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Sandwich Complexes of Lutetium with Tetraanthraquinoneporphyrazine and Asymmetric Alkoxy-substituted Phthalocyanines. Preparation and Spectral Properties

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Abstract—Interaction of 3,6-di(hexadecyloxy)phthalonitrile with tetrachlorophthalonitrile and lutetium chloride in alcoholic medium yields lutetium complexes with asymmetric phthalocyanines. Their heating with dinitrile of anthraquinone-2,3-dicarboxylic acid gives the sandwich complexes containing fragments of tetraanthraquinoneporphyrazine and asymmetric phthalocyanines; their spectral properties has been studied.

Keywords: phthalocyanine, chromophore, anthraquinone, lutetium complex, porphyrazine

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Sandwich complexes of rare earth metals with tetrapyrrole ligands are stable compound with unique structure, being of fundamental as well as applied interest. They can be used as sensor materials [1, 2], optical limiters [3] as well as electrochromic [4] or liquid-crystalline [5] materials.

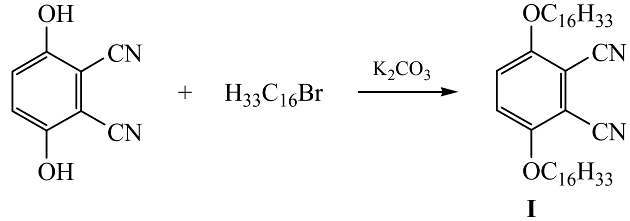
So far the homoligand sandwich complexes of lanthanides have been studied in detail, including these based on phthalocyanines or naphthocyanines [6, 7]. Similar heteroligand complexes, for example, com-bining phthalo-cyanines and porphyrins as ligands [8–11], have been scarcely studied. To the best of our knowledge, information about compounds containing fragments of tetraanthraquinoneporphyrazine and asymmetric phthalocyanine has not been reported in the literature.

Herein, we report on preparation and spectral properties of lutetium complexes with asymmetric alkoxy-substituted phthalocyanines of the AABB and ABAB types as well as of the related sandwich complexes, containing fragments of tetraanthraquinoneporphyrazine.

Asymmetric phthalocyanines were prepared from 3,6-di(hexadecyloxy)phthalonitrile **I** (component A) and tetrachlorophthalonitrile **II** (component B). In turn, compound **I** was synthesized by alkylation of 2,3-dicyanohydroquinone with *n*-hexadecylbromide in the presence of K_2CO_3 in DMF.

Compound **I** was light-yellow powder, readily soluble in benzene and chloroform, and poorly soluble in DMF and acetone. Its composition and structure

Scheme 1.



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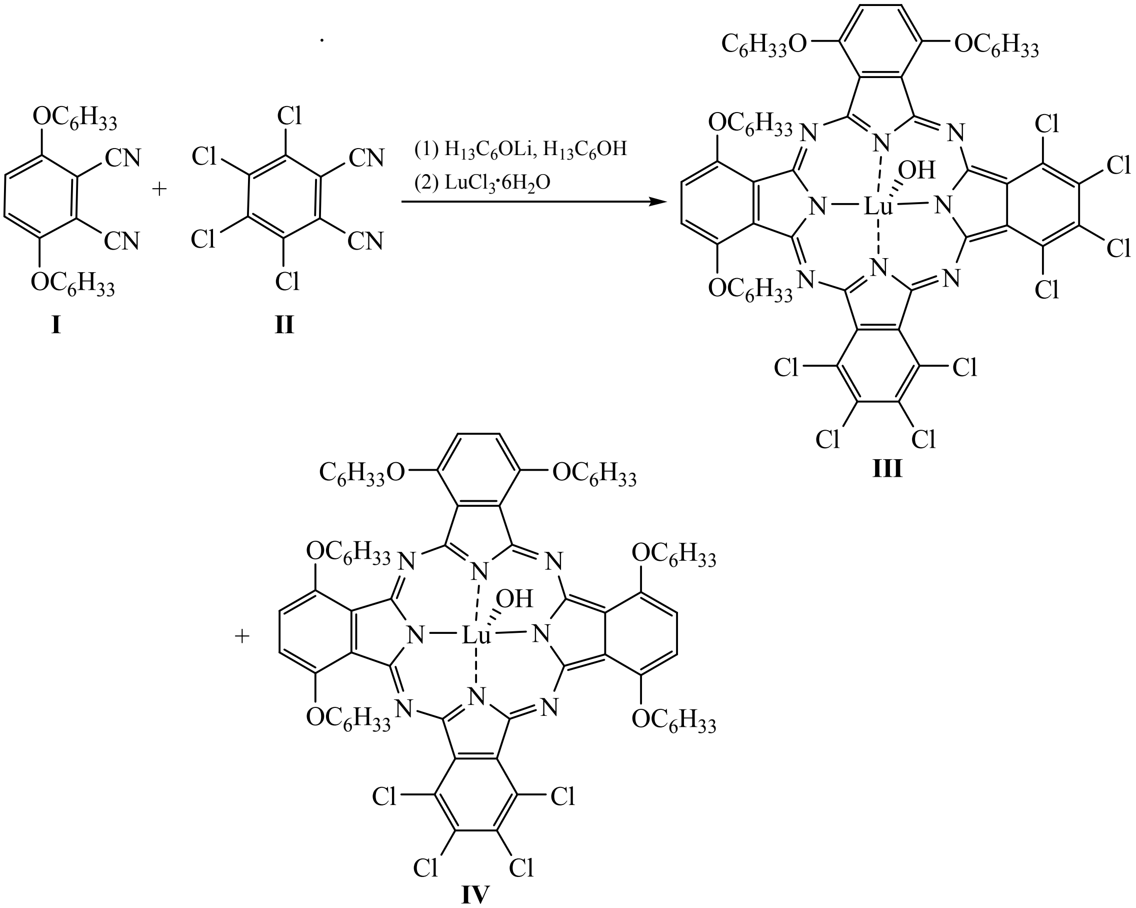
Scheme 2.



were confirmed by elemental analysis, IR, and ^1H NMR spectroscopy data (Scheme 1).

Heating of the mixture of nitriles **I** and **II** (1 : 6 ratio) in boiling hexanol-1 in the presence of lithium hexanolate-1 with subsequent addition of excess of lutetium chloride led to formation of a mixture of phthalocyanines (Scheme 2).

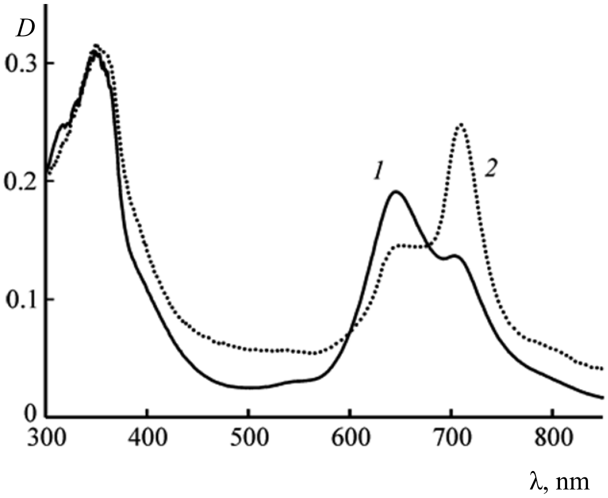
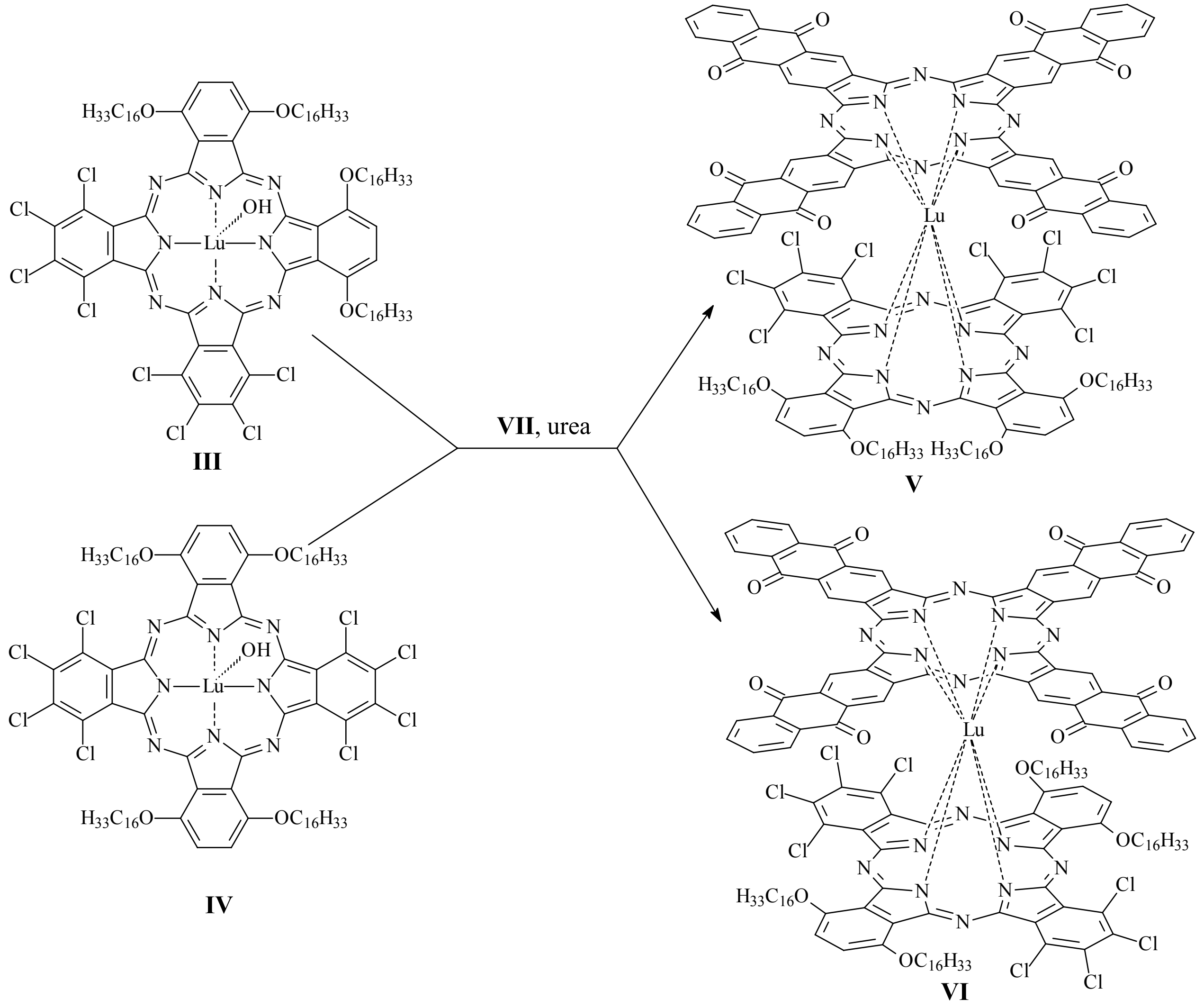


Fig. 1. Electronic absorption spectra of solutions in CH_2Cl_2: compounds **III** (*1*) and **IV** (*2*).

By column chromatography, the following products were isolated: hydroxylutetium 1,4,8,11-tetra(hexadecyloxy)-15,16,17,18,22,23,24,25-octachlorophthalocyaninate **III** (AABB) and hydroxylutetium 1,4,15,18-tetra(hexadecyloxy)-8,9,10,11,22,23,24,25-octachlorophthalocyaninate **IV** (ABAB).

Composition and structure of compounds **III** and **IV** were confirmed by elemental analysis, ^1H NMR, and electronic spectroscopy data. In the ^1H spectra of the products, broadened and poorly resolved signals of benzene rings and alkoxy substituents were observed. That could point at association of phthalocyanines in the solution. Indeed, the spectra quality was improved upon dilution of the solutions. Noteworthily, signals of protons of the hydroxyl groups bound to lutetium were not observed in the spectra, likely, due to deuterium exchange.

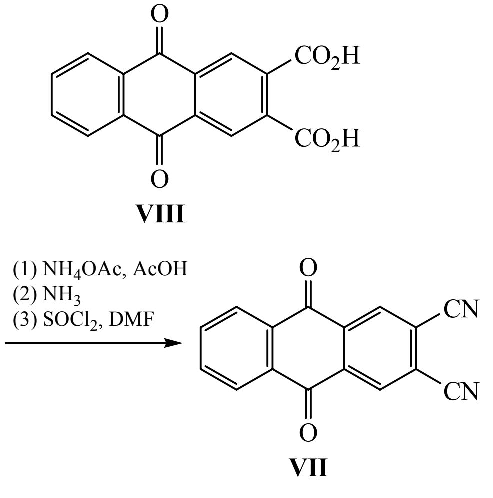
Scheme 3.



Under the reaction conditions, the phthalocyanine A_4 was not formed; compound of the A_3B type was found in trace amounts; the AB_3 and B_4 type complexes were poorly soluble in organic solvents and could not be isolated by chromatography. Hydroxylutetium complexes were formed, evidently, due to partial alkaline hydrolysis.

In the long-wave range of electronic absorption spectrum of compound **III** (Fig. 1, curve *1*), the *Q* band was observed, split into two components with λ_{max} of 704 and 646 nm and the intensity ratio of 0.71 : 1; in the short-wave range, the B band was found (λ_{max} 349 nm). In the spectrum of compound **IV** (Fig. 1, curve *2*), the *Q* band was split into two components as well (λ_{max} 709 and 647 nm), their intensities ratio being

Scheme 4.



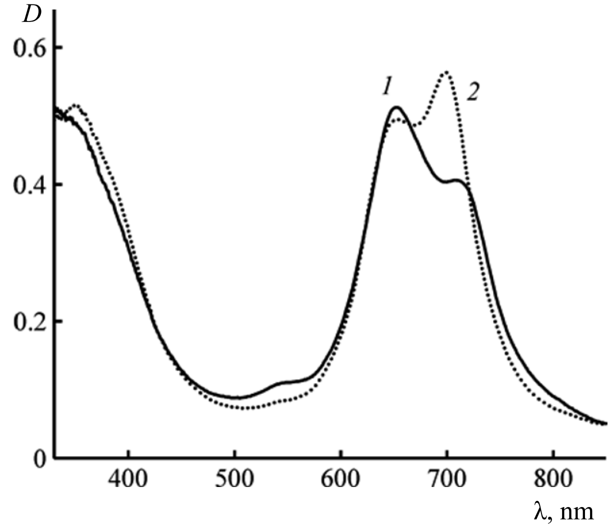


Fig. 2. Electronic absorption spectra of solution of compound **V** in CH_2Cl_2 (*1*) and in DMF (*2*).

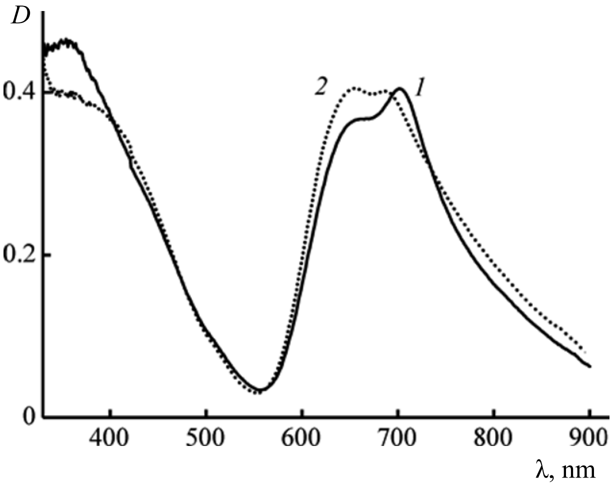


Fig. 3. Electronic absorption spectra of solution of compound **VI** in CH_2Cl_2 (*1*) and in DMF (*2*).

of 1 : 0.58. The B band maximum was found at λ_{max} 351 nm in the case of complex **IV**.

The observed splitting of the long-wave band is typical of the ABAB-type phthalocyanines and can be explained by the four-orbital Gouterman's model [12]. In particular, the long-wave maxima in absorption spectra of symmetric phthalocyanines are assigned to electronic transition from the a_{1u} orbital to two perpendicular degenerate orbitals e_g^*. In the case of asymmetric phthalocyanines, the degeneration was removed, and the *Q* was split into several components. The splitting then should be the highest in the case of the ABAB-type compounds, being in agreement with the experiment.

The heteroligand sandwich compounds, the second chromophore being tetraanthraquinoneporphyrazine, could be prepared via template interaction of the heteroligand complex with phthalonitrile [13–19] or its derivative. In this work, the heteroligand sandwich complexes of lutetium with phthalocyanines AABB (**V**) and ABAB (**VI**) were prepared via heating of phthalocyanines **III** or **IV**, respectively, with excess of dinitrile of anthraquinone-2,3-dicarboxylic acid (**VII**) in urea melt (Scheme 3).

The dinitrile **VII** was in turn prepared from anthraquinone-2,3-dicarboxylic acid **VIII** via sequential treatment with ammonium acetate in acetic acid, ammonia solution, and thionyl chloride in DMF (Scheme 4).

Heteroligand complexes **V** and **VI** were extracted from the reaction mixtures with dichloromethane and purified via column chromatography. They were dark-green compounds, readily soluble in benzene, chloroform, and dichloromethane, and poorly soluble in acetone and DMF. Their composition and structure were confirmed by elemental analysis, ^{1}H NMR, and electronic spectroscopy data.

Electronic absorption spectrum of complex **V** in dichloromethane (Fig. 2, curve *1*) contained the *Q* band split into two components in the long-wave range, λ_{max} of 707 and 653 nm (Δλ 54 nm), intensity ratio of 0.79 : 1. It is known that in the absence of reducing agents phthalocyanine complexes of lanthanides exist in the neutral-radical "green" form in the solutions [19]. Presence of weak absorption band at λ_{max} 549 nm, typical of transition of the unpaired electron confirmed that complex **V** in dichloromethane also existed in the "green" form. Probably, the unpaired electron was majorly localized at the more electron-acceptor fragment of tetraanthraquinoneporphyrazine. Furthermore, the *B* band was found in the spectrum (λ_{max} 339 nm).

As compared with the above-described spectrum, in the case of solution of **V** in DMF (Fig. 2, curve *2*) splitting of the *Q* band decreased (Δλ 46 nm), the ratio of intensity of the components with λ_{max} 698 and 652 nm being changed to 1:0.88. The band at λ_{max} 549 nm disappeared, and the *B* band was shifted (λ_{max}

348 nm). The described featured pointed at transition of complex **V** into its reduced "blue" form.

In the absorption spectrum of the "green" form of complex **VI** (solution in dichloromethane, Fig. 3, curve *1*), the *Q* band was split into two components as well, λ_{max} of 702 and 656 nm, the intensities ratio being of 1 : 0.91. In the spectrum of the "blue" form (solution in DMF), $\Delta\lambda$ was down to 30 nm, the intensities ratio being of 0.99 : 1. The *B* band maximum in the spectra of the both forms of complex **VI** was found at 350 nm. As expected, electronic absorption bands of compound **VI**, containing the ABAB-type phthalocyanine, were significantly broadened as compared with those of complex **V**, containing the AABB-type ligand.

EXPERIMENTAL

Electronic absorption spectra of the solutions were recorded using the Helios Zeta spectrophotometer. IR spectra of thin films on thallium iodide crystal were recorded with the Avatar 360 FT-IR spectrometer (400–4000 cm^{-1}). ^{1}H NMR spectra in $CDCl_3$ or DMSO-d_6 (TMS as internal reference) were recorded using the Bruker Avance-500 spectrometer. Elemental analysis was performed using the FlashEA 1112 CHNS–O Analyzer instrument.

Commercial 2,3-dicyanohydroquinone (98%) and tetrachlorophthalonitrile **II** (98%) (Aldrich) were used. Anthraquinone-2,3-dicarboxylic acid was prepared as described elsewhere [20].

3,6-Di(hexadecyloxy)phthalonitrile (I). A mixture of 2.0 g (12.5 mmol) of compound **II**, 8.4 g (27.5 mmol) of 1-bromohexadecane, 6.9 g (50 mmol) of K_2CO_3, and 30 mL of DMF was stirred at 150°C during 5 h, and then cooled down and diluted with 100 mL of water. The formed precipitate was filtered off, washed successively with 50 mL of HCl solution (10%), 100 mL of water, and 400 mL of acetone, and then dried. Yield 7.5 g (98%), light-yellow powder, readily soluble in benzene, chloroform, poorly soluble in acetone. IR spectrum, ν, cm^{-1}: 3085 (C–H, Ar), 2921 (C–H, Alk), 2223 (C≡N), 1498, 1461, 1281; 1192, 1071 (C–O–C); 836, 477. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.17 s (2H, Ar), 4.08 t (4H, *J* 6.5 Hz, Alk), 1.86 t (4H, *J* 6.6 Hz, Alk), 1.49 t (4H, *J* 6.4 Hz, Alk), 1.30–1.25 m (48H, *J* 6.9 Hz, CH_2), 0.86 t (6H, *J* 6.6 Hz, CH_3). Found, %: C 78.91; H 11.32; N 4.47. $C_{40}H_{68}N_2O_2$. Calculated, %: C 78.89; H 11.25; N 4.60.

Complexes III and IV. 1.00 g (1.6 mmol) of compound **I** was added to the boiling solution of lithium hexanolate-1 (prepared by dissolution of 0.1 g of lithium in 30 mL of hexanol-1), the mixture was incubated during 10 min, and then 2.53 g (9.6 mmol) of compound **II** was added. The mixture was incubated during 2 h, then 2.38 g (6.0 mmol) of lutetium(III) chloride hexahydrate was added, and the mixture was further incubated during 2 h. 20 mL of the alcohol was distilled off the mixture, the residue was cooled down, suspended in 40 mL of acetone, and 5 mL of acetic acid was added. After 5 min of incubation, the formed precipitate was filtered off, washed with 50 mL of acetone, and dried. The product was suspended in 30 mL of dichloromethane and filtered. The filtrate was subject to column chromatography (Kieselgel 60 silica gel, Merck; dichloromethane–THF 50 : 1 as eluent). From the eluted fractions, individual complexes **III** and **IV** were isolated in the form of green waxy substances.

Hydroxylutetium 1,4,8,11-tetra(hexadecyloxy)-15,16,17,18,22,23,24,25-octachlorophthalocyaninate (III) (AABB). Yield 0.32 g (10%), readily soluble in benzene, dichloromethane, and chloroform, poorly soluble in acetone. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.18–7.12 m (4H, Ar), 4.30 t (4H, *J* 6.5 Hz, Alk), 4.14 t (4H), 1.89–1.82 m (8H), 1.30–1.21 m (104H), 0.88 t (12H, *J* 7.2 Hz). Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm (D/D_{max}): 704 (0.44), 646 (0.62), 349 (1.00). Found, %: C 60.01; H 7.93; N 5.38. $C_{96}H_{137}Cl_8LuN_8O_5$. Calculated, %: C 59.38; H 7.11; N 5.77.

Hydroxylutetium 1,4,15,18-tetra(hexadecyloxy)-8,9,10,11,22,23,24,25-octachlorophthalocyaninate (IV) (ABAB). Yield 0.58 g (18%), readily soluble in benzene, dichloromethane, and chloroform, poorly soluble in acetone. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.16–7.10 m (4H, Ar), 4.20 t (8H, *J* 7.2 Hz), 1.88–1.83 m (8H), 1.31–1.25 m (104H), 0.89 t (12H, *J* 6.6 Hz). Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm (D/D_{max}): 800 (sh), 709 (0.79), 647 (0.46), 351 (1.00). Found, %: C 60.33; H 7.56; N 5.27. $C_{96}H_{137}Cl_8LuN_8O_5$. Calculated, %: C 59.38; H 7.11; N 5.77.

Dinitrile of anthraquinone-2,3-dicarboxylic acid (VII). A mixture of 2.90 g (0.01 mol) of the acid **VIII**, 2.50 g (0.03 mol) of ammonium acetate, and 20 mL of glacial acetic acid was refluxed during 2 h. 15 mL of acetic acid was distilled off, and the residue was diluted with 50 mL of water. The formed precipitate was filtered off, washed with water till pH 7, and suspended in 100 mL of ammonia (30 %) solution. The suspension was stirred during 5 days and then filtered off. The precipitate was washed with water till pH 7 and dried. The product was dissolved in 30 mL of DMF, cooled down to 3°C, 8 mL of thionyl chloride was added, and the mixture was stirred during 5 h. The reaction mixture was diluted with 100 mL of water; the formed precipitate was filtered off, washed with water till pH 7, and dried. Yield 1.61 g (61%), grey powder, soluble in DMF and DMSO, poorly soluble in acetone and chloroform. IR spectrum, ν, cm^{-1}: 3071, 2223, 1678, 1447, 897, 748. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.65 s (2H), 8.31–8.28 m (2H), 7.95–7.90 m (2H). Found, %: C 74.13; H 2.87; N 10.61. $C_{16}H_6N_2O_2$. Calculated, %: C 74.42; H 2.34; N 10.85.

Preparation of sandwich complexes V and VI. A mixture of 0.20 g (0.1 mmol) of compound **III** or **IV**, 0.20 g (0.8 mmol) of compound **VII**, and 1.0 g of urea was heated at 190°C during 3 h, and then cooled down. The reaction mixture was crushed, extracted with dichloromethane; the extract was dried and washed with acetone. The residue was dissolved in dichloromethane and subject to column chromatography (Kieselgel 60 silica gel Merck, dichloromethane–THF mixture 10 : 1 as eluent), the major green zone was collected. After the solvent removal, the target products were obtained.

[1,4,8,11-Tetra(hexadecyloxy)-15,16,17,18,22,23,-24,25-octachlorophthalocyaninato]tetraantraquinoneporphyrazinatolutetium(III) (V). Yield 0.17 g (56%), dark-green powder, readily soluble in dichloromethane, chloroform, and benzene, poorly soluble in acetone and DMF. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.78–7.75 m (8H), 7.55–7.53 m (8H), 7.22 s (8H), 7.07 s (4H), 4.33–4.25 m (4H), 4.15 t (4H, *J* 7.2 Hz), 1.87–1.81 m (8H), 1.32–1.20 m (104H), 0.88 t (12H, *J* 7.3 Hz). Electronic absorption spectrum, λ_{max}, nm (D/D_{max}): CH_2Cl_2, 707 (0.79), 653 (1.00), 549 (0.22), 339 (0.98); DMF, 698 (1.00), 652 (0.88), 348 (0.91). Found, %: C 65.21; H 5.87; N 7.13. $C_{160}H_{160}Cl_8 \cdot LuN_{16}O_{12}$. Calculated, %: C 64.97; H 5.45; N 7.58.

[1,4,15,18-Tetra(hexadecyloxy-8,9,10,11,22,23,-24,25-octachlorophthalocyaninato]tetraantraquinoneporphyrazinatolutetium(III) (VI). Yield 0.12 g (40%), dark-green powder, readily soluble in dichloromethane, chloroform, and benzene, poorly soluble in acetone and DMF. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.80–7.76 m (8H), 7.56–7.54 m (8H), 7.25 s (8H), 7.09 s (4H), 4.25–4.18 m (8H), 1.85–1.82 m (8H), 1.32–1.19 m (104H), 0.88 t (12H, *J* 7.2 Hz). Electronic absorption spectrum, λ_{max}, nm (D/D_{max}): CH_2Cl_2, 702 (0.88), 656 (0.79), 350 (1.00); DMF, 685 (0.99), 655 (1.00), 351 (0.99). Found, %: C 65.17; H 5.98; N 7.09. $C_{160}H_{160}Cl_8 \cdot LuN_{16}O_{12}$. Calculated, %: C 64.97; H 5.45; N 7.58.

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