possible positional isomers (C_{4h}, C_{2v}, C_s, and D_{2h}, Figure 2) can be formed during the cyclotetramerization reaction and the size of substituent in

the 3-substituted precursor can dictate predominant formation of the least sterically crowded and least soluble phthalocyanine of C_{4h} symmetry. It is interesting that the mild reaction conditions (*i.e.* alkoxide promoted cyclotetramerization) lead to formation of the pure least sterically crowded isomer of 'C_{4h}' symmetry (since it is metal-free phthalocyanine, the actual symmetry of this compound is C_{2h}) in low yield (1%).[15] On the other hand, harsh reaction conditions and use of a template (*e.g.* transition-metal ions) result in formation of a mixture of all four possible positional isomers in significantly higher yields even in the cases when 3-substituted phthalic acids were used as the precursors. Of course, when comparison is possible, 3-substituted phthalonitriles result in better yields of phthalocyanines as compared to corresponding phthalic acids or anhydrides. For instance, vanadyl 1,8(11),15(18),22(25)-tetraphenyl phthalocyanine can be prepared in 90% yield when 3-phenylphthalonitrile was used as the precursor at 180 ^{o}C, while only 55% yield was observed when 3-phenylphthalic acid and urea were used as the precursors at 250 ^{o}C.[16]

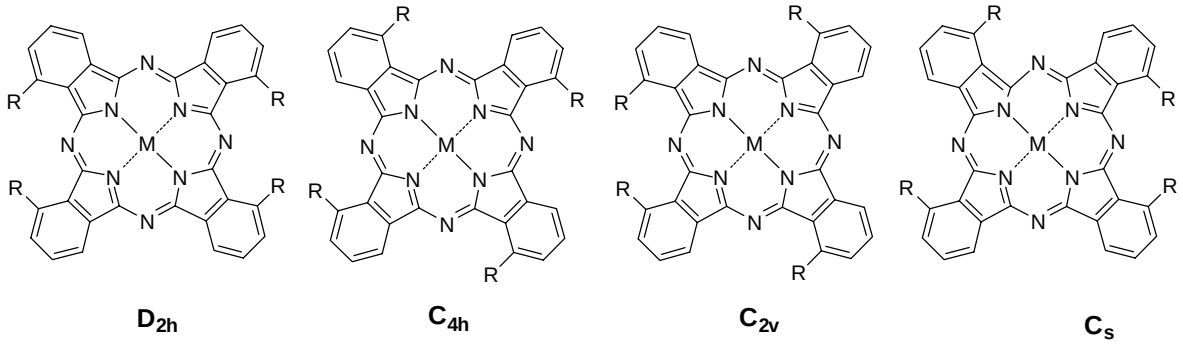
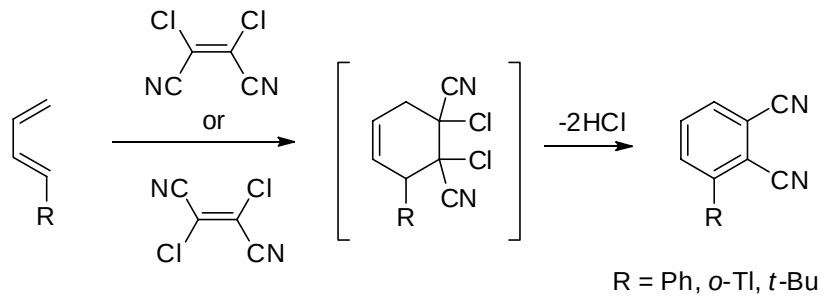


Figure 2. Four possible positional isomers of 1,8(11),15(18),22(25)-tetrasubstituted phthalocyanines.

Catalytic ammonolysis is probably the most important synthetic pathway for the multi-gram preparation of 3-alkyl- and 3-aryl-substituted phthalonitriles in a single step.[17] The reaction is typically conducted using appropriately substituted phthalic acids, anhydrides, or imides, gaseous ammonia and a borophosphate catalyst[18] at *ca.* 400 °C. The yields of the target phthalonitriles vary between 45 and 80%.

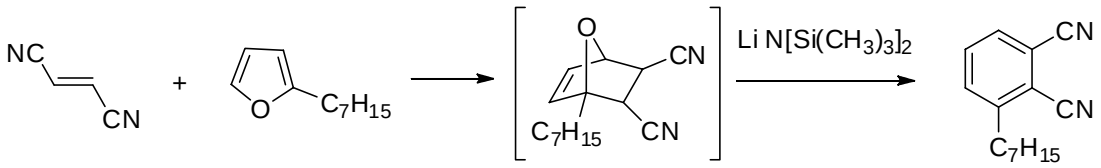
Although the Diels-Alder reaction is rarely used for preparation of the 3-substituted phthalonitriles, several examples can be found in the literature. For instance, the [4+2] cycloaddition reaction between 1-aryl or 1-alkylbutadiene and dichloromaleo(fumaro)nitrile results in formation of a cyclic reaction intermediate, which can be aromatized at elevated temperature with elimination of hydrogen chloride and formation of the target nitriles (Scheme 2).[19]



Scheme 2

The dichloromaleo(fumaro)nitrile[20] can be easily prepared by the direct chlorination of inexpensive succinonitrile with chlorine gas at elevated temperatures.

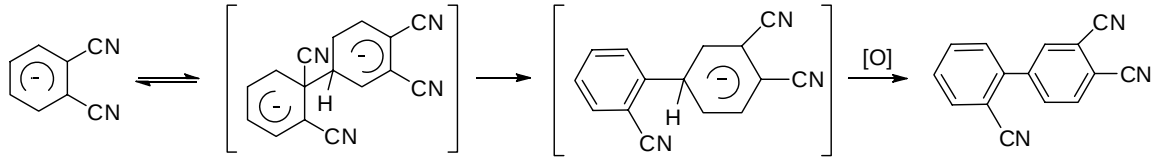
Another analogous reaction pathway for preparation of 3-alkyl substituted phthalonitriles was explored by Hanack's group.[21,22] They used as proposed by Cook *et al.*[23-26] the cycloaddition reaction between 2-substituted furans and fumaronitrile. Thus, the reaction of 2-heptylfuran and fumaronitrile leads to formation of a bicyclic intermediate, which can be aromatized by treatment with lithium bis(trimethylsilyl)amide at low temperature with formation of 3-heptylphthalonitrile in 28% yield (Scheme 3).



Scheme 3

The palladium catalyzed Suzuki-Miyaura coupling reaction between 2,3-dicyanophenyl trifluoromethanesulfonate and phenylboronic acid was also used for preparation of 3-phenylphthalonitrile in 80% yield.[27]

The interesting route to 3-(2'-cyanophenyl) phthalonitrile with overall yield up to 80% was recently proposed[28] utilizing reactivity of sodium or lithium salt of phthalonitrile radical anion in liquid ammonia at -40°C (Scheme 4).



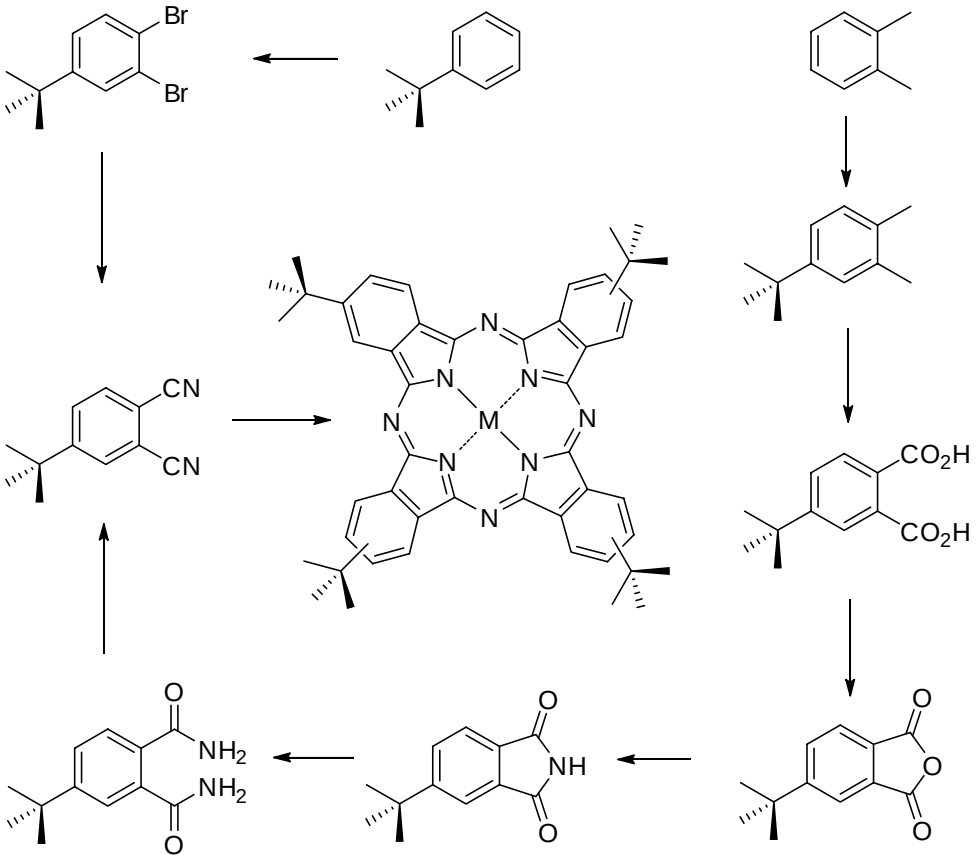
Scheme 4

2.1.2. 2,9(10),16(17),23(24)-Tetrasubstituted compounds. Alkyl-, alkenyl, alkynyl-, and aryl substituted phthalocyanines with 2,9(10),16(17),23(24)-tetrasubstituted patterns are probably the most common and well-explored in the field of phthalocyanine chemistry. 2,9(10),16(17),23(24)-Tetramethyl-[29] and -tetraethyl-[30-32] substituted phthalocyanines still have fair solubility in common organic solvents and thus have generated only limited scientific interest, while the examples of the other, more soluble, analogs are very scarce.[33] Preparation of zinc 2,9(10),16(17),23(24)-tetra(cyclopropyl)phthalocyanine was also reported although the solubility of this compound remains low.[34]

Probably the most used and convenient alkyl substituted phthalocyanines is the metal-free 2,9(10),16(17),23(24)-tetra-*tert*-butylphthalocyanine[35] and its metallic complexes. This phthalocyanine was introduced in the late 1960s when a variety of main group, transition-metal and lanthanide complexes were described; this was followed by an enormous number of research papers reporting studies of this macrocycle.[36] Similarly to 1,8(11)15(18),22(25) tetrasubstituted phthalocyanines, 2,9(10),16(17),23(24)-tetrasubstituted phthalocyanines exist as a mixture of four positional isomers (Figure 2). Since the influence of *tert*-butyl substituents at "β-peripheral" positions of the phthalocyanine core on the electronic structure and thus on the spectroscopic and redox properties is negligibly small, such an isomeric mixture is suitable for the majority of applications. The presence of bulky *tert*-butyl substituents on the phthalocyanines results in a dramatic increase of solubility of these compounds in a variety of common organic solvents without significant shift of the Q-band in the UV-vis spectra as compared to that observed in the corresponding unsubstituted analogs.[37] Indeed, 2,9(10),16(17),23(24)-tetra-*tert*-butylphthalocyanines are readily soluble in saturated hydrocarbons (*e.g*. hexane or petroleum ether), aromatic solvents (benzene, toluene, etc.), and chlorinated hydrocarbons (chloroform, dichloromethane, etc.). Moreover, the introduction of the *tert*-butyl group onto the phthalocyanine periphery prohibits their aggregation, which is one of the common phenomena in phthalocyanine chemistry.

The synthesis of the key precursor 4-*tert*-butylphthalonitrile starts from inexpensive *ortho*-xylene, which undergoes a Friedel-Crafts reaction resulting in formation of 4-*tert*-butyl-*ortho*-xylene[35]. Its oxidation leads to formation of 4-*tert*-butylphthalic acid, which represents the starting reagent for the so-called 'acidic route' to substituted phthalonitriles (substituted phthalic acid → anhydride → imide → amide → nitrile), yielding *ca* 25% of the target nitrile (Scheme 5). The large-scale laboratory preparation of 4-*tert*-butylphthalonitrile was later simplified by using a two-step procedure, which first requires the regioselective bromination of readily available *tert*-butylbenzene followed by the classic Rosenmund-von Braun or a palladium-catalyzed reaction of 1,2-dibromo-4-*tert*-butylbenzene with CuCN or $Zn(CN)_2$.[38,39] Similarly, the preparation of even more sterically crowded 4-adamantylphthalonitriles and the corresponding complexes of 2,9(10),16(17),23(24)-tetraadamantyl- and 2,9(10),16(17),23(24)-tetra(trimethyladamantyl)-phthalocyanines has been reported.[40] The increase of steric bulk of the substituent can be achieved using triphenylmethyl-[41] and (1,1,3,3-tetramethyl)butyl[30] substituents providing excellent solubility of the target phthalocyanines in non-polar solvents. In addition,

several compounds functionalized at the ω-position with amino, ammonium, phosphonate, carboxylate, trifluoromethyl and alkoxy groups (-$(CH_2)_n$-X type of substituents) as well as malonic acid derivatives of 2,9(10),16(17),23(24)-tetrasubstituted phthalocyanines, were reported by a number of research groups.[42]



Scheme 5

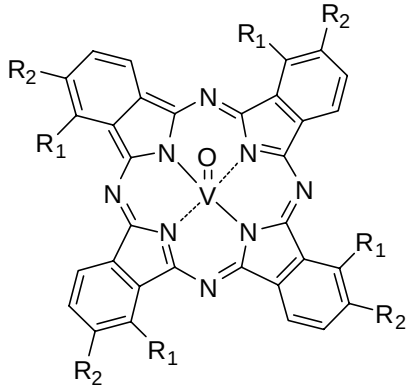
Since substituents in the 4-substituted derivatives of phthalic acid provide less steric crowding during the cyclotetramerization reaction as compared with the corresponding 3-substituted derivatives, the usual yield of C_{4h}, D_{2h}, C_{2v}, and C_s symmetry regioisomers is close as a rule to what would be statistically expected (C_s = 50%, C_{2v} = 25%, C_{4h} = 12.5%, and D_{2h} = 12.5%). In 1993, Hanack reported successful separation of C_{2v} and C_s isomers of nickel 2,9(10),16(17),23(24)-tetra-*tert*-butyl phthalocyanine using direct phase HPLC and MPLC methods.[43] Eight years later, the isomer distribution in metal-free 2,9(10),16(17),23(24)-tetraethyl- and In($C_6H_4CF_3$-p) 2,9(10),16(17),23(24)-tetra-*tert*-butylphthalocyanines was tested by the same research group.[44] The peak area for 'C_{4h}' (C_4) and 'D_{2h}' (D_2) isomers was found to be the same as predicted by statistics for the cyclotetramerization reaction, while the combined area for the 'C_{2v}' (C_2)/ C_s isomers is expected to be 75%. These new observations are differ from those in an earlier publication,[45] where it was claimed that the pure C_{2v} isomer of zinc

2,9(10),16(17),23(24)-tetra-*tert*-butylphthalocyanine can be prepared in the reaction between 4-*tert*-butylphthalonitrile and zinc powder.

A variety of 2,9(10),16(17),23(24)-tetra-aryl substituted phthalocyanines were prepared.[16] In the case of the phenyl, *p*-chlorophenyl, and *p*-nitrophenyl substituents, the solubility of the target phthalocyanines in common organic solvents remains quite low. Enhanced solubility can be achieved by introduction of *ortho*-substituents in the isomeric tetraphenyl-Pc due to steric hindrance of conjugation of the phenyl groups with the macrocycle. The introduction of even more bulky (pentaphenyl)phenyl substituents into phthalocyanines results in high solubility and the absence of aggregation properties in these compounds because of the perpendicular orientation of the substituents with respect to the phthalocyanine core.[46]

The influence of coplanarity on the position of the Q-band in UV-vis spectra in tetraphenyl-substituted phthalocyanines was first investigated in the late 1960s (Figure 3).[16] First, when π-conjugation between the phthalocyanine core and aromatic substituents is broken because of the presence of a chlorine atom in the *ortho*-position of the phenyl ring (*ortho*-chloro substituted complexes), the Q-band position is almost indistinguishable from that in an unsubstituted phthalocyanine. The partial π-orbital overlap between the aromatic substituents and phthalocyanine core in other complexes, however, results in an appreciable (11–27 nm for vanadyl complexes) red shift of the Q-band. Similar to the chlorine substituted phthalocyanines, the influence of aromatic substituents at the β-positions is significantly smaller compared with those located at α-positions (Figure 3).

In the case of 2,3,9,10,16,17,23,24-octaphenylphthalocyanine complexes, two phenyl groups are located next to each other forcing them out of the phthalocyanine plane. As a result, it can be expected that the Q-band in UV-vis spectra in these compounds will be close to the position of the Q-band in 2,9(10),16(17),23(24)-tetraphenylphthalocyanines. Indeed, the Q-band is located at 691 nm in copper 2,9(10),16(17),23(24)-tetraphenylphthalocyanine, while it is observed at 698 nm in copper 2,3,9,10,16,17,23,24-octaphenylphthalocyanine.



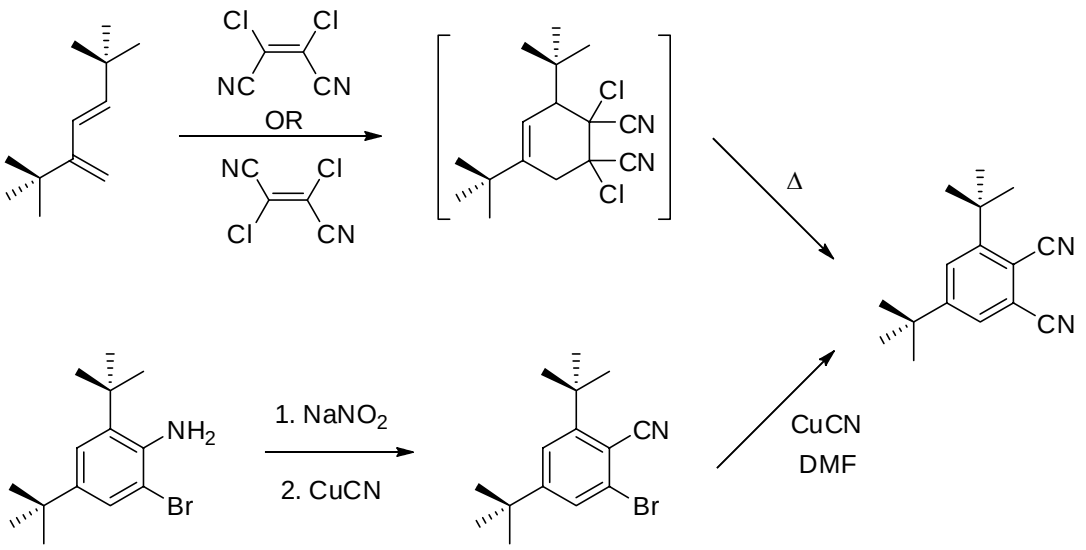
R_1	R_2	Q-band, nm
H	C_6H_5	715
H	*p*-ClC_6H_4	716
H	*o*-ClC_6H_4	707
Ph	H	723
p-ClC_6H_4	H	731
o-ClC_6H_4	H	704

Figure 3. Influence of position and coplanarity of aromatic ring substituents on the position of the Q-band.

2.1.3 Octasubstituted compounds. So far, only two examples of 1,2,8,9(10,11),15,16(17,18), 22,23(24,25)-substitution pattern have been described[47,48] for chloro- and alkynyl-substituted phthalocyanine derivatives. The quite rare 1,3,8,10(9,11),15,17(16,18),22,24(23,25)-type of octasubstituted phthalocyanine compounds with octamethyl- and octa-*tert*-butyl derivatives was only published during last decade. An attempt to control the favorable formation of the least sterically crowded C_{4h} constitutional isomer of nickel 1,3,8,10(9,11),15,17(16,18),22,24(23,25)-octa-*tert*-butylphthalocyanine failed.[49] In this case, the isomer distribution pattern was tentatively explained to be a result of the specificity of the template tetramerization of the 3,5-di-*tert*-butylphthalonitrile precursor which leads to the initial formation of sterically unrestricted phthalonitrile-based "dimers", whereupon further dimerization favors formation of C_s isomer (69%). The preparation of 3,5-dimethylphthalonitrile as well as metal-free and double-decker lanthanide phthalocyanines with the 1,3,8,10(9,11),15,17(16,18),22,24(23,25)-octamethylphthalocyanine core was reported in several papers.[50] As expected, the solubility of these target octasubstituted phthalocyanines is significantly lower as compared to that achieved by introduction of the *tert*-butyl groups.

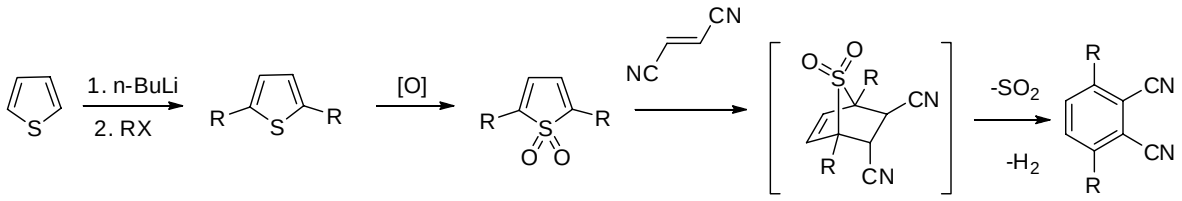
The first report of preparation of the 3,5-di-*tert*-butylphthalonitrile occurred in 1972, when a high-temperature Diels-Alder reaction between 1,3-di-*tert*-butylbutadiene and dichloromaleo (fumaro)nitrile was explored (Scheme 6).[19] Twenty-five years later Hanack et al. reported the preparation of 3,5-di-*tert*-butylphthalonitrile starting from 3,5-di-*tert*-butyl-2-bromoaniline, which was transformed into 3,5-di-*tert*-butyl-2-bromobenzonitrile by a diazotization reaction followed by standard the Sandmeyer reaction. 3,5-Di-*tert*-butyl-2-bromobenzonitrile can be easily converted into the target 3,5-di-*tert*-butyl-phthalonitrile using the Rosenmund-von Braun reaction and a similar synthetic strategy was used for preparation of the 3,5-dimethylphthalonitrile.[49]

Unlike the previously discussed alkylsubstituted phthalocyanines, 1,4,8,11,15,18,22,25-octasubstituted compounds exist as a single D_{4h} or C_{4v} (metal inside or above the phthalocyanine cavity, correspondingly) symmetry isomer because of their symmetric nature.[5] Similarly to the other alkylsubstituted phthalocyanines, the presence of bulky or long chain alkyl substituents results in high solubility of these phthalocyanines in a variety of non-polar solvents. In addition, the introduction of long alkyl chains into the 1,4,8,11,15,18,22,25-octasubstituted phthalocyanine core results in liquid crystal properties.[51,52]



Scheme 6

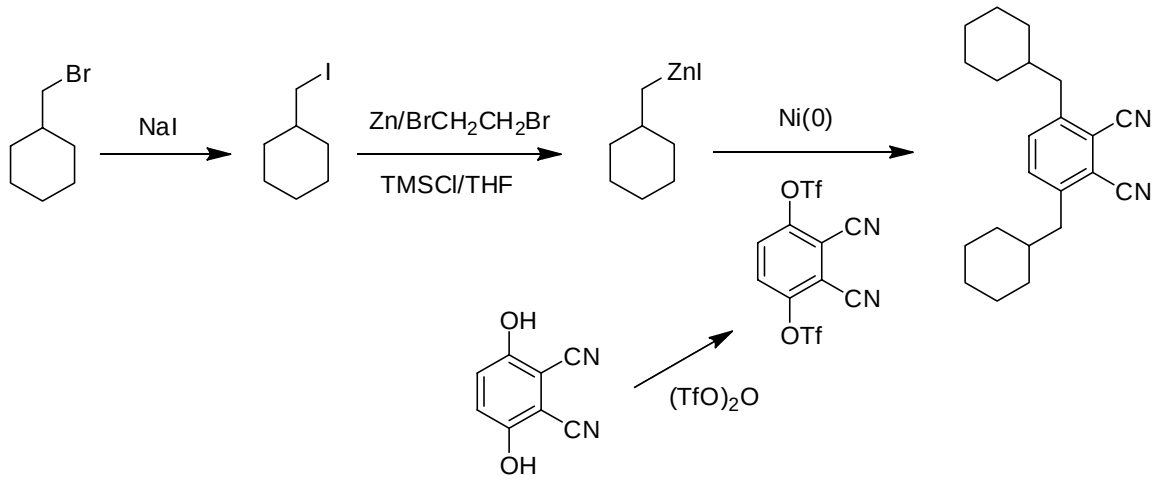
Most of this type of phthalocyanine compounds have originated from Cook's group,[53] which developed a very elegant way for preparation of the key precursors, *e.g.* 3,6-dialkylphthalonitriles, using the Diels-Alder reaction (Scheme 7). The reaction utilizes a readily available 2,5-dialkylthiophenes **(**via a double lithiation-alkylation reaction), which can be oxidized to 2,5-dialkylthiophene-1,1-dioxides forming in Diels-Alder reaction with fumaronitrile the bicyclic intermediate. The latter undergoes *in situ* extrusion of a bridging SO_2 fragment and forms the target 3,6-dialkylphthalonitriles in good yield. Recently, it was found that 2,5-dialkylfurans are useful precursors for preparation of alkenyl and ω-functionalized 3,6-disubstituted phthalonitriles.[33,54]



Scheme 7

The alternative reaction pathway developed by Cammidge and Cook for preparation of the 3,6-dialkylphthalonitrile employs a Negishi coupling reaction between phthalonitrile-3,6-bistriflate (easily obtained from the commercially available 2,3-dicyanohydroquinone[55,56]) and an alkylzinc halide (Scheme 8).[57] The best yields of the alkylzinc halides can be achieved using the appropriate alkyl iodides. Typical yields of the target phthalonitriles are 40–50%. It was found that reaction of the 5-hexenyliodide and zinc powder in DMF at 45 ^{o}C leads to formation of the cyclopentylmethylzinc iodide rather than the 5-hexenylzinc iodide. Thus, if the linear alkenyl

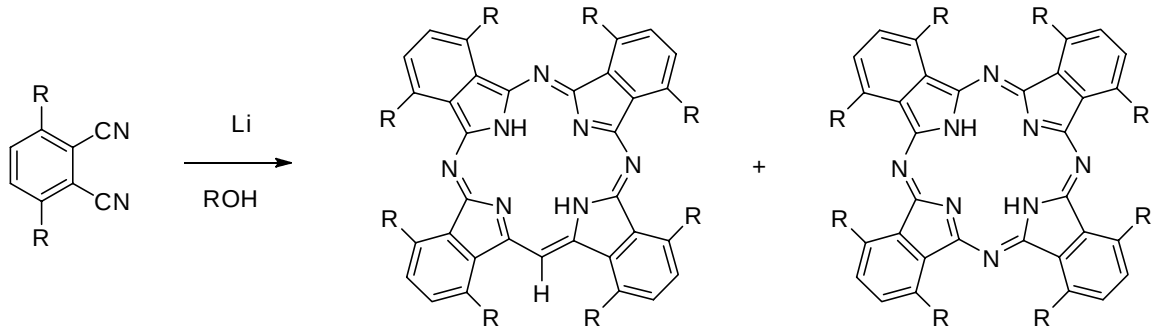
chains are required at the 3 and 6 positions of phthalonitrile, the Diels-Alder reaction pathway (starting from 2,5-dialkenylfuran) can be considered as a preferable synthetic pathway.[33]



Scheme 8

Finally, it was shown that 3-alkyl-6-arylsubstituted phthalonitriles can be prepared by the multistep reaction between dicyanoacetylene and 1-alkyl-4-arylcyclohexa-1,3-diene.[58] Alkoxide-initiated or transition-metal templated cyclotetramerization reactions of 3,6-dialkylphthalonitriles in alcohols afford metal-free or transition-metal 1,4,8,11,15,18,22,25-octaalkylphthalocyanines, respectively. Alternatively, transition-metal 1,4,8,11,15,18,22,25-octaalkylphthalocyanines can be prepared by standard metalation of metal-free phthalocyanine precursors.[57] Taking into consideration the restrictions provided by eight alkyl substituents at αα-peripheral positions, it is not surprising that the yields of metal-free and transition-metal 1,4,8,11,15,18,22,25-octaalkylphthalocyanines (prepared by a direct cyclotetramerization reaction) are in general lower than those from similar reactions of 4- and 4,5-alkylsubstituted phthalonitriles. For instance, refluxing of 3,6-dibutylphthalonitrile in a butanol/lithium butanolate mixture results in formation of metal-free 1,4,8,11,15,18,22,25-octabutylphthalocyanine in 20% yield, while the similar cyclotetramerization of isomeric 4,5-dibutylphthalonitrile leads to formation of metal-free 2,3,9,10,16,17,23,24-octabutylphthalocyanine in 38% yield. Interestingly, although in general substituted 1-amino-3-iminoisoindolenines are better precursors for formation of metal-free substituted phthalocyanines as compared to the respective phthalonitriles, the 3,6-dialkyl-1-amino-3-iminoisoindolenines cannot be prepared by the usual methods, probably because of the steric restrictions provided by the alkyl substituents.[59] Some caution should be used in preparation of metal-free 1,4,8,11,15,18,22,25-octaalkylphthalocyanines also because their formation depends upon the order of the added reagents.[60,61] For instance, when freshly cut lithium was added to a solution of 3,6-dihexylphthalonitrile in pentanol, formation of metal-free 1,4,8,11,15,18,22,25-octahexyl-29*H*,31*H*-tetrabenzo[*b,g,l,q*]-[5,10,15]triazaporphyrin (Scheme 9) was observed as a by-product, along with the expected 1,4,8,11,15,18,22,25-

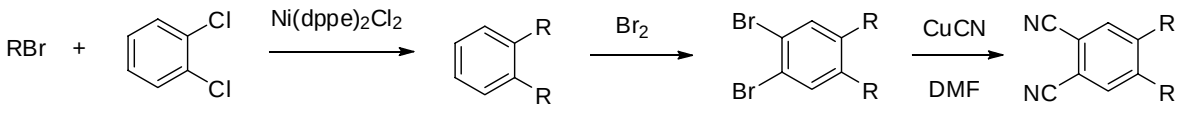
octahexylphthalocyanine. The relative yields of these two macrocycles depend on the nature of the alcohol and the amount of added lithium. For instance, when pentanol was used as a solvent, addition of 2.1 equivalents of lithium resulted in a 5:95 tetrabenzotriazaporphyrin: phthalocyanine ratio, while increasing the amount of lithium up to 19 equivalents shifted this ratio to 23:77.



Scheme 9

Although aryl substituents in 1,4,8,11,15,18,22,25-octaaryl substituted phthalocyanines are expected to provide more steric strain compared with 1,4,8,11,15,18,22,25-octaalkyl compounds, Kobayashi et al. were able to prepare several transition-metal 1,4,8,11,15,18,22,25-octaphenylphthalocyanines.[59] The available X-ray crystal structures of these complexes clearly suggest a highly distorted phthalocyanine core, which leads to a tremendous red-shift of the Q-band in UV-vis spectra. Of course, increase of steric hindrance by phenyl substituents compared to the more conformationally flexible alkyl groups results in very low yields of the target compounds. The initial 3,6-diphenylphthalonitriles used in the above mentioned tetracyclization reaction was prepared using a Diels-Alder reaction between 1,4-disubstituted butadiene and dichloromaleo(fumaro)nitrile. Alternatively, 3,6-diaryl- or 3,6-bis(heteroaryl)phthalonitriles can be prepared using the Suzuki cross-coupling reaction between readily available 3,6-bis(trifluoromethanesulfonyloxy)phthalonitrile and aryl(heteroaryl) boronic acids.[55,56]

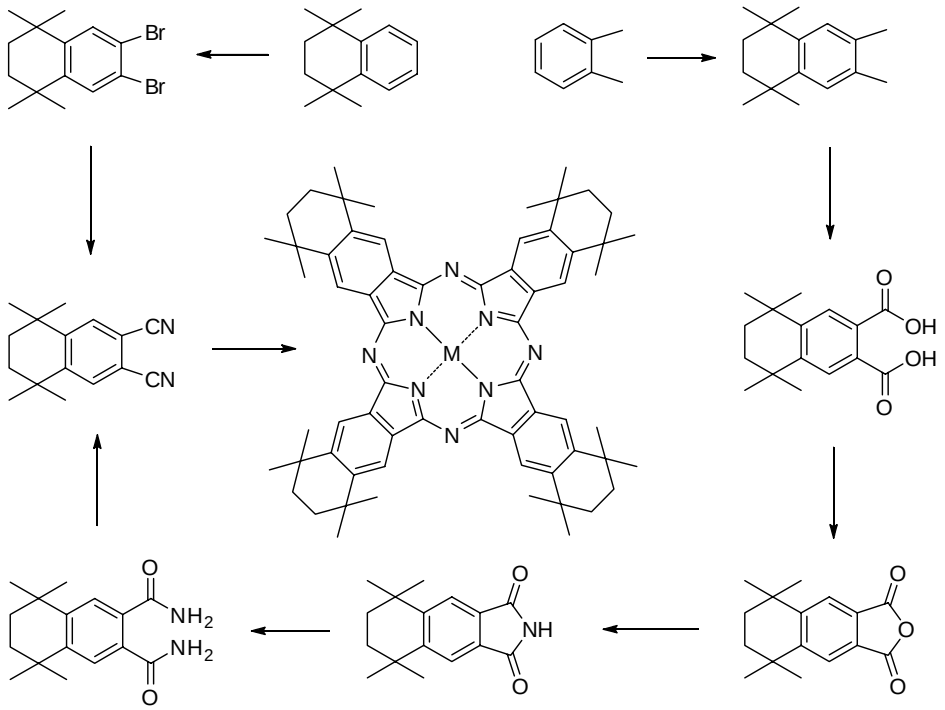
The unsubstituted metal-free phthalocyanine can be very selectively, if not exclusively, lithiated and then deuterated to the 'α-peripheral' positions at low temperature.[62] Thus, reaction of H_2Pc and lithium 2,2,6,6-tetramethylpiperidine (Li-TMP) in the presence of D-TMP at -23 ^oC leads to selective formation of 1,4,8,11,15,18,22,25-octadeuterophthalocyanine.



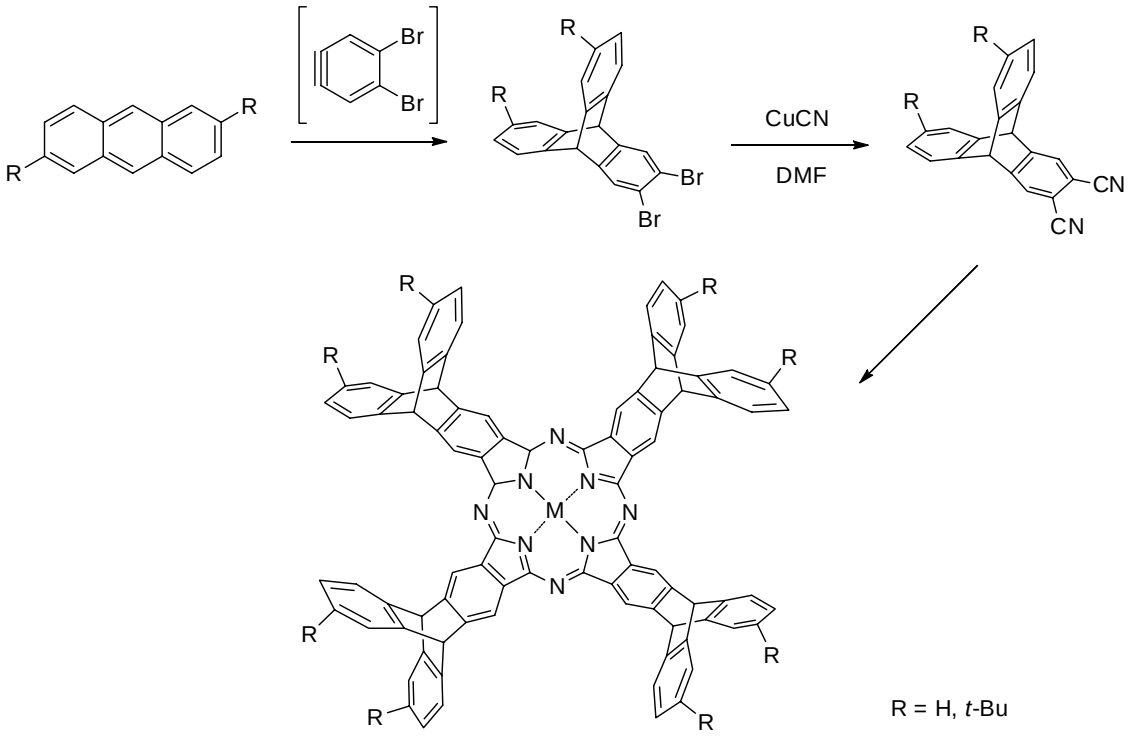
Scheme 10

Similar to 1,4,8,11,15,18,22,25-octasubstituted phthalocyanines, 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines exist as a single isomer. The bromination of the 1,2-dialkylbenzenes followed by the Rosenmund-von Braun reaction, and tetracyclization is one of the most effective ways for preparation of the 2,3,9,10,16,17,23,24-octaalkyl substituted phthalocyanines.[63] Although some 1,2-dialkylbenzenes are commercially available, the corresponding 2,3,9,10,16,17,23,24-octaalkylphthalocyanines have low solubility and thus have little academic interest. Introduction of longer alkyl chains usually can be achieved by the catalytic coupling of *ortho*-dihalobenzenes with the appropriate haloalkanes following by bromination and finally Rosenmund-von Braun reactions (Scheme 10).

Alternatively, cross-coupling reactions between 4,5-dichlorophthalonitrile and alkylzinc halides can be used for preparation of 4,5-dialkylphthalonitriles.[33] Finally, as shown in the late 1980s, alicyclic alkyl substituents can be introduced onto the phthalocyanine core by the 'acidic' methodology presented in Scheme 11.[64] An alternative reaction pathway for preparation of 6,7-dicyano-1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene starts from the bromination reaction of commercially available 1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene, following by the Rosenmund-von Braun reaction.[65] Phthalocyanines prepared from this nitrile as well as their alicyclic five-membered analogs[66] have, like tetra-*tert*-butylphthalocyanines good solubility in common organic solvents, and moreover the presence of alicyclic substituents on the molecule does not significantly affect their optical properties. Metal-free phthalocyanine can be used as a luminescence sensor for laser-induced singlet oxygen generation in solution.[67]



Scheme 11



Scheme 12

The preparation of other interesting sterically crowded, so-called 'concave' phthalocyanine complexes, also includes an initial Diels-Alder reaction between anthracene and 4,5-dibromobenzyne generated *in situ* from 4,5-dibromoanthranilic acid (Scheme 12).[68]

The resulting 2,3-dibromotriptycene can be introduced into the Rosenmund-von Braun reaction to afford 2,3-dicyanotriptycene in moderate yield. The latter can be easily cyclized into the corresponding sterically crowded phthalocyanine complexes using general methods for the preparation of substituted phthalocyanines. The sterically crowded triptycene skeleton creates a double 'concave' cavity, while not affecting the optical properties of phthalocyanines.

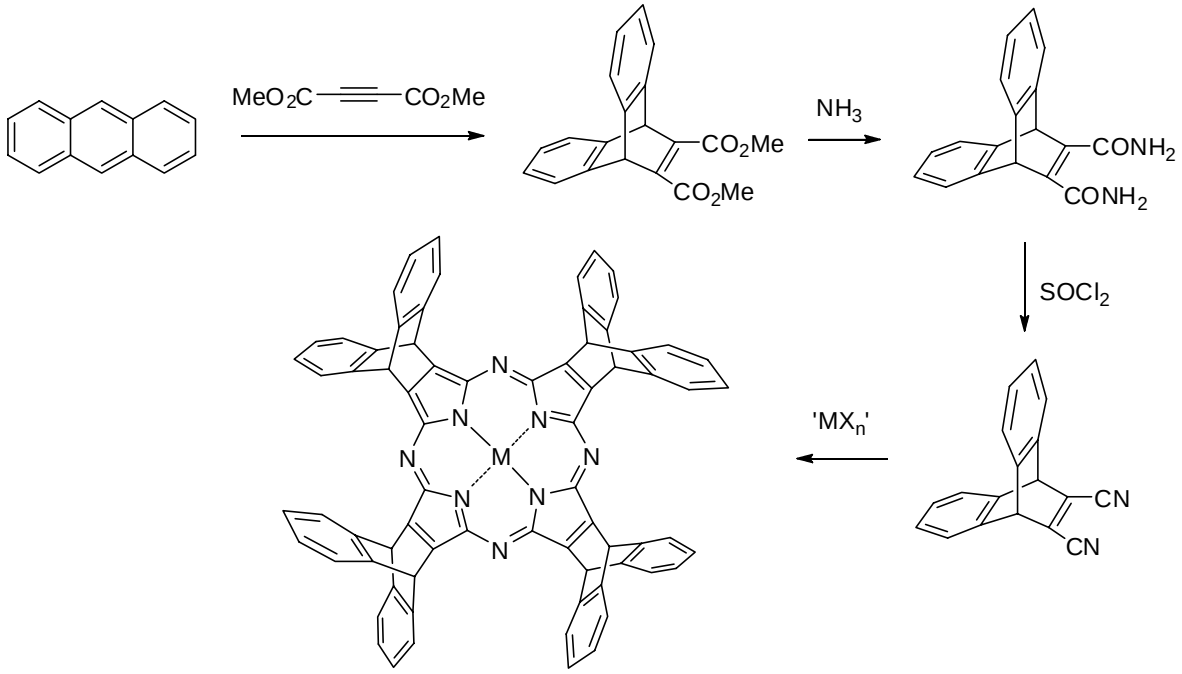
The smaller and larger 'concave' tetraazaporphyrin and 2,3-naphthalocyanine analogs can be prepared in the similar Diels-Alder transformation sequences (Schemes 13 and 14). For instance, 2,3-dicyanodibenzobarrelene can be prepared by the reaction between anthracene and dimethyl acetylenedicarboxylate followed by formation of the amide and the nitrile under standard reaction conditions.[69-71] The Diels-Alder reaction of anthracene with chloromaleo(fumaro)nitrile can be also used for preparation of 2,3-dicyanodibenzobarrelene.[72,73] Direct cyclotetramerization reactions of this nitrile using a magnesium template lead to formation of a small cavity "concave" tetraazaporphyrin (Scheme 13).[69,71-73]

The reaction pathway for preparation of the "concave" analog of 2,3-naphthalocyanine complexes is presented in Scheme 14. It starts from dimethyltriptycene, which can be further brominated by a radical mechanism using *N*-bromosuccinimide to result in formation of 1,2-bis(dibromomethyl)triptycene in high yield. This compound as well as many other substituted

1,2-bis(dibromomethyl)benzenes [for instance 4-adamantyl-1,2-bis(dibromomethyl)benzene], which can be prepared in a similar way, is an extremely useful precursor for Diels-Alder reactions between *in situ* generated diene and an appropriate dienophile (*e.g.* fumaronitrile).[74-76]

The reaction intermediate can be easily aromatized by elimination of two hydrogen bromide molecules with formation of 2,3-dicyano-(4,5-dibenzobarelleno)naphthalene, which under regular template high-temperature reaction conditions generates the target "concave" 2,3-naphthalocyanines.[77]

Similar to 2,3,9,10,16,17,23,24-octaalkyl substituted phthalocyanines, their phenyl analogs can be prepared by the cyclotetramerization reaction of 4,5-diphenylphthalonitrile, which can be prepared by the high-temperature Diels-Alder reaction between 2,3-diphenylbutadiene and dichloromaleo(fumaro)nitrile.

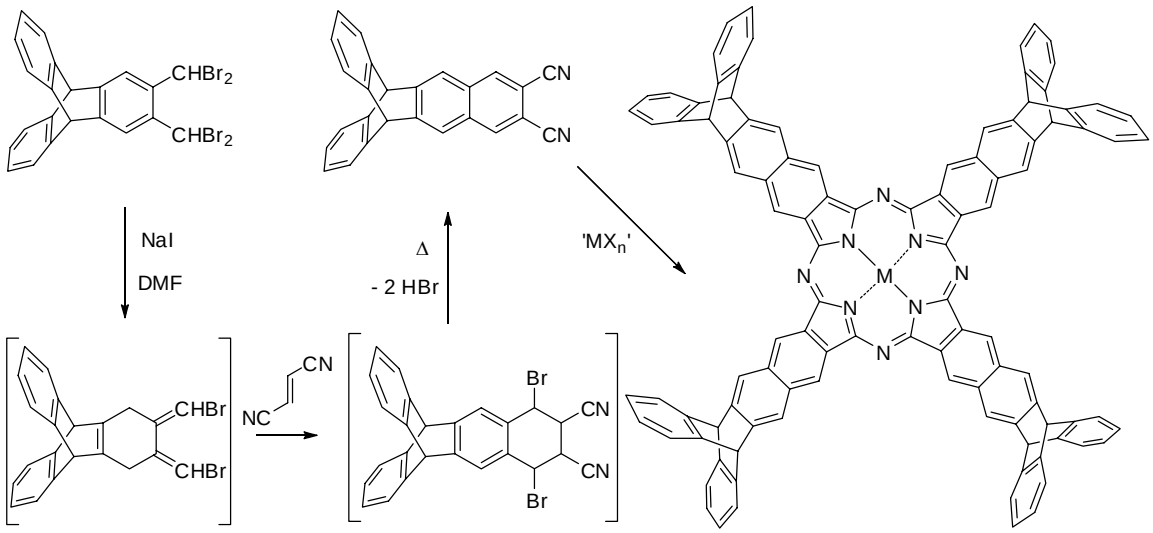


Scheme 13

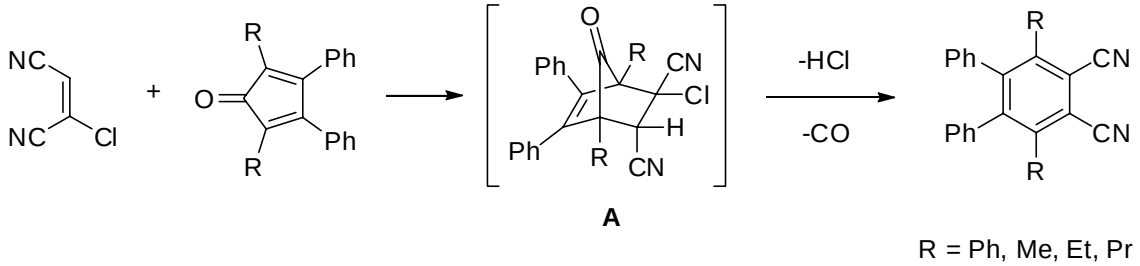
2.1.4 Dodecaalkyl- or aryl- substituted phthalocyanines. Although there are several reports of the preparation of dodecasubstituted phthalocyanines, "all alkyl" or "all aryl" dodecasubstituted phthalocyanines are yet to be reported.

2.1.5 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadecasubstituted compounds. The Diels-Alder reaction is, probably, the easiest synthetic approach for the preparation of tetrasubstituted phthalonitriles, which can, at least theoretically, form 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecasubstituted phthalocyanines. The key precursors for this [4+2] cycloaddition reaction are well-documented tetrasubstituted cyclopentadienone ('cyclone')[78] compounds, which can

usually be prepared by a condensation reaction between α-diketones and ketones with two αCH_2 groups (Scheme 15). The Diels-Alder reaction between appropriate 'cyclone' and chloromaleo(fumaro)nitrile or fumaronitrile leads to formation of bicyclic intermediates **A**, which can be aromatized either by a bromination/elimination reaction sequence or simply by heating the reaction mixture.[79] The typical yields of the target tetrasubstituted nitrile vary with the nature of the substituted diene and were found to be between 16 and 73%. Use of readily available tetrasubstituted cyclopentadienone precursors allows preparation of several tetrasubstituted phthalonitriles with both aryl- and alkyl-substituents on the benzene ring.



Scheme 14

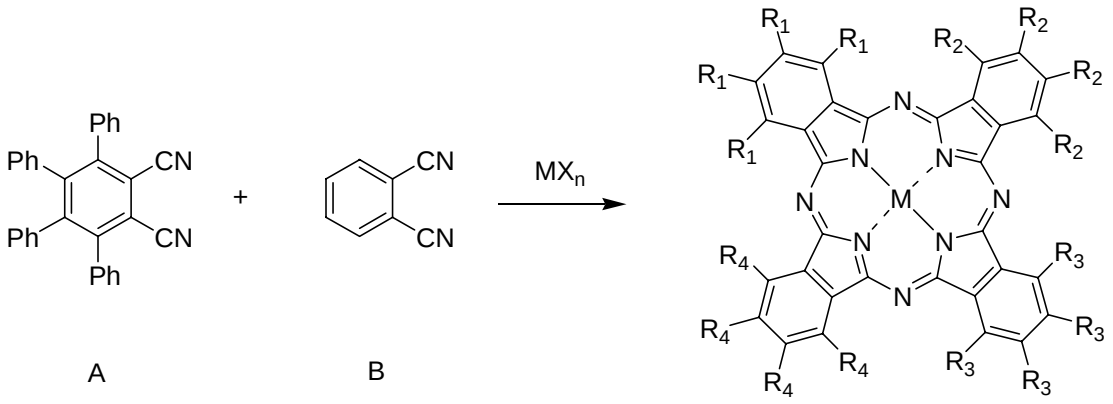


Scheme 15

Sterically hindered nitriles can be used for preparation of low-symmetry phthalocyanine analogs using the so-called sterically-controlled method (Scheme 16).[80] In this method, the low-symmetry phthalocyanines can be prepared by cross-condensation of sterically hindered and sterically unhindered phthalonitriles **A** and **B**, respectively. Target compounds can be easily separated by preparative TLC, while the yields of the isolated reaction products follows the order of increase of steric hindrance, *i.e.* AAAA>AAAB>ABAB>AABB>ABBB. Although steric

interactions between phenyl groups located at the 1,4-positions of each isoindole fragment prevent direct formation of hexadecaphenylsubstituted transition-metal phthalocyanines, the analog zinc complexes substituted at the 1,4,8,11,15,18,22,25-positions can be prepared using a modified approach in low yield.[81]

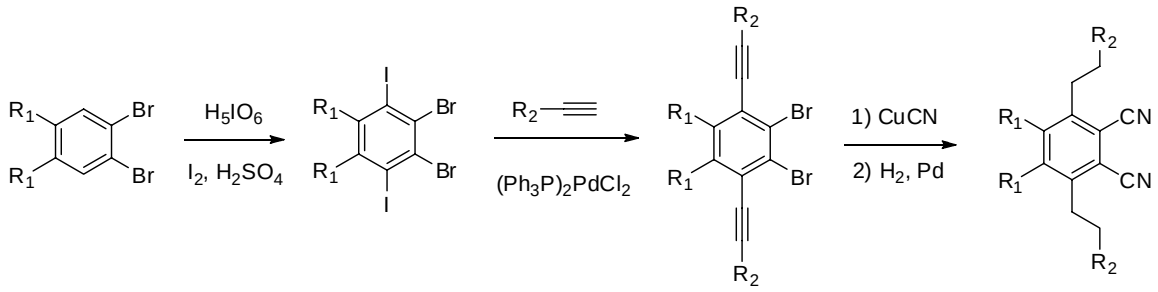
Another synthetic strategy for preparation of tetrasubstituted phthalonitriles was explored by Hanack et al. (Scheme 17).[82] The reaction sequence starts by iodination of 1,2-dibromo-4,5-dialkylbenzene with formation of 1,2-dibromo-3,6-diiodo-4,5-dialkylbenzene. Further selective coupling reactions between 1,2-dibromo-3,6-diiodo-4,5-dialkylbenzene and an appropriate alkyne leads to formation of 1,2-dibromo-3,6-dialkynyl-4,5-dialkylbenzene, which can be transformed into the corresponding phthalonitrile by the Rosenmund-von Braun reaction. Finally, reduction of the tetrasubstituted acetylenic phthalonitriles leads to formation of the target tetraalkylphthalonitriles.



Scheme 16

Taking into consideration steric restrictions induced by substituents at the α-peripheral positions, it is not surprising that only a few examples of 1,2,3,4,8,9,10,11,15,16,17,18, 22,23,24,25-hexadecaalkyl- or aryl substituted phthalocyanines have been reported in the literature. Two of hexadecaalkyl substituted nickel phthalocyanines were prepared by Hanack et al. by template condensation of the respective tetraalkyl substituted phthalonitriles in octanol for 7 days.[82] Interestingly, when tetra(*n*-hexyl)phthalonitrile was used, the yield of the target nickel hexadecahexylphthalocyanine is low (< 1%), while a similar template condensation of 3,6-diheptyl-4,5-dimethylphthalonitrile results in a 10% yield of the target phthalocyanine. So far, all attempts to obtain hexadecaphenyl phthalocyanine by template condensation of tetraphenylphthalonitrile failed to provide the target compound. On the other hand, a

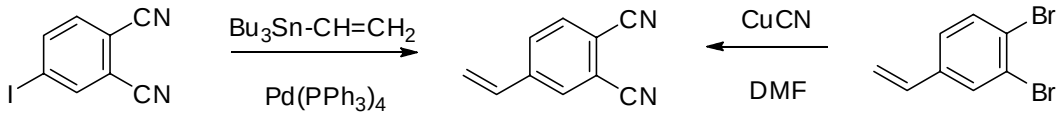
cyclotetramerization reaction of tetrapyrazolylphthalonitrile in hydroquinone at 180 ^{o}C leads to formation of metal-free hexadecapyrazolylphthalocyanine in 70% yield.[83]



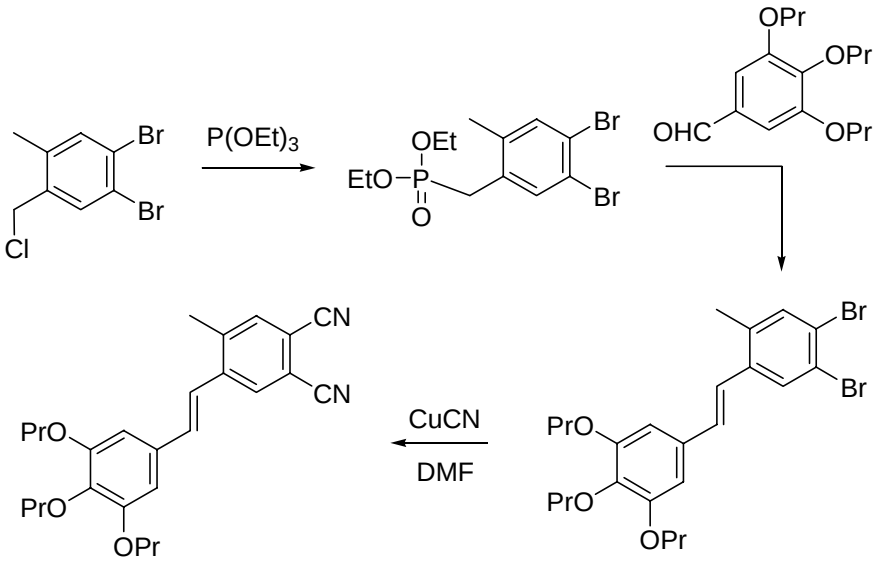
Scheme 17

2.2 Phthalocyanines with alkenyl- and alkynyl-substituents

Several synthetic strategies for preparation of vinyl-containing phthalonitriles have been proposed since the early 1990s, when Leznoff et al. reported the synthesis of *cis*-1,2-bis(3,4-dicyanophenyl)ethene.[84] In general, reduction of the carbon-carbon triple bond, a Rosenmund-von Braun reaction, and various coupling reactions were suggested for preparation of the target alkenylphthalonitriles with a typical example shown in Scheme 18.[85]



Scheme 18

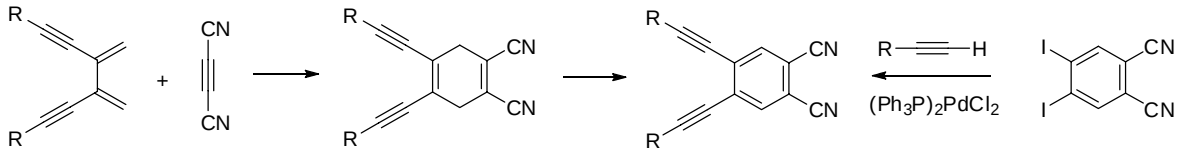


Scheme 19

Although preparation of alkenyl-substituted phthalonitriles was described by the Leznoff, Hanack, Kimura and Torres groups, in most cases these compounds were used for synthesis of asymmetric phthalocyanines, while to date, there are only a few examples on the preparation of alkenyl-containing symmetric phthalocyanines, which include the metal-free 2,9(10),16(17),23(24)-tetravinylphthalocyanine reported by Hanack in 1993.[85] This compound was prepared by a cyclotetramerization reaction of 1,3-dihydro-1,3-diimino-5-vinyl-isoindole in DME and the product was characterized by IR-, UV-vis, and ^{13}C CP/MAS-NMR spectroscopy. In addition, several star-shaped stilbenoid phthalocyanines with extended π-conjugated oligo(*p*-phenylenevinylene)s were reported by Kimura et al.[85] The target nitriles for these compounds were prepared using the Michaelis-Arbuzov and Wittig-Horner reaction sequences (Scheme 19).

Unlike 2,9(10),16(17),23(24)-tetra-alkenyl substituted phthalocyanines, their tetra-alkynyl substituted analogs are relatively abundant. The target 4-alkynyl substituted phthalonitriles can be prepared by palladium-catalyzed coupling reactions between 4-iodophthalonitrile and specific terminally monosubstituted acetylenes.[86] Cyclotetramerization of 4-alkynylphthalonitriles leads to formation of the target 2,9(10),16(17),23(24)-tetra-alkynyl substituted phthalocyanine compounds. If alkynyl substituents are sensitive to the reaction conditions, formation of oligomeric materials, which originate from partial degradation of the alkynyl chain, can also be observed. Several interesting phthalocyanine-porphyrin assemblies connected via the -C≡C- fragment were reported by Lindsey and co-workers.[87] In each of these assemblies, the 2,9(10),16(17),23(24)-tetraalkynyl substituted phthalocyanine core is connected to four or eight porphyrin units resulting in interesting redox and photophysical properties. The introduction of the alkynyl substituents into the phthalocyanine core can also be achieved by the Sonogashira coupling reaction using 2,9(10),13(14),23(24)-tetraiodophthalocyanines as was demonstrated in the preparation of the deoxyribose-phthalocyanine conjugate.[88]

So far, the only example of the 1,2,8,9,15,16,22,23-octakis substitution pattern was described in 1999 by Leznoff and co-workers.[48] A palladium-catalyzed coupling reaction between 3,4-dibromophthalonitrile and *tert*-butylacetylene results in formation of 3,4-bis(*tert*-butylethynyl)phthalonitrile in 40% yield. This nitrile undergoes a cyclotetramerization reaction with lithium 1-pentanolate and results in formation of a single C_{4h} (ignoring inner protons) isomer of 1,2,8,9,15,16,22,23-octakis(3,3-dimethyl-1-butynyl)phthalocyanine in 35% yield. Formation of a single isomer in this reaction is not surprising taking into consideration the size and conformational rigidity of *tert*-butylacetylene groups at the α-peripheral positions of the phthalocyanine core. Similar palladium catalyzed couplings between alkynes and 3,4-diiodophthalonitrile were also explored by Leznoff et al.[48]



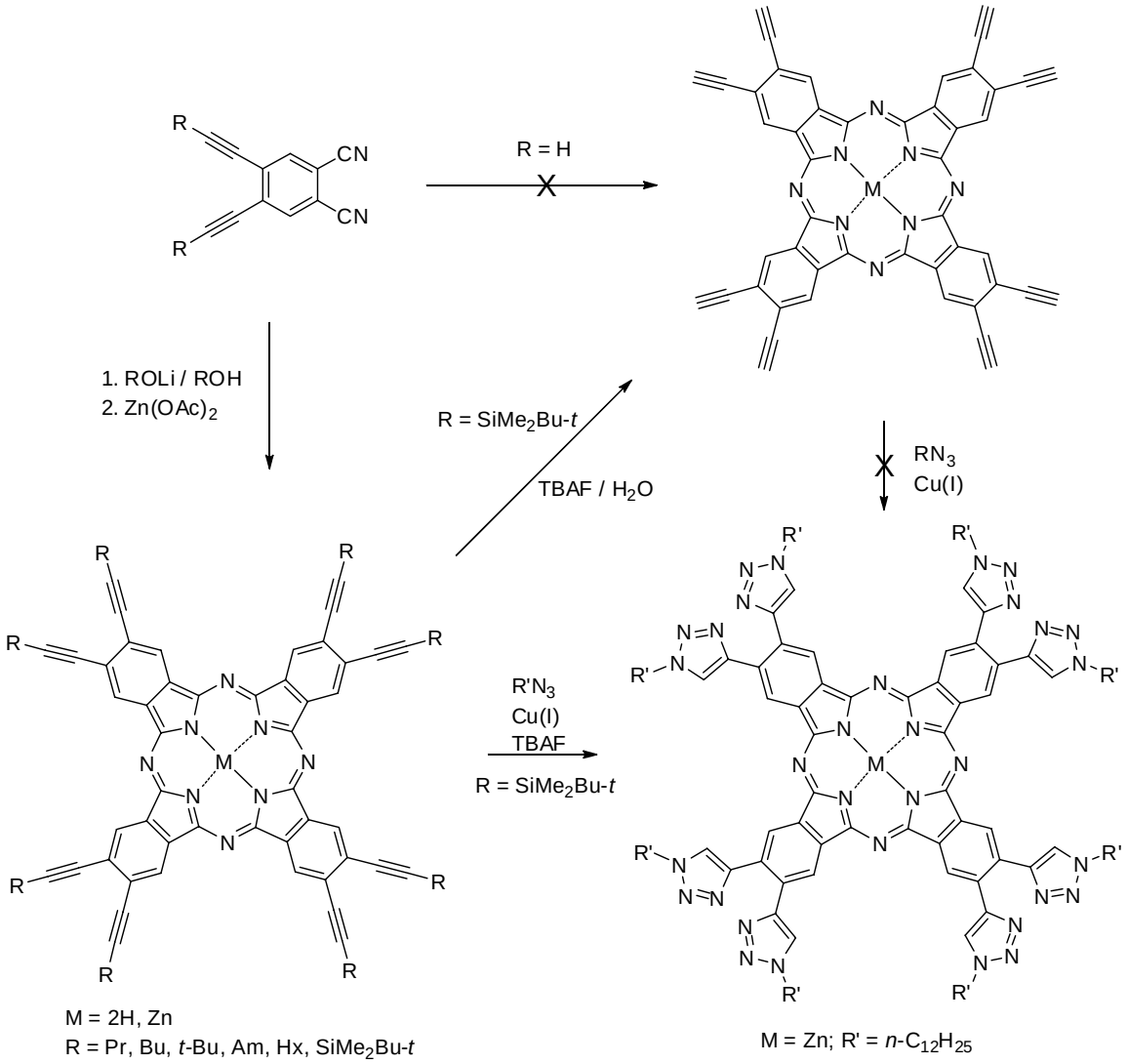
Scheme 20

The preparation of 4,5-dialkynyl substituted phthalonitriles and their respective 2,3,9,10,16,17,23,24-octaalkynyl substituted phthalocyanines was explored in detail by Leznoff and Torres in the 1990s. The original preparation of 4,5-dialkynylphthalonitriles was accomplished using a simple Heck coupling reaction between 4,5-dibromo- or diiodo-phthalonitrile and the corresponding substituted or terminal alkynes in the presence of a palladium catalyst (Scheme 20). Alternatively, 4,5-dialkynyl substituted phthalonitriles can be prepared by the Diels-Alder reaction between dimethylenehexadiynes and dicyanoacetylene, followed by a hydrogen subtraction reaction with DDQ.

In the case when 4,5-disubstituted phthalonitriles have alkyl or silyl terminal groups directly connected to the acetylene moieties, the target 2,3,9,10,16,17,23,24-octaalkynyl substituted phthalocyanines can be prepared with reasonable yields by a direct cyclomerization reaction in the presence of a metal salt (if necessary) in DMAE, with or without continuous ammonia gas flow.[48] The 2,3,9,10,16,17,23,24-octaalkynyl substituted phthalocyanines with terminal -C≡C-H groups, however, must be prepared by modification of the peripheral -C≡C-R substituents. For instance, they can be prepared by cleavage of the C-Si bond in C≡C-SiMe$_2$Bu-*t* using tetrabutylammonium fluoride under mild conditions (Scheme 21).[48] In addition, *in situ* deprotection of *tert*-butyldimethylsilyl groups with tetrabutylammonium fluoride and "clicking" of terminal acetylene substituents with alkylazides in the presence of copper(I) ions results in a highly efficient and quantitative route to the octatriazole-functionalized phthalocyanines. It has been demonstrated that these triazole containing phthalocyanines can form well-defined supramolecular structures when doped with zinc triflate.[89]

2.3 Trialkylsilyl substituted phthalocyanines

4-Trimethylsilylphthalonitrile and isomeric 3-trimethylsilylphthalonitrile were first prepared by Hopff and Gallegra in 1968 using the 'acidic' synthetic pathway starting from the corresponding trimethylsilylphthalic acids, or by catalytic ammonolysis of their anhydrides with gaseous ammonia and borophosphate catalyst.[18] 4-Trimethylsilylphthalic anhydride and 4-trimethylsilylphthalonitrile were the starting compounds for preparation of 2,9(10),16(17),23(24)-tetrakis(trimethylsilyl)-phthalocyanines, the first soluble in organic solvents phthalocyanine derivatives with bulky silyl substituents. Trimethylsilylphthalic acids were obtained by the coupling reaction between 4- or 3-chloro-*o*-xylene and trimethylsilylchloride in the presence of sodium in benzene, with subsequent oxidation of the resulting trimethylsilyl-*o*-xylenes.



Scheme 21

An alternative preparation of the 3-trimethylsilylphthalonitrile was reported by Chen et al., who used a direct silylation reaction of unsubstituted phthalonitrile. Upon its cyclotetramerization, metal-free 1,8(11),15(18),22(25)-tetrakis(trimethylsilyl)phthalocyanine was prepared.[90] The target phthalocyanine is readily soluble in chlorinated hydrocarbons and gives a single ^{29}Si NMR peak at δ = -2.366 ppm relative to TMS.

Chen et al. suggested that the direct lithiation of the phthalocyanine core predominantly, if not exclusively, occurs at the α-peripheral positions of the phthalocyanine ring, and this can be used to selectively introduce α-peripheral substituents onto the phthalocyanine core. Thus, treatment of the unsubstituted metal-free phthalocyanine with lithium 2,2,6,6-tetramethylpiperidine in the presence of chlorotrimethylsilane results in formation of a mixture of trimethylsilyl-substituted phthalocyanines, $H_2Pc(SiMe_3)_n$ (n = 2–4), which can be separated by

column chromatography. The yield of tetrakis(trimethylsilyl)phthalocyanine depends upon the phthalocyanine : base ratio. For instance, when this ratio is 1 : 7.8, the yield of tetrakis(trimethylsilyl)phthalocyanine is 13%, which can be increased if a 1 : 32 ratio is used.[62,90] It is interesting to note that despite the bulkiness of the trimethylsilyl groups, all four possible isomers of $H_2Pc(SiMe_3)_4$ were observed in the ^{29}Si NMR spectrum. Similarly, lithiation of the zinc phthalocyanine followed by treatment with Me_3SiCl leads to formation of polysilylated zinc phthalocyanine.[91]

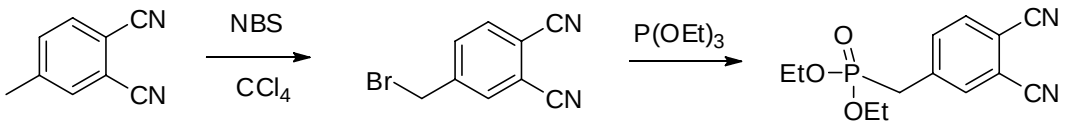
The silylated analogs of octaalkylsubstituted phthalocyanines are presented in a single report in which 1-imino-5,6-bis(trimethylsilyl)-1*H*-isoindol-3-amine (prepared from 4,5-bis(trimethylsilyl)-1,2-benzenedicarbonitrile in four steps with an overall yield of 32%) was used for preparation, in a pentanol/DBU mixture in the presence of appropriate metal salts, of the corresponding zinc and manganese 2,3,9,10,16,17,23,24-octakis(trimethylsilyl)phthalocyanines.[92]

2.4 Phthalocyanines with substituents connected via a methylene group to the phthalocyanine core

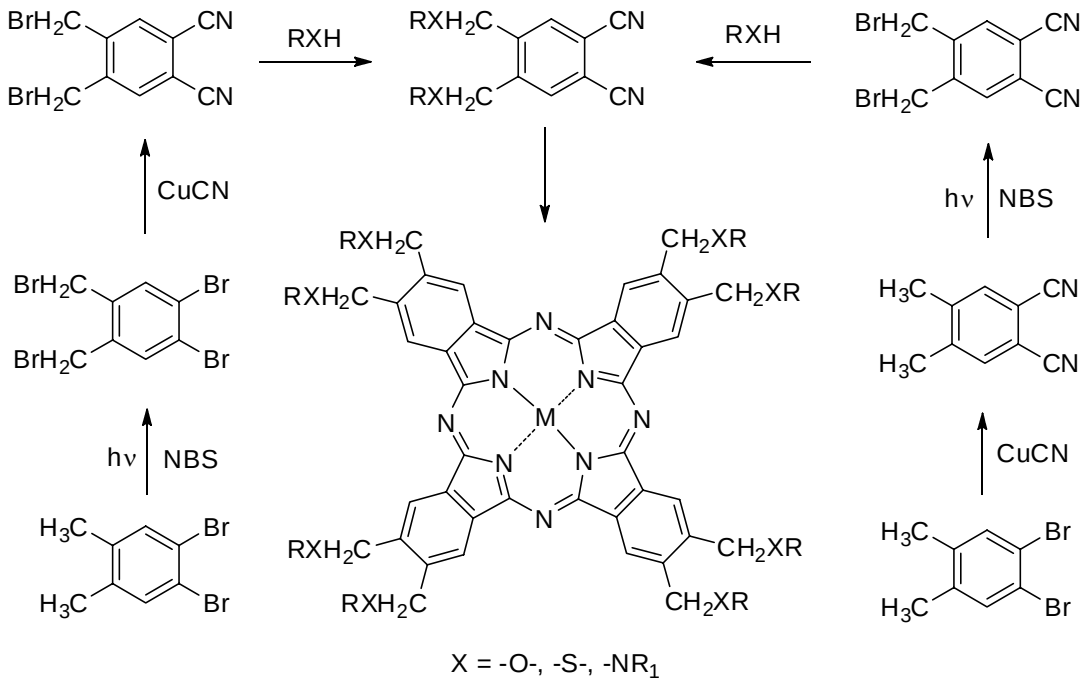
Phthalocyanines with substituents connected via a methylene group to the phthalocyanine core represent another important class of substituted phthalocyanine compounds. These complexes can be prepared using two major synthetic strategies – by the cyclotetramerization reaction of appropriately substituted phthalonitriles or by substitution reactions on the phthalocyanine macrocycle.

Thus, by reaction of 4-bromomethylphthalonitrile with triethylphosphite 4-diethoxyphosphinylmethylphthalonitrile was synthesized; this is the starting compound for the preparation of the corresponding diethoxyphosphinylmethyl substituted phthalocyanines (Scheme 22).[93]

The typical synthetic pathway for preparation of 4,5-disubstituted phthalonitriles with $ArCH_2X$ groups is presented in Scheme 23.[94] The bromination of *o*-xylene results in formation of 4,5-dibromo-*o*-xylene, which can be converted into 4,5-dimethylphthalonitrile under the regular Rosenmund-von Braun reaction conditions. This nitrile then can be converted into 1,2-bis(bromomethyl)-4,5-dicyanobenzene by a radical chain halogenation reaction. Finally, nucleophilic substitution of the bromine atoms at the benzylic positions in 1,2-bis(bromomethy)-4,5-dicyanobenzene leads to formation of the target 4,5-disubstituted phthalonitriles. Alternatively, 4,5-dibromo-*o*-xylene can be brominated under radical chain bromination conditions to form 1,2-dibromo-4,5-bis(bromomethy)benzene. 1,2-Dibromo-4,5-bis(bromomethyl)benzene then undergoes the Rosenmund-von Braun reaction to form 1,2-bis(bromomethyl)-4,5-dicyanobenzene, which can be converted into the target 4,5-disubstituted phthalonitriles. In the majority of cases, alcohols and thiols were used in the final nucleophilic substitution step, although several examples of aminosubstituted analogs are also present in the literature.



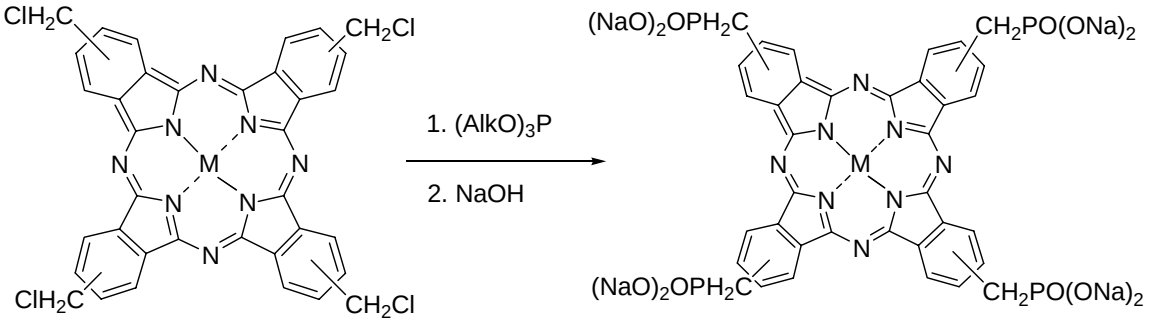
Scheme 22



Scheme 23

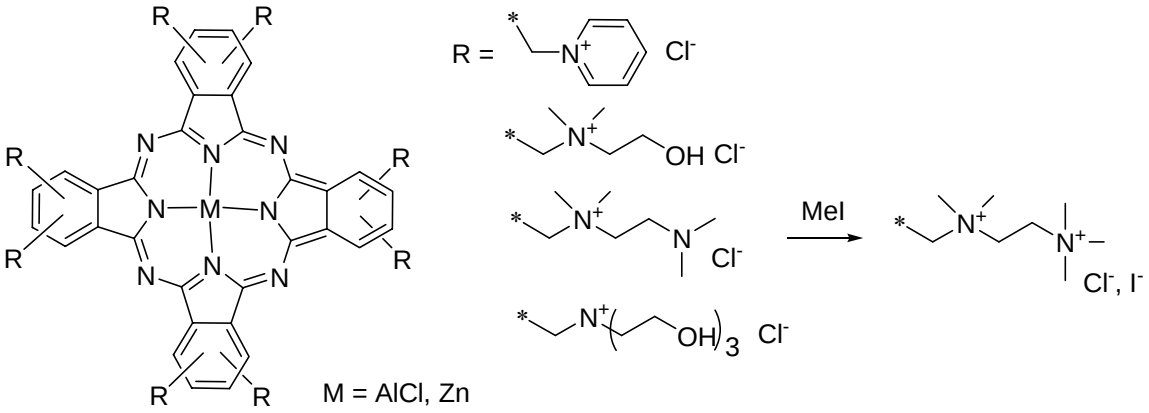
Chloromethylation of the phthalocyanine core represents the second synthetic strategy for preparation of phthalocyanines with substituents connected to the phthalocyanine core via a methylene group. This reaction results in formation of tetra- and octa-chloromethylphthalocyanine macrocycles as a mixture of unknown positional isomers. These chloromethylphthalocyanines can be used as the universal precursors for preparation of a variety of functionalized phthalocyanine derivatives. Thus, polysubstituted phthalocyanine metal complexes of general formula $PcM[CH_2PO(OR)_2]_n$ where M=AlX, Zn, SnX_2, SiX_2, TiO, R=H, Et, X = OH, OPOR(OR), Br, n = 4-8, can be prepared from corresponding chloromethylated phthalocyanines and trialkylphosphites using the Arbuzov-Michaelis reaction (Scheme 24).[95]

Such compounds are highly soluble in water and do not aggregate in aqueous solutions.



Scheme 24

They absorb at longer wavelengths than the corresponding sulfo-derivatives and have generated interest as efficient photosensitizers for PDT, allowing deeper located tumors to be treated. So, aluminum octakis(diethylphosphinylmethyl)phthalocyanine has intense absorption with maximum at 698 nm ($\varepsilon > 10^5$ $M^{-1}cm^{-1}$).[96]



Scheme 25

Similar to the preparation of anionic phosphomethylphthalocyanines, water-soluble cationic phthalocyanines can be prepared using the octachloromethylphthalocyanine precursor (Scheme 25). In this case, the reaction of a tertiary aliphatic amine or pyridine leads to formation of a quaternary ammonium or pyridinium salt, which (in the case where other tertiary amino groups are present) can be transformed into dicationic (per substituent) derivatives.[97] Some of these derivatives are very active in cancer PDT as well as in antimicrobial photodynamic treatment of biologically relevant substances and water.

Use of tetra- and octa-chloromethylphthalocyanine precursors also provides the possibility for introduction of carborane cages, useful in boron neutron capture therapy. A covalent conjugate of cobalt phthalocyanine with carborane –closocarboranylphthalocyanine was prepared earlier, starting from dimethyl(3,4-dicyanophenyl)(o-carboranylmethyl)malonate[42a] and other[98] precursors. Tetrakis and octakis(chloromethyl)phthalocyanines, when treated with

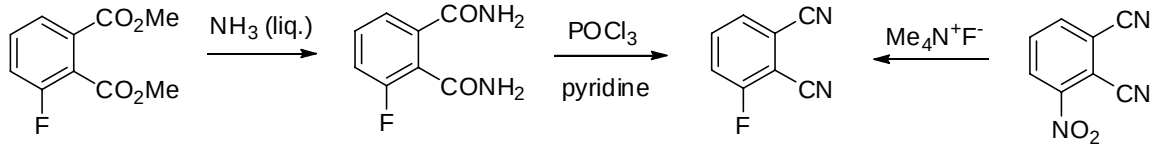
$B_{12}H_{11}NH_2^{2-}$, form sodium salts of tetrakis and octakis(undecahydro-closododecacarboranylaminomethyl) phthalocyanines which are soluble in water because of the presence of anionic boranyl moieties.[99]

3. Phthalocyanines with electron-withdrawing groups

3.1 Halogen-substituted phthalocyanines

In general, the interest in substituted phthalocyanines with direct C(aryl)-F bonds relates to their molecular semiconducting properties.[52,100] In spite of the commercial availability of 3-fluorophthalonitrile, there are only a few reports on the preparation of the corresponding phthalocyanines published so far.[101]

Thus, copper and zinc complexes of 1,8(11),15(18),22(25)-tetrafluorophthalocyanines were investigated as molecular semiconductor thin films and as prospective compounds for solar energy conversion.[101a] The key precursor for formation of these complexes (3-fluorophthalonitrile) can be prepared either by an aromatic nucleophilic substitution reaction between 3-nitrophthalonitrile and tetramethylammonium fluoride or from 3-fluorodimethylphthalate, which can be treated first with liquid ammonia and then with $POCl_3$/pyridine to form 3-fluorophthalonitrile (Scheme 26).[101] 4-Fluorophthalonitrile can be prepared similarly starting from 4-fluorodiethylphthalate.[101c] A template cyclotetramerization of 4-fluorophthalonitrile under normal reaction conditions leads to formation of the target 2,9(10),16(17),23(24)- tetrafluorophthalocyanines.



Scheme 26

There are three types of octafluorophthalocyanines reported to date. Transition-metal 1,3,8,10(11,9),15,17(18,16),22,24(25,23)-octafluorophthalocyanines were prepared by the diazotization reaction of the corresponding octaaminophthalocyanines followed by the treatment of the diazonium salts with $NaBF_4$ at 5 ^oC.[102] Although the reported elemental analyses of these complexes are in agreement with the proposed structures, the molar extinction coefficients reported for Q- and B-bands (ε = 690 – 6025) are more than an order of magnitude lower than the expected (for phthalocyanines) values of ~100,000. Zinc 1,4,8,11,15,18,22,25-octafluorophthalocyanine was investigated by Mayer et al.[101a] as a potentially useful compound for solar energy conversion. Several transition-metal 2,3,9,10,16,17,23,24-octafluorophthalocyanines were investigated using photoelectron and photoemission spectroscopies, while their optical and redox properties were studied by electro- and

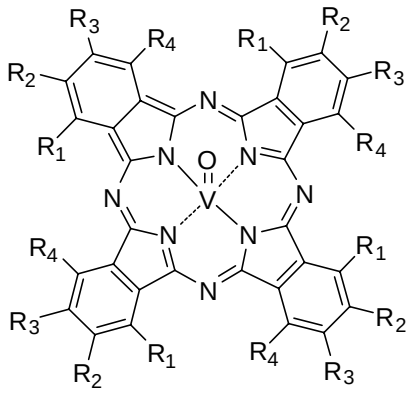
spectroelectro-chemical methods.[101a,103] The starting 4,5-difluorophthalonitrile can be prepared using the aromatic nucleophilic substitution reaction between commercially available 4,5-dichlorophthalonitrile and potassium fluoride, or by a palladium-catalyzed reaction between 1,2-dibromo-4,5-difluorobenzene and $Zn(CN)_2$.[39,101] Metal-free and transition-metal 1,2,3,4,8,9,10, 11,15,16,17,18,22, 23,24,25-hexadecafluoro phthalocyanines, prepared in the normal way using commercially available 3,4,5,6-tetrafluorophthalonitrile, have been intensively studied during last decade because of their potential application as low-voltage thin-film transistors.[104] Unlike unsubstituted phthalocyanine, these compounds are soluble to some extent in a variety of organic solvents such as DMF, chlorobenzene, acetone, and chloroform.

One of the first reports on the preparation of chlorinated copper phthalocyanines with different degrees of chlorination was published in 1959.[105] It was found that the copper complexes of 1,8(11),15(18),22(25)-tetrachloro-, 2,9(10),16(17),23(24)-tetrachloro-, 1,4,8,11,15, 18,22,25-octachloro-, 1,2,8,9(10,11),15,16(17,18),22,23(24,25)-octachloro-, 2,3,9,10,16,17,23, 24-octachloro-, 1,2(3),4,8,9(10),11,15,16(17),18,22, 23(24),25-dodecachloro-, 1,2,3,8(11),9,10, 15(18),16,17,22(25),23,24-dodecachloro-, and hexadecachlorophthalocyanine can be prepared in excellent yields from the corresponding chlorinated phthalic anhydrides, urea, and copper salt. Again, when comparisons were possible, the yields of the less sterically crowded polychloro-containing phthalocyanines were higher compared with those with chlorine atoms located at the α-positions.[5,105] Another interesting observation was that formation of hexadecachlorophthalocyanine from tetrachlorophthalic anhydride and urea leads to the partial dechlorination of the phthalocyanine core. The pure hexadecachlorophthalocyanine could be prepared from the commercially available tetrachlorophthalonitrile, avoiding urea and other potential nucleophiles in the reaction mixture.[106,107] After the initial report, a large number of the other chlorinated phthalocyanines were published. In the majority of cases, chlorine-containing phthalonitriles were used as the key precursors in the cyclotetramerization reaction. It has been recently shown[108] that yields of chlorinated transition-metal phthalocyanines from chlorinated anhydrides can be improved by using an ionic liquid as the reaction media.

In general, introduction of chlorine atoms into the phthalocyanine core increases the first oxidation potential of the respective phthalocyanine,[109] and changes the color of the target compounds from blue to green. Indeed, commercial green-colored phthalocyanine-based pigments usually contain 14-15 chlorine atoms.[110] The position of long wavelength Q-band in UV-vis spectra of chlorinated phthalocyanines depends on number and position of chlorine atoms in macrocycle – it is red shifted in the case of substituents at α-position, especially in polysubstituted compounds (Figure 4).

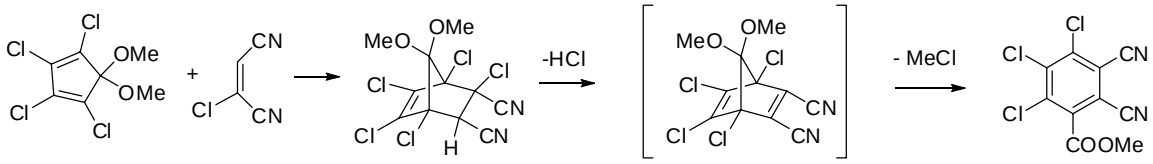
Use of chloromaleonitrile[111] for preparation of the methyl 2,3,4-trichloro-5,6-dicyanobenzoate is a rare example of the Diels-Alder reaction being used for synthesis of precursors for phthalocyanines with electron-withdrawing groups.[79] The interaction of commercially available 1,2,3,4-tetrachloro-5,5-dimethoxycyclopenta-1,3-diene and chloromaleonitrile leads to formation of a bicyclic intermediate, which can be aromatized in two

steps, first eliminating hydrogen chloride and then unexpectedly eliminating methyl chloride from a second unstable bicyclic reaction intermediate.



R_1	R_2	R_3	R_4	Q-band, nm
H	H	H	H	704
H	Cl	H	H	698
Cl	H	H	H	709
Cl	Cl	H	H	714
Cl	H	H	Cl	736
H	Cl	Cl	H	712
Cl	Cl	Cl	Cl	745

Figure 4. Wavelength of the Q-band in UV-vis spectra of chlorinated vanadyl phthalocyanines.



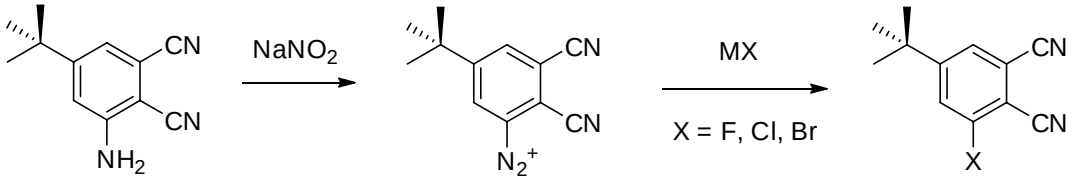
Scheme 27

The preparation, UV-vis spectra, and electronic structures of several transition-metal 1,8(11),15(18),22(25)-tetrabromophthalocyanines are available in the literature.[112] Their preparation can be achieved by the cyclotetramerization reaction between 3-bromophthalonitrile and an appropriate metal salt at 220–240 ^{o}C. All complexes have limited solubilities in common organic solvents, with DMF and DMSO providing the best choices. A similar synthetic strategy leads to preparation of transition-metal complexes of 2,9(10),16(17),23(24)-tetrabromophthalocyanines.[112,113] It is interesting to note that the conductivity of doped and undoped nickel and copper tetrahalogen substituted phthalocyanines is about 100 times higher than for the parent unsubstituted phthalocyanines.[114] Not surprisingly, these compounds were tested as potentially useful blocks for NO_2 gas sensors.[115] Also, the copper 2,9(10),16(17),23(24)-tetrabromophthalocyanine was tested as one of the first phthalocyanines to be used in the cumene autoxidation reaction.[116] So far, only one example of copper 1,4,8,11,15,18,22,25-octabromophthalocyanine is known,[117] while several reports on preparation, characterization, and fluorescence properties of copper and silicon 2,3,9,10,16,17,23,24-octabromophthalocyanines have been published.[118] Both complexes were prepared from the corresponding substituted phthalonitriles and cuprous chloride or silicon tetrachloride. Hexadecabromophthalocyanines have received less attention than the fluoro- and chloro-

analogs, probably because of their lower stability, as confirmed in radiation damage experiments.[119]

Several 1,8(11),15(18),22(25)-tetraiodophthalocyanines were prepared either by a direct cyclotetramerization reaction between 3-iodophthalonitrile and the appropriate metal salt, or by phthalocyanine core modification.[88,112,120]

In the latter case, copper 1,8(11),15(18),22(25)-tetranitrophthalocyanine was first reduced to the corresponding tetraamino derivative, which was diazotized and treated with sodium iodide to form copper 1,8(11),15(18),22(25)-tetraiodophthalocyanine.[121] Similarly, starting from 4-iodophthalonitrile, several transition-metal 2,9(10),13(14),23(24)-tetraiodophthalocyanines were prepared and characterized by a variety of spectroscopic methods.[88,112,122] As was mentioned earlier, zinc 2,9(10),13(14),23(24)-tetraiodophthalocyanine can be employed in Sonogashira reaction to form tetra-deoxyribose-phthalocyanine conjugate[88] or other alkynyl substituted derivatives useful for photodynamic therapy of cancer.[86] Copper 1,4,8,11,15,18,22,25- and 2,3,10,11,16,17,23,24-octaiodophthalocyanines were prepared by heating the corresponding iodine substituted anhydrides with, urea, cupric chloride, and a catalytic amount of $TiCl_4$ in trichlorobenzene for about 1 hour.[123] Similar to formation of hexadecachlorophthalocyanines, the reaction of 3,4,5,6-tetraiodophthalic anhydride with urea, cupric chloride, and a catalytic amount of $TiCl_4$ in trichlorobenzene leads to substantial loss of the iodine atoms from the phthalocyanine core.

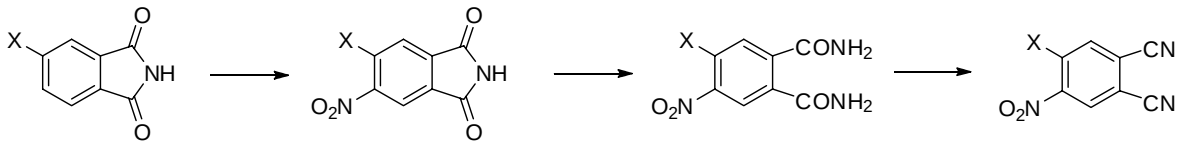


Scheme 28

As usual, the solubility of the halogenated phthalocyanines can be dramatically increased by introduction of *tert*-butyl substituents into peripheral positions. Indeed, metal-free and transition-metal 1,8(11),15(18),22(25)-tetrahalo-3,10(9),17(16),24(23)-tetra-*tert*-butylphthalocyanines are readily soluble in saturated hydrocarbons, aromatic compounds, and chlorinated solvents.[124,125] Preparation of these compounds can be achieved by using 3-halo-5-*tert*-butylphthalonitriles, which can be prepared by the diazotization reaction of 3-amino-5-*tert*-butylphthalonitrile followed by treatment of the respective diazonium salts with an appropriate halogen salt (Scheme 28). Alternatively, a similar diazotization reaction can be conducted on copper 1,8(11),15(18),22(25)-tetraamino-3,10(9),17(16),24(23)-tetra-*tert*-butylphthalocyanine.[121]

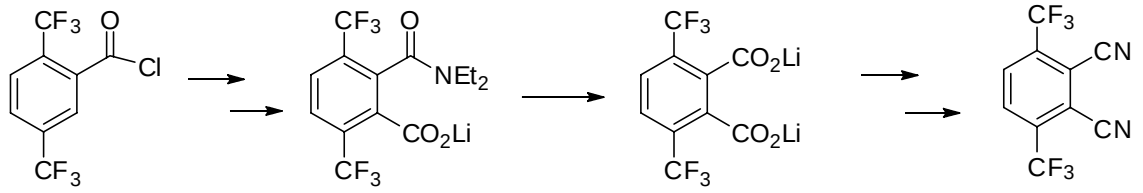
A set of the main-group and transition-metal 2,9(10),16(17),23(24)-tetrachloro(bromo)-3,10(9),17(16),24(23)-tetranitrophthalocyanines has been recently reported. The required 4-chloro(bromo)-5-nitrophthalonitriles were prepared from 4-chloro(bromo)phthalimides using stereoselective nitration, amidation, and nitrile formation reactions (Scheme 29).[126] The nitro

group in synthesized octasubstituted phthalocyanines with *ortho*-located halogen atoms is not coplanar with the macrocycle plane, and this reduces its effect on the absorption spectra.



Scheme 29

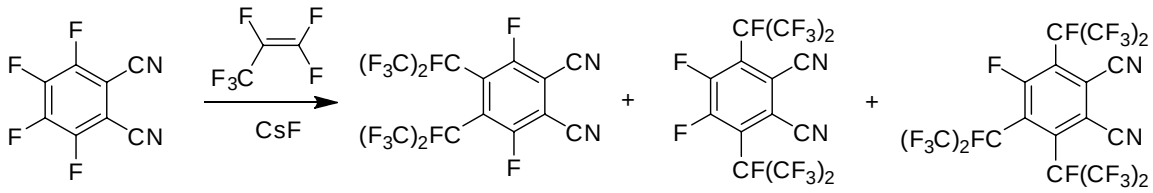
A separate class of halogenated phthalocyanines consists of chain-fluorinated substituted compounds, because fluorinated substituents tend to be among the most powerful electron-withdrawing groups that can be introduced into phthalocyanine core. The first tetra-, octa-, and dodeca-substituted with trifluoromethyl groups phthalocyanine compounds were reported at the end of the 1970s by Yagupol'skii et al.[101c,127] The presence of trifluoromethyl groups in these complexes results in an increase of their solubility in chloro- and nitrobenzene, as well as in DMF, while solubility in other common organic solvents remains quite low. Similar to the alkyl substituted phthalocyanines, introduction of two trifluoromethyl groups into the α-positions of phthalocyanine rings results in better solubility compared with the 2,3,9,10,16,17,23,24-octakis(trifluoromethyl) analogs. The six steps preparation of the 3,6-bis(trifluoromethyl) phthalonitrile is presented in Scheme 30 and, in general, it follows the 'acidic' synthetic route.[127a,128]



Scheme 30

Another possibility to introduce perfluoroalkyl substituents into phthalonitriles and thus into phthalocyanines is based on the reaction between 3,4,5,6-tetrafluorophthalonitrile and perfluoropropene in the presence of cesium fluoride in acetonitrile at -78 ^{o}C (Scheme 31).[129] This reaction leads to formation of 3,6-bis(perfluoroisopropyl)-4,5-difluoro-, 4,5-bis(perfluoroisopropyl)-3,6-difluoro-, and 3,4,6-tris(perfluoroisopropyl)-5-fluoro-phthalonitrile with 4,5-bis(perfluoroisopropyl)-3,6-difluorophthalonitrile being the major product. The prepared from it zinc, iron, and cobalt 2,3,9,10,16,17,23,24-octakis(pefluoroisopropyl)-1,4,8,11,15,18,22,25-octafluorophthalocyanines are rare examples of fluorophthalocyanines lacking C-H bonds what results in higher stabilities towards self-oxidation.[130] Not surprisingly,

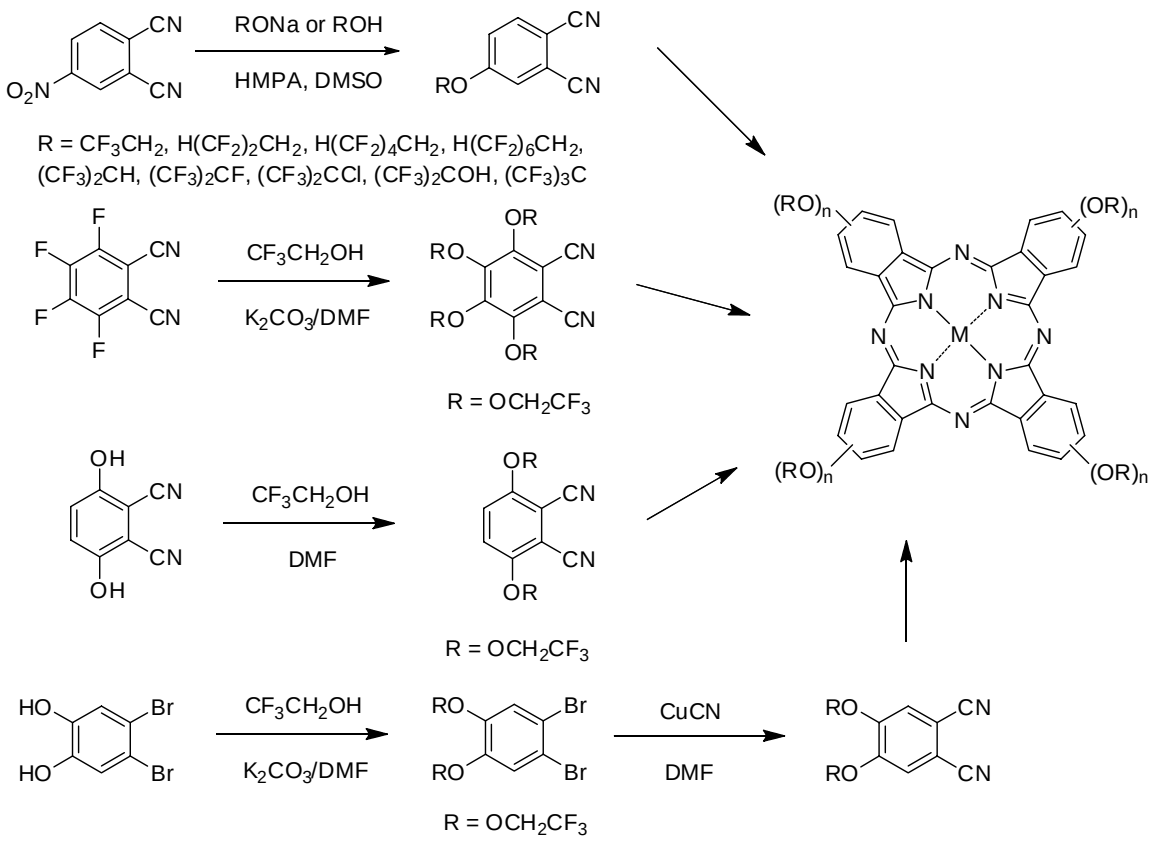
the cobalt complex was tested as a prospective catalyst for oxidative C=P bond formation reactions.[131]



Scheme 31

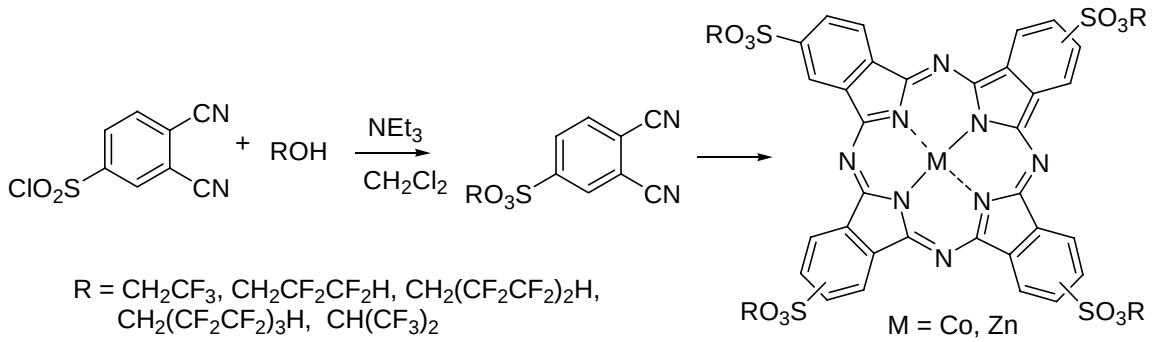
Trifluorosulfanyl and trifluorosulfonyl substituted phthalocyanines can be prepared using the corresponding 4-trifluoromethylsulfanyl-, 4-trifluoromethylsulfonyl-, and 4,5-di(trifluoromethylsulfanyl)phthalonitriles.[132] Trifluoromethylsulfanyl substituted phthalonitriles were prepared starting from the reaction between diethyl 4-iodo- or 4,5-diiodo-phthalate and copper trifluoromethylthiolates followed by an amidation reaction with liquid ammonia and then a dehydration reaction using phosphorus oxychloride. Oxidation of the trifluoromethylsulfanyl group in the abovementioned compounds leads to formation of the diethyl 4-trifluoromethylsulfonyl- and 4,5-di(trifluoromethylsulfonyl)-phthalates, of which only the former can be amidated with liquid ammonia and eventually converted into substituted phthalocyanine.[132] Again, the solubility of trifluoromethylsulfanyl- and trifluoromethylsulfonyl substituted phthalocyanine in common organic solvents remains low. Interestingly, the introduction of any fluorinated substituents into the phthalocyanine core has no significant effect on the position of the Q-band in the UV-vis spectra of these complexes, compared with the unsubstituted phthalocyanine analogs, although a small bathochromic effect was observed.

The solubility of fluoroalkyl complexes can be significantly increased by replacement of the trifluoromethyl substituents with fluoroalkoxy groups (Scheme 32).[133] The preparation of target nitriles can be achieved by nucleophilic aromatic substitution of the nitro group in 4-nitrophthalonitrile, substitution of fluorine atoms in 3,4,5,6-tetrafluorophthalonitrile, and alkylation of aromatic OH bonds. Since the nucleophilicity of fluorinated alcohols is very small, it is necessary to transform these into the corresponding alkoxides using an appropriate base prior to substitution conducted at elevated temperatures in aprotic polar solvents. Phthalocyanines prepared from these nitriles are soluble in a variety of organic solvents and have optical properties similar to those observed in tetra-*tert*-butylphthalocyanines. The electron-withdrawing nature of fluoroalkoxy groups can be clearly seen from the first oxidation potential of the appropriate phthalocyanines. For instance, the oxidation potential of zinc phthalocyanine substituted with four OCH_2CF_3 groups is ~200 mV higher than that observed in zinc 2,9(10),16(17),23(24)-tetra-*tert*-butylphthalocyanine.[134]



Scheme 32

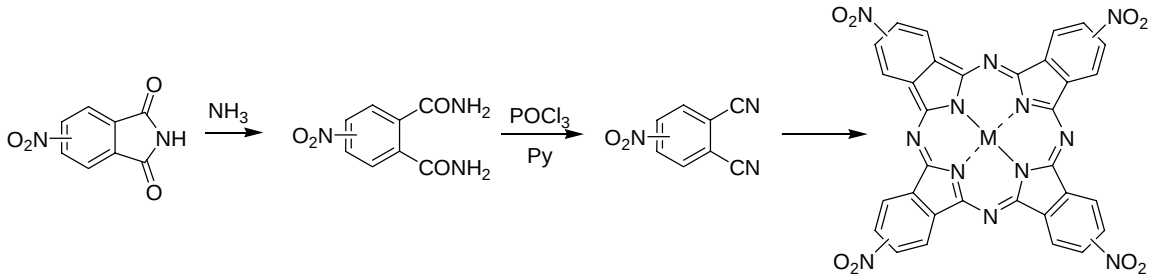
Esterification of 4-chlorosulfonylphthalonitrile with fluoroalkyl-containing alcohols leads to formation of polyfluoroalkoxysulfonylphthalonitriles, which can be converted into the appropriate 2,9(10),16(17),23(24)-tetrakis(fluoroalkoxysulfonyl)phthalocyanines (Scheme 33).[135] These complexes are also highly soluble in a variety of organic solvents, which makes them potential candidates for applications in homogeneous catalytic reactions. The polyfluoroalkoxysulfonyl groups in these complexes were shown to stabilize both the HOMO and LUMO of the complexes in comparison with the alkoxy- or polyfluoroalkoxy-substituted analogs. Although never observed (because of solvent electrochemical window limitations) the first oxidation potential for zinc 2,9(10),16(17),23(24)-tetra(fluoroalkyl)sulfonylphthalocyanines is estimated to be between 1.47 and 1.65 V.



Scheme 33

3.2 Nitro substituted phthalocyanines

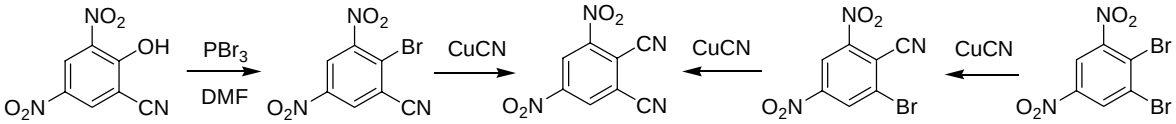
Introduction of the nitro group into the α- or β-positions of the phthalocyanine core (Figure 1) is a well-known method for preparation of transition-metal phthalocyanines with four electron-withdrawing groups.[5,116,136] The preparation of both 1,8(11),15(18),22(25)- and 2,9(10),16(17),23(24)-tetranitrophthalocyanine can be easily achieved using 3- and 4-nitrophthalonitrile, respectively (Scheme 34)[112a,137] a method proposed in the late 1960s used the more exotic treatment of 1,2-bis(dichloromethyl)-4-nitrobenzene with gaseous ammonia in the presence of transition-metal salts.[138]



Scheme 34

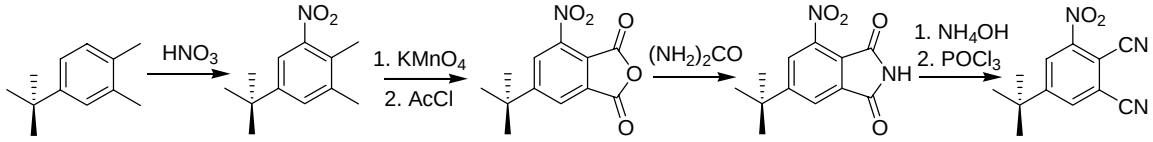
In 1991 a new methodology for synthesis of transition-metal 1,3,8(11),10(9),15(18),17(16),22(25),24(23)-octanitrophthalocyanines was developed.[139] The key precursor for preparation of these compounds is 3,5-dinitrophthalonitrile, which can be prepared by two different ways using nucleophilic aromatic substitution reactions on either 1,2-dibromo-3,5-dinitrobenzene or 2-hydroxy-3,5-dinitrobenzonitrile (Scheme 35). Although both methods look similar to each other, it is interesting to note that the 3,5-dinitrophthalonitrile can be obtained in high yield only by using 2-hydroxy-3,5-dinitrobenzonitrile, because in the case of 1,2-dibromo-3,5-dinitrobenzene the copper 1,3,8(11),10(9),15(18),17(16),22(25),24(23)-octanitrophthalocyanine is the major reaction product. The presence of eight strongly electron-withdrawing groups at both the α- and β-positions of the phthalocyanine ring results in very

unusual redox properties of these compounds. Specifically, no phthalocyanine-based oxidation was found within the solvent range, while reduction potentials of these complexes are ~1 V more positive compared with those observed in alkyl substituted complexes.[140] In general, transition-metal octanitrophthalocyanines are so easily to reduce that special care should be taken for solvent purification in order to eliminate any traces of minor reducing agents. For instance, the traces of dimethylamine in regular grade DMF can easily reduce cobalt(II) octanitrophthalocyanine to the corresponding cobalt(I) compound, which was confirmed by UV-vis spectra compared with those obtained using the spectroelectrochemical approach.[139,140] Electrochemical and chemical reduction data indeed suggest that the eight nitro groups present in octanitrophthalocyanines have more electron-withdrawing power compared with 2,3,9,10,16,17,23,24-octacyanophthalocyanines.[141] The reluctance to undergo oxidation makes transition-metal complexes of 1,3,8(11),10(9),15(18),17(16),22(25),24(23)-octanitrophthalocyanine potentially useful candidates for a variety of oxidative catalytic reactions, for instance C-H bond activation in organic compounds.[142]



Scheme 35

The low solubility of 1,8(11),15(18),22(25)-tetranitrophthalocyanines, 2,9(10),16(17),23(24)-tetranitrophthalocyanines and 1,3,8(11),10(9),15(18),17(16), 22(25),24(23)-octanitrophthalocyanines, which are soluble only in dipolar aprotic solvents and acids, has stimulated exploratory work on the preparation of nitrophthalocyanines soluble in organic solvents. As a result, a synthetic pathway for the preparation of 1,8(11),15(18),22(25)-tetranitro-3,10(9),17(16),24(23)-tetra-*tert*-butylphthalocyanines has been developed (Scheme 36).[143] Nitration of readily available 4-*tert*-butyl-*ortho*-xylene results in formation of 5-*tert*-butyl-1,2-dimethyl-3-nitrobenzene, the methyl groups of which can be oxidized to carboxylic ones by potassium permanganate. Treatment of 5-*tert*-butyl-3-nitro-*ortho*-phthalic acid sequentially with acetyl chloride, urea, concentrated ammonia solution, and finally phosphorus oxychloride leads to the target 5-*tert*-butyl-3-nitro-phthalonitrile. This nitrile can also be obtained using 3-nitro-4,5-dibromo-*tert*-butylbenzene by the Rosenmund-von Braun reaction. Macrocyclization of 5-*tert*-butyl-3-nitro-phthalonitrile results in formation of 1,8(11),15(18),22(25)-tetranitro-3,10(9),17(16),24(23)-tetra-*tert*-butylphthalocyanines which are highly soluble in common organic solvents.



Scheme 36

3.3 Phthalocyanine sulfoacids and their derivatives

Phthalocyanine sulfoacids and their derivatives - alkali metal salts, sulfoacid esters, sulfamides, and sulfones - are an important class of substituted phthalocyanine compounds, mostly used as textile and printing dyes and more recently, in photodynamic therapy of cancer and catalysis. A general transformation pattern for preparation of phthalocyanine sulfoacids and their derivatives is presented in Scheme 37. It was found that direct sulfonation of a variety of metal-free or metal-containing phthalocyanines using chlorosulfonic acid in trichlorobenzene leads to formation of the corresponding polysulfonated (n = 2–4) phthalocyanine compounds. In the case where the central metal is labile under acidic conditions, it can be easily introduced into the phthalocyanine cavity by treating the metal-free polysulfonated phthalocyanine, or its alkali metal salt, with an appropriate metalating agent.[144]

Water-soluble phthalocyanines with peripheral solubilizing groups are very important for photodynamic therapy of cancer (PDT).[7,145] The sodium salt of hydroxyaluminum average trisulfophthalocyanine ("photosens") is approved and has been in use for 14 years for PDT in Russia for the treatment of cancer of various indications, and the sodium salt of metal-free trisulfophthalocyanine ("phthalosens")[146] is undergoing preclinical studies.

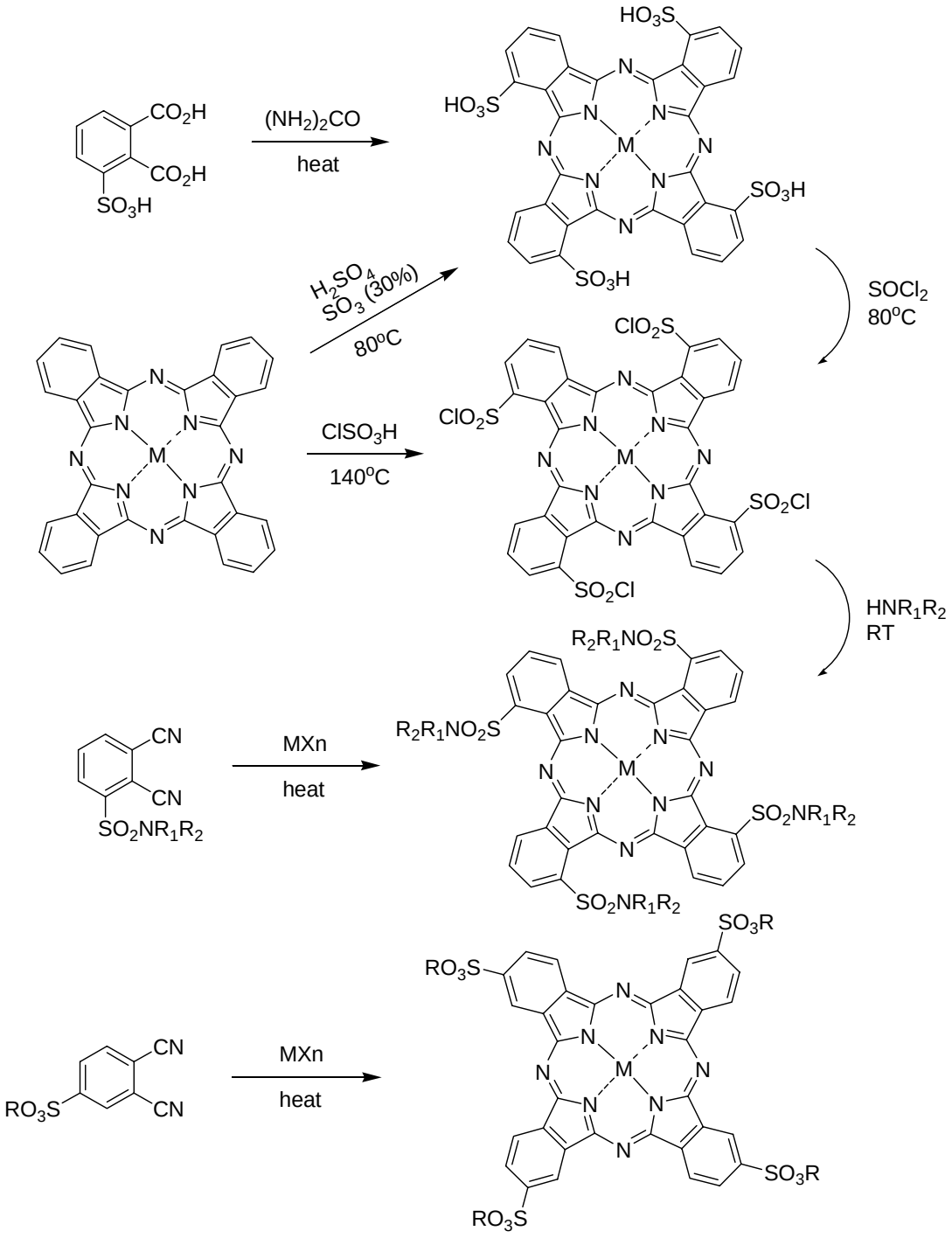
The use of bio-conjugates of water-soluble phthalocyanines, e.g. biotin-linked assemblies, can significantly improve the targeted delivery of the photosensitizer into cancer cells. Some conjugates of phthalocyanines with oligonucleotides can also be used as reagents for photosensitized or catalytic DNA modifications.

The tetra- and octasulfonamide-containing phthalocyanines with $SO_2NR_1R_2$ residues that are highly soluble in organic solvents without significantly affecting the absorption spectra.[147] They can be prepared from dicyanobenzenesulfonamides or from the corresponding dibromides and CuCN[148] as well as by the reaction between phthalocyanine sulfochlorides and appropriate amines at room temperature. The anchoring of corresponding sulfochlorides to amino group containing silica gels and carbons is, probably, the most useful synthetic pathway for heterogenization of transition-metal phthalocyanines.[149] These heterogeneous catalysts can be used in a variety of catalytic transformations of organic substrates, for instance in oxidation of organic thiols to the corresponding disulfides ('Merox' process).[150]

The application of phthalocyanines in organic photovoltaic cells and pH sensors requires the presence of specifically designed peripheral substituents.[151] Some recent examples are the rhodamine-phthalocyanine conjugates, which have different optical and electron-transfer properties at different values of pH (Figure 5).[152] An appropriate Rhodamine B and 6G substituents can be linked to the phthalocyanine core via electron-withdrawing imide- or sulfonyl groups with formation of the corresponding N-alkylimide or sulfamoyl bonds.

In neutral and alkaline media these compounds have typical phthalocyanine electronic absorption spectra dominated by Q- and B-bands, while the influence of the closed form of rhodamine is negligible. In acidic conditions, however, the lactam ring of the rhodamine substituent transforms into an open ionic form, resulting in new, characteristic for rhodamine band at 530 nm in addition to phthalocyanine-based transitions. The conjugates with rhodamine

B 2-aminoethyl ester perchlorate preserve their spectral characteristics independent of acidity (Figure 5). On the other hand, the emission spectrum of the aluminum complex of the rhodamine 6G phthalocyanine conjugate suggests effective energy transfer from the rhodamine substituents to the phthalocyanine core.



Scheme 37

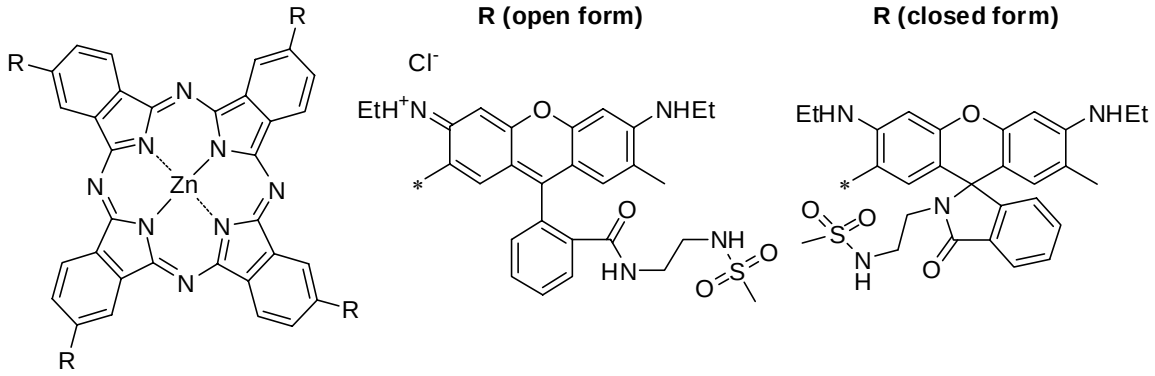
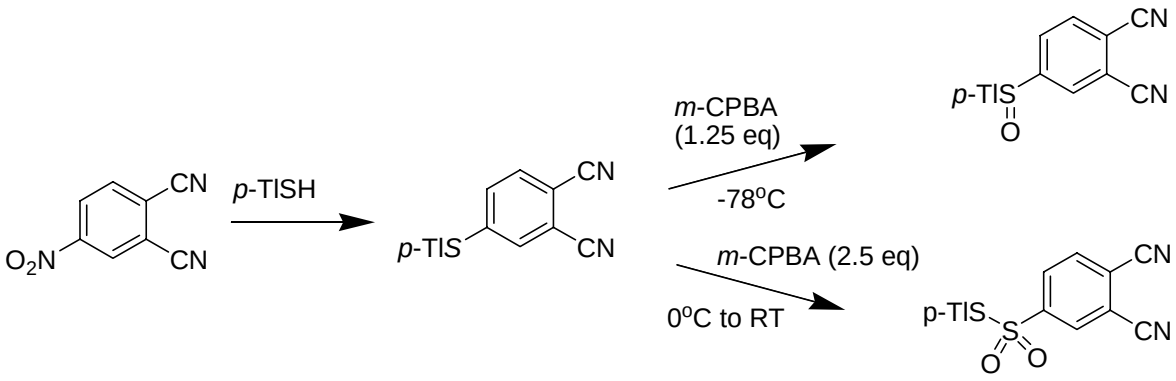


Figure 5. The open and closed forms of the conjugate of tetra-4-sulfo substituted zinc phthalocyanine with the spirolactam of N-(2-aminoethyl)rhodamine 6G.

3.4 Alkyl- and arylsulfonyl and sulfinyl substituted phthalocyanines

Alkyl- and arylsulfonyl and sulfinyl substituted phthalocyanines can be prepared using standard approaches, *i.e*. macrocyclization reaction of corresponding nitriles,[153] aminoiminoisoindolenines,[154] and oxidation of thioalkyl substituents on the phthalocyanine core.[155] The alkyl- and arylsulfonyl and sulfinyl substituted phthalonitriles can be prepared by oxidation of the corresponding alkyl- or arylthiophthalonitriles obtained by nucleophilic aromatic substitution reactions between nitro- or chloro-phthalonitriles and an appropriate thiol under basic conditions (Scheme 38). Higher reaction temperatures favor formation of the sulfonyl substituents, while low reaction temperatures result in isolation of the sulfinyl-containing phthalonitriles. Hydrogen peroxide and *m*-perchlorobenzoic acid were used so far as the oxidants for this reaction.[94b,156]



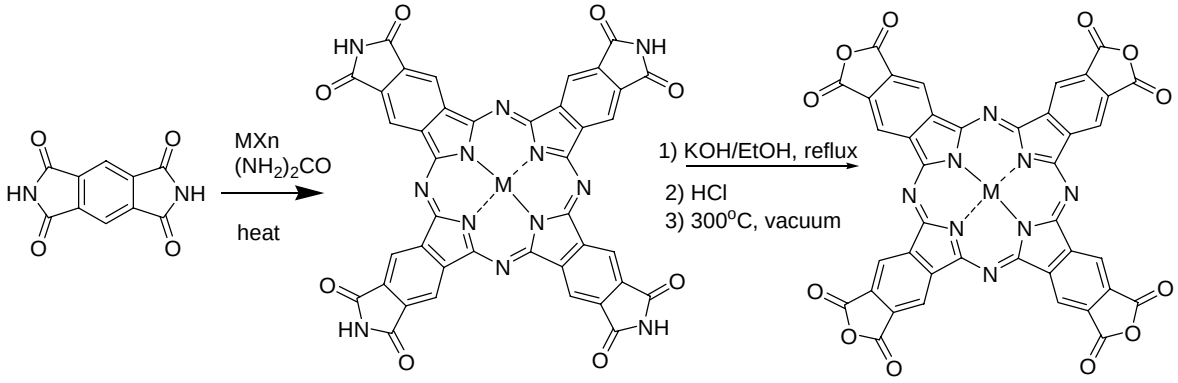
Scheme 38

Metal-containing tetra- and octasulfonyl- or sulfinylphthalocyaines can be prepared in reasonable yields by the direct cyclotetramerization reaction using the corresponding nitriles or aminoiminoisoindolenines. The preparation of the metal-free sulfonyl-containing

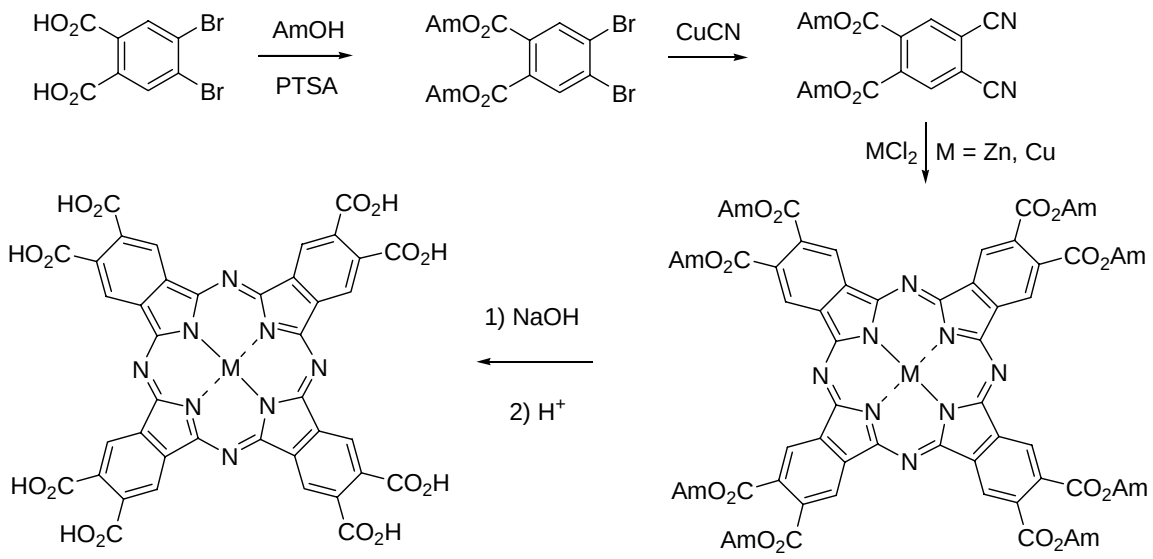
phthalocyanines requires some caution because of possible aromatic nucleophilic substitution of the sulfonyl group by alkoxide ion.[155] This problem can be overcome by oxidation of 2,3,9,10,16,17,23,24-octakis(alkylsulfanyl)phthalocyanines to corresponding octakis-(alkylsulfonyl)phthalocyanines in 53–79% yield using *m*-chloroperoxybenzoic acid in CH_2Cl_2.

3.5 Phthalocyanines with carboxylic groups and their derivatives

Phthalocyanines substituted with carboxylic groups and their derivatives represent another large group of macrocycles with electron-withdrawing substituents. To date, 2,9(10),16(17),23(24)-tetra-, 2,3,9,10,16,17,23,24-octa-, 1,3,8,10(9,11),15,17(16,18),22, 24(23,25)-octa- and 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecasubstituted patterns are known in this series. The parent phthalocyanine carboxylic acids (for instance 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine) can be prepared by the high-temperature reaction between the corresponding anhydrides or imides, urea, and transition-metal salt (Scheme 39).[157] The resulting imides can be hydrolyzed using concentrated alkali hydroxides in ethanol with formation of water soluble salts of phthalocyanine carboxylic acids. Acidification of these salts leads to formation of the usually water insoluble phthalocyanine carboxylic acids. Finally, heating of the phthalocyanine carboxylic acids in vacuum leads to formation of the corresponding phthalocyanine anhydrides (Scheme 39). Alternatively, 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine can be prepared by hydrolysis of the 2,3,9,10,16,17,23,24-octacyanoxyphthalocyanine, which can be prepared from 1,2,4,5-tetracyanobenzene.[158]



Scheme 39



Scheme 40

It should be noted, however, that, as expected, the cyclotetramerization reaction of the pyromellitic anhydride or imide (Scheme 39) also unavoidably leads to formation of polymeric by-products. In order to avoid these polymeric by-products, Opris et al. developed a synthetic pathway, as shown in Scheme 40.[159] Oxidation of the methyl groups in 1,2-dibromo-4,5-dimethylbenzene results in formation of 4,5-dibromophthalic acid, which undergoes esterification and the Rosenmund-von Braun reaction to form dipentyl 4,5-dicyanophthalate. The latter can be cyclotetramerized to give the corresponding phthalocyanine octaesters, which finally can be hydrolysed to give the target 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines.

Water-soluble alkali salts of phthalocyanine carboxylic acids can be used in catalysis as well as medicine. For example, the water-soluble sodium salt of cobalt 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine, known as "theraphthal",[160] is currently under clinical trials for so-called catalytic therapy of cancer. In this approach, molecular oxygen can be involved in specifically triggered catalytic reactions of transition-metal phthalocyanines with reductants, e.g. ascorbic acid, giving reactive oxygen species.[161] The pentanuclear tetraplatinate complex (Figure 6) can be easily prepared by the reaction between octasodium cobalt(II) phthalocyanine-2,3,9,10,16,17,23,24-octacarboxylic acid and K_2PtCl_4. In this case, the catalytic activity of cobalt 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine can be enhanced by the well-known cytotoxic properties of platinum(II) fragments.[162]

Esters of phthalocyanine carboxylic acids can be prepared either from the appropriate esters of carboxyphthalonitriles[163] or by phthalocyanine core modification[164] (Scheme 41). In the latter case, phthalocyanine carboxylic acids can react directly with appropriate alkyl halides in the presence of DBU as a base. Alternatively, phthalocyanine carboxylic acids can first be converted the corresponding carboxylic acid chloroanhydrides and then refluxed in the appropriate alcohols.[165]

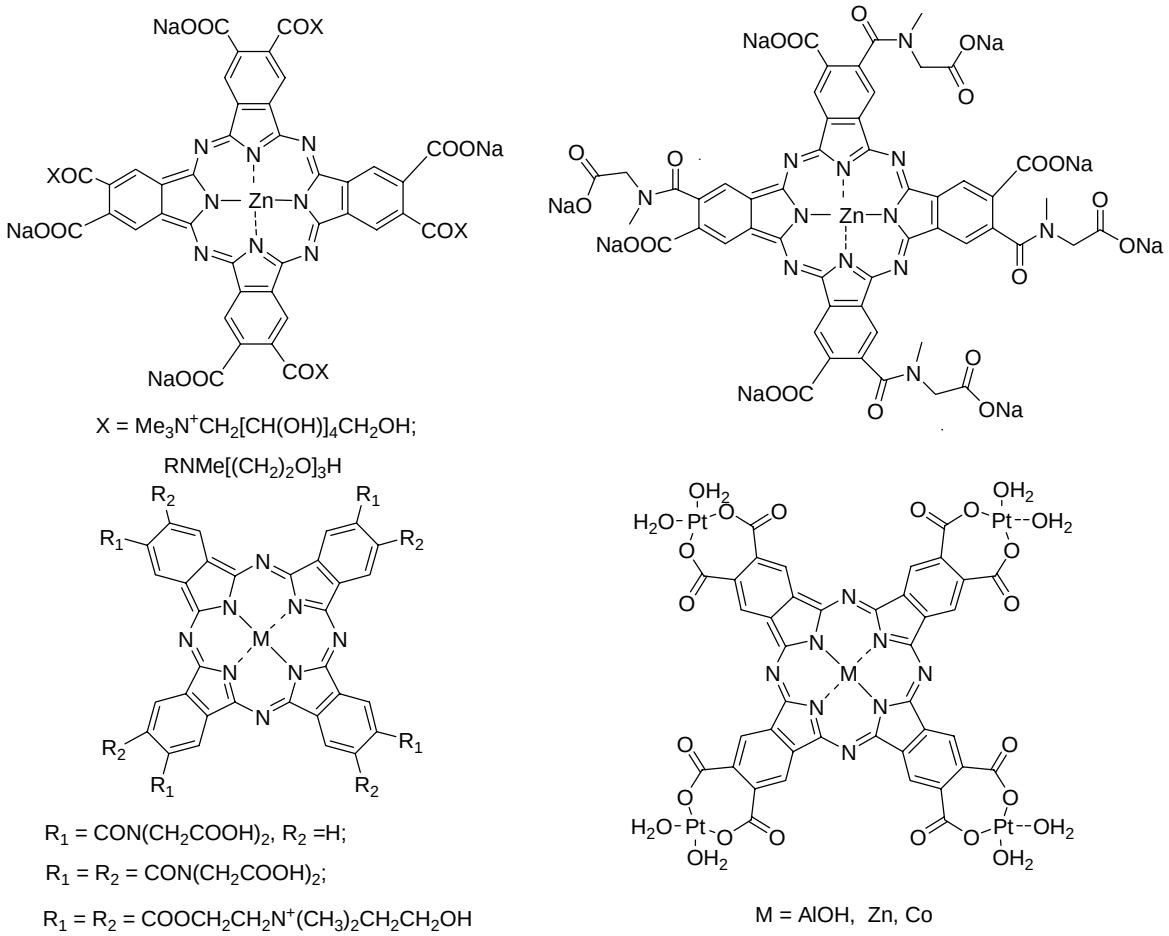
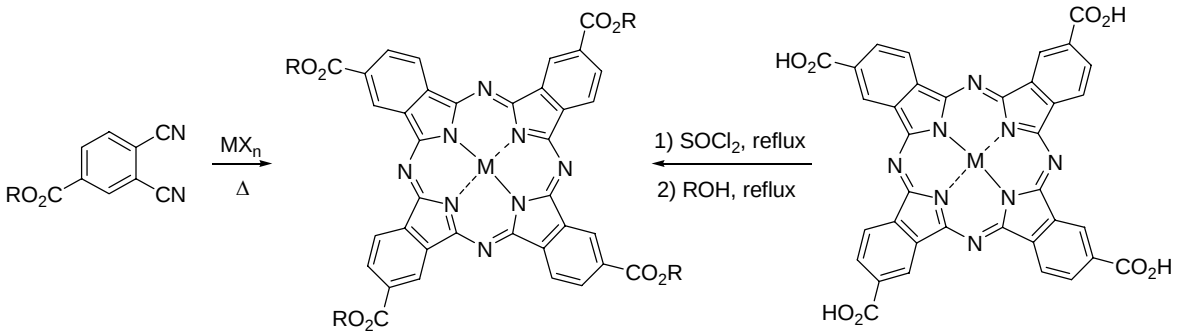


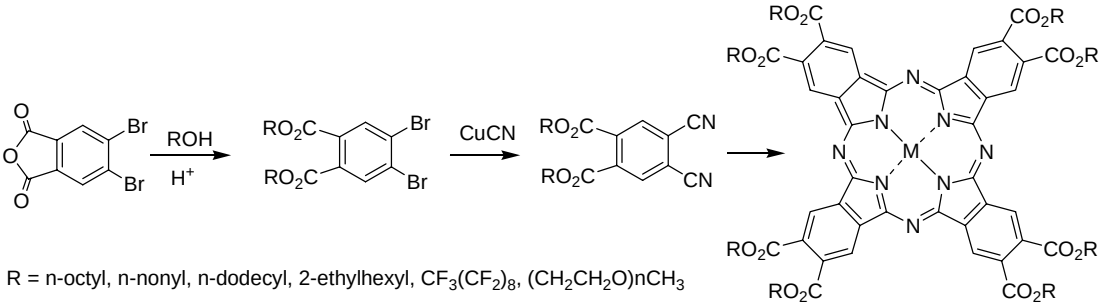
Figure 6. Water-soluble carboxyphthalocyanine derivatives useful for potential application in PDT and catalytic therapy of cancer.



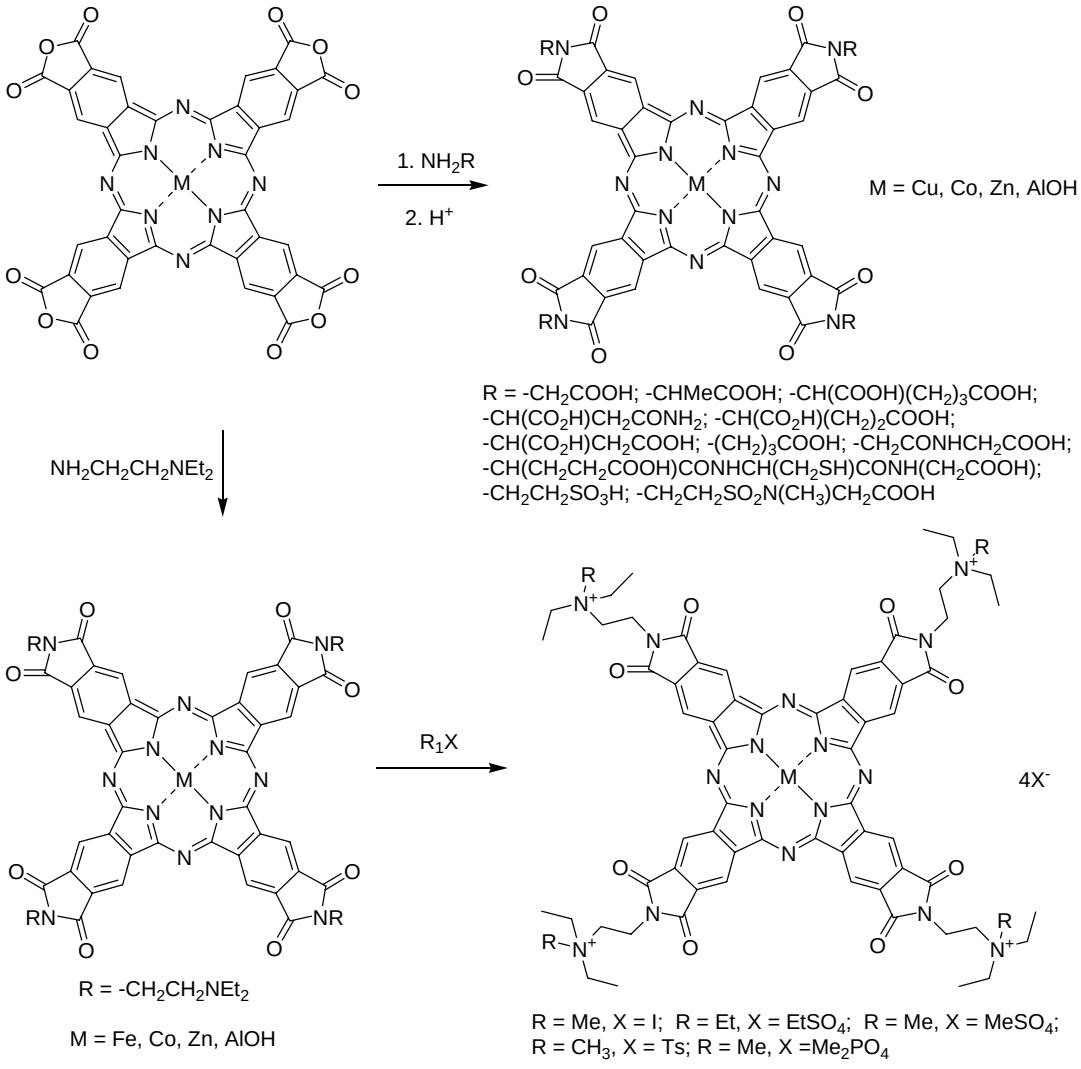
Scheme 41

Esters of carboxyphthalonitriles can be prepared in several different ways. For instance, a very convenient method for selective preparation of the esters of phthalonitrile starts from the esterification of 4,5-dibromophthalic anhydride, which then can be used in the Rosenmund-von

Braun reaction with formation of the 4,5-bis(alkoxycarbonyl)phthalonitriles. These nitriles can then be easily converted into the appropriate transition-metal phthalocyanines, some of which show typical phthalocyanine discotic liquid crystal properties (Scheme 42).[166]



Scheme 42



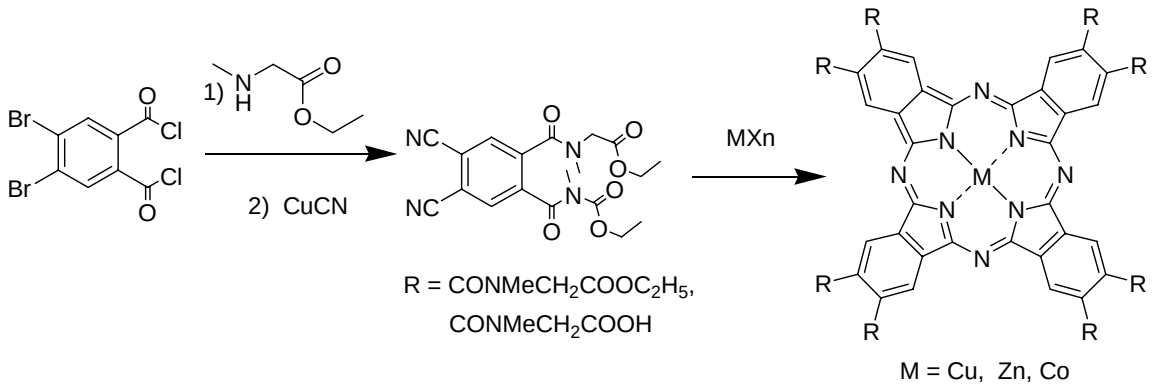
Scheme 43

N-Unsubstituted phthalocyanine tetra- and octacarboximides can be prepared by the direct cyclotetramerization reaction between the appropriate anhydrides and transition-metal salts (Scheme 39),[163,167] or by partial hydrolysis of peripheral cyano substituents.[157d,168] N-Substituted imides of 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines can be prepared using two major strategies (Scheme 43). The first utilizes transformation of the octa-4,5-carboxyphthalocyanine anhydrides by reaction with an appropriate primary amino group.[152,169] This methodology was used for preparation of a large number of water-soluble anionic and cationic conjugates of phthalocyanines with α-, β-, and γ-aminoacids, di- and tripeptides, taurine, and β-diethylmethylammoniummethyl substituents.[170] In the case of anionic conjugates with α-, β-, and γ-aminoacids, di- and tripeptides, as well as taurine, the reaction was conducted in N-methylpyrrolidone and directly resulted in the target compounds, while in the case of cationic β-diethylmethylammoniummethyl substituents the quaternary ammonium salts can be obtained by an additional alkylation step using the appropriate alkylating agent. The electronic absorption spectra of the quaternary salts demonstrate significant aggregation in aqueous solution, and this can be controlled by addition of polar aprotic solvents such as DMSO.

An alkylation reaction of the N-unsubstituted phthalocyanine imides was used as an alternative way for preparation of the N-substituted phthalocyanine imides. Deprotonation of the imide N-H bond was achieved using NaH followed by alkylation of the resulting anion with an alkyl bromide.[171]

The parent 2,3,9,10,16,17,23,24-octacarboxamide phthalocyanine can be prepared from N-unsubstituted phthalocyanine tetraimide using aqueous ammonia for 7 days.[157d] In the majority of cases, however, phthalocyanine 2,9(10),16(17),23(24)-tetra- and 2,3,9,10,16,17,23,24-octa amides can be prepared by the direct cyclotetramerization reaction between carboxamide-substituted phthalonitriles and transition-metal salt[163,170a,172] or by using an excess of an appropriate amine during its reaction with octa-4,5-carboxyphthalocyanine chlorides.[173] The derivatives of phthalonitrile-4,5-dicarboxamides can be prepared starting from 4,5-dibromophthaloyl chloride using the standard Rosenmund-von Braun reaction (Scheme 44).[163,170a]

The terminal ester groups in the target phthalocyanines can be selectively hydrolyzed with formation of water-soluble terminal carboxylic acids. The presence of eight substituents in phthalocyanines improves their solubility compared with that observed for anionic imide analogs.



Scheme 44

The water-soluble amides of phthalocyanine octacarboxylic acid are complementary to the highly organic soluble N-mono- and N-disubstituted amide derivatives of phthalocyanine tetra- and octacarboxylic acids reported earlier (Figure 7).[163,174]

Currently, the only reliable way to introduce cyano groups into the phthalocyanine core is to use 1,2,4-tricyano-[112a,175] or 1,2,4,5-tetracyanobenzene precursors[176] although preparation of the iron(III) 2,9(10),16(17),23(24)-tetracyanophthalocyanine from the the iron(III) 2,9(10),16(17),23(24)-tetraaminophthalocyanine has been reported.[177] The direct cyclotetramerization reaction between 1,2,4-tricyanobenzene or 3,6-dialkyl-1,2,4-tricyanobenzene[178] and transition-metal salt leads to formation of the target phthalocyanines in good yields. Similarly, the cyclotetramerization reaction of commercially available 1,2,4,5-tetracyanobenzene and transition-metal salts results in formation of the transition-metal 2,3,9,10,16,17,23,24-octacyanophthalocyanines. Unavoidable side-products in this reaction are oligomeric and polymeric substituted phthalocyanines. In addition, it can be expected that the standard reaction conditions for formation of metal-free 2,3,9,10,16,17,23,24-octacyanophthalocyanine (refluxing of the 1,2,4,5-tetracyanobenzene with lithium alkoxide in alcohol) can result in partial hydrolysis of the terminal cyano groups. Based on MALDI-TOF mass spectrometry data it was found, however, that in the case of the room-temperature heterogeneous reaction between 1,2,4,5-tetracyanobenzene and sodium methoxide in THF, hydrolysis of the terminal cyano groups is negligible.[179]

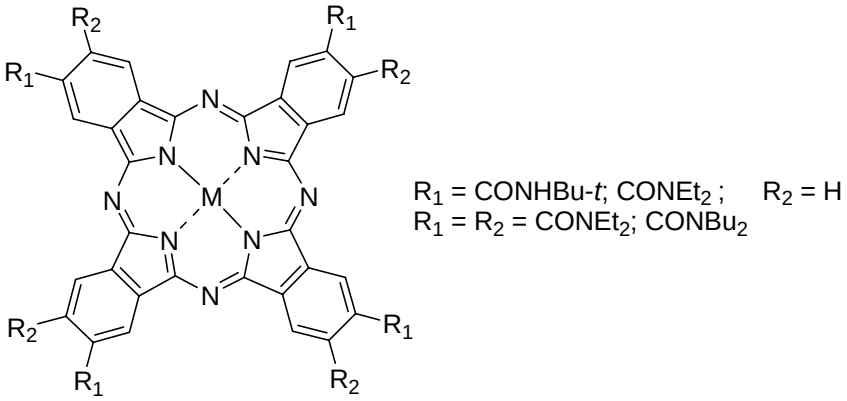
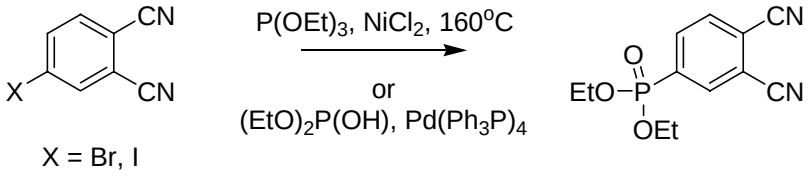


Figure 7. Highly soluble in organic solvents tetra- and octasubstituted phthalocyanine amides.

3.6 Phthalocyanines functionalized with phosphoric acid derivatives

Phthalocyanines functionalized with phosphoric acid residues are a relatively new class of compounds for which only a limited number of 2,9(10),16(17),23(24)-tetrasubstituted derivatives with direct C(Pc)-P bonds are known. Preparation of the starting protected phosphoric acid-containing phthalonitriles can be achieved by coupling reactions of 4-halophthalonitrile (Scheme 45).[180]



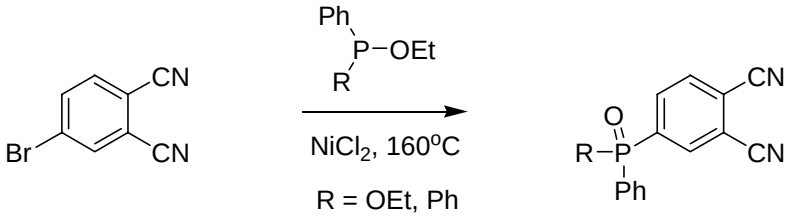
Scheme 45

Template cyclotetramerization reactions of the diethyl (3,4-dicyanophenyl)phosphonate with transition-metal salts results in formation of the expected copper or zinc 2,9(10),16(17),23(24)-tetrakis(diethylphosphonate)phthalo-cyanines. Similarly, cyclotetramerization reactions of diethyl (3,4-dicyanophenyl)-phosphornate with organic base (DBU) in ethanol results in formation of metal-free 2,9(10),16(17),23(24)-tetrakis(diethylphosphonate)phthalocyanine.[181] All of these phthalocyanines can be hydrolyzed in high yields to give the corresponding phosphoric acid derivatives.

Some metal complexes have also been prepared starting from the corresponding substituted phthalic anhydrides as well as by direct phosphorylation of the corresponding unsubstituted phthalocyanines. The latter reaction was conducted by heating with dialkylphosphite and *tert*-butyl peroxide for several hours.[182,183]

Coupling of the mono- and di-phenylethoxyphosphine with 4-bromophthalonitrile leads to formation of ethyl-(3,4-dicyanophenyl)phenylphosphinate and 4-(diphenylphosphinyl) benzol-

1,2-dicarbonitrile, respectively (Scheme 46); these can be converted into the corresponding metal-free or metal phthalocyanines in ~35% yield under standard cyclotetramerization conditions.[181]



Scheme 46

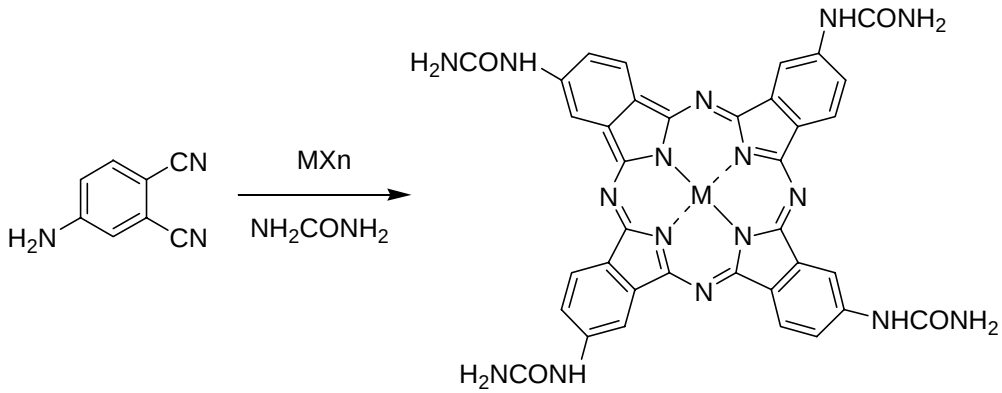
Zinc and copper complexes can be hydrolyzed to the corresponding 2,9(10),16(17)23(24)-tetrakis(phenylphosphinato)phthalocyanines using a sodium hydroxide/methanol mixture.

4. Phthalocyanines with electron-donating groups

4.1 Aminosubstituted phthalocyanines and their derivatives

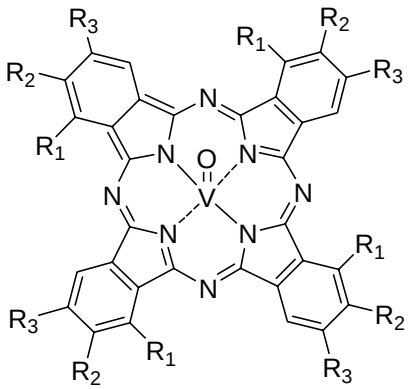
Although the solubility of the parent 1,8(11),15(18),22(25)- and 2,9(10),16(17),23(24)-tetraaminophthalocyanines is limited to polar aprotic and halogenated aromatic solvents, these macrocycles have attracted attention because they are potentially useful for preparation of chemically modified electrodes for electrocatalytic reactions, as well as good candidates for immobilization on chemically modified surfaces.[184] For instance, a self-assembled monomolecular film of the nickel 1,8(11),15(18),22(25)- tetraaminophthalocyanine adsorbed on gold electrodes can be used for selective electrochemical detection of epinephrine.[185] Based on the surface coverage and intensity of the in-plane stretching bands from Raman studies, it has been suggested that the cobalt(II) 1,8(11),15(18),22(25)-tetraaminophthalocyanine adopts a nearly parallel orientation on the gold surface, while its 2,9(10),16(17),23(24)-isomer adopts the perpendicular orientation.[186] Besides adsorption, electropolymerization of transition-metal tetraaminophthalocyanines can be used for preparation of modified glassy carbon electrodes.[187] The resulting electrodes can be used in the electrocatalytic oxidation *e.g.* of nitrite to nitrate. Typically, tetraaminophthalocyanines can be prepared by hydrolysis of the appropriately protected amino groups (*e.g.* acetamido) or by reduction of nitro group in tetrasubstituted phthalocyanines.[188] An attempt was reported also of a direct tetramerization of 3- and 4-aminophthalonitrile, or the corresponding phthalimides, into the corresponding transition-metal phthalocyanines (Scheme 47).[189] It was found that 3-aminophthalonitrile can indeed form the expected transition-metal 1,8(11),15(18),22(25)- tetraaminophthalocyanines upon heating with an appropriate metal salt, with or without urea. The reaction of 4-aminophthalonitrile with transition-metal salts produces uncharacterized black polymers, while similar reaction in the

presence of urea results in formation of 2,9(10),16(17),23(24)-tetraureidophthalocyanines. Such difference in reactivity can be explained on the basis of steric restrictions in 3-aminophthalonitrile, which therefore cannot easily participate in the intermolecular nucleophilic attack of nitrile group.



Scheme 47

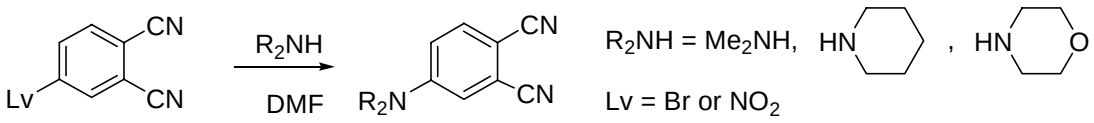
Similar to tetraaminophthalocyanines, preparation of the transition-metal complexes of 1,3,8,10(11,9),15,17(18,16),22,24(25,23)-octaaminophthalocyanines by the reduction of the corresponding 1,3,8,10(11,9),15,17(18,16),22,24(25,23)-octanitrophthalocyanines has been reported.[190] Another strategy was used by Ahsen et al. for preparation of nickel 2,3,9,10,16,17,23,24-octaaminophthalocyanine.[191] In this approach, the target compound was prepared by hydrolysis of the octatosylamido derivative using concentrated sulfuric acid at 100 ^{o}C. The metal-free, nickel, and zinc 2,3,9,10,16,17,23,24-octakis(tosylamido)phthalocyanines can be formed from 4,5-dicyano-N,N'-ditosyl-*o*-phenylenediamine.[191]



	Q, nm
R_1 = NMe_2, R_2 = R_3 = H	828
R_1 = NMe_2, R_2 = H R_3 = *t*-Bu	821
R_1 = R_3 = H, R_2 = NMe_2	775
R_1 = H, R_2 = R_3 = NMe_2	760
R_1 = NH_2, R_2 = H R_3 = *t*-Bu	806
R_1 = R_3 = H, R_2 = $NHCOCH_3$	704
R_1 = R_3 = H, R_2 = $NHCONH_2$	730
R_1 = R_3 = H, R_2 = NH_2	762

Figure 8. Structures and Q-band positions of selected amino and dialkylamino vanadyl phthalocyanines.

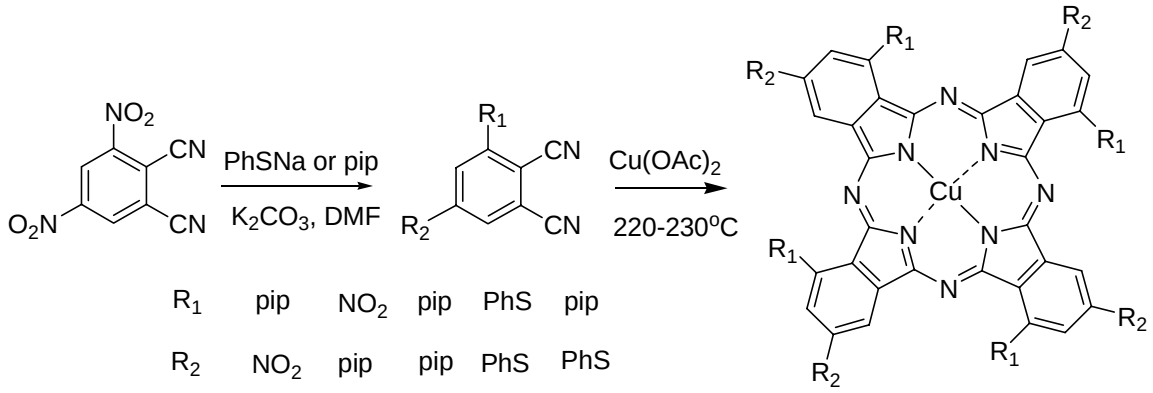
Transformation of the peripheral amino groups in amino substituted phthalocyanines into their derivatives is rarely used, although preparation of several transition-metal 1,8,15,22-tetrakis(3-phenylprop-2-enylideneamino)- and 1,8,15,22-tetrakis(*p*-methoxy-phenylimino) phthalocyanines by the reaction between 1,8(11),15(18),22(25)-tetraaminophthalocyanines and cinnamaldehyde or anisaldehyde, respectively, have been reported.[192] In another example, nickel 2,3,9,10,16,17,23,24-octaaminophthalocyanine was acylated with excess hexanoyl or lauroyl chloride giving in moderate yields 2,3,9,10,16,17,23,24-octahexanoyl- and octalaurylamidophthalocyanines, respectively.[193]



Scheme 48

One of the most convenient methods, which results in formation of the target phthalonitriles bearing electron-donating substituents, utilizes nucleophilic aromatic substitution reactions, with nitro or bromide leaving group proven to be the best in this reaction. Aromatic nucleophilic substitution of the bromine atom in 4-bromophthalonitrile with secondary amines was reported in mid 1970s (Scheme 48).[194] Similarly, nucleophilic aromatic substitution of bromine in 3-bromo-5-*tert*-butylphthalonitrile leads to formation of 3-(N,N-dimethylamino)-5-*tert*-butylphthalonitrile.[194b] Alternatively, 3- and 4-(N,N-dimethylamino)phthalonitrile can be prepared by methylation of readily available 3- and 4-aminophthalonitrile with dimethyl sulfate in aprotic polar solvents.[194] Analogous results can be obtained with the nucleophilic substitution reactions of 3- or 4-nitrophthalonitrile with dialkylamino precursors in aprotic polar solvents (Scheme 48).[194b] The substituted phthalonitriles obtained in this way can be easily used in reactions with appropriate metal salts to give the corresponding tetrasubstituted phthalocyanines bearing electron-donor groups; these are soluble in variety of organic solvents.

The other useful precursors for preparation of dialkylamino substituted phthalocyanines are 3- and 4-dialkylamino substituted phthalimides, which can be easily prepared in high yield by aromatic nucleophilic substitution of the bromo or nitro groups in 3- and 4-substituted phthalimides.[195] Similarly, the aromatic substitution reaction between 4,5-dichlorophthalonitrile and tosyl-protected tetraazamacrocyclic precursors in polar aprotic solvents in the presence of base results in formation of 4,5-disubstituted tetraazamacrocyclic precursors, which were converted into 2,3,9,10,16,17,23,24-tetrakis(tetraaza)substituted phthalocyanines in reasonable yields.[196]



Scheme 49

It is interesting to compare the reactivity of the nitro groups in 3,5-dinitrophthalonitrile toward nucleophilic aromatic substitution reactions with dialkylamines as well as other nucleophiles.[197] Reaction of 3,5-dinitrophthalonitrile with piperidine in DMF in the presence of potassium carbonate as a base leads to formation of all three expected nucleophilic substitution products bearing one or two piperidine residues. The monosubstituted 3(5)-nitro-5(3)-piperidinophthalonitriles are interesting examples of precursors which lead to preparation of octasubstituted phthalocyanines with push-pull substituents in each isoindole subunit. It was shown that an unreacted nitro group in 3(5)-nitro-5(3)-piperidinophthalonitriles can be further substituted with a different nucleophile, *e.g.* phenylthiolate, with formation of 3-piperidino-5-phenylsulfanyl-phthalonitrile (Scheme 49); this is a useful precursor for preparation of 1(4),8(11),15(18), 22(25)-tetrapiperidino-3(2),10(9),17(16),24(23)-tetraphenylsulfanylphthalocyanines.

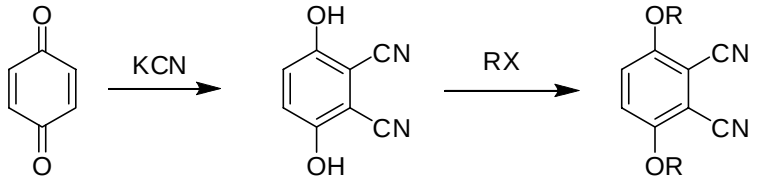
4.2 Hydroxy-, alkoxy- and aryloxy substituted phthalocyanines

The availability of simple methods for preparation of alkoxy- and aryloxy-substituted phthalocyanines has resulted in the appearance of an enormous number of compounds of this type in the literature.[3b] 1,8(11),15(18),22(25)-Tetra-, 2,9(10),16(17),23(24)-tetra-, and 2,3,9,10,16,17,23,24-octasubstituted patterns represent the majority of these compounds, while 1,4,8,11,15,18,22,25-octa- as well as dodeca- and hexadecasubstituted patterns are quite rare. In general, alkylation of phenolic hydrogens,[198] aromatic nucleophilic substitution of nitro[199] and halogeno[200] atoms, the Rosenmund-von Braun,[201] and Diels-Alder[202] reactions can be used for preparation of alkoxy- and aryloxyphthalonitriles and their related phthalocyanines. As usual, when 3- and 4-substituted phthalonitriles are used in the cyclotetramerization reaction, a mixture of all possible isomeric forms is obtained (Figure 2), although as pointed out by Leznoff et al.,[203] the room-temperature template (Zn^{2+}) cyclization of 3-alkoxyphthalonitriles leads to formation of a single C_{4h} symmetry 1,8,15,22-tetrasubstituted isomer. This isomer forms not only when sterically hindered 3-neopentoxy- and 3-(*p*-*tert*-butylbenzyl)oxyphthalonitriles were used but also in the case of 3-methoxyphthalonitrile suggesting that electronic influences of strongly electron-donating alkoxy groups decrease the activity of the closest nitrile group toward

nucleophilic attack during the cyclotetramerization reaction. One precaution which should be addressed during preparation of the alkoxysubstituted phthalocyanines is the lability of some alkoxy groups during the cyclotetramerization reactions when conducted in alcohols.[204] As a result it is generally recommended to 'match' the alkyl in the substituted phthalonitrile with the length of the side chain in the alcohol.

Another interesting feature of transition-metal alkoxysubstituted phthalocyanines is the prominent basicity of the *meso*-nitrogen atoms. For instance, the *meso*-nitrogen atoms in zinc(II) 1,8(11),15(18),22(25)-tetramethoxyphthalocyanine can be protonated even by water compared with the basicity of the unsubstituted analog, which can be protonated by only strong acids.[205] During such protonation reactions in organic solvents, 1,8(11),15(18),22(25)-tetra- and 1,4,8,11,15,22,25-octa-alkoxyphthalocyanines change the color from green to brown.

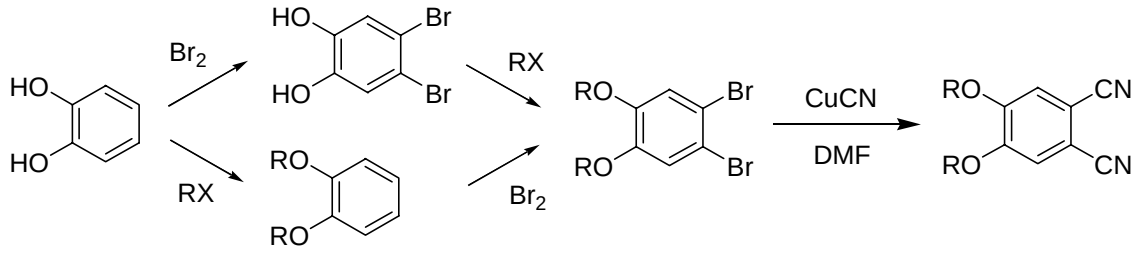
The alkylation of phenolic hydrogen atoms with appropriate alkyl halides along or in combination with the Rosenmund-von Braun reaction is a common synthetic pathway for preparation of 3,6- and 4,5-alkoxy- or aryloxysubstituted phthalonitriles and the corresponding 1,4,8,11,15,18,22,25- or 2,3,9,10,16,17,23,24-octaalkyl(aryl)oxy-phthalocyanines. For example, preparation of the 3,6-dialkoxyphthalonitriles can be viewed as an example of an alkylation reaction used for preparation of alkoxyphthalo-nitriles (Scheme 50).[206] The alkylation reaction typically proceeds under slightly basic conditions with a variety of alkyl halides, including those with terminal functional groups. These terminal functional groups can then be used for a variety of applications (*e.g.* preparation of water-soluble salts for PDT, coordination of transition-metal complexes, preparation of supramolecular frameworks, and heterogeneous catalysis etc.).



Scheme 50

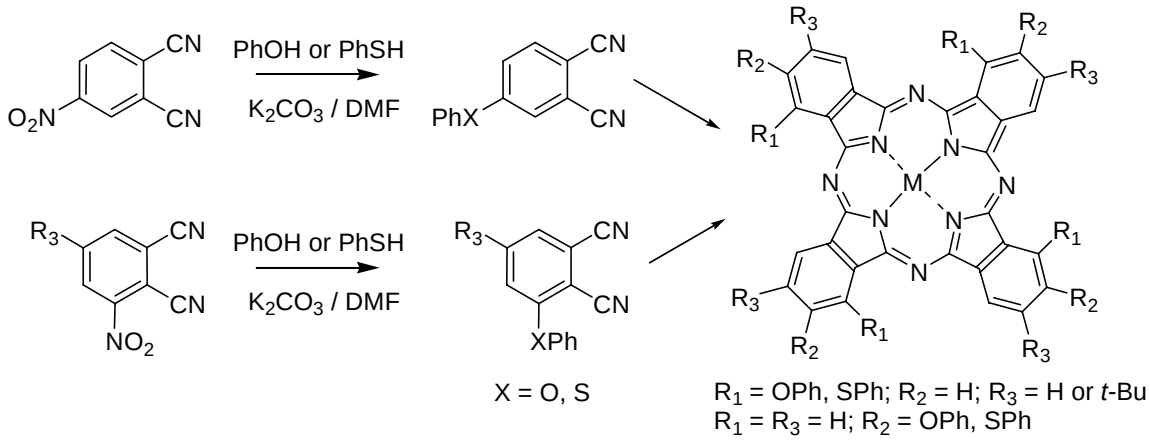
The typical reaction pathways for preparation of alkoxysubstituted phthalonitriles by alkylation and Rosenmund-von Braun reactions are presented in Scheme 51.[38,207] The key precursor, 1,2-dibromo-4,5-dialkoxybenzene can be prepared either from 4,5-dibromocatechol or from 1,2-dialkoxybenzene. 4,5-Dibromocatechol can be alkylated using a variety of alkyl halides to form 1,2-dibromo-4,5-dialkoxybenzenes. Alternatively, catechol can first be alkylated followed by the bromination reaction. Finally, 1,2-dibromo-4,5-dialkoxybenzenes can be introduced into the standard Rosenmund-von Braun reaction to form the target 1,2-dicyano-4,5-dialkoxybenzenes. The strategy presented in Scheme 51 can also be used for preparation of the crown-ether (or other macrocycle) substituted phthalocyanines and for the preparation of 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines with two different substituents on each benzo unit. In this case, catechol undergoes stepwise alkylation of its hydroxyl groups with

formation of 1,2-dialkoxybenzenes with two different alkoxy groups. Although the Rosenmund-von Braun reaction is a very simple reaction pathway for preparation of alkoxy- and aryloxysubstituted phthalonitriles, the reaction yields depend upon the number and type of substituents present in the dibromo precursors.



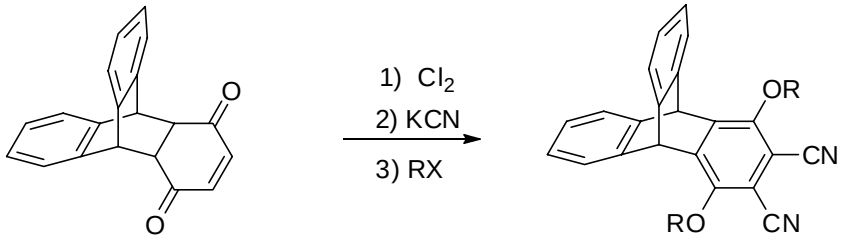
Scheme 51

Aromatic nucleophilic substitution of nitro groups in 3- and 4-mono, as well as 4,5- and 3,5-disubstituted phthalonitriles by phenols and thiophenols was reported in 1980.[208] This reaction, which became a standard method for introduction of ArO and ArS substituents into 3- and 4-substituted phthalonitriles and the corresponding 1,8(11),15(18),22(25)- and 2,9(10),16(17),23(24)-tetraalkyl(aryl)oxysubstituted phthalocyanine complexes, proceeds smoothly in aprotic polar solvents (DMSO, DMF, MeCN etc) in the presence of large excess of potassium carbonate as a base; it affords phthalonitrile precursors in high yields (Scheme 52).[208a,209] In the case of 3- and 4-substituted phthalonitriles, readily available 3- and 4-nitrophthalonitriles are usually used for aromatic nucleophilic substitution reactions with alcohols, phenols, thiols, or thiophenols, while the 4,5-dichlorophthalonitrile is a convenient precursor for preparation of 4,5-disubstituted phthalonitriles.



Scheme 52

A synthetic strategy for preparation of the 1,4,8,11,15,18,22,25-octaalkoxy substituted 'concave' phthalocyanines was reported by Kenney et al. (Scheme 53).[210] In this case, a Diels-Alder reaction between anthracene and *p*-benzoquinone leads to formation of triptycene-1,4-dihydroquinone, which can be chlorinated by the chlorine gas in acetic acid and then used in the reaction with potassium cyanide and finally an alkylation reaction. The resulting 2,3-dicyano-1,4-dibutoxytriptycene can be cyclotetramerized to the corresponding phthalocyanine compounds.

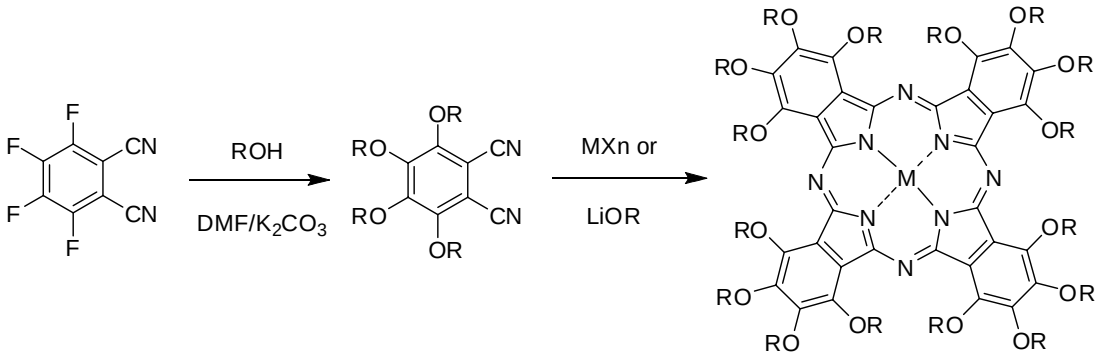


Scheme 53

Preparation of transition-metal 1,2,4,5,8,9,10,11,15,16,17,18,22,23,24,25-hexadecaalkyl(aryl)oxysubstituted phthalocyanines was pioneered by the groups of Kobayashi,[211] Hanack,[212] Ng,[213] Leznoff,[214] Wöhrle[176c] and others.[215] In all cases, aromatic nucleophilic substitution reactions between tetrafluorophthalonitrile and the respective alcohols in DMF/K_2CO_3 was used for preparation of the 3,4,5,6-tetraalkyl(aryl)oxyphthalonitriles in 51-92% yield (Scheme 54). As was shown by Leznoff and co-workers, the reaction is sensitive to the steric properties of the alcohols. For instance, all four fluorine atoms in tetrafluorophthalonitrile can be substituted by alkoxygroups when 1-adamantanemethanol or 2-(1-adamantanyl)ethanol were used, while only three fluorine atoms undergo substitution if more sterically crowded 1-adamantanol was used in the reaction.[214c]

Introduction of hydroxyl groups into the phthalocyanine core can be achieved by (i) the diazotization of aminosubstituted phthalocyanines followed by hydrolysis in the presence of copper(II) sulfate;[112a,177] (ii) demethylation of methoxy substituted phthalocyanines with BBr_3, HCl/pyridine, trifluoroacetic acid, or $AlCl_3$;[207a,216] (iii) desilylation of $OSiMe_2$(*t*-Bu) groups with HF or metal fluorides;[216d] (iv) deprotection of OCH_2OMe, $OCHPh_2$, or benzylic substituents with trifluoroacetic acid;[217] and (v) hydrolysis of isopropylidendioxy substituents with strong acids.[218] In a limited number of reports, 2,9(10),15(16),23(24)-tetrahydroxyphthalocyanines were prepared either by reaction between the metal-free 2,9(10),15(16),23(24)-tetrahydroxyphthalocyanine and zinc acetate in DMF/toluene mixture[217] or by direct cyclotetramerization reaction of 4-hydroxyphthalonitrile and metal salts at 220 ^oC.[216a] Metal chelation to peripheral hydroxyl substituents in metal-free and nickel 2,3,9,10,16,17,23,24-octahydroxyphthalocyanines was investigated by the Pierpont[216d] and Kobayashi[216e] groups. Both groups found that 2,3,9,10,16,17,23,24-octahydroxyphthalocyanines can form stable

supramolecular assemblies with appropriate transition-metal complexes. It is interesting to note that both partially protonated as well as completely deprotonated nickel 2,3,9,10,16,17,23,24-octahydroxyphthalocyanines were able to form supramolecular compounds with substituted tris(3-*p*-tert-butylphenyl-5-methyl)pyrazolyl borate (scorpionate) zinc complex.

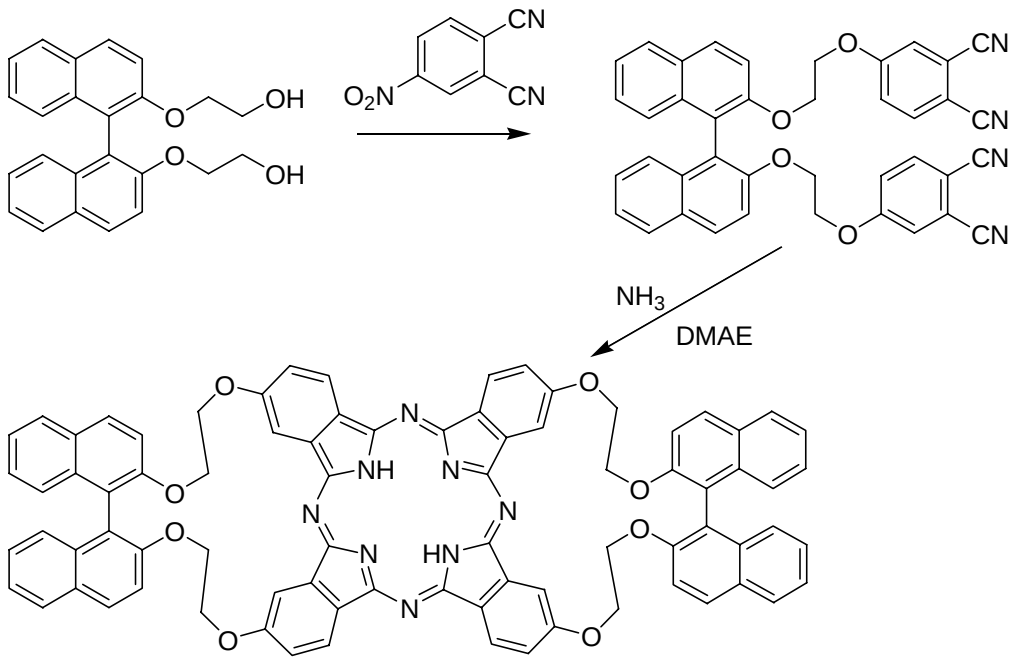


Scheme 54

Similar to heterobimetallic complex (Figure 6), the electron-donating pyridyloxy substituents in zinc 2,9(10),16(17),23(24)-tetrakis(3-pyridyloxy)phthalocyanine can be used as anchor groups in the preparation of tetraplatinum(II) derivatives with $PtCl_2NH_3$ and $PtCl_2$(dmso) fragments.[219] The platinum fragments in these heterobimetallic complexes are stable in solution up to 90 ^oC, which makes them excellent potential candidates for combined PDT/chemotherapy treatments.

Another interesting class of alkoxy- and aryloxy-substituted phthalocyanines are 1:25,11:15- and 2:24,10:16-bridged phthalocyanines first explored by Leznoff and Kobayashi research groups.[220] The precursor phthalonitriles can be prepared by aromatic nucleophilic substitution of 3- or 4-nitrophthalonitrile with appropriate diols in DMF using K_2CO_3 as a base (Scheme 55). The resulting bisphthalonitriles can be cyclotetramerized into the corresponding symmetric bridged phthalocyanines. Their low yields (usually less than 10%) can be explained by the expected formation of oligomeric products.

As expected, the length of the bridging fragment for preparation of 1:25,11:15-bridged phthalocyanines can be significantly shorter compared with the bridging group for preparation of 2:24,10:16-bridged phthalocyanines.[221]



Scheme 55

4.3 Alkylthio- and arylthio-substituted phthalocyanines

In general, alkylthio- and arylthio-substituted phthalocyanines can be prepared following many of the synthetic procedures for preparation of alkyloxy- and aryloxy-substituted phthalocyanines described in the previous section. For instance, aromatic nucleophilic substitution reactions between 3-nitro-,[208a,222] 4-nitro-,[208a,223] 3,5-dinitrophthalonitrile[224] as well as 4,5-dichlorophthalonitrile,[225] 3,6-bistosyloxyphthalonitrile,[55,226] tetrafluorophthalonitrile[227]or tetrachlorophthalonitrile[228] with a variety of thiols and thiophenols in DMF/K_2CO_3 results in formation of the target 3-mono or 4-mono as well as 4,5-di and 3,4,5,6-tetraalkylsulfanyl- or diarylsulfanyl-phthalonitriles, which can be cyclotetramerized into the corresponding phthalocyanines using standard procedures. As a rule, formation of alkylsulfanyl- and arylsulfanyl-phthalonitriles by aromatic substitution reaction proceeds more easily than formation of the analogous alkyloxy- and aryloxy-phthalonitriles because of the better nucleophilicity of thiolates compared with alkoxides. As a result, aromatic nucleophilic substitution of all halogen atoms on alkyl- or aryl-sulfanyl substituents in transition-metal hexadecafluoro(chloro)phthalocyanines can be achieved simply by heating of these macrocycles with the appropriate thiols or thiophenols in diglyme or quinoline.

The Q-band in phenylsulfanyl derivatives is located at longer wavelengths compared with the corresponding phenoxy complexes.[226a] 1,8(11),15(18),22(25)-Tetraphenylthiophthalocyanines have a Q-band in the NIR region and are potential candidates for PDT applications.[229] Another useful property of the alkylsulfanylphthalocyanines is their easy adsorption onto the surface of

gold electrodes, which results in the preparation of surface-modified electrodes for a variety of electrocatalytic reactions.[230]

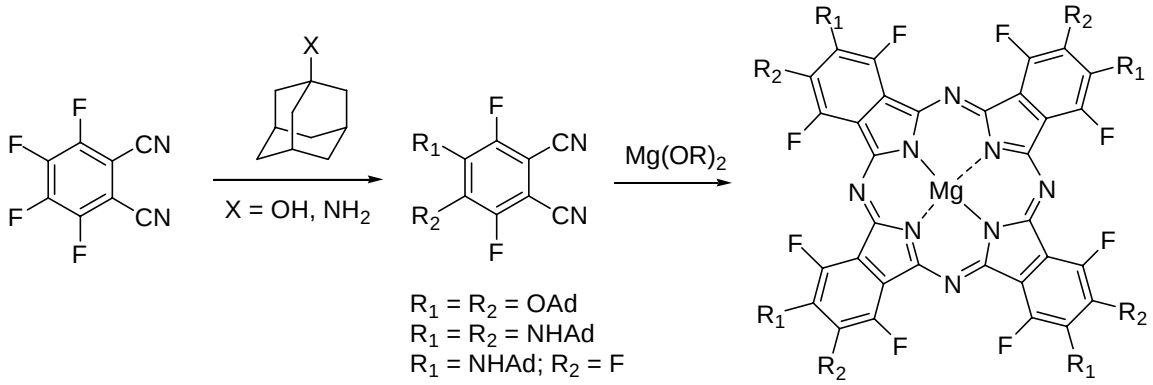
5. Phthalocyanines with electron-donating and electron-withdrawing substituents on the same benzene rings

Symmetric phthalocyanines bearing both electron-donating and electro-withdrawing substituents on the same benzene ring represent a relatively new class of phthalocyanine compounds.[178,197,206,214c,228,231] The pioneering work on these compounds originates from the research groups of Lukyanets, Shaposhnikov, Bekaroglu, Leznoff, and the others. As usual, direct cyclotetramerization of appropriately substituted phthalonitriles or aromatic nucleophilic substitution of halogen atoms in hexadecahalogenated phthalocyanines have been used.

The latter approach was extensively investigated by Leznoff's group, which studied aromatic nucleophilic substitution of the fluorine atoms in zinc hexadecafluorophthalocyanine by oxygen-, nitrogen-, sulfur-, and carbon-centered nucleophiles (Scheme 56).[214c,232] The distribution of the reaction products was monitored by mass spectrometry. Based on these data, it was found that, as expected, aromatic nucleophilic substitution of the fluorine atoms results in a broad distribution of reaction products rather than formation of individual complexes, although in some cases narrowly defined mixtures of polysubstituted products were observed. In general, the average number of oxygen-, nitrogen-, sulfur-, and carbon-centered nucleophiles incorporated into the reaction product follows their relative nucleophilicity and increases in the order: HNRR' < RO < CN^- < RS^-.[232] The reactivity of zinc hexadecafluorophthalocyanine was further studied in substitution reactions with primary and secondary amines as well as *tert*-butyl esters of aminoacids as nucleophiles, using various reaction conditions.[233] It was found that mild reaction conditions lead to formation of mono- and di-substituted fluorophthalocyanines, while higher degrees of substitution can be achieved using amines as solvents. In the case when diamines were used as the nucleophiles, reaction products consisted of cyclic substituted phthalocyanines, binuclear and trinuclear (amine bridged) compounds, or mixtures of both of these types depending on the structure of the diamines used.

Aromatic nucleophilic substitution of the nitro group in polysubstituted phthalonitriles provides an alternative controllable synthetic strategy for preparation of push-pull symmetric phthalocyanines with both electron-donating and electron-withdrawing groups on the same benzene ring. It was found that the reaction between 3,5-dinitrophthalonitrile and piperidine leads to formation of both 5-nitro-3-piperidonophthalonitrile (major product) and 3-nitro-5-piperidinophthalonitrile (minor product).[197] The former phthalonitrile can be easily converted into copper 1,8(11),15(18),22(25)-tetrapiperidino-3,10(9),17(16),24(23)-tetranitro-phthalocyanine. Besides the polynitrophthalonitriles (which are relatively more difficult to prepare), partial nucleophilic substitution in polyhalophthalonitriles can also provide the desired push-pull phthalonitriles.[228,231] For instance, it was shown that the substitution of a single

chlorine atom in 4,5-dichlorophthalonitrile with sulfur-based nucleophiles resulted in formation of 4-chloro-5-arylsulfonylphthalonitriles, which were converted into the corresponding phthalocyanine compounds.[231e] Similarly, the reaction between 3,4,5,6-tetrafluorophthalonitrile and 1-adamantanol or 1-adamantylamine leads to formation of 4,5-di-(1-adamantyloxy)- or 4,5-di-(1-adamantylamino)-3,6-difluorophthalonitrile and 4-(1-adamantylamino)-3,5,6-trifluorophthalonitrile, respectively (Scheme 56).[214c] These nitriles were converted into the corresponding magnesium, nickel, and metal-free phthalocyanines.



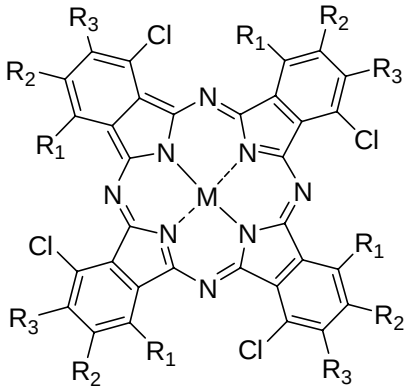
Scheme 56

Several cobalt 2,9(10),16(17),23(24)-tetranitro-3,10(9),17(16),24(23)-tetraacetylamino-phthalocyanines were prepared by cyclotetramerization of the corresponding phthalonitriles.[231f] Hydrolysis of cobalt 2,9(10),16(17),23(24)-tetranitro-3,10(9),17(16),24(23)-tetraacetylaminophthalocyanine results in formation of 2,9(10),16(17),23(24)-tetranitro-3,10(9),17(16),24(23)-tetraaminophthalocyanine.

Nucleophilic aromatic substitution of the chlorine atoms in tetrachlorophthalonitrile by phenols, thiols, and amines is relatively new but is a very promising method for introduction of electron-donating groups into the phthalocyanine core.[231] It was found that the selectivity and degree of substitution predominantly depend on the nature of the nucleophile. For instance, it is possible to substitute all chlorine atoms in tetrachlorophthalonitrile with alkyl- and aryl-thiols, while only three chlorine atoms can be substituted by aryloxy- and pyridyloxy- groups. Moreover, only two chlorine atoms can be substituted by cyclic secondary amines, whereas only one chlorine atom can be replaced by monoalkyl-, monoaryl-, and dialkylamine nucleophiles. The first point of substitution is independent of the type of nucleophile and always leads to formation of 2,4,6-trichloro-5-nucleophilophthalonitrile. When the nucleophiles are aryl and alkyl thiols as well as phenols, or cyclic secondary amines, introduction of the second group results in formation of 3,6-dichloro-4,5-dinucleophilophthalonitrile; in the case of pyridine-3-ol as the nucleophile both 3,6-dichloro-4,5-di(3-pyridyloxy)oxyphthalonitrile and 3,5-dichloro-4,6-di(3-pyridyloxy)oxyphthalonitrile were observed in the reaction mixture. Finally, when three

chlorine atoms are substituted by nucleophiles, only 3-chloro-4,5,6-trinucleophilophthalonitrile was observed in the reaction mixture.

Similar nucleophilic substitutions in polychlorophthalonitriles already substituted by electron-donor group can result in substituted phthalonitriles with two different electron-donating groups.[231] For example, the room-temperature reaction of 3,4,6-trichloro-5-(phenylamino)phthalonitrile with one, two, or three equivalents of phenyl or butyl thiols results in formation of pure 3,6-dichloro-4-(aryl or alkylsulfanyl)-5-(phenylamino)phthalonitrile, 3-chloro-5,6-di(aryl or alkylsulfanyl)-4-(phenylamino)-phthalonitrile, and 3,4,6-tri(aryl or alkylsulfanyl)-5-(phenylamino)phthalonitrile, respectively. Another example of such a clean transformation is the reaction of 3,6-dichloro-4,5-di(piperidino)benzene-1,2-dinitrile with phenylthiol, which exclusively leads to formation of 3,6-di(phenylsulfanyl)-4,5-di(piperidino)benzene-1,2-dinitrile. If an electron-donor group is already present in the substituted polychlorophthalonitrile and is 3-pyridyloxy or phenylsulfanyl, an additional nucleophilic substitution leads to a variety of products which originate from a scrambling reaction and thus these products are less useful from the synthetic point of view. 3,6-Dichloro-4,5-di(phenyl or alkyl sulfanyl)benzene-1,2-dinitriles, 3,4,5,6-tetra(phenylsulfanyl)benzene-1,2-dinitrile, 3,6-dichloro-4,5-di(aryloxy)benzene-1,2-dinitriles, 3,5-dichloro-4,6-di(3-pyridyloxy)-benzene-1,2-dinitrile, 3,4,6-trichloro-5-(3-pyridyloxy)benzene-1,2-dinitrile, and 3,4,6-dichloro-5-aminobenzene-1,2-dinitrile can be readily tetramerized to the corresponding transition-metal or main group phthalocyanines, which in the majority of cases are only slightly soluble in aprotic dipolar solvents (Figure 9). On the other hand, purification of transition-metal 2,3,9,10,16,17,23,24-octa(substituted amino)-1,4-8,11,15,18,22,25-octachlorophthalocyanines was unsuccessful because of the low stability of the target phthalocyanine complexes.



	Q, nm
$R_1 = R_2 = R_3 = OPh$, M = Zn	700
$R_1 = R_2 =$ Cl, $R_3 = NHPh$ M = Zn	714
$R_1 = Cl$, $R_2 = R_3 = NEt_2$, M = Zn	714
$R_1 = Cl$, $R_2 = R_3 = SPh$, M=Cu	746
$R_1 = Cl$, $R_2 = R_3 = SBu$,M = Cu	741

Figure 9. Q-band positions in selected examples of chlorinated phthalocyanines bearing electron-donating groups.

Acknowledgements

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