SCHOOL OF CHEMISTRY

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Synthesis and crystal structures of phthalocyanine derivatives containing bulky phenyloxy substituents

Thesis submitted for the degree of Doctor of Philosophy by:

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To my Family

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Abstract

The planar extended shape of the phthalocyanine macrocycle results in a strong tendency of its derivatives to form densely packed co-facial aggregates. The strategy to avoid co-facial self-association that forms the basis of this thesis involves the use of substituents that can introduce severe steric crowding adjacent to the phthalocyanine core. Previous work showed that the introduction of 2,6-di-*iso*-propylphenoxy groups on the peripheral positions of the phthalocyanine seems to be perfect for this purpose. Of particular interest is zinc octa(2,6-di-*iso*-propylphenoxy) phthalocyanine (**Pc1Zn**), which forms a remarkable cubic crystal structure, containing interconnected solvent-filled voids 2 nm across. The aim of the research programme was to investigate the crystal forming properties of related phthalocyanine derivatives containing different metal cations and bulky phenoxyl substituents.

A range of metal cations were introduced into 2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy) phthalocyanine (**Pc1**) to establish which, if any, were compatible with the formation of the nanoporous cubic crystal observed for the zinc derivative. It was found that any metal capable of binding to a ligand at its axial site formed the cubic crystal including metals of primary catalytic relevance such as cobalt, iron, manganese and ruthenium. Single crystal X-ray diffraction studies demonstrated the exchange of axial ligands to confirm the interconnectivity of the nanovoids, which is essential for the potential exploitation of these molecules in heterogeneous catalysis. Of particular interest is the introduction of bidentate ligands, which act as structural wall ties that bind metals between cubic subunits.

Since loss of crystallinity occurs after removal of the guest solvent from the cubic clathrates, the introduction of substituents at the 4-position of the phenoxy groups was also investigated in order to induce stronger dipole-dipole (e.g., R = Br, Cl, CN, OMe) or hydrogen bond interactions (e.g., R = OH), which might stabilise the crystal structure. Unfortunately, these derivatives formed non-cubic crystals, although in each case solvent was included within the structure to form novel clathrates.

Abbreviations

Å	Angstrom
APCI	Atmospheric pressure chemical ionisation
aq	aqueous
bipy	4,4'-bipyridyl
BisIm	1,2-bisimida-zol-1-ylethane
br	Broad
calc.	Calculated
DABCO	1,4-diazabicyclo[2.2.2]octane
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DBU	1,8-diazabicyclo[5.4.0]undecene
DCM	Dichloromethane
1,6-diahex	1,6-diaminohexane
dimepy	3,5-dimethylpyridine
DMAc	N,N-Dimethylacetamide
DMAE	N,N-dimethylaaminoethanol
DMF	*N,N*–Dimethylformamide
DMSO	Dimethyl sulphoxide
EI	Electron Impact
ES	Electrospray
Et	Ethyl
Et_2O	Diethylether
EtOAc	Ethyl acetate
EtOH	Ethanol
g	Grams
GPC	Gel Permeation Chromatography
h	Hour/s
HRMS	High Resolution Mass Spectrometry
Hz	Hertz
Im	imidazole
IR	Infra Red
IUPAC	International Union of Pure and Applied Chemistry
J	Coupling constant (in Hz)
lit.	Literature
LRMS	Low Resolution Mass Spectrometry
m	Multiplet
MALDI	Matrix-assisted laser desorptio/ionisation
Me	Methyl
MeIm	1-methyl imidazolyl
MeOH	Methanol
mmol	Millimole(s)

MOF	Metal Organic Framework
MOP	metal-organic polyhedra
M.p.	Melting point
nm	nano meters
NMIm	N-methylimidazole
NMP	*N*-methyl pyrrolidone
NMR	Nuclear Magnetic Resonance
NOESY	Nuclear Overhauser Enhancement Spectroscopy
OBu	Butoxide
Pc	Phthalocyanine
Ph	Phenyl
Phic	1,4-phenyleneisocyanide
pic	4-picoline
PIM	Polymers of Intrinsic Microporosity
py	pyridine
q	quartet
r.t.	room temperature
s	singlet
t	triplet
t-Bu	tert butyl
t-BuNC	*tert*-butylisocyanide
t-Bupy	*t*-butylpyridine
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	Trimethylsilyl
TpyP	5,10,15,20-tetra-4'-pyridylporphyrin
UV	Ultraviolet
V	volume
XRD	X-ray diffraction

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Chapter 1

1. Introduction

1.1 History of phthalocyanine research

Phthalocyanines are 18-π electron aromatic macrocycles, consisting of four isoindole units connected by nitrogen atoms (Figure 1.1 a). Their structure is closely related to the naturally occurring porphyrin ring system, the differences being the four benzo-subunits and the nitrogen atoms at each of the *meso* positions[1] (Figure 1.1 b).

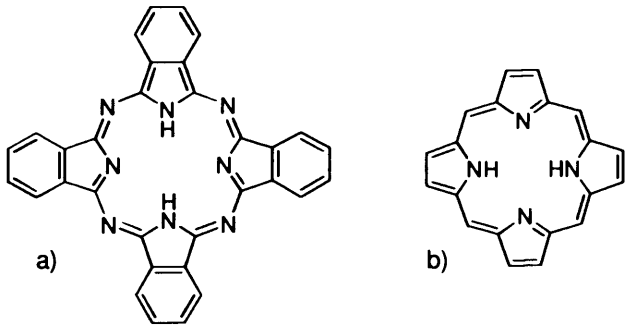


Figure 1.1. a) The structure of phthalocyanine. b) The structure of the simplest porphyrin; porphine.

The name phthalocyanine, which is a combination of the prefix phthal, from the Greek naphtha (rock oil), and the Greek cyanine (blue), was given to this class of compound by Reginald P. Linstead (Imperial College, London). He was the first academic to investigate the structure of phthalocyanines after their accidental discovery in 1928 at the Grangemouth plant of Scottish Dyes Ltd, during the industrial preparation of phthalimide from phthalic anhydride and ammonia. The glass-lined reaction vessel had cracked exposing the outer steel vessel to the reaction, resulting in the formation of a iron containing blue impurity.[2,3] Imperial Chemical Industries (ICI), which had acquired Scottish Dyes in 1928 were interested in understanding the structure of this substance that, after preliminary studies, appeared to be exceptionally stable and exploitable as an insoluble pigment. Hence they sent a sample to Professor Jocelyn F. Thorpe at Imperial College London who in turn gave it to Linstead for investigation. The preparation and the properties of the substance were covered in a patent in 1928.[4]

Actually, substances which could be later interpreted as the metal free[5] and copper phthalocyanines[6] had been observed already in 1907 and 1927 respectively, but it was only

after the third accidental event that there was sufficient interest to elucidate the structure of these highly coloured by-products.

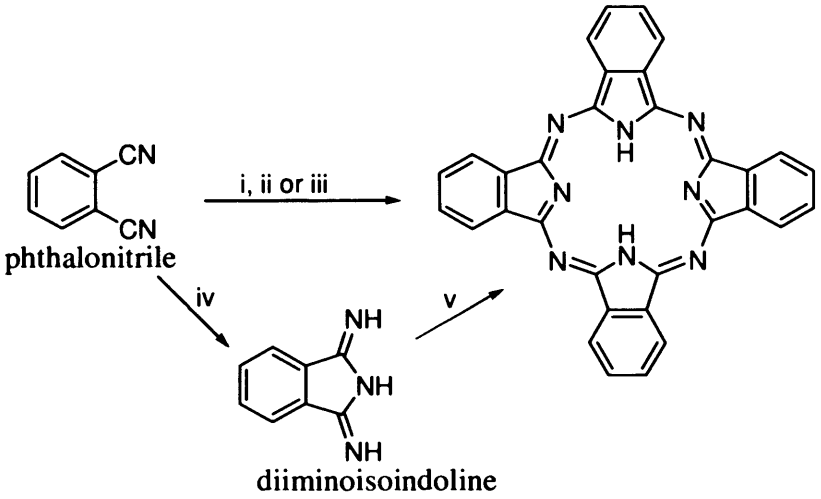
After a series of investigations, in 1934 Linstead published six papers where the structure of Pc and the synthesis of some of its metal derivatives were described.[7-12] The proposed structure was confirmed by mean of X-ray diffraction techniques by Robertson in 1936.[13]

Pcs, especially the copper derivative, were soon exploited as pigments,[1] but more recently they have been investigated as molecular materials and their synthesis and study has developed into a fascinating area of research.[14]

1.2 Phthalocyanine synthesis

1.2.2 Metal free phthalocyanine

Metal free Pc can be synthesised starting from different 1,2-disubstituted benzene precursors but are usually prepared from phthalonitrile in the laboratory[1,15] (Scheme 1.1).

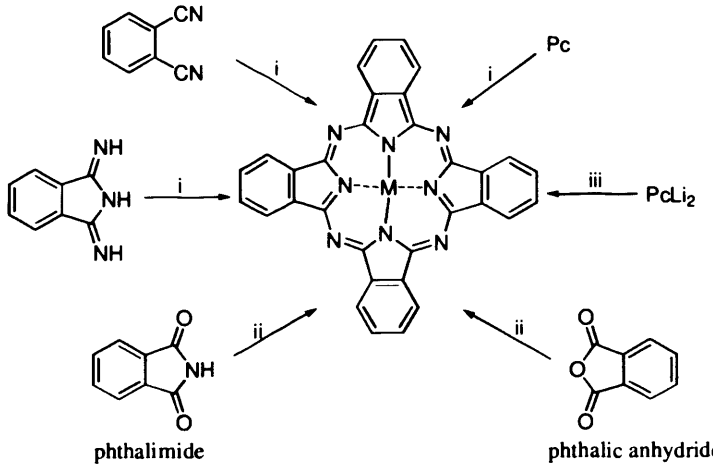


Scheme 1.1. *Synthetic routes to metal free* **Pc**. *Reagents and conditions:* i) lithium, refluxing pentanol, aqueous hydrolysis. ii) Heat with DBU or DBN or NH_3 in refluxing pentanol or heat in DMAE. iii) Fuse with hydroquinone. iv) NH_3, refluxing MeOH, NaOMe. v) Reflux in a high-boiling-point alcohol.

Phthalonitrile cyclotetramerisation to form Pc can be performed by heating the phthalonitrile in a solvent such as *n*-pentan-1-ol in presence of a base (DBU, DBN)[16,17] or in a basic solvent such as N,N-dimethylaminoethanol (DMAE).[18-20] Lithium, sodium, or magnesium alkoxides, generally formed *in situ* by the addition of the metal to a primary alcohol (e.g. *n*-pentan-1-ol) can be used as a base to form the respective alkali-metal Pcs, which can be easily converted into the metal free macrocycle by acidic work-up (the Linstead method).[21-23] Phthalonitrile cyclotetramerisation can be achieved without solvent at a temperature (> 180 °C) above which the phthalonitrile melts and in presence of a reducing agent, generally hydroquinone. Furthermore, phthalonitrile can be initially converted by reaction with NH_3 in diiminoisoindoline which under relatively mild conditions condenses to form Pc.[1]

1.2.3 Metal phthalocyanine

It is possible to place around seventy different elements in the central cavity of Pc[1,24] which can strongly influence its physical properties. Metal Pcs are generally prepared from the precursor using the metal salt as a template for the cyclotetramerisation (**Scheme1.2**).



Scheme 1.2. Synthetic routes to **MPc**. *Reagents and conditions*: i) Heat in a high-boiling-point solvent (e.g. quinoline) with metal salt. ii) Heat in a high-boiling-point solvent with metal salt and urea. iii) Heat in ethanol with metal salt.

When phthalic anhydride[25] or phthalimide[26] are employed it is necessary to add a source of nitrogen (urea). In most cases, the metallation can be achieved also by refluxing Pc or $PcLi_2$ in the presence of the metal salt.[1,10,22] The presence of the metal cation allows the possibility of axial substitution, which could enhance the solubility and reduce the Pcs co-facial aggregation due to the strong π-π interaction.

Along with the axial sites, 16 possible sites of substitution are present in the phthalocyanine ring. In general the substituents are introduced in the phthalonitrile precursors before the cyclotetramerisation reaction. Incorporation of substituents, both in axial and in the ring, apart from increasing its solubility, allows fine-tuning of the physical properties.[24]

1.3 Phthalocyanine applications as materials

Phthalocyanine and its derivative are largely studied as molecular materials[1,23] due to their optical and electronic properties,[1] which arise from their electronic delocalization.[24] They have been used as blue and green colorants since their discovery and more recently have attracted great interest for applications in nonlinear optics,[27-29] as photoconductors,[30] optical data storage,[31] molecular electronics,[32,33] photodynamic cancer therapy,[34,35] solar energy conversion,[36,37] catalysis[38] and as the active component of gas sensors.[39] Their planarity along with their high symmetry and synthetic versatility make them suitable building block for use in supramolecular[24] and polymer chemistry.[40]

Consequently an intense synthetic activity around these molecules has developed, which is clearly represented by the increasing number of publications in this field (**Chart 1**).[24]

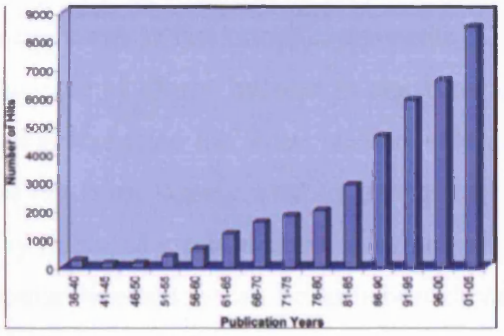


Chart 1. Number of scientific documents on phthalocyanines.[24]

The physical properties of Pcs are strongly influenced by the spatial molecular arrangement in the solid state, which is dependent on the molecular structure.[40] In particular, the optical and electronic properties of the material highly depend on the relative orientation and distance of the phthalocyanine moieties from one another.

Various crystalline polymorphs,[1,23,41,42] formed from low molar mass derivatives, have been used for the preparation of ordered thin films by vacuum sublimation,[1,23,43] Langmuir-Blodgett[1,23,44,45] technique and spin coating.[1,23,46] Liquid crystals in which the molecules self assemble forming ordered columnar stacks have been obtained from numerous Pc derivatives which have flexible side chains as substituents.[1,23]

The incorporation of phthalocyanines into polymers offers the possibility to exert strong control on their relative orientation based on covalent bonding. The numerous sites of potential functionalisation of the phthalocyanine ring allow their incorporation into polymers as the main chain, side groups or within highly cross-linked network structures.[40]

1.4 Supramolecular organization of phthalocyanines.

The self-organizing properties of phthalocyanines are mainly determined by the strong π-π interaction between the extended aromatic rings, and can be tuned with structural modifications.[24,47] The overlap between the π-orbitals within a well organized stack of Pc molecules may result in interesting uni-dimensional materials with conducting properties.[48]

Depending on the degree of stacking and the nature of the central metal, assemblies based on these molecules can serve as functional components in, for example, gas sensors and as conductive wires capable of charge transfer in electronic devices. The aggregation behaviour of crowned phthalocyanines has been studied extensively.[49] The substitution with crown ether moieties has been largely used to improve molecular stacking.[50] They self-assemble into stacks by means of π-π interactions, and, by adding (alkali) metal ions to the stacks, the intermolecular interaction can be enhanced because these ions complex between the crown ether fragments. In this way fine tuning of the self-assembled architecture at the molecular level is possible and results in dramatic structural changes at the mesoscopic level.[49]

Interesting supramolecular chemistry based on phthalocyanines was presented by Nolte *et al.*[50] They described the 10-step synthesis of a disk-shaped molecule with chiral tails, which form long fibres of molecular diameter and micrometer length by self-assembly, derived from molecules containing a phthalocyanine ring to which four benzo-crown ether moieties are attached.[51] These structures self-assemble to form coiled aggregates (organogels) with left-handed helicity which have potential in optoelectronic applications and as components in sensor devices. This unusual example of helix and superhelix formation is driven by π–π stacking interactions (**Figure 1.2**).

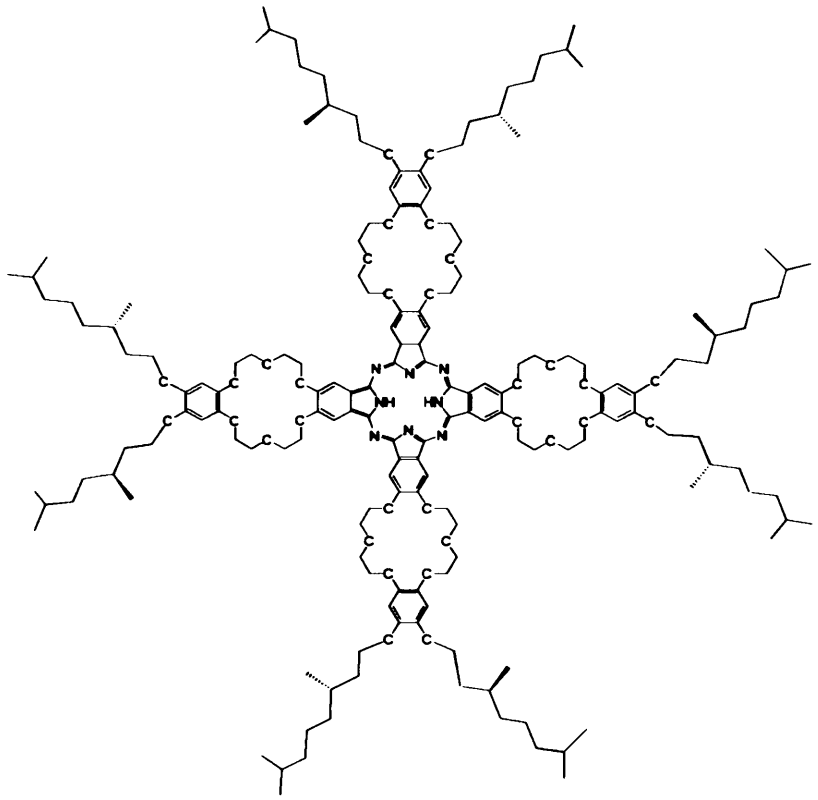


Figure 1.2 Chemical structures of crown ether phthalocyanine **Pc-18-crown-6.**

Apart from π-π interactions metal-ligand coordination can be also used to construct supramolecular entities based on phthalocyanines.[52] In this sense, among M(II) metallated phthalocyanines, ruthenium(II) phthalocyanines have received particular attention due to their strong tendency to coordinate axial ligands.[53,54] This particular feature has been exploited by Hanack and co-workers for the synthesis of the so-called 'shish-kebab' polymers, in which the ruthenium Pc are linked together through bidentate ligands such as unsubstituted and substituted *p*-diisocyanobenzenes (**Figure 1.3**).[55-57]

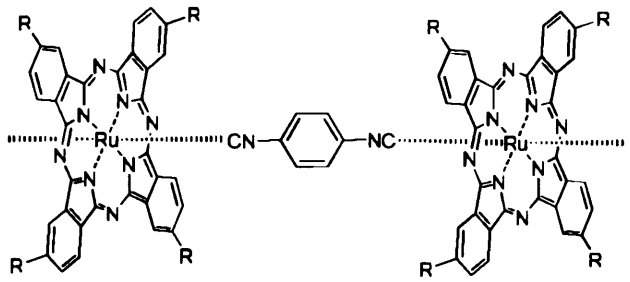
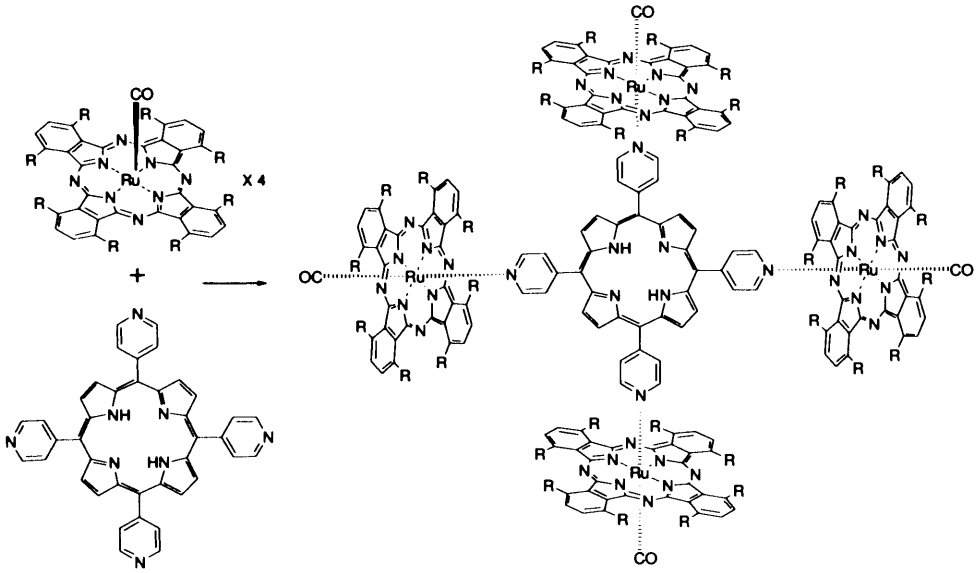


Figure 1.3 Phthalocyaninatoruthenium 'shish-kebab' complex.

The level of synthetic control possible in these ruthenium Pcs permits their exploitation as useful building-blocks in supramolecular chemistry. An interesting example of a supramolecular array in which coordination to the ruthenium ions in the centre of the Pc cavity of an octasubstituted-phthalocyanine allow four Pc molecules to be assembled around a tetrakis(4-pyridyl)porphyrin has been reported by Cammidge, Cook and co-workers[53] (**Scheme 1.3**). Due to the presence of complementary red and violet absorbing chromophoric units these kinds of arrays are not only interesting from a synthetic point of view but could find applications in optical devices and as light harvesters.



Scheme 1.3 Supramolecular assembly of porphyrins and phthalocyanine molecules through pyridine-ruthenium axial ligand coordination.

1.5 Porphyrins and Phthalocyanines in catalysis as mimics of cytochrome P-450

1.5.1 Cytochrome P-450

Cytochrome P-450 belongs to the group of ubiquitous enzymes known as monooxygenases, which catalyze the oxidation of many organic substrates by incorporating an oxygen atom from molecular oxygen into the substrates, with the other being converted into water. The electrons necessary for these reactions come from the oxidation of NAPDH via electron transfer proteins, such as cytochrome P-450 reductase, which are coupled to the cytochrome P-450. These enzymes play a key role in the removal of foreign compounds in the body.[58,59]

The active site of the enzyme contains a Fe(III) protoporphyrin IX to which a cysteinate ligand essential for catalytic activity is axially coordinated.[60] It seems that thiol ligand is not only responsible for the remarkable red shift of the heme absorption band from 420 to 450 nm upon CO complexation to the reduced enzyme, from which cytochrome P450 takes its name, but enhances the rate of the O-O cleavage in the catalytic process and promotes the heterolytic splitting of the molecular oxygen as well.[59]

1.5.2 Porphyrins as mimic models of cytochrome P-450

Synthetic iron porphyrin complexes have been extensively[59,61,62] investigated as models for the catalytic action of cytochrome P-450.[63] Starting in 1975, many synthetic model systems that mimic the activity and selectivity of the natural enzyme have been developed with the dual purpose of understanding the structure and mechanistic behaviour of the iron complexes involved in the P-450 and to develop metalloporphyrin catalytic systems that could be active in typical P-450 reactions such as hydroxylation of alkanes, the epoxidation of alkenes , N-, S-, and O-oxidative dealkylations, sulfoxidations etc.[58]

In general, it has been found that the combination of molecular oxygen and a cofactor in the enzyme is complex and not easily reproducible *in vitro,* and furthermore the reducing agent can compete with the substrate for the active oxidant. This problem has been addressed by using 'single oxygen donors', *e.g.* sodium periodate, iodosobenzene,

hypochlorite, hydrogen peroxide, peroxy acids and *tert*-butyl hydroperoxide.[64-68] Another problem encountered in model systems is the instability of thiol-ligated metal-oxo complexes, which has led to the use of simple iron(III) porphyrins with a halide axial ligand and/or porphryrin systems with imidazole or pyridine ligands.

The first model systems with nitrogen base ligands were simple functional iron porphyrins, in which bulky groups were inserted in order to avoid the dimerization with free heme, and porphyrin ligand oxidation. In order to avoid binding of the nitrogen ligands in both positions, which would inhibit the binding of the molecular oxygen or the single oxygen donor, models using capped porphyrins were developed.[69]

More recently, model systems have focused on the development of functionalised porphyrins for regio- and stereoselective oxidation reactions.[70,71] In this context an interesting example is represented by the metal-porphyrin model developed by Elemans and coworkers,[72] in which the metal porphyrin is appended with a diphenylglycoluril-based cavity, which effectively shields one side of the porphyrin plane (**Figure 1.4**). The cavity is capable of binding N-containing axial ligands very strongly as the result of a combination of metal–ligand coordination and cavity-filling effects, so that only one equivalent of ligand is required to achieve an essentially complete occupation of the manganese metal. This is reflected in a high activity in the catalytic epoxidation of olefins by this system which is furthermore more stereoselective in the epoxidation of, for example, *cis*-stilbene into *cis*-stilbene oxide than normal *meso*-substituted porphyrins catalytic systems. This could be interpreted in terms of the strong coordination of the axial ligand, which pulls the metal centre into the plane of the porphyrin prohibiting the rotation of the C–C bond of the *cis*-stilbene substrate coordinated to the other face of the porphyrin in the transition state.

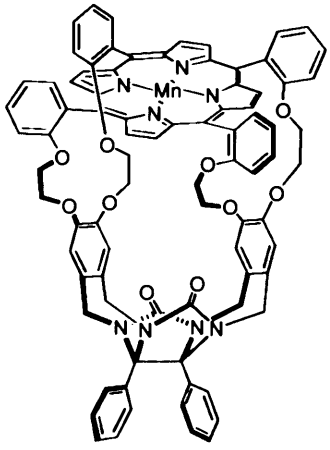


Figure 1.4 Diphenylglycoluril-based cavity Mn porphyrin.

Other interesting Cytochrome P-450 mimics are the ones that contain a porphyrin attached to a cavitand like a cyclodextrin or a cyclophane. For example, Fang and Breslow[73,74] have described hydroxylations of steroids directed by geometric control, in complexes of the substrates with cytochrome P-450 mimics based on manganese porphyrins carrying cyclodextrin binding groups.

In their initial attempts, they used as catalyst **TPhcyDP1** (**Figure 1.5**) which binds and hydroxylates the steroid substrate, which contains two ester groups attached at C-3 and C-17, in water with iodosobenzene as the oxidant. The product was exclusively the 6α hydroxy of the diester steroid, which was not further oxidized to ketone because of the inaccessibility of the product 6β hydrogen in the complex. However, the turnover of the catalyst was small before it was oxidatively destroyed. The catalyst was improved by fluorinating the *meso* phenyl substituents **TPFcyDP4** , which stabilizes the catalyst against oxidative destruction and improved significantly the turnover before the catalyst was oxidatively destroyed[75](**Figure 1.5**).

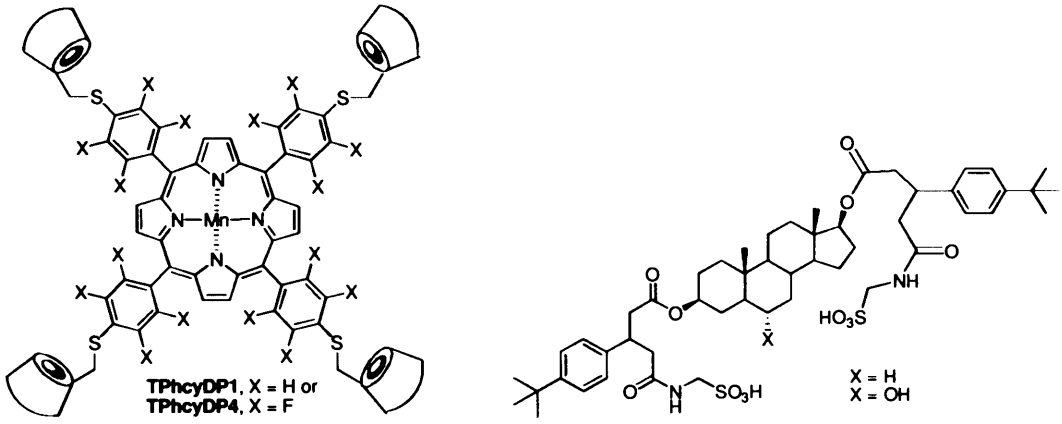


Figure 1.5 Cyclodextrin substituted porphyrin catalysts.

They also showed that using the perfluorinated **TPFcyDP4** with thiol ligands bridging two of the four cyclodextrins at the opposite sides of the porphyrin, the substrate oxidation could be achieved even with hydrogen peroxide, which did not work with the previous two catalysts.

An interesting aspect of cytochrome P-450 is the fact that it is a membrane-bound enzyme, and that phospholipids stimulate the transfer of electrons to the isolated enzyme and enhance its affinity for the substrate. This has inspired the preparation of some cytochrome P-450 mimics in which a hydrophobic porphyrin is incorporated in the bilayer

of a vesicle membrane,[76] or encapsulated within dendrimers,[77] mainly employed to study the effect of site isolation.

Furthermore, the immobilisation of metalloporphyrin catalysts onto solid supports could lead to their commercial application. This strategy could make possible the separation and the reuse of the catalyst from the products and enhance the catalyst stability toward oxidative decomposition through site isolation. An interesting example is the one reported by Che and co-workers,[78] who prepared polymer supported catalytic systems employing simple porphyrinato ligands, which showed high stability and versatility, and which efficiently and diasteoselectively catalyse alkenes epoxydation reactions. In their first attempts they immobilised two ruthenium porphyrins onto a surface-modified mesoporous molecular sieve (MCM-41) to form the heterogenized catalysts **P1Ru-H_2N-MCM-41** and **P2Ru-H_2N-MCM-41** (**Figure 1.6**) and examined their catalytic behaviour toward alkene epoxidation.[79,80]

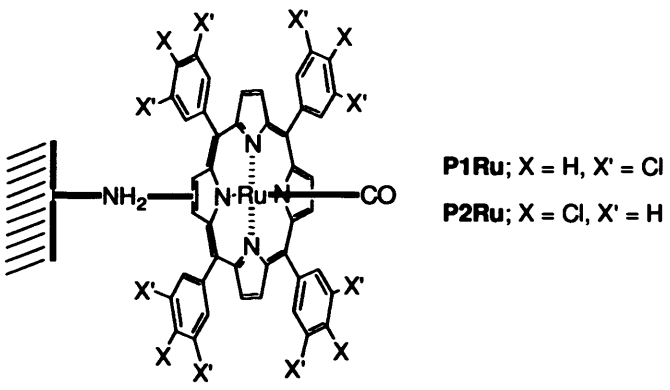
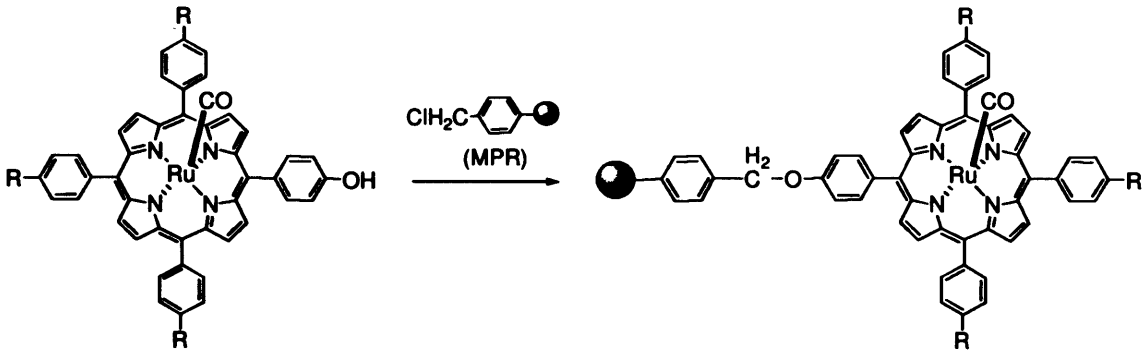


Figure 1.6. Schematic structures of Ruthenium porphyrins. a) coordinatively grafted onto the surface modified MCM-41 .

P2Ru-NH_2-MCM-41, was highly efficient and selective in alkene epoxidations by C 2,6-dichloropyridine *N*-oxide,[80] but subsequent reuse experiments showed significant catalyst leaching and/or deactivation. As an alternative approach, ruthenium porphyrins were covalently attached to Merrifield's peptide resin (MPR), a chloromethylated styrene-divinylbenzene copolymer, which swells greatly in certain organic solvents and allows the metalloporphyrins to be attached not only at the surface of the polymer bead but also within its interior. Two asymmetrically substituted *meso*-tetraarylporphyrin-5,10,15-tris(4-R-phenyl)-20-(4-hydroxyphenyl)porphyrins (R = Cl or Me) were attached to the resin by

treating the complexes with MPR in DMF at 80 °C for 4 h in the presence of anhydrous potassium carbonate (**Scheme 1.4**).



Scheme1.4. Ruthenium porphyrins covalently immobilized onto Merrifield's peptide resin.

Preliminary experiments revealed their efficiency, stability and recyclability as catalysts for epoxidation with 2,6-dichloropyridine *N*-oxide for a wide variety of alkenes, with high number of turnovers.

Numerous other heterogenous metalloporphyrins catalytic systems, especially with iron and manganese porphyrins[81,82] have been reported in the literature. In some cases new hybrid organic-inorganic materials have been developed, such as the so-called porphyrinosilicas developed by Battioni and co-workers.[83]

1.5.3 Phthalocyanines as mimic models of cytochrome P-450

Metallophthalocyanines have been studied as catalysts due to their structural similarities to the porphyrins, although less extensively. They offer some advantages over porphyrins because they are more easily synthesised, more stable to degradation and, furthermore are readily accessible on an industrial scale.[84] Indeed, Pcs are already used as industrial catalysts in the Merox process, in which mercaptans are removed from petroleum via their oxidation to disulfides.[85-87]

Metal-containing Pcs, like porphyrins, have been shown to exhibit good biomimetic catalytic activity which is enhanced by ring substitution with electronegative substituents or in particular cases, such in the oxidation of cyclohexane, when supported derivatives are required.[63] Incorporation into heterogeneous systems may allow easier recovery and recycling as well as reduce the degradation of the catalyst. Many examples in which they

have been encapsulated in zeolites,[88,89] immobilized in mesoporous materials[90] and supported on polymers[91] are reported in the literature.

Impressive results were obtained by Parton *et al.*, who reported[92] a catalytic system that achieves similar performances to the P-450 enzyme and with a turnover rate that makes the system industrially viable. The catalyst is based on iron phthalocyanine complexes encapsulated in crystals of zeolite Y (**FePcY**), synthesised within the pores using a version of the metallocene method.[93] The zeolite encapsulated Pc was then immobilised in a polydimethyl siloxane (PMDS) membrane. The polymer acts as mimic of the phospholipid membrane in which the cytochrome P-450 resides acting as interface between two immiscible phases avoiding the need of phase transfer (**Figure 1.7**). The system revealed to oxidize alkanes at room temperature at rates that proved comparable to the one exerted by the enzyme.

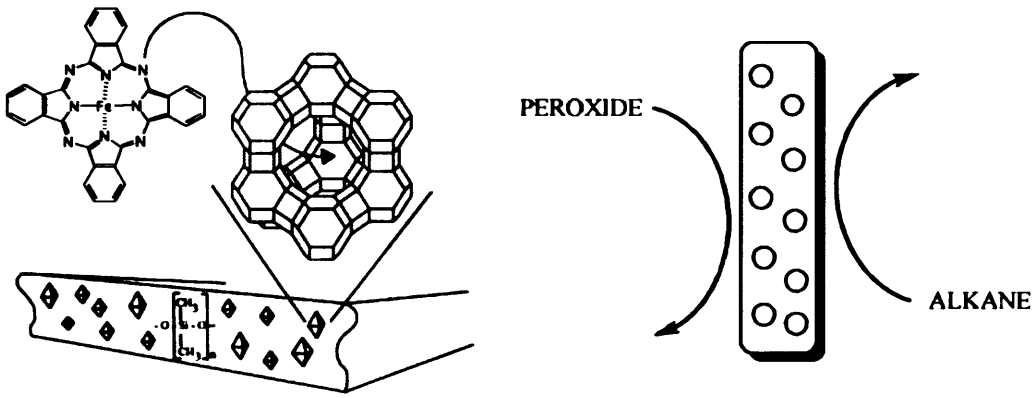


Figure1.7. Schematic representation of the incorporation of **PcFe** complex in the supercages of zeolite Y and subsequent incorporation of these zeolite crystals in the PDMS-membrane.

This system proved to be a big improvement compared to heterogeneous mimics of the enzyme previously designed in which organometallic complexes were encapsulated in zeolites supercages,[94] which did not show the same mechanism as the enzymatic process of the cytochrome P-450 and had low oxidation rate.

In other work Parton *et al.*[95] tested carbon black as a support for iron phthalocyanine in alkane oxidation with *t*-butylhydroperoxide, showing that there is a relation between the polarity of the carrier surface and the activity of the heterogeneous complex. In this case the iron phthalocyanine complexes were adsorbed onto the carbon black, which had been demonstrated to have a macroporous structure by previous characterisation. In direct

comparisons between carbon black and zeolite Y as support materials for **PcFe**, the first system showed a better conversion rate in the oxidation reaction of cyclohexane. This was attributed to improved alkane absorption on carbon due to its high hydrophobicity. The major problem with this system was the catalyst leaching from the support, which led to oxidative degradation of the complex and a drop in activity after regeneration.

1.6 Microporous organic materials

In the last few years there has been growing interest in the preparation of organic nanoporous materials. Such organic-based materials are expected to allow the introduction of specific molecular recognition or catalytic sites for their potential exploitation in adsorption, separations and heterogeneous catalysis.[96]

Organic compounds, especially those with rigid molecular structures can crystallise forming clathrates, from which the loss of the included solvent could form a nanoporous solid, but, in general, the removal of the solvent causes loss of crystalline order.[97] Nevertheless, quite recently remarkable crystals from organic–inorganic hybrid materials, in which rigid and extended organic components are linked together by coordination to metal ions, the so called metal organic frameworks (MOFs)[98] have been shown to survive the removal of the included solvent to give highly microporous materials.[99]

Numerous crystalline porphyrin-based clathrates[100,101] and nanoporous coordination polymers[102-104] have been reported and some of these are stable to the removal of the crystallisation solvent.[105,106] In contrast, there are few reports of phthalocyanine-based clathrates in the literature, perhaps due to the strong tendency of Pcs to form densely packed cofacial aggregates, owing to their extended planar shape. It is clear that cofacial self-association needs to be prohibited in order to obtain open nanoporous structure that will allow access of reagent to the metal cation to facilitate catalysis.

1.6.1 Metal-organic frameworks

Metal–organic frameworks (MOFs), extensively developed by Yaghi and co-workers, are crystalline solids that are assembled by the connection of metal ions or clusters through molecular (i.e. organic) bridges.[107] They are widely considered as

promising materials for applications[108] in catalysis, separation, gas storage and molecular recognition. Compared to conventional microporous materials such as zeolites and activated carbons, these organic structures offer the possibility for more flexible rational design. Yaghi and co-workers have named reticular chemistry "the process of assembling judiciously designed rigid molecular building blocks into predetermined ordered structures (networks), which are held together by strong bonding".[109] They have largely used the carboxylate functionality to chelate metal ions in order to lock them into rigid and therefore directional metal–oxygen–carbon clusters creating geometrical shapes defined as secondary building units (SBUs).[110] The same approach has led to the synthesis and the use of numerous inorganic and organic SBUs with different geometries. By reticulating these units into extended networks, porous structures with various pore size and functionality have been prepared.[110-112]

An outstanding example by Yaghi is **MOF-5**,[113] in which units containing four ZnO_4 tetrahedra with a common vertex and six carboxylate C atoms, belonging to benzenedicarboxylate molecules, are joined together by benzene links to form a cubic network, in which the vertices are the octahedral subunits and the edges are the benzene molecules (**Figure 1.8**).

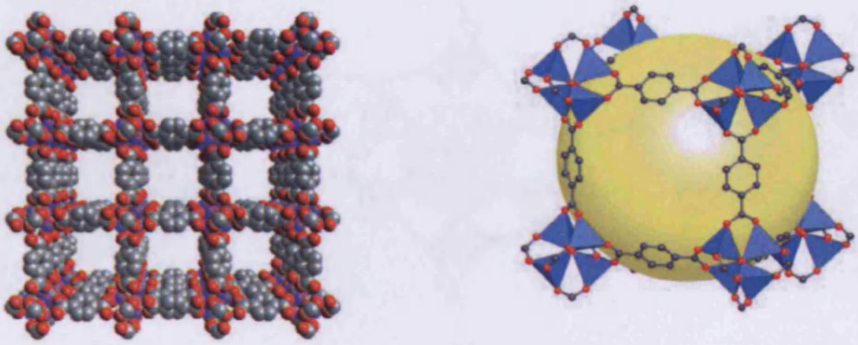


Figure 1.8. MOF-5 X-ray single crystal structure. The yellow sphere represents the size of the largest sphere that would occupy the cavity without contacting the interior van der Waals surface.

MOF-5 cubic crystals were obtained by the slow diffusion of triethylamine into a solution of zinc (II) nitrate and benzenedicarboxylic acid in DMF/chlorobenzene that led to deprotonation of the dicarboxylic acid and its consequent reaction with Zn^{2+}. A small amount of hydrogen peroxide was added to the reaction in order to provide the O^{2-} at the centre of the secondary building unit. The elemental analysis of the cubic crystals so

obtained suggested that the formula was $Zn_4O(BDC).3(DMF)8(C_6H_5Cl)$ and the presence of the solvents was confirmed by solid-state ^{13}C NMR.

The framework atoms in **MOF-5** occupy a small fraction of the available space in the crystal and if overlapping spheres with van der Waals radii are placed at the atomic positions, the unoccupied space results in the 80% of the total volume. In practice, it was shown that 55-61% of the space was available to the guest species. The guest molecules could be completely exchanged with chloroform and the latter could be evacuated without loss of crystallinity. The stability of the desolvated crystals was confirmed by their X-ray analysis after heating them in air at 300 °C for 24h. The density (0.59 g cm^{-3}) of desolvated crystals was among the lowest recorded for any crystalline material.

Using different inorganic and organic SBUs they were able to produce various crystalline MOFs and MOPs (metal-organic polyhedra)[111,114] for which cavities were occupied by solvent molecules (some examples in **Figure 1.9**). In many cases it was demonstrated that the crystals were stable upon removal of the guest species and their porosity was attested by measurement of gas adsorption isotherms. In some case they showed very high surface areas (4500 m^2g^{-1} for **MOF-177**) (**Figure 1.9 b**) a property which gives them potential as materials for hydrogen storage.[114]

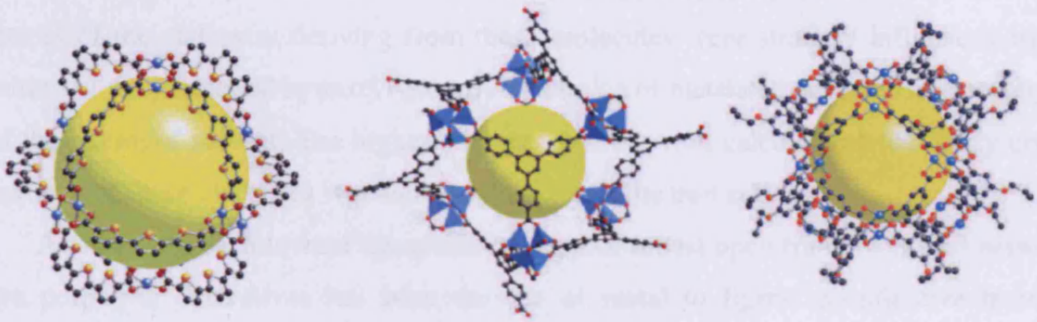


Figure 1.9. Ball and stick model of **MOP-28**, **MOF-177** and **MOP-17** with yellow sphere showing the internal cavity.

1.6.2 Porphyrin clathrates

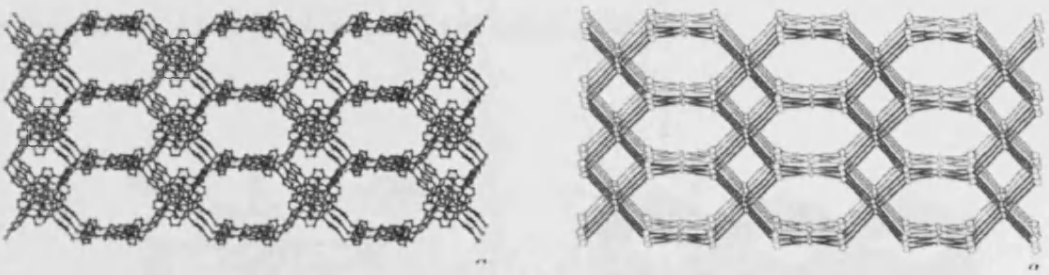
Porphyrins represent ideal building blocks for functional supramolecular materials,[115] due to their extended planar shape, the possible functionalisation at different sites, and their well established catalytic activity. Hence, numerous *meso*-substituted porphyrins have been studied as possible components for the design of nanoporous materials.

Strouse and co-workers[116] examined the crystal structure of a large number of porphyrin clathrates in which the predominant intermolecular bonding interactions were weak van der Waals forces. All these clathrates showed similar structural features with a recurrent planar packing due the interaction between the meso-phenyl groups on adjacent tetraphenylporphyrins. Unfortunately, none of these crystals survived the removal of the solvent.

Goldberg and co-workers have tried to obtain more robust frameworks introducing different substituents[117] onto the *meso*-phenyl subunits to provide new dipole-dipole interactions and hydrogen bonding. However, only a modest stabilisation of the solids was observed once the included solvent was removed.[118]

Suslick and coworkers explored supramolecular networks based on hydrogen bonding between *ortho* and *meta*-tetrakis(dihydroxyphenyl)porphyrins.[119] The structural features of the clathrates deriving from these molecules were strongly influenced by the position of the peripheral hydroxyl groups, the choice of metalated or metal-free porphyrin, and the nature of solvate. The highest channel volume void calculated from X-ray crystal structures of these clathrates was equal to the 67% of the unit cell.

Another approach toward the synthesis of more robust open framework and networks from porphyrin derivatives has been the use of metal to ligand coordinative bonding. Interesting examples prepared by Robson and co-workers[102] are three-dimensional network solids formed by copper complexes of 5,10,15,20-tetra-4'-pyridylporphyrin, **Cu(TPyP)**, and 5,10,15,20-tetra-4'-cyanophenylporphyrin, **Cu(T(*p*-CN)PP)**. For **Cu(TpyP)** a framework **$((Cu(II)(TPyP)Cu(I))^{n+}$** which occupied less than a half the volume of the crystal was obtained (**Figure 1.10 a**), with solvent molecules and anions occupying the remaining space. For **Cu(T(*p*-CN)PP)** two independent but interpenetrating **$((Cu(II)(T(p\text{-}CN)PP)Cu(I)_n)^{n+}$** frameworks were present (**Figure 1.10 b**). Even in this case the channels were occupied by solvent molecules and anions. However, both frameworks did not survive the removal of the solvent.[102]



a) b)

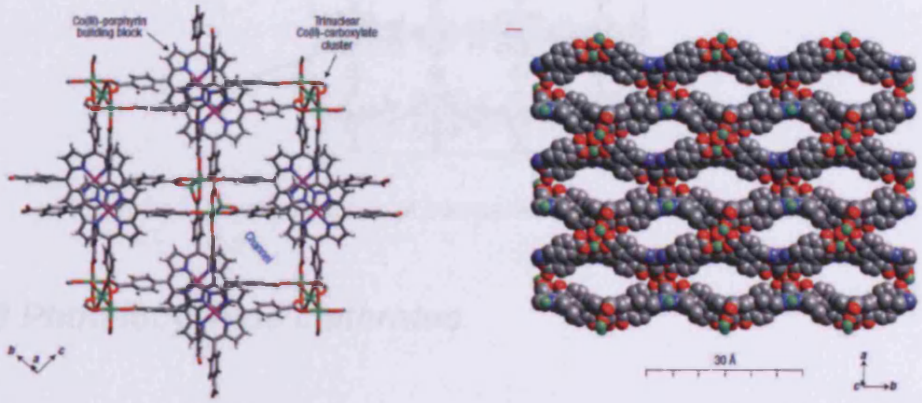
Figure 1.10. Extended structure of a) the $((Cu(II)(tpp)Cu(I))^{n+}$ framework and b) the two interpenetating frameworks of $((Cu(II)(tcp)Cu(I)_n)^n$.

A similar approach was used to prepare a three dimensional coordination polymer from **Zn(II)(TpyP)**, by coordinative bonding of the central zinc by the *meso*-pyridine substituents, forming a porous material with ~0.6 nm wide channels with a quite high thermal stability. Identical frameworks were obtained from **Co(II)(TpyP)** and **Mn(II)(TpyP)**.[120]

A layered framework with large cavities obtained from both **Co(II)(TpyP)** and **Mn(II)(TpyP)** was reported by Lin.[121] Each metal centre is octahedrally coordinated by four nitrogen atoms of the porphyrin and two nitrogen atoms of the *trans* pyridyl groups of the TpyP. The structure presents a hexameric cage which results in an infinite hexagonal channel along the crystallographic c axis, owing to the π-π interactions between the porphyrins molecules. The porous structure was stable to the removal of the included solvent.

Goldberg and co-workers[105] have also reported the formation of three-dimensional supramolecular architectures based on coordinative bonding and cooperative intermolecular (O–H...OH and O–H...N) hydrogen bonding from the reaction of meso-(4-hydroxyphenyl)porphyrinato zinc and various bipyridyl derivatives. In this case the supramolecular arrangement is affected by the competition between the two kinds of interactions along with the different length and functionality of the bipyridyl ligands. In addition, interesting structures have been obtained by using *meso*-(carboxypheny)porphyrins as building blocks. Suslik and co-workers reported[104] the synthesis of a functional microporous material, closely related to a MOF, based on the supramolecular assembly of carboxylate-substituted porphyrins with cobalt ions. The

compound, named **PIZA-1** (**Figure 1.11**), was prepared solvothermally by heating a mixture of metal free porphyrin acid and cobalt chloride.



a) b)

Figure 1.11. **PIZA-1** network a) structure along the ***a*** axis. b) Space filling view along b or ***c*** axes.

By single crystal x-ray diffraction it was found that the distorted porphyrin derivatives (with the pyrrole rings alternatively displaced above and below the porphyrin plane) are connected by bridging trinuclear Co(II)- carboxylate clusters to form a neutral network with oval-shaped channels (9 x 7 Å) along the crystallographic **b** and **c** axes and another set of large (14 x 7 Å) channels along **a.** Crystallographic analysis showed the presence of fifty six pyridine molecules per unit cell (12 coordinated ligands and 44 disordered solvate guests). The void volume of the solvate-free material was calculated to be 74 % of the unit cell volume. The clathrate was stable to the removal of the solvent as showed by powder X-ray diffraction studies on the solvate-filled and evacuated framework solids. Its stability was also confirmed by nitrogen absorption studies.

Suslik and co-workers[103] have also reported the synthesis of Zn_4O framework with zinc-(II) *trans*-biscarboxylate-tetraarylporphyrin bridges (named **PIZA-4**). The X-ray analysis showed an interpenetrated three-dimensional framework of zinc *trans*-biscarboxylate tetraarylporphyrins whose carboxylates coordinate the six edges of tetrahedral Zn_4O^{6+} clusters (**Figure 1.12**). Even in this case, the structure demonstrated stability to the removal of the solvent.

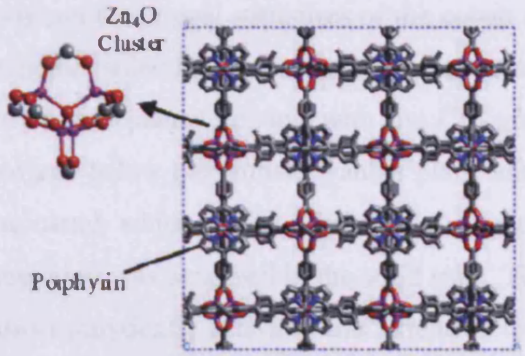


Figure 1.12. Crystal structure of interpenetrated **PIZA-4** along the cubic axis.

1.6.3 Phthalocyanine clathrates

Phthalocyanines have been less investigated than porphyrins as possible building units of nanoporous solid materials, although some benefits would be gained from their use. They are more resistant to chemical and oxidative degradation and possess a major advantage in that, unlike porphyrins, they are made routinely in large scale by industry.

There are several hundred Pc XRD crystal structures in Cambridge Structural Database (CSD).[122] However, up to now, only few examples of clathrates formed by phthalocyanine derivatives are reported in the literature. Gorun *et al.*[123] reported the synthesis of a perfluorinated metal free phthalocyanine with peripheral perfluoro-isopropyl substituents (**$F_{64}PcH_2$**) that form crystals containing fluorine lined channels which accounted for ~39% of the unit cell volume and were occupied by acetone molecules (**Figure 1.13**). The phthalocyanine ring exhibited a dome-like distortion which is normally observed for metallated phthalocyanines with large metal ions such as Pb^{2+}. The interplanar distance was quite short indicating a strong aggregation between the molecules.

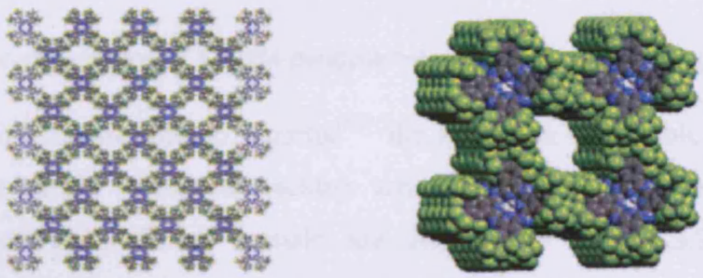


Figure 1.13. Packing arrangement of **$F_{64}PcH_2$** along the ***c*** axis.

The synthesis and the crystal structures of the cobalt and zinc derivatives of the same perfluorinated phthalocyanine had been previously reported.[124,125] For both complexes, an X-ray structure reveals a planar Pc ring with the CF_3 groups of the perfluoro-isopropyl substituents above and below the phthalocyanine plane and two acetone molecules axially coordinated to the metal, which impart a biconcave character to the complex. In this case no strong π-π interaction was observed in the solid state. They demonstrated that the cobalt derivative was also catalytically active in the oxidative formation of carbon phosphorous double bond.

More recently Zeng and co-workers reported the synthesis and characterisation of supramolecular complexes obtained from the reaction of PcZn with different bipyridyl ligands,[126] whose conformations played an important role in the molecular arrangement in the crystals. They obtained crystals with some included molecules for three supramolecular complexes. In two of them two PcZn molecules were linked by 1,2-bis(4-pyridyl)ethane, 1,2-di(4-pyridyl)ethylene (**Figure 1.14**) respectively to form a H shape complex. In the third, where 1,3-di(4-pyridyl)-propane was used as axial ligand, only one of the nitrogen atoms of the bipyridyl coordinated the Zn forming a T shape complex. In all three complexes the molecules seem to pack quite efficiently and no presence of significant free volume or other molecules was indicated.

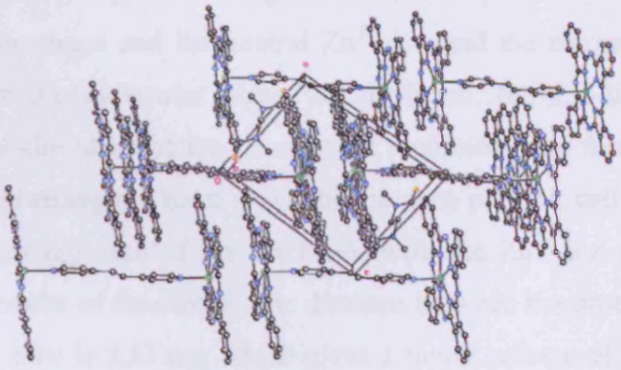
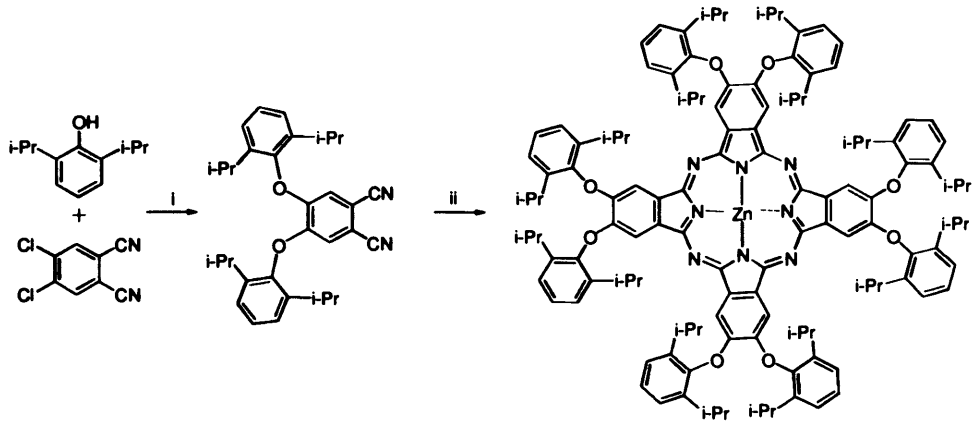


Figure 1.14. The crystal-packing of 1,2-di(4-pyridyl)ethylene **PcZn** complex along the ***b*** axis.

Recently, our research group reported[127] the formation of a cubic clathrate crystal with a very interesting molecular packing arrangement that provides interconnected solvent-filled nanovoids. These crystals are formed by zinc 2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyanine (**Pc1Zn**), which was prepared via metal template cyclotetramerisation of the preformed phthalonitrile obtained from the reaction of

4,5-dichlorophthalonitrile and 2,6-di-*iso*-propylphenol (**Scheme 1.5**).[20] This phthalocyanine derivative was originally designed to avoid cofacial self-association by the introduction of substitutents (2,6-di-*iso*-propylphenoxy groups) that cause severe steric crowding adjacent to the phthalocyanine core.[46]



Scheme 1.5. The synthesis of **Pc1Zn**. *Reagents and conditions*: i) K_2CO_3, DMF, 70 °C; ii) $Zn(OAc)_2$, NMP, 150 °C.

Single crystal X-ray analysis found a remarkable crystal structure, with 12 phthalocyanine molecules in the cubic unit cell (a=3.77 nm), which belongs to the exceptionally rare space group *Pn-3n* (**Figure 1.15**). The phthalocyanine core of **Pc1Zn** adopts a shallow cone-shape and the central Zn^{2+} ion and the oxygen atom of its axial ligand protrude from the molecular plane. As predicted, the 2,6-di-*iso*-propylphenoxy substituents lie out of the plane of the macrocycle prohibiting the formation of columnar stacks. The molecules arrange to form two cubic cavities per unit cell with a molecule of phthalocyanine comprising each of the six faces, with the Zn^{2+} ion and its axial ligand pointing toward the centre of the cavity. The distance between the protruding Zn^{2+} ions on opposite sides of the cube is 2.33 nm, which gives a cavity volume of at least 8 nm^3, even if the width, calculated from the sum of the van der Waals radii, of the phthalocyanine unit (0.33 nm) is taken into account.

By X-ray analysis, other than 24 water molecules per unit cell which seems to be associated through hydrogen-bonding interactions to the *meso* nitrogen atoms of the phthalocyanine ring, no further solvent could be located within the crystal structure. The solvent-accessible void was calculated to be 38.2% of the total volume. Thermogravimetric analysis (TGA) showed a mass loss of 25.5% on heating up to 120 °C, for which the water of solvation observed in the crystal structure could account for only 1.6%.

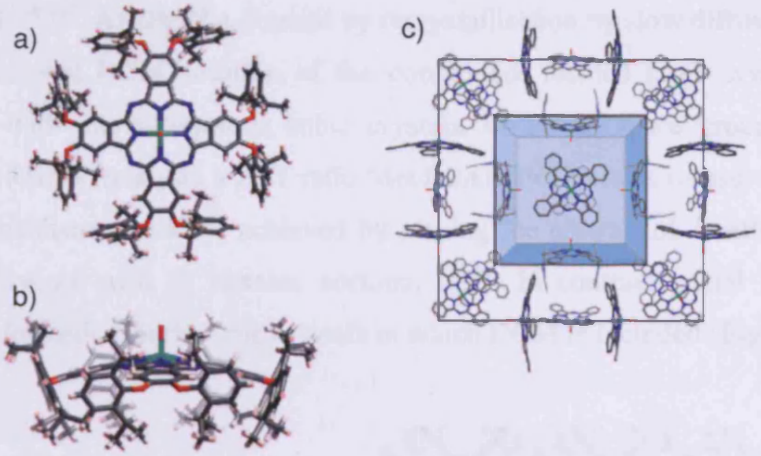


Figure 1.15. The molecular and crystal structure of **Pc1Zn**. a) Face-on and b) edge-on molecular views c) The cubic packing arrangement of **Pc1Zn,** the phenoxy substituents have been removed for clarity. The outer cube represents the unit cell, the inner cube represents one of the two voids of volume 8 nm^3 found in each unit cell, and the second nanovoid is distributed at each corner of the unit cell in 8 x1 nm^3 portions

The additional mass loss could be attributed to included disordered solvent of recrystallisation which was estimated to be present approximately in the ratio 1/11, Pc/acetone. This value was confirmed by ^{1}H NMR spectroscopic analysis of dissolved crystals. X-ray analysis showed that the crystal was not stable to the removal of the included solvent although no change in the macroscopic appearance was observed.

The void space appears almost fully enclosed by the six phthalocyanine units, but narrow cylindrical channels (~0.4 nm in diameter) that connect the voids are situated at each corner of the cubic arrangement. The interconnectivity of the voids was demonstrated by solvent exchange experiments, followed by ^{1}H NMR analysis which showed that the included solvent was readily exchanged by acetone-d_6, MeOH and water. Subsequent X-ray analysis showed that the solvent exchange does not affect the basic crystal structure.

Based on these results it was envisaged to prepare similar clathrates by inserting catalytically active metals within the phthalocyanine to allow for exploitation in heterogeneous catalysis. Furthermore, it was hoped that the insertion of substituents in the 2,6-diisopropyl units would stabilise the structure.

More recently the synthesis and formation of clathrates from the analogous 2,3,9,10,16,17,23,24-octa(2,6-di-*iso*-propyl-phenoxy)-1,4,8,11,15,18,22,25-octaazaphthalocyanine (**AzaPc1**; M = H_2, Ni, Zn) and also 2,3,9,10,16,17,23,24-octa(2,6-diphenylphenoxy)-1,4,8,11,15,18,22,25-octaazaphthalocyanine (**AzaPc2**; M = H_2, Ni, Zn)

were reported.[128,129] **AzaPc1Zn**, formed by recrystallisation by slow diffusion of methanol into a concentrated DCM solution of the compound, formed large crystals which are isomorphous with the nanoporous cubic crystals, of *Pn-3n* space group, derived from **Pc1Zn**. By ^{1}H NMR analysis a 20/1 ratio MeOH/**AzaPc1Zn** was measured. Exchange of the included methanol could be achieved by placing the crystals of **AzaPc1Zn** in contact with other solvents such as hexane, acetone, H_2O. In contrast, metal free and nickel **AzaPc1** both formed orthorhombic crystals in which DCM is included (**Figure 1.16**).

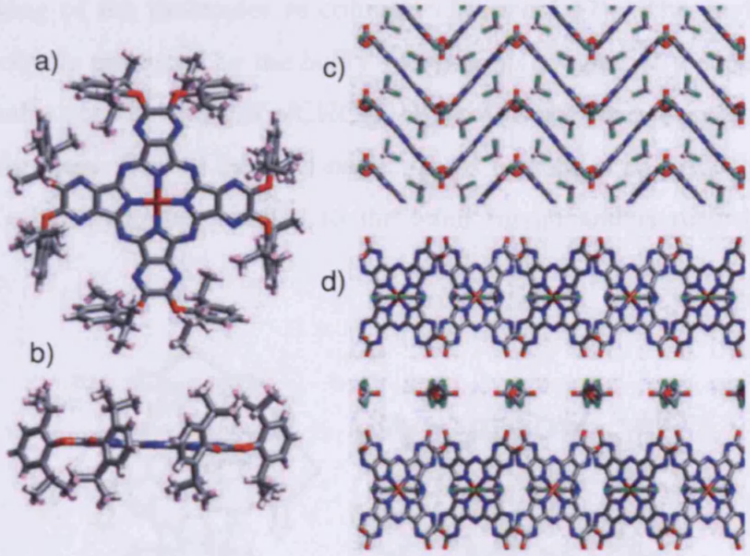


Figure 1.16 The molecular and crystal structure of **AzaPc1** (M = Ni). a) Face-on and b) side views. c) A view of the herrringbone arrangement of the macrocycles looking down the ***x*** axis of the crystal. d) A view along the ***z*** axis of the crystal showing the disordered solvent (DCM, acetone and H_2O) the 2,6-di-iso-propylphenoxyl groups are not shown in for clarity c) and d).

The **AzaPc** cores are planar with the phenoxy substituents disposed almost perpendicular to the plane of the **AzaPc** prohibiting cofacial self-association of the AzaPc and providing a cavity above and below the macrocycle. The molecules adopt a planar packing structure in which the **AzaPc** cores form a herringbone structure with the 2,6-di-*iso*-propylphenoxy groups of one molecule placed within the cavity of its neighbour. In the metal free **AzaPc1** crystals, four solvent molecules of DCM for each AzaPc molecule are present, two of which are weakly hydrogen-bonded to the benzo-nitrogens of the **AzaPc** and placed mid-way within the plane of the herringbone arrangement, instead the

other two DCM molecules are highly disordered and lie in between these planes (**Figure 1.16 c**). Within the isomorphous crystal structure derived from **AzaPc1Ni**, the included guest is composed of a disordered mixture of DCM, acetone and water.

For the **AzaPc2** derivatives only the zinc-containing derivative gave suitable crystals for X-ray analysis. The crystals are of tetragonal symmetry, of *P-42$_1$c* spacegroup, where the macrocycle is slightly twisted from planarity and the phenyl groups of the eight 2,6-diphenylphenoxy substituents lie out of the plane of the macrocycle assuming a configuration which gives the whole molecule a square shape, which in turn leads to tetrahedral packing of the molecules in columns (**Figure 1.17**). The cavities above and below the macrocycle produced by the bulky substituents are partially occupied by $CHCl_3$ and H_2O molecules (1/2/2 **AzaPc2Zn**/$CHCl_3$/ H_2O) with the former hydrogen bonded to the four *meso*-nitrogens. One of the H_2O molecules is present as an axial ligand on the Zn cation and the other hydrogen bonded to the axial ligand and is disordered over four equivalent sites.

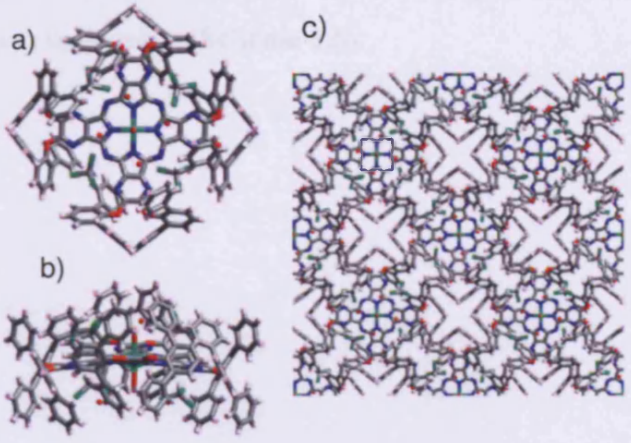


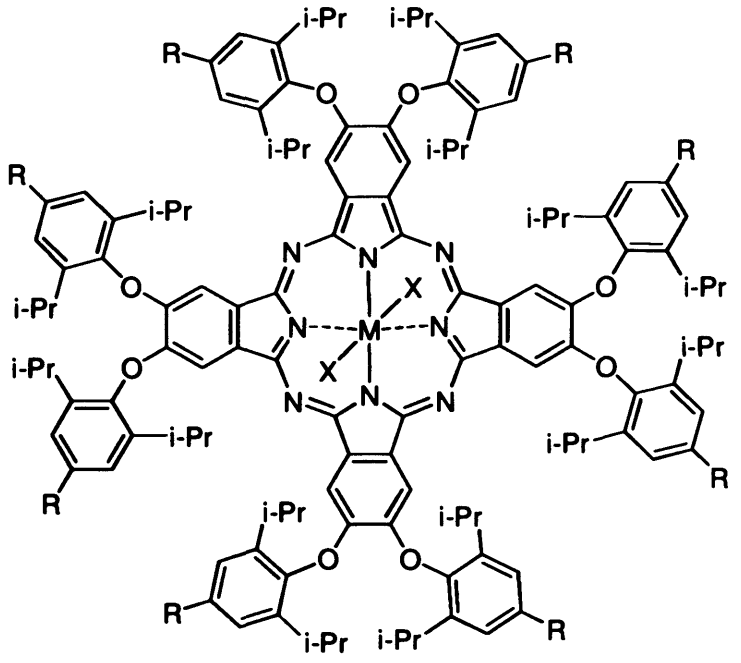
Figure 1.17. The molecular and crystal structure of **AzaPc2-Zn**. a) Face-on and b) side views of the molecule. c) A view of the tetragonal arrangement of the macrocycles looking down the ***z*** axis of the crystal.

It can be concluded that placing eight bulky phenoxyl substituents at the periphery of **Pcs** or **AzaPc** proved successful in prohibiting self-association of the macrocycle, so that efficient packing of the molecules in the crystalline state is only achieved by the inclusion of solvent molecules.

1.7 Aims and objectives

The remarkable crystal structure containing 8 nm^3 cubic voids, interconnected by narrow channels, formed from zinc 2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy) phthalocyanine (**PcIZn**) suggested the possibility of applications in heterogeneous catalysis. Since up to 70 elemental ions can be placed within the central cavity of the phthalocyanine macrocycle, our first aim was to synthesise novel metal derivatives of **PcI**, especially with metals of primary catalytic relevance such as iron, manganese and ruthenium and evaluate the reproducibility of the nanoporous cubic crystal structure (**Scheme 1.6**).

Secondly, the cubic packing arrangements of **PcI** seems to be due to the van der Waals interactions between the eight interleaved phenoxy rings present at each edge of the phthalocyanine cube. Therefore, the insertion of substituents at the 4-position of the phenoxy groups, in order to enhance the stability of the crystal structure, due to stronger dipole-dipole (e.g., R = Br, Cl, CN, OMe, NO_2) or hydrogen bond interactions (e.g., R = OH, COOH, NH_2), was undertaken (**Scheme 1.6**).



M = 2H, Zn, Co, Fe, Mn, Ru, Cu, Ni, etc

R = H, Br, Cl, CN, OMe, NO_2, OH, COOH, NH_2

Scheme 1.6. Target molecules

Used nomenclature:

PcRM(X)

Pc : 2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy) phthalocyanine

R : substituent at the 4-position of the phenoxy groups, when this is a proton **R = 1**

M : central metal cation

X : axial ligands.

Chapter 2

2. Results and discussion: metal and ligand modifications

2.1. Introduction

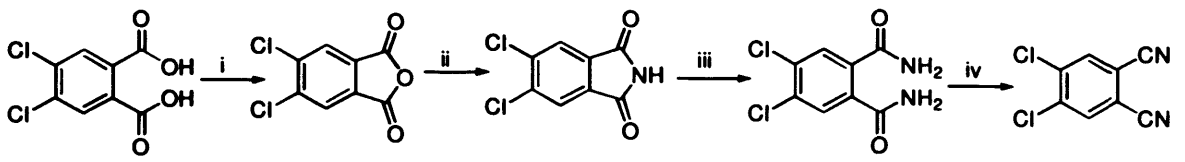
Previous experiments on the cubic crystal formed by zinc 2,3,9,10,16,17,23,24-octa-(2',6'-di-*iso*-propylphenoxy)phthalocyanine (**Pc1Zn**), such as exchange of included solvent, showed that the 8 nm^3 cubic voids present in the structure are interconnected, thus demonstrating the accessibility of the central metal ion. That suggested the possibility of exploitation of this kind of molecule for heterogeneous catalysis. In order to do so, it is necessary to introduce active metals, that possess catalytic properties such as cobalt, iron, manganese,[61,84,87] into the central cavity of the phthalocyanine macrocycle. In addition, since it is possible for phthalocyanines to form complexes with more than seventy metal ions we decided to prepare a number of metal 2,3,9,10,16,17,23,24-octa-(2',6'-di-*iso*-propylphenoxy)phthalocyanine complexes (Co, Ni, Cu, Fe, Ru, Mn, etc.) to test the generality of the cubic crystal packing.

2.2. Preparation of phthalonitrile starting material

Synthesis of octa-substituted phthalocyanines can be achieved starting from 4,5-disubstituted derivatives of 1,2-dicyanobenzene (phthalonitrile) that can be obtained by nucleophilic aromatic substitution of 4,5-dichlorophthalonitrile using different phenol or thiol compounds.[20]

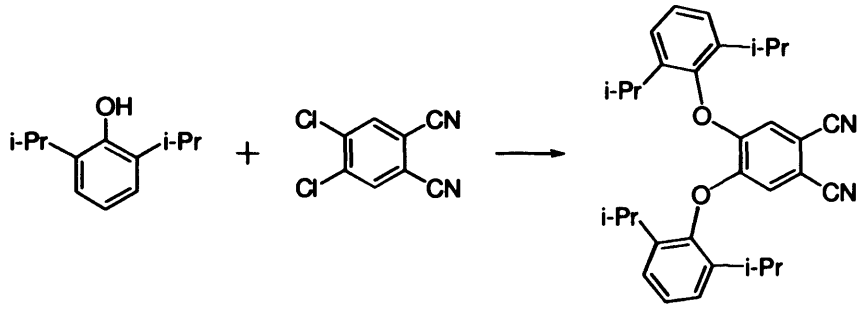
In order to carry out the synthesis of a good number of novel metal derivatives of **Pc1** we needed a large quantity of 4,5-di(2',6'-di-*iso*-propylphenoxy)phthalonitrile (**Pn1**) and therefore a big amount of 4,5-dichlorophthalonitrile, which although commercially available, is quite expensive. Therefore, this precursor was prepared following an existing four step procedure,[20] a route (**Scheme 2.1**) which starts with the dehydration of the cheap precursor 4,5-dichlorophthalic acid to form the anhydride, which is then reacted with formamide to give the imide, which then reacts with ammonium hydroxide to form the diamide. In the last step, the diamide is dehydrated with thionyl chloride to form the 4,5-

dichlorophthalonitrile. The overall yield of the synthesis was 49%, as reported in literature.[20]



Scheme 2.1. Synthesis of 4,5-dichlorophthalonitrile. *Reagents and conditions*: i) acetic anhydride, reflux, 5h; ii) formamide, reflux, 3h; iii) ammonia solution, r.t., 48h, iv thionyl chloride, DMF, 0-5 °C, 5h, r.t. 24 h

The next step was the synthesis of 4,5-di(2',6'-di-*iso*-propylphenoxy)phthalonitrile, which was carried out under nitrogen at 70 °C over three days, using dry dimethylformamide as solvent and an excess of anhydrous potassium carbonate to activate the phenol, also in excess, via deprotonation[127] (**Scheme 2.2**). The desired product was obtained in a yield of 65%.



Scheme 2.2. Synthesis of **Pn1**. *Reagents and conditions*: K_2CO_3, DMF 80 °C.

2.3. Synthesis of metal derivatives of Pc1

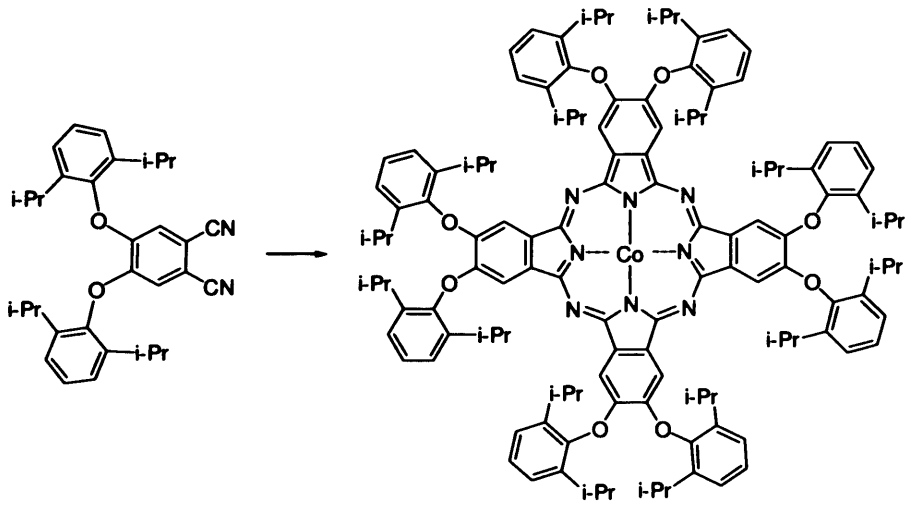
A good number of metal complexes of **Pc1** have been prepared, following known or modified existing procedures. In most cases the synthesis was straightforward and gave the desired compounds in reasonable or good yields, but for other derivatives problems were encountered and different approaches were attempted in order to obtain the product in sufficient quantity for crystallisation studies.

2.3.1. Synthesis of zinc derivative of Pc1

The synthesis of the cube-forming **Pc1Zn** was repeated in order to have sufficient material for solvent and ligand exchange reactions. The molecule was synthesised following the reported procedure[127] by stirring a mixture of 4,5-di(2',6'-di-*iso*-propylphenoxy) phthalonitrile and anhydrous Zn(II)acetate in dry NMP at 165 °C. **Pc1Zn** was obtained with a yield of 67%.

2.3.2. Synthesis of the cobalt derivative Pc1Co

The first metal that we decided to insert in our **Pc1** was cobalt for its well-established catalytic properties. Cobalt phthalocyanines are, in fact, already used commercially in homogeneous catalysis for oxidation reactions[87,130] (e.g. Merox process). They have also been studied as potential biomimetic catalysts of vitamin B_{12} in alkyl transfer reactions.[131,132] **Pc1Co** was synthesised in the same way as **Pc1Zn**, starting from **Pn1** but using cobalt acetate as the metal salt (**Scheme 2.3**). The yield of **Pc1Co** was 40%, slightly lower than that of **Pc1Zn**, but satisfactory.

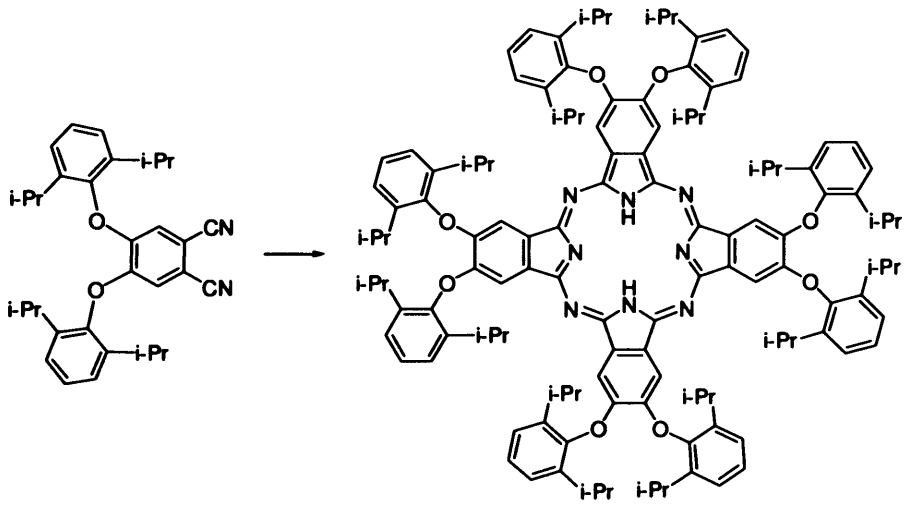


Scheme 2.3. Synthesis of **Pc1Co**. *Reagents and conditions*: $CoAc_2$, NMP, 165 °C.

2.3.3. Synthesis of metal-free and copper derivatives of Pc1

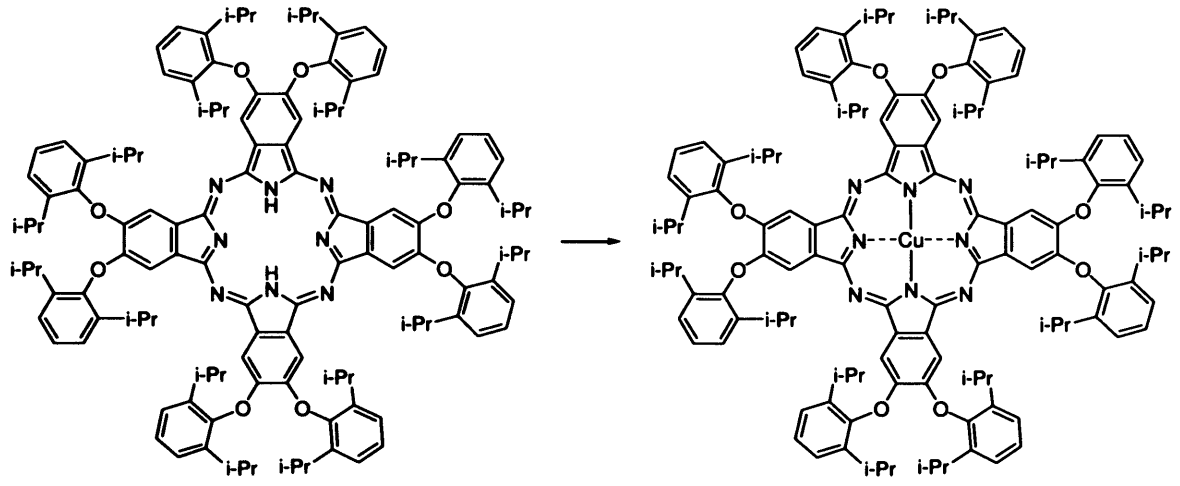
It was of interest to insert copper into **Pc1**. The first attempt of the synthesis of **Pc1Cu** was based upon the method previously used successfully for **Pc1Co** and **Pc1Zn**, but unfortunately in this case the reaction led only to traces of the desired compound. Hence, we decided to try another general route used for the synthesis of metal phthalocyanines, which starts from the metal free derivative.[1,14]

Metal free phthalocyanines are generally prepared[1,133] via the lithium derivative which is formed from addition of lithium metal to a refluxing solution of the corresponding phthalonitrile in *n*-pentanol (the 'Linstead method'). The resulting dilithium derivative is then hydrolysed during an acidic work up with diluted acetic acid to give the metal free phthalocyanine. Following this route, **Pc1** was obtained with a yield of 40%. (**Scheme 2.4**)



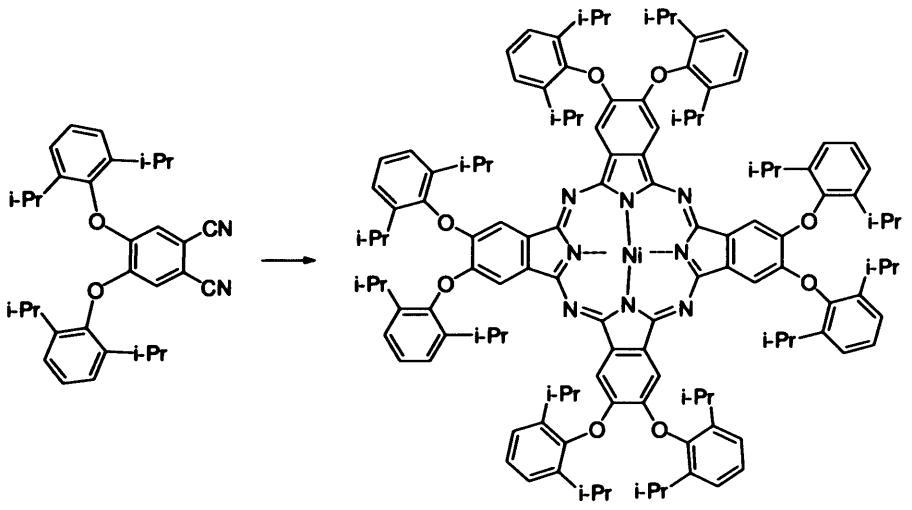
Scheme 2.4. Synthesis of **Pc 1**. *Reagents and conditions*: i) Li, n-pentanol, reflux; ii) dilute CH_3COOH.

The copper derivative **Pc1Cu** was readily prepared via a metal insertion reaction starting from **Pc1** with a good yield of 77% achieved by stirring the **Pc1** in refluxing *n*-pentanol with a large excess of copper(II)acetate[22] (**Scheme 2.5**).



Scheme 2.5 Synthesis of **Pc1Cu**. *Reagents and conditions*: Copper(II) acetate, n-pentanol, reflux.

2.3.4. Synthesis of the nickel derivative Pc1Ni



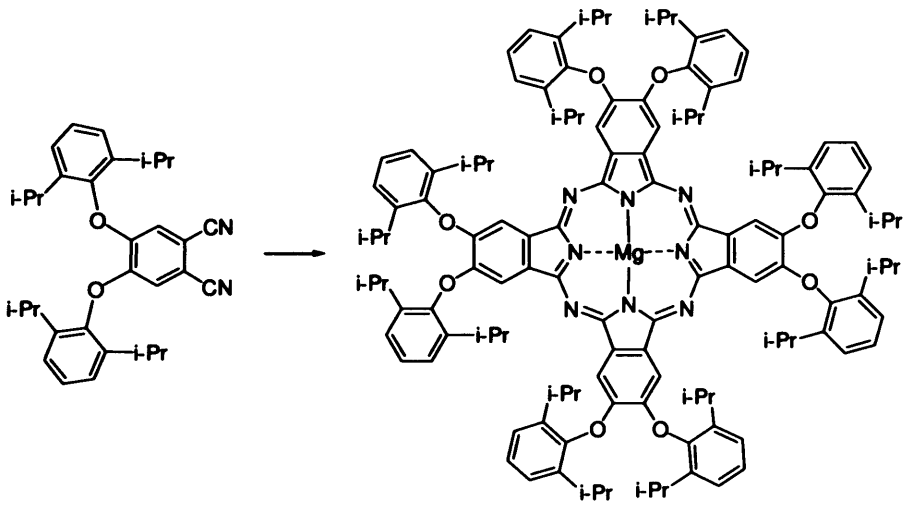
Scheme 2.6. Synthesis of **Pc1Ni**. *Reagents and conditions*: $NiCl_2$, quinoline, 165 °C

The initial attempt at the synthesis of **Pc1Ni** was the same as that employed successfully for the zinc and cobalt derivatives, using Ni(II)acetate as metal salt. However, in this case, the phthalocyanine was formed only in traces. It was decided to change the metal salt and leave all the other conditions unchanged. Our choice was $NiCl_2$, since it is often employed in this kind of reaction.[14,134,135] This time the desired compound was obtained with a modest, but sufficient, yield of 15%. Even though this method enabled us

to have the nickel derivative in such an amount that could allow various recrystallization experiments, we tried to increase the yield. Because nickel(II) chloride had already led to an improvement of the reaction it was used again as metal template, but in addition, the solvent was changed from the usual NMP to another high boiling solvent often used for the synthesis of phthalocyanines, quinoline.[18,136,137] In this case **Pc1Ni** was obtained with the much improved yield of 50% (**Scheme 2.6**).

2.3.5. Synthesis of the magnesium derivative Pc1Mg

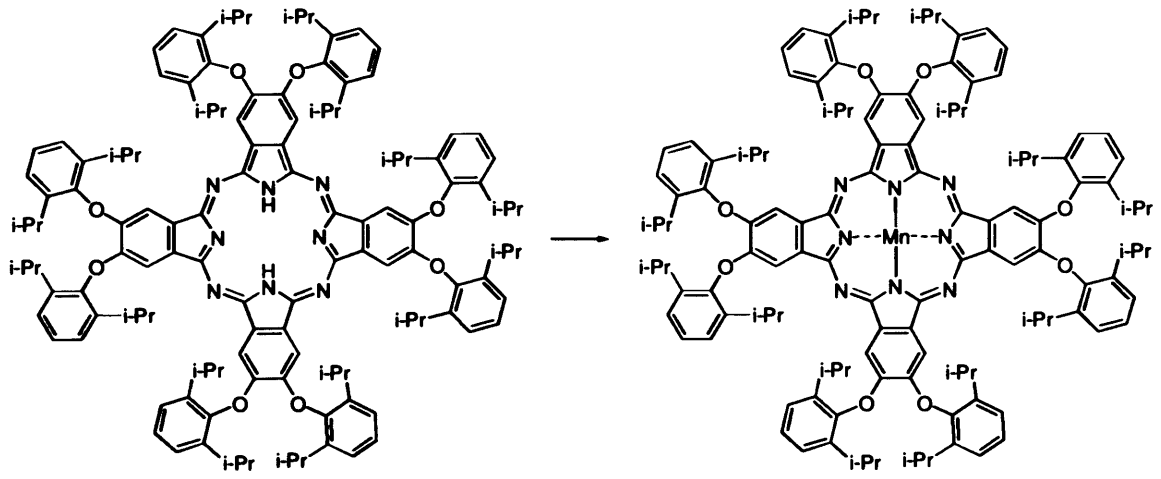
Pc1Mg was easily synthesised, adapting a recently reported procedure[138] for the synthesis of some substituted porphyrazines (**Scheme 2.7**). The reaction involved stirring magnesium metal, in presence of iodine, in *n*-pentanol at reflux, in order to form $Mg(OC_5H_{11})_2$ and then adding the phthalonitrile and leaving the mixture to heat at reflux for an additional two hours. The crude product was easily purified by reprecipitation to give the desired compound in a reasonable yield of 40%.



Scheme 2.7. Synthesis of **Pc1Mg**. *Reagents and conditions*: Magnesium, pentanol, iodine, reflux.

2.3.6. Synthesis of the manganese derivative Pc1Mn

It was reported in the literature[139] that highly hindered hexadecasubstituted manganese phthalocyanines can be formed from their equivalent metal free derivatives in appreciable yields, therefore it was anticipated that this would be a suitable method for the synthesis of the hindered manganese phthalocyanine **Pc1Mn**. Indeed, following this reported procedure, the metal free phthalocyanine was successfully metallated in the presence of an excess of manganese (II) acetate in refluxing dimethylformamide (**Scheme 2.8**). The reaction was complete after five hours and the product was isolated with a yield of 30 %.



Scheme 2.8. Synthesis of **Pc1Mn**. *Reagents and conditions*: Manganese(II) acetate, DMF, reflux.

In analogy with the results obtained in the literature, a Mn(III) phthalocyanine with an acetate ion in the axial position should have been the product of the reaction, but the experimental data suggested that in our case a Mn(II) derivative was formed. The UV spectrum showed a Q band at 732 nm, which is typical for Mn(II)phthalocyanine.[139-142] This was further confirmed from the MALDI spectrum where there was not sign of the peak corresponding to **acetate-Pc1Mn(III)** but a main cluster of peaks centred at m/z 1978.14 consistent with the MH^+ ion of **Pc1Mn**. Further confirmation was given later from X-ray analysis and from elemental analysis of the crystals of this derivative, both indicating the presence of two molecules of water which were linked to the metal in the axial position.

2.3.7. Synthesis of the iron derivative Pc1Fe

So far, the synthesis of the different metal **Pc1** derivatives had not been problematic. However, the synthesis of the iron derivative proved much more challenging. Nevertheless, the insertion of this metal into **Pc1** was of critical importance due to its potential exploitation as a heterogeneous mimic of the cytochrome P450 enzyme in oxidation reactions.

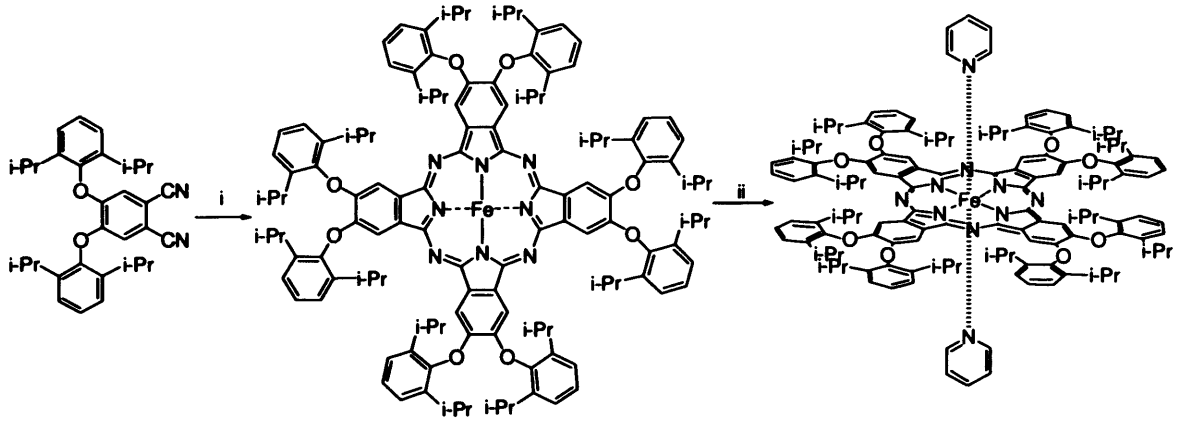
Since many reported methods for synthesis of iron phthalocyanines start from the corresponding phthalonitrile and since in numerous cases the iron acetate[19,143] is employed as metal template, our first attempt in the synthesis of **Pc1Fe** was similar to that used previously for the zinc derivative. Unfortunately, after one day, only the starting material was observed by TLC from the reaction mixture.

We then tried another general procedure that had previously been used to make the copper derivative, by refluxing the metal free phthalocyanine in pentanol for one day in the presence of a large excess of iron(II) acetate. We could observe by TLC, UV and MALDI spectra that a very small amount of the desired compound was formed but that the reaction mixture largely consisted of starting material. A very small amount of desired product was isolated from the reaction between **Pc1** and iron(II) acetate in refluxing DMF, which produced crystals suitable for XRD analysis.

We then tried the reaction between the phthalonitrile, iron pentacarbonyl as a metal template and ethylene glycol as a solvent at a temperature of 210 °C, as described in the literature.[144] In this case, after two hours the starting material disappeared. We were puzzled by the very dark brown colour of the compound obtained from this reaction, as it was not the characteristic green or blue expected for a phthalocyanine. The compound was not easily purified and after flash chromatography, a very poor amount of it was obtained. In its MALDI spectrum a cluster of peaks centred on the expected mass of **Pc1Fe** plus a molecule of water was present together with other clusters centred at M + 481, M + 962 and M - 481, (481 being the mass of the starting phthalonitrile). Even using a larger amount of iron pentacarbonyl, we were able to isolate only a very small amount of green product, which gave a MALDI spectrum similar to that obtained previously. Attempts to grow crystals of this compound resulted only in decolouration of the solution, indicating that decomposition had occurred.

We anticipated that the use of microwave irradiation could be useful to improve the reaction yield, since it allows the maintenance of higher temperatures (e.g. 235 °C) compared to traditional heating. So a mixture of **Pn1** and iron pentacarbonyl in dry ethylene glycol was irradiated with microwaves (200 W). The temperature of 235 °C was reached within five minutes and the reaction was kept at this temperature for fifteen minutes at which time, by TLC and UV, it seemed complete. In the UV-visible spectrum the Q band was observed at 669 nm.

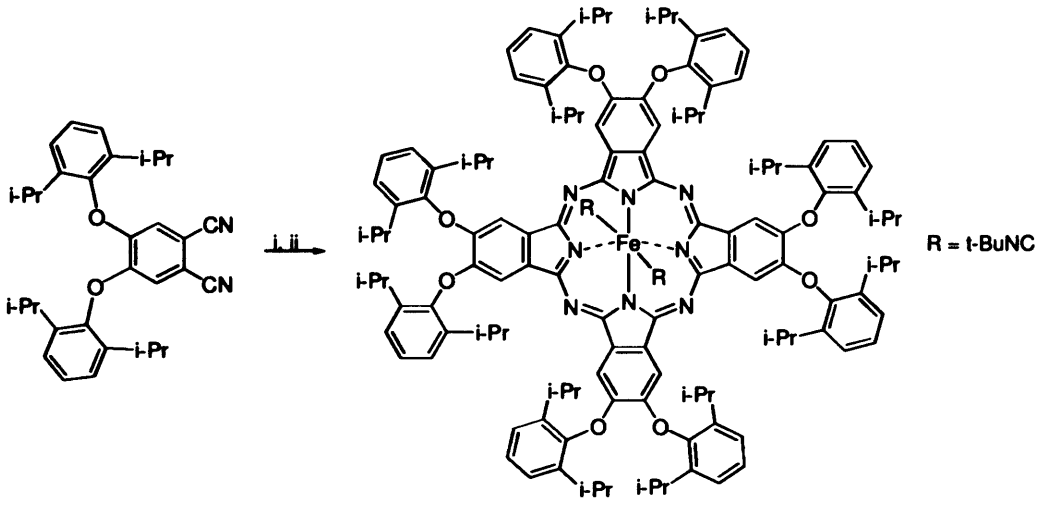
In previous work[143-145] it had been demonstrated that the addition of axial ligands such as pyridine facilitate the isolation of iron-containing phthalocyanine as $PcFe(py)_2$. Thus, before purification the crude product was dissolved in pyridine and the solution was heated at 90 °C, in order to promote the formation of **PcIFe(py)$_2$**, (**Scheme 2.9**). Purification was assisted by the use of column chromatography for which the silica gel was passivated by pyridine or triethylamine prior to use.



Scheme 2.9. Synthesis of **PcIFe** and **PcIFe(py)$_2$**. *Reagents and condition*: i) $Fe(CO)_5$, Ethylene glycol, μW, 200 W, 235 °C, 240 psi. ii) pyridine.

In the MALDI spectrum the cluster of peaks corresponding to **PcIFe** was present. We concluded that little advantage had been obtained from the use of microwave irradiation, apart from shortening the time of reaction. Instead, the isolation of a larger amount of product was due to the addition of pyridine to the crude reaction, which avoided the formation of the bridged-oxo complex. We found in the literature[146,147] that *tert*-butylisocyanide can be used in the same way to form bis(*tert*-butylisocyanide)-phthalocyaninatoiron(II). Hence, we attempted to prepare **PcIFe** by the simple application of the well-established method in which metal phthalocyanines are prepared via metal

exchange from lithium derivatives.[14,148] Lithium metal was added to a refluxing mixture of **Pn1** in pentanol within which an excess of iron acetate was present. After two hours the reaction was complete. The crude product was stirred in tert-butylisocyanide for 24 hours at 50 °C, then the solvent was evaporated to give a bright blue solid, with 63% of yield obtained following purification by column chromatography (**Scheme 2.10**)



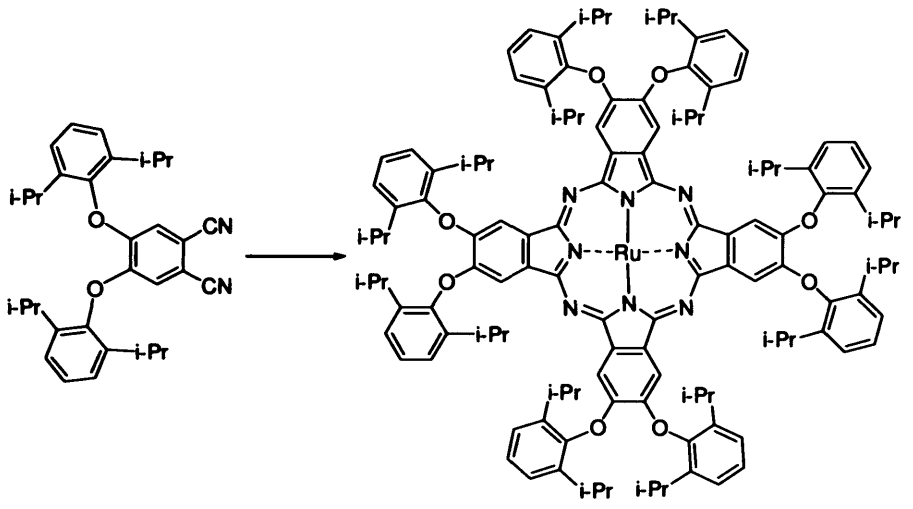
Scheme 2.10. Synthesis of **Pc1Fe.** *Reagents and conditions*: i) Lithium metal, iron(II) acetate, n-pentanol, reflux; ii) *t*-butylisocyanide 50 °C.

2.3.8. Synthesis of the ruthenium derivative Pc1Ru

As for **Pc1Fe,** difficulties were initially encountered in the synthesis and isolation of the ruthenium derivative **Pc1Ru**. We were particularly interested to obtain this molecule and its crystal, not only for its possible employment as catalyst[54] but also because it would provide a direct comparison with the iron derivative. Furthermore, since ruthenium phthalocyanines are widely employed to form polymeric and oligomeric bridged macrocyclic complexes,[56,149] we would have had the opportunity to try to form some oligomers with **Pc1Ru** as macrocyclic component and perhaps the chance to study their crystalline structure.

The first attempt at the synthesis of **Pc1Ru** was the reaction of metal free **Pc1** with $RuCl_3 \cdot H_2O$,[55] but after 40 h at reflux in pentanol or DMF only the starting material was present as indicated from UV-Vis spectroscopy and by TLC. In the second attempt, the

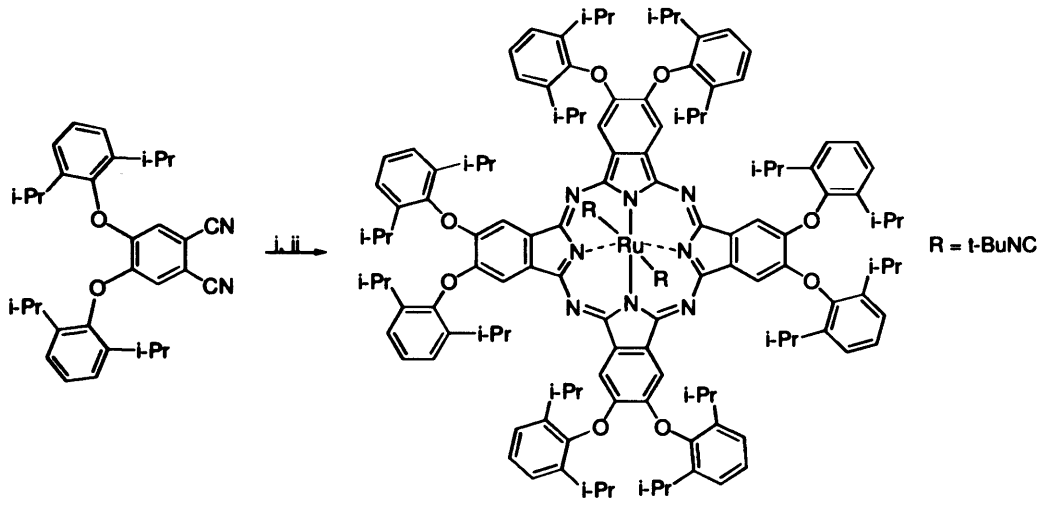
crude lithium derivative, which was synthesised *in situ* by the cyclotetramerization of **Pn1** with lithium in pentanol, was added to $RuCl_3 \cdot H_2O$. In this case we expected, as had been reported in the literature for similar procedures,[55] the formation of a complex in which a carbonyl group would have been the axial ligand on the metal. Unfortunately, we were unable to recover any of the expected compound.



Scheme 2.11. Synthesis of **Pc1Ru.** *Reagents and conditions*: Ruthenium(III) chloride, DBU, 160 °C.

Finally, starting from the phthalonitrile and reacting with $RuCl_3 \cdot H_2O$ in DBU[55] (**Scheme 2.11**) we were able to isolate the desired compound with a yield of 13%. The TLC of the reaction mixture showed that other weak blue-green spots were present, probably corresponding to the ruthenium phthalocyanine coordinated with unspecified additional ligands,[15] but we were not able to isolate any other compound.

On the basis of this encouraging result, we tried another reaction starting again from the phthalonitrile and using the same metal salt, but using NMP as solvent. Due to the ability of ruthenium to bind further axial ligands,[54-56,149,150] we anticipated that the introduction of two *tert*-butylisocyanide molecules in axial position would help the isolation of the product as was shown to be the case for **Pc1Fe**. Hence, the crude product obtained from the latter reaction was stirred in t-butylisocyanide for 24 hours (**Scheme 2.12**). Following chromatographic purification, a blue solid corresponding to the expected compound was isolated with a yield of 17%. This yield was not as good as for **Pc1Fe** but it gave sufficient compound to grow some crystals.



Scheme 2.12. Synthesis of **Pc1Ru(*t*-BuNC)$_2$**. *Reagents and condition*: i) Ruthenium(III) chloride, NMP, 170 °C; ii) *t*-BuNC, 50 °C.

2.3.9. Synthesis of the titanium derivative Pc1Ti

As for the previous two molecules, many attempts were carried out before finding a successful way of preparing the titanium phthalocyanine derivative **Pc1Ti**.

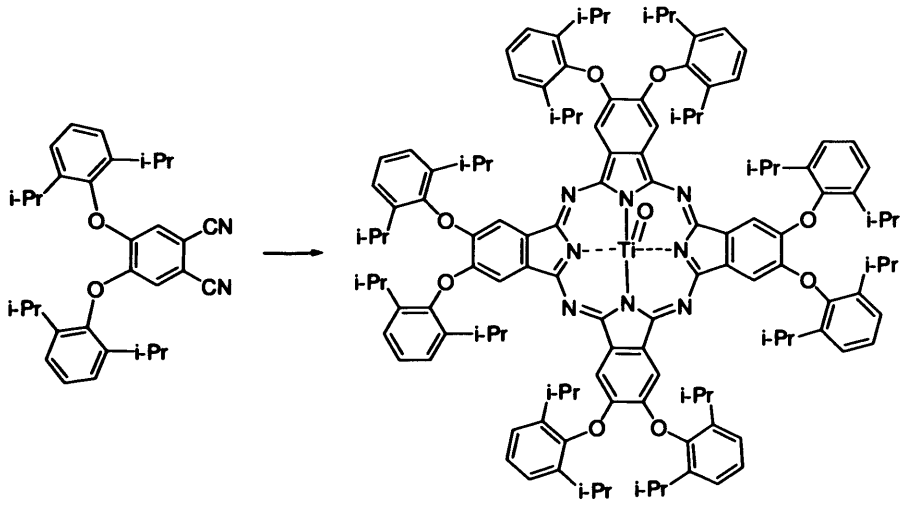
Since phthalocyaninatotitanium(IV)oxide, together with peripherally substituted and naphthalocyaninatotitanium(IV) oxides have been thoroughly investigated as charge generation materials and this property depends not only on the central metal atom but also on the crystal structure, we thought that it would be interesting to study the structure of the crystals grown from **Pc1Ti.**

Following a procedure for the synthesis of peripherally substituted titanium phthalocyanines,[151,152] **Pn1** was reacted with an excess of $Ti(OBu)_4$ in pentanol at 110 °C. After forty hours there was no sign of phthalocyanine, so the temperature was raised to 130 °C and some DBU was added to the reaction mixture. After a further ten hours from the addition of DBU, the TLC indicated a trace of phthalocyanine together with other unidentified spots. However, the addition of DBU seemed to have helped the reaction so it was used in the following two experiments that we carried out.

In the first experiment a solution of **Pn1** and $Ti(OBu)_4$ in DBU was heated at 195°C for 24 hours and a very small amount of a greenish solid was isolated by column chromatography, but MALDI revealed that it was a complex mixture of compounds.

In the second experiment a mixture of **Pn 1** and DBU in pentanol was heated at 140 °C, then titanium(IV) butoxide was added. In this case a mixture of **Pc1** and **Pc1TiO** was obtained. Unfortunately, the former product was the major one and the latter was present only in a small amount. Then, a similar procedure was attempted in which, instead of DBU, lithium pentoxide was used as the initiator of the cyclotetramerisation. This procedure was very similar to the one successfully used for the synthesis of the iron derivative, except that titanium(IV) butoxide was used as source of the metal. Even this reaction was a failure.

The next attempt was carried out without any solvent[14] so that **Pn 1** and titanium(IV) butoxide were heated at 200 °C for several hours, but even this did not succeed in producing significant quantities of the desired **Pc1TiO**. At this point, quite discouraged from the previous results, we attempted the reaction in NMP (**Scheme 2.13**). Fortunately this time the right product was formed and isolated with a yield of 29%.

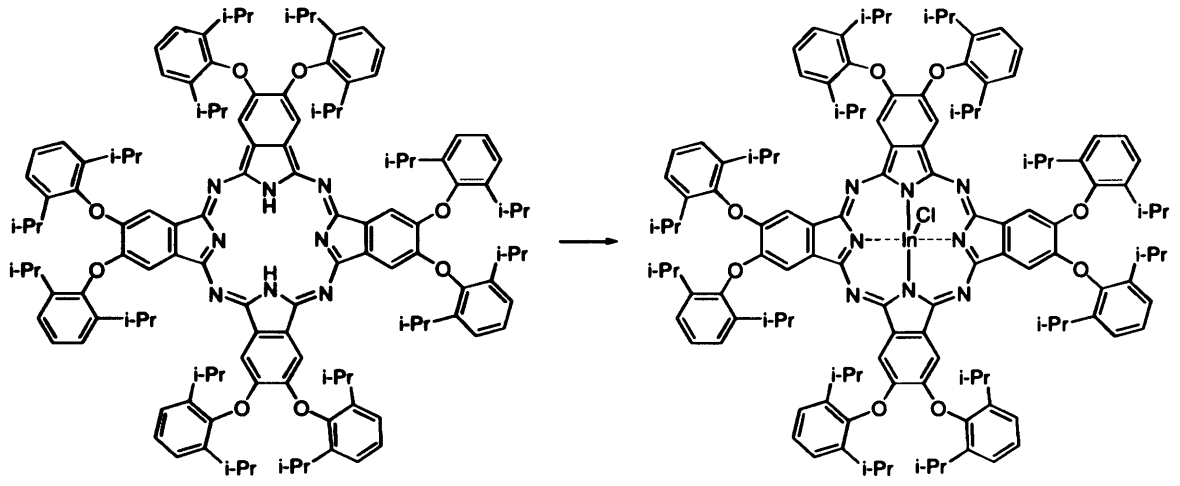


Scheme 2.13. Synthesis of **Pc1TIO**. *Reagents and conditions*: Titanium(IV) butoxide, NMP, 165°C.

2.3.10. Synthesis of the Indium derivative Pc1InCl

Literature provides[153] some examples of substituted indium(III) phthalocyanines on which X-ray crystallographic studies, focusing on the effects of the axial ligand and peripheral substituents, were carried out. Therefore, it was of interest to insert this metal into **Pc1** and try to obtain suitable crystals for X-ray analysis. **Pc1InCl** was synthesised,

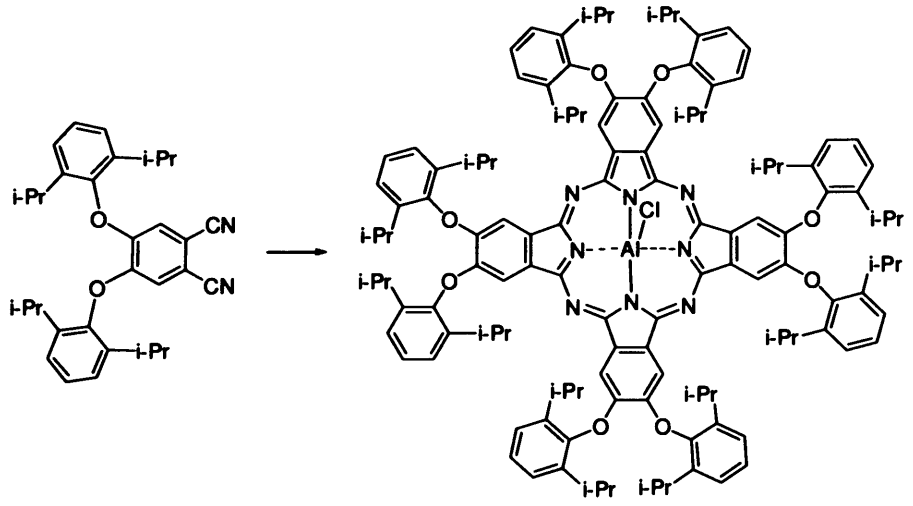
with a satisfactory yield of 36%, following a reported procedure in which the metal free phthalocyanine is stirred with indium(III) chloride in pentanol at reflux[153] (**Scheme 2.14**).



Scheme 2.14. Synthesis of **Pc1InCl**. *Reagents and conditions*: Indium(III)chloride, pentanol, reflux.

2.3.11. Synthesis of the aluminium derivative Pc1AlCl

To complete our study of the effect of the central metal cation on packing arrangement, we inserted aluminium into **Pc1**. This synthesis was achieved quite easily by reacting **Pn 1** with aluminium(III) chloride in quinoline at 160 °C. The product was obtained with a reasonable yield of 25% (**Scheme 2.15**)



Scheme 2.15. Synthesis of **Pc1AlCl**. *Reagents and conditions*: Aluminum(III) chloride, quinoline, 160 °C.

2.4. Crystallographic studies

Suitable crystals for X-ray analysis were grown for the metal free and all the various metal derivatives of **Pc1** synthesised. In every case, the technique used for the crystallization was slow diffusion of a non-solvent into a solution of the phthalocyanine in a suitable solvent.

To our initial disappointment, the first attempts to recrystallise **Pc1Co** from DCM/acetone gave a non-cubic form, which was identified as a monoclinic clathrate crystal belonging to the space group $P2_1/c$, with four phthalocyanine molecules in the unit cell. **Figure 2.1** shows a view of the crystal packing along the cell axis *a*. From this view the Pc molecules seem to have a herringbone arrangement and form channels in which DCM molecules are present (ratio 2:1 DCM/Pc) the maximum width of which is approximately 0.86 nm.

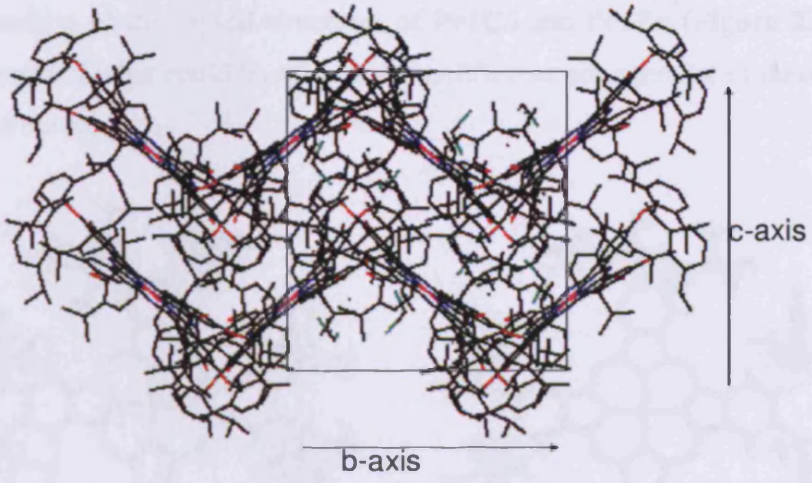


Figure 2.1 The monoclinic packing of **Pc1Co**, view along ***a*** axis.

However, the real packing is quite different from the impression given by this picture, so that even in this case the 2,6-di-*iso*-propylphenoxy substituents are quite efficient at blocking the cofacial aggregation of the phthalocyanine molecules.

By taking a closer look at the packing structure and considering one molecular layer along the a axis (**Figure 2.2**) it is possible to see that within the b-c plane Pc molecules lie oriented in two different directions which form an angle of 86.08° to each other. Between two molecules of the same orientation there is always a Pc molecule that lies in the near-perpendicular plane. Every Pc molecule in this layer is surrounded by four other Pc

molecules, which are parallel to each other and more or less perpendicular to the central molecule. The molecules adopt the same arrangement in every monomolecular layer but with a shift along *c* of half the length of this cell axis

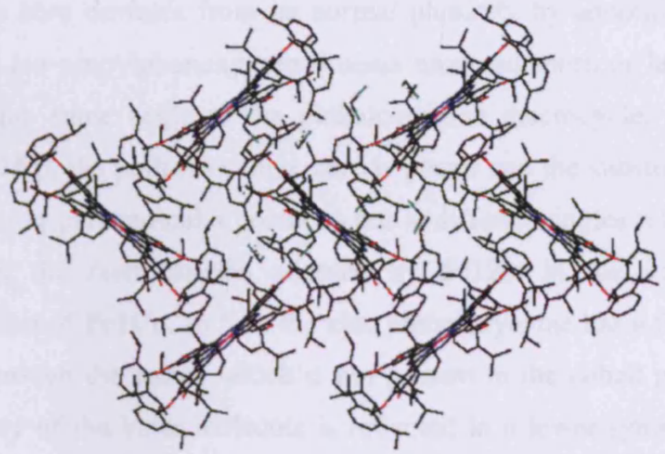


Figure 2.2 A monomolecular layer along ***a*** axis in the packing of **Pc1Co**

A comparison of the crystal structures of **Pc1Co** and **Pc1Zn (Figure 2.3)** has been useful to understand what could have caused the different arrangement of these molecules in their crystalline forms.

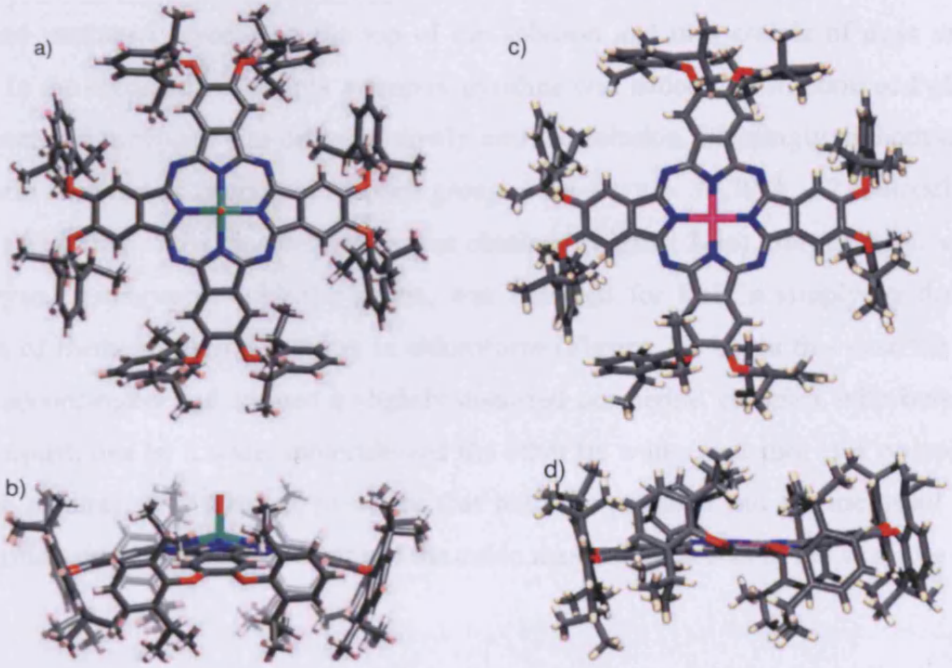


Figure 2.3 The molecular structure of **Pc1Zn**. a) Face-on and b) edge-on molecular views, and **Pc1Co**. c) Face-on and d) edge-on molecular views

The zinc cation of **Pc1Zn** in the cubic crystal is pentacoordinate and has one water molecule as an axial ligand and assumes a distorted square-pyramidal conformation whereas the cobalt is only tetracoordinated and forms a planar square complex. For **Pc1Zn** the phthalocyanine core deviates from its normal planarity by adopting a conical shape, with all the 2,6-di-*iso*-propylphenoxy substituents arranged more or less perpendicularly and always with the same angle to the phthalocyanine macrocycle. For the non-cubic crystal form of **Pc1Co**, the phthalocyanine core is planar and the substituents are disposed always more or less in perpendicular positions but at different angles relative to the central plane. Therefore, the conformation adopted by **Pc1Zn** in the solid state is more symmetrical than that of **Pc1Co**. In fact, the zinc phthalocyanine has a four-fold symmetry axis that passes through the metal, which is not present in the cobalt phthalocyanine and the lower symmetry of the latter molecule is reflected in a lower symmetry in its crystal packing.

In view of these results and in order to confirm the necessity for the presence of an axial ligand on the metal for the molecules to adopt the more symmetrical cubic packing in the solid state, a pyridine molecule was introduced on the cobalt phthalocyanine. This was done in two different ways. In the first case a solution of **Pc1Co** in pyridine was heated at 90 °C for 3 h and then the pyridine was evaporated, but not completely, chloroform was added and methanol layered on the top of the solution and in a couple of days crystals formed. In the second case, simply a drop of pyridine was added to a solution of **Pc1Co** in chloroform and methanol was diffused slowly into the solution. Pleasingly, in both cases a cubic form which was isomorphic (space group = *Pn-3n*, a = 37.39 Å, 12 molecules per unit cell) with that of the zinc derivative was obtained (**Figure 2.4a**). Surprisingly, another cubic crystal, isomorphic with the others, was obtained for **Pc1Co** simply by the slow diffusion of methanol into a solution in chloroform (**Figure 2.4 b**). In this case the metal was hexacoordinated and formed a slightly distorted octahedral complex with both axial sites occupied, one by a water molecule and the other by water/methanol (1:1 occupancy). From the pictures, it is possible to notice that both the pyridine and the methanol in the axial position point towards the centre of the cubic nanovoids present in the structure

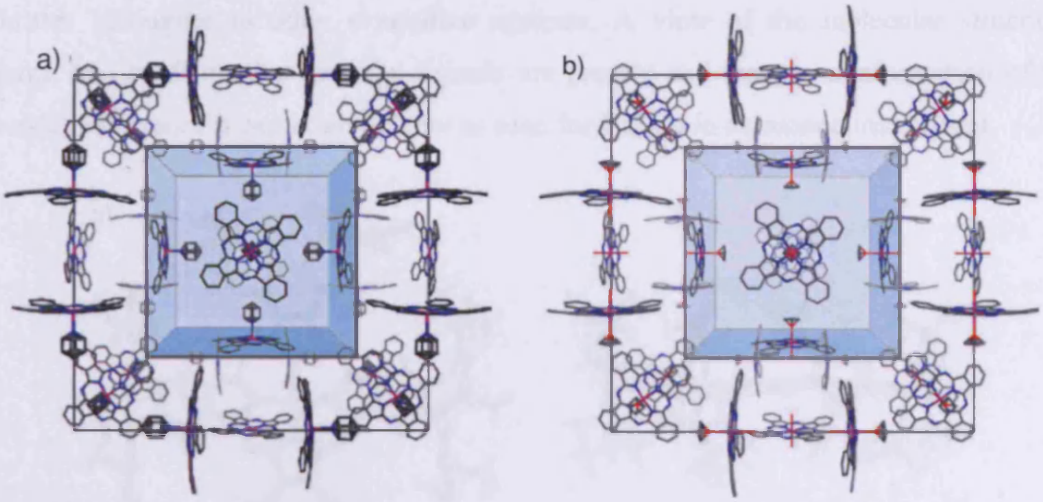


Figure 2.4 The cubic packing arrangement of **Pc1Co** (the 2,6-di-isopropylphenoxy substituents have been removed for clarity) a) recrystallised from pyridine/$CHCl_3$/MeOH – note the pyridine axial ligands; b) recrystallized from slow diffusion of MeOH into DCM – note the H_2O and MeOH axial ligands (MeOH pointing towards the centre of the cubic void).

These results seem to confirm that the presence of the axial ligand or ligands seems to be essential for the molecules to adopt a cone shape and to be more symmetrical (**Figure 2.5**) and therefore arrange in a cubic form.

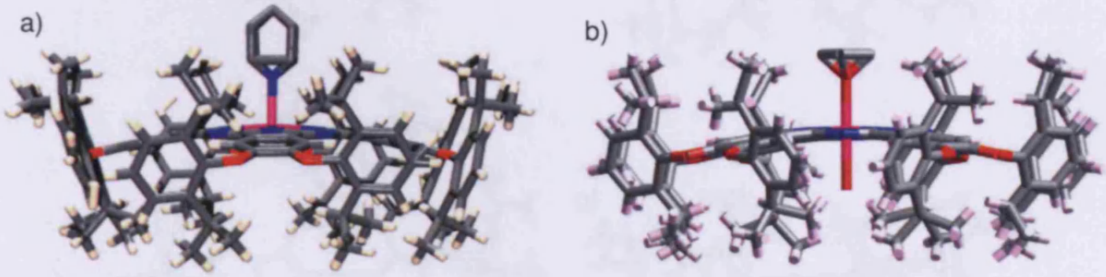


Figure 2.5 Edge-on molecular views of the molecular structure of a) **Pc1CoPy**, and b) **Pc1Co** recrystallized from $CHCl_3$/MeOH.

These results were quite encouraging, especially as a good number of the seventy or so metals that could be placed within the central cavity of the phthalocyanine could form penta or hexacoordinated complexes. The necessity of the presence of axial ligands on the metal for the molecule to adopt a cubic morphology was confirmed from the fact that metal free, copper and nickel derivatives, in which no axial ligands would be expected, formed

clathrates belonging to other crystalline systems. A view of the molecular structures (**Figure 2.6**) confirms that no axial ligands are present and that the conformation of the phthalocyanine core is essentially planar as seen for **Pc1Co** in its monoclinic crystal.

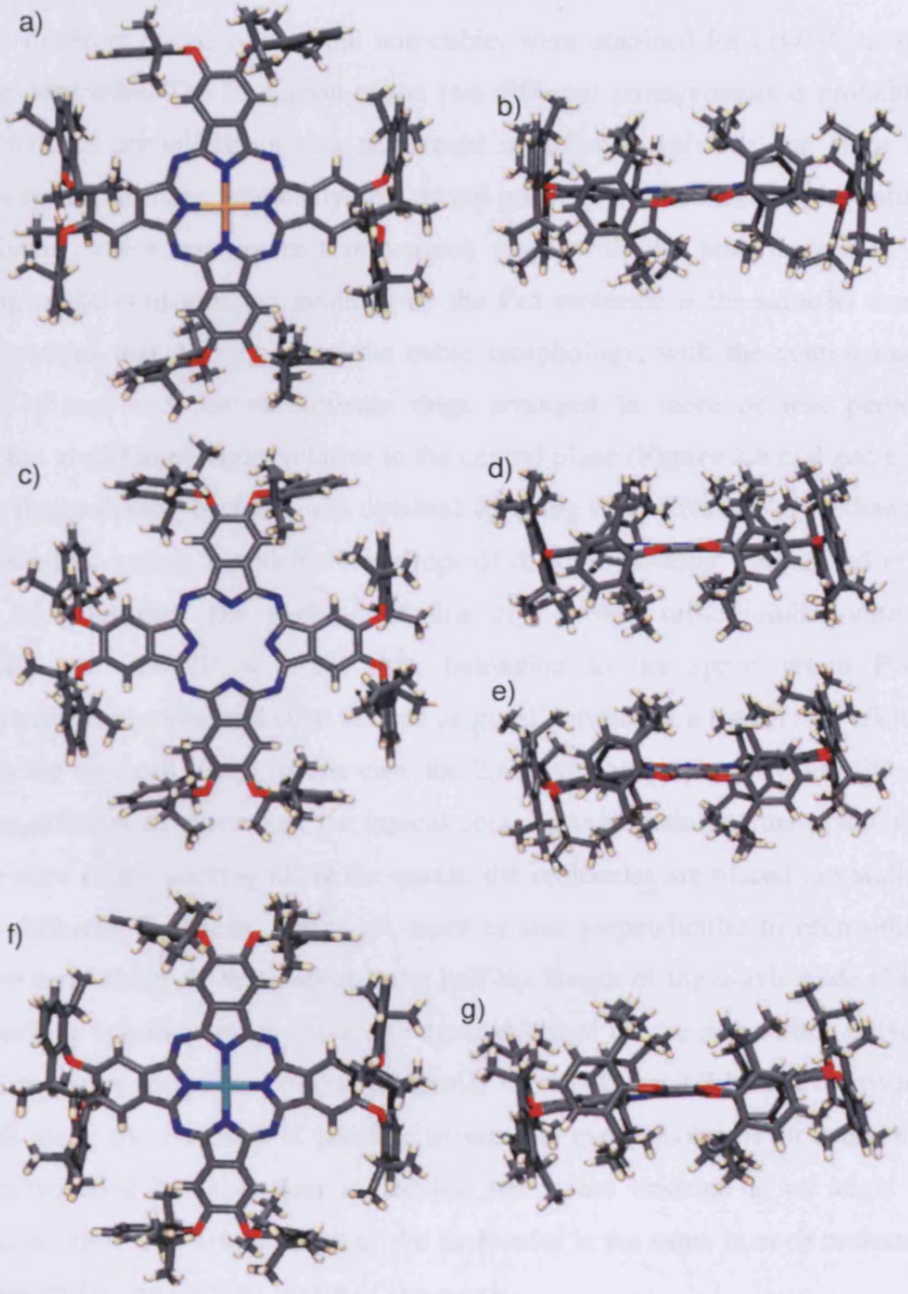


Figure 2.6. The molecular structures of **Pc1Cu**, **Pc1** and **Pc1Ni**. **Pc1Cu** a) Face-on and b) edge-on views; **Pc1** c) Face-on and edge-on molecular views d) in the orthorhombic packing e) in the monoclinic packing. **Pc1Ni** f) Face-on and g) edge-on molecular views.

Pc1Cu crystallized with a monoclinic arrangement (space group $P2_1/c$, a = 38.60, b = 16.86, c = 18.42 Å, β = 91.37°, V = 11997 Å ^{3}) which was isomorphic with the non-cubic crystal previously obtained for **Pc1Co**. In this case the crystal hosts an acetone molecule per Pc and some disordered solvent assumed to be DCM.

Two different polymorphs, both non-cubic, were obtained for crystallization of the metal free derivative. The formation of the two different arrangements is probably due to the fact that the crystallisation was performed in different solvents and since all these molecules form clathrates, obviously, the crystal packing is influenced by the nature of the guest solvent, which can interact in various ways with the host molecules. In both morphologies the conformation assumed by the **Pc1** molecule is the same as seen for the other derivatives that did not adopt the cubic morphology, with the central macrocycle practically planar and the substituents rings arranged in more or less perpendicular positions but at different angles relative to the central plane (**Figure 2.6 c, d** and **e**).

The first polymorph of **Pc1** was obtained by using slow diffusion of methanol into its solution in ethyl acetate to which a few drops of dichloromethane were added in order to improve its solubility. The packing of this crystal was orthorhombic with a quite voluminous unit cell (V = 12201 Å^3), belonging to the space group *Pbca*. Four phthalocyanine molecules and ethyl acetate as guest solvent, in a ratio 1:1 (Pc/EtOAc) are present in the unit cell. Even in this case the 2,6-di-*iso*-propylphenoxy substituents have been quite efficient in preventing the typical cofacial aggregation of the phthalocyanines. From the view of the packing along the c-axis, the molecules are placed in parallel planes with two different directions, which are more or less perpendicular to each other (angle 74.73°), to form channels that appear to be half the length of the a-axis wide (**Figure 2.7 a**). The packing is quite similar to the one showed before for the monoclinic polymorph of **Pc1Co.** Comparing the picture of one molecular layer (**Figure 2.7 b**) and the overall view of the cell along the c-axis, it is possible to see that every molecule in every molecular layer is surrounded by other four molecules, which are oriented at an angle of 74.7° relative to the first. The arrangement of the molecules is the same in each molecular layer but they are shifted by half the length of the a-axis.

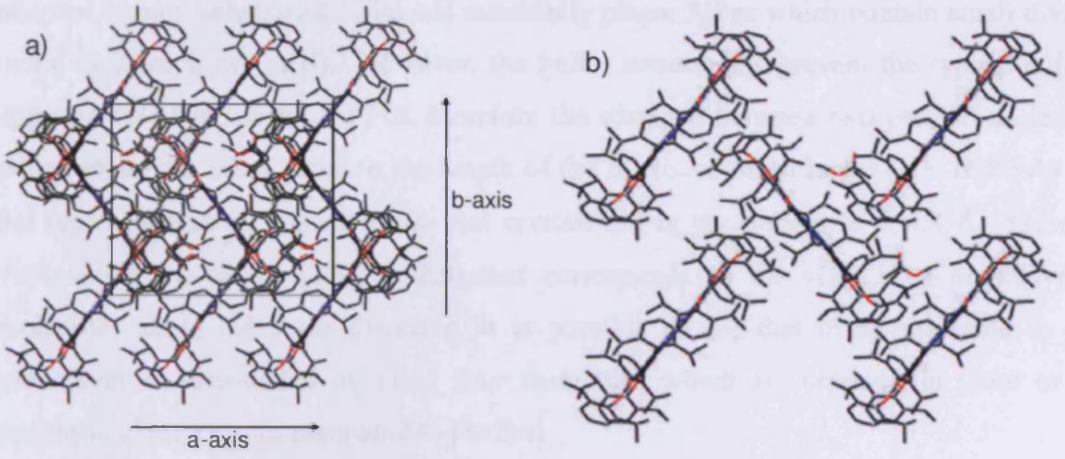


Figure 2.7 a) The orthorhombic packing of **Pc1**, view along ***c*** axis. b) A monomolecular layer along ***c***.

The second polymorph of **Pc1** was obtained by the slow diffusion of acetone into dichloromethane solution. In the unit cell (a = 21.29, b = 16.90, c = 18.28 Å, β = 114.65°, V = 5977.8 Å^3), which belongs to the space group $P2_1/c$, there are two phthalocyanine molecules and one acetone molecule as guest solvent (**Figure 2.8).**

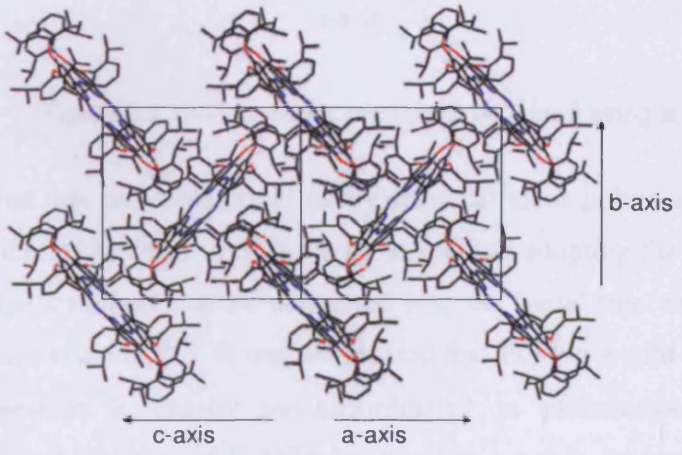


Figure 2.8. The monoclinic packing of **Pc1**, view along a face diagonal.

In this case, the herringbone-packing is similar to the commonly encountered phthalocyanine crystal morphology, defined as β-form (monoclinic, space group $P2_1/a$, typical cell parameters a = 19.4, b = 4.8, c = 14.6 Å, β = 120° two molecules per unit cell),

adopted by non substituted H_2Pc and essentially planar MPcs which contain small divalent metal ions, such as Cu(II).[1] However, the bulky substituents prevent the typical cofacial aggregation of unsubstituted Pcs, therefore the distance between two parallel molecules, which is in both cases equal to the length of the *b*-axis, is much larger (*b* = 16.89 Å) than the typical found for the molecule that crystallized in the β-form (*b* = 4.8 Å). From the view along the *a*-axis (**Figure 2.9**) that corresponds to the view of a monolayer of molecules along the same direction, it is possible to see that every molecule in each monolayer is surrounded by other four molecules which are oriented in more or less perpendicular direction compared to the first.

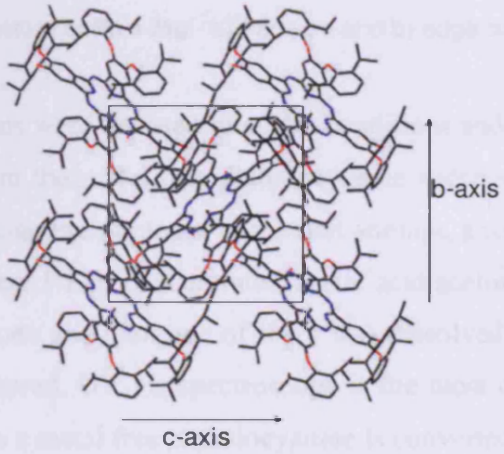


Figure 2.9 The monoclinic packing of **Pc1**, view along ***a***.

The fact that this molecule could easily form different polymorphs made us think about some artifice, with which to trick the molecule into adopting the cubic arrangement. Magnesium phthalocyanines can be converted into the metal-free analogues by simple reaction with aqueous acids.[14,139] It was anticipated that **Pc1Mg** would form cubic crystals since the magnesium is usually pentacoordinated in phthalocyanine complexes.[154] Fortunately, the crystallization of **Pc1Mg** led to cubic crystals, isomorphic with the ones from the cobalt and zinc derivatives. As expected, the magnesium was pentacoordinated, with a water molecule in the axial position. The phthalocyanine molecule in the crystal assumed the typical conical shape already seen for the zinc and the cobalt derivatives (**figure 2.10**).

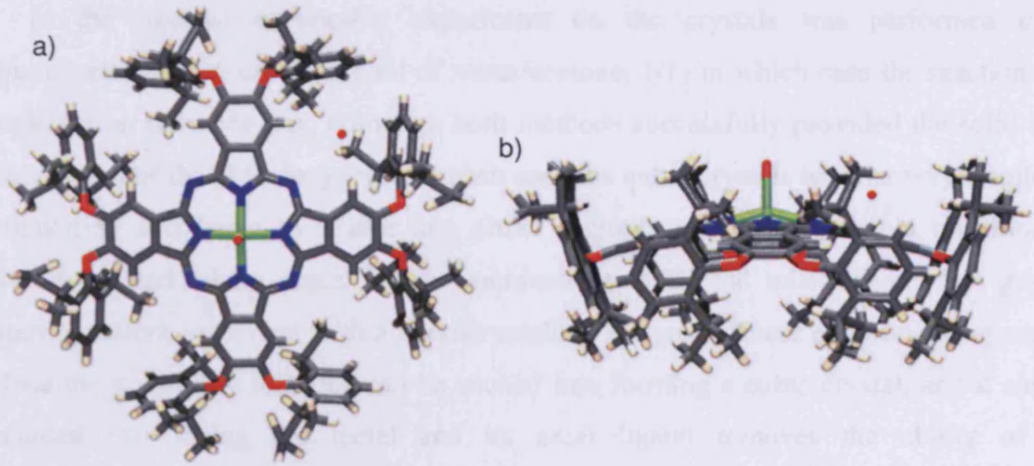


Figure 2.10 The molecular structure of **Pc 1 Mg**. a) Face-on and b) edge-on molecular view.

At this point, the crystals were exposed to acidic conditions and it was hoped that not only was the reaction to form the metal free phthalocyanine successful but also that the crystal would maintain the same morphology. In the first attempt, a couple of **Pc1Mg** cubic crystals were put in a solution 1:1 of concentrated acetic acid/acetone and after 24 hours they were washed with acetone and then one of them was dissolved in DCM to allow its UV-vis spectrum to be measured. UV-vis spectroscopy is the most convenient method of following a reaction in which a metal free phthalocyanine is converted into a metal one and vice versa. All simple phthalocyanines show a strong absorption between 670 and 700 nm, termed the Q band, which is responsible for the characteristic intense blue-green colour of the phthalocyanines and which has a different shape for the metal and metal free derivatives. For the latter the Q band is split in two because of its lower symmetry in comparison to the metal phthalocyanine.

Initially the spectrum showed no splitting in the Q band, which was at 681 nm, meaning that the reaction did not work. We thought that more time and addition of water would help the hydrolysis and therefore the crystals were exposed to a solution of 1:1:1 acetic acid/water/acetone and their status was checked after two weeks. The crystals were filtered from solution, thoroughly washed with acetone and then one of them was dissolved in DCM to allow the measurement of the UV-vis spectrum, which revealed that the reaction had worked since the split Q band, typical for metal free phthalocyanines, was observed.

In the meanwhile, another experiment on the crystals was performed using trifluoroacetic acid (6 drops in 1 ml of water/acetone, 1/1) in which case the reaction was complete after only one day. Although both methods successfully provided the solid state demetallation of the phthalocyanine, in each case the cubic crystals became very fragile on manipulation and liable to shatter into small fragments suggesting that a transition in crystal form had taking place. When examined by XRD the modified crystals gave a scattering pattern consistent with a microcrystalline material. These experiments appear to exclude the possibility that **Pc1** can be tricked into forming a cubic crystal, and it can be concluded that losing the metal and its axial ligand removes the ability of the phthalocyanine to adopt the cubic packing arrangement.

Given the apparent requirement of an axial ligand it was not expected that the nickel derivative of **Pc1** would crystallize with a cubic packing. Indeed, crystals which are isomorphic (a = 21.37, b = 16.88, c = 18.72 Å, β = 115.06°, V = 6098.7 Å ^{3}) with the monoclinic polymorph of **Pc1** were obtained for this molecule. In this case chloroform is the guest solvent and is present in a ratio of 1:1 with the phthalocyanine molecule. The molecular structure of **Pc1Ni** is very similar to the ones obtained for **Pc1** and **Pc1Cu** (**Figure 2.6 f** and **g**).

A monoclinic polymorph, similar to that obtained for the non-cubic crystal of **Pc1Co**, was formed by the iron derivative of **Pc1** that had been isolated without previous addition of *t*-butylisocyanide, although, in this case a water molecule was axially bonded to the metal cation. Instead, **Pc1Fe(t-BuNC)$_2$** gave cubic crystals with different axial ligands from changing only the solvent of crystallization, so that when the crystals of **Pc1Fe(*t*-BuNC)$_2$** were grown from deuterated chloroform/methanol, the displacement of one isocyanide by one water molecule occurred, perhaps due to the greater acidity of the chloroform. Instead, for the crystals grown from DCM/methanol or either $CHCl_3$/MeOH both the isocyanide ligands were retained.

The ruthenium derivative also gave cubic crystals with different axial ligands, as two different derivatives **Pc1Ru** and **Pc 1 Ru(*t*-BuNC)$_2$** were crystallized. Therefore, we had the possibility to assess how the presence of different ligands bonded to the axial sites of the metal influences the deviation from planarity of the phthalocyanine core. For example, when two *t*-butylisocyanide molecules are the axial ligands the distortion is slightly more pronounced. The opposite might be expected, especially for the iron derivative, since the effect on the two sides of the molecule of two identical ligands should be the same.

However, looking at these structures it is evident that the two *t*-butylisocyanide ligands are bonded in different ways to the metal (**Figure 2.11**).

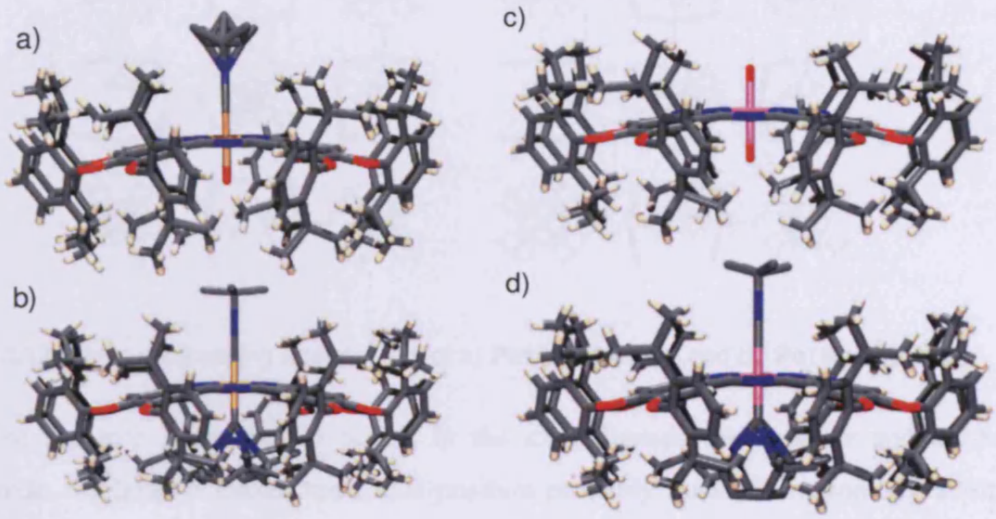


Figure 2.11 Edge-on molecular views of the molecular structure of a) **Pc1Fe(*t*-BuNC)(H_2O)**, b) **Pc1Fe(*t*-BuNC)$_2$**, c) **Pc1Ru(H_2O)$_2$** and d) **Pc1Ru(*t*-BuNC)$_2$**.

In both the IR spectrum of **Pc1Fe(*t*-BuNC)$_2$** and **Pc1Ru(*t*-BuNC)$_2$**, only one band, at 2144 cm^{-1} and at 2135 cm^{-1} respectively, was present for C-N stretching, showing that the two ligands must be bound in the same way or, more likely, there is a dynamic equilibrium between the two forms. Since the stretching band of the iron-bound isocyanides is more or less at the same frequency of that of the free isocyanide (2135 cm^{-1}) we would expect to find the same features for the two t-butyl isocyanides in the crystal molecular structure, with a linear arrangement for N-C-Fe and an angle for C-N-C close to 180° both sides of the iron cation. Instead, from the edge-views of the molecular structures of **Pc1Fe(*t*-BuNC)$_2$** and **Pc1Ru(*t*-BuNC)$_2$** in **figure 2.11 b** and **d,** it is possible to see that only one of the two ligands is linear but the other is tilted. The different configurations of the ligands could be due to packing interactions as the tilted ligands are outside the cubic nanovoids and interact sterically with the axial ligand of a neighbouring phthalocyanine (**Figure 2.12**).

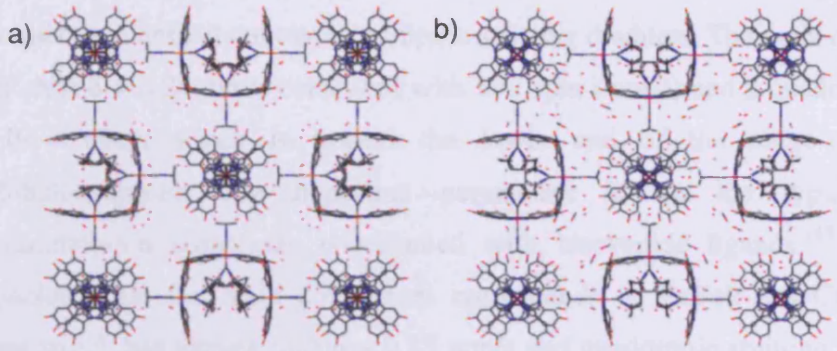


Figure 2.12. The cubic packing arrangement of a) **Pc1Fe(*t*-BuNC)$_2$**,and b) **Pc1Ru(*t*-BuNC)$_2$**.

For the iron derivative in which in the axial ligands are a water and a *t*-butyl isocyanide, the latter occupies the apical position probably for steric reasons. In addition, for this complex a water cluster is present at the non-apical site and chloroform is also localised within the nanoscale voids (**Figure 2.13**).

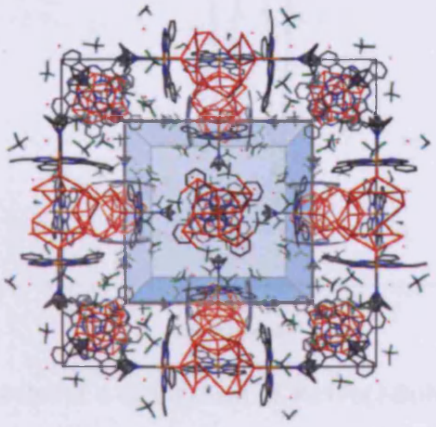


Figure 2.13. The cubic packing arrangement of **Pc1Fe(*t*-BuNC)(H$_2$O)**.

Even in the ruthenium derivative which contains two molecules of water in the axial positions, the Ru-O distances are different, the water molecule in apical site is closer (1.957 Å) than the other (2.193 Å), indicating stronger bonding at the apical axial site.

The electronic structure and the coordination state of the central iron in the cubic crystal have been investigated by mean of ^{57}Fe Mossbauer spectroscopic technique. The ^{57}Fe Mossbauer spectrum was measured at University of East Anglia in Norwich by Prof.

David Evans. The spectrum of a frozen suspension of **PcFe(*t*-BuNC)$_2$** grown from $CHCl_3$/MeOH and dispersed in FOMBLIN Y® oil was recorded at 80 K (**Figure 2.14**).

The spectrum consists of two quadrupole splitting doublets. The main component has an isomer shift δ = 0.24 mm/s consistent with low spin iron(II) and a quadrupole splitting ΔE_Q = 0.67 mm/s which is toward the lower end of the range for low spin iron(II)phthalocyanines. The hyperfine parameters lie in the typical range of phthalocyaninatoiron complexes coordinated with isocyanide ligands,[143] therefore we could conclude that the main component corresponds to **PcFe(*t*-BuNC)$_2$**. The minor component which has isomer shift δ = 0.25 mm/s and quadrupole splitting ΔE_Q = 1.75(2) mm/s may correspond to **PcFe(*t*-BuNC)(H_2O)**, present due to hydrolysis.[155]

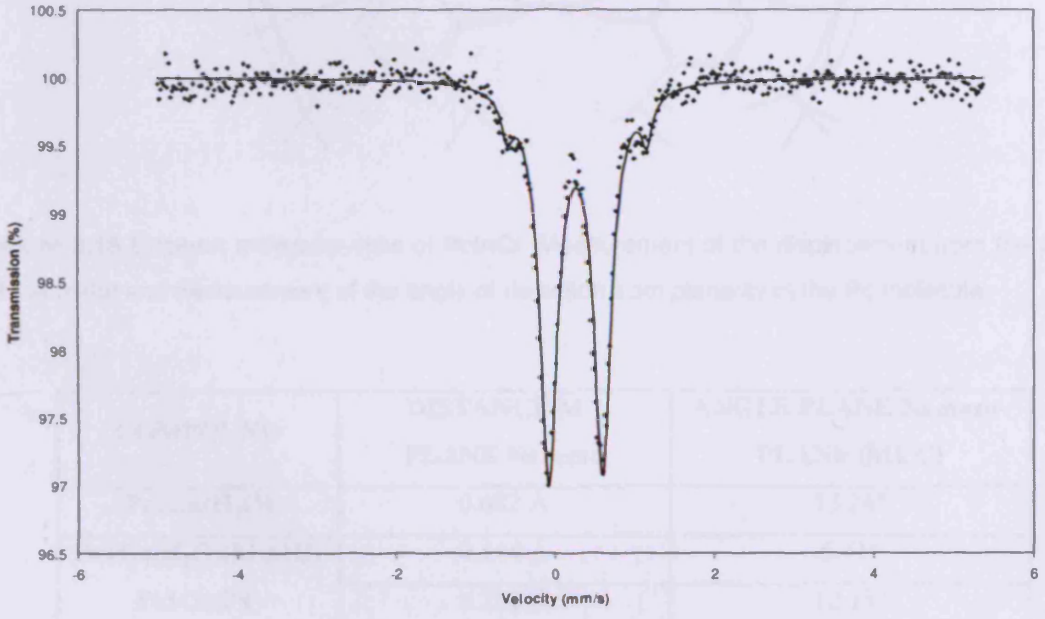


Figure 2.14. Mossbauer spectrum of a suspension of **Pc1Fe(*t*-BuNC)$_2$** crystals in FOMBLIN Y ® measured at **80 K**.

It was very pleasing that clathrates isomorphic with the cubic form of **Pc1Zn** have been obtained for most of the metal **Pc1** derivatives investigated. Indeed, the cubic arrangement formed for all cases in which the central metal could bind to either one or two ligands in its axial positions.

For all these molecules the central core of the phthalocyanine deviates, to a greater or lesser degree, from planarity by the adoption of a conical shape. A good indication of the degree of deviation from planarity of these phthalocyanine molecules is given from the measure of the distance of the metal ion from the plane formed from the four nitrogen in

the *meso* positions of the macrocycle. More indicative still is the angle formed between the latter and the plane passing through the metal and the two carbon atoms on the benzo-subunits where the phenoxy substituents are bonded. The program Mercury was used to make these measurements for all our metal **Pc1** derivatives and in **figure 2.15** an example of the molecule for which the biggest distortion was observed, **Pc1In(Cl/OH)** is shown. A summary of these data for all the molecules within the cubic crystals is reported in **table 2.1**.

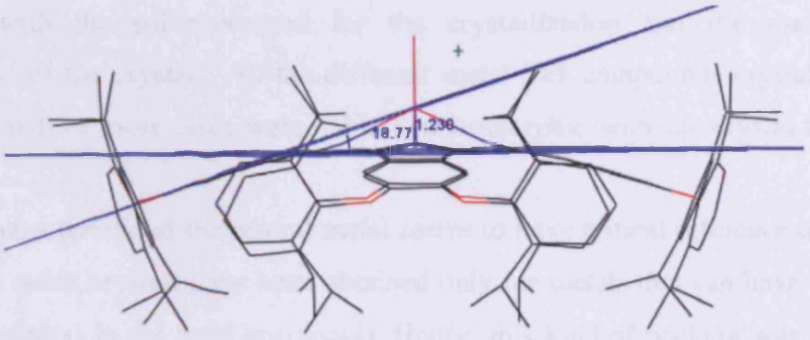


Figure 2.15 Edge-on molecular view of **PcInCl**. Measurement of the displacement from the plane of the metal and measurement of the angle of deviation from planarity of the Pc molecule.

COMPOUND	DISTANCE M - PLANE Ns *meso*	ANGLE PLANE Ns *meso*- PLANE (MCC)
Pc1Zn(H_2O)	0.682 Å	13.24°
Pc1Co(H_2O)(MeOH)	0.144 Å	6.71°
Pc1Co(Py)	0.252 Å	12.13°
Pc1Fe(*t*-BuNC)$_2$	0.195 Å	8.36°
Pc1Fe(*t*-BuNC)(H_2O)	0.141 Å	7.02°
Pc1Ru (*t*-BuNC)$_2$	0.229 Å	8.78°
Pc1Ru (H_2O)$_2$	0.200 Å	7.45°
Pc1Mn (H_2O)$_2$	0.185 Å	7.10°
Pc1Mg (H_2O)	0.800 Å	14.66°
Pc1Ti	0.908 Å	14.02°
PcIn (Cl/OH)	1.230 Å	18.77°
PcAl(Cl)	0.189 Å	7.78°

Table 2.1. The displacement from the macrocyclic plane of the metal and the angle of deviation from planarity of the Pc molecule.

It is possible to notice that the deviation from planarity is bigger in the cases in which the metal is pentacordinated and assumes a distorted pyramidal square conformation and that, predictably, it increases with the radius of the metal (In>Mg>Ti>Zn>Co).

In all the other cases, the metals are hexacordinated and assume a slightly distorted octahedral conformation. Even here, it is observed that when the axial ligands are the same the distortion increases with the radius of the metal (Ru>Mn and Ru>Fe).

Table 2.2 summarises the crystal structures of the metal phthalocyanines derived from **Pc1**, with the solvents used for the crystallization and the main structural characteristics of the crystal. All the different metal **Pc1** compounds crystallise to form clathrates, which in most cases were cubic and isomorphic with the crystal formed from **Pc1Zn**.

One characteristic of the central metal seems to have critical influence on the crystal arrangement: cubic crystals have been obtained only for metals that can have one (or two) additional ligand(s) in the axial position(s). Hence, this kind of packing was not obtained for the metal free, the nickel and the copper derivatives for which axial ligands are either impossible (metal free) or highly unusual in phthalocyanine chemistry (Cu, Ni).

For the metal free and cobalt derivatives of **Pc1** different polymorphs were obtained, depending upon the different conditions of crystallization. Also different polymorphs were obtained for the **Pc1Fe** including a monoclinic crystal, despite the iron bearing a water molecule as axial ligand.

COMPOUND	SOLVENTS OF CRYSTALLIZATION	INCLUDED SOLVENT PER Pc	CRYSTAL SYSTEM	SPACE GROUP	UNIT CELL PARAMETERS	Z	AXIAL LIGAND(S)
Pc1	DCM/ Acetone	2 acetone	Monoclinic	*P2₁/c*	a = 21.29, b = 16,89, c = 18.28 Å, β= 114,66°	2	none
	(EtOAc-DCM/MeOH)	2 EtOAc	Orthorhombic	*Pbca*	a = 19.49, b = 16.29, c = 38.42 Å	4	none
Pc1Co	DCM/acetone	2 DCM	Monoclinic	*P2₁/c*	a = 38.71, b = 16.84, c = 18.21 Å, β =90.73°	4	none
	DCM/MeOH)	33(DCM +MeOH)[a]	Cubic	*Pn-3n*	a = 37.39 Å	12	MeOH , H_2O
	$CHCl_3$/MeOH/pyridine	162 acetone[a]	Cubic	*Pn-3n*	a = 37.55 Å	12	pyridine
Pc1Cu	DCM/Acetone	1 DCM + 1 acetone	Monoclinic	*P2₁/c*	a = 38.61, b = 16.87, c = 18.43 Å, β =91.37°	4	none
Pc1Ni	$CHCl_3$/MeOH	1 $CHCl_3$	Monoclinic	*P2₁/c*	a = 21.37, b = 16.88, c = 18.72 Å , β =115.06°	2	none
Pc1Mg	$CHCl_3$/ Acetone	12 Acetone + 6 H_2O[b]	Cubic	*Pn-3n*	a = 37.33 Å	12	H_2O
Pc1Mn	$CHCl_3$/MeOH	Not determined	Cubic	*Pn-3n*	a = 37.25 Å	12	2 H_2O
Pc1Fe	$CDCl_3$/MeOH	_	Monoclinic	*P2₁/c*	a =18.94, b =18.66, c =33.27 Å, β = 92.83°	4	H_2O
Pc1Fe(t-BuNC)$_2$	$CDCl_3$/MeOH	20 MeOH + 14 H_2O[b]	Cubic	*Pn-3n*	a = 37.57 Å	12	*t*-BuNC, H_2O
	DCM /MeOH	_	Cubic	*Pn-3n*	a = 37,36 Å	12	2 *t*-BuNC
Pc1Ru	$CHCl_3$/MeOH	_	Cubic	*Pn-3n*	a = 37.56 Å	12	2 H_2O
Pc1Ru(t-BuNC)$_2$	$CHCl_3$/MeOH	33 MeOH + 7H_2O[b]	Cubic	*Pn-3n*	a = 37.63 Å	12	2 *t*-BuNC
Pc1Ti	$CHCl_3$/MeOH	8 (MeOH + $CHCl_3$)[a]	Cubic	*Pn-3n*	a = 37.51 Å	12	=O
Pc1In(Cl)	$CHCl_3$/MeOH	12 $CHCl_3$ + 13 MeOH[a]	Cubic	*Pn-3n*	a = 37.44 Å	12	$^-$OH, Cl^-, (1:1)
Pc1Al(Cl)	$CHCl_3$/MeOH	14 MeOH + 2 $CHCl_3$+ 20 H_2O[b]	Cubic	*Pn-3n*	a = 37.41 Å	12	$^-$OH

Table 2.2 Crystals structures of the different metal derivatives of **Pc1**, solvent of crystallization and main features of the crystals packings. (a) SQUEEZE, (b) NMR

2.5 Solvent and ligand exchange

In order to further investigate the interconnectivity between the cubic nanovoids, solvent-exchange experiments were repeated and extended to the use of other solvents. As previously reported,[127] the experiments were performed by placing the clathrate crystals in the desired solvent, followed by NMR spectroscopic analysis of the crystals dissolved in $CDCl_3$. The results, which are summarised in **table 2.3,** prove the accessibility of the crystals pores confirming the preliminary experiments. Other experiments were tried using 1/1(V/V) mixture of solvents in order to examine whether the crystals had shown some selectivity for one of the solvents. In no case was high selectivity of one solvent over another observed (**Table 2.3**).

SOLVENT	Pc1Zn/ SOLVENT	Pc1Zn/ H_2O
acetone	1:11	1:3
H_2O	1:1[a]	1:30
MeOH	1:20	1:2
EtOH	1:21	_
iso-propanol	1:14	1:2
hexane	1:9	1:1
Hexane/cyclohexane[b]	1:7:6	_
MeOH/ *t*-BuOH[b]	1:24:7	_

Table 2.3. Composition of the included solvent within the cubic crystals of **Pc1Zn.** (a) Residual amount of acetone remained included with the crystals of **Pc1Zn** on exchange with water. (b) solution 1/1, w/w.

In addition, ligand exchanges on the central metal ion were attempted to ascertain the accessibility of the metal, which is essential for the possible exploitation of these molecules for catalytic purposes. As for the solvent exchange, preliminary experiments were carried out on **Pc1Zn.** These experiments were performed by adding a small excess of a chosen ligand to some **Pc1Zn** crystals in the solution of crystallization. In this way the water molecule present as axial ligand on the metal was partially exchanged with ligands such as pyridine, 3,5-dimethylpyridine, DABCO and *t*-butylpyridine. The exchange was complete when picoline or N-methyl imidazole were employed.

LIGAND(L)	Pc1Zn(L)
Pyridine	50%
t-butylpyridine	48%
3,5-dimethylpyridine	72%
DABCO	68%
4-Picoline	100%
N-methylimidazole	100%

Table 2.4 Extent of exchange of axial ligands on **Pc1Zn.**

Meanwhile, the ligand exchange experiments were attempted on **Pc1Co(Py)** with picoline, *t*-butylpyridine and *n*-butylamine. The substitution of pyridine in the axial position was incomplete for picoline (60%) and *t*-butylpyridine (18%) and did not occur for *n*-butylamine. Instead, a cubic crystal of the cobalt derivative with *n*-butylamine in axial position on the metal was afforded from the crystallization of this molecule by slow diffusion of methanol into its chloroform solution, to which had been previously added the amine. Surprisingly the amine was not in the usual apical position and did not point toward the centre of the cube as had been found with all the other ligands, but was instead on the other side of the metal. A detailed look at the cubic crystal structure showed that the access of small ligands to the non apical side of the metal is allowed by the presence of narrow channels (0.25 nm) running through the crystal. This result showed that it could be possible to exert control over the coordination chemistry on both sides of the central metal cation and furthermore, of particular interest, is the fact that the non-apical ligands could behave analogously to the proximal ligands found at the active metal centres of enzymes[73,156-158] to provide biomimetic catalysis. Hence, the possibility of incorporating small bidentate ligands such as 1,6-diaminohexane, which could act as proximal ligands and tune the reactivity of the metal site for catalysis was envisaged. In addition, by simultaneously binding two phthalocyanine molecules in different cubic subunits it is possible that the crystal structure could be stabilised in the same way as wall-ties stabilise buildings with cavity brick walls.

Cubic crystals containing 1,6-diaminohexane binding two **Pc1Co** molecules were obtained successfully from a crystallization experiment in which methanol was diffused slowly into a solution of the cobalt derivative in chloroform to which a very small amount of 1,6-diaminohexane had been previously added (**Figure 2.17**). From the crystal structure

it appears that the 1,6-diaminohexane ligand pulls the two cobalt cations closer, shortening the distance by about 0.8 Å (Co-Co = 11.766 Å) in comparison with the same distance in all the other **Pc1Co** derivatives structures obtained (for example Co-Co = 12.568 Å and 12.801 Å for the derivatives with methanol and pyridine in axial position respectively). From **figure 2.16** it is clearly visible that the carbon atoms in the aliphatic chain of 1,6-diaminohexane are disordered due to the flexibility of the chain. This suggested that shorter or more rigid bidentate ligands could be used for the same purpose.

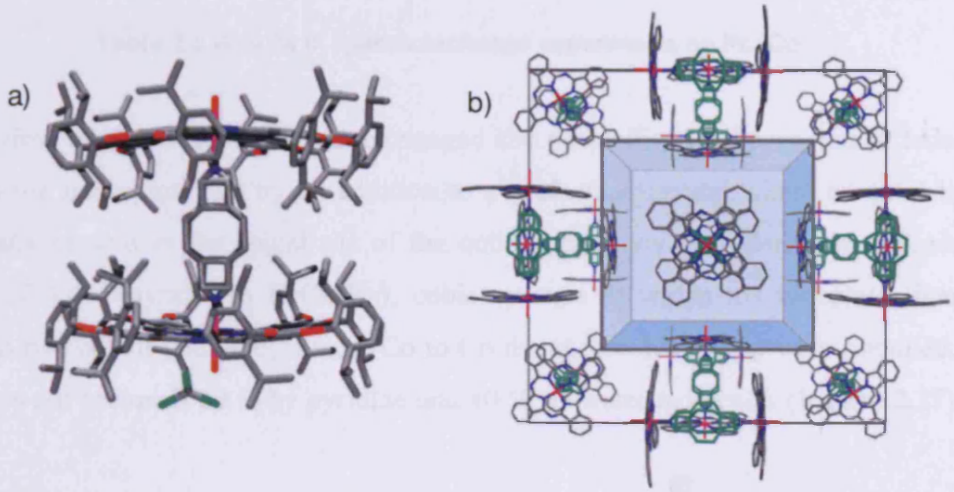


Figure 2.16 a) Edge-on molecular view of the molecular structure and b) cubic packing arrangement of **Pc1Co(1,6-diaminohexane)(H_2O).**

Therefore the same kind of experiment was repeated with different bidentate ligands (**Table 2.5**). Unfortunately, all these experiments failed to give the expected results. Crystals in which these ligands were coordinated in the apical axial position to the cobalt cation, therefore with their other coordinating end pointing toward the centre of the cubic nanovoid, were obtained only with 4,4'-bipyridyl and 1,2-bisimidazol-1-ylethane. The latter procedure of crystallization was employed even with monodentate ligands, such as 4-picoline and imidazole, since the exchange of ligands experiments on the cobalt phthalocyanine had led only to a partial substitution of the pyridine. Following this method, cubic crystals in which the cobalt cation in all the molecules was bearing respectively 4-picoline as axial ligand in the apical site and imidazole in both axial positions were obtained.

LIGAND	APICAL SITE	NON-APICAL SITE
1,5-diaminopentane	H_2O	H_2O
1,4-diaminobutane	MeOH	MeOH
1,3-diaminopropane	MeOH	MeOH
4,4'-bipyridyl	4,4'-bipyridyl (100%)	-
1,2-bisimidazol-1-ylethane	1,2-bisimidazol-1-ylethane (100%)	MeOH
p-Xylylenediamine	H_2O	H_2O

Table 2.5 Results of ligands exchange experiments on **Pc1Co.**

In view of these results it was envisaged the possibility to incorporate a bidentate ligand in the non-apical site by its addition to a preformed crystal where an axial ligand was already present in the apical site of the cobalt phthalocyanine derivative. Hence, by addition of 4,4'-bipyridyl to **PcCo(Py)**, cubic crystals in which the bidentate ligand is bonded to two cobalt phthalocyanines (Co to Co distance = 12.121 Å) were obtained. The apical sites are occupied 60 % by pyridine and 40 % by water molecules (**Figure 2.17**).

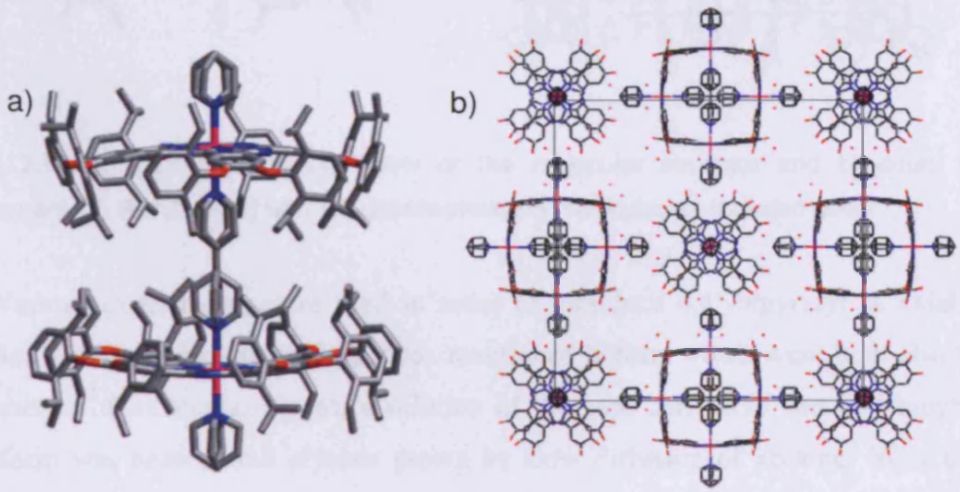


Figure 2.17 a) Edge-on molecular view of the molecular structure and b) cubic packing arrangement of **Pc1Co(bipy)(Py).**

In addition, experiments to try to incorporate mono and bidentate ligands on other metal (Zn, Mn, Fe, Ru) **Pc1** derivatives were carried out, using both exchange of ligands on preformed crystals and crystallization in presence of the ligand in solution. Interesting but sometimes contrasting results were obtained.

In particular, for the cubic crystals derived from **Pc1Zn**, not one of the bidentate ligands was found axially bonded to the metal. However, some of the aliphatic diamines such as 1,5-diaminopentane and 1,6-diaminohexane molecules were included in the crystals, but outside of the void, in the confined space between two phthalocyanine molecules. For these crystals a large amount of chloroform was present in the cubic pores of the crystals (**Figure 2.18**). The same results were obtained even when molecular sieves were added to both the solution and to the non-solvent of crystallization as drying agent in order to help the displacement of the axial water by these ligands.

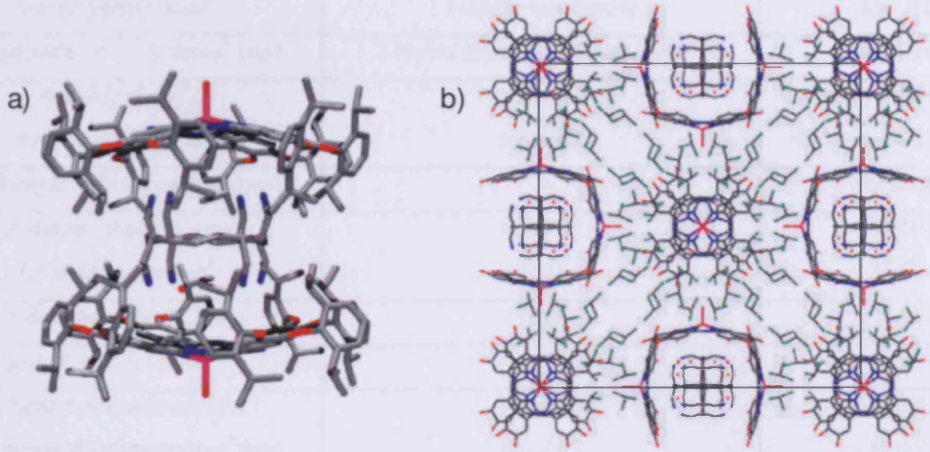


Figure 2.18 a) Edge-on molecular view of the molecular structure and b) cubic packing arrangement of **Pc1Zn(H_2O)** with **1,6-diaminohexane** molecules as included guest.

Various experiments were tried in order to introduce 4,4'-bipyridyl as axial ligand onto the Zn. Apart from the two methods mentioned before, which were both also tried in the presence of molecular sieves, a solution of the zinc derivative and 4,4'-bipyridyl in chloroform was heated, and crystals grown by slow diffusion of acetone. None of these techniques proved successful and no trace of the ligand was found in the crystals.

Pc1Mn showed even less reactivity toward axial substitution than **Pc1Zn**. Although exchange with pyridine, imidazole, 1,2-bisimidazol-1-ylethane, 4,4'-bipyridyl, and 1,4-phenylenediisocyanide were tried, only imidazole was incorporated in the crystals to occupy the axial apical position on the metal. This result was achieved by exchange of ligand on the preformed crystals in presence of molecular sieves.

In contrast, quite interesting results were obtained for the iron derivative, especially considering the fact that this molecule could be employed for catalysis purposes and

therefore the possibility to exert control on the coordination of the central metal assumes more importance. Most of the ligand exchange experiments were carried out starting from **PclFe(*t*-BuNC)$_2$**. For this molecule, both techniques of ligand substitution on the preformed crystals and also ligand addition into the solution of the metal derivative followed by crystallization, proved efficient in most cases (**Table 2.6**).

LIGAND	APICAL SITE	NON-APICAL SITE
Pyridine[a] (ms)	Py (70%), *t*-BuNC (30%)	t-BuNC
Imidazole[b]	imidazole	H_2O
1-methylimidazole[a]	1-methylimidazole	MeOH
1,2-bisimidazol-1-ylethane[b] (ms)	1,2-bisimidazol-1-ylethane, t-BuNC	MeOH
4,4'-bipyridyl[a]	*t*-BuNC	4,4'-bipyridyl (<80%)
4,4'-bipyridyl[b](ms)	*t*-BuNC	4,4'-bipyridyl (80%)
1,4-phenylenediisocyanide[a] (ms)	O_2	1,4-PhNC (83%)
1,4-diaminobutane[a] (ms)	*t*-BuNC	*t*-BuNC
1,4-diaminobutane[b]	H_2O	H_2O
1,5-diaminopentane[b](ms)	H_2O	H_2O
p-Xylylenediamine[a,b]	?	?
1,4-benzenedimethanethiol [a]	*t*-BuNC	*t*-BuNC
1,4-benzenedimethanethiol [b](ms)	*t*-BuNC	*t*-BuNC

Table 2.6 Results of ligands exchange experiments on **PclFe(*t*-BuNC)$_2$** (a) substitution on the preformed crystals experiments, (b) previous addition of the ligand to the solution of the phthalocyanine derivative experiments, (ms) experiments carried out in presence of molecular sieves.

Particularly interesting results were obtained with the bidentate ligands 4,4'-bipyridyl and 1,4-phenyleneisocyanide. In both cases the ligands were found in the non-apical axial position and joining together two phthalocyanine molecules. However, the results of the XRD analysis of the crystals obtained from both kind of exchange procedure with p-xylylendiamine were highly ambiguous. The structure could not be completely solved and the axial ligands were indistinct.

4,4'-Bipyridyl was easily incorporated into the crystals using both of the above methodologies, even though the substitution was not complete (at about 80% exchange) and it proved slightly more efficient to add the new ligand before crystallization. In both cases, the structure was composed of a minor component for which it was impossible to

locate the axial ligands. As seen previously for the cobalt derivative, the two metal cations are pulled closer by the bidentate ligand with their distance (Fe to Fe distance = 11.353 Å) significantly shorter than in **Pc1Fe(*t*-BuNC)$_2$** (Fe to Fe distance = 13.006 Å), **Pc1Fe(*t*-BuNC)(H$_2$O)** (Fe to Fe distance = 12.699Å) and the same distance in the minor component in the same structure (Fe to Fe distance = 12.355 Å).

Even with 1,4-phenylenediisocyanide the exchange achieved by its addition to the preformed crystals of **Pc1Fe(*t*-BuNC)$_2$** was not quite complete (about 83% exchange). An interesting feature is showed by the molecular structure, the substitution of the metal of the *t*-BuNC by what appears to be molecular oxygen in the apical position (**Figure 2.19**). Crystals with the same structure were obtained also from the addition of 1,4-phenylenediisocyanide to **Pc1Fe** crude and crystallization by slow diffusion of methanol into its solution in chloroform.

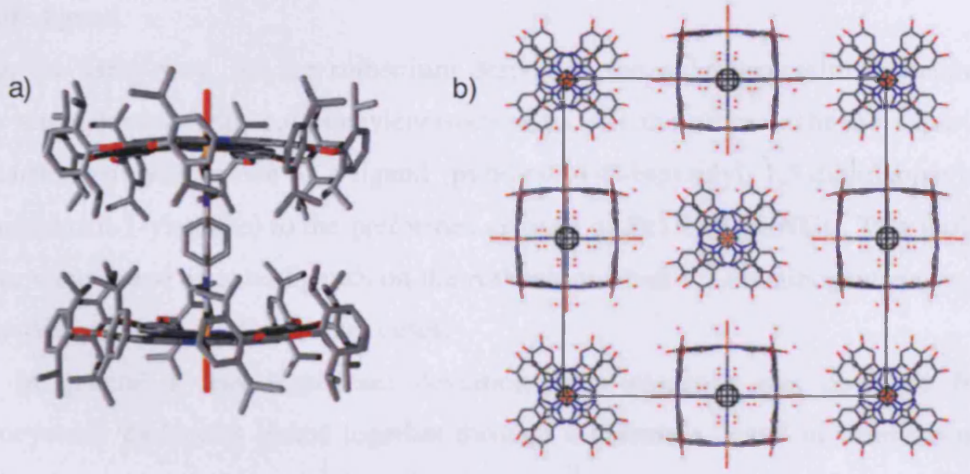


Figure 2.19 a) Edge-on molecular view of the molecular structure and b) cubic packing arrangement of **Pc1Fe(1,4-phenylenediisocyanide)(O$_2$)**.

Analogous crystal structure was obtained for the ruthenium derivative. The crystallization experiment was carried out by diffusion of methanol into a solution of **Pc1Ru(*t*-BuNC)$_2$** in chloroform to which had been previously added 1,4-phenyleneisocyanide. In this case the axial ligand substitution was complete.

Surprisingly, for both derivatives the oxygen molecule does not adopt the bent disposition usually found in oxygenated iron porphyrins,[159-161] but it is completely aligned along the central axis. Therefore, the possibility that the axial ligand could be carbon monoxide was considered, especially because in some cases of ruthenium phthalocyanine

formation reported in the literature the CO complex was isolated even though a carbon monoxide-containing precursors was not used during the reaction.[55] In order to ascertain the nature of the axial ligand, the IR spectra of both of these crystals were measured. For both of them there was no sign of coordinated CO stretching band but there was one at 1138.9 cm^{-1} and one at 1143.8 cm^{-1} for the iron and the ruthenium derivatives respectively which could plausibly correspond to O-O stretching.[161] Even in these crystals the central metals which are bonded by the ligand are pulled closer (Fe to Fe distance = 11.693 Å).

Other experiments were carried out on the recrystallisation of crude **Pc1Fe** with different bidentate ligands such as 1,4-diaminopentane, 1,5-diaminopentane and 4,4'-bipyridyl, but unfortunately suitable crystals for XRD analysis were obtained only with 1,5-diaminopentane. Even in this case and despite the addition of molecular sieves to the solution, two molecules of water were found axially bonded to the metal rather than the bidentate ligand.

In the same way, for the ruthenium derivative the only successful inclusion of a ligand was achieved with 1,4-phenyleneisocyanide. All the other exchange experiments were carried out adding one of a ligand (pyridine, 4,4'-bipyridyl, 1,5-diaminopentane or 1,2-bisimidazol-1-ylethane) to the preformed crystals of **Pc1Ru(*t*-BuNC)$_2$**. Two molecules of water were found as axial ligands on the ruthenium when 1,5-diaminopentane was used and *t*-butylisocyanide in all the other cases.

In general a less significant deviation from planarity was observed for the phthalocyanine molecules linked together through a bidentate ligand in comparison with those bearing monodentate axial ligands giving the impression that the bidentate ligands "pull" the metals closer (**Figure 2.20**). To give an indication of the different degree of deviation, the measure of the distance of the metal ion from the plane formed from the four nitrogens in the *meso* positions of the macrocycle, and in addition, the angle between this plane and the plane passing through the metal and the two carbons on the benzo-subunits, where the phenoxy substituents are bonded, were calculated and compared to the data previously obtained for the same phthalocyanines with monodentate ligands. Indeed from these data it is possible to observe that the closer the metals are "pulled" by the bidentate ligands, the smaller is the deviation from planarity of the molecule (**Table 2.7**). Even for these crystals, it is observed that when the axial ligands are the same the distortion increases with the radius of the metal (Ru>Fe).

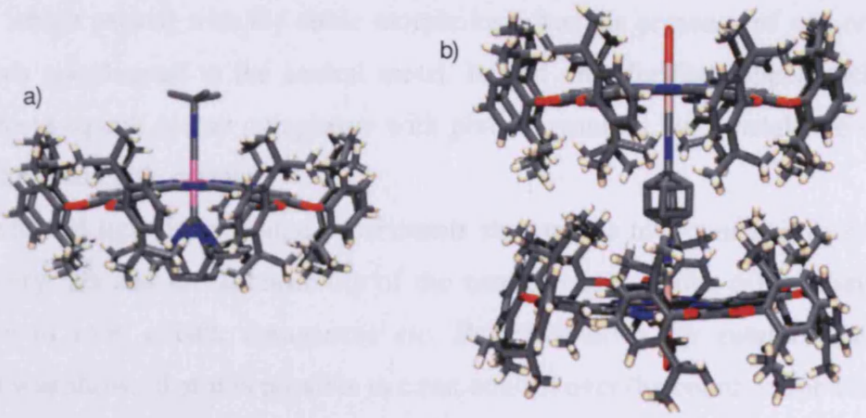


Figure 2.20. Edge-on molecular view of the molecular structures of a) **Pc1Ru(*t*-BuNC)$_2$** and b) **Pc1Ru(1,4-phenylenediisocyanide)(O$_2$)**

COMPOUND		DISTANCE M –PLANE Ns *meso*	ANGLE PLANE Ns *meso*- PLANE (MCC)	DISTANCE M-M
Pc1Co(H$_2$O)(MeOH)	monodentate	0.144 Å	6.71°	12.568 Å
Pc1Co(Py)		0.252 Å	12.13°	12.801 Å
Pc1Co(1,6-diahex)	bidentate	0.043 Å	4.2°	11.766 Å
Pc1Co(py)(bipy)		0.108 Å	5.52°	12.121 Å
Pc1Fe(*t*-BuNC)$_2$	monodentate	0.195 Å	8.36°	13.006 Å
Pc1Fe(*t*-BuNC)(H$_2$O)		0.141 Å	7.02°	12.699 Å
Pc1Fe(*t*-BuNC)(bipy)	bidentate	0.033 Å	3.57°	11.353 Å
Pc1Fe(O$_2$)(Phic)		0.061 Å	3.82°	11.693 Å
Pc1Ru (*t*-BuNC)$_2$	monodentate	0.229 Å	8.78°	13.193 Å
Pc1Ru (H$_2$O)$_2$		0.200 Å	7.45°	12.756 Å
Pc1Ru(O$_2$)(Phic)	bidentate	0.082 Å	4.50°	11.831 Å

Table 2.7. The displacement from the macrocyclic plane of the metal, the angle of deviation and the distance between the metals.

2.6 Conclusions

Various **Pc1** metal derivatives (Co, Cu, Ni, Fe, Ru, Mn, Mg, In, Al, Ti) were synthesised and crystallised forming clathrates, which in most of the cases were isomorphic with the cubic crystal obtained for **Pc1Zn.** A common feature showed by the

molecules which packed with the cubic morphology was the presence of one or two extra axial ligands coordinated to the central metal. Indeed only for the copper, nickel, which generally form square planar complexes with phthalocyanines, and metal-free derivatives were not obtained cubic crystals.

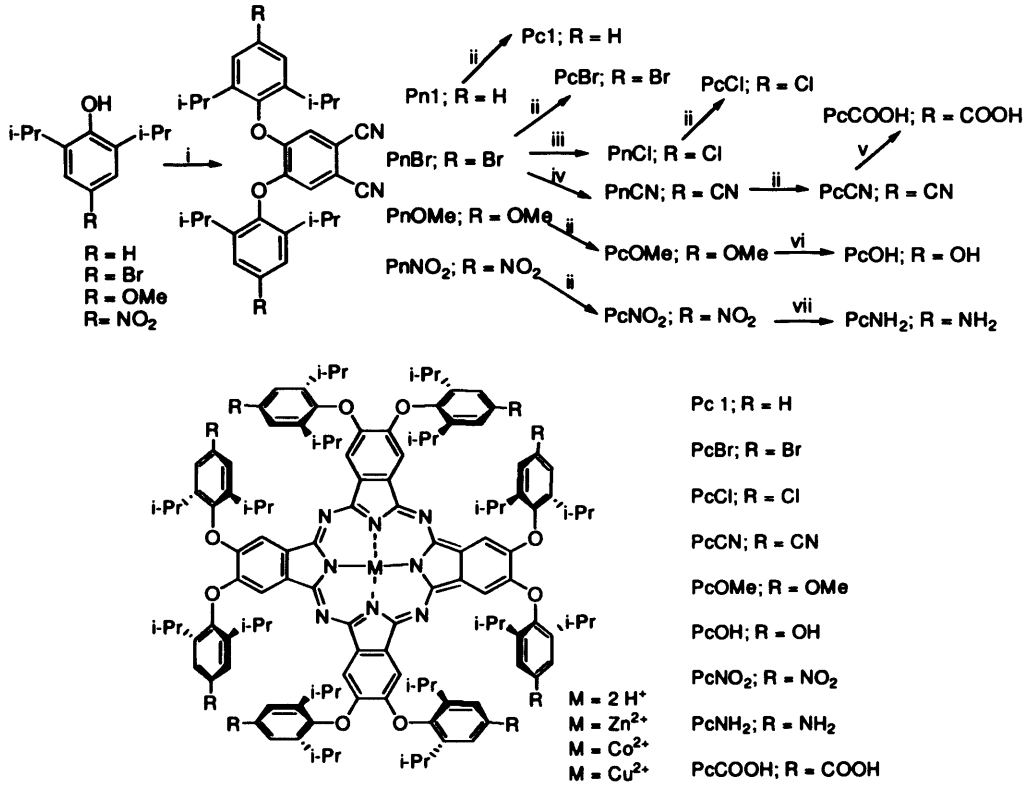
Solvent and ligands exchange experiments showed the interconnectivity of the voids within the crystals and the accessibility of the central metal, which offer possibilities for exploitation of iron, cobalt, manganese *etc.* **Pc1** derivatives for catalytic purposes. In addition, it was shown that it is possible to exert control over the coordination chemistry on both sides of the central metal. Bidentate ligands of appropriate size were successfully placed in the non apical site of the metal to link together two **PcsM** molecules. This may enhance the stability of the crystal structure and furthermore could have an important role in tuning the catalytic activity of the metal complexes.

Chapter 3

3. Results and discussion: addition of substituents.

3.1 Introduction

Unfortunately, XRD analysis indicates that the cubic crystals formed by the zinc 2,3,9,10,16,17,23,24-octa-(2',6'-di-*iso*-propylphenoxy)phthalocyanine are not stable to the loss of the included solvent although macroscopically they appear unchanged. Careful analysis of the crystal structure of zinc 2,3,9,10,16,17,23,24-octa-(2',6'-di-*iso*-propylphenoxy)phthalocyanine reveals that each edge of the phthalocyanine cube contains eight interleaved phenoxy rings and it is the van der Waals interactions between these groups that appear to induce its cubic packing arrangement. Therefore, we thought that the introduction of substituents in the 4-position of the phenoxy groups could enhance the stability of the crystal structure, due to stronger dipole-dipole (e.g., R = Br, Cl, CN, OMe, NO_2) or hydrogen bond interactions (e.g., R = OH, COOH, NH_2). An outline of possible phthalocyanine synthetic targets is given in **Scheme 3.1**.

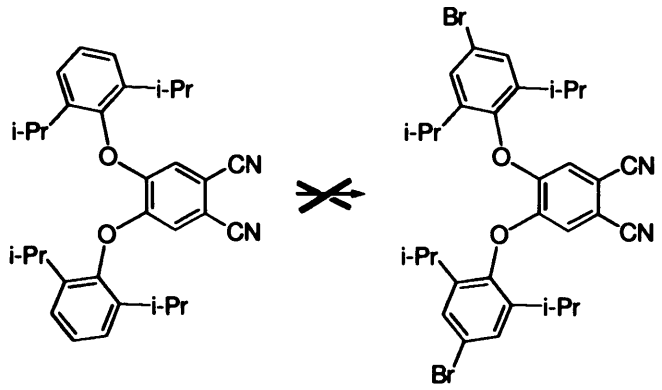


Scheme 3.1. The outline synthesis of **PcR**. *Reagents and conditions*: i) 4,5-Dichlorophthalonitrile, K_2CO_3, DMF 80 °C; ii) Metal acetate, NMP, 165 °C; iii) CuCl, DMF, 150 °C; iv) CuCN, DMF, 150 °C; v) KOH, EtOH, reflux; vi) BBr_3, CH_2Cl_2, rt; vii) Sn, HCl

3.2 Synthesis of Phthalonitriles

3.2.1 Synthesis of 4,5-di(4'-bromo-2',6'-di-*iso*-propylphenoxy) phthalonitrile

The bromine was the first substituent which we tried to introduce in the 4-position on the phenoxy groups. The 4,5-di(4'-bromo-2',6'-di-*iso*-propylphenoxy)phthalonitrile, **PnBr**, could constitute, in fact, the starting material not just for the synthesis of the corresponding phthalocyanine but also for the 4,5-di(4'-chloro-2',6'-di-*iso*-propylphenoxy) and 4,5-di(4'-cyano-2',6'-di-*iso*-propylphenoxy)phthalonitriles, (**PnCl** and **PnCN**). As shown in **Scheme 3.1,** a possible strategy for the synthesis of this molecule involves the introduction of bromine via the electrophilic aromatic substitution 2,6-di-*iso*-propylphenol, followed by nucleophilic aromatic substitution of the phenol on the dichlorophthalonitrile. However, the 4,5-di(2',6'-di-*iso*-propylphenoxy)phthalonitrile was available and the possibility of preparing **PnBr** by electrophilic aromatic substitution of bromine directly on this molecule was explored (**Scheme 3.2**).

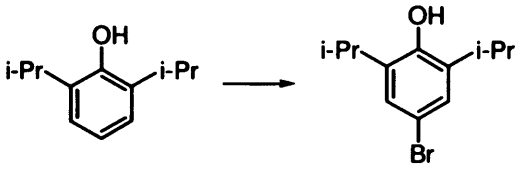


Scheme 3.2. Bromination of **Pn1**.

We tried this reaction under a number of different conditions, always starting by dropwise addition, of bromine at 0 °C to a solution of 4,5-(2,6-di-*iso*-propylphenoxy)-phthalonitrile in dichloromethane.[162] The reaction was then heated to room temperature, and later at reflux. Because of the lack of reaction, the addition of $FeBr_3$ as catalyst and greatly increased time of reaction were used to try and force the reaction, but unfortunately, the desired product was not obtained in good yield. From the first reaction, achieved for 1h at room temperature and further 5h at reflux, without catalyst, we only obtained the starting material. In all the other conditions, a mixture of mono-substituted

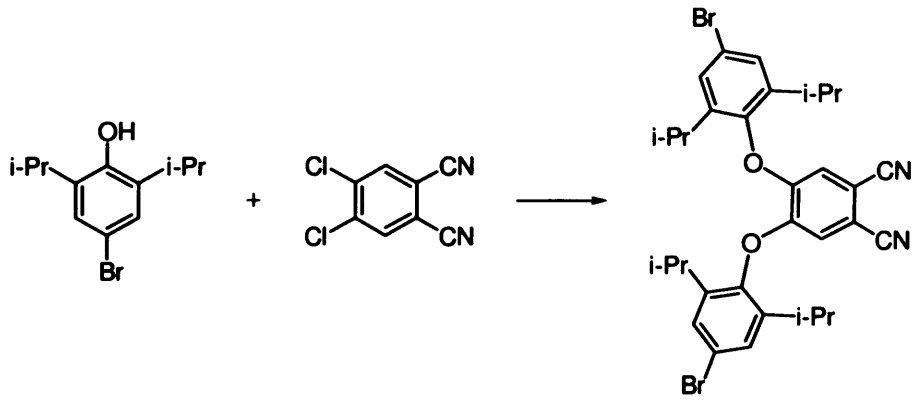
and di-substituted compounds was obtained, which could not be separated by column chromatography.

The presence of the electron-withdrawing nitrile groups appeared to deactivate the phenoxy group towards electrophilic aromatic substitutions, even in the presence of a Lewis acid catalyst. After these failed attempts, we decided to return to the original strategy: the bromination of 2,6-di-*iso*-propylphenol (**Scheme 3.3**). The reaction was achieved, as described in literature[162] adding bromine dropwise, at 0 °C to a stirred solution of 2,6 di-*iso*-propylphenol in dichloromethane. The reaction was left for 1h at room temperature then the temperature was increased to 45 °C to drive-off the remaining hydrogen bromine. The desired product was obtained with almost quantitative yield.



Scheme 3.3. Bromination of 2,6-di-*iso*-propylphenol. *Reagents and conditions*: Br_2, DCM.

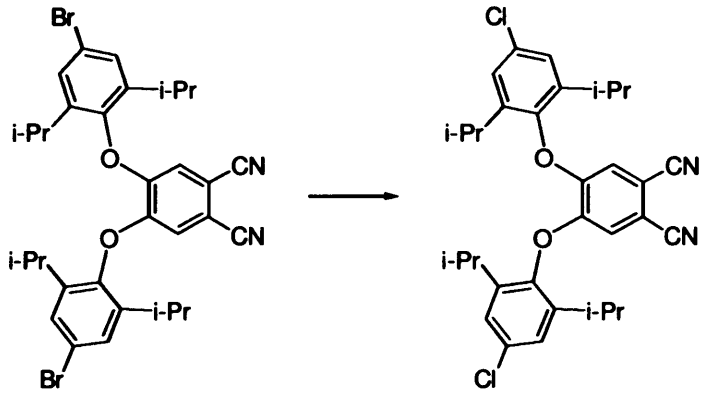
The synthesis of 4,5-bis(4'-bromo-2',6'-di-*iso*-propylphenoxy)phthalonitrile, **PnBr**, has been achieved, as for **Pn1**, by nucleophilic aromatic substitution of the phenol on the 1,2-dichlorophthalonitrile, using potassium carbonate as base and DMF as solvent.[20,127,163] The bromine, which acts as an electron withdrawing group, facilitated the formation of the phenoxy anion, leading to an improvement on the yield of reaction, which increased from 65%, for **Pn1**, to 82% for **PnBr** (**Scheme 3.4**).



Scheme 3.4. Synthesis of **PnBr**. *Reagents and conditions*: K_2CO_3, anhydrous DMF 70 °C

3.2.2 Synthesis of 4,5-bis(4'-chloro-2',6'-di-*iso*-propylphenoxy) phthalonitrile

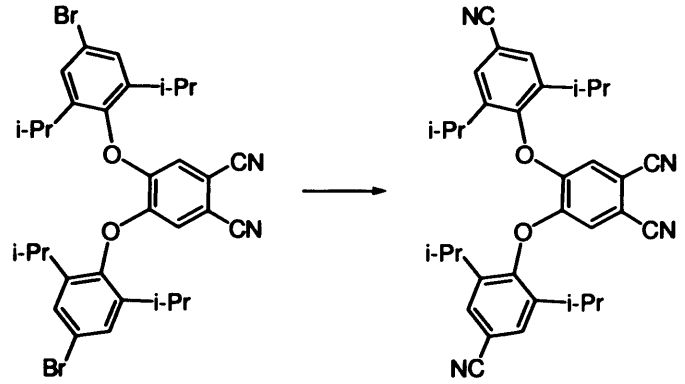
In accordance with the synthetic strategy, 4,5-bis(4'-chloro-2',6'-di-*iso*-propylphenoxy)phthalonitrile, **PnCl**, was prepared by the reaction of **PnBr** with an excess of copper (I) chloride in dry dimethylformamide at 150 °C (**Scheme 3.5**).[164] The high temperature and the presence of a copper salt favoured the formation of a complex mixture of phthalocyanines together with the desired product, which was isolated in a yield of 35% by column chromatography.



Scheme 3.5. Synthesis of **Pn3**. *Reagents and conditions*: CuCl, anhydrous DMF, 150 °C

3.2.3 Synthesis of 4,5-bis(4'-cyano-2',6'-di-*iso*-propylphenoxy) phthalonitrile

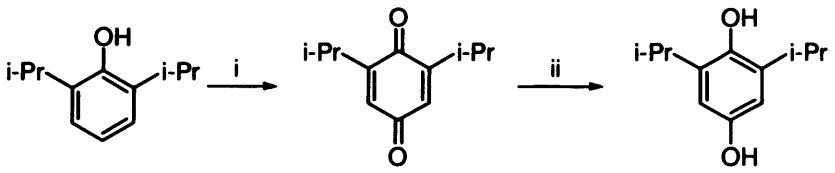
A similar procedure was used to synthesise 4,5-bis(4'-cyano-2',6'-di-*iso*-propylphenoxy)phthalonitrile, **PnCN** (**Scheme 3.6**).[165] A large excess of CuCN was added to a solution of **PnBr** in dry dimethylformamide under nitrogen and the reaction was complete at 150 °C after 24 h to give a yield of 54 %.



Scheme 3.6. *Synthesis of* **Pn4**. *Reagents and conditions*: CuCN, anhydrous DMF, 150 °C

3.2.4 Synthesis of 4,5-bis(4'-methoxy-2',6'-di-*iso*-propylphenoxy) phthalonitrile

Our next target molecule was 4,5-bis(4'-methoxy-2',6'-di-*iso*-propylphenoxy), phthalonitrile, **PnOMe.** Our original strategy was to synthesise the 4-methoxy-2,6-di-*iso*-propylphenol via 2,6-di-isopropylhydroquinone using a previously reported four step route involving the diazotisation of 4-aminophenol and then employing a selective methylation of the less hindered 4-hydroxyl group.[166] However, we decided to synthesise the hydroquinone starting from 2,6-di-*iso*-propylphenol, via its previous oxidation to quinone (**Scheme 3.7**). The oxidation was achieved using lead (IV) oxide and perchloric acid in acetic acid,[167] in 83% yield. After using several different reagents the reduction to the hydroquinone was achieved with sodium borohydride in methanol at 0 °C in 93% yield.[168]



Scheme 3.7. Synthesis of 2,6-di-iso-propyl-p-quinone and of 2,6-di-*iso*-propyl-p-hydroquinone. *Reagents and Conditions*: i) $HClO_4$ (70%), PbO_2, acetic acid; ii) $NaBH_4$, MeOH, 0 °C

The selective methylation of the 4-hydroxyl group proved more problematic. The initial attempts using Methyl iodide as methylating agent, potassium carbonate as base and 2-butanone as solvent under various conditions failed to give the required product selectively.[169,170] However, with careful chromatography, the desired isomer was isolated

but in a very poor yield. In order to confirm that the correct isomer was isolated, a ^{1}H NOESY NMR spectrum was obtained (**Figure 3.1**) from which it is possible to see that the protons of the methoxy group interact through space with the aromatic protons and that the hydroxyl proton interacts with the isopropyl groups, as indicated from the cross peaks that have been is circled in red.

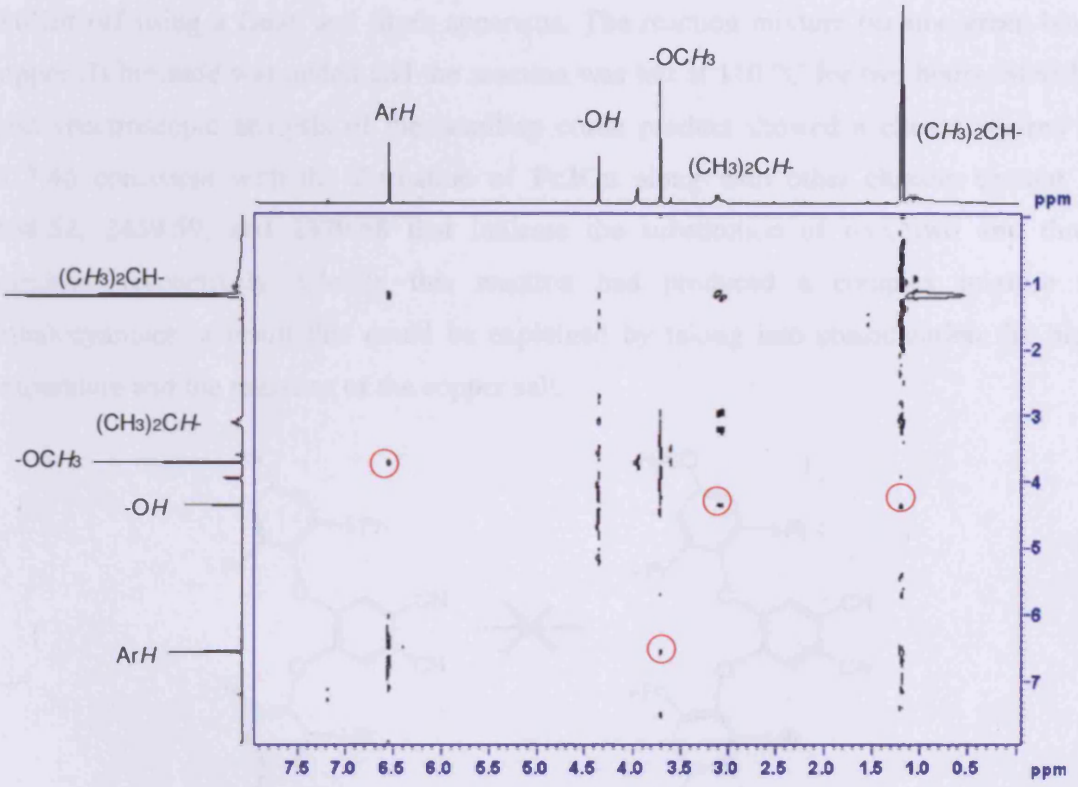
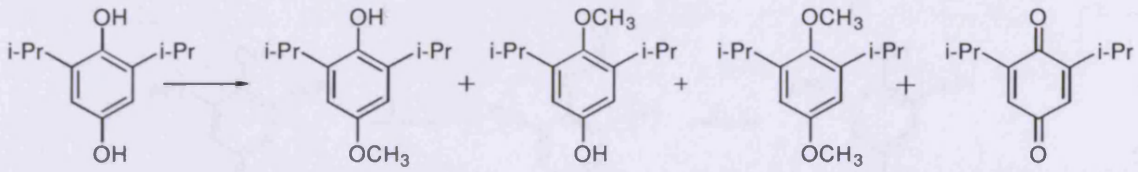


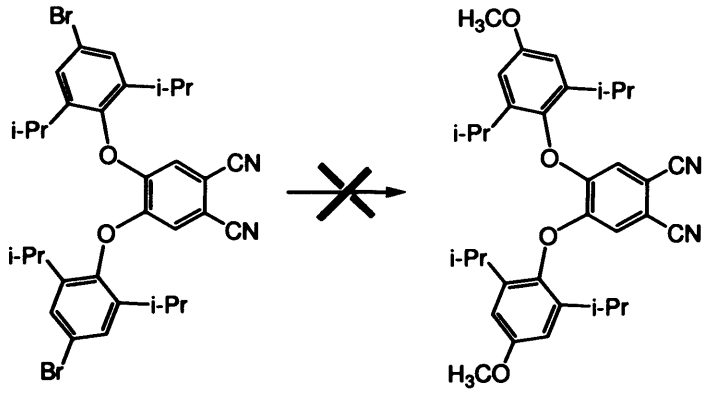
Figure 3.1. ^{1}H NOESY NMR of 4-methoxy-2,6-di-*iso*-propylphenol.

The low yield of this reaction prompted the use of other bulkier methylating agents and for such as dimethylsulfate[171-173] and *para*-toluene-methylsulfonate[174] but despite a range of reaction conditions only a mixture of products was obtained in each case.



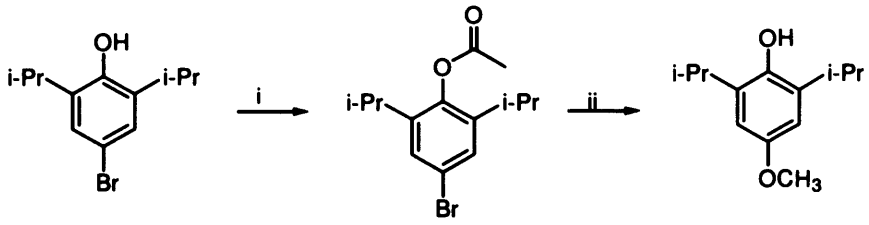
Scheme 3.8. Synthesis of 4 methoxy-2,6-di-*iso*-propylphenol. *Reagents and Conditions*: a) CH_3I, K_2CO_3, 2-butanone; b) $(CH_3)_2SO_4$, K_2CO_3, acetone; c) p-toluene-methylsulfonate, NaOH (20%) or K_2CO_3, acetone

Instead, the synthesis of **PnOMe** from **PnBr** was attempted using a copper mediated substitution of bromine by methoxide anion (**Scheme 3.9**). Following a reported procedure[175] for the synthesis of methyl aryl ethers from aryl bromides, the reaction was carried out adding sodium methoxide in methanol to a solution of **PnBr** in anhydrous dimethylformamide. The temperature was increased to 110 °C and the methanol was distilled off using a Dean and Stark apparatus. The reaction mixture became green-blue. Copper (I) bromide was added and the reaction was left at 110 °C for two hours. MALDI mass spectroscopic analysis of the resulting crude product showed a cluster centred at 2617.46 consistent with the formation of **Pc2Cu** along with other clusters centred at 2538.52, 2459.59, and 2379.68 that indicate the substitution of one, two and three bromines, respectively. Clearly this reaction had produced a complex mixture of phthalocyanines, a result that could be explained by taking into consideration the high temperature and the presence of the copper salt.



Scheme 3.9. Synthesis of **PnOMe**. *Reagents and Conditions*: $NaOCH_3$/MeOH, DMF, CuBr, 110 °C

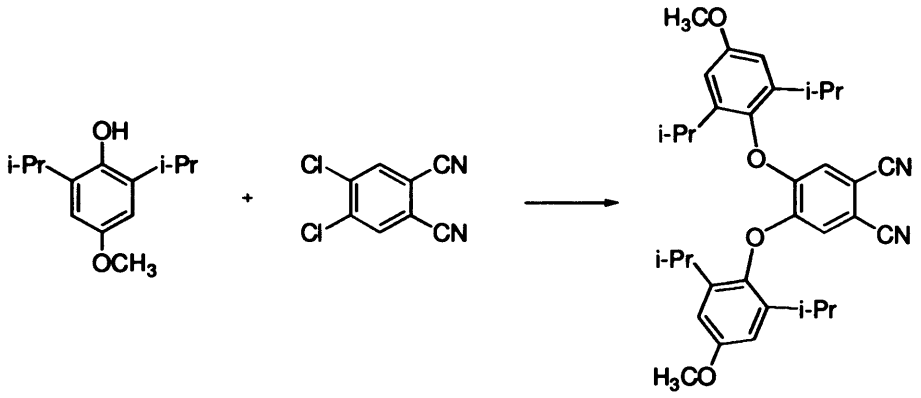
Therefore a similar substitution reaction was attempted on the acetyl ester of 4-bromo-2,6-di-*iso*-propylphenol readily prepared in 90.5% yield by adding sulphuric acid to a solution of the phenol in acetic anhydride (**Scheme 3.10**).[176]



3.10. Protection of 4-bromo-2,6-di-iso-propylphenol and synthesis of 4-methoxy-2,6-di-iso-propylphenol. *Reagents and Conditions*: i) Acetic anhydride, H_2SO_4.ii) $NaOCH_3/CH_3OH$, DMF, CuBr, 110 °C

An excess of sodium methoxide in methanol was added to a solution of 4-acetoxy-3,5-di-*iso*-propyl-bromobenzene in anhydrous dimethylformamide and, the temperature was increased to 110 °C in order to allow the methanol to distil off, then copper(I)bromide was added.[175] As an added benefit, the ester protecting group was removed during the course of the reaction to give pure 4-methoxy-2,6-di-*iso*-propylphenol in 89% yield (**Scheme 3.10**).

At this point we could proceed with the synthesis of 4,5-bis(4'-methoxy-2',6'-di-*iso*-propylphenoxy)phthalonitrile, **PnOMe**. We followed the same procedure used for the synthesis of **Pn1** (**Scheme 3.11**).[127,163] The product was isolated by recrystallization from methanol with a yield of 72%.

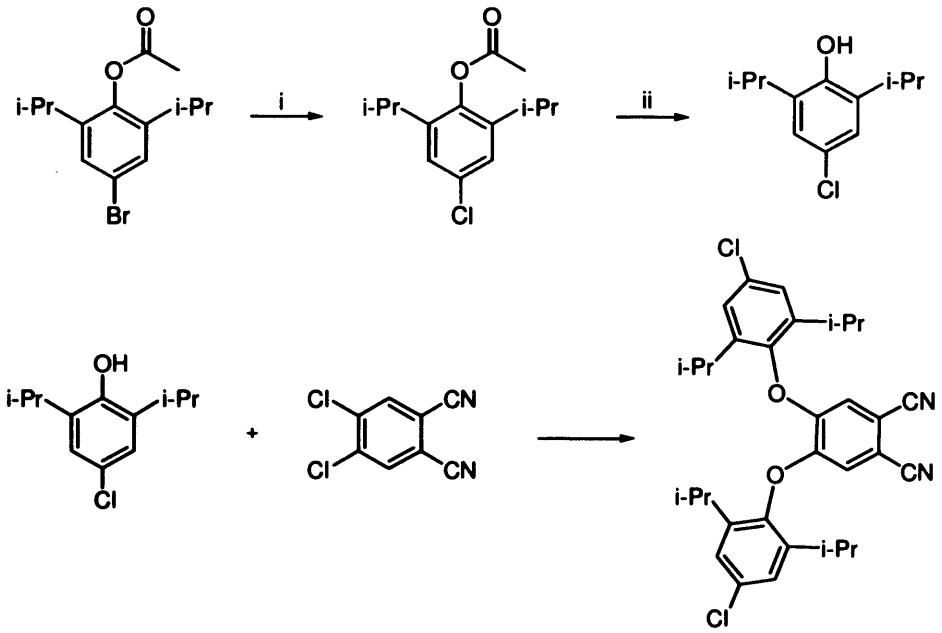


Scheme 3.11. Synthesis of **PnOMe**. *Reagents and conditions:* K_2CO_3, DMF, 70 °C.

3.2.5 Alternative route for PnCl synthesis

Considering the simplicity and the high yields of the various steps that led to the synthesis of **PnOMe**, an analogous approach to **PnCl** was tried and proved successful with a near quantitative yield of the 4-chloro-2,6-di-*iso*-propylphenol precursor[176] (**Scheme 3.13**) and avoided any need for chromatographic purification, which was necessary with the previous synthesis to get rid of the mixture of phthalocyanines formed during the reaction.

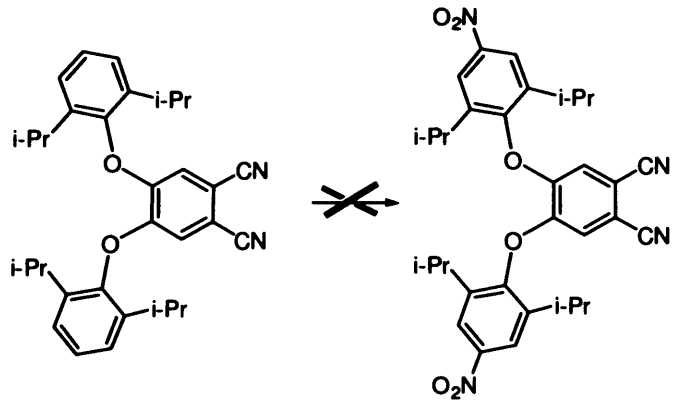
PnCl was synthesised from 4-chloro-2,6-di-*iso*-propylphenol and 4,5-dichlorophthalonitrile in 77% yield.[20,127,163]Despite requiring more steps, this route proved effective with a much higher overall yield of 62% versus only 29% for the previous transhalogenation reaction (**Scheme 3.5**).



Scheme 3.13. Synthesis and hydrolysis of the 4-acetoxy-3,5-di-*iso*-propyl-chlorobenzene. *Reagents and conditions*: i) CuCl, DMF, 150°C.ii) NaOH (40%), MeOH and synthesis of **PnCl**. *Reagents and conditions*: K_2CO_3, anhydrous DMF, 70 °C.

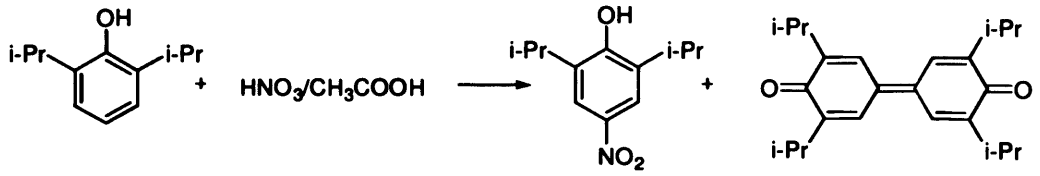
3.2.6 Attempted synthesis of nitro-containing phthalonitrile

The preparation of 4,5-bis(4'-nitro-2',6'-di-*iso*-propylphenoxy)phthalonitrile, **Pn7**, proved highly problematic. Attempts to obtain **Pn7** by direct nitration of **Pn1** (**Scheme 3.16**) failed instead it gave a complex mixture of products.[177](19)



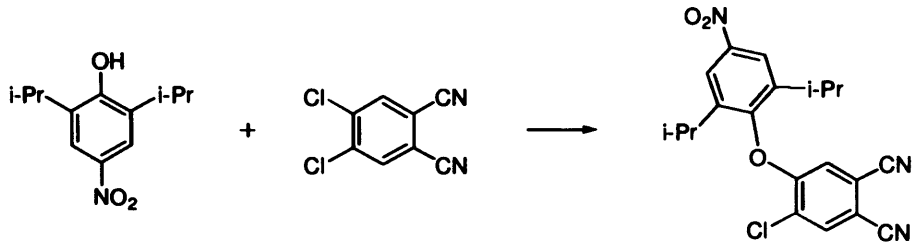
Scheme 3.16. Nitration of **Pn1**. *Reagents and conditions*: a) HNO_3/H_2SO_4; b) HNO_3/CH_3COOH, DCM.

Due to the difficulties encountered during the nitration of **Pn1**, the direct electrophilic nitration of the phenol was attempted following literature reports[166,177]. However in most cases the oxidatively coupled product was formed rather than the desired nitrated phenol as had been previously reported for this reaction.[162,178]



Scheme 3.17. Synthesis of 4-nitro-2,6-di-*iso*-propylphenol. *Reagents and condition*: HNO_3, acetic acid, DCM, 0 °C.

However, after much effort the synthesis of the 4-nitro-2,6-di-*iso*-propylphenol was finally achieved with a yield of 60%. Unfortunately, the synthesis of **PnNO$_2$** by adapting the usual reaction with 4,5-dichlorophthalonitrile[20,127,163] gave after four days at 70 °C only the monosubstituted product. Even under forcing conditions (i.e. large excess of phenol, extended reaction period) only the monosubstituted product was obtained.

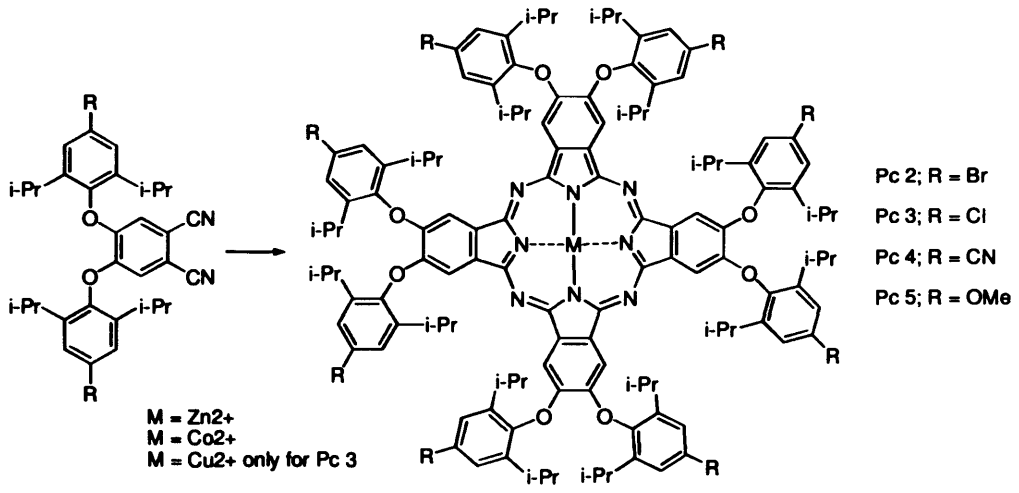


Scheme 3.19. Attempted Synthesis of **PnNO$_2$**. *Reagents and conditions*: K_2CO_3, DMF 70 °C

3.3 Synthesis of phthalocyanines

3.3.1 Zinc and cobalt phthalocyanine derivatives

All the zinc and cobalt phthalocyanines were synthesised using the same reaction that proved effective for the synthesis of **Pc1Zn**.[127] The appropriate metal salt (zinc or cobalt acetate) was added to a solution of the phthalonitrile in NMP and the reaction mixture was heated at 165 °C for 20 h (**Scheme 3.20**). Each phthalocyanine derivative was obtained in reasonable yields and purified by column chromatography (**Table 3.1**)



Scheme 3.20. Synthesis of **PcsM**. *Reagents and conditions*: Metal salt, NMP, 165 °C.

3.3.2 Metal free and copper phthalocyanine derivatives

The same procedure (i.e. reaction with copper acetate) was attempted for the synthesis of the copper-containing phthalocyanine derivatives but unfortunately this procedure proved successful only for the chlorinated phthalonitrile, **PnCl** (**Scheme 3.20**).

During the attempted synthesis of **PcBrCu**, instead, a complex mixture of copper phthalocyanines was formed. We tried to separate the mixture by means of column chromatography but without success. The mixture was analysed by MALDI mass spectrometry showed a cluster of peaks corresponding to **PcBrCu** together with numerous other clusters of peaks which indicated loss of bromine (**Figure 3.2**).

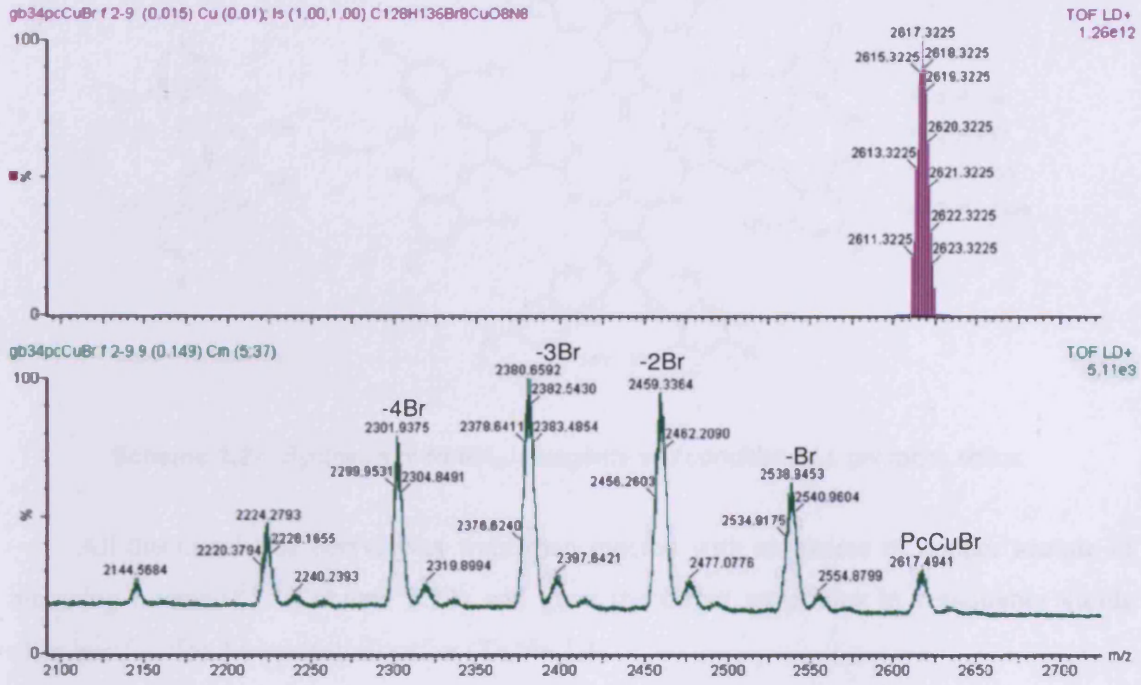
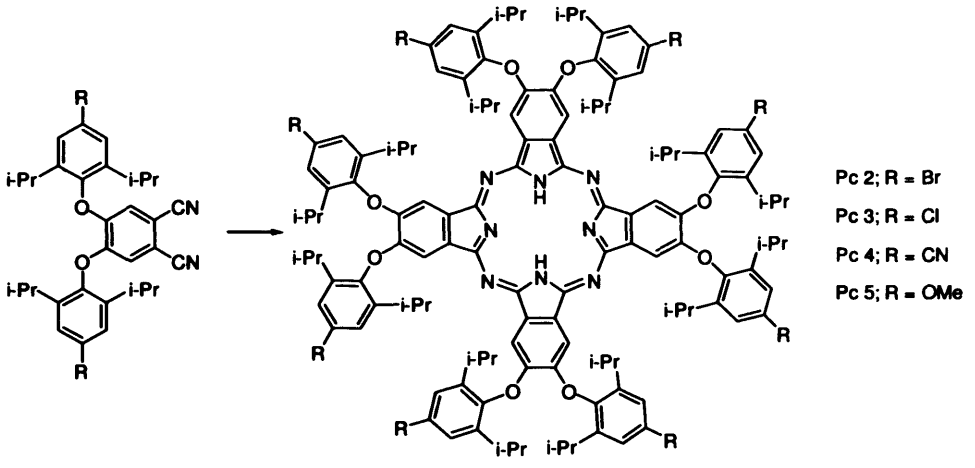


Figure 3.2 MALDI spectrum of a column chromatography fraction deriving from the attempted synthesis of **PcBrCu** using copper acetate.

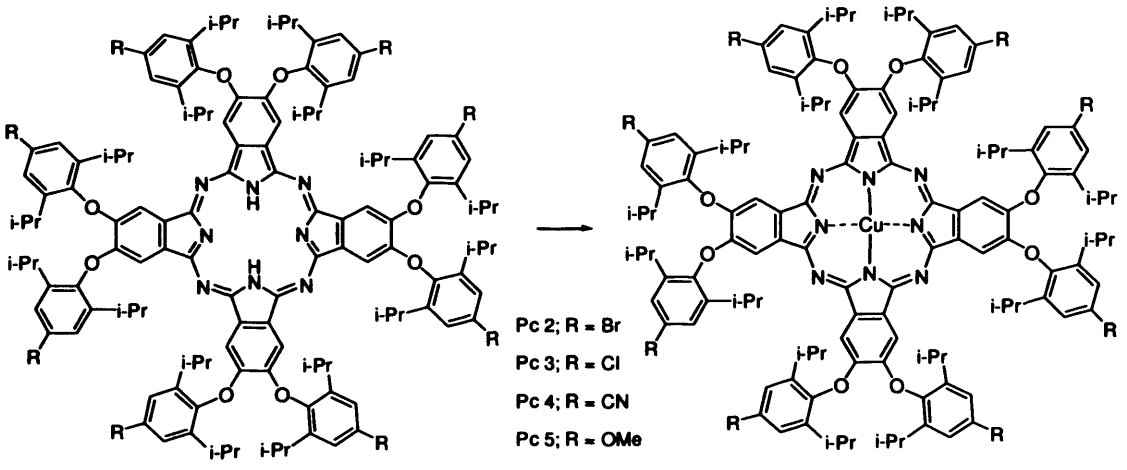
Clearly, this method was not suitable for the synthesis for **PcBrCu** since the copper salt mediates the removal of bromine. Copper phthalocyanines, along with many other metal derivatives, are prepared easily by the metal-insertion reaction of the metal free derivative and so attention was switched to the prepared of the metal-free derivatives. [1,14,22]

All metal free phthalocyanines were synthesised quite efficiently following the 'Linstead method' in which lithium metal is added to refluxing solution of the phthalonitrile in *n*-pentanol[1,14,133,148] (**Scheme 3.21**). These molecules were purified by column chromatography and were obtained in satisfactory yields (**Table 3.1**).



Scheme 3.21. Synthesis of **$PcRH_2$**. *Reagents and conditions*: Li, pentanol, reflux.

All the metal free derivatives were then reacted with an excess of copper acetate in refluxing pentanol[22] (**Scheme 3.22**) and gave the target molecules in reasonable yields after purification by recrystallization (**Table 3.1**).

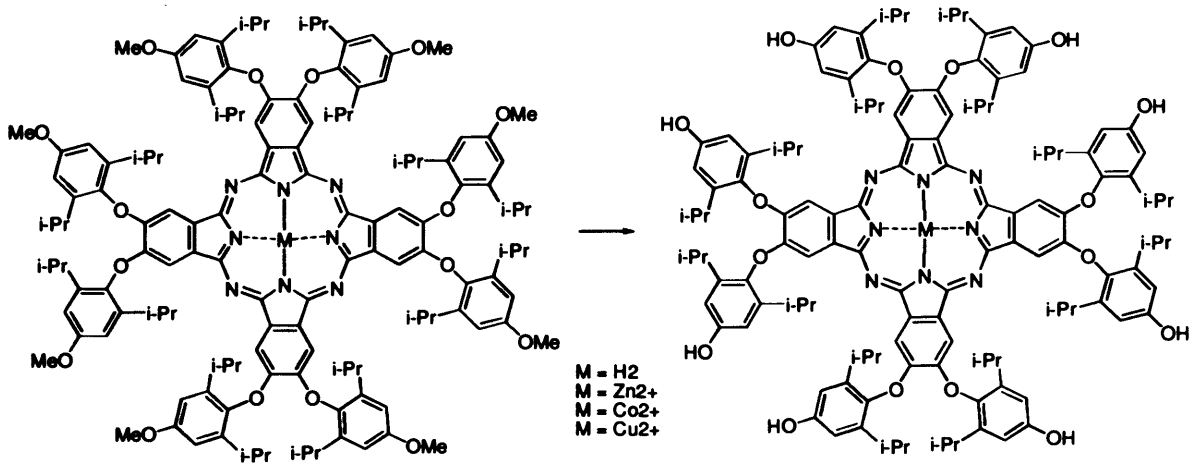


Scheme 3.22. Synthesis of **PcCus**. *Reagents and conditions*: $Cu(OOCCH_3)_2$, DCM, 0 °C.

3.3.3 Preparation of PcOHs and $PcCO_2Hs$

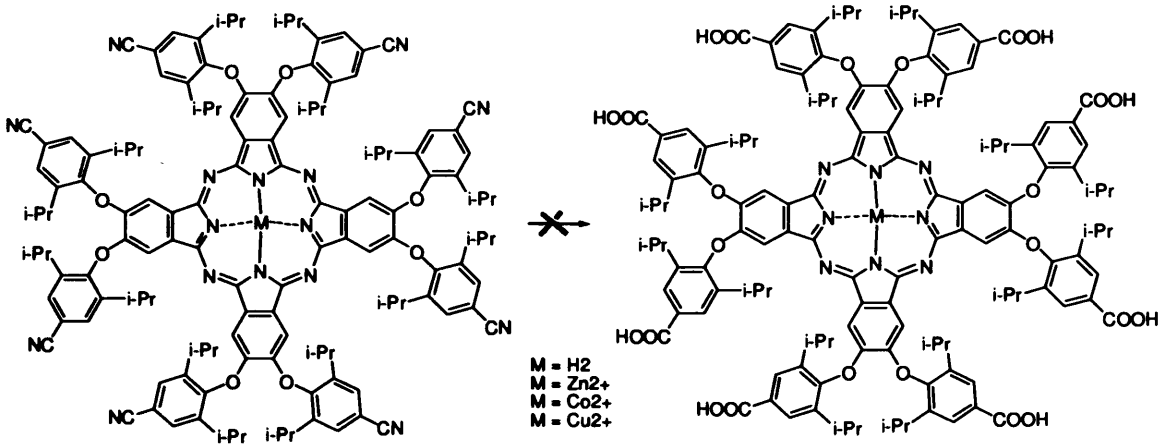
PcOH and **PcCOOH** contain hydroxyl and carboxylic groups at each of the 4-positions of the eight phenoxy-rings, respectively. **PcOHs** were readily obtained in good

yield by the demethylation reactions of the appropriate **PcOMes** using an excess of boron tribromide in anhydrous DCM[179,180] (**Scheme 3.23**; **Table 3.1**).



Scheme 3.23. Synthesis of **PcOHs**. *Reagents and conditions*: BBr_3, DCM, 0 °C.

For the synthesis of the **PcCOOHs** the nitrile groups on the corresponding **PcCNs** had to be hydrolysed to carboxylic acids. The simultaneous and complete hydrolysis of the eight nitrile substituents proved to be challenging. Initially a basic hydrolysis performed with KOH (85%)[181,182] in refluxing ethanol was attempted on **PcCNCo** but MALDI analysis of the product formed after 8 h revealed that it was practically all amide. Therefore, the reaction mixture was refluxed for a further 24 hours. A green solid, which was only partially soluble in polar solvent such as methanol and acetone, was obtained (**Scheme 3.24**). Despite the low solubility, the MALDI spectrum of the product showed a cluster of peaks which was close to the right mass, but still two units lower, together with other peaks, which we were not able to assign. Therefore, the hydrolysis seemed to be slowly taking place, but it was not complete. Other reaction conditions were tried in order to obtain the fully hydrolysed product but with similar results. The low solubility of this product mixture suggested that the completely hydrolysed compound could be even less soluble and therefore would be difficult to purify and study for clathrate formation.



Scheme 3.24. Attempted synthesis of **PcCOOHs.** *Reagents and conditions*: KOH (85% aqueous solution), ethanol, reflux.

To conclude, most of the target molecules were prepared in reasonable yields (**Table 3.1**), and therefore it was possible to determine if the different substituents placed in the 4-position of the phenoxy rings, with their possible dipole-dipole (Br, Cl, CN, OMe) or hydrogen bonding (OH) interactions, were compatible with the formation of stable cubic crystals.

	M = H_2	M = Zn	M = Co	M = Cu
PcBr	40%[a]	20%[b]	50%[b]	90%[c]
PcCl	56%[a]	42%[b]	44%[b]	31%[b]
PcCN	10%[a]	15%[b]	16%[b]	32%[c]
PcOMe	45%[a]	70%[b]	60%[b]	34%[c]
PcOH	85%[d]	61%[d]	55%[d]	70%[d]

Table 3.1 Summary of the yields for each of the phthalocyanine derivatives Pcs 1-6. a) by "Linstead method" b) Metal salt, NMP, 165 °C, c) $Cu(OOCCH_3)_2$, *n*-pentanol, reflux, d) BBr_3, DCM, 0 °C.

3.4 Crystallographic studies

Suitable crystals for XRD analysis were obtained for most of the substituted phthalocyanines synthesised with all of these crystals being clathrates that play host to a number of different solvent molecules, but unfortunately, none of them has the cubic arrangement seen for **Pc1**.

Based upon the crystals formed by the metal-free and copper derivatives of **Pc1** (R = H), the lack of cubic crystal formation from the metal-free and copper derivatives of **PcsR** (R = Br, Cl, CN, OMe, OH) was expected as axial ligands appear to be a necessary condition for cubic packing. However, in order to understand the reasons why the substituted phthalocyanines containing zinc and cobalt do not crystallize with a cubic arrangement their molecular structures are examined and compared with that of **Pc1Zn**.

In **figure 3.3** the molecular structures of **Pc1Zn** and **PcOHZn** are shown together for comparison. In their crystalline form, all the substituted molecules **PcsR** (R = Br, Cl, CN, OMe, OH) assumed a conformation which is less symmetric than that of **Pc1Zn**.

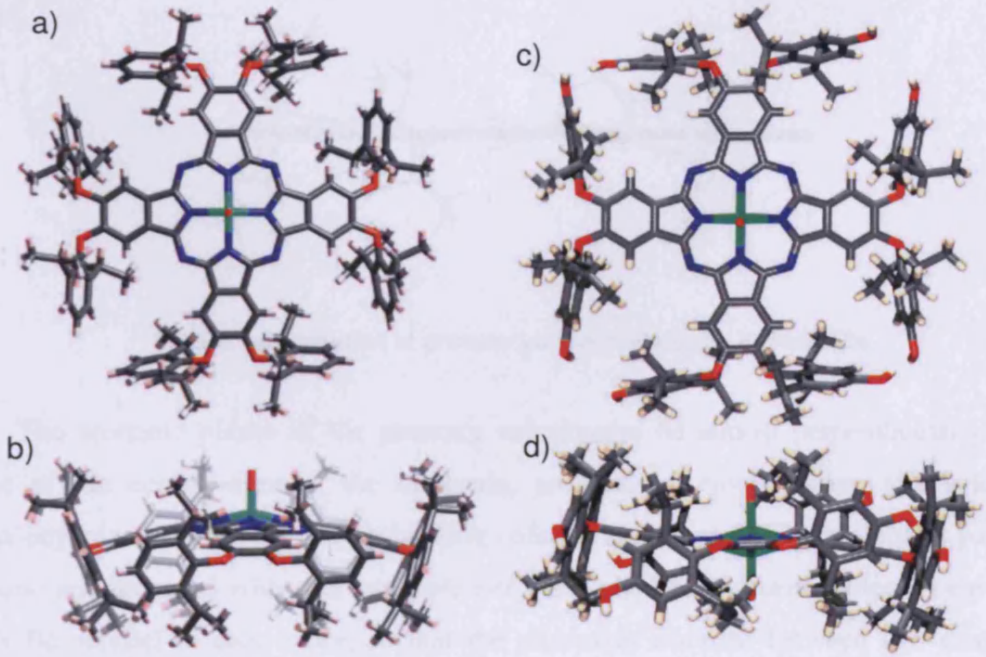


Figure 3.3 The molecular structure of **Pc1Zn**. a) Face-on and b) edge-on molecular views, and **PcOHZn**. c) Face-on and d) edge-on molecular views.

For all PcR, as seen earlier for the non-cubic forming derivatives of **Pc1,** the central core of the phthalocyanine is practically planar and the phenoxy substituents are disposed more or less perpendicularly to this plane, but at different angles. For these molecules the presence of axial ligands does not induce the conical conformation, which seems an essential prerequisite for them to pack with a cubic arrangement.

Of course, the substituents have a fundamental effect on the molecular conformation and the molecular packing within the crystals. For example, for **PcOHZn** it is possible to see that four of the hydroxyl substituents form two intramolecular hydrogen bonds and, in order to do that, four of the phenoxy rings are pushed up and four down relative to the plane of the phthalocyanine core. This causes a slight deviation from planarity in the phthalocyanine macrocycle with two benzo-subunits lying in the same plane passing through the four meso-nitrogen atoms and one is above this plane whereas the other is below (**figure 3.4**). This arrangement, together with steric effects between the bulky isopropyl groups prohibits the formation of the other two possible intramolecular hydrogen bonds between the other hydroxyl groups (**Figure 3.5**).

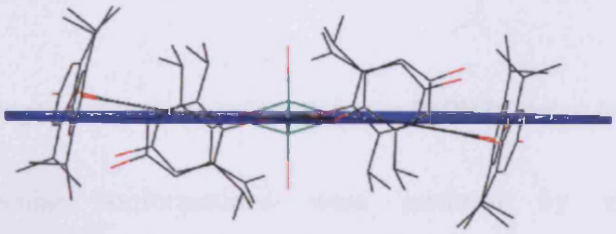


Figure 3.4 Distortion of phthalocyanine macrocycle **in PcOHZn**

The aromatic planes of the phenoxy substituents lie almost perpendicularly to the plane of the central core of the molecule, providing a cavity above and below the phthalocyanine macrocycle and prohibiting cofacial aggregation. The molecules pack in a triclinic arrangement, with one molecule per unit cell. The phthalocyanine's near-planar cores lie parallel to each other, so that the minimum distance between two central Zn cations is equal to the length of the *a* axis (Zn-Zn = 13.299 Å) and two of the 2,6-di-*iso*-propylphenoxy of one molecule are accommodated in the cavity of its neighbour. The central metal ion is disordered over two sites that protrudes from the macrocycle and is bound to a water molecule (Zn-O = 2.091 Å). Four acetone molecules per phthalocyanine are present, two of them, at 0.5 of occupancy, are hydrogen bonded to the axial water

($O_{acetone}$-H_{water} = 2.716 and 2.793 Å respectively), and to another water molecule, which has an occupancy of 0.25. The other two acetone molecules form hydrogen bonds with two of the eight hydroxyl groups ($O_{acetone}$-$H_{hydroxy}$ = 2.657 Å). Some other disordered water molecules are present. Considering the whole structure, it is possible to see that numerous intermolecular hydrogen bonds are formed between different phthalocyanines molecules, these must contribute to the conformation assumed by the **Pc** molecule. In **figure 3.5** both the intramolecular, which are highlighted in blue, and some of the intermolecular hydrogen bonding interactions (pink lines)for **PcOHZn** are shown.

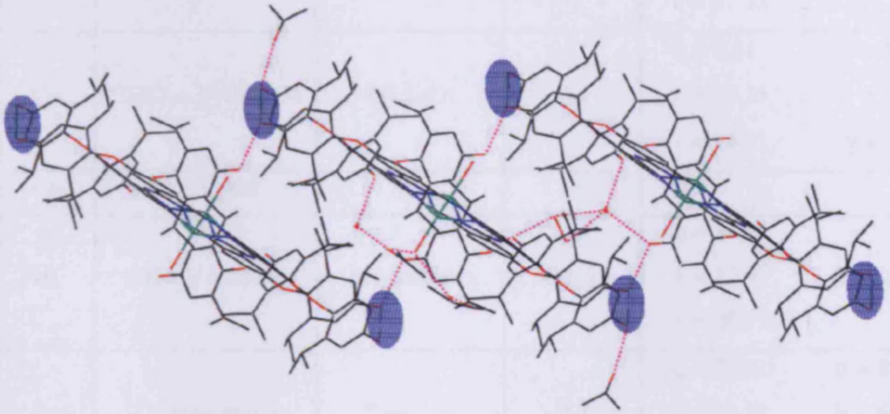


Figure 3.4 Hydrogen bonding interactions between **PcOHZn** molecules in the crystals

Similar molecular conformations were assumed by all the substituted phthalocyanines, as the molecules have to distort in comparison with the Pc molecules within the cubic crystals of **Pc1** in order to accommodate the bulkier substituents. In fact, considering the distance between two hydrogen atoms in the 4-position in the phenoxy rings in the cubic crystal of **Pc1**, which is 2.706 Å (calculated with Mercury), it is evident that two bulkier substituents could not occupy the same positions deforming the structure significantly. A summary of the crystals structures of the various phthalocyanine derivatives with the main characteristics of the unit cell is reported in **Table 3.2**.

PARA-SUBST.	M	SOLVENTS OF CRYST.	CRYSTAL SYSTEM	SPACE GROUP	UNIT CELL PARAMETERS	Z
Br	H_2	DCM/MeOH	Monoclinic	$P2_1/n$	$a = 23.28$ $b = 12.46$ $\beta = 114.18$ $c = 24.19$	2
	Zn	DCM/acetone	Monoclinic	$P2_1/n$	$a = 9.38$ $b = 31.86$ $\beta = 100.16$ $c = 23.56$	2
		DCM/MeOH	Monoclinic	$P2_1/n$	$a = 22.24$ $b = 9.42$ $\beta = 92.44$ $c = 31.33$	2
	Co	$CHCl_3$+ Py/MeOH	Triclinic	$P\text{-}1$	$a = 9.61$ $\alpha = 67.28$ $b = 18.31$ $\beta = 79.15$ $c = 21.51$ $\gamma = 77.24$	1
	Cu	No crystal				
Cl	H_2	$CHCl_3$/ acetone	Monoclinic	$P2_1/c$	$a = 17.64$ $b = 12.82$ $\beta = 103.49$ $c = 28.75$	
	Zn	DCM/acetone	Triclinic	$P\text{-}1$	$a = 20.91$ $\alpha = 86.39$ $b = 22.71$ $\beta = 66.92$ $c = 25.94$ $\gamma = 63.23$	3
	Co	DCM/acetone	Triclinic	$P\text{-}1$	$a = 20.96$ $\alpha = 72.78$, $b = 22.87$ $\beta = 66.31$, $c = 26.09$ $\gamma = 62.73$	3
		DCM/hexane	Monoclinic	$P2_1/n$	$a = 23.51$ $b = 12.58$ $\beta = 115.60$ $c = 23.64$	2
	Cu	No crystal				
CN	H_2	DCM/acetone	Triclinic	$P\text{-}1$	$a = 11.66$ $\alpha = 106.43$ $b = 16.81$ $\beta = 97.04$ $c = 21.29$ $\gamma = 106.58$	1
	Zn	DCM/MeOH	Triclinic	$P\text{-}1$	$a = 11.69$ $\alpha = 105.88$ $b = 16.69$ $\beta = 96.31$ $c = 21.03$ $\gamma = 107.27$	1
	Co	$CHCl_3$ + Py/MeOH	Triclinic	$P\text{-}1$	$a = 9.75$ $\alpha = 69.15$ $b = 18.10$ $\beta = 78.33$, $c = 22.47$ $\gamma = 76.76$	1
	Cu	No crystal				

PARA-SUBST.	M	SOLVENTS OF CRYST.	CRYSTAL SYSTEM	SPACE GROUP	UNIT CELL PARAMETERS		Z
OMe	H_2	DCM/MeOH	Monoclinic	*C2/c*	*a* = 39.95 *b* = 13.08 *c* = 34.11	β = 121.08	4
	Zn	$CHCl_3$/MeOH	Triclinic	*P-1*	*a* = 9.68 *b* = 19.18 *c* = 20.61	α = 65.32 β = 79.78 γ = 79.10	1
	Co	$CHCl_3$/MeOH	Triclinic	*P-1*	*a* = 9.69 *b* = 19.14 *c* = 20.49	α = 65.49, β = 79.79 γ = 78.93	1
	Cu	$CHCl_3$/MeOH	Triclinic	*P-1*	*a* = 9.71 *b* = 19.15 *c* = 20.65	α = 65.23 β = 79.56 γ = 78.94	1
OH	H_2	No crystal					
	Zn	Acetone/hex	Triclinic	*P-1*	*a* = 13.29 *b* = 14.52 *c* = 19.68	α= 76.51 β = 76.06 γ = 86.81	1
	Co	No crystal					
	Cu	Acetone/hex	Monoclinic	*I2/a*	*a* = 18.76 *b* = 16.47 *c* = 44.59	β = 90.56	

Table 3.2 Summary of the crystals structures of phthalocyanine derivatives

Monoclinic and triclinic seem to be the favoured crystal systems for these molecules. In some cases, as for **PcsBr and OMe** the same crystal morphology is assumed by different metal derivatives. This suggests that the crystal packing is controlled by the substituents. However, it is not possible to find a particular trend of morphology based upon the substituents or the solvent of crystallization. In fact, **PcBr** and **PcClCo** formed isomorphic crystals, despite having different substituents, central cations and recrystallisation solvents.

Five compounds, the three metal derivatives of **PcOMe** with methoxy substituents and the cobalt phthalocyanines containing bromine (**PcCoBr**) and nitrile (**PcCoCN**) substituents and two molecules of pyridine in the axial sites, crystallise with the same triclinic cell. The molecular packing is very similar to the one described previously for

PcOHZn. The molecules are arranged so that there is one in every vertex of the unit cell and are shared by four contiguous unit cells (**figure 3.5**). In all these isomorphous crystals apart from **PcBrCoPy,** chloroform is the main guest solvent. For the zinc and cobalt **PcsOMe,** a molecule of methanol as axial ligand is present for each molecule of phthalocyanine. An acetone molecule, at 0.5 occupancy, per phthalocyanine is present as guest solvent in the copper derivative crystal. The distance between the metal and the oxygen of the acetone molecule is equal to 2.751 Å, which indicates only a weak coordination of the acetone to the central cation.[183,184] Acetone is the main guest solvent in **PcBrCoPy**.

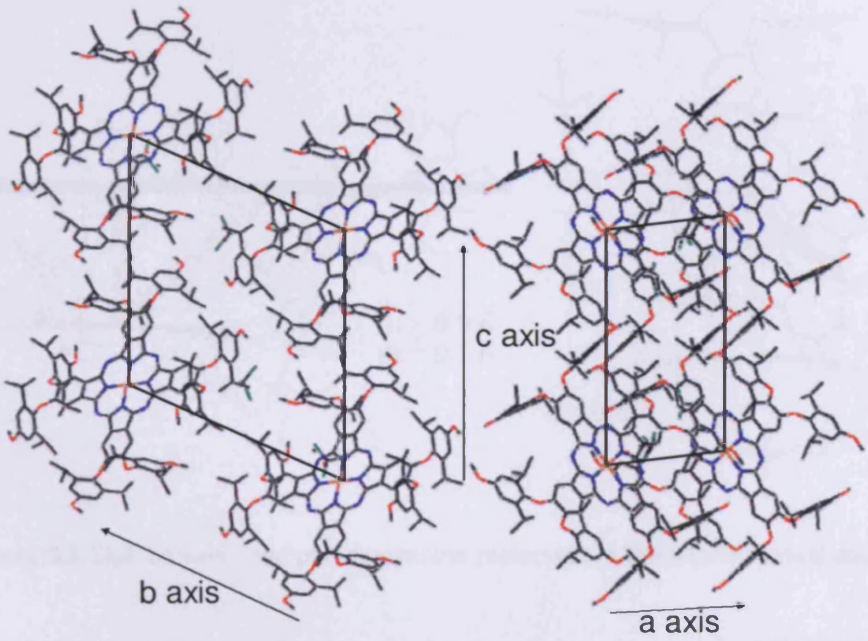


Figure 3.5. The triclinic packing of **PcOMeCu**

In **figure 3.5** the triclinic cell of **PcOMeCu** is shown as an example of the molecular arrangement for these molecules. The molecules lie parallel to each other and the minimum distance between two central Cu cations is equal to the length of the *a* axis (Cu-Cu = 9.719 Å). Therefore, they are closer as compared to analogous distance within the crystals of **PcOHZn** molecules but the bulky substituents still prohibit π–π interactions between the phthalocyanine macrocycles, and as seen before, the molecules are shifted so that the cavities above and below the macrocycle can accommodate two 2,6-di-*iso*-propylphenoxy substituents of a neighbour molecule. This shift is equivalent to the *a*-axis orthogonal projection onto one of the planes where the central core of the phthalocyanine lies and

therefore, it can be easily determined. Using Mercury version 1.4.2 it is possible to determine the distance between two consecutive parallel planes where two closest molecule lie and then work out the shift using the Pythagoras theorem (**Figure 3.6 a**).

The centres of these two molecules are separated by 6.7 Å, which is practically double the distance between the central metal and each meso-nitrogen in the phthalocyanine. In fact, as shown in (**figure 3.6 b**) where, for clarity, only two molecules of the unit cell are represented, the correspondence of the shift is readily seen in the perpendicular direction to the macrocyclic plane of the phthalocyanine.

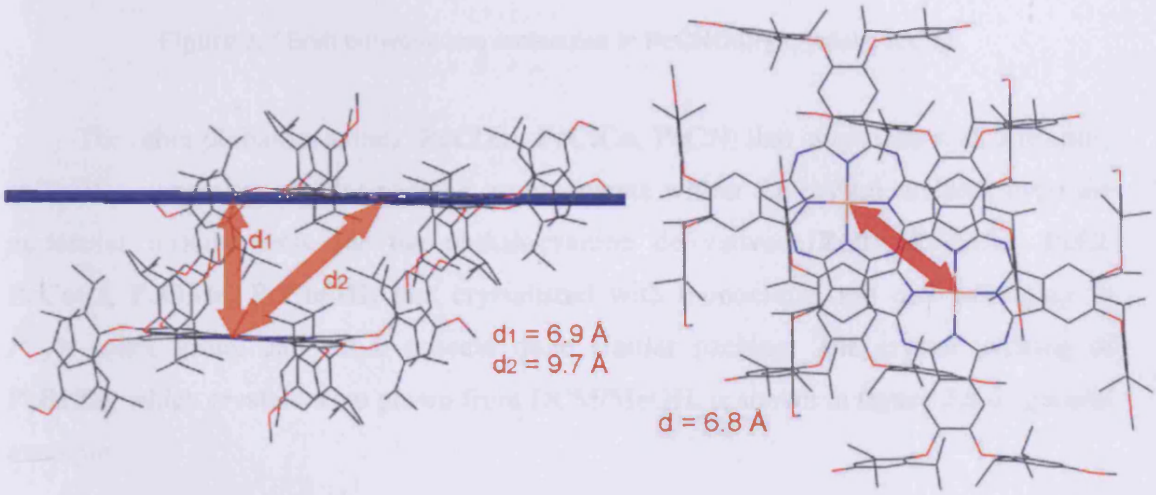


Figure 3.6 Shift between two phthalocyanine molecules in **PcOMeCu** crystal packing.

This is more easily visualised by looking at the packing of both **PcOMeCo.Py** and **PcCNCo.Py**, where the perpendicular axial pyridine ligands give a clear indication of the shift between the phthalocyanine molecules (**Figure 3.7**). This seems due to the interaction of the the axial pyridine on one molecule with one of the meso-nitrogen and the 2,6-di-*iso*-propylphenoxy substituents of the neighbouring phthalocyanine molecule.

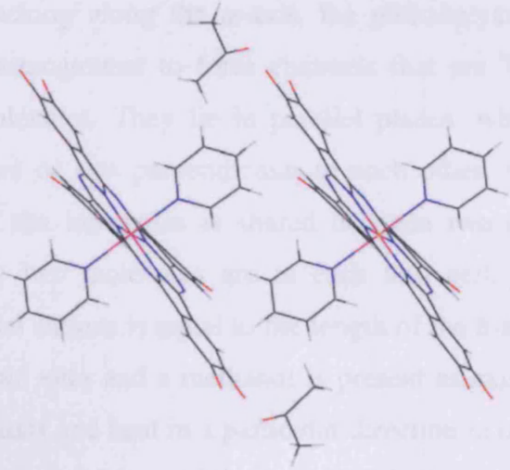


Figure 3.7 Shift between two molecules in **PcCNCoPy** crystal packing.

The other phthalocyanines (**PcClZn**, **PcClCo**, **PcCN**) that crystallise with a triclinic cell, all assume very similar packing arrangements within the crystal. Indeed, even the molecular arrangements for the phthalocyanine derivatives (**PcBr**, **PcZnBr**, **PcCl**, **PcCoCl**, **PcOMe**, **PcCuOH**) that crystallized with monoclinic unit cell belonging to $P2_1/n$ space group and $P2_1/c$ possess quite similar packing. The crystal packing of **PcBrZn**, which crystals were grown from DCM/MeOH, is shown in **figure 3.8** as general example.

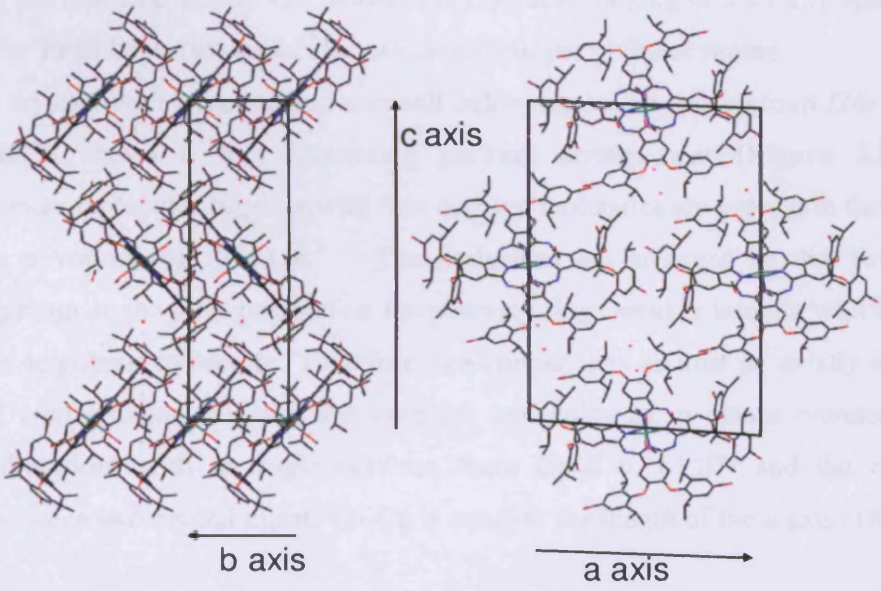


Figure 3.8 The monoclinic packing of **PcBrZn** crystals from DCM/MeOH.

Looking at the packing along the *a*-axis, the phthalocyanine molecules seem to assume a herringbone arrangement to form channels that are 7.11 Å wide, containing water and methanol molecules. They lie in parallel planes, which are oriented in two different directions, more or less perpendicular to each other, with an angle of 82.14° between them. Each of the molecules is shared between two contiguous repeat units. Therefore, overall, only two molecules are in each unit cell. The minimum distance between two central metal cations is equal to the length of the *b*-axis (9.424 Å). The zinc ion is disordered over two sites and a methanol is present as axial ligand (Zn-O = 2.162 Å). The methanol is off axis and bent in a particular direction in order to interact with one of the isopropyl groups of a neighbour phthalocyanine. In this case each cavity above and below the core of every phthalocyanine accommodates three of the phenoxy substituents of a neighbouring molecule. Another methanol, at 0.50 occupancy, weakly interacts with two meso-nitrogens (N_{meso}-$H_{methanol}$ = 3.329 Å). Some other disordered water molecules are present.

In the other monoclinic polymorph obtained for **PcBrZn** there are disordered acetone and methanol in 50:50 ratio in the axial site. Some other disordered acetone together with disordered water and DCM are present in the unit cell. Isomorphic monoclinic crystals belonging to the $P2_1/n$ space group were grown from **PcBr** and **PcClCo**. In both of them DCM is the guest solvent, which is present in the ratio of two molecules per phthalocyanine. The monoclinic crystal belonging to the $P2_1/c$ space group obtained for **PcCl** hosts two molecules of chloroform per phthalocyanine.

The crystals with a monoclinic unit cell belonging to the space group *I2/a* obtained for **PcOHCu** shows a very interesting packing arrangement (**Figure 3.9**). Four phthalocyanine molecules together with four acetone molecules are present in the unit cell which has a volume of 13788 $Å^3$. The molecules are arranged so that two of the hydroxyl groups in the *para* position on the phenoxy rings weakly interact with the metal ion of two neighbour molecules. Therefore, the copper ions assume an axially elongated octahedral conformation. Even in this case the molecules lie in planes oriented in two different directions with an angle between them equal to 61.07° and the minimum distance between two central metals Cu-Cu is equal to the length of the *a* axis (18.76 Å).

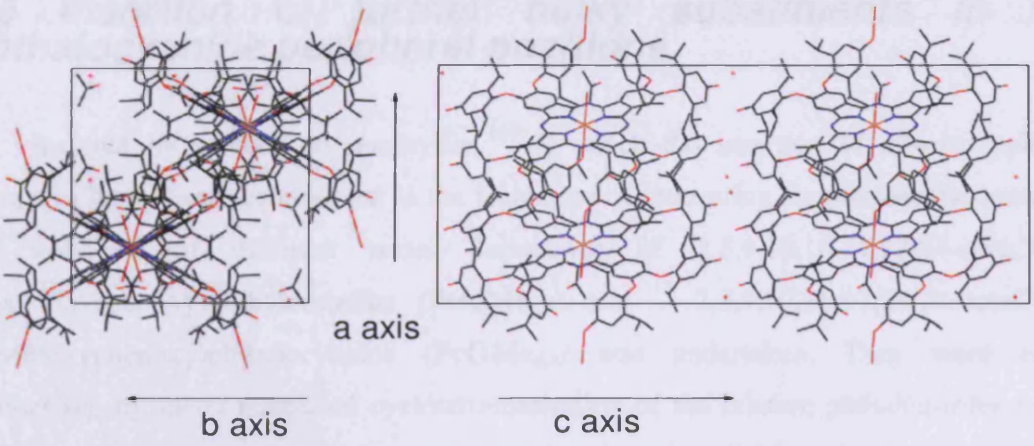


Figure 3.9. The monoclinic packing of **PcOHCu** crystals

The monoclinic crystal, belonging to the *C2/c* space group, obtained for the metal free phthalocyanine derivative **PcOMe** with methoxy substituents in the *para* position of the phenoxy rings is not dissimilar from the previously described structure (**Figure 3.10**). The bulky substituents also prohibit an efficient packing of the phthalocyanine molecules, which as a result assume a herringbone arrangement, forming channels 13.08 Å large. These channels host some disordered methanol and water molecules. The angle between the molecules is equal to 68.14°, which is narrower than seen in the preceding example.

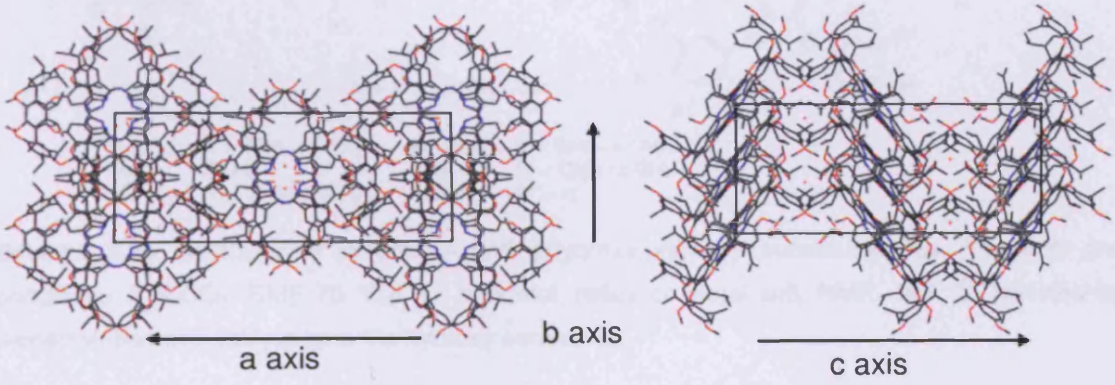
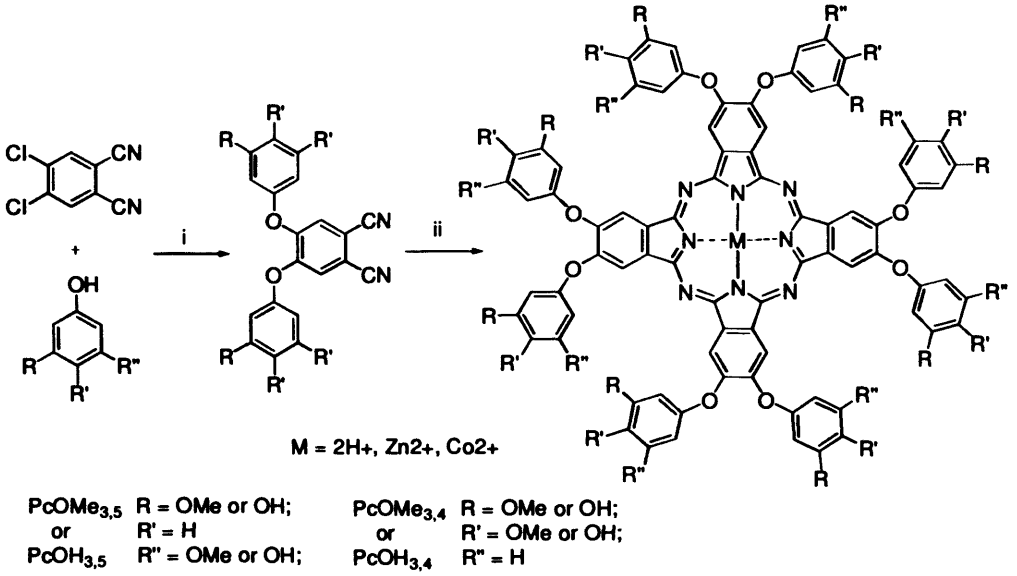


Figure 3.10. *The monoclinic packing of* **PcOMe** *crystals*

3.5 Insertion of further bulky substituents in the phthalocyanine peripheral positions.

Inspired by a work on porphyrins,[119] in which the insertion of dihydroxyphenyl groups in their *meso* positions led to the formation of interesting supramolecular network, the synthesis of different metal derivatives of 2,3,9,10,16,17,23,24-octa(3',5'-dimethoxyphenoxy)phthalocyanine (**$PcOMe_{3,5}$**) and 2,3,9,10,16,17,23,24-octa(3',5'-dimethoxyphenoxy)phthalocyanine (**$PcOMe_{3,4}$**) was undertaken. They were easily synthesised by metal templated cyclotetramerisation of the relative phthalonitriles which had been obtained reacting the starting phenols with dichlorophthalonitrile, then demethylated by reaction with an excess of BBr_3 in DCM to give the corresponding octa-dihydroxyphenoxy substituted phthalocyanines **$PcOH_{3,4}$** and **$PcOH_{3,4}$** (**Scheme 3.25**).



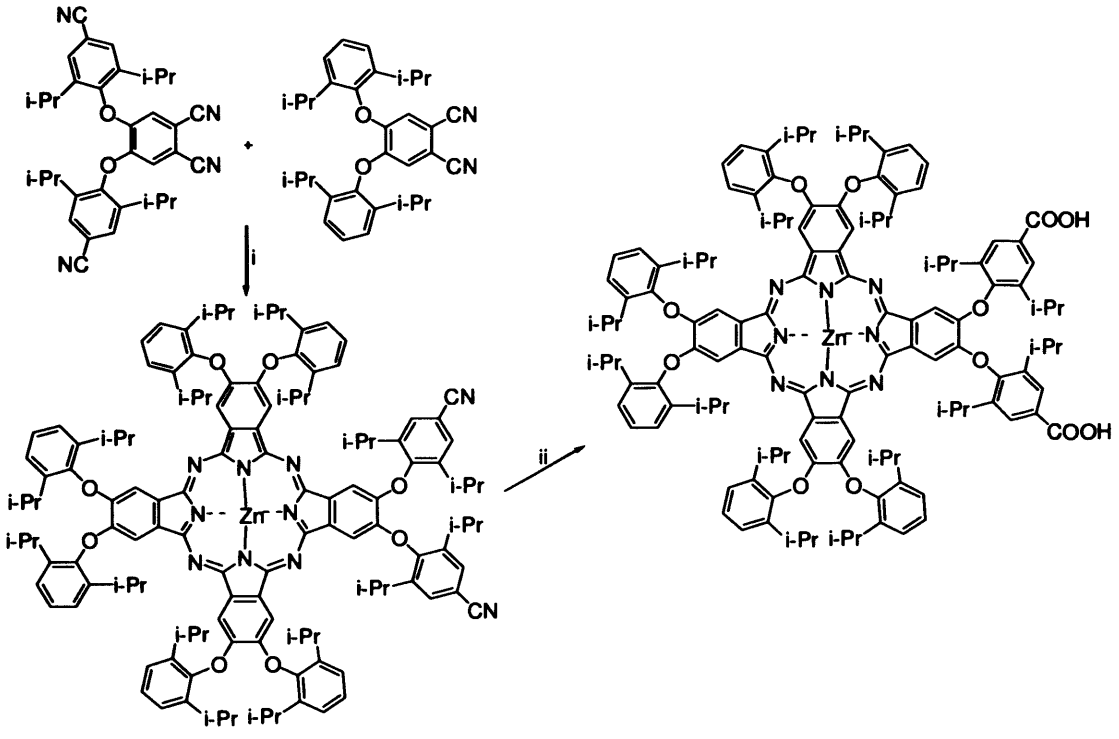
Scheme 3.25. Synthesis of dimethoxy- and dihydroxy-phenoxyl substituted Pcs. *Reagents and conditions*: i) K_2CO_3, DMF 70 °C.ii) Li, pentanol, reflux or metal salt, NMP, 165 °C, followed by demethylation with BBr_3 to form the hydroxy derivatives.

Unfortunately both methoxy an hydroxy phenyl substituents did not seem to sufficiently prohibit the usual co-facial aggregation and the compounds that resulted were quite difficult to purify and characterise. Indeed, UV spectra were recorded for very diluted solutions and aggregation was also confirmed by ^1H NMR spectra that showed very broad peaks, that did not allow a proper characterisation by this technique. Some crystallisation experiments were attempted, but these molecules seemed to form microcrystalline clusters and no suitable crystals for XRD analysis were obtained.

3.6 Synthesis of asymmetric phthalocyanines using Pn1.

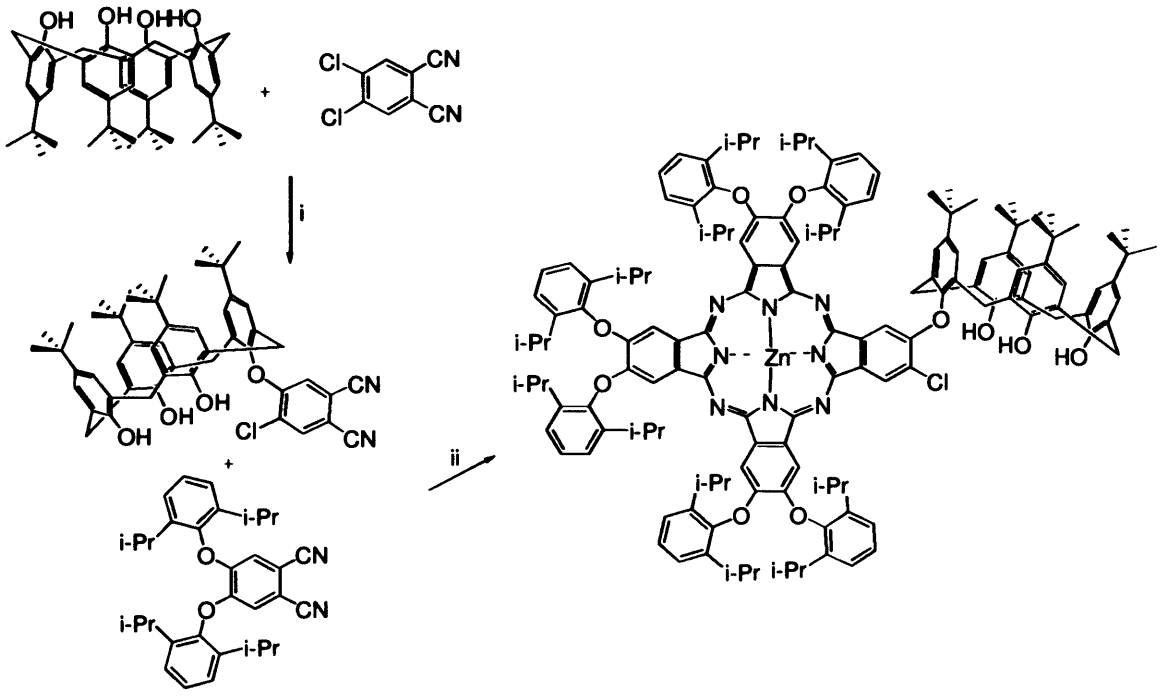
The synthesis of asymmetric phthalocyanines consisting of three **Pn1** units and a fourth differently functionalised phthalonitrile was also envisaged especially for their evaluation as materials for sensor and thin film fabrication (e.g. photovoltaic devices).[1]

It would be desirable to prepare amphiphilic molecules which could form LB- thin films. We outlined the synthesis of 2,3,9,10,16,17-hexakis(2',6'-di-*iso*-propylphenoxy)-23,24-bis(4'-carboxy-2',6'-di-*iso*-propylphenoxy) phthalocyaninato zinc (**$Pc1_3PcCOOHZn$**), starting from 2,3,9,10,16,17-hexakis(2',6'-di-*iso*-propylphenoxy)-23,24-bis(4'-cyano-2',6'-di-*iso*-propylphenoxy) phthalocyaninato zinc (**$Pc1_3PcCNZn$**), which could be easily prepared by metal template mixed cyclotetramerisation reaction of **Pn1** with **PnCN,** that we had previously obtained. (**$Pc1_3PcCNZn$**) was successfully prepared but some difficulties were encountered in the hydrolysis reaction of the nitrile substituents to carboxyl groups (**Scheme 3.26**).



Scheme 3.26. Synthesis of **$Pc1_3PcCNZn$** i) Zn(II)acetate, NMP, 165 °C. Synthesis **$Pc1_3PcCOOHZn$** ii) KOH, ethylene glycol, 24h, 160 °C. H_2PO_4, 160°C, 24h.

In addition, another asymmetric phthalocyanine composed of three **Pn1** units and a 4-*tert*-butylcalix(4)arene substituted phthalonitrile (**Pncalix**) was synthesised. **Pncalix** was prepared reacting 4-*tert*-butylcalix(4)arene with 4,5-dichlorophthalonitrile (**Scheme 3.27**). Double substitution by two of the hydroxy groups on the calixarene on the phthalonitrile was expected, but surprisingly only one of the two chlorines was substituted even forcing the conditions of reactions. It was envisaged that this substituent would introduce a cavity in the molecule which could be a site of recognition for some organic molecules offering possibilities for its exploitation as an optical sensor. The potential of application of this molecule as sensor will be investigated by studying its interaction with appropriate organic molecules by mean of fluorescence experiments and possibly XRD analysis of the complexes will be carried out. A monoclinic clathrate belonging to the $P2_1/n$ space group, with three phthalocyanine molecules per unit cell, was obtained for this molecule. Two acetone molecules per **Pc** are present as guest solvent and one of which is axially bonded to the central cation (**Figure 3.11**)



Scheme 3.27. Synthesis of **Pncalix** and **$Pc1_3PccalixZn$**. *Reagents and conditions:* i) K_2CO_3, 70 °C, 72 h. Synthesis ii) Zn(II)acetate, NMP, 165 °C.

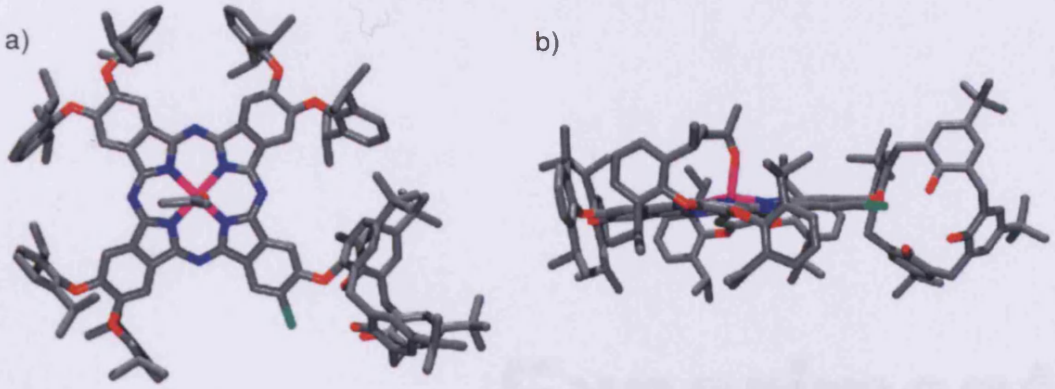


Figure 3.11. The molecular structure of **$Pc1_3$PccalixZn.** a) Face-on and b) edge-on molecular

3.7 Conclusions

Numerous metal-free and metal (M = Zn, Co, Cu) derivatives of **Pc1** with substituent at the 4-position (R = Br, Cl, CN, OMe, OH) of the phenoxy groups were synthesised.

Most of these molecules crystallised forming clathrates, which were examined by X-ray diffraction. Unfortunately, the introduction of substituents in the 4-position of the phenoxy groups in these molecules did not lead to the desired enhancement of the cubic crystal arrangement, but induced different unit crystal structures. The amount of included solvent in these crystals was unremarkable in comparison with that found in the cubic structure.

Experimental

1600 series FTIR i

chloride plates. All

Ultraviolet visible

Absorption Uv-vis s

UV/vis/NIR spectro

Nuclear Magnetic Resonance (NMR)

^{1}H NMR spectra were recorded in $CDCl_3$ (unless otherwise stated) using an Avance Bruker DPX 400 instrument (400 MHz) or an Avance Bruker DPX 500 (500 MHz), with ^{13}C NMR spectra recorded at 100 MHz or 125 MHz respectively. Chemical shifts (δ_H and δ_C) were recorded in parts per million (ppm) from tetramethylsilane (or chloroform) and are corrected to 0.00 (TMS) and 7.26 ($CHCl_3$) for ^{1}H NMR and 77.00 ($CHCl_3$), centre line, for ^{13}C NMR. The abbreviations s, d, t, q, m and br. denote singlet, doublet, triplet, quartet, multiplet and broadened resonances; all coupling constants were recorded in Hertz (Hz).

Mass spectrometry

Low-resolution mass spectrometric data were determined using a Fisons VG Platform II quadrupole instrument using electrospray ionisation (ES) unless otherwise stated.

High-resolution mass spectrometric data were obtained in electrospray (ES) mode unless otherwise reported, on a Waters Q-TOF micromass spectrometer. MALDI-TOF analyses were performed with a Waters MALDI Micro MX spectrometer.

Elemental analysis

Elemental analyses were obtained using a Carlo Erba Instruments CHNS-O EA 108 elemental analyzer.

X-Ray crystal structure determination

X-ray crystal structures data were recorded at Manchester University X-Ray Crystallography Facility, at 100 K or 150 K, on a Bruker APEX CCD diffractometer (graphite monochromated MoK_α radiation λ = 0.71073 Å) or using synchrotron radiation at Daresbury SRS, UK (Station 9.8), on a Bruker APEXII CCD diffractometer (λ = 0.6710 Å) and the structures were solved by direct methods. All calculations were carried out by using the SHELX-97 package.

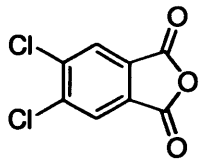
General experimental procedures

a) General procedure for the synthesis of substituted phthalonitriles. In a typical procedure, anhydrous potassium carbonate (100.0 mmol) was added to a solution of 4,5-dichlorophthalonitrile (25.0 mmol) and phenol (75.0mmol) in anhydrous dimethylformamide (70 ml). The mixture was stirred under nitrogen atmosphere for 72 h at 70 °C. After cooling, the reaction mixture was poured into water (200 ml) and neutralised with hydrochloric acid (2N). The aqueous solution was extracted with dichloromethane (3 x 150 ml), dried over magnesium sulphate and filtered. The solvent was evaporated under vacuum to give the crude product.

b) General procedure for the synthesis of metal free phthalocyanines. In a typical procedure, to a solution of phthalonitrile (1mmol) in refluxing anhydrous 1-pentanol (3 ml), under nitrogen and with stirring, lithium (0.02 g) was added. The mixture of reaction was refluxed for 5 h and then cooled and acetic acid added (1 ml, 0.1 M). The solvent was removed under reduced pressure to give the crude product.

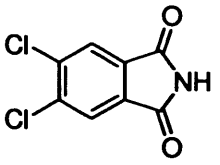
c) General procedure for the synthesis of metal phthalocyanines. A stirred solution of phthalonitrile (1mmol) and the appropriate metal salt (1 mmol) in anhydrous N-methylpyrrolidone (1.5 ml) was heated at 165 °C for 20 h under nitrogen. The reaction mixture was cooled to room temperature and poured into water (15 ml). The crude product was collected by filtration.

5,6-Dichloroisobenzofuran-1,3-dione[20]



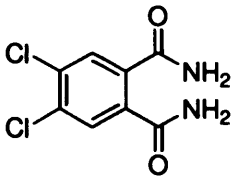
4,5-Dichlorophthalic acid (90 g, 381 mmol) and acetic anhydride (150 ml) were heated under gentle reflux for 5 h with slow distillation of solvent (20 ml). After cooling, the solid was filtered, washed with petroleum ether, then dried under vacuum (77.8 g, 95%). M.p.184-186 (lit[20] m.p. 184-186°C); IR (film)/cm^{-1} 1830, 1786, 1378, 1310, 1248, 1094, 915, 733; ^1H NMR (400 MHz; $CDCl_3$) δ 8.44 (s, 2H, Ar*H*); ^{13}C NMR (100 MHz; $CDCl_3$) δ 161.1, 139.1, 131.1, 127.0; LRMS, (EI), m/z: ($M^{\bullet+}$ 216, 35%).

5,6-Dichloroisoindoline-1,3-dione[20]



5,6-Dichlorobenzofuran-1,3-dione (77 g, 356 mmol) in formamide (100 ml) was heated at reflux for 3 h, under stirring. After cooling, the precipitate formed was filtered, washed with water and dried under vacuum (75.36 g, 98%). M.p. 202-203 (lit[20] m.p. 193-195°C); IR 3225, 1711, 1345, 1059, 906, 742 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 8.05 (s, 2H, Ar*H*); ^{13}C NMR (100 MHz; $CDCl_3$) δ 167.0, 136.9, 132.4, 124.9; LRMS, (EI), m/z: 215 ($M^{\bullet+}$, 100%).

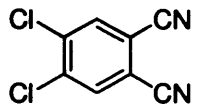
4,5-Dichlorobenzene-1,2-diamide[20]



5,6-Dichloroisoindoline-1,3-dione (75 g, 347 mmol) was stirred for 24 h in 25% NH_4OH (900 ml) then 33% NH_4OH was added and stirring was continued for other 24 h. The precipitate was filtered, washed with water and dried under vacuum (60 g, 70%). M.p. 235-

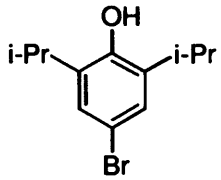
237 °C (lit[20] m.p. 245-247 °C); IR (nujol)/cm^{-1} 3426, 3296, 3131, 1667, 1608, 1173, 1121, 916, 897; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.84 (s, 2H, N*H*$_2$), 7.71 (s, 2H, Ar*H*), 7.46 (s, 2H, N*H*$_2$); ^{13}C NMR (100 MHz; $CDCl_3$) δ 167.3, 136.2, 131.4, 129.3; LRMS, (EI), m/z: 232 ($M^{\bullet+}$, 100%).

4,5- Dichlorophthalonitrile[20]



At 0 °C, $SOCl_2$ (200 ml) was added under stirring and under N_2 to anhydrous DMF (300 ml). After 2 h, 4,5-dichlorobenzene-1,2-diamide (60g, 257 mmol) was added and the mixture was stirred at 0 °C for 5 h then at r.t. for 20 h. The mixture was slowly added to ice water to quench the excess of $SOCl_2$. The product was collected by filtration and washed with water, then recrystallized twice from methanol (38 g, 75%). M.p. 180-183 °C (lit[20] m.p. 182-184°C); IR (film)/cm^{-1} 2916, 2237, 1815, 1467, 1348, 1262, 1217, 1132, 917, 683; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.91 (s, 2H, Ar*H*); ^{13}C NMR (100 MHz; $CDCl_3$) δ 139.0, 134.9, 114.9, 113.6; LRMS, (APCI), m/z: 197 (MH^+, 100%).

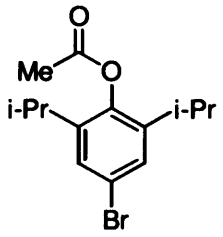
4-Bromo-2,6-di-*iso*-propylphenol [162]



To a solution of 2,6-di-iso-propylphenol (2.00g, 11mmol) in dichloromethane (10ml), under stirring at 0°C, was added dropwise bromine (1.80g, 11 mmol). Hydrogen bromide was evolved copiously. The solution was stirred for one hour at room temperature, and then heated at 50°C to drive off solvent and the remaining hydrogen bromide. After two hours, the solution was allowed to return to room temperature, then poured into 50 ml of water and sodium bisulphite was added to eliminate excess bromine. The aqueous solution was extracted with dichloromethane (3 x 20 ml), dried over magnesium sulphate, filtered and evaporated under vacuum to give a pink pale oil (2.82 g, 98%). IR (film)/cm^{-1} 3581, 2963, 1599, 1462, 1301, 1198, 865, 726 ; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.15 (s, 2H, Ar*H*),

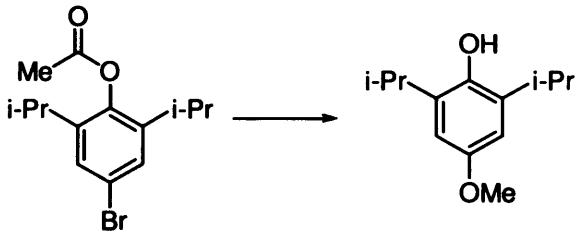
4.08 (s, 1H, O*H*), 3.16 (sept, 2H, *J* = 6.8 Hz, CH_3CHCH_3), 1.29 (d, 12H, *J* = 6.8 Hz, CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 148.9, 135.9, 126.4, 113.2, 27.2, 22.5; HRMS Calc. for $C_{12}H_{17}O^{79}Br$ 256.0463 found 256.0458.

4-Acetoxy-3,5-di-*iso*-propyl-bromobenzene



To a solution of 4-bromo-2,6-di-*iso*-propylphenol (14.15 g, 55 mmol) in acetic anhydride (70 ml) was added sulphuric acid (0.25 ml) with stirring. Instantly, formation of a white precipitate was observed and TLC analysis showed that after 15 minutes the reaction was complete. The solid was filtered and washed with methanol (14.88 g, 90.5%). M.p. 95-98 °C; IR (film)/cm^{-1} 2962, 1761, 1449, 1364,1322, 1214, 1163, 1011, 911, 871, 782; ^1H NMR (400 MHz; $CDCl_3$) δ 7.26 (s, 2H, Ar*H*), 2.87 (sept, 2H, *J* = 6.8 Hz, CH_3CHCH_3), 2.35 (s, 3H, CH_3CO), 1.19 (d, 12H, *J* = 6.8 Hz, CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 169.3, 144.6, 142.7, 127.2, 120.0, 27.7, 22.9, 20.5, LRMS, (APCI), m/z: 299 (MH^+, 100%).

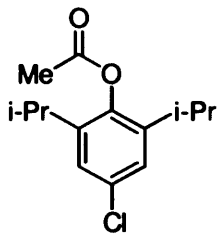
4-Methoxy-2,6-di-*iso*-propylphenol



In a three-necked round bottomed flask equipped with a Dean-Stark apparatus to a solution of 4-acetoxy-3,5-di-*iso*-propyl-bromobenzene (14.4 g, 48 mmol) in anhydrous dimethylformamide (100 ml) was added sodium methoxide in methanol (25%; 52 ml) at room temperature, under stirring and under nitrogen. The temperature was increased to 110 °C while methanol was collected in the Dean-Stark apparatus.

Copper (I) bromide (1.38 g, 9.6 mmol) was then added to the reaction mixture. During the reaction methanol was continuously distilled off. The reaction was monitored by TLC and after 3 h the starting material had completely disappeared. After cooling, the reaction mixture was poured into 250 ml of water, dichloromethane was added and then was filtered over Celite® in order to eliminate the copper metal which was formed during the reaction. The mixture was extracted with dichloromethane (3 x 150 ml) and then washed with water (3 x 200 ml) and brine (1 x 100 ml). The organic layer was dried over magnesium sulphate, filtered and the solvent evaporated to give a dark orange oil (8.93 g, 89%). The compound was pure by NMR and was used for the next reaction without any further purification. IR (film)/cm^{-1} 3484, 2961, 2869, 1603, 1486, 1436, 1320, 1197, 1041, 941, 863, 780; ^1H NMR (400 MHz; $CDCl_3$) δ 6.62 (s, 2H, Ar*H*), 4.33(br s, 1H, OH),3.78 (s, 3H, CH_3O) 3.16 (sept, 2H, *J* = 6.8 Hz, CH_3CHCH_3),1.25 (d, 12H, *J* = 6.8 Hz, CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 153.5, 143.7, 135.0, 108.7, 55.5, 27.3, 22.7; LRMS, (APCI), m/z: 209.1 (MH^+, 100%); HRMS Calc. for $C_{13}H_{20}O_2$ 208.1463 found 208.1462.

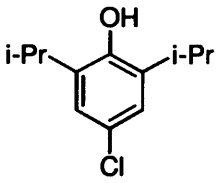
4-Acetoxy-3,5-di-*iso*-propyl-chlorobenzene



To a solution of 4-acetoxy-3,5-di-*iso*-propyl-bromobenzene (2.5 g, 8.3 mmol) in anhydrous DMF (40 ml), under stirring and under N_2, copper(I) chloride (1,65g, 17mmol) was added. The temperature was increased to 150 °C for 24 h. After cooling, the mixture was filtered through Celite® to eliminate the copper metal, then poured into water and extracted with DCM (3 x 100 ml). The combined organic layers were washed repeatedly with water in order to eliminate the DMF, then dried over $MgSO_4$ and evaporated under reduced pressure to give the crude product. Purification was achieved by recrystallization from methanol to yield a white solid (2.1 g, 99%). M.p. 85-86 °C; IR (film)/ cm^{-1} 2964, 2752, 1560, 1458, 1364, 1214, 1166, 874, 795; ^1H NMR (400 MHz; $CDCl_3$) δ 7.10 (s, 2H, Ar*H*), 2.89 (sept, 2H, *J* = 6.8 Hz, CH_3CHCH_3), 2.34 (s, 3H, CH_3CO), 1.17(d, 12H, *J* = 6.8 Hz,

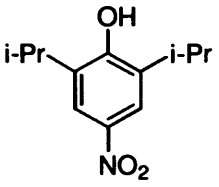
CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 169.5, 144.1, 142.4, 132.0, 124.3, 27.8, 23.37, 20.60; HRMS Calc.for $C_{14}H_{19}O_2{}^{35}Cl$ 254.1074 found 254.1074.

4-Chloro-2,6-di-*iso*-propylphenol



To a solution of 4-acetoxy-3,5-di-*iso*-propyl-chlorobenzene (2.0 g, 7.9 mmol) in methanol (20 ml) was added NaOH (40%; 20 ml). The reaction was left stirring for 3h. Water (100 ml) was added to the reaction mixture and *conc.* HCl was added at 0 °C, dropwise, until neutral pH. The aqueous layer was extracted with DCM (3 x 100 ml), the organic layer was then washed with brine (100 ml). The solvent was dried over $MgSO_4$, filtered and evaporated under vacuum to give a pale yellow oil (1.6g, 90%). IR (film)/cm^{-1} 3584, 2964, 1461, 1435, 1303, 1198, 1149, 868, 745; ^1H NMR (400 MHz; $CDCl_3$)[177] δ 6.99 (s, 2H, Ar*H*), 3.12 (sept, 2H, *J* = 6.8 Hz, CH_3CHCH_3), 1.24 (d, 12H, *J* = 6.8 Hz, CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 148.5, 135.6, 125.7, 123.5, 27.3, 22.6 HRMS Calc. for $C_{12}H_{17}O^{35}Cl$ 212.0968 found 212.0967.

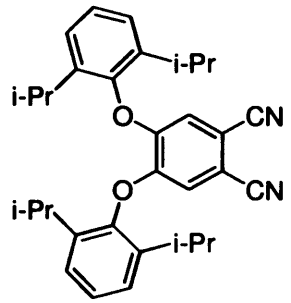
4-Nitro-2,6-di-*iso*-propylphenol[166]



Conc. HNO_3 (1.12ml) in glacial acetic acid (11 ml) was added, dropwise, at 0 °C with stirring, to a solution of 2,6-di-*iso*-propylphenol (2.00 g, 11.2mmol) in acetic acid (18ml)/DCM(11 ml). The mixture became yellow then orange. After 2h of stirring at room temperature, water was added and the mixture was extracted with DCM. The solution was dried with $MgSO_4$ and the solvent removed under reduced pressure. The crude compound was recrystallized by diethyl ether/ hexane to give a pale yellow solid (1.50 g, 60%). M.p. 118-120 °C (lit[166] m.p. 121°C); IR (film)/cm^{-1}3488, 2960, 1587, 1518, 1459, 1334, 1193, 1144, 934, 900; ^1H NMR (400 MHz; $CDCl_3$) δ 7.99, (s, 2H, Ar*H*), 5.66 (s, 1H, OH), 3.18

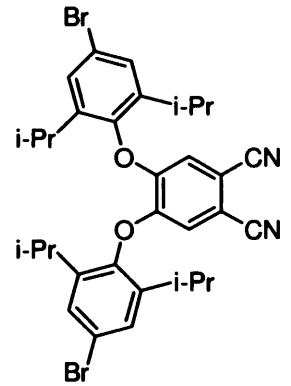
(sept, 2H, J = 6,8 Hz, CH_3CHCH_3),1.30 (d, 12H, J = 6.8 Hz, CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 155.71, 141.6, 134.5, 120.0, 27.2, 22.3; HRMS Calc.for $C_{12}H_{17}NO_3$ 223.1208, found 223.1207.

4,5-Bis(2',6'-di-*iso*-propylphenoxy)phthalonitrile (Pn1).[127]



Anhydrous potassium carbonate (26.24 g, 190.0mmol) was added to a solution of 2,6-di-*iso*-propylphenol (25.40 g, 142.5 mmol) and 4,5-dichlorophthalonitrile (9.35 g, 47.5 mmol) in anhydrous dimethylformamide according to the general procedure (a) to give the crude compound which was purified by recrystallization from methanol (14.69 g, 65%). Mp 161-163 °C; IR (nujol)/cm^{-1} 3080, 2228, 1589, 1503, 1332, 1096, 881, 795; ^1H NMR (400 MHz; $CDCl_3$) δ 7.26 (m, 6H, Ar*H*), 6.69 (s, 2H, Ar*H*), 2.87 (sept, 4H, J = 6.7 Hz, CH_3CHCH_3), 1.18 (d, 12H, J = 6.7 Hz, CH_3CHCH_3), 1.10 (d, 12H, J = 6.7 Hz, CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 151.4, 147.0, 140.6, 127.3, 125.1, 117.7, 115.3, 109.1, 27.4, 24.1, 22.4; LRMS, (APCI), m/z: 481 (MH^+, 100%); HRMS Calc.for $C_{32}H_{36}O_2N_2$ 480.2777 found 480.2796.

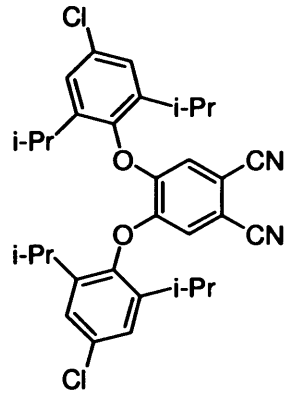
4,5-Bis(4'-bromo-2',6'-di-*iso*-propylphenoxy)phthalonitrile (PnBr).



Anhydrous potassium carbonate (8.3 g, 60.0mmol) was added to a solution of 4-bromo-2,6-di-*iso*-propylphenol (11.35 g, 45.0 mmol) and 4,5-dichlorophthalonitrile (2.9 g, 15.0

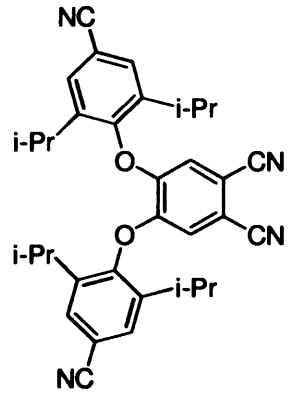
mmol) in anhydrous dimethylformamide according to the general procedure (a) to give the crude compound which was purified by recrystallization from methanol (7.8 g, 82%) M.p. 203-204 °C ; IR (nujol)/cm^{-1} 3100, 2230, 1584, 1503, 1342, 1202, 876, 795, 755; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.40 (s, 4H, Ar*H*), 6.76 (s, 2H, Ar*H*), 2.87 (sept, *J* = 6.8 Hz, 4H, CH_3CHCH_3), 1.23 (d, 12H, *J* = 6.8 Hz, CH_3CHCH_3), 1.16(d, 12H, *J* =6.8 Hz, CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) 150.8, 146.0, 143.0, 128.5, 121.0, 117.7, 114.9, 109.7, 27.7, 23.9, 22.1; LRMS, (APCI), m/z,: 639 (MH^+, 100%); HRMS Calc. for $C_{32}H_{34}N_2O_2{}^{79}Br_2$ 636.0987, found 636.1005.

4,5-Bis(4'-chloro-2',6'-di-*iso*-propylphenoxy)phthalonitrile (PnCl).



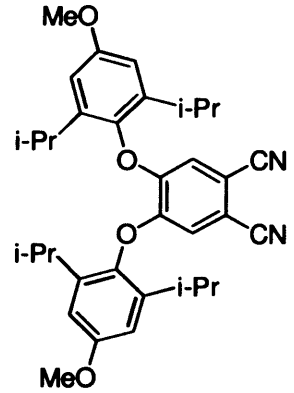
4,5-Dichlorophthalonitrile (1.5 g, 7.5 mmol), 4-chloro-2,6-di-*iso*-propylphenol (4.8 g, 22.5 mmol) and potassium carbonate (4,2 g, 30 mmol) were reacted according to the general procedure (a). The compound was recrystallized by methanol (3.18 g, 77%). M.p. 185-186 °C; IR (nujol)/cm^{-1} 2227, 1589, 1503, 1348, 1207, 1177, 1061, 865, 800; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.19 (s, 4H, Ar*H*), 6.69 (s, 2H, Ar*H*), 2.81 (sept, 4H, *J* = 6.9 Hz, CH_3CHCH_3), 1.17 (d, 12H, *J* = 6.9 Hz, CH_3CHCH_3), 1.10 (d, 12H, *J* = 6.9 Hz, CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 150.9, 145.4, 142.6, 133.0, 125.5, 117.7, 114.9, 109.7, 27.7, 23.9, 22.1; LRMS, (EI), m/z: 548 ($M^{\bullet+}$60%); HRMS Calc. for $C_{32}H_{34}N_2O_2{}^{35}Cl_2$ 548.1997, found 548.1997.

4,5-Bis(4'-cyano-2',6'-di-*iso*-propylphenoxy)phthalonitrile (PnCN).



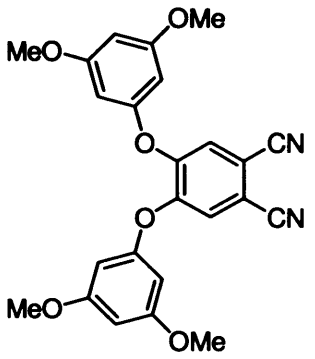
To a solution of **PnBr** (4,5 g, 7 mmol) in anhydrous dimethylformamide (100 ml), under nitrogen and with stirring, copper cyanide (5 g, 55 mmol) was added, then the temperature was increased to 120 °C for 3 h and then 140 °C. The reaction was monitored by TLC and after 20 h all starting material had been consumed. The reaction mixture was poured into 1 litre of ammonia solution and left under stirring for 2 h then filtered. The solid was washed with ammonia solution until the solution became colourless, then with water and finally with methanol. The compound was recrystallized from methanol (2.1 g, 54%). M.p. 254-255 °C; IR (film)/cm^{-1} 2969, 2232, 1586, 1503, 1465, 1400, 1337, 1284, 1205, 1118, 1007, 886; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.62 (s, 4H, Ar*H*), 6.72 (s, 2H, Ar*H*), 2.92 (sept, 4H, *J* = 6.8 Hz, CH_3CHCH_3), 1.25 (d, 12H, *J* = 6.8 Hz, CH_3CHCH_3), 1.21 (d, 12H, *J* = 6.8 Hz, CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 150.3, 150.1, 142.6, 129.6, 118.3, 117.6, 114.5, 111.8, 110.4, 27.7, 23.8, 21.9; LRMS, (APCI), m/z: 531 (MH^+, 100%); HRMS Calc. for $C_{34}H_{34}N_4O_2$ 530.2682, found 530.2697.

4,5-Bis(4'-methoxy-2',6'-di-*iso*-propylphenoxy)phthalonitrile (PnOMe).



4,5-Dichlorophthalonitrile (1.5 g, 7.5 mmol), 4-methoxy-2,6-di-*iso*-propylphenol (4,7 g, 22,5 mmol) and potassium carbonate (4,2 g, 30 mmol) were reacted according to the general procedure (a). The compound was recrystallized from methanol (2.91 g, 72%). M.p. 177-178 °C. IR (film)/cm^{-1} 2966, 2226, 1595, 1503, 1462, 1336, 1285, 1196, 1074, 1032, 869; ^{1}H NMR (400 MHz; $CDCl_3$) δ 6.81 (s, 4H, Ar*H*), 6.78 (s, 2H, Ar*H*), 3.88 (s, 6H, C*H*$_3$O), 2.90 (sept, 4H, *J* = 6.8 Hz, CH_3CHCH_3), 1.23 (d, 12H, *J* = 6.8 Hz, CH_3CHCH_3), 1.15 (d, 12H, *J* = 6.8 Hz, CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 158.2, 151.8, 141.8, 140.6, 117.8, 115.3, 110.2, 109.0, 55.4, 27.6, 24.0, 22.4; LRMS, (APCI), m/z: 541 (MH^+, 100 %); HRMS Calc. for $C_{34}H_{40}N_2O_4$ 540.2988, found 540.2987

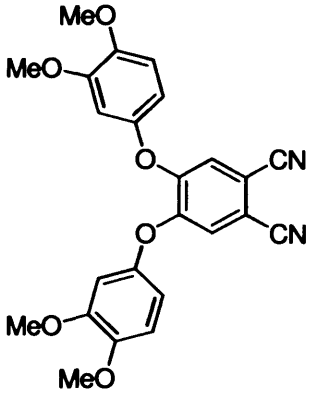
4,5-Bis(3',5'-di-methoxyphenoxy)phthalonitrile (PnOMe$_{3,5}$).



Anhydrous potassium carbonate (4.2 g, 30.4 mmol) was added to a solution of 3,5-dimethoxyphenol (3.5 g, 22.8 mmol) and 4,5-dichlorophthalonitrile (1.5 g, 7.6 mmol) in anhydrous dimethylformamide and were reacted according to the general procedure (a). After 24 h TLC indicated the complete consumption of 4,5-dichlorophthalonitrile. After cooling, the reaction mixture was poured into water and neutralised with hydrochloric acid

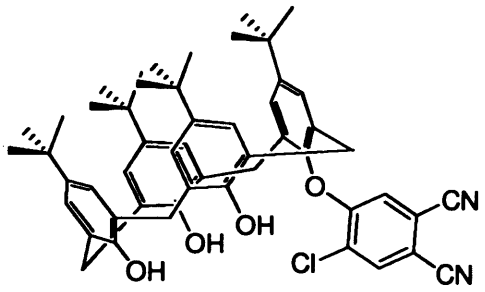
(2N), then the solid was filtered and thoroughly washed with methanol (2.75 g, 84%). M.p. 234-235 °C; IR (nujol)/cm^{-1} 2230,1621, 1572, 1503,1341, 1293, 1191, 1160, 1061, 972, 876, 829,612; ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.23 (s, 2H, Ar*H*), 6.37 (t, 2H, *J* = 2.2 Hz, Ar*H*), 6,22 (d, 4H, *J* = 2.2 Hz, Ar*H*), 3.79 (s, 12H, OC*H*$_3$); ^{13}C NMR (125 MHz; $CDCl_3$) δ 162.1, 122.3, 98.4, 97.7, 60.6, 55.5, some Cs are missing due to low solubility of the sample; HRMS Calc. for $C_{24}H_{20}N_2O_6$ 432.1321, found 432.1330.

4,5-Bis(3',4'-di-methoxyphenoxy)phthalonitrile (PnOMe$_{3,4}$).



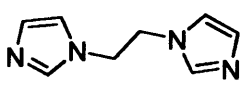
Anhydrous potassium carbonate (4.2 g, 30.4 mmol) was added to a solution of 3,4-dimethoxyphenol (3,5 g, 22.8 mmol) and 4,5-dichlorophthalonitrile (1.5 g, 7.6 mmol) in dry dimethylformamide according to the general procedure (a). After 24 h, the 4,5-dichlorophthalonitrile was fully consumed as shown by TLC. After cooling, the reaction mixture was poured into water and neutralised with hydrochloric acid (2N). The resulting solid was filtered and thoroughly washed with methanol (3.15 g, 95%). M.p. 165-167 °C; IR (nujol)/cm^{-1} 3090, 2225, 1603, 1584, 1508,1396, 1346, 1289, 1231, 1073, 1025, 947, 881, 635; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.08 (s, 2H, Ar*H*), 6.91 (d, 2H, *J* = 7.8 Hz, Ar*H*), 6,67(m, 4H, Ar*H*), 3.92 (s, 6H, OC*H*$_3$) 3.88 (s, 6H, OC*H*$_3$); ^{13}C NMR (100 MHz; $CDCl_3$) δ 151.2, 149.3, 146.1, 145.9, 119.3, 114.1, 110.7, 110.6, 108.6, 103.6, 55.2, 55.0; HRMS Calc. for $C_{24}H_{20}N_2O_6$ 432.1321, found 432.1328.

4-Chloro-5-(4-*tert*-butylcalix(4)arene)phthalonitrile (Pncalix)



Anhydrous potassium carbonate (2.1 g, 15.2 mmol) was added to a solution of *tert*-butylcalix(4)arene (1.65 g, 2.5 mmol) and 4,5-dichlorophthalonitrile (0.50 g, 2.5 mmol) in anhydrous dimethylformamide (20 ml). The mixture was stirred under nitrogen atmosphere for 72 h at 70 °C. After cooling, the reaction mixture was poured into water (200 ml) and the aqueous solution was neutralised with hydrochloric acid (2N). The resulting solid was filtered and washed with water. Purification by column chromatography on SiO_2, eluting with hexane-ethyl acetate, gave the title compound as a white solid (1.5 g, 73%). M.p. 185-186 °C; IR (nujol)/cm^{-1} 3461, 3288, 2234, 1585, 1302, 1269, 1202, 1012, 897, 872, 740; ^{1}H NMR (500 MHz; $CDCl_3$) δ 9.19 (br s, 1H, O*H*), 7.72 (br s, 2H, O*H*), 7.28 (s, 2H, Ar*H*), 7.09 (s, 2H, Ar*H*), 7.05 (s, 2H, Ar*H*), 7.04 (s, 1H, Ar*H*), 6,79 (s, 1H, Ar*H*), 6.74 (s, 2H, Ar*H*), 3.99 (m, 2H, ArCH_2Ar), 3.72 (m, 4H, ArCH_2Ar), 3.61 (m, ArCH_2Ar), 1.29 (s, 9H, C(CH_3)$_3$), 1.25 (s, 9H, C(CH_3)$_3$), 1.15 (s, 18H, C(CH_3)$_3$); ^{13}C NMR (100 MHz; $CDCl_3$) δ 156.7, 151.1, 148.4, 147.2, 144.0, 143.4, 135.3, 131.9, 128.7, 128.0, 127.9, 127.6, 127.1, 126.2, 125.9, 125.4, 124.8, 117.6, 115.2, 114.7, 114.2, 109.2, 34.5, 34.0, 33.8, 32.2, 31.4, 31.1; LRMS, (EI), m/z: 808.42 ($M^{\bullet+}$, 100%). Crystal data (*calix*): crystal size 0.3 x 0.07 x 0.02 mm, triclinic, space group *P-1*, a = 1.5385(12) nm, b = 1.7110(13) nm, c = 2.0965(16) nm, α= 91.613(10, β = 109.176(10), γ= 112.248(10), V = 4.750(6) nm^3, Z = 2, R_1 = 0.1156, the asymmetric unit contains 2 molecules together with some solvent methanol and H_2O molecules, the latter at partial occupancy.

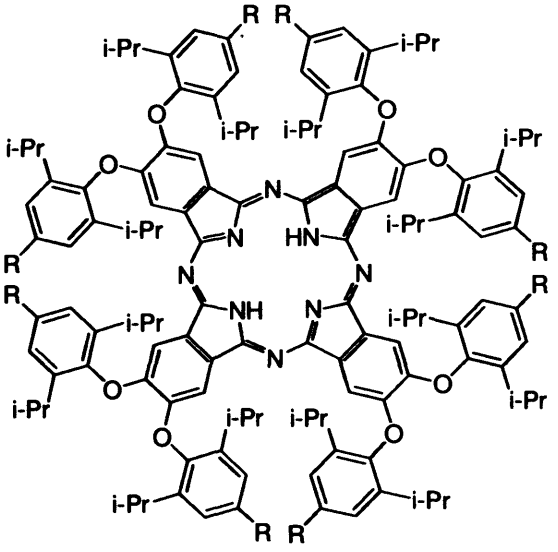
1,2-Di(1H-imidazol-1-yl)ethane[185]



A mixture of imidazole (2.00 g, 29 mmol), 10 ml of 40% aqueous sodium hydroxide terabutylammonium bromide (0.45 g, 1.4 mmol) and 1,2-dibromoethane (2.72 g, 14.5

mmol) in 25 ml of toluene were heated at reflux for 72h. After cooling, the aqueous layer was extracted with dichloromethane (3 x 40 ml) and the extracts combined with the organic phase. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on SiO_2 eluting with DCM: methanol 10:1 to give the title compound as white solid (1.00 g, 43%). M.p. 137-138 °C (lit[185] m.p. 142-144 °C); IR (nujol)/cm^{-1} 1748, 1586, 1294, 1231, 1108, 1075, 909, 808, 778, 659; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.22 (s, 2H, Ar*H*), 7.02 (s, 2H, Ar*H*), 6.65 (s, 2H, Ar*H*), 4.24 (s, 4H, ArCH_2); ^{13}C NMR (100 MHz; $CDCl_3$) δ 137.2, 130.5, 118.7, 48.0; LRMS, (APCI), m/z: 163.09 ($M^{\bullet+}$, 100%).

Metal free phthalocyanine derivatives



Pc 1; R = H
Pc 2; R = Br
Pc 3; R = Cl
Pc 4; R = CN
Pc 5; R = OMe
Pc 6; R = OH

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyanine (Pc1). 4,5-Bis(2,6-di-*iso*-propylphenoxy)phthalonitrile (**Pn1**) (0.20 g, 0.42 mmol) was reacted according to the general procedure (b). Purification by column chromatography on SiO_2, eluting with DCM, gave the title compound as a green solid (0.08 g, 40%). M.p. > 300 °C; IR (film)/cm^{-1} 3576, 2962, 1439, 1328, 1265, 1184, 1093, 1017, 877, 754; UV/vis (DCM): λ_{max} 702.5, 667.5, 607, 420.5, 348.5, 297, 229.5 nm; ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.13 (br , 8H), 7.50(m, 24H, Ar*H*), 3.37 (sept, 16H, *J* = 6.5 Hz, CH_3CHCH_3), 1.28 (br m, 96 H, CH_3CHCH_3), -0.84 (s, 2H, N*H*); ^{13}C NMR (125 MHz; $CDCl_3$) δ 151.0, 149.1, 141.7, 126.4, 124.7, 107.4, 27.4, some Cs are missing; MS (MALDI-TOF): cluster centred at m/z 1925.71(MH^+); elemental analysis calc (%) for $C_{128}H_{146}N_8O_8$: C 79.88, H 7.65, N 5.82, found C 80.04, H 7.70, N 5.70. Crystal data: first polymorph (DCM/acetone): crystal size:

0.6 x 0.6 x 0.05 mm, monoclinic, space group $P2_1/c$, a = 2.1293(7) nm, b = 1.6896(5) nm, c = 1.8283(6) nm, β = 114,657(4), V = 5.9778(7) nm^3, Z = 2, R_1 = 0.0838. The asymmetric unit contains ½ of **Pc1** with a solvent acetone molecule; second polymorph (EtOAc-DCM/MeOH): crystal size: 0.8 x 0.6 x 0.10 mm, orthorhombic, space group *Pbca*, a = 1.94927(12) nm, b = 1.62918(10) nm, c = 3.8420(2) nm, V =1.2201(1) nm^3, Z = 4, R_1 = 0.0677. The asymmetric unit contains ½ of **Pc1** with 2 solvent ethyl acetate molecules.

2,3,9,10,16,17,23,24-octa(4'-bromo-2',6'-di-*iso*-propylphenoxy)phthalocyanine (PcBr). 4,5-Bis(4'-bromo-2',6'-di-*iso*-propylphenoxy)phthalonitrile (**PnBr**) (0.20 g, 0.31 mmol) was reacted according to the general procedure (b). The crude product was purified by column chromatography on SiO_2, eluting with hexane-DCM (7:3) to give a green solid (0.08 g, 40%). M.p. > 300 °C; IR (film)/cm^{-1} 3298, 2962, 1613, 1443, 1328, 1265, 1185, 1091, 1009, 877, 797, 757 UV/vis (DCM): λ_{max} 702, 667, 607, 400, 349, 294, 234 nm; ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.24 (s, 8H, Ar*H*), 7.67 (s, 16 H, Ar*H*), 3.40 (sept, 16 H, J = 6.7 Hz, CH_3CHCH_3),1.29 (br m, 96 H, CH_3CHCH_3), -0.78 (s, 2H, NH_2); MS ^{13}C NMR (125 MHz; $CDCl_3$) δ 150.7, 148.2, 144.3, 128.3, 120.2, 107.7, 27.74 some C are missing; (MALDI-TOF): cluster centred at m/z 2556.60 (MH^+); elemental analysis calc (%) for $C_{128}H_{138}Br_8N_8O_8$: C 60.15, H 5.44, N 4.38, Br 25.01, found C 60.48, H 5.69, N 4.06, Br 23.82. Crystal data:(DCM/MeOH): the crystal was found to be twinned, crystal size 0.2 x 0.05 x 0.02 mm, monoclinic, space group $P2_1/n$, a = 2.3287(5) nm, b = 1.2468(5) nm, c = 2.4191(5) nm, β = 114.185(5), V = 6.407(19) nm^3, Z = 2, R_1 = 0.1103. The asymmetric unit contains ½ of **PcBr** with a solvent DCM molecule.

2,3,9,10,16,17,23,24-octa(4'-chloro-2',6'-di-*iso*-propylphenoxy)phthalocyanine (PcCl). 4,5-Bis(4'-chloro-2',6'-di-*iso*-propylphenoxy)phthalonitrile (**PnCl**) (0.50 g, 0.91 mmol) was reacted according to the general procedure (b). The crude product was purified by column chromatography on SiO_2, eluting with hexane-DCM (7:3) to give a green solid (0.28 g, 56%). M.p. > 300 °C; IR (film)/cm^{-1} 2962, 1609, 1442, 1326, 1270, 1185, 1091, 1007, 876, 811, 758, 699; UV/vis (DCM): λ_{max} 702, 667, 396, 350,295, 230 nm; ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.22 (s, 8H, Ar*H*), 7.51 (s, 16 H, Ar*H*), 3.40 (sept, 16 H, J = 6.7 Hz, CH_3CHCH_3),1.29 (br m, 96 H, CH_3CHCH_3), -0.80 (s, 2H, NH_2); ^{13}C NMR (125 MHz; $CDCl_3$) δ 150.7, 147.6, 143.8, 132.0, 125.2, 114.0, 107.6, 27.7, some C are missing; MS (MALDI-TOF): cluster centred at m/z 2201.94 (MH^+); elemental analysis calc (%) for $C_{128}H_{138}Cl_8N_8O_8$: C 69.88, H 6.32, N 5.09, Cl 12.89, found C 69.93, H 6.41, N 4.77, Cl

13.27. Crystal data:($CHCl_3$/MeOH): crystal size 0.30 x 0.03 x 0.01 mm, monoclinic, space group $P2_1/c$, a = 1.7641(12) nm, b = 1.2824(9) nm, c = 2.875(2) nm, β = 103.486(7), V = 6324(8) nm^3, Z = 2, R_1 = 0.0725. The asymmetric unit contains ½ of **PcCl** with a solvent $CHCl_3$ molecule.

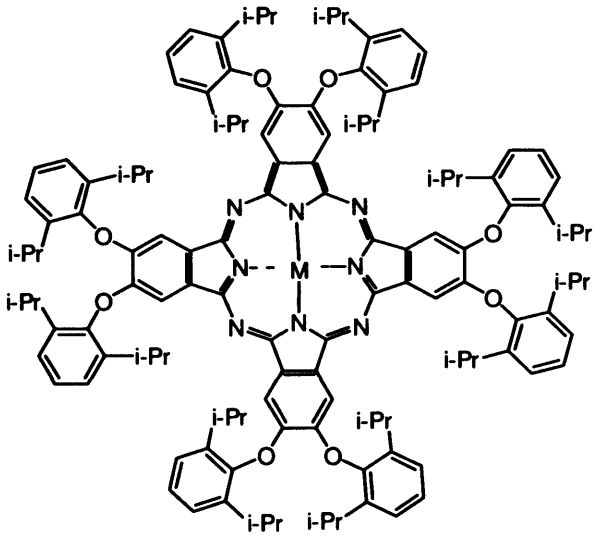
2,3,9,10,16,17,23,24-octa(4'-cyano-2',6'-di-*iso*-propylphenoxy)phthalocyanine (PcCN). 4,5-bis(4'-cyano-2',6'-di-*iso*-propylphenoxy)phthalonitrile (**PnCN**) (0.20 g, 0.37 mmol) was reacted according to the general procedure (b). The crude product was purified by column chromatography on SiO_2 eluting with DCM to give a green solid (0.02 g, 10%). M.p. > 300 °C; IR (film)/cm^{-1} 2965, 2232, 1613, 1443, 1334, 1283, 1198, 1092, 1016, 887; UV/vis (DCM): λ_{max} 700, 666, 605, 396, 349, 233 nm; ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.09 (s, 8H, Ar*H*), 7.92 (s, 16 H, Ar*H*), 3.40 (sept, 16 H, J = 6.8 Hz, CH_3CHCH_3) 1.33 (br m, 96 H, CH_3CHCH_3), -0.87(s, 2H, NH_2); ^{13}C NMR (125 MHz; $CDCl_3$)152.7, 150.3, 143.8, 129.5, 119.2, 111.1, 107.7, 27.8, 23.92, 22.43, some Cs are missing; MS (MALDI-TOF): cluster centred at m/z 2125.81 (MH^+); elemental analysis calc (%) for $C_{136}H_{138}N_{16}O_8$: C 76.88, H 6.55, N 10.55 found C 76.98, H 6.90, N 10.13. Crystal data: (DCM/acetone): crystal size 0.2 x 0.1 x 0.02 mm, triclinic, space group *P-1*, a = 1.16617(9) nm, b = 1.68193(13) nm, c = 2.1294(2) nm, α= 106.4350(10), β = 97.0490(10), γ= 106.5810(10), V = 3.74419 nm^3, Z = 1, R_1 = 0.1056, the asymmetric unit contains ½ of **PcCN** with some disordered solvent, acetone and H_2O or O atom with occupancies of 0.5 or 0.25.

2,3,9,10,16,17,23,24-octa(4'-methoxy-2',6'-di-*iso*-propylphenoxy)phthalocyanine (PcOMe). 4,5-bis(4'-methoxy-2',6'-di-*iso*-propylphenoxy)phthalonitrile (**PnOMe**) (0.75 g, 1.4 mmol) was reacted according to the general procedure (b).The crude product was purified by column chromatography on SiO_2 eluting with DCM/hexane/ethyl acetate, 2/8/1 to give a green solid (0.34g, 45%). M.p. > 300 °C; IR (film)/cm^{-1} 2963, 1608, 1456, 1334, 1198, 1090, 1040, 1016, 878; UV/vis (DCM): λ_{max} 704, 671, 420.5, 347, 292, 205 nm; ^{1}H NMR (500 MHz; $CDCl_3$) δ8.27 (s, 8H, Ar*H*), 6.99 (s, 16 H, Ar*H*), 4.09 (s, 24 H, OCH_3), 3.44 (sept, 16 H, J = 6.9 Hz, CH_3CHCH_3), 1.28 (br m, 96 H, CH_3CHCH_3), -0.75 (s, 2H, N*H*); ^{13}C NMR (125 MHz; $CDCl_3$) 157.7, 151.5, 142.9, 142.8, 110.0, 107.7, 55.5, 27.6; MS (MALDI-TOF): cluster centred at m/z 2164.22 (M^+); elemental analysis calc (%) for $C_{136}H_{162}N_8O_{16}$: C 75.46, H 7.54, N 5.18 found C 75.58, H 7.26, N 4.74. Crystal data: DCM/MeOH: crystal size 0.8 x 0.1 x 0.05 mm, monoclinic, space group *C2/c*, a =

3.9950(5) nm, b = 1.3082(5) nm, c = 3.4112(5) nm, β =121.087(5), V=15.267(5) nm^3, Z = 4, R_1 = 0.1161, the asymmetric unit contains ½ of **PcOMe** with a number of MeOH and H_2O molecules mostly at partial occupancy.

2,3,9,10,16,17,23,24-octa(4'-hydroxy-2',6'-di-*iso*-propylphenoxy)phthalocyanine (PcOH). Boron tribromide (0.1ml, 1 mmol) was added dropwise to a solution of **PcOMe** (0.19 g, 0.09mmol) in anhydrous dichloromethane (5 ml), with stirring and under nitrogen, at 0 °C. The reaction was monitored by TLC and after 1 h **PcOMe** was fully consumed. The excess of boron tribromide was left to evaporate, then the reaction was quenched with water and a green precipitate isolated. The solid was purified by recrystallization from acetone/hexane (0.16 g, 85%). M.p. > 300 °C; IR (nujol)/cm^{-1} 3345, 1601, 1188, 1088, 1013, 876; UV/vis (DCM): λ_{max} 701, 667, 346, 206 nm; ^{1}H NMR (400 MHz; AcD6) δ 8.69 (br, 8 H, O*H*), 8.30 (s, 8H, Ar*H*), 7.14 (s, 16 H, Ar*H*), 3.46 (sept, 16 H, J = 6.9 Hz, CH_3CHCH_3), 1.27 (br m, 96 H, CH_3CHCH_3), -0.65(s, 2H, N*H*) ; ^{13}C NMR (100 MHz; AcD6) δ 157.2, 144.5, 143.9, 143.7, 113.5, 113.3, 109.1, 29.4, some Cs are missing; MS (MALDI-TOF): cluster centred at m/z 2052.28 (M^+); elemental analysis calc (%) for $C_{128}H_{154}N_8O_{20}$ (**PcOH** + 4H_2O, hygroscopic): C 72.36, H 7.31, N 5.27 found C 71.69, H 7.31, N 4.82.

Pc1 Metal derivatives



Pc 1; M = Zn^{2+}

Pc 1; M = Co^{2+}

Pc 1; M = Cu^{2+}

Pc 1; M = Ni^{2+}

Pc 1; M = Mg^{2+}

Pc 1; M = Mn^{2+}

Pc1; M = Ru^{2+}

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato zinc (Pc1Zn).[127] 4,5-Bis(2,6-di-*iso*-propylphenoxy)-phthalonitrile (**Pn1**) (0.3 g, 0.6 mmol) and zinc(II)acetate (0.11 g, 0.6 mmol) in anhydrous NMP (1 ml) were reacted according to the

procedure (c). Purification by column chromatography on SiO_2, eluting with hexane-DCM (3:7), gave the title compound as a green solid (0.2 g, 67%). M.p. > 300 °C; IR (film)/cm^{-1} 2963, 1609, 1456, 1400, 1329, 1271, 1186, 1092, 1025, 894, 795; UV/vis (DCM): λ_{max} 683, 653, 615, 347,296, 229 nm; ^1H NMR (400 MHz; $CDCl_3$) δ 8.16 (s, 8H, Ar*H*), 7.51(m, 24 H, Ar*H*), 3.46 (sept, 16 H, *J* = 6.9 Hz, CH_3CHCH_3), 1.30 (br m, 96 H, CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 152.6, 150.7, 149.3, 141.8, 139.8, 132.2, 126.3, 124.7, 107.4, 27.5, 23.8, 23.6;MS (MALDI-TOF): cluster centred at m/z 1988.62 (MH^+); elemental analysis calc (%) for $C_{129}H_{146}N_8O_8Zn$: C 76.64, H 7.34, N 5.59 found C 76.95, H 7.53, N 5.58.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato cobalt (Pc1Co). 4,5-Bis(2,6-di-*iso*-propylphenoxy)-phthalonitrile (**Pn1**) (0.50 g, 1.04 mmol) and cobalt(II)acetate (0.18 g, 1.01 mmol) in anhydrous NMP (1 ml) were reacted according to the procedure (c). Purification by column chromatography on SiO_2, eluting with hexane-DCM (4:6), gave the title compound as a green solid (0.22 g, 40%). M.p. >300 °C; IR (film)/cm^{-1} 2961, 1612, 1456, 1462, 1413, 1353, 1269, 1186, 1095, 1050, 904, 864, 799, 777, 755, 729; UV/vis (DCM): λ_{max} 673, 608, 404, 331, 302, 229 nm; MS (MALDI-TOF): cluster centred at m/z 1982.055 (MH^+); elemental analysis calc (%) for $C_{128}H_{144}N_8O_8Co$: C 77.59, H 7.32, N 5.66 found C 77.68, H 7.52, N 5.52. Crystal data: first isomorph DCM/acetone: crystal size 0.3 x 0.3 x 0.1 mm, monoclinic, space group $P2_1/c$, a = 3.8714(3) nm, b = 1.68469(12) nm, c = 1.82104(13) nm, β =90.7290(10), V = 11.8761(15) nm^3, Z = 4, R_1 = 0.0792, the asymmetric unit contains 1 molecule of **Pc1Co** with 2 disordered DCM solvent molecules; second polymorph (DCM/MeOH): crystal size 1.00 x 0.80 x 0.50 mm cubic, $Pn\text{-}3n$, a = 3.7391(3), V = 52.2759, Z = 12, R_1 = 0.0983. The asymmetric unit contains ¼ of **Pc1Co** molecule together with a solvent atom, assumed to be water at an occupancy of 0.5. In the axial sites there is a water molecule at one site and a water/MeOH at the other site.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato copper (Pc1Cu). A solution of **Pc1** (0.10g, 0.05 mmol) and a large excess of Cu(II)acetate (0.47g, 2.5 mmol) in dry *n*-pentanol (5ml) was heated at reflux for four hours. After cooling, the slurry of reaction was dissolved in toluene and filtered to remove the excess of Cu(II)acetate, the solvent was evaporated under reduced pressure. The crude product was purified by repeated reprecipitation with methanol from its solution in DCM to give a

green solid (0.08 g, 77%).M.p. > 300 °C; IR (film)/cm^{-1} 2962, 1611, 1461, 1406, 1351, 1271, 1186, 1095, 1034, 899, 797, 775; UV/vis (DCM): λ_{max} 682, 614, 405, 343, 295, 230 nm; MS (MALDI-TOF): cluster centred at m/z 1988.33(MH^+); elemental analysis calc (%) for $C_{128}H_{144}N_8O_8Cu$: C 77.41, H 7.31, N 5.64 found C 77.97, H 7.52, N 5.36. Crystal data (DCM/acetone): crystal size 0.4 x 0.2 x 0.04 mm, monoclinic, space group $P2_1/c$, a = 3.8607(2) nm, b = 1.68676(10) nm, c = 1.84282(11) nm, β =91.3750 , V =11.997 nm^3, Z = 4, R_1 = 0.0747, the asymmetric unit contains 1 molecule of **Pc1Cu** with a solvent acetone molecule and some disordered solvent assumed to be DCM over 2 sites whose occupancies sum to 0.5 and water at 0.5 occupancy.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato nickel (Pc1Ni). A stirred solution of 4,5-bis(2,6-di-*iso*-propylphenoxy)-phthalonitrile **Pn1** (0.5 g,1.0 mmol) and nickel(II)chloride (0.10 g , 0.77 mmol) in anhydrous quinoline (1 ml), was heated at 165 °C for 30h under nitrogen. The reaction mixture was cooled to room temperature, poured into a mixture of methanol - water (20 ml, 1:1) then filtered off. The crude product was purified by reprecipitation with methanol from DCM solution to give a green solid (0.26 g, 50%). M.p. > 300 °C; IR (film)/cm^{-1} 2962,1464, 1417, 1359, 1272, 1189, 1095, 1051, 905; UV/vis (CH_2Cl_2): λ_{max} = 673, 608, 405, 309, 234nm ; ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.03(s , 8H, Ar*H*), 7.56 (t, 8H, J = 7.7 Hz, Ar*H*), 7.45 (d, 16H, J = 7.7 Hz, Ar*H*), 3.42 (sept, 16H, J = 6.8 Hz, CH_3CHCH_3), 1.25 (br m, 96 H, CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) 150.8, 149.1, 145.3, 141.7, 131.4, 106.5, 27.4, some Cs are missing; MS (MALDI-TOF): cluster centred at m/z 1980.65 (M^+); elemental analysis calc (%) for $C_{128}H_{144}N_8O_8Ni$: C 77.60, H 7.33, N 5.66 found C 77.67, H 7.22, N 5.27. Crystal data (CHCl3/): crystal size 0.45 x 0.3 x 0.04 mm, monoclinic, space group $P2_1/c$, a = 2.1370(2) nm, b = 1.688255(18) nm, c = 1.8726(2) nm, β =115.0680(10), V = 6.0987(11) nm^3, Z = 2, R_1 = 0.0550, the asymmetric unit contains ½ molecule of **Pc1Ni** with a fully occupied $CHCl_3$ molecule.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato magnesium (Pc1Mg). Magnesium turnings (0.02 g, 0.35 mmol), iodine (1 crystal) were stirred in pentanol (10 ml) at reflux, in inert atmosphere, for 2 h, then 4,5-bis(2,6-di-*iso*-propylphenoxy)-phthalonitrile (**Pn1**) (0.50 g, 1 mmol) was added. After 2 h the solvent was left to evaporate and the solid was dissolved in DCM. The crude product was purified by reprecipitation with methanol from DCM solution to give a green solid (0.20 g, 40%).

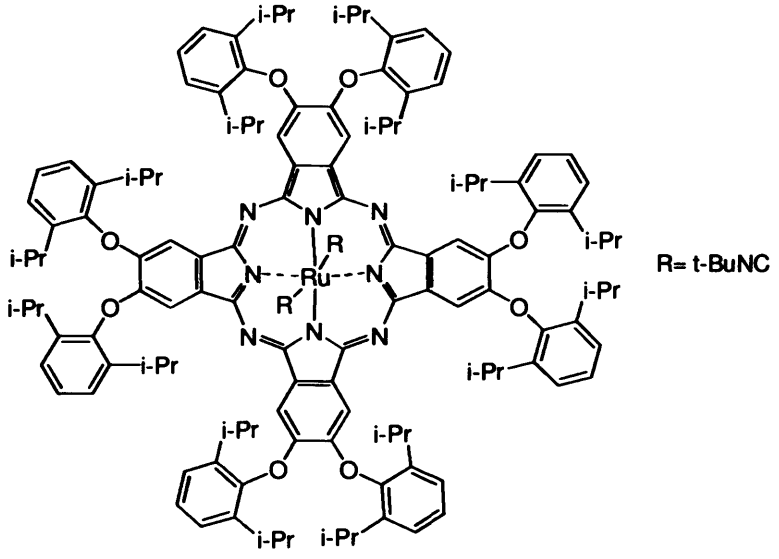
M.p. > 300 °C; IR (film)/cm^{-1} 2963, 1610, 1455, 1399, 1330, 1270, 1186, 1084, 1025, 896, 795; UV/vis (DCM): λ_{max} 681, 616, 421, 359, 294 nm; ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.13 (s, 8H, Ar*H*), 7.56(t, 9 H, *J* = 7.7 Hz, Ar*H*), 7.46 (t, 18 H, *J* = 7.7 Hz, Ar*H*), 3.46 (sept, 16 H, *J* = 6.8 Hz, CH_3CHCH_3), 1.28 (br m, 96 H, CH_3CHCH_3); ^{13}C NMR (125 MHz; $CDCl_3$) δ 153.2, 150.4, 149.3, 141.8, 132.6, 126.3, 124.7, 107.3, 27.4, 24.2, 22.9; MS (MALDI-TOF): cluster centred at m/z 1946.43 (M^+); elemental analysis calc (%) for $C_{128}H_{144}N_8O_8Mg$: C 78.97, H 7.46, N 5.76 found C 78.62, H 7.54, N 5.62. Crystal data ($CHCl_3$/acetone): crystal size 0.6 x 0.45 x 0.4 mm, cubic, space group *Pn-3n*, *a* = 3.73320(5) nm, *V* = 52.02888(12) nm^3, *Z* = 12, R_1 = 0.1377, the asymmetric unit contains ¼ of **PclMg** molecule together with a solvent atom, assumed to be water at an occupancy of 0.5. One axial site appears to be occupied by a water molecule.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato manganese (PclMn). A mixture of **Pcl** (0.1 g, 0.05 mmol) and Mn(II)acetate (0.1g, 0.6 mmol) in anhydrous DMF (2 ml) were refluxed for 5 hours. After cooling, water was added to the reaction mixture and the resulting solid formed was filtered. The crude product was purified by column chromatography on SiO_2 eluting with hexane-dichloromethane (7:3) to give the title compound as a green-reddish solid (0.03 g, 30%). M.p. > 300 °C; IR (film)/cm^{-1} 2963, 1610, 1463, 1406, 1352, 1272, 1188, 1087, 904; UV/vis (DCM): λ_{max} 733, 658, 435, 397, 282, 241 nm; MS (MALDI-TOF): cluster centred at m/z 1978.14 (MH^+); elemental analysis calc (%) for $C_{128}H_{154}N_8O_{13}Mn$ (**PclMn** + $5H_2O$): C 74.36, H 7.51, N 5.42 found C 74.26, H 7.21, N 5.32. Crystal data ($CHCl_3$/MeOH): crystal size 0.28 x 0.2 x 0.2 mm, cubic, space group *Pn-3n*, *a* = 3.72511(5) nm, *V* = 51.6913(12) nm^3, *Z* = 12, R_1 = 0.1374, the asymmetric unit contains ¼ of **PclMn** molecule together with 5 solvent atom, assumed to be water at partial occupancy. In the axial sites there is a water molecule at both sites.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato ruthenium (PclRu). A mixture of 4,5-bis(2,6-di-*iso*-propylphenoxy)-phthalonitrile (**Pnl**) (0.15 g, 0.31 mmol) and ruthenium(III)chloride trihydrate(0.06 g, 0.31 mmol) in DBU was stirred at 150 °C in inert atmosphere for 3 h. After cooling, the reaction mixture was poured into water-methanol (1:1; 10ml) then filtered. The crude product was purified by column chromatography on SiO_2 eluting with dichloromethane-methanol (98:2) to give the title compound as a green (0.02 g, 13%). M.p. > 300 °C. IR (film)/cm^{-1} 2962, 1609, 1465, 1405,

1351, 1270, 1186, 1094, 1025, 899; UV/vis (DCM): λ_{max} 630, 327, 252, 231; MS (MALDI-TOF): cluster centred at m/z 2024.28 (M^+); Crystal data ($CHCl_3$/MeOH): crystal size 0.4 x 0.3 x 0.3 mm, cubic, space group *Pn-3n*, a = 3.75645(8) nm, V = 53.007(2) nm^3, Z = 12, R_1 = 0.1009, the asymmetric unit contains ¼ of **PclRu** molecule together with 3 solvent atoms, assumed to be water at an occupancy of 0.25. In both axial sites there is a water molecule.

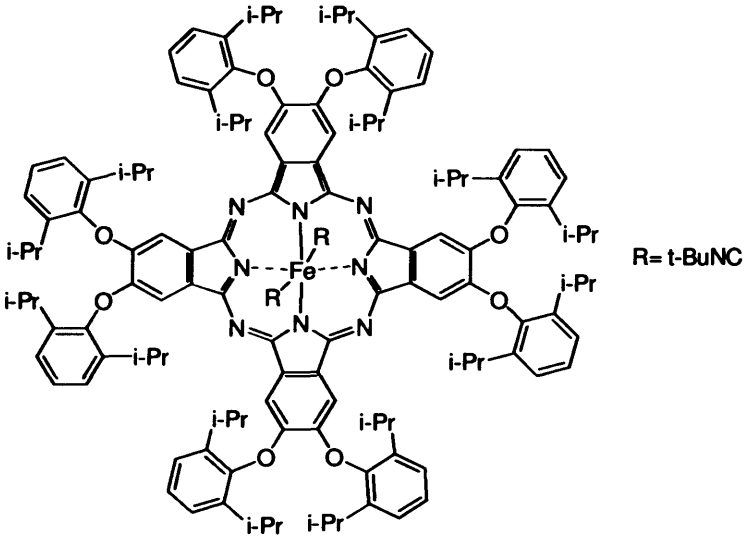
2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato ruthenium bis(t-butylisocyanide) (PclRu)(*t*-BuNC)$_2$.



A mixture of 4,5-bis(2,6-di-*iso*-propylphenoxy)-phthalonitrile (**Pn1**) (0.20 g, 0.42 mmol) and ruthenium(III)chloride hydrate (0.05 g, 0.21 mmol) in dry NMP (1 ml) was stirred at 170 °C in inert atmosphere for 3 h. After cooling, the reaction mixture was poured into water-methanol (1:1, 10ml) then filtered. To the dark brown solid, *t*-butylisocyanide (0.25 ml) was added and the mixture was stirred at 50 ° C for 24 h, then the excess of t-butylisocyanide was left to evaporate. The crude product was purified by column chromatography on SiO_2 eluting with hexane-DCM (7:3) to give the title compound as a blue solid 0.04 g, 17%). M.p. > 300 °C; IR (film)/cm^{-1} 2965, 2135, 1685, 1438, 1404, 1267, 1184, 1034, 864; UV/vis (DCM): λ_{max} 648, 327, 238, 206; ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.89 (s, 8H, Ar*H*), 7.51(t, 8H, J = 7.5 Hz, Ar*H*), 7.42 (t, 16H, J = 7.5 Hz, Ar*H*), 3.50 (sept, 16 H, J = 6.8 Hz, CH_3CHCH_3), 1.28 (br m, 96 H, CH_3CHCH_3), -0.64 (s, 18H, $(CH_3)_3C$); ^{13}C NMR (125 MHz; $CDCl_3$) δ 149.5, 149.1, 142.6, 141.8, 134.0, 126.0, 124.5, 106.7, 28.4, 27.3, some Cs are missing; MS (MALDI-TOF): cluster centred at m/z 2107.90

(M^+) (**PclRu(*t*-BuNC)$_2$**); elemental analysis calc (%) for $C_{138}H_{162}N_{10}O_8$ Ru: C 75.69, H 7.46, N 6.40, found C 75.49, H 7.61, N 6.28. Crystal data ($CHCl_3$/MeOH): crystal size 0.6 x 0.4 x 0.4 mm, cubic, space group *Pn-3n*, a =3.76390(4) nm, V = 53.322(10) nm^3, Z = 12, R_1 = 0.0872; the asymmetric unit contains ¼ of the molecule with some disordered solvent assumed to be water and MeOH. In both axial sites there is a *t*-butylisocyanide molecule, of which one is out of axis.

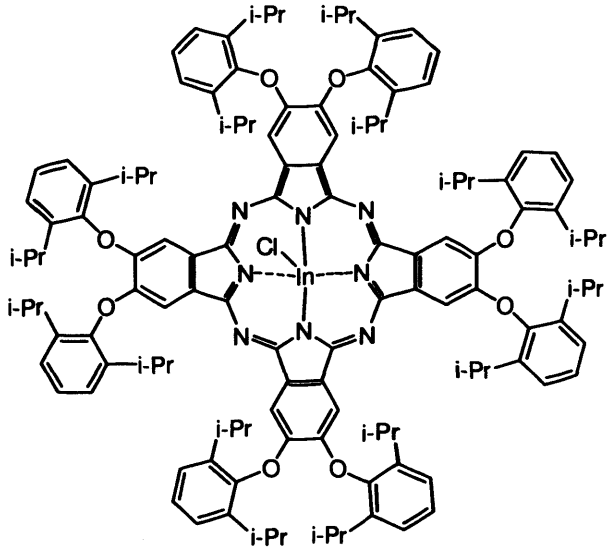
2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato iron bis(*t*-butylisocyanide) (PclFe)(*t*-BuNC)$_2$



Lithium metal (0.005 g) was added to a refluxing mixture of 4,5-bis(2,6-di-*iso*-propylphenoxy)-phthalonitrile (**Pn1**) (0.15 g, 0.31mmol) and iron(II) acetate (0.10 g 0.58 mmol) in anhydrous pentanol (2 ml), under nitrogen and with stirring. The reaction was monitored by TLC and UV and after 2 h was complete. The solvent was evaporated and distilled water (10 ml) was added to the dark solid. After filtration, the solid was stirred with *t*-butylisocyanide (0.5 ml) for 24 h under nitrogen, at 50°C. Then the excess of *t*-butylisocyanide was left to evaporate and the crude product was purified by column chromatography on SiO_2 eluting with hexane-DCM (5:5) to give the title compound as a blue solid (0.1 g, 63%). M.p. > 300 °C; IR (film)/cm^{-1} 2963, 2144, 1456, 1410, 1268, 1185, 1139,1097; UV/vis (DCM): λ_{max} 664, 349, 238, 222; ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.95 (s, 8H, Ar*H*), 7.51(t, 8H, J = 7.5 Hz, Ar*H*), 7.43 (d, 16H, J = 7.5 Hz, Ar*H*), 3.49 (sept, 16 H, J = 6.8 Hz, CH_3CHCH_3), 1.25 (br m, 96 H, CH_3CHCH_3), -0.68 (s, 18H, $(CH_3)_3C$); ^{13}C

NMR (125 MHz; $CDCl_3$) δ 149.6, 149.2, 145.8, 141.8, 134.8, 126.0, 124.5, 106.1, 28.3, 27.3, some Cs are missing; MS (MALDI-TOF): cluster centred at m/z 1979.48 (M^+) (**PcIFe**); elemental analysis calc (%) for $C_{133}H_{154}$ Fe N_9O_9 (**PcIFe(H_2O)(*t*-BuNC)**) (crystals obtained by crystallisation from($CDCl_3$/MeOH): C 76.85, H 7.47, N 6.06, found C 76.64, H 7.80, N 6.20.C; Crystal data ($CDCl_3$/MeOH): crystal size 0.70 x 0.45 x 0.40 mm, cubic, space group *Pn-3n*, a = 3.757680(10) nm, V = 53.0590(2) nm^3, Z = 12, R_1 = 0.1386, the asymmetric unit contains ¼ of the molecule together with 4 solvent atoms, assumed to be water at an occupancy of 0.5 and a $CHCl_3$. In the axial sites there is a t-butylisocyanide molecule at one site and a water molecule at the other site; (DCM/MeOH): crystal size 0.80 x 0.60 x 0.60 mm, cubic, space group *Pn-3n*, a = 3.7362(4) nm, V = 52.154(10) nm^3, Z = 12, R_1 = 0.1202, the asymmetric unit contains ¼ of the molecule and in the axial sites there are *t*-butylisocyanide ligands.

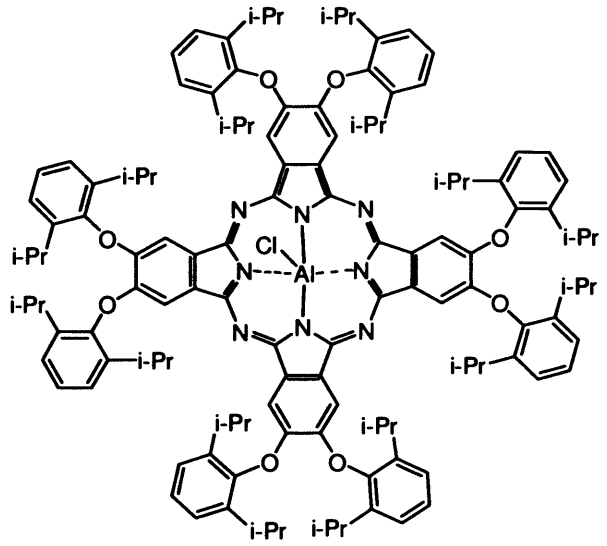
2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato indium chloride (PcIInCl).



Indium(III) chloride(0.16g, 0.72 mmol) was added to a solution of 2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyanine (**PcI**) (0.08g, 0.04mmol) in refluxing anhydrous 1-pentanol (3 ml), under nitrogen and with stirring. After 24 h, the solvent was evaporated and methanol (5 ml) was added to the resultant solid. The crude product was filtered off and purified by column chromatography on SiO_2 eluting with DCM to give the title compound as a green solid (0.03 g, 36%). M.p. > 300 °C; IR (film)/cm^{-1} 2963, 1607, 1460, 1410, 1270, 1186, 1094; UV/vis (DCM): λ_{max} 700, 683, 364, 279, 228; ^1H NMR

(500 MHz; $CDCl_3$) δ 8.17 (s, 8H, Ar*H*), 7.61 (t, 8H, *J* = 7.5 Hz, Ar*H*), 7.50 (br s, 16H, Ar*H*), 3.37 (br m, 16 H, CH_3CHCH_3), 1.28 (br m, 96 H, CH_3CHCH_3); ^{13}C NMR (125 MHz; $CDCl_3$) δ 152.2, 151.4, 148.9, 141.6, 131.5, 126.5, 124.8, 107.4, 27.5, 24.4, 23.0; MS (MALDI-TOF): cluster centred at m/z 2072.09 (M^+); elemental analysis calc (%) for $C_{128}H_{144}ClInN_8O_8$: C 74.17, H 7.00, N 5.41, Cl 1.71 found C 73.62, H 7.36, N 4.93, Cl 1.81; Crystal data ($CHCl_3$/MeOH): crystal size 1.00 x 0.70 x 0.40 mm, cubic, space group *Pn-3n*, *a* = 3.74428(8) nm, *V* = 52.4934(19) nm^3, *Z* = 12, R_1 = 0.1008, the asymmetric unit contains ¼ of the molecule and in the axial site there is part Cl- and part OH- in 1:1 ratio.

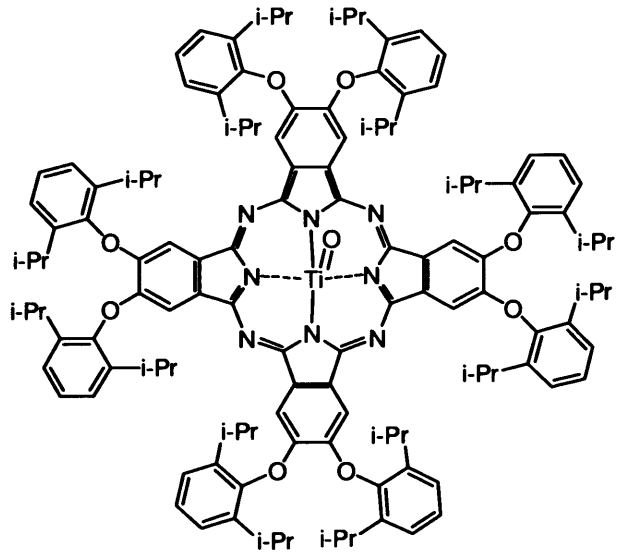
2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato aluminum chloride (PclAlCl).



A mixture of 4,5-bis(2,6-di-*iso*-propylphenoxy)-phthalonitrile (**Pn1**) (0.50 g, 1.04 mmol) and aluminum(III)chloride (0.27 g, 2.04 mmol) in quinoline (1 ml) was stirred at 160 °C in an inert atmosphere for 24 h. After cooling, the reaction mixture was poured into water-methanol (1:1; 10ml) then filtered. The crude product was purified by column chromatography on SiO_2 eluting with hexane-DCM-ethyl acetate (6:4:1) to give the title compound as a green solid (0.13 g, 25%). M.p. > 300 °C; IR (film)/cm^{-1} 2963, 1611, 1465, 1414, 1356, 1328, 1273, 1188, 1093, 900, 776; UV/vis (DCM): λ_{max} 691, 626, 421, 348, 299, 252 nm; ^1H NMR (500 MHz; $CDCl_3$) δ 8.21 (s, 8H, Ar*H*), 7.60(t, 8H, *J* = 7.8 Hz, Ar*H*), 7.48 (br s, 16H, Ar*H*), 3.43 (br s, 16 H, CH_3CHCH_3), 1.28 (br m, 96 H, CH_3CHCH_3) 151.8, 151.6, 148.9, 141.7, 131.0, 126.5, 124.7, 107.3, 27.4, 24.4, 24.3, 23.0, 22.9, 22.9; ^{13}C NMR (100 MHz; $CDCl_3$) δ 151.8, 151.6, 148.9, 141.7, 131.0, 126.5, 124.7, 107.3,

27.4, 24.4, 23.0; MS (MALDI-TOF): cluster centred at m/z 1985.16; elemental analysis calc (%) for $C_{128}H_{144}ClAlN_8O_8$: C 77.45, H 7.31, N 5.65, Cl 1.49 found C 77.09, H 7.44, N 5.59, Cl trace; Crystal data ($CHCl_3$/MeOH): crystal size 0.30 x 0.30 x 0.25 mm, cubic, space group *Pn-3n*, a = 3.74064(4) nm, V = 52.3405(10) nm^3, Z = 12, R_1 = 0.1106, the asymmetric unit contains ¼ of the molecule and in the axial sites there are water molecules.

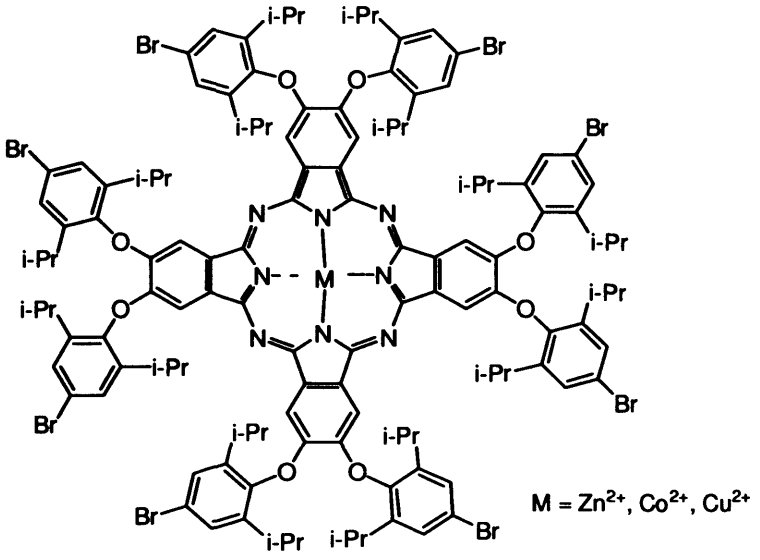
2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato titanium oxide (PclTiO).



4,5-Bis(2,6-di-*iso*-propylphenoxy)-phthalonitrile (**Pn1**) (0.20g, 0.42 mmol) and titanium(IV) butoxide (0.14 g, 0.42 mmol) were reacted according to the general procedure (c). Purification by column chromatography on SiO_2 eluting with hexane-DCM-ethyl acetate (7:3:0.5) gave the title compound as a green solid (0.06 g, 29%). M.p. > 300 °C; IR (film)/cm^{-1} 2963, 1607, 1462, 1401, 1327, 1270, 1186, 1081, 900, 795; UV/vis (DCM): λ_{max} 702, 634, 430, 348, 302, 230; ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.17 (s, 8H, Ar*H*), 7.52 (t, 8H, J = 7.5 Hz, Ar*H*), 7.42 (br s, 16H, Ar*H*), 3.38 (br, 16 H, CH_3CHCH_3), 1.25 (br m, 96 H, CH_3CHCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 151.8, 151.1, 148.9, 141.7, 140.9, 131.3, 126.6, 124.9, 124.8, 107.7, 27.5; MS (MALDI-TOF): cluster centred at m/z 1986.55; elemental analysis calc (%) for $C_{128}H_{144}Cl\ TiN_8O_9$: C 77.39, H 7.31, N 5.64 found C 76.10, H 7.14, N 5.39; Crystal data ($CHCl_3$/MeOH): crystal size 0.20 x 0.20 x

0.20 mm, cubic, space group *Pn-3n*, a = 3.75117(9) nm, V = 52.784(2) nm^3, Z = 12, R_1 = 0.1259.

Bromo substituted Pcs



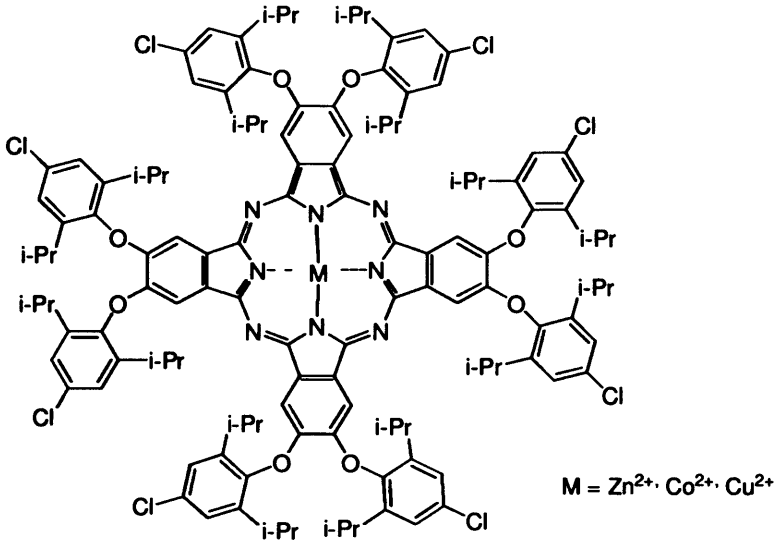
2,3,9,10,16,17,23,24-octa(4'-bromo-2',6'-di-*iso*-propylphenoxy)phthalocyaninato zinc (PcBrZn). 4,5-Bis(4'-bromo-2',6'-di-*iso*-propylphenoxy)phthalonitrile (**PnBr**) (0.50 g, 0.78 mmol) and zinc acetate were reacted according to the general procedure (c). The crude product was purified by column chromatography on SiO_2 eluting with hexane-DCM (4:6) to give a green solid (0.10 g, 20%). M.p.> 300°C; IR (film)/cm^{-1} 2964, 1453, 1400, 1328, 1271, 1186, 1092, 1027, 897; UV/vis (DCM): λ_{max} 683, 615, 371, 345, 294 nm; ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.26 (s, 8 H, Ar*H*), 7.67 (s, 16 H, Ar*H*), 3.42 (sept, 16 H, J = 6.7 Hz, CH_3CHCH_3), 1.36 (br m, 96 H, CH_3CHCH_3); ^{13}C NMR (125 MHz; $CDCl_3$) δ 152.6, 150.3, 148.3, 144.3, 132.4, 128.3, 120.1, 107.7, 27.7 some Cs are missing; MS (MALDI-TOF): *m/z* 2619.66 (M^+); elemental analysis calc (%) for $C_{128}H_{138}Br_8N_8O_9Zn$ (**PcBrZn** + H_2O): C 58.30, Br 24.41, H 5.27, N 4.25, found C 57.80, Br 23.47, H 5.33, N 4.28. Crystal data: first polymorph (DCM/acetone): crystal size 0.7 x 0.05 x 0.02 mm, monoclinic, space group $P2_1/n$, a = 0.93801(3) nm, b = 3.18629(11) nm, c = 2.35605(8) nm, β = 100.1600(10), V = 6.9313 nm^3, Z = 2, R_1 = 0.0602, the asymmetric unit contains ½ of the molecule; second polymorph (DCM/MeOH) (*gbznbr2a*): crystal size 0.4 x 0.2 x 0.5 mm, monoclinic, space group $P2_1/n$, a = 2.22409(16) nm, b = 9.4245(7) nm, c = 3.1332(2) nm, β = 92.4490(10); V =6.5616(8) nm^3, Z = 2, R_1 = 0.0712, the asymmetric unit contains ½ of molecule.

2,3,9,10,16,17,23,24-octa(4'-bromo-2',6'-di-*iso*-propylphenoxy)phthalocyaninato cobalt (PcBrCo). 4,5-Bis(4'-bromo-2',6'-di-*iso*-propylphenoxy)phthalonitrile (**PnBr**) (0.50 g, 0.78 mmol) was reacted according to the general procedure (c). The crude product was purified by column chromatography on SiO_2 eluting with hexane-ethyl acetate (8:2) to give a green solid (0.26 g, 50%). M.p. > 300 °C; IR (film)/cm^{-1} 2971, 1610, 1461, 1413, 1325, 1270, 1188, 1094, 1044, 903, 866; UV/vis (DCM): λ_{max} 674, 302, 230 nm; MS (MALDI-TOF): *m/z* 2612.594 (M^+); elemental analysis calc (%) for $C_{128}H_{136}Br_8CoN_8O_8$: C 58.84, H 5.25, N 4.29, Br 24.47, found C 58.13, H 4.88, N 4.03 (insufficient sample for Br). Crystal data ($CHCl_3$+ Py/acetone): crystal size 0.175 x 0.095 x 0.05 mm, triclinic, space group *P-1*, a = 0.9619(3) nm, b = 1.8313(5) nm, c = 2.1519(6) nm, α= 67.283(3), β = 79.158(3), γ= 77.249(3), V = 3.3879(15) nm^3, Z = 1, R_1 = 0.0940, the asymmetric unit contains ½ of the molecule with a solvent acetone molecule. In both the axial sites there is a pyridine molecule.

2,3,9,10,16,17,23,24-octa(4'-bromo-2',6'-di-*iso*-propylphenoxy)phthalocyaninato copper (PcBrCu).

A solution of **PcBr** (0.15g, 0.06 mmol) and a large excess of Cu(II)acetate (0.65g, 3.6 mmol) in dry *n*-pentanol (5ml) was heated at reflux for 24 h. After cooling, the pentanol was evaporated and the resulting slurry was dissolved in DCM and filtered to remove the excess of $Cu(OOCCH_3)$. The solvent was evaporated under reduced pressure and the crude product was purified by reprecipitation with methanol from DCM solution to give a green solid (0.14 g, 90%). M.p. > 300 °C; IR (film)/cm^{-1} 2963, 1613, 1461, 1408, 1348, 1328, 1271, 1188, 1094, 1036, 899, 880, 866, 826, 728; UV/vis (DCM): λ_{max}682, 615, 371, 340 265 nm; MS (MALDI-TOF): *m/z* 2617.15 (M^+). Elemental analysis calc (%) for $C_{128}H_{136}Br_8CuN_8O_8$: C 58.74, H 5.24, N 4.28, Br 24.42, found C 58.07, H 4.92, N 4.11 (insufficient sample for Br).

Chloro substituted Pcs



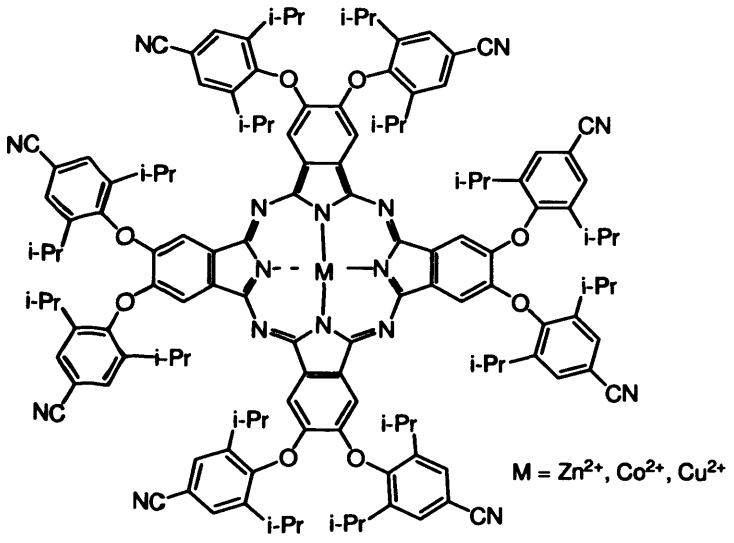
2,3,9,10,16,17,23,24-octa(4'-chloro-2',6'-di-*iso*-propylphenoxy)phthalocyaninato zinc (PcClZn). 4,5-Bis(4'-chloro-2',6'-di-*iso*-propylphenoxy)phthalonitrile (**PnCl**) (0.30 g, 0.55 mmol) was reacted with zinc acetate according to the general procedure (c). The crude product was purified by column chromatography on SiO_2 eluting with hexane-DCM-ethyl acetate (7.5:2:0.5) to give a green solid (0.13 g, 42%). M.p.> 300°C; IR (film)/cm^{-1} 2965, 1609, 1455, 1401, 1328, 1273, 1186, 1094, 1028, 888, 830; UV/vis (DCM): λ_{max} 682, 615, 348, 294, 230 nm; ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.25 (s, 8 H, Ar*H*), 7.51 (s, 16 H, Ar*H*), 3.42 (sept, 16 H, J = 6.7 Hz, CH_3CHCH_3), 1.29 (br m, 96 H, CH_3CHCH_3); ^{13}C NMR (125 MHz; $CDCl_3$) δ 152.6, 150.4, 147.7, 143.8, 132.3, 131.9, 125.2, 107.6, 27.7 some Cs are missing; MS (MALDI-TOF): *m/z* 2263.86(MH^+); elemental analysis calc (%) for $C_{129}H_{138}Cl_{10}N_8O_8Zn$ (**PcClZn** + DCM) : C 65.97, Cl 12.53, H 5.92, N 4.77, found C 65.91, H 5.97, N 4.55 (insufficient sample for Cl). Crystal data (DCM/acetone): crystal size 1 x 0.1 x 0.02 mm, triclinic, space group *P-1*, a = 2.0917(5) nm, b = 2.2711(5) nm, c = 2.5941(5) nm, α= 86.390(5), β = 66.921(5), γ= 63.231(5), V = 10.0125(4) nm^3, Z = 3, R_1 = 0.0789, the asymmetric unit contains 1.5 of the molecule with 4 ordered solvent acetone molecules.

2,3,9,10,16,17,23,24-octa(4'-chloro-2',6'-di-*iso*-propylphenoxy)phthalocyaninato cobalt (PcClCo). 4,5-Bis(4'-chloro-2',6'-di-*iso*-propylphenoxy)phthalonitrile (**PnCl**)

(0.40 g, 0.73 mmol) was reacted with cobalt acetate according to the general procedure (c). The crude product was purified by column chromatography on SiO_2 eluting with hexane-dichloromethane (7:3) to give a green solid (0.18 g, 44%). M.p. > 300°C; IR (film)/cm^{-1} 2965, 1608, 1461, 1414, 1351, 12712, 1188, 1093, 1044, 905, 869, 836, 730; UV/vis (DCM): λ_{max} 672, 610, 303, 278, 230 nm; MS (MALDI-TOF): *m/z* 2257.83(MH^+). elemental analysis calc (%) for $C_{128}H_{136}Cl_8CoN_8O_8$: C 68.11, Cl 12.57, H 6.07, N 4.96, found C 67.82, H 5.78, N 4.75, (insufficient sample for Cl). Crystal data: first polymorph (DCM/acetone): crystal size 0.2 x 0.02 x 0.02 mm, triclinic, space group *P-1*, a = 2.0961(10) nm, b = 2.2872(11) nm, c = 2.609(2) nm, α= 72.786(4), β = 66.31, γ= 62.73, V =10.084(10) nm^3, Z = 3, R_1 = 0.0959, the asymmetric unit contains 1.5 of the molecule together with 3 acetone molecules and 2 water molecules the latter with 0.5 occupancy; second polymorph (DCM/hexane):the crystal was a twinned crystal of size 1.0 x 0.5 x 0. 2 mm, monoclinic, $P2_1/n$, a = 2.3518(6) nm, b = 1.2582(3) nm, c = 2.3640 (6) nm, β = 115.601(12), V = 6.309(3) nm^3, Z = 2, R_1 = 0.1431, the asymmetric unit contains ½ of molecule together with a DCM molecule whose occupancy is 0.5.

2,3,9,10,16,17,23,24-octa(4'-chloro-2',6'-di-*iso*-propylphenoxy)phthalocyaninato copper (PcClCu). 4,5-Bis(4'-chloro-2',6'-di-*iso*-propylphenoxy)phthalonitrile (**PnCl**) (0.50 g, 0.91 mmol) was reacted with copper(II) acetate according to the general procedure (c). The crude product was purified by column chromatography on SiO_2 eluting with hexane-dichloromethane (8:2) to give a green solid (0.16g, 31%). M.p. > 300°C; IR (film)/cm^{-1} 2965, 1723, 1609, 1461, 1408, 1326, 1273, 1189, 1096, 1037, 904, 868, 836, 728; UV/vis (DCM): λ_{max} 681, 613, 340, 294, 229 nm; MS (MALDI-TOF): *m/z* 2261.91 (MH^+); elemental analysis calc (%) for $C_{128}H_{136}Cl_8CuN_8O_8$: C 67.98, Cl 12.54, H 6.06, N 4.95, found C 67.88, H 6.17, N 4.83 (insufficient sample for Cl).

Nitrile substituted Pcs



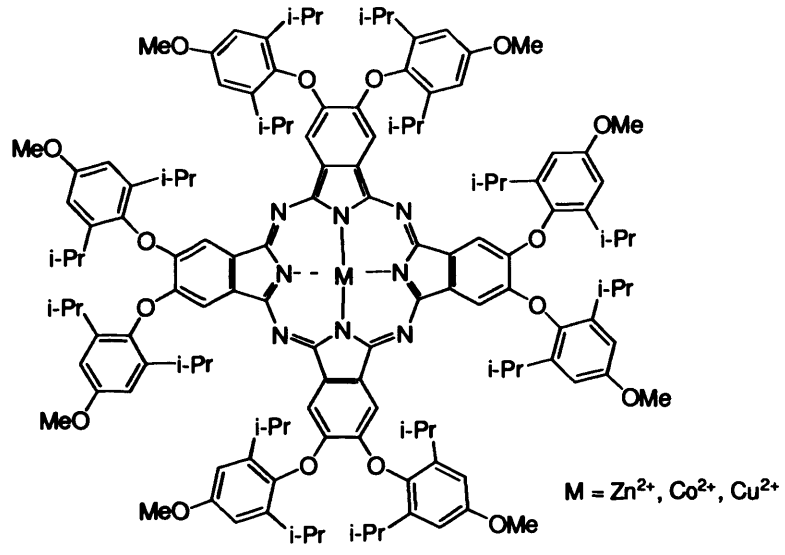
2,3,9,10,16,17,23,24-octa(4'-cyano-2',6'-di-*iso*-propylphenoxy)phthalocyaninato zinc (PcCNZn). 4,5-Bis(4'-cyano-2',6'-di-*iso*-propylphenoxy)phthalonitrile (**Pn4**) (0.50 g, 0.94 mmol) was reacted with zinc acetate according to the general procedure (c). The crude product was purified by column chromatography on SiO_2 eluting with hexane-DCM-ethyl acetate (5.5:4:1) to give a green solid (0.08 g, 15%). M.p. > 300°C; IR (film)/cm^{-1} 2966, 2231, 1448, 1400, 1338, 1282, 1198, 1091, 1026, 890; UV/vis (DCM): λ_{max} 680, 651, 613, 349, 294, 232 nm; ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.07 (s, 8H, Ar*H*), 7.88 (s, 16 H, Ar*H*), 3.43 (br m, 16 H, CH_3CHCH_3), 1.29 (br m, 96 H, CH_3CHCH_3); ^{13}C NMR (125 MHz; $CDCl_3$) δ 152.9, 143.8, 132.7, 129.4, 129.3, 119.1, 110.8, 107.5, 27.7, some Cs are missing; MS (MALDI-TOF): cluster centred at m/z 2188.97 (MH^+); elemental analysis calc (%) for $C_{138}H_{140}Cl_4N_{16}O_8Zn$ (**PcCNZn** + 2 DCM): C 70.29, H 5.98, N 9.50, found C 70.58, H 5.17, N 9.29. Crystal data (DCM/MeOH): crystal size 0.5 x 0.5 x 0.1 mm, triclinic, space group *P-1*, a = 1.1691(5) nm, b = 1.6694(5) nm, c = 2.1039(5) nm, α= 105.880(5), β = 96.314(5), γ= 107.278, V =3.689(2) nm^3, Z = 1, R_1 = 0.0961, the asymmetric unit contains ½ of the molecule together with some disordered solvent DCM, MeOH, and water, some at an occupancy of 0.5. In the axial site there is a methanol molecule.

.2,3,9,10,16,17,23,24-octa(4'-cyano-2',6'-di-*iso*-propylphenoxy)phthalocyaninato cobalt (PcCNCo). 4,5-Bis(4'-cyano-2',6'-di-*iso*-propylphenoxy)phthalonitrile (**PnCN**) (0.40 g, 0.75 mmol) was reacted with cobalt acetate according to the general procedure (c).

The crude product was purified by column chromatography on SiO_2 eluting with DCM/hexane/ethyl acetate (7:2.5:0.5) to give a green-blue solid (0.07g, 16%). M.p. > 300 °C; IR (film)/cm^{-1} 2965, 2225, 1608, 1451, 1414, 1282, 1198, 1097, 1044, 904, 851 UV/vis (DCM): λ_{max} 671, 606, 334, 304, 230nm; MS (MALDI-TOF): cluster centred at m/z 2182.01 (M^+); elemental analysis calc (%) for $C_{137}H_{137}Cl_3CoN_{16}O_8$ (**PcCNCo** + $CHCl_3$): C 71.51, H 6.00, N 9.74 found C 70.89, H 5.48, N 9.33 . Crystal data ($CHCl_3$ + pyridine/acetone): crystal size 0.60 x 0.02 x 0.02 mm, triclinic, space group *P-1*, a = 0.9759(3) nm, b = 1.8102(6) nm, c = 2.2476(8) nm, α= 69.154(4), β = 78.334(4), γ= 76.760(4), V = 3.580(2) nm^3, Z = 1, R_1 = 0.0774, the asymmetric unit contains ½ of the molecule together with an acetone and a $CHCl_3$ molecules each at 0.5 occupancy.

2,3,9,10,16,17,23,24-octa(4'-cyano-2',6'-di-*iso*-propylphenoxy)phthalocyaninato copper (PcCNCu) A solution of **PcCN** (0.10 g, 0.05 mmol) and a big excess of Cu(II)acetate (0.54 g, 3.0 mmol) in anhydrous *n*-pentanol (5 ml) was heated at reflux for four hours. After cooling, the pentanol was evaporated and the reaction mixture was dissolved in DCM and filtered to remove the excess of Cu(II)acetate. The solvent was evaporated under reduced pressure and the crude product was purified by reprecipitation with methanol from its solution in DCM to give a green solid (0.03 g, 32%). M.p. > 300 °C; IR (film)/cm^{-1} 2963, 2223, 1607, 1411, 1283, 1196, 1094, 1042, 899, 856; UV/vis (DCM): λ_{max}682, 614, 340, 246 nm; MS (MALDI-TOF): *m/z* 2186.07 (M^+), elemental analysis calc (%) for $C_{136}H_{136}CuN_{16}O_8$: C 74.72, H 6.27, N 10.25, found C 74.58, H 6.16, N 9.86.

Methoxy substituted Pcs

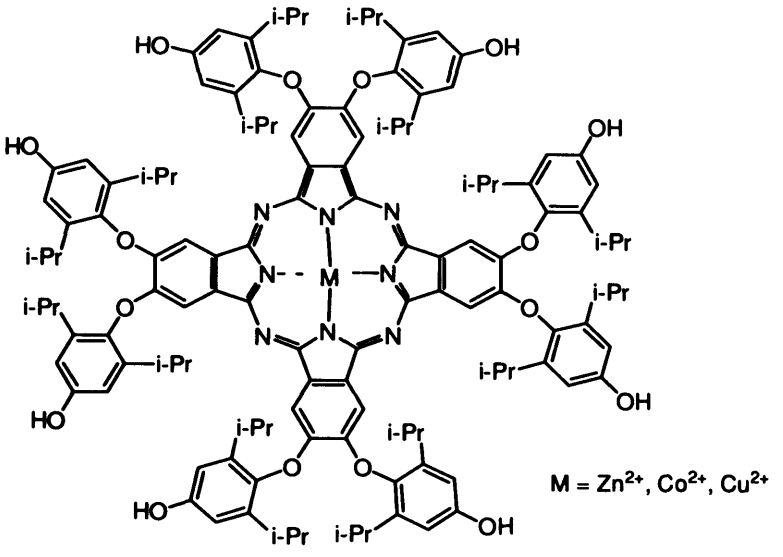


2,3,9,10,16,17,23,24-octa(4'-methoxy-2',6'-di-*iso*-propylphenoxy)phthalocyaninato zinc (PcOMeZn). 4,5-Bis(4'-methoxy-2',6'-di-*iso*-propylphenoxy)phthalonitrile (**PnOMe**) (0.50 g, 0.92 mmol) was reacted with zinc acetate according to the general procedure (c). The crude product was purified by column chromatography on SiO_2 eluting with hexane- DCM- ethyl acetate (7:2:1) to give a green solid (0.36g, 70%). M.p. > 300 °C; IR (film)/cm^{-1} 2963, 1607,1453, 1398, 1335, 1266,1198, 1088, 1040, 889, 846; UV/vis (DCM): λ_{max} 684, 656, 618, 346, 294, 230 nm; ^{1}H NMR (500 MHz; $CDCl_3$) δ8.28 (s, 8 H, Ar*H*), 6.97(s, 16 H, Ar*H*), 4.08 (s, 24 H, OCH_3), 3.45 (sept,16 H, *J* = 6.7 Hz, CH_3CHCH_3), 1.26 (br m, 96 H, CH_3CHCH_3); ^{13}C NMR (125 MHz; $CDCl_3$) δ 157.7, 152.6, 151.1, 143.1, 142.8, 132.1, 109.9, 107.7, 55.5, 27.6, some Cs are missing; MS (MALDI-TOF): cluster centred at m/z 2228.04 (M^+); elemental analysis calc (%) for $C_{136}H_{162}N_8O_{17}Zn$(**PcOMeZn** + H_2O): C 72.72, H 7.27, N 4.99, found C 72.56, H 7.31, N 4.82. Crystal data ($CHCL_3$/MeOH): crystal size 0.42 x 0.05 x 0.05 mm, triclinic, space group *P-1*, *a* = 0.9688(15) nm, *b* = 1.9183(3) nm, *c* = 2.0601(3) nm, α= 65.324(2), β = 79.787(2), γ= 79.107(2), *V* =3.3957(9) nm^3, *Z* = 1, R_1 = 0.0769, the asymmetric unit contains ½ of the molecule together with a disordered chloroform solvent molecule at 0.5 occupancy. In the axial site there is a methanol molecule.

2,3,9,10,16,17,23,24-octa(4'-methoxy-2',6'-di-*iso*-propylphenoxy)phthalocyaninato cobalt (PcOMeCo). 4,5-Bis(4'-methoxy-2',6'-di-*iso*-propylphenoxy)phthalonitrile (**PnOMe**) (0.50 g, 0.92 mmol) was reacted with cobalt acetate according to the general procedure (c). The crude product was purified by column chromatography on SiO_2 eluting with hexane- DCM- ethyl acetate (7.5:2:0.5) to give a green-blue solid (0.30g, 60%). M.p. > 300 °C; IR (film)/cm^{-1} 2962, 1609, 1455, 1412, 1334, 1268, 1197, 1096, 1047, 855; UV/vis (DCM): λ_{max} 676, 610, 302, 230 nm; MS (MALDI-TOF): cluster centred at m/z 2222.07 (M^+); elemental analysis calc (%) for $C_{136}H_{160}CoN_8O_{16}$: C 73.52, H 7.26, N 5.04, found C 73.26, H 7.44, N 5.02. Crystal data ($CHCl_3$/MeOH): crystal size 0.4 x 0.1 x 0.06 mm, triclinic, space group *P-1*, a = 0.96955(13) nm, b = 1.9140(3) nm, c = 2.0491(3) nm, α= 65.492(2), β = 79.794(2), γ= 78.938(2), V =3.3752(8) nm^3, Z = 1, R_1 = 0.0584, the asymmetric unit contains ½ of the molecule together with a disordered chloroform solvent molecule at 0.5 occupancy. In the axial site there is a methanol molecule.

2,3,9,10,16,17,23,24-octa(4'-methoxy-2',6'-di-*iso*-propylphenoxy)phthalocyaninato copper (PcOMeCu). An excess of lithium metal (0.01 g) was added to a solution of **PnOMe** (0.40 g, 0.74mmol) and a big excess of Cu(II)acetate (0.67 g, 3.7 mmol) in dry *n*-pentanol (5ml) at reflux with stirring and under N_2,. After 20 h, the cooled reaction was quenched with water/methanol (50:50) and the resulting precipitate was collected by filtration. Purification was achieved by reprecipitation from DCM solution with methanol to give a green solid (0.14 g, 34%,). M.p. over 300 °C; IR (film)/cm^{-1} 2963, 1608, 1455, 1406, 1334, 1268, 1197, 1095, 1041, 895, 851; UV/vis (DCM): λ_{max} 684,, 616, 395, 340, 286, 235 nm; MS (MALDI-TOF): cluster centred at m/z 2225.88 (MH^+); elemental analysis calc (%) for $C_{136}H_{160}CuN_8O_{16}$ C 73.37, H 7.24, N 5.03, found C 72.98, H 7.38, N 4.87. Crystal data ($CHCl_3$/acetone): crystal size 0.4 x 0.08 x 0.05 mm, triclinic, space group *P-1*, a = 0.97190(4) nm, b = 1.91522(8) nm, c = 2.06589(9) nm, α= 65.2300(10), β = 79.5650(10), γ= 78.9490(10), V =3.4049(2) nm^3, Z = 1, R_1 = 0.0599, the asymmetric unit contains ½ of the molecule together with a disordered chloroform solvent molecule at 0.5 occupancy.

Hydroxy substituted Pcs

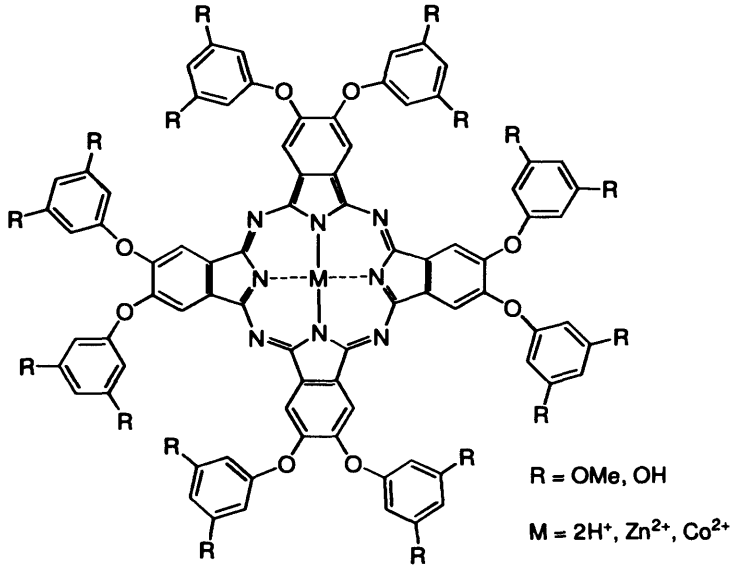


2,3,9,10,16,17,23,24-octa(4'-hydroxy-2',6'-di-*iso*-propylphenoxy)phthalocyaninato zinc (PcOHZn). Boron tribromide (0.1ml, 1 mmol) was added dropwise to a solution of **PcOMeZn** (0.10 g, 0.05mmol) in anhydrous DCM (5 ml), with stirring and under nitrogen, at 0 °C. The reaction was monitored by TLC and after 4 h was finished. The excess of boron tribromide was left to evaporate, then the reaction was quenched with distilled water and the purple precipitate and crushed and collected by filtration. The solid was dissolved in ethyl acetate, then washed with water. The organic layer was dried over magnesium sulphate and evaporated to give a green solid that was purified by recrystallization from ethyl acetate/hexane (0.065 g, 61%). M.p. > 300 °C; IR (nujol)/cm^{-1} 3306, 1604, 1455, 1397, 1339, 1265, 1222, 1183, 1088, 1026, 967, 891, 851, 748; UV/vis (methanol): λ_{max} 676, 646.5, 610, 357 nm; ^{1}H NMR (500 MHz; AcD_6) δ 8.66 (br s, 8 H, OH), 8.27 (s, 8H, Ar*H*), 7.11 (s, 16H, Ar*H*), 3.44 (sept, 16 H, J = 6.8 Hz, CH_3CHCH_3,), 1.27 (br m, 96H, CH_3CHCH_3); ^{13}C NMR (125 MHz; AcD_6) 157.0, 154.6, 152.7, 144.6, 143.9, 134.2, 113.4, 108.8, 25.7, 25.5, 24.1, 24.0; MS (MALDI-TOF): cluster centred at m/z 2115.88 (M^+); elemental analysis calc (%) for $C_{128}H_{146}N_8O_{17}Zn$ (**PcOHZn** + H_2O): C 72.04, H 6.90, N 5.25, found C 71.54, H 7.62, N 5.03 . Crystal data (acetone/hexane): crystal size 0.9 x 0.4 x 0.08 mm, triclinic, space group *P-1*, a = 1.3299(2) nm, b = 1.4527(3) nm, c = 1.9689(4) nm, α= 76.518(2), β = 76.060(2), γ= 86.816(2), V =3.580(2) nm^3, Z = 1, R_1 = 0.1171, the asymmetric unit contains ½ of the molecule together with a number of acetone and water molecules, some at 0.5 or 0.25 occupancies.

2,3,9,10,16,17,23,24-octa(4'-hydroxy-2',6'-di-*iso*-propylphenoxy)phthalocyaninato cobalt (PcOHCo). The title compound was obtained by the same procedure as above. (0.08 g, 55%) M.p. over 300 °C; IR (nujol)/cm^{-1} 3297, 1599, 1525, 1455, 1413, 1363, 1339, 1270, 1221, 1186, 1096, 1047, 861; UV/vis (methanol): λ_{max} 673, 607, 364 nm; MS (MALDI-TOF): cluster centred at m/z 2110.00 (M^+).

2,3,9,10,16,17,23,24-octa(4'-hydroxy-2',6'-di-*iso*-propylphenoxy)phthalocyaninato Copper (PcOHCu) The title compound was obtained by the same procedure as above. (0.045 g, 70%) M.p. over 300 °C; IR (nujol)/cm^{-1} 3373, 1607, 1407, 1340, 1268, 1186, 1096, 1037, 897, 856; UV/vis (methanol): λ_{max} 677, 611, 409, 342 nm; MS (MALDI-TOF): cluster centred at m/z 2114.08 (M^+); elemental analysis calc (%) for $C_{128}H_{148}CuN_8O_{18}$ C 72.72, H 6.87, N 5.30, found C 72.34, H 6.69, N 4.87. Crystal data (acetone/hexane) crystal size not measured, monoclinic, space group *I2/a*, a = 1.8757(10) nm, b = 1.6486(7)nm, c = 4.459(2) nm, β = 90.563(17), V =13.786(11)nm^3, Z = 4, R_1 = 0.1231, the asymmetric unit contains ½ of the molecule together with a acetone and a water molecules.

3,5 methoxy substituted Pcs



2,3,9,10,16,17,23,24-octa(3',5'-dimethoxyphenoxy)phthalocyanine (PcOMe$_{3,5}$). 4,5-bis(3',5'-dimethoxyphenoxy)-phthalonitrile (0.5 g, 1.1 mmol) was reacted according to the general procedure (b). The crude product was thoroughly washed with methanol and further purified by reprecipitation with methanol from DCM solution to afford a green

solid (0.32 g, 67%). M.p. > 300 °C; IR (film)/cm^{-1} 3292, 2997, 2939, 2837, 1608, 1472, 1439, 1320, 1267, 1205, 1176, 1153, 1130, 1063, 1016, 820, 751; UV/vis (DCM): λ_{max} 700, 667, 608, 345, 290, 230 nm; MS (MALDI-TOF): cluster centred at m/z 1733.32 (MH^+); elemental analysis calc (%) for $C_{96}H_{82}N_8O_{24}$: C 66.58, H 4.77, N 6.47, found C 66.23, H 4.84, N 6.13

2,3,9,10,16,17,23,24-octa(3',5'-dimethoxyphenoxy)phthalocyaninato zinc ($PcOMe_{3,5}$ Zn). 4,5-Bis(3',5'-dimethoxyphenoxy)-phthalonitrile **$PnOMe_{3,5}$** (0.3 g, 0.7mmol) and zinc(II)acetate (0.13 g, 0.7 mmol) were reacted according to the procedure (c). The crude product was washed with methanol and reprecipitated with methanol from its solution in DCM to give the title compound as a green solid (0.11 g, 35%). M.p. over 300 °C; IR (film)/cm^{-1} 2939, 2837, 1606, 1471, 1400, 1266, 1205, 1176, 1152, 1130, 1086, 1053, 985, 822; UV/vis (DCM): λ_{max} 686, 621, 349, 285, 230 nm;MS (MALDI-TOF): cluster centred at m/z 1796.30 (MH^+).

2,3,9,10,16,17,23,24-octa(3',5'-dimethoxyphenoxy)phthalocyaninato cobalt ($PcOMe_{3,5}$ Co). 4,5-Bis(3',5'-dimethoxyphenoxy)-phthalonitrile **$PnOMe_{3,5}$** (0.5 g, 1.1 mmol) and cobalt(II)acetate (0.20 g, 1.1 mmol) were reacted according to the procedure (c). The crude product was washed with methanol and then reprecipitated with methanol from DCM solution to give the title compound as a green-blue solid (0.15 g, 30%). M.p. > 300 °C; IR (film)/cm^{-1} 3004, 2938, 2840, 1598, 1455, 1415, 1269, 1205, 1153, 1131, 1097, 1054, 823; UV/vis (DCM): λ_{max} 681, 612, 292, 241 nm; MS (MALDI-TOF): cluster centred at m/z 1790.22 (MH^+); elemental analysis calc (%) for $C_{96}H_{80}N_8O_{24}$: C 64.46, H 4.51, N 6.26, found C 64.18, H 4.62, N 6.16.

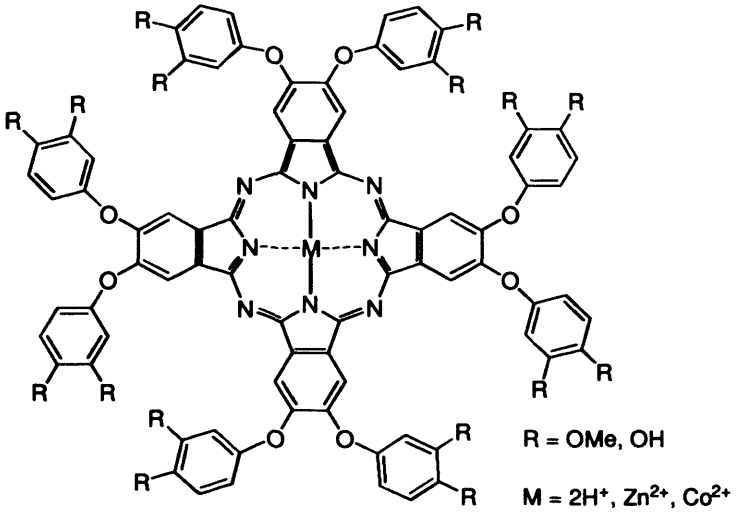
2,3,9,10,16,17,23,24-octa(3',5'-dihydroxyphenoxy)phthalocyanine ($PcOH_{3,5}$). Boron tribromide (0.17 ml, 1.8 mmol) was added dropwise to a stirred solution of **$PcOMe_{3,5}$** (0.15 g, 0.09mmol) in dry DCM (10 ml), under nitrogen, at 0 °C. The reaction was monitored by TLC and after 20 h the starting material had been consumed. The excess of boron tribromide was left to evaporate, then the reaction was quenched with distilled water. The resulting solid was crushed and thoroughly washed with water and with DCM, then purified by reprecipitation with DCM from methanol solution to give a green solid (0.08 g, 58%). M.p. over 300 °C; IR (nujol)/cm^{-1} 3372, 1609, 1267,1155, 1126, 1035, 1001;

UV/vis (MeOH): λ_{max} 698, 665, 340, 292, 229 nm; MS (MALDI-TOF): cluster centred at m/z 1508.00 (MH^+).

2,3,9,10,16,17,23,24-octa(3',5'-dihydroxyphenoxy)phthalocyaninato zinc ($PcOH_{3,5}Zn$). Boron tribromide (0.16 ml, 1.7 mmol) was added dropwise to a stirred solution of **$PcOMe_{3,5}Zn$** (0.15 g, 0.08mmol) in dry DCM (10 ml), under nitrogen, at 0 °C. The reaction was monitored by TLC and after 20 h the starting material was fully consumed. The excess of boron tribromide was left to evaporate, then the reaction was quenched with distilled water. The resulting purple solid was crushed and thoroughly washed with water and with DCM, then purified by reprecipitation with DCM from its solution in methanol to give a green solid (0.09 g, 72%). M.p. > 300 °C; IR (nujol)/cm^{-1} 3373, 1609, 1268, 1155, 1126, 1036, 1002; UV/vis (methanol): λ_{max} 677, 612, 354, 286, 211 nm; MS (MALDI-TOF): cluster centred at m/z 1571.86 (MH^+).

2,3,9,10,16,17,23,24-octa(3',5'-dihydroxyphenoxy)phthalocyaninato cobalt ($PcOH_{3,5}Co$). Boron tribromide (0.11 ml, 1.1 mmol) was added dropwise to a stirred solution of **$PcOMe_{3,5}Co$** (0.10 g, 0.06mmol) in dry DCM (8 ml), under nitrogen, at 0 °C. The reaction was monitored by TLC and after 20 h the starting material was fully consumed. The excess of boron tribromide was left to evaporate, then the reaction was quenched with distilled water and a purple precipitate collected by filration. The solid was thoroughly washed with water and with DCM, then purified by reprecipitation with DCM from a methanol solution to give a green solid (0.07 g, 75%). M.p.> 300 °C; IR (nujol)/cm^{-1} 3365, 1610, 1520, 1268, 1175, 1125, 1034, 1001; UV/vis (methanol): λ_{max} 665, 313, 223 nm; MS (MALDI-TOF): cluster centred at m/z 1564.40 (MH^+).

3,4 methoxy substituted Pcs



2,3,9,10,16,17,23,24-octa(3',4'-dimethoxyphenoxy)phthalocyanine (PcOMe$_{3,4}$). 4,5-Bis(3',4'-dimethoxyphenoxy)-phthalonitrile (0.5 g, 1.1 mmol) was reacted according to the general procedure (b). The crude product was thoroughly washed with methanol and further purified by reprecipitation with methanol from DCM solution to afford a green solid (0.33g, 69%). M.p. over 300 °C; IR (film)/cm^{-1} 2937, 2830, 1602, 1509, 1439, 1260, 1229, 1192, 1085, 1025, 956, 862, 749; UV/vis (DCM): λ_{max} 702, 669, 608, 343, 289, 238 nm; MS (MALDI-TOF): cluster centred at m/z 1732.74 (M^+); elemental analysis calc (%) for $C_{96}H_{82}N_8O_{24}$: C 66.58, H 4.77, N 6.47, found C 65.91, H 4.59, N 6.21.

2,3,9,10,16,17,23,24-octa(3',4'-dimethoxyphenoxy)phthalocyaninato zinc (PcOMe$_{3,4}$Zn). 4,5-Bis(3',4'-dimethoxyphenoxy)-phthalonitrile **PnOMe$_{3,4}$** (0.5 g, 1.1mmol) and zinc(II)acetate (0.20 g, 1.1 mmol) were reacted according to the procedure (c). The crude product was washed with methanol and reprecipitated with methanol from DCM solution and further purified by column chromatography on SiO_2 eluting with DCM-methanol (9:1) to give the title compound as a green solid (0.31 g, 65%). M.p. > 300 °C; IR (film)/cm^{-1} 2998, 2937, 2834, 1604, 1509, 1447, 1401, 1260, 1229, 1193, 1128, 1091, 1028, 957, 879, 731; UV/vis (DCM): λ_{max} 690, 618, 354, 288, 231 nm; MS (MALDI-TOF): cluster centred at m/z 1796.12 (MH^+); elemental analysis calc (%) for $C_{96}H_{80}N_8O_{24}$: C 64.23, H 4.49, N 6.24, found C 63.84, H 4.32, N 6,54.

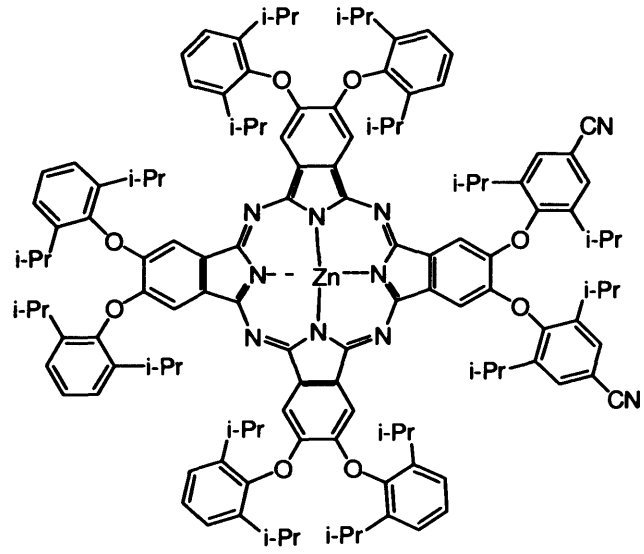
2,3,9,10,16,17,23,24-octa(3',4'-dimethoxyphenoxy)phthalocyaninato cobalt ($PcOMe_{3,4}Co$). 4,5-Bis(3',4'-dimethoxyphenoxy)-phthalonitrile **$PnOMe_{3,4}$** (0.5 g, 1.1 mmol) and cobalt(II)acetate (0.20 g, 1.1 mmol) were reacted according to the procedure (c). The crude product was washed with methanol and reprecipitated with methanol from its solution in DCM and further purified by column chromatography on SiO_2 eluting with DCM- methanol (98:2) to give the title compound as a green-blue solid (0.12 g, 25%). M.p. > 300 °C; IR (film)/cm^{-1} 3003, 2937, 2834, 1603, 1509, 1455, 1415, 1261, 1229, 1193, 1095, 1027, 957, 889, 753; UV/vis (DCM): λ_{max} 688, 610, 349, 313, 236 nm; MS (MALDI-TOF): cluster centred at m/z 1790.17 (MH^+); elemental analysis calc (%) for $C_{96}H_{80}N_8O_{24}$: C 64.46, H 4.51, N 6.26, found C 64.09, H 4.48, N 6.26.

2,3,9,10,16,17,23,24-octa(3',4'-dihydroxyphenoxy)phthalocyanine ($PcOH_{3,4}$). Boron tribromide (0.17 ml, 1.8 mmol) was added dropwise to a stirred solution of **$PcOMe_{3,4}$** (0.15 g, 0.09mmol) in dry DCM (10 ml), and under nitrogen, at 0 °C. The reaction was monitored by TLC and after 20 h the starting Pc was fully consumed. The excess of boron tribromide was left to evaporate, then the reaction was quenched with distilled water and a purple precipitate collected by filtration. The crushed solid was thoroughly washed with water and with DCM, then purified by reprecipitation with DCM from methanol solution to give a green solid (0.11 g, 81%). M.p. > 300 °C; IR (nujol)/cm^{-1} 3358, 1612, 1515, 1267, 1176, 1089, 1018, 967, 873, 746; UV/vis (MeOH): λ_{max} 700, 665, 607, 338, 290, 206 nm; ^1H NMR (500MHz; MeOD) δ 8.34 (br s, 8H, Ar*H*), 7.02 (br s, 8H Ar*H*), 6.90 (br,16 H, Ar*H*); MS (MALDI-TOF): cluster centred at m/z 1508.92 (MH^+).

2,3,9,10,16,17,23,24-octa(3',4'-dihydroxyphenoxy)phthalocyaninato zinc ($PcOH_{3,4}Zn$). Boron tribromide (0.16 ml, 1.7 mmol) was added dropwise to a stirred solution of **$PcOMe_{3,4}Zn$** (0.15 g, 0.08mmol) in dry DCM (10 ml), under nitrogen, at 0 °C. The reaction was monitored by TLC and after 20 h the starting Pc was fully consumed. The excess of boron tribromide was left to evaporate, then the reaction was quenched with distilled water and a purple precipitate collected by filtration. The crushed solid was thoroughly washed with water and with DCM, then purified by reprecipitation with DCM from a methanol solution to give a green solid (0.09 g, 72%). M.p. > 300 °C; IR (nujol)/cm^{-1} 3360, 1607, 1512, 1264, 1174, 1137, 1095, 1025, 965, 880, 788; UV/vis (MeOH): λ_{max} 679, 616, 347, 289, 209 nm; MS (MALDI-TOF): cluster centred at m/z 1571.75 (MH^+).

2,3,9,10,16,17,23,24-octa(3',4'-dihydroxyphenoxy)phthalocyaninato cobalt ($PcOH_{3,4}Co$). Boron tribromide (0.21 ml, 2.2 mmol) was added dropwise to a stirred solution of **$PcOMe_{3,4}Co$** (0.20 g, 0.11 mmol) in dry DCM (10 ml), under nitrogen, at 0 °C. The reaction was monitored by TLC and after 20 h the starting Pc was fully consumed. The excess of boron tribromide was left to evaporate, then the reaction was quenched with distilled water and a purple precipitate collected by filtration. The crushed solid was thoroughly washed with water and with DCM, then purified by reprecipitation with DCM from its solution in methanol to give a green solid (0.15 g, 87%). M.p. > 300 °C; IR (nujol)/cm^{-1} 3368, 1610, 1518, 1266, 1175, 1127, 1035, 1003; UV/vis (MeOH): λ_{max} 664, 309, 222 nm; MS (MALDI-TOF): cluster centred at m/z 1565.90 (MH^+); elemental analysis calc (%) for $C_{80}H_{48}CoN_8O_{24}$: C 61.43, H 3.09, N 7.16, foundC 59.26, H 2.44, N 7.01.

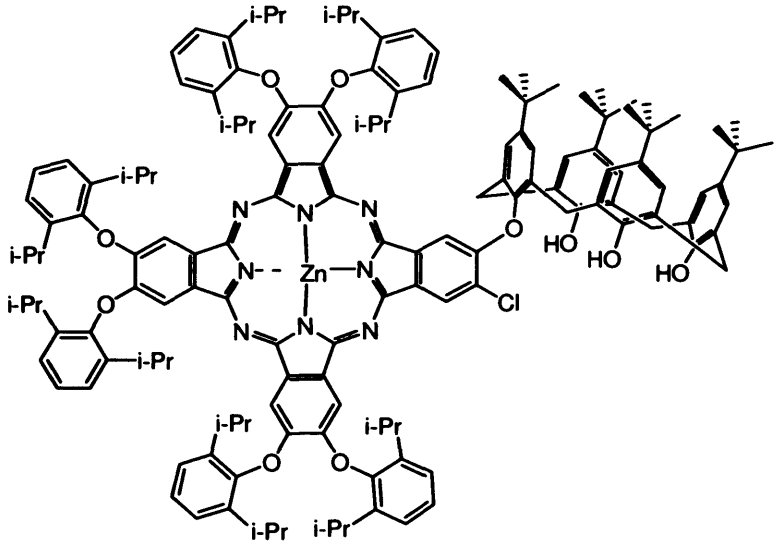
2,3,9,10,16,17-hexakis(2',6'-di-*iso*-propylphenoxy)-23,24-bis(4'-cyano-2',6'-di-*iso*-propylphenoxy) phthalocyaninato zinc ($Pcl_3PcCNZn$).



A mixture of **Pn1** (2.04 g, 4.23 mmol) and **PnCN**(0.25 g, 0.47 mmol) and zinc(II) acetate (0.86 g, 4.7 mmol) in dry N-methylpyrrolidone (3ml) was heated at 150 °C for twenty hours. The reaction mixture was cooled to room temperature, poured in 20 ml of distilled water and the precipitate collected by filtration. Purification by column chromatography on SiO_2 eluting with dichloromethane-hexane (7:3), led to 0.7g of **Pc1Zn** (yield 48%) and

0.3g of **Pcl$_3$PcCNZn** (yield 31 %). M.p. > 300 °C; UV/vis (DCM): λ_{max} 682, 615, 370, 351, 340, 292, 235 nm; IR (film)/cm^{-1} 2964, 2869, 2233,1610, 1452, 1400, 1364, 1330, 1269, 1183, 1094, 1025, 893, 748, 725; ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.13(s, 4H, Ar*H*), 8.11 (s, 2H, Ar*H*), 8.07 (s, 2H, Ar*H*), 7.75 (s, 4H, Ar*H*), 7.67 (t, 2H, J = 7.8 Hz, Ar*H*), 7.54 (m, 8H, Ar*H*), 7.45 (d, 8H, J = 7.8 Hz, Ar*H*), 3.43 (br m, 16H, Ar*H*), 1.26 (br m, 96H, Ar*H*); ^{13}C NMR (500Mhz; $CDCl_3$) δ 154.0, 153.7, 153.0, 152.9, 151.6, 150.6, 150.5, 149.3, 148.7, 143.9, 141.7, 136.8, 132.7, 132.5, 132.4, 132.3, 129.2, 126.5, 126.3, 124.8, 124.6, 123.2, 119.4, 110.4, 107.3, 107.0, 106.9, 29.7, 27.8, 27.5, 24.2 ; MS (MALDI-TOF): cluster centred at m/z 2038,51 (M^+); elemental analysis calc (%) for $C_{130}H_{142}N_{10}O_8Zn$: C 76.61, H 7.02, N 6.87, found C 75.65, H 6.89, N 6.73.

2,3,9,10,16,17-Hexakis(2',6'-di-*iso*-propylphenoxy)-23-(4-*tert*-butylcalix(4)arene)-24-chloro phthalocyaninato zinc (Pcl$_3$Pccalix Zn).

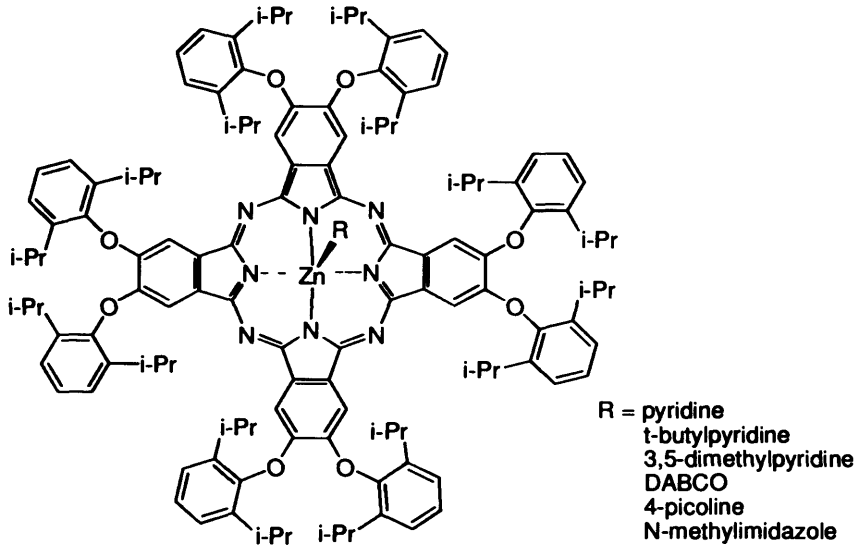


A mixture of **Pn1** (1.60 g, 3.35 mmol) and **Pncalix** (0.30 g, 0.37 mmol) and zinc(II) acetate (0.55 g, 2.96 mmol) in dry N-methylpyrrolidone (5ml) was heated at 150 °C for twenty hours. The reaction mixture was cooled to room temperature, poured in 20 ml of distilled water and then filtered off. Purification by column chromatography on SiO_2, eluting with toluene, gave the title compound as a green solid (0.10 g, 12 %) and 0.68 g of **Pc1Zn** (62%). M.p. > 300 °C; UV/vis (DCM): λ_{max} 684, 615, 348, 292, 230 nm; IR (film)/cm^{-1}3387, 2963, 2869, 1609, 1440, 1397, 1269, 1183, 1095, 1025, 893, 794, 724; MS (MALDI-TOF): cluster centred at m/z 2038,51 (M^+); elemental analysis calc (%) for

$C_{148}H_{165}ClN_8O_{10}Zn$: C 76.73, H 7.18, Cl 1.53, N 4.84, found C 76.20, H 7.38, N 4.71, not enough sample for Cl analysis. Crystal data ($CHCl_3$/acetone): crystal size 0.8 x 0.5 x 0.4 mm, monoclinic, space group $P2_1/n$, a = 2.60440(3) nm, b = 1.98390(2)nm, c = 3.08170(4) nm, β= 101.8030(10), V =15.5861(3)nm^3, Z = 3, R_1 = 0.1378.

Insertion of different axial ligands

Axial substituted Pc1Zn derivatives



An excess of the appropriate ligand was added to some **Pc1Zn** crystals in contact with acetone. XRD analysis of the crystals showed that the axial water molecule had been exchanged to at least some extent by the different ligands.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato pyridyl zinc (Pc1Zn(py)). 50% exchange of water by pyridine. Crystal data: crystal size 0.35 x 0.35 x 0.25 mm, cubic, *Pn-3n* , a = 3.73006(3) nm, V = 51.8976(7) nm^3, Z = 12, R_1 = 0.1203. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. Py and water at 50:50 ratio, are axially bonded to Zn.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato *t*-butylpyridyl zinc (Pc1Zn(*t*-bupy)). 48% exchange of water by t-butylpyridine. Crystal data: crystal size 0.50 x 0.40 x 0.25 mm, cubic, *Pn-3n* , a = 3.72390(8) nm, V = 51.6409(19) nm^3, Z = 12,

R_1 = 0.134. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. t-butylpyridine and water at 48:52 ratio, are axially bonded to Zn.

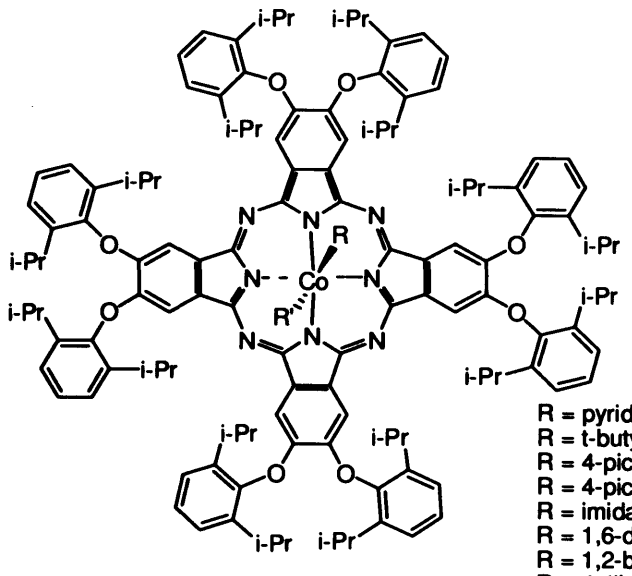
2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato 3,5-dimethyl pyridyl zinc (PcIZn(dimepy)). 72% exchange of water by 3,5-dimethylpyridine. Crystal data: crystal size 0.40 x 0.40 x 0.30 mm, cubic, *Pn-3n* , *a* = 3.71952(3) nm, *V* = 51.4589(7) nm^3, *Z* = 12, R_1 = 0.1019. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. 3,5-dimethylpyridine and water at 72:28 ratio, are axially bonded to Zn.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato dabco zinc (PcIZn(dabco)). 68% exchange of water by DABCO. Crystal data: crystal size 1.00 x 1.00 x 1.00 mm, cubic, *Pn-3n* , *a* = 3.72379(9) nm, *V* = 51.636(2) nm^3, *Z* = 12, R_1 = 0.1673. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. DABCO and water at 68:32 ratio, are axially bonded to Zn.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato 4-picolyl zinc (PcIZn(pic)). 100% exchange of water by 4-picoline. Crystal data: crystal size 0.70 x 0.70 x 0.50 mm, cubic, *Pn-3n* , *a* = 3.75099(9) nm, *V* = 52.776(2) nm^3, *Z* = 12, R_1 = 0.0777. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. 4-picoline was axially bonded to Zn.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato N-methylimidazolyl zinc (PcIZn(NMIm)). 100% exchange of water by N-methylimidazole. Crystal data: crystal size 0.60 x 0.60 x 0.60 mm, cubic, *Pn-3n* , *a* = 3.74277(6) nm, *V* = 52.4300(15) nm^3, *Z* = 12, R_1 = 0.0899. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. N-methylimidazole was axially bonded to Zn.

Axial substituted Pc1Co derivatives



R = pyridine
R = t-butylpyridine/pyridine (18/82)
R = 4-picoline/pyridine (60/40)
R = 4-picoline, R' H_2O
R = imidazole, R' = imidazole
R = 1,6-diaminohexane, R' = H_2O
R = 1,2-bisimidazolyl-ethane, R' = MeOH
R = 4,4'bipyridyl
R = 4,4'bipyridyl, R' = pyridine/H_2O (60/40)

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato pyridyl cobalt (Pc1Co(py)). A solution of **Pc1Co** (0.02 g, 0.01 mmol) in pyridine (1 ml) was stirred at 90 °C for 3 h in an inert atmosphere, then most of the pyridine was evaporated under N_2. The pyridine-soaked product was dissolved in chloroform (1 ml) and methanol (3 ml) was layered above this solution. After 2 days at 4°C, cubic crystals of **Pc1Co(Py)** formed.

The same result was obtained for slow diffusion of methanol into a solution **Pc1Co** (0.01 g, 0.005 mmol), to which was previously added 2 drops of pyridine to the compound. Crystal data: crystal size 0.80 x 0.60 x 0.60 mm, cubic, *Pn-3n* , a = 3.75596(4) nm, V = 52.9862(10) nm^3, Z = 12, R_1 = 0.0625. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. In the axial site there is a pyridine molecule.

An excess of the appropriate ligand was added to some **Pc1Co(Py)** crystals in contact with acetone. XRD analysis of the crystals showed that the axial pyridine molecule had been exchanged at least to some extent by 4-picoline and t-butylpyridine.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato t-butylpyridyl cobalt (Pc1Co(*t*-Bupy)). 18% exchange of pyridine by *t*-butylpyridine. Crystal data: crystal size 0.60 x 0.60 x 0.50 mm, cubic, *Pn-3n*, a = 3.75512(3) nm, V = 52.9507(7) nm^3,

Z = 12, R_1 = 0.0876. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. t-butylpyridine and pyridine in 18:82 ratio, are axially bonded to Zn in the apical position.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato picolyl cobalt (PcICo(pic)). 60% exchange of pyridine by 4-picoline. Crystal data: crystal size 0.25 x 0.25 x 0.20 mm, cubic, *Pn-3n*, a = 3.71172(4) nm, V = 51.1358(10) nm^3, Z = 12, R_1 = 0.1432. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. 4-Picoline and pyridine 60:40 ratio, are axially bonded to Zn in the apical position and a water molecule is axially bonded in the other side of the metal at 0.5 occupancy.

The following cubic **PcICo** crystals with different axial ligands were obtained for slow diffusion of methanol in a solution of **PcICo** (about 0.01 g, 0.005 mmol) in chloroform (0.5 ml), to which an excess of the desired ligand had been added.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato picolyl cobalt (PcICo(pic)). Crystal data: crystal size 0.90 x 0.60 x 0.60 mm, cubic, *Pn-3n*, a = 3.75208 nm, V = 52.8222(5) nm^3, Z = 12, R_1 = 0.0611. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. In the axial site there is a picoline molecule.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(1,6-diamino-hexane) cobalt (PcICo(1,6-diahex)). Crystal data: crystal size 0.35 x 0.28 x 0.1 mm, cubic, *Pn-3n* , a = 3.74908 nm, V = 52.6956(5) nm^3, Z = 12, R_1 = 0.1458. The asymmetric unit contains ¼ of the molecule together with a $CHCl_3$ solvent molecule. A 1,6-diaminohexane molecule which links together two **PcICo** is in the non-apical axial site of the metal and a water molecule is in the apical axial site.

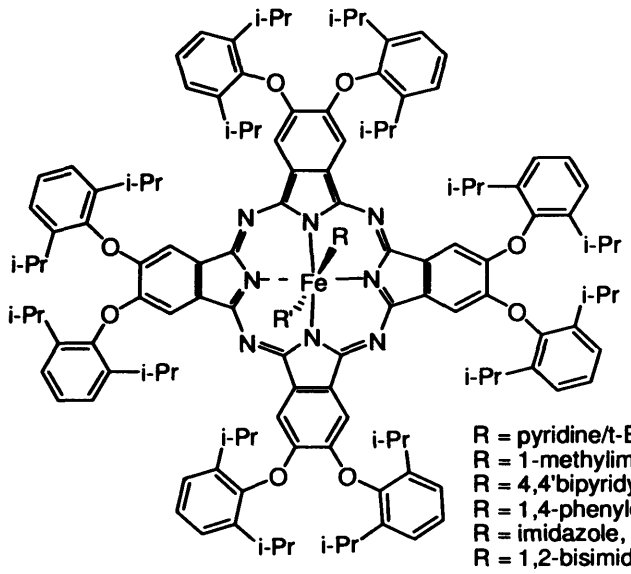
2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(1,2-bisimida-zol-1-ylethane) cobalt (PcICo(BisIm)). Crystal data: crystal size 0.20 x 0.16 x 0.16 mm, cubic, *Pn-3n* , a = 3.75504(3) nm, V = 52.9473(7) nm^3, Z = 12, R_1 = 0.2880. The asymmetric unit contains ¼ of the molecule. In the apical axial site there is a bisimidazole ligand and in the other axial site a methanol molecule.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(4,4'-bipyridyl) cobalt (PcICo(bipy)). Crystal data: crystal size 0.80 x 0.60 x 0.60 mm, cubic, *Pn-3n* , a = 3.74921 nm, V = 52.701(2) nm^3, Z = 12, R_1 = 0.1792. The asymmetric unit contains ¼ of the molecule. In the axial site there is a 4,4-bipyridyl molecule.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(imidazole)$_2$ cobalt (PcICo(Im)$_2$). Crystal data (*coimlsqa*): crystal size 0.25 x 0.20 x 0.15 mm, cubic, *Pn-3n* , a = 3.75719(16) nm, V = 53.038(4) nm^3, Z = 12, R_1 = 0.0835. The asymmetric unit contains ¼ of the molecule. Imidazole is axially bonded in both sides of the metal.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(pyridine)(4,4'-bipyridyl)cobalt (PcICo(py)(bipy). Crystal data: crystal size 0.22 x 0.22 x 0.22 mm, cubic, *Pn-3n* , a = 3.7647(3) nm, V = 53.359(7) nm^3, Z = 12, R_1 = 0.1051. A 4,4-bipyridyl molecule which links together two **PcICo** is in the non-apical axial site of the metal and pyridine/water in 60/40 ratio are is in the apical axial site.

Axial substituted PcIFe derivatives



R = pyridine/t-BuNC(70/30), R' = t-BuNC
R = 1-methylimidazol, R' = MeOH
R = 4,4'bipyridyl, R' = t-BuNC
R = 1,4-phenylenediisocyanide, R' = O_2
R = imidazole, R' = H_2O
R = 1,2-bisimidazolyl-ethane/t-BuNC, R' = t-BuNC

The exchange of axial ligands in the following crystals was performed adding an excess of the appropriate ligand to some **PcIFe(*t*-BuNC)$_2$** crystals in contact with methanol and was evaluated by mean of XRD analysis of the crystals .

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(pyridyl)(t-butylisocyanide) iron (PcIFe(py)(*t*-BuNC)). This experiment was performed as above, but in presence of molecular sieves. 70% one side exchange of *t*-BuNC by pyridine. Crystal data: crystal size 0.55 x 0.50 x 0.50 mm, cubic, *Pn-3n*, a = 3.75004(9) nm, V = 52.736(2) nm^3, Z = 12, R_1 = 0.1015. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. Pyridine and t-BuNC 60:40 ratio, are axially bonded to Fe in the apical position and a *t*-BuNC is axially bonded in the other side of the metal.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(1-methyl imidazolyl) iron (PcIFe(MeIm)) 100% both sides exchange of t-BuNC by 1-methylimidazole and MeOH respectively. Crystal data: crystal size 0.30 x 0.25 x 0.25 mm, cubic, *Pn-3n*, a = 3.75202(5) nm, V = 52.8196(12) nm^3, Z = 12, R_1 = 0.1091. The asymmetric unit contains ¼ of the molecule together with some solvent molecules. In the axial sites there is a 1-methylimidazole in the apical site and a methanol molecule in the other side.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(1,4-phenylene-isocyanide) iron (PcIFe(Phic)). This experiment was performed as above but in presence of molecular sieves. 83% exchange of t-BuNC by 1,4-phenyleneisocyanide in one side and 100% by O_2 in the other. Crystal data: crystal size 0.30 x 0.20 x 0.15 mm, cubic, *Pn-3n*, a = 3.76840(14) nm, V = 53.514(3) nm^3, Z = 12, R_1 = 0.1233. The asymmetric unit contains ¼ of the molecule together with some solvent molecules. In the non apical site there is 1,4-phenileneisocyanide acting as bridge between two molecules and in the apical site there appears to be a oxygen molecule.

The following cubic **PcIFe** crystals with different axial ligands were obtained for slow diffusion of methanol in a solution of **PcIFe(*t*-BuNC)$_2$** (about 0.01 g, 0.005 mmol) in chloroform (0.5 ml), to which an excess of the desired ligand had been added.

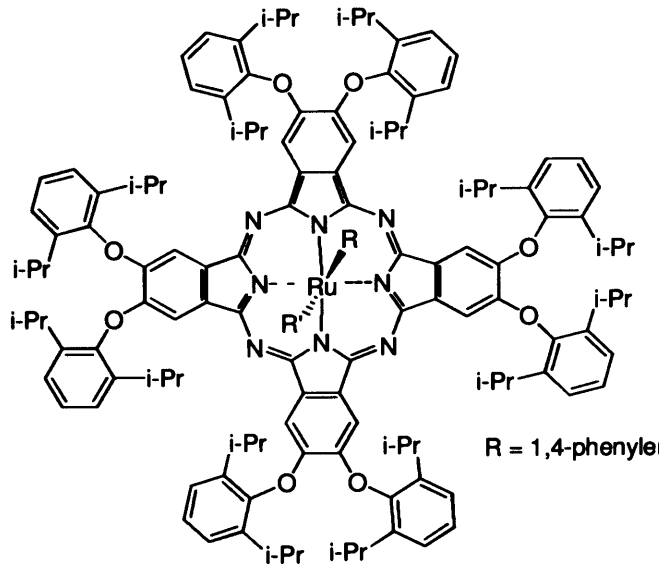
2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(*t*-BuNC)(4,4'-bipyridyl) iron (PcIFe(*t*-BuNC)(bipy)). This experiment was carried out as above with addition of molecular sieves. 80% one side exchange of t-BuNC by 4-4'-bipyridyl. Crystal data: crystal size 0.468 x 0.35 x 0.239 mm, cubic, *Pn-3n*, a = 3.76091(3)nm, V =

53.196.0(7) nm^3, Z = 12, R_1 =0.1212. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. In the non apical site there is a 4,4'-bipyridyl ligand acting as bridge between two molecules and in the apical site there is t-BuNC.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(imidazolyl) (H_2O) iron (PcIFe(Im)(H_2O)). 100% one side exchange of *t*-BuNC by imidazole and H_2O in the other. Crystal data: crystal size 0.30 x 0.25 x 0.25 mm cubic, *Pn-3n*, a = 3.75202(5)nm, V = 52.8196(12) nm^3, Z = 12, R_1 =0.1091. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. In the axial sites there is a imidazole molecule in the apical site and a H_2O molecule in the other side.

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(1,2-bisimidazol-1-ylethane)(*t*-BuNC) iron (PcIFe(BisIm)(*t*-BuNC)). Crystal data: crystal size 0.36 x 0.30 x 0.30 mm, cubic, *Pn-3n*, a = 3.74367(4) nm, V = 52.4678(10) nm^3, Z = 12, R_1 =0.1359. The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. One of the axial sites seems to be occupied by bisimidazole and t-BuNC but neither ligand can be fully developed and t-BuNC is axially bonded in the other side.

Axial substituted PcIRu derivatives



2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(1,4-phenylene-isocyanide) iron (PcIRu(Phic)). The crystals of this derivative were obtained for slow

diffusion of methanol in a solution of **PclRu(*t*-BuNC)$_2$** (about 0.01 g, 0.005 mmol) in chloroform (0.5 ml), to which an excess of the 1,4-phenileneisocyanide had been added. 100 % exchange of t-BuNC by 1,4-phenyleneisocyanide in one side and by O_2 in the other. Crystal data: crystal size 0.40 x 0.40 x 0.40 mm, cubic, *Pn-3n* , a = 3.77453(4) nm, V = 53.770(10) nm^3, Z = 12, R_1 = 0.0894. The asymmetric unit contains ¼ of the molecule together with some solvent molecules. In the non apical site there is 1,4-phenileneisocyanide acting as bridge between two molecules and in the apical site there seems to be a oxygen molecule.

Bibliography

(1) McKeown, N. B. *Phthalocyanine Materials: Structure, Synthesis and Function*, 1998.
(2) Gregory, P. *J. Porphyrins Phthalocyanines* **2000**, *4*, 432-437.
(3) Cronshaw, C. T. J. *Endeavour* **1942**, *1*, 79-83.
(4) Dandridge, A. G.; Drescher, H. A. E.; Thomas, J.; (Scottish Dyes, Ltd.). GB, 1928.
(5) Braun, A.; Tscherniac, J. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 2709-14.
(6) de Diesbach, H.; von der Weid, E. *Helv. Chim. Acta* **1927**, *10*, 886-8.
(7) Linstead, R. P. *J. Chem. Soc.* **1934**, 1016-17.
(8) Byrne, G. T.; Linstead, R. P.; Lowe, A. R. *J. Chem. Soc.* **1934**, 1017-22.
(9) Linstead, R. P.; Lowe, A. R. *J. Chem. Soc.* **1934**, 1022-7.
(10) Dent, C. E.; Linstead, R. P. *J. Chem. Soc.* **1934**, 1027-31.
(11) Linstead, R. P.; Lowe, A. R. *J. Chem. Soc.* **1934**, 1031-3.
(12) Dent, C. E.; Linstead, R. P.; Lowe, A. R. *J. Chem. Soc.* **1934**, 1033-9.
(13) Robertson, J. M. *J. Chem. Soc.* **1936**, 1195-1209.
(14) McKeown, N. B. *Porphyrin Handb.* **2003**, *15*, 61-124.
(15) Hanack, M.; Heckmann, H.; Polley, R. *Methods of Organic Chemistry* fourth ed.; Georg Thieme Verlag: Stuttgart, 1998; Vol. E-9.
(16) Tomoda, H.; Saito, S.; Shiraishi, S. *Chem. Lett.* **1983**, 313-16.
(17) Guerek, A. G.; Bekaroglu, O. *J. Chem. Soc., Dalton Trans.* **1994**, 1419-23.
(18) Cuellar, E. A.; Marks, T. J. *Inorg. Chem.* **1981**, *20*, 3766-70.
(19) Kobayashi, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1987**, *109*, 7433-41.
(20) Woehrle, D.; Eskes, M.; Shigehara, K.; Yamada, A. *Synthesis* **1993**, 194-6.
(21) Mikhalenko, S. A.; Derkacheva, V. M.; Luk'yanets, E. A. *Zh. Obshch Khim.* **1981**, *51*, 1650-7.
(22) McKeown, N. B.; Chambrier, I.; Cook, M. J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1169-77.
(23) Leznoff, C. C.; Lever, A. B. P.; Editors *Phthalocyanines: Properties and Applications*, 1989.
(24) de la Torre, G.; Claessens, C. G.; Torres, T. *Chem. Commun.* **2007**, 2000-2015.
(25) Shaabani, A. *J. Chem. Res., Synop.* **1998**, 672-673.
(26) Kempa, A.; Dobrowolski, J. *Can. J. Chem.* **1988**, *66*, 2553-5.
(27) de la Torre, G.; Vazquez, P.; Agullo-Lopez, F.; Torres, T. *Chem. Rev.* **2004**, *104*, 3723-3750.
(28) O'Flaherty, S. M.; Hold, S. V.; Cook, M. J.; Torres, T.; Chen, Y.; Hanack, M.; Blau, W. J. *Adv. Mater.* **2003**, *15*, 19-32.
(29) Chen, Y.; Hanack, M.; Blau, W. J.; Dini, D.; Liu, Y.; Lin, Y.; Bai, J. *J. Mater. Sci.* **2006**, *41*, 2169-2185.
(30) Law, K. Y. *Chem. Rev.* **1993**, *93*, 449-86.
(31) Emmelius, M.; Pawlowski, G.; Vollmann, H. W. *Angew. Chem.* **1989**, *101*, 1475-502.
(32) Wang, J.; Wang, H.; Yan, X.; Huang, H.; Jin, D.; Shi, J.; Tang, Y.; Yan, D. *Adv. Funct. Mater.* **2006**, *16*, 824-830.
(33) Bao, Z.; Lovinger, A. J.; Brown, J. *J. Am. Chem. Soc.* **1998**, *120*, 207-208.
(34) Ogura, S.-i.; Tabata, K.; Fukushima, K.; Kamachi, T.; Okura, I. *J. Porphyrins Phthalocyanines* **2006**, *10*, 1116-1124.
(35) Rosenthal, I. *Photochem Photobiol* **1991**, *53*, 859-70.

(36) Brumbach, M.; Placencia, D.; Armstrong, N. R. *J. Phys. Chem. C* **2008**, *112*, 3142-3151.
(37) Nazeeruddin, M. K.; Humphry-Baker, R.; Gratzel, M.; Murrer, B. A. *Chem. Commun.* **1998**, 719-720.
(38) Robert, A.; Benoit-Vical, F.; Meunier, B. *Coord. Chem. Rev.* **2005**, *249*, 1927-1936.
(39) Guillaud, G.; Simon, J.; Germain, J. P. *Coord. Chem. Rev.* **1998**, *178-180*, 1433-1484.
(40) McKeown, N. B. *J. Mater. Chem.* **2000**, *10*, 1979-1995.
(41) McKeown, N. B. *Chem. Ind.* **1999**, 92-98.
(42) Chambrier, I.; Cook, M. J.; Helliwell, M.; Powell, A. K. *J. Chem. Soc., Chem. Commun.* **1992**, 444-5.
(43) Dogo, S.; Germain, J. P.; Maleysson, C.; Pauly, A. *Thin Solid Films* **1992**, *219*, 244-50.
(44) McKeown, N. B.; Cook, M. J.; Thomson, A. J.; Harrison, K. J.; Daniel, M. F.; Richardson, R. M.; Roser, S. J. *Thin Solid Films* **1988**, *159*, 469-78.
(45) Cook, M. J.; Daniel, M. F.; Harrison, K. J.; McKeown, N. B.; Thomson, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1148-50.
(46) Hassan, B. M.; Li, H.; McKeown, N. B. *J. Mater. Chem.* **2000**, *10*, 39-45.
(47) Engelkamp, H.; van Nostrum, C. F.; Nolte, R. J. M.; Picken, S. J. *Chem. Commun.* **1998**, 979-980.
(48) van Nostrum, C. F.; Nolte, R. J. M. *Chem. Comm.* **1996**, 2385-2392.
(49) Elemans, J. A. A. W.; van Hameren, R.; Nolte, R. J. M.; Rowan, A. E. *Advanced Materials (Weinheim, Germany)* **2006**, *18*, 1251-1266.
(50) Engelkamp, H.; Middelbeek, S.; Nolte, R. J. M. *Science* **1999**, *284*, 785-788.
(51) Engelkamp, H.; Nolte, R. J. M. *J. Porphyrins Phthalocyanines* **2000**, *4*, 454-459.
(52) Ballesteros, B.; De la Torre, G.; Torres, T.; Hug, G. L.; Rahman, G. M. A.; Guldi, D. M. *Tetrahedron* **2006**, *62*, 2097-2101.
(53) Cammidge, A. N.; Berber, G.; Chambrier, I.; Hough, P. W.; Cook, M. J. *Tetrahedron* **2005**, *61*, 4067-4074.
(54) Rawling, T.; McDonagh, A. *Coord. Chem. Rev.* **2007**, *251*, 1128-1157.
(55) Hanack, M.; Hees, M.; Witke, E. *New J. Chem.* **1998**, *22*, 169-172.
(56) Kobel, W.; Hanack, M. *Inorg. Chem.* **1986**, *25*, 103-7.
(57) Hanack, M.; Osio-Barcina, J.; Witke, E.; Pohmer, J. *Synthesis* **1992**, 211-14.
(58) Mansuy, D. *C. R. Chim.* **2007**, *10*, 392-413.
(59) Feiters, M. C.; Rowan, A. E.; Nolte, R. J. M. *Chem. Soc. Rev.* **2000**, *29*, 375-384.
(60) Elemans, J. A. A. W.; Bijsterveld, E. J. A.; Rowan, A. E.; Nolte, R. J. M. *Eur. J. Org. Chem.* **2007**, 751-757.
(61) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411-56.
(62) Rose, E.; Andrioletti, B.; Zrig, S.; Quelquejeu-Etheve, M. *Chem. Soc. Rev.* **2005**, *34*, 573-583.
(63) Sehlotho, N.; Nyokong, T. *J. Mol. Catal. A: Chem.* **2004**, *209*, 51-57.
(64) Van Keulen, J.; Warmerdam, T. W.; Nolte, R. J. M.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 534-6.
(65) Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fort, M.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110*, 8462-70.
(66) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8443-52.

(67) Okochi, E.; Mochizuki, M. *Chem. Pharm. Bull.* **1995**, *43*, 2173-6.
(68) Ruf, H. H.; Wende, P. *J. Am. Chem. Soc.* **1977**, *99*, 5499-5500.
(69) Collman, J. P.; Fu, L. *Acc. Chem. Res.* **1999**, *32*, 455-463.
(70) Collman, J. P.; Zhong, M.; Wang, Z.; Rapta, M.; Rose, E. *Chem. Commun.* **1999**, *18*, 1783-84.
(71) Gross, Z.; Ini, S. *Org. Lett.* **1999**, *1*, 2077-2080.
(72) Elemans, J. A. A. W.; Claase, M. B.; Aarts, P. P. M.; Rowan, A. E.; Schenning, A. P. H. J.; Nolte, R. J. M. *J. Org. Chem.* **1999**, *64*, 7009-7016.
(73) Fang, Z.; Breslow, R. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 5463-5466.
(74) Breslow, R.; Dong, S. D. *Chem. Rev.* **1998**, *98*, 1997-2011.
(75) Breslow, R.; Gabriele, B.; Yang, J. *Tetrahedron Lett.* **1998**, *39*, 2887-2890.
(76) Schenning, A. P. H. J.; Hubert, D. H. W.; van Esch, J. H.; Feiters, M. C.; Nolte, R. J. M. *Angew. Chem., Int. Ed.Engl.* **1994**, *33*, 2468-70.
(77) Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1998**, *120*, 10895-10901.
(78) Yu, X.-Q.; Huang, J.-S.; Yu, W.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2000**, *122*, 5337-5342.
(79) Liu, C.-J.; Li, S.-G.; Pang, W.-Q.; Che, C.-M. *Chem. Commun.* **1997**, 65-66.
(80) Liu, C.-J.; Yu, W.-Y.; Li, S.-G.; Che, C.-M. *J. Org. Chem.* **1998**, *63*, 7364-7369.
(81) Woehrle, D.; Gitzel, J.; Krawczyk, G.; Tsuchida, E.; Ohno, H.; Okura, I.; Nishisaka, T. *J. Macromol. Sci., Chem.* **1988**, *A25*, 1227-54.
(82) Barloy, L.; Lallier, J. P.; Battioni, P.; Mansuy, D.; Piffard, Y.; Tournoux, M.; Valim, J. B.; Jones, W. *New J. Chem.* **1992**, *16*, 71-80.
(83) Battioni, P.; Cardin, E.; Louloudi, M.; Schollhorn, B.; Spyroulias, G. A.; Mansuy, D.; Traylor, T. G. *Chem. Commun.* **1996**, 2037-2038.
(84) Kaliya, O. L.; Lukyanets, E. A.; Vorozhtsov, G. N. *J. Porphyrins Phthalocyanines* **1999**, *3*, 592-610.
(85) Brouwer, W. M.; Traa, P. A. M.; De Weerd, T. J. W.; Piet, P.; German, A. L. *Angew. Makromol. Chem.* **1984**, *128*, 133-47.
(86) Leitao, A.; Costa, C.; Rodrigues, A. *Chem. Eng. Sci.* **1987**, *42*, 2291-9.
(87) Basu, B.; Satapathy, S.; Bhatnagar, A. K. *Catal. Rev. - Sci. Eng.* **1993**, *35*, 571-609.
(88) Thibault-Starzyk, F.; Van Puymbroeck, M.; Parton, R. F.; Jacobs, P. A. *J. Mol. Catal. A: Chem.* **1996**, *109*, 75-79.
(89) Paez-Mozo, E.; Gabriunas, N.; Maggi, R.; Acosta, D.; Ruiz, P.; Delmon, B. *J. Mol. Catal. A: Chem.* **1994**, *91*, 251-8.
(90) Alcaraz, J. J.; Arena, B. J.; Gillespie, R. D.; Holmgren, J. S. *Catal. Today* **1998**, *43*, 89-99.
(91) Mackintosh, H. J.; Budd, P. M.; McKeown, N. B. *J. Mater. Chem.* **2008**, *18*, 573-578.
(92) Parton, R. F.; Vankelecom, I. F. J.; Casselman, M. J. A.; Bezoukhanova, C. P.; Uytterhoeven, J. B.; Jacobs, P. A. *Nature (London)* **1994**, *370*, 541-4.
(93) Parton, R. F.; Uytterhoeven, L.; Jacobs, P. A. *Stud. Surf. Sci. Catal.* **1991**, *59*, 395-403.
(94) De Vos, D. E.; Thibault-Starzyk, F.; Knops-Gerrits, P. P.; Parton, R. F.; Jacobs, P. A. *Macromol. Symp.* **1994**, *80*, 157-84.
(95) Parton, R. F.; Neys, P. E.; Jacobs, P. A.; Sosa, R. C.; Rouxhet, P. G. *J. Catal.* **1996**, *164*, 341-346.
(96) McKeown, N. B.; Budd, P. M. *Chem. Soc. Rev.* **2006**, *35*, 675-683.

(97) MacNicol, D. D.; Robertson, C. D. *Nature* **1988**, *332*, 59-61.
(98) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319-330.
(99) McKeown, N. B.; Hanif, S.; Msayib, K.; Tattershall, C. E.; Budd, P. M. *Chem. Commun.* **2002**, 2782-2783.
(100) Byrn, M. P.; Curtis, C. J.; Goldberg, I.; Hsiou, Y.; Khan, S. I.; Sawin, P. A.; Tendick, S. K.; Strouse, C. E. *J. Am. Chem. Soc.* **1991**, *113*, 6549-57.
(101) Goldberg, I. *Chem.--Eur. J.* **2000**, *6*, 3863-3870.
(102) Abrahams, B. F.; Hoskins, B. F.; Michall, D. M.; Robson, R. *Nature* **1994**, *369*, 727-9.
(103) Smithenry, D. W.; Wilson, S. R.; Suslick, K. S. *Inorg. Chem.* **2003**, *42*, 7719-7721.
(104) Kosal, M. E.; Chou, J.-H.; Wilson, S. R.; Suslick, K. S. *Nat. Mater.* **2002**, *1*, 118-121.
(105) Diskin-Posner, Y.; Patra, G. K.; Goldberg, I. *CrystEngComm* **2002**, *4*, 296-304.
(106) Kosal, M. E.; Suslick, K. S. *J. Solid State Chem.* **2000**, *152*, 87-98.
(107) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670-4679.
(108) Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. *Chem. Mater.* **1999**, *11*, 2633-2656.
(109) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705-714.
(110) Kim, J.; Chen, B.; Reineke, T. M.; Li, H.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 8239-8247.
(111) Furukawa, H.; Kim, J.; Ockwig, N. W.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2008**, *130*, 11650-11661.
(112) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469-472.
(113) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, M. *Nature* **1999**, *402*, 276-279.
(114) Chae, H. K.; Siberio-Perez, D. Y.; Kim, J.; Go, Y. B.; Eddaoudi, M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523-527.
(115) Goldberg, I. *CrystEngComm* **2008**, *10*, 637-645.
(116) Byrn, M. P.; Curtis, C. J.; Khan, S. I.; Sawin, P. A.; Tsurumi, R.; Strouse, C. E. *J. Am. Chem. Soc.* **1990**, *112*, 1865-74.
(117) Kumar, R. K.; Balasubramanian, S.; Goldberg, I. *Inorg. Chem.* **1998**, *37*, 541-552.
(118) Kosal, M. E.; Suslick, K. S. *J. Solid State Chem.* **2000**, *152*, 87-98.
(119) Bhyrappa, P.; Wilson, S. R.; Suslick, K. S. *Supramol. Chem.* **1998**, *9*, 169-174.
(120) George, S.; Goldberg, I. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2005**, *E61*, m1441-m1443.
(121) Lin, K.-J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2730-2732.
(122) Engel, M. K. *Porphyrin Handb.* **2003**, *20*, 1-242.
(123) Lee, H.-J.; Brennessel, W. W.; Lessing, J. A.; Brucker, W. W.; Young, V. G., Jr.; Gorun, S. M. *Chem. Commun.* **2003**, 1576-1577.
(124) Bench, B. A.; Beveridge, A.; Sharman, W. M.; Diebold, G. J.; Van Lier, J. E.; Gorun, S. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 747-750.
(125) Bench Barbara, A.; Brennessel William, W.; Lee, H.-J.; Gorun Sergiu, M.

Angew Chem Int Ed Engl **2002**, *41*, 750-4.
(126) Zeng, Q.; Wu, D.; Wang, C.; Lu, J.; Ma, B.; Shu, C.; Ma, H.; Li, Y.; Bai, C. *CrystEngComm* **2005**, *7*, 243-248.
(127) McKeown, N. B.; Makhseed, S.; Msayib, K. J.; Ooi, L.-L.; Helliwell, M.; Warren, J. E. *Angew. Chem., Int. Ed.* **2005**, *44*, 7546-7549.
(128) Maksheeed, S.; Ibrahim, F.; Samuel, J.; Helliwell, M.; Warren, J. E.; Bezzu, C. G.; McKeown, N. B. *Chem.--Eur. J.* **2008**, *14*, 4810-4815.
(129) Makhseed, S.; Ibrahim, F.; Bezzu, C. G.; McKeown Neil, B. *Tetrahedron Lett.* **2007**, *48*, 7358-61.
(130) Tyapochkin, E. M.; Kozliak, E. I. *J. Mol. Catal. A: Chem.* **2005**, *242*, 1-17.
(131) Galezowski, W. *Inorg. Chem.* **2005**, *44*, 1530-1546.
(132) Galezowski, W.; Kubicki, M. *Inorg. Chem.* **2005**, *44*, 9902-9913.
(133) Brewis, M.; Clarkson, G. J.; Humberstone, P.; Makhseed, S.; McKeown, N. B. *Chem.Eur. J.* **1998**, *4*, 1633-1640.
(134) Agar, E.; Sasmaz, S.; Akdemir, N.; Keskin, I. *J. Chem. Soc., Dalton Trans.* **1997**, 2087-2090.
(135) Sommerauer, M.; Rager, C.; Hanack, M. *J. Am. Chem. Soc.* **1996**, *118*, 10085-10093.
(136) Ahsen, V.; Yilmazer, E.; Ertas, M.; Bekaroglu, O. *J. Chem. Soc., Dalton Trans.* **1988**, 401-6.
(137) Kandaz, M.; Yilmaz, I.; Bekaroglu, O. *Polyhedron* **2000**, *19*, 115-121.
(138) Lee, S.; Vesper Benjamin, J.; Zong, H.; Hammer Neal, D.; Elseth Kim, M.; Barrett Anthony, G. M.; Hoffman Brian, M.; Radosevich James, A. *Met Based Drugs* **2008**, *2008*, 391418.
(139) Leznoff, C. C.; Black, L. S.; Hiebert, A.; Causey, P. W.; Christendat, D.; Lever, A. B. P. *Inorg. Chim. Acta* **2006**, *359*, 2690-2699.
(140) Seoudi, R.; El-Bahy, G. S.; El Sayed, Z. A. *Opt. Mater.* **2006**, *29*, 304-312.
(141) Liu, W.; Lee, C.-H.; Chan, H.-S.; Mak, T. C. W.; Ng, D. K. P. *Eur. J. Inorg. Chem.* **2004**, 286-292.
(142) Lever, A. B. P. *Advan. Inorg. Chem. Radiochem.* **1965**, *7*, 27-105.
(143) Hanack, M.; Knecht, S.; Polley, R.; Subramanian, L. R. *Synth. Met.* **1996**, *80*, 183-189.
(144) Metz, J.; Schneider, O.; Hanack, M. *Inorg. Chem.* **1984**, *23*, 1065-71.
(145) Bayo, K.; Saba, A.; Ouedraogo, G. V.; Terzian, G.; Benlian, D. *J. Mol. Struct.* **1992**, *271*, 19-26.
(146) Schmid, G.; Witke, E.; Schlick, U.; Knecht, S.; Hanack, M. *J. Mater. Chem.* **1995**, *5*, 855-9.
(147) Polley, R.; Hanack, M. *J. Org. Chem.* **1995**, *60*, 8278-82.
(148) Barrett, P. A.; Frye, D. A.; Linstead, R. P. *J. Chem. Soc.* **1938**, 1157-63.
(149) Pohmer, J.; Hanack, M.; Osio Barcina, J. *J. Mater. Chem.* **1996**, *6*, 957-962.
(150) Bossard, G. E.; Abrams, M. J.; Darkes, M. C.; Vollano, J. F.; Brooks, R. C. *Inorg. Chem.* **1995**, *34*, 1524-7.
(151) Haisch, P.; Winter, G.; Hanack, M.; Luer, L.; Egelhaaf, H. J.; Oelkrug, D. *Adv. Mater.* **1997**, *9*, 316-321.
(152) Winter, G.; Heckmann, H.; Haisch, P.; Eberhardt, W.; Hanack, M.; Lueer, L.; Egelhaaf, H.-J.; Oelkrug, D. *J. Am. Chem. Soc.* **1998**, *120*, 11663-11673.
(153) Auger, A.; Burnham, P. M.; Chambrier, I.; Cook, M. J.; Hughes, D. L. *J. Mater. Chem.* **2005**, *15*, 168-176.
(154) Guzei, I. A.; McGaff, R. W.; Kieler, H. M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2005**, *C61*, m472-m475.

(155) Valenti, V.; Fantucci, P.; Cariati, F.; Micera, G.; Petrera, M.; Burriesci, N. *Inorg. Chim. Acta* **1988**, *148*, 191-7.
(156) Collman, J. P.; Decreau, R. A.; Zhang, C. *J. Org. Chem.* **2004**, *69*, 3546-3549.
(157) Ueyama, N.; Nishikawa, N.; Yamada, Y.; Okamura, T.-A.; Nakamura, A. *Inorg. Chim. Acta* **1998**, *283*, 91-97.
(158) Tani, F.; Nakayama, S.; Ichimura, M.; Nakamura, N.; Naruta, Y. *Chem. Lett.* **1999**, 729-730.
(159) Collman, J. P.; Gagne, R. R.; Reed, C. A.; Robinson, W. T.; Rodley, G. A. *Proc. Nat. Acad. Sci. U. S. A.* **1974**, *71*, 1326-9.
(160) Collman, J. P.; Eberspacher, T.; Fu, L.; Herrmann, P. C. *J. Mol. Catal. A: Chem.* **1997**, *117*, 9-20.
(161) Schappacher, M.; Ricard, L.; Fischer, J.; Weiss, R.; Bill, E.; Montiel-Montoya, R.; Winkler, H.; Trautwein, A. X. *Eur. J. Biochem.* **1987**, *168*, 419-29.
(162) Wheatley, W. B.; Holdrege, C. T. *J. Org. Chem.* **1958**, *23*, 568-71.
(163) Brewis, M.; Clarkson, G. J.; Helliwell, M.; Holder, A. M.; McKeown, N. B. *Chem. Eur. J.* **2000**, *6*, 4630-4636.
(164) Bacon, R. G. R.; Hill, H. A. O. *J. Chem. Soc.* **1964**, 1097-1107.
(165) Friedman, L.; Shechter, H. *J. Org. Chem.* **1961**, *26*, 2522-4.
(166) Helfenbein, J.; Lartigue, C.; Noirault, E.; Azim, E.; Legailliard, J.; Galmier, M. J.; Madelmont, J. C. *J. Med. Chem.* **2002**, *45*, 5806-5808.
(167) Omura, K. *Synthesis* **1998**, 1145-1148.
(168) Germeraad, P.; Weyler, W., Jr.; Moore, H. W. *J. Org. Chem.* **1974**, *39*, 781-5.
(169) Horie, T.; Tsukayama, M.; Kourai, H.; Yokoyama, C.; Furukawa, M.; Yoshimoto, T.; Yamamoto, S.; Watanabe-Kohno, S.; Ohata, K. *J. Med. Chem.* **1986**, *29*, 2256-62.
(170) Sabui, S. K.; Venkateswaran, R. V. *Tetrahedron* **2003**, *59*, 8375-8381.
(171) Newman, E. M.; Lin, A. J.; Sartorelli, A. C. *J Med Chem* **1980**, *23*, 627-31.
(172) Mukherjee, S.; Kumar, V.; Prasad, A. K.; Raj, H. G.; Bracke, M. E.; Olsen, C. E.; Jain, S. C.; Parmar, V. S. *Bioorg. Med. Chem.* **2001**, *9*, 337-345.
(173) Petranek, J.; Pilar, J. *Collect. Czech. Chem. Commun.* **1970**, *35*, 830-7.
(174) Dobronravova, Z. A.; Meshcheryakov, V. I.; Prishenko, Y. E.; Gavrilov, L. D.; Vereshchagin, L. I. *J.Org.Chem.USSR (Engl.Transl.)* **1980**, *16*, 910-914.
(175) Aalten, H. L.; Van Koten, G.; Grove, D. M.; Kuilman, T.; Piekstra, O. G.; Hulshof, L. A.; Sheldon, R. A. *Tetrahedron* **1989**, *45*, 5565-78.
(176) Tamura, K.; Kato, Y.; Ishikawa, A.; Kato, Y.; Himori, M.; Yoshida, M.; Takashima, Y.; Suzuki, T.; Kawabe, Y.; Cynshi, O.; Kodama, T.; Niki, E.; Shimizu, M. *J. Med. Chem.* **2003**, *46*, 3083-3093.
(177) Trapani, G.; Latrofa, A.; Franco, M.; Altomare, C.; Sanna, E.; Usala, M.; Biggio, G.; Liso, G. *J. Med. Chem.* **1998**, *41*, 1846-1854.
(178) v. Auwers, K.; Wittig, G. *Ber. Dtsch. Chem. Ges. B* **1924**, *57B*, 1270-5.
(179) McOmie, J. F. W.; Watts, M. L.; West, D. E. *Tetrahedron* **1968**, *24*, 2289-92.
(180) Vickery, E. H.; Pahler, L. F.; Eisenbraun, E. J. *J. Org. Chem.* **1979**, *44*, 4444-6.
(181) Cava, M. P.; Mitchell, M. J. *J. Org. Chem.* **1962**, *27*, 631-2.
(182) Sekiyama, Y.; Palaniappan, N.; Reynolds, K. A.; Osada, H. *Tetrahedron*

2003, *59*, 7465-7471.
(183) Valach, F. *Polyhedron* **1999**, *18*, 699-706.
(184) Ishimaru, Y.; Kitano, M.; Kumada, H.; Koga, N.; Iwamura, H. *Inorg. Chem.* **1998**, *37*, 2273-2280.
(185) Torres, J.; Lavandera, J. L.; Cabildo, P.; Claramunt, R. M.; Elguero, J. *J. Heterocycl. Chem.* **1988**, *25*, 771-82.

Appendix

Crystallographic data (CIF files)on CD at the back of the thesis