

# Bi- and polynuclear phthalocyanines: synthesis and study of physicochemical properties

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**Abstract.** Various approaches to the synthesis of different types of binuclear phthalocyanines ('clamshell', planar, 'ball') and their polynuclear analogues are considered. Particular attention is focused on the behaviour of binuclear phthalocyanines in solutions. The bibliography includes 91 references.

## I. Introduction

For many years phthalocyanines have been the subject of intensive studies due to widening of their practical application. Being traditionally used as dyes and pigments, at present phthalocyanines attract attention due to their unique spectral, electrochromic, magnetic, semiconducting and other properties owing to a multicontour system of aromatic conjugation and to the ability to form complexes with virtually all elements of the Periodic Table.<sup>1–6</sup> Binuclear phthalocyanines of different structures are especially interesting. These compounds exhibit unique spectroelectrochemical and nonlinear optical properties due to existence of electronic interaction between macrocycles (in the case of binuclear 'clamshell' phthalocyanines<sup>7–19</sup>) or to electron transfer from one macrocycle to another (in the case of planar phthalocyanines<sup>20–31</sup>).

However, the synthesis of binuclear phthalocyanines is labourious, which limits substantially their investigation and particularly their practical application. In most cases, binuclear phthalocyanines are synthesised from two phthalogens of

different structures, which usually results in a hardly separable mixture of phthalocyanine products and in extremely low yields of target compounds (see<sup>6, 8–11, 14–16, 20, 22–24, 28, 32–45</sup>). The development of convenient and accessible methods for the synthesis of binuclear phthalocyanines is an important and topical goal. Recently we have suggested an alternative route for the synthesis of binuclear phthalocyanines from unsymmetrically substituted mononuclear phthalocyanines.<sup>46, 47</sup> This approach allows the control over the number of possible products and, therefore, over selectivity of the process.

Binuclear phthalocyanines are of interest from both theoretical and practical viewpoints. By controlling the mutual position of the macrocycles and the nature of central complexing ions, one can design novel supramolecular structures with unique physicochemical properties.

In this review, the attention is focused on the methods for the synthesis of different types of bi- and polynuclear phthalocyanines and on their physicochemical properties.

## II. Methods for the synthesis of binuclear phthalocyanines of different structures

### 1. Binuclear clamshell phthalocyanines

In the mid-1980s, binuclear phthalocyanines 'linked' by one covalent bridge were first synthesised.<sup>15</sup> This type of compounds was termed 'clamshell' by analogy with porphyrins of related structures, which means 'a shell of a bivalve mollusc'.

Binuclear clamshell phthalocyanines with six neopentyloxy substituents on the periphery are well-soluble in most organic solvents, which facilitates their isolation in the individual state and studies of their physicochemical properties. It was noted<sup>9, 11, 14, 15, 17</sup> that the presence of chromatographically unseparable regioisomers prevents crystallisation of binuclear phthalocyanines and makes impossible X-ray analysis for establishing their structures.

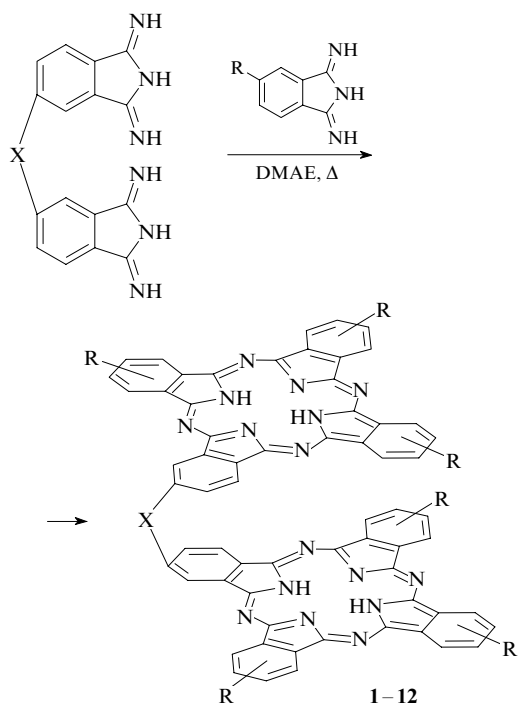
The traditional approach to the synthesis of binuclear clamshell phthalocyanines consists in cyclisation of bis(1,3-diiminoisindolines) with a large excess of substituted 1,3-di-

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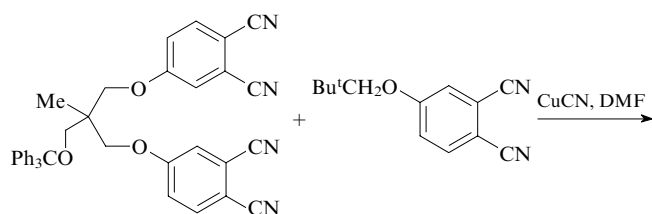
iminoisoindolines<sup>†</sup> in refluxing *N,N*-dimethylaminoethanol (DMAE) for 48–60 h in an argon atmosphere.



In this case, a significant amount of side mononuclear phthalocyanines is formed; the yields of the target binuclear products **1–12**, in most cases, do not exceed 15% (Table 1).<sup>9, 11, 14, 15, 17</sup>

Binuclear phthalocyanine **11** with the macrocycles linked through the C–C bond between the benzene rings was prepared by prolonged refluxing of the corresponding bis(1,3-diiminoisoindoline) with 5-neopentyloxy-1,3-diiminoisoindoline in DMAE in a maximum yield of 33%.<sup>9</sup> Binuclear phthalocyanines **1–12** are readily metallated to give the corresponding complexes with different metals (Zn, Cu, Ni, Co).<sup>9, 11, 14, 15, 17</sup>

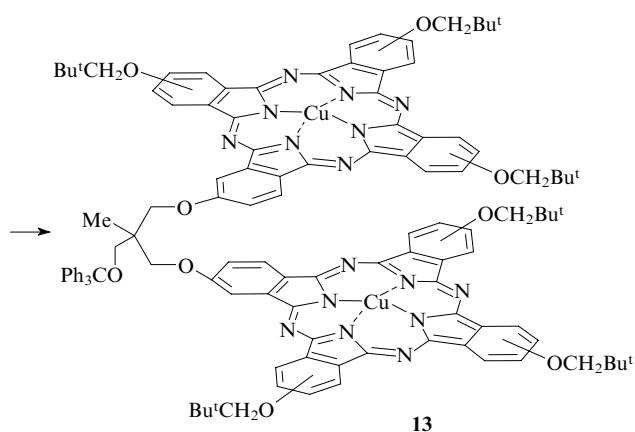
The synthesis of binuclear phthalocyanines can easily be performed by cross-cyclisation of bis(phthalonitrile) with different covalent bridges and substituted phthalonitriles in the presence of bases.<sup>17, 33, 48</sup> Thus, prolonged refluxing of a solution of parent phthalonitriles in DMF in the presence of CuCN gives the target binuclear copper phthalocyanine **13** in 1% yield.



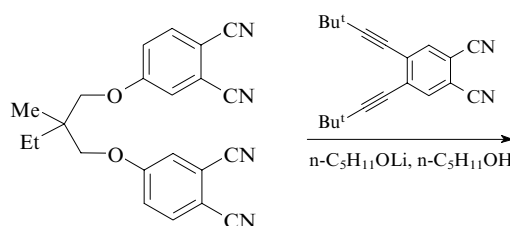
<sup>†</sup> Bis(1,3-diiminoisoindolines) are usually obtained by cross-linking two molecules of 4-substituted phthalonitrile with the corresponding bifunctional compounds playing the role of spacers.

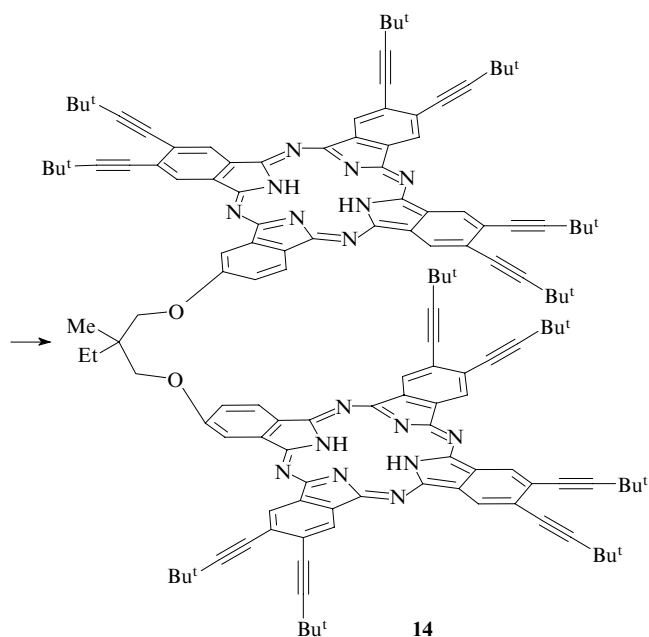
**Table 1.** Binuclear clamshell phthalocyanines.

| ~X~                                | R   | Compound    | Yield (%)    | Ref.   |
|------------------------------------|---|-------------|--------------|--------|
|                                    | Bu <sup>t</sup> CH <sub>2</sub> O                 | <b>1</b>    | 10           | 15     |
|                                    | Bu <sup>t</sup> CH <sub>2</sub> O                 | <b>2</b>    | 13           | 15     |
| ~(CH <sub>2</sub> ) <sub>2</sub> ~ | Bu <sup>t</sup> CH <sub>2</sub> O                 | <b>3a</b>   | 10           | 15     |
| ~(CH <sub>2</sub> ) <sub>2</sub> ~ | Bu <sup>t</sup> (CH <sub>2</sub> ) <sub>2</sub>   | <b>3b</b>   | 8            | 15     |
| ~(CH <sub>2</sub> ) <sub>2</sub> ~ | Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>2</sub> | <b>3c</b>   | 7            | 15     |
| ~(CH <sub>2</sub> ) <sub>4</sub> ~ | Bu <sup>t</sup> CH <sub>2</sub> O                 | <b>4</b>    | 1.4          | 15     |
|                                    | Bu <sup>t</sup> CH <sub>2</sub> O                 | <b>5</b>    | 17           | 17     |
|                                    | Bu <sup>t</sup> CH <sub>2</sub> O                 | <b>6</b>    | 10           | 15, 17 |
| ~C≡C~                              | Bu <sup>t</sup> CH <sub>2</sub> O                 | <b>7</b>    | 7.4          | 11     |
| ~CH=CH~<br>( <i>cis, trans</i> )   | Bu <sup>t</sup> CH <sub>2</sub> O                 | <b>8a,b</b> | 28 (overall) | 11     |
|                                    | Bu <sup>t</sup> CH <sub>2</sub> O                 | <b>9</b>    | 8.7          | 9      |
|                                    | Bu <sup>t</sup> CH <sub>2</sub> O                 | <b>10</b>   | 12           | 9      |
| None                               | Bu <sup>t</sup> CH <sub>2</sub> O                 | <b>11</b>   | 33           | 9      |
| ~O~                                | Bu <sup>t</sup> CH <sub>2</sub> O                 | <b>12</b>   | 11           | 14     |

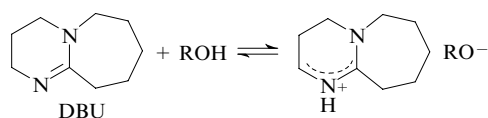


Isagot *et al.*<sup>33</sup> used a strong base *n*-C<sub>5</sub>H<sub>11</sub>OLi in the synthesis of binuclear phthalocyanine **14**. The yield of the target product was 3.5%.

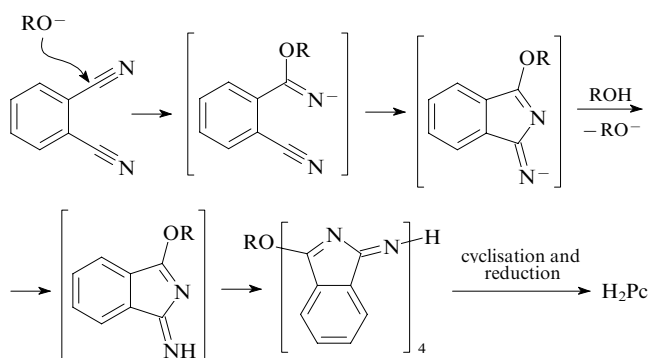




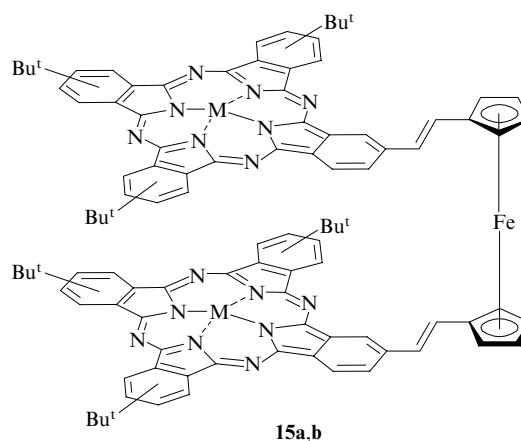
Nitrogen-containing heterocyclic compounds, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and pyridine, are often used as alternative and convenient bases for preparation of phthalocyanines.<sup>49</sup> Their interaction with alcohols employed as solvents in the synthesis of polynuclear phthalocyanines resulted in alkoxides.<sup>49</sup> For example,



The alkoxides formed attack the carbon atom of the CN group of phthalonitrile as nucleophiles.



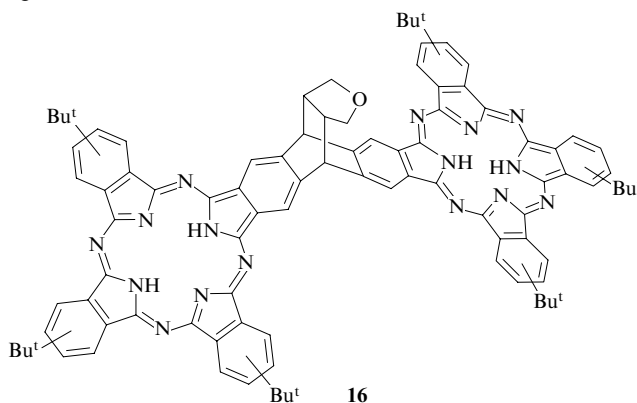
With DMAE as a solvent, tetramerisation of phthalonitriles occurs without bases. In this case, radicals Me<sub>2</sub>NCH<sub>2</sub>·CH<sub>2</sub>O<sup>·</sup> are believed<sup>50,51</sup> to be the reactive species that induce the reaction. In this way González *et al.*<sup>48</sup> obtained binuclear phthalocyanines **15a,b**.



M = Zn (a), Co (b).

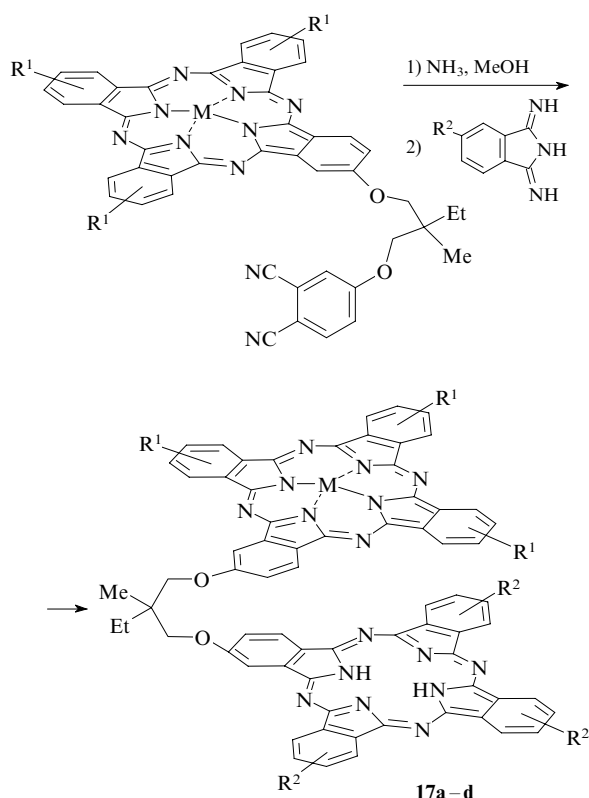
Ceyhan *et al.*<sup>52</sup> showed that thermal activation of phthalonitriles and conducting the reaction in quinoline in the presence of zinc or cobalt acetates increase the yield of the target binuclear phthalocyanines (in some cases, the yield exceeded 30%).

Recently, Asano and Kobayashi<sup>53</sup> have reported the synthesis of a novel binuclear phthalocyanine **16** with the macrocycles linked through a rigid polycyclic bridge. They ascribed a gable configuration to this phthalocyanine; however, in our opinion, its conformation should be considered as a partially open 'shell'.<sup>16</sup>



The synthesis of unsymmetrical binuclear phthalocyanines by cross-cyclisation of phthalogens of different nature is impossible due to labourious separation of the products of several cross-cyclisation reactions<sup>10</sup> and due to a well-known phenomenon of aggregation of phthalocyanine molecules;<sup>7,54</sup> for these reasons, special approaches to preparation of these compounds have been developed.

Leznoff *et al.*<sup>10</sup> suggested a rather interesting approach to the synthesis of unsymmetrical binuclear clamshell phthalocyanines (compounds **17a–d**) containing phthalocyanine fragments differing in either the nature of substituents or the presence/absence of the metal atom. Leznoff *et al.*<sup>10</sup> used unsymmetrically substituted monophthalocyanines containing the phthalonitrile fragment as starting compounds. The authors believe that unsymmetrical complexes obtained can substitute binuclear porphyrins used in electro- and photocatalytic processes.



$R^1 = \text{OCH}_2\text{Bu}^t$ ;  $R^2 = \text{H}$  (**a**),  $\text{Bu}^t$  (**b**),  $\text{OCH}_2\text{Bu}^t$  (**c**, **d**);  
 $M = \text{H}_2$  (**a–c**),  $\text{Cu}$  (**d**).

We found<sup>18</sup> that if the cross-cyclisation of the corresponding bis- and monophthalonitriles is conducted by fusion in the presence of a metal diacetate, the unsymmetrically substituted mononuclear complex **19** with the phthalocyanine fragment can be isolated along with binuclear metal complex **18** (Scheme 1).

The formation of compound **19** in the synthesis of binuclear phthalocyanine **18** is rather demonstrative because formally this unsymmetrically substituted phthalocyanine is a precursor of binuclear phthalocyanine, *i.e.* binuclear phthalocyanines are formed in two stages: cyclisation of one macrocycle occurs first and then that of the other macrocycle. In this respect, the question arises why these precursors have not been found earlier by other researches? It is known that compounds

like **19** practically fully oligomerise upon prolonged refluxing in solutions in the presence of strong bases, therefore, it cannot be ruled out that after the reaction was over, the researchers simply did not notice the presence of these compounds in the reaction mixtures against a background of a considerable amount of phthalocyanine oligomers.

Thus Leznoff<sup>17</sup> notes that when the cyclisation of bis(1,3-diiminoisindolines) with 4-neopentyloxy-1,3-diiminoisindoline) was completed and the excess of mononuclear 2,9,16,23-tetrakis(neopentyloxy)phthalocyanine was removed by flash chromatography, in the isolated fraction containing mainly binuclear phthalocyanine, an unknown compound<sup>‡</sup> was found, which had higher chromatographic mobility than the binuclear phthalocyanine. Marcuccio *et al.*,<sup>15</sup> when purifying binuclear phthalocyanines by chromatography, also isolated a fraction, along with monophthalocyanines, which they took without proof for a trinuclear phthalocyanine. Unfortunately, the authors<sup>15, 17</sup> did not pay proper attention to these facts, as these unidentified compounds might have been precursors of binuclear phthalocyanines.

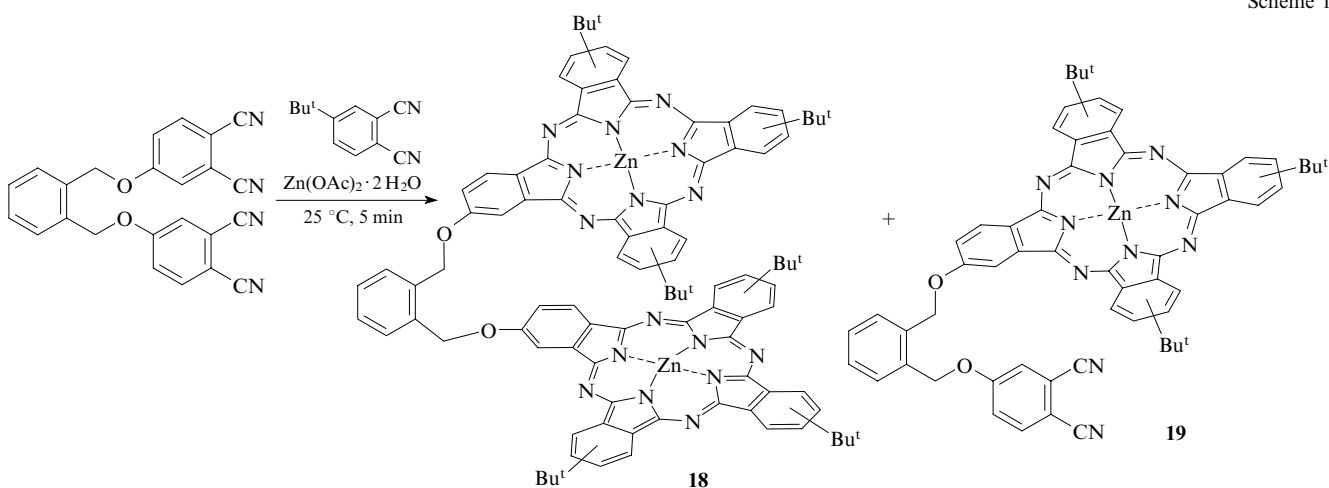
Unsymmetrically substituted monophthalocyanines **20** served as starting compounds in the synthesis of heterometallic and heteroligand binuclear phthalocyanines **21a,b**. We found<sup>47</sup> that in order to achieve efficient cross-cyclisation of complex **20** and phthalonitriles, it is practical to fuse reactants in the presence of metal salts (Scheme 2).

A comparison of the yields of binuclear clamshell phthalocyanines obtained by the above methods permits one to draw the conclusion that refluxing of bis- and mono-1,3-diiminoisindolines in DMAE or fusion of bis- and monophthalonitriles in the presence of metal salts are the most promising methods. Notably that in all cases, monophthalocyanines are formed as by-products complicating chromatographic purification of target binuclear products.

## 2. Planar binuclear phthalocyanines

The synthesis of planar binuclear phthalocyanines **22a–c** (Table 2), in which the macrocycles share a common benzene ring was first performed by Canadian researchers.<sup>22, 28</sup>

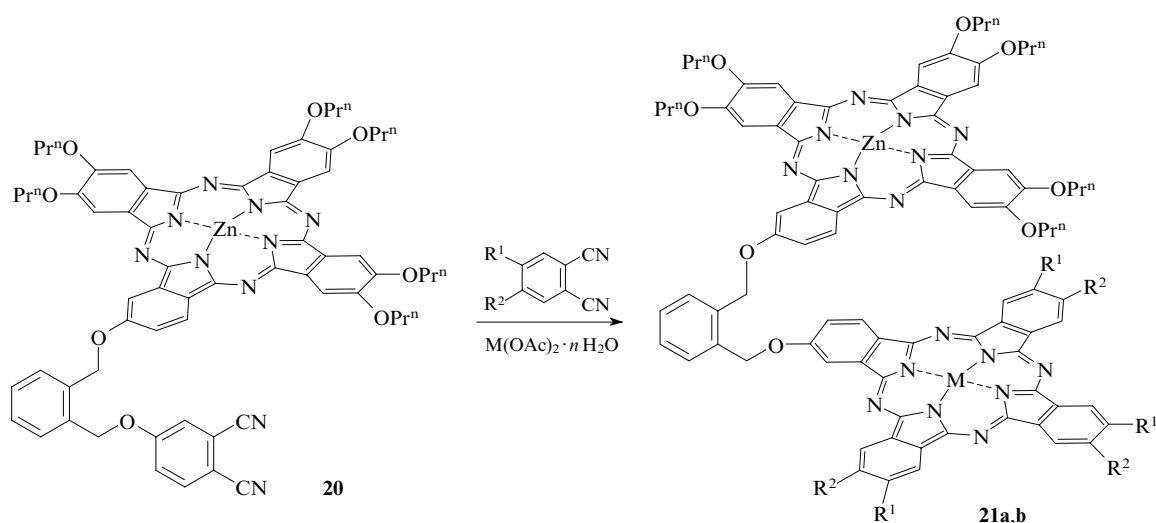
By now a large number of planar binuclear phthalocyanines connected through a common benzene or naphthalene



Scheme 1

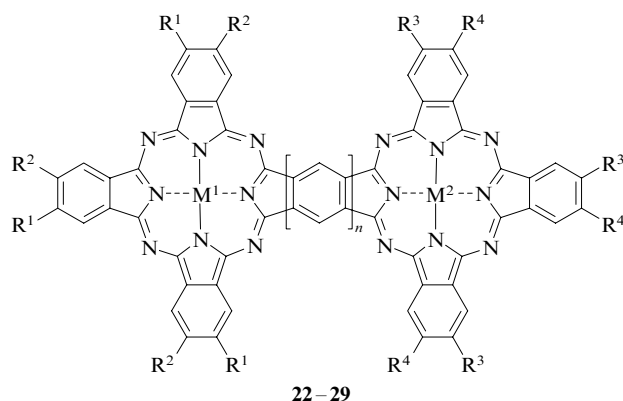
<sup>‡</sup> This compound was detected in the stage of purification of binuclear phthalocyanine by the TLC.

Scheme 2



$R^1 = \text{Bu}^t$ ,  $R^2 = \text{H}$ ,  $M = \text{Zn}$  (**a**);  $R^1 = R^2 = \text{OPr}^n$ ,  $M = \text{Cu}$  (**b**).

core has been synthesised.<sup>30, 41, 43, 55–57</sup> Derivatives of mono- and bis(diiminoisoindolines) serve usually as parent compounds for the synthesis of this type ligands, as in the synthesis of binuclear clamshell phthalocyanines. The ligands formed are easily metallated to give complexes.<sup>22, 28, 30, 40, 41, 55</sup>



$n = 1, 2$ .

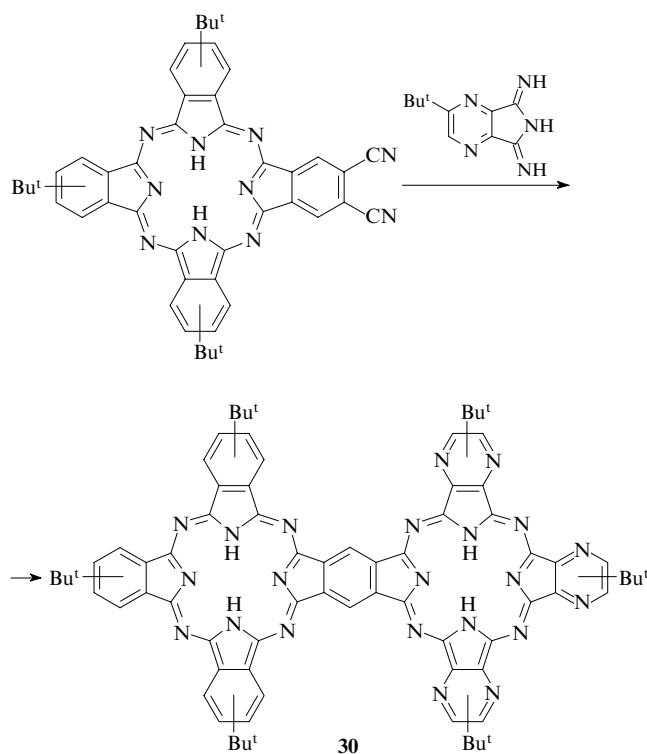
There are other approaches to the synthesis of planar binuclear phthalocyanines. For example, sulfo-substituted binuclear cobalt phthalocyanine **26** was prepared by fusing pyromellitic anhydride, ammonium 4-sulfophthalate, urea and  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ .<sup>36</sup> This change in the nature of phthalogens did not increase the yield of the target product, moreover, in this case, strongly corrosive media had to be avoided.

The synthesis of unusual planar heteronuclear complex **30** is reported.<sup>21</sup> This synthesis is similar to that of unsymmetrical binuclear phthalocyanines **17a–d**. Unsymmetrically substituted phthalocyanine with active CN groups and 6*H*-pyrrolo[3,4-*b*]pyrazine-5,7-diimine were used as starting compounds.

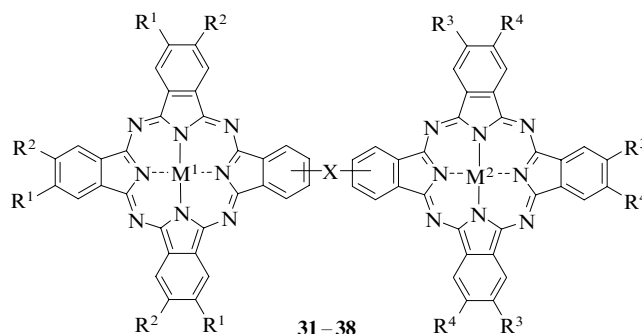
**Table 2.** Planar binuclear phthalocyanines with the macrocycles joined through a common benzene or naphthalene core.

| $R^1 - R^4$  | $M^1, M^2$                               | $n$ | Com-<br>pound | Yield<br>(%)    | Ref.   |
|--|--|-----|---------------|-----------------|--------|
| $R^1 = R^3 = \text{H}$ ,<br>$R^2 = R^4 = \text{OCH}_2\text{Bu}^t$                            | $M^1 = M^2 = \text{H}_2$                 | 1   | <b>22a</b>    | 12              | 22, 28 |
|  | $M^1 = M^2 = \text{Zn}$                  | 1   | <b>22b</b>    | 92 <sup>a</sup> | 22, 28 |
|  | $M^1 = M^2 = \text{Co}$                  | 1   | <b>22c</b>    | 63 <sup>a</sup> | 22, 28 |
|  | $M^1 = M^2 = \text{Zn}$                  | 1   | <b>22d</b>    | 10              | 31, 57 |
| $R^1 = R^3 = \text{H}$ ,<br>$R^2 = R^4 = \text{Bu}^t$  | $M^1 = M^2 = \text{H}_2$                 | 1   | <b>23a</b>    | 8               | 30     |
|  | $M^1 = M^2 = \text{Ni}$                  | 1   | <b>23b</b>    | 60 <sup>a</sup> | 30     |
| $R^1 = R^2 = R^3 =$<br>$= R^4 = \text{OC}_{12}\text{H}_{23-n}$                               | $M^1 = M^2 = \text{H}_2$                 | 1   | <b>24a</b>    | 10              | 41     |
|  |  | 2   | <b>24b</b>    | 6               | 41     |
| $R^1 = R^2 = R^3 =$<br>$= R^4 = \text{OCH}_2\text{CH}(\text{Et})\text{Bu}^n$                 | $M^1 = M^2 = \text{H}_2$                 | 1   | <b>25a</b>    | 1               | 55     |
|  | $M^1 = M^2 = \text{Cu}$                  | 1   | <b>25b</b>    | 2               | 55     |
|  | $M^1 = M^2 = \text{Ni}$                  | 2   | <b>25c</b>    | 20              | 43     |
|  | $M^1 = \text{Ni}$ ,<br>$M^2 = \text{Cu}$ | 2   | <b>25d</b>    | 18              | 43     |
| $R^1 = R^3 = \text{H}$ ,<br>$R^2 = R^4 = \text{SO}_3\text{NH}_4$                             | $M^1 = M^2 = \text{Co}$                  | 1   | <b>26</b>     | 8               | 36     |
| $R^1 = \text{Bu}^t$ , $R^2 = \text{H}$ ,<br>$R^3 = R^4 = \text{OC}_8\text{H}_{17-n}$         | $M^1 = M^2 = \text{Zn}$                  | 1   | <b>27a</b>    | 10              | 56     |
|  | $M^1 = \text{Zn}$ ,<br>$M^2 = \text{Ni}$ | 1   | <b>27b</b>    | 9               | 56     |
| $R^1 = R^2 =$<br>$= \text{OCH}_2\text{CH}(\text{Et})\text{Bu}^n$ ,<br>$R^3 = R^4 = \text{H}$ | $M^1 = \text{Ni}$ ,<br>$M^2 = \text{Cu}$ | 2   | <b>28a</b>    | 20              | 43     |
|  | $M^1 = M^2 = \text{Ni}$                  | 2   | <b>28b</b>    | 23              | 43     |
| $R^1 = R^2 = R^3 =$<br>$= R^4 = \text{Et}$   | $M^1 = M^2 = \text{Zn}$                  | 1   | <b>29a</b>    | 8               | 31, 57 |
| $R^1 = R^2 = R^3 =$<br>$= R^4 = \text{Bu}^n$   | $M^1 = M^2 = \text{Zn}$                  | 1   | <b>29b</b>    | 9               | 31, 57 |
| $R^1 = R^2 = R^3 =$<br>$= R^4 = \text{OPr}^n$  | $M^1 = M^2 = \text{Zn}$                  | 1   | <b>29c</b>    | 8               | 31, 57 |

<sup>a</sup> The yields of metal complexes synthesised by metallation of the corresponding ligands are presented.



Since 1997, wide-scale research on the synthesis and properties of planar phthalocyanines linked by different spacers has been performed.<sup>58–68</sup>



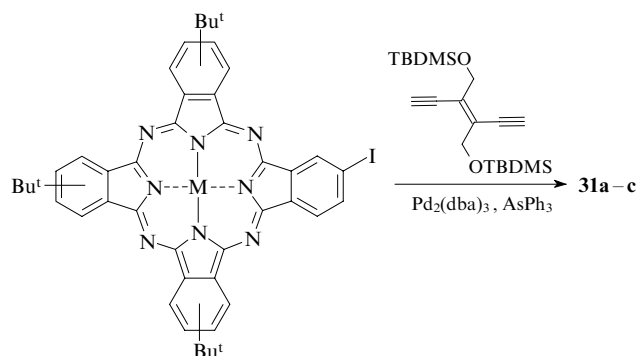
Notations see in Table 3.

The conjugated electronic systems in complexes **31–38** are attractive because they favour electron transfer. By now a large variety of this type complexes have been synthesised (Table 3).<sup>58, 60, 63, 68–70</sup> The basic approach to their synthesis consists in cross-coupling of unsymmetrically substituted monophthalocyanines with bifunctional compounds playing the role of a covalent bridge.<sup>38, 58–60, 63</sup> Functionally substituted monophthalocyanines with a halogen atom (most often iodine) is one of the substituents used as building blocks, compounds with terminal acetylene fragments are used as

**Table 3.** Planar binuclear phthalocyanines with the macrocycles joined by different covalent bridges.

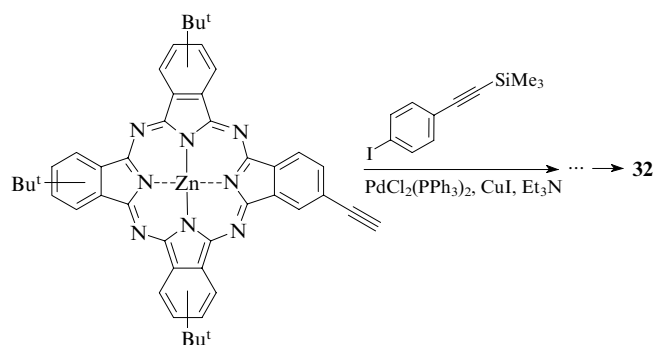
| $R^1 - R^4$                               | X  | $M^1, M^2$           | Compound   | Ref. |
|---|--|----------------------|------------|------|
| $R^1 = R^3 = Bu^t, R^2 = R^4 = H$         | <p>(TBDMS = <math>SiMe_2Bu^t</math>)</p> | $M^1 = M^2 = Co$     | <b>31a</b> | 58   |
|   |  | $M^1 = M^2 = Zn$     | <b>31b</b> | 58   |
|   |  | $M^1 = Zn, M^2 = Co$ | <b>31c</b> | 58   |
|   |  |                      |            |      |
| $R^1 = R^2 = R^3 = R^4 = Bu^t$            |  | $M^1 = M^2 = Zn$     | <b>32</b>  | 68   |
| $R^1 = R^2 = R^3 = R^4 = Bu^t$            |  | $M^1 = M^2 = Zn$     | <b>33a</b> | 63   |
|   |  | $M^1 = Zn, M^2 = Ni$ | <b>33b</b> | 63   |
|   |  | $M^1 = M^2 = Zn$     | <b>34a</b> | 63   |
|   |  | $M^1 = M^2 = Ni$     | <b>34b</b> | 63   |
|   |  |                      |            |      |
| $R^1 = R^2 = R^3 = R^4 = OCH_2CH(Et)Bu^n$ |  | $M^1 = M^2 = Zn$     | <b>35</b>  | 60   |
|   |  | $M^1 = M^2 = Ni$     | <b>36</b>  | 63   |
| $R^1 = R^2 = R^3 = R^4 = OC_8H_{17-n}$    |  | $M^1 = M^2 = Ni$     | <b>37</b>  | 69   |
|   |  | $M^1 = Zn, M^2 = Ni$ | <b>38</b>  | 70   |

linking covalent bridges.<sup>24</sup> For example, complexes **31a–c** were obtained in this way.



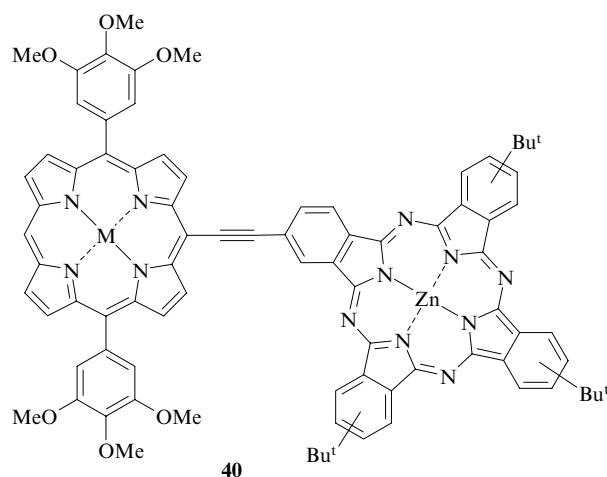
TBDMS is  $\text{SiMe}_2\text{Bu}^t$ , dba is *trans,trans*-dibenzylideneacetone.

Phthalocyanines with the acetylene fragment and covalent bridges containing iodine atoms are used more seldom. Binuclear phthalocyanine **32** was prepared in this way. In this case, the synthesis was carried out in several stages. After the addition of 4-(trimethylsilyl)ethynyl iodobenzene to monophthalocyanine, the protecting  $\text{Me}_3\text{Si}$  group was removed and the cross-coupling was repeated by the addition of first the bridging reagent and then the starting monophthalocyanine.



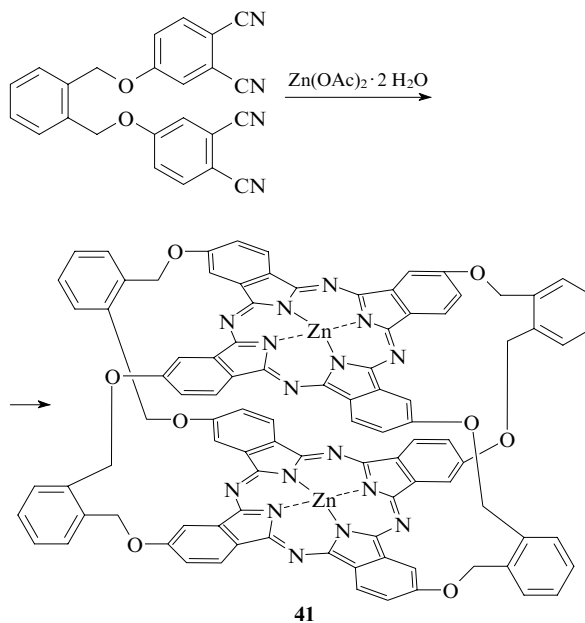
An interesting planar binuclear phthalocyanine is formed upon dimerisation of unsymmetrically substituted monophthalocyanine **39** with two *ortho* acetylene substituents in one of the benzene rings (Scheme 3).<sup>61</sup>

The cross-coupling reaction is used for the preparation of various heteronuclear complexes,<sup>59</sup> for example, phthalocyanine–porphyrin complexes **40**.



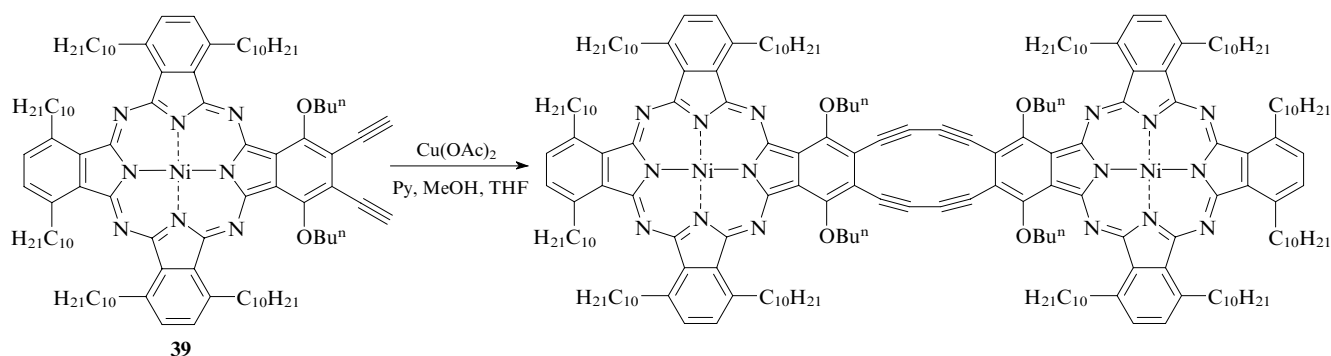
### 3. 'Ball'-type binuclear phthalocyanines

In 2002 we synthesised<sup>71</sup> novel binuclear phthalocyanine **41** that we termed as 'ball'. The macrocycles in this type phthalocyanines are strapped by four covalent bridges, in our case, by 1,2-bis(oxymethyl)benzene bridges.



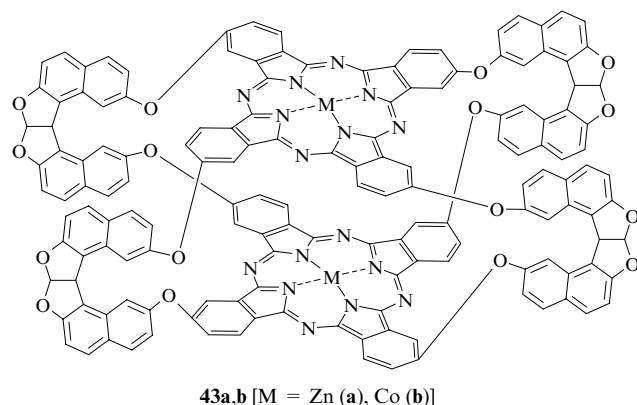
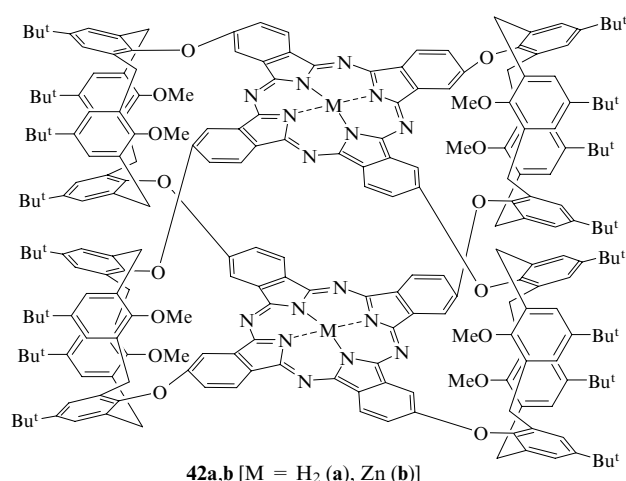
Complex **41** results from self-cyclisation of 1,2-bis(3,4-dicyanophenoxymethyl)benzene in the presence of zinc ace-

Scheme 3



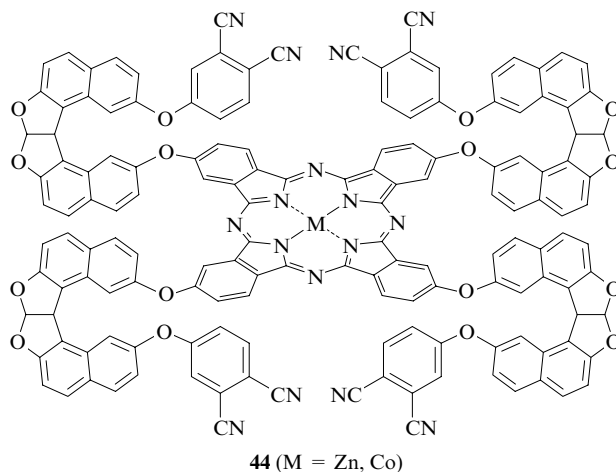
tate. Earlier, self-cyclisation of bis(phthalonitriles) has been used for the preparation of side-strapped monophthalocyanines cross-linked from the opposite sides by two covalent bridges<sup>72–75</sup> and of polymers.<sup>76–80</sup> We suggested the optimal<sup>§</sup> method for the synthesis of complex **41** by fusion of the parent bis(phthalonitrile) with a large excess of zinc acetate. In this case, the yield of the product reached 33%. Later, phthalocyanines of similar structure but with shorted bridges were prepared.<sup>81</sup>

Recently Turkish scientists<sup>19, 44, 45</sup> have prepared binuclear phthalocyanines **42** and **43** in which the macrocycles are linked by calixarene and bis(naphthofuran) bridges. Citing our paper,<sup>71</sup> they also termed these compounds as binuclear ball phthalocyanines.



It was noted<sup>19</sup> that, if tetramerisation of bis(phthalonitrile) is performed in a sealed ampoule in the presence of an excess of metallic lithium, binuclear ligand **42a** can be obtained in 55% yield. The use of a zinc salt instead of metallic lithium leads to a more than twofold decrease in the yield of the target complex **42b** as compared to the yield of corresponding ligand.

<sup>§</sup> Using standard approaches, the target binuclear complex was formed in trace amounts; the main reaction products were phthalocyanine polymers and oligomers.



Monophthalocyanines **44** containing four phthalonitrile fragments are formed as by-products in the synthesis of complexes **43**. They seem to be considered as precursors of binuclear ball phthalocyanines.

In our opinion, phthalocyanines **41–43** are promising compounds for the synthesis of host–guest complexes. Manipulating with the nature of spacers and central metal atoms, it is possible to tune the distance between the macrocycles and to place molecules of a suitable size into the cavity between the macrocycles.

\* \* \*

We considered the basic approaches to the synthesis of binuclear phthalocyanines of different structures: cross-cyclisation of mono- and bis(1,3-diiminoisoindolines) or phthalonitriles, cross-coupling and self-cyclisation reactions of bis(phthalonitriles). In all cases, the synthesis of binuclear phthalocyanines is a time- and labour-consuming process resulting in target products in overall yields not exceeding, as a rule, 30%. In our opinion, the preference should be given to the method of cross-coupling, which permits quite easy preparation of different unsymmetrical heterometallic heteroligand phthalocyanines and their analogues. This is a really unique method for ‘assembling’ binuclear phthalocyanines from existing unsymmetrically substituted monophthalocyanines playing the role of ‘building blocks’.

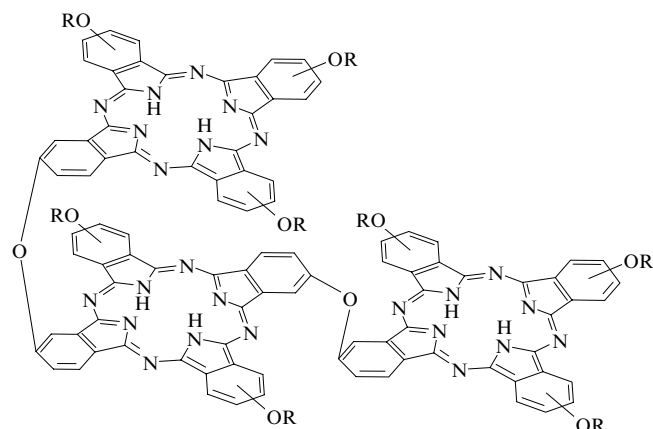
### III. Methods for the synthesis of polynuclear phthalocyanines

In addition to the data on the synthesis of binuclear phthalocyanines, numerous reports on the synthesis and properties of tri-, tetra-, penta- and polynuclear phthalocyanines are available in the literature.

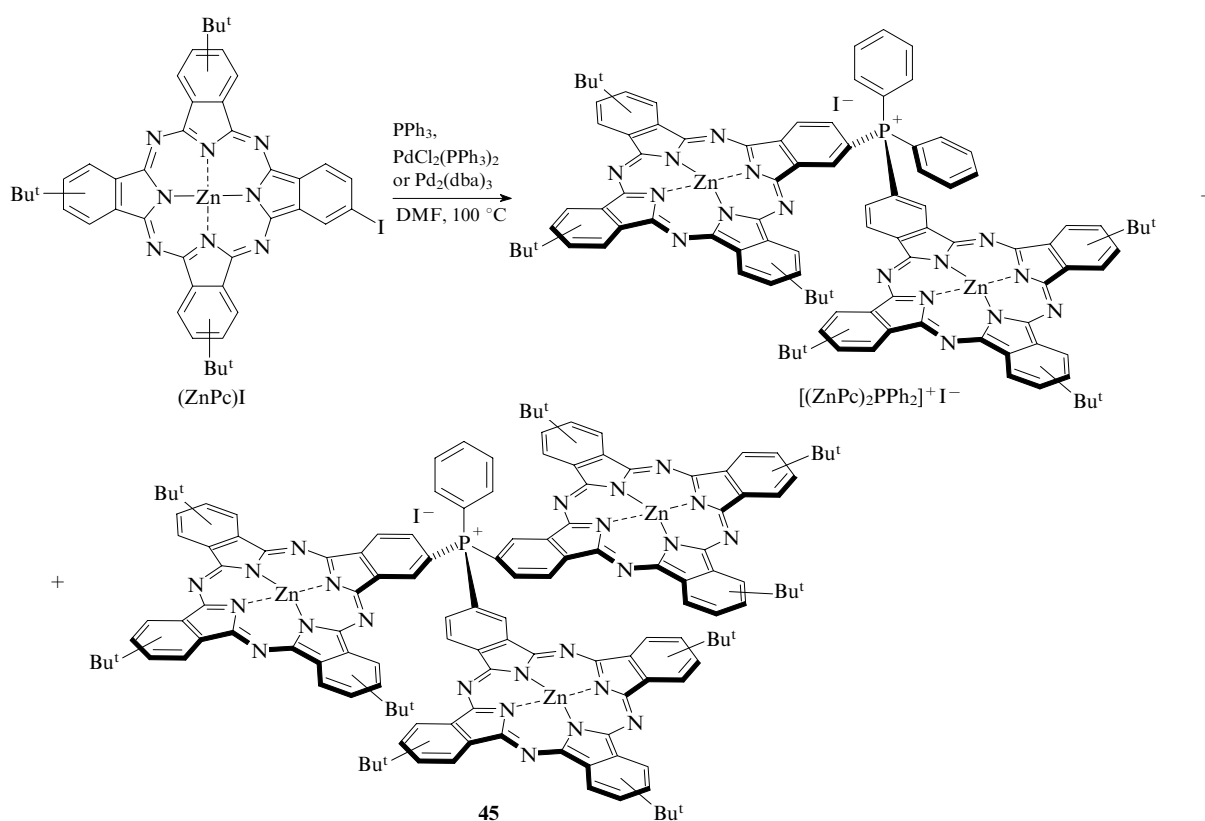
Trinuclear phthalocyanines were first found as by-products in the synthesis of binuclear clamshell phthalocyanines.<sup>15, 17</sup>

These compounds were detected by mass spectrometry, however, the attempts to isolate them in the individual state failed. Later it was shown that trinuclear phthalocyanines can be obtained in large amount using cross-cyclisation [for instance, of bis(diiminoisoindolines) with phthalonitriles].<sup>14</sup>

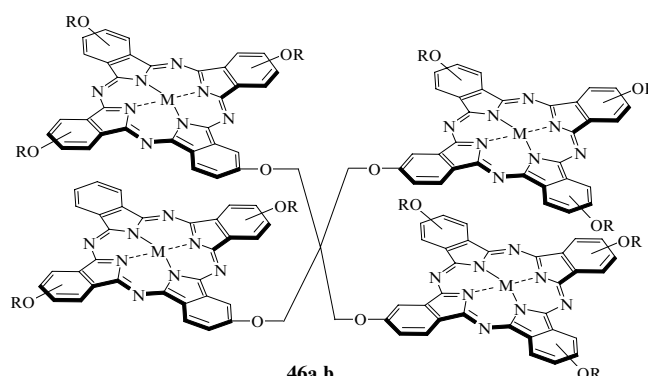




Unusual phosphonium salts  $[L_nPPh_{4-n}]^+X^-$  ( $n = 1-3$ ) containing macrocyclic zinc phthalocyanines ( $L = ZnPc$ ) as one, two or three ligands have been synthesised by Torre *et al.*<sup>82</sup> They were prepared from zinc 2-iodo-9,16,23-tris(*tert*-butyl)phthalocyanine and triphenylphosphine in the presence of palladium catalysts,  $Pd_2(dba)_3$ ,  $Pd(PPh_3)_2Cl_2$  or  $Pd(Ac)_2$ . The catalysis with complexes  $Pd_2(dba)_3$  and  $Pd(PPh_3)_2Cl_2$  results in binuclear phthalocyanine  $[(ZnPc)_2PPh_2]^+I^-$  as the major reaction product, which is formed due to ligand exchange (Scheme 4), catalysis with  $Pd(Ac)_2$  gave trinuclear zinc phthalocyanine  $[(ZnPc)_3PPh]^+I^-$  (**45**, yield 3%) as a by-product. The latter is formed upon reaction of the major product *viz.*, binuclear phthalocyanine  $[(ZnPc)_2PPh_2]^+I^-$ , with monophthalocyanine. The yield of compound **45** can be increased to 10%, if zinc 2-iodo-9,16,23-tris(*tert*-butyl)phthalocyanine is added to the reaction mixture in the stoichiometric ratio with respect to the binuclear complex.



Metal-free tetranuclear phthalocyanine **46a** was obtained in 12% yield upon random cyclisation of tetrakis(1,3-diiminoisoidoline), the derivative of pentaerithritol, with 4-neopentyloxyphthalonitrile.<sup>7</sup> Metallation of ligand **46a** with anhydrous  $CoCl_2$  results in the corresponding complex **46b** in 89% yield.



R = Bu<sup>t</sup>CH<sub>2</sub>; M = H<sub>2</sub> (**a**), Co (**b**).

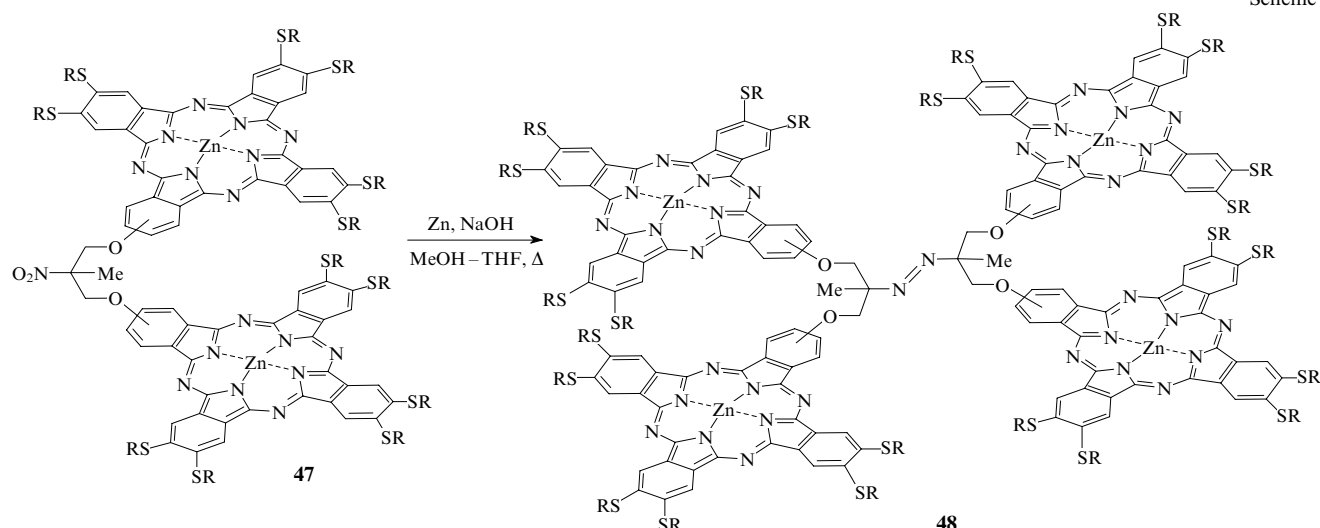
The authors consider compound **46** as an ensemble consisting of two binuclear clamshell phthalocyanines bound through common carbon atom.

An unusual method for the synthesis of tetranuclear phthalocyanines was suggested by Ceyhan *et al.*<sup>52</sup> Binuclear phthalocyanine **47** containing the nitro group in the covalent bridge was used as a starting compound. The presence of the nitro group made possible condensation of compound **47** to give tetranuclear complex **48** in a high yield (Scheme 5).

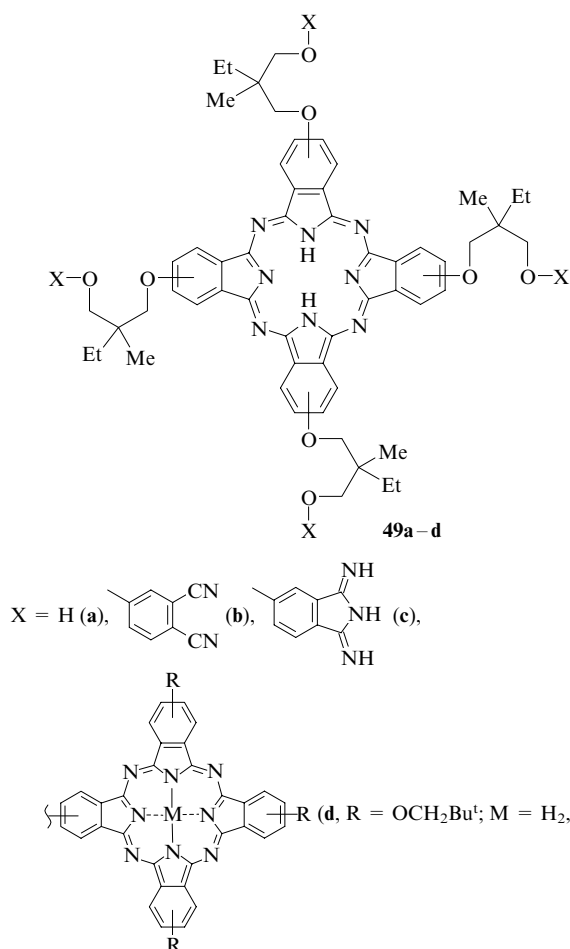
Leznoff *et al.*<sup>10</sup> used somewhat different approach to the synthesis of pentanuclear phthalocyanine **49d**. First phthalocyanine **49b** with four phthalonitrile fragments was obtained by the reaction of symmetrical monophthalocyanine **49a** con-

Scheme 4

Scheme 5



taining four OCH<sub>2</sub>C(Et)(Me)CH<sub>2</sub>OH substituents in the benzene rings with 4-nitrophthalonitrile. The phthalonitrile fragments in compound **49b** were transformed to the corresponding 1,3-diiminoisoindoline ones. Cross-cyclisation of derivative **49c** obtained with 5-neopentyloxy-1,3-diiminoisoindoline resulted in pentanuclear phthalocyanine **49d**.



As for phthalocyanine polymers and polynuclear phthalocyanines, they are inevitably formed as by-products in the

synthesis of binuclear phthalocyanines by random cyclisation.<sup>18, 47, 57</sup> These polymers have ordered structures and are of no interest. Special methods for the synthesis of polynuclear phthalocyanines of predetermined structures have been developed.<sup>83, 84</sup>

#### IV. Peculiarities of isolation and purification of bi- and polynuclear phthalocyanines

Isolation of bi- and polynuclear phthalocyanines from reaction mixtures is a labourious procedure. In most cases, DMAE and 2-methoxyethanol, which are infinitely water-soluble, are used as solvents in the synthesis of binuclear phthalocyanines. After the reaction is completed, the mixtures obtained are poured into water and suspensions formed are refluxed for several hours.<sup>9, 11, 15, 17</sup> Phthalocyanine products are filtered off, washed with water, methanol or acetonitrile until filtrates become colourless.<sup>7, 10, 14</sup>

The use of lithium pentoxide for the synthesis of compound **14** necessitated the treatment of the reaction mixture with a mixture of concentrated hydrochloric acid, methanol and ethanol in a ratio of 1 : 1 : 1 for the isolation of the product. This treatment led to demetallation and to formation of free binuclear ligand.

Standard column chromatography is used for purification of bi- and polynuclear phthalocyanines. Silica gel is usually used as a sorbent.<sup>7, 14, 15, 17, 33, 58–64, 82</sup> At first, more usually phthalocyanines are isolated from reaction mixtures, then, with an increase in eluent polarity, the target bi- and polynuclear phthalocyanines. Sometimes thin-layer chromatography is used for more thorough purification.<sup>10</sup>

It was noted<sup>9, 11, 15, 17</sup> that binuclear phthalocyanines obtained from unsymmetrically substituted 1,3-diiminoisoindolines exist as a mixture of a large number of geometrical isomers. It is impossible to separate these isomers by standard column or thin-layer chromatography. Chromatographic isolation of the target products is significantly facilitated, if symmetrical phthalogens were used in the synthesis.<sup>33</sup>

For chromatographic purification of bi- and polynuclear phthalocyanines, standard approaches should often be modified, for example, flash chromatography<sup>9–11, 14, 15, 17</sup> or vacuum liquid chromatography should be used.<sup>9, 14, 15, 85</sup> One of the most promising methods for purification of bi- and

polynuclear phthalocyanines is the use of gel chromatography. The BioBeads SX1 carrier (Bio-Rad) and tetrahydrofuran as an eluent were used for the isolation of bi- (compounds **8–11**)<sup>9–11</sup> and tetranuclear (compound **46a**)<sup>7</sup> phthalocyanines. The advantage of this method over absorption methods consists, in our opinion, in easy regeneration of the carrier (it is sufficient to wash the column with the same solvent, and it can be reused). However, the preparation of the target phthalocyanine in the individual state requires several purification cycles (at least, three).<sup>7,9–11</sup> Sometimes gel chromatography is supplemented with standard chromatographic methods, column chromatography or TLC.

## V. Behaviour of binuclear phthalocyanines in solutions

Among huge amount of publications devoted to the synthesis of binuclear phthalocyanines of different structures, some publications can be found concerning the behaviour of these compounds in solutions.<sup>16,23,24,33,86</sup> UV-vis spectroscopy is the simplest and the most available method for studies of behaviour of complicated compounds in solutions.<sup>16</sup> Actually, characteristic positions of the bands in the absorption spectra of binuclear phthalocyanines and, above all, the sensitivity of the bands to different changes are a reliable tool for identification of the latter. In addition, the structure of binuclear phthalocyanines, the degree of their aggregation in solutions and different conformational equilibria can be revealed from the shape and the character of changes in the electronic absorption spectra.<sup>16,33,34</sup>

It is known that only intermolecular aggregation is possible to occur in planar binuclear phthalocyanines;<sup>16</sup> they are detected by changes in the electronic absorption spectra related to deviations from the Lambert-Beer law.<sup>34,54</sup> Not only intermolecular, but also intramolecular aggregation is typical of binuclear clamshell phthalocyanines.<sup>6,7,14–16,22</sup> Intramolecular aggregation is associated with the interactions between two phthalocyanine macrocycles. Dilution results in gradual weakening of intermolecular interaction, while intramolecular interaction remains unchanged.<sup>7,16</sup> It was shown that the interaction between the phthalocyanine macrocycles in these binuclear molecules is first of all determined by the length of the covalent spacer linking the macrocycles.<sup>7,9,11,15,17,33,48</sup>

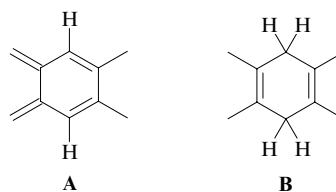
Several conformations can exist in binuclear clamshell phthalocyanines: open, partially open and closed or face-to-face conformation. These conformations originate from the rotation of the phthalocyanine rings around C—C bonds of the spacer in the absence of steric hindrances.<sup>16</sup> Thus phthalocyanines **11** and **12** with rigid spacers can exist only in the open conformation; for compounds **1**, **4** and **6**, in which the distances between the macrocycles are 4–5 nodal atoms, in solutions there is an equilibrium between two conformations, partially open and closed. Compounds **2**, **3** and **5** occupy an intermediate position in this classification: all three conformations exist in solutions.

Intramolecular interaction between the macrocycles can be revealed from electronic absorption spectra. The electronic spectra of different types of binuclear phthalocyanines differ from those of their mononuclear analogues; this difference is the greater the stronger the interaction between the chromophore centres.<sup>16,58–60</sup> This difference manifests itself first of all in the shape of the Q-bands, which are, as a rule, broadened and ill-resolved in the case of binuclear phthalocyanines. For binuclear clamshell phthalocyanines, this complication of the spectra is explained by the presence of an equilibrium between

different conformers. Notably that the spectra of binuclear clamshell phthalocyanines are complicated regardless of the concentration of the solution thus evidencing for intramolecular interaction between the macrocycles in these compounds. If there is no interaction between the macrocycles of binuclear clamshell phthalocyanines, their electronic spectra are identical to those of the corresponding mononuclear analogues.<sup>16</sup>

The electronic absorption spectra of metal-free binuclear phthalocyanines are complicated and noninformative; Dodsworth *et al.*<sup>16</sup> carried out an analysis of the spectra of their dianionic forms. The authors believe that the interaction between the macrocycles in compounds **1–6**, **11** and **12** depends on the length of the covalent spacer. The change in the intensity of the band in the range of 710 nm in the absorption spectra is indicative of the degree of the interaction between the macrocycles.

Planar binuclear phthalocyanines and their analogues with the macrocycles sharing common benzene or naphthalene cores are characterised by extended  $\pi$ -systems. The latter provide efficient intraelectron conjugation between two macrocycles.<sup>23,24,28,36,55,87</sup> Until recently there has been contradictory information in the literature concerning spectral properties of these phthalocyanines.<sup>20,22,25,41</sup> Electronic spectra of planar binuclear phthalocyanines reported in different papers (see, for example,<sup>9,25,55,69</sup>) provided no possibility to assign distinctly these compounds to the type under consideration. Thus Lelièvre *et al.*,<sup>55</sup> while studying the electronic absorption spectra of binuclear phthalocyanines **25a,b** with an extended  $\pi$ -conjugated electronic system, found that the absorption band for these compounds is observed in the same range where the related monophthalocyanine (2-EtC<sub>6</sub>H<sub>12</sub>O)<sub>8</sub>PcCu absorbs, namely, in the range of 670 nm. This fact gave the authors reason to conclude that there is no conjugation between two phthalocyanine macrocycles. Later<sup>25</sup> they pointed out the erroneous assignment of the spectral data to planar binuclear phthalocyanines. In their opinion, the electronic spectrum described<sup>55</sup> does not characterise the target planar binuclear phthalocyanine **25** with a common benzene ring, but is associated with the compound, in which the macrocycles are linked by a common cyclohexadiene ring (type **B**). They note that the interaction of 4,5-bis(2-ethylhexyloxy)-1,2-phthalonitrile with 1,2-diiminisindoline gives at least three products: bisphthalocyanines with the type **A** and **B** bridges and monophthalocyanine. Lelièvre *et al.*<sup>25</sup> explain this hypothesis by the possibility for protonation of the benzene ring upon cyclisation of the tetrameric fragments formed in the course of the reaction. Phthalocyanines with the protonated benzene ring are not planar, therefore, no significant bathochromic shift of the absorption band in the range of 670 nm in the electronic absorption spectra is observed as compared to that in the spectrum of monophthalocyanine.



It is very difficult to distinguish between pseudo-planar and really planar binuclear phthalocyanines on the basis of standard physicochemical data. We believe that in this case, NMR studies are also complicated due to shielding of the protons of the common benzene ring by two phthalocyanine macrocycles,

which results in much lower intensities of the signals of these protons as compared to theoretical values. That is why the key role in establishing the structure of polynuclear phthalocyanines belongs to mass spectrometry. Yang and Van De Mak<sup>41</sup> note that in the mass spectrum of the target product, the only peak  $M + 2$  is observed, which seems to belong to the structure **B**, that is why one can agree with the critical remark of Lelièvre *et al.*<sup>25</sup>

The doubts were finally settled only in 2006 when intense absorption in the range of 850 nm was found in the electronic spectra of binuclear phthalocyanines with the common benzene ring.<sup>57,88</sup> It is important that, in contrast to the spectra of binuclear clamshell phthalocyanines, the character of electronic absorption spectra strongly depends on the solvent nature.<sup>57</sup> Thus in such noncoordinating solvents as  $C_6H_6$ ,  $CHCl_3$ ,  $Et_2O$ , a broad absorption band is observed in the range of 600–900 nm. The absorption band is better resolved in more polar solvents (dioxane, THF), the intensity of the band in the range of 850 nm is gradually increasing; in coordinating solvents (pyridine) this band undergoes an additional bathochromic shift by 14 nm (Fig. 1).

A shift of the Q-band of planar binuclear phthalocyanines with the common benzene ring to the near infrared range as compared to its position in the spectrum of the corresponding monophthalocyanines evidences for a high degree of electronic conjugation in binuclear phthalocyanines and for strong intramolecular interaction between the macrocycles.

Recently studies of binuclear phthalocyanines by other physicochemical methods have been reported. Thus the interaction between the macrocycles in binuclear phthalocyanines was found by the method of scanning tunnelling microscopy.<sup>24</sup> The authors, using planar phthalocyanine **22c** as an example, showed that the mixed-valence form  $PcCo(I)-PcCo(III)$  is energetically more stable than the form  $PcCo(II)-PcCo(II)$  and compound **22c** exists primarily in the mixed-valence form. As a result of this asymmetry, a dipole moment arises leading to the intramolecular electron transfer. The Co(I) and Co(III) atoms in molecule **22c** are considered as electron donor and acceptor, respectively, the benzene ring is considered as a covalent bridge providing the electronic interaction between the macrocycles.

The interaction between the macrocycles of binuclear phthalocyanines can be quantitatively estimated by time resolved EPR (TREPR). Ishii *et al.*<sup>23</sup> studied metal-free 2,9,16,23-tetra(*tert*-butyl)phthalocyanine and binuclear

phthalocyanine **23a** in the lowest excitation triplet state ( $T_1$ ). It was shown that delocalisation of electron density in two phthalocyanine macrocycles in the state  $T_1$  is characteristic of compound **23a**, in contrast to monophthalocyanine. This result was confirmed by the calculation of molecular orbitals of phthalocyanines. The value of stabilisation energy ( $D = -3F_z/2$ ) for binuclear compound was determined, which appeared to be smaller than the  $D$  value for the corresponding monophthalocyanine.<sup>23</sup>

NMR spectroscopy is seldom used for studies of binuclear phthalocyanines. As was already mentioned above, the NMR spectra of binuclear phthalocyanines are far from being always informative.<sup>9,11,14,15,17</sup> However, while studying symmetrical dodecasubstituted metal-free phthalocyanine **14**, Isagot *et al.*<sup>33</sup> managed to find appropriate parameters for measurement and to obtain quite satisfactory  $^1H$  NMR spectrum of this compound. It was found in the course of investigation that the character of the  $^1H$  NMR spectrum stands in close relation to concentration and temperature of the solution of phthalocyanine **14**. Thus it was shown that good resolution is observed only at high temperatures (above 360 K) or at low concentrations of solutions ( $\sim 10^{-4}$  mol litre $^{-1}$ ).

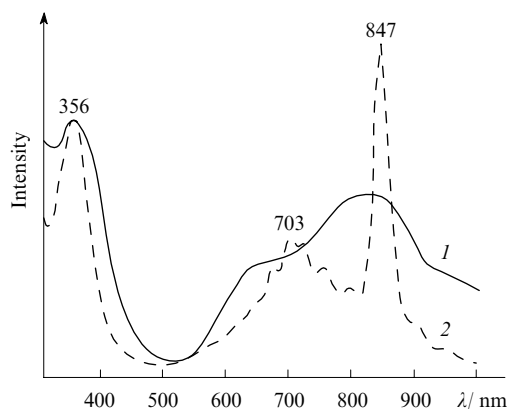
The authors note the difference between the  $^1H$  NMR spectra of binuclear phthalocyanine **14** and the corresponding mononuclear analogue. If gradual dilution of a monophthalocyanine solution induces a smooth downfield shift of the signals for inner NH-protons, in the case of the binuclear analogue, the saturation phenomenon is observed, *i.e.* the downfield shift occurs only to a certain degree of dilution; further dilution does not lead to a change in the spectrum. Similar phenomenon is observed upon increasing the temperature. The signals for some aromatic protons are also somewhat shifted, whereas the position of the signals for aliphatic protons does not change in any of the cases considered.

Isagot *et al.*<sup>33</sup> associate the phenomena observed with intramolecular aggregation of a binuclear phthalocyanine. Thus in solutions of binuclear phthalocyanines at high concentrations, both intra- and intermolecular aggregation are observed. Dilution results in an increase of the distance between macromolecules, which weakens intermolecular interactions between macrocycles. Starting with some limiting concentration, only separate binuclear molecules are present in solution, where only intramolecular interactions remain. This is also confirmed by EPR spectra.<sup>33</sup>

Thus investigation of the behaviour of binuclear phthalocyanines in solutions is an important problem, the solution of this problem might result in targeted development of new catalysts, in particular, multielectron redox catalysts for studies of energy transformation in biological systems.<sup>16,33</sup>

## VI. Application of bi- and polynuclear phthalocyanines

Porphyrins are unique catalysts for numerous redox reactions occurring in biological systems. Thus in the process of oxygen reduction to water, two iron(II) porphyrin molecules are required per oxygen molecule; in this case, the complex with the composition porphyrin–O–porphyrin in the face-to-face conformation is a catalytic species.<sup>89</sup> Collman *et al.*<sup>90,91</sup> showed that the use of binuclear cobalt and silver porphyrins increases the efficiency of the reduction process, because only one metal porphyrin molecule is required per oxygen molecule. In this case, hydrogen peroxide, the by-product of two-electron reduction of dioxygen, is not formed. However, with time porphyrin catalysts lose their activity due to gradual destruc-



**Figure 1.** Electronic absorption spectra for compound **29b** in chloroform (curve 1) and THF (curve 2).<sup>57</sup>

tion; for this reason, catalysts that could substitute porphyrins have been searched for. It is known that phthalocyanine ring is thermally and chemically more stable than porphyrin. This fact gave impetus to intensive studies of binuclear clamshell phthalocyanines.

Only binuclear macrocyclic molecules with the face-to-face conformation of the macrocycles are able to exhibit catalytic properties.<sup>9, 11, 17</sup> Leznoff *et al.*<sup>9, 10, 11, 14, 15, 17</sup> synthesised and investigated different binuclear clamshell phthalocyanines with various substituents, metals and bridges, as well as unsymmetrical binuclear complexes. In virtually all cases, the interaction between the macrocycles was found, which was indirectly confirmed by electronic and emission spectra, however, this interaction was not sufficient for these complexes to adopt the conformation of a closed shell. That might be the reason why only two-electron reduction of dioxygen to hydrogen peroxide was observed upon their use. Numerous attempts to obtain binuclear phthalocyanines with the closed shell conformation using structural modifications, as well as the target synthesis of tri-,<sup>14</sup> tetra-<sup>7</sup> and pentanuclear phthalocyanines<sup>10</sup> failed.

Lever, the initiator of studies in the field of creation of catalysts based on binuclear phthalocyanines for electro- and photoelectric processes, noted on the 2nd International Conference on Porphyrins and Phthalocyanines, ICPP-2 that, though binuclear clamshell phthalocyanines are extremely promising, their synthesis in sufficient amount is very labourious. This seems to be a reason why the Leznoff's group stopped their work in this field.

At the same time, one cannot help noting that it is possible to regulate the degree of the interaction between the phthalocyanine rings in binuclear clamshell phthalocyanines by controlling the mutual arrangement of the macrocycles and the amount of spacers. By increasing the number of spacers, it is possible to fix the spacial location of the macrocycles and to increase the selectivity of their binding to ditopic molecules, which is important for development of ion-selective electrodes.

In 2003 Blikova *et al.*<sup>81</sup> reported the synthesis and study of binuclear phthalocyanines as anion-selective electrodes for recognition and specific binding of maleic and terephthalic acids. The authors supposed that the strict face-to-face conformation of binuclear phthalocyanines achieved by the introduction of several bridges is not so obligatory for ion-selective electrodes; the nature of the central metal atom is much more important because the key principle of anion binding is the formation of a host–guest complex stable under given conditions (Fig. 2).

The authors<sup>81</sup> believe that binuclear phthalocyanines with the macrocycles joined only to one side due to a large number

of conformations will have a lot of opportunities for structural match to the anion under determination, therefore, they can find application as ion-selective electrodes.

Planar binuclear phthalocyanines **22–29** and **31–37** attract attention by unusual spectral properties.<sup>58–64</sup> Now it can be stated with assurance that this type of complexes are novel promising materials for nonlinear optics.<sup>20–31</sup> Whereas in clamshell phthalocyanines **1–12**<sup>9, 11, 14, 15, 17</sup> the through-space interaction between the macrocycles mainly occurs,<sup>16</sup> in planar binuclear complexes, the interaction between the macrocycles occurs through the unsaturated covalent spacer. As a consequence, a bathochromic shift of the Q-band in the electronic absorption spectra occurs resulting in unusual optical properties of these compounds.<sup>57, 88</sup>

Valkova *et al.*<sup>87</sup> report on the possibility of using planar binuclear phthalocyanine **23b** as a sensor for benzene and cyclohexane. The data of the X-ray diffraction study of Langmuir–Blodgett films based on this complex allowed the authors to draw a conclusion on the mechanisms of the interaction of films with these hydrocarbons. Two mechanisms were suggested: molecular (molecules of gaseous benzene and cyclohexane are condensed on active centres) and supramolecular (the analysed molecules penetrate into macrocyclic ensembles). It was found that the sensitivity of the sensor based on **23b** to benzene is much higher than to cyclohexane, which is important in view of high toxicity of benzene.

Polynuclear phthalocyanines, especially those of the net-shaped structure, are of interest as new semiconducting materials.<sup>78–80</sup> Agar *et al.*<sup>78</sup> synthesised polyphthalocyanine by fusing 1,2,4,5-tetracyanobenzene with Cu<sub>2</sub>Cl<sub>2</sub> and studied its p- and n-conductivity; semiconducting materials based on copper, nickel, cobalt, zinc and iron polyphthalocyanines obtained by polymerisation of bis(phthalonitriles) with different binding bridges have also been studied.<sup>79, 80</sup>

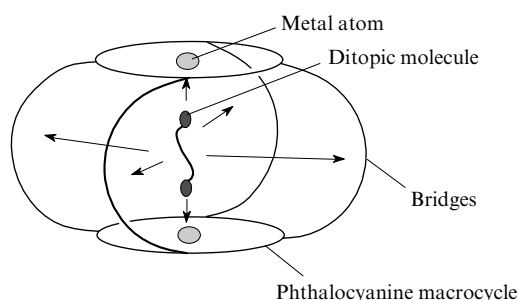
The possibility of using binuclear clamshell phthalocyanine **13** as a precursor in the synthesis of monohydroxy-substituted phthalocyanine has been demonstrated (Ref. 39).<sup>¶</sup>

\* \* \*

In this review, approaches to the synthesis of bi- and polynuclear phthalocyanines of different structures are considered. Among a variety of binuclear phthalocyanines, special attention is paid to binuclear clamshell phthalocyanines as promising catalysts for photo- and electrocatalytic processes. However, the number of publications devoted to planar bi- and polynuclear phthalocyanines has also been growing. It can be expected that in the nearest future these systems will find wide application in laser technique of new generation. This is associated with the fact that planar conjunction of the macrocycles in these systems favours maximum interaction of the latter and results in extension of the electronic system.

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**Figure 2.** Schematic image of the complex 'binuclear phthalocyanine–ditope molecule'.<sup>81</sup>

<sup>¶</sup>In our opinion, it is no point of using this approach to the synthesis of asymmetrically substituted monophthalocyanines.

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