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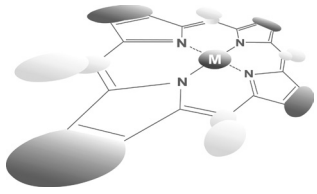

Er(III) and Lu(III) complexes of 2(3),9(10),16(17),23(24)-tetrakis- and 2,3,9,10,16,17,23,24-octakis-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninato. Synthesis and spectroscopic properties

Tatyana Tikhomirova*[a], Kseniya Nalimova[a], Anastasiya Kerner[b], Artur Vashurin[b,c] and Serafima Znoyko[c]

[a]*Department of Technology of Fine Organic Synthesis, Ivanovo State University of Chemistry and Technology, Ivanovo 153000, Russia*
[b]*Department of Inorganic Chemistry, Ivanovo State University of Chemistry and Technology, Ivanovo 153000, Russia*
[c]*Research Institute of Macroheterocycles of Ivanovo State University of Chemistry and Technology, Ivanovo 153000, Russia*

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ABSTRACT: 4-[4-(1-Methyl-1-penylethyl)phenoxy]- and 4,5-di-[4-(1-methyl-1-phenylethyl)phenoxy]phthalonitriles are obtained by nucleophilic substitution. Mono- and double-decker lutetium and erbium complexes of 2(3),9(10),16(17),23(24)-tetrakis- and 2,3,9,10,16,17,23,24-octakis-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanines are synthesized based on the phthalonitriles. Synthesized complexes are studied spectrophotometrically.

KEYWORDS: phthalocyanines, synthesis, rare-earth metals, redox, kinetics.

INTRODUCTION

Phthalocyanine metal complexes are compounds with prospective properties [1, 2] originating from high chemical, thermal and photo-stability [3] One can apply phthalocyanine compounds to develop novel functional materials with a wide range of applications [4]. Among the most promising applications, fields of *d*- and *f*-metal phthalocyanine complexes are useful for photosensitivity and PDT [5], catalysis and photocatalysis [6], organic electronic devices [7], development of MOF [8] and molecular machines [9].

There are several ways to modify phthalocyanine molecules. These include introducing various natural functional substituents into peripheral and non-peripheral positions [10] or, for example, varying the nature of the central metal cation. Such modifications are the tool for fine tuning spectroscopic [11] and other physico-chemical characteristics of the compounds [12].

To date, there have been many synthetic approaches to various substituted metal phthalocyanines developed [13]. In addition, bifunctional phthalocyanines can be obtained by extension of already tetra-substituted macrocycles with other substituents resulting in octa-derivatives. Promising applications of such bifunctional macrocycles include nonlinear optics and photonics [14]. The materials are also of great importance as protectors of photosensitive objects toward intense radiation due to their conjugated π systems being sensitive toward photons and susceptible to third order response [15]. But spectroscopic properties of tetrapyrrolic macroheterocycles are known to strongly depend on the nature of the peripheral substitution [16].

Double-decker sandwich complexes of *f*-metal phthalocyaninates are of certain interest from this point of view. The nature of the central metal ion and

*Correspondence to: Tatyana Tikhomirova, email tararjkina@mail.ru.

substituents significantly affect the power of the π–π interaction between two phthalocyanine macrocycles [17–20]. Moreover, the value of the central metal's ionic radius affects the resulting yield upon synthesis [21]. Tetrasubstituted phthalocyanines containing four bulky substituents without extended alkyl chains are able to form a mesomorphic "flying seed-like" state existing in wide temperature range. However, the literature provides very little information on such compounds, namely on those having (1,1-diphenylethyl)phenoxy, (1-methyl-1-phenylethyl)phenoxy- and (*tert*-butyl)phenoxy-substituents containing copper as the central ion [22]. There is no information found on complexes of such structures with lanthanides.

Developing synthesis of aryloxy-substituted phthalocyanine lanthanide complexes [23] of both planar and sandwich structure is intriguing due to the need to overcome the main limitation of formation of mixed products of various composition. The current work provides a synthetic approach for novel phthalocyanine metal complexes containing peripheral 4-(1-methyl-1-phenylethyl)phenoxy-groups with lutetium and erbium. Analysis of spectroscopic properties is performed in order to find out whether or not it is possible to use the obtained compounds as photosensors and photocatalysts.

EXPERIMENTAL

Electron absorption spectra were registered in organic solvents (DMF and chloroform) by means of a Shimadzu UV-1800 spectrophotometer with a wave range of 200–1000 nm at a temperature of 298.15 K.

IR spectra were registered by means of an Avatar 360 FT-IR ESP device using a frequency range of 400–4000 cm^{-1} from KBr pellets.

MALDI-TOF mass spectra were registered by means of a Shimadzu Biotech Axima Confidence Time-of-Flight mass spectrometer in positive and negative ion modes. 2,5-Dihydroxybenzoic acid, α-cyano-4-hydroxycinnamic acid were used as a matrix. Samples were gained by dissolving the compounds in chloroform (10^{-4}–10^{-5} mol × L^{-1}) followed by mixing it with a DMF matrix solution (30 mg × mL^{-1}) in 1:1 (v/v) ratio.

^{1}H NMR spectra were registered in a DMSO-D_6: $CDCl_3$ mixture (2:1) under 294 K by means of an Avance 500 (Bruker) spectrometer. The working frequency for ^{1}H nuclei was 500.17 MHz. The error of chemical shift value obtained was not higher than 0.005 ppm. Chemical shifts for ^{1}H were determined regarding TMS.

***Synthesis of* 4-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*] *phthalonitrile* (1).** Synthesis was carried out according to a known technique [21]. 4-Nitrophthalonitrile (0.9 mmol) and 4-(1-methyl-1-phenylethyl)phenole (0.9 mmol) were dissolved in 30 ml of DMSO. K_2CO_3 (0.2 g) was added every 30 min for 5 h under constant stirring. The reaction mixture was then stirred at 20 °C for 24 h. The insoluble precipitate was filtered off. Water (40 ml) was rapidly added to the filtrate. The resulting suspension was neutralized by hydrochloric acid. The obtained mixture was maintained for a night and the resulting precipitate was filtered off, washed with water until the filtrate became transparent and dried under 50 °C. Yield: 80% (2.43 g). Elemental analysis found: C, 81.45; H, 5.46; N, 5.30%; Anal. calculated for ($C_{23}H_{18}N_2O$) C, 81.63; H, 5.36; N, 8.28. IR (KBr): υ, cm^{-1}; 3050, 3031 (Ar-H); 2964, 2924, 2854 (CH_3); 2229 (C≡N); 1232 (Ar-O-Ar). MS (MALDI-TOF) *m/z* 339 $[M + H]^+$; calculated [M] 338.

***Synthesis of* 4,5-*di*[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*]*phthalonitrile* (5)** was carried out according to [24]. 4-Bromo-5-nitrophthalonitrile (1 mmol) and 4-(1-methyl-1-phentlethyl)phenole (2 mmol) were dissolved in DMF (70 ml). A solution of K_2CO_3 (2 mmol) in water (10 ml) was added and the mixture was stirred for 8 h at 80–90 °C. The resulting precipitate was filtered off by means of a paper filter, washed with 2-propanol followed with water until 2-propanol was absent and dried at 70–80 °C. Yield: 44% (2.40 g). Elemental analysis found: C, 82.95; H, 6.02; N, 5.11%; Anal. calculated for ($C_{38}H_{32}N_2O_2$) C, 83.19; H, 5.88; N, 4.96. ^{1}H NMR ($CDCl_3$): δ, ppm 7.33 s (H1; 2H), 7.01–7.03 m (H2; 4H), 6.96–6.98 m (H3; 4H), 7.09–7.17 m (H4–6; 10H), 2.19 s (CH_3; 12H). IR (KBr): υ, cm^{-1} 3050, 3029 (Ar-H); 2967, 2929, 2869 (CH_3); 2233 (C≡N); 1217 (Ar-O-Ar). MS (MALDI-TOF) *m/z* 549.19 $[M + H]^+$; 588.13 $[M + K]^+$; calculated [M] 548.68.

General synthetic approach for metal complexes of* 2(3),9(10),16(17),23(24)-*tetrakis- and* 2,3,9,10,16,17,-23,24-*octakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*] *phthalocyaninato. A mixture of phthalonitrile (**1** or **5**) (0.80 mmol), a corresponding metal (0.60 mmol) chloride (method **A**) or acetate (method **B**), DBU (0.8 mmol) and *iso*-amyl alcohol (3 ml) was refluxed for 8 h or 12 h (for erbium chloride), cooled down to room temperature and a mixture of ethanol and water (4:1) was added. A precipitate was filtered off and washed with a mixture of ethanol and water until the filtrate became transparent. The precipitate was dried and the product was extracted by chloroform. Separation of the products was performed by means of column chromatography utilizing silica gel M60 as a sorbent and chloroform (double-decker phthalocyanine), mixture of chloroform and ethanol of 8:1 ratio (phthalocyaninate) as eluent.

2(3),9(10),16(17),23(24)-*tetrakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*]*phthalocyaninato Lu*(III) *chloride* (2*a*) was obtained according to method **A**. Yield: 19% (0.06 g). Elemental analysis found: C, 70.65; H, 4.64; N, 7.16%; Anal. calculated for ($C_{92}H_{72}ClLuN_8O_4$) C, 70.52; H, 4.78; N, 7.98. ^{1}H NMR (DMSO-d_6: $CDCl_3$): δ, ppm 8.19 s (H3; 4H), 7.79–7.76 m (H1; 4H), 7.26–6.95 m (H2,5,6,7,8; 32H), 6.63 d (H4; 8H; *J* 8.57 Hz), 1.65 s (CH_3; 24 H) (**Suppl. 7**). IR (KBr): υ, cm^{-1} 3052, 3030 (Ar-H), 2964, 2924, 2854 (CH_3), 1232 (Ar-O-Ar) (**Suppl. 8**). MS (MALDI-TOF) *m/z* 1683 $[M + 3K]^-$ (**Suppl. 3**); calculated [M] 1564.

2(3),9(10),16(17),23(24)-*tetrakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*]*phthalocyaninato Lu*(III) *acetate* (3*a*) was obtained according to method **B**. Yield: 32% (0.10 g). Elemental analysis found: C, 71.11; H, 4.76; N, 7.06%; Anal. calculated for ($C_{94}H_{75}LuN_8O_6$) C, 70.99; H, 4.82; N, 7.01. ^{1}H NMR (DMSO-d_6: $CDCl_3$): δ, ppm 8.29 s (H3; 4H), 7.86–7.78 m (H1; 4H), 7.44–7.13 m (H2,5,6,7,8; 32H), 7.07–7.00 m (H4; 8H), 2.09 s (CH_3; 3H), 1.66 s (CH_3; 24H)IR (KBr): υ, cm^{-1} 3051, 3030 (Ar-H), 2966, 2926, 2855 (CH_3), 1230 (Ar-O-Ar). MS (MALDI-TOF) *m/z* 1588 $[M + H]^+$; calculated [M] 1587.

***Bis*(2(3),9(10),16(17),23(24)-*tetrakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*]*phthalocyaninato*) *Lu*(III) (4*a*)** was obtained according to method **A**. Yield: 7% (0.04 g). Elemental analysis found: C, 76.68; H, 5.04; N, 7.78%; Anal. calculated for ($C_{184}H_{144}LuN_{16}O_8$) C, 76.42; H, 5.11; N, 7.71. IR (KBr): υ, cm^{-1} 3052, 3030 (Ar-H), 2963, 2925, 2850 (CH_3), 1234 (Ar-O-Ar). MS (MALDI-TOF) m/z 2884 $[M + 2H]^+$; calculated [M] 2882. Method **B**. Yield: 9% (0.05 g).

2(3),9(10),16(17),23(24)-*tetrakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*]*phthalocyaninato Er*(III) *chloride* (2*b*) was obtained according to method **A**. Yield: 48% (0.14 g). Elemental analysis found: C, 70.00; H, 4.66; N, 7.20%; Anal. calculated for ($C_{92}H_{72}ClErN_8O_4$) C, 69.89; H, 4.71; N, 7.17. IR (KBr): υ, cm^{-1} 3052, 3029 (Ar-H), 2966, 2924, 2856 (CH_3), 1232 (Ar-O-Ar). MS (MALDI-TOF) *m/z* 1675 $[M + 3K]^+$ (**Suppl. 2**); calculated [M] 1556.

2(3),9(10),16(17),23(24)-*tetrakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*]*phthalocyaninato Er*(III) *acetate* (3*b*) was obtained according to method **B**. Yield: 38% (0.21 g). Elemental analysis found: C, 71.46; H, 4.78; N, 7.09%; Anal. calculated for ($C_{94}H_{75}ErN_8O_6$) C, 71.32; H, 4.80; N, 7.02. IR (KBr): υ, cm^{-1} 3050, 3029 (Ar-H), 2964, 2926, 2854 (CH_3), 1232 (Ar-O-Ar).

***Bis*(2(3),9(10),16(17),23(24)-*tetrakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*]*phthalocyaninato*) *Er*(III) (4*b*)** was obtained according to method **A**. Yield: 10% (0.06 g). Elemental analysis found: C, 76.88; H, 5.05; N, 7.80%; Anal. calculated for ($C_{184}H_{144}ErN_{16}O_8$) C, 76.52; H, 5.08; N, 7.76. IR (KBr): υ, cm^{-1} 3051, 3030 (Ar-H), 2962, 2926, 2851 (CH_3), 1231 (Ar-O-Ar). MS (MALDI-TOF) m/z 2875 $[M + H]^+$ (**Suppl. 1**); calculated [M] 2874. Method **B**. Yield: 21% (0.12 g).

2,3,9,10,16,17,23,24-*octakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*]*phthalocyaninato Lu*(III) *chloride* (6*a*) was obtained according to method **A**. Yield: 35% (0.16 g). Elemental analysis found: C, 75.87; H, 5.40; N, 4.66%; Anal. calculated for ($C_{152}H_{129}ClLuN_8O_8$) C, 75.72; H, 5.48; N, 4.59. IR (KBr): υ, cm^{-1} 3055, 3026 (Ar-H), 2967, 2930, 2869 (CH_3), 1266 (Ar-O-Ar).

2,3,9,10,16,17,23,24-*octakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*]*phthalocyaninato Lu*(III) *acetate* (7*a*) was obtained according to method **B**. Yield: 29% (0.14 g). Elemental analysis found: C, 76.16; H, 5.44; N, 4.61%; Anal. calculated for ($C_{154}H_{131}LuN_8O_{10}$) C, 76.21; H, 5.52; N, 4.54. IR (KBr): υ, cm^{-1} 3056, 3027 (Ar-H), 2966, 2930, 2867 (CH_3), 1267 (Ar-O-Ar) (**Suppl. 9**). MS (MALDI-TOF) *m/z* 2430 $[M + 2H]^-$ (**Suppl. 4**); calculated [M] 2428.

***Bis*(2,3,9,10,16,17,23,24-*octakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*]*phthalocyaninato*) *Lu*(III) (8*a*)** was obtained according to method **A**. Yield: 16% (0.15 g). Elemental analysis found: C, 80.00; H, 5.65; N, 4.66%; Anal. calculated for ($C_{304}H_{256}LuN_{16}O_{16}$) C, 79.94; H, 5.71; N, 4.59. IR (KBr): υ, cm^{-1} : 3059, 3026 (Ar-H), 2963, 2925, 2859 (CH_3), 1266 (Ar-O-Ar) (**Suppl. 10**). MS (MALDI-TOF) m/z 4562 $[M + 2H]^+$; calculated [M] 4564. Method **B.** Yield: 0.19 g (21%).

2,3,9,10,16,17,23,24-*octakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*]*phthalocyaninato Er*(III) *chloride* (6*b*) was obtained according to method **A**. Yield: 46% (0.22 g). Elemental analysis found: C, 76.12; H, 5.42; N, 4.67%; Anal. calculated for ($C_{152}H_{129}ClErN_8O_8$) C, 76.03; H, 5.46; N, 4.60. ^{1}H NMR (DMSO-d_6: $CDCl_3$): δ, ppm 8.26–8.20 m (H1; 8H), 7.97–7.95 m (H4; 16H), 7.61–6.59 m (H5,6; 24H), 7.21–6.93 m (H2,3; 32H), 1.63 s (CH_3; 24 H). IR (KBr): υ, cm^{-1} 3055, 3026 (Ar-H), 2966, 2929, 2865 (CH_3), 1267 (Ar-O-Ar).

2,3,9,10,16,17,23,24-*octakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*]*phthalocyaninato Er*(III) *acetate* (7*b*) was obtained according to method **B**. Yield: 35% (0.17 g). Elemental analysis found: C, 76.40; H, 5.45; N, 4.63%; Anal. calculated for ($C_{154}H_{131}ErN_8O_{10}$) C, 76.36; H, 5.50; N, 4.60. ^{1}H NMR (DMSO-d_6: $CDCl_3$): δ, ppm 8.39–8.19 m (H1, 8H), 7.97–7.95 m (H4, 16H), 7.61–6.59 d (H5,6; 24H, *J* 10.60 Hz), 7.24–7.17 m (H3, 16H), 6.96–9.92 d (H2, 16H, *J* 9.00 Hz), 2.09 s (CH_3; 3H) 1.63 s (CH_3; 24 H) (**Suppl. 6**). IR (KBr): υ, cm^{-1} 3055, 3026 (Ar-H), 2966, 2931, 2858 (CH_3), 1266 (Ar-O-Ar).

***Bis*(2,3,9,10,16,17,23,24-*octakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*]*phthalocyaninato*) *Er*(III) (8*b*)** was obtained according to method **A**. Yield: 19% (0.17 g). Elemental analysis found: C, 80.13; H, 5.66; N, 4.92%; Anal. calculated for ($C_{304}H_{256}ErN_{16}O_{16}$) C, 80.09; H, 5.70; N, 4.90. IR (KBr): υ, cm^{-1} : 3055, 3026 (Ar-H), 2967, 2930, 2866 (CH_3), 1265 (Ar-O-Ar). MS (MALDI-TOF) m/z 4559 $[M + 3H]^+$ (**Suppl. 5**); calculated [M] 4556. Method **B**. Yield: 23% (0.21 g).

RESULTS AND DISCUSSION

Selection of rare-earth complexes synthesis conditions

For the first time, the influence of synthesis conditions and nature of reagents on yield and composition of resulting products has been studied. Synthetic procedures for lanthanide complexes have been carried out under equal conditions utilizing a general set of compounds, namely phthalonitrile derivatives containing one or two 4-(1-methyl-1-phenylethyl)phenol fragments, chlorides

and acetates of erbium and lutetium. Previously [25] we obtained data on synthesis of double-decker complexes containing peripheral phenoxy-substituents by metalation of free ligand in refluxing *o*-dichlorobenzene (DCB) using 2:1 ligand:salt molar ratio. However, metalation of 2(3),9(10),16(17),23(24)-tetrakis and 2,3,9,10,16,17,23,24-octakis-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninato failed under the same conditions. This is probably caused by steric hindrances originating from the peripheral environment of desired macrocycle. Addition of DBU enhances basicity of a medium, although the monoligand complex only is obtained yielding less than 1%.

In this way, we assumed the only mild way for obtaining phthalocyanine lanthanide complexes containing peripheral 4-(1-methyl-1-phenylethyl)phenoxy groups to be template synthesis utilizing corresponding nitriles (**1**, **5**) and excess of metal cation within *iso*-amyl alcohol in presence of DBU. The reaction was controlled by electronic spectroscopy. Metal complex formation was noted to proceed slower when utilizing erbium chloride as a template. The resulting mixture contained both planar and sandwich-type phthalocyanines is due to the presence of DBU. The first step of the reaction is the formation of mono-decker phthalocyanines, which in turn form sandwich complexes. The same behavior was previously observed for alkyl-substituted phthalocyanines [18]. Separation of the products was performed by means of column chromatography. Fractions could be controlled

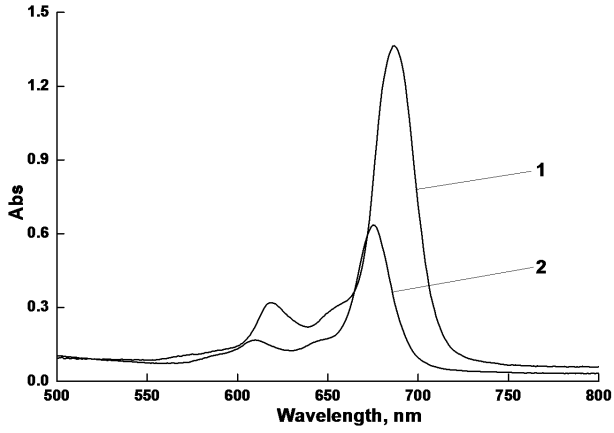
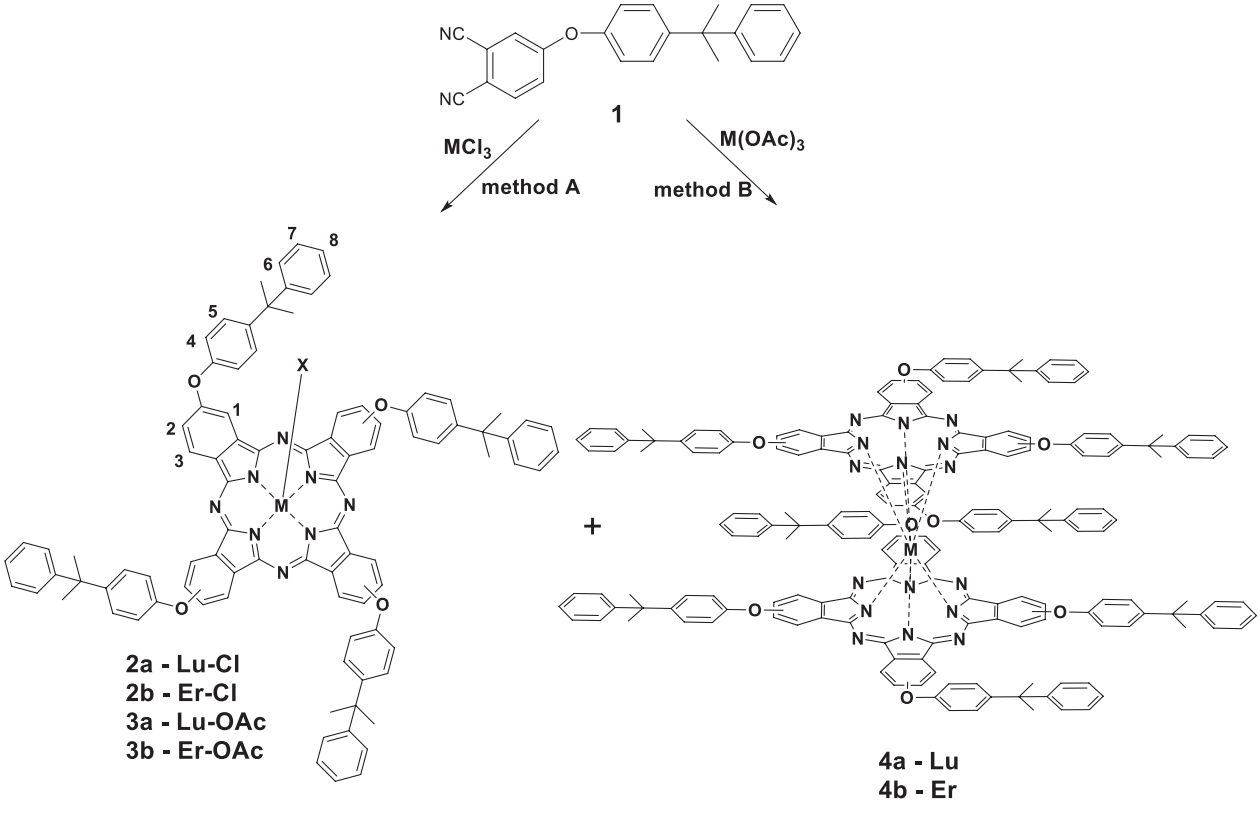


Fig. 1. UV-vis spectra in $CHCl_3$ (3.3×10^{-5} M): 1 – **6a**; 2 – **8a**

spectrophotometrically due to the fact that each of the complexes has its own UV-vis spectral shape (Fig. 1). The compounds were identified by means of IR, ^{1}H NMR, electronic spectroscopy and MALDI-TOF spectrometry.

Synthesis of erbium and lutetium* 2(3),9(10),16(17),-23(24)-*tetrakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*] *phthalocyaninato complexes. The synthetic approach for 2(3),9(10),16(17),23(24)-tetrakis-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninato metal complexes corresponds to Scheme 1, utilizing 4-[4-(1-methyl-1-phenylethyl)phenoxy]phthalonitrile **(1)** obtained by nucleophilic



Scheme 1. General route to synthesis of tetra-substituted phthalocyanines with *f*-metals

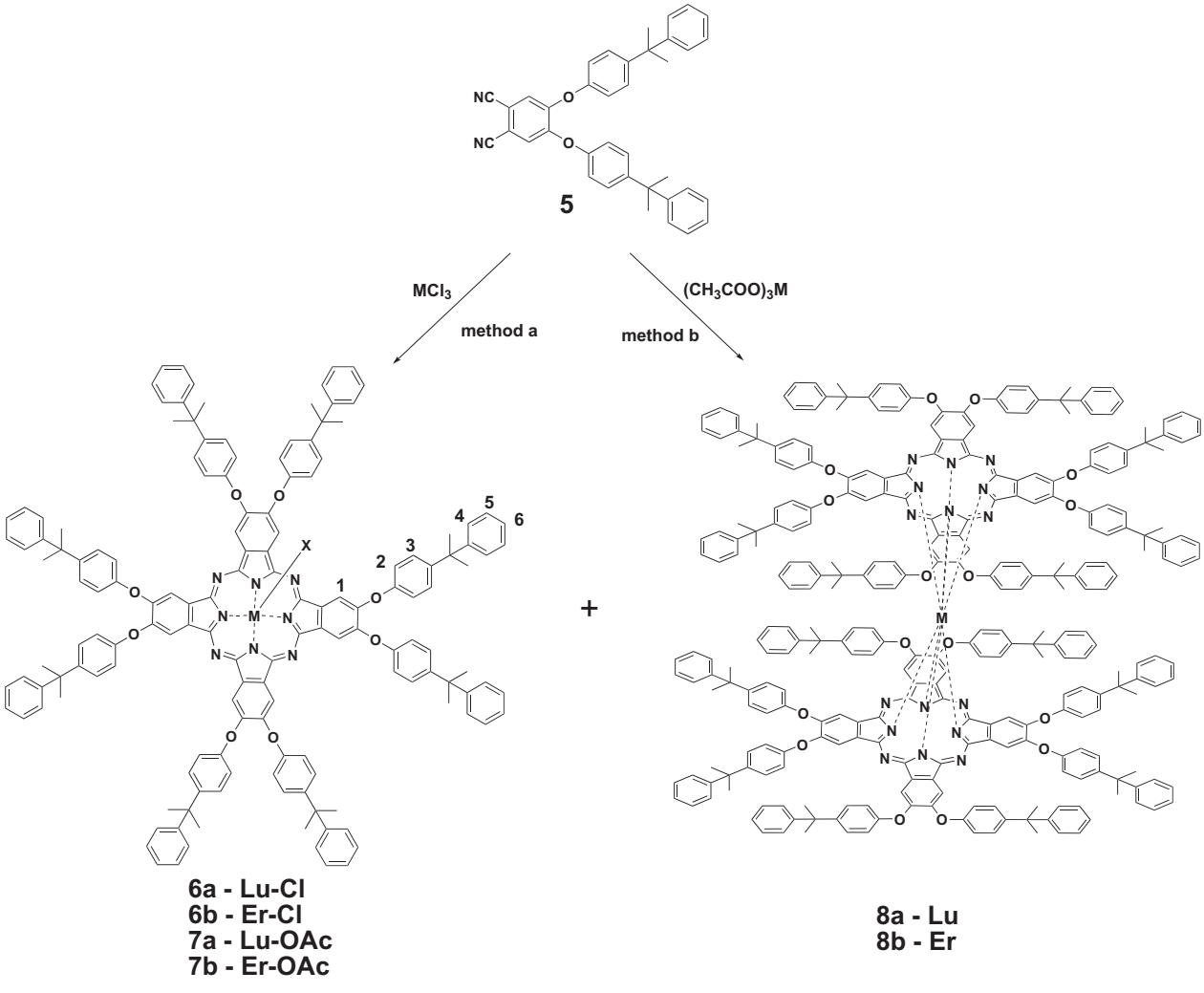
replacement of 4-nitrophthalonitrile's nitro-group with 4-(1-methyl-1-phenylethyl)phenol fragment [22].

A mixture containing both planar and sandwich-type complexes was gained resulting from synthesis using phthalonitrile **1** and lutetium acetate of chloride within refluxing *iso*-amyl alcohol in presence of DBU for 8 h. Chromatography utilizing chloroform as eluent allowed separation of the ligand, the double-decker phthalocyanine and the triphthaloctanine from the mixture, whereas applying chloroform-ethanol (8:1) allowed extraction of monocomplex **3a**. Lutetium acetate compared to the chloride showed a noteworthy increase in containment of double-decker phthalocyanine and decrease in containment of free ligand.

^{1}H NMR identification of phthalocyanine mono-complexes in $CDCl_3$ has failed because aromatic proton signals are covered by resonance of chloroform protons and widened. This phenomenon is explained by self-association of the macrocycle [26]. In turn, the DMSO-d_6 solvent is unsuitable because of low solubility. Taking these two facts into account, a DMSO-d_6:$CDCl_3$ (2:1) mixture was used in order to inhibit an association and enhance a solubility of phthalocyanines up to sufficient level (see supporting information).

The ^{1}H NMR spectrum of **2a** contains weak field region signals of corresponding aromatic protons of the substituent and protons of another phthalocyanine unit as multiplets at 7.26–6.95 ppm, characteristic of aromatic protons. A resonance of 4 phenyl protons in *ortho*-position regarding oxygen is observed as doublet at 6.63 ppm exhibiting a spin–spin interaction constant equal to J_{HH} = 8.37 Hz. The weakest field signal at 8.19 ppm corresponds to the resonance of macrocycle 3 protons, while multiplet at 7.79–7.76 ppm signals four protons being part of first phthalocyanine unit. A singlet at 1.65 ppm signals the presence of a methyl group.

The slowest complexation among all used salts is observed for erbium chloride. An application of the salt



Scheme 2. General route to synthesis of octa-substituted phthalocyanines with *f*-metals

increases containment of mono-decker phthalocyanine and decreases the amount of phthalocyanine ligand and triple-decker complexes in the resulting mixture. As a proof, erbium acetate used as a template source was able to extract mono- and double-decker phthalocyanines only. Thus one can conclude that application of acetates contributes to formation of double-decker complexes.

The literature [18, 21] shows that increasing a template metal's ionic radius increases the yield of a double-decker phthalocyanine. Thus, salt of lutetium, having the smallest ionic radius resulted in predominant formation of mono-decker complex of phthalocyanine, though the mixture contained trace amounts of free ligand, double-decker and triple-decker complexes. Even when using erbium, monocomplexes remained the predominant product, but double-decker phthalocyanine containment increased. Phthalocyanine ligand and triple-decker complex, although present in the mixture, were less than 0.01% at mass.

***Synthesis of erbium and lutetium* 2,3,9,10,16,17,-23,24-*octakis*-[4-(1-*methyl*-1-*phenylethyl*)*phenoxy*].** Since synthesis of tetrasubstituted phthalocyanines is carried out using corresponding asymmetrically substituted phthalonitriles [27], a mixture of isomers with various structure can be formed [28–30]. The isomers are difficult to separate because of similar physico-chemical behavior, which is notably very sensitive towards homogeneity of a compound's composition [31, 32]. As an example, presence of optically inseparable isomers affects not only temperature parameters of mesophase existence but also the ability of a compound to form a mesophase itself [31]. One should be able to obtain highly symmetric phthalocyanines based on phthalonitriles containing two equal substituents in 3,6- or 4,5-positions of phenyl ring in order to prevent formation of such an isomer mixture. Regarding this, synthesis of 2,3,9,10,16,17,23,24-octakis-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninato complexes of lanthanides is of great interest.

The same method as for tetra-derivatives has been applied for obtaining lanthanide complexes based on 2,3,9,10,16,17,23,24-octakis-[4-(1-methyl-1-phenyl-ethyl)phenoxy]phthalocyanine. Refluxing phthalonitrile **5** combined with excess of lutetium or erbium salt within *iso*-amyl alcohol in presence of DBU (Scheme 2) gave a mixture containing both planar and sandwich complexes as in the case of tetrasubstituted phthalocyanines. Free ligands were notably absent from the reaction mass in contrast to tetrasubstituted complexes. We also found that applying chlorides (*method* **A**) as template salts resulted in formation of mono- and double-decker phthalocyanines as well as trace amounts of triple-decker complexes. Only mono- and double-decker phthalocyanines were extracted when using acetates (*method* **B**). Acetates also contributed to formation of double-decker complexes.

Table 1. Detail of the Q-band region of the electronic spectra of phthalocyanines in DMF and in $CHCl_3$

Ref.	λ_Q, nm ($\log_{10}\varepsilon$)	
	DMF	$CHCl_3$
2a	680 (4.84)	686 (4.86)
3a	679 (5.16)	685 (5.07)
2b	679 (4.90)	685 (4.98)
3b	679 (4.76)	685 (4.81)
4a	—	673 (4.91)
4b	—	676 (5.08)
6a	679 (4.84)	685 (4.92)
7a	679 (5.21)	685 (5.23)
6b	679 (4.81)	686 (4.91)
7b	679 (5.11)	686 (5.01)
8a	—	674 (5.26)
8b	—	678 (5.21)

Spectrophotometric studies of synthesized phthalocyaninates

Analysis of electronic absorption spectra obtained for the metal complexes of metal:ligand (1:1) composition revealed that neither the nature of the template metal or extra ligand bonded with the metal ion nor the number of cumylphenolic fragments contained in the phthalocyanine molecule significantly affected the position of bands represented in the UV-vis spectra (Table 1). Only a small hypsochromic shift was registered when using DMF instead of chloroform.

The shape of the electronic absorption spectra obtained for double-decker complexes depends on the solvent nature. Chloroform gives spectra similar to single-decker complexes except having negligible hypsochromic shifts of the Q band-maximum. Sandwich-type complexes demonstrate hypsochromic shifts of absorption Q bands compared to mono- double-decker phthalocyanines. The shape of sandwich-complex spectra appears to depend on the nature of the template metal. The absorption Q band of erbium complex (**4b**, **8b**) is bathochromically shifted compared to the corresponding lutetium complex (**4a**, **8a**) (Table 1). A distinctive feature of double-decker complexes is a wide band of low intensity at 450–500 nm, characteristic of neutrally-radical "green" form lanthanide sandwich complexes [33]. Additionally, near-IR absorption is registered in the range of 915–940 nm (Fig. 2).

Exchanging DMF for chloroform gave new UV-vis spectra for **4** and **8**. The long wavelength region presents a dual band shape with maxima at 672–676 nm and 630–632 nm. The short-wavelength component becomes

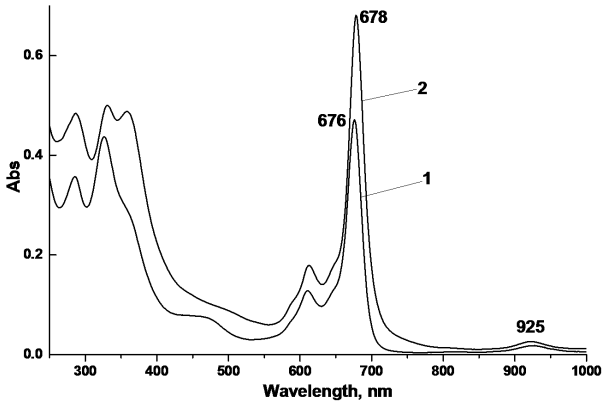


Fig. 2. UV-vis spectra in $CHCl_3$ (4.15×10^{-5} M) : 1 – **4b**; 2 – **8b** at 298.15 K

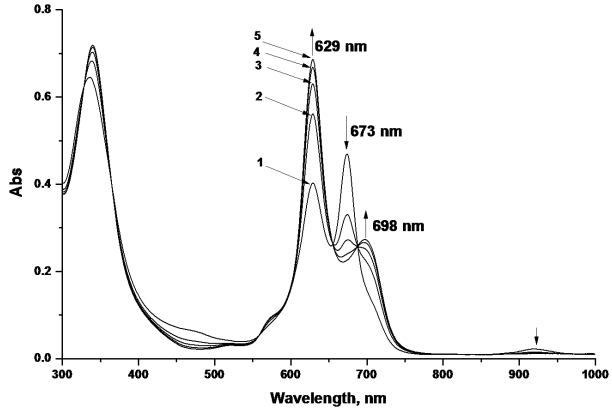


Fig. 3. UV-vis spectral changes of erbium bis(2,9,16,23-tetra-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanine (**4b**) DMF solution (2.73×10^{-5} M) at 298.15 K under storing, 1 – initial, 2 – 2 min 30 s, 3 – 4 min 30 s, 4 – 6 min 30 s, 5 – 8 min 30 s

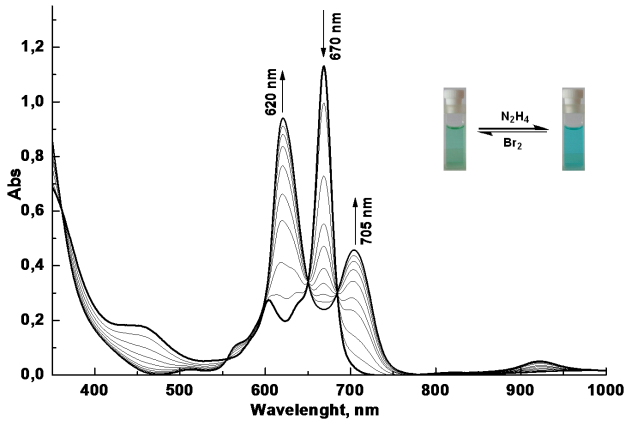


Fig. 4. UV-vis spectral changes of **4a** solution in THF (2.41×10^{-5} M) at 298.15 K in the presence of hydrazine hydrate

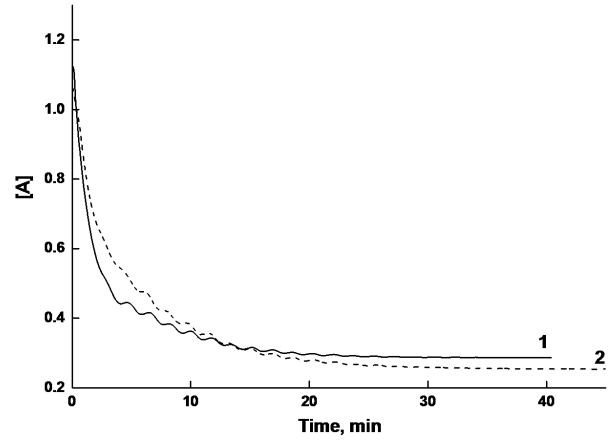


Fig. 5. Kinetic curve of green-blue transformation of **4a** in THF in presence of hydrozinehydrate at 298.15 K (**1**) and 305.15 K (**2**)

predominant with wide bands at 450–500 nm as bands in the IR region disappear.

Figure 3 represents the transformation of neutral sandwich complexes of erbium into corresponding reduced forms. This transformation of bis(2(3),9(10),-16(17),23(24)-tetrakis-[4-(1-methyl-1-phenylethyl) phenoxy]phthalocyaninato) Er(III) (**4b**) in DMF takes place spontaneously within several minutes without adding any reducing agent at room temperature.

Kinetics of redox transfer for freshly obtained solutions of erbium (**4b**) and lutetium (**4a**) bis(2(3),9(10),-16(17),23(24)-tetrakis-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninato) have been studied. The UV-vis spectra of **4b** demonstrate degeneration of absorption bands at 476, 673 and 925 nm, characteristics of neutrally-radical forms of general formula $[Pc^{2-}Er^{3+}Pc^{-\bullet}]^0$ and appearance of a new band at 698 nm indicating the reduced anionic form of general formula $[(Pc^{-})_2Er^{3+}]^+$. Observed transformations are accompanied by formation of isosbestic points that prove existence of two equilibrium processes, in other words suggesting the process to be reversible. Similar transformations are revealed for sandwich complexes of lutetium phthalocyaninate.

The process has been studied in tetrahydrofurane in order to investigate the possibility of controlling transformation of neutrally-radical forms into reduced ones. Hydrazine hydrate was taken as a reducing agent.

Figure 4 represents transformation of lutetium phthalocyanine **4a** from a neutrally-radical form into a reduced one. An unpaired electron of a "green" form occupies a single-time occupied molecular orbital (SOMO). The stability of such a radical can be explained by the presence of electron delocalization between two phthalocyanine macrocycles, which are located at a short distance from each other. SOMO of the "blue" neutral-radical form transforms into the highest occupied molecular orbital (HOMO). In this way, a one-electron transition from HOMO to LUMO occurs in the presence of hydrazine hydrate.

The kinetic study of the process at different temperatures (Fig. 5) made it possible to calculate its activation

parameters. The calculated value of the activation energy is found to be $E^{\neq}$ 40.38 kJ, which characterizes the diffusion nature of this process. Obviously, the relatively low activation barrier toward a transfer of an electron from a single-time occupied molecular orbital (SOMO) shows the possibility of controlling this process due to minor external influences, such as increasing or decreasing the temperature within 5 degrees.

CONCLUSION

In sum, series of Lu(III) and Er(III) complexes with substituted phthalocyanines has been synthesized. Application of phthalonitrile containing only one 4-(1-methyl-1-phenylethyl)phenol fragment in the presence of a triple excess of the corresponding metal salt has been found to result in formation of metal-free phthalocyanine and its metal complex of metal:ligand (1:1) composition, as well as corresponding double- and triple-decker complexes. Di-4,5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalonitrile in contrast to 4-(1-methyl-1-phenylethyl)phenol-derived phthalonitrile results in absence of free ligand from the reaction mixture. Moreover, symmetrically-substituted phthalocyanines have higher yields than tetrasubstituted ones. Metal salt has been found to affect the composition of resulting mixture. The effect is higher yields of sandwich metal complexes when replacing lutetium with erbium and acetates with chlorides. Based on studies of transformation from neutrally-radical forms into reduced ones for lutetium and erbium sandwich phthalocyanines, one can suppose the studied complexes could be applied in various redox processes as, for example, electrochromic components of displaying devices.

Acknowledgments

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Supporting information

MALDI-TOF, ^{1}H NMR and FT-IR spectra for selected compounds are available in the supplemental material (Figs S1–S10). This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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