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Non-symmetrically substituted phthalocyanines: synthesis and structure modification

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Abstract. The presently known approaches to the synthesis of non-symmetrically substituted phthalocyanines of the A_3B and A_2B_2 types are surveyed. The prospects for the use of these compounds for the synthesis of binuclear and heteronuclear complexes and phthalocyanine oligomers and polymers are demonstrated. The bibliography includes 84 references.

I. Introduction

Phthalocyanines, being synthetic analogues of porphyrins wide spread in nature attract attention of many researchers owing to their prominent chemical and thermal non-stability. Over the last decade, non-symmetrically substituted phthalocyanines bearing different types of substituents came into the focus of interest. These compounds manifest a number of valuable properties enabling their application as advanced materials, in particular in non-linear optics.[1–12] Non-symmetrically substituted phthalocyanines readily form ordered single layers (*i.e.*, the Langmuir–Blodgett films)[11–14] and linear polymers.[15] Furthermore, their zinc complexes are promising substrates in the photodynamic anticancer therapy.[16,17]

It is of note that the synthesis of non-symmetrical phthalocyanines is a very labourious task, which hinders their studies and practical applications. In the vast majority of cases, non-symmetrically substituted phthalocyanines are synthesised by random cyclisation of phthalogens, which gives rise, naturally, to mixtures of phthalocyanines that are difficult to separate in extremly low yields of the target products.

Non-symmetrically substituted phthalocyanines are of interest from both theoretical and practical standpoints. The presence of different functional substituents in these macrocyclic compounds enables the design of novel supramolecular structures with unique physicochemical properties.[18–21] That is why the developement of methods for the directed synthesis of this class of compounds is one of the topical directions in the chemistry of phthalocyanines.

In the present review, the emphasis is placed on the methods for the synthesis of non-symmetrically substituted phthalocyanines and their modifications aimed at the introduction of new functional substituents required for the design of bi- and polynuclear assemblies of any complexity.

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II. Methods for the synthesis of non-symmetrically substituted phthalocyanines

As has been noted above, the directed synthesis of non-symmetrically substituted phthalocyanines remains a challenging problem. The known methods of synthesis do not provide sufficiently high yields[15–17,22–41] comparable to those achievable in the synthesis of symmetrical phthalocyanines.

There are two major approaches to the synthesis of non-symmetrically substituted phthalocyanines, *viz.*, the random cyclisation of different phthalonitriles and their synthetic analogues, 1,3-diiminoisoindolines,[15–17,22–32,40,42–50] and the macrocycle ring expansion in subphthalocyanines, *i.e.*, compounds with three rather than four isoindole fragments.[33–39,51–56]

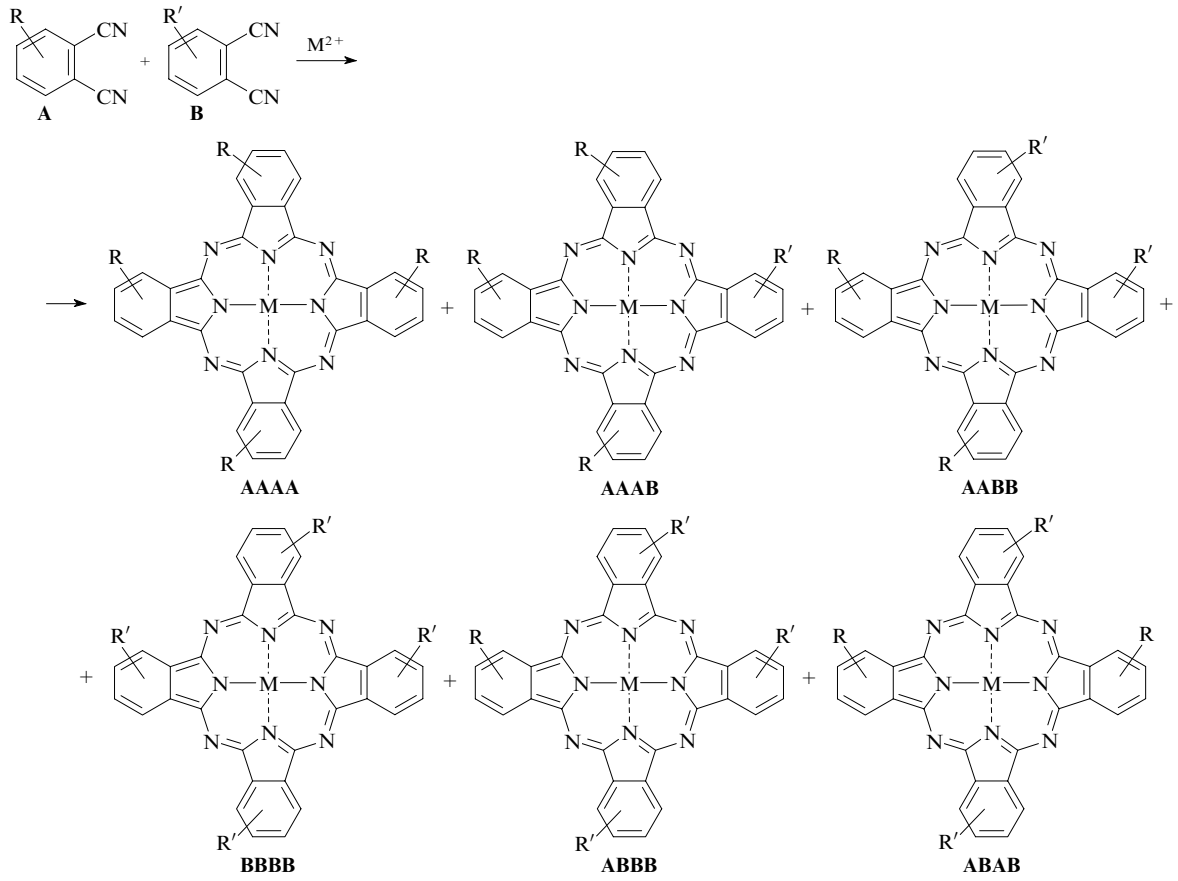
1. Methods of synthesis based on the phthalogen random cyclisation

The random cyclisation is presently used the most often for the synthesis of different types of non-symmetrically substituted phthalocyanines, despite its intrinsically low selectivity. Thus the joint cyclisation of two phthalogens **A** and **B** may theoretically afford six products, *viz.*, **AAAA** (A_4), **BBBB** (B_4), **AABB**, **ABAB** (two isomers with the A_2B_2 stoichiometry), **AAAB** (A_3B) and **ABBB** (AB_3) (Scheme 1).

The separation of the resultant random mixture requires the application of sophisticated chromatographic techniques. Due to the high proneness of phthalocyanine molecules to self-aggregation, the isolation of the target product represents a rather difficult problem.[23,57] Typically, it can be solved with the use of phthalogens with substituents of different nature. In particular, bulky substituents prevent the self-aggregation and increase the solubility thus facilitating the chromatographic isolation and purification of the target product.[43,58,59]

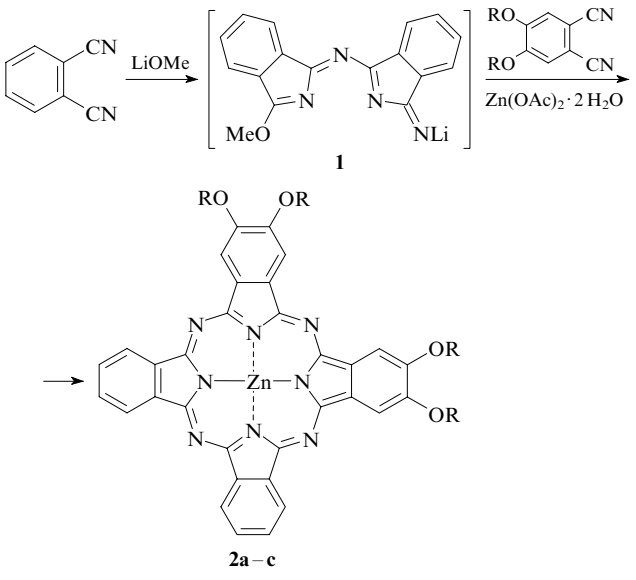
The yield of a target product is strongly affected by the ratio of the reactants.[16,17,22–27] According to a theoretical analysis, the reaction of phthalogens **A** and **B** with similar reactivities taken in a molar ratio of 3 : 1 yields a mixture containing phthalocyanines A_4 and A_3B in a ratio of 3 : 4.[58] The total yield of the A_3B products does not exceed 10% – 20%. Leznoff and co-workers[17] noted that

Scheme 1



the content of the product A_3B in the reaction mixture can be increased with respect to other possible phthalocyanines by increasing the amount of the phthalogen **A** to 9–10 equivalents. But even in this case, the yield of the target product rarely exceeds 20%.

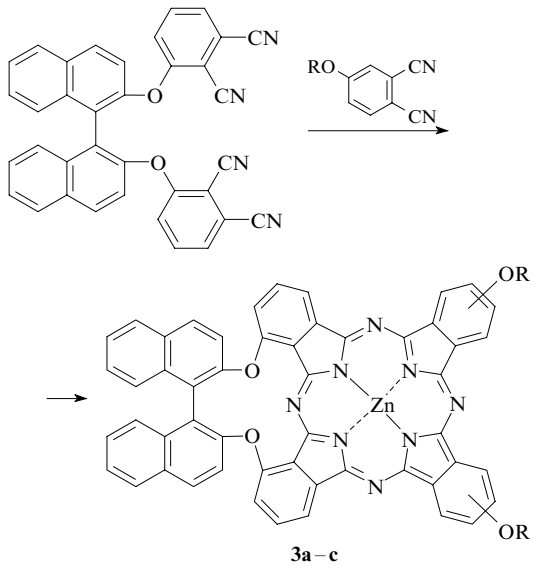
In the synthesis of the A_2B_2 type phthalocyanines, the formation of two isomers with the identical fragments arranged either next to (**AABB**), or opposite to (**ABAB**), each other is possible.[15–17,27,28,43–45] These isomers cannot be separated by adsorption chromatography, thus a two-step process has been elaborated [17] for the selective synthesis of the isomer **AABB**.



R = Me (**a**), CH_2Ph (**b**), $CHPh_2$ (**c**).

The reaction of lithium methoxide with phthalonitrile taken in the equimolar ratio in methanol at 40–60 °C yields mainly intermediate **1**. Its subsequent cyclisation with alkoxy-substituted phthalonitriles in n-octanol affords complexes **2**.

An alternative approach to the synthesis of structures **AABB** consists of the use of the mixed cyclisation of bis(phthalonitriles) prepared from 3-nitrophthalonitrile and diols with closely arranged OH groups.[7,8,27,60,61] Such phthalocyanines synthesised for the first time in the mid 1990s [61] are commonly referred to as side-strapped.



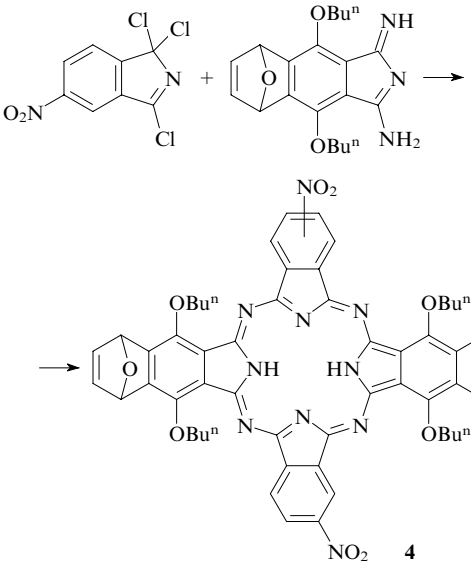
R = Ph (**a**), 4-$Bu^tC_6H_4$ (**b**), 4-$C_6H_4SO_3Na$ (**c**).

Since in the starting compound the phthalonitrile groups are located close to each other, the probability of the oligomerisation and formation of binuclear products is rather low, such that non-symmetrically substituted phthalocyanines of the **AABB** type are preferably formed. Nevertheless, the possible formation of a phthalocyanine with two cross-links at the opposite sides is not totally ruled out even in the presence of phthalonitrile.[27]

Young and Onyebuagu [28] proposed a method for the selective synthesis of phthalocyanines **ABAB** based on the cyclisation of 6-nitro-1,3,3-trichloroisoindole and substituted 1,3-diiminoisoindoline taken in an equimolar ratio.

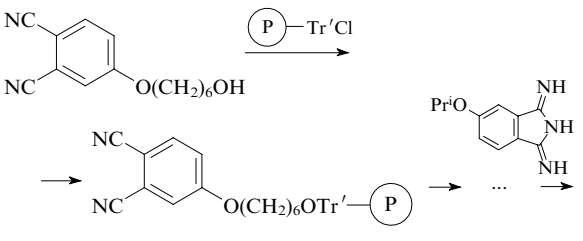
The target product **4** is formed in 50% yield, which is record high for non-symmetrically substituted phthalocyanines. However, other authors who employed this method [15, 62] observed the formation of the phthalocyanine **AAAB** as a by-product with the total yield of the target phthalocyanine **ABAB** not exceeding 15% – 25%. It was also noted [63] that the selectivity of the reaction increases with an increase in the bulk of substituents in one of the phthalogens.

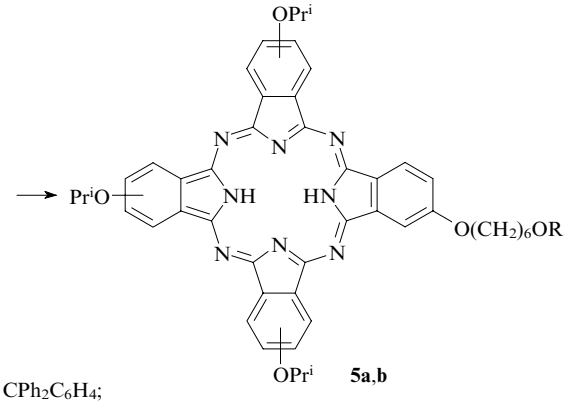
Therefore, the random cyclisation as a method for the synthesis of non-symmetrically substituted phthalocyanines provides low selectivity, which weakly depends on the nature and ratio of the starting phthalogens.



4

The synthesis on a polymer support (P) represents a promising modification of the random cyclisation method. This approach involves grafting of a phthalonitrile contaning an OH group in a substituent to a polymer, converting the thus modified phthalogen into the respective 1,3-diiminoisoindoline analogue followed by its mixed cyclisation with another substituted 1,3-diiminoisoindoline.[40, 49]





5a,**b**

Tr′ = $CPh_2C_6H_4$;

R = Tr′—(P) (**a**), H (**b**).

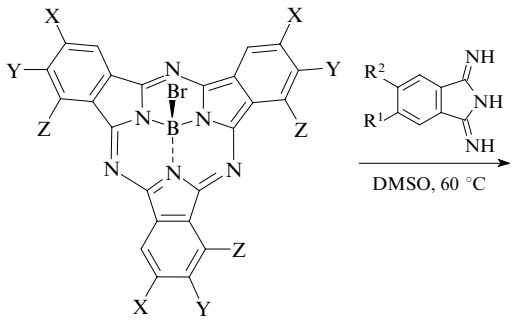
An acid treatment of the immobilised phthalocyanine **5a** afforded compound **5b** in 20% yield. The simplicity of the isolation of the target product is an evident advantage of this method — it is sufficient to wash the immobilised phthalocyanine with an appropriate solvent to remove concomitant symmetrical phthalocyanine. Wöhrle and co-workers [50] proposed to use modified silica gel as a support for the assembly of the target phthalocyanine.

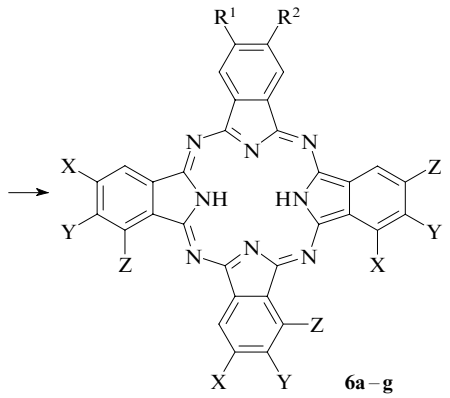
The synthesis on a polymeric support requires that substituents in the starting phthalonitriles should contain suitable reactive groups, which limits the diversity of substituted phthalocyanines that can be synthesised by this method.

2. A method of synthesis based on the ring expansion in subphthalocyanine macrocycles

A rather convenient and elegant method for the synthesis of A_3B-type phthalocyanines has been suggested by Kobayashi *et al.*[53] and further developed by Torres and co-workers,[37, 38, 51] van Lier and co-workers [33, 54, 56] and Wöhrle and co-workers.[52] These studies showed that energetically strained subphthalocyanines undergo ring opening in the presence of 1,3-diiminoisoindolines giving rise to phthalocyanines. In a recent paper, van Lier and co-workers [56] reported on the synthesis of a number of functionally substituted phthalocyanines **6a**–**g** by this method. This method provides a substantial advantage over the statistical cyclisation: the reaction selectivity can be finely controlled.

The ring expansion reaction is shown [64, 65] to be of the first order with respect to subphthalocyanine and its selectivity is mainly governed by the nature of substituents in the reactants. The reaction proceeds with the maximum selectivity and the target products are obtained in the maximum yields (> 20%) provided that the subphthalocyanine is either non-substituted [51] or bears acceptor substituents,[39] whereas the 1,3-diiminoisoindoline bears electron-releasing substituents.[35, 38, 51, 52] Highly reactive 1,3-diiminoisoindolines with electron-withdrawing groups yield random mixtures of products.[36, 37]





6a–g

Compound **6**	R^1	R^2	X	Y	Z
a	H	H	I	H	H
b	H	Bu^t	I	H	H
c	CH=CHCH=CH		I	H	H
d	H	H	H	H	I
e	H	Bu^t	H	H	I
f	CH=CHCH=CH		H	H	I
g	H	H	I	I	H

Mixtures of DMSO with α-chloronaphthalene or *o*-dichlorobenzene are typically used as solvents for the subphthalocyanine ring expansion.[33–39,51–54] Dimethyl sulfoxide is the optimum medium for the reaction, but subphthalocyanines are only moderately soluble in DMSO and thus co-solvents are necessary. The use of such solvents as DMF or alcohols results exclusively in the decomposition of subphthalocyanines.[39]

Torres and co-workers[37,38,66] suggested a mechanism of this reaction. In the first step, an 'open' phthalocyanine, which is an intermediate with four isoindole framgents, is formed. Then the intermediate undergoes either ring closure to yield phthalocyanine or fragmentation to a random mixture of products. However, the mechanism of the attack at subphthalocyanine, which is central, in our opinion, for the selection of optimum conditions for the subphthalocyanine ring expansion, remains largely unexplored.

3. A comparison of the methods for the synthesis of non-symmetrically substituted phthalocyanines

A comparison of yields of non-symmetrically substituted phthalocyanines with the stoichiometry A_3B provided by the subphthalocyanine ring expansion and random cyclisation reveals their similar efficiencies. In both cases, the total yields do not exceed 20%. Thus since the former method requires an additional step of synthesis and purification of subphthalocyanines, the random cyclisation is considered as the method of choice by the majority of researchers despite the laborious isolation of the target products. Furthermore, the random cyclisation of phthalogens with bulky substituents seems to be preferable for the synthesis of A_2B_2-type phthalocyanines.

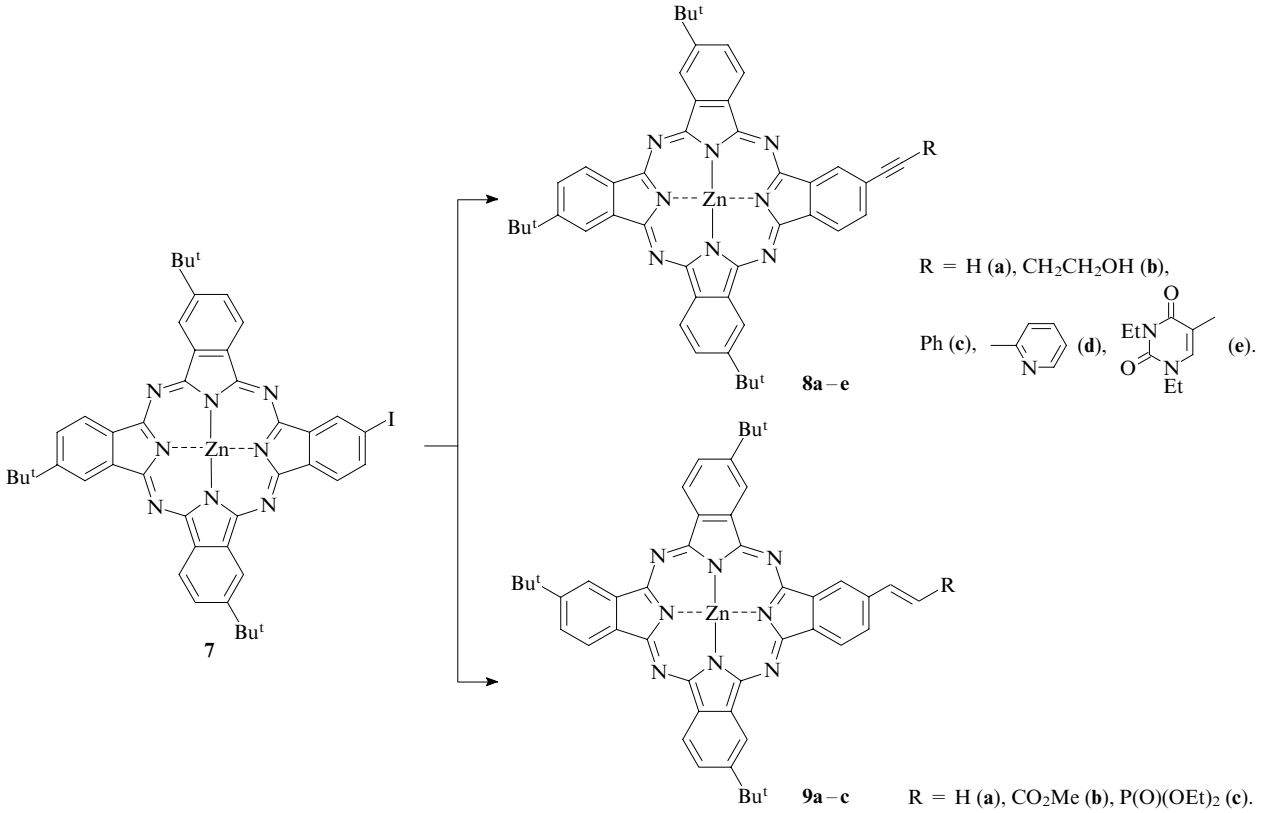
III. Structure modification of non-symmetrically substituted phthalocyanines

The majority of non-symmetrically substituted phthalocyanines described in the literature bear functional groups, which allow their post-synthetic modifications.[2–6,9,13,18,26,31,67–70] In particular, a selective method for the synthesis of planar bi- and trinuclear phthalocyanines with the macrocycles linked by ethylene,[71,72] ethynyl,[67,68,73] ferrocenediethynyl,[3,4] dehydroannulene[20,70] or anthraquinone[2] spacers has been developed. These phthalocyanines are of great potential as new-generation functional materials due to their extended conjugated π-systems providing efficient interactions between the phthalocyanine macrocycles.

1. Structure modification of halogen-substituted phthalocyanines

In the late 1990s, Ali and van Lier[74] found that zinc 9,16,23-tri(*tert*-butyl)-2-iodophthalocyanine (**7**) readily undergoes the Heck and Stille reactions affording products **8a–e**, **9b**,**c** and **9a**, respectively, in preparative yields (Scheme 2).

Scheme 2

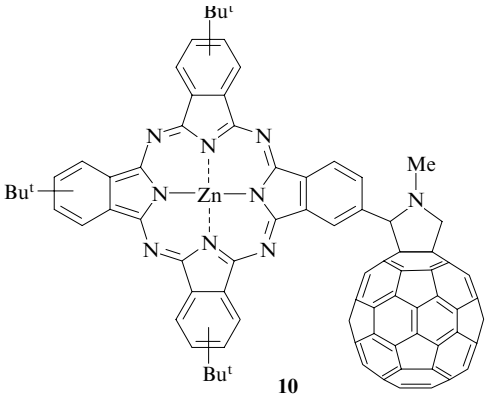


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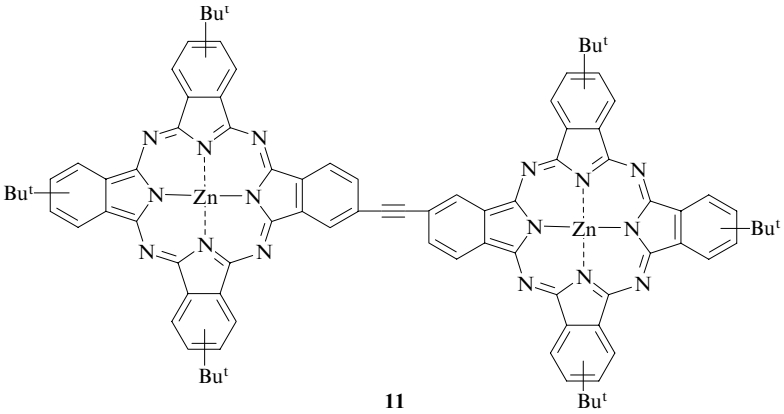
8a–e

R = H (**a**), CH_2CH_2OH (**b**), Ph (**c**), (**d**), (**e**).

9a–c R = H (**a**), CO_2Me (**b**), $P(O)(OEt)_2$ (**c**).



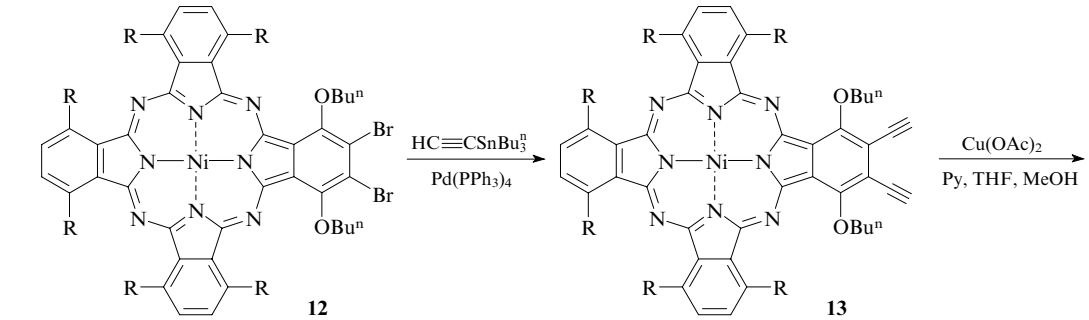
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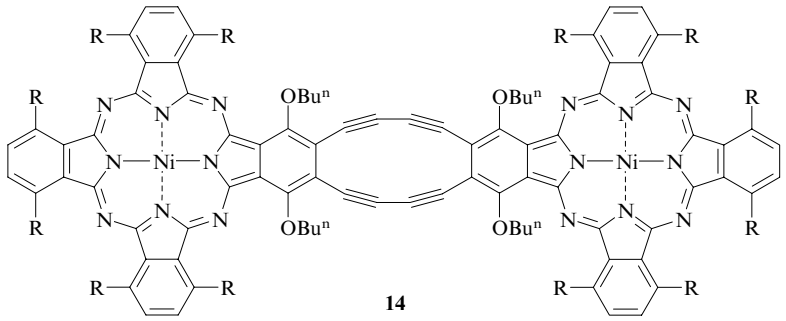
11

Later, other cross-coupling products were synthesised [26] based on the phthalocyanine **7**. Thus, halogen-substuted phthalocyanines can be regarded as the basic synthetic precursors of both other non-symmetrically substituted phthalocyanines (with the composition A_3B) and binuclear phthalocyanines.[2–4, 18, 26, 67–69, 73–75]

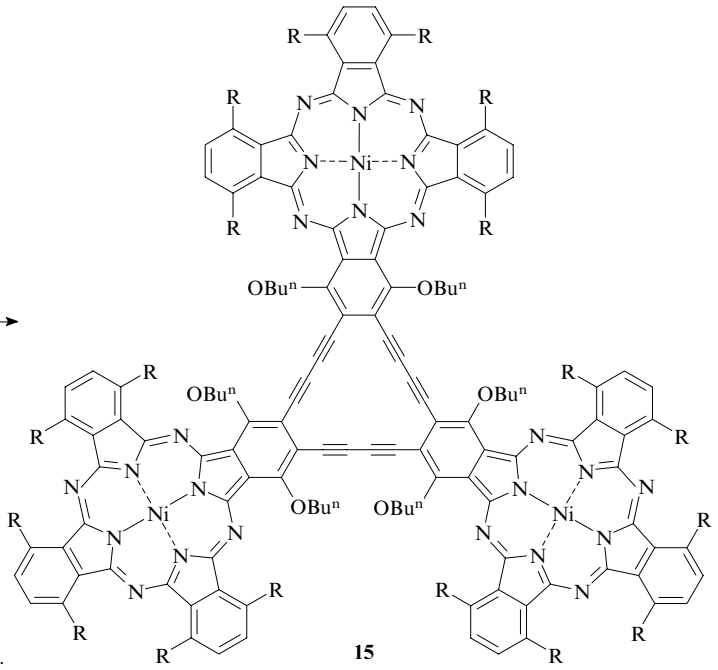
Scheme 3



12 **13**



14



15

R = n-$C_{10}H_{21}$.

In this way, a fullerene-substituted phthalocyanine (**10**) and a planar binuclear phthalocyanine (**11**) have been prepared. Both compounds manifest unique photophysical properties owing to the efficient intramolecular interaction between the macrocycles.[70, 73]

The starting phthalocyanine **7** is usually synthesised by co-cyclisation of 4-(*tert*-butyl)phthalonitrile and 4-iodonaphthonitrile,[26, 73] although an alternative more complex two-step modification of the respective nitro-substituted phthalocyanine has been reported.[69]

Phthalocyanine **12** with two bromine atoms in the *ortho*-position is no less important from the synthetic viewpoint. Its cross-coupling with tributylstannylacetylene yields diethynylphthalocyanine **13**. This compound can also be prepared from the respective diiodo-substituted complex.[18]

Starting from phthalocyanine **13**, bi- and trinuclear phthalocyanines **14** and **15** can be synthesised, which can well be regarded as supramolecular structures: the phthalocyanine macrocycles therein are fused through the dehydroannulene spacers (Scheme 3).[20, 70] This fusion provides even more efficient intramolecular conjugation, which is important for the practical utilisation.

o-Dihalogen-sibstituted phthalocyanines can be synthesised by co-cyclisation using respective 4,5-dibromo- or 4,5-diiodo-substituted phthalonitriles as one of the phthalogens.[18, 20, 70]

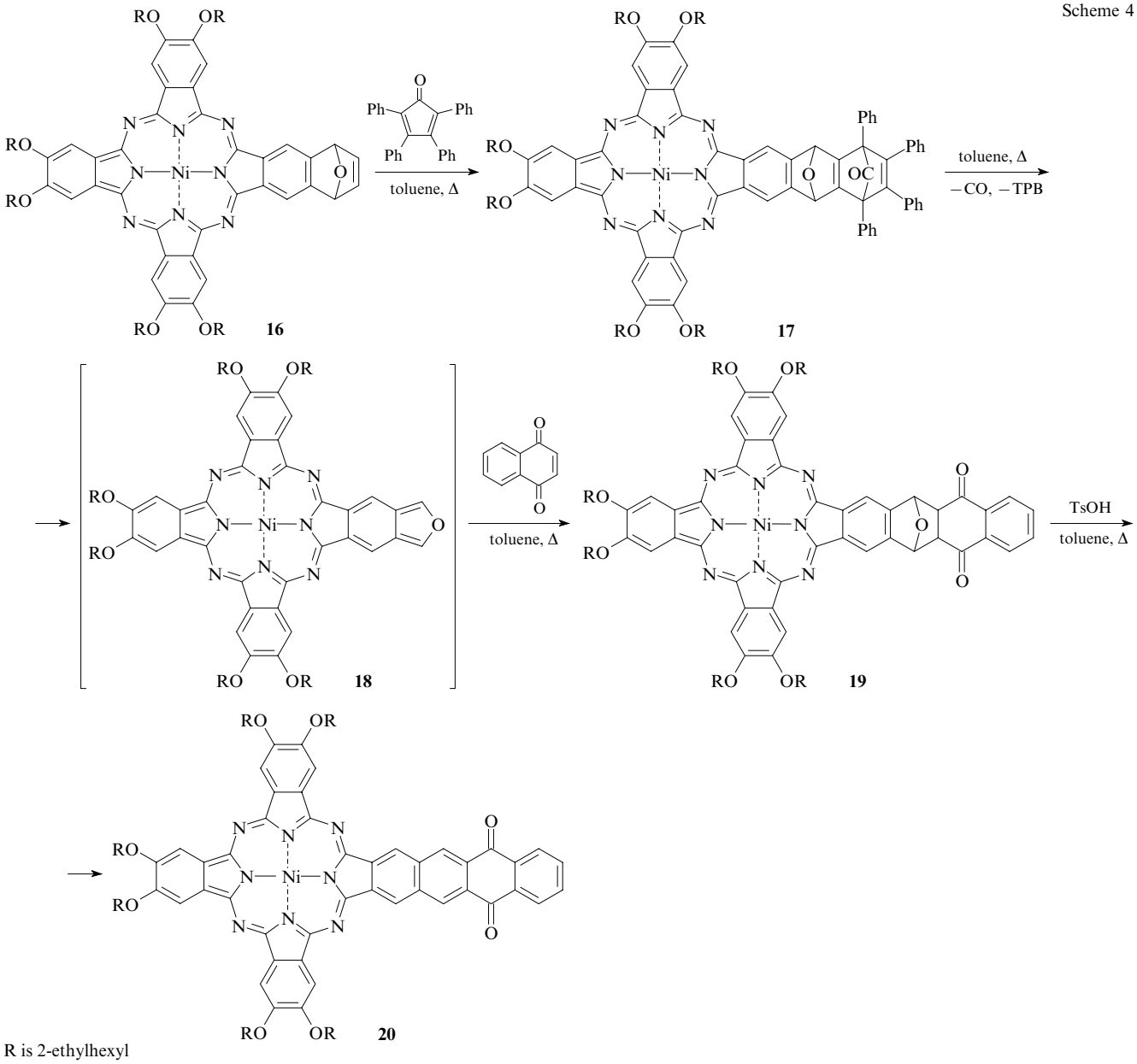
2. Structure modification of phthalocyanines using the Diels – Alder and Wittig reactions

The Diels – Alder and Wittig reactions are among few classical organic reactions that enable the stereo- and regioselective construction of compounds with specified structures under mild conditions in high yields. The possibility of utilisation of phthalocyanines in these reactions opens broad synthetic prospects.[71, 72, 76, 77]

The Diels – Alder reaction of non-symmetrically substituted phthalocyanines has been realised for the first time by Hanack and co-workers[72, 76] aimed at the preparation of linear phthalocyanine-based oligomers and polymers. It was demonstrated first for symmetrically and then for non-symmetrically substituted phthalocyanines (*e.g.*, **16**) that the isobenzofuran fragments in peripheral substituents in phthalocyanine macrocycles readily react as dienophiles with 2,3,4,5-tetraphenylpentadienone as a diene (Scheme 4).

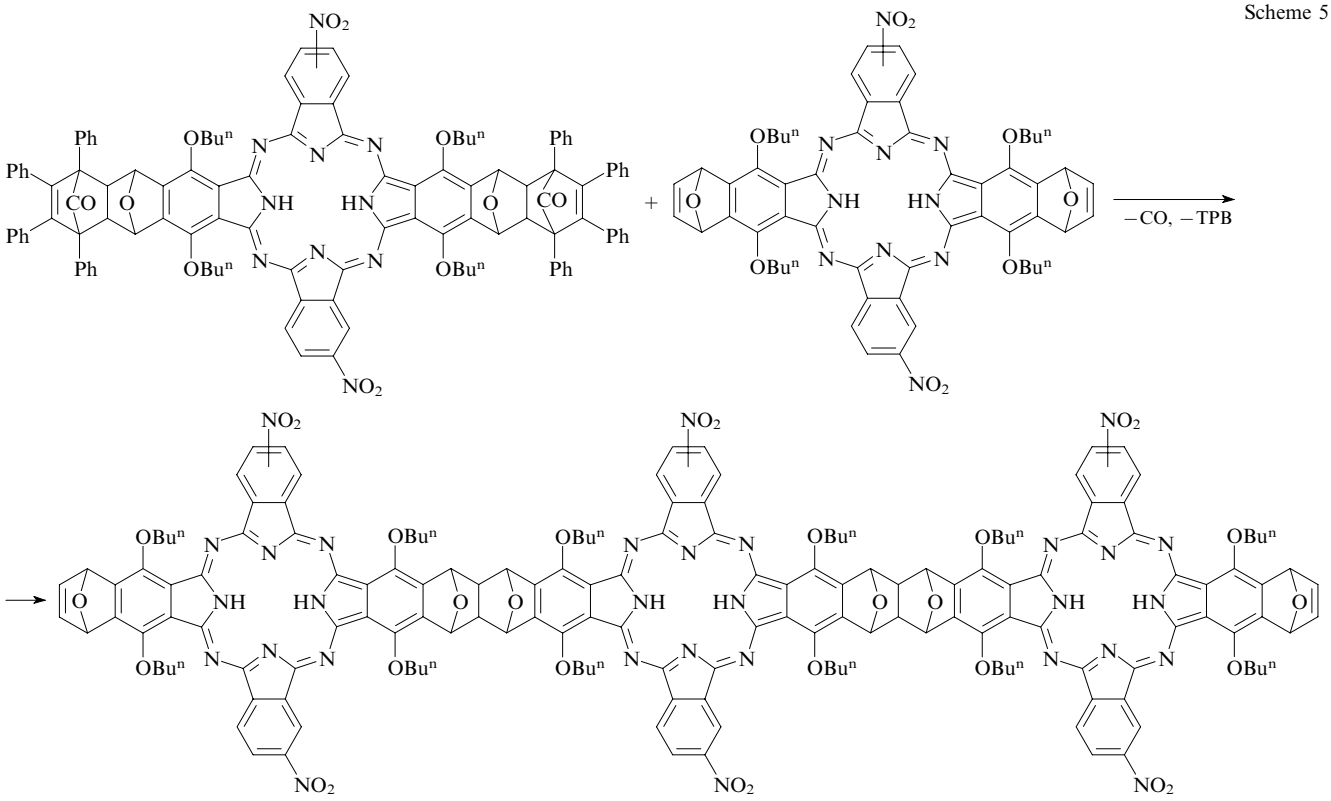
Complex **17** loses CO and tetraphenylbenzene (TPB) molecules upon boiling in toluene yielding an unstable intermediate **18**

Scheme 4



R is 2-ethylhexyl

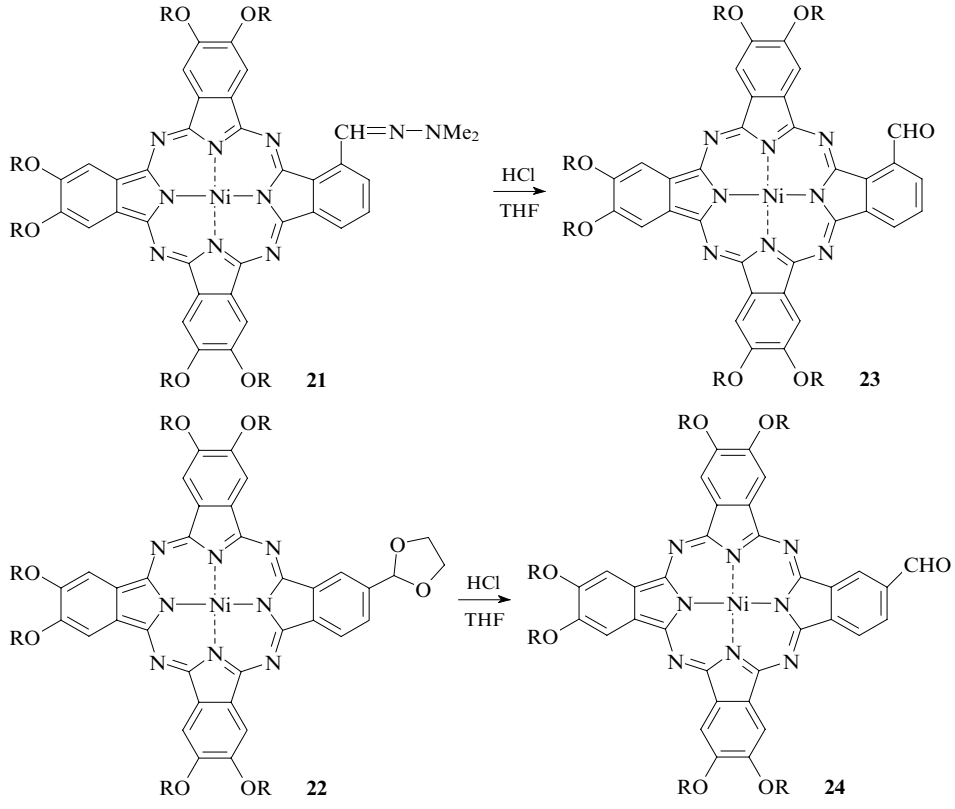
Scheme 5



with a diene structure capable of reacting with dienophiles, *e.g.*, with 1,4-naphthoquinone. Product **19** has to be only aromatised to afford the target phthalocyanine **20**. However, standard reagents used for similar naphthalocyanine substrates (*e.g.*, TsOH) react with phthalocyanines, as a rule, with partial decomposition of the macrocycles. Therefore, the use of a mild Lewis acid, trimethylsilyl triflate is more appropriate.

The Diels–Alder reaction was also successfully applied to prepare ordered polymeric structures. Non-symmetrically substituted phthalocyanines **ABAB** can be converted into linear polymers (Scheme 5).[15, 62]

Scheme 6



R is 2-ethylhexyl.

The Wittig reaction necessitates a phthalocyanine to bear at least one aldehyde group. Such phthalocyanines cannot be directly synthesised by the standard method based on the random cyclisation since dicyanobenzaldehydes yield no phthalocyanine products.[72,77] Therefore, the required aldehyde-functionalised phthalocyanines should by synthesised by a structure modification of other non-symmetrically substituted phthalocyanines (Scheme 6).

Hydrolysis of hydrazone **21** or acetal **22** yields phthalocyanines **23** and **24**, respectively. The starting derivatives **21** and **22** can easily be prepared by the random cyclisation of the corresponding phthalogens.[77]

The Wittig reaction makes it possible not only to modify the structure of non-symmetrically substituted phthalocyanines but also to synthesise planar binuclear phthalocyanines. The structure of the target product in this case is governed by the number of ylide groups in the selected spacer (Scheme 7).

The simple control over the structure of the target products and nearly quantitative yields make this method very useful for both the modification of monophthalocyanines and the preparation of bi- and polynuclear phthalocyanines with a specified spatial orientation of the macrocycles.

The phthalocyanines synthesised by the Diels–Alder or Wittig reactions are characterised by extended conjugated electron systems, which results in bathochromic shifts of the Q band in their UV-Vis absorption spectra.[71,72,76,77]

3. Functionalisation of nitro-substituted phthalocyanines

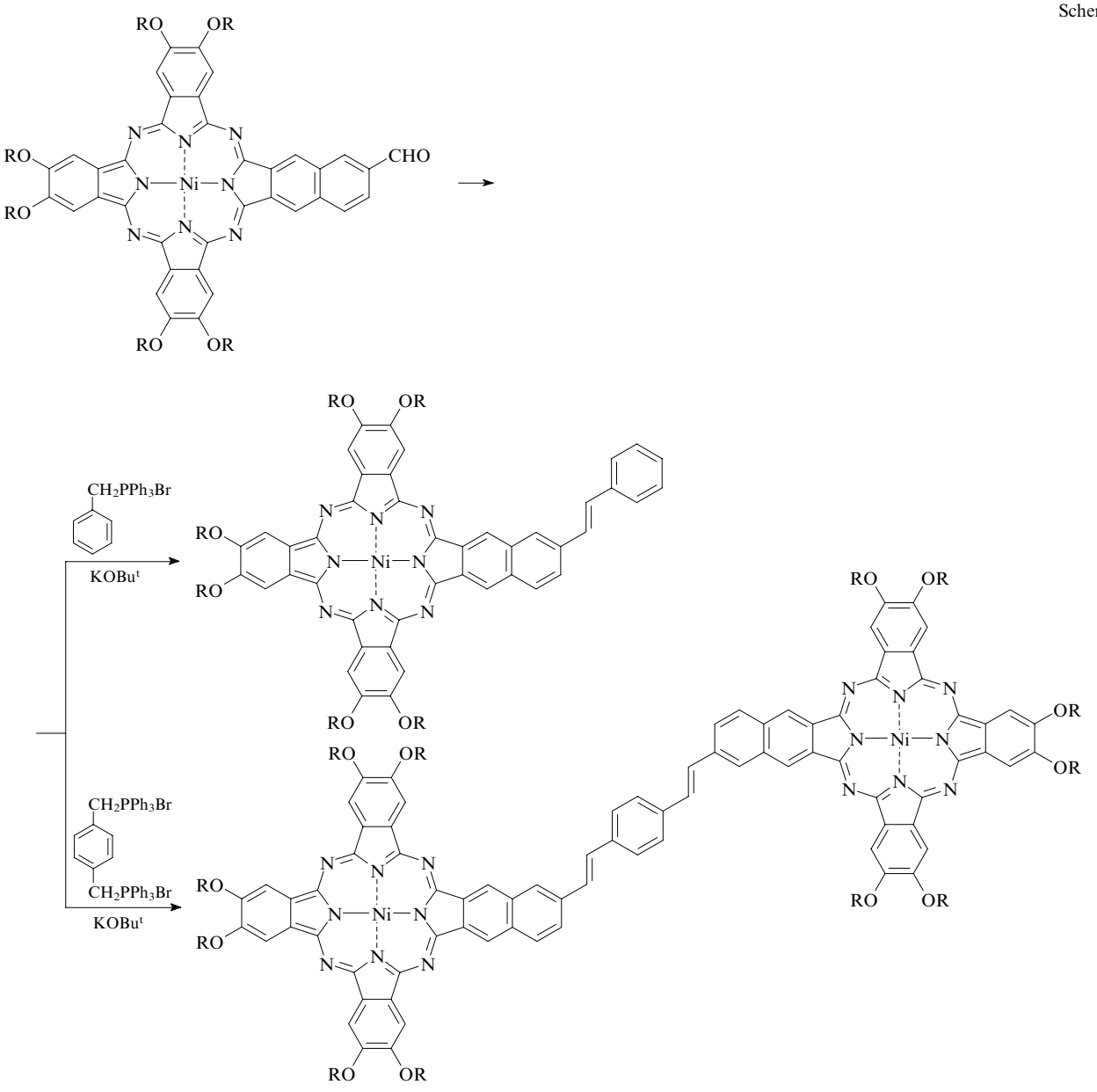
A nitro group as an electron-withdrawing substituent activates the aromatic nucleophilic substitution. Furthermore, it can readily be reduced to amino and diazo groups, which can further be involved in the preparation of various alkylation and coupling products.

One possible way to modify nitro groups in non-symmetrically substituted phthalocyanines, *viz*., the reduction to the amino group, has been mentioned above in the description of the synthesis of monoiodo-substituted phthalocyanine **7**. A unique synthesis of planar trinuclear phthalocyanine **25** (Scheme 8) is based on the easy alkylation of the amino group.[19]

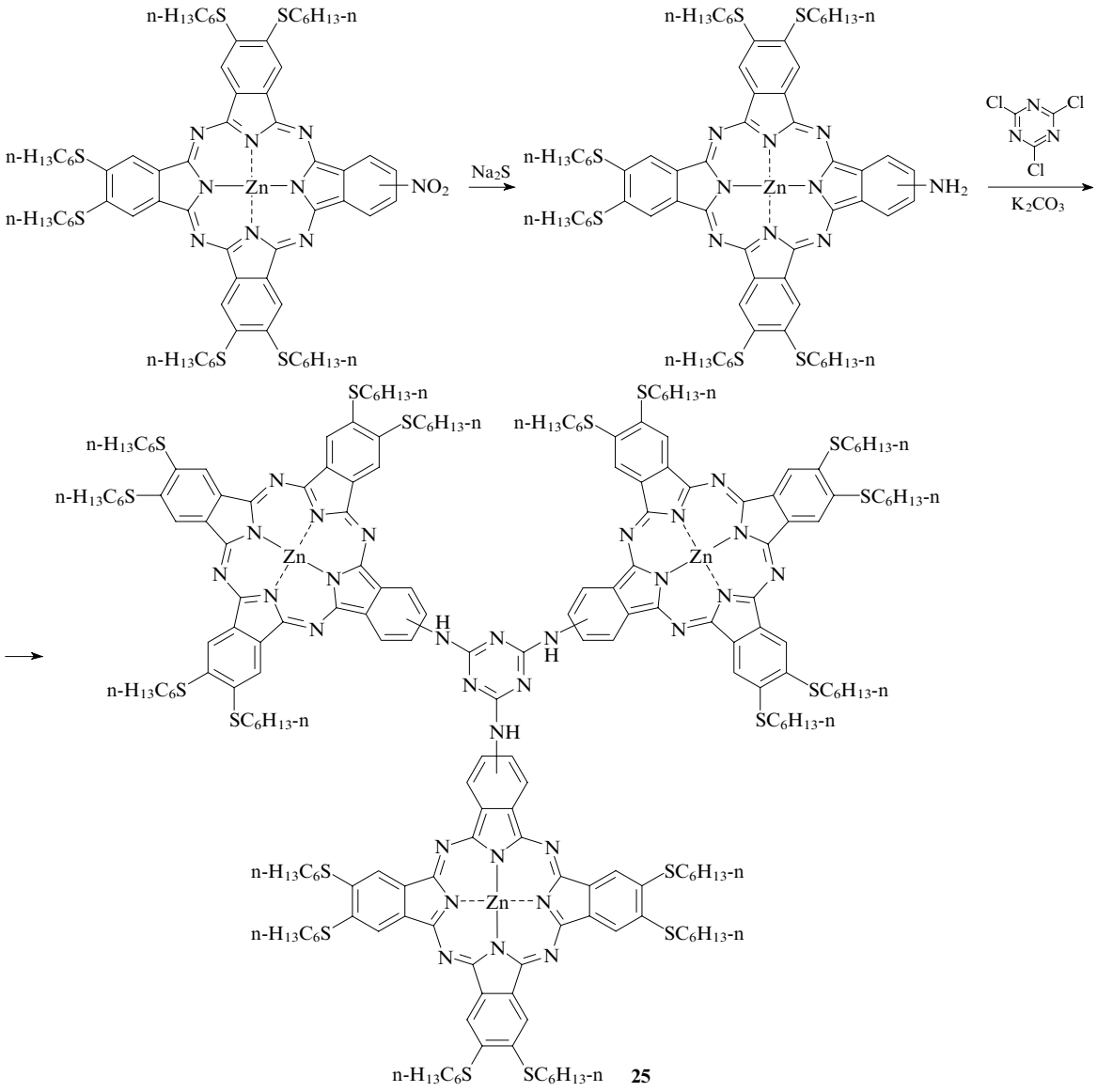
A similar alkylation reaction has been realised for monohydroxy-substituted phthalocyanine.[21]

Yet another method for the structure modification of mononitrophthalocyanines, *viz*., the nucleophilic substitution of the nitro group, has been developed[78,79] for the synthesis of new functionally substituted phthalocyanines, which served as precur-

Scheme 7

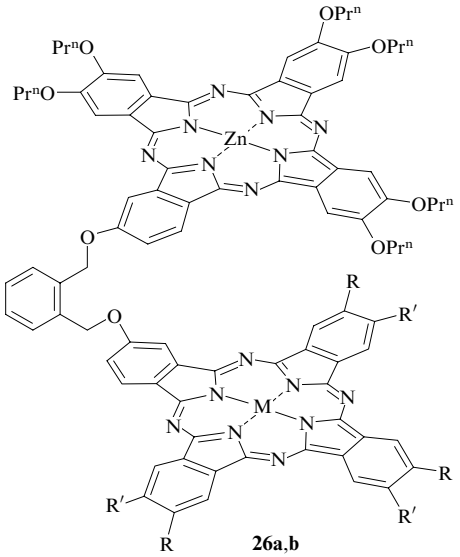


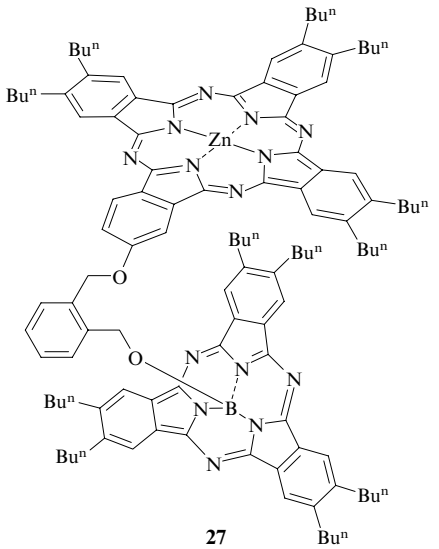
Scheme 8



sors of binuclear clamshell phthalocyanines **26a**,**b** [80] and a heteronuclear complex phthalocyanine – spacer – subphthalocyanine **27**.[81, 82]

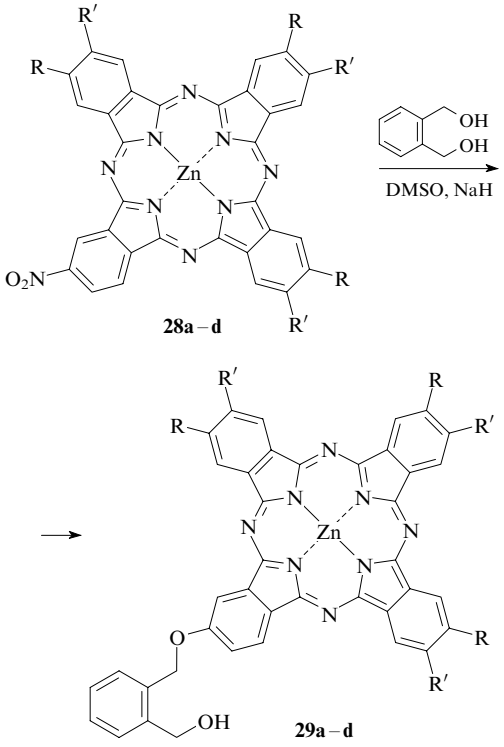
The *ipso*-substitution of the nitro group is typically accomplished in substrates with strong electron-withdrawing substituents, such as CN groups. Such an approach is used





R = Bu^t, R′ = H, M = Zn (**a**); R = R′ = OPr^n, M = Cu (**b**).

for the synthesis of bis(phthalonitriles)[83] and the majority of alkoxy-substituted phthalonitriles.[27,84] However, this reaction has not been applied to phthalocyanines so far. The feasibility of the nucleophilic substitution of a nitro group in non-symmetrically substituted phthalocyanines **28a–d** has been demonstrated for the first time and the optimum reaction conditions have been found by our group.[78] The target complexes **29a–d** containing a benzyl alcohol fragment in a peripheral substituent were isolated in preparative yields.

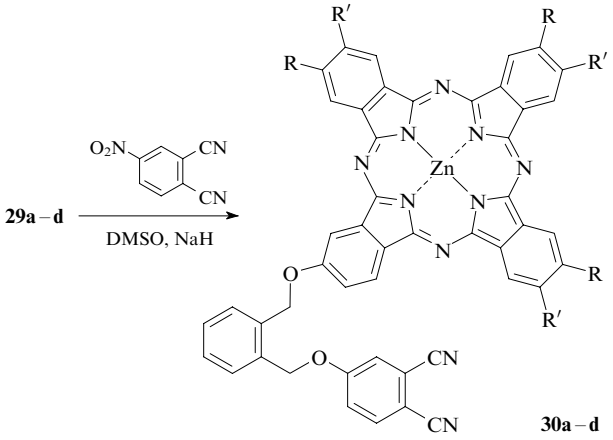


R = R′ = Et (**a**), Bu^n (**b**), OPr^n (**c**); R = Bu^t, R′ = H (**d**).

When K_2CO_3 was used as the base, the reaction was completed in 50 h and the products **29a–d** formed in trace concentrations. The use of a stronger base, *viz*., sodium hydride, made it possible to both accelerate the reaction and increase the yields of the target products **29a–d**. The course of the reaction can conveniently be monitored by means of UV-Vis absorption spectroscopy (Fig. 1). The starting nitrophthalocyanines **28a–d** manifest split Q bands. The products **29a–d** devoid of both electron-releasing and -withdrawing substituents should be characterised by spectra typical of mononuclear metal complexes, which is indeed observed experimentally.

As the nucleophilic substitution reaction proceeds, the splitting of the Q band gradually disappears. Meanwhile, it was found that a prolonged contact of phthalocyanines with a strong base should be avoided, since it results in a gradual decomposition, which was confirmed by control experiments.

A similar reaction of the aromatic nucleophilic *ipso*-substitution was utilised for the synthesis of phthalocyanines **30a–d** containing reactive phthalonitrile fragment.[78]



R = R′ = Et (**a**), Bu^n (**b**), OPr^n (**c**); R = Bu^t, R′ = H (**d**).

Phthalocyanines **30a–d** are synthetic precursors of non-symmetric binuclear clamshell phthalocyanines. The feasibility of the synthesis of such compounds has been demonstrated with complex **30c** as an example.[80] The co-cyclisation of phthalocyanine **30c** with substituted phthalonitriles in the presence of copper and zinc acetates afforded binuclear phthalocyanines **26a**,**b**.

The presence of a benzylic OH group in complexes **29a–d** enables the synthesis of heteronuclear complexes and supramolecular structures. In particular, the reaction of phthalocyanine **29b** with boron μ-chlorohexabutylsubphthalocyanine yields complex **27** involving a phthalocyanine and a subphthalocyanine moieties.

Therefore, the functionalisation of monosubstituted phthalocyanines together with the structure modification of non-symmetrically substituted phthalocyanines considered above make it possible to prepare diverse bi- and polynuclear (including heteronuclear) macrocyclic compounds.

IV. Prospects for the use of non-symmetrically substituted phthalocyanines

Non-symmetrically substituted phthalocyanines attract attention not only from synthetic chemists but also from physicists. Primarily, this concerns complexes of the push–pull type. The

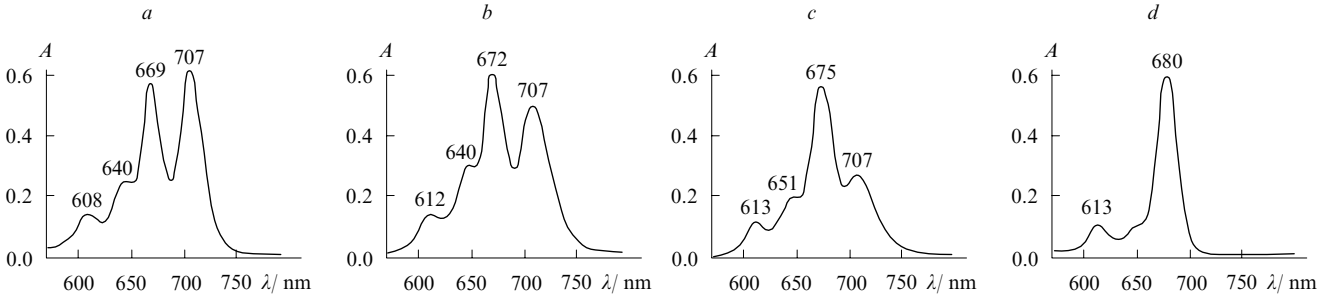
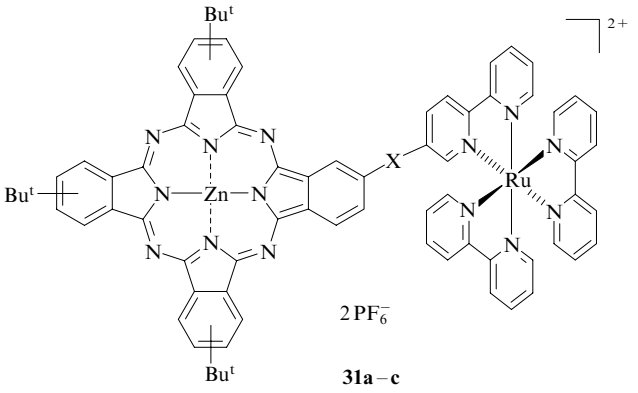


Figure 1. Changes in the UV-Vis absorption spectra (in DMSO) in the course of the nucleophilic substitution of the nitro group in phthalocyanine **28d** in the presence of NaH at 25 °C.
Reaction time (min): 5 (*a*), 15 (*b*), 30 (*c*), 45 (*d*).

simultaneous presence of substituents of the opposite character modifies, first of all the spectral properties of these macrocyclic compounds.[31,46,78] In particular, an intramolecular electron transfer from a donating to a withdrawing substituent has been observed in A_3B phthalocyanines.[11,14,47]

Non-symmetrically substituted phthalocyanines possess no inversion centre and thus they are prone to the formation of oriented dipoles upon irradiation with coherent light. They manifest non-linear optical properties and thus can be used for the second harmonic generation.[11,12] Furthermore, it was found that these phthalocyanines readily form Langmuir – Blodgett films,[11–14] which significantly facilitates the above studies.

Recently, the capability of fullerene-substituted A_3B phthalocyanines to separate and accumulate for a long time electric charges in a solid phase has attracted considerable attention. A possible application of such compounds as components of solar cells has already been demonstrated.[6,9] The chemical conversion of solar energy was achieved with heteronuclear complexes zinc phthalocyanine – ruthenium(II) tris(bipyridine) **31a**–**c**.[5]



31a–**c**

X = CH═CH (**a**), NHCO (**b**), C≡C (**c**).

Thus, non-symmetrically substituted phthalocyanines are very promising compounds and the progress in the methods for their synthesis will certainly extend fields of their practical utilisation.

* * *

The well-known methods for the formation of a phthalocyanine macrocycle has recently been supplemented with regioselective reactions giving rise to new classes of macrocyclic compounds and unveiling new avenues in the synthesis of supramolecular structures for emerging areas of science and technology. The methods for the synthesis and structure modification of non-symmetrically substituted phthalocyanines are being successfully developed, which makes the macrocyclic compounds accessible for the investigations and practical applications. We hope that the number of structurally diverse non-symmetrically substituted phthalocyanines will expand substantially in the nearest future and some day they will come into practice as advanced functional materials.

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