Selective synthesis and spectroscopic properties of alkyl-substituted lanthanide(III) mono-, di-, and triphthalocyanines*

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Methods for the selective synthesis of mono- (^{R}PcLnOAc), di- ($^{R}Pc_2Ln$), and triphthalocyanines ($^{R}Pc_3Ln_2$) of rare-earth metals (Ln = Lu, Er, Eu) from symmetrically substituted 2,3,9,10,16,17,23,24-octaalkylphthalocyanines $^{R}PcH_2$ (R = Et, Bu) were developed. The synthesized complexes were characterized by NMR spectroscopy, mass spectrometry, and electronic absorption spectra. The conditions for ^{1}H NMR spectra recording were optimized. Regularities in changing the spectral properties of the synthesized compounds, depending on the lanthanide nature and the planarity of metal phthalocyanine complexes, were found.

Key words: phthalocyanines, rare-earth metals, selective methods of synthesis, ^{1}H NMR spectra, electronic absorption spectra.

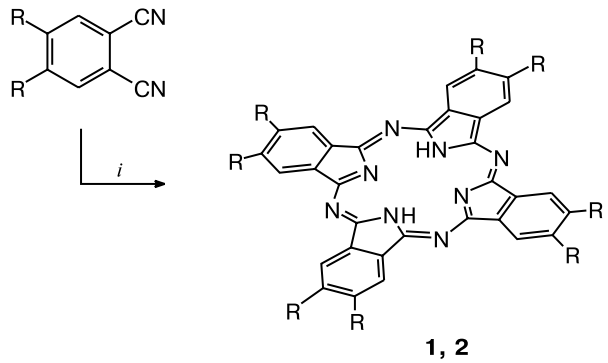
Rare-earth metals (REM) have high coordination numbers and, hence, can form complexes of different compositions with phthalocyanines.[1—3] The unique physicochemical properties of these complexes provide wide potentialities for their use in different fields of science and technology.[4—8] Accessibility of the phthalocyanine complexes is a determining factor for practical use. However, their synthesis often produces a mixture of compounds, which impedes isolation and decreases the yields of target products. Therefore, the development of selective methods for the synthesis of lanthanide mono-, di-, and triphthalocyanines and studies of their structure and properties are of great significance.

In this work, we studied conditions for the directed synthesis of several symmetric alkyl-substituted mono-, di-, and triphthalocyanine complexes of REM and determined their spectral characteristics. The use of free phthalocyanines as the starting compounds was shown to be more efficient than the use of the corresponding phthalodinitriles,[9] because the reaction time is shortened substantially, isolation and purification become simpler, and, in most cases, the yield of target products increases.

Results and Discussion

Ethyl- and butyl-substituted phthalocyanines **1** and **2** were used as phthalocyanine ligands. Earlier, these compounds were obtained in 21 and 38% yields, respectively, by the reflux of diethyldiiminoisoindoline in *N*,*N*-dimethylaminoethanol[10] or dibutylphthalodinitrile in *n*-pentanol in the presence of metallic sodium.[11] It turned out that the reflux of solutions of 4,5-diethyl- or 4,5-dibutylphthalodinitriles in isoamyl alcohol in the presence of lithium methoxide affords phthalocyanines **1** and **2** in 62—64% yields (Scheme 1).

Scheme 1



R = Et (**1**), Bu (**2**)

Reagents and conditions: *i*. $C_5H_{11}{}^{i}OH$, MeOLi, 130 °C, 5—6 h.

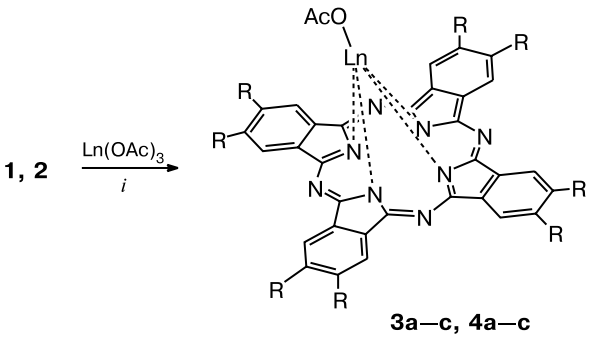
Monophthalocyanine complexes **3** and **4** were synthesized under the conditions similar to the preparation of the tetracrown-substituted lanthanide complexes.[12] The

* Dedicated to Academician A. L. Buchachenko on the occasion of his 70th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 2024—2030, September, 2005.

reactions were carried out under argon for 3—4 h by the reflux of stoichiometric amounts of compounds **1** or **2** and the corresponding REM acetates in *o*-dichlorobenzene (*o*-DCB) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 2). It seems that the role of DBU in this reaction is the formation of the phthalocyanine dianion Pc^{2-}, which reacts with lanthanide acetate. Under these conditions, Lu, Er, and Eu monophthalocyanines were obtained in high yields (Table 1), which are virtually independent of the lanthanide nature.

Scheme 2



R = Et (**3**), Bu (**4**); Ln = Lu (**a**), Er (**b**), Eu (**c**)

Reagents and conditions: *i*. *o*-DCB, DBU, 180 °C, 3—4 h (method *A*).

We have previously[9] described the synthesis of lutetium and europium ethyl- and butyl-substituted diphthalocyanines using the corresponding phthalodinitriles as the starting compounds. However, this method is accompanied by considerable tarring, and the target diphthalocyanines are obtained in a yield of ≤53%. In addition, the first step of the reaction is the formation of a monophthalocyanine complex,[13,14] whose subsequent transformations are complicated by several factors. Therefore, the diphthalocyanines prepared from phthalodinitriles often contain admixtures of planar complexes and free phthalocyanines, which impede their isolation and purification.

The method for the synthesis of gadolinium and ytterbium diphthalocyanine complexes by the reaction of a pre-formed phthalocyanine ligand, in particular, tetracrown-substituted phthalocyanine, with REM acetates in boiling 1-chloronaphthalene in the presence of DBU was reported.[15] However, the yield of the corresponding diphthalocyanines was only 15—20%, and comparable amounts of the corresponding triphthalocyanine complexes were formed during the reaction.

Nevertheless, we applied an approach based on the use of free phthalocyanine ligands **1** or **2** for the synthesis of the corresponding diphthalocyanines. We found that

Table 1. Yields of phthalocyanine complexes **3—8**

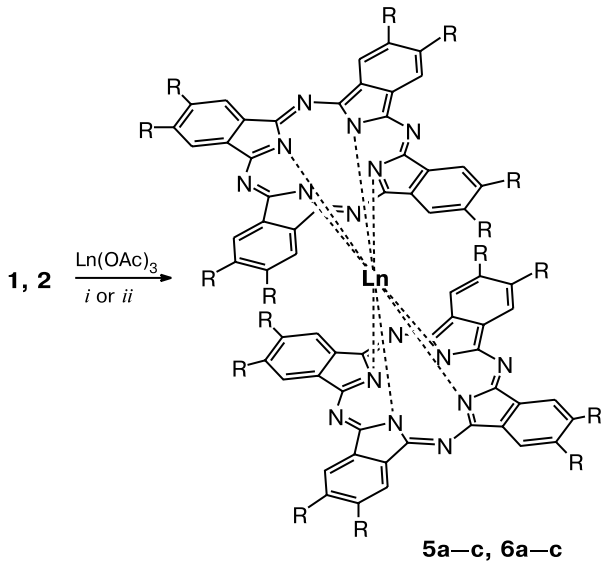
Compound	R	Ln	Method of synthesis*	Yield (%)
3a	Et	Lu	*A*	89
3b	Et	Er	*A*	96
3c	Et	Eu	*A*	96
4a	Bu	Lu	*A*	96
4b	Bu	Er	*A*	95
4c	Bu	Eu	*A*	97
5a	Et	Lu	*B*	14
			C	90
5b	Et	Er	*B*	23
			C	89
5c	Et	Eu	*B*	95
6a	Bu	Lu	*B*	10
			C	85
6b	Bu	Er	*B*	20
			C	90
6c	Bu	Eu	*B*	87
7a	Et	Lu	*D*	53
			E	89
7b	Et	Er	*D*	61
			E	92
7c	Et	Eu	*D*	92
8a	Bu	Lu	*D*	49
			E	93
8b	Bu	Er	*D*	46
			E	88
8c	Bu	Eu	*D*	94

* The conditions for the syntheses are given in Schemes 2—4.

triphthalocyanine formation can be prevented when the reaction is conducted in boiling *n*-hexanol in the presence of DBU (Scheme 3, method *B*). In the case of europium, complexes **5c** and **6c** were isolated in 95 and 87% yields, respectively (see Table 1). However, under the same conditions, lutetium and erbium produce the diphthalocyanine complexes in substantially lower yields: the main reaction products are monophthalocyanines in this case. These differences can be caused by steric factors, which appear upon the addition of the second phthalocyanine ligand due to smaller ion radii of Er and Lu compared to that of Eu.

Taking into account this fact, we found conditions for the synthesis of compounds **5a**,**b** and **6a,b** that enable one to exclude the use of additives of strong bases (see Scheme 3, method *C*). It turned out that the reaction can be carried out at a higher temperature (~230 °C) by heating a mixture of phthalocyanine **1** or **2** and lutetium or erbium acetates (in a molar ratio of 2 : 1) in hexadecan-1-ol for 1 h. This method is similar, in essence, to that of the high-temperature template synthesis in a melt of phthalodinitrile.[16—22] However, the use of the pre-formed phthalocyanine ligands makes it possible to exclude tarring, which is characteristic of template reactions. In this

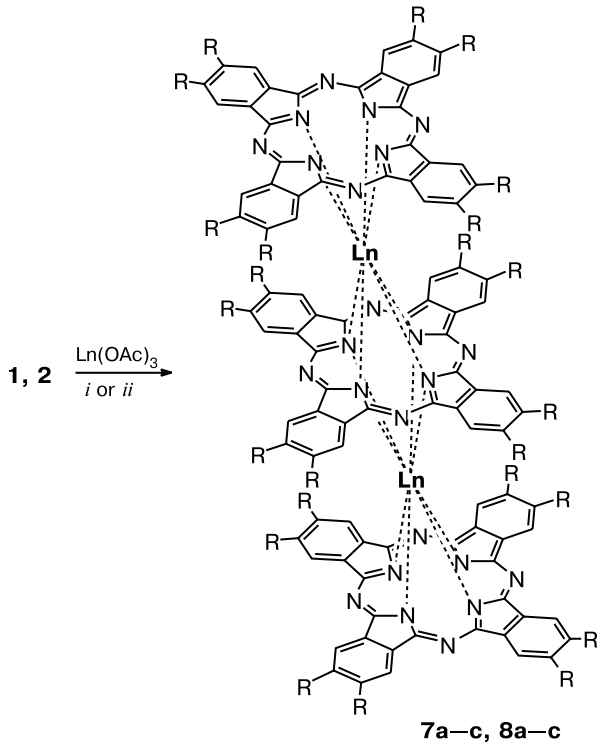
Scheme 3



R = Et (**5**), Bu (**6**); Ln = Lu (**a**), Er (**b**), Eu (**c**)

Reagents and conditions: *i*. $C_6H_{13}{}^nOH$, DBU, 160 °C, 2—3 h (method *B*); *ii*. $C_{16}H_{33}{}^nOH$, 230 °C, 1 h (method *C*).

Scheme 4



R = Et (**7**), Bu (**8**); Ln = Lu (**a**), Er (**b**), Eu (**c**)

Reagents and conditions: *i*. $C_8H_{17}{}^nOH$, 190 °C, 1—1.5 h (method *D*); $C_{16}H_{33}{}^nOH$, 280 °C, 1 h (method *E*).

case, the yields of diphthalocyanines **5a,b** and **6a,b** are 85—90% (see Table 1).

Triple-decked phthalocyanines **7** and **8** were primarily synthesized according to procedures that have been used earlier[2,23] for the preparation of the complexes containing butoxy groups in the phthalocyanine macrocycle. The reaction was carried out by the reflux of a mixture of phthalocyanine **1** or **2** with REM acetates (in a molar ratio of 1 : 1) in *n*-octanol (Scheme 4, method *D*). Optimization of this method showed that a threefold decrease in the solvent volume, as compared to the amount described,[23] results in an almost fourfold shortening of the reaction time, while this provides 92 and 87% yields of triphthalocyanines **7c** and **8c**, respectively, in the case of europium acetate (see Table 1). For the lutetium and erbium salts, the yields of the triple-deckers decrease along with the formation of considerable amounts of mono- and diphthalocyanines, which is caused, most likely, by an insufficiently rigid temperature regime of the reaction (~190 °C). In fact, the heating of a mixture of phthalocyanine **1** or **2** with lutetium and erbium acetates (in a molar ratio of 1 : 1) in hexadecan-1-ol at 280 °C for 1 h produces triphthalocyanines **7a,b** or **8a,b** in 88—93% yield (see method *E* in Scheme 4 and Table 1).

The structures of all synthesized complexes were studied by ^{1}H NMR spectroscopy and mass spectrometry. No satisfactory NMR spectra were obtained for monophthalocyanine complexes **3** and **4** using $CDCl_3$ as the solvent. The signals of aliphatic protons are considerably broadened, and the absorption in the aromatic region is virtually absent, which can be associated with aggregation of macromolecules in a low-polarity solvent.[12] However, the spectra with well resolved signals from both aromatic and aliphatic protons are obtained when more polar DMSO-d_6 (10—30 vol.%) is added to $CDCl_3$ (Table 2). It is difficult to record NMR spectra in neat DMSO-d_6 because of a low solubility of the samples under study in this solvent. In the case of erbium (**3b** and **4b**) and europium phthalocyanines (**3c** and **4c**), all signals exhibit a downfield shift compared to lutetium complexes **3a** and **4a**, which is caused by the paramagnetic nature of these metal ions.[24] A similar regularity obeys for di- and triphthalocyanine complexes **5—8**.

A specific feature of diphthalocyanines is a radical fragment $Pc^{\bullet-}$ in their molecules, which prevents to obtain satisfactory NMR spectra in usual solvents. Therefore, the ^{1}H NMR spectra of compounds **5** and **6** were recorded in a $CDCl_3$—$(CD_3)_2SO$ (3 : 1, vol/vol) mixture in the presence of 1—2 vol.% hydrazine hydrate, which allows the reduction of the $Pc^{\bullet-}$ fragment to the corresponding dianion[9] to be carried out (see Table 2).

A characteristic feature of the ^{1}H NMR spectra of the triple-decked phthalocyanines is two sets of similar sig-

Table 2. ^{1}H NMR spectra of compounds **3—8**

Compound	δ[a]				
	H_{Ar}	α-CH_2	β-CH_2	γ-CH_2	Me[b]
3a	9.20 (8 H)	3.20 (16 H)			1.65 (24 H)
3b	23.07 (8 H)	8.86 (8 H); 8.10 (8 H)			6.33 (24 H)
3c	9.90 (8 H)	3.55 (16 H)			1.90 (24 H)
4a	9.20 (8 H)	3.15 (16 H)	1.95 (16 H)	1.65 (16 H)	1.10 (24 H)
4b	23.14 (8 H)	8.71 (8 H); 8.30 (8 H)	7.12 (8 H); 6.92 (8 H)	6.51 (16 H)	5.31 (24 H)
4c	9.90 (8 H)	3.55 (16 H)	2.30 (16 H)	1.93 (16 H)	1.32 (24 H)
5a[c]	8.65 (16 H)	3.31 (32 H)			1.75 (48 H)
5b	36.79 (16 H)	16.68 (16 H); 15.03 (16 H)			11.44 (48 H)
5c[c]	10.91 (16 H)	4.31 (32 H)			2.57 (48 H)
6a[c]	8.61 (16 H)	3.28 (32 H)	2.15 (32 H)	1.79 (32 H)	1.26 (48 H)
6b	38.60 (16 H)	15.73 (16 H); 14.71 (16 H)	13.16 (16 H); 12.88 (16 H)	9.90 (16 H); 9.73 (16 H)	6.76 (48 H)
6c[c]	10.94 (16 H)	4.27 (32 H)	3.09 (32 H)	2.57 (32 H)	1.77 (48 H)
7a	8.24 (16 H); 8.68 (8 H)	3.23 (32 H); 3.81 (16 H)			1.61 (48 H); 2.23 (24 H)
7b	21.35 (16 H); 44.29 (8 H)	10.91 (16 H); 9.28 (16 H); 17.69 (16 H)			7.33 (48 H); 14.83 (24 H)
7c	9.47 (16 H); 12.72 (8 H)	4.15 (32 H); 4.87 (16 H)			2.35 (48 H); 3.66 (24 H)
8a	8.08 (16 H); 8.61 (8 H)	3.12 (32 H); 3.69 (16 H)	1.96 (32 H); 2.61 (16 H)	1.76 (32 H); 2.29 (16 H)	1.24 (48 H); 1.60 (24 H)
8b	21.61 (16 H); 44.39 (8 H)	10.82 (16 H); 9.64 (16 H); 18.13 (16 H)	8.33 (16 H); 7.92 (16 H); 15.80 (16 H)	7.17 (16 H); 6.99 (16 H); 12.39 (16 H)	5.42 (48 H); 7.72 (24 H)
8c	9.52 (16 H); 12.72 (8 H)	4.02[d]; 4.85 (16 H)	2.71 (32 H); 4.09[d]	2.45 (32 H); 3.47 (16 H)	1.78 (48 H); 2.28 (24 H)

[a] The spectra of compounds **3** and **4** were recorded in a $CDCl_3$—$(CD_3)_2SO$ (3 : 1, vol/vol) mixture; those of compounds **5** and **6** were recorded in a $CDCl_3$—$(CD_3)_2SO$ (3 : 1, vol/vol) mixture with an additive of 1—2 vol.% $N_2H_4 \cdot H_2O$; the spectra of compounds **7** and **8** were obtained in $CDCl_3$.
[b] Triplet ($J \approx 7.3$ Hz) for the compounds containing Lu (**a**) and Eu (**c**); multiplet ($\Delta_{1/2} = 20$—28 Hz) for the Er-containing phthalocyanines (**b**).
[c] See Ref. 9.
[d] Overlapping signals (48 H).

nals with a ratio of integral intensities of 1 : 2 (Fig. 1), which is related to a stronger deshielding of protons of the internal ligand compared to the two external ligands. The resonance signals of protons of the internal ligands of triphthalocyanines **7** and **8** undergo a downfield shift compared to the signals of the corresponding mono- and diphthalocyanines (see Table 2), which indicates the maximum deshielding of these protons in the series of compounds under study. The signals of protons of the alkyl substituents of erbium phthalocyanines appear as broad signals ($\Delta_{1/2}$ = 20—60 Hz) in which spin-spin coupling constants cannot be determined. The spectra contain a double set of signals of the methylenic protons, which is most pronounced for the CH_2 fragments adjacent to the macrocycle. This effect can be caused by either geminal nonequivalence of the methylenic protons due to a low mobility of the alkyl substituents, or nonequivalence of the methylene fragments themselves because of a turn of the phthalocyanine rings.

The synthesized complexes were studied by MALDI-TOF mass spectrometry (see Table 3, Fig. 2). The spectra of di- and triphthalocyanines **5—8** contain only molecular ion peaks $[M]^+$. In the case of monophthalocyanines **3** and **4**, the most intense are the signals caused by counterion elimination under the action of laser ionization. These spectra also exhibit the low-intensity peaks of the di- and triphthalocyanine ions, indicating that ion-molecular reactions occur during ionization. The data of MALDI-TOF and electronic absorption spectra for diphthalocyanines **5a,c** and **6a,c** coincide with our

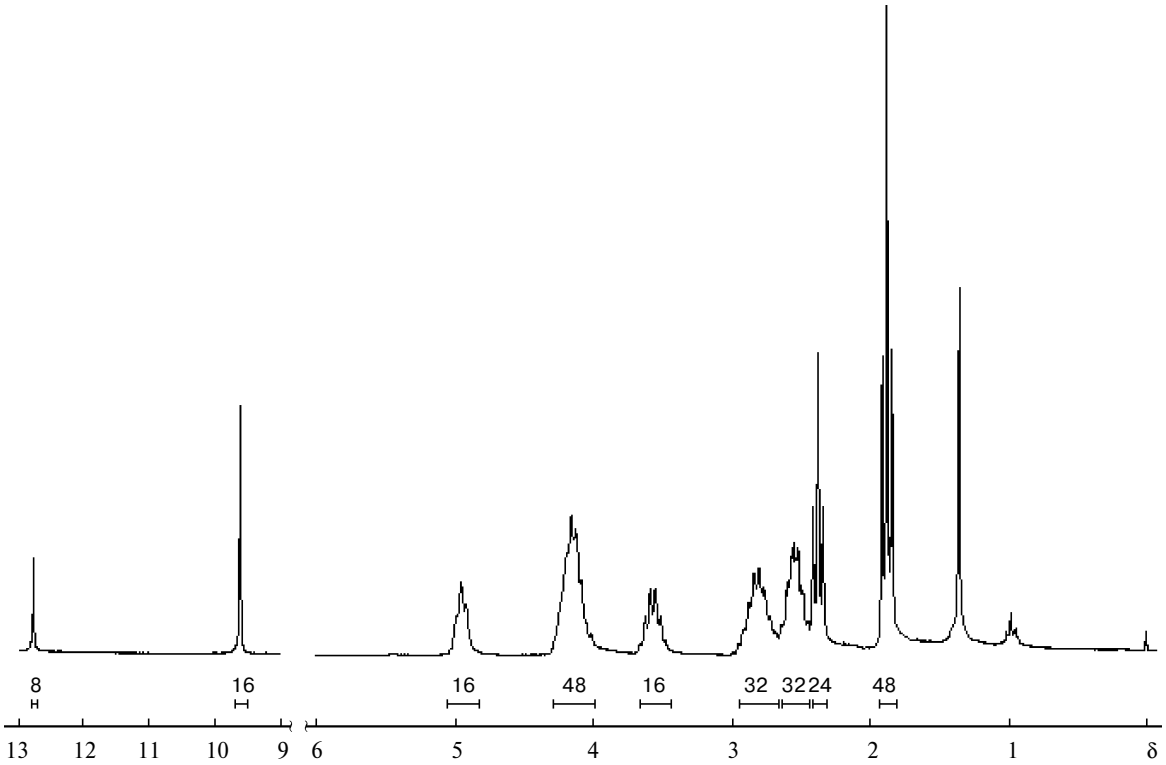


Fig. 1. ^{1}H NMR spectrum of europium triphthalocyanine **8c** ($CDCl_3$).

earlier results[9] and, hence, are not considered in the present work.

Each type of complexes **3—8** is characterized by a specific shape of electronic absorption spectra (see Table 3), whose common feature is the bathochromic shift of the Q band on going from the ethyl-substituted to butyl-substituted phthalocyanines. The REM nature also affects both the character and position of the Q band. A specific feature of monophthalocyanines **3** and **4** is the absence of Q band splitting, which is typical of free phthalocyanines **1** and **2**. No Q band splitting is related to an increase in the symmetry from D_{2h} to D_{4h}. In the case of the monophthalocyanines, the position of the Q band is independent of the lanthanide nature. The absorption spectra of diphthalocyanines **5** and **6** exhibit the characteristic absorption band at 470—490 nm that corresponds to the $Pc^{\bullet -}$ radical fragment. The Q band undergoes a hypsochromic shift on going from europium to lutetium.

The band at 490 nm is not observed in the absorption spectra of triple-deckers **7** and **8** because of electron equivalence of the three ligands (Pc^{2-}). However, the Q band is split into the blue and red components due to the exciton π—π-interaction of orbitals of the external and internal macrocycles.[24] In the case of complexes **7a** (Fig. 3) and **8a**, this splitting is more pronounced, because the smallest (in the series under study) ion radius of lutetium induces the maximum overlap of the π-orbitals of the ligands. As in the case of the diphthalocyanines, the Q band undergoes a hypsochromic shift from the beginning to the end of the lanthanide series (see Table 3). Butyl-substituted phthalocyanines **8**, compared to ethyl-substituted phthalocyanines **7**, manifest an additional absorption at 570—600 nm, which is observed, for example, for europium complexes **7c** and **8c** (see Fig. 3). This fact is related, most likely, to an increase in distortion of the phthalocyanine ring affected by bulky substituents. However, this effect needs additional studies.

Experimental

^{1}H NMR spectra were obtained on a Bruker AM-300 instrument (300.13 MHz) using $CDCl_3$, $CDCl_3$—$(CD_3)_2SO$ (3 : 1, vol/vol), and $CDCl_3$—$(CD_3)_2SO$ as solvents with an additive of 1—2 vol.% $N_2H_4 \cdot H_2O$. Chemical shifts are presented in the δ scale relative to Me_4Si. Mass spectra of the phthalocyanines were recorded on an Autoflex II instrument (MALDI-TOF) using 3,5-dihydroxybenzoic acid as the matrix. Electronic absorption spectra were obtained on a Helios-α spectrophotometer in 0.5- and 1.0-cm cells, using $CHCl_3$ and *o*-dichlorobenzene as solvents. The reaction mixtures were analyzed and purity of the isolated compounds was monitored using TLC on plates with silica gel 60 F_{254} and aluminium oxide 60 F_{254} (Merck). Column chromatography was carried out by gel filtration on the polymeric support Bio-Beads S-X1 using THF as the eluent. The starting 4,5-diethyl- and 4,5-dibutylphthalodinitriles were synthesized according to a previously described procedure.[9] Solvents were purified according to standard procedures imme-

Table 3. MALDI-TOF mass spectra and the electronic absorption spectra of phthalocyanines **1** and **2** and complexes **3—8**

Compound	Molecular formula	Mass spectrum, m/z[a] $[M]^+$	λ_{max}/nm (in $CHCl_3$)
1	$C_{48}H_{50}N_8$	738	347, 611, 644, 673, 708[b]
2	$C_{64}H_{82}N_8$	962	348, 613, 645, 674, 709[b]
3a	$C_{50}H_{51}N_8OLu$	911[c], 1065[d]	352, 620, 688
3b	$C_{50}H_{51}N_8O_2Er$	902, 904[c], 1054, 1058[d]	353, 618, 687
3c	$C_{50}H_{51}N_8O_2Eu$	889[c]	353, 621, 688
4a	$C_{66}H_{83}N_8O_2Lu$	1135[c], 1289[d]	353, 621, 690
4b	$C_{66}H_{83}N_8O_2Er$	1127, 1128[c] 1279, 1282[d]	353, 622, 691
4c	$C_{66}H_{83}N_8O_2Eu$	1113[c]	354, 624, 692
5b	$C_{96}H_{96}N_{16}Er$	1638, 1640	327, 352, 480, 611, 678
6b	$C_{128}H_{160}N_{16}Er$	2086, 2088	329, 353, 481, 612, 680
7a	$C_{144}H_{144}N_{24}Lu_2$	2558, 2559	347, 644, 727
7b	$C_{144}H_{144}N_{24}Er_2$	2540, 2544	345, 645, 705
7c	$C_{144}H_{144}N_{24}Eu_2$	2514	346, 657
8a	$C_{192}H_{240}N_{24}Lu_2$	3230, 3232	348, 667, 726 sh
8b	$C_{192}H_{240}N_{24}Er_2$	3212, 3216	347, 667
8c	$C_{192}H_{240}N_{24}Eu_2$	3186	347, 590, 670

[a] The values corresponding to the most abundant isotope (^{153}Eu, ^{166}Er, ^{175}Lu) and the most intense peak in the spectrum are presented.
[b] The electronic absorption spectra were obtained in *o*-dichlorobenzene.
[c] Fragment $[M - OAc]^+$.
[d] Fragment $[M - OAc + HY]^+$, where HY is a matrix molecule (3,5-dihydroxybenzoic acid).

diately before use. Diazabicycloundecene (DBU, Aldrich) was used without additional purification.

The yields and spectral data for compounds **3—8** are given in Tables 1—3.

2,3,9,10,16,17,23,24-Octaalkylphthalocyanines (1, 2) (general procedure). A mixture of 4,5-diethyl- or 4,5-dibutylphthalodinitrile (4 mmol) and MeOLi (0.342 g, 12 mmol) was refluxed in isoamyl alcohol (10 mL) until the starting phthalodinitrile disappeared completely (5—6 h). The course of the reaction was monitored by TLC (SiO_2, C_6H_6 as eluent). After the end of the reaction, ethyl acetate (50 mL) and acetic acid (20 mL) were added to the resulting mixture. A precipitate that formed was filtered off, washed with boiling MeOH (3×50 mL), and dried in a vacuum desiccator. Compounds **1** and **2** were obtained in 62—64% yield as dark blue powders. The spectral data are presented in Table 2.

(2,3,9,10,16,17,23,24-Octaalkylphthalocyanine)lanthanides (3, 4) (general procedure). A mixture of free phthalocyanine **1** (or **2**) (0.14 mmol), $Ln(OAc)_3 \cdot nH_2O$ (Ln = Lu, Er, Eu) (0.14 mmol), and DBU (35 mg, 0.23 mmol) was refluxed in *o*-dichlorobenzene (3 mL) (method *A*) until the starting ligand disappeared completely (3—4 h). The course of the reaction was monitored by TLC (Al_2O_3, C_6H_6 as eluent) and spectrophotometry. At the end of the reaction, $CHCl_3$ (25 mL) was added to the resulting mixture, insoluble admixtures were filtered off on a glass filter, and the solvent was distilled off. The residue was washed with boiling 80% aqueous MeOH (3×50 mL), filtered off, and dried in a vacuum desiccator.

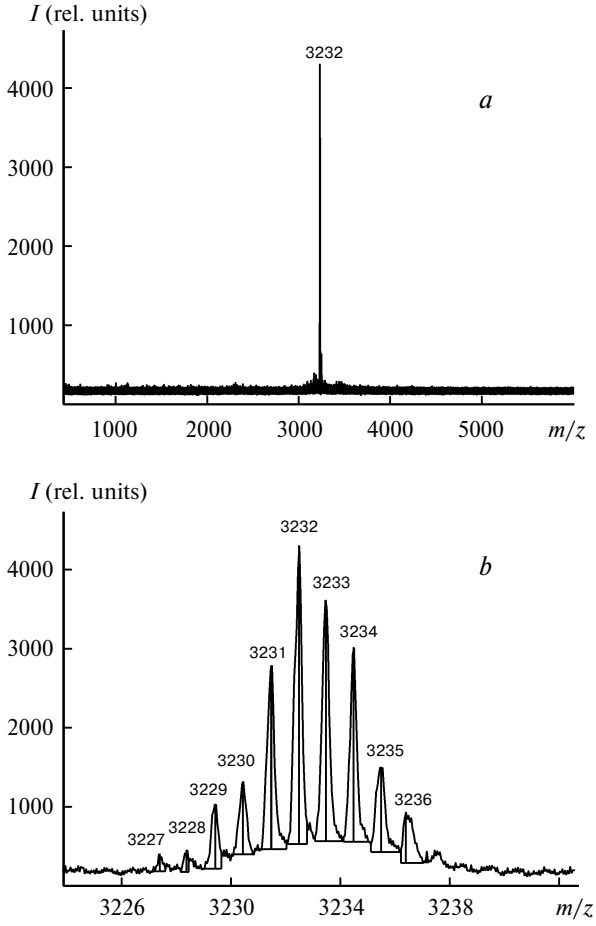


Fig. 2. MALDI-TOF mass spectrum of lutetium triphthalocyanine **8a** (*a*) and the isotope splitting of the molecular ion peak (*b*).

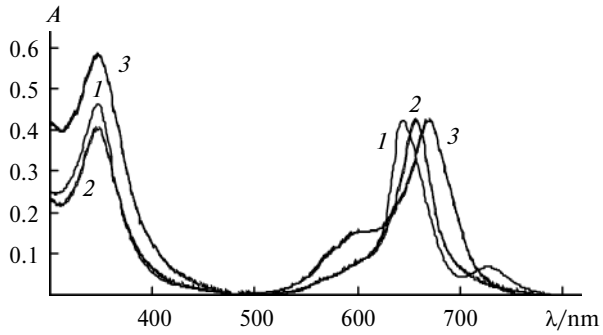


Fig. 3. Electronic absorption spectra of triple-decked phthalocyanines $^{Et}Pc_3Lu_2$ **7a** (*1*), $^{Et}Pc_3Eu_2$ **7c** (*2*), and $^{Bu}Pc_3Eu_2$ **8c** (*3*) in $CHCl_3$.

Bis(2,3,9,10,16,17,23,24-octaalkylphthalocyanine)lanthanides (5, 6) (general procedure). A mixture of free phthalocyanine **1** (or **2**) (0.14 mmol), $Ln(OAc)_3 \cdot nH_2O$ (Ln = Lu, Er, Eu) (0.07 mmol), and DBU (100 mg, 0.66 mmol) was refluxed for 2—3 h in *n*-hexanol (2 mL) (method *B*) or a mixture of free phthalocyanine **1** (or **2**) (0.14 mmol), $Ln(OAc)_3 \cdot nH_2O$ (Ln = Lu, Er) (0.07 mmol), and hexadecan-1-ol (400 mg) was heated for 1 h at 230 °C (method *C*) in an Ar flow until the starting ligand disappeared completely. The course of the reaction was monitored by TLC (Al_2O_3, C_6H_6 as eluent) and spectrophotometry. After the end of the reaction, the resulting mixture was diluted with $CHCl_3$ (25 mL) and filtered on a glass filter, and the solvent was distilled off. The residue was washed with boiling 80% aqueous MeOH (3×50 mL), filtered off, and dried in a vacuum desiccator. The resulting powder was dissolved in THF and chromatographed on a column (2.5×40 cm, Bio-Beads S-X1, THF as eluent), collecting a green-colored fraction.

Tris(2,3,9,10,16,17,23,24-octaalkylphthalocyanine)lanthanides (7, 8). A mixture of free phthalocyanine **1** (or **2**) (0.05 mmol) and $Ln(OAc)_3 \cdot nH_2O$ (Ln = Lu, Er, Eu) (0.05 mmol) was refluxed for 1—2 h in *n*-octanol (1 mL) at 196 °C (method *D*) or a mixture of free phthalocyanine **1** (or **2**) (0.05 mmol), $Ln(OAc)_3 \cdot nH_2O$ (Ln = Lu, Er) (0.05 mmol), and hexadecan-1-ol (100 mg) was heated in an Ar flow for 1 h at 280 °C (method *E*). After the end of the reaction, the resulting mixture was diluted with $CHCl_3$ (25 mL), insoluble admixtures were filtered off, and the solvent was distilled off. The residue was washed with boiling 80% aqueous MeOH (3×50 mL), filtered off, and dried in a vacuum desiccator. The resulting powder was dissolved in THF and chromatographed on a column (2.5×40 cm, Bio-Beads S-X1, THF as eluent), collecting a blue-colored fraction.

This work was financially supported by the Presidium of the Russian Academy of Sciences (Program of Fundamental Research "Directed Synthesis of Organic Compounds with Specified Properties and Creation of Related Functional Materials") and the International Scientific Technical Center (Grant No. 1526).

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Received June 6, 2005;
in revised form July 26, 2005