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Synthesis of phthalocyanines with an extended system of π-electron conjugation

T V Dubinina, L G Tomilova, N S Zefirov

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Abstract. Synthetic approaches to phthalocyanines with an extended system of π-electron conjugation are described. Compounds of planar and sandwich structure are presented that possess intensive absorption in the near-IR region of the spectrum. Particular attention is devoted to electronic absorption spectra of these systems and their correlation with structure. The bibliography includes 97 references.

I. Introduction

Phthalocyanines which possess an extended system of π-electron conjugation (hereinafter, π-system) attract attention owing to absorption in the near-IR region. This feature allows for consideration of these compounds as promising objects for the creation of photovoltaic elements,[1] photosensitizers for photodynamic therapy of hypodermal tumours[2, 3] and IR labels.[4] The main features that favourably distinguish phthalocyanine complexes from porphyrin complexes are their high thermal and photochemical stability, the presence of a narrow Q-band in electronic absorption spectra and high extinction coefficients ($\log\varepsilon \geqslant 5$). Moreover, owing to the high quantum yields of luminescence,[2] phthalo- and naphthalocyanine complexes can be considered as promising luminophores.

The first annulated analogues of phthalocyanines, tetra-3,4-benzophthalocyanines or 1,2-naphthalocyanines, were synthesized in 1936;[5] and in 1938, a bathochromic shift of the absorption maximum of these compounds compared to those of phthalocyanines was revealed.[6] One of the main drawbacks of 1,2-naphthalocyanines is a possibility of existence of four geometric isomers differing in the mutual disposition of naphthalene fragments (C_{4h}, C_s, D_{2h} and C_{2v} symmetry), which creates additional complications during their isolation and identification. Therefore, isomers of 1,2-naphthalocyanines — 2,3-naphthalocyanines — were prepared.[5] However, their application scope was limited due to the low solubility of these compounds in common organic solvents.[7] This drawback was overcome by the introduction of substituents around the naphthalocyanine moiety periphery.[8] Further extension of the π-system by structural modifications of the macrocycle was reported.[4, 9, 10]

Nowadays, there are two main groups of phthalocyanines with extended system of π-conjugation: planar and sandwich complexes. The planar phthalocyanines are compounds which contain one or several macrocycles lying in one plane, without considering spatial arrangement of the peripheral substituents; therewith, the extension of the π-system occurs owing to the linear annulation. Structures of the sandwich type, which usually include a rare-earth metal ion, feature axial interaction of the ligand π-systems that depends on the lanthanide ionic radius.

The goal of the present review is to generalize and analyze the published and authors' own data on synthesis of phthalocyanines with the extended π-system and to investigate the effect of this extension on the displacement of absorption bands in the near IR region. Because of the existence of different terminologies for designation of the compounds under consideration, the current review will utilize the most popular terms. In bi-, tri-, and polynuclear phthalocyanine complexes of a planar structure, the number of central metal ions (if its valency is $\geqslant 2$) is two, three, and > 3, respectively. Di- and triphthalocyanines are sandwich complexes; the numeral in their names corresponds to the number of ligands involved.

The present review will not consider sandwich heteroleptic complexes of naphthalocyanines, since they were exhaustively considered in another publication.[11] Planar

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mono- and binuclear complexes bearing heterocyclic fragments [12, 13] are not discussed either, since these compounds predominantly possess a porphyrazine nature, and systematization of the methods for their synthesis and properties is a topic of a separate publication.

To date, there are no single-crystal XRD data for almost any class of phthalocyanines with the extended π-system (planar polynuclear phthalo- and naphthalocyanines, lanthanide dinaphthalocyanines, hybrid sandwich-planar compounds), and only few papers deal with the data of powder X-ray diffraction (see, *e.g.*, Ref. 14). All phthalocyanines are characterized, apart from UV/Vis spectra, by means of matrix assisted laser desorption ionization mass spectrometry with a time-of-flight mass analyzer (MALDI TOF), the mass spectra exhibiting most often only a molecular ion peak. Original works containing fast atom bombardment (FAB) mass spectra, which typically show fragment ions, are rare.[15] In a series of papers, phthalocyanine complexes were additionally characterized by high resolution mass spectrometry [16] or elemental analysis.[17] Due to an aggregation effect, the ^{1}H and ^{13}C NMR spectra are very complicated and are specific to each class of compounds; their unambiguous interpretation requires the introduction of various additives into NMR tubes [18] and quantum chemical calculations.[19] In this respect, the present review will focus on the detailed description of electronic spectra, which are characteristic of structures of each type and reflect the structure–property correlation.

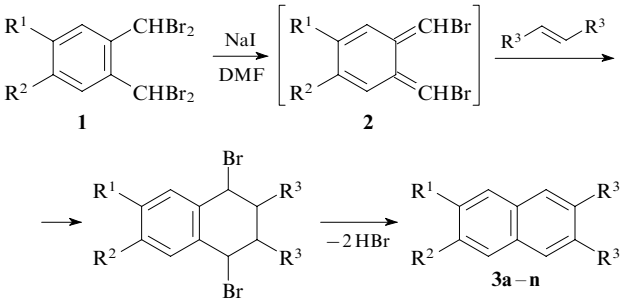
II. Synthesis of planar phthalocyanines with an extended π-system

The simplest analogues of phthalocyanines that are most extensively studied in recent years are 2,3-naphthalocyanines. One of the key stages in the preparation of these compounds and their derivatives is the synthesis of initial dinitriles, which can be carried out using approaches outlined below.

1. The Diels–Alder reaction in the synthesis of substituted 2,3-dicyanonaphthalenes

Most of approaches to the synthesis of substituted 2,3-dicyanonaphthalenes are based on the Diels–Alder reaction involving *o*-quinodimethane derivatives as dienes.[20] A series of substituted 2,3-dicyanonaphthalenes and their analogues was obtained [21–26] according to Scheme 1.

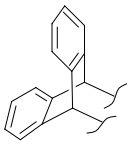
Scheme 1



The starting compounds in this synthetic method are bis(dibromomethyl)benzenes **1**, which are converted to highly reactive *o*-quinodimethanes **2** under the action of NaI. The reaction of these dienes with maleic or fumaric acid derivatives followed by the aromatization leads to substituted dinitriles **3a–n** (Table 1).

Table 1. Yields of compounds **3a–n**.

Compound **3**	R^1	R^2	R^3	Yield (%)	Ref.
a	H	H	CN	98	21
b	H	Br	CN	92	21
c	H	NO_2	CN	89	21
d	H	CN	CN	78	21
e	H	Bu^t	CN	87	21
f	Cl	Cl	CN	91	21
g	Br	Br	CN	95	21
h	see [a]		CN	88	22
i	3-$CF_3C_6H_4$	3-$CF_3C_6H_4$	CN	67	23
j	$CMe_2(CH_2)_2CMe_2$		CN	76	26
k	CN	CN	CN	33	24
l	H	OBz	CN	83	25
m	CN	CN	see [b]	80	24
n	CN	CN	CO_2H	64	24

[a] $R^1–R^2$ =  ; [b] $R^3–R^3$ = C(O)N(Ph)C(O).

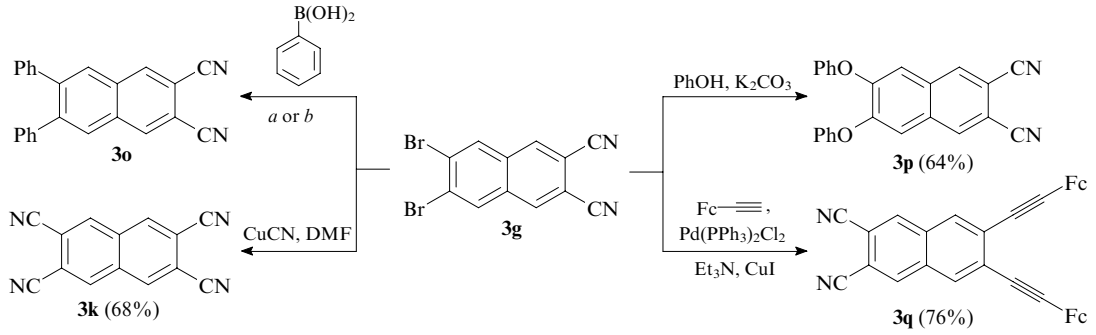
As can be seen from the data of Table 1, the introduction of electron-withdrawing substituents into the molecule of *o*-quinodimethane derivative **2** leads, in most cases, to a reduction in the yield of the Diels–Alder product (see compounds **3d**,**i**,**k**,**m**,**n**), which is in line with the normal electron requirements. A low yield of dinitrile was also observed in the case of diene **3j** bearing sterically hindered substituents.

Dibromo-substituted dinitrile **3g** attracted particular interest of researchers, since it can be used as the initial compound in the synthesis of substituted dicyanonaphthalenes (Scheme 2).

Based on dibromide **3g**, we obtained novel substituted dinitriles **3o** [16, 19] and **3p**.[27] Several approaches to the synthesis of dinitrile **3o** were studied. The first one involved two stages: the Diels–Alder reaction between compound **1** and the corresponding *trans*-stilbene followed by cyanation of the resulting dibromide by the Rosenmund–von Braun reaction (see Scheme 1). However, this approach was not implemented, since, even the first stage gave the corresponding compound **2** in only trace amount. The second approach, described in Scheme 2, consisted in the Suzuki–Miyaura cross-coupling between compound **3g** and phenylboronic acid. It was shown that the application of the Pd(II) compounds instead of the Pd(0) compounds as catalysts allows for an increase in the yield of target dinitrile **3o** owing to the presence of two active groups, namely, the Cl atoms, in the catalyst molecule.[16]

Dintrile **3p** was obtained by the nucleophilic substitution of the bromine atoms in the presence of potassium carbonate as a base.[27] In this case, the yield of product **3p** appeared to be slightly lower than the yield of the analogous phenyloxy-substituted phthalodinitrile.[28] This feature stems from the greater remoteness of the electron-withdrawing cyano groups from the site of nucleophilic attack in the

Scheme 2



(*a*) $Pd(PPh_3)_4$ (yield 61%); (*b*) $Pd(PPh_3)_2Cl_2$ (yield 85%); Fc is ferrocenyl

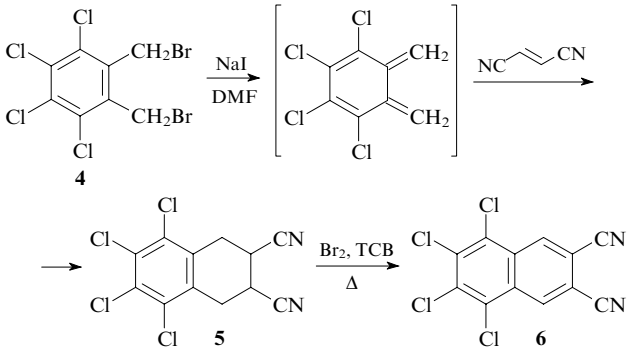
molecule of naphthalodinitrile compared with phthalodinitrile.

In order to introduce additional redox-active sites into the phthalocyanine molecule, 6,7-bis(ferrocenylethynyl)-substituted dinitrile **3q** was obtained from compound **3g** by the Sonogashira reaction.[29]

The cyanation of dinitrile **3g** by the Rosenmund–von Braun method affords tetracyano-substituted naphthalene **3k**.[18] An important role in this reaction is played by the molar ratio of compound **3g** and CuCN, which, as it was shown earlier,[30] must be 1 : 5 to achieve a high yield of the target nitrile. This synthetic route to tetranitrile **3k** is most preferred, since in another approach[24] which utilizes 4,5-dimethylpthalonitrile the target product is formed in a low total yield (11%). Upon reproduction of this method, we showed[18] that radical bromination of 4,5-dimethylphthalonitrile already affords hardly separable less brominated products, which precluded isolation in a high yield and reliable characterization of compound **3k** in the mentioned study.[24]

In the synthetic approach to chloro-substituted dicyanonaphthalenes presented in Scheme 3, the starting compound is dibromo derivative **4**.[31] In this case, an additional stage of aromatization of tetrahydronaphthalene **5** is required. The yield of product **6** at the last stage comprises 86%.

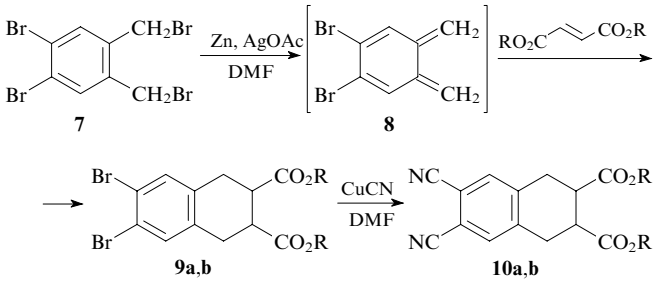
Scheme 3



TCB is 1,2,4-trichlorobenzene

Yet another example of the synthesis of substituted tetrahydronaphthalenes, which were used subsequently as the initial compounds in the synthesis of dicyanonaphthalenes, was described.[32] The target dintiriles were obtained based on dibromo derivative **7** (Scheme 4).

Scheme 4



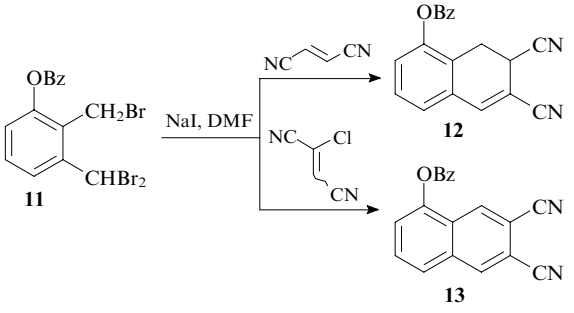
R = Me (**9a**, yield 42%; **10a**, 49%), Et (**9b**, 40%; **10b**, 87%)

The starting tetralin was synthesized by the Diels–Alder reaction from 1,2-bis(bromomethyl)-4,5-dibromobenzene (**7**) and the corresponding dialkyl fumarate. *o*-Quinodimethane derivative **8** was obtained *in situ* under the action of zinc activated with silver acetate. The resulting 2,3-bis(alkoxycarbonyl)-6,7-dibromo-1,2,3,4-tetrahydronaphthalenes **9a**,**b** were then introduced into the Rosenmund–von Braun cyanation, which yielded compounds **10a**,**b**.

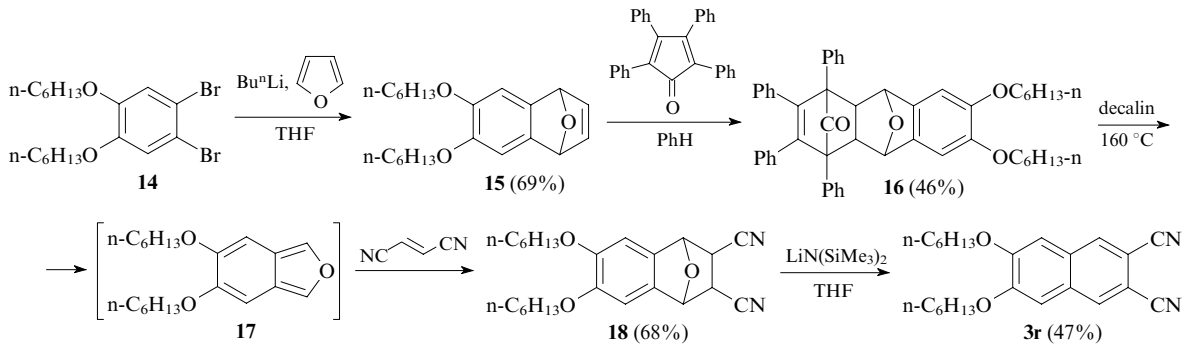
Earlier it was shown[33] that a dibromide : DMF mass ratio of 1 : ⩾10 is a necessary condition for the cyanation of aromatic *o*-dibromides. This allows terminating the process after dinitrile formation preventing the subsequent formation of copper phthalocyanine.

It was reported[34] that application of tribromide **11** as the starting compound in the synthesis of substituted 2,3-dicyanonaphthalenes leads to derivative **12**, which does not form an aromatic naphthalene system under reaction conditions. However, the replacement of fumarodinitrile by a mixture of chlorofumaro- and chloromaleo-dinitriles afforded compound **13** (Scheme 5). The yield of the target product was 20%, which is several times lower than the yields of substituted 2,3-dicyanonaphthalenes synthesized from tetra- and dibromides (see Schemes 1, 3).

Scheme 5



Scheme 6



A synthesis of 6,7-di(hexyloxy)-2,3-dicyanonaphthalene (**3r**) from bromo derivative of pyrocatechol was proposed [34] (Scheme 6). This route includes three sequential diene syntheses. At the first stage, the diene is furan and the dienophile is dehydrobenzene derivative obtained from dibromide **14**. The reaction of compound **15** with tetraphenylcyclopentadiene affords adduct **16**. Heating of this compound in decalin leads, as a result of the retro Diels–Alder reaction, to isobenzofuran **17**, which reacts *in situ* with fumarodinitrile, yielding compound **18**. Upon treatment with lithium bis(trimethylsilyl)amide, the latter converts to dinitrile **3r**.

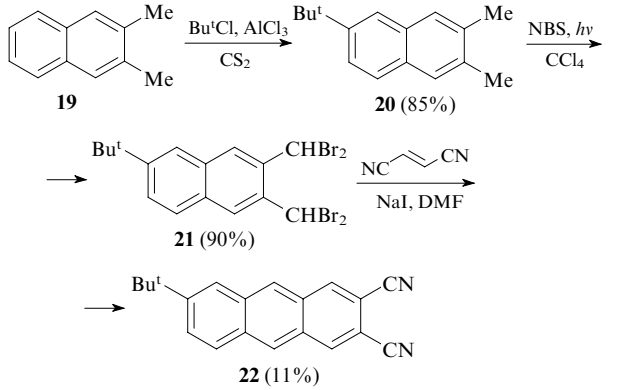
2. Synthesis of annulated derivatives of 2,3-dicyanonaphthalenes

A key stage in the synthesis of most annulated derivatives of 2,3-dicyanonaphthalenes is also the Diels–Alder reaction.

The synthesis of 2,3-dicyano-substituted anthracene based on 2,3-dimethylnaphthalene (**19**) was reported.[35] Compound **19** was alkylated with *tert*-butyl chloride in the presence of aluminium chloride, resulting in 6-*tert*-butyl-2,3-dimethylnaphthalene (**20**). The bromination of the latter under irradiation afforded tetrabromide **21**, which was introduced into the Diels–Alder reaction with fumarodinitrile. As a consequence, target 6-*tert*-butyl-2,3-dicyanoanthracene (**22**) was formed (Scheme 7).

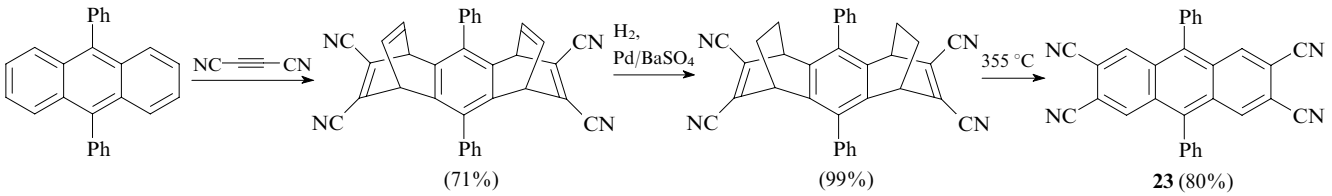
A synthesis of cyano-substituted anthracene **23** using 9,10-diphenylanthracene as the starting compound was

Scheme 7

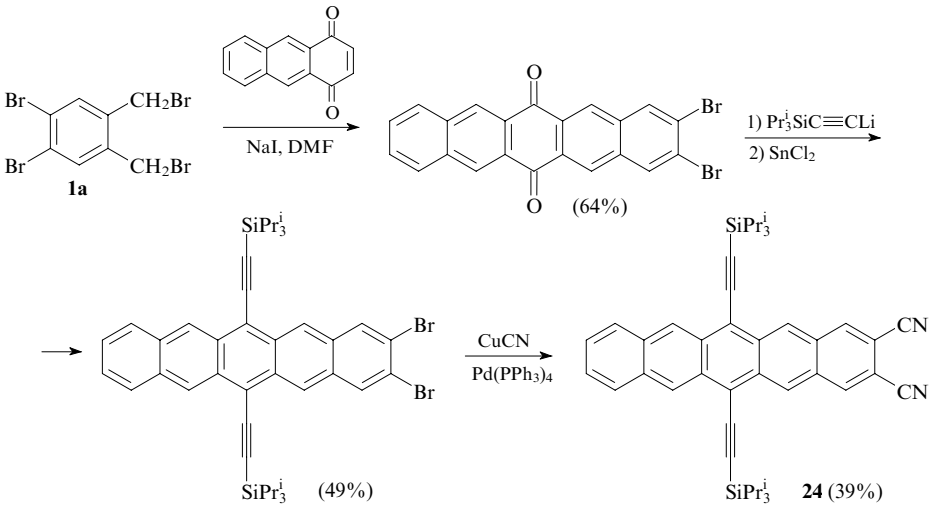


NBS is *N*-bromosuccinimide

Scheme 8



Scheme 9

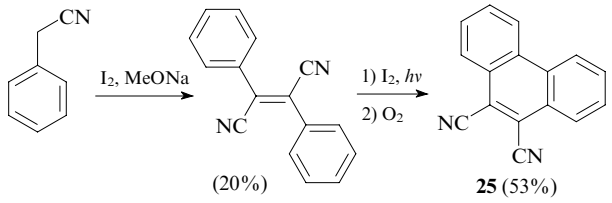


proposed [36] (Scheme 8). This approach includes the Diels–Alder reaction, hydrogenation, and subsequent high-temperature aromatization.

Moreover, using the Diels–Alder reaction, the substituted dicyano- and tetracyanopentacenes were synthesized from dibromo-*o*-xylene derivative **1a**.[37] For example, the application of 1,4-anthraquinone as a dienophile in the Diels–Alder reaction yielded dicyanopentacene **24** (Scheme 9).

9,10-Dicyanophenanthrene (**25**) was obtained based on phenylacetonitrile.[38] The oxidative coupling of the starting compound in the presence of sodium methoxide and iodine leads to the corresponding *trans*-dicyanostilbene, which undergoes photocyclization followed by the aromatization under the action of iodine (Scheme 10).

Scheme 10



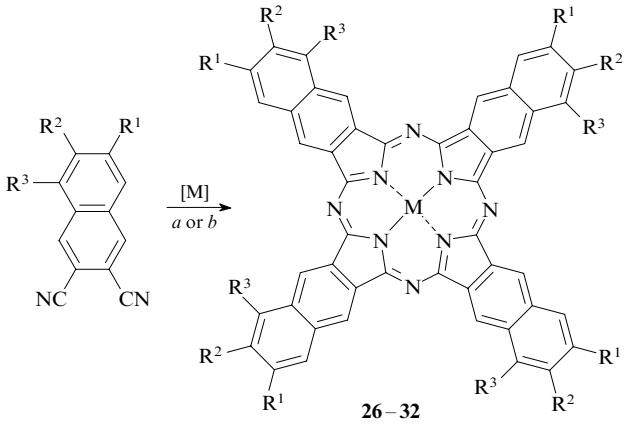
3. Synthesis of 2,3-mononaphthalocyanines

a. Template synthesis in melt

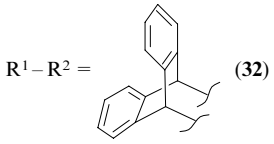
The synthesis of 2,3-naphthalocyanines can be carried out in a melt of the starting dinitrile (Scheme 11, conditions *a*) or in the presence of a solvent (conditions *b*). Method *a*, which is simpler and more facile, is used most frequently, as in this case, the starting dinitrile serves simultaneously both as a reactant and as a reaction medium.

The possibility of the synthesis of 2,3-naphthalocyanine complexes *via* fusing together 2,3-dicyanonaphthalene and the corresponding metal was mentioned for the first time in the work of Bradbrook and Linstead,[5] published in 1936. However, the reaction conditions, the yields of the target compounds, and their properties were not described. The detailed synthetic procedure and the spectral properties of 2,3-naphthalocyanines were reported later.[7] The authors obtained unsubstituted 2,3-naphthalocyanine and its metal complexes **26a–c**. The complexes synthesized by fusing together 2,3-dicyanonaphthalene with the corresponding metal salts (acetates or chlorides) or directly with metals (*e.g.*, magnesium chips). The reaction conditions are presented in Table 2. The authors point out that the application of metal chlorides in the presence of a solvent (1-bromonaphthalene) affords partially chlorinated naphthalocyanine complexes as by-products, and the yields of the target compounds range from 12% to 67%.

Scheme 11



[M] is metal or metal salt; (*a*) fusion, (*b*) solvent;
$R^2 = R^3 = H$: $R^1 = H$ (**26**), Bu^t (**27**); $R^1 = Bu^t$, $R^2 = H$, $R^3 = Br$ (**28**);
$R^3 = H$: $R^1 = R^2 = 3\text{-}CF_3C_6H_4$ (**29**), $3\text{-}CF_3C_6H_4O$ (**30**), FcC≡C (**31**),



The main advantages of 2,3-naphthalocyanines compared to analogous 1,2-naphthalocyanines are the absence of isomers and the higher thermal and chemical stability. However, these complexes are soluble in sulfuric acid but are poorly soluble in organic solvents, which essentially complicates their isolation and identification.[7]

In order to increase the solubility of 2,3-naphthalocyanines, by analogy with phthalocyanine complexes, tetra-6-(*tert*-butyl)-2,3-naphthalocyanines **27** were obtained [8] (see Table 2). These complexes were synthesized under milder conditions than unsubstituted 2,3-naphthalocyanines, namely, at 185–240 °C in an urea melt. A considerable increase in the solubility allowed the authors to use column chromatography for purification and record the electronic absorption spectra of these compounds in a wide wavelength range.

Fusing together dinitriles with metal salts in the presence of urea and ammonium sulfate [10] at 220–230 °C afforded metal complexes **28** based on 5-bromo-7-*tert*-butyl-2,3-dicyanonaphthalene in 15%–50% yields.

Upon comparison of the data presented in Table 2, it is obvious that the yields of substituted 2,3-naphthalocyanines

Table 2. Template synthesis of 2,3-naphthalocyanine complexes **26–28** in melt ($R^2 = H$).

Compound	R^1	R^3	M	[M]	Fusing conditions	Yield (%)	Ref.
26a	H	H	Cu	CuCl	ammonium molybdate, 260–270 °C, 5–6 h	58	7
26b	H	H	VO	VCl_3	NH_4VO_3, 260–270 °C, 5–6 h	62	7
26c	H	H	Mg	Mg	ammonium molybdate, 260–270 °C, 5–6 h	64	7
27a	Bu^t	H	Cu	CuCl	ammonium molybdate, 230–240 °C, 3 h	42	8
27b	Bu^t	H	VO	VCl_3	urea, 185–195 °C, 30 min	39	8
27c	Bu^t	H	Co	$CoCl_2$	urea, 210–215 °C, 1 h	28	8
28a	Bu^t	Br	Cu	CuCl	urea, $(NH_4)_2SO_4$, ammonium molybdate, 220 °C, 4 h	35	10
28b	Bu^t	Br	VO	VCl_3	urea, $(NH_4)_2SO_4$, ammonium molybdate, 220 °C, 4 h	38	10

are lower than those of unsubstituted analogues. However, it should be taken into account that an increase in the solubility of substituted 2,3-naphthalocyanines enabled their isolation by chromatographic methods. Just this circumstance was likely to lead to a reduction in the yields but gave rise to more pure target compounds.

b. Template synthesis in solution

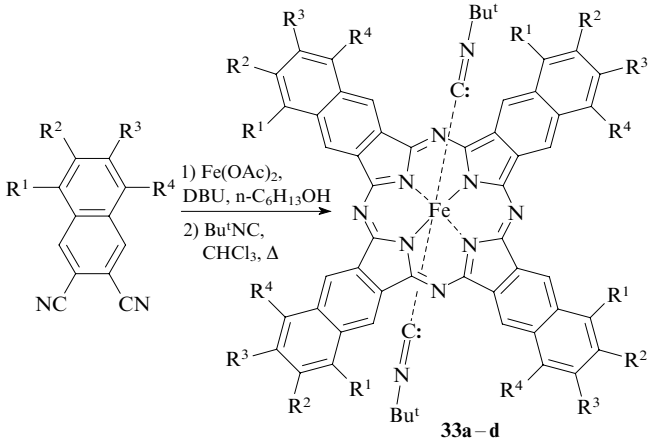
A number of publications [22, 23, 29] devoted to naphthalocyanine complexes with more complicated substituents describe their template synthesis in solution.

The application of quinoline and pentanol–octanol mixture (1 : 1 ratio) as solvents allowed the authors [23] to obtain magnesium and zinc octakis(3-trifluoromethylphenyl)- (**29**) and octakis(3-trifluoromethylphenoxy)-2,3-naphthalocyanines (**30**) in the yields ranging from 27% to 62%. As an example, Table 3 shows the conditions for synthesis of Zn complexes.

Zinc octakis(ferrocenylethynyl)-substituted naphthalocyanine **31** is formed upon refluxing of the reactants in n-pentanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base. As it was already mentioned, these substituents were introduced to create additional independent redox-active sites in the molecule.

By heating to 290 °C in 1-bromonaphthalene, the authors [22] obtained di(benzo)barrelene-substituted 2,3-naphthalocyanines **32**. The introduction of bulky substituents around the macrocycle periphery weakens intermolecular interactions and reduces the degree of aggregation of the target compounds both in solution and in films.

Scheme 12

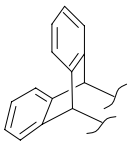


Compound **33**	R^1	R^2	R^3	R^4	Yield (%)
a	H	n-$C_6H_{13}O$	H	H	35
b	n-$C_6H_{13}O$	H	H	H	42
c	H	n-$C_6H_{13}O$	n-$C_6H_{13}O$	H	33
d	n-C_7H_{15}	H	H	n-C_7H_{15}	42

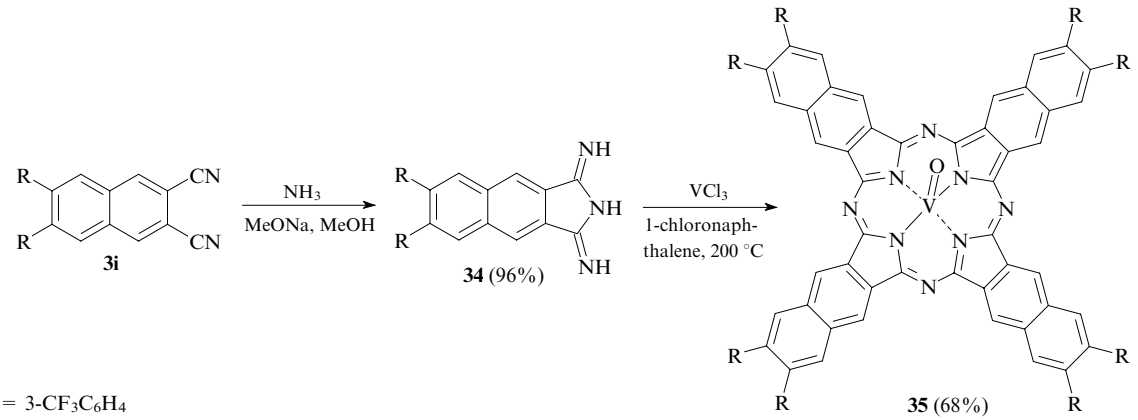
It was shown [34] that intermolecular interaction is also reduced by the introduction of axial substituents. For this purpose, iron alkoxy-substituted 2,3-naphthalocyanines were obtained by refluxing the corresponding reactants in hexanol in the presence of DBU (Scheme 12); on heating

Table 3. Template synthesis 2,3-mononuclear naphthalocyanines **29**–**32** in solution (R^3 = H).

Compound	$R^1 = R^2$	M	[M]	Conditions	Yield (%)	Ref.
29	3-$CF_3C_6H_4$	Zn	$ZnCl_2$	quinoline, 210 °C, 30 min	27	23
30	3-$CF_3C_6H_4O$	Zn	$ZnCl_2$	quinoline, 210 °C, 1 h	50	23
31	FcC≡C	Zn	$Zn(OAc)_2$	n-pentanol, DBU, 150 °C, 10 h	27	29
32a	see [a]	Cu	CuCl	urea, 1-bromonaphthalene, Na_2SO_4, ammonium molybdate, 290 °C, 3 h	10	22
32b	see [a]	VO	VCl_3	urea, 1-bromonaphthalene, Na_2SO_4, ammonium molybdate, 290 °C, 3 h	25	22

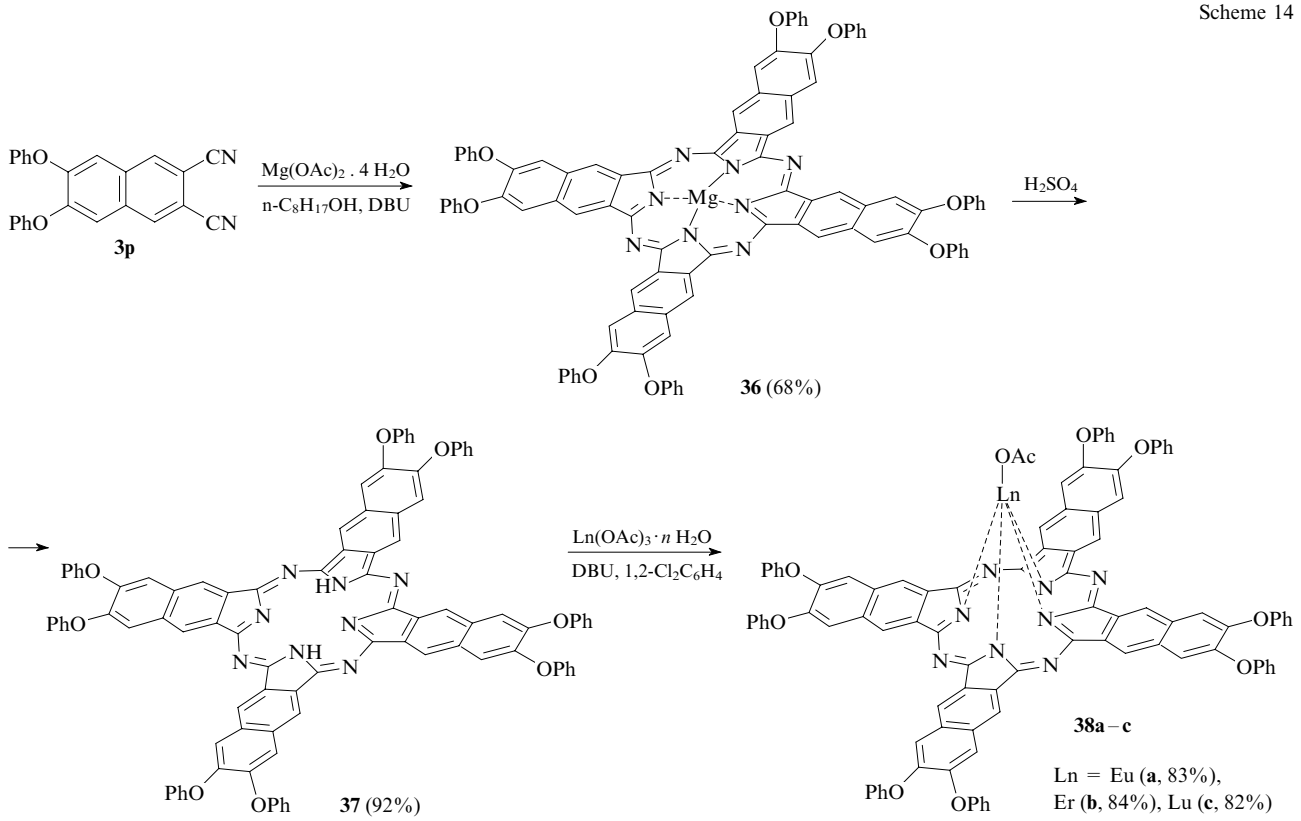
[a] R^1-R^2 = .

Scheme 13



R = 3-$CF_3C_6H_4$

Scheme 14



with *tert*-butyl isocyanide in chloroform, they form the corresponding axially substituted complexes **33a–d**.

To increase the activity of the starting 2,3-naphthalodinitrile in the template synthesis, diiminoisoindoline derivative **34** was synthesized[23] (Scheme 13). It is formed upon treatment of bis(3-trifluoromethylphenyl)-substituted 2,3-dicyanonaphthalene **3i** with gaseous ammonia in methanol in the presence of sodium methoxide.

Upon heating with vanadium chloride in 1-chloronaphthalene, compound **34** converts to oxovanadium complex **35**. The yield of a target product is twice higher than the yield of analogous 3-trifluoromethylphenoxy-substituted oxovanadium complex, which results from the corresponding dinitrile.

c. Synthesis based on a free ligand

Another approach to complexes of 2,3-naphthalocyanines is the synthesis based on a free ligand. Unsubstituted 2,3-naphthalocyanines were synthesized for the first time by the demetallation of disodium complexes, which result from refluxing of 2,3-dicyanonaphthalene with sodium isoamylate in isoamyl alcohol.[7] This method for synthesis of free ligands was used in most of works on the synthesis of substituted 2,3-naphthalocyanines (see, *e.g.*, works[10,26]). The yields of the target compounds did not exceed 26%.

An alternative approach based on the interaction of magnesium di(benzo)barrelene-substituted 2,3-naphthalocyanine **32** with concentrated sulfuric or trifluoroacetic acid or with gaseous hydrogen halides was reported.[22] However, in this reaction, too, the yield of the free ligand was not high.

tert-Butyl-substituted 2,3-naphthalocyanine complexes were obtained by refluxing a free ligand, namely, *tert*-butyl-substituted 2,3-naphthalocyanine, and the corresponding lanthanide acetates in DMSO.[39] The yield of the reaction products was about 50%.

The most efficient approach was implemented in our study to prepare lanthanide phenoxy-substituted naphthalocyanines.[27] Based on dinitrile **3p**, magnesium complex **36** was obtained. The yield of product **37** at the demetallation stage was raised almost to quantitative by dissolution of the initial magnesium complex in a small amount of THF followed by treatment with concentrated sulfuric acid (Scheme 14).

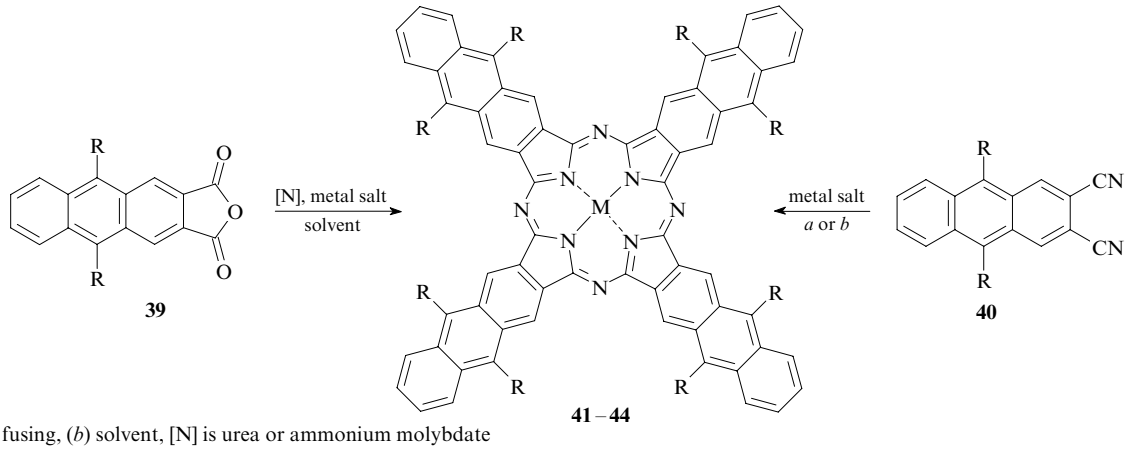
The reactions of ligand **37** with the corresponding lanthanide acetates afforded lanthanide complexes of 2,3-naphthalocyanines **38**, by analogy with the method for synthesis of lanthanide monophthalocyanines.[40] The base of choice was DBU. Owing to its coordination by the central metal ion, the formation of a mononaphthalocyanine is associated with steric restrictions, which hampers the subsequent formation of dinaphthalocyanine complex as a reaction by-product.

4. Synthesis of 2,3-mononaphthalocyanine derivatives

Based on anhydride **39** or dinitrile **40**, the first linearly annulated derivatives of 2,3-naphthalocyanines, anthracocyanines **41–44**, were obtained by the template synthesis in melt[41,42] or in a high-boiling solvent[42,43] (Scheme 15). According to this strategy, a series of metal complexes of unsubstituted and 9,10-substituted anthracocyanines was obtained, some of which are presented in Table 4. The researchers cited[42] also attempted to obtain a complex based on tetracene dinitrile, but they did not manage to isolate and characterize a product.

A paper[35] deals with the synthesis of cobalt *tert*-butyl-substituted anthracocyanine **45** by refluxing dinitrile **22** and

Scheme 15



(*a*) fusing, (*b*) solvent, [N] is urea or ammonium molybdate

Table 4. Template synthesis of anthracocyanines **41**–**44**.

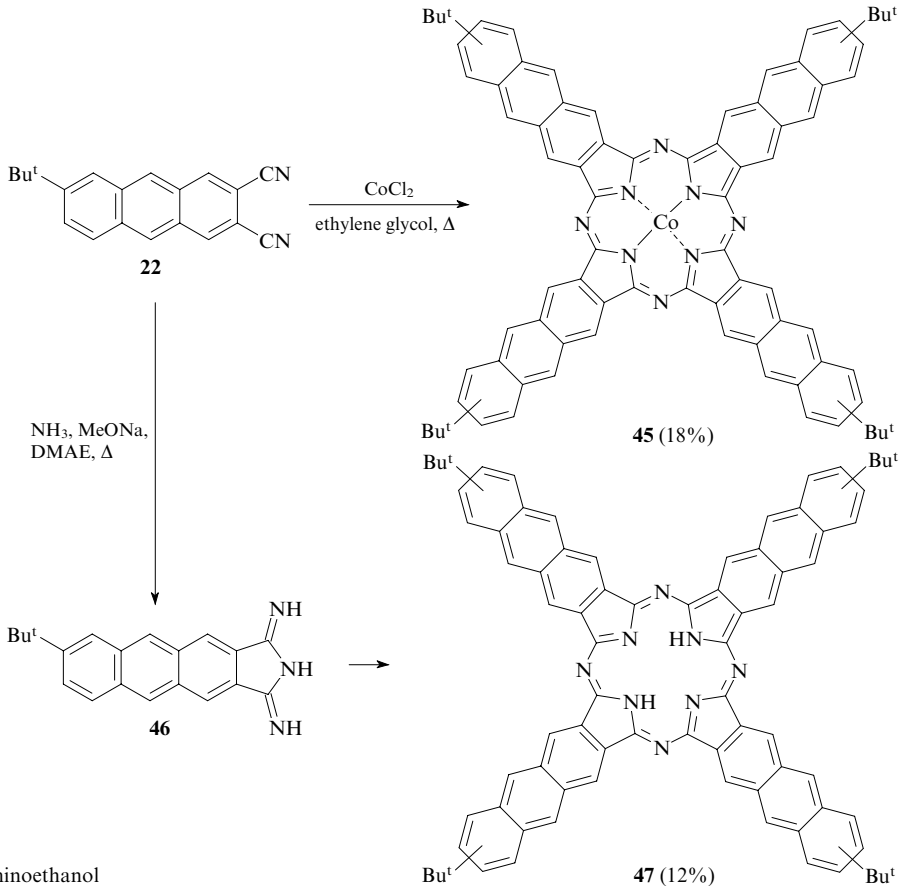
Compound	R	Metal salt (M)	Conditions	Yield (%)	Ref.
41a	H	VCl_3 (VCl)	urea, ammonium molybdate, 1-chloronaphthalene, 235 °C, 4 h	84	42
41b	H	$InCl_3$ (InCl)	ammonium molybdate, DMF, 220 °C, 2 h	–	43
42	Br	VCl_3 (VCl)	urea, ammonium molybdate, fusing, 300–310 °C, 5 h	86	42
43	Ph	VCl_3 (VCl)	urea, fusing, 200–290°C, 6 h	52	42
44	Ph	K_2PdCl_4 (Pd)	urea, 290 °C	20	41

cobalt chloride in ethylene glycol; the product yield appeared to be rather low (Scheme 16).

The free anthracocyanine ligand was obtained[35] from diiminoisoindoline derivative **46** (see Scheme 16). However, the authors do not mention the synthesis conditions and point out that compound **47** is less stable than the corresponding metal complexes. It decomposes during several days upon storage in the dark under nitrogen atmosphere, whereas metal complex **45** is stable under these conditions for a year.

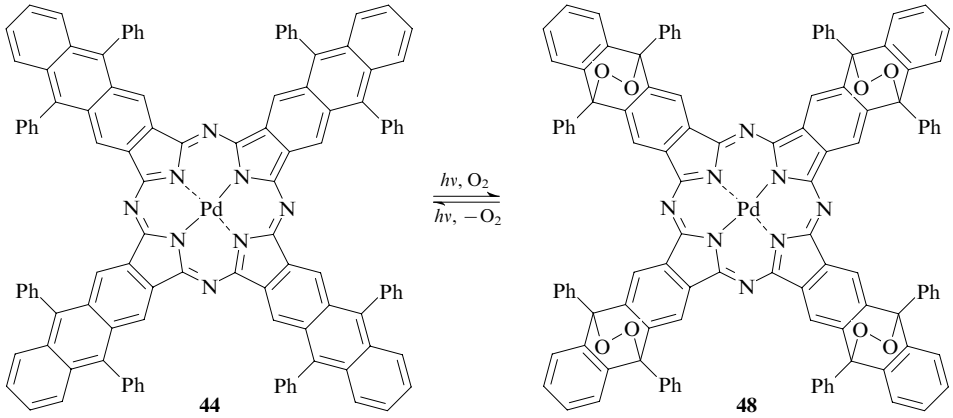
In general, the stability of linearly annulated monophthalocyanine derivatives reduces in the following series: phthalocyanines > 2,3-naphthalocyanines > anthracocyanines.[35] This fact can be explained by a decrease in the first oxidation potential, which is observed upon extension of the π-system.

Scheme 16



DMAE is 2-dimethylaminoethanol

Scheme 17



Furthermore, the low stability of anthracocyanines can be caused by the interaction with oxygen. To confirm this hypothesis, researchers[41,44] isolated adduct **48**, which results from the reaction of substituted anthracocyanine **44** with oxygen on exposure to light with the excitation wavelength of (λ_{ex}) > 750 nm (Scheme 17).

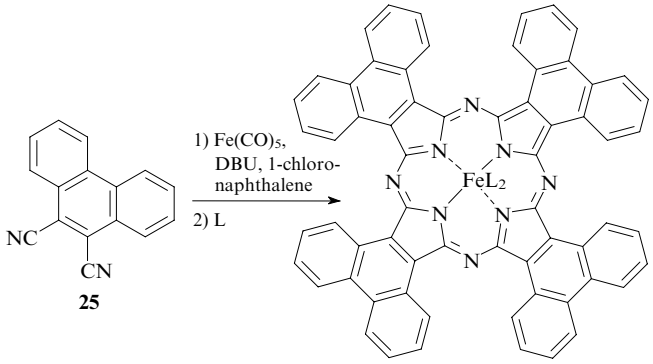
The formation of analogous endoperoxides of substituted anthracenes on exposure to solar light was known earlier[45] and was explained by the predominantly diene nature of the double bond of the anthracene central fragment.[46] This [4 + 2]-cycloaddition is partially reversible both for anthracene derivatives [45] and for anthracocyanines.[41,47] In the latter case, the elimination of oxygen is initiated by irradiation with nitrogen laser (λ_{ex} > 337 nm).

Compared to naphthalocyanines and anthracocyanines, other annulated derivatives of phthalocyanines are substantially less studied. Only several examples of generation of these systems are reported.

The synthesis of iron 9,10-phenanthrenocyanines **49** with different axial substituents was described.[38] Dicyanophenanthrene **25** was heated with iron pentacarbonyl in 1-chloronaphthalene in the presence of a catalytic amount of DBU in the temperature range of 220–250 °C, then the corresponding ligand was added, and the reaction mixture was stirred at 60 °C (Scheme 18).

As in the case of iron naphthalocyanine complexes **33** (see Scheme 12), the axial substituents were introduced to weaken intermolecular interactions and to simplify the isolation and spectral investigations of the target complexes. It should be noted that as regards spectral and electrochemical characteristics, phenanthrenocyanines are similar to 1,2-naphthalocyanines.[38]

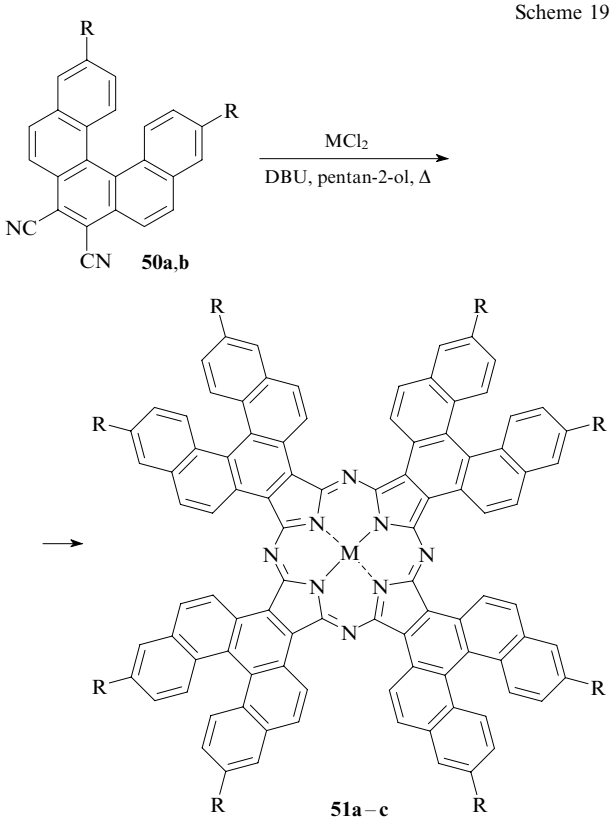
Scheme 18



L = Bu^{t}NC, BnNC, cyclo-C_6H_{11}NC

Based on 7,8-dicyano[5]helicene (3,4-dicyanodibenzo[*c*,*g*]phenanthrene, **50a**), complexes **51a**,**b**, which are phenanthrenocyanine analogues benzoannulated around the periphery, were synthesized for the first time[48] and were called by the authors helicenocyanines (Scheme 19). The subsequent publication[49] of the same authors deals with substituted helicenocyanine **51c** obtained in a similar manner from compound **50b** (the yield of the reaction product is not mentioned in the article).

Scheme 19

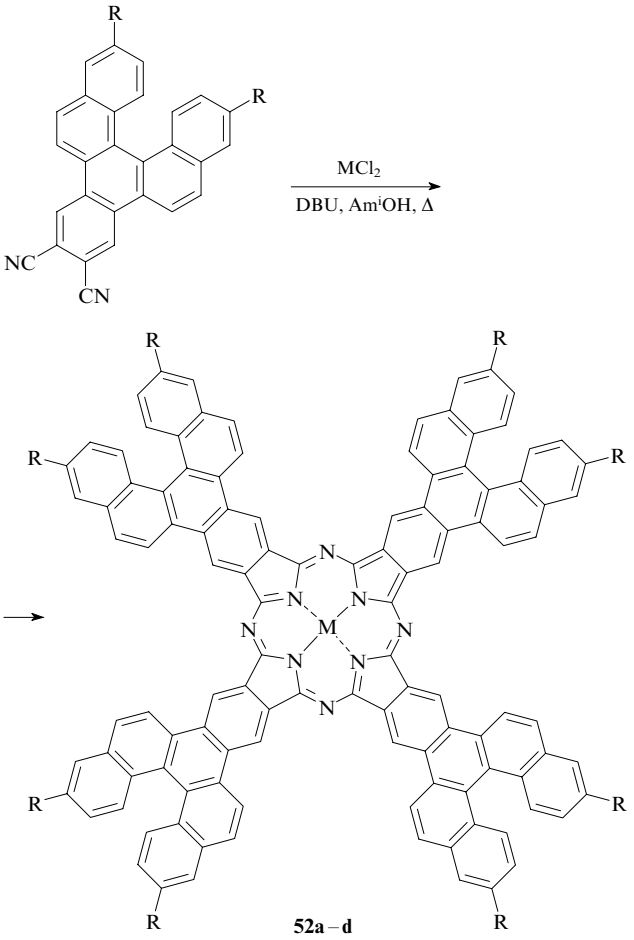


50: R = H (**a**), n-$C_{12}H_{25}O$ (**b**);

51: R = H: M = Zn (**a**, 36%), Pb (**b**, 34%); R = n-$C_{12}H_{25}O$, M = Zn (**c**)

The structure of helicenocyanine **51c** was studied in detail.[48] According to the data of small angle X-ray scattering (SAXS) obtained for a dimeric face-to-face aggregate, the conjugation inside the π-system of the helicenocyanine is

Scheme 20



R = H: M = Zn (**a**, 42%), Pb (**b**, 18%);
R = n-$C_{12}H_{25}O$: M = Zn (**c**, 37%), Pb (**d**, 23%)

weakened due to a non-planar disposition of the peripheral helicene moieties according to the lock washer conformation.[50] The alkoxy substituents adopt a *trans*-configuration relative to each other. A monomolecular form of the helicenocyanine was detected by recording the electronic spectrum in a liquid crystalline phase (octylbiphenylcarbonitrile).

Two publications[48,49] deal with the synthesis of benzohelicenocyanines **52a–d** under relatively mild conditions including refluxing in isoamyl alcohol (Am^iOH) in the presence of DBU as a base (Scheme 20).

Hence, based on the overview of the literature, it can be concluded that the extension of the mononaphthalocyanine π-system owing to the linear benzannulation reduces the stability of the target compounds and increases the aggregation degree. Moreover, preparation of these compounds becomes much more complicated. In this respect, a topical problem is the additional extension of the π-system owing to structural modifications in a macrocycle. One of the ways to address this problem is the synthesis of planar polynuclear phthalocyanine complexes.

5. Binuclear phthalocyanines of a planar structure

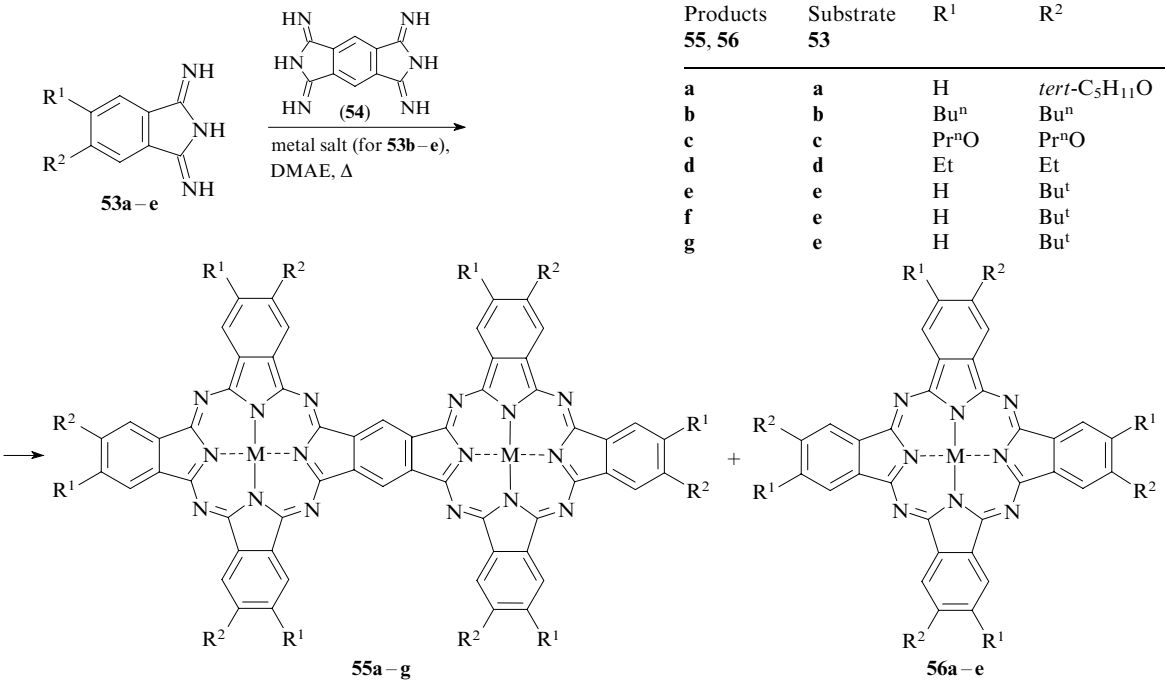
Important representatives of planar polynuclear phthalocyanines are binuclear phthalocyanines. The extension of the π-system in this case is possible owing to the introduction of an aromatic bridge and peripheral π-system.

a. Extension of the π-system owing to an aromatic bridge

The most explored binuclear phthalocyanines of planar structure are those bearing a benzene ring common to two moieties.[51–54] There are two main approaches to the synthesis of these compounds

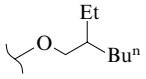
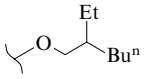
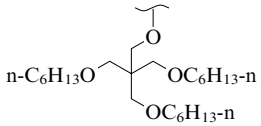
(i) statistical condensation during which the binuclear macrocycle is assembled in one stage;

Scheme 21



Products **55**, **56**	Substrate **53**	R^1	R^2	M	Yield (%)
a	**a**	H	*tert*-$C_5H_{11}O$	2 H	12
b	**b**	Bu^n	Bu^n	Zn	9
c	**c**	Pr^nO	Pr^nO	Zn	8
d	**d**	Et	Et	Zn	8
e	**e**	H	Bu^t	Zn	10
f	**e**	H	Bu^t	Mg	14
g	**e**	H	Bu^t	2 H	8

Table 5. Synthesis of binuclear phthalocyanines **55h–n** from phthalo dinitriles.

Products **55**, **56**	Substrate **57**	R^1	R^2	Ratio **54** : **57**	Conditions	M	Yield (%)	Ref.
h	**a**			see [a]	DMAE, Δ	2 H	5	14
i	**b**	2,6-$Me_2C_6H_3O$	2,6-$Me_2C_6H_3O$	1 : 7	1) Mg, Bu^nOH, Δ, 48 h; 2) CF_3CO_2H	2 H	11	56
j	**c**		H	1 : 15	Li, n-$C_5H_{11}OH$, 130 °C, Δ, 12 h	2 H	8	57
k	**d**	Ph	Ph	1 : 20	$Mg(OAc)_2 \cdot 4H_2O$, DBU, Am^iOH, Δ, 19 h	Mg	17	16
l	**e**	Bu^t	H	1 : 10	$Lu(OAc)_3 \cdot 4H_2O$, MeOLi, Am^iOH, Δ, 2.5 h	Lu(OAc)	26	55
m	**e**	Bu^t	H	1 : 10	$Yb(OAc)_3 \cdot 4H_2O$, MeOLi, Am^iOH, Δ, 2.5 h	Yb(OAc)	21	55
n	**e**	Bu^t	H	1 : 10	$Dy(OAc)_3 \cdot 4H_2O$, MeOLi, Am^iOH, Δ, 2.5 h	Dy(OAc)	23	55

[a] The reactant ratio was not mentioned in the original paper.

(ii) *via* formation of an unsymmetrically substituted mononaphthalocyanine of the A_3B-type followed by building up the second moiety of a binuclear phthalocyanine.

The first representative of binuclear phthalocyanines with shared benzene ring was described in 1987.[9] It was prepared using the former approach. As the starting compounds, the authors used substituted diiminoisoindoline **53a** (R^1 = H, R^2 = *tert*-$C_5H_{11}O$), forming a peripheral system of π-electron conjugation, and 1,3,5,7-tetraiminopyrrole[3,4-*f*]isoindoline (**54**). However, in 1993 based on the NMR spectroscopic data, it was shown[14] that the structure of the compound obtained earlier[9] was not elucidated correctly. It was a binuclear phthalocyanine linked by a cyclohexadiene bridge, which was formed upon protonation. The synthesis and full identification of binuclear phthalocyanine **55a** (R^1 = H, R^2 = *tert*-$C_5H_{11}O$), derived from diiminoisoindoline derivative, were described[51] (Scheme 21). The reaction medium was dimethylaminoethanol, which served both as a solvent and as a base during the reaction.

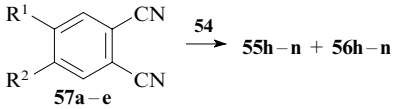
Using this strategy, zinc and magnesium complexes **55b–f** with different substituents[53] and binuclear *tert*-butyl-substituted free ligand **55g**[52] were obtained. The by-products of statistical condensation are the products of self-cyclization of the corresponding iminoisoindoline **53**, namely, symmetrical mononaphthalocyanine complexes **56**. Moreover, the formation of different products of oligomerization of the starting iminoisoindoline derivatives is possible.[53]

In our laboratory it was shown[53] that free binuclear phthalocyanine ligand **55g** can be obtained in an almost quantitative yield (98%) upon treatment of magnesium complex **55f** with concentrated H_2SO_4.

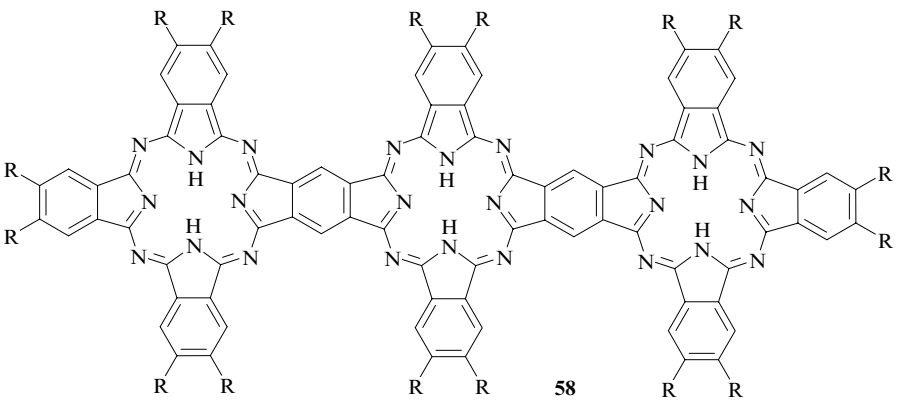
Hence, the synthesis of a binuclear free ligand through the formation of a Mg-complex is realized in the higher total yield than in the single-stage approach demonstrated in Scheme 21.

It was proposed[14] to use tetraimine **54** and substituted phthalonitriles **57a–e** as the initial compounds (Scheme 22). These reactions afford the corresponding mononaphthalocyanine complexes **56h–n** as by-products (Table 5).[55, 56]

Scheme 22

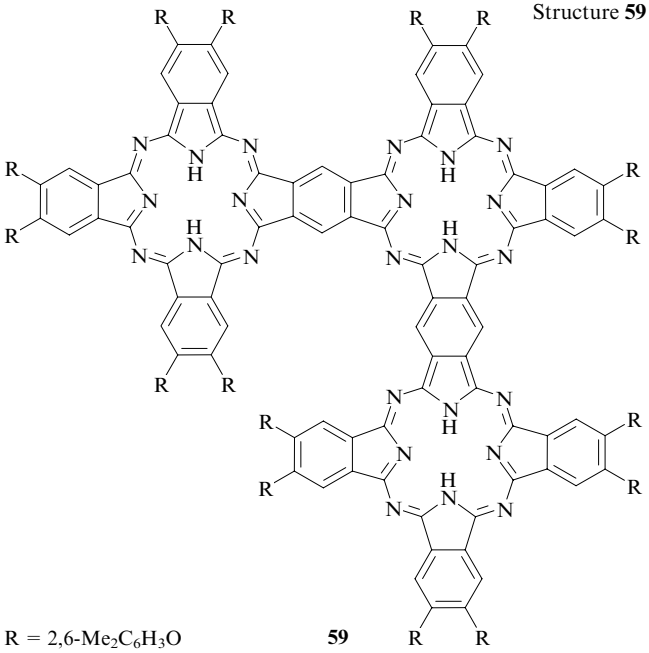


Structure **58**



R = 2,6-$Me_2C_6H_3O$ **58**

Structure **59**



R = 2,6-$Me_2C_6H_3O$ **59**

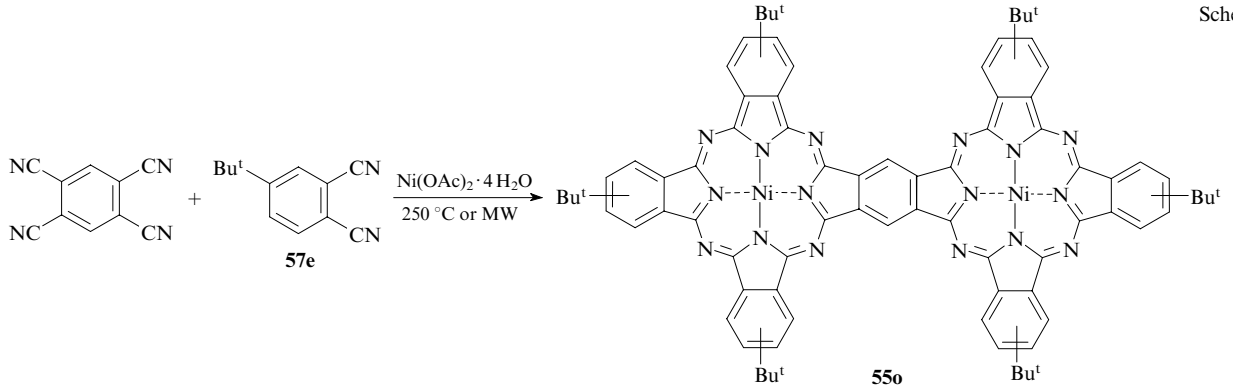
The application of a 10-fold excess of compound **57** relative to tetraimine **54** increases the yields of target compounds **55h–n**.

The highest yields of lanthanide complexes were achieved using isoamyl alcohol as a solvent and lithium methoxide as a base.[55] The process of formation of binuclear lanthanide phthalocyanines proceeds in two stages: initially a tetralithium complex is formed, which reacts with lanthanide acetate to give the target product.

The most optimal conditions for magnesium complexes were the conditions selected in our study[16] for phenyl-substituted binuclear phthalocyanine **55k**. The lower yield of the magnesium complex compared to those of the lanthanide complexes obtained under similar conditions is likely to be caused by the high coordination ability of the lanthanide ion. This also explains the fact that the synthesis of free ligands is characterized by even lower yields.[57]

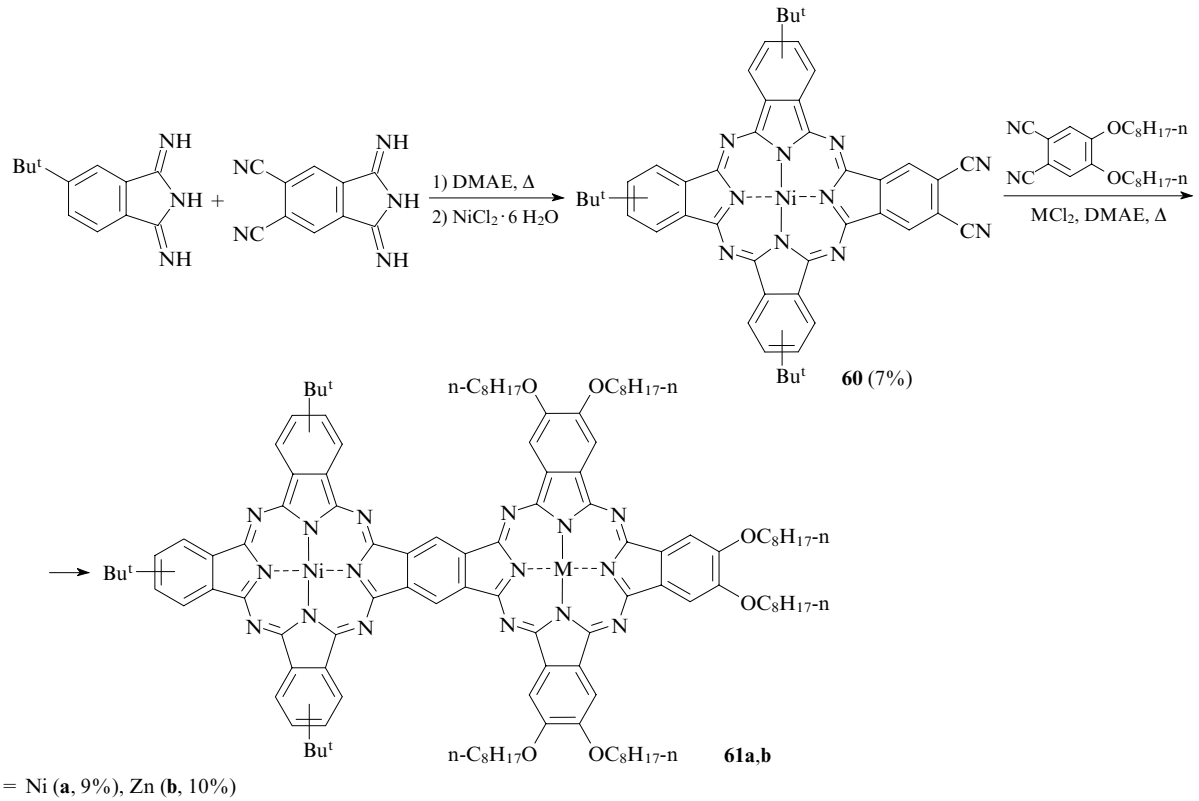
It was found[56] that the reaction of dinitrile **57b** affords, besides monophthalocyanine **56i** ($R^1 = R^2 =$ 2,6-$Me_2C_6H_3O$), trinuclear phthalocyanine **58** in trace amounts as a by-product (0.2%). Subsequently, the authors managed to isolate also angular isomer **59** by column chromatography.[58] The ratio of the linear and angular

Scheme 23



57e **55o**

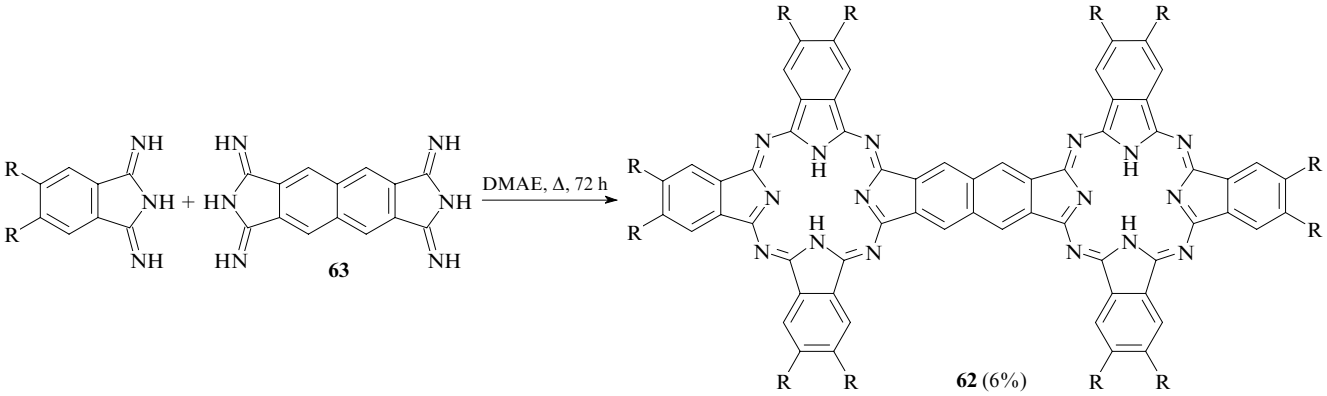
Scheme 24



60 (7%)

M = Ni (**a**, 9%), Zn (**b**, 10%) **61a,b**

Scheme 25



R = $OC_{12}H_{25}$-n

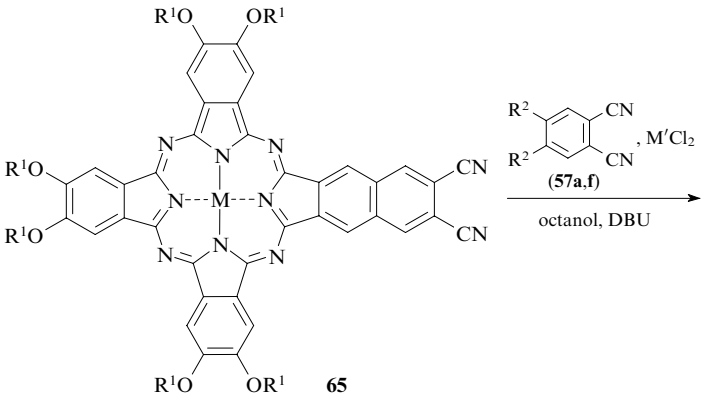
forms comprised 1 : 2. The structures of the linear and angular isomers were determined based on ^{1}H NMR spectroscopic data.

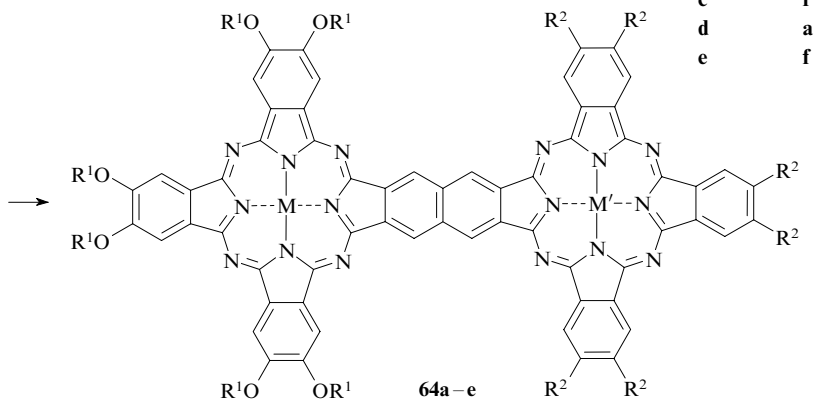
The solid-phase synthesis of binuclear nickel complexes in a melt of the initial nitrile was also reported.[52] This approach is most facile, since the nitrile is used both as a reactant and as a reaction medium. Initially, complex **55o** (R^1 = Bu^t, R^2 = H, M = Ni) was synthesized by fusing together 1,2,4,5-tetracyanobenzene and 4-*tert*-butylphthalonitrile and nickel acetate (Scheme 23, 250 °C), but the target product was isolated in trace amounts, and the main reaction direction appeared to be oligomerization of 4-*tert*-butylphthalonitrile. The yield of complex **55o** was increased to 18% using microwave radiation (MW), the reaction time being 5 min.[52]

Another modification of the synthesis of binuclear phthalocyanines in a melt consists in the reaction of pyromellitic anhydride, the corresponding metal chloride and urea. The yields of binuclear Co and Fe phthalocyanines bearing the amide groups reach 24%. However, using this method, the authors [59] failed to isolate a pure product to analyze it by NMR.

An alternative two-stage approach to the synthesis of binuclear phthalocyanines of a planar structure through the formation of an unsymmetrically substituted monophthalocyanine of the A_3B-type (*e.g.*, complex **60**) followed by building-up the second phthalocyanine moiety was described.[60] This method can be used to obtain heteroligand and heterometallic binuclear phthalocyanines of a planar structure (*e.g.*, **61a**,**b**) (Scheme 24). An essential drawback of this method is low yield of the target compounds.

Scheme 26





Product **64**	Substrate **57**	R^2	M	M′	Yield (%)
a	**f**	H	Ni	Cu	20
b	**a**	$OCH_2CH(Et)Bu^n$	Ni	Cu	18
c	**f**	H	Ni	Ni	23
d	**a**	$OCH_2CH(Et)Bu^n$	Ni	Ni	20
e	**f**	H	Mg	Mg	35

R^1 = $CH_2CH(Et)Bu^n$

A binuclear phthalocyanine with a naphthalene rather than benzene bridge was described for the first time in Ref. 4. Complex **62** was synthesized based on bis(diiminoisoindoline) derivative **63** (Scheme 25). A low yield of the product is likely to be caused by the absence of a complexing ion, which would provide the spatial proximity of intermediates during statistical condensation.

Bis(diiminoisoindoline) **63** was obtained by passing an ammonia flow through a solution of 2,3,6,7-tetracyanonaphthalene (**3k**) in a methanol–dioxane mixture (1 : 1) (dioxane was added to improve the solubility of the starting tetranitrile) in the presence of sodium methoxide.

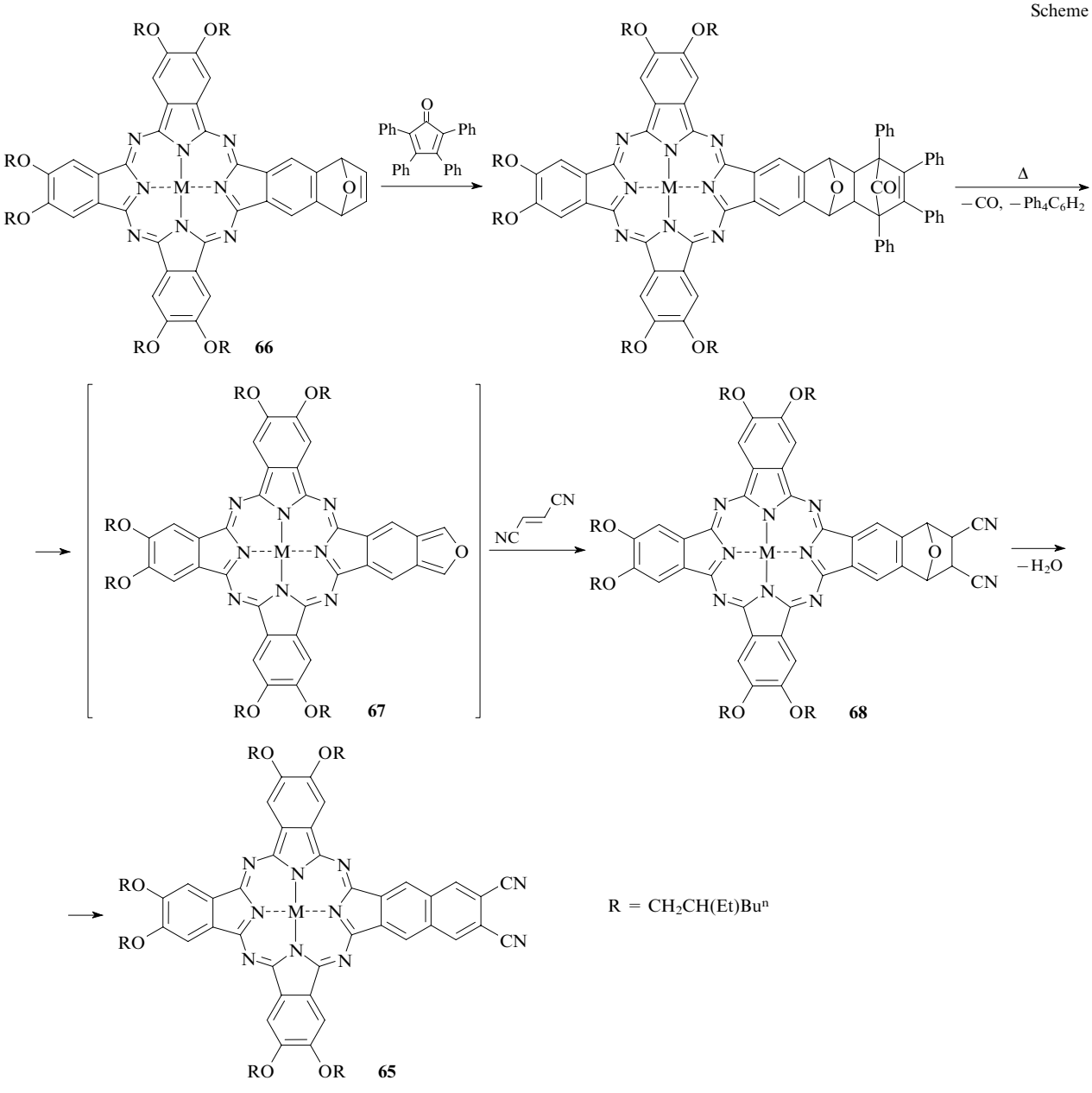
Two papers [17,61] deal with the synthesis of different binuclear phthalocyanines connected by a naphthalene bridge. Compounds **64a–e** were obtained by analogy with planar binuclear phthalocyanines connected by a benzene bridge [60] starting from unsymmetrically substituted phthalocyanine **65** of the A_3B-type and dinitriles **57a**,**f** (Scheme 26). The reaction was carried out in n-octanol in the presence of DBU as a base.

Unsymmetrically substituted monophthalocyanine **65** was synthesized in several stages based on complex **66** [61,62] through the formation of intermediate isobenzofuran derivative **67**. Compound **67** was introduced then into the Diels–Alder reaction with fumarodinitrile followed by the dehydration of the resulting adduct **68** (Scheme 27). Essential drawbacks of this method for synthesis of binuclear phthalocyanines are multiple stages and low yields of the target compounds **64**.[61]

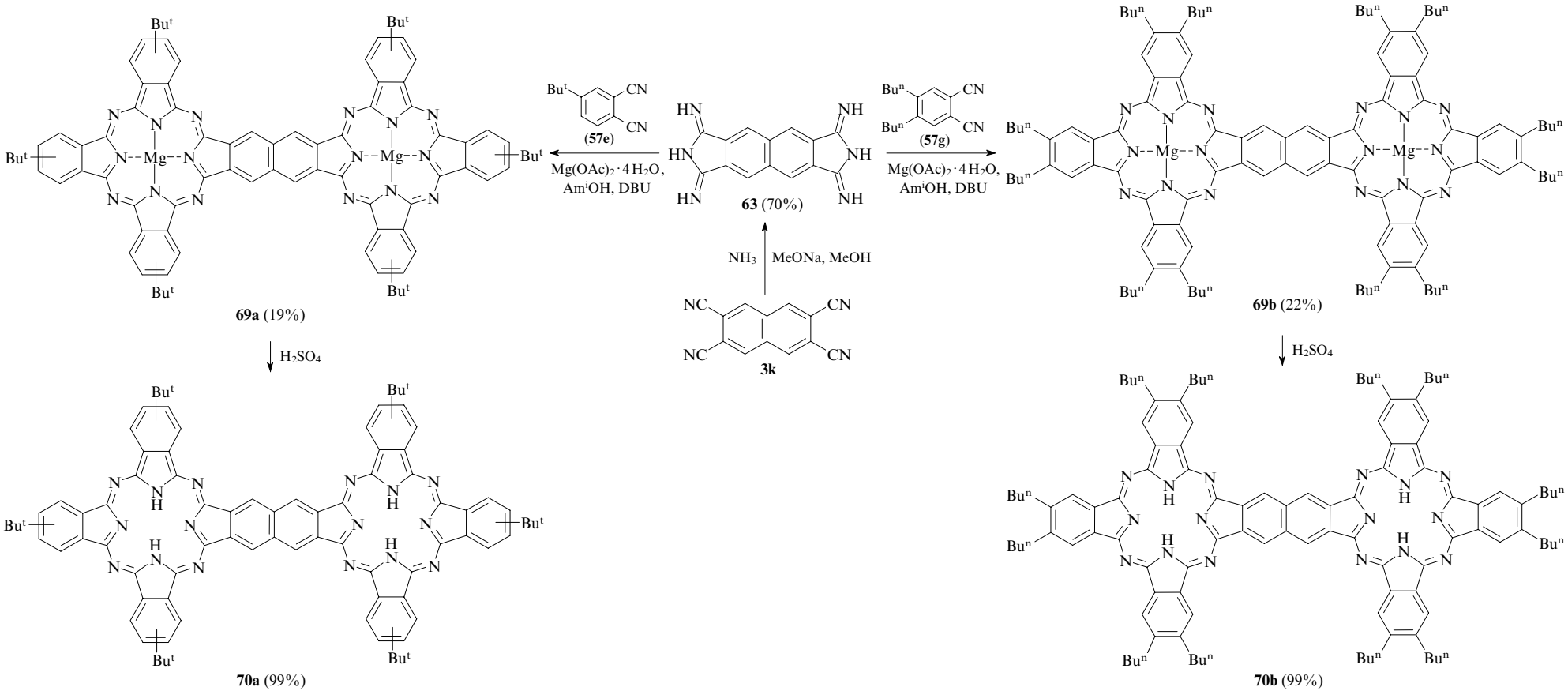
Hence, the suggested methods for synthesis of naphthalene-bridged binuclear phthalocyanines did not allow for the production of complexes in preparative amounts, which complicated further investigation of their electrochemical and spectral properties.

In order to optimize the conditions for formation of these compounds, we chose statistical condensation of bis(diiminoisoindoline) derivatives and the corresponding

Scheme 27



Scheme 28


Bu^t
CN
(57e)
Mg(OAc)2·4H2O,
Am^iOH, DBU
63 (70%)
NH3
MeONa, MeOH
3k
Bu^n
(57g)
69a (19%)
69b (22%)
H2SO4
70a (99%)
70b (99%)

alkyl-substituted dinitriles (Scheme 28).[18] It was established that the application of a bis(diiminoisoindoline) bridging component, more reactive than nitrile, decreases the yield of the resulting by-product — alkyl-substituted monophthalocyanine. This approach was used earlier mostly in the synthesis of benzene-bridged binuclear phthalocyanines.[55] The bis(diiminoisoindoline) derivative of pyromellitonitrile served as the initial compounds for the introduction of a benzene bridge. An advantage of this method compared to the reported synthesis *via* unsymmetrically substituted phthalocyanine [17, 61] consists in the fewer number of stages and the higher yield of the target compound.

The reaction of tetranitrile **3k** with ammonia in methanol in the presence of sodium methoxide afforded the corresponding bis(diiminoisoindoline) derivative **63**. This method appeared to be more efficient than a similar reaction in a methanol–1,4-dioxane mixture (1 : 1),[4] since in the latter case, the high solubility of the reaction product leads to essential complications upon its isolation.

The methods for synthesis of alkyl-substituted binuclear phthalocyanines **69a**,**b** are presented in Scheme 28.

Taking into account the availability of the initial nitrile and high solubility of the target complexes, we found the optimal conditions for the statistical condensation by varying the reactant ratio and the solvent–base system in relation to magnesium *tert*-butyl-substituted planar binuclear phthalocyanine **69a** as an example (Table 6). Binuclear magnesium phthalocyanines **69a**,**b** were chosen in order to convert them to free ligands **70a**,**b**, which can be used in complexation with different metals. Ligands **70a**,**b** were prepared in almost quantitative yields by treatment of magnesium complexes **69a**,**b** with concentrated sulfuric acid (see Scheme 28).[18]

Table 6. Synthesis of magnesium binuclear phthalocyanine **69a**.[18]

Solvent (base)	Ratio **63** : 4-*tert*-butylphthalonitrile	Reaction time /h	Yield (%)
DMAE	1 : 5	61	2
	1 : 20	17	6
Am^{i}OH (DBU)	1 : 20	8	19.5

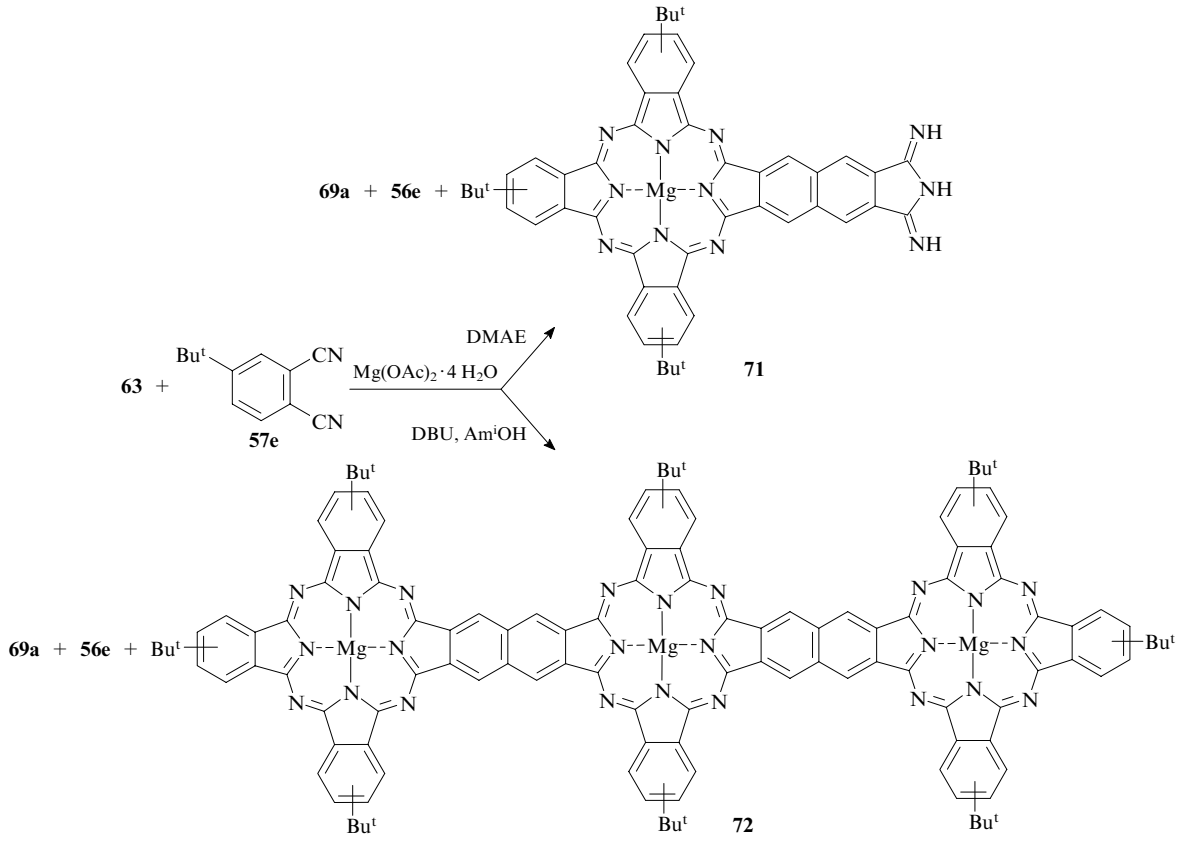
The reaction of bis(diiminoisoindoline) **63** with 4–*tert*-butylphthalonitrile yields, along with the target binuclear complex **69a**, by-products, which is typical for such reactions. One of them is symmetrically substituted monophthalocyanine **56e** (Bu^{t}PcMg).[14, 51] Moreover, depending on the reaction conditions, previously unknown unsymmetrically substituted monophthalocyanine of the A_3B-type (**71**) and trinuclear phthalocyanine **72** were isolated (Scheme 29).

Trinuclear phthalocyanine of an angular structure analogous to trinuclear complex **59** was also detected.

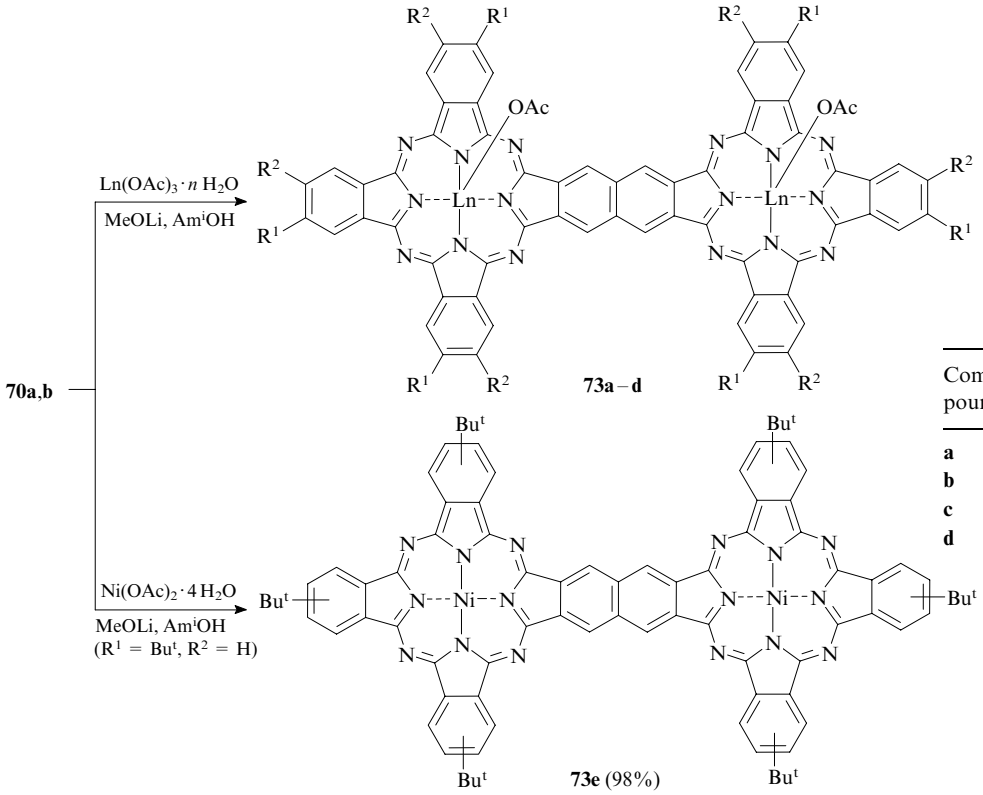
The reaction of ligands **70** with the corresponding metal acetates afforded in high yields lanthanide and nickel binuclear phthalocyanines (Scheme 30).[18] Lanthanide complexes **73a**–**d** can exist as *syn*- and *anti*-forms relative to the position of the axial ligand. According to the computation data,[15] the *anti*-form is energetically more stable for this type of compounds in the gas phase.

The procedure developed for butyl-substituted binuclear complexes was used to synthesize phenyl-substituted binuclear phthalocyanine **74**.[16] Octaphenyl-substituted monophthalocyanine **75** and unsymmetrically substituted monophthalocyanine **76** of the A_3B-type were isolated as by-products (Scheme 31).

Scheme 29

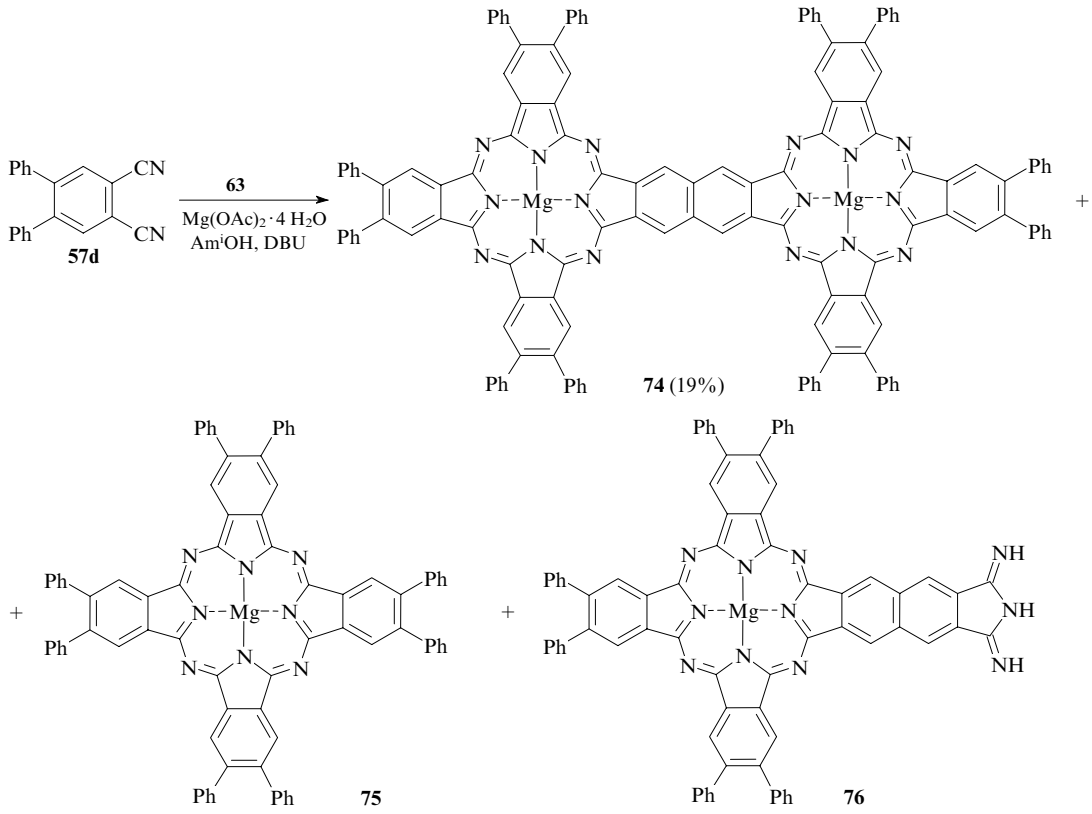


Scheme 30



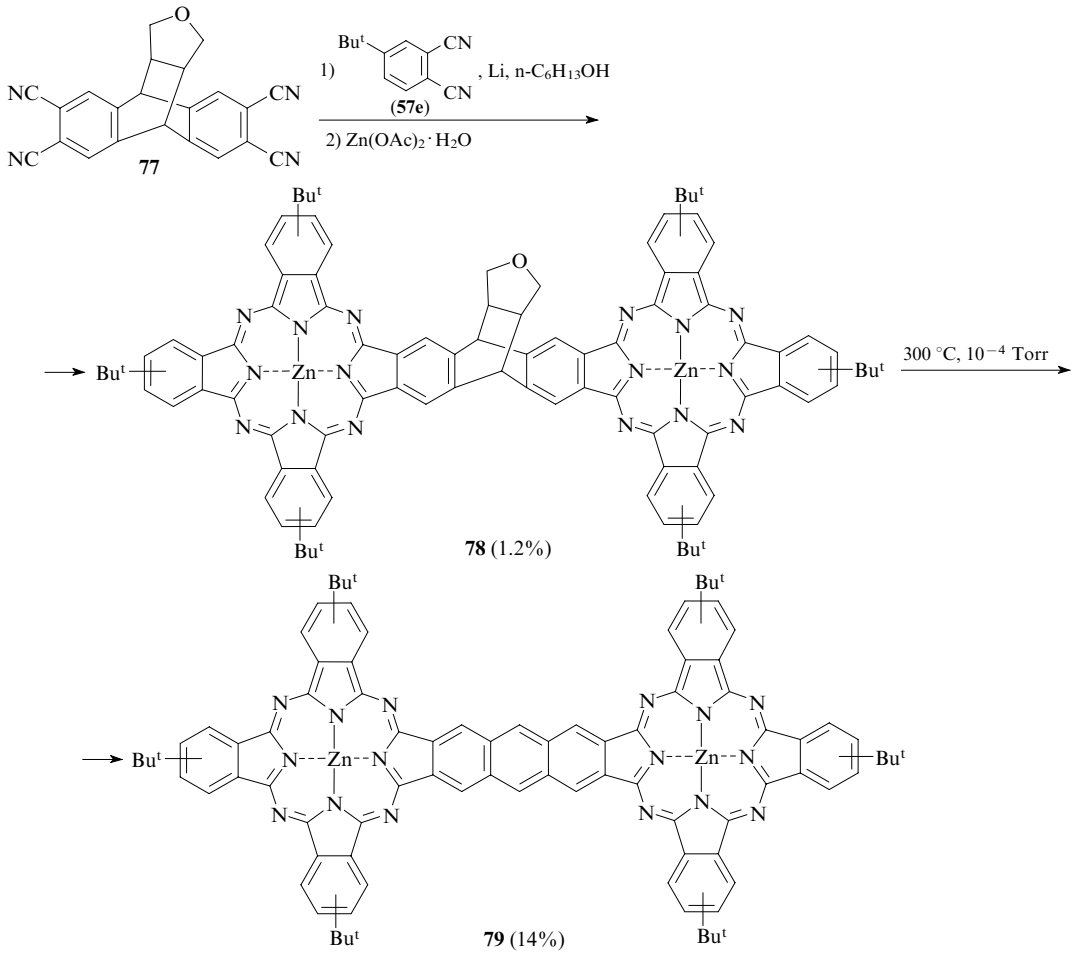
Compound **73**	R^1	R^2	Ln	Yield (%)
a	Bu^t	H	Lu	98
b	Bu^t	H	Er	90
c	Bu^t	H	Gd	94
d	Bu^n	Bu^n	Lu	97

Scheme 31



An original two-stage approach to the synthesis of binuclear phthalocyanines with an anthracene bridge was devised.[63] The first stage was statistical condensation of tetracyano-substituted hexahydrofuranoanthracene **77** and *tert*-butyl-substituted phthalodinitrile in n-hexanol in the presence of lithium. The subsequent reaction with zinc acetate afforded Zn complex **78**. The yield of the reaction product was rather low, which is related to a similar reactivity of the initial nitriles in the cyclization (Scheme 32). The second stage consisted in the thermal aromatization of compound **78** by the retro-Diels–Alder reaction, accompanied by the formation of the aromatic

Scheme 32



anthracene bridge in product **79**. A similar method was used earlier for synthesis of binuclear porphyrin complexes.[64]

The subsequent extension of an aromatic bridge was accomplished[65] for binuclear tetracene-bridged phthalocyanine. This compound was synthesized based on monophthalocyanine **80** of the A_3B-type bearing a dienophile moiety. The synthetic scheme comprised several sequential transformations: the Diels–Alder reaction (resulting in compound **81**), the retro Diels–Alder reaction (**82**), and deoxygenation (**83**), which afforded target complex **84** (Scheme 33).

The initial phthalocyanine **80** was synthesized by statistical condensation according to Scheme 34. The by-products formed in this reaction are phthalocyanines **85** and **86** of the A_4- and B_4-types, respectively.[65]

b. Extension of the peripheral π-system

The peripheral system of π-electron conjugation of binuclear phthalocyanines can be extended for one or both macrocycles, resulting in hetero- and homoligand binuclear phthalocyanines, respectively.

Previously, only the first version of this extension was reported.[66,67] Thus, the synthesis of binuclear phtalo-naphthalocyanine complexes was carried out *via* formation of an A_3B-type phthalocyanine bearing cyano groups. To increase the reactivity, compound **87** was converted to diiminoisoindoline derivative, which was used to obtain target complex **88** (Scheme 35).

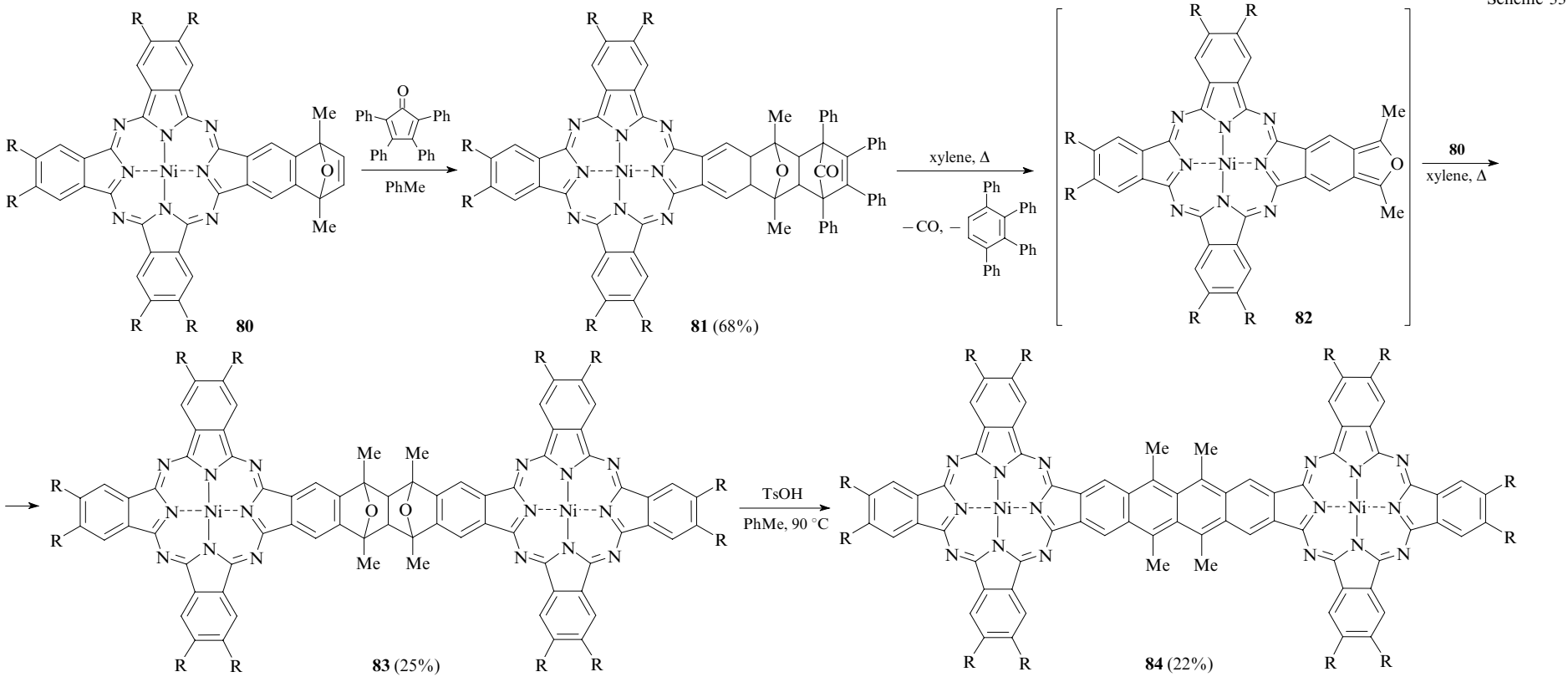
The initial unsymmetrically substituted phthalocyanine **87** was synthesized by a method similar to that presented in Scheme 24 for compound **60**.

The first representatives of binuclear naphthalocyanine complexes of a symmetrical structure **89** and **90**, in which the π-system is extended owing to both the periphery and aromatic bridge, were described in our papers.[16,19] These complexes were obtained by the single-stage statistical condensation (Scheme 36) using the conditions[18] selected in relation to binuclear phthalocyanines **69**. The initial compound for the synthesis of complexes of this type was 6,7-diphenyl-2,3-dicyanonaphthalene (**3o**).

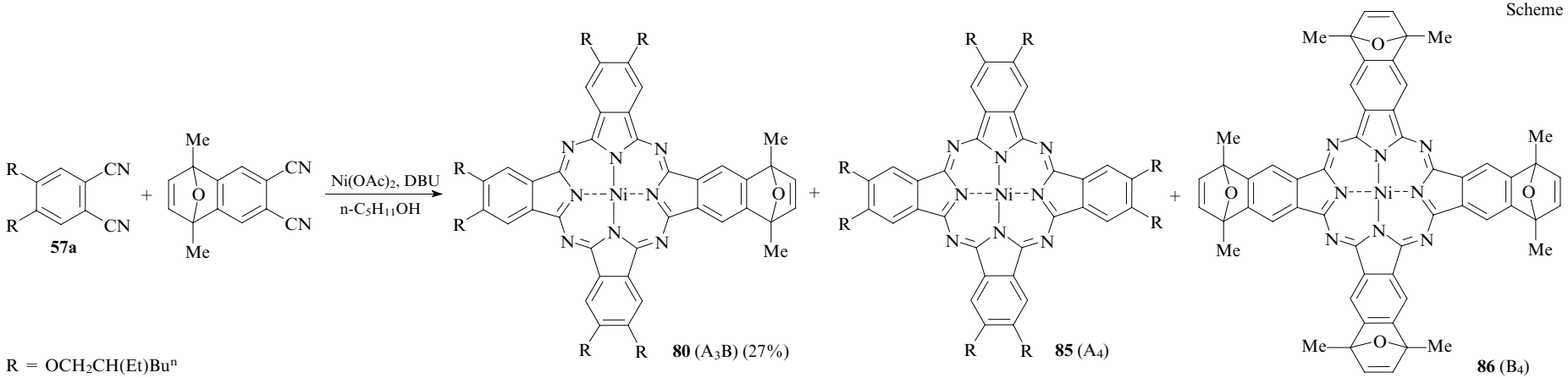
The yields of the target binuclear naphthalocyanine complexes exceeded those of the binuclear phthalocyanine analogues. As a by-product, both reactions gave only the corresponding mononaphthalocyanine **91**, which is likely to be caused by the high reactivity of naphthalocyanine intermediates of the A_3B-type. The more complete cyclization than in the case of binuclear phthalocyanines **55k** and **74** (see Schemes 22 and 31) may be responsible for increase in the yields of binuclear naphthalocyanine complexes **89** and **90**.

Using this approach, Zn-complex **92** was prepared[68] from benzene-bridged *tert*-butyl-substituted binuclear naphthalocyanine (Scheme 37). A by-product was zinc *tert*-butyl-substituted mononaphthalene **93**.

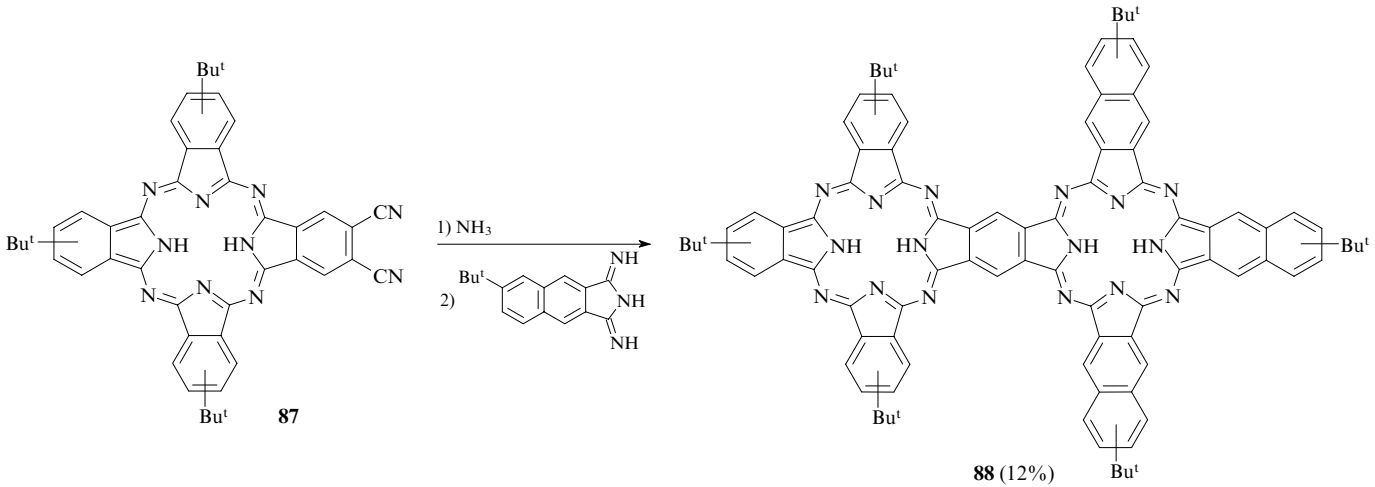
Scheme 33



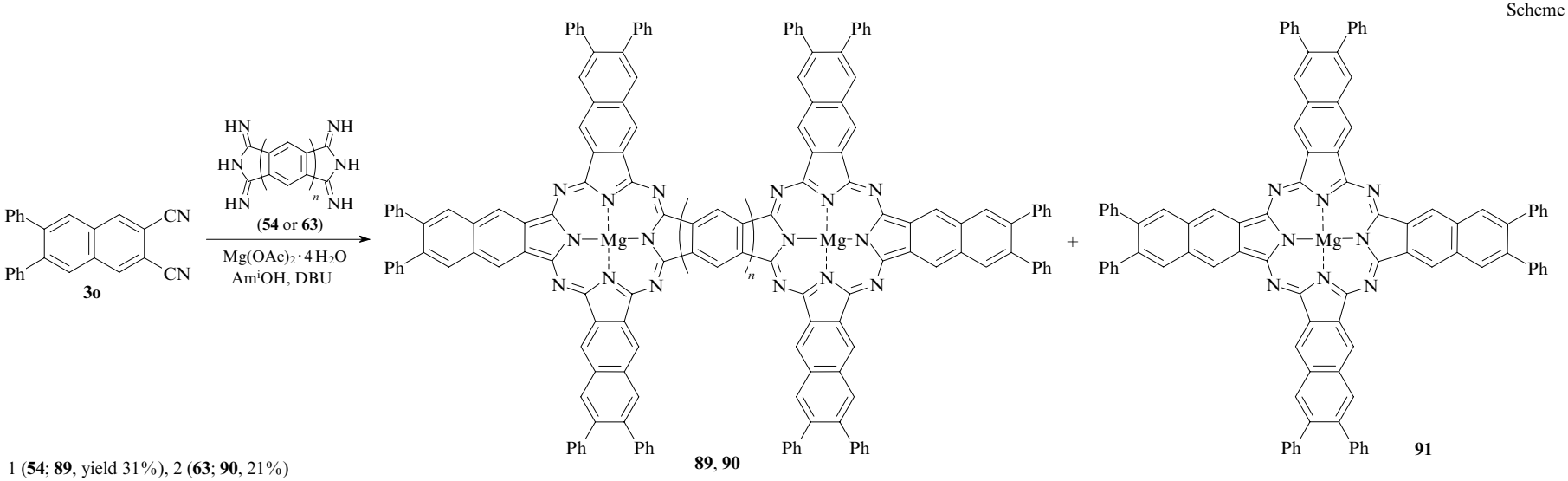
Scheme 34



Scheme 35

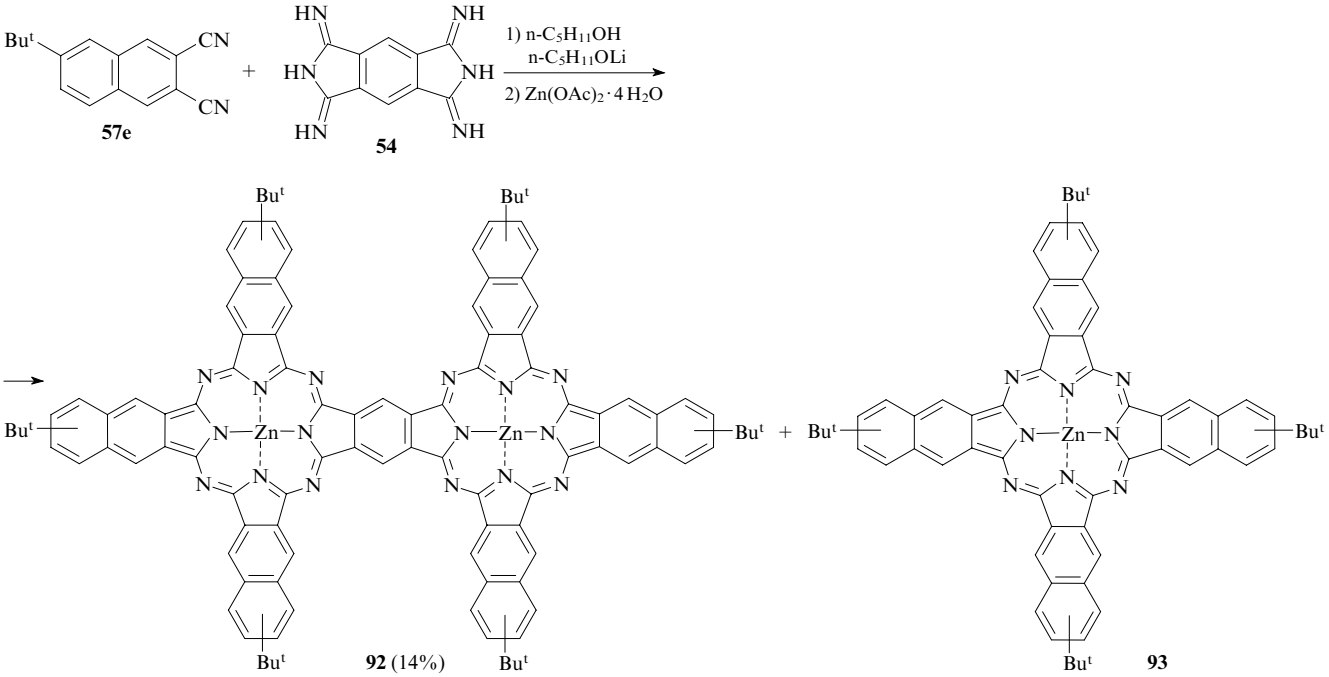


Scheme 36

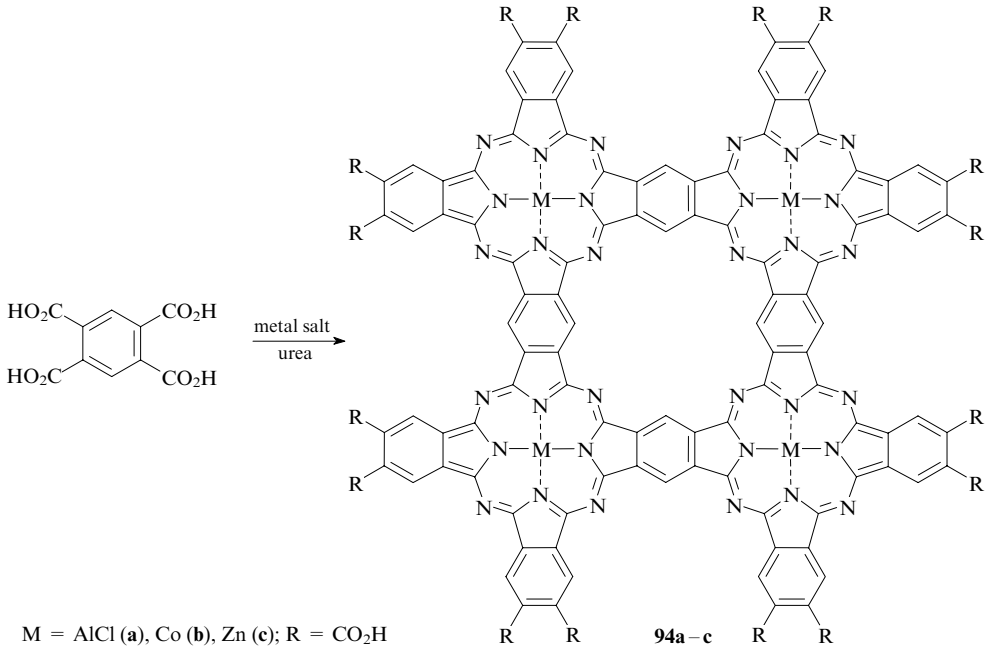


n = 1 (**54**; **89**, yield 31%), 2 (**63**; **90**, 21%)

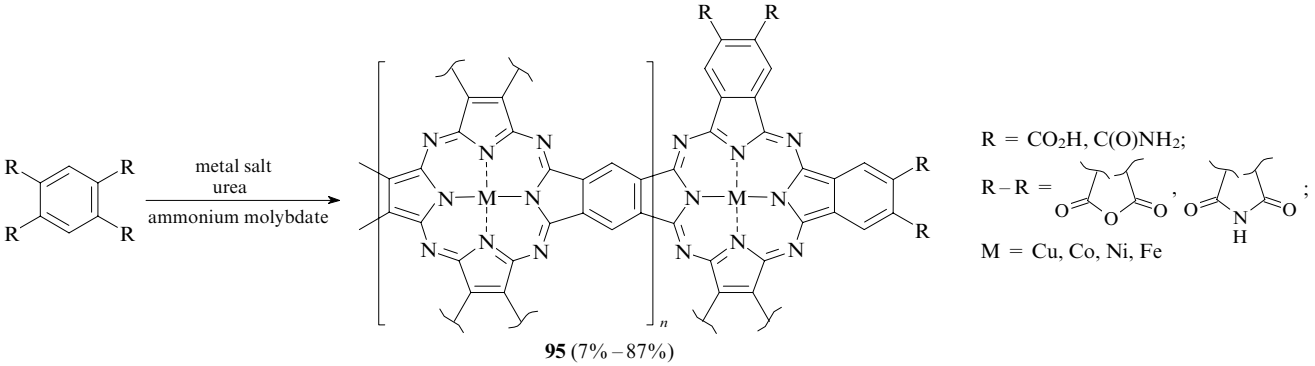
Scheme 37



Scheme 38



Scheme 39



c. Polynuclear phthalocyanines of a planar structure

The reported planar polynuclear phthalocyanines with extended π-system can be divided into three groups: trinuclear complexes, tetranuclear ('two-dimensional' polynuclear phthalocyanines) and polymeric phthalocyanines.

The synthesis and strcuture of trinuclear complexes were discussed above in Section II.5.a. These compounds were isolated by column chromatography as by-products in the synthesis of binculear phthalocyanines.[18, 56, 58] Targeted synthesis of tetramers was documented.[69] Zinc, cobalt and aluminium complexes **94a–c** were obtained by fusing technique in the presence of urea (Scheme 38).

It was shown that tetramers are intermediates in the formation of polymeric phthalocyanines, which were characterized.[70] The synthesis of polymeric phthalocyanines **95** was conducted both in melt (Scheme 39) and in a high-boiling solvent (nitrobenzene) based on different derivatives of pyromellitic acid.

It should be noted that attempts to synthesize polymeric phthalocyanines bridged by benzene rings based on pyromellitonitrile led to mononaphthalocyanine derivatives with the imide and carboxylic groups around the macrocycle periphery.[71]

Metal complexes **95** of polymeric phthalocyanines are insoluble in most organic solvents but are readily soluble in concentrated sulfuric acid (solutions are stable for 24 h). Free ligands obtained in the same way as metal complexes are unstable and decompose in the concentrated acid medium over a period of 1 h.[70]

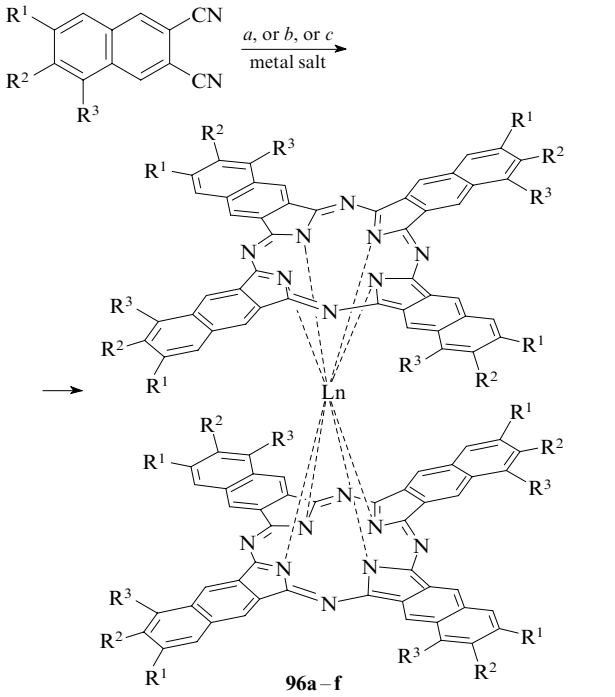
III. Synthesis of sandwich phthalocyanines with an extended π-system

A result of the combination of approaches to the extension of π-system by linear annulation and by axial interaction of π-systems are sandwich-like lanthanide complexes of naphthalocyanines.

1. Template synthesis based on 2,3-dicyanonaphthalene

The first example[10] of preparation of dinaphthalocyanine complexes **96** is the template synthesis in the melt of 2,3-dicyanonaphthalene (Scheme 40). Accoridng to this strategy, lutetium complexes of substituted dinaphthalocyanines **96a**,**b** (Table 7) and, subsequently, lanthanide phenoxy-substituted dinaphthalocyanines **96e–g** were obtained.[27] Having selected the conditions (replacement of heating by microwave irradiation), we were able to appreciably reduce the reaction time from several hours to several minutes. It should be noted that on going from late lanthanides (**96g**) to early lanthanides (**96e**), an increase in the yield of dinaphthalocyanine is observed. This is caused by the increase in the ionic radius of complexing metal and, consequently, by weakening of the π-interaction between naphthalocyanine ligands.

Scheme 40



(*a*) fusing, (*b*) synthesis in solution, (*c*) MW

A publication[72] deals with the template syntesis of lanthanide *tert*-butyl-substituted dinaphthalocyanines **96c**,**d** in boiling n-octanol in the presence of a base (see Table 7). A drawback of this method is a rather low yeild of double-decker complexes on going from early lanthanides (**96c**) to late lanthanides (**96d**). Furthermore, the presence of small amounts of impurities of unknown nature which could not be separated by standard chromatographic techniques did not allow the authors to characterize the products by elemental analysis and NMR spectroscopy.

Table 7. Template synthesis of sandwich complexes **96**.

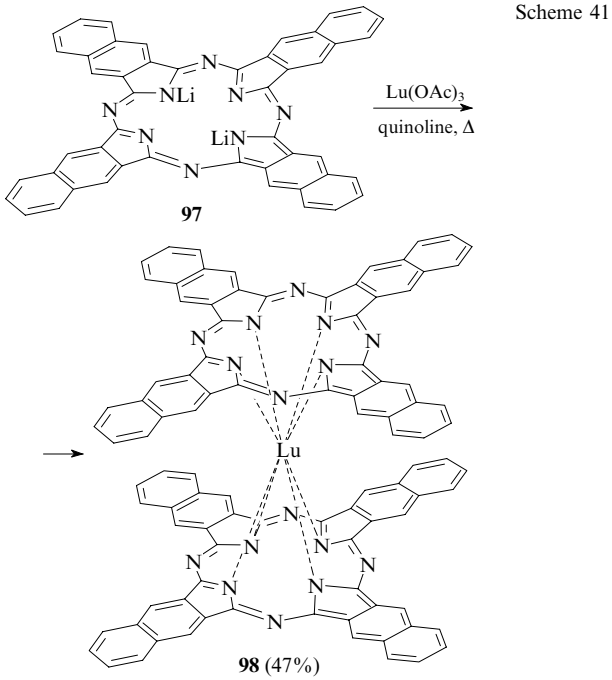
Compound **96**	R^1	R^2	Ln	Conditions	Yield (%)	Ref.
a	Bu^t	H	Lu	$Lu(OAc)_3 \cdot 3H_2O$, 280 °C, 2 h	60	10
b[a]	Bu^t	H	Lu	$Lu(OAc)_3 \cdot 3H_2O$, 280 °C, 2 h	42	10
c	Bu^t	H	La	$La(OAc)_3 \cdot nH_2O$, DBU, n-$C_8H_{17}OH$, Δ, > 18 h	69	72
d	Bu^t	H	Er	$Er(OAc)_3 \cdot nH_2O$, DBU, n-$C_8H_{17}OH$, Δ, > 18 h	35	72
e	PhO	PhO	Eu	$Eu(OAc)_3 \cdot 3H_2O$, 230–310 °C, 2 h	55	27
	PhO	PhO	Eu	$Eu(OAc)_3 \cdot 3H_2O$, MW (700 W), 5–7 min	39	27
f	PhO	PhO	Er	$Er(OAc)_3 \cdot 4H_2O$, 230–310 °C, 2 h	47	27
	PhO	PhO	Er	$Er(OAc)_3 \cdot 4H_2O$, MW (700 W), 5–7 min	33	27
g	PhO	PhO	Lu	$Lu(OAc)_3 \cdot 4H_2O$, 230–310 °C, 2 h	41	27

[a] R^3 = Br, in the other cases R^3 = H.

2. Synthesis based on dilithium 2,3-naphthalocyanine

A synthetic route to unsubstituted lutetium 2,3-naphthalocyanine based on dilithium complex **97** was proposed.[73] The reaction was carried out in boiling quinoline for 3 h, the yield of compound **98** (in the form of a stable π-radical) was 47% (Scheme 41). The initial dilithium complex **97** was obtained by the template synthesis from 2,3-dicyanonaphthalene in solution, by analogy with disodium mononaphthalocyanines.[7]

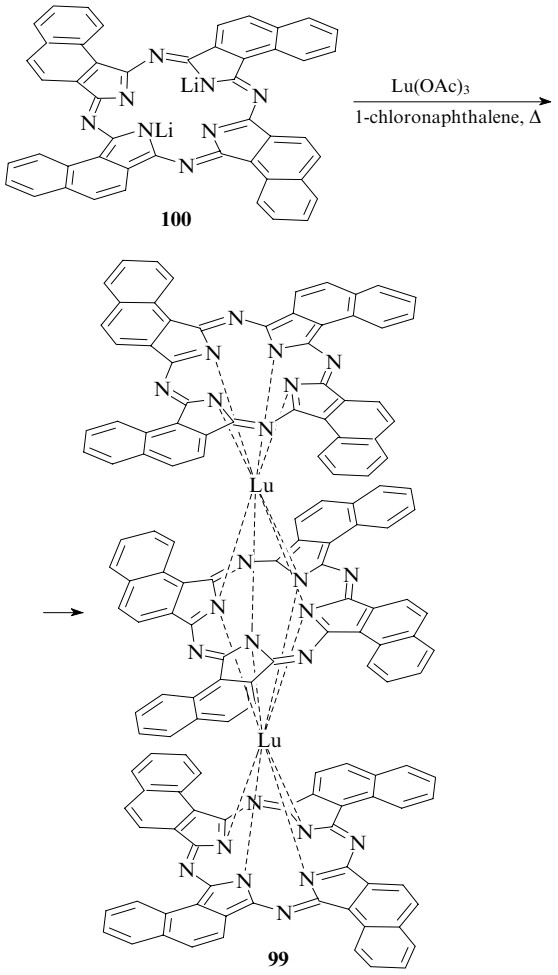
Scheme 41



A drawback of this approach to the synthesis of dinaphthalocyanine complexes is the neccessity of an additional stage of formation of complex **97**, which reduces the overall yield of the compound to 30%.

The only known representative of trinaphthalocyanines, lutetium complex **99**,[74] was obtained from dilithium complex of 1,2-naphthalocyanine **100** in 1-chloronaphthalene (Scheme 42). As by-product, the corresponding dinaphthalocyanine was isolated.

Scheme 42



IV. Synthesis of hybrid sandwich-planar phthalocyanines

Our research team obtained the first representatives of a new class of hybrid compounds of the sandwich-planar type[75] (Scheme 43). These compounds were synthesized based on both benzene-bridged free binuclear ligands (**55g**,**p**) and lutetium binuclear phthalocyanine **55l**. The reaction was carried out under the standard conditions for the synthesis of lanthanide phthalocyanines, using a mixture of high-boiling solvents and lithium methoxide as a base (see Scheme 43).[11] This strategy was exploited to obtain Eu (**101a**, **102a**) and Lu (**101b**, **102b**) complexes in the reduced forms. Using gel permeation chromatography, the corresponding triple- and quadruple-decker complexes were isolated as by-products.

Dynamic light scattering revealed that the diameter of particles of complexes **101a** and **102a** in THF solution comprises 60 nm.[75]

The interaction of complex **101a** with concentrated sulfuric acid afforded compound **103** in almost a qunatitative yield. It is noteworthy that the demetallation of only the planar moieties of the binuclear complex rather than its sandwich part was observed. Owing to this, complex **103** can be used subsequently as a building block in the design of heteroleptic complexes.

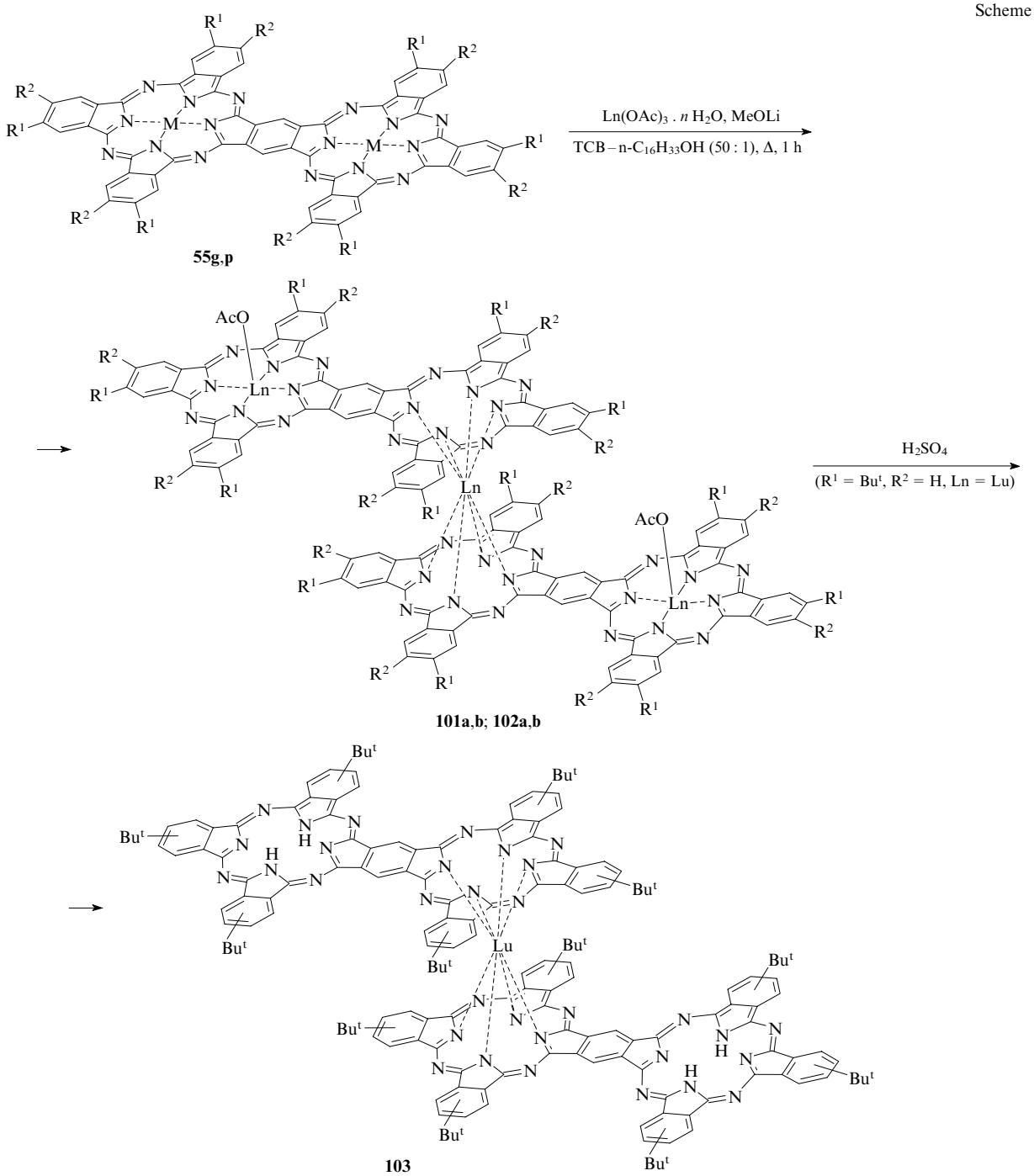
V. Investigation of phthalocyanines with an extended π-system by electronic spectroscopy

Each type of phthalocyanines with extended π-system and their metal complexes feature a particular pattern of absoprtion spectrum, which makes electronic absorption spectroscopy a convenient technique for both identification and estimation of the degree of purity of compounds.

1. Electronic absorption spectra of planar phthalocyanines with extended π-system

The electronic absorption spectrum of a mononuclear phthalocyanine is characterized by one principal absorption maximum in the range of 660–680 nm, Q-band due to the $\pi \rightarrow \pi^*$ electron transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and a vibrational satellite of lower intensity in the range of 600 nm. In Fig. 1, the Q-band of zinc phthalocyanine (PcZn) corresponds to the $a_{1u} \rightarrow e_g$ transition. Moreover, in the vicinity of the boundary between the visible and UV regions (350 nm), the absorption spectra of phthalocyanines show an intensive absorption peak, the

Scheme 43



55: M = 2H: R^1 = Bu^t, R^2 = H (**g**); R^1 = R^2 = Bu^n (**p**);
101: R^1 = Bu^t, R^2 = H: Ln = Lu (**a**), Eu (**b**); **102**: R^1 = R^2 = Bu^n: Ln = Lu (**a**), Eu (**b**)

Soret band (B-band), which corresponds to the $a_{2u} \rightarrow e_g$ transition (see Fig. 1).[35]

Upon extension of the π-system by the linear annulation, the frontier orbitals are destabilized; this affects, most of all, the HOMO level (see Fig. 1, orbital a_{1u}). Owing to this, the HOMO–LUMO energy gap decreases, and, as a consequence, the electronic spectrum shows a bathochromic shift of the Q-band by ~100 nm on going from phthalocyanines to 2,3-naphthalocyanines and further to anthracocyanines. Figure 2 depicts an example of the longer-wavelength shift of the absorption maximum on going from ferrocenylethynyl-substituted phthalocyanine to 2,3-naphthalocyanine **31**.[29]

This effect was aslo observed in the case of sandwich complexes on going from diphthalocyanines to dinaphthalocyanines;[73] it was called 'the 100 nm' rule.[20] This rule can be formulated as follows: each successive linear benzannulation of tetraazaporphyrin core leads to ~100 nm low-energy shift of Q band. However, this rule holds only upon linear annulation (*e.g.*, on going from 2,3-naphthalocyanine **27c** to anthracocyanine **45**) and does not hold for such

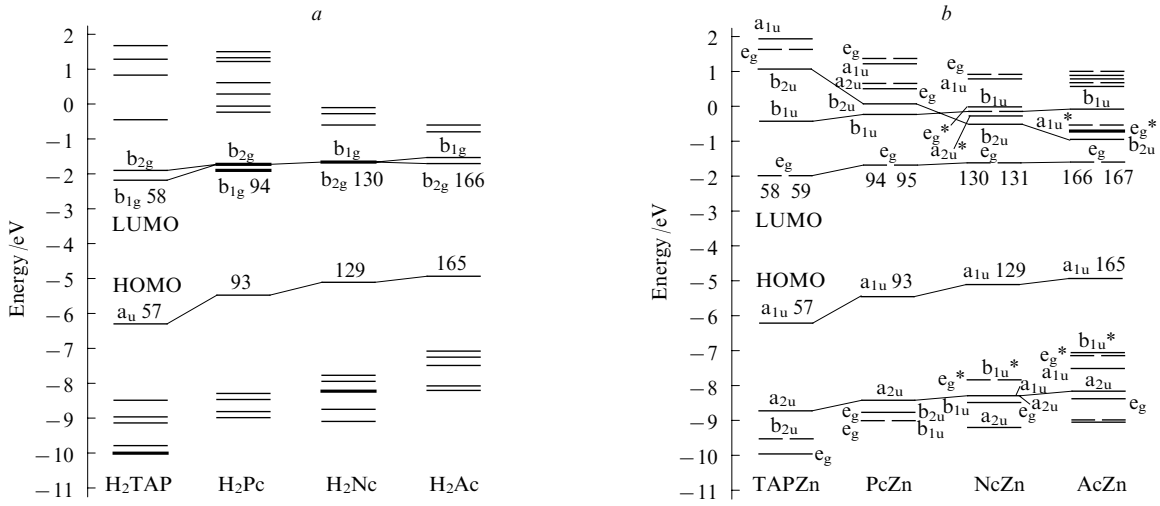


Figure 1. Partial diagram of molecular orbitals of free ligands (*a*) and zinc complexes (*b*) with tetraazaporphyrin (TAP), phthalocyanine (Pc), naphthalocyanine (Nc) and anthracocyanine (Ac).[35]
The asterisked orbitals denote naphthalene- and anthracene-centred orbitals.

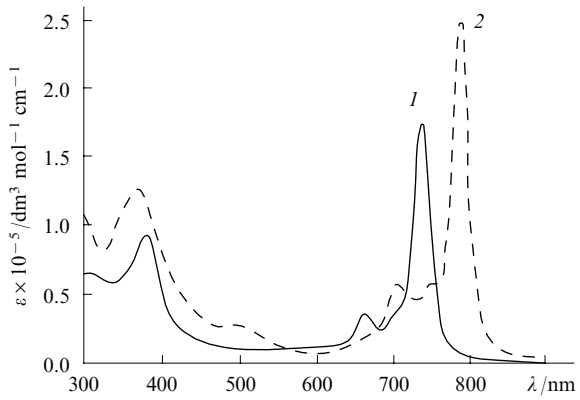


Figure 2. Absorption spectra of zinc ferrocenylethynyl-substituted phthalocyanine (*1*) and naphthalocyanine **31** (*2*) in THF.[29]

derivatives as phenanthreno- and helicenocyanines (Table 8).

Thus, it was shown [6] that for 1,2-naphthalocyanines, the bathochromic displacement of the Q-band is only 20 nm compared to that for phthalocyanines.

Table 8. Data of electronic absorption spectra of planar monophthalocyanine complexes with extended π-system.

Compound	Class	M	Q-band (λ/nm)	Solvent	Ref.
27c	2,3-naphthalocyanine	Co	752	pyridine	35, 76
45	anthracocyanine	Co	831.5	"	35, 76
49	9,10-phenanthrenocyanine	Fe	664	"	38
51a	helicenocyanine	Zn	748	octylbiphenylcarbonitrile	48
52c	benzohelicenocyanine	Zn	781	toluene	49

It should be noted that the absence of degeneracy of the b_{1g}- and b_{2g}-orbitals in electronic absorption spectrum of free porphyrazine and phthalocyanine ligands (see Fig. 1 *a*) leads to splitting of the Q-band into two components. Unlike phthalocyanines, the LUMO of naphthalocyanines are degenerate; therefore, no splitting of the absorption band is observed.[35]

Molecular orbital calculations for planar binuclear phthalocyanines were reported.[51] The authors proceeded from the assumption that both phthalocyanine macrocycles are planar and the structure of the molecule corresponds to D_{2h} symmetry. The results of these calculations for binuclear phthalocyanines coupled by benzene and naphthalene bridges are presented in Fig. 3.

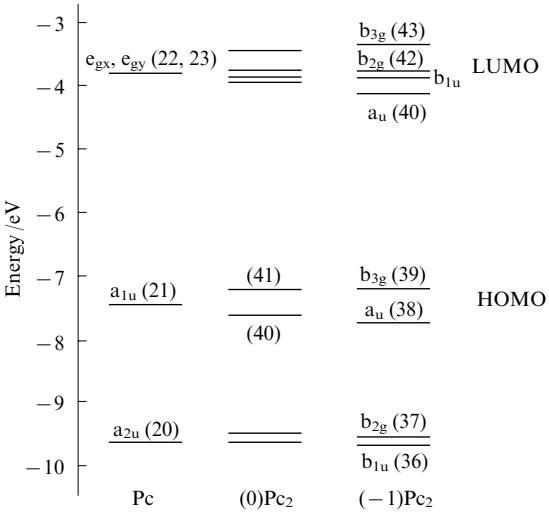


Figure 3. Diagrams of molecular orbitals of the dianion form of unsubstituted monophthalocyanine (Pc) and tetraanions of binuclear phthalocyanines bridged by benzene [$(-1)Pc_2$] and naphthalene [$(0)Pc_2$] rings.[51]

Due to the presence of two phthalocyanine moieties in the molecule of binuclear complexes, the splitting of the frontier orbitals and, as a consequence, the splitting of the Q-band as compared with those for mononaphthalocyanine are observed. The splitting intensifies with a decrease in the size of the aromatic bridge. The Soret band features insignificant splitting.

Owing to the extension of the aromatic π-system of binuclear phthalocyanines $(-1)Pc_2$ and $(0)Pc_2$ relative to mononaphthalocyanines, the destabilization of the HOMO levels of the former is observed, which must lead to a displacement of the absorption band to the near IR region. The inaccuracy of calculations being cited [51] is rather high, as the structure of binuclear phthalocyanines in solution can deviate from planarity. However, the data on the relative shift of the Q-band in electronic absorption spectrum obtained from molecular orbital diagrams possess high accuracy.

A ~200 nm bathochromic shift of the Q-band relative to the band of the corresponding mononaphthalocyanine was revealed for the first time [14] in the absorption spectrum of binuclear phthalocyanine ligand **55p** bridged by a benzene ring. The analogous long-wavelength shift of the absorption maximum was also observed for other binuclear phthalocyanines with a benzene bridge.[53, 56]

A characteristic feature of binuclear complexes is the presence of a series of electron transitions in the near-IR reigion, which results in splitting of the Q-band, and several vibrational satellites, which allows for covering rather wide range of wavelengths.[53, 77, 78] This is important for the practical application of these compounds, since it is difficult to precisely focus laser radiation in a narrow range of wavelengths.[66]

For binuclear phthalocyanines with naphthalene [4, 15, 17, 61, 79] (Fig. 4) and tetracene [65] bridges, no absorption in the near-IR region was detected earlier. The authors explain this fact by the possible hydrogenation of the aromatic moiety during the reaction or too weak delocalization of the electron density between the phthalocyanine moieties in the binuclear complex.[61]

However, it can be assumed that the absence of absorption in the near-IR region for these compounds stems from the strong aggregation effects, since electronic absorption spectra were recorded in non-coordinating solvents such as dichloromethane and benzene. This assumption was confirmed in our publication.[16] We showed that on going from

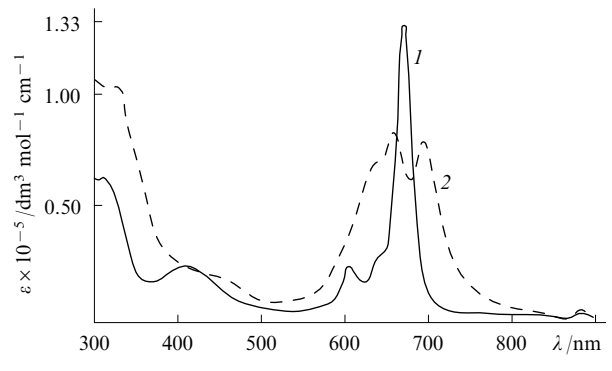


Figure 4. Absorption spectra of n-C_8H_{17}OPcNi (*1*) and analogous binuclear phthalocyanine $(0)Pc_2Ni_2$ (*2*) in CH_2Cl_2.[79]

Table 9. Absorption bands of phenyl-substituted planar binuclear phthalo- and naphthalocyanines in THF.[16]

Compound	λ /nm (I/I_{max})
55k	846 (0.66), 698 (0.56), 372 (1)
74	798 (0.29), 716 (0.86), 368 (1)
89	960 (0.17), 772 (0.33), 327 (1)
90	905 (0.18), 776 (0.34), 331 (1)

binuclear phthalocyanines with a benzene bridge (**55k**, **89**) to their analogues with a naphthalene bridge (**74**, **90**), the Q_2-band in the near-IR region does not disappear and shifts hypsochromically (Table 9), the distance between the Q_1 and Q_2 bands also reduces. This is caused by the fact that an increase in the length of the aromatic bridge disrupts the interaction of the two phthalocyanine chromophores.

From the viewpoint of the molecular orbital theory,[51] this phenomenon can be explained as follows: LUMO of $(0)Pc_2$ is destabilized relative to LUMO of $(-1)Pc_2$ (see Fig. 3), which results in an increase in the HOMO–LUMO energy gap and a hypsochromic shift of the Q_2-band. A similar hypsochromic shift is observed on going from the naphthalene bridge to the anthracene one.[63]

The extension of the peripheral π-system on going from planar binuclear phthalo- to naphthalocyanine complexes with similar bridges leads to a bathochromic shift of the Q_2-band by more than 100 nm (see Table 9). This value essentially exceeds the hypsochromic shift caused by the elongation of an aromatic bridge. The largest bathochromic shift is observed for benzene-bridged binuclear naphthalocyanine complex **89** (Fig. 5).[80] Hence, in this case as well as for mononaphthalocyanines and their derivatives, the 100 nm rule was found to hold.

It should be noted that owing to the extension of the peripheral π-system, transition from monophthalocyanine to binuclear and trinuclear phthalocyanines [18, 81] also affords a displacement of the Q-band to the near-IR region (Fig. 6), up to 856 nm.

The aggregation in solutions of phthalocyanines is observed, as a rule, at concentrations $>10^{-5}$ mol litre^{-1} and is caused by strong intermolecular interaction of the π-systems.[82] However, in the case of phthalocyanines with extended π-system, in particular, binculear phthalocyanines, this phenomenon is also observed at lower concen-

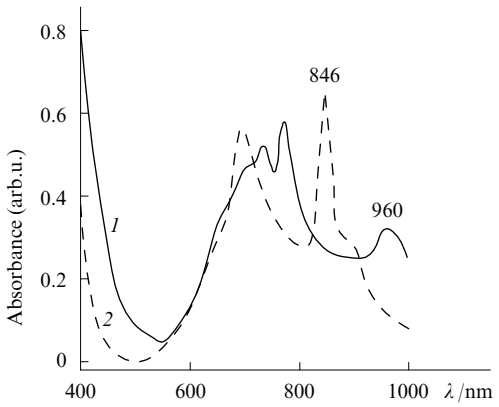


Figure 5. Absorption spectra of complexes **89** (*1*) and **55k** (*2*).[81]

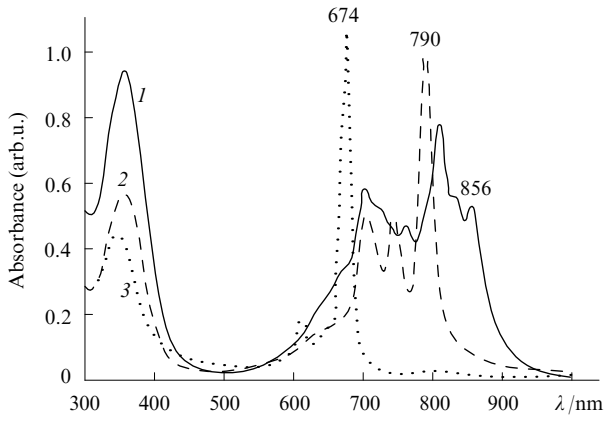


Figure 6. Absorption spectra of compounds **72** (*1*), **69a** (*2*) and phthalocyanine analogue Bu^{t}PcMg (*3*).[81]

trations. It is manifested as the substantial broadening of absorption bands and reduction of the intensity ratio of the Q- and B-bands.[83] Figure 7 demonstrates the absorption spectra of complex **55k** in a coordinating solvent (THF) and in thin film. In the latter case, the interaction of the π-systems is most pronounced; it is accompanied by considerable broadening of all absorption bands and regular reduction in the intensity of the Q_2-band. It was shown[16,53] that, owing to the steric effect, coordinating solvents (THF, pyridine) hamper the aggregation of binuclear phthalocyanines, substantially increasing the intensity of the absorption band in the near-IR region. Atomic force microscopy (AFM) showed that upon film deposition from a coordinating solvent, the resulting particle size is several times lower than that obtained upon deposition from a non-coordinating solvent.[16] This fact indirectly supports the hypothesis about the aggregation nature of changes in the electronic absorption spectrum on going from coodinating to a non-coordinating solvent.

For phthalocyanines and their analogues, two types of aggregates are possible. *H*-aggregates are formed at the face-to-face arrangement of the macrocycles, while the interaction of the peripheral π-systems results in *J*-aggregates[84] ('brickwork' type[85,86]). According to Kasha's molecular exciton theory, the absorption of the *H*-aggregates is hypsochromically shifted relative to the Q-band of a monomeric form, while that of the *J*-aggregates is bathochromically shifted.[84] Therefore, the essential broadening of absorption bands of binuclear complexes is caused by the formation of both *J*- and *H*-aggregates.

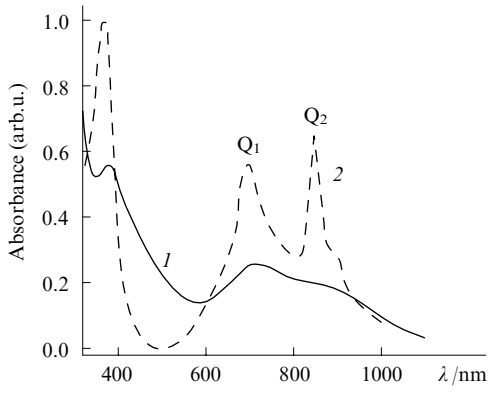


Figure 7. Absorption spectra of complex **55k** in thin film (*1*) and in THF (*2*).[81]

2. Electronic absorption spectra of sandwich phthalocyanines with extended π-system

As a consequence of the presence of a free radical in the molecules of diphthalocyanines and their analogues, electronic absorption spectra of these compounds show a series of features which are not characteristic of planar phthalocyanines. For dinaphthalocyanines, the HOMO level is a singly occupied molecular orbital (SOMO). Hence, in addition to the Q- ($2b_1 \rightarrow 6e_3$ transition) and B-band ($3a_1 \rightarrow 6e_3$ and $3b_2 \rightarrow 6e_1$), the spectra show a series of bands of lower intensity that correspond to the electron transitions from the fully occupied MO to SOMO. In the range of 550–600 nm, a broad medium-intensity π-radical band ($5e_1 \rightarrow 2a_2$) is observed, which is called also the charge transfer band.[87] Furthermore, two main transitions were registered in the near-IR region, called intervalence (IV) and red valence (RV) and related to the $2b_1 \rightarrow 2a_2$ (Ref. 88) and $2a_2 \rightarrow 6e_3$ (Ref. 89) [or $2a_2 \rightarrow 6e_1$ (Ref. 90)] transitions, respectively (Fig. 8).

It was pointed out[91,92] that an increase in the ionic radius of a complexing metal leads to a bathochromic shift of the principal absorption bands of lanthanide dinaphthalocyanine complexes, as in the case of diphthalocyanines.[91,93] This is likely to be caused by weakening of the interligand interaction (Fig. 9). The strongest displacement (relative to the Q-band) is observed for the IV band (from 1818 to 2346 nm) on going from Er to La.[72]

Upon comparsion of the absorption spectra of diphthalocyanines and dinaphthalocyanines, as in the case of their mono derivatives, the radical absorption band and Q- and IV-bands shift bathochromically by ~100 nm to the near-IR region. The Soret band virtually does not shift.[7]

The spectra of hybrid sandwich-planar phthalocyanines feature a broadened absorption band in the range of 600–800 nm, which corresponds to the planar binuclear phthalocyanine moiety of the molecule (Fig. 10).[75] The radical band is situated in the range of 450–500 nm, being characteristic of diphthalocyanines.

VI. Applications of phthalocyanines with an extended π-system

The above review of the literature and our own data indicates that by extending the system of π-electron conjugation of planar phthalocyanines and their analogues, one can control the position of the absorption band in the wavelength range from 600 to 1000 nm. In the case of sandwich complexes, the absorption range broadens to 2200 nm, and an additional possibility of changing the absorption band position by variation of the central metal ion arises. Owing to these properties, these compounds can find wide application in different fields of science and engineering.

Most of phthalocyanine complexes possess pronounced non-linear third-order optical susceptibilities χ^3 (Ref. 94) that exceed the second-order values. Furthermore, phthalocyanines relate to optical limiters whose mechanism of action is based on the decrease in transmittance upon

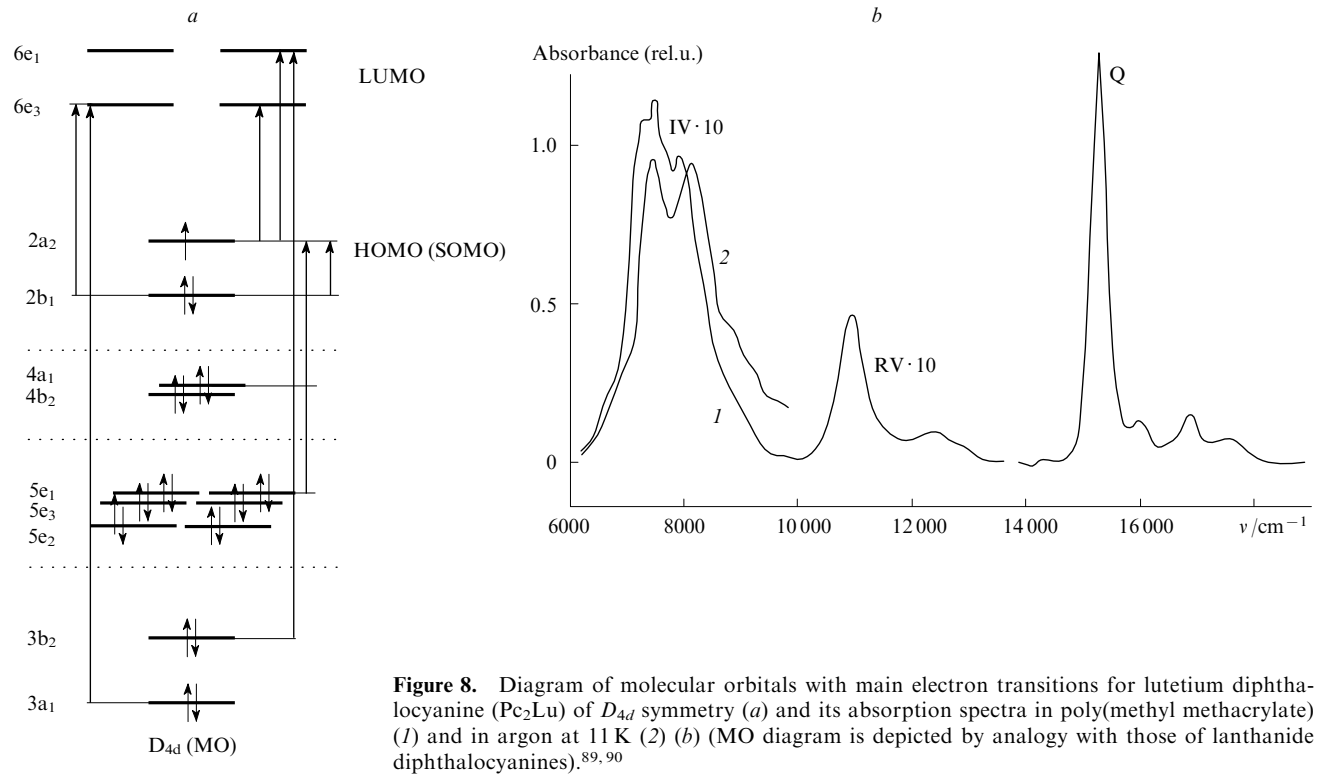


Figure 8. Diagram of molecular orbitals with main electron transitions for lutetium diphthalocyanine (Pc_2Lu) of D_{4d} symmetry (*a*) and its absorption spectra in poly(methyl methacrylate) (*1*) and in argon at 11 K (*2*) (*b*) (MO diagram is depicted by analogy with those of lanthanide diphthalocyanines).[89, 90]

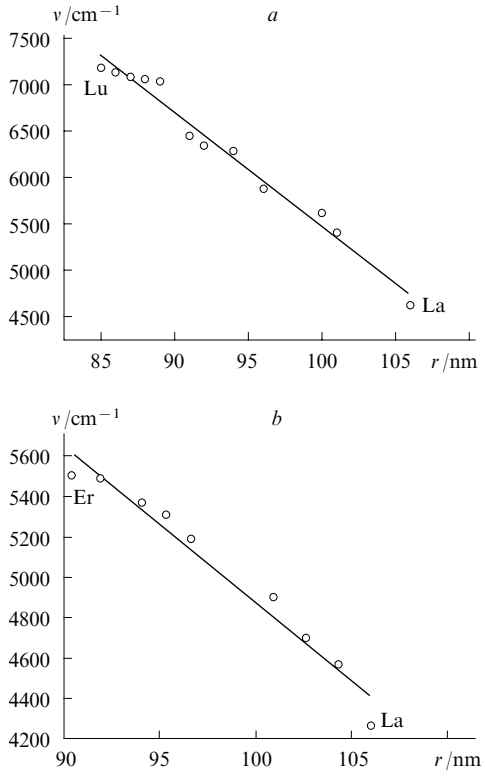


Figure 9. Position of band IV in the absorption spectra of Bu^tPc_2Ln (*a*)[93] and Bu^tNc_2Ln (*b*)[72, 92] *vs.* lanthanide ionic radius (*r*) in CCl_4.

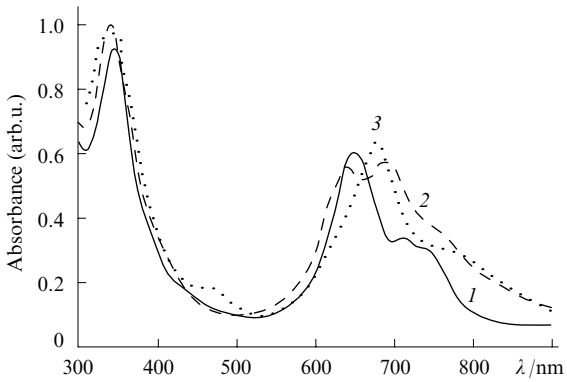


Figure 10. Absorption spectra of the reduced form of compound **101a** (*1*) and the reduced (*2*) and neutral (*3*) forms of complex **103** in THF.[75]

increase in the intensity of the light flux. In the ideal case, the intensity of radiation transmitted by a limiter increases linearly to reach the threshold value I_{lim} (Fig. 11).

The main values that characterize χ^3 are the absorption factor (α_2), which consists of a linear (radiation intensity-independent) and nonlinear parts, and nonlinear refractive index (n_2).

As was mentioned,[94, 95] for compounds that possess an extended system of conjugation, the value of nonlinear susceptibility χ^3 essentially increases. In this respect, such phthalocyanines are important objects for investigation of their nonlinear optical properties.[15]

A series of metal complexes of water-soluble anthracocyanines were patented.[43] These compounds can be used as

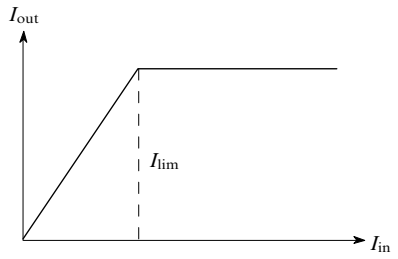


Figure 11. Model of behaviour of an optical limiter (I_{out} is the intensity of radition transmitted by the limiter; I_{in} is the intensity of incident radition).[94]

additives for dyes for ink-jet printers in order to control the dye supply, and owing to the presence of absorption in the near-IR region, they can be used for secret marking of documents.[43]

Phthalocyanines and their analogues are able to pass into the excited state under the action of light. This is particularly important in photodynamic therapy of cancer. Serving as photosensitizers, these molecules transfer energy to triplet oxygen, which is accompanied by generation of active singlet oxygen capable of annihilating tumour cells. It is known that human skin integument is most transparent for radiation of the near-IR region.[2] In this respect, of particular interest are investigations on the propensity of phthalocyanines for photooxidative catalysis. In particular, oxidation of 1,3-diphenylisobenzofuran in toluene saturated with oxygen in the presence of a palladium planar binuclear phthalocyanine on exposure to radiation at $\lambda > 780$ nm was desrcibed.[96] This photosensitizer manifested the activity in this range of wavelengths (2.28×10^{-6} mol litre^{-1} min^{-1}), whereas the corresponding monophthalocyanine appeared to be almost inactive.[96]

A considerbale part of the sunlight spectrum is in the near-IR region; therefore, phthalocyanines that absorb in this range are of particular interest as components for photovoltaic cells. Owing to the presence of the electron-excess heterocyclic macrocycle, these compounds can be used as electron donors. It was proposed[1] to employ naphthalocyanines grafted to nanotubes *via* π–π-stacking interaction as a working layer of photovoltaic cells. The larger the π-system, the more pronounced this interaction.

Yet another effect, which was observed earlier only for diphthalocyanine complexes,[97] was found in our studies for lutetium dinaphthalocyanine **96g**.[27] Using cyclic voltammetry, the electrochemical properties of an electrode made of highly oriented pyrolytic graphite (HOPG) modified with a thin film of phenoxy-substituted lutetium dinaphthalocyanine were studied (Fig. 12).

It is known[97] that redox-transition II (one-electron reduction) is accompanied by transfer of K^+ ions from water to an organic phase and back, whereas redox transition I (one-electron oxidation) is accompanied by transfer of Cl^- ions to the organic phase. Different intensity of peaks I and II is caused by a difference in the phase transfer rate of anions and cations. Curve *2* obtained for an aqueous solution of potassium perchlorate shows only one couple of redox activity peaks I which is associated with the transfer of ClO_4^- ion. The potential of this redox transition is shifted

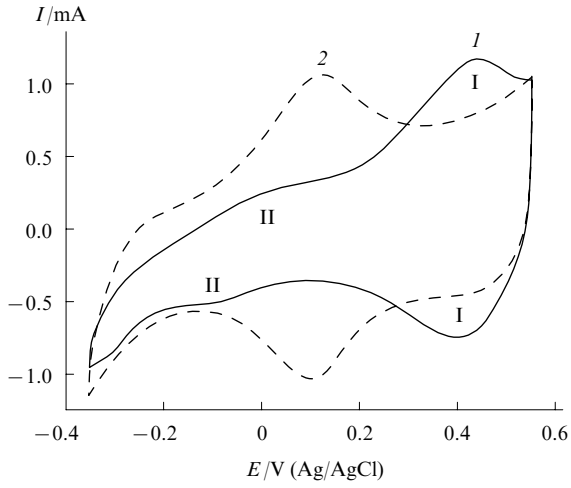


Figure 12. Cyclic voltammograms ($v = 20$ mV s^{-1}) of lutetium dinaphthalocyanine (a solution of 0.2 μl in *p*-nitrophenyl octyl ether; concentration 1 mg ml^{-1}) on HOPG of diameter ~3 mm in 0.1 M KCl (*1*) and $KClO_4$ (*2*).[27]

toward cathodic potentials relative to the position of redox activity peaks observed in a solution containing Cl^- ions (curve *1*). Different positions of redox activity peaks II is caused by different hydrophobicity of the transferred anion: as it increases, the redox activity potential shifts toward cathodic potentials. The peaks II of redox activity, which is accompanied by phase transfer of cations, cannot be obsered in curve *2* due to strong cathodic shift of redox activity peaks I caused by the increase in the hydrophobicity of the aqueous phase anion (ClO_4^-).

Hence, it was shown that lutetium dinaphthalocyanine **96g** can be used to estimate the hydrophobicity of anions upon their transfer through the interface between two immiscible liquids (*p*-nitrophenyloctyl ether – H_2O).

* * *

The presented review considers the methods for synthesis and electronic absorption spectra of planar and sandwich-like phthalocyanines with extended π-system and listed some of their practical applications. Since absorption in the near-IR region is the most widely used property of this class of compounds, particular attention was drawn to the correlations between structural features and the pattern of electronic absorption spectra. This allowed for establishing a series of general regularities, which was especially important for the representatives of novel classes of compounds: hybrid sandwich-planar structures, binuclear naphthalocyanine complexes and some other. In particular, it was found that the 100 nm rule holds not only for monophthalocyanines and sandwich-like complexes, but also for binuclear complexes. Hence, the extension of the system of π-electron conjugation of phthalocaynines and their analogues can be used to control the position of the absorption maximum in a rather wide range of wavelengths, and in some cases, there is additional possibility for variation of the position of absorption bands by varying the nature of the central metal ion.

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