Electrochemical and electrochromic properties of rare-earth metal diphthalocyanine complexes

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The electrochemical and spectroelectrochemical properties of several new rare-earth metal diphthalocyanine complexes with different substituents containing both electron-withdrawing and -donating substituents in the phthalocyanine rings were studied. The influence of structural modification of the phthalocyanine complexes (*viz.*, the nature of the central metal atom and substituents in the phthalocyanine rings and the number of phthalocyanine rings in the complexes) on the total number of redox transitions, their potentials, and spectral characteristics of anionic and cationic forms of the complexes was examined. The potentials of the first anodic and cathodic redox transitions of the diphthalocyanine complexes are in a good linear correlation with the ionic radii of lanthanides. The potentials of the observed redox transitions of the complexes under study correlate well with the sums of Hammett constants for the substituents and the minimum molecular electrostatic potential of the benzene rings in the phthalocyanine moiety, which serves as a measure of electron perturbations introduced by the substituents. The revealed regularities allow the prediction of the redox properties and structure of rare-earth element diphthalocyanine complexes, which are redox-active in a specified potential range.

Key words: rare-earth metals, diphthalocyanine complexes, electrochemistry, spectroelectrochemistry, redox transitions, Hammett constants, semiempirical quantum-chemical calculations.

Phthalocyanine complexes of transition and rare-earth metals are of great interest from both theoretical and practical viewpoints due to their capability of undergoing multiple reversible redox transitions in the anodic and cathodic regions. Few systems with these properties are known. Among them are fullerenes and their derivatives,[1,2] some polynuclear bridged complexes of transition metals (see, *e.g.*, Ref. 3), and several other compounds.[4,5] The distinctive feature of phthalocyanine complexes is a possibility to create on their basis "tuned redox systems" because the phthalocyanine structure allows wide modification, in particular, by the variation of the nature of the central metal atom or introduction of various substituents into the phthalocyanine ring. Note that rare-earth metals form both mono- and diphthalocyanine and even three-decker phthalocyanine complexes. These modifications allow a smooth variation in a wide interval of potentials of electrochemical redox transitions of phthalocyanine complexes.

This work is aimed at systematic studying of the electrochemical and spectral parameters of a series of substituted diphthalocyanine complexes of rare-earth metals and comparing with the monophthalocyanine complexes, whose parameters have been studied in detail.[6] We were interested in the question: how do changes in the phthalocyanine structure affect the total number and potentials of redox transitions, as well as the spectral parameters of anionic and cationic forms of the complexes?

Revelation of these regularities allows the prediction of the properties of the complexes and structure of the catalysts, which are redox-active in a required range of potentials, and estimation of the properties of materials for electrochromic devices with a specified chrominance.

Experimental

Diphthalocyanine complexes of rare-earth metals were synthesized according to the previously described procedure.[7—10] The purity of complexes was monitored by chromatographic, spectral, and elemental analysis data.

Acetonitrile (pure grade) was stirred with CaH_2 for 24 h and filtered. Then KNO_3 (5 g) and conc. H_2SO_4 (5 mL) were

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added. The resulting mixture was boiled for 3 h and distilled. Then MeCN was boiled above P_2O_5 for 2 h and distilled, and the fraction with b.p. 81—82 °C (760 Torr) was taken.

o-Dichlorobenzene (DCB) was dried with $CaCl_2$, filtered, and distilled to take the fraction with b.p. 65 °C (13 Torr). The fraction was passed through a column with neutral Al_2O_3 prior to experiments.

Commercial $Bu^n{}_4NBF_4$ (Aldrich) and DMF (A.C.S. reagent, Aldrich) were used.

Electrochemical measurements were carried out by a PI-50-1.1 potentiostat, a PR-8 programmator, and a PDA1 XY-recorder using the three-electrode scheme on a graphite electrode (pyrolyzed polyacrylonitrile) and a disk Pt electrode with a working surface area of 20.7 mm^2 against the $Bu^n{}_4NBF_4$ supporting electrolyte with a concentration of 0.05—0.15 mol L^{-1} for different solvents at 20 °C. A Pt wire served as an auxiliary electrode, and a saturated Ag|AgCl|KCl electrode was used as a reference. Dioxygen was removed from the cell by a dry argon flow. Voltammetric curves were recorded by cyclic voltammetry (CV) at a sweep rate of 200 mV s^{-1}. The electrode was mechanically polished after recording of each curve. The measured peak potentials were recalculated taking into account the electrolyte resistance calculated by the shift of the anodic and cathodic peaks of ferrocene oxidation $(E^c - E^a) - 0.059 = i \cdot R$, where E^c and E^a are the potentials of the cathodic and anodic peaks of ferrocene oxidation, respectively; i is the sum of currents of the cathodic and anodic processes; and R is the resistance of the electrolyte. Anhydrous MeCN, its mixture with DCB, pure DCB, and DMF were used as solvents. The concentration of solutions of the compounds under study was $7 \cdot 10^{-5}$—$7 \cdot 10^{-4}$ mol L^{-1}.

Spectroelectrochemical studies were carried out at 20 °C in the potentiostatic mode in a special quarts cell connected up to a P-5827M potentiostat by the three-electrode scheme. A Pt wire with a surface area of 120 mm^2 served as the working electrode, and $Bu^n{}_4NBF_4$ with a concentration of 0.05—0.15 mol L^{-1} (depending on the solvent) was used as the supporting electrolyte. The auxiliary and working electrode compartments were separated by a porous glass membrane. Potentials were measured *vs.* a saturated Ag|AgCl|KCl electrode. The concentration of solutions was $3 \cdot 10^{-5}$—$7 \cdot 10^{-5}$ mol L^{-1}. Stirring of a solution in the cell during electrolysis and removal of dioxygen before electrolysis were carried out by a dry argon flow. Spectra of electrochemically generated forms of the complexes were recorded directly in a quartz cell on a Hitachi 124 spectrophotometer in the 200—800 nm region using $Bu^n{}_4NBF_4$ in the same solvent as a reference solution.

Results and Discussion

Paramagnetic[11] diphthalocyanine complexes of Sm, Tb, Dy, Er, Tm, and Lu, the elements of the beginning, middle, and end of the lanthanide series, which contained various substituents in the phthalocyanine rings, were chosen as objects for the study. Previously[12] we have studied the electrochemical properties of 2,9,16,23,2′,9′,16′,23′-octa-*tert*-butylphthalocyanines of Lu, Dy, and Pr ($^{2\text{-}Bu^t}Pc_2Ln$). In this work, the study of these complexes was supplemented with Lu, Er, and Dy 2,9,16,23,2′,9′,16′,23′-octaminophthalocyanines ($^{2\text{-}NH_2}Pc_2Ln$); Lu and Tb 2,3,9,10,16,17,23,24,2′,3′,9′,10′,16′,17′,23′,24′-hexadecamethylphthalocyanines ($^{2,3\text{-}Me}Pc_2Ln$); Lu, Tm, and Er 1,3,8,10,15,17,22,24,1′,3′,8′,10′,15′,17′,22′,24′-hexadecamethylphthalocyanines Lu, Tm, Er ($^{1,3\text{-}Me}Pc_2Ln$); Lu, Tm, and Sm 2,3,9,10,16,17,23,24,2′,3′,9′,10′,16′,17′,23′,24′-hexadecapentoxyphthalocyanines ($^{2,3\text{-}C_5H_{11}O}Pc_2Ln$); and Lu and Er 2,9,16,23,2′,9′,16′,23′-octanitrophthalocyanines ($^{2\text{-}NO_2}Pc_2Ln$).

The electrochemical and spectroelectrochemical properties of some substituted rare-earth metal diphthalocyanine complexes were published, but (unlike data for monophthalocyanines) these data are few and concern only donating substituents. In particular, the electrochemical properties of the lutetium and ytterbium hexadeca-*p*-butoxy-substituted complexes,[13] europium and gadolinium hexadecapentoxy- and hexadecaheptyl-substituted complexes[14] have been studied. The introduction of the octyl and dodecyl groups into the phthalocyanine ring only slightly affects the spectroelectrochemical properties of the diphthalocyanine complexes.[15] The synthesis of the polyethoxyethylene-substituted lutetium complex, which is soluble in many solvents including water, has been described,[16] and its spectroelectrochemical properties were studied. The influence of the substituents in the phthalocyanine rings on the electro- and spectroelectrochemical properties of the rare-earth metal diphthalocyanine complexes has been demonstrated[11] for lutetium octaphenyl-, octaphenoxy-, octa-*tert*-butyl-, and octa-1-bromocta-3-*tert*-butyl-substituted complexes. The electrochemical properties of the nonsubstituted Pc_2Ln complexes[17] and spectroelectrochemical properties of the octa-4-*tert*-butyl-substituted complexes have been studied for a wide series of rare-earth elements.[7]

A low solubility of many diphthalocyanine complexes in the most organic solvents used in electroanalytical methods is the main difficulty for the study of their electrochemical properties. A method for the solution of this problem is the use of a conducting material with a large specific surface area, for example, pyrolyzed polyacrylonitrile (PAN), as a working electrode. In fact, this is a graphite variety with a strongly developed surface area (~12 m^2 g^{-1}).

Table 1. Redox potentials (E/V) of the diphthalocyanine complexes on the smooth platinum and graphite (PAN) electrodes

Complex	Solvent	E^{Ox}		E^{Red}	
		Pt	PAN	Pt	PAN
$^{2,3\text{-}Me}Pc_2Lu$	DMF	0.42	0.46	0.01	−0.06
$^{2\text{-}Bu^t}Pc_2Y$	MeCN	0.41	0.39	0.06	0.06
Pc_2Y	DCB	0.51	0.56	0.15	0.15

Note. Experimental conditions: 0.05 mol L^{-1} $Bu^n{}_4NBF_4$; Ag|AgCl|KCl; v = 200 mV s^{-1}; 20 °C.

The data in Table 1 show that the influence of the material on the potentials of redox transitions of the compounds under study is insignificant and independent of the solvent, which is characteristic of thermodynamically reversible processes. The shape of the CV curve and character of the peaks remain almost unchanged. This allowed us to use, in several cases, the potentials of transitions obtained on the PAN electrode where the potentials of the complexes on smooth platinum in a chosen solvent are inaccessible due to the restricted solubility of the complexes.

However, even the use of PAN as a material of the working electrode does not allow the study of the electrochemical properties of all diphthalocyanine complexes in one appropriate solvent, *e.g.*, MeCN in which both oxidation and reduction potentials can be measured in a wide range.

Solubility of the complexes in DMF is somewhat higher, as a rule, than in MeCN. However, the most part of the anodic region of potentials is inaccessible in this solvent. By contrast, dichlorobenzene restricts the measurements in the cathodic region of potentials, especially for low concentrations. Therefore, we often had to measure the potentials of redox transitions of different diphthalocyanine complexes in different solvents. To confirm correctness of comparison of the obtained values, we measured the potentials of redox transitions for several complexes (when possible) in various solvents. The changes in the potentials of redox transitions with changing the solvent are not high. For example, for $^{1,3\text{-Me}}\text{Pc}_2\text{Dy}$ the potentials of the first two redox transitions are 0.40, −0.06 V in DCB and 0.30, −0.07 V in DMF (*vs.* Ag|AgCl|KCl).

A change in the solvent has often a stronger effect on the oxidation potentials of the ferrocene derivatives than for the most diphthalocyanine complexes. This is most likely related to the stronger hindrances of the metal atom in the diphthalocyanine complexes than in ferrocene. In addition, molecules of the diphthalocyanine complexes are larger in size and form more delocalized ions by reduction or oxidation. Therefore, the role of solvation in these systems is virtually reduced to a minimum.

The obtained potentials for the studied series of diphthalocyanine complexes are presented in Table 2.

Influence of the nature of the metal on the potentials of redox transitions of the rare-earth metal diphthalocyanine complexes. As follows from the data in Table 2 and Fig. 1, the influence of the nature of the central metal ion on the potential of the same redox transition for different complexes is much weaker than the difference in the potentials of subsequent redox transitions for the same complex. Moreover, if this influence can still be monitored by changes in the potentials of the first anodic (Ox^1) and first cathodic (Red^1) redox transitions, the differences are almost aligned for processes of deeper oxidation and reduction (see Fig. 1).

Table 2. Electrochemical potentials (*E*/V) of the first redox transitions of the substituted diphthalocyanine complexes[a]

Complex	Solvent	Ln	E^{Ox}, Ox^1	E^{Red}	
				Red^1	Red^2
$^{2\text{-NH}_2}\text{Pc}_2\text{Ln}$[b]	DMF	Lu	0.42	−0.15	−1.38
		Er	0.42	−0.10	−1.43
		Dy	0.33[c]	−0.16[c]	−1.54[c]
$^{2,3\text{-Me}}\text{Pc}_2\text{Ln}$	DCB	Lu	0.39[c]	0.04[c]	−1.07
		Tb	0.47	0.10	
$^{1,3\text{-Me}}\text{Pc}_2\text{Ln}$	DMF	Lu	0.46[c]	−0.06[c]	−1.23[c]
		Tm	0.46[c]	−0.07[c]	
		Er	0.47[c]	−0.07[c]	−1.19[c]
$^{2\text{-Bu}^t}\text{Pc}_2\text{Ln}$	MeCN	Lu	0.35	0.02	−1.10
		Dy	0.39	0.05	−1.12
		Tb	0.40	0.06	−1.11
		Pr	0.51	0.17	−1.10
$^{2,3\text{-OC}_5\text{H}_{11}}\text{Pc}_2\text{Ln}$	DCB	Lu	0.39[c]	−0.06[c]	
		Tm	0.42[c]	−0.03[c]	
		Sm	0.50[c]	0.05[c]	
Pc_2Ln	DCB—MeCN (1 : 1)	Lu	0.53	0.13	−1.02
		Dy	0.55	0.15	−0.95
		Gd	0.63	0.22	−0.97
$^{2\text{-NO}_2}\text{Pc}_2\text{Ln}$[b]	DMF	Lu	1.01[c]	0.54[c]	−0.57[c]
		Er	1.05[c]	0.58[c]	−0.53[c]

[a] Experimental conditions: Pt electrode; 0.05—0.15 mol L^{-1} $\text{Bu}^n{}_4\text{NBF}_4$; Ag|AgCl|KCl; $v = 200$ mV s^{-1}; 20 °C.

[b] We failed to prepare high-purity samples of these complexes; therefore, insignificant peaks at −0.66, −0.91 V ($^{2\text{-NH}_2}\text{Pc}_2\text{Lu}$); −0.56, −0.78, −0.98 V ($^{2\text{-NH}_2}\text{Pc}_2\text{Er}$); −0.53, −0.96 ($^{2\text{-NH}_2}\text{Pc}_2\text{Dy}$); 0.26, −0.11, −0.76 V ($^{2\text{-NO}_2}\text{Pc}_2\text{Lu}$); and 0.23, −0.18, −0.69 V ($^{2\text{-NO}_2}\text{Pc}_2\text{Er}$) were observed in the CV along with the indicated peaks.

[c] Graphite electrode (PAN).

The regularities observed agree well with the previous calculations[18] for Pc_2Ln using the extended Hückel method. Due to the very high difference in the energies of MOs of the phthalocyanine rings and AOs of the metal ion, their interaction is very weak. Therefore, the influence of the nature of the metal in the complex on the energy of its MOs is reduced to the influence of a change in the distance between two interacting phthalocyanine rings, which is determined by the radius of the lanthanide ion. As the radius of the lanthanide ion decreases, the π—π-interaction of the phthalocyanine rings increases, which increases the energy of the a_2 HOMO and decreases the energy of the e_3 LUMO (Fig. 2). Since the first anodic and first cathodic redox transitions are related to the singly occupied a_2 orbital of the complex, the potentials corresponding to these processes should be shifted to the cathodic region with a decrease in the radius of the lanthanide ion. However, the influence of the radius of the lanthanide ion on LUMO, the more so as on other MOs, is much weaker, which should result in a weaker influence of the lanthanide radius on the potentials of deeper oxidation and reduction processes.

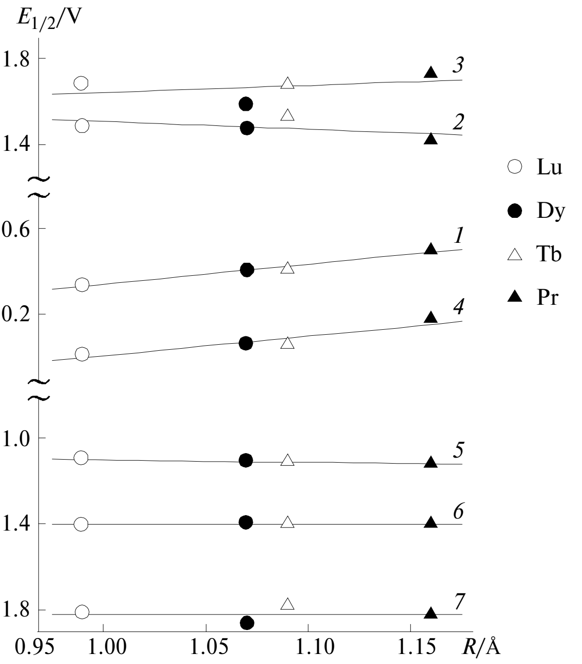


Fig. 1. Influence of the metal ion radius (*R*) on the redox potentials of $^{2\text{-}Bu^t}Pc_2Ln$ ($E_{1/2}$): oxidation Ox^1—Ox^3 (*1—3*, respectively) and reduction Red^1—Red^4 (*4—7*, respectively).

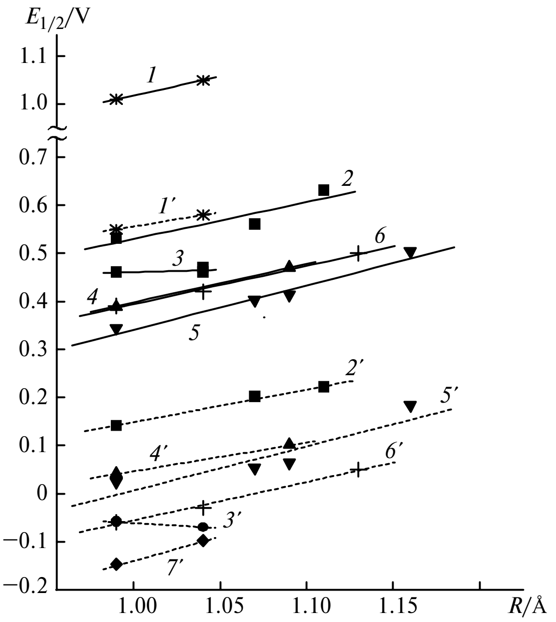


Fig. 3. Influence of the lanthanide radius (*R*) on the potentials of the first anodic (*1—7*) and first cathodic (*1′—7′*) transitions of the substituted diphthalocyanine complexes of rare-earth metals $^{X}Pc_2Ln$: X = 2-NO_2 (*1, 1′*), H (*2, 2′*), 1,3-Me (*3, 3′*), 2,3-Me (*4, 4′*), 2-Bu^t (*5, 5′*), 2,3-$C_5H_{11}O$ (*6, 6′*), and 2-NH_2 (*7′*).

The slope of the straight plots (Fig. 3) of the potentials of the first anodic and first cathodic redox transitions *vs.* ion radius of the lanthanide amounts to ~0.6—1.0 V $Å^{-1}$ (R = 0.912—0.996). As can be seen in Fig. 3, this is the common regularity for the most substituted complexes.

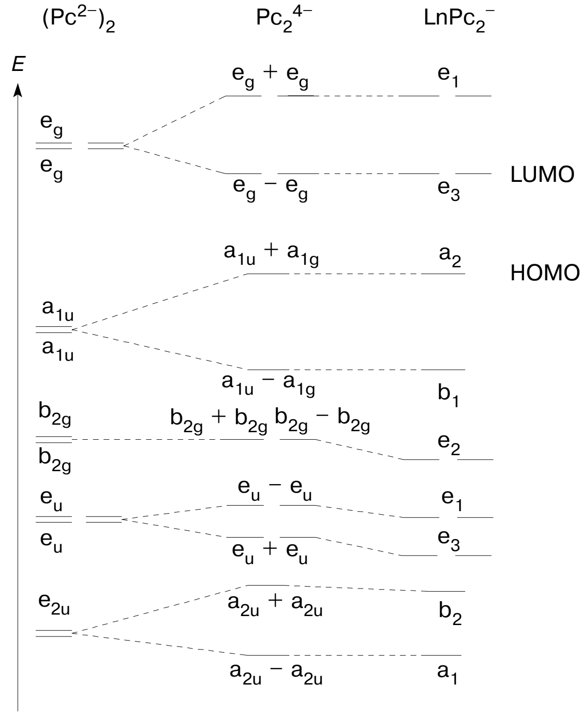


Fig. 2. Correlation diagram of molecular orbitals of $(Pc_2Ln)^-$ calculated by the extended Hückel method.

Since the lanthanide radii change in a narrow interval (from 0.99 to 1.22 Å),[19] the range of changing the redox potentials for the oxidation and reduction of lanthanides of the beginning, middle, and end of the series is also comparatively narrow, ~0.2 V.

Influence of the nature of substituents in the phthalocyanine ring on the potentials of redox transitions of the complexes. The introduction of substituents into the phthalocyanine rings and a change in the nature of the central metal atom can be considered as a perturbation of the frontier MOs, whose energy is mainly contributed by the MOs of the phthalocyanine rings. It follows from the data in Table 2 that the potentials of redox transitions of the diphthalocyanine complexes are very sensitive to the introduction of substituents. The slope of the straight lines in Fig. 4 is small and equal to ~0.07—0.08 V/σ. However, the electron-donating and -withdrawing abilities of the substituents in the ligand can be varied within wide limits (for example, from σ_p = 0.778 and σ_m = 0.710 (NO_2) to σ_p = −0.66 and σ_m = −0.16 (NH_2)). Therefore, we can change potentials of the redox transitions in a broad interval.

Similar studies have previously been performed for several series of the monophthalocyanine complexes.[20] The slope of the plot of the potentials of the redox transitions *vs.* σ was ~0.11 V/σ for all studied redox

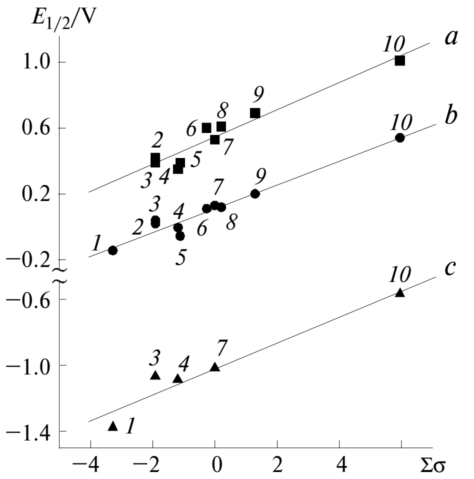


Fig. 4. Potentials ($E_{1/2}$) of the first oxidation process (*a*) and the first (*b*) and second reduction processes (*c*) of the substituted lutetium diphthalocyanine complexes $^{X}Pc_2Lu$ as functions of the sums of Hammett constants (Σσ) of the substituents (the potentials of the redox transitions of $^{PhO}Pc_2Lu$, $^{Ph}Pc_2Lu$, and $^{1\text{-Br-3-Bu}^t}Pc_2Lu$ are taken from Ref. 9): X = 2-NH_2 (*1*), 1,3-Me (*2*), 2,3-Me (*3*), 2-Bu^t (*4*), 2,3-$C_5H_{11}O$ (*5*), 2-PhO (*6*), H (*7*), 2-Ph (*8*), 1-Br-3-Bu^t (*9*), and 2-NO_2 (*10*).

transitions. The authors of Ref. 20 compared this value with that for the Re and Ru bipyridyl complexes and explained the much smaller slope for the phthalocyanine complexes by a larger size of the phthalocyanine ring as compared to that of the bipyridyl ligand.

The Hammett constants σ_p or their sum $\Sigma\sigma_p$ were used[11,20] for the quantitative description of the influence of the substituents in the phthalocyanine ring on the potentials of redox transitions of the phthalocyanine complexes. As a rule, this estimation gave satisfactory correlations (R = 0.830—0.995). We used the following combination of the Hammett constants σ_p and σ_m of all substituents in the diphthalocyanine ligands:

$$\Sigma\sigma = \sum_{i=1}^{k} n_i(\sigma_{pi} + \sigma_{mi})/2,$$

where n_i is the number of the same substituents in the molecule; summation was performed over all substituents (if they are different). The use of the half-sums σ_p and σ_m instead of those proposed previously[11,20] (σ_p) is most likely more correct especially for substituents with σ_p and σ_m with unlike signs such as alkoxy groups. Our correlations (see Fig. 4) are satisfactory (R = 0.963—0.974).

A new quantitative parameter, the so-called "minimum electrostatic potential of a molecule" ($V_{\min}$), has recently[21] been proposed for the estimation of the electron effects of substituents in the aromatic ring. This parameter was calculated[21] for five different substituents, and a good linear correlation between $V_{\min}$ and the Hammett constants for monosubstituted benzenes was shown. In the case of di- and polysubstituted benzenes, the use of $V_{\min}$ for the quantitative estimation of the electron density redistribution in the benzene ring gives more exact results than the usually used sum of the Hammett constants. We used the previously[21] calculated $V_{\min}$ values for methyl, amino, and nitro groups to describe the influence of the substituents in the phthalocyanine ring (Fig. 5) on the potentials of electrochemical oxidation and reduction of the diphthalocyanine complexes. Since the correlation coefficient, as in the case discussed above, is satisfactory (R = 0.950—0.994), both methods of the quantitative description of the influence of substituents in the phthalocyanine ring are valid.

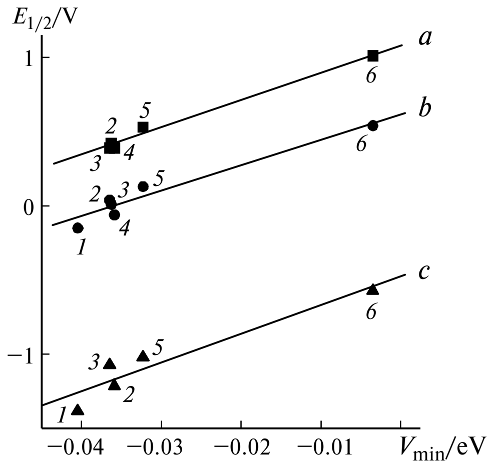


Fig. 5. Potentials ($E_{1/2}$) of the first oxidation process (*a*) and the first (*b*) and second reduction processes (*c*) of the substituted lutetium diphthalocyanine complexes $^{X}Pc_2Lu$ as functions of the minimum molecular electrostatic potential ($V_{\min}$): X = 2-NH_2 (*1*), 1,3-Me (*2*), 2,3-Me (*3*), 2,3-$C_5H_{11}O$ (*4*), H (*5*), and 2-NO_2 (*6*).

The influence of different substituents in the phthalocyanine rings of the diphthalocyanine complexes of lanthanides on their electrochemical properties is confirmed by the results of PM3 semiempirical quantum-chemical calculations of the model substituted tin diphthalocyanine complexes. Since the PM3 method is not parametrized by lanthanides, we used tin, which forms complexes similar to the rare-earth metal diphthalocyanine complexes, as the central metal atom. The results obtained coincide qualitatively with the X-ray diffraction data[22—24] for some lanthanide diphthalocyanine complexes, indicating correctness of this simulation. Calculations show that the phthalocyanine rings are nonplanar, concave toward the central metal atom, and turned relatively to each other by ~45°. Note that the previously proposed[12] simulation of the rare-earth element diphthalocyanine complexes by the yttrium complexes with the preliminary optimization of the geometry by the molecular mechanics method gave less satisfactory results: the skew angle of the rings was 22.7°.

Semiempirical calculations were performed with the convergence limit <10 cal Å^{-1} mol^{-1} except the $^{1,3\text{-Me}}Pc_2Sn$ complex for which we restricted our consideration with a limit of 20 cal Å^{-1} mol^{-1}.

The calculated energies of HOMO (ε^{HOMO}) for several substituted tin diphthalocyanine complexes are presented below.

Complex	ε^{HOMO}/eV
$^{2\text{-}NH_2}Pc_2Sn$	−7.00
$^{2,3\text{-Me}}Pc_2Sn$	−7.00; −7.14
$^{1,3\text{-Me}}Pc_2Sn$	−7.05; −7.18
Pc_2Sn	−7.23
$^{2\text{-}NO_2}Pc_2Sn$	−8.79

It should be emphasized that, in the case of $^{1,3\text{-Me}}Pc_2Ln$ and $^{2,3\text{-Me}}Pc_2Ln$, two HOMO are virtually degenerate.

The correlation between the calculated HOMO energies of the substituted tin diphthalocyanine complexes and experimental values of the potentials of the first reduction peaks of the corresponding lutetium diphthalocyanine complexes is presented in Fig. 6. The possibility of this correlation is based on the fact that in the tin (oxidation state +4) complexes both phthalocyanine rings have the formal charge −2. According to the Koopmans theorem, the value of the energy of HOMO of the next, more reduced form with the $+(n-1)$ or $-(n-1)$ charge is taken as an electron affinity of the particle with the $\pm n$ charge. Therefore, in our case, the potentials of the first reduction of the substituted lutetium diphthalocyanine complexes should correlate, most likely, with the energies of HOMO of the both reduced forms of the $[(^XPc)^{2-}Lu^{3+}(^XPc)^{2-}]^-$ complexes and neutral $[(^XPc)^{2-}Sn^{4+}(^XPc)^{2-}]^0$ complexes, which also contain two dianionic phthalocyanine rings. The correlation coefficient of this plot is 0.954.

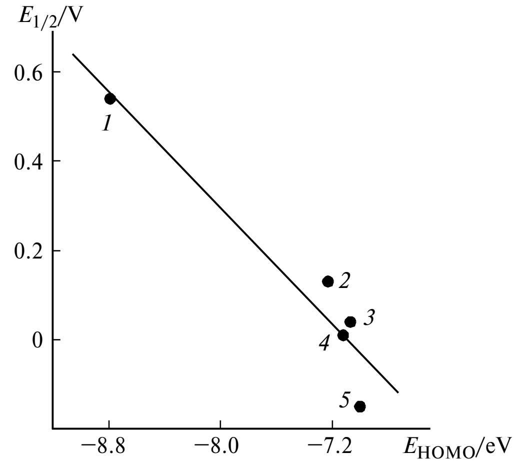


Fig. 6. Correlation of the potentials ($E_{1/2}$) of the first reduction process of the substituted lutetium diphthalocyanine complexes $^XPc_2Lu$ to the HOMO energies (E_{HOMO}) of the substituted tin diphthalocyanine complexes $^XPc_2Sn$ calculated by the PM3 method: X = 2-NO_2 (*1*), H (*2*), 2,3-Me (*3*), 1,3-Me (*4*), and 2-NH_2 (*5*).

Influence of the number of phthalocyanine rings in the molecule on the electrochemical properties of the corresponding complexes. The number of phthalocyanine rings in the molecule is another structural factor that has a great effect on the electrochemical parameters of phthalocyanine complexes. Rare-earth metals are capable of forming both planar and sandwich-type complexes with phthalocyanine ligands. The electrochemical properties of the rare-earth metal monophthalocyanine complexes have been studied in detail (see Ref. 6 and references cited therein). The following points result from the comparison of the electrochemical behavior of the rare-earth metal mono- and diphthalocyanine complexes.

1. The number of the observed redox transitions for diphthalocyanines is greater than that for monophthalocyanines. For example, for $^{2\text{-Bu}^t}Pc_2Lu$ and $^{2\text{-Bu}^t}PcLuOAc$ the number of the observed redox transitions is seven and five, respectively (under comparable conditions, in the potential interval from −2.0 to +2.0 V).

2. The electrochemical gap (*i.e.*, the difference of potentials for the first anodic and first cathodic redox transitions) of the diphthalocyanine complexes is much smaller than the corresponding value for the monophthalocyanines. This is a very important parameter related to the relative arrangement of the frontier orbitals and determining the "chemical face" of the molecule. For example, for the complexes in Table 2 this value is only 0.32—0.52 V, whereas for the rare-earth metal monophthalocyanine complexes it usually amounts[25] to 1.6 V.

3. For the diphthalocyanine complexes, the first anodic and first cathodic redox transitions occur, in most cases, at low overvoltages (see Table 2). This property can be fruitful for their use in electrocatalytic transformations because the reaction at low overvoltages enhances selectivity.

Influence of the nature of the metal and substituents in the phthalocyanine ring on the spectroelectrochemical parameters of the rare-earth metal diphthalocyanine complexes. The spectroelectrochemical parameters of a series of the rare-earth metal diphthalocyanine complexes Pc_2Ln (Ln = Lu, Er, Sm, Nd),[8] $^{2\text{-Bu}^t}Pc_2Ln$ (Ln = Lu, Yb, Er, Dy, Gd, Sm, Nd, Pr, La),[7] as well as $^{2,3\text{-}O(CH_2CH_2O)nCH_2CH_2OMe}Pc_2Lu$,[16] $^{C_8H_{17}}Pc_2Lu$, $^{C_{12}H_{25}}Pc_2Lu$,[15] $^{PhO}Pc_2Lu$, $^{Ph}Pc_2Lu$, and $^{1\text{-Br-}3\text{-Bu}^t}Pc_2Lu$ [11] have been studied to date.

In this work, we studied the spectroelectrochemical parameters of some substituted diphthalocyanine complexes of Lu, Tm, Er, Dy, and Tb.

The spectral parameters of the diphthalocyanine complexes under study and their oxidized and reduced forms are presented in Table 3. It can be seen that an increase in the radius of the central metal atom results in the bathochromic shift of the absorption bands of the redox forms of the complexes, except the long-wave component of the split Q band, which is shifted toward shorter wavelengths. The introduction of various substituents

Table 3. Maxima of the electronic absorption spectra (λ) of the neutral, reduced, and oxidized forms of the substituted diphthalocyanine complexes $^{\mathrm{X}}\mathrm{Pc}_2\mathrm{Ln}$ and visual coloration of the solutions

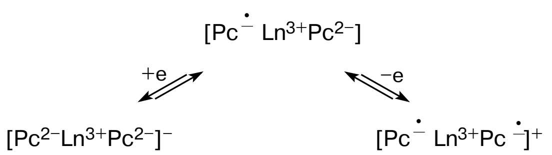
Complex	Solvent	Ln	λ/nm (color)		
			$[^{\mathrm{X}}\mathrm{Pc}_2\mathrm{Ln}]^-$	$[^{\mathrm{X}}\mathrm{Pc}_2\mathrm{Ln}]^0$	$[^{\mathrm{X}}\mathrm{Pc}_2\mathrm{Ln}]^+$
$^{2\text{-}\mathrm{NH}_2}\mathrm{Pc}_2\mathrm{Ln}$[a]	DMF	Lu	727 (green)	650, 720 (green)	[b]
		Er	726 (green)	651, 721 (green)	[b]
		Dy	696 (green)	645, 695 (greenish-blue)	[b]
$^{2,3\text{-}\mathrm{Me}}\mathrm{Pc}_2\mathrm{Ln}$	DCB	Lu	634, 704 (greenish-blue)	672 (green)	494, 704 (pink)
		Tb	638, 693 (greenish-blue)	678 (green)	503, 714 (pink)
$^{1,3\text{-}\mathrm{Me}}\mathrm{Pc}_2\mathrm{Ln}$	DMF	Lu	637, 708 (greenish-blue)	685 (green)	510, 730 (orange-pink)
		Tm	639, 704 (greenish-blue)	687 (green)	514, 734 (orange-pink)
		Er	639, 703 (greenish-blue)	689 (green)	515, 736 (orange-pink)
$^{2\text{-}\mathrm{Bu^t}}\mathrm{Pc}_2\mathrm{Ln}$	MeCN	Lu	624, 702 (blue)	664 (green)	485, 697 (orange)
		Tb	631, 689 (blue)	672 (green)	491, 709 (orange)
$^{2,3\text{-}\mathrm{OC}_5\mathrm{H}_{11}}\mathrm{Pc}_2\mathrm{Ln}$	DCB	Lu	623, 681 (greenish-blue)	669 (green)	502, 701 (pink)
		Tm	626, 678 (greenish-blue)	670 (green)	504, 702 (pink)
		Sm	633, 684 (greenish-blue)	675 (green)	520, 718 (pink)
$\mathrm{Pc}_2\mathrm{Ln}$	DCB—MeCN (1 : 1)	Lu	616, 690 (blue)	659 (green)	477, 693 (orange)
$^{2\text{-}\mathrm{NO}_2}\mathrm{Pc}_2\mathrm{Ln}$[a]	DMF	Lu	705 (green)	638, 692 (greenish-blue)	645 (blue)
		Er	706 (green)	634, 693 (greenish-blue)	652 (blue)

[a] Broad, poorly resolved peaks.

[b] Very weak coloration likely due to the partial decomposition of the complex.

into the phthalocyanine ring also shifts the absorption bands to the long-wave spectral region. It is of interest that an increase in the donating ability of the substituents decreases color visibility of the transitions (Scheme 1)

Scheme 1



Among the compounds presented above, $\mathrm{Pc}_2\mathrm{Ln}$ and $^{2\text{-}\mathrm{Bu^t}}\mathrm{Pc}_2\mathrm{Ln}$ possess the maximum color visibility.

Thus, variation of the nature of the metal and substituents in the phthalocyanine ring of the rare-earth metal diphthalocyanine complexes allows the smooth monitoring of the shifts of potentials of redox transitions toward the cathodic or anodic regions. Therefore, the diphthalocyanine complexes are attributed to redox systems that can easily be "tuned" to the desired potential range and, hence, they can serve as promising electrocatalysts or materials for electrochromic devices active in a specified narrow potential region.

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