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The development of highly selective approaches to sandwich-type heteroleptic double- and triple-decker lutetium(III) and europium(III) phthalocyanine complexes

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Abstract—The selective synthesis of heteroleptic (heteronuclear) sandwich-type lanthanide phthalocyanines has been accomplished. Double-decker complexes ^{Bu}PcLnPc, and ^{Bu}PcLnPc^{Cl} (Ln = Lu, Eu; ^{Bu}Pc = 2,3,9,10,16,17,23,24-octabutylphthalocyaninate; Pc = phthalocyaninate, ^{Cl}Pc = 2,3,9,10,16,17,23,24-octachlorophthalocyaninate) were obtained in good yields by a direct interaction of metal-free ligand ^{Bu}PcH$_2$ with the monophthalocyanines PcLnOAc or ^{Cl}PcLnOAc. Heteronuclear triple-decker phthalocyanines PcEu^{R}PcLu^{R}Pc, ^{Cl}PcEu^{R}PcLu^{R}Pc and ^{Bu}PcEu^{R}PcLu^{R}Pc (^{R}Pc = ^{Bu}Pc, ^{tBu}Pc; ^{tBu}Pc = 2(3),9(10),16(17),23(24)-tetra-*tert*-butylphthalocyaninate) were obtained from the corresponding mono-(PcEuOAc, ^{Cl}PcEuOAc, ^{Bu}PcEuOAc) and bisphthalocyanines (^{R}Pc$_2$Lu) under similar conditions.

Sandwich-type phthalocyanine complexes of rare-earth elements (REE) are a well-studied class of coordinating compounds with tetrapyrrole ligands.[1] Owing to characteristic overlapping of ligand π-orbitals,[2] which is supplemented with a specific interaction of two *f*-electronic systems in the case of triple-decker complexes,[3] these compounds possess a wide range of unique properties determining a variety of applications.[4] The possibility of a structural modification in sandwich-type phthalocyanines, implying synthesis of mixed-ligand and heteronuclear derivatives,[5] makes effective control of the intramolecular interactions and preparation of the materials with required properties possible.[6]

Mixed-ligand REE phthalocyanines were first reported by Tomilova and co-workers[7] as early as 1986. However, recent synthetic approaches to these complexes often reveal low selectivity, which prevents progress in their chemistry and limits accessibility for technological developments. In particular, syntheses of heteroleptic bisphthalocyanines are based either on template reactions of monophthalocyanines with corresponding phthalonitriles in a melt[7,8] or in a solution,[9] or on direct complexation of two different ligands in the presence of REE salts.[10] However, both methods inevitably result in difficult to separate mixtures of products and do not lead to acceptable yields of target compounds.

To simplify purification by suppression of homoleptic by-product formation, Ishikawa suggested the so-called ‘raise-by-one-story’ method consisting of the interaction of the preliminarily obtained or formed in situ half-sandwich REE monophthalocyanine with the corresponding ligand or its sodium derivative in a high-boiling solvent.[11] It is noteworthy, that the yields of the target heteroleptic compounds obtained by this procedure did not exceed 32%.[9c,11,12] A series of heteroleptic and heteronuclear triple-decker complexes were synthesized analogously by reaction of the corresponding bisphthalocyanines and monophthalocyanines generated in situ from REE acetylacetonates and metal-free ligands[3] or their lithium salts.[13] Starting from lithium salts, Jiang and co-workers[13a] noticed the formation of unexpected isomeric trisphthalocyanines, which could

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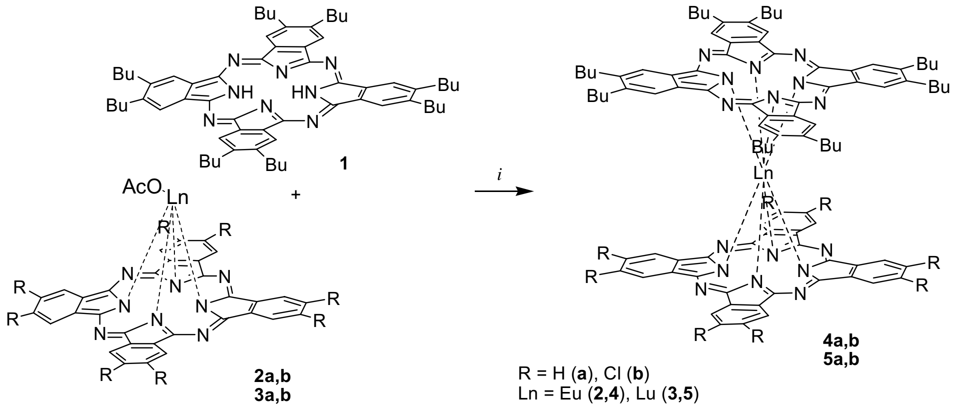
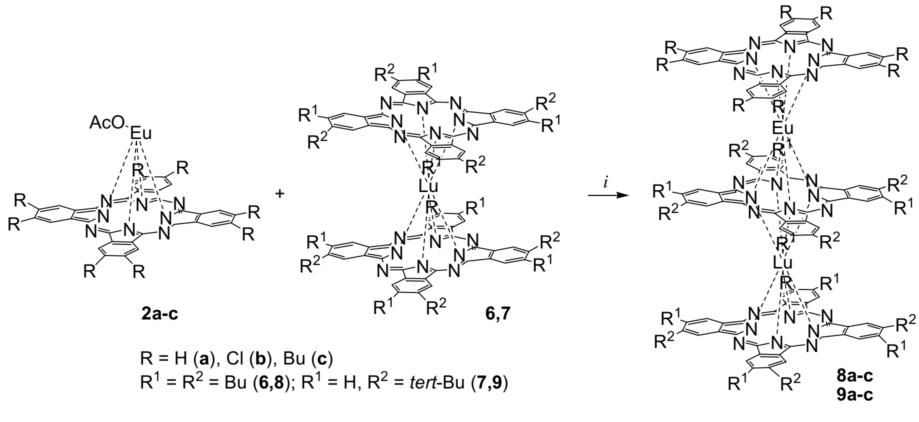
only be obtained via thermal degradation of the initial bisphthalocyanines. In Ishikawa's works,[3] it is stated that the side processes can be avoided by preparation of monophthalocyanines from the corresponding metal-free ligands. However, in our attempts to apply these procedures for the current investigation we failed to achieve the selective formation of the target heteroleptic products, moreover, the overall yields of a mixture of triple-decker products were not more than 20–30%.

In our previous work[14] we developed conditions for the selective formation of homoleptic sandwich-type complexes of some lanthanides with octaalkylphthalocyanines and optimized the synthesis of the starting ligands, which turned out to be useful in the development of selective synthetic approaches to heteroleptic bis- and trisphthalocyanines (Schemes 1 and 2). This issue was briefly discussed,[15] and in the present work, we report more detailed studies.

Starting from octabutylphthalocyanine **1** and monophthalocyanines **2** or **3** (molar ratio 2:1) obtained in high yields according to earlier procedures,[14] heteroleptic europium(III) and lutetium(III) bisphthalocyanines **4** and **5** were synthesized (Scheme 1).[16] Initially, europium complexes **4a**,**b** were obtained in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in refluxing *n*-octanol. Unfortunately, under these conditions, formation of the corresponding homoleptic derivatives in considerable amounts was observed along with the target compounds, that is, the reaction was non-selective and side processes involving decomplexation–complexation took place. Lutetium bisphthalocyanines **5a**,**b** were synthesized in the absence of DBU, because of the reasons discussed previously,[14] at higher temperatures (about 230 °C) using *n*-hexadecanol as solvent. However, formation of heteroleptic products was also non-selective, and their yields did not exceed 30–40%. It turned out that conducting the reaction in the low-polar aprotic solvent 1,2,4-trichlorobenzene (TCB) in the presence of catalytic amounts of high-boiling alcohol (Scheme 1, methods A and B)[16] minimized the formation of side products and resulted in good yields of the target double-deckers. In particular, method A gave the best results for europium complexes **4a**,**b** with yields of 85% and 80%, and method B led to the isolation of lutetium compounds **5a**,**b** in 78% and 71% yields, respectively (Table 1). While trying to carry out the reaction in pure TCB we observed virtually no formation of sandwich-type products. This fact is evidence of the key role



Scheme 1. Reagents and conditions: (i) TCB–*n*-hexadecanol (50:1), cat. DBU, reflux, 2 h (method A); TCB–*n*-hexadecanol (50:1), reflux, 1 h (method B).



Scheme 2. Reagents and conditions: (i) TCB–*n*-hexadecanol (50:1), reflux, 20–30 min (method B).

Table 1. Yields, MALDI-TOF mass spectra, UV–vis and ^{1}H NMR spectroscopic data of complexes **4**, **5**, **8**, and **9**

Compd	Molecular formula	Method[a]	Yield (%)	Mass spectrum, m/z,[b] $[M]^+$	λ_{max} (nm) (in C_6H_6)	δ[c]	
						α-H_{Ar}	β-H_{Ar}
4a	$C_{96}H_{96}N_{16}Eu$	A (B)	85 (37)	1625	326, 348, 488, 609, 675	11.34, 11.28	9.23
4b	$C_{96}H_{88}N_{16}Cl_8Eu$	A (B)	80 (33)	1901	331, 352, 512, 613, 678	11.04, 10.92	
5a	$C_{96}H_{96}N_{16}Lu$	A (B)	20 (78)	1648	323, 341, 472, 600, 665	8.96, 8.75	8.13
5b	$C_{96}H_{88}N_{16}Cl_8Lu$	A (B)	14 (71)	1923	328, 347, 488, 603, 668	8.86, 8.75	
8a	$C_{160}H_{176}N_{24}EuLu$	B	89	2761, 2762	345, 649	10.90, 10.23, 7.80	8.60
8b	$C_{160}H_{168}N_{24}Cl_8EuLu$	B	75	3036, 3037	346, 651	10.78, 9.92, 7.62	
8c	$C_{192}H_{240}N_{24}EuLu$	B	83	3209, 3210	347, 659	10.74, 9.87, 7.81	
9a	$C_{128}H_{112}N_{24}EuLu$	B	82	2312, 2313	341, 642	10.08–11.42, 8.56–8.70, 7.78–8.34	
9b	$C_{128}H_{104}N_{24}Cl_8EuLu$	B	70	2588, 2589	342, 644	9.92–10.73,[d] 9.95,[d] 7.41–8.20	
9c	$C_{160}H_{176}N_{24}EuLu$	B	87	2761, 2762	343, 647	9.54–10.42,[d] 9.89,[d] 7.74–8.48	

[a] The conditions for the synthesis are given in Scheme 1.

[b] The values calculated for the most abundant isotope (^{153}Eu, ^{175}Lu) and the most intense peak in the spectrum are presented (matrix—3,5-dihydroxybenzoic acid).

[c] The spectra of compounds **4** and **5** were recorded in THF-d_8 containing 1–2 vol % $N_2H_4{\cdot}H_2O$ as additive; the spectra of compounds **8** and **9** were obtained in $CDCl_3$.

[d] Overlapping signals.

of the OH-function in the mechanism of bisphthalocyanine formation according to Scheme 1, although this requires further detailed study.

It should be pointed out that bisphthalocyanines **4b** and **5b** represent a new family of sandwich-type phthalocyanines—namely, complexes containing ligands bearing donor and acceptor substituents. These compounds are specifically polarized, resulting in the appearance of interesting spectral features which allows them to be considered as potential materials for non-linear optics. Analogous heteroleptic complexes were recently described by L'Her and co-workers[17] from the point of their aggregating ability in solutions. However, the synthetic procedure employed was based on condensation of two different dilithium phthalocyanines with lutetium acetate and gave the desired compounds in only 24–31% yields accompanied by the formation of symmetrical sandwich products. The main advantages of the present work are the good yields and high selectivity.

The conditions used in method B also proved to be appropriate for the synthesis of novel heteronuclear triple-decker phthalocyanines (Scheme 2). Thus, complexation of monophthalocyanines **2a**–**c** with bisphthalocyanines **6** or **7** in the molar ratio 1:1 gave triple-decker products **8** and **9** in yields ranging from 70% to 89% depending on the nature of peripheral substituents in the initial compounds (Table 1).[18] The optimal reaction time was 20–30 min; formation of side products in trace amounts was observed only in the case of complex **8c**. These minor by-products were isolated and characterized as homonuclear europium and lutetium trisphthalocyanines. Their formation is likely due to high temperature degradation of both bisphthalocyanine **6** and target compound **8c** followed by further recomplexation. On heating for a long time (up to 2 h), formation of side compounds was observed for all complexes **8** and **9**, leading to reduced yields and complicated purification. It is important to note that for the first time, the described approach leads to triple-decker phthalocyanine complexes **8b** and **9b** containing ligands with donor and acceptor substituents in the same molecule.

The compositions of the complexes were confirmed by MALDI-TOF mass spectrometry (Table 1). In the spectra of compounds **4**, **5**, **8**, and **9**, molecular ion $[M]^+$ peaks or the corresponding protonated molecular ions $[MH]^+$ were observed. Additional fragmentation under the ionization conditions was not registered.

There were some interesting peculiarities in the electronic absorption spectra of the compounds obtained. According to UV–vis spectral data, bisphthalocyanines **4** and **5** were synthesized as the green forms $[(Pc)^{\cdot-}M^{3+}(Pc')^{2-}]^0$ wherein one unpaired electron is delocalized over the two macrocycles. In the spectra of these compounds, an intense Q-band at 665–678 nm, a split B-band (Soret) with maxima at 323–331 and 341–352 nm, and a characteristic band in the region 472–512 nm caused by the radical fragment $Pc^{\cdot-}$ were present (Table 1). The position of the band at 475–512 nm for homoleptic bisphthalocyanines is well known to change synchronously with the Q-band while going from La to Lu, undergoing a hypsochromic shift.[14]

For heteroleptic complexes **4b** and **5b**, containing octabutyl- and octachloro-substituted ligands, this band underwent a significant bathochromic shift in comparison with the corresponding homoleptic hexadecabutyl-substituted bisphthalocyanines (16 nm for **5b** and 26 nm for **4b**), and the Q-band was shifted hypsochromically. This effect was found by us for the first time and is evidence of the peculiar interaction between donor- and acceptor-substituted ligands in heteroleptic bisphthalocyanines, which can intensify magnetic, semi-conducting, and non-linear optical properties of the materials based on these compounds.

In the UV–vis spectra of triple-decker complexes **8** and **9**, the band near 480–490 nm was not observed due to the electronic equivalence of all three ligands (Pc^{2-}). In the visible region, only the Q-band and non-split B-band were present. The Q-band was gradually shifted to the short-wave region on decreasing the bulk of the substitutents in the complex (Table 1).

NMR spectroscopy is an important instrument in structural determination of different phthalocyanine complexes and investigation of their properties,[3a,19] however, developments are limited by a range of factors, mainly connected with the low solubility of phthalocyanines. Nevertheless, our work with substituted complexes and optimization of conditions for each type of phthalocyanines allowed us to use NMR spectroscopy both for structural investigations and for determination of the purity of prepared samples.

A specific feature of bisphthalocyanines is the radical fragment $Pc^{\bullet-}$, which prevents satisfactory NMR spectra being obtained in common solvents. Therefore, the ^1H NMR spectra of compounds **4** and **5** were recorded in THF-d_8 in the presence of 1–2 vol % hydrazine hydrate, which reduced the π-radical fragment to the corresponding dianion. After reduction the ^1H NMR spectra of **4** and **5** demonstrated well-resolved signals for each of the phthalocyanine decks (Table 1).

A characteristic feature of the ^1H NMR spectra of heteronuclear trisphthalocyanines **8** and **9** is the triple set of signals with a ratio of integral intensities 1:1:1 (Fig. 1), which results from different deshielding of the ligand protons. The highest deshielding was characteristic for the inner deck protons while the latter of the outer (Lu) deck were the most shielded. These results together with UV–vis and mass-spectrometry data unambiguously confirm the structures of the compounds obtained.

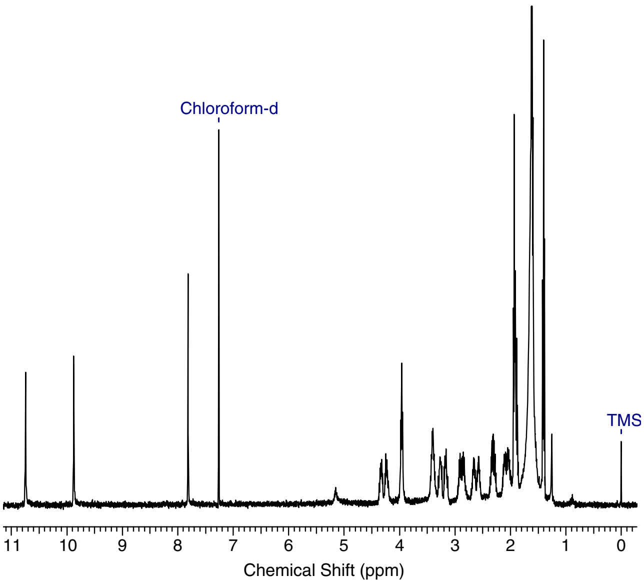


Figure 1. ^1H NMR spectrum of heteronuclear triple-decker **8c** in $CDCl_3$.

In summary, reaction conditions have been developed for the selective synthesis of heteroleptic double- and triple-decker phthalocyanine REE complexes containing europium or lutetium. These compounds are easily accessible allowing detailed investigation of their unique physico-chemical properties and open the possibility for development of new technologies.

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Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.05.128.

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16. *Typical procedure*: A mixture of free-base phthalocyanine **1** (135 mg, 0.14 mmol) and monophthalocyanine **2** (or **3**) (0.07 mmol) in TCB (5 mL) with *n*-hexadecanol (0.1 mL) was refluxed under argon in the presence of DBU (100 mg, 0.66 mmol) for about 2 h (Method A) or in the absence of DBU for about 1 h (Method B) until the starting monophthalocyanine had completely disappeared. The course of the reaction was monitored by TLC (Al_2O_3, benzene as eluent) and UV–vis spectroscopy. The resulting solution was diluted with THF (25 mL), rinsed through a glass filter, and the solvent was removed under reduced pressure. The residue was washed with boiling 80% aqueous MeOH (3 × 50 mL), filtered, and dried in a vacuum desiccator. The resulting powder was dissolved in THF and chromatographed on a column (2.5 × 40 cm, Bio-Beads S-X1, THF as eluent), to afford a grey-greenish (for Ln = Eu), or green-colored (for Ln = Lu) fraction. To achieve the extra purity, preparative TLC on silica gel using benzene/hexane (2/1) as eluent was employed. The yields and spectral data for compounds **4** and **5** are given in Table 1.
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