

## Sandwich–Type Lanthanide(III) Dinaphthalocyanine Complexes Possessing an Intensive Absorption in the Near IR Region: Synthesis and Investigation of Properties

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*Dedicated to Academician Aslan. Yu. Tsvadze on the occasion of his Anniversary*

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*Phenoxy-substituted sandwich-type naphthalocyanine complexes of lanthanides were synthesized in a melt under the heating and using microwave irradiation assisted approach. The intensive absorption in the near IR region up to 2000 nm was found. All complexes obtained were characterized using MALDI-TOF mass spectrometry, UV/Vis/NIR and <sup>1</sup>H NMR spectroscopy. The presence of reversible redox properties was demonstrated by cyclic voltammetry for a wide range of potentials (-1.6÷1.6 V).*

**Keywords:** Dinaphthalocyanine, lanthanide, near IR region, electrochemistry, microwave irradiation.

## Динафталоцианиновые комплексы лантанидов(III) сэндвичевого строения, обладающие интенсивным поглощением в ближнем ИК диапазоне: синтез и исследование свойств

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*Посвящается академику Аслану Юсуповичу Цивадзе по случаю его 70-летнего юбилея*

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*Синтезированы феноксизамещенные динафталоцианиновые комплексы РЗЭ. Обнаружено интенсивное поглощение данных соединений в ближней ИК области вплоть до 2000 нм. Установлены корреляции между радиусами ионов РЗЭ и значениями редокс потенциалов.*

**Ключевые слова:** Динафталоцианин, лантанид, ближняя ИК область, электрохимия, микроволновое излучение.

## Introduction

Phthalocyanines with an extended  $\pi$ -conjugation system are of increasing importance due to the presence of absorption in the near-IR region.<sup>[1-4]</sup> It is known that the widening of the conjugation system causes a considerable (up to 100 nm) bathochromic shift of the *Q*-band in the electronic absorption spectra of naphthalocyanines in comparison with the spectra of phthalocyanines.<sup>[5-8]</sup> An introduction of functional groups into naphthalocyanine ligands, a possibility of a central ion incorporation into the macrocycle, and an ability, similarly to phthalocyanines, to form double decker complexes allows one to vary their properties within a wide range.<sup>[9]</sup> So a direct synthesis of new substituted naphthalocyanines is an important problem, as well as a study of their properties in order to establish the structure-properties relationship and to broaden the scope of their application. The main purpose of present work was the synthesis of phenoxy-substituted dinaphthalocyanine complexes of lanthanides and determination of correlations between their spectral and electrochemical properties and values of radius of central ion.

## Experimental

Column chromatography was carried out on neutral MN-Aluminiumoxid. The electrolyte  $[\text{Bu}_4\text{N}]^+[\text{BF}_4]^-$  (Sigma-Aldrich) was recrystallized twice from ethyl acetate/hexane (9:1, V/V) and dried under vacuum at 70 °C. All other reagents and solvents were obtained or distilled according to standard procedures. The salts  $\text{Ln}(\text{OAc})_3 \cdot n\text{H}_2\text{O}$  were dried immediately before use in a vacuum desiccator for 4 h at 70 °C. 6,7-Diphenoxynaphthalene-2,3-dicarbonitrile **1** was obtained by the earlier published procedure.<sup>[10]</sup>

Electronic absorption (UV-vis) spectra were recorded on a ThermoSpectronic Helios- $\alpha$  spectrophotometer using quartz cells (0.5×1cm). UV/Vis/NIR measurements were made with a Hitachi U-4100 spectrophotometer in quartz cells (1×1cm) using  $\text{CCl}_4$  as a solvent. MALDI-TOF mass spectra were taken on a VISION-2000 mass spectrometer with  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA) as the matrix. <sup>1</sup>H NMR spectra of reduced forms of dinaphthalocyanine complexes, which were generated by the addition of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (1-2 vol.%), were recorded on a Bruker AVANCE 400 spectrometer (400.13 MHz) at 20 °C (if not additionally specified). Chemical shifts are given in ppm relative to  $\text{SiMe}_4$ .

Cyclic voltammetry was performed with IPC-Pro (Econix, Moscow, Russia) electrochemical interface using a conventional three-electrode cell with a Pt-disk (2.0 mm in diameter) working and Pt-foil counter electrodes. The calomel reference electrode (SCE, 3.5 M KCl) was connected to the solution through a salt bridge and a Luggin capillary, the tip of which was placed close to the working electrode. The junction potential of the reference electrode was corrected to a ferrocenium<sup>+</sup>/ferrocene ( $\text{Fc}^+/\text{Fc}$ ) couple. *o*-Dichlorobenzene (*o*-DCB, 99 % Sigma-Aldrich, HPLC-grade) freshly passed through an  $\text{Al}_2\text{O}_3$  was used as a solvent. Blank voltammograms were recorded in the solution of 0.15 mol/l  $\text{Bu}_4\text{NBF}_4$  (Sigma-Aldrich, dried under vacuum at +80 °C) before 0.2-1 mmol/l of sample was introduced. All solutions were bubbled with argon for 20 min before measurements were taken.

*Synthesis of lanthanide bis[(3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanines] (2-4) in a melt of compound 1 (general procedure).* The mixture of 6,7-diphenoxynaphthalene-2,3-dicarbonitrile **1** (0.3 g, 0.83 mmol) and  $\text{Ln}(\text{OAc})_3 \cdot n\text{H}_2\text{O}$  (0.17 mmol) (Ln = Lu, Er, Eu) was heated with gradual increasing of temperature from 220 to 310 °C. The reaction mixture was kept at this temperature for 2 h until the reaction mass solidified.

Then, the reaction mixture was dissolved in DMF and target dinaphthalocyanine was precipitated with methanol. The precipitate was filtered off and dried at 70 °C, dissolved in benzene, and purified by column chromatography ( $\text{THF}-\text{C}_6\text{H}_6$  (1:10),  $\text{Al}_2\text{O}_3$ ).

*Lutetium bis[(3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanine] (2).* The yield was 130 mg (41 %). UV-vis (THF)  $\lambda_{\text{max}}$  nm (lg $\epsilon$ ): 339 (5.38), 590 (4.74), 677 (4.78), 758 (5.24). MS (MALDI-TOF), *m/z*: 3073  $[\text{M}]^+$ , 2980  $[\text{M}-\text{OPh}]^+$ , 2888  $[\text{M}-2\text{OPh}]^+$ , 2796  $[\text{M}-3\text{OPh}]^+$ , 2703  $[\text{M}-4\text{OPh}]^+$ . <sup>1</sup>H NMR ( $\text{THF}-d_8 + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (1-2 vol.%), 298 K)  $\delta_{\text{H}}$  ppm: 7.21 (t, 16 H, *p*- $\text{H}_{\text{OPh}}$ ,  $J = 7.1$  Hz); 7.29 (d, 32 H, *o*- $\text{H}_{\text{OPh}}$ ,  $J = 7.7$  Hz); 7.50 (t, 32 H, *m*- $\text{H}_{\text{OPh}}$ ,  $J = 7.2$  Hz); 8.04 (s, 16 H,  $\beta\text{-H}_{\text{Ar}}$ ); 9.07 (s, 16H,  $\alpha\text{-H}_{\text{Ar}}$ ).

*Erbium bis[(3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanine] (3).* The yield was 150 mg (47 %). UV-vis (THF)  $\lambda_{\text{max}}$  nm (lg $\epsilon$ ): 336 (5.42), 591 (4.77), 679 (4.87), 762 (5.33). MS (MALDI-TOF), *m/z*: 3065  $[\text{M}]^+$ , 2973  $[\text{M}-\text{OPh}]^+$ , 2881  $[\text{M}-2\text{OPh}]^+$ . <sup>1</sup>H NMR ( $\text{THF}-d_8 + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (1-2 vol.%), 298 K)  $\delta_{\text{H}}$  ppm: 9.95-12.04 (m, 40H,  $\text{H}_{\text{OPh}}$ ); 19.87 (s, 16H,  $\beta\text{-H}_{\text{Ar}}$ ); 36.72 (s, 16H,  $\alpha\text{-H}_{\text{Ar}}$ ).

*Europium bis[(3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanine] (4).* The yield was 174 mg (55 %). UV-vis (THF)  $\lambda_{\text{max}}$  nm (lg $\epsilon$ ): 339, 594, 623, 682, 769. MS (MALDI-TOF), *m/z*: 3050  $[\text{M}]^+$ , 2958  $[\text{M}-\text{OPh}]^+$ . <sup>1</sup>H NMR ( $\text{THF}-d_8 + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (1-2 vol.%), 298 K)  $\delta_{\text{H}}$  ppm: 7.07-7.70 (m, 40H,  $\text{H}_{\text{OPh}}$ ); 8.96 (s, 16H,  $\beta\text{-H}_{\text{Ar}}$ ); 11.06 (s, 16 H,  $\alpha\text{-H}_{\text{Ar}}$ ).

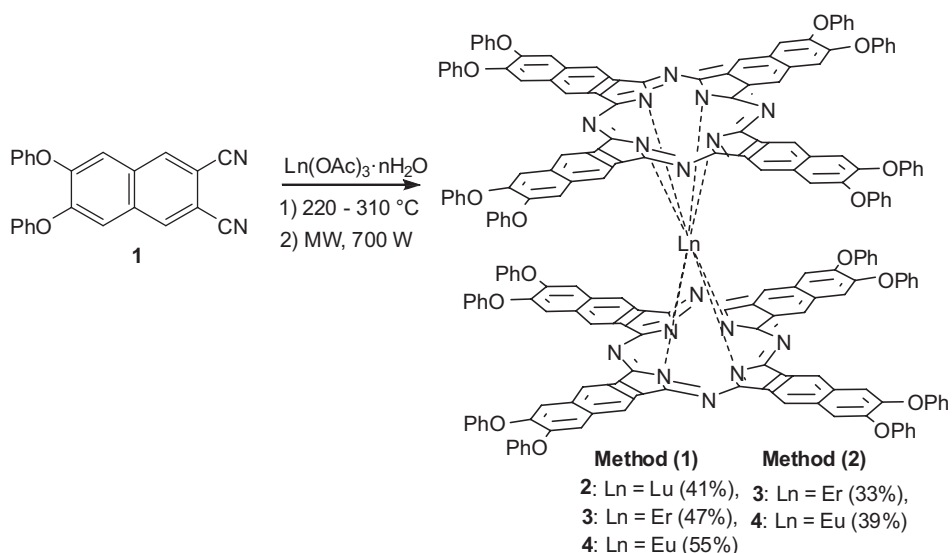
*Synthesis of lanthanide bis[(3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanines] (3, 4) using microwave irradiation (general procedure).* The mixture of compound **1** (0.3 g, 0.83 mmol) and  $\text{Ln}(\text{OAc})_3 \cdot n\text{H}_2\text{O}$  (0.17 mmol) (Ln = Er, Eu) was placed into a microwave oven with the power of irradiation of 700 W. The reaction time was 5-7 min. Then, the reaction mixture was dissolved in DMF, and dinaphthalocyanine was precipitated with methanol. The precipitate was filtered off and dried at 70 °C, dissolved in benzene, and purified by column chromatography ( $\text{THF}-\text{C}_6\text{H}_6$  (1:10),  $\text{Al}_2\text{O}_3$ ). The yields of compounds **3** and **4** were 105 mg (33 %) and 123 mg (39 %), respectively. The characteristics were identical with those obtained by the first method.

## Results and Discussion

### Synthesis

Starting dinitrile **1** was obtained by the earlier published procedure<sup>[10]</sup> Dinaphthalocyanine complexes **2-4** were synthesized by the melting of naphthalodinitrile **1** and corresponding salts of lanthanide (Scheme 1).

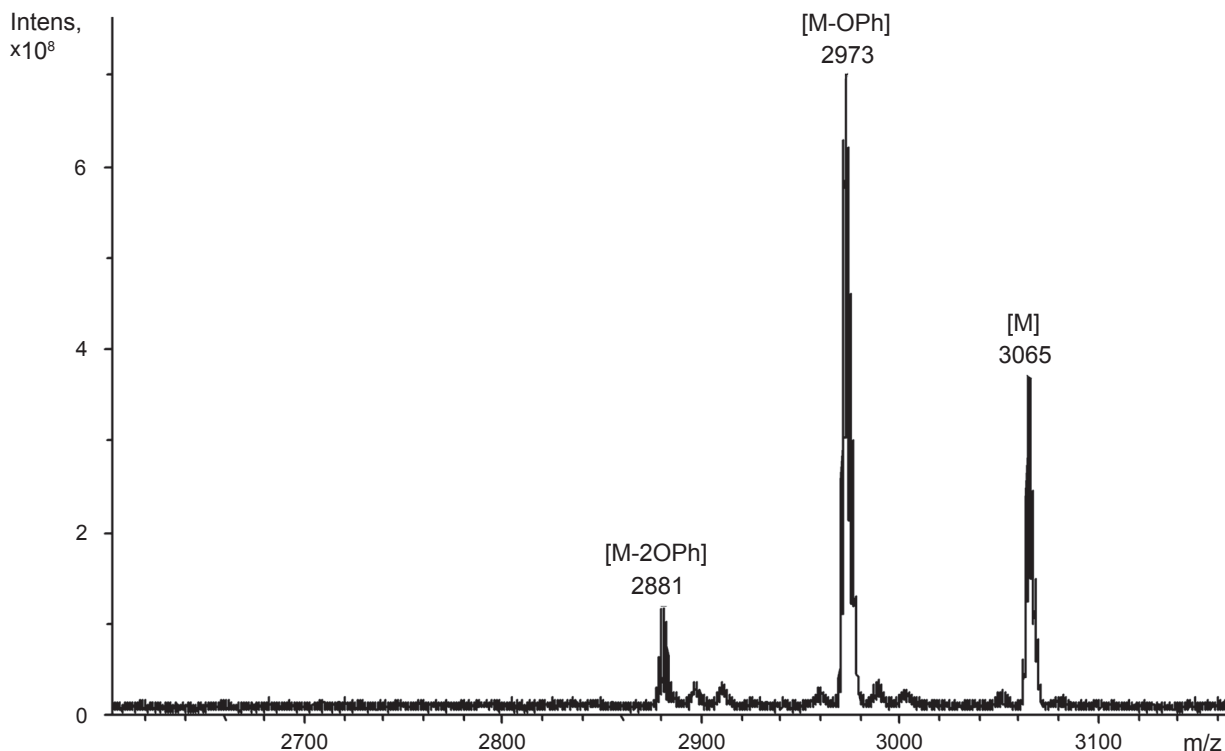
This method considerably differs from the synthesis in solution<sup>[11-13]</sup> since the starting nitrile serves simultaneously as the reagent and the reaction medium. According to this method, the synthesis of dinaphthalocyanines **2-4** was performed by melting of a mixture of dinitrile **1** with the corresponding lanthanide acetates by the gradual increase of temperature from 220 to 310 °C and by keeping at this temperature until the reaction mixture was solidified (~2 h). Compounds **2-4** were purified using chromatography. It was found that the yields of dinaphthalocyanine complexes gradually decrease on going from europium to lutetium that agrees with the literature data.<sup>[14]</sup> It was noted that the change of the yield correlates with the size of the central ion. Apparently, this is caused by a decrease in the lanthanide ionic radius from europium to lutetium and by the corresponding increase in the steric effect. Using of this approach allowed us to decrease the time of reaction and increase the yields of target complexes comparing to their analogues, which were obtained by the synthesis in solution.<sup>[13]</sup>



Scheme 1.

In addition to the melting method, the europium and erbium dinaphthalocyanine complexes were synthesized using microwave irradiation (MW). This method has been suggested for the first time for the synthesis of unsubstituted and octa-*tert*-butyl-substituted lanthanide diphthalocyanines<sup>[15]</sup> and so far has not been used for preparation of naphthalocyanine complexes. Naphthalodinitrile **1** and acetates of the corresponding lanthanide salts were used to obtain the dinaphthalocyanine complexes. The synthesis was carried out by irradiation of a

mixture of reagents in a microwave oven (Samsung, 1714R model). The power of irradiation was varied from 300 to 1000 W, the time, from 3 to 10 min. The following conditions were found to be optimal for the synthesis of dinaphthalocyanines with the use of the MW energy: the power of 700 W and the reaction time of 5-7 min. The use of microwave irradiation of higher power led to destruction of 2,3-naphthalodinitrile **1**. The use of MW allowed us to considerably simplify the synthesis (which can be carried out solvent-free), as well as to decrease the synthesis time from several hours to several

Figure 1. MALDI-TOF mass spectrum of **3**.

minutes. In the case of MW experiment, the main energy source is a MW irradiation, which more powerful, than the heating. Therefore, the reaction time decreased. The yields of dinaphthalocyanines are comparable with the results obtained by the melting method.

All complexes obtained were characterized using MALDI-TOF mass spectrometry, UV/Vis/NIR and  $^1\text{H}$  NMR spectroscopy of reduced forms.

The MALDI-TOF mass spectra of these compounds (Figure 1, CHCA used as the matrix) revealed intense molecular ion  $[M]^+$  peak. It is also noteworthy that in the case of **3**, two additional fragmentation peaks with molecular weight  $[M-OPh]^+$  and  $[M-2OPh]^+$  which were formed during laser ionization were observed.

### Spectral Properties

Comparing to planar complexes some peculiarities were observed in the UV/Vis/NIR spectra of dinaphthalocyanines (Figure 2). There are three bands referring to single-occupied molecular orbital (SOMO):<sup>[16]</sup> blue valence (BV), red valence (RV) and intervalence (IV). IV band occupies

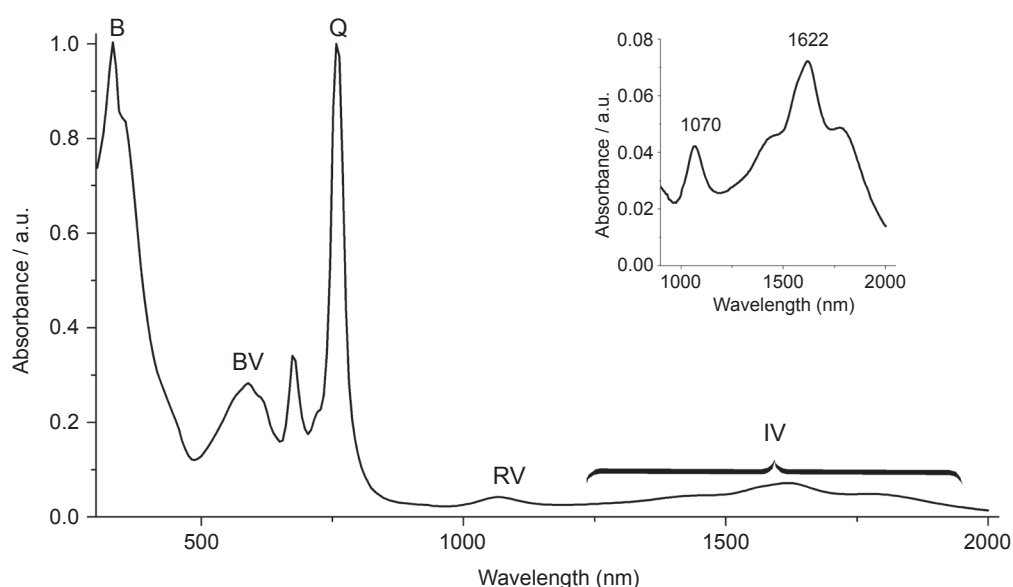
wide region and possesses multiple peak nature, which is referred to equilibrium processes in sandwich molecule<sup>[17]</sup> and corresponding splitting of energy levels.<sup>[18,19]</sup> In contrast to diphthalocyanines<sup>[16]</sup> of lanthanide the shape of this band doesn't exhibit dramatic changes for different central ions.

Noteworthy, that about 100 nm bathochromic shift of the Q, BV and IV bands was shown for dinaphthalocyanine complexes obtained in comparison with diphthalocyanines described in literature.<sup>[20]</sup> The increasing of the ionic radius of lanthanide ion from Lu to Eu leads to the bathochromic shift of Q, BV and IV bands (Table 1). The stabilization of SOMO orbital results in the high values of shift for BV (transition HOMO-2 - SOMO) and IV (transition HOMO - SOMO) bands. The IV-band of Eu complex **4** was the most red-shifted up to 1640 nm.

At the same time the RV (transition SOMO - LUMO) exhibits a hypsochromic shift going from Lu to Eu (Table 1).

### Electrochemical Properties

The redox properties of the dinaphthalocyanine complexes were investigated by cyclic voltammetry in a



**Figure 2.** UV/Vis/NIR spectrum of **3** with magnified NIR region (inset) in  $\text{CCl}_4$ .

**Table 1.** UV/Vis/NIR data and radii of central ion for dinaphthalocyanine complexes **2-4** in  $\text{CCl}_4$ .

Compound	$\lambda_{\text{max}}$ , nm ( $I/I_{\text{max}}$ )	ionic radii, pm <sup>[21]</sup>
<b>2</b>	337 (1.00), 588 (0.26), 675 (0.30), 756 (0.98), 1074 (0.05), 1596 (0.06)	85
<b>3</b>	336 (0.93), 590 (0.24), 676 (0.30), 760 (1.00), 1068 (0.04), 1616 (0.06)	89
<b>4</b>	332 (1.00), 630 (0.42), 681 (0.44), 769 (0.61), 1056 (0.05), 1640 (0.05)	98

**Table 2.** Half-wave potentials (V) for dinaphthalocyanine complexes **2-4** in *o*-DCB.

Compound	$E_{1/2}(\text{Ox}_1)$	$E_{1/2}(\text{Ox}_2)$	$E_{1/2}(\text{Red}_1)$	$E_{1/2}(\text{Red}_2)$	$E_{1/2}(\text{Red}_3)$	$\Delta E(\text{Red}_1 - \text{Red}_2)$
<b>2</b>	0.34 (-0.32) <sup>[a]</sup>	1.33 (0.67)	-0.05 (-0.71)	-0.96 (-1.62)	-1.25 (-1.91)	0.91
<b>3</b>	0.36 (-0.30)	1.32 (0.66)	0.00 (-0.66)	-0.96 (-1.62)	-1.25 (-1.91)	0.96
<b>4</b>	0.31 (-0.35)	-	0.05 (-0.61)	-0.98 (-1.64)	-1.34 (-2.00)	1.03

<sup>[a]</sup>Values versus  $\text{Fc}/\text{Fc}^+$  given in parentheses. The experimental error for obtained values is estimated to be 10 mV.

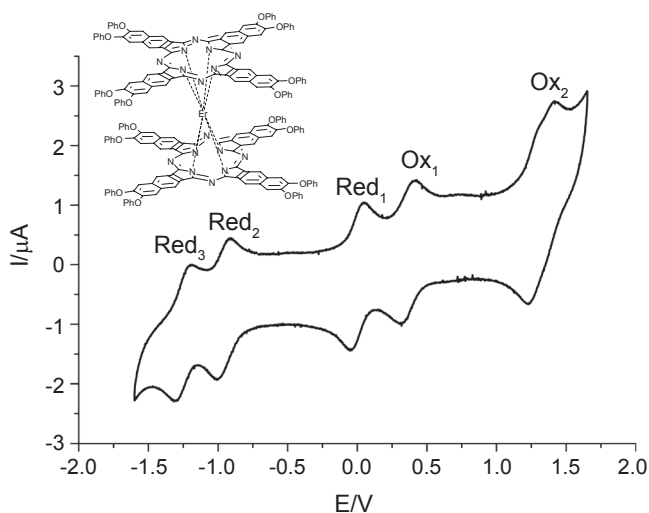


Figure 3. Cyclic voltammogram of **3** in *o*-DCB.

potential range of -1.6 – 1.6 V and summarized in Table 2. Erbium complex **3** demonstrated three reversible reductions and two reversible oxidations (Figure 3). Redox potential for Ox<sub>2</sub> has not been determined in case of complex **4**, since the peaks for relatively diluted solutions of **4** were weak and Ox<sub>2</sub> was probably located near the border or even out of the available window of potentials.

We observed a shift of Red<sub>1</sub> to negative direction along with decreasing of ionic radii from Eu<sup>3+</sup> to Lu<sup>3+</sup>. The similar shift of Red<sub>1</sub> together with Ox<sub>1</sub> is known for diphthalocyanines<sup>[22]</sup> and explained by destabilization of SOMO with decreasing of distance between macrocycles. In case of the studied dinaphthalocyanines the shift of Ox<sub>1</sub> was not obvious, probably because of an effect of peripheral substituents on interaction between macrocycles. The increase in  $\Delta E$  (Red<sub>1</sub> - Red<sub>2</sub>) from Lu to Eu complexes is in accordance with the increase of HOMO-LUMO gap for single-electron reduced forms of diphthalocyanines, which was described in literature.<sup>[16]</sup>

## Conclusions

Phenoxy-substituted sandwich-type naphthalocyanine complexes of lanthanides were synthesized in a melt under the heating and using microwave irradiation assisted approach. This approach was used to obtain dinaphthalocyanines for the first time. About 100 nm bathochromic shift of the Q, BV and IV bands was shown for dinaphthalocyanine complexes obtained in comparison with diphthalocyanines described earlier. IV-Band of Eu complex **4** was the most red-shifted up to 1640 nm. The redox properties of the dinaphthalocyanine complexes were investigated by CVA. The presence of reversible redox processes was shown for all complexes obtained. The correlations between the radius

of central ion of lanthanides and values of redox potentials were established.

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