Russian Chemical Reviews **77** (10) 875 – 907 (2008) © 2008 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2008v077n10ABEH003879

Synthetic approaches to lanthanide complexes with tetrapyrrole type ligands

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Contents

I.	Introduction	875
II.	Synthesis of single-decker complexes	876
III.	Synthesis of homoleptic double-decker complexes	879
IV.	Synthesis of homoleptic triple-decker complexes	885
V.	Synthesis of heteroleptic and mixed-ligand double-decker complexes	888
VI.	Synthesis of heteroleptic and mixed-ligand triple-decker complexes	896

Abstract. Approaches to the synthesis of single-, double- and triple-decker complexes of lanthanides with phthalocyanines and their analogues known to date are considered. Examples of preparation of sandwich-type complexes based on other metals of the Periodic System are given. The bibliography includes 222 references.

I. Introduction

In recent decades, complexes of phthalocyanines and their analogues with various metals have been the subject of vigorous research. Owing to their structural features, in particular, multiple-circuit aromatic conjugation system, these compounds possess unique physicochemical properties. Among the chemical elements capable of coordination to phthalocyanines,[1] lanthanides are of particular interest. Having large ionic radii and high coordination numbers, lanthanides form compounds of both planar and sandwich structure with phthalocyanines and their analogues. Sandwich-type compounds are characterised by the overlap of ligand π-orbitals, which depends on the lanthanide ionic radius and, in the case of trisphthalocyanine complexes, is supplemented by a specific interaction of the f electrons of two metal ions. These effects give rise to unique characteristics of these compounds and open up new prospects for their use as materials for molecular electronics[2] and nonlinear optics.[3] The prospects for preparing heteroleptic, mixed-ligand or heterometallic sandwich complexes based on phthalocyanines[4, 5] create grounds for the development of materials with specified properties.[6, 7] Thus, studies of phthalocyanine derivatives of lanthanides are important from both the fundamental and applied standpoints. Of particular significance is the development of efficient and selective methods for the synthesis of complexes of a required structure.

The synthesis of lanthanide phthalocyanines is based on either template tetramerisation of phthalonitriles with lanthanide salts or direct reaction of the salts with free phthalocyanine ligands.[4, 5, 8 – 13] The recent progress in the latter method stimulated the search for optimal approaches to the preparation of complexes containing different tetrapyrrole-type ligands.[4, 5, 10 – 13]

The key tasks of this review are to generalise and analyse the literature and the authors' data on the synthesis of coordination compounds of lanthanides with phthalocyanines and their analogues and to elucidate the advantages and drawbacks of each method. The attention is focused on the selective methods for the preparation of various types of lanthanide phthalocyanine complexes developed to date.

Since some classes of the title compounds have been obtained quite recently, different literature sources use different terminology for their naming.[4, 5, 13] In this review, we use the most common terms and notions. In single-, double- and triple-decker complexes, the number of metal ion-coordinated macrocyclic ligands is one to three, respectively. Complexes with identical ligands are called homoleptic. Heteroleptic complexes comprise ligands of the same type but with different substituents. In addition, phthalocyanine – naphthalocyanine and porphyrin – tetraazaporphyrin complexes are usually classified into this group. Mixed-ligand complexes contain ligands of different type, for example, phthalocyanine – porphyrin or naphthalocyanine – porphyrin. Triple-decker complexes with different metals are called heteronuclear. The terms 'dimer' and 'trimer' can be used to designate both sandwich complexes and oligomers coupled by covalent bridges. The designa-

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Received 25 May 2008
Uspekhi Khimii **77** (10) 938 – 972 (2008); translated by Z P Svitanko

tions Pc, Nc and Por (sometimes P) stand for phthalocyanine, naphthalocyanine and porphyrin, respectively, while the left superscript (*e.g.*, ^{R}Pc) refers to substituents in the macrocyclic ligands.

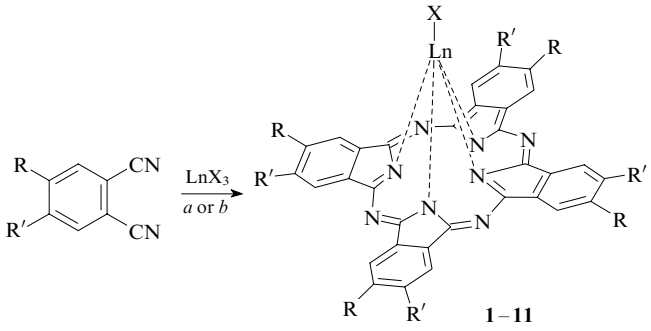
II. Synthesis of single-decker complexes

A distinctive feature of lanthanide monophthalocyanines compared to the complexes of most other elements is the unsaturation of the metal coordination sphere, which accounts for their existence as solvates $[Pc^{2-}Ln^{3+}X^{-}](Solv)_n$, where X^{-} is the counter-ion, Solv are the external ligands (solvent or base molecules). Effective solvation of lanthanide ions during the reaction, which prevents the undesirable formation of sandwich complexes, is a condition of successful synthesis of lanthanide monophthalocyanines. The methods for the synthesis of lanthanide monophthalocyanines developed to date can be classified into three groups depending on the type of reactants.

1. Template synthesis from phthalonitriles

The simplest method for the preparation of monophthalocyanine complexes is fusion of appropriate phthalonitriles with lanthanide salts in the temperature range of 200–300 °C followed by extraction of impurities with organic solvents (Scheme 1, conditions *a*).

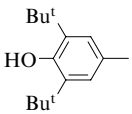
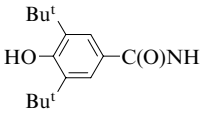
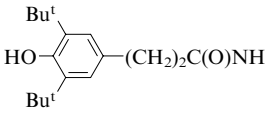
Scheme 1



(*a*) 200–300 °C, 2–3 h; (*b*) DBU, n-$C_6H_{13}OH$ or iso-$C_5H_{11}OH$, 130–160 °C, 2–7 h; DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene. (Hereinafter all Ln–N bonds are shown by dashed lines to emphasise their equivalence).

This method has been used to prepare unsubstituted complexes **1** (Table 1),[14,15] tetracrown-substituted lutetium phthalocyanine **2**[17] and tetrachloro-substituted ytterbium complex **3**.[18] The authors of the cited studies did not report the yields of the target compounds but noted that sandwich complexes were also formed along with monophthalocyanine complexes under the conditions used.[17] This suggests low selectivity of the method and requires additional chromatographic purification of the products. However, tetra-

Table 1. Template synthesis of lanthanide monophthalocyanine complexes from phthalonitriles (see Scheme 1).

Compound	R	R′	Ln	X	Conditions	Yield (%)[a]	Ref.
1	H	H	Sm, Gd, Yb, Lu, Y	AcO	*a*	–	14
			Nd, Y	AcO	*a*	–	15
			Lu	AcO	*b*[b]	5	16
2	$O(CH_2CH_2O)_4$		Lu	AcO	*a*	–	17
3	H	Cl	Yb	Cl	*a*	–	18
			Sm, Ho, Lu	Cl	*a*	74–76	19
			Y, Er	Cl	*a*	32–34	20
4	H	NO_2	Nd, Sm, Ho, Lu	Cl	*a*	66–74	19
			Y, Er	Cl	*a*	55–56	20
5	H	Br	Y, Er	Cl	*a*	29–31	20
6	Cl		Nd, Eu, Lu	AcO	*a*	53–83	21
7	H		Nd, Eu, Lu	AcO, HCO_2	*a*	77–82	22
8	H		Nd, Eu, Lu	AcO, HCO_2	*a*	70–84	22
9	H	$Ph_2CHC(O)NH$	Nd, Eu, Lu	AcO, HCO_2	*a*	70–80	22
10	H	cyclo-C_3H_7	Lu	AcO	*b*[c]	< 25	23
11	$OCMe_2O$		Sm, Eu, Tb, Dy, Yb, Lu	AcO	*b*[c]	22–75	24

[a] The dash means that the yield is not indicated; [b] n-hexanol as the solvent; [c] isopentanol as the solvent.

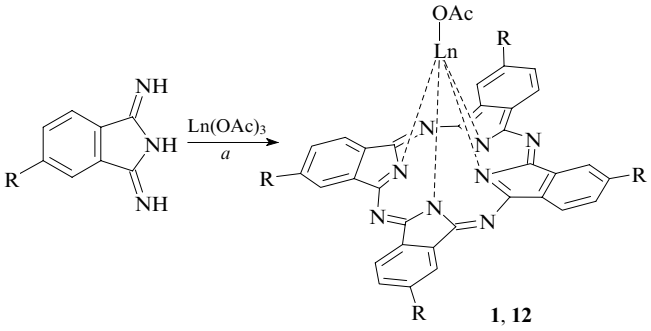
chloro- (**3**) and tetranitro-substituted (**4**) monophthalocyanine complexes were obtained by this method in up to 76% yields.[19] More recently,[20] the same research group synthesised tetrabromo-substituted metal phthalocyanines **5**, but in lower yields (see Table 1).

It was claimed[21,22] that the reactions of nitriles containing bulky substituents with lanthanide salts afford monophthalocyanine complexes **6**–**9** (yields 53%–84%). However, only UV/Vis spectra of the products were reported rather than their detailed analysis, which is clearly inadequate to draw such a conclusion.

In alcohols in the presence of bases, the template synthesis of metal monophthalocyanines can be carried out at lower temperatures, for example, at 130–160 °C (see Scheme 1, conditions *b*). This method was used to prepare unsubstituted (**1**)[16] and cyclopropyl-substituted (**10**)[23] lutetium complexes and a series of metal isopropylidenedioxyphthalocyanines **11** (yields from 5% to 75%).[24]

Isoindolines resulting from addition of ammonia to phthalonitriles can be used as the starting compounds for the synthesis of metal monophthalocyanines (Scheme 2). Unsubstituted (**1**)[25] and propoxy-substituted (**12**)[26] metal monophthalocyanines were prepared in this way in 40%–70% yields.

Scheme 2



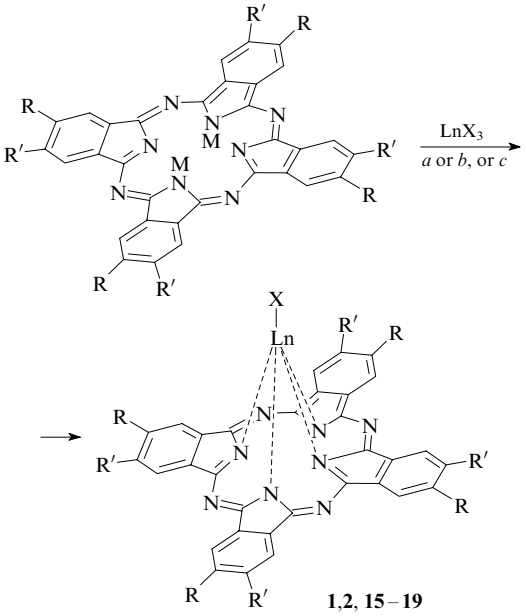
R = H (**1**), OPr^n (**12**);
(*a*) DMF or $Me_2N(CH_2)_2OH$, 135–150 °C, 5–7 h.

The template method (see Scheme 1, conditions *a*) was also used to prepare lanthanide complexes with 1,2-naphthalocyanine (1,2-NcLnCl, **13**)[27] and octaphenyltetraazaporphyrin (^{Ph}TAPLnCl, **14**).[28]

2. Metallation of a free phthalocyanine ligand

The methods of synthesis of monophthalocyanine complexes from phthalonitriles and their derivatives described in the previous Section suffer from a number of drawbacks, the most substantial being the relatively low yields of some of the target products and difficulty of purification.

Scheme 3



M = H, Li;
(*a*) DBU, DCB, 180 °C; (*b*) Bu^{n}Li, $Ca(OAc)_2$, DMSO, 190 °C;
(*c*) solvent, 65–190 °C; DCB is *o*-dichlorobenzene.

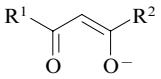
More advanced methods for the synthesis of monophthalocyanine complexes are based on the reactions of a free macrocyclic ligand (or its dianion) with lanthanide salts (Scheme 3).

In these reactions, the dianion is generated *in situ* to achieve high yields of monophthalocyanine complexes. Lanthanide chlorides or acetates react with the dianions obtained upon treatment of the appropriate ligands with butyllithium (see Scheme 3, conditions *b*) to give single-decker[29–31] complexes **1**, **15**, **16** in >90% yields in 1–5 min (Table 2). When DBU or 1,10-phenanthroline was used as the base, tetracrown-substituted (**2**)[36,37] and octaalkyl-substituted (**17**, **18**)[39,40] monophthalocyanine complexes formed in yields above 90%.

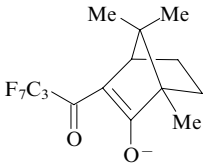
A similar reaction can be carried out between phthalocyanines and lanthanide β-diketonates (β-Dik = acac, dbm, dpm, fod, btfa, hfbc) in DMSO in the absence of strong base additives (see Scheme 3, conditions *c*).

Table 2. Synthesis of lanthanide monophthalocyanine complexes according to Scheme 3.

Compound	R	R′	M	Ln	X	Conditions	Solvent	Yield (%)	Ref.
1	H	H	H	Pr, Nd, Sm–Lu	Cl, AcO	*b*	DMSO	>90	29, 31
			H	Sm, Eu, Gd, Lu	fod, btfa, hfbc	*c*	DMSO	<86	32
			Li	Eu–Yb, Y	dbm	*c*	MeOH	<90	33
			Li	Eu–Tm, Lu, Y	dpm, acac	*c*	MeOH	60–90	34, 35
2	$O(CH_2CH_2O)_4$		H	Lu	AcO	*a*	DCB	>93	36
			H	Sm, Dy, Tm	AcO	*a*	DCB	>95	37
15	Me	Me	H	Pr, Nd, Sm–Lu	Cl, AcO	*b*	DMSO	>90	30
16	H	Bu^t	H	Pr, Nd, Sm–Lu	Cl, AcO	*b*	DMSO	>90	30
			H	Er	acac	*c*	DCB	59	38
17	Et	Et	H	Eu, Er, Lu	AcO	*a*	DCB	89–96	39, 40
18	Bu^n	Bu^n	H	Eu, Er, Lu	AcO	*a*	DCB	95–97	39, 40
19	H	n-$C_5H_{11}O$	H	Er	acac	*c*	DCB	61	38



$R^1 = R^2 =$ Me (acac), Bu^t (dpm), Ph (dbm);
$R^1 =$ Bu^t, $R^2 = C_3F_7$ (fod);
$R^1 =$ Ph, $R^2 = CF_3$ (btfa).



(hfbc)

This method was used [32] to prepare a number of unsubstituted complexes **1** in up to 86% yields (see Table 2). A similar reaction was carried out [38] in *o*-dichlorobenzene as the solvent; the yields of erbium phthalocyanines **16** and **19** synthesised in this way were 59% and 61%, respectively.

The second version of this type of reaction is the reaction of alkali metal (most often, lithium) phthalocyanine with various lanthanide derivatives (see Scheme 3, conditions *c*). Unlike free ligands, lithium phthalocyanine is readily soluble in methanol, tetrahydrofuran, acetone and other organic solvents and hence the reaction can be carried out under homogeneous conditions at relatively low temperatures. A number of monophthalocyanine complexes **1** with diketonates as the anions X were prepared in this way [33–35] (see Table 2).

When using lanthanide tris(β-diketonates) as the source of lanthanide, it is important to choose an appropriate solvent. If the reaction is carried out in methanol or DMSO, the complexes ^{R}PcLn(β-Dik)(Solv)$_n$ are formed as the major products.[32–34] In some cases, these complexes can be prepared in THF [34] or on treatment of the lithium salts Li[PcLn(acac)$_2$] with water.[35] The complexes Li[PcLn(β-Dik)$_2$] and H[PcLn(β-Dik)$_2$] are the major reaction products formed from lithium phthalocyanine and lanthanide tris(β-diketonate) in acetone.[33–35,41] However, these compounds become by-products when the reaction is carried out in THF [34] or DMSO.[32,42] The reaction of lithium phthalocyanine with M(acac)$_4$ (M = U, Th) in THF affords complexes described by the formula PcM(acac)$_2$ in yields of ~40%.[43] It was noted that a similar reaction with the corresponding tetrachlorides cannot be performed.

Refluxing of a mixture of lithium phthalocyanine with Ln(dpm)$_3$ (Ln = Sm–Yb, Y) in THF followed by a multistage workup of the reaction mixture afforded complexes PcLn$_2$(dpm)$_4$ (**20**). This is a unique type of binuclear monophthalocyanine complexes with additional ligands (Fig. 1).[34,44,45]

It was shown [32,42] that if the axial β-diketonate ligand contains electron-withdrawing groups (for example, fod, hfbc, btfa), the reaction of free phthalocyanine and lanthanide tris(β-diketonate) in DMSO or 1,2,4-trichlorobenzene (TCB) yields minor amounts (up to 6.5%) of the complexes [Pc$^{-\bullet}$]Ln(β-Dik)$_2$ (**21**), which can be isolated by chromatography. According to EPR spectroscopy data, these compounds are of radical nature and are rather stable when stored in air and in solutions.[32]

The reactions of the appropriate ligands or their lithium salts with lanthanide chlorides, acetates, acetylacetonates or dipivaloylmethanates afforded lutetium tetra(*tert*-butyl)-pyrazinoporphyrazine [46] (**22**), lutetium octaphenyl-, octaethylthio- and octadecylthiotetraazaporphyrins [46,47] (**23**) lutetium 2-naphthalocyanine [48,49] (**13**), lanthanide tetra(*tert*-butyl)-2,3-naphthalocyanines [50] (**24**), lutetium 1,2,3,4,19,20,21,22-octaphenyldiphthalo-11(12),29(30)-di(*tert*-butyl)dinaphthalotetraazaporphyrin [51] (**25**), and a number of complexes with *meso*-substituted porphyrins in 50%–80% yields.[52–55]

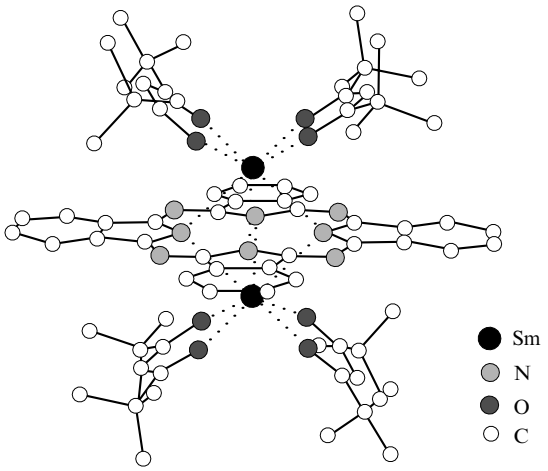
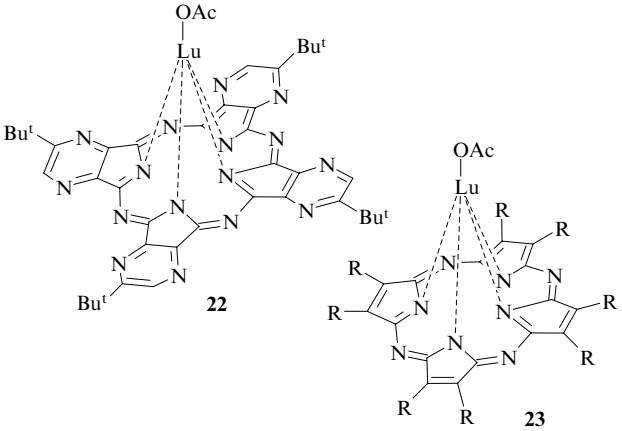


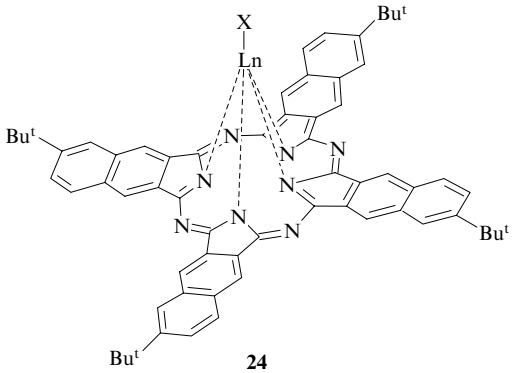
Figure 1. Crystal structure of binuclear samarium phthalocyanine **20**.[45]

The reactions were carried out in DMF,[46] DMSO [46,47,50,51] or n-octanol.[47] Note that metallation of octa(alkylthio)tetraazaporphyrin ligand with lutetium acetate in DMSO gives complexes **23** even at room temperature.



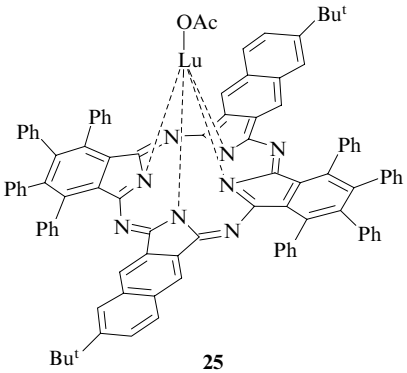
22 **23**

R = Ph, SEt, $SC_{10}H_{21}$-n.



24

Ln = Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Tm, Lu;
X = Cl, OAc, acac, dpm.



25

Thus, metallation of free ligands or their dianions with lanthanide derivatives is a highly efficient and selective method for the synthesis of single-decker lanthanide complexes with phthalocyanine and its analogues; it is characterized by high yields and purity of the target products.

3. Axial substitution at the metal atom

Substitution reactions of counter-ions as axial ligands in a series of indium,[56,57] zirconium and hafnium,[58,59] and lutetium[60] monophthalocyanine complexes are presently now known. These reactions are promising for both modification of the composition of metal complexes and study of their relative stabilities.

The reactions of indium monophthalocyanine PcInCl with the salts $Bu^n_4N^+X^-$ (X = F, Cl, Br, CN, HCO_2) in dichloromethane or THF occur under mild conditions and result in high yields of the complexes $[Bu^n_4N]^+$ $[PcInX_2]^-$.[56]

Substituted metal phthalocyanines ^{R}PcInCl react with the Grignard reagents R′MgCl (R′ = Me, Ph, 4-FC_6H_4, 4-$CF_3C_6H_4$, 3-$CF_3C_6H_4$, C_6F_5) in ether or THF to form the phthalocyanine complexes of the general formula ^{R}PcInR′ in yields of 12%–70%.[57,61]

The reactions of metal phthalocyanines $PcMCl_2$ with β-diketones in toluene yielded the complexes PcM(β-Dik)$_2$ (M = Zr, Hf),[59] while the reactions with the clathrochelate oximate complexes containing Fe^{2+} ions in a methanol–dichloromethane mixture afforded the clathrochelate complexes PcMClat (M = Zr, Hf, Lu; Clat is the clathrate anion).[58,60]

III. Synthesis of homoleptic double-decker complexes

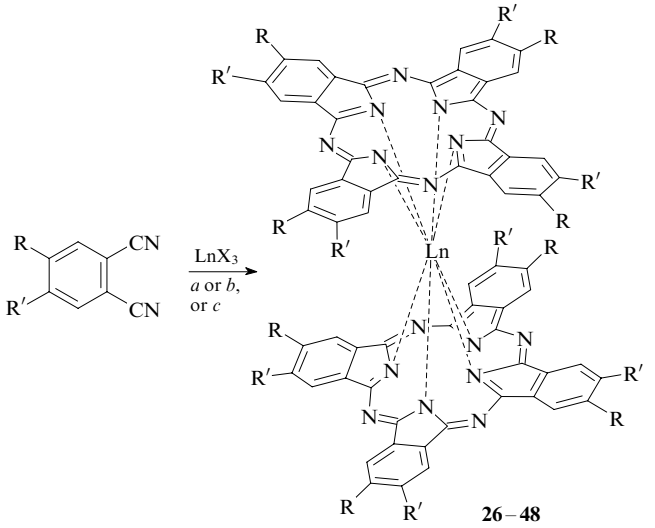
Metal bisphthalocyanines the first representatives of which were prepared by Russian scientists[62] back in 1965 are the best studied sandwich complexes. The key methods for the synthesis of bisphthalocyanine complexes can be conveniently divided into three groups depending on the type of the initial compound. The homoleptic double-decker complexes are prepared most often by the template method and by metallation of the free ligand or its dianion.

1. Template synthesis based on phthalonitrile and its derivatives

The extensive use of the template method for the preparation of phthalocyanine complexes is caused, first of all, by its technical simplicity (see Section II.1). However, in the case of lanthanides and other metals able to form phthalocyanine complexes with different metal : ligand ratios, the selectivity of the template synthesis depends on many factors. Of these, the most significant are the temperature, the reaction time, the nature of the starting compounds, lanthanide salts and phthalic acid derivatives (mainly phthalonitriles), and their ratio. The preparation of sandwich complexes requires higher temperature and longer reaction time than the synthesis of monophthalocyanine analogues. The stability of metal bisphthalocyanines increases on going from lanthanum to lutetium; however, the introduction of bulky substituents into the peripheral positions of ligands can break this trend.

The first lanthanide bisphthalocyanines **26** were prepared and spectrally characterised by Kirin and Moskalev.[62,63] Heating (280–290 °C) of a mixture of phthalonitrile with lanthanide acetates in 1 : (4–8) molar ratio for 40–90 min resulted in bisphthalocyanine complexes in 10%–15% yields (Scheme 4, conditions *a*).

Scheme 4



26–48

(*a*) 250–350 °C, 0.5–4 h; (*b*) DBU, solvent, 130–160 °C; (*c*) microwave radiation (300–700 W), 5–10 min.

This method was subsequently optimised and used by a number of other researchers to prepare unsubstituted[64–67] complexes **26** and a series of substituted bisphthalocyanine complexes **27**–**36** (Table 3).[17,26,65,69–74] Note that apart from Ln bisphthalocyanines **36**, Gd, Yb and Lu complexes with covalently linked decks were isolated and spectrally characterised;[96] however, their yields did not exceed 1%. The UV/Vis spectra of these complexes contained no Q-band, which is due to disruption of aromatic conjugation in the macrocycles upon C–C covalent bonding of the ligands. The formation of such structures has also been noted for titanium[97] and niobium[98] phthalocyanine complexes.

Compounds **26** could be synthesised by reaction of the components at 300–310 °C followed by vacuum sublimation of the products;[66,67] this allowed the target complexes to be isolated in 5% to 60% yields depending on the lanthanide nature. On going from the end to the beginning of the lanthanide series, the yields of Ln bisphthalocyanines decrease, while the yields of free ligands PcH_2 formed as by-products increase from 2% to 75%. The yields of bisphthalocyanine complexes **26** for the beginning of the lanthanide series were increased to 50%–60% by performing the process in a sealed tube at 290 °C and using chromatography on alumina for purification of the resulting complexes instead of sublimation.[65]

Table 3. Template synthesis of lanthanide bisphthalocyanines (see Scheme 4).

Compound	R	R′	Ln	X	Conditions	Solvent	Time /h	Yield (%)	Ref.
26	H	H	La, Pr, Nd, Sm – Lu	AcO	*a*	–	0.5 – 4	10 – 15	62 – 64
			Lu	AcO	*b*	n-$C_6H_{13}OH$	5	10	16
			Nd, Sm, Er, Lu	AcO	*a*	–	0.5 – 4	50 – 60	65
			Pr, Nd, Sm – Lu	AcO	*a*	–	0.5 – 4	5 – 60	66, 67
			Tb, Dy, Lu	AcO	*c*	–	see [a]	> 70	68
27	H	Bu^t	La, Pr, Nd, Sm, Gd, Er, Lu	AcO	*a*	–	0.5 – 4	60 – 80	65, 69
			Er, Gd, Lu	HCO_2, Cl	*a*	–	0.5 – 4	70	70
			Ce	BzO	*a*	–	0.5 – 4	52	71
			Er	acac	*b*	n-$C_5H_{11}OH$	12	24	38
28	H	$(CF_3)_3C$	Lu	AcO	*a*	–	0.5 – 4	–	72
29	H	Ph	Lu	HCO_2	*a*	–	0.5 – 4	< 70	70
30	H	PhO	Lu	HCO_2	*a*	–	0.5 – 4	70	70
31	Br	Bu^t	Lu	HCO_2	*a*	–	0.5 – 4	70	70
32	H	Pr^nO	Lu	AcO	*a*	–	0.5 – 4	–	26
33	H	Bu^tCH_2	Lu	AcO	*a*	–	0.5 – 4	–	26
34	Me	Me	Tb, Lu	AcO	*a*	–	2 – 3.5	–	73
	Et	Et	Eu, Dy, Lu	AcO, acac	*b*	iso-$C_5H_{11}OH$	15 – 20	11 – 53	74
	Bu^n	Bu^n	Eu, Dy, Lu	AcO, acac	*a*	–	2 – 8	22 – 49	74
			Eu, Dy, Lu	AcO, acac	*b*	iso-$C_5H_{11}OH$	15 – 20	6 – 46	74
			Eu, Dy, Lu	AcO, acac	*c*	–	see [a]	16 – 23	74
	n-C_7H_{15}	n-C_7H_{15}	Eu, Gd	acac	*b*	n-$C_5H_{11}OH$	13	68 – 72	75
			Y	acac	*b*	n-$C_5H_{11}OH$	13	68 – 72	76
35	MeO	MeO	Lu	AcO	*a*	–	0.5 – 4	–	73
	Pr^nO	Pr^nO	Sm, Tm, Lu	HCO_2, AcO	*b*	n-$C_5H_{11}OH$	8	61 – 66	77
	Bu^nO	Bu^nO	Er	AcO	*b*	n-$C_6H_{13}OH$	20	–	78
	n-$C_5H_{11}O$	n-$C_5H_{11}O$	Eu, Gd	acac	*b*	n-$C_5H_{11}OH$	8	75 – 79	75
			Y	acac	*b*	n-$C_5H_{11}OH$	8	75 – 79	76
	n-$C_6H_{13}O$	n-$C_6H_{13}O$	Er	AcO	*b*	n-$C_6H_{13}OH$	20	–	78
	n-$C_8H_{17}O$	n-$C_8H_{17}O$	Er	AcO	*b*	n-$C_6H_{13}OH$	20	–	78
			La – Nd, Sm – Tm, Y	acac	*b*	n-$C_5H_{11}OH$	12	9 – 63	79
	n-$C_9H_{19}O$	n-$C_9H_{19}O$	Er	AcO	*b*	n-$C_6H_{13}OH$	20	–	78
	n-$C_{10}H_{21}O$	n-$C_{10}H_{21}O$	Er	AcO	*b*	n-$C_6H_{13}OH$	20	24	80
			Lu	AcO	*b*	n-$C_6H_{13}OH$	24	20	81
	n-$C_{12}H_{25}O$	n-$C_{12}H_{25}O$	Lu	AcO	*b*	n-$C_6H_{13}OH$	20	20	82
			Nd, Eu, Er, Lu	AcO	*b*	n-$C_6H_{13}OH$	20	15 – 23	80
			Pr, Nd, Eu – Lu	AcO	*b*	n-$C_6H_{13}OH$	20	20 – 30	78
			Ce	acac	*b*	n-$C_5H_{11}OH$	12	22	83
	n-$C_{14}H_{29}O$	n-$C_{14}H_{29}O$	Er	AcO	*b*	n-$C_6H_{13}OH$	20	–	78
			Lu	AcO	*b*	n-$C_6H_{13}OH$	24	14	81
	n-$C_{16}H_{33}O$	n-$C_{16}H_{33}O$	Er	AcO	*b*	n-$C_6H_{13}OH$	20	–	78
			Lu	AcO	*b*	n-$C_6H_{13}OH$	24	11	81
	n-$C_{18}H_{37}O$	n-$C_{18}H_{37}O$	Er	AcO	*b*	n-$C_6H_{13}OH$	20	27	80
			Lu	AcO	*b*	n-$C_6H_{13}OH$	24	12	81
36	$O(CH_2CH_2O)_4$		Lu	AcO	*b*	n-$C_6H_{13}OH$	20	–	84
			Lu	AcO	*b*	n-$C_6H_{13}OH$	20	19	85
			Lu	AcO	*a*	–	0.5 – 4	35	17
37	$O(CH_2CH_2O)_5$		Lu	AcO	*b*	n-$C_6H_{13}OH$	20	7	85
38	$MeO(CH_2CH_2O)_n$ (n = 1, 3, 4)	$MeO(CH_2CH_2O)_n$ (n = 1, 3, 4)	Lu	AcO	*b*	n-$C_6H_{13}OH$	8 – 22	6.5 – 12	85, 86
	$MeO(CH_2CH_2O)_2$	$MeO(CH_2CH_2O)_2$	Lu	AcO	*b*	n-$C_6H_{13}OH$	18	6	85, 86
			Eu	acac	*b*	n-$C_5H_{11}OH$	8	31	87
39	3,4-$(C_nH_{2n+1}O)_2$. .C_6H_3O (n = 12, 13)	3,4-$(C_nH_{2n+1}O)_2$. .C_6H_3O (n = 12, 13)	Lu	AcO	*b*	n-$C_6H_{13}OH$	8	20	88
40	BnO	BnO	Nd, Sm, Dy, Lu	HCO_2, AcO	*b*	n-$C_6H_{13}OH$	8	37 – 55	89

Table 3 (continued).

Compound	R	R′	Ln	X	Conditions	Solvent	Time /h	Yield (%)	Ref.
41	n-$C_nH_{2n+1}S$ (n = 8, 10, 12, 14, 16, 18)	n-$C_nH_{2n+1}S$ (n = 8, 10, 12, 14, 16, 18)	Eu, Tb, Lu	AcO	*b*	n-$C_6H_{13}OH$	21.5–44	26–44	90
	n-$C_6H_{13}S$	n-$C_6H_{13}S$	Sm, Gd, Dy	AcO	*b*	n-$C_6H_{13}OH$	48	29–36	91
42	H	n-$C_{12}H_{25}S$	Lu	AcO	*b*	n-$C_6H_{13}OH$	20	8.1	92
43	H	cyclo-C_3H_7	Lu	AcO	*b*	iso-$C_5H_{11}OH$	12	<25	23
44	H	n-$C_5H_{11}O$	Er	acac	*b*	n-$C_5H_{11}OH$	12	30	38
45	PhO	PhO	Eu, Ho, Lu	acac	*b*	n-$C_5H_{11}OH$	8	36–43	93
46	PhS	PhS	Eu	acac	*b*	n-$C_5H_{11}OH$	8	42	93
47	Me[b]	Me[b]	Dy, Er, Tm, Lu	HCO_2, AcO	*b*	n-$C_6H_{13}OH$	5	66–72	94
48	CN	CN	Nd	AcO	*b*	sulfolane	3	–	95

[a] The reaction time was 5–10 min; [b] the substituents are in positions 1, 3, 8, 10, 15, 17, 22 and 24 of the phthalocyanine ligand.

This modification of the template method was also used successfully [65, 69–72] for the synthesis of substituted double-decker complexes **27**–**31** (see Table 3). Although monophthalocyanine complexes are formed initially,[65, 73, 99, 100] lanthanides of the beginning of the series form bisphthalocyanine complexes as soon as 5–10 min after the onset of heating, and the elements of the end of the series, after 1–1.5 h.

The template synthesis carried out in the presence of basic additives, in particular, sodium carbonate, potassium hydroxide or methoxide, at 270–280 °C for 15–25 min results in Ln bisphthalocyanines **26** as the salts $M^+[Pc_2Ln]^-$ (Ln = La, Pr, Nd, Sm–Lu, Y; M = Na, K) in 36%–41% yields.[101–104] Treatment of the salts with tetrabutylammonium or tris(dodecyl)octylammonium bromides afforded ionic products $[Alk_4N]^+[Pc_2Ln]^-$ in quantitative yields. Electrooxidation of these bisphthalocyanine anions in dichloromethane results in neutral complexes $[Pc^{2-}Ln^{3+}Pc^{-\bullet}]\cdot CH_2Cl_2$ in high yields.[102] The formation of radical species from anions on exposure to UV radiation has also been noted [105] for solutions of bisphthalocyanine complexes in a dichloromethane–acetonitrile mixture.

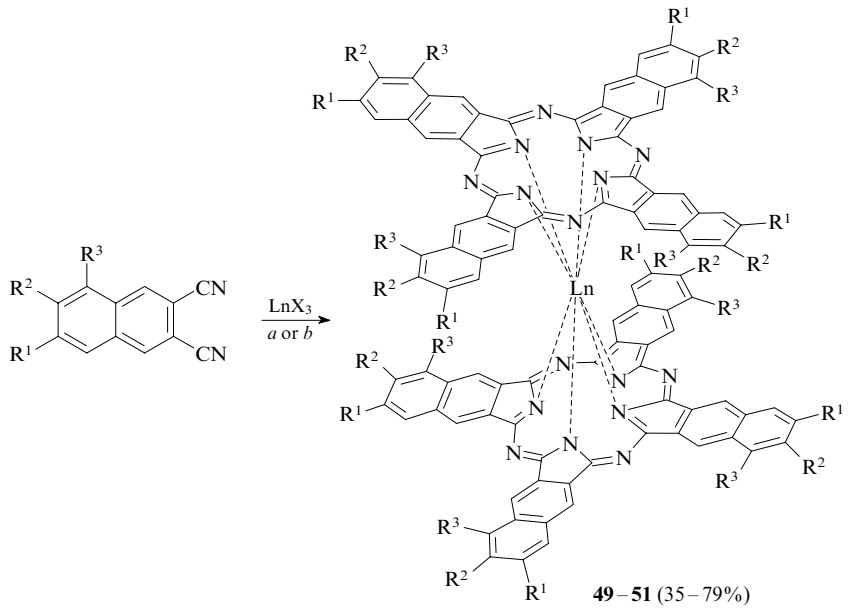
The template synthesis of bisphthalocyanine complexes can be carried out not only with lanthanide salts, but also with metallic lanthanides. Heating of a compacted mixture of ytterbium powder, phthalonitrile and iodine (molar ratio 1 : 8 : 2) in a sealed tube at 200 °C for 6 h afforded ytterbium bisphthalocyanine **26** $[Pc_2Yb]I_2$ as dark violet crystals.[106] Under above-described conditions, similar zirconium(IV) and indium(III) complexes have also been synthesised, indium being introduced in the reaction as an alloy with thallium.[107] Zirconium(IV) and hafnium(IV) bisphthalocyanines were prepared by the traditional method, *i.e.*, by fusing unsubstituted phthalonitrile or 4-*tert*-butylphthalonitrile with metal chlorides at 310–315 °C for 4–5 h (yields 60%–70%).[108, 109]

Apart from thermal fusion, complexation has been initiated by microwave radiation (see Scheme 4, conditions *c*). The use of microwave radiation reduces the reaction time from several hours to several minutes. There are only two publications [68, 74] devoted to the template synthesis of lanthanide bisphthalocyanines by this method. Unsubstituted complexes Pc_2Ln (Ln = Tb, Dy, Lu) (**26**) were prepared [68] by irradiation (650–700 W) of a mixture of phthalonitrile with an appropriate lanthanide salt for 6–10 min (yields >70%). However, in the case of *tert*-butyl-substituted bisphthalocyanine complexes **27**, the yields of the target complexes did not exceed 10%. More recently,[74] n-butyl-substituted complexes **34** were prepared in higher yields (see Table 3). For their synthesis, milder conditions proved to be preferred, in particular, radiation power 300–450 W and reaction time 5–8 min, which suggests higher reactivity of the starting 4,5-dibutylphthalonitrile in the microwave-assisted complexation compared to 4-*tert*-butylphthalonitrile.

The third method of template synthesis of bisphthalocyanine complexes used most often in recent years to obtain complexes with substituents of different nature requires rather mild reaction conditions: refluxing of a mixture of the appropriate phthalonitrile and a lanthanide salt in the presence of DBU in a protic solvent (usually pentanol or hexanol) for 5–48 h (see Scheme 4, conditions *b*). The target products are mainly purified by filtering the reaction mixture to remove the insoluble impurities followed by chromatography of the filtrate. The yields of unsubstituted (**26**) [16] and substituted (**27**, **34**–**48**) bisphthalocyanine complexes are in the range of 6%–79% (see Table 3),[38, 74–95] the lowest values being typical of lutetium complexes and the highest corresponding to the middle of the lanthanide series (Eu, Gd). As the bulk of the peripheral substituents in the ligands increases, the yields of the bisphthalocyanine complexes decrease (see Table 3).

The template method has also been used for the synthesis of a number of substituted Ln dinaphthalocyanine complexes **49**–**51** (Scheme 5).[110–112] Lutetium acetate reacts with a melt of 5-bromo-7-*tert*-butylnaphthalonitrile (see Scheme 5, conditions *a*) to give dinaphthalocyanine complex **49**, and no formation of a mononaphthalocyanine complex can be detected, which attests to its fast transformation into a target double-decker complex.[110] Compounds **50** and **51** were prepared by refluxing a mixture of naphthalonitriles and lanthanide acetylacetonates in n-octanol in the presence of DBU (conditions *b*). The product yields were 35%–79% and decreased gradually on going from the beginning to the end of the lanthanide series.[109, 110] As has been noted,[111] the solvent and the temperature have a considerable effect on the reaction route: if n-octanol is replaced by n-pentanol, n-hexanol, TCB or 1-chloronaphthalene (1-ClN), no target products are formed in the reaction.

Scheme 5



49: R^1 = Bu^t, R^2 = H, R^3 = Br, Ln = Lu; **50:** R^1 = Bu^t, R^2 = R^3 = H; Ln = La, Ce, Pr, Nd, Eu, Gd, Tb, Er, Y;
51: R^1 = R^2 = n-$C_{12}H_{25}S$, R^3 = H, Ln = Eu; X = OAc, acac; (*a*) 280 °C, 2 – 4 h; (*b*) DBU, n-$C_8H_{17}OH$, 190 °C, > 18 h.

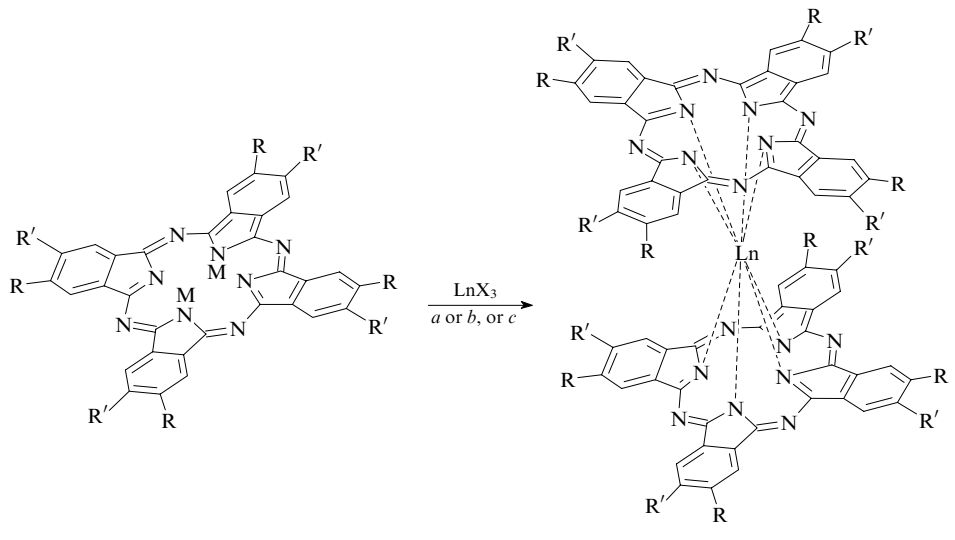
2. Metallation of free phthalocyanine ligand

The synthesis of double-decker lanthanide complexes using metal-free phthalocyanines allows one to avoid side processes typical of template reactions, first of all, resinification of the starting phthalogens. However, control of the transformation selectivity is often complicated in this case by steric factors arising in the complexation of the Ln monophthalocyanine formed initially with the second free ligand. Therefore, bisphthalocyanine complexes often cannot be obtained in high yields, especially for the end of the lanthanide series where the ionic radii of the metals are small.

The approaches to the synthesis of bisphthalocyanine complexes from the ligands (or their lithium derivatives) and lanthanide acetates (or acetylacetonates) are summarised in Scheme 6. The reaction is carried out in a basic medium using either alkali metal (most often, lithium) phthalocyanine or a weakly basic solvent: quinoline, n-octanol, *etc*. A number of unsubstituted phthalocyanine complexes **26** were obtained by this method (see Scheme 6, conditions *c*) in quinoline or TCB (yields 9% – 33%);[75, 76, 113, 114] the use of n-octanol as the solvent results in alkoxy-substituted bisphthalocyanine complexes **35** and **52**[115, 116] (Table 4). Meanwhile, attempts at the synthesis of hexadeca-n-heptyl- (**34**, R = R′ = n-C_7H_{15}) and hexadeca-n-pentoxy-substituted (**35**, R = R′ = n-$C_5H_{11}O$) europium and gadolinium bisphthalocyanines in TCB at 220 °C failed.[75]

The synthetic routes to alkyl-substituted bisphthalocyanine complexes **34** (n = 2, 4) developed to date[39, 40] selectively give lanthanide complexes of both the middle (see

Scheme 6



M = H, Li; (*a*) base, solvent, Δ, 1 – 3 h; (*b*) DBU, microwave radiation (240 W), 10 min; (*c*) solvent, Δ.

Table 4. Synthesis of lanthanide bisphthalocyanines according to Scheme 6.

Compound	R	R′	M	Ln	X	Conditions	Base	Solvent	T /°C	Time /h	Yield (%)	Ref.
26	H	H	H	Lu	AcO	*c*	–	quinoline	240	22	9	113
			Li	La, Pr, Nd, Sm – Lu	acac	*c*	–	TCB	220	4	12 – 33	114
			Li	Eu, Gd	acac	*c*	–	TCB	220	10	32, 25	75
			Li	Y	acac	*c*	–	TCB	220	10	27	76
27	H	Bu^t	H	La, Tb, Dy	AcO	*b*	DBU	–	20	see [a]	61 – 63	117, 118
34	n-C_nH_{2n+1} (n = 2, 4)	n-C_nH_{2n+1} (n = 2, 4)	H	Lu	AcO	*c*	–	n-$C_{16}H_{33}OH$	230	1	85 – 90	39, 40
			H	Er	AcO	*c*	–	n-$C_{16}H_{33}OH$	230	1	89 – 90	39, 40
			H	Eu	AcO	*a*	DBU	n-$C_6H_{13}OH$	160	2 – 3	87 – 95	39, 40
	n-C_nH_{2n+1} (n = 8, 12, 18)	n-C_nH_{2n+1} (n = 8, 12, 18)	H	Lu	AcO	*a*	n-$C_5H_{11}OK$	n-$C_5H_{11}OH$	135	–	–	119, 120
35	Bu^nO	Bu^nO	H	Yb, Lu	AcO	*c*	–	n-$C_8H_{17}OH$	190	–	–	115
36	$O(CH_2CH_2O)_4$		H	Gd, Yb, Y	AcO	*a*	DBU	1-$ClC_{10}H_7$	260	2	15 – 35	121 – 124
			H	La	AcO	*a*	DBU	1-$ClC_{10}H_7$	260	1	70	124, 125
			H	Sm, Dy, Tm	AcO	*a*	DBU	1-$ClC_{10}H_7$	260	2	40 – 45	37
52	Et_2HCO [b]	H	H	Eu, Lu, Y	acac	*c*	–	n-$C_8H_{17}OH$	190	9	21 – 49	116
53	4-(n-$C_{18}H_{37}O$)C_6H_4	4-(n-$C_{18}H_{37}O$)C_6H_4	H	Lu	AcO	*a*	n-$C_5H_{11}OK$	n-$C_5H_{11}OH$	135	–	–	126
54	n-$C_nH_{2n+1}OCH_2$ (n = 8, 12, 18)	n-$C_nH_{2n+1}OCH_2$ (n = 8, 12, 18)	H	Lu	AcO	*a*	n-$C_5H_{11}OK$	n-$C_5H_{11}OH$	135	–	< 40	127, 128

[a] The reaction time was 10 min; [b] the substituents are in positions 1, 8, 15 and 22 of the phthalocyanine ligand.

Scheme 6, conditions *a*) and the end (conditions *c*) of the series in high yields (see Table 4).

In some studies (see, for example [37–40, 117, 118, 121–125]), DBU was used as the solvent (see Scheme 6, conditions *a*, *b*). For example, Liu *et al.*[117, 118] reported a microwave-assisted (240 W) synthesis carried out in the presence of DBU to give lanthanum, terbium and dysprosium octa(*tert*-butyl)-substituted bisphthalocyanines (**27**) in yields of 61%–63% (see Table 4). However, the spectral data presented by the authors, in particular, UV/Vis spectra, indicate that they have obtained monophthalocyanine complexes as the final products.

The synthesis of some lanthanide and yttrium octa(15-crown-5) bisphthalocyanines (**36**) has been reported.[37, 121–124] The target products were obtained by refluxing a mixture of the ligand, a lanthanide salt and DBU (molar ratio 1.5 : 1 : 2) in 1-ClN in yields of 15%–45%. It is noteworthy that the structure of the thus synthesised ytterbium bisphthalocyanine was confirmed by not only spectral methods but also by X-ray diffraction.[123] Further optimisation of the conditions of synthesis consisting of the change in the ligand : (lanthanide salt) : DBU ratio to 1 : 1.5 : 10 gave [124, 125] lanthanum octa(15-crown-5) bisphthalocyanine as a mixture of radical $\{[(R_4Pc^{2-})La^{3+}(R_4Pc^{-\bullet})]^{\bullet}\}$ and anionic $\{[La^{3+}(R_4Pc^{2-})_2]^{-}\}$ forms in an overall yield of 70%.

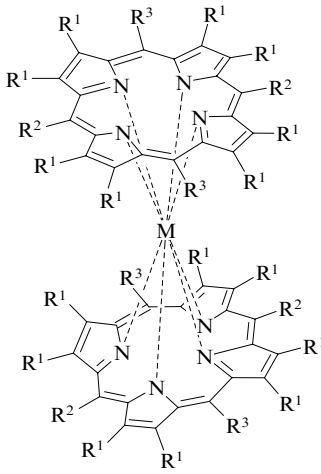
A number of lutetium bisphthalocyanines (**34**, **53** and **54**) with bulky substituents exhibiting mesogenic properties have been described.[119, 120, 126–128] These compounds were obtained in yields of up to 40% using potassium pentoxide as the base prepared *in situ* by dissolving metallic potassium in pentyl alcohol (see Table 4).

The synthesis of bisphthalocyanine complexes from free ligands was accomplished not only for lanthanides, but also for some other metals. Thus the reaction of unsubstituted sodium phthalocyanine with uranium(IV) or thorium(IV) chloride (1-ClN, 12 h) gave sandwich complexes Pc_2M (M = U, Th) (**55**) in yields of 7.8% and 6.2%, respectively.[129] The yields of titanium(IV) unsubstituted and octa(*tert*-butyl)-substituted bisphthalocyanines $^{R}Pc_2Ti$ (R = H, Bu^t) (**56**) formed upon the reaction of free ligands with titanium tetrachloride in boiling DMSO for 15–20 min reach 40%.[130]

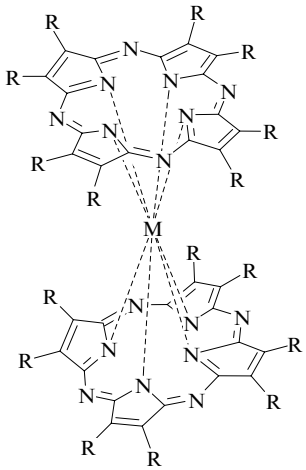
Unsubstituted lutetium complexes with 2,3-naphthalocyanine [131] (**57**) and 1,2-naphthalocyanine [48] (**58**, Ln = Lu) were prepared from the corresponding lithium salts and lutetium acetate in quinoline or 1-ClN (yields 47% and 60%, respectively).

Since each of 1,2-naphthalocyanine macrocycles in complex **58** (Ln = Lu) exists as four structural isomers (symmetry groups C_{4h}, D_4, C_{2v}, C_s), we show only one of the possible dinaphthalocyanine isomers with C_{4h} symmetry of the ligands. The preparation of similar complexes of neodymium and europium has been reported.[27] However, neither the conditions of synthesis nor the yields of final compounds were discussed in the publication; no convincing evidence for the structures of the obtained products was reported either.

Note that double-decker complexes of lanthanides and other metals with porphyrins (**59**–**61**) and tetraazaporphyrins (**62**, **63**) are synthesised using only the free ligands as the starting compounds.



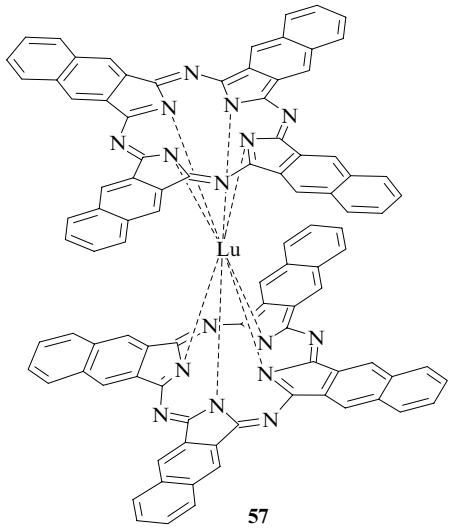
59–**61**



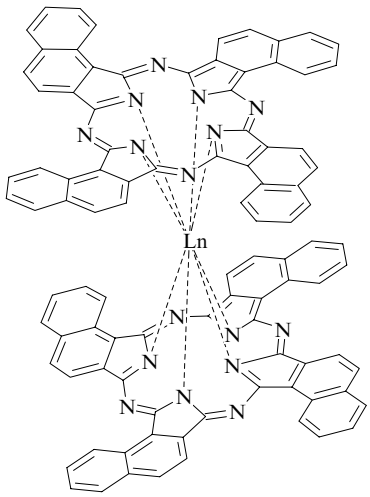
62, **63**

59: R^1 = H, R^2 = 4-$MeOC_6H_4$, R^3 = 4-Py, M = La;
60: R^1 = Et, R^2 = R^3 = H; M = La, Ce, Pr, Nd, Sm–Lu, Y;
61: R^1 = H, Et; R^2 = R^3 = H, Ph; M = Zr, Hf;
62: R = Pr^n: M = Ce, Eu, Lu;
63: R = Et, M = Zr.

Compounds **59** (M = La),[132] **60** (M = La, Ce, Pr, Nd, Sm–Gd) [133, 134] and **62** (M = Ce) [135] are prepared by refluxing free porphyrins and tetraazaporphyrins with lanthanide acetylacetonates in TCB for 20–48 h (yields of up to 80%). Zirconium and hafnium are introduced into this reaction as



57



58 (Ln = Lu, Nd, Eu)

diethylamides $M(NEt_2)_4$ (M = Zr, Hf), which react with the ligands in toluene to give complexes **61** and **63** in 54% – 61% yields.[136, 137] Bis-porphyrin complexes of lanthanides of the middle and the end of the series are synthesised either in n-hexanol [compounds **62** (M = Eu, Lu) were formed in yields of 36% and 44%, respectively][135] or using the so-called raise-by-one-story method (see the next Section) [complexes **60** (M = Tb – Lu, Y) were prepared in yields of 60% – 80%, respectively].[134]

3. Axial substitution at the metal ion

The direct reaction of the previously obtained single-decker complex with a free ligand resulting in the corresponding sandwich derivatives has been called the 'raise-by-one-story' method. It is used mainly for the synthesis of heteroleptic and mixed-ligand complexes described in the next Section. However, several examples of synthesis of homoleptic double-decker derivatives by this method are also known. The reaction of tin(IV) monophthalocyanine $PcSnCl_2$ with sodium phthalocyanine in boiling 1-ClN for 1.5 h affords Pc_2Sn.[138] The reaction of single-decker lanthanide complexes (TPyP)Ln(acac) [Ln = Sm, Eu, Gd; TPyP is the *meso*-tetrakis(4-pyridyl)porphyrin dianion] with the required ligands on refluxing in TCB for 24 – 72 h results in bisporphyrin complexes $(TPyP)_2Ln$ in 25% – 40% yields.[139] This method was also used successfully to prepare complexes of the second half of the lanthanide series and yttrium **60** (M = Tb – Lu, Y) from single-decker lanthanide complexes and the lithium salt of free porphyrin (yields 60% – 80%).[134]

IV. Synthesis of homoleptic triple-decker complexes

1. Template synthesis in phthalonitrile melts

The first assumption about the formation of triple-decker lanthanide phthalocyanines was made by Russian scientists[63, 140] in 1967. Fusion of a phthalonitrile mixture with lanthanide acetates at 280 – 290 °C for 1 h gave, along with double-decker complexes, compounds for which the structure of binuclear trisphthalocyanine complexes Pc_3Ln_2 (Ln = Pr, Nd, Er, Lu) (**64**) was proposed on the basis of spectral data and elemental analysis.

Later, unsubstituted triple-decker complexes **64** for the whole lanthanide series including yttrium[141-143] as well as lutetium crown-substituted[17] phthalocyanine **65** have been obtained by heating the corresponding phthalonitriles with lanthanide acetates or chlorides in 230 - 290 °C temperature range. However, clear elucidation of the triphthalocyanine structure has long been debated. Only in 1999 an X-ray diffraction study[144] of compound **65** was carried out and its binuclear triple-decker structure was unambiguously proved (Fig. 2).

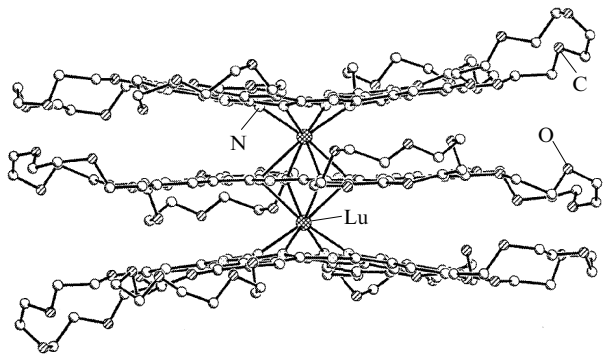
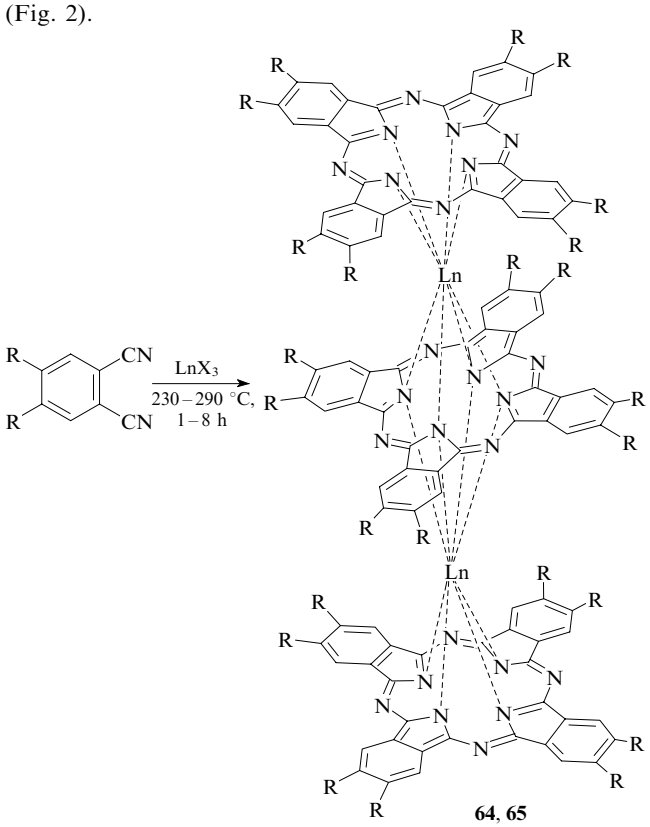


Figure 2. Crystal structure of crown-substituted lutetium trisphthalocyanine **65**.[144]



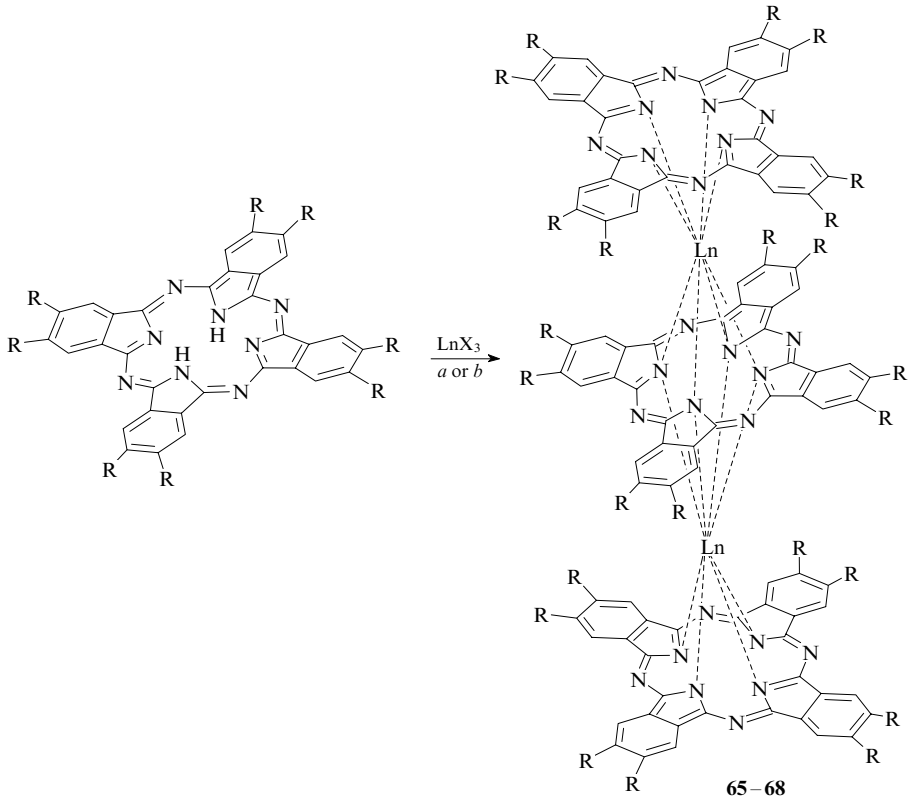
64: R = H; Ln = La, Pr, Nd, Sm – Lu, Y;
65: R – R = $O(CH_2CH_2O)_4$, Ln = Lu.
X = OAc, Cl.

Triple-decker indium and bismuth phthalocyanine complexes were synthesised using the template method. Heating of a mixture of phthalonitrile with a powdered indium – tin alloy at 210 °C yielded the triple-decker complex Pc_3In_2,[145] while fusion of phthalonitrile with bismuth selenide in a molar ratio 12 : 1 in an evacuated tube (220 °C, 24 h) afforded trisphthalocyanine complex Pc_3Bi_2.[146] The product yields were not given in either of the studies cited; however, X-ray diffraction data confirming the structure of the target complexes were reported. Another research group[147] synthesised the bismuth complex by heating phthalonitrile and bismuth acetate at 310 °C. This reduced the reaction time to 30 min and afforded the target compound Pc_3Bi_2 in 63% yield.

2. Metallation of a free phthalocyanine ligand

Crown phthalocyanine complexes **65** (Ln = Gd, Yb) were prepared[121, 124] by the reaction of the ligand with lanthanide acetates in the presence of DBU [molar ratio ligand : (lanthanide salt) : DBU = 1.5 : 1 : 2] in a 1-ClN solution (Scheme 7, conditions *a*); the yields of the complexes proved to be relatively low (10% – 15%). Later, this reaction was modified,[148] in particular, it was carried out without a base and with lanthanide acetylacetonates as the starting compounds (molar ratio ligand : salt = 1 : 3); this resulted in metal trisphthalocyanines **65** (Ln = Nd, Tb) in 62% and 68% yields, respectively, under milder conditions (TCB, 210 °C). The rather unstable triple-decker lanthanum com-

Scheme 7

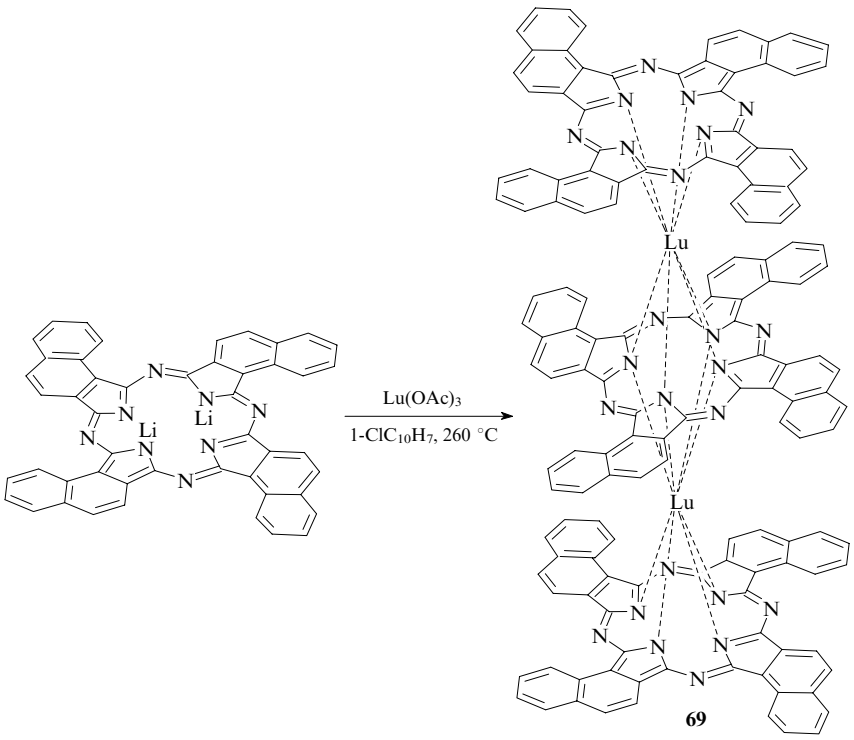


65: R – R = $O(CH_2CH_2O)_4$; Ln = La, Nd, Gd, Tb, Yb; **66**: R = Bu^nO; Ln = La, Dy, Yb, Lu, Y; Ln = Lu, Er, Eu: R = Et (**67**), Bu^n (**68**); X = OAc, acac; (*a*) DBU, 1-$ClC_{10}H_7$, 260 °C, 2 h; (*b*) solvent (TCB or n-$C_8H_{17}OH$, or n-$C_{16}H_{33}OH$), Δ.

plex **65** (Ln = La), which cannot be obtained by other methods, was prepared in this way.[149]

Butoxy-substituted complexes **66** were synthesised[150,151] in n-octanol (see Scheme 7, conditions *c*) by refluxing (190 °C) a mixture of the free ligand and lanthanide acetate taken in a molar ratio of 1 : 2.6 (yields 76% – 83%). Diphthalocyanine complexes formed as by-products were removed by column chromatography on silica gel (elution with $CHCl_3$)[150] or on basic alumina using CH_2Cl_2[151] or $CHCl_3$ – MeOH mixture (97.5 : 2.5) as

Scheme 8

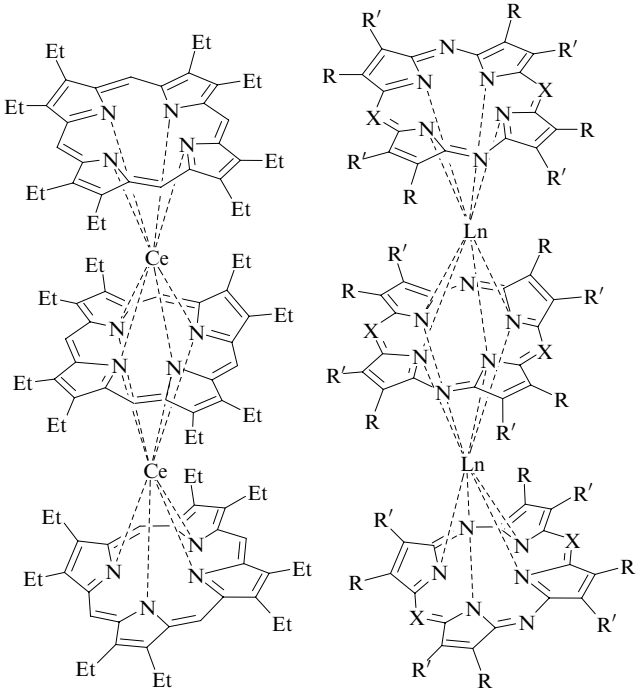


the eluent.[148] More efficient separation of the products was performed[150, 151] by gel permeation chromatorgaphy on a polymeric support Bio-Beads S-X1 (elution with benzene).

The above-described synthetic method served as the basis for the development of selective approaches to the preparation of alkyl[40] trisphthalocyanine complexes **67** and **68** (see Scheme 7). Thus the reaction of the starting ligand and the lanthanide salt (molar ratio 1 : 1) in n-octanol with amount of the solvent being decreased threefold resulted, in the case of europium acetate, in complexes **67** and **68** in 92% and 87% yields, respectively. In the case of lutetium and erbium, the yield of triple-decker complexes decreased, and considerable amounts of mono- and bisphthalocyanine complexes were formed; this was attributed[40] to too low reaction temperature (190 °C). Indeed, heating of the initial compounds in n-hexadecanol at 280 °C for 1 h furnished erbium and lutetium trisphthalocyanines (**67**, **68**) in 88% – 93% yields.

Transmetallation of lithium 1,2-naphthalocyanine with lutetium acetate in 1-ClN gave compound **69** in 55% – 60% yield. By analogy with dinaphthalocyanine complex **58** (Ln = Lu), this product was isolated as a mixture of structural isomers (see Section III.2), one of which is shown in Scheme 8 (C_{4h} symmetry of the ligands). This is so far the only example of a homoleptic triple-decker lanthanide complex with naphthalocyanines.[48, 152]

Triple-decker lanthanide complexes containing other tetrapyrrole type ligands have been reported in the literature. The reaction of free octaethylporphyrin or tetramethyltetraethyldiazaporphyrins with cerium and europium acetylacetonate in boiling TCB for 18 – 20 h gave sandwich complexes **70**[133] and **71**[153] in up to 12% yields. Octapropyltetraazaporphyrin reacts with europium(II) iodide in n-hexanol for 24 h giving rise to complex **72** (yield 9%).[135]

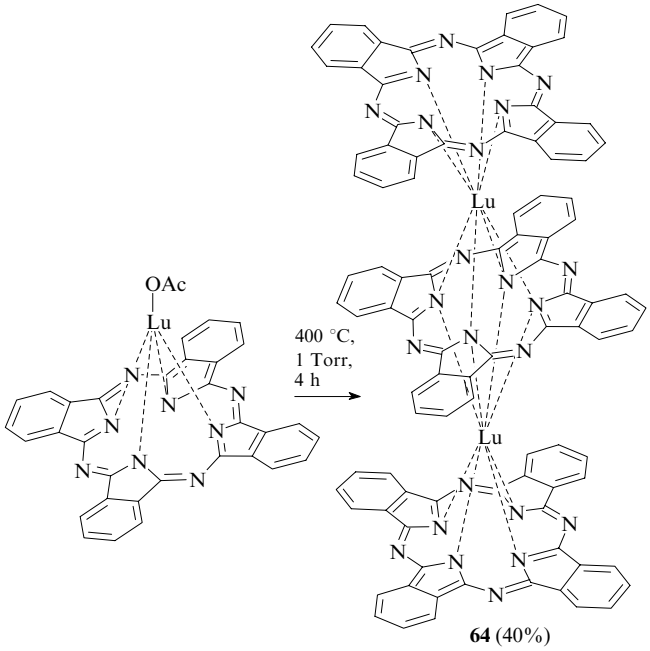


70 **71**, **72**

71: X = CH, R = Me, R′ = Et; Ln = Ce, Eu;
72: X = N, R = R′ = Pr^n, Ln = Eu.

3. Vacuum sublimation of monophthalocyanine complex

An unusual method for the synthesis of unsubstituted lutetium trisphthalocyanine **64** (R = H) was proposed.[154] Heating of PcLu(OAc)·2 H_2O *in vacuo* (~1 Torr) at 400 °C for 4 h yielded the target product in 40% yield.



64 (40%)

It is noteworthy that the formation of triple-decker complexes of the type **64** upon vacuum sublimation (10^{-6} Torr) of the products of template reaction of phthalonitrile with lanthanide acetates (Ln = La, Nd, Eu, Gd, Dy, Er, Yb, Lu) at 300 – 420 °C was assumed back in 1986.[142] However, by that time the structure of trisphthalocyanine complexes was not unambiguously proved (see Section IV.2), which was an essential obstacle hampering correct interpretation of many experimental facts and development of targeted synthesis of these compounds.

Unique triple-decker cadmium complex **73** was prepared by Cook and co-workers[155] by slow crystallisation of cadmium phthalocyanine from a THF – MeOH mixture (Fig. 3). The structure of complex **73** was proved by X-ray diffraction. The complex was poorly stable, as was indicated by the absence of the molecular ion peak in the

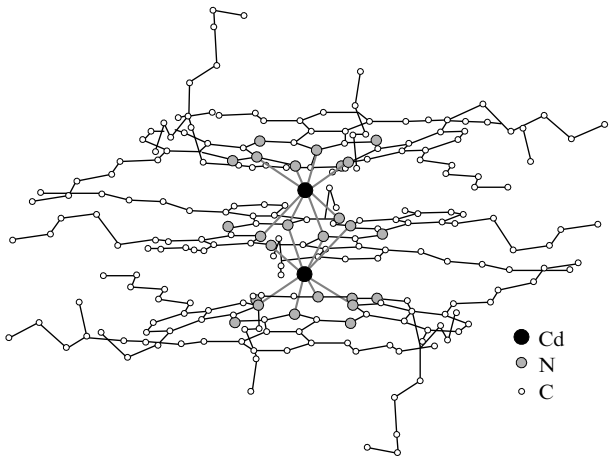


Figure 3. Crystal structure of n-hexyl-substituted cadmium trisphthalocyanine **73**.[155]

MALDI-TOF mass spectrum. Moreover, neutral divalent cadmium trisphthalocyanine should contain two additional protons, *i.e.*, its composition should be $[2\,H]\cdot[Pc_3Cd_2]$; however, neither the protons nor other counter-ions were found in the structure of the complex. No examples of synthesis of sandwich complexes of lanthanides and other metals by a similar method were reported.

V. Synthesis of heteroleptic and mixed-ligand double-decker complexes

Five types of double-decker lanthanide complexes containing various tetrapyrrole ligands have now been synthesised. Three of these are heteroleptic complexes (phthalocyanine – phthalocyanine, phthalocyanine – naphthalocyanine or porphyrin – porphyrin complexes) and two other are mixed-ligand complexes (phthalocyanine – porphyrin, naphthalocyanine – porphyrin).

The existing approaches to the synthesis of heteroleptic and mixed-ligand lanthanide complexes with phthalocyanines can be divided into four groups depending on the types of reactants: (i) reaction of two different phthalonitriles in the presence of lanthanide salts; (ii) reaction of single-decker lanthanide complexes with substituted or unsubstituted phthalonitriles or their analogues; (iii) reaction of two different phthalocyanine ligands or their metal (usually lithium) derivatives with lanthanide salts; (iv) reaction of single-decker lanthanide complexes with free ligands or their metal derivatives. The first two approaches should be classified as template synthesis, and the last two approaches as direct synthesis.

This part of the review is classified according to the type of target complexes. The synthetic methods used to prepare each class of structures are considered in relevant sections in the order of increasing efficiency according to published data.

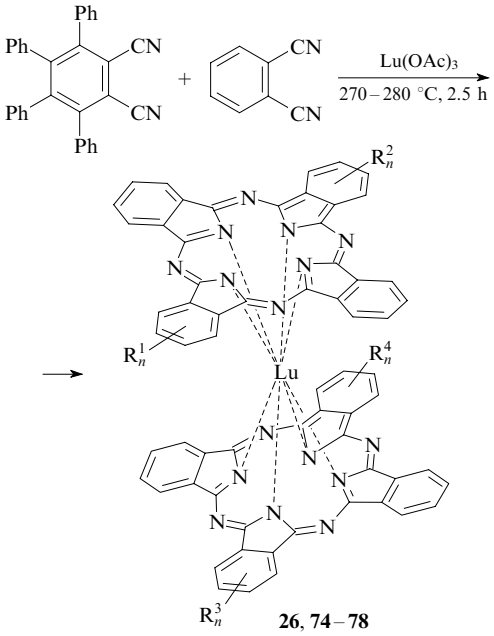
1. Phthalocyanine – phthalocyanine complexes

The simplest and still the most efficient method for the preparation of heteroleptic phthalocyanine complexes is the template reaction of two different phthalonitriles in the presence of a lanthanide salt. Formally, this reaction is expected to give nine randomers of bisphthalocyanine complexes. In addition, if two to six isoindole fragments differ from the other ones, up to 17 structural isomers may be formed. Thus, all other conditions being the same (approximately equal reactivities of the reacting dinitriles, the absence of steric factors, *etc.*), the total number of potential complexes reaches 21.

Liu *et al.*[156] fused an equimolar mixture of 4-propoxyphthalonitrile and 4-*tert*-butylphthalonitrile with lutetium acetate at 270 – 280 °C for 4 h and the mixture thus formed was chromatographed. A fraction of bisphthalocyanine positional isomers with four *tert*-butyl and four propoxy groups was thus isolated in 4.6% yield and characterised by FAB mass spectrometry.

Tomilova *et al.*[157] used a strategy of sterically targeted synthesis, which markedly reduced the number of reaction products, which were isolated in a pure state. The reaction of unsubstituted and tetraphenyl-substituted phthalonitriles (the latter creates steric restrictions to template condensation) in the presence of lutetium acetate (Scheme 9) afforded three homoleptic (**26**, **74**, **75**) and three heteroleptic (**76** – **78**) complexes. All six products obtained were separated by TLC and characterised by elemental analysis and UV/Vis spectroscopy data.

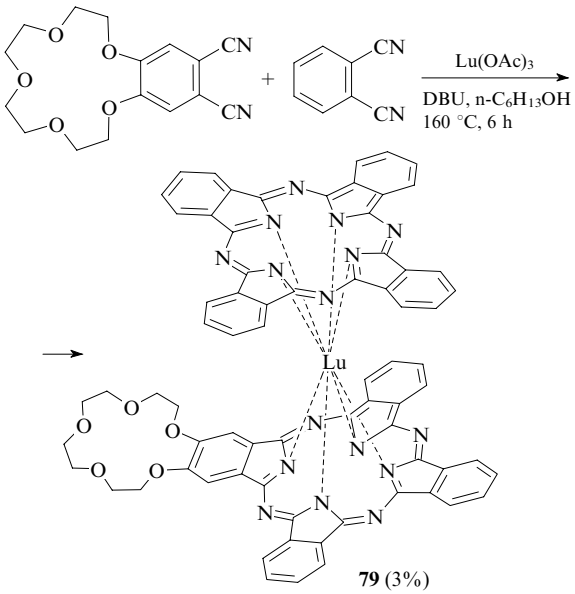
Scheme 9



26, **74** – **78**

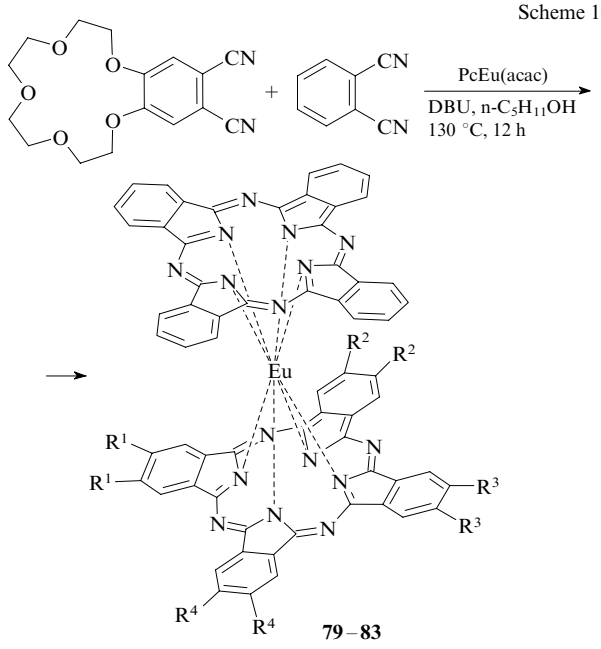
26: $R^1 = R^2 = R^3 = R^4 = H$;
74: $R^1_4 = R^3_4 = Ph_4$, $R^2 = R^4 = H$;
75: $R^1_4 = R^2_4 = R^3_4 = R^4_4 = Ph_4$;
76: $R^1 = R^2 = R^4 = H$, $R^3_4 = Ph_4$;
77: $R^1 = R^2 = H$, $R^3_4 = R^4_4 = Ph_4$;
78: $R^1_4 = R^3_4 = R^4_4 = Ph_4$, $R^2 = H$.

The template reaction of unsubstituted and crown-substituted phthalonitriles with lutetium acetate was carried out [158, 159] in boiling n-hexanol in the presence of DBU. This gave a multicomponent mixture containing, along with Ln bisphthalocyanines, single-decker complexes, starting dinitriles and their oligomerisation products. The separation of this mixture by multistep chromatography gave compound **79** in 3% yield. Subsequently, the interaction of the crown-ether substituent of this complex with alkali metal ions was studied.[159]



79 (3%)

Scheme 10



79–**83**

79: $R^1–R^1 = O(CH_2CH_2O)_4$, $R^2 = R^3 = R^4 = H$ (13%);
80: $R^1–R^1 = R^3–R^3 = O(CH_2CH_2O)_4$, $R^2 = R^4 = H$ (5%);
81: $R^1–R^1 = R^2–R^2 = O(CH_2CH_2O)_4$, $R^3 = R^4 = H$ (8%);
82: $R^1–R^1 = R^2–R^2 = R^3–R^3 = O(CH_2CH_2O)_4$, $R^4 = H$ (12%);
83: $R^1–R^1 = R^2–R^2 = R^3–R^3 = R^4–R^4 = O(CH_2CH_2O)_4$ (11%).

The reaction of single-decker lanthanide complexes with dinitriles is a more selective method for the synthesis of heteroleptic metal bisphthalocyanines. Thus the reaction of unsubstituted and crown phthalonitrile with europium monophthalocyanine (Scheme 10) afforded compound **79** in 13% yield.[160] In addition to this product, heteroleptic bisphthalocyanine complexes **80**–**83** were isolated by chromatography of the reaction mixture on silica gel (elution with $CHCl_3$) and characterised by spectral methods.

The reaction of monophthalocyanine complexes with nitriles of one type was used to prepare heteroleptic complexes **83**–**97** (Scheme 11, Table 5).

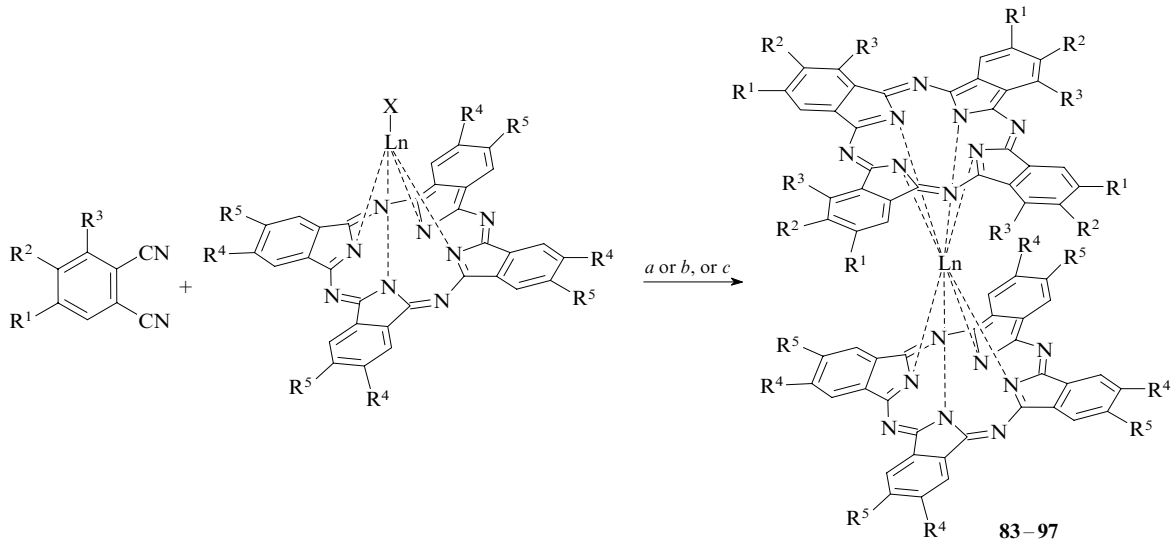
Lanthanide phthalocyanines **83**–**90** were also prepared by fusing the reactants at high (usually 20-fold) molar excess of the corresponding nitriles, which act simultaneously as the reactant and the medium (see Scheme 11, conditions *a*).[19, 20, 22, 30, 161, 162]

According to published data,[19–21] heteroleptic complexes containing electron-withdrawing (**85**–**87**) and bulky (**88**–**90**) substituents in the ligands are formed in yields from 28% to 75% (see Table 5). The structures of the compounds obtained were proved by elemental analysis data, IR spectra and UV/Vis spectra; however, no studies based on mass spectrometry or NMR spectroscopy are presented in these publications. In addition, some of the complexes obtained do not show the bathochromic shift of Q absorption bands in the UV/Vis spectra typical of lanthanide bisphthalocyanines on going from the end to the beginning of the lanthanide series. Thus, despite the high yields of the target products, the proof of the product structure given by the authors is not sufficiently convincing.

Heteroleptic bisphthalocyanine complexes are also formed in solutions of alcohols under the action of DBU (see Scheme 11, conditions *b*). A number of publications[37, 76, 85, 93, 163–165] reported the synthesis and reliable characterisation of complexes **83**, **91**–**96** containing alkyl or alkoxyl substituents of different nature. The yields of target products were 7.5%–43% depending on the substituent bulk and the lanthanide nature (see Table 5). Note that compounds **96** represent[164, 165] a unique example of chiral bisphthalocyanine complex. The presence of a bulky substituent in the α-position of the benzene ring results in the formation of a ligand with only C_{4h} symmetry and, as a consequence, in the existence of compound **96** as a pair of enantiomers. When lithium pentoxide prepared *in situ* by dissolution of metallic lithium in pentanol was used as the base (see Scheme 11, conditions *c*), lutetium bisphthalocyanine **97** was obtained in 31.6% yield as a mixture of structural isomers.[156]

Special mention should be made of the unique method used[37] to synthesise heteroleptic complex **83** (Ln = La). Since it is impossible to prepare lanthanum monophthalocyanine,[123] the synthesis of compound **83** cannot be performed according to Scheme 11. Moreover, an attempt of random reaction between unsubstituted and 15-crown-5-substituted lithium phthalocyanines in the presence of $La(acac)_3 \cdot H_2O$ has also failed. Therefore, unsubstituted

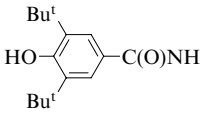
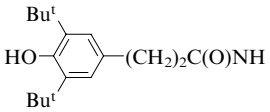
Scheme 11



83–**97**

(*a*) 240–310 °C, 0.5–3 h; (*b*) DBU, solvent, 130–160 °C, 2–20 h; (*c*) Li, n-$C_5H_{11}OH$, 130 °C, 17 h.

Table 5. Synthesis of heteroleptic lanthanide bisphthalocyanines according to Scheme 11.

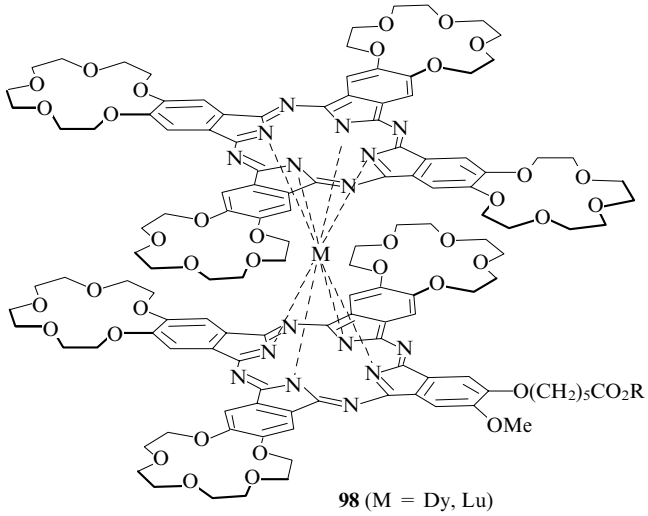
Compound [a]	R^1	R^2	R^4	R^5	Ln	X	Conditions	Solvent	Yield (%)	Ref.
83	$O(CH_2CH_2O)_4$		H	H	Lu	AcO	*a*	–	14	161
	H	H	$O(CH_2CH_2O)_4$		Sm, Dy, Tm	AcO	*b*	see [b]	31–43	37
84	H	H	H	Bu^t	Lu	Cl	*a*	–	–	30, 162
85	H	H	H	Cl	Sm, Ho, Er, Lu, Y	Cl	*a*	–	28–61	19, 20
			H	Bu^n	Er	Cl	*a*	–	28–61	19, 20
86	H	H	H	Br	Er, Y	Cl	*a*	–	43–55	20
			H	Bu^n	Er	Cl	*a*	–	43–55	20
87	H	NO_2	H	H	Nd, Sm, Ho, Er, Lu, Y	Cl	*a*	–	31–57	19, 20
88	H	H	H		Nd, Eu, Lu	AcO, HCO_2	*a*	–	62–75	22
89	H	H	H		Nd, Eu, Lu	AcO, HCO_2	*a*	–	52–67	22
90	**H**	**H**	H	$Ph_2CHC(O)NH$	Nd, Eu, Lu	AcO, HCO_2	*a*	–	56–71	22
91	n-C_7H_{15}	n-C_7H_{15}	H	H	Eu, Y	acac	*b*	n-$C_5H_{11}OH$	32, 28	76, 163
92	n-$C_5H_{11}O$	n-$C_5H_{11}O$	H	H	Eu, Y	acac	*b*	n-$C_5H_{11}OH$	27, 25	76, 163
93	PhO	PhO	H	H	Eu, Ho, Lu	acac	*b*	n-$C_5H_{11}OH$	26–29	93
94	PhS	PhS	H	H	Eu	acac	*b*	n-$C_5H_{11}OH$	30	93
95	$MeO(CH_2CH_2O)_3$	$MeO(CH_2CH_2O)_3$	$O(CH_2CH_2O)_4$		Lu	AcO	*b*	n-$C_6H_{13}OH$	7.5	85
96	H	H	H	H	Sm–Lu, Y	acac	*b*	n-$C_5H_{11}OH$	15–31	164, 165
97	H	Bu^t	H	Pr^nO	Lu	AcO	*c*	n-$C_5H_{11}OH$	31.6	156

[a] In compound **96**, $R^3 = Et_2HCO$, in other cases, $R^3 = H$; [b] 1-$ClC_{10}H_{17}$–Bu^nOH, 1 : 1 (vol.) as the solvent.

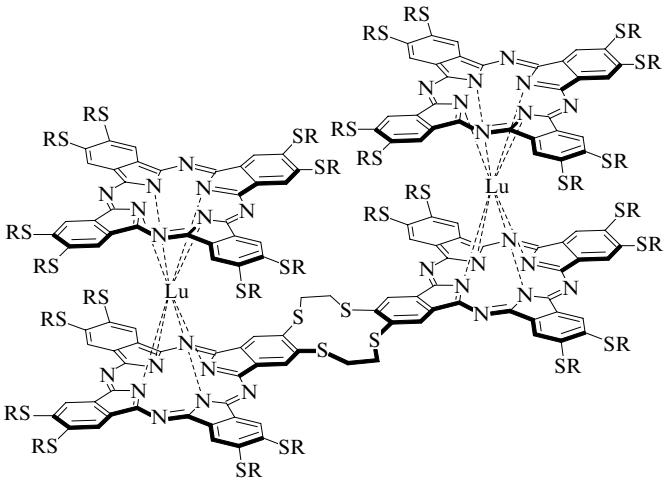
lanthanum bisphthalocyanine and the 15-crown-5-substituted ligand were made to react to prepare the trisphthalocyanine complex $[(R_4Pc^{2-})La^{3+}(Pc^{2-})La^{3+}(Pc^{2-})]$ (R is 15-crown-5 ether fragment), which decomposed on storage in $CHCl_3$ to give product **83** in a overall yield of 31%. Presumably, compound **83** (Ln = La) is formed according to Scheme 6 (conditions *b*), because it is by this method that the homoleptic lanthanum bisphthalocyanine **36** was prepared in high yield [123] (see Table 4). However, the authors [33] did not mention this reaction, probably, due to the formation of a complex product mixture.

According to Scheme 11, dysprosium and lutetium bisphthalocyanines **98** (conditions *b*, n-$C_6H_{13}OH$ as the solvent) [166] and bi- (**99**) and trinuclear (**100**) lutetium complexes (conditions *c*) [167–169] were obtained.

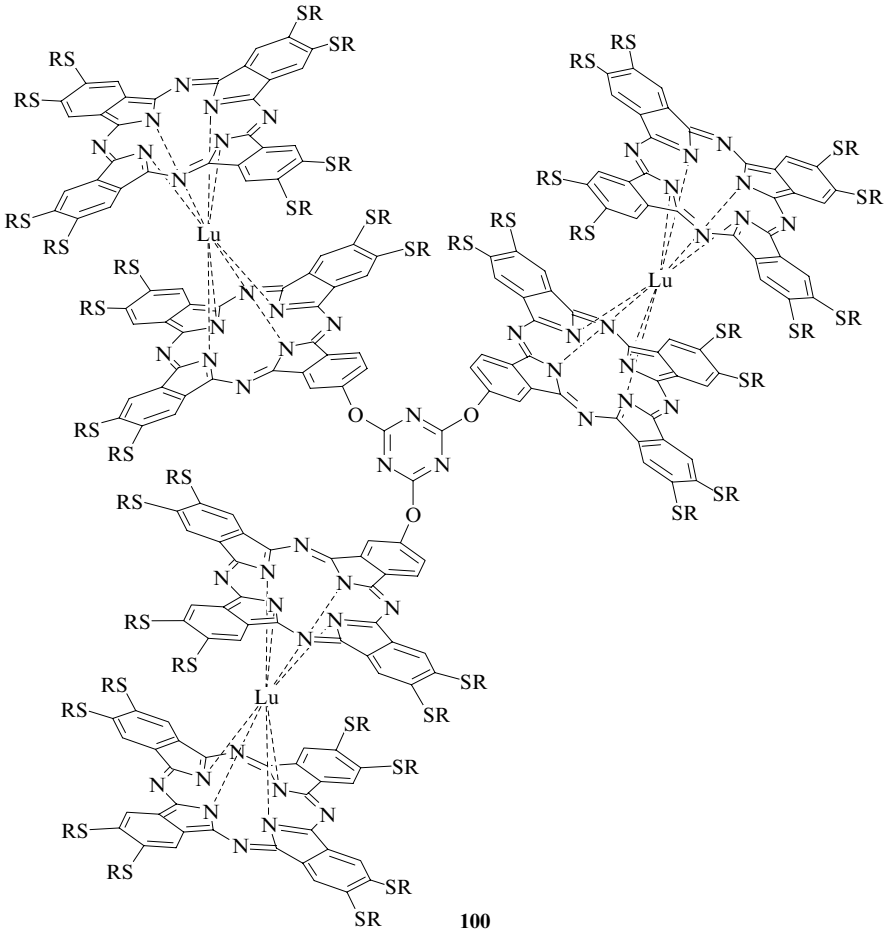
The initial Ln monophthalocyanines used in these reactions were unsymmetrical complexes based on A_3B type ligands obtained in no more than 20% yields by random condensation of appropriate nitriles [166] or diiminoisoindolines.[167–169] After the formation of heteroleptic bisphthalocyanine complexes, the yields of compounds **98** were 10%–20%,[166] those of **99** and **100** were 34.4% and 41%, respectively.[167–169] However, the overall yield of compounds **98**–**100** over two steps only slightly exceeded 8%. In addition, unfortunately, no data from mass spectrometry



98 (M = Dy, Lu)



99



100

R = n-C_6H_{13}.

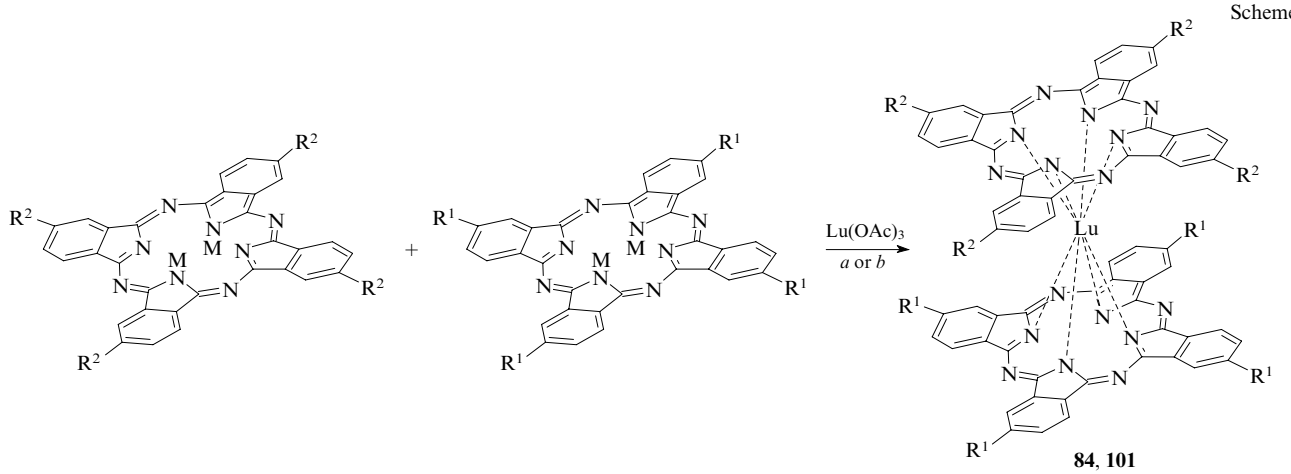
were reported for **99** and **100**, which casts doubt on the reliability of the presented structures.

Heteroleptic bisphthalocyanine complexes **84** and **101** were synthesised by the reaction of the ligands with lutetium acetate [170–172] (Scheme 12). For preparing complex **84**, a reactant mixture was exposed to microwave radiation in the presence of DBU;[170] however, the researchers cited did not indicate the product yield and the UV/Vis spectrum rather corresponds to a monophthalocyanine complex. The reliably characterised complex **84** was prepared [171] in 20% yield by refluxing a mixture of lithium salts of the ligands and lutetium acetate in 1-ClN for 1 h (see Scheme 12, conditions *b*). The replacement of chloronaphthalene by basic quinoline and increase in the reaction time to 24 h resulted in the synthesis of amphiphilic bisphthalocyanine complex **101** possessing mesogenic properties (yield 47%).[172]

Yet another route to heteroleptic bisphthalocyanine complexes is the reaction of single-decker lanthanide complex with the appropriate ligands in an aprotic or protic solvent (Scheme 13, conditions *a*). This reaction first carried out by Japanese scientists [173] in 1993 is also an example of the raise-by-one-story method, because the diphthalocyanine complex is formed in one step during the synthesis.

According to Scheme 13, complexes **83**,[159, 173, 174] **96** [165] and **102** [175, 176] were obtained; however, the conditions of synthesis proposed by the authors provided the target compounds in yields < 32%. Moreover, as in all cases described above (see Schemes 9–12), the formation of heteroleptic products is accompanied by the formation of approximately equal amounts of the corresponding homoleptic bisphthalocyanine complexes, which accounts for the low yields of the target compounds. In another work,[177] the formation of by-products was avoided by changing the reaction conditions (see Scheme 13, conditions *b*, *c*) in the synthesis of bisphthalocyanines **103** and **104** containing ligands with both electron-donating (Bu^n) and electron-withdrawing (Cl) substituents. It was shown that conditions *b* are the conditions of choice for the formation of

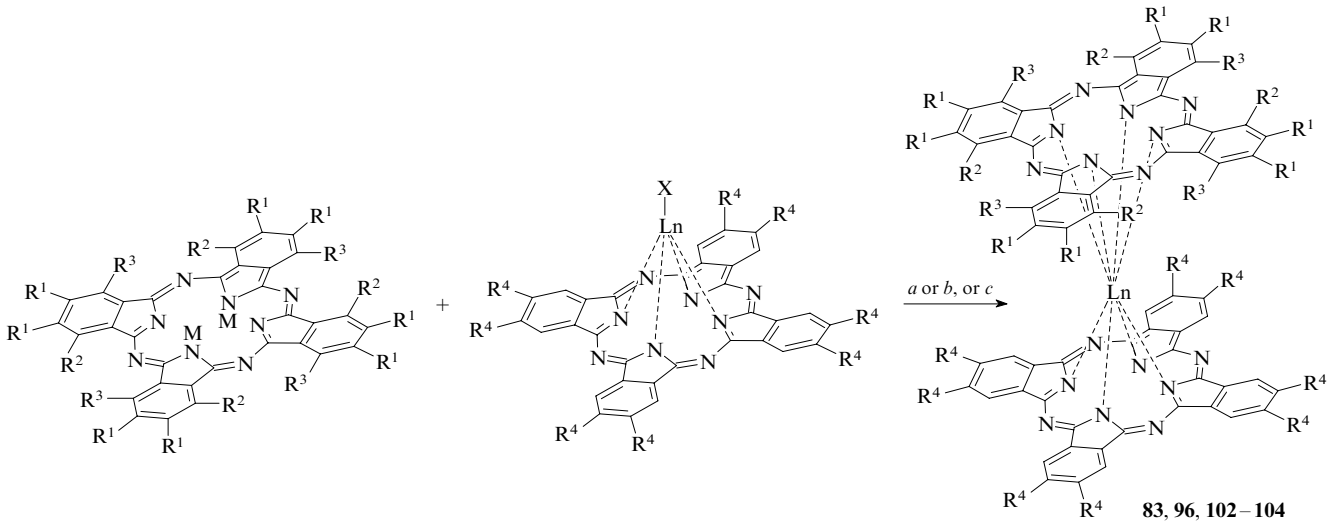
Scheme 12



84, **101**

M = H, Li; R^1 = H, R^2 = Bu^t (**84**); R^1 = $MeO(CH_2CH_2O)_8$, R^2 = n-$C_{12}H_{25}O$ (**101**);
(*a*) DBU, microwave radiation (240 W), 10 min; (*b*) quinoline or 1-$ClC_{10}H_7$, 240–260 °C, 1–24 h.

Scheme 13

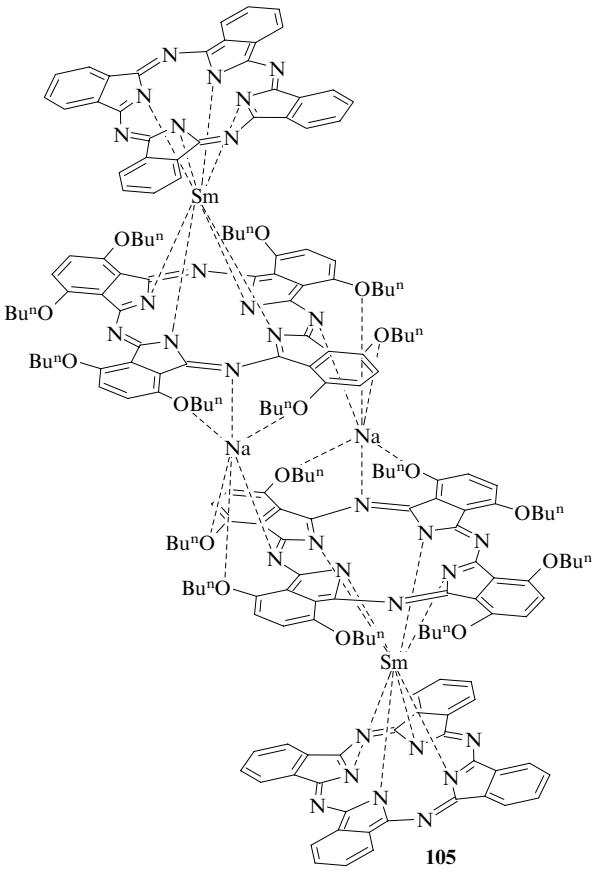


83, **96**, **102**–**104**

83: R^1–R^1 = $O(CH_2CH_2O)_4$, R^2 = R^3 = R^4 = H, Ln = Lu; **96**: R^1 = R^2 = R^4 = H, R^3 = Et_2HCO; Ln = Sm–Lu, Y;
102: R^1 = R^4 = H, R^2 = R^3 = Bu^nO; Ln = Sm, Eu, Gd; **103**: R^1 = Bu^n, R^2 = R^3 = R^4 = H; Ln = Eu, Lu;
104: R^1 = Bu^n, R^2 = R^3 = H, R^4 = Cl, X = OAc; Ln = Eu, Lu; , X = OAc, acac;
(*a*) n-$C_8H_{17}OH$ or 1-$ClC_{10}H_7$, 190–260 °C, 8 h; (*b*) DBU, TCB–n-$C_{16}H_{33}OH$ [50 : 1 (vol.)], 220 °C, 2 h; (*c*) TCB–n-$C_{16}H_{33}OH$ [50 : 1 (vol.)], 220 °C.

europium complexes, while lutetium complexes are formed selectively under conditions *c*. The yields of compounds **103** and **104** are 71% – 85%.

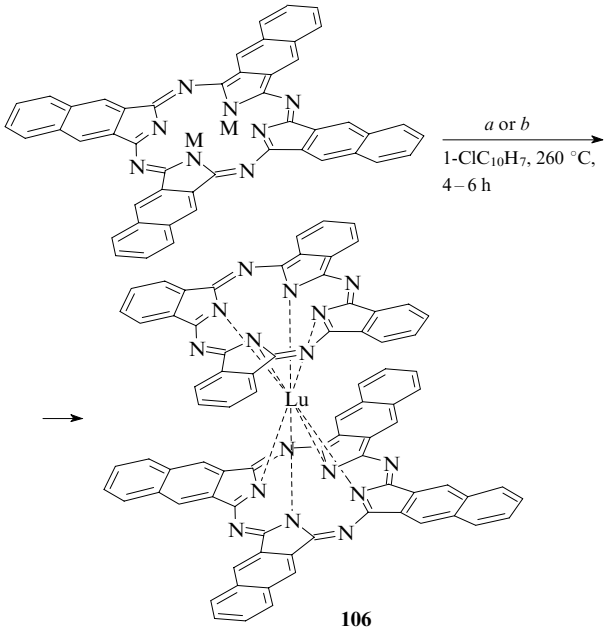
Among the compounds obtained by Scheme 13, complexes **102** with Bu^nO substituents in the α- positions of one phthalocyanine ligand deserve special note. Owing to this structural feature, these compounds were converted by treatment with sodium hydroxide into the so-called 'pseudo-quadruple-decker' complexes **105**,[175] which are ionic compounds with the single-electron-reduced diphthalocyanine acting as the anion.



105

2. Phthalocyanine – naphthalocyanine complexes

The first mention of the phthalocyanine – naphthalocyanine complexes dates back to 1986 (Subbotin *et al.*[162]). Relatively few complexes containing both phthalocyanine and naphthalocyanine macrocycles are known, first of all, due to insufficiently developed methods for their synthesis. The reaction of equimolar amounts of phthalonitrile and 2,3-naphthalonitrile in the presence of lutetium salts induced by DBU in boiling n-hexanol yielded [178] complexes with the following ratios of isoindole to benzoisoindole fragments [the values in parentheses are their contents (%)]: 8 : 0 (1), 7 : 1 (5.5) and a mixture of randomers 6 : 2 (20), 5 : 3 (37), 4 : 4 (28), 3 : 5 (7), 2 : 6 (1.5). The heteroleptic complex NcLuPc (**106**) could not be isolated from this mixture.[178] Somewhat later, this compound was synthesised by direct reaction of alkali metal naphthalocyanine with lutetium monophthalocyanine [179] or with lithium phthalocyanine in the presence of lutetium acetate.[131] However, in both cases, the authors noted the formation of considerable amounts of homoleptic products, the yield of complex **106** being not higher than 17%.

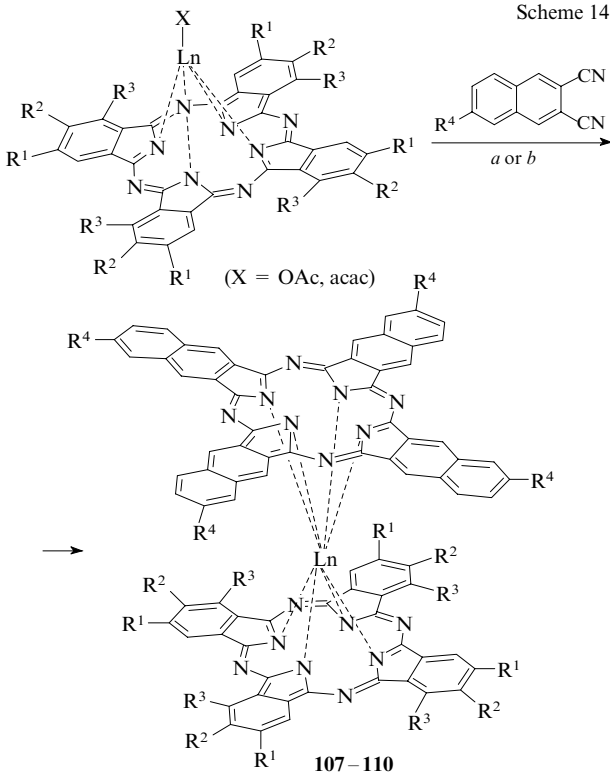


106

M = Li, Na; (*a*) PcLuOAc; (*b*) $PcLi_2$, $Lu(OAc)_3$.

By analogy with heteroleptic bisphthalocyanine complexes (see Section V.1, Scheme 11), substituted complexes **107 – 110** were obtained. The synthesis was carried out by the template method starting from lanthanide monophthalocyanines in a melt [162] or in a solution of naphthalonitriles in n-octanol (Scheme 14).[180] The selectivity of this approach proved to be rather low: the yields of compounds **107 – 110**

Scheme 14



107 – 110

107: $R^1 = R^2 = R^3 = H$, $R^4 = Bu^t$; Ln = Lu, Sm;
108: $R^1 = Et_2HCO$, $R^2 = R^3 = R^4 = H$, Ln = Sm;
109: $R^1 = R^2 = n\text{-}C_8H_{17}O$, $R^3 = R^4 = H$, Ln = Sm;
110: $R^1 = R^2 = R^4 = H$, $R^3 = Et_2HCO$; Ln = Sm, Eu, Y;
(*a*) 250 – 270 °C, 1.5 – 2 h; (*b*) DBU, $n\text{-}C_8H_{17}OH$, 190 °C, 7 h.

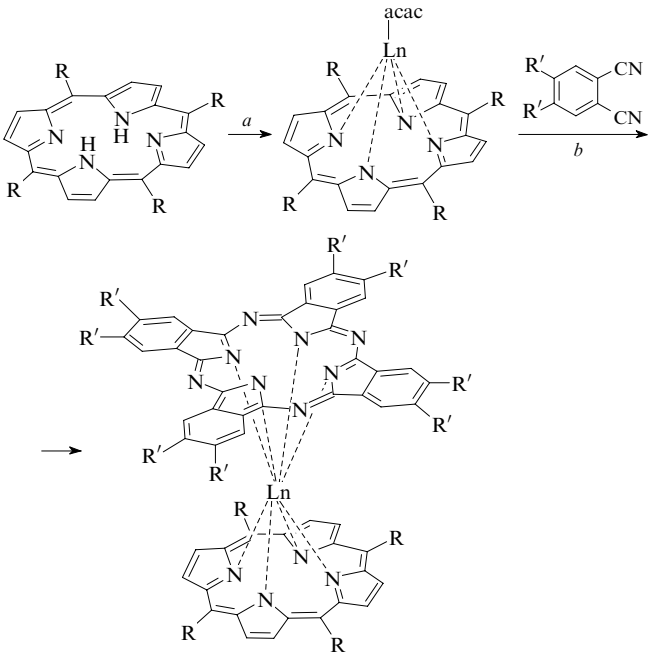
were 25% – 59%, which is due not only to the formation of homoleptic by-products but also to oligomerisation and resinification of the starting nitriles. Note that chiral compound **110**, by analogy with bisphthalocyanine complexes **96** (see Section V.1), exists as a mixture of enantiomers.[180]

3. Phthalocyanine – porphyrin complexes

The main specific feature of the synthesis of porphyrin complexes, in particular, mixed-ligand sandwich lanthanide complexes, is introduction of a porphyrin fragment only as a formed ligand. As in the case of heteroleptic bisphthalocyanine complexes (see Section V.1), phthalocyanine – porphyrin complexes are prepared using template and direct synthetic strategies.

Thus metallation of free porphyrins with lanthanide salts in TCB or n-octanol leads to single-decker complexes, which then react with phthalonitriles under the action of DBU in alcoholic media[181–183] to give compounds **111** – **121** (Scheme 15). The product yields ranging from 2% to 69% depend on both the lanthanide nature and substituents in the ligands. For example, in the case of complexes **116**, the highest yields (up to 36%) were noted[183] for the middle of the lanthanide series; in the authors' opinion, the ionic radii of these elements specify the optimal distance between the ligands, thus ensuring the most efficient stabilising overlap of their π-orbitals. Meanwhile, the introduction of bulky substituents into the peripheral positions of the macrocycles results in a regular decrease in the yields of the target compounds.[181]

Scheme 15



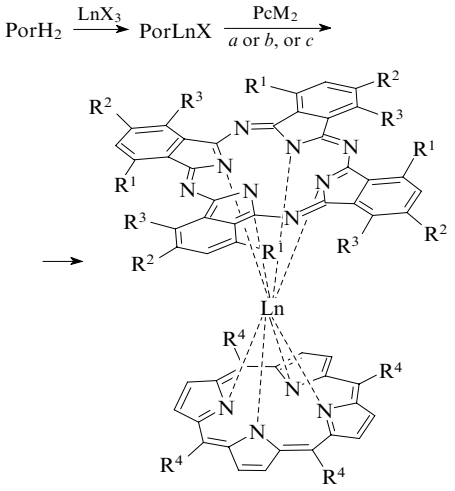
111 – **121**

R = Ph: Ln = Eu, Y; R′ = H (**111**), n-C_7H_{15} (**112**); Ln = Eu, R′ – R′ = O(CH_2CH_2O)$_4$ (**113**); R = 4-Py, Ln = Eu, Y: R′ = H (**114**),
n-C_7H_{15} (**115**); R = 4-ClC_6H_4: Ln = La, Nd, Pr, Sm – Lu, Y; R′ = H (**116**); Ln = Eu, R′ = n-C_7H_{15} (**117**);
R = 4-$MeOC_6H_4$, Ln = Eu: R′ = H (**118**), n-C_7H_{15} (**119**);
R = 4-$Bu^tC_6H_4$, Ln = Eu: R′ = H (**120**), n-C_7H_{15} (**121**);
(*a*) Ln(acac)$_3$, TCB or n-$C_8H_{17}OH$, 190 – 220 °C, 4 – 6 h;
(*b*) DBU, n-$C_5H_{11}OH$ or n-$C_8H_{17}OH$, 130 – 190 °C, 12 h.

Direct reaction of single-decker lanthanide porphyrins with free phthalocyanine or its lithium derivatives is generally more efficient than the template synthesis and gives rise to mixed-ligand complexes **111**,[184] **114**,[185] **122** – **127**[186–189] (Scheme 16) in yields ranging from low to high. Thus compounds **111** and **114** were synthesised[184, 185] in TCB in 60% – 85% yields and complexes **122** and **123** were prepared in boiling n-octanol[186] in 24% – 61% yields (see Scheme 16, conditions *b*).

For europium complex **122**, the first nanotubes formed from sandwich phthalocyanine-containing lanthanide complexes were prepared using a nanoporous anodised alumina as the template.[187]

Scheme 16



111, **114**, **122** – **127**

M = H, Li; X = acac, OAc, Cl, I;
111: $R^1 = R^2 = R^3$ = H, R^4 = Ph; Ln = La, Pr, Nd, Eu, Gd, Er, Lu, Y;
114: $R^1 = R^2 = R^3$ = H, R^4 = 4-Py; Ln = Ce, Eu, Gd;
122: $R^1 = R^2$ = H, R^3 = Et_2HCO, R^4 = 4-ClC_6H_4; Ln = Sm, Eu, Y;
123: $R^1 = R^3$ = Bu^nO, R^2 = H, R^4 = 4-ClC_6H_4, Ln = Y;
124: $R^1 = R^3$ = H, R^2 = Bu^t, R^4 = 4-$Bu^tC_6H_4$, Ln = Lu;
125: $R^1 = R^2 = R^3$ = H, R^4 = 4-MeC_6H_4, Ln = Eu;
126: $R^1 = R^3$ = H, R^2 = Bu^t, R^4 = 4-MeC_6H_4; Ln = Ce, Eu;
127: $R^1 = R^3$ = H, R^2 = Bu^t, R^4 = n-C_5H_{11}, Ln = Ce;
(*a*) DBU, microwave radiation (440 W), 10 min; (*b*) TCB or n-$C_8H_{17}OH$, 190 – 220 °C, 8 – 12 h; (*c*) LiN($SiMe_3$)$_2$, diglyme, 160 °C, 18 h.

Complex **124** was synthesised using microwave radiation (see Scheme 16, conditions *a*), the product yield being 66%.[188] Compounds **125** – **127** were prepared by, first, treating europium and cerium halides with two equivalents of LiN($SiMe_3$)$_2$ in diglyme. The salts LnX[N($SiMe_3$)$_2$]$_2$ (Ln = Ce, Eu; X = Cl, I) thus formed were made to react *in situ* with free porphyrins to give single-decker complexes.[189] The subsequent reaction of lanthanide monoporphyrins with unsubstituted or tetra(*tert*-butyl)-substituted lithium phthalocyanine in boiling diglyme resulted in mixed-ligand products **125** – **127** in moderate to high yields (38% – 94%) (see Scheme 16, conditions *c*).

An alternative procedure of direct synthesis (Scheme 17) implies the opposite sequence of complexation stages. The reaction of lithium phthalocyanine with lanthanide acetylacetonates results in single-decker complexes, which react *in situ* with free porphyrins to give mixed-ligand derivatives.

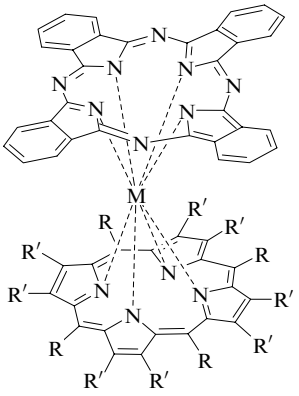
Compounds **111** [184, 190] and **114** [97] were prepared in this way for the first half of the lanthanide series.

Scheme 17

$PcLi_2 \xrightarrow[\text{TCB, 120 °C, 3–4 h}]{Ln(acac)_3} PcLn(acac) \xrightarrow[\text{TCB, 220 °C, 8–12 h}]{PorH_2} \mathbf{111}, \mathbf{114}$ (36%–69%)

Ln = La–Nd, Eu, Gd.

Of special note is the fact that direct synthesis gives sandwich complexes of trivalent metals as anionic species, which are gradually transformed into neutral paramagnetic species under the action of oxidants, for example, O_2. The stability of the anionic species decreases in the series of alike lanthanide complexes with a decrease in the ionic radii of the elements.[184] Conversely, tetravalent metals form only neutral diamagnetic double-decker compounds with phthalocyanines and their analogues. Thus direct reaction of metal monoporphyrins $PorMCl_2$ (M = U, Th, Zr, Hf) with sodium phthalocyanine in boiling 1-chloronaphthalene afforded [129, 191] complexes **111**, **125** and **128** with tetravalent metals.



111, **125**, **128**

111: R = Ph, R′ = H; M = U, Th, Zr, Hf;
125: R = 4-MeC_6H_4, R′ = H; M = U, Th;
128: R = H, R′ = Et; M = U, Th, Zr, Hf.

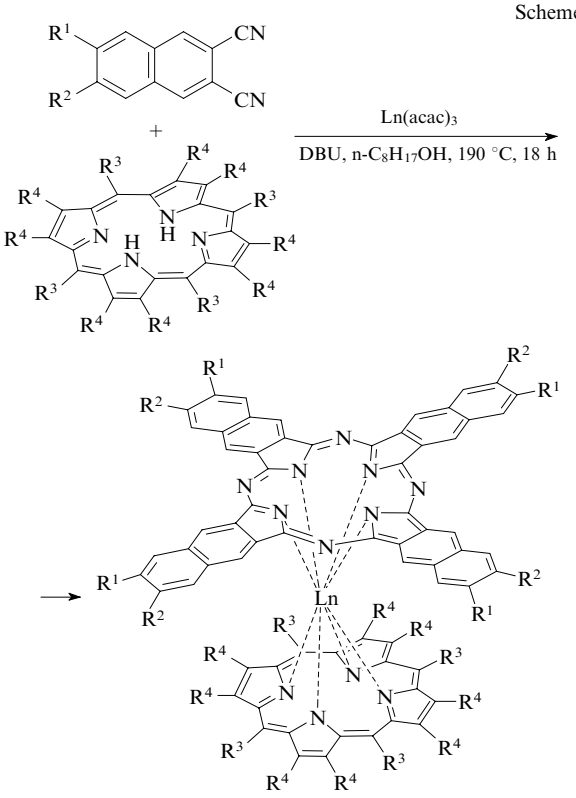
In the case of uranium and thorium, the synthesis is carried out for 40 h (the yields of mixed-ligand products are equal to 20%–45%),[129] whereas zirconium and hafnium give the target compounds as soon as 3 h after onset of the reaction (yields 25%–69%).[191]

4. Naphthalocyanine–porphyrin complexes

The first double-decker complexes containing naphthalocyanine and porphyrin ligands, *viz*., compounds **129** and **130**, were prepared by Jiang *et al*.[192] in 1999 by template tetramerisation of unsubstituted and 6,7-bisdodecylthio-substituted naphthalonitriles in the presence of europium monoporphyrins (Scheme 18) in 52% and 69% yields, respectively.

Jiang *et al*.[192] prepared monoporphyrin complexes by metallation of the ligand with europium acetylacetonate in boiling TCB, which was then evaporated. The subsequent reaction with naphthalonitriles was carried out according to Scheme 18. More recently, it was demonstrated [83, 193–195] that direct reaction between free porphyrin, naphthalonitrile and a lanthanide salt (see Scheme 18) gives mixed-ligand complexes **131**–**133** in comparable yields. For compounds **131** [193] and **133**,[195] the trend for a decrease in the yields from 73% to 29% and from 45% to 21%, respectively, following a decrease in the metal ionic radii was noted and attributed to enhancement of the steric effects.

Scheme 18



129–**133**

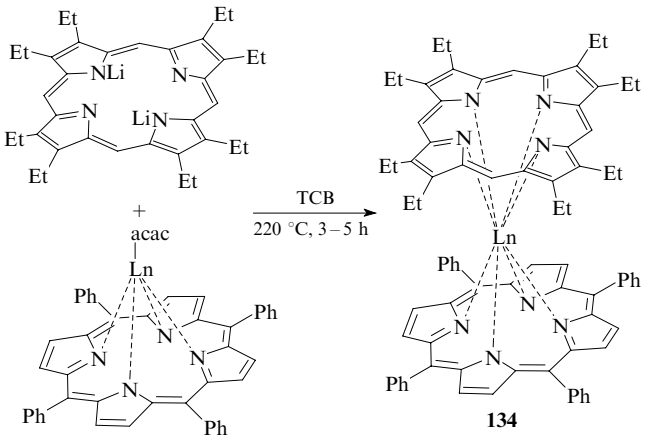
129: $R^1 = R^2 = R^4 = H$, R^3 = 4-Py, Ln = Eu;
130: $R^1 = R^2$ = n-$C_{12}H_{25}S$, R^3 = 4-Py, R^4 = H, Ln = Eu;
131: $R^1 = R^2 = R^4 = H$, R^3 = 4-$Bu^tC_6H_4$; Ln = La, Ce, Pr, Nd, Sm–Tm, Y;
132: $R^1 = R^3 = H$, $R^2 = Bu^t$, R^4 = 4-ClC_6H_4, Ln = Eu;
133: $R^1 = R^2 = R^3 = H$, R^4 = Et; Ln = La, Ce, Pr, Nd, Sm–Lu, Y.

Notably, all of the studies of naphthalocyanine–porphyrin dimers have been reported so far by one research group. This may account for the use of only one synthetic approach for the synthesis of this type of complex.

5. Porphyrin–porphyrin complexes

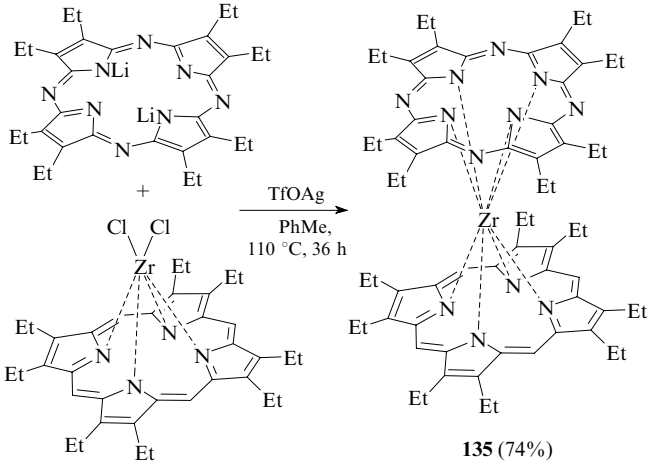
Synthesis of heteroleptic lanthanide diporphyrins is based on direct reaction of single-decker metal complexes with dianions of the required ligands.

The reaction of Ln *meso*-tetraphenylporphyrin (TPP)Ln(acac) with lithium octaethylporphyrin obtained *in situ* by treatment of metal-free porphyrin $(OEP)H_2$ with butyllithium [196] results in compounds **134** (yield 5%–35%) [196, 197] and homoleptic derivatives $(TPP)_2Ln$, $(OEP)_2Ln$ and $(OEP)_3Ln_2$. The separation of this mixture containing also non-consumed starting compounds was carried out by a four-stage chromatography on basic alumina using several types of eluents. Under similar conditions, tetravalent metal complexes (OEP)(TPP)M (M = U, Th) were prepared,[129] the process being over in 40 h and the yields of uranium and thorium diporphyrins after chromatographic purification being 30% and 16%, respectively.



Ln = Nd, Sm–Lu.

It was shown [137] that complexation involving porphyrins occurs more efficiently in the presence of silver triflate. By exchange reaction, $(OEP)ZrCl_2$ was converted into zirconium monoporphyrin $(OEP)Zr(OTf)_2$, which reacted with lithium octaethyltetraazaporphyrin under mild conditions to give complex **135**.



VI. Synthesis of heteroleptic and mixed-ligand triple-decker complexes

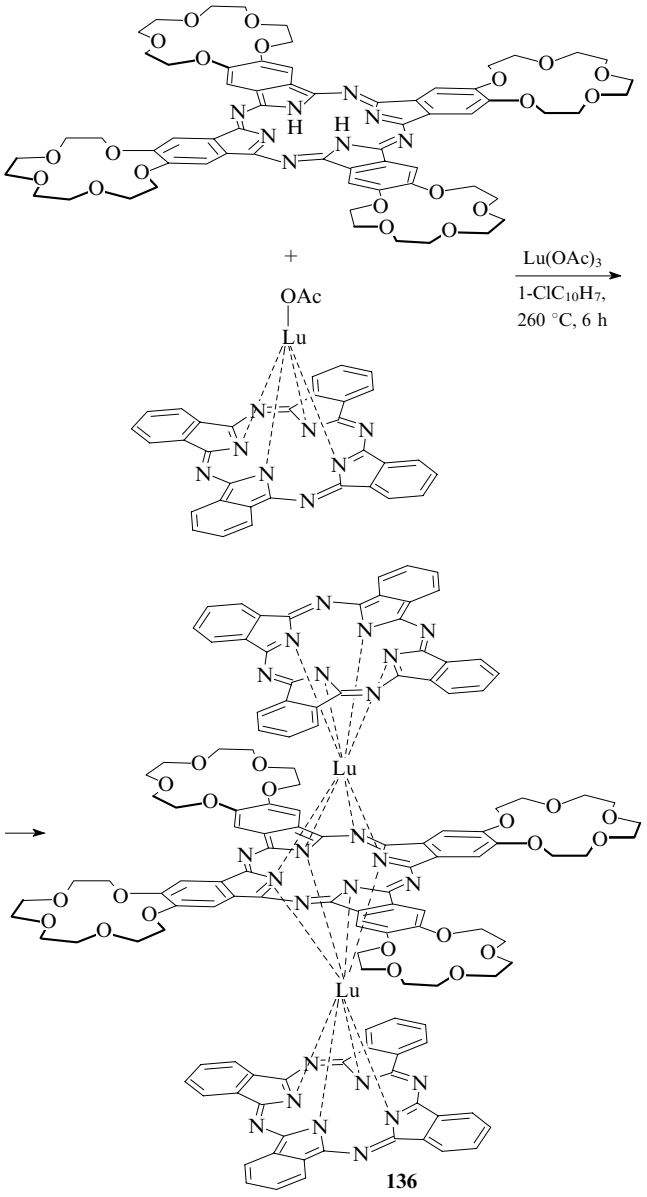
Triple-decker lanthanide complexes containing various tetrapyrrole type ligands have been known for more than a decade. The vast majority of papers on this subject were published in 2000–2007. It was shown that in the synthesis of heteroligand and heteronuclear derivatives the π–π interactions between the ligands and f–f interactions of metal ions in triple-decker complexes can effectively be controlled, the complexes being thus imparted with clear-cut magnetic [198] and nonlinear-optical [6] properties; this opens up the way of using these complexes in the high-capacity information storage devices.[189, 199]

The complexes of this type known to date can be classified into three groups depending on the nature of ligands: (i) heteroleptic phthalocyanine complexes; (ii) mixed-ligand complexes of phthalocyanines with porphyrins; (iii) mixed-ligand complexes of naphthalocyanines with porphyrins. With few exceptions, the approaches to the synthesis of these compounds represent modifications of the direct complexation method and have low selectivity.

By analogy with Section V, this part of the review is classified according to the type of the target compounds.

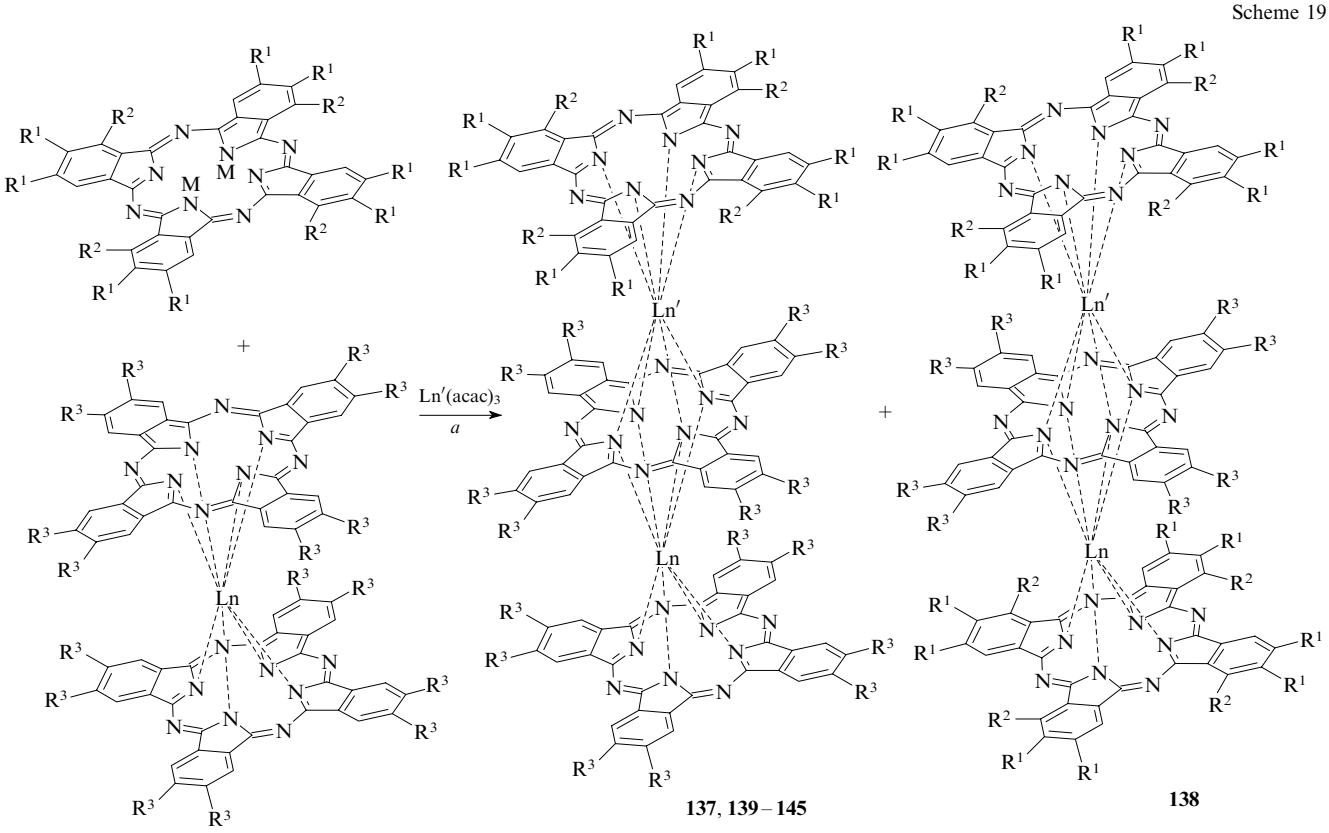
1. Heteroleptic phthalocyanine complexes

The heteroleptic lutetium phthalocyanine **136** prepared by Ishikawa *et al.*[200] in 1994 was the first example of a triple-decker lanthanide complex containing single-type ligands with different substituents. The reaction was carried out with a threefold excess of lutetium monophthalocyanine with respect to the tetracrown-substituted ligand, whereas the corresponding bisphthalocyanine **83** (see Scheme 13) was obtained from an equimolar mixture of these reactants.[173] Complex **136** was isolated in a pure state by several chromatographic stages and characterised by elemental analysis, FAB mass spectrometry and ^1H NMR spectroscopy. Unfortunately, the yield of this compound was not reported.[200]



The first series of heteroleptic trisphthalocyanine complexes for the whole lanthanide series (except for La, Pm,

Scheme 19



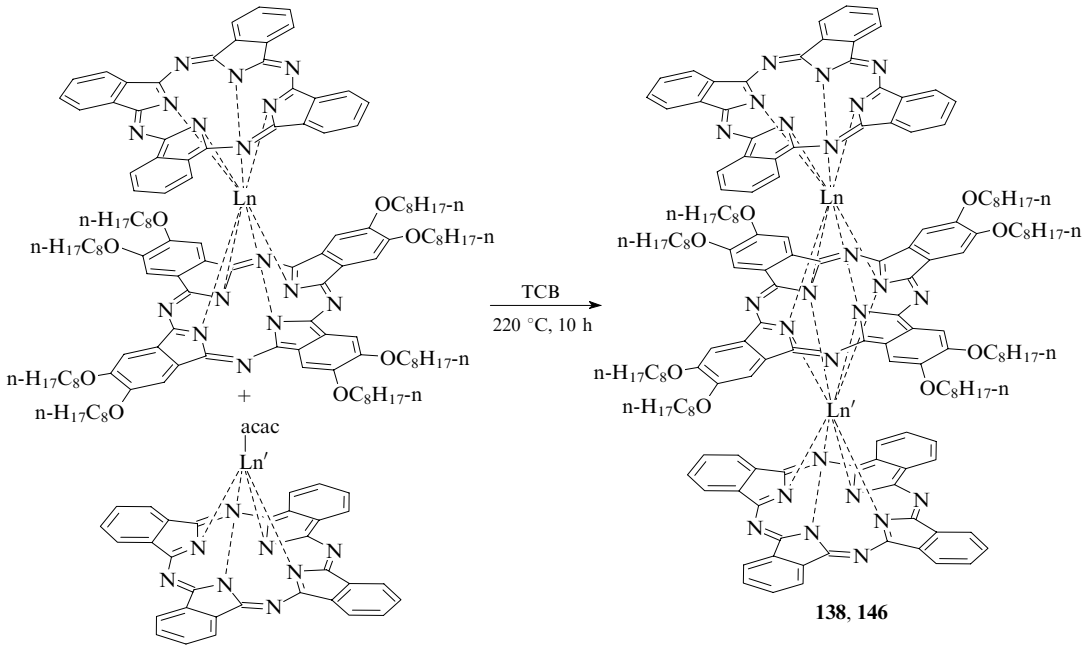
M = Li (**137**, **138**), H (**139** – **145**); $R^1 = R^2 = H$, R^3 = n-$C_8H_{17}O$; Ln = Ln′ = Pr, Nd, Sm – Tm (**137**, **138**);
R^1 = Bu^nO, $R^3 = R^2 = H$: Ln = Ln′ = Tb, Dy, Ho, Er, Tm, Yb (**139**); Ln = Tb, Dy, Ho, Er, Tm, Yb; Ln′ = Y (**140**); Ln = Y; Ln = Tb, Dy, Ho, Er, Tm, Yb (**141**); R^1 = n-$C_nH_{2n+1}O$ (n = 6, 8, 10, 12), $R^2 = H$, R^3 = $MeO(CH_2CH_2O)_2$, Ln = Ln′ = Eu (**142**);
R^1 = n-$C_nH_{2n+1}O$ (n = 4, 6, 8, 10, 12), $R^2 = H$, $R^3 – R^3$ = $O(CH_2CH_2O)_4$, Ln = Ln′ = Eu, Ho, Lu (**143**);
$R^1 – R^1$ = $O(CH_2CH_2O)_4$, $R^2 = R^3 = H$, Ln = Ln′ = Sm, Dy, Tm, Y (**144**); $R^1 = R^3 = H$, R^2 = Et_2HCO, Ln = Ln′ = Sm, Gd, Lu (**145**);
(*a*) TCB or n-$C_8H_{17}OH$, 190 – 220 °C, 3 – 12 h.

Lu) was obtained in 2000 by a group of Chinese scientists headed by Jiang.[201] Long-term (> 12 h) refluxing of lanthanide acetylacetonate, lithium phthalocyanine and the specified bisphthalocyanine complex in boiling TCB resulted in compounds **137** (Scheme 19) in 26% – 79% yields. Apart from the major products, the authors were able to isolate (yields 3% – 17%) and characterise complexes **138** (except for Ln = Pr). This result was attributed to the fact that the starting bisphthalocyanine complex and products **137** can undergo thermolysis during the synthesis to give monophthalocyanine complexes ^{R}PcLn(acac) and heteroleptic complexes ^{R}PcLn′Pc (R = n-$C_8H_{17}O$), respectively, which then react with excess PcLn(acac) giving rise to compounds **138**. This assumption is confirmed by the increase in the content of complexes **138** in the reaction products proportionally to the reaction time. In addition, the control experiment, *viz*., a reaction of PcLn(acac) (Ln = Tb) with ^{R}PcH$_2$ (R = n-$C_8H_{17}O$) in boiling TCB afforded complex **138** in 51% yield, whereas trisphthalocyanine complex **137** was obtained in 37% yield.

Using free ligands instead of lithium phthalocyanine, Ishikawa *et al*.[198,202] synthesised heteroleptic homo- and heteronuclear complexes **139** – **141** under similar conditions (see Scheme 19) in yields of about 60%. No by-products such as compounds **138** were formed in this case. Compounds **139** – **141** were characterised by elemental analysis and ^{1}H NMR spectroscopy data.[203] Amphiphilic complexes **142** and **143** were prepared in a similar way in 23% – 48% yields;[87,204,205] trisphthalocyanine complexes **144**[206] containing two unsubstituted and one external 15-crown-5-phthalocyanine ligands were obtained in 39% – 70% yields.

The formation of heteroleptic trisphthalocyanine complexes is also possible in protic solvents. Thus a number of isomeric samarium, gadolinium and lutetium complexes (**145**) were produced in 40%, 42% and 24% yields, respectively, in boiling n-octanol for 3 h.[207] The low product yield in the case of lutetium was attributed to steric hindrance to complexation caused by the smaller ionic radius of this lanthanide compared to the samarium and europium radii.

Jiang and co-workers[208] synthesised trisphthalocyanines **138** and their heteronuclear analogues **146** by refluxing monophthalocyanine complexes with heteroleptic double-decker complexes in TCB for 10 h. The target compounds **138** and **146** were isolated in yields of 8% – 15%, not even trace amounts of alternative complexation products being detected, which is quite surprising, especially in view of earlier studies by the same research group.[201] They only assumed that such selectivity of the process may be due to the electron-donating properties of the substituents in octakis(octyloxy)phthalocyanine ligand, resulting in an increase in the electronic density on the isoindole nitrogen



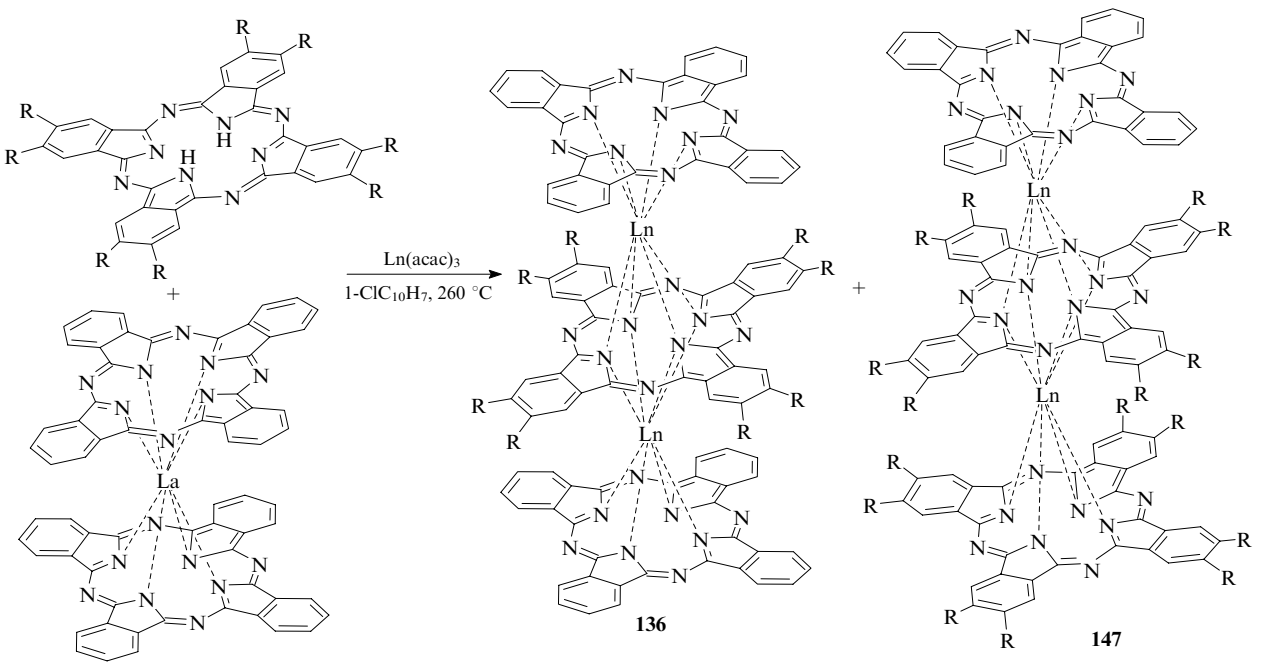
Ln = Ln′ = Nd, Sm – Tm (**138**); Ln′ = Lu, Ln = Gd – Yb (**146**).

atoms and, as a consequence, in easier formation of coordination bonds with lanthanide ions.

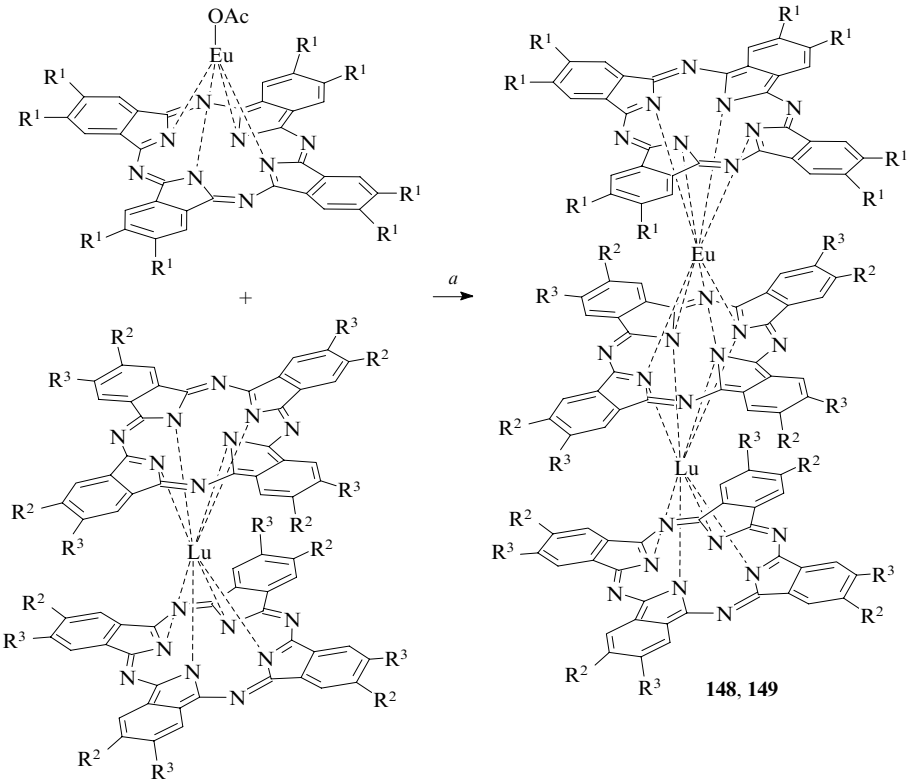
An original approach to the synthesis of trisphthalocyanine complexes **136** and **147** has been proposed.[209] As the source of unsubstituted ligand, the poorly stable lanthanum bisphthalocyanine was used, which reacted with lanthanide acetylacetonates in the presence of 15-crown-5-substituted Ln phthalocyanine to give compounds **136** in 10% – 25% yields, while the major products formed in this reaction were phthalocyanine complexes **147**, their yields being 39% – 46% (Scheme 20).

Conditions for the selective preparation of heteronuclear europium – lutetium complexes **148** and **149** from the respective Ln mono- and bisphthalocyanines in 70% – 89% yields were reported.[177] Note that compounds **148** and **149** (R^1 = Cl) are the first examples of triple-decker phthalocyanine complexes containing both ligands with electron-donating and -withdrawing substituents.

Scheme 20



R – R = $O(CH_2CH_2O)_4$; Ln = Sm, Tb, Dy, Tm, Y.



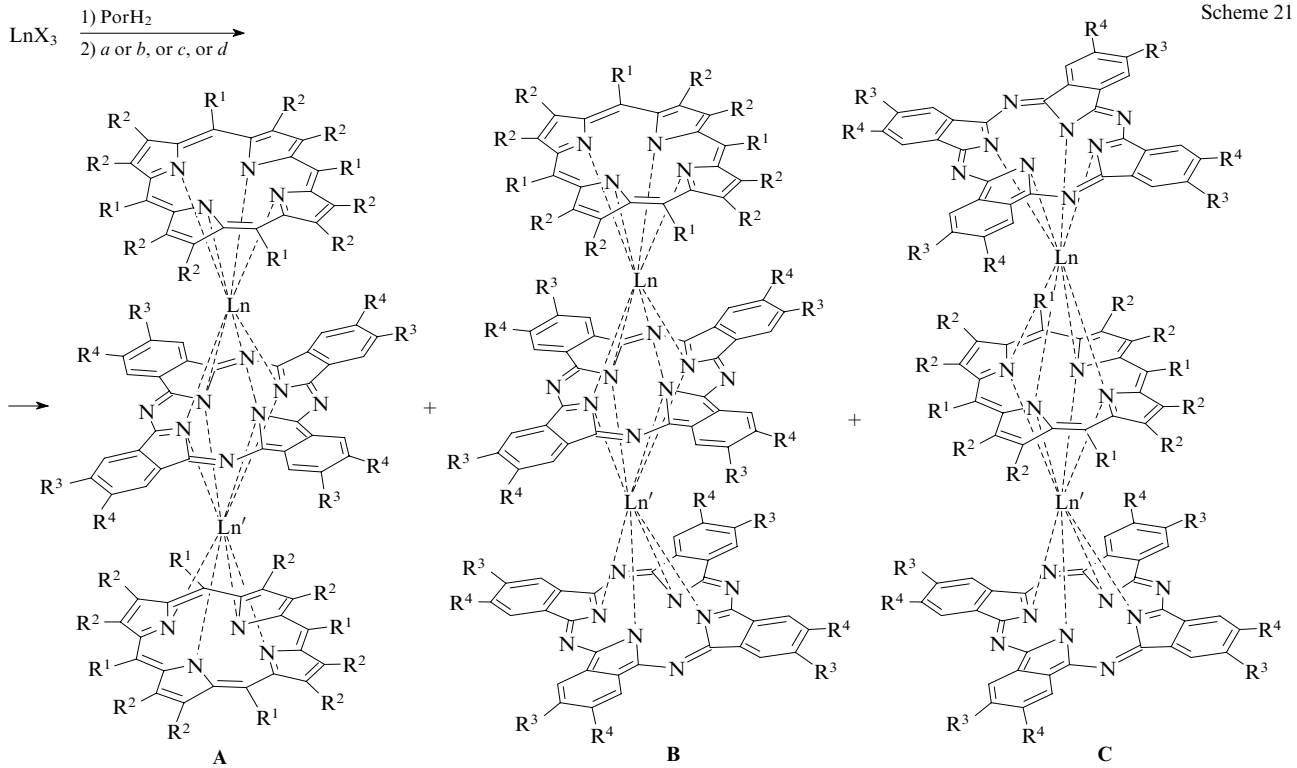
R^1 = H, Cl, Bu^n: $R^2 = R^3 = Bu^n$ (**148**); R^2 = H, $R^3 = Bu^t$ (**149**); (*a*) TCB – n-$C_{16}H_{33}OH$ [50 : 1 (vol.)], 220 °C, 20 – 30 min.

2. Mixed-ligand phthalocyanine and porphyrin complexes

This type of triple-decker complexes is much more abundant than heteroleptic phthalocyanine complexes. The main reason is that the chemistry of porphyrins is generally more developed, which extends the possibilities of preparation of products with specified properties. Nevertheless, the existing approaches to the synthesis of porphyrin-containing heteroligand complexes have most often low selectivity and often produce mixtures of compounds.

Three types of phthalocyanine – porphyrin trimers differing in the composition and mutual arrangement of ligands are known by now. The synthetic methods used for their preparation can also be divided into three main groups depending on the nature of the substrates (Scheme 21). Table 6 presents

Scheme 21



(*a*) $PcLi_2$; (*b*) PcLn′Por; (*c*) Pc_2Ln'; (*d*) substituted phthalonitrile, DBU.

Table 6. Synthesis of triple-decker lanthanide complexes according to Scheme 21.

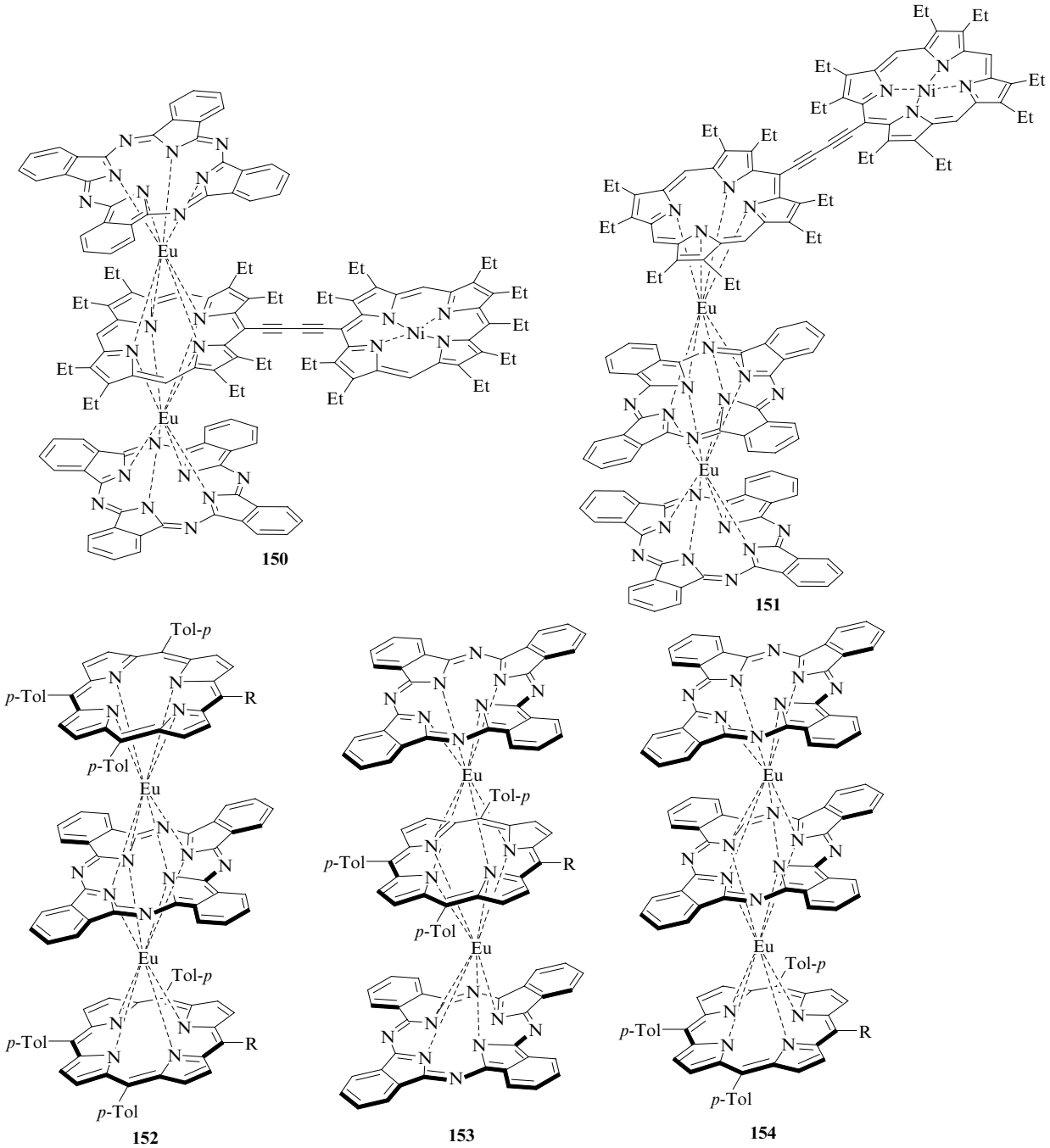
Run	R^1	R^2	R^3	R^4	Ln	Ln′	X	Path	Yield (%)			Ref.
									A	**B**	**C**	
1	H	H	Ph	H	Gd	Gd	acac	*a* [a]	78	–	–	190
2	H	H	Ph	H	Sm, Eu, Gd	Sm, Eu, Gd	acac	*a*	62 – 68	15 – 17		210
3	H	H	Ph	H	Gd, Lu, Y	Ce	acac	*b*	64 – 79	–	–	211
4	H	H	Ph	H	Y	La	acac	*b*	69	–	–	211
5	Me	Me	Ph	H	Eu	Eu	acac	*a*	14	8.9	–	199
6	$O(CH_2CH_2O)_4$		Ph	H	Eu	Eu	acac	*b*	50	–	–	182
7	$O(CH_2CH_2O)_4$		Ph	H	Eu	Eu	acac	*c*	–	42	–	182
8	H	H	4-MeC_6H_4	H	Eu	Eu	acac	*a*	23	10	3	212
9	n-$C_8H_{17}O$	n-$C_8H_{17}O$	4-MeC_6H_4	H	Eu	Eu	acac	*a*	42	11	–	199
10	n-$C_8H_{17}O$	n-$C_8H_{17}O$	4-MeC_6H_4	H	Ce	Eu	I	*c*	–	39	–	189
11	H	Bu^t	4-MeC_6H_4	H	Eu	Eu	acac	*a*	13	17	2.7	199
12	H	Bu^t	4-MeC_6H_4	H	Ce	Ce	I	*a*	13	–	–	189
13	H	Bu^t	4-MeC_6H_4	H	Ce	Eu	I	*c*	–	53	–	189
14	H	H	4-$MeOC_6H_4$	H	Eu	Eu	acac	*a*	49	21	–	213
15	H	H	4-$MeOC_6H_4$	H	Nd, Eu, Gd	Nd, Eu, Gd	acac	*a*	–	see [b]	–	214
16	H	H	4-$Bu^tC_6H_4$	H	Eu	Eu	acac	*a*	63	30	–	213
17	H	H	4-$Bu^tC_6H_4$	H	Eu	Eu	acac	*a*	36	11	0.7	199
18	H	H	4-C_6H_4	H	Eu	Eu	acac	*a*	45	20	–	213
19	H	H	4-C_6H_4	H	Eu	Eu	acac	*d*	35	31	–	215
20	H	H	4-C_6H_4	H	Tb	Tb	acac	*d*	3	28	–	215
21	H	H	4-C_6H_4	H	La, Pr, Nd, Sm – Er, Y	La, Pr, Nd, Sm – Er, Y	acac	*a*	5 – 48	4 – 40	–	216
22	H	H	4-Py	H	La	La	acac	*c*	47	see [b]	–	217
23	H	H	4-Py	H	Eu	Eu	acac	*c*	51	see [b]	–	217
24	n-$C_8H_{17}O$	n-$C_8H_{17}O$	4-(n-$C_{12}H_{25}O$)C_6H_4	H	Eu	Eu	acac	*d*	35	32	–	215
25	n-$C_8H_{17}O$	n-$C_8H_{17}O$	4-(n-$C_{12}H_{25}O$)C_6H_4	H	Tb	Tb	acac	*d*	4	21	–	215
26	n-$C_8H_{17}O$	n-$C_8H_{17}O$	4-(n-$C_{12}H_{25}O$)C_6H_4	H	Eu	Tb	acac	*c*	–	58	–	215
27	n-$C_8H_{17}O$	n-$C_8H_{17}O$	4-(n-$C_{12}H_{25}O$)C_6H_4	H	Tb	Eu	acac	*c*	–	44	–	215
28	H	H	n-C_5H_{11}	H	Eu	Eu	acac	*a*	39	30	–	199
29	Me	Me	n-C_5H_{11}	H	Eu	Eu	acac	*a*	8	2	–	199
30	H	Bu^t	n-C_5H_{11}	H	Eu	Eu	acac	*a*	39	11	–	199
31	H	Bu^t	n-C_5H_{11}	H	Ce	Ce	I	*a*	13	–	–	189
32	Me	Me	H	Et	Eu	Eu	acac	*a*	20	–	–	199
33	n-C_7H_{15}	n-C_7H_{15}	H	Et	Eu	Eu	acac	*a*	–	18	–	199
34	H	Bu^t	H	Et	Eu	Eu	acac	*c*	–	76	–	189
35	H	Bu^t	H	Et	Ce	Eu	I	*c*	–	38	–	189

[a] The opposite order of addition of reactants is possible; [b] the yield was not indicated, in other cases, the dash means that the compound was not isolated.

data on the methods of synthesis and yields of triple-decker complexes of three types: **A**, **B** and **C** (the substituents R^1 and R^2 are located in the porphyrin macrocycle, while R^3 and R^4 are in the phthalocyanine ring).

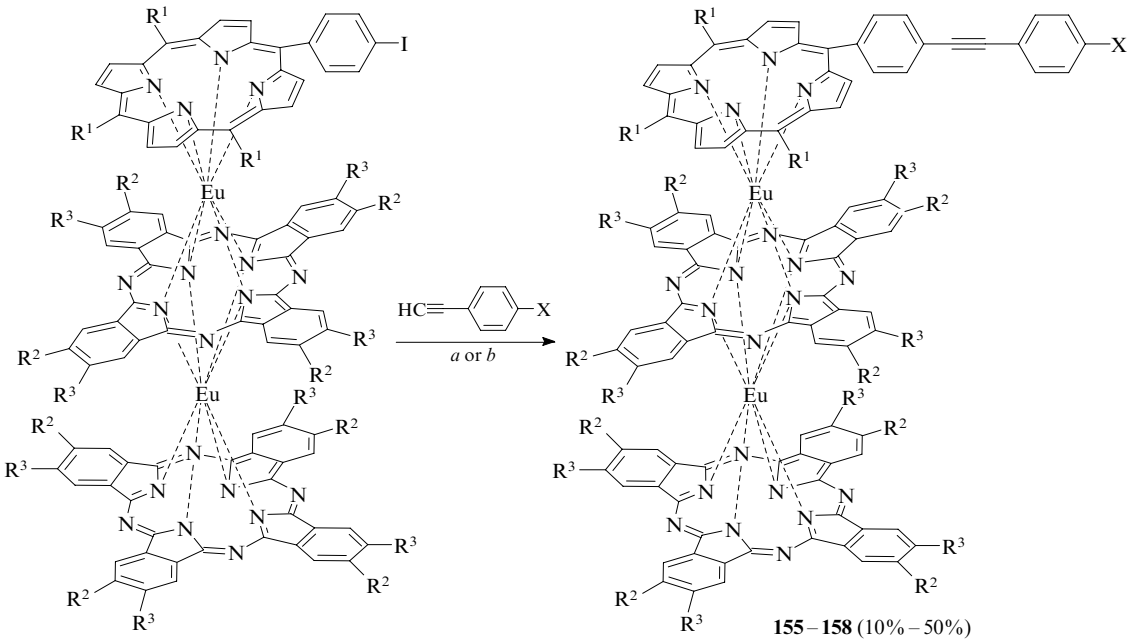
The first method (see Scheme 21, path *a*) includes successive reactions of a lanthanide salt with the porphyrin and phthalocyanine ligands. In the initial stage, lanthanide acetylacetonate reacts with free porphyrin in TCB to give a single-decker complex, which is further complexed with an excess of lithium phthalocyanine for 2–6 h to give a mixture containing both triple-decker and double-decker sandwich products. The trimers synthesised in this way are presented in Table 6; note that the yields of target complexes usually decrease regularly on going from type **A** compounds to type **B** compounds. The formation of complexes **B** in an acceptable yield (18%) was reported only in one publication [199] (see Table 6, run 33), which is indicative of their relatively low stability. By varying the reactant ratio, it is possible to shift the equilibrium toward one or another product; however, no pronounced increase in the selectivity can be attained along path *a*.[199] The complexation in the opposite order (first $PcLi_2$ is added to LnX_3 and then $PorH_2$ is added) has almost no effect on the yields of the target compounds.[190, 210]

The second method (see Scheme 21) implies the interaction of lanthanide monoporphyrin obtained *in situ* with double-decker complexes $PcLn'Por$ (path *b*) or Pc_2Ln' (path *c*), resulting in products **A** and **B**, respectively, in good yields (see Table 6). Path *c* was also used for the synthesis of heteronuclear trimers with different porphyrin ligands, (TPP)CePcGd(OEP) [211] and (PnP)Ce(Bu^t_4Pc)Eu(TTP).[189] Nevertheless, the selectivity of this approach, as in the case of path *a*, depends considerably on the reaction conditions. Thus compounds **A** (runs 22, 23 in Table 6) were formed as



R = 4-[$(CH_2{=}CHCH_2)_3C$]C_6H_4; *p*-Tol = 4-MeC_6H_4.

Scheme 22



R^1 = 4-MeC_6H_4, R^2 = R^3 = H: X = AcS (**155**), [4-$(AcSCH_2)C_6H_4]_3C$ (**156**); R^1 = n-C_5H_{11}, X = AcS: R^2 = R^3 = Me (**157**); R^2 = H, R^3 = Bu^t (**158**); (*a*) $Pd(PPh_3)_2Cl_2$, CuI, Pr^i_2EtN, THF, 30 °C, 20 h; (*b*) $Pd_2(dba)_3$, P(*o*-Tol)$_3$, Pr^i_2EtN, PhMe, 35 °C, 44 h; dba is dibenzylideneacetone.

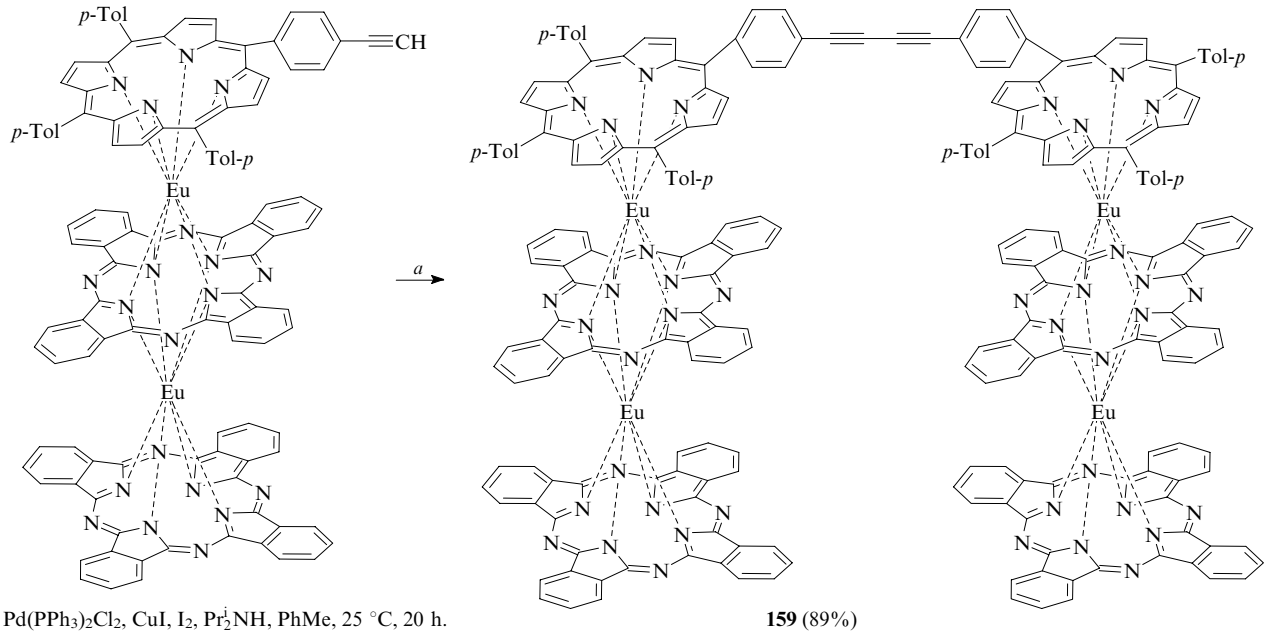
the major products of synthesis along path *c* when the reactants were refluxed in TCB for 18 h, while the expected trimers **B** were isolated only in trace amounts.[217]

Unlike the first two methods, the third one is a template method where lanthanide monoporphyrin reacts with phthalonitriles in the presence of DBU (see Scheme 21, pathway *d*). This approach was tested for preparing complexes **A** and **B** (runs 19, 20, 24, 25);[215] relatively low selectivity comparable with that of synthesis along path *a* was noted (see Table 6).

According to Scheme 21, a number of trimers containing unsymmetrically substituted porphyrin ligands have been synthesised. Thus complexes **150** and **151**[218] containing two A_3B type porphyrin ligands connected by a butadiyne bridge were prepared by path *a* in 33% and 17% yields, respectively.

Compounds **152** – **154**[219] containing triallyl fragments were prepared in a similar way. Owing to the introduction of these functional groups, ordered trimer monolayers were formed upon adsorption on silicon electrodes. The effective binding of trimers to the Si(100) surface produces high concentration of redox-active species (phthalocyanine – porphyrin complexes) on the surface, which results in an increase in the generated charge density. The attainment of the highest charge density is the key issue in the development of molecular materials for high-capacity information storage devices.[219]

Functionally substituted and bridged double-decker lanthanide complexes were prepared[199, 212, 220 – 222] using Pd(0)-catalysed cross-coupling reactions. The starting complexes obtained according to Scheme 21 (path *c*) were then introduced into the Sonogashira cross-coupling with terminal alkynes (Scheme 22, conditions *a*). The corresponding thioacetyl derivatives **155** – **158** were isolated in 10% – 50% yields.[199, 214, 222]

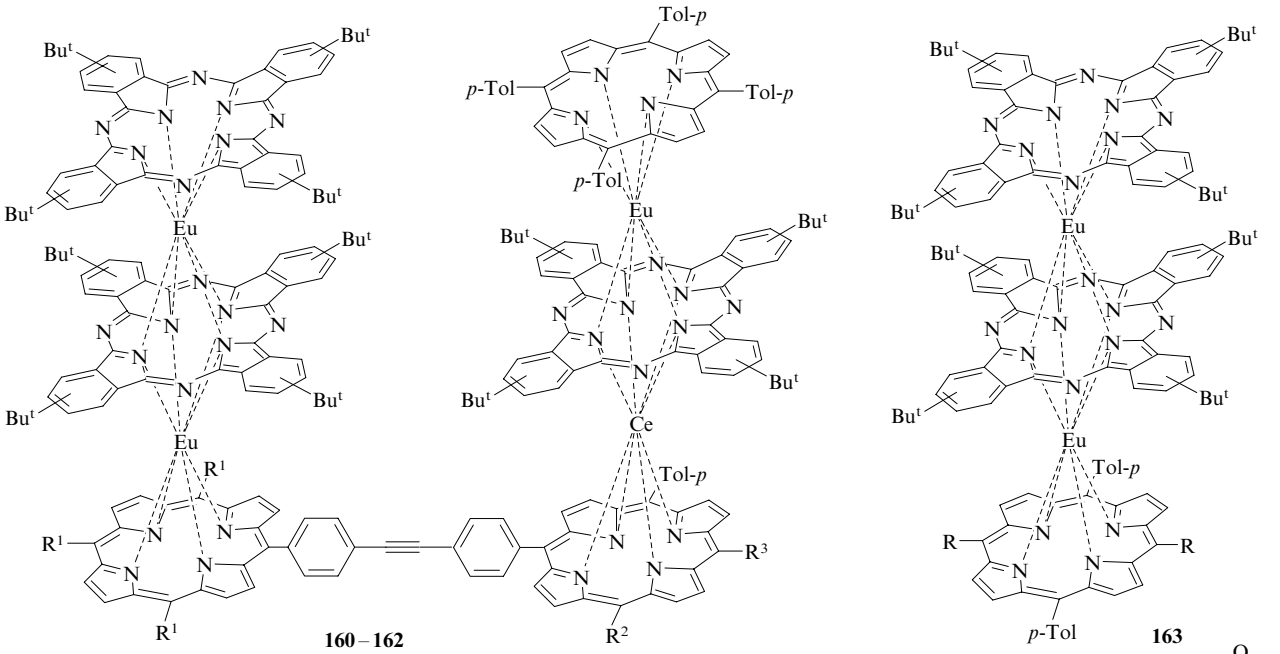


(*a*) $Pd(PPh_3)_2Cl_2$, CuI, I_2, Pr^i_2NH, PhMe, 25 °C, 20 h.

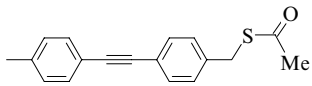
However, under these conditions, large amount of by-products is formed, most of all, homocoupling products of the initial alkynes, which markedly complicates the isolation of the target complexes. For solving this problem, alternative conditions (see Scheme 22, conditions *b*) minimising undesirable side processes have been found.[199, 212]

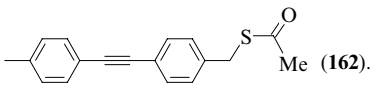
By modified Eglinton–Glaser coupling of the terminal ethynyl groups, triple-decker complexes linked by a butadiyne bridge have been obtained.[212] Homocoupling giving dimer **159** is presented as an example.

The above-described methods were used[220, 221] to synthesise complicated functionally substituted porphyrin–phthalocyanine complexes **160**–**165**.



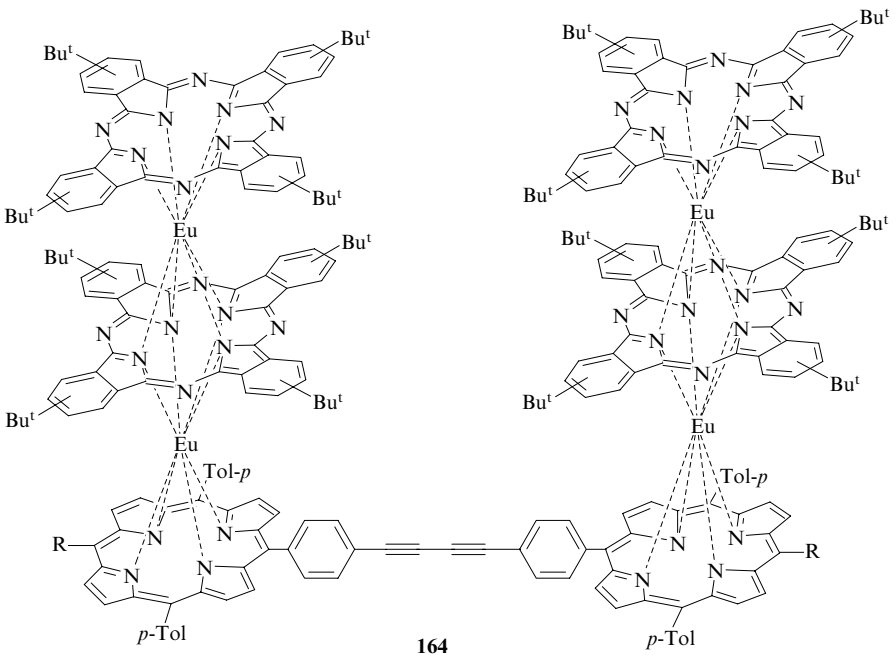
160–**162**

R^3 =  : R^1 = n-C_5H_{11}, R^2 = *p*-Tol (**160**);

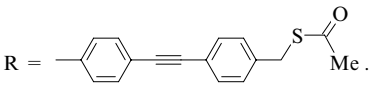
$R^1 = R^2$ = *p*-Tol (**161**); $R^1 = R^3$ = *p*-Tol, R^2 =  (**162**).

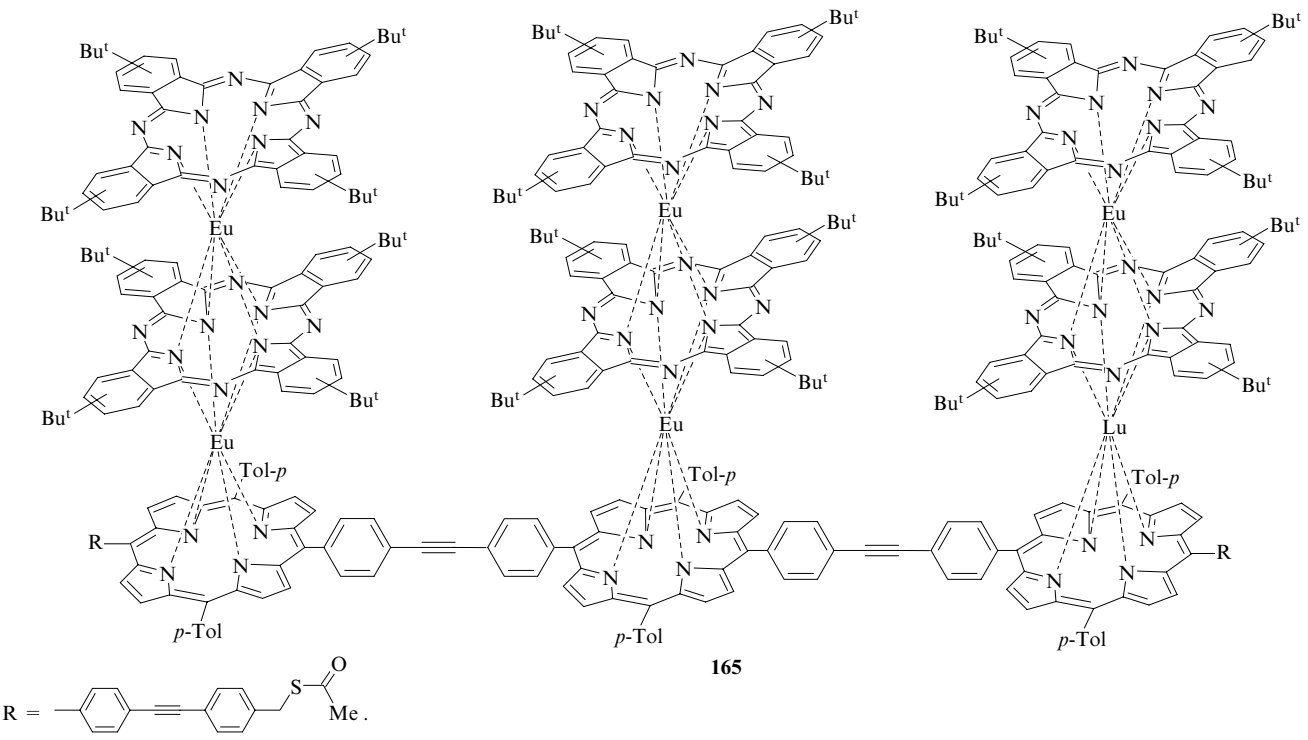
163

R =



164

R = 



165

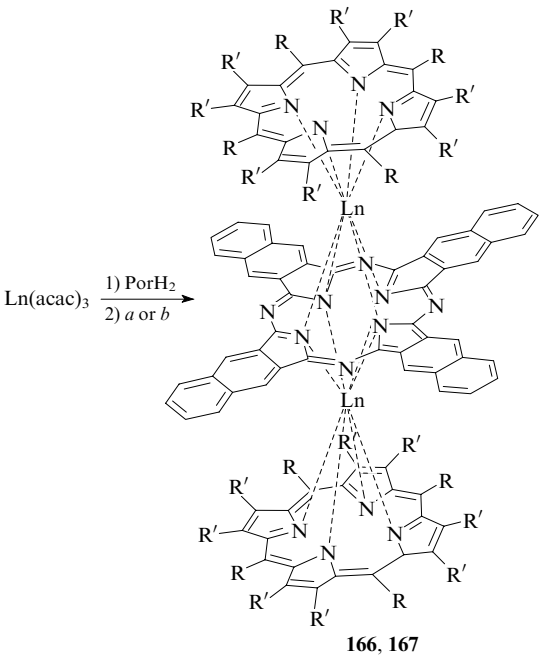
R =

3. Mixed-ligand complexes of naphthalocyanines and porphyrins

Among the possible combinations of naphthalocyanines and porphyrins in triple-decker complexes, only representatives of one structural type are known to date (Scheme 23). Moreover, compounds **166**, **167** are still the only example of sandwich trimers containing a 2,3-naphthalocyanine ligand.

The synthesis is carried out only by the direct method. First, the free porphyrin was metallated by lanthanide acetylacetonate to give a single-decker complex, which then reacted with lithium naphthalocyanine (see Scheme 23, conditions *a*) or with mixed-ligand naphthalocyanine–porphyrin dimer (see Scheme 23, conditions *b*). In the former case, refluxing of a reactant mixture in TCB for 5 h gave europium trimer **166** in 3% yield.[199] The yields of products **167** synthesised according to the second route in TCB over a period of 18 h were 46% and 63% for neodymium and europium, respectively.[195]

Scheme 23



166, **167**

R = n-C_5H_{11}, R′ = H, Ln = Eu (**166**); R = H, R′ = Et; Ln = Nd, Eu (**167**);
(*a*) $NcLi_2$; (*b*) NcLnPor.

* * *

Thus, currently single-, double- and triple-decker lanthanide complexes with tetrapyrrole type ligands are known. Also, some heteroleptic, mixed-ligand and heteronuclear lanthanide derivatives have been obtained. Among homoleptic complexes, bisphthalocyanine complexes have been studied in most detail, while among heteroleptic and mixed-ligand complexes, porphyrin–phthalocyanine complexes are best known. In recent years, convenient and selective methods for the synthesis of these compounds have been developed, which promotes the development of the chemistry of phthalocyanine derivatives and makes them available for practical use.

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