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Phthalocyanines and Naphthalocyanines with Sulfur–Containing Functional Groups: Synthesis, Preparation of Hybrid Gold Nanoparticles and Some Application Areas

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Dedicated to memory of our teacher – Professor Larisa Godvigovna Tomilova

Synthetic approaches to the phthalocyanines and their polynuclear and sandwich-type derivatives, bearing sulfur-containing functional groups, are classified. Additionally complexes, possessing an extended π-conjugation system (planar and sandwich-type 2,3-naphthalocyanines) are reviewed. Principal application areas are covered. Special attention is paid to the formation of conjugates with gold nanoparticles – prospective materials for organic electronics.

Keywords: Phthalocyanine, naphthalocyanine, gold nanoparticles, sulfur, hybrid materials.

Фталоцианины и нафталоцианины, замещенные функциональными группами, содержащими серу: синтез, получение гибридов с наночастицами золота и некоторые области применения

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Посвящается памяти нашего учителя – профессора Ларисы Годвиговны Томиловой

Представлены синтетические подходы к фталоцианинам, их полиядерным производным и сэндвичевым комплексам, замещенным функциональными группами, содержащими серу. Дополнительно рассмотрены комплексы, обладающие протяженной системой π-сопряжения (2,3-нафталоцианины плоского и сэндвичевого типа). Рассмотрены основные области применения данных соединений. Особое внимание уделяется образованию конъюгатов с наночастицами золота – перспективным материалам для органической электроники.

Ключевые слова: Фталоцианин, нафталоцианин, наночастицы золота, сера, гибридные материалы.

Introduction

The nature of the functional groups in phthalocyanine molecules plays a crucial role in many practical applications. The introduction of electron-releasing or electron-withdrawing substituents leads to the manifestation of *p*- or *n-type* semiconductor properties, respectively.[1,2] Asymmetrically substituted phthalocyanines containing both electron-rich and electron-deficient fragments are characterized by the presence of nonlinear optical properties.[3] The preparation of phthalocyanines containing hydrophilic fragments offers opportunities for their use in catalysis,[4] as well as as photosensitizers in photodynamic therapy (PDT).[5,6] Besides, functionally substituted phthalocyanines can be used as starting compounds to create complexes of a sandwich structure.[7–11]

2,3-Naphthalocyanines are among the most widely studied and promising annelated analogs of phthalocyanines. Expansion of the π-system leads to a bathochromic shift of the main absorption maxima up to almost 900 nm,[12] shift of the first oxidation potential to the cathode region, and enhancement of π-π interactions.[13,14]

Due to the extended π-system, wide coordination possibilities and the ability to form new covalent bonds due to peripheral substituents, phthalocyanines and their analogs can form hybrid systems with nanotubes,[15,16] fullerenes,[16] nanoparticles.[4,17,18] Compared to compositions in which the components do not form chemical bonds with each other,[19] hybrid materials have several advantages. For instance, in photovoltaics the use of hybrid materials can improve the efficiency of energy transfer[20] and accordingly reduce the thickness of the photoactive layer.

Hybrids of phthalocyanines and gold nanoparticles are of greatest interest. In our research group[21] a hybrid of *tert*-butyl-substituted aluminum phthalocyanine and gold nanoparticles was obtained, for which a plasmon absorption increase at wavelengths of 535–550 nm was observed by more than 8 times. This phenomenon can lead to an increase in the yield of singlet oxygen.[22]

The presence of nanoparticles in the conjugate can provide better delivery of the photosensitizer to tumor cells during PDT.[23] Also, for such hybrid materials, enhancement of fluorescence[24] and nonlinear optical response can be observed.[25]

For this area of research, phthalocyanines and their analogs substituted with functional groups containing sulfur are promising. They can form strong S-Au bonds due to the “soft” nature of these elements.[17,18,26–28]

The purpose of this review is to systematize approaches to the synthesis of phthalocyanines and 2,3-naphthalocyanines substituted with sulfur-containing functional groups. Methods for the preparation of phthalonitriles and 2,3-dicyanonaphthalenes as starting compounds in the synthesis of the corresponding phthalocyanines and 2,3-naphthalocyanines are considered. The review presents several groups of substituted phthalocyanines and 2,3-naphthalocyanines, which can be subdivided as follows:

- free-base ligands, planar metal complexes containing one phthalocyanine or 2,3-naphthalocyanine macrocycle;
- sandwich-type double decker complexes, containing two phthalocyanine or naphthalocyanine macrocycles sharing a central metal ion – diphthalocyanines and dinaphthalocyanines respectively.
- bi- and polynuclear complexes containing two or more covalently linked phthalocyanine macrocycles.

Over the past 10 years, two reviews have been published devoted to the study of the role of substituents in the chemistry of phthalocyanines and their analogues.[29,30] However, they mention only a few examples of phthalocyanines substituted with sulfur-containing functional groups. Besides, these reviews do not provide data on the corresponding 2,3-naphthalocyanines, diphthalocyanines, and polynuclear complexes. In the review[29] methods for the synthesis of symmetrically and unsymmetrically substituted phthalocyanines containing sulfogroups were considered in detail; therefore, these compounds were not included in our review.

The review considers some promising areas of application of phthalocyanines substituted by functional groups containing sulfur: materials for the near-IR range, gas sensors, photovoltaics. Special attention is paid to hybrid materials based on gold nanoparticles coated with a phthalocyanine shell.

1. Synthetic approaches to *o*-phthalonitriles bearing sulfur-containing functional groups

The starting compounds in the synthesis of phthalocyanines and their metal complexes are *o*-phthalonitriles. Varying the substituents allows to control the properties of target phthalocyanine complexes: to reduce aggregation,[31] to enhance nonlinear optical[32] and semiconductor properties,[1] to create additional redox-active centers.[33] It is important to note that the introduction of substituents can be implemented in the peripheral – 4,5 and non-peripheral – 3,6 positions of *o*-phthalonitrile.

1.1. Nucleophilic substitution in the synthesis of o-phthalonitriles with sulfur-containing functional groups

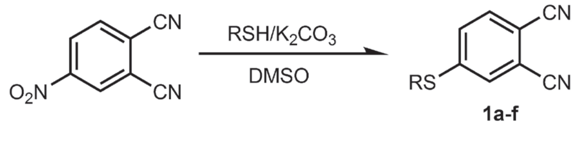
The introduction of sulfur-containing functional groups into *o*-phthalonitrile molecules can be realized in several ways. The most common method is nucleophilic substitution. The following options for carrying out this reaction in *o*-phthalonitriles are described:

- substitution of nitro group;
- substitution of the halogen;
- substitution of *p*-toluenesulfonyl group;
- nucleophilic substitution reactions in an ionic liquid.

The substitution of the nitro group in 4-nitrophthalonitrile with various thiols takes place at room temperature, the reaction time is 14–29 h. Potassium carbonate is used as a base (Scheme 1).

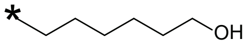
Using this technique, various alkylthio- and arylthio-substituted phthalonitriles **1** were obtained in high yields (Table 1).

The simplicity of this reaction is since the substrate is activated to nucleophilic substitution by the cyano group, which is located in the *para*-position to the nucleofuge.

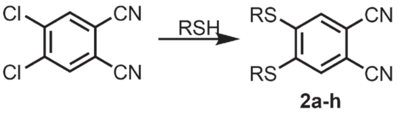


Scheme 1.

Table 1. Reaction time and yields of compounds **1a-f**, obtained via Scheme 1.

Compound	R	Reaction time, h	Yield, %	Reference
1a	C_8H_{17}	18	83	[34]
1b	Ph	14	85	[35]
1c	$PhCH_2$	14	92	[35]
1d		29	90	[36]
1e	$C_{12}H_{25}$	18	62	[37]
1f	$C_{16}H_{33}$	18	66	[37]

The starting compound in the synthesis of dialkylthio-substituted *o*-phthalonitriles **2a-h** can be 4,5-dichlorophthalonitrile (Scheme 2).

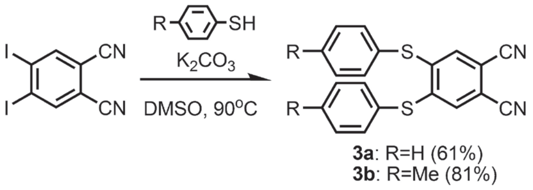


Scheme 2.

The reaction is carried out at a temperature not higher than 90 °C, in the presence of potash. DMSO or *N,N*-dimethylacetamide is used as a solvent (Table 2).

In *N,N*-dimethylacetamide, the reaction time is significantly shorter than in the syntheses carried out in DMSO. However, by carrying out the reaction in a DMSO medium, M. Mayukh *et al.*[39] managed to increase the yield of nitrile **2c**. A decrease in the yield of hexylthio-substituted nitrile **2a** with an increase in the reaction temperature may be due to a change in the method of isolation of the target compound. A.G. Gurek *et al.*[38] used recrystallization while M. Mayukh *et al.*[39] isolated nitrile **2a** using column chromatography.

It was found, that[34,42] 4,5-diiodophthalonitrile can be used as starting compound in the synthesis of 1,2-dicyano-4,5-phenylthio and 1,2-dicyano-4,5-*p*-tolylthiobenzenes **3a** and **3b**, respectively (Scheme 3).



Scheme 3.

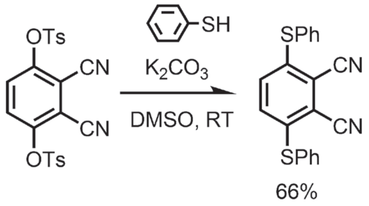
It is interesting to note that the reaction was carried out with heating, in contrast to the method described

Table 2. Reaction conditions and yields of compounds, obtained via Scheme 2.

Compound	R	Reaction conditions	Yield, %	Reference
2a	C_6H_{13}	DMSO, K_2CO_3, RT, 14 h	79	[38]
2a	C_6H_{13}	DMSO, K_2CO_3, 80 °C, 12 h	70	[39]
2b	C_7H_{15}	DMSO, K_2CO_3, 80 °C, 12 h	84	[39]
2c	C_8H_{17}	*N,N*-Dimethylacetamide, K_2CO_3, 90 °C, 6 h	79	[34]
2c	C_8H_{17}	DMSO, K_2CO_3, 80 °C, 12 h	86	[39]
2d	C_9H_{19}	DMSO, K_2CO_3, 80 °C, 12 h	78	[39]
2e	$C_{10}H_{21}$	DMSO, K_2CO_3, 80 °C, 12 h	76	[39]
2f	$C_{12}H_{25}$	DMSO, K_2CO_3, RT, 14 h	80	[38]
2g	$C_{16}H_{33}$	*N,N*-Dimethylacetamide, K_2CO_3, 70 °C, 6 h	79	[40]
2h	Pr^i	*N,N*-Dimethylacetamide, K_2CO_3, 100 °C, 6 h	75	[41]

by the authors[38] (Table 2). In this case, the target compounds were obtained in high yields, and the reaction time was reduced to 30 min.

The introduction of phenylthio groups into non-peripheral positions 3,6 was carried out in DMSO at room temperature (Scheme 4).[43]



Scheme 4.

In this case, *p*-tolyl sulfonate (OTs) was used as a leaving group. The yield of the target compound is comparable to the yield of compound 3a, which contains phenylthio substituents at the 4,5 positions.

Due to its high ionic conductivity,[44] ionic liquids can increase the activity of nucleophiles in reactions proceeding by S_{NAr} mechanism. The melt of inexpensive and fairly stable ionic liquid Bu_4NBr was chosen by P.-C. Lo *et al.* [45] as a medium for nucleophilic substitution. According to the classification presented in the review [46] this ionic liquid can be classified as basic/strongly coordinating. Thus, Bu_4NBr plays a double role in the nucleophilic substitution reaction: the medium and the base.

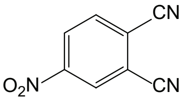
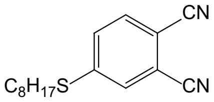
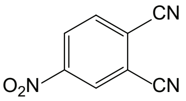
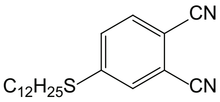
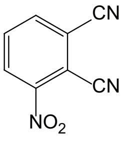
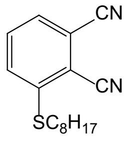
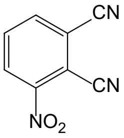
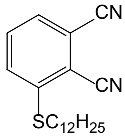
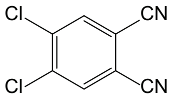
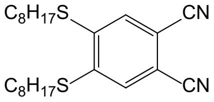
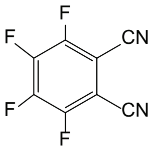
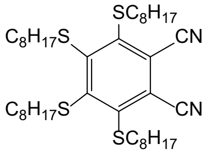
Using this approach, a number of alkylthio-substituted phthalonitriles was obtained (Table 3). All reactions were carried out at a temperature of 100 °C approximately corresponding to the melting point of Bu_4NBr (m.p. 102–106 °C). Thiol is taken in two-fold excess. At a lower temperature (90 °C) and using a stoichiometric amount of the starting thiol, the yields are reduced by several times.[45]

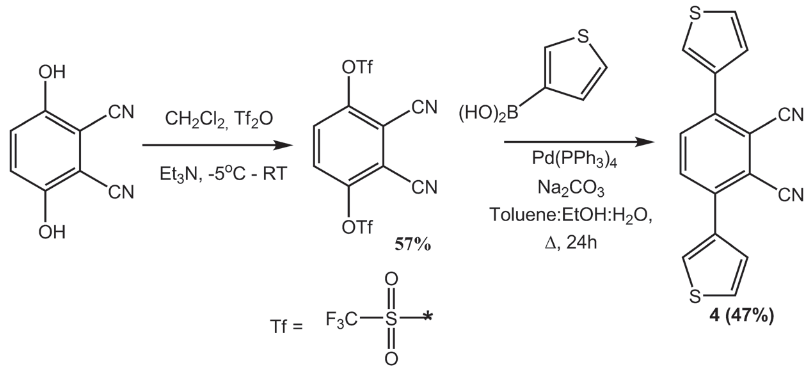
In the case of di- and tetrasubstituted phthalonitriles, the reaction yields are decreased. In addition, to replace chlorine atoms in 4,5-dichlorophthalonitrile, an additional introduction of two equivalents of potash is required.

1.2. Suzuki reaction in the synthesis of o-phthalonitriles with sulfur-containing functional groups

A method for introducing functional groups containing sulfur into phthalonitrile by Suzuki cross-coupling reaction is presented in the literature. Trifluoromethanesulfonate was introduced into the molecule as a leaving group (Scheme 5).[47] This choice is due to the availability of the parent phenol. In addition, the rate-limiting stage of the Suzuki reaction is often oxidative addition; therefore, the relative activity of substrates decreases in the row of substituents: I > OTf > Br >> Cl.[48] It is also important to note that electron-

Table 3. Reagents and yields of target compounds when carrying out nucleophilic substitution in the melt of Bu_4NBr.[45]

Initial phthalonitrile	Thiol	Product	Yield, %
	$C_8H_{17}SH$		77
	$C_{12}H_{25}SH$		79
	$C_8H_{17}SH$		91
	$C_{12}H_{25}SH$		93
	$C_8H_{17}SH$		50
	$C_8H_{17}SH$		55



Scheme 5.

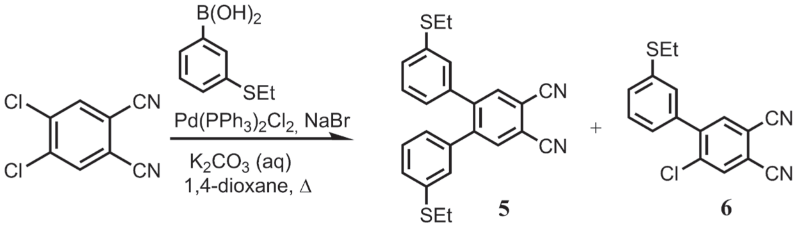
withdrawing substituents (for example, cyano groups) activate halides and pseudohalides to oxidative addition. S. Al-Raqa[47] used tetrakis(triphenylphosphine) palladium as a catalyst.

Starting from 4,5-dichlorophthalonitrile and 3-(ethylthio)phenylboronic acid under the conditions of the Suzuki cross-coupling reaction, we obtained substituted phthalonitrile **5** (Scheme 6).[49] It is well known that cross-coupling reactions for aryl chlorides are ineffective and require the addition of special ligands ($P(Bu^t)_3$; tricyclohexylphosphine (PCy_3)).[50–52] Due to steric hindrance, such ligands promote the dissociation of the complex of zero-valent palladium entering the catalytic cycle to a coordinatively unsaturated state, for example: $Pd(PBu^t_3)$. In addition, their electron donating properties facilitate the oxidative addition step.[52]

However, the presence of electron-withdrawing CN groups in the molecule leads to the activation of 4,5-dichlorophthalonitrile to oxidative addition.[48,51] This allowed us to use only dichlorobis(triphenylphosphine) palladium as a catalyst, without introducing additional ligands. It is important to note that the synthesis of diaryl-substituted *o*-phthalonitriles was carried out from 4,5-dichlorophthalonitrile, using Pd(II) as a catalyst, in the presence of 2-(2′,6′-dimethoxybiphenyl)dicyclohexylphosphine (S-Phos).[50] We were lucky to obtain nitrile **5** without the introduction of S-Phos and in a higher yield.

A study of the influence of the molar ratio of the starting reagents on the yield of the target nitrile **5** was carried out. It was shown that the use of a molar ratio of 1:4 (4,5-dichlorophthalonitrile : 3-(ethylthio)phenylboronic acid), which was previously used in our scientific group for the synthesis of 4,5-diphenylphthalonitrile,[53] results in the formation of a mixture of mono- (**6**) and disubstituted (**5**) compounds (Table 4). It is very difficult to separate these compounds, since their R_f values are close.

An increase in the amount of 3-(ethylthio)phenylboronic acid (molar ratio 1:6, 4,5-dichlorophthalonitrile : 3-(ethylthio)phenylboronic acid) led to the selective formation of nitrile **5**.

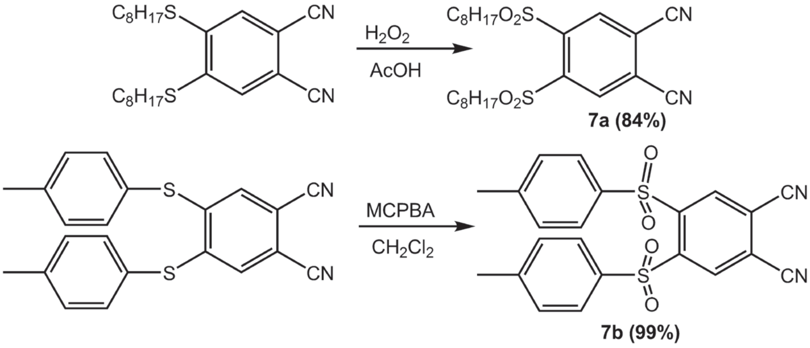


Scheme 6.

Table 4. Reaction conditions and the yields for Scheme 6.[49]

Molar ratio of 4,5-dichlorophthalonitrile : 3-(ethylthio)phenylboronic acid	Yield, %	
	5	**6**
1:2.5	0	19
1:4	37[a]	16[a]
1:6	70	0

[a] – yields calculated from ^{1}H NMR spectroscopy data.



Scheme 7.

It was found that when a 2.5 fold molar excess of arylboronic acid was used, compound **6** was formed.

1.3. Synthesis of sulfonyl substituted o-phthalonitriles

An important feature of functional groups containing sulfur is the possibility of changing the oxidation state of sulfur (Scheme 7). Sulfonyl-substituted phthalonitriles **7** are easily and in high yields obtained by the oxidation reaction of alkylthio-substituted phthalonitriles.[34]

When using hydrogen peroxide in acetic acid, the reaction is carried out first at 90 °C for 4 hours and then stirred overnight at room temperature. When using *meta*-chloroperbenzoic acid, the reaction mixture is kept at room temperature for 2 days.

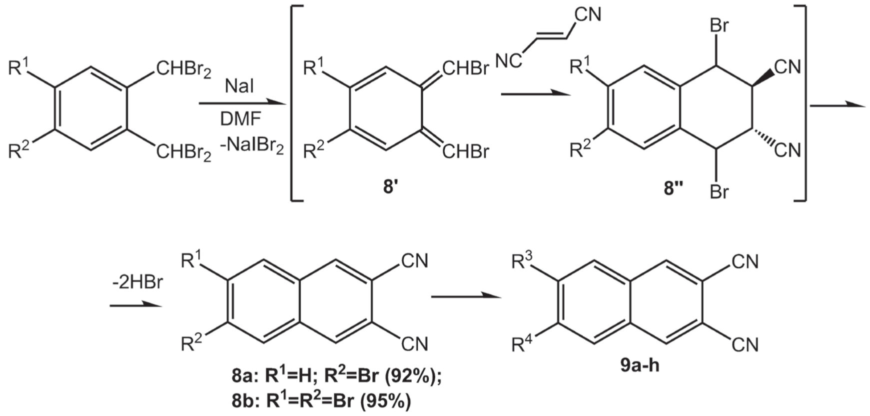
2. Synthesis of 2,3-dicyanonaphthalenes with sulfur-containing functional groups

The closest analogues of phthalocyanines with an extended π-system, 2,3-naphthalocyanines, can be synthesized on the basis of substituted 2,3-dicyanonaphthalenes.[14] Previously, only one approach to the synthesis of 2,3-dicyanonaphthalenes substituted with functional groups containing sulfur was described in the literature.[54–57] Bromo-substituted 2,3-dicyanonaphthalenes **8**, which are obtained starting from *bis*(dibromomethyl)benzenes, are used as the initial compound.[14,58] These tetrabromides under the action of sodium iodide are converted into *o*-quinodimethanes **8′**, which enter into the Diels-Alder reaction with fumaronitrile. In this case, tetralins **8′′** are formed, which are aromatized to the target compounds with the formation of an energetically favorable naphthalene π-system. The resulting naphthalodinitrile **8** reacts with alkyl thiolates (Scheme 8)

Alkylthio- and arylthio-substituted 2,3-dicyanonaphthalenes **9** obtained from compounds **8a,b** are presented in Table 5. Copper salts of alkylthiols,[54,55,57] or thiolate obtained by the action of 1,8-diazabicyclo[5.4.0]undecene-7 (DBU)[56] were used in the synthesis (Table 5). Copper salts of alkyl thiols can be formed in situ or can be prepared and isolated in advance. The synthesis of copper salts of alkyl thiols was carried out in boiling ethanol by analogy with the procedure for the synthesis of copper *n*-butyl mercaptide from Cu_2O and the corresponding alkyl thiol.[59]

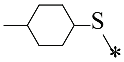
The decrease in the yields of the nucleophilic substitution reaction (up to 30 % in the case of compound **9h**), as compared to *o*-phthalonitriles, is probably since the cyano groups activating the substitution are distant one benzene ring from the nucleophile attack site. The authors managed to achieve the best yields.[55]

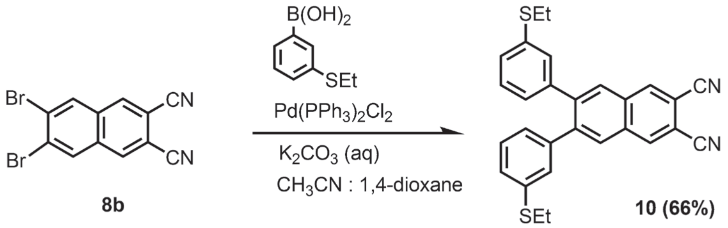
Based on 2,3-dicyanonaphthalene **8b** by the Suzuki reaction, we selectively obtained 3-(ethylthio)phenyl-substituted nitrile **10** (Scheme 9).[49]



Scheme 8.

Table 5. Reaction conditions and the yields of **9a-h**, obtained via Scheme 8.

Compounds	R^3	R^4	Reaction conditions	Yield, %	Reference
9a	$C_{10}H_{21}S$	H	CuR^3; quinoline; Py; Δ; 6h	53	[54]
9b	$C_6H_{13}S$	H	CuR^3; quinoline; Py; Δ; 6h	52	[54]
9c	C_4H_9S	H	CuR^3; quinoline; Py; Δ; 6h	70	[54]
9d	$C_{16}H_{33}S$	H	CuR^3; quinoline; Py; Δ; 6h	58	[54]
7e		H	CuR^3; quinoline; Py; Δ; 6h	46	[54]
9f	C_3H_7S	C_3H_7S	C_3H_7SNa; Cu_2O; DMF; Δ; 3h	89	[55]
9g	PhS	PhS	PhSNa; Cu_2O; DMF; Δ; 3h	84	[55]
9h	$C_{12}H_{25}S$	$C_{12}H_{25}S$	$C_{12}H_{25}SH$; DBU; DMF; 90 °C; 6h	65	[56]
9h	$C_{12}H_{25}S$	$C_{12}H_{25}S$	$C_{12}H_{25}SNa$; Cu_2O; *solvent and temperature not specified*	30	[57]



Scheme 9.

In the synthesis, the ratio of reagents selected for 3-(ethylthio)phenyl substituted phthalonitrile **5** was used. However, a mixture of 1,4-dioxane : acetonitrile was used as a solvent, since the initial 6,7-dibromo-2,3-dicyanonaphthalene is poorly soluble in pure 1,4-dioxane.

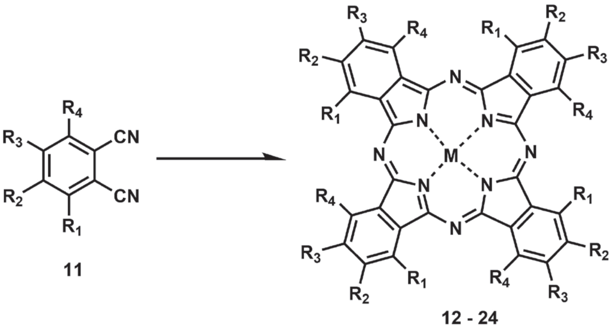
3. Synthesis of phthalocyanines bearing the sulfur-containing functional groups

3.1. Synthesis, based on o-phthalonitriles

To obtain phthalocyanines substituted with functional groups containing sulfur, and their metal complexes, the template method is most often used. The starting compounds are the corresponding *o*-phthalonitriles **11**. The synthesis is carried out in boiling solvents or in melts (Scheme 10, Table 6).

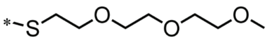
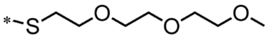
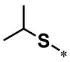
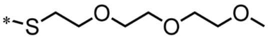
1,8-Diazabicycloundec-7-ene (DBU) can be used as the base initiating the cyclization process.[38,60,62] Probably, in these cases, alcoholates are not used as bases due to possible transesterification processes.

Two high-temperature methods for the synthesis of phthalocyanine ligands substituted by sulfur-containing groups are described (Table 6).[37,38,41] In the method described by I. Gurol *et al.*,[37] freshly distilled hydroquinone was used as a redox-active particle and simultaneously a source of protons to obtain ligand **12a**. In the process of template cyclization of the phthalocyanine macrocycle, the 18 π-electron system is formed from the 16 π-electron



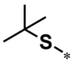
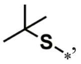
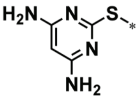
Scheme 10.

Table 6. Reaction conditions and the yields of **12–24**, obtained via Scheme 10.

Compounds	R	M	Reaction conditions	Yield, %	Reference
12a	$R_2 = C_{12}H_{25}S$, $R_1 = R_3 = R_4 = H$	HH	Hydroquinone, 200 °C, 5 h	24	[37]
12b	$R_2 = C_{12}H_{25}S$, $R_1 = R_3 = R_4 = H$	Ni	$NiCl_2$, quinoline, 200 °C, 5 h	26	[37]
12c	$R_2 = C_{16}H_{33}S$, $R_1 = R_3 = R_4 = H$	Ni	$NiCl_2$, quinoline, 200 °C, 5 h	34	[37]
13a	$R_2 = R_3 = C_6H_{13}S$, $R_1 = R_4 = H$	HH	Pentanol, DBU, Δ, 60 h	39	[38]
13b	$R_2 = R_3 = C_6H_{13}S$, $R_1 = R_4 = H$	Ni	$NiCl_2$, quinoline, 200 °C, 5 h	38	[38]
13c	$R_2 = R_3 = C_{12}H_{25}S$, $R_1 = R_4 = H$	Ni	$NiCl_2$, quinoline, 200 °C, 5 h	19	[38]
13d	$R_2 = R_3 = C_6H_{13}S$, $R_1 = R_4 = H$	Cu	$CuCl_2$, urea, 100 °C, 2 h	62	[38]
13e	$R_2 = R_3 = C_6H_{13}S$, $R_1 = R_4 = H$	Co	$CoCl_2$, ethylene glycol, 200 °C, 4 h	26	[38]
13f	$R_2 = R_3 = C_6H_{13}S$, $R_1 = R_4 = H$	Zn	$ZnCl_2$, quinoline, 200 °C, 6 h	48	[38]
14a	$R_1 = PhS$, $R_2 = R_3 = R_4 = H$	TiO	$Ti(OBu)_4$, $C_8H_{17}OH$, urea, 150 °C, 14 h	40	[35]
14b	$R_1 = PhCH_2S$, $R_2 = R_3 = R_4 = H$	TiO	$Ti(OBu)_4$, $C_8H_{17}OH$, urea, 150 °C, 14 h	43	[35]
14c	$R_2 = PhS$, $R_1 = R_3 = R_4 = H$	TiO	$Ti(OBu)_4$, $C_8H_{17}OH$, urea, 150 °C, 14 h	52	[35]
14d	$R_2 = PhCH_2S$, $R_1 = R_3 = R_4 = H$	TiO	$Ti(OBu)_4$, $C_8H_{17}OH$, urea, 150 °C, 14 h	48	[35]
15a	$R_2 =$ , $R_1 = R_3 = R_4 = H$	Zn	$Zn(OAc)_2$, *n*-hexanol, Δ, DBU, 18 h	33	[60]
15b	$R_3 = R_2 =$ , $R_1 = R_4 = H$	Zn	$Zn(OAc)_2$, *n*-hexanol, Δ, DBU, 18 h	18	[60]
16a	$R_2 = C_{16}H_{33}S$, $R_1 = R_3 = R_4 = H$	Pb	PbO, 210 °C, 5 h	19	[61]
16b	$R_2 = R_3 = C_6H_{13}S$, $R_1 = R_4 = H$	Pb	PbO, 210 °C, 5 h	26	[61]
17	$R_2 = R_3 =$ , $R_1 = R_4 = H$	HH	DBU, pentanol, Δ, 8 h	40	[41]
18a	$R_2 = R_3 = C_8H_{17}S$, $R_1 = R_4 = H$	Cu	$CuCl_2$, DBU, *n*-hexanol, Δ , 24 h	58	[62]
18b	$R_2 = R_3 = C_{16}H_{33}S$, $R_1 = R_4 = H$	Cu	$CuCl_2$, DBU, *n*-hexanol, Δ , 24 h	23	[62]
18c	$R_3 = R_2 =$ , $R_1 = R_4 = H$	Cu	$CuCl_2$, DBU, *n*-hexanol, Δ , 24 h	52	[62]
19a	$R_1 = R_4 = C_5H_{11}S$, $R_2 = R_3 = H$	VO	VCl_4, DBU, pentanol, Δ , 6 h	42	[63]
19b	$R_1 = R_4 = C_5H_{11}S$, $R_2 = R_3 = H$	Mn(OAc)	$Mn(OAc)_3$, DBU, pentanol, Δ , 6 h	42	[64]
19c	$R_1 = R_4 = C_5H_{11}S$, $R_2 = R_3 = H$	TiO	$Ti(OBu)_4$, DBU, pentanol, Δ , 6 h	22	[64]
20	$R_2 = PhS$, $R_1 = R_3 = R_4 = H$	Pd	$PdCl_2$, urea, 190 °C, 12 h	72	[65]
21a	$R_2 = R_3 = C_6H_{13}S$, $R_1 = R_4 = H$	TiO	$Ti(OPr^i)_4$, urea, melt, 150 °C, 24 h	16	[39]
21b	$R_2 = R_3 = C_7H_{15}S$, $R_1 = R_4 = H$	TiO	$Ti(OPr^i)_4$, urea, melt, 150 °C, 24 h	42	[39]
21c	$R_2 = R_3 = C_8H_{17}S$, $R_1 = R_4 = H$	TiO	$Ti(OPr^i)_4$, urea, melt, 150 °C, 24 h	34	[39]
21d	$R_2 = R_3 = C_9H_{19}S$, $R_1 = R_4 = H$	TiO	$Ti(OPr^i)_4$, urea, melt, 150 °C, 24 h	42	[39]
21e	$R_2 = R_3 = C_{10}H_{21}S$, $R_1 = R_4 = H$	TiO	$Ti(OPr^i)_4$, urea, melt, 150 °C, 24 h	35	[39]
22a	$R_2 = R_3 =$ 3-(ethylthio) phenyl, $R_1 = R_4 = H$	Zn	$Zn(OAc)_2 \cdot 2H_2O$, Am^iOH, Δ, MeOLi, 5 h	88	[49]
22b	$R_2 =$ 3-(ethylthio) phenyl $R_3 = Cl$ $R_1 = R_4 = H$	Zn	$Zn(OAc)_2 \cdot 2H_2O$, Am^iOH, Δ, MeOLi, 5 h	55	[49]
22c	$R_2 = R_3 =$ 3-(ethylthio) phenyl, $R_1 = R_4 = H$	Er(OAc)	$Er(OAc)_3 \cdot 4H_2O$, Am^iOH, Δ, MeOLi, 4 h	91	[66]
22d	$R_2 = R_3 =$ 3-(ethylthio) phenyl, $R_1 = R_4 = H$	Lu(OAc)	$Lu(OAc)_3 \cdot 4H_2O$, Am^iOH, Δ, MeOLi, 4 h	70	[66]

(continued)

Table 6. Continued.

23a	$R_2 = R_3 =$  , $R_1 = R_4 = H$	HH	1) LDA/THF, 25 °C, 3 h; 2) H^+/H_2O	19.2	[67]
23b	$R_2 =$  , $R_1 = R_3 = R_4 = H$	HH	1) LDA/THF, 25 °C, 3 h; 2) H^+/H_2O	27	[67]
24	$R_2 =$  , $R_1=R_4=R_3=H$	Zn	$Zn(OAc)_2$, *n*-hexanol, Δ, DBU, 6 h	48	[68]

system consisted from four isoindole fragments. I. Gurol *et al.*[37] suggest that hydroquinone is a reducing agent.

In the second method[38,41] the synthesis of the ligands **13a** and **17** was carried out under milder conditions - boiling pentanol (138 °C) and DBU, as a base. Compared to the first method, the yield of the target ligand is more than 1.5 times higher. Probably, the decrease in the yield in the first case is due to the polymerization of the nitrile under harsh conditions of the synthesis.

An interesting example of low-temperature synthesis of phthalocyanine ligands was realized by the authors.[67] The reaction was carried out in THF at room temperature, in the presence of lithium diisopropylamide (LDA) as a base. Compared to lithium methoxide, diisopropylamide is more basic. Its main disadvantage is steric hindrance created by isopropyl fragments. However, they are insignificant in the formation of the phthalocyanine macrocycle. This is due to the flat structure of the cyano group, which is attacked by the nucleophile during template cyclization.[67]

When obtaining metal complexes, we have achieved the best yield for erbium and lutetium complexes[66] using boiling Am^{i}OH and lithium methoxide as base.

For titanium complexes, carrying out the reaction in solution,[35] as a rule, leads to higher yields of the target compounds, in comparison with the synthesis in the melt in the presence of urea.[39]

The synthesis of thiophene-substituted complexes **25a-c** was carried out using the template method (Scheme 11). 2-Ethoxyethanol was used as a solvent, and DBU as a base. The main peculiarity of approach used by the authors[69] is that the starting thiophene-substituted phthalonitrile was obtained from the corresponding dibromo derivative without isolation of intermediate compounds. The choice of such a strategy is since at the first stage (cross-coupling according to Suzuki), in addition to the target disubstitution product, Z. Chen *et al.*[69] obtained a monosubstitution product, and also isolated a part of the unreacted starting compound. These substances have the same R_f values and cannot be separated chromatographically; therefore, the undivided reaction mass was introduced into the hydrolysis reaction (second stage, Scheme 11). Separation was carried out at the stage of nitrile preparation (Scheme 11, insert). For this, the reaction mass was treated with an excess of hydroquinone in the presence of potash.

The obtained products of the reaction of nucleophilic substitution are easily separated from the target phthalonitrile in an aqueous alkali solution. The total yield of nitrile was 19%.

Metal complexes of phthalocyanines substituted with sulfur-containing functional groups can be obtained not only by the template cyclization method, but also by the metallation reaction of the phthalocyanine ligand (Scheme 12).[41,70]

Ligand **27** was prepared[41] from the corresponding nitrile (Table 6). Metallation was performed with lead or copper acetates in boiling DMF.

In the second case,[70] 4-octylthio-substituted phthalonitrile was used as the starting compound, which was introduced into the reaction of template synthesis with lead oxide. The reaction medium was the melt of initial nitrile. The lead phthalocyaninate **26** was treated with acetic acid to form ligand **26′**. The last stage was the metallation of ligand **26′** in boiling *n*-hexanol. Copper phthalocyaninate **27** was obtained in high yield. This compound, due to the different positions of the peripheral substituents, is a mixture of isomers. It is important to note that complex **26** and ligand **26’** were introduced into the reaction without preliminary purification; therefore, their yields were not calculated.

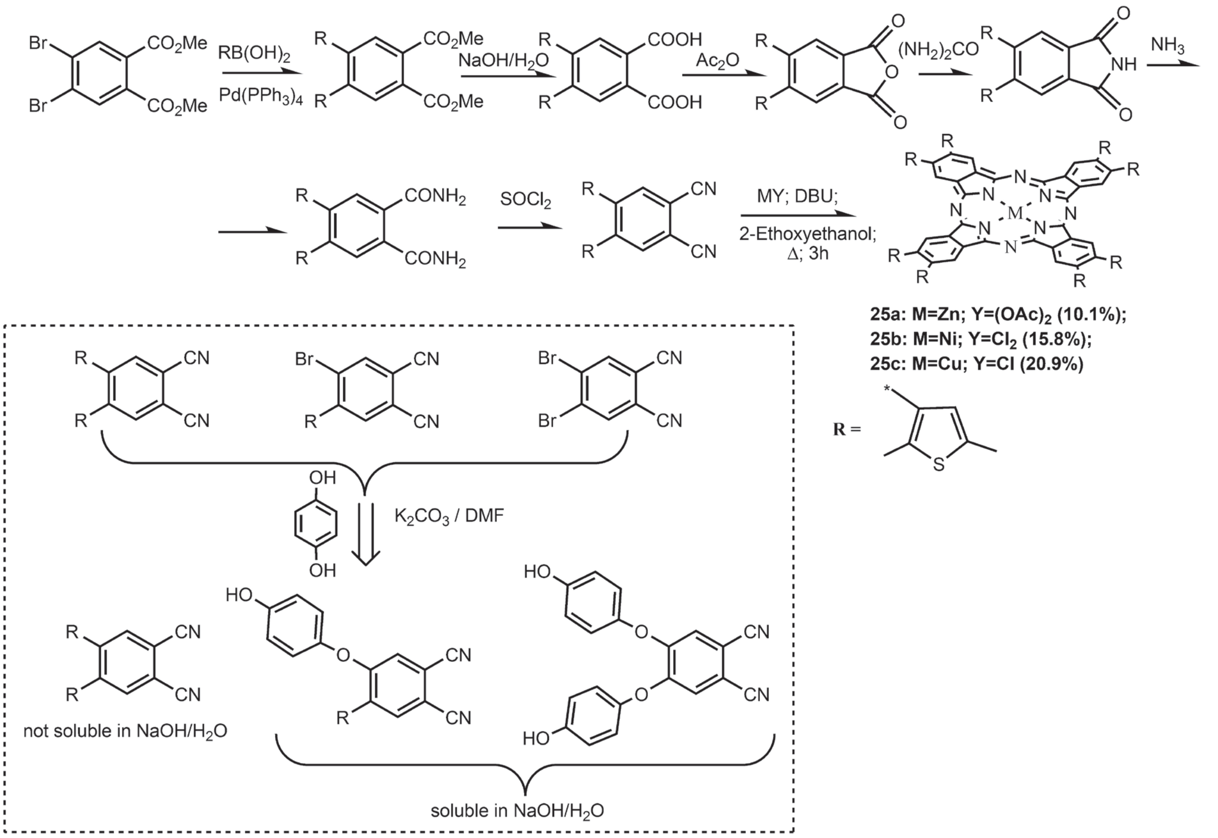
The total yields of copper complexes **17a** and **27**, starting from the corresponding substituted nitriles, are 34% and 85%, respectively. The low total yield of the first approach is due to losses at the stage of isolation of ligand **17** by the template method.

Nombona *et al.*[36] described an example of the synthesis of unsymmetrically substituted phthalocyanine ligand of A_3B type. This classification is based on the number of fragments of the two nitriles that make up the phthalocyanine macrocycle. The target compound was obtained by a statistical condensation reaction between two different nitriles (Scheme 13). Dilithium complex was obtained *in situ,*[36] and then demetallated by acetic acid. Interestingly, to achieve the best contact between nitriles **28** and **29**, they were mixed and ground in a mortar before being dissolved in pentanol.

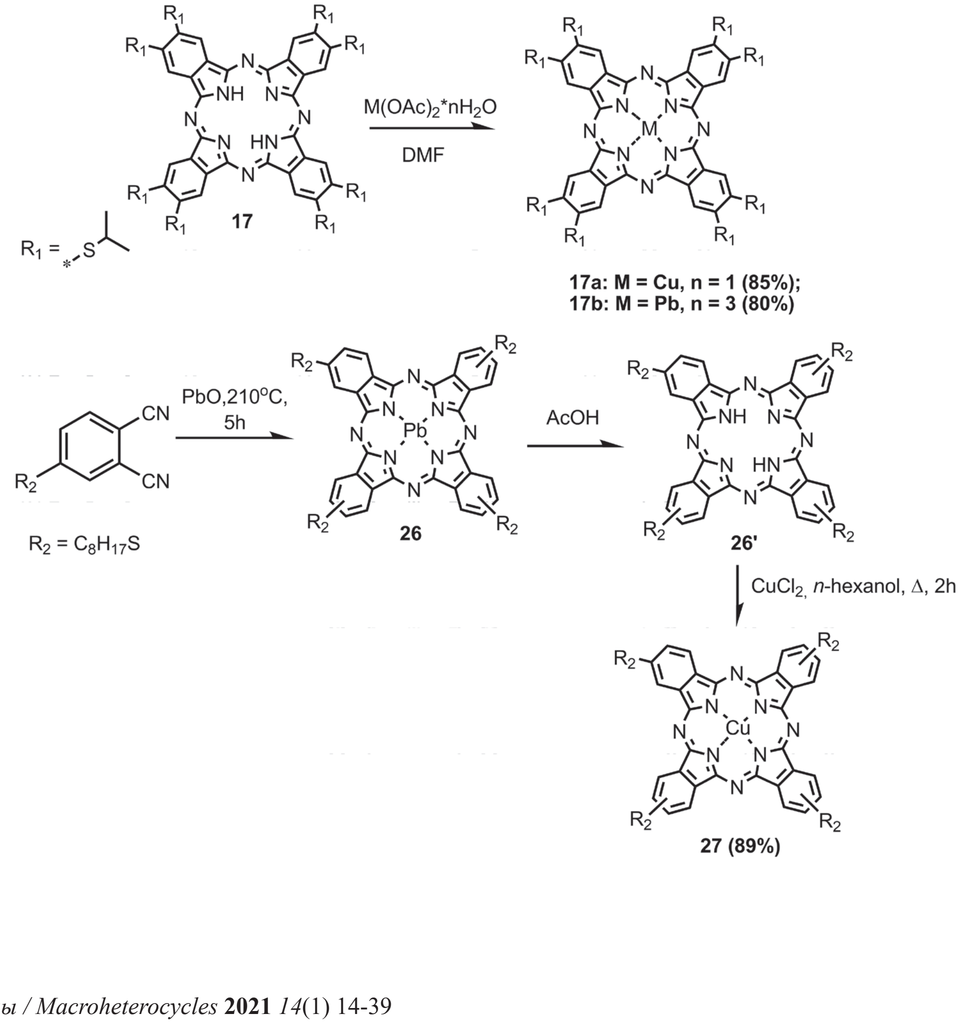
The yield of the target ligand **30** was 13%. The low yield is due to the formation of difficult-to-separate self-cyclization by-products of starting compounds **28** and **29**. A few more examples of A_3B phthalocyanines will be given in Section 3.2.

3.2. Modification of substituents at the stage of cyclization of the phthalocyanine macrocycle and in the formed macrocycle

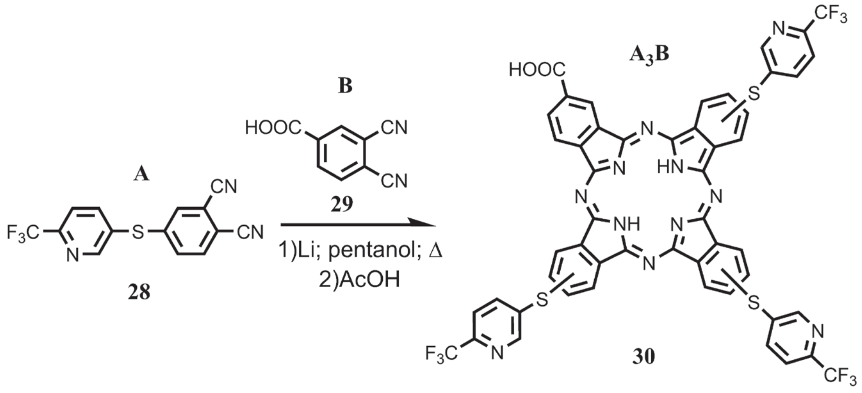
The literature describes examples of the introduction of functional groups containing sulfur into the phthalocyanine molecule both at the stage of template cyclization of the macrocycle and in the formed phthalocyanine.



Scheme 11.



Scheme 12.



Scheme 13.

P.-C. Lo *et al.*[45] succeeded in synthesizing alkylthio-substituted phthalocyanines **31** in an ionic liquid starting from 4-nitrophthalonitrile (Scheme 14). Alkylthiol was introduced into the reaction in a fourfold excess. The reaction was carried out at a temperature of 100 °C approximately corresponding to the melting point of Bu$_4$NBr (m.p. 102–106 °C, decomposes at 133 °C). The use of a twofold excess leads to the formation of a nucleophilic substitution reaction product.

Thus, both the formation of a macrocycle and the reaction of nucleophilic substitution of the nitro group took place during the synthesis. A similar reaction for 3-nitrophthalonitrile results in only trace amounts of the target phthalocyanine ligand.

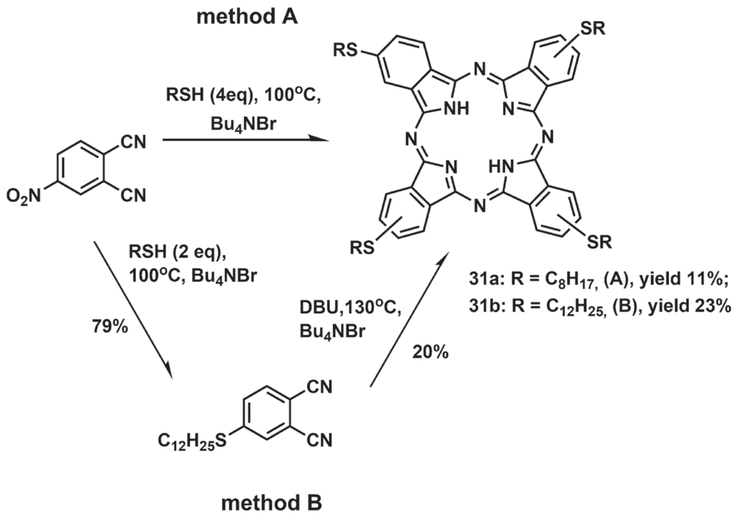
It is important to note that the yield of phthalocyanine **31b** when using a one-step technique (method A, Scheme 14) is higher than when using a two-step approach (total yield - 16%).[45]

The approach described by the N. Nombona *et al.*[36] includes: synthesis of a zinc complex with a terminal hydroxy group, introduction of a protective group, alkylation of thiourea with compound **32**, and hydrolysis to form a terminal SH group. The introduction of terminal thiol groups is necessary for the further formation of covalent bonds with gold nanoparticles. Scheme 15 shows the overall yield for complex **33**. Intermediates were not isolated and characterized.

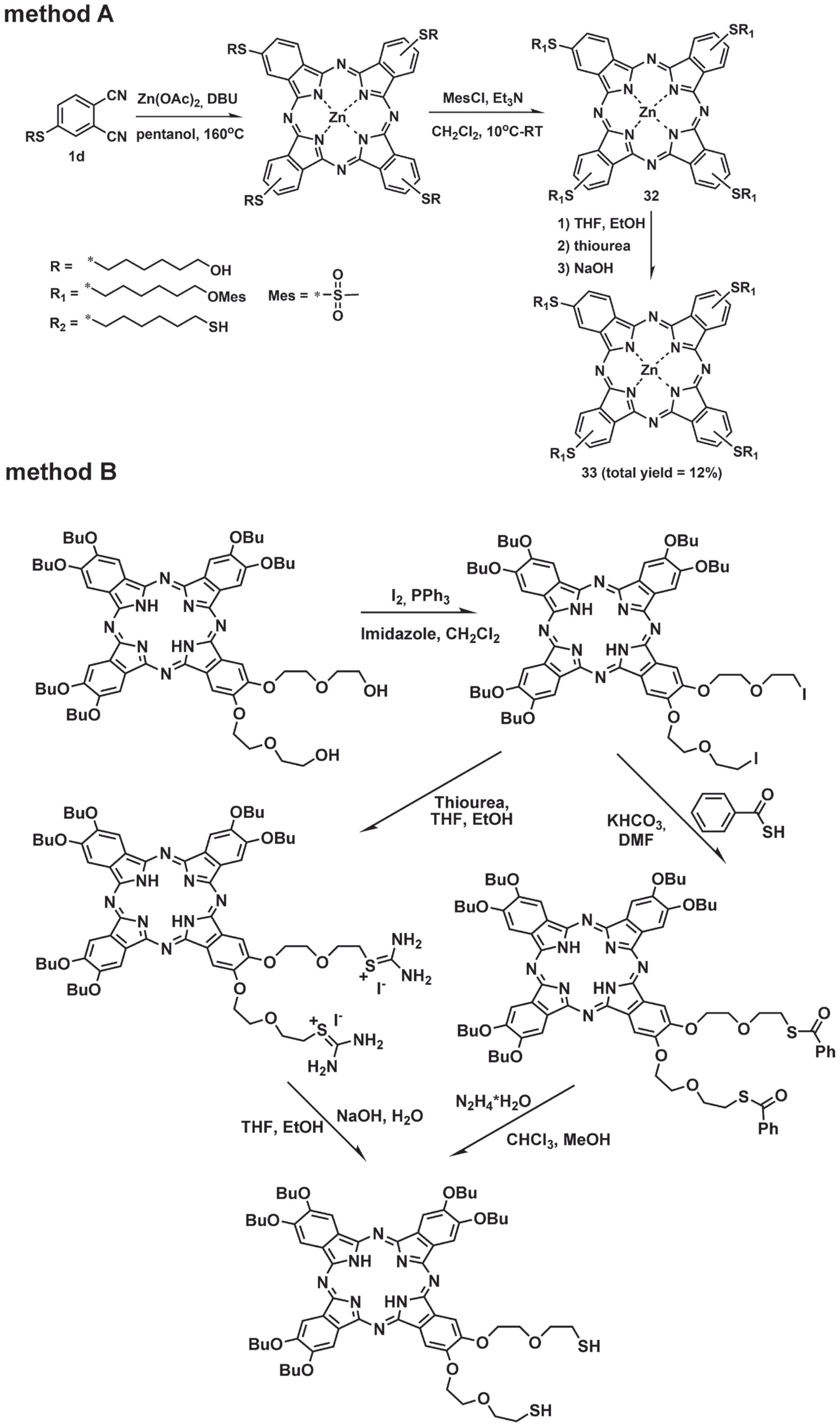
Alternative method (method B, Scheme 15) of conversion of OH groups to SH was demonstrated by D.O. Oluwole *et al.* This approach includes substitution of iodine atoms with thiourea or thiobenzoyl fragments. In the case of thiobenzoyl group the last stage implied mild cleavage of benzoyl protective groups.[71] Due to the presence of thiol groups, this phthalocyanine could be conjugated with triocylphosphineoxide-capped CdSe quantum dots or oleylamine capped silver nanoparticles (Ag-NPs). These conjugates possess enhanced nonlinear optical response in comparison with individual components.

It was found by A.V. Shokurov *et al.*,[72] that thiobenzoate-bearing phthalocyanine have a tendancy to form densely packed self-assembled monolayers on gold without the need in additional *ex situ* deprotection synthetic step.

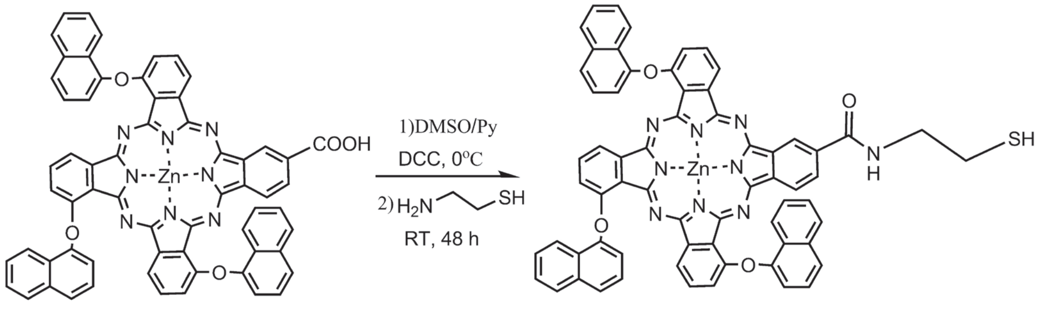
Carboxyl-substituted A$_3$B phthalocyanine appears to be initial compound for the introduction of thiol-containing spacer, which was useful for the preparation of hybrid nanoparticles.[36] Zinc complex **34** bearing three



Scheme 14.


method A
1d
Zn(OAc)$_2$, DBU
pentanol, 160°C
MesCl, Et$_3$N
CH$_2$Cl$_2$, 10°C-RT
32
1) THF, EtOH
2) thiourea
3) NaOH
33 (total yield = 12%)
R =
R$_1$ =
R$_2$ =
Mes =
method B
I$_2$, PPh$_3$
Imidazole, CH$_2$Cl$_2$
Thiourea, THF, EtOH
KHCO$_3$, DMF
THF, EtOH
NaOH, H$_2$O
N$_2$H$_4$*H$_2$O
CHCl$_3$, MeOH

Scheme 15.



34 **35 (10%)**

Scheme 16.

α-naphthoxy-groups and one carboxyl group was activated by dicyclohexyl carbodiimide (DCC) and then the amide bond was formed (Scheme 16).

The synthesis of A_3B phthalocyanine with three decyl-substituted moieties and one thiol functional group in nonperipheral (α-position) of phthalocyanine macrocycle was carried out by I. Chambrier *et al.*[73] (Scheme 17). Heptadecyl-hydroxypropyl-substituted zinc phthalocyanine **36** was chosen as initial compound.

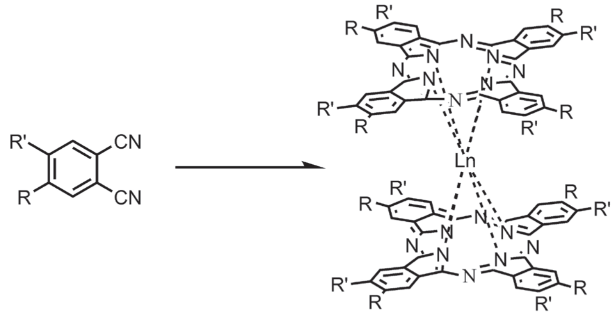
Then by the analogy with approach, which was depicted in Scheme 15 (method A),[36] the protective group was introduced and the alkylation of thiourea by compound **37** was realized. All intermediate compounds were isolated and characterized. Target compound **38** was isolated using column chromatography and subsequent recrystallization.

4. Synthesis of lanthanide(III) diphthalocyanines bearing sulfur-containing functional groups

All methods described in the literature for the synthesis of lanthanide(III) diphthalocyanines with sulfur-containing functional groups include the use of corresponding substituted phthalonitriles as starting compounds (Scheme 18, Table 7).

Diphthalocyanines and their analogs (dinaphthalocyanines) exist in the form of stable π-radicals.[7,74,81–84] The radical is delocalized between the pyrrole fragments of the phthalocyanine macrocycle.

The rather low yield of target compounds **39–43** is probably due to: (1) the formation of by-products of the polymerization of the starting nitriles, (2) steric hindrances created by DBU, coordinating with the central lanthanide ion during the reaction.[7,85]



39-43

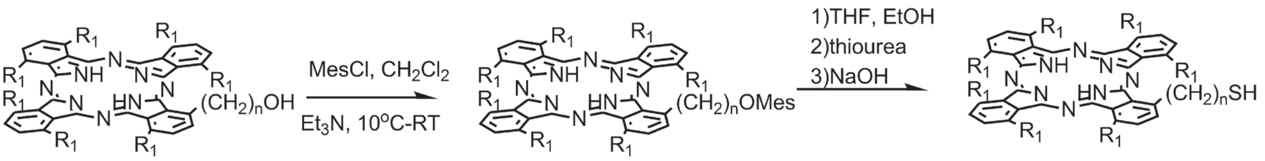
Scheme 18.

Using electrochemical measurements,[74] it was found that complex **39** is easier to reduce and more difficult to oxidize than the corresponding unsubstituted diphthalocyanine. On this basis, phenylthio-substituents in this case refer to electron-withdrawing ones.

In the case of complex **41a**, the compliance with the declared structure can be questioned. This compound was not characterized by either mass spectrometry or ^1H NMR spectroscopy. The hypothesis of the π-radical nature of the obtained compound is based on the presence of a low-intensity broadened absorption band at 440 nm[76] and is not confirmed by the data of electron paramagnetic resonance (EPR) spectroscopy.

An important representative of the class of diphthalocyanine complexes of a sandwich structure are heteroleptic complexes. This review considers heteroleptic complexes containing phthalocyanine ligands with various substituents.

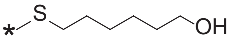
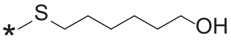
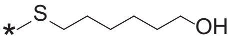
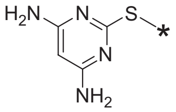
The authors of [74] described the synthesis of a heteroleptic diphthalocyanine complex **44** containing an unsubstituted phthalocyanine and octaphenylthio-substituted decks (Scheme 19).



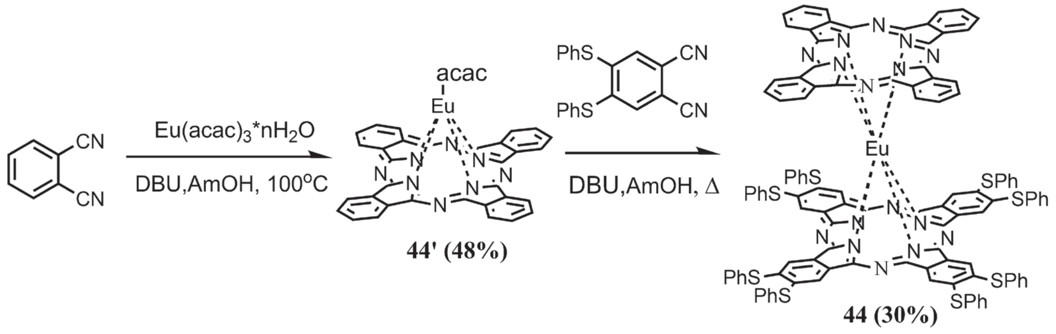
36: $R_1 = C_{10}H_{21}$; n=3 **37: $R_1 = C_{10}H_{21}$; n=3 (98%)** **38: $R_1 = C_{10}H_{21}$; n=3 (77%)**

Scheme 17.

Table 7. Reaction conditions and yields of compounds **39–43**, obtained via Scheme 18.

Compound	R	R´	Ln	Reaction conditions[a]	Yield, %	Reference
39	PhS	PhS	Eu	$Eu(acac)_3\cdot nH_2O$, pentanol, Δ	42	[74]
40a		R	Eu	$Eu(acac)_3\cdot nH_2O$, hexanol, Δ	10.52	[75]
40b		R	Yb	$Yb(acac)_3\cdot nH_2O$, hexanol, Δ	11.54	[75]
40c		R	Lu	$Lu(acac)_3\cdot nH_2O$, hexanol, Δ	12.71	[75]
41a		H	Lu	$Lu(OAc)_3\cdot 2H_2O$, hexanol, Δ	49	[76]
41b	$C_8H_{17}S$	$C_8H_{17}S$	Eu	$Eu(OAc)_3\cdot 4H_2O$, hexanol, Δ	61	[77]
41c	$C_{10}H_{21}S$	$C_{10}H_{21}S$	Eu	$Eu(OAc)_3\cdot 4H_2O$, hexanol, Δ	15	[77]
41d	$C_{12}H_{25}S$	$C_{12}H_{25}S$	Eu	$Eu(OAc)_3\cdot 4H_2O$, hexanol, Δ	44	[77]
41e	$C_{14}H_{29}S$	$C_{14}H_{29}S$	Eu	$Eu(OAc)_3\cdot 4H_2O$, hexanol, Δ	43	[77]
41f	$C_{16}H_{33}S$	$C_{16}H_{33}S$	Eu	$Eu(OAc)_3\cdot 4H_2O$, hexanol, Δ	40	[77]
41g	$C_8H_{17}S$	$C_8H_{17}S$	Tb	$Tb(OAc)_3\cdot 4H_2O$, hexanol, Δ	19	[77]
41h	$C_{10}H_{21}S$	$C_{10}H_{21}S$	Tb	$Tb(OAc)_3\cdot 4H_2O$, hexanol, Δ	39	[77]
41i	$C_{12}H_{25}S$	$C_{12}H_{25}S$	Tb	$Tb(OAc)_3\cdot 4H_2O$, hexanol, Δ	42	[77]
41j	$C_{14}H_{29}S$	$C_{14}H_{29}S$	Tb	$Tb(OAc)_3\cdot 4H_2O$, hexanol, Δ	44	[77]
41k	$C_{16}H_{33}S$	$C_{16}H_{33}S$	Tb	$Tb(OAc)_3\cdot 4H_2O$, hexanol, Δ	32	[77]
41l	$C_{18}H_{37}S$	$C_{18}H_{37}S$	Tb	$Tb(OAc)_3\cdot 4H_2O$, hexanol, Δ	22	[77]
41m	$C_8H_{17}S$	$C_8H_{17}S$	Lu	$Lu(OAc)_3\cdot 4H_2O$, hexanol, Δ	8	[77]
41n	$C_{10}H_{21}S$	$C_{10}H_{21}S$	Lu	$Lu(OAc)_3\cdot 4H_2O$, hexanol, Δ	9	[77]
41o	$C_{12}H_{25}S$	$C_{12}H_{25}S$	Lu	$Lu(OAc)_3\cdot 4H_2O$, hexanol, Δ	28	[77]
41p	$C_{14}H_{29}S$	$C_{14}H_{29}S$	Lu	$Lu(OAc)_3\cdot 4H_2O$, гексанол, Δ	16	[77]
41q	$C_{16}H_{33}S$	$C_{16}H_{33}S$	Lu	$Lu(OAc)_3\cdot 4H_2O$, hexanol, Δ	20	[77]
41r	$C_{18}H_{37}S$	$C_{18}H_{37}S$	Lu	$Lu(OAc)_3\cdot 4H_2O$, hexanol, Δ	44	[77]
42a	$C_6H_{13}S$	$C_6H_{13}S$	Gd	$Gd(OAc)_3$, hexanol, Δ	29	[78]
42b	$C_6H_{13}S$	$C_6H_{13}S$	Dy	$Dy(OAc)_3$, hexanol, Δ	36	[78]
42c	$C_6H_{13}S$	$C_6H_{13}S$	Sm	$Sm(OAc)_3$, hexanol, Δ	30	[78]
43a	$C_6H_{13}S$	H	Lu	$Lu(OAc)_3$, pentanol, Δ	12	[79]
43b	$C_8H_{17}S$	H	Lu	$Lu(OAc)_3$, pentanol, Δ	14	[79]
43c	$C_{10}H_{21}S$	H	Lu	$Lu(OAc)_3$, pentanol, Δ	13	[79]
43d	$C_{12}H_{25}S$	H	Lu	$Lu(OAc)_3$, pentanol, Δ	8.1	[79]
43d	$C_{12}H_{25}S$	H	Lu	$Lu(OAc)_3$, hexanol, Δ	8.1	[80]
43e	$C_{16}H_{33}S$	H	Lu	$Lu(OAc)_3$, pentanol, Δ	12	[79]

[a] – DBU was chosen as a base.



Scheme 19.

This compound was obtained in two stages. First, the synthesis of the monophthalocyanine complex **44´** was carried out, and then the template assembly of the second phthalocyanine macrocycle and the formation of the target compound **44**.

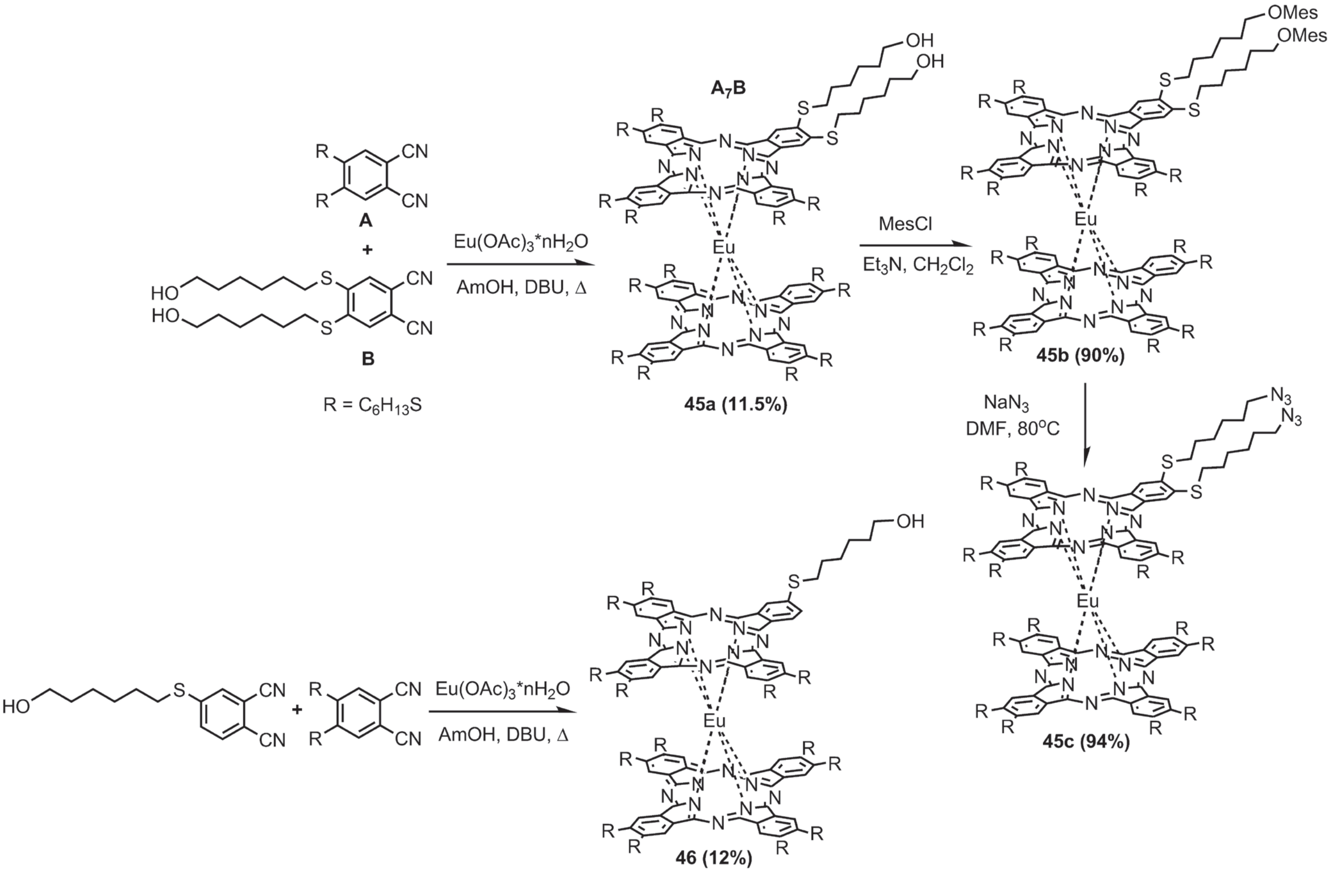
The authors of [86] have synthesized heteroleptic diphthalocyanine complexes of europium **45** and **46** (Scheme 20). The authors classify these compounds as A_7B type.

The synthesis was carried out under the conditions of a statistical condensation reaction by mixing two nitriles in a ratio of 20:1 (A:B). The target compounds were purified by column chromatography. Only the corresponding symmetrically substituted diphthalocyanines were isolated as by-products. In order to show the synthetic potential of the terminal hydroxy groups, the authors additionally carried out their modification into azido groups and methanesulfonyl groups.

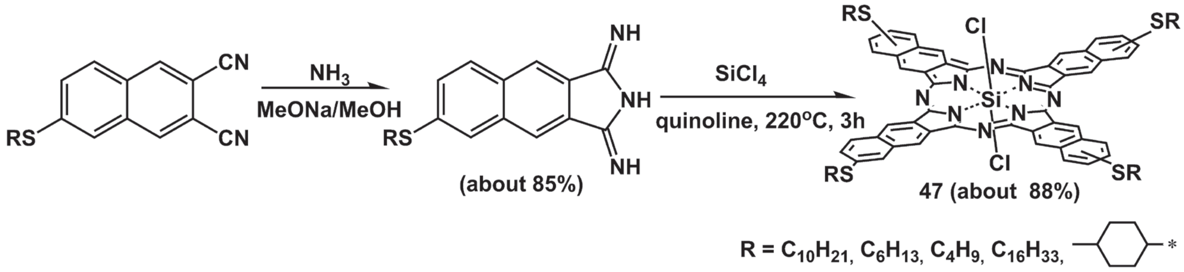
5. Synthesis of 2,3-naphthalocyanines bearing sulfur-containing functional groups

The literature describes only a few examples of synthesis of 2,3-naphthalocyanines substituted with functional groups containing sulfur. Scheme 21 shows the synthesis of silicon naphthalocyaninates **47**.

As a starting compound, the authors of [54] used not 2,3-dicyanonaphthalenes, but diiminoisoindolines, which are more active in the process of macrocyclization. This



Scheme 20.



Scheme 21.

approach was used to synthesize a series of alkylthio-substituted silicon naphthalocyaninates. Unfortunately, the exact yields of the target compounds were not presented in the work.

The authors of [55,56] carried out the synthesis of naphthalocyanine complexes under milder conditions (Scheme 22, Table 8): boiling 1-pentanol or 1-hexanol. Both the diiminoisoindoline derivative (**1**) and the corresponding nitrile (**2**) were used as starting compounds.

Using isoamyl alcohol as a solvent and lithium methoxide as a base, we managed to obtain 3-(ethylthio)phenyl-substituted zinc naphthalocyaninate **48e**[49] with a yield of 90%, which is significantly higher than those presented earlier for 2,3-naphthalocyanines substituted by functional groups containing sulfur.

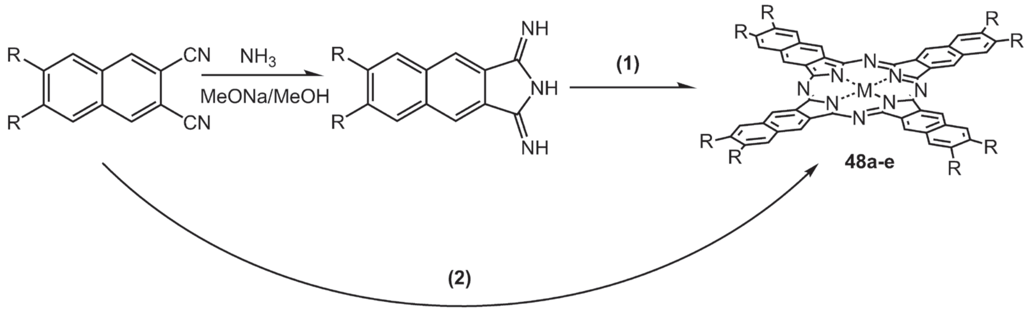
The authors of [87] described the synthesis of dodecylthio-substituted dinaphthalocyanine europium **49** with a sandwich structure (Scheme 23).

This compound, like diphthalocyanine, is a stable π-radical. This is confirmed by the data of the EPR spectrum recorded in toluene. The spectrum contains a structureless singlet with a g-factor of 2.01.

It is interesting to note that a higher-boiling solvent (octanol, 195 °C) was used in the synthesis of dinaphthalocyanine **49** than in the synthesis of diphthalocyanine **41d** (hexanol, 157 °C).[77] In this case, the output of compound **49** is almost twice as high.

6. Synthesis of bi- and polynuclear phthalocyanines

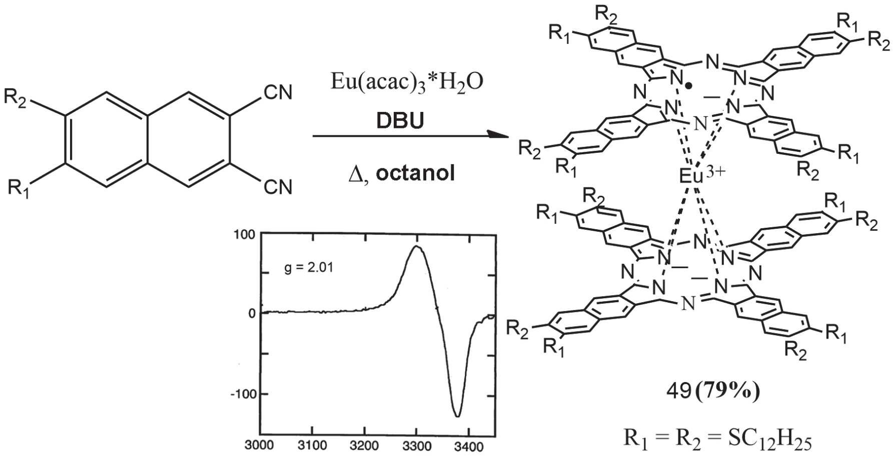
The main method for the synthesis of binuclear complexes is statistical condensation between the nitrile, which forms the periphery of the binuclear complex, and the compound, which forms the spacer.[14] Using this approach, the authors of [88] obtained binuclear cobalt complexes containing amino, nitro-, and ferrocenyl groups at the periphery of the macrocycle (Scheme 24).



Scheme 22.

Table 8. Reaction conditions and yields of compounds **48**, obtained via Scheme 22.

Compound	R	M	Reaction conditions	Method	Yield, %	Reference
48a	C_3H_7S	Zn	$Zn(OAc)_2 \cdot 2H_2O$; DBU; 1-hexanol; Δ; 5h	**(2)**	53	[55]
48b	PhS	Zn	$Zn(OAc)_2 \cdot 2H_2O$; DBU; 1- hexanol; Δ; 5h	**(2)**	48	[55]
48c	$C_{12}H_{25}S$	HH	DBU; 1-pentanol; Δ; 10h	**(1)**	38	[56]
48d	$C_{12}H_{25}S$	Cu	CuCl; DBU; 1- pentanol; Δ; 10h	**(2)**	41	[56]
48e	3-(ethylthio)phenyl	Zn	$Zn(OAc)_2 \cdot 2H_2O$; MeOLi; Am^{i}OH; Δ; 6h	**(2)**	90	[49]



Scheme 23. Scheme of synthesis of dinaphthalocyanine complex **49**. Insert - EPR spectrum of a solution of dinaphthalocyanine **49** in toluene.

Tetracyanobenzo(1,4,7,10-tetrathio(12-crown)) **50** was used as a starting compound to create a spacer. In contrast to nitro-substituted **51** and amino-substituted complexes **52**, compound **53** was found to be insoluble in organic solvents. Its structure was confirmed by the data of elemental analysis and IR spectroscopy (on the disappearance of vibrations of aldehyde and amino groups).

Based on the asymmetrically substituted monophthalocyanine complex of zinc **54** and the binuclear complex **51**, a polynuclear complex **55** was obtained.

During the synthesis, the nitro groups were transformed *in situ* to amino groups, and then azo spacers were formed. The good solubility of the target complex **55** was presumably provided by hexylthio groups.

Despite the fact that the authors of[88] postulate the overlap of the π-systems of the macrocycles of compound **55**, no absorption bands in the near IR range are observed in its electronic absorption spectrum (UV-Vis). This may be due to either the aggregation of this complex as it was observed for other polynuclear phthalocyanines,[14] or to its insufficient purity.

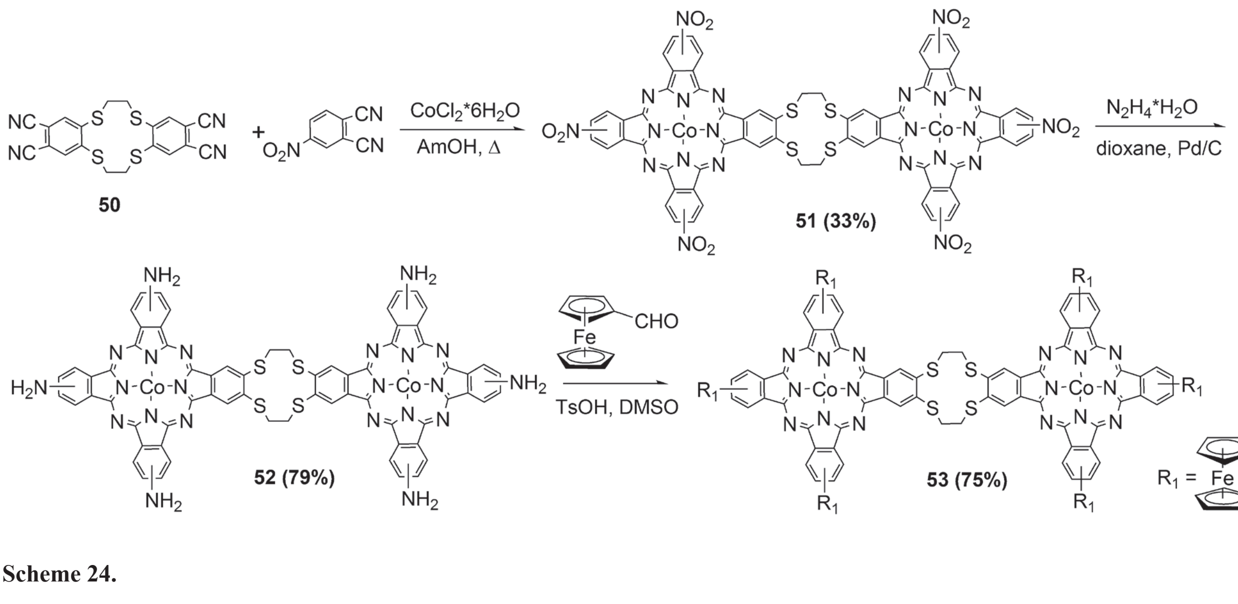
The synthesis of the tetranuclear complex **56** based on the corresponding binuclear complex is based on a similar principle for creating an azo spacer (Scheme 26).[89]

An interesting example of a complex containing both sandwich and binuclear structural units was obtained.[90]

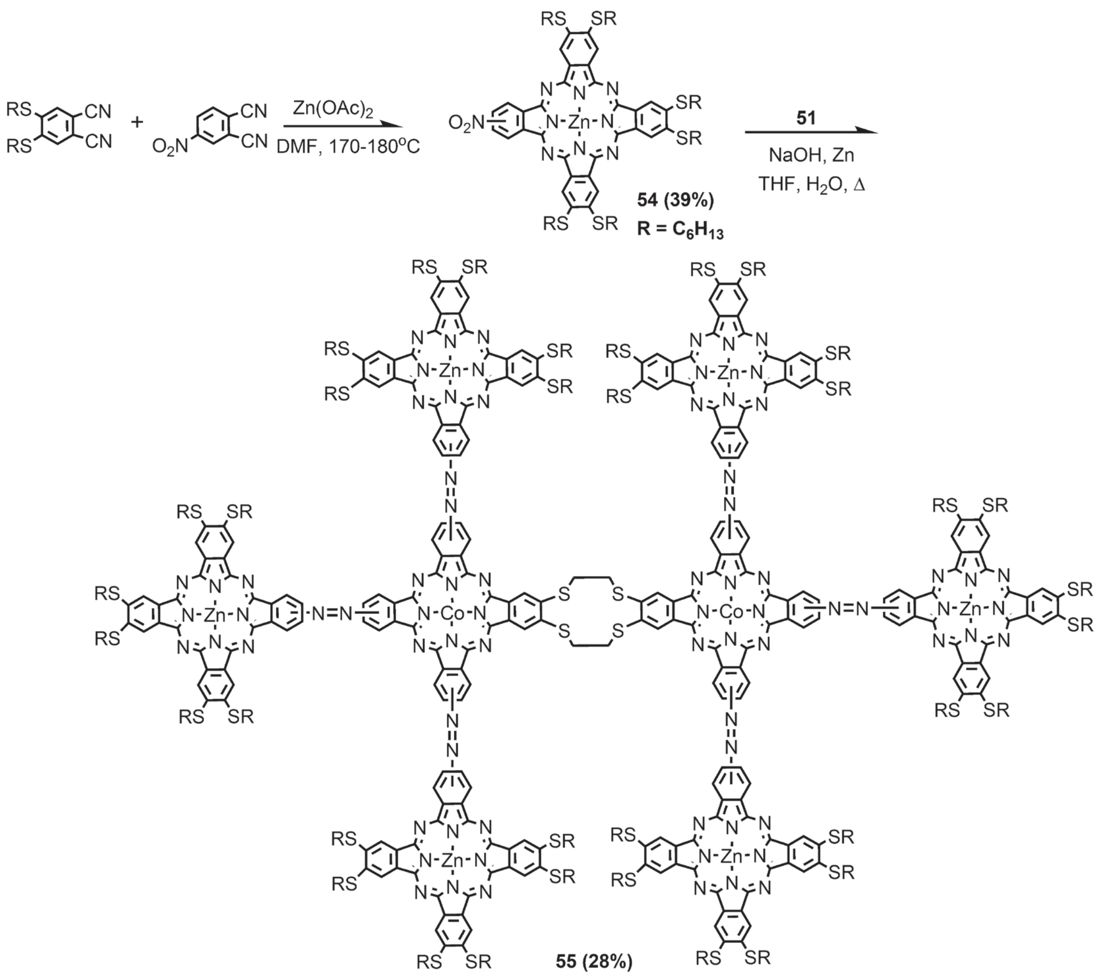
Compound **57** was used as the initial binuclear complex. The corresponding binuclear free ligand and its hexylthio-substituted cobalt complex are also described in the literature.[91,92]

The sandwich-type complex **58** was obtained by the interaction of the binuclear complex and diiminoisoindoline **57´**. Lithium amylate formed *in situ* served as the base. We assume that, based on the UV-Vis data of compound **58**, it may contain an admixture of the initial binuclear complex and/or lutetium diphthalocyanine. This research group has published a number of works on sandwich complexes containing common calixarene and heteroaromatic bridges.[93–95] A detailed analysis of these studies is given in the review.[7]

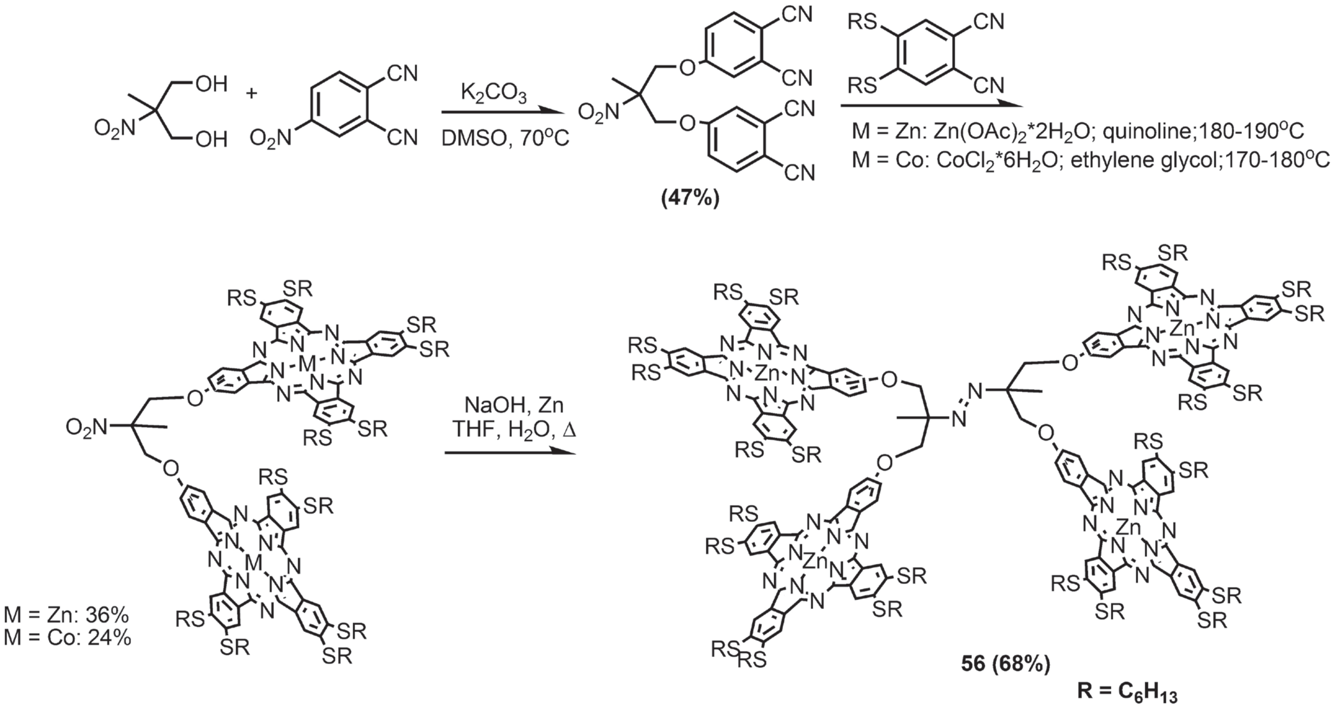
As a conclusion to this section, it can be noted that the low yields of bi- and polynuclear complexes obtained



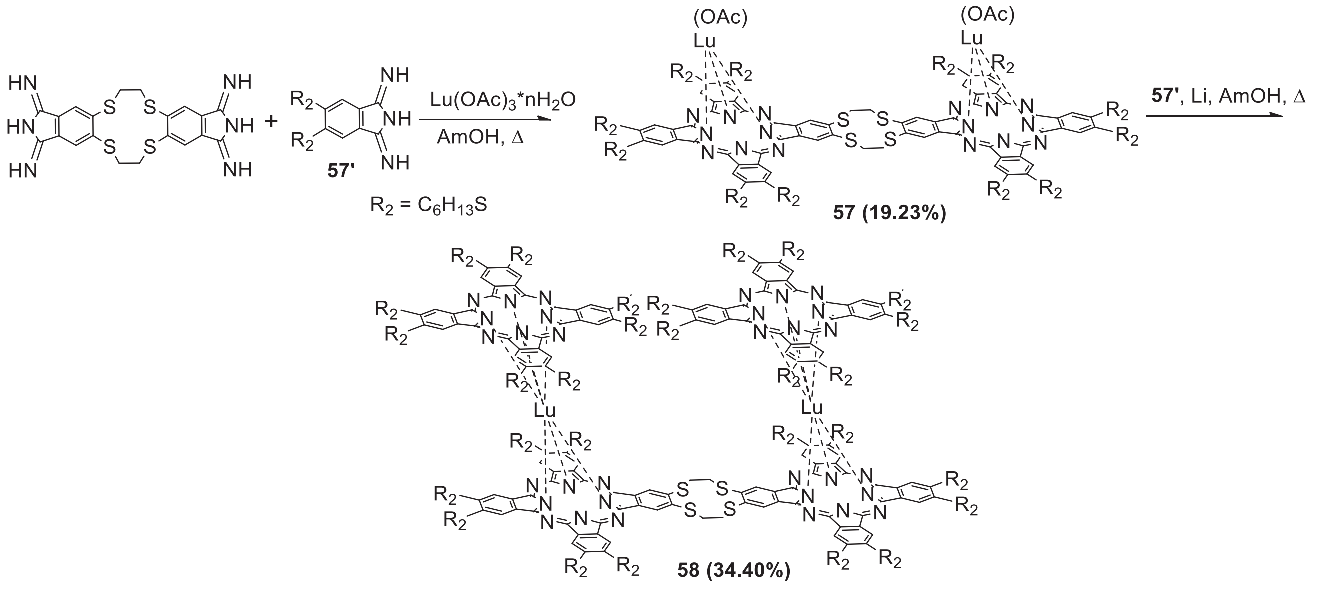
Scheme 24.



Scheme 25.



Scheme 26.



Scheme 27.

by the statistical condensation reaction are due to the close reactivity of the starting nitriles (forming the periphery of the binuclear complex and the spacer). This leads to the formation of the corresponding monophthalocyanines as by-products, as well as oligomers of the starting nitriles.[14]

7. Application areas of phthalocyanines and 2,3-naphthalocyanines with functional groups containing sulfur

The introduction of functional groups containing sulfur into the molecules of phthalocyanines and 2,3-naphthalocyanines gives them properties that are important for their practical application.

First, due to the high affinity between sulfur and gold,[17,26] it is possible to obtain hybrids with gold nanoparticles. Hybrids of phthalocyanines and gold nanoparticles can be subdivided according to the type of bonding: covalently bonded, formed due to coordination or electrostatic interactions.

Second, the introduction of substituents containing sulfur into the non-peripheral positions 3 and/or 6 of the phthalocyanine macrocycle promotes the bathochromic shift of the main absorption band (Q-band corresponding to the transition of an electron from HOMO to LUMO).[43]

Finally, the introduction of bulky substituents containing sulfur helps to reduce aggregation. This is especially important for the formation of thin films based on phthalocyanines from solutions.

7.1. Hybrids with gold nanoparticles: preparation and application

The synthesis of hybrid systems based on metal nanoparticles and phthalocyanines can significantly improve the characteristics of materials based on phthalocyanines. Besides, the presence of phthalocyanines on the surface of nanoparticles leads to their stabilization.[96]

The authors of [18,27] carried out the functionalization of the surface of gold nanoparticles with benzylmercapto- and thiophenyl-substituted zinc phthalocyaninate (Figure 1). For this purpose, a solution of gold nanoparticles stabilized with tetraoctylammonium bromide was first prepared. The aqueous solution of gold chloride was stirred with a solution of tetraoctylammonium in toluene, and then $NaBH_4$ was added. The stabilized nanoparticles were separated together with the organic phase. Then, solutions of nanoparticles and zinc phthalocyaninate were mixed. Molecules of thiophenyl- and benzylmercapto-substituted phthalocyanines can interact with the surface of gold nanoparticles due to S-Au coordination bonds.

The formation of conjugates was confirmed by transmission electron and atomic force microscopy data. An increase in the size of nanoparticles in solution in the presence of zinc phthalocyanine was shown. The photochemical characteristics of arylmercapto-substituted zinc phthalocyanines were determined. It is shown that, due to the presence of residual bromine atoms on the surface of nanoparticles, the yield of singlet oxygen generation in hybrid nanoparticles is higher than that of the initial complex $(BenzylS)_4Pc$.

By the method of electrospinning, the authors of [27] succeeded in obtaining polymethyl methacrylate fibers with hybrid gold nanoparticles coated with a phthalocyanine shell. The resulting modified fibers efficiently generate singlet oxygen. They can potentially be used in antibacterial linen and ointments.

O.M. Bankole[68] modified the surface of alloys with the composition of Ag_1Au_3 and Ag_3Au_1 using zinc phthalocyaninate **24**. The peripheral diaminopyrimidine groups of phthalocyanine form coordination bonds with the surface of nanoparticles. The resulting conjugates have improved nonlinear optical characteristics in comparison with complex **24**. In this case, the highest value of the coef-

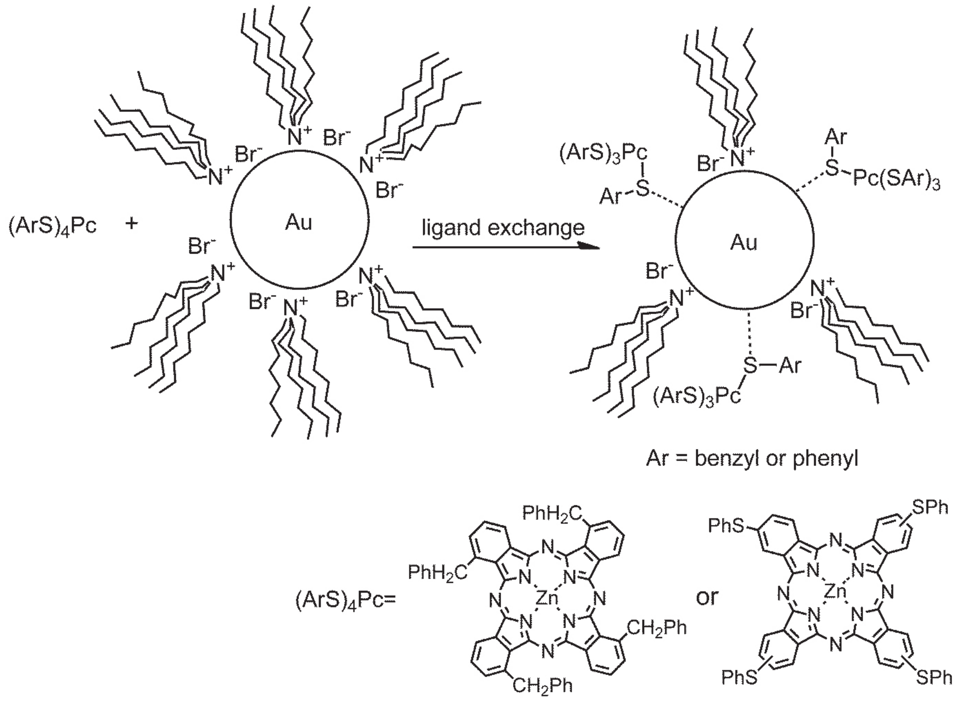


Figure 1. Surface modification of gold nanoparticles with benzyl mercapto-substituted zinc phthalocyaninate.[18,27]

Table 9. Photophysical characteristics for solutions in toluene of arylmercapto-substituted zinc phthalocyanines and corresponding hybrid gold nanoparticles.

Compound	λ_{abs}, nm	λ_{em}, nm	Φ_F	Φ_Δ	τ_F, ns
$(PhenylS)_4Pc$[18]	692	702	0.15	not presented	2.60 ± 0.01 (1.00)
$(PhenylS)_4Pc$+Au[18]	685	698	0.09	not presented	4.23 ± 0.07 (0.73) 1.74 ± 0.11 (0.27)
$(BenzylS)_4Pc$ [27]	710	725	0.03	0.33	2.40 ± 0.01 (1.00)
$(BenzylS)_4Pc$+Au [27]	699	708	<0.01	0.54	0.88 ± 0.03 (0.74)[a] 2.17 ± 0.04 (0.26)[a]

[a] Abundances are given in brackets.

ficient of effective nonlinear absorption (β_{eff}) is observed for the conjugate with Ag_1Au_3 nanoparticles.

Hybrid gold nanoparticles (AuNPs) coated with tetrasulfo-substituted aluminum phthalocyaninate (AlPcTS) molecules due to electrostatic interactions are presented in literature[24] (Figure 2). The surface of gold nanoparticles was preliminarily immobilized with a polyelectrolyte, and then a layer of sulfo-substituted aluminum phthalocyanine was applied by the *Layer-by-Layer* method.

For the obtained hybrid material, a plasmon enhancement of fluorescence was observed, which can be used in biomarkers. An important role is played by the distance between phthalocyanine and the surface of nanoparticles. It has been shown that the best effect can be achieved at a distance of 7 polyelectrolyte layers.

Phthalocyanine complexes can get a sulfur-containing substituent due to the formation of conjugates with nanoparticles. N. Nwaji *et al.*[97] described a series of conjugates of nanoparticles (Au, Ag) and quantum dots (CdTeSe, CdTeSe/ZnO) with *ball*-type indium phthalocyaninate (Scheme 28).

Covalent bonding of the surface of nanoparticles and phthalocyanine **59** molecules was carried out through the amide bond between the carboxyl group of phthalocyanine and the amino group of glutathione molecules that is comprised of the shell of the nanoparticles. The reaction was carried out in the presence of 4-dimethylamino pyridine (DMAP) and DCC. The resulting conjugates have nonlinear optical properties and high quantum yields of the triplet state.

A similar approach to the synthesis of a conjugate of gold nanoparticles and an asymmetrically substituted complex **60** was used in the work by O.M. Bankole *et al.*[98] (Scheme 29).

The covalent bond was formed due to the interaction of the carboxyl groups of mercaptopropionic acid, which forms the shell of nanoparticles, and the amino group of complex **60**. Carboxyl groups were preliminarily activated by interaction with *N*-hydroxysuccinimide in the presence of *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride.

Figure 3 shows a hybrid material formed due to covalent interactions between the surface of gold nanoparticles

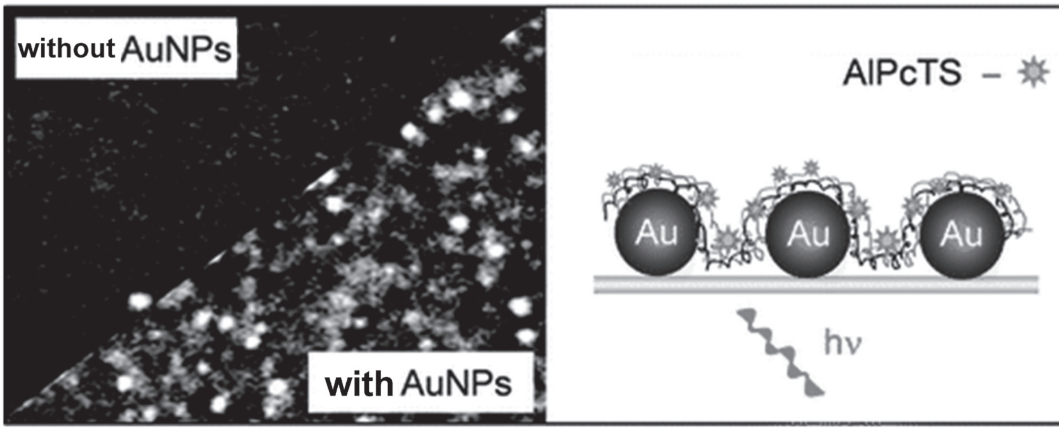


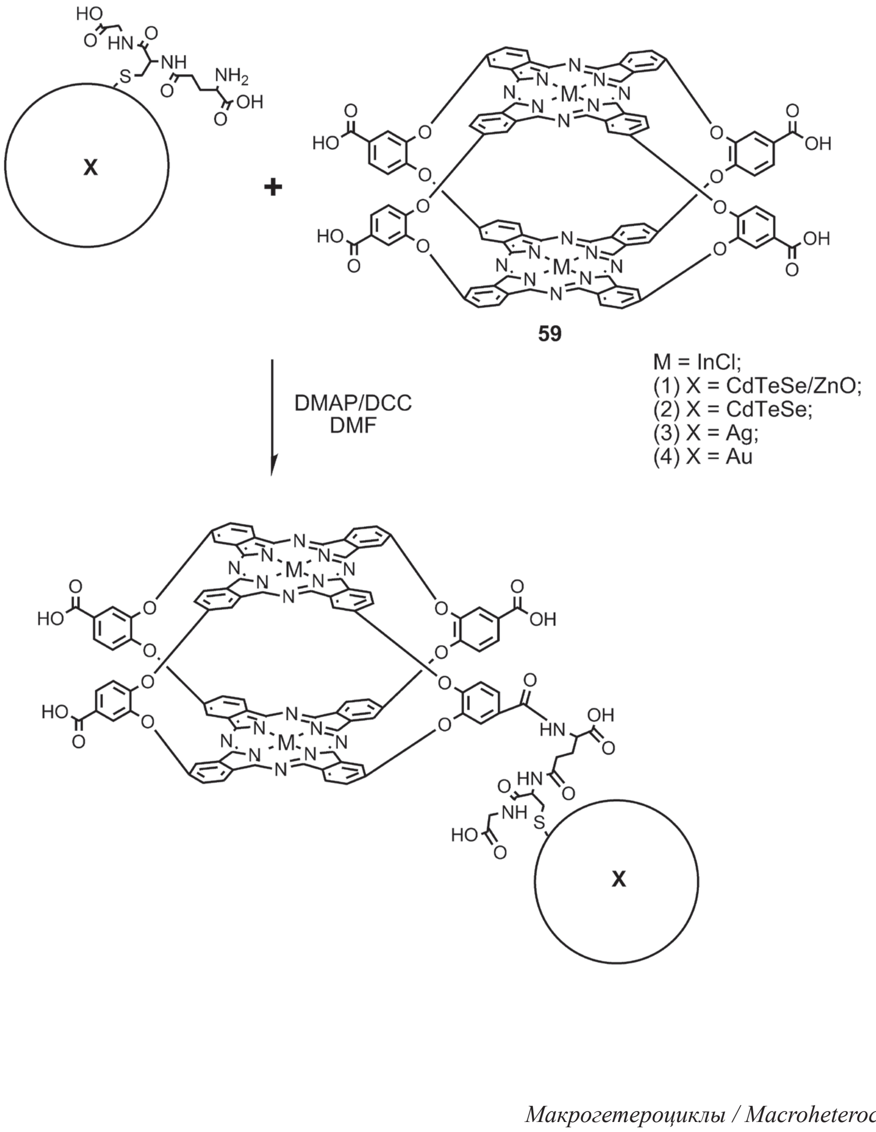
Figure 2. Fluorescence microscopy (left) and schematic representation of gold nanoparticles modified with tetrasulfo-substituted aluminum phthalocyanine (right).[24]

and A_3B type phthalocyanine containing a terminal thiol group.[36]

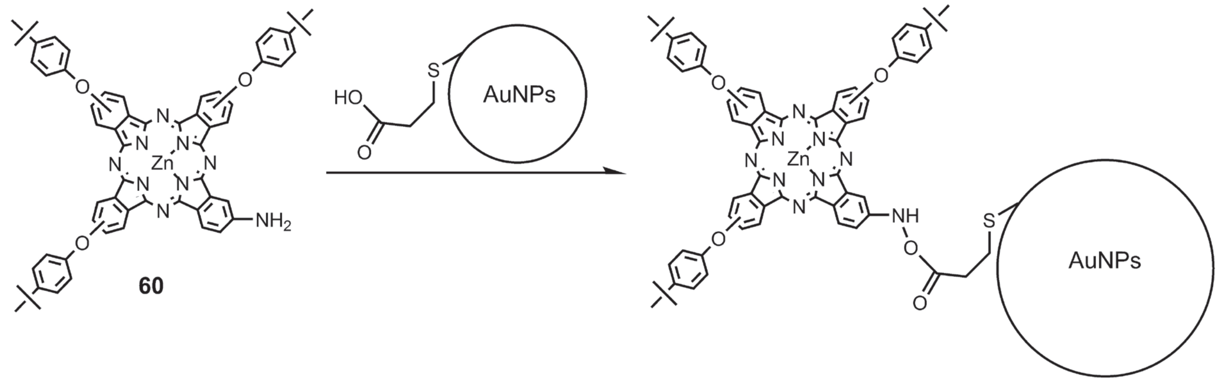
The resulting hybrid material is a promising photosensitizer for photodynamic therapy, since it has a high quantum yield of the triplet state.

7.2. Near infrared absorption

The presence of absorption in the near IR range is necessary for the creation of photovoltaic cells,[99] the synthesis of photosensitizers for photodynamic therapy



Scheme 28.



Scheme 29.

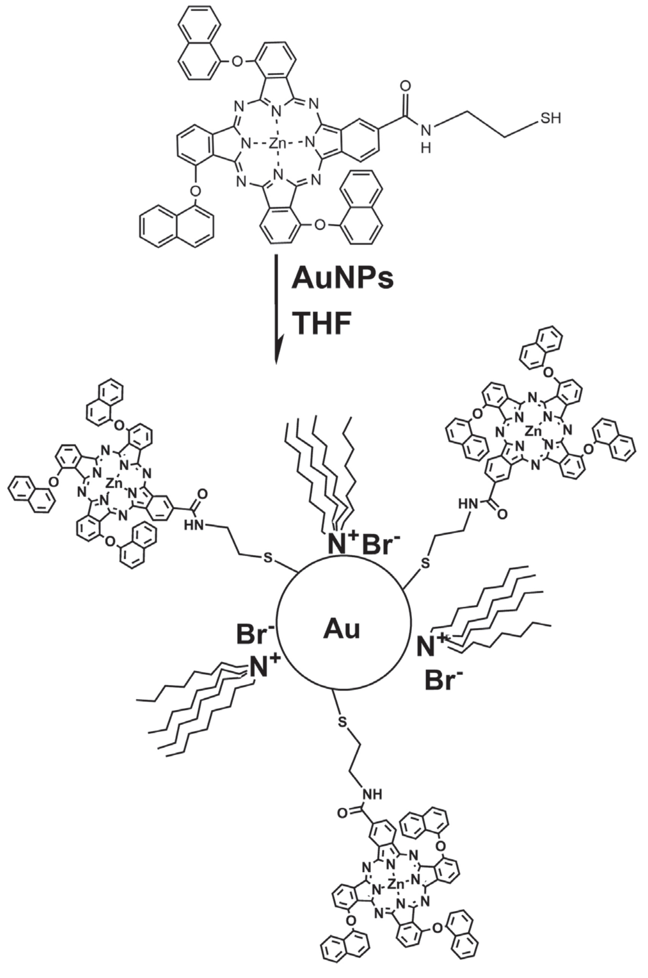


Figure 3. Obtaining a hybrid by covalent bonding.[36]

of subcutaneous cancerous tumors,[100] in the preparation of catalysts for photooxidative processes,[101,102] as well as the creation of IR labels.[103]

This section provides examples of the shift of the main absorption maximum of phthalocyanines (*Q* bands) to the near-IR region due to the presence of functional groups containing sulfur in non-peripheral positions of molecules (Table 9). In order not to take into account the effect of the nature of the macrocycle on the position of the absorption maximum, only phthalocyanine complexes are considered here.

Due to the effective interaction between the phthalocyanine π-orbitals and the sulfur 3p orbitals, an increase in the total π-system of the complex is achieved. In this case, the absorption maximum of compounds substituted with functional groups containing sulfur shifts bathochromically.[42] For example, the absorption maximum of complex **21a** is shifted by 20 nm bathochromically more than the unsubstituted analogue.[39]

Using phenylthio- and benzylthio-substituted complexes as the examples, it was shown in [35] that the introduction of the substituents in the non-peripheral position (complexes **14a** and **14b**) promotes a bathochromic shift of the *Q* band relative to the peripherally substituted complexes **14c** and **14d**. The absorption maxima of octasubstituted complexes **19** are shifted more bathochromically than tetrasubstituted **14**. In this case, the absorption maximum of the Mn(III) complex is located most bathochromically.

N. Kobayashi *et al.*[43] described the synthesis of stable phosphorus(V) phthalocyanine **61a** possessing absorption band beyond 1000 nm. Such a strong bathochromic shift is explained by the following factors:

– destabilization of HOMO due to electron-donor PhS groups in non-peripheral positions of the phthalocyanine macrocycle;

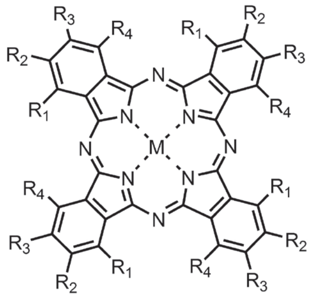
– deformation of the phthalocyanine macrocycle relative to the plane due to the steric effect of substituents;

– stabilization of both LUMO and HOMO due to the electron-withdrawing central phosphorus atom in a high oxidation state.

The largest bathochromic shift of the *Q* band was achieved only when functional groups containing another representative of chalcogenides, Se.[43]

Y. Zorlu *et al.* showed the correlation between the distortion of phthalocyanine macrocycle by bulky substituents and the position of the *Q* band maximum. Two complexes **62a** and **62b** with alkylthio groups in nonperipheral positions were obtained. The presence of bulky *tert*-butyl groups resulted in hypsochromic shift of *Q* band maximum for complex **62b** in comparison with hexyl-substituted compound **62a**.

Table 9.



Compound	R_1	R_2	R_3	R_4	M	*Q* band	Reference
14a	PhS	H	H	H	TiO	747^b	[35]
14c	H	PhS	H	H	TiO	714^b	[35]
14b	PhCH$_2$S	H	H	H	TiO	746^b	[35]
14d	H	PhCH$_2$S	H	H	TiO	714^b	[35]
19b	$C_5H_{11}S$	H	H	$C_5H_{11}S$	Mn(OAc)	893^b	[64]
19c	$C_5H_{11}S$	H	H	$C_5H_{11}S$	TiO	808^b	[64]
19a	$C_5H_{11}S$	H	H	$C_5H_{11}S$	VO	850^b	[63]
21a	H	$C_6H_{13}S$	$C_6H_{13}S$	H	TiO	736^b	[39]
61a	PhS	H	H	PhS	P(OMe)$_2^a$	1018^c	[43]
61b	PhSe	H	H	PhSe	P(OMe)$_2^a$	1033^c	[43]
62a	$C_6H_{13}S$	H	H	$C_6H_{13}S$	HH	810^c	[104]
62b	tBuS	H	H	tBuS	HH	755^c	[104]

^{a} – the complex with a positive charge, counterion – $[PF_6]^-$.
^{b} – CH_2Cl_2 used as a solvent.
^{c} – $CHCl_3$ used as a solvent.

7.3. Gas sensors

Dinaphthalocyanine complexes of a sandwich structure can be easily and reversibly oxidized due to the presence of an extended π-system, as well as a π-radical nature. This peculiarity allowed Y. Chen *et al.* to create a NO_2 sensor based on them (Figure 4).[105]

It was noted that the synthesis of the complexes was carried out by analogy with the method.[87] However, the detailed synthesis and yields of the target compounds are not given. Thin films were prepared by the Langmuir-Blodgett method and then treated with nitric oxide vapor. The process was monitored spectrophotometrically. A reversible change like the spectrum under the action of an oxidizing agent (NO_2) is shown.

For tetranuclear complex **56**, the sensitivity to volatile organic compounds (chloroform, acetone, CCl_4, methanol, ethanol) was studied. The current is shown to be increased by several times during the interaction of a thin film of phthalocyanine and vapors of the analyzed compounds.[89]

7.4. Photovoltaic cells

M. Mayukh *et al.*[99] described photovoltaic cells based on titanium phthalocyaninates substituted with alkylthio groups at the periphery of the macrocycle (complexes **21a**, **21d**, **21e**, Table 6) - an electron donor with *p*-type semiconducting properties and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate - an electron acceptor with *n*-type semiconductor properties. Phenyl-C_{61}-butyric acid methyl ester was used as an additional electron acceptor. The function of the electrodes was performed by a layer of In_2O_3: Sn (anode) and Al (cathode). LiF was used as an additive to improve ion transport.

Due to the central titanium ion and peripheral groups containing sulfur in the film obtained by the spin-coating method, these complexes absorb at a wavelength of about 900 nm. The authors[99] succeeded in obtaining a material with a bulk heterojunction with a sufficiently high (0.71 V) value of the open circuit potential (Figure 5).

Conclusions

This review considers the main methods for the synthesis of phthalocyanines and 2,3-naphthalocyanines bearing sulfur-containing functional groups. Both approaches based on substituted nitriles and methods for modifying functional groups in the formed phthalocyanine macrocycle are presented. Compounds of both planar and sandwich structures are considered.

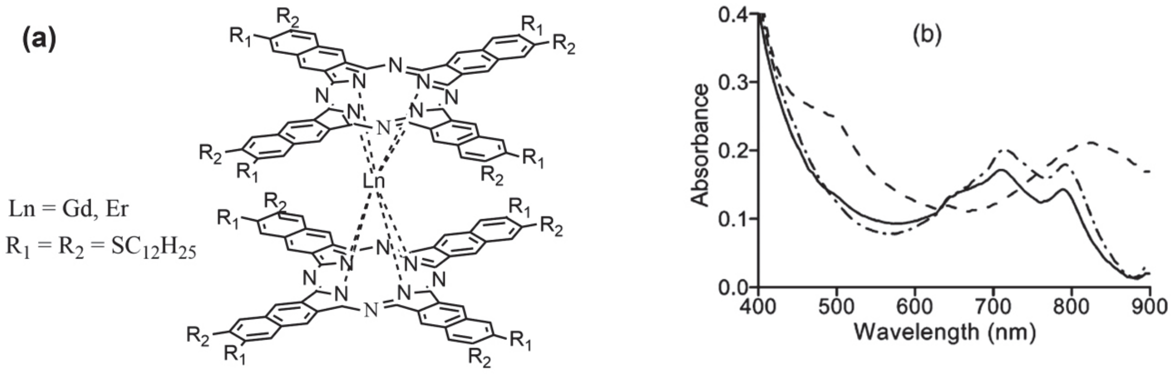


Figure 4. Structures of the Ln complexes (a) and their UV-Vis spectra (b): dash-dotted line - thin film of dinaphthalocyanine Gd; dotted line - after NO_2 oxidation; solid line - 2 days after oxidation (adopted from [105]).

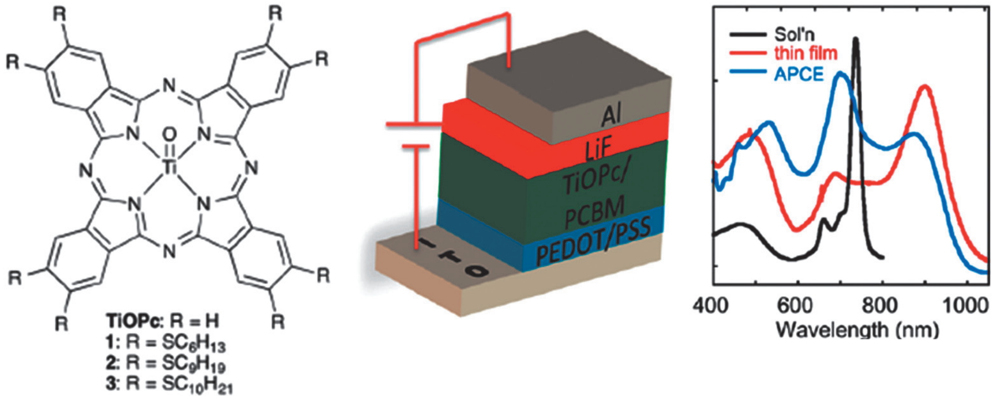


Figure 5. Titanium phthalocyaninate structure, scheme of the photovoltaic cell and absorption spectra of titanium phthalocyanine in solution (black line), thin film (red line) and absorbed photon to current efficiency (APCE) (blue line) (adopted from [99]).

According to the methods for the synthesis of phthalocyanines and 2,3-naphthalocyanines substituted with functional groups containing sulfur, the following conclusions can be drawn:

– the most accessible, in synthetic terms, are alkylthio- and arylthio-substituted compounds.

– the main disadvantage of thiol-terminated phthalocyanines is the tendency to form compounds with disulfide bonds as by-products.[73]

– the least amount of by-products and, accordingly, the ease of isolation is characteristic of symmetrically substituted complexes.

– in the case of unsymmetrically substituted phthalocyanines of the A_3B type, the yields at the stage of statistical condensation are rather low.[36]

Noteworthy are those phthalocyanines, which form coordination bonds with the surface of nanoparticles, which are promising for the creation of hybrid materials with gold nanoparticles. Their preparation is less laborious than in the case of hybrids with covalent bonds.

The introduction of functional groups containing sulfur into non-peripheral positions 3 and 6 of the phthalocyanine macrocycle promotes the bathochromic shift of the *Q* band to the near-IR region up to 1018 nm.[43]

For other applications, the most widely used compounds are those containing long-chain alkylthio groups. These compounds are readily available and have good solubility. On their basis, homogeneous thin films can be easily obtained by the Langmuir-Blodgett and spin-coating methods. This makes these compounds promising for the creation of photovoltaic cells and gas sensors.

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References

1. Chen Y., Li D., Yuan N., Gao J., Gu R., Lu G., Bouvet M. *Journal of Materials Chemistry* **2012**, 22, 22142–22149.
2. Schlettwein D., Woehrle D., Karmann E., Melville U. *Chemistry of Materials* **1994**, 6, 3–6.
3. de la Torre G., Vázquez P., Agulló-López F., Torres T. *Chemical Reviews* **2004**, *104*, 3723–3750.

4. Khoza P., Nyokong T. *Journal of Molecular Catalysis A: Chemical* **2015**, *399*, 25–32.
5. Lamch Ł., Tsirigotis-Maniecka M., Kulbacka J., Wilk K.A. *Arkivoc* **2017**, part ii, 433–445.
6. Kimani S.G., Shmigol T.A., Hammond S., Phillips J.B., Bruce J.I., MacRobert A.J., Malakhov M.V., Golding J.P. *Photochemistry and Photobiology* **2013**, *89*, 139–149.
7. Pushkarev V.E., Tomilova L.G., Nemykin V.N. *Coordination Chemistry Reviews* **2016**, *319*, 110–179.
8. Wang H., Qi D., Xie Z., Cao W., Wang K., Shang H., Jiang J. *Chemical Communications* **2013**, *49*, 889–891.
9. Wang H., Kobayashi N., Jiang J. *Chemistry – A European Journal* **2012**, *18*, 1047–1049.
10. Wang H., Wang K., Bian Y., Jiang J., Kobayashi N. *Chemical Communications* **2011**, *47*, 6879–6881.
11. Wang H., Qian K., Wang K., Bian Y., Jiang J., Gao S. *Chemical Communications* **2011**, *47*, 9624–9626.
12. Gao S., Zhao H., Huo L.H., Zhao J.G., Wu Y.Q., Xi S.Q. *Sensors and Actuators B: Chemical* **2004**, *97*, 319–323.
13. Vagin S., Hanack M. *European Journal of Organic Chemistry* **2003**, *2003*, 2661–2669.
14. Dubinina T.V., Tomilova L.G., Zefirov N.S. *Russian Chemical Reviews* **2013**, *82*, 865.
15. Tolbin A.Y., Khabashesku V.N., Tomilova L.G. *Mendeleev Communications* **2012**, *22*, 59–61.
16. Bottari G., de la Torre G., Torres T. *Accounts of Chemical Research* **2015**, *48*, 900–910.
17. Kotiaho A., Lahtinen R., Efimov A., Metsberg H.-K., Sariola E., Lehtivuori H., Tkachenko N.V., Lemmetyinen H. *The Journal of Physical Chemistry C* **2010**, *114*, 162–168.
18. Forteath S., Antunes E., Chidawanyika W., Nyokong T. *Polyhedron* **2012**, *34*, 114–120.
19. Nikitenko S.L., Spitsina N.G., Kaplunov M.G., Tomilova L.G. *Fullerenes, Nanotubes and Carbon Nanostructures* **2010**, *19*, 141–146.
20. Martinez-Diaz M.V., de la Torre G., Torres T. *Chemical Communications* **2010**, *46*, 7090–7108.
21. Zasedatelev A.V., Dubinina T.V., Krichevsky D.M., Krasovskii V.I., Gak V.Y., Pushkarev V.E., Tomilova L.G., Chistyakov A.A. *The Journal of Physical Chemistry C* **2016**, *120*, 1816–1823.
22. Hone D.C., Walker P.I., Evans-Gowing R., FitzGerald S., Beeby A., Chambrier I., Cook M.J., Russell D.A. *Langmuir* **2002**, *18*, 2985–2987.
23. Manoto S.L., Oluwole D.O., Malabi R., Maphanga C., Ombinda-Lemboumba S., Nyokong T., Mthunzi-Kufa P. *Optical Methods for Tumor Treatment and Detection: Mechanisms and Techniques in Photodynamic Therapy XXVI* **2017**, 1004716.
24. Teixeira R., Paulo P.M.R., Viana A.S., Costa S.M.B. *The Journal of Physical Chemistry C* **2011**, *115*, 24674–24680.
25. Kuzmina E.A., Dubinina T.V., Zasedatelev A.V., Baranikov A.V., Makedonskaya M.I., Egorova T.B., Tomilova L.G. *Polyhedron* **2017**, *135*, 41–48.
26. Beloglazkina E.K., Majouga A.G., Romashkina R.B., Zyk N.V., Zefirov N.S. *Russian Chemical Reviews* **2012**, *81*, 65.
27. Tombe S., Chidawanyika W., Antunes E., Priniotakis G., Westbroek P., Nyokong T. *Journal of Photochemistry and Photobiology A: Chemistry* **2012**, *240*, 50–58.
28. Daniel M.-C., Astruc D. *Chemical Reviews* **2004**, *104*, 293–346.
29. Lukyanets E.A., Nemykin V.N. *Journal of Porphyrins and Phthalocyanines* **2010**, *14*, 1–40.
30. Nemykin V.N., Luk'yanets E. A. *Arkivoc* **2010**, i, 136–208.
31. Gobo N.R.S., Brocksom T.J., Zukerman-Schpector J., de Oliveira K.T. *European Journal of Organic Chemistry* **2013**, *2013*, 5028–5031.
32. Bankole O.M., Yılmaz Y., Nyokong T. *Optical Materials* **2016**, *51*, 194–202.
33. Poon K.-W., Liu W., Chan P.-K., Yang Q., Chan T.W.D., Mak T.C.W., Ng D.K.P. *The Journal of Organic Chemistry* **2001**, *66*, 1553–1559.
34. del Rey B., Keller U., Torres T., Rojo G., Agulló-López F., Nonell S., Martí C., Brasselet S., Ledoux I., Zyss J. *Journal of the American Chemical Society* **1998**, *120*, 12808–12817.
35. Tau P., Nyokong T. *Dalton Transactions* **2006**, 4482–4490.
36. Nombona N., Antunes E., Litwinski C., Nyokong T. *Dalton Transactions* **2011**, 11876–11884.
37. Gurol I., Ahsena V., Bekaroglu O. *Journal of the Chemical Society, Dalton Transactions* **1994**, 497–500.
38. Gurek A.G., Bekaroglu O. *Journal of the Chemical Society, Dalton Transactions* **1994**, 1419–1423.
39. Mayukh M., Sema C.M., Roberts J.M., McGrath D.V. *The Journal of Organic Chemistry* **2010**, *75*, 7893–7896.
40. Rey B., Martinez-Diaz M.V., Barbera J., Torres T. *Journal of Porphyrins and Phthalocyanines* **2000**, *4*, 569–573.
41. Hao Z., Wu X., Sun R., Ma C., Zhang X. *ChemPhysChem* **2012**, *13*, 267–273.
42. Kobayashi N., Ogata H., Nonaka N., Luk'yanets E.A. *Chemistry – A European Journal* **2003**, *9*, 5123–5134.
43. Kobayashi N., Furuyama T., Satoh K. *Journal of the American Chemical Society* **2011**, *133*, 19642–19645.
44. Dupont J., de Souza R.F., Suarez P.A.Z. *Chemical Reviews* **2002**, *102*, 3667–3692.
45. Lo P.-C., Cheng D.Y.Y., Ng D.K.P. *Synthesis* **2005**, *2005*, 1141–1147.
46. Wasserscheid P., Keim W. *Angewandte Chemie International Edition* **2000**, *39*, 3772–3789.
47. Al-Raqa S.Y. *Journal of Porphyrins and Phthalocyanines* **2006**, *10*, 55–62.
48. Miyaura N., Suzuki A. *Chemical Reviews* **1995**, 95, 2457–2483.
49. Dubinina T.V., Tychinsky P.I., Borisova N.E., Maklakov S.S., Sedova M.V., Kosov A.D., Tomilova L.G., Zefirov N.S. *Dyes and Pigments* **2017**, *144*, 41–47.
50. Eu S., Katoh T., Umeyama T., Matano Y., Imahori H. *Dalton Transactions* **2008**, 5476–5483.
51. Littke A.F., Fu G.C. *Angewandte Chemie International Edition* **2002**, *41*, 4176–4211.
52. Littke A.F., Dai C., Fu G.C. *Journal of the American Chemical Society* **2000**, *122*, 4020–4028.
53. Dubinina T.V., Trashin S.A., Borisova N.E., Boginskaya I.A., Tomilova L.G., Zefirov N.S. *Dyes and Pigments* **2012**, *93*, 1471–1480.
54. Katayose M., Tai S., Kamijima K., Hagiwara H., Hayashi N. *Journal of the Chemical Society, Perkin Transactions 2*, **1992**, 403–409.
55. Yeung Y.-O., Liu R. C. W., Law W.-F., Lau P.-L., Jiang J., Ng D.K.P. *Tetrahedron* **1997**, 53, 9087–9096.
56. Kitahara K., Asano T., Hamano K.-i., Tokita S., Nishi H. *Journal of Heterocyclic Chemistry* **1990**, *27*, 2219–2220.
57. Ng D.K.P., Yeung Y.-O., Chan W.K., Yu S.-C. *Tetrahedron Letters* **1997**, *38*, 6701–6704.
58. Dubinina T.V., Ivanov A.V., Borisova N.E., Trashin S.A., Gurskiy S.I., Tomilova L.G., Zefirov N.S. *Inorganica Chimica Acta* **2010**, *363*, 1869–1878.
59. Adams R., Reifschneider W., Ferretti A. In: *Organic Syntheses, Vol. 42*, John Wiley & Sons, Inc., **1962**. p. 22.
60. Atilla D., Saydan N., Durmuş M., Gürek A.G., Khan T., Rück A., Walt H., Nyokong T., Ahsen V. *Journal of Photochemistry and Photobiology A: Chemistry* **2007**, *186*, 298–307.
61. Atilla D., Gürek A.G., Basova T.V., Kiselev V.G., Hassan A., Sheludyakova L.A., Ahsen V. *Dyes and Pigments* **2011**, *88*, 280–289.

62. Basova T.V., Çamur M., Esenpınar A.A., Tuncel S., Hassan A., Alexeyev A., Banimuslem H., Durmuş M., Gürek A.G., Ahsen V. *Synthetic Metals* **2012**, *162*, 735–742.
63. Mbambisa G., Nyokong T. *Polyhedron* **2008**, 27, 2799–2804.
64. Mbambisa G., Tau P., Antunes E., Nyokong T. *Polyhedron* **2007**, 26, 5355–5364.
65. Lokesh K.S., Adriaens A. *Dyes and Pigments* **2013**, *96*, 269–277.
66. Dubinina T.V., Tychinsky P.I., Borisova N.E., Krasovskii V.I., Ivanov A.S., Savilov S.V., Maklakov S.S., Sedova M.V., Tomilova L.G. *Dyes and Pigments* **2018**, *156*, 386–394.
67. Zheng W., Wan C.-Z., Zhang J.-X., Li C.-H. and You X.-Z., *Tetrahedron Letters*, **2015**, 56, 4459–4462.
68. Bankole O.M., Osifeko O., Nyokong T. *Journal of Photochemistry and Photobiology A: Chemistry*, **2016**, *329*, 155–166.
69. Chen Z., Niu L., Cheng Y., Zhou X., Zhong C., Zhang F. *Dalton Transactions* **2011**, *40*, 393–401.
70. Gülmez A.D., Polyakov M.S., Volchek V.V., Kostakoğlu S.T., Esenpinar A.A., Basova T.V., Durmuş M., Gürek A.G., Ahsen V., Banimuslem H.A., Hassan A.K. *Sensors and Actuators B: Chemical* **2017**, *241*, 364–375.
71. Oluwole D.O., Yagodin A.V., Britton J., Martynov A.G., Gorbunova Y.G., Tsivadze A.Y., Nyokong T. *Dalton Transactions* **2017**, *46*, 16190–16198.
72. Shokurov A.V., Yagodin A.V., Martynov A.G., Gorbunova Y.G., Selektor S.L. *ECS Journal of Solid State Science and Technology* **2020**, *9*, 051006.
73. Chambrier I., Cook M.J., Russell D. A. *Synthesis* **1995**, *1995*, 1283–1286.
74. Lu G., Bai M., Li R., Zhang X., Ma C., Lo P.-C., Ng D.K.P., Jiang J. *European Journal of Inorganic Chemistry* **2006**, *2006*, 3703–3709.
75. Kandaz M., Bilgiçli A.T., Altındal A. *Synthetic Metals* **2010**, 160, 52–60.
76. Yağlıoğlu H.G., Arslan M., Abdurrahmanoğlu Ş., Ünver H., Elmali A., Bekaroğlu Ö. *Journal of Physics and Chemistry of Solids* **2008**, *69*, 161–167.
77. Ban K., Nishizawa K., Ohta K., van de Craats A.M., Warman J.M., Yamamoto I., Shirai H. *Journal of Materials Chemistry* **2001**, *11*, 321–331.
78. Gürek A.G., Basova T., Luneau D., Lebrun C., Kol’tsov E., Hassan A.K., Ahsen V. *Inorganic Chemistry* **2006**, *45*, 1667–1676.
79. Atilla D., Kilinç N., Yuksel F., Gürek A.G., Öztürk Z.Z., Ahsen V. *Synthetic Metals* **2009**, *159*, 13–21.
80. Kadish K.M., Nakanishi T., Gürek A., Ahsen V., Yilmaz I. *The Journal of Physical Chemistry B* **2001**, 105, 9817–9821.
81. Magdesieva T.V., Zhukov I.V., Tomilova L.G., Korenchenko O.V., Kalashnikova I.P., Butin K.P. *Russian Chemical Bulletin* **2001**, *50*, 396–403.
82. Jiang J., Liu W., Poon K.-W., Du D., Arnold D.P., Ng D.K.P. *European Journal of Inorganic Chemistry* **2000**, *2000*, 205–209.
83. Dubinina T.V., Piskovoi R.A., Tolbin A.Y., Pushkarev V.E., Vagin M.Y., Tomilova L.G., Zefirov N.S. *Russian Chemical Bulletin* **2008**, *57*, 1912–1919.
84. Dubinina T.V., Paramonova K.V., Trashin S.A., Borisova N.E., Tomilova L.G., Zefirov N.S. *Dalton Transactions* **2014**, *43*, 2799–2809.
85. Gorbunova Y.G., Lapkina L.A., Martynov A.G., Biryukova I.V., Tsivadze A.Y. *Russian Journal of Coordination Chemistry* **2004**, *30*, 245–251.86. Alpugan S., Isci U., Albrieux F., Hirel C., Gurek A.G., Bretonniere Y., Ahsen V., Dumoulin F. *Chemical Communications* **2014**, *50*, 7466–7468.
87. Nyokong T., Furuya F., Kobayashi N., Du D., Liu W., Jiang J. *Inorganic Chemistry* **2000**, *39*, 128–135.
88. Abdurrahmanoğlu Ş., Altındal A., Bulut M., Bekaroğlu Ö. *Polyhedron* **2006**, *25*, 3639–3646.
89. Ceyhan T., Altındal A., Erbil M.K., Bekaroğlu Ö. *Polyhedron* **2006**, *25*, 737–746.
90. Abdurrahmanoglu S., Altindal A., Riza Ozkaya A., Bulut M., Bekaroglu O. *Chemical Communications* **2004**, 2096–2097.
91. Yilmaz I., Burkut Koçak M. *Polyhedron* **2004**, *23*, 1279–1285.
92. Gürek A.G., Bekaroglu Ö. *Journal of Porphyrins and Phthalocyanines* **1997**, *1*, 67–76.
93. Ceyhan T., Altındal A., Özkaya A.R., Erbil M.K., Bekaroğlu Ö. *Polyhedron* **2007**, *26*, 73–84.
94. Ceyhan T., Korkmaz M., Erbil M.K., Bekaroğlu Ö. *Journal of Porphyrins and Phthalocyanines* **2005**, *9*, 423–429.
95. Şen P., Dumludağ F., Salih B., Özkaya A.R., Bekaroğlu Ö. *Synthetic Metals* **2011**, *161*, 1245–1254.
96. Noda Y., Noro S.-i., Akutagawa T., Nakamura T. *Scientific Reports* **2014**, *4*, 3758.
97. Nwaji N., Oluwole D.O., Mack J., Louzada M., Khene S., Britton J., Nyokong T. *Dyes and Pigments* **2017**, *140*, 417–430.
98. Bankole O.M., Nyokong T. *Journal of Photochemistry and Photobiology A: Chemistry* **2016**, *319*, 8–17.
99. Mayukh M., Macech M.R., Placencia D., Cao Y., Armstrong N.R., McGrath D.V. *ACS Applied Materials & Interfaces* **2015**, *7*, 23912–23919.
100. Quartarolo A.D., Pérusse D., Dumoulin F., Russo N., Sicilia E. *Journal of Porphyrins and Phthalocyanines* **2013**, *17*, 980–988.
101. Yao Y., Chen W., Lu S., Zhao B. *Dyes and Pigments* **2007**, *73*, 217–223.
102. Ikeue T., Sonoda M., Kurahashi S., Tachibana H., Teraoka D., Sugimori T., Kasuga K., Handa M. *Inorganic Chemistry Communications* **2010**, *13*, 1170–1172.
103. Yang J., Van De Mark M.R. *Tetrahedron Letters* **1993**, *34*, 5223–5226.
104. Zorlu Y., Kumru U., İşci Ü., Divrik B., Jeanneau E., Albrieux F., Dede Y., Ahsen V., Dumoulin F. *Chemical Communications* **2015**, *51*, 6580–6583.
105. Chen Y., Liu H.-G., Pan N., Jiang J. *Thin Solid Films* **2004**, *460*, 279–285.

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