

Voltammetry of microparticles of lutetium bisphthalocyanine

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Abstract Oxidation of microparticles of lutetium (bis-*tert*-butylphthalocyaninato) complex immobilized on the surface of paraffin-impregnated graphite electrode and immersed into an aqueous electrolyte was investigated by cyclic voltammetry and square wave voltammetry. The electrode reaction exhibits the typical features of insertion electrochemistry where the anions of the aqueous electrolyte are transferred into the solid phase upon oxidation of the redox centers there in. The reaction is quasi-reversible and influenced by the ohmic resistance of the compound. The formal potentials of the electrode reaction involving the transfer of perchlorate, nitrate, and chloride ions follow the same order as the Gibbs energies of ion transfer in the systems water–nitrobenzene and water–octanol. Bromide and thiocyanate ions are not intercalated.

Keywords Lutetium (bis-*tert*-butylphthalocyaninato) complex · Graphite electrode · Solid microparticle electrochemistry · Cyclic voltammetry · Square wave voltammetry

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Introduction

Lutetium bisphthalocyanine, LuPc₂, has been well known since its discovery for quite unusual properties, particularly as being a promising electrochromic compound [1, 2]. Electrochemistry of its solutions in organic media revealed that LuPc₂ can be reduced, or oxidized, through many reversible one-electron steps, being green in the neutral state, brownish-yellow as the oxidized form, and blue in the reduced state [3, 4]. In methylene chloride, the apparent standard potentials for the oxidation of dissolved LuPc₂ to LuPc₂⁺ and electro-reduction to LuPc₂⁻ ions are 0.03 and -0.45 V vs the formal potential of the ferricinium/ferrocene couple. The first oxidation and reduction potentials of monophthalocyanines are ≥1.5 V apart [5]. The unusual electronic properties of the bisphthalocyanines come from their sandwich-like nature that associates two unsaturated macrocycles, the distance between the phthalocyanine planes being short enough to induce strong π–π interactions between the two units [6]. Molecular lanthanide bisphthalocyanines bear one unpaired electron that is delocalized over the two macrocycles and gives them very interesting physico-chemical properties that are promising for optoelectronic applications [7]. The compound is the first characterized intrinsic molecular semiconductor, with an electronic conductivity of 2 × 10⁻⁶ S/cm in thin film, while monophthalocyanines are insulators [8]. Considering their potential applications, the electrochemistry of the lanthanide bisphthalocyanines has been studied, not only in solution but also as thin layers of organic phases on electrodes [9] as well as solid phases, e.g., deposited by sublimation on transparent electrodes for the study of their electrochromic properties [10], as Langmuir–Blodgett films [11]. Their intrinsic semiconductivity is an advantage for such experiments. As possible redox mediators for the development of

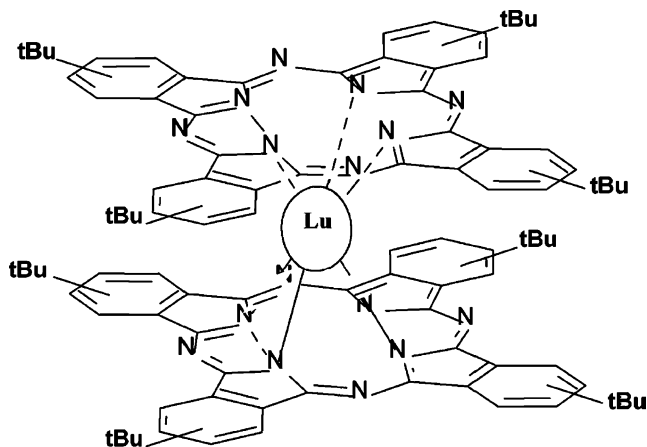
sensors in food analysis, LuPc₂ microparticles have been studied incorporated in carbon paste electrodes [12, 13].

In this short communication, voltammetric properties of lutetium (bis-*tert*-butylphthalocyaninato) microparticles (Lu(*t*-bu₄Pc)₂, Scheme 1) immobilized on the graphite electrode surface are reported. The method is based on the mechanical transfer of solid particles by pressing the electrode into powder of the compound under investigation [14–18]. The purpose of the work was to investigate electrochemical properties of solid Lu(*t*-bu₄Pc)₂.

Experimental

Analytical-grade KNO₃, NaClO₄, KCl, KSCN, KBr, NaOH, HCl, citric acid, acetic acid, and boric acid (all Merck) were used as received. Lutetium (bis-*tert*-butylphthalocyaninato) complex (Lu(*t*-bu₄Pc)₂) was synthesized and purified according to the procedure described previously [5]. Supporting electrolytes and 0.1 M buffer solutions pH 2 (sodium citrate, HCl), pH 4.7 (acetic acid, NaOH), pH 8 (sodium borate, HCl), and pH 10 (sodium borate, NaOH) were prepared with double distilled water. Buffered electrolytes were prepared by adding 1 ml of buffer solution to 4 ml of electrolyte.

The experiments were performed with a spectral-grade paraffin-impregnated graphite rod as the working electrode (PIGE), which was used in conjunction with a platinum gauze counter electrode and an Ag|AgCl|3 M KCl (Metrohm) reference electrode. Before each measurement, the circular surface of the graphite rod was rinsed with distilled water, polished on a wet polishing cloth, rinsed again, dried with a fine-grade paper tissue, and carefully polished on a dry, white paper sheet. Then it was pressed into Lu(*t*-bu₄Pc)₂ powder on a highly glazed ceramic tile and moved circularly for about 5 s. By this procedure, the



Scheme 1 Molecular structure of Lu(*t*-bu₄Pc)₂

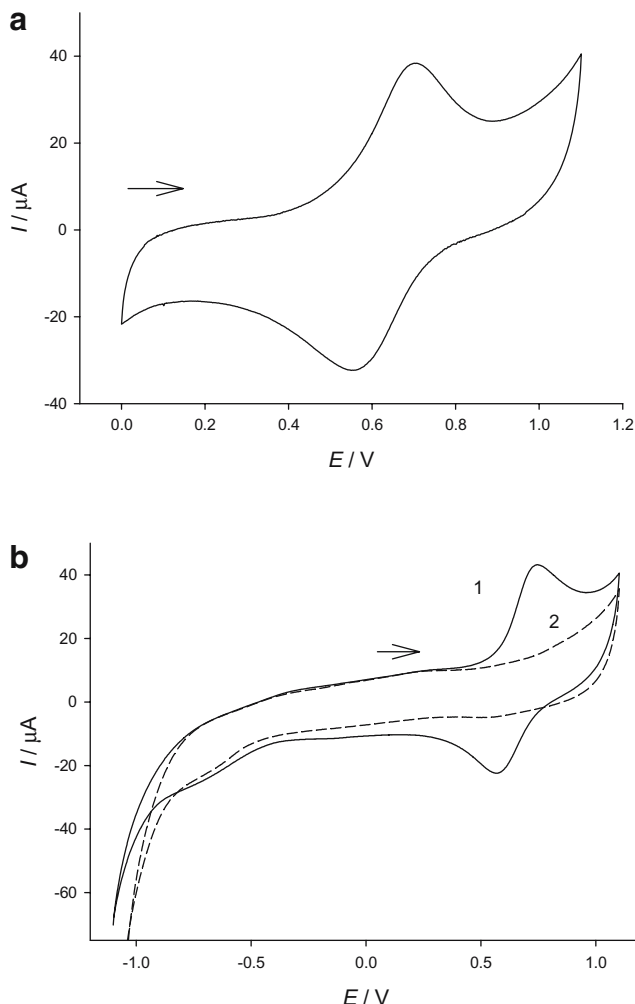


Fig. 1 **a** Cyclic voltammetry of Lu(*t*-bu₄Pc)₂ microparticles immersed into 1 M KNO₃ solution and **b** cyclic voltammetry of solid Lu(*t*-bu₄Pc)₂ precipitate on PIGE (1) and of bare PIGE (2) in 1 M KNO₃ buffered to pH 4.66; $\nu=100$ mV/s, $E_{\text{start}}=0$ V vs Ag/AgCl|3 M KCl

surface is contaminated by traces of a pigment and can be used as a modified working electrode. Only less than 1 mm of the graphite rod was immersed in the electrolyte.

Additional experiments were performed with precipitates of Lu(*t*-bu₄Pc)₂. A drop of solution of Lu(*t*-bu₄Pc)₂ in dichloroethane was deposited on the surface of PIGE and left in the air until the solvent evaporated. The electrode modified by dry precipitate was immersed into an aqueous electrolyte and used in voltammetric experiments. The same procedure was applied to the basal plane and edge plane graphite electrodes.

Voltammetric measurements were performed by using an Autolab PGSTAT 12 potentiostat (EcoChemie, Utrecht). Solutions were degassed with high-purity nitrogen for 30 min before the measurements. A nitrogen blanket was maintained thereafter.

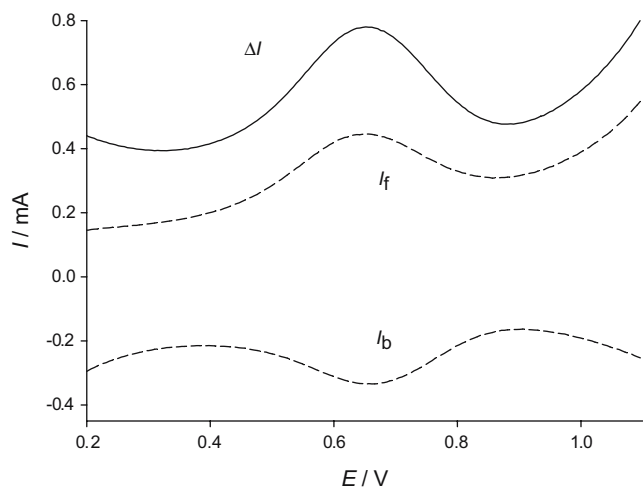


Fig. 2 Square wave voltammetry of solid Lu(*t*-bu₄Pc)₂ in 1 M KNO₃; a net response (ΔI), and its oxidative (I_f) and reductive (I_b) components; $f=100$ Hz, $E_{sw}=100$ mV, and $\Delta E=5$ mV

Results and discussion

Figure 1a shows a cyclic voltammogram (CV) of Lu(*t*-bu₄Pc)₂ microparticles immobilized on PIGE surface and immersed into 1 M KNO₃ solution. The oxidation and reduction peak potentials are 0.702 and 0.553 V, respectively, with the median $E_m=0.628$ V vs Ag|AgCl|3 M KCl. The response can be ascribed to one-electron reversible electrode reaction: Lu(*t*-bu₄Pc)₂ ⇌ Lu(*t*-bu₄Pc)₂⁺ + e⁻ [9].

Figure 1b shows CV of precipitate of Lu(*t*-bu₄Pc)₂ on PIGE (curve 1). The response of bare PIGE is shown as curve 2. Oxidation and re-reduction peaks of solid Lu(*t*-bu₄Pc)₂ appear at 0.750 and 0.583 V, respectively, with the median 0.667 V. However, no reduction in Lu(*t*-bu₄Pc)₂ microparticles can be noted. In nitrobenzene, the reduction of dissolved Lu(*t*-bu₄Pc)₂ occurs at -0.35 V vs aqueous Hg/Hg₂Cl₂ reference electrode [9]. Similar responses were obtained with Lu(*t*-bu₄Pc)₂ precipitates on the basal plane and edge plane graphite electrodes. Moreover, mechanically transferred microparticles of Lu(*t*-bu₄Pc)₂ exhibited no reduction as well.

Square wave voltammogram (SWV) of abrasively transferred Lu(*t*-bu₄Pc)₂ microparticles in 1 M KNO₃ is shown in Fig. 2. The net peak potential is 0.654 V. The oxidation and reduction components of the response indicate reversible electrode reaction.

Figure 3 shows the dependence of the median potential in CV and the peak potential in SWV on the logarithm of electrolyte concentration. Both relationships are linear, with the slopes -0.066 and -0.071 V, respectively. They can be explained by the theory of electrode reaction of solid insertion compounds [18, 19]:



where the subscript ss denotes the solid state. In CV of the reaction (1), the median potential is:

$$E_m = E_{Ox/Red}^0 - \frac{RT}{F} \ln K - \frac{RT}{F} \ln [X_{aq}^-] \quad (2)$$

where K is the equilibrium constant of the reaction: $X_{aq}^- + \{\text{Ox}^+\}_{ss} \rightleftharpoons \{\text{Ox}^+X^-\}_{ss}$. It is related to the energy of transfer of anion X^- from the aqueous phase into the solid phase. It is postulated that the product of oxidation of Lu(*t*-bu₄Pc)₂ is not dissolved ion Lu(*t*-bu₄Pc)₂⁺ but an ion pair Lu(*t*-bu₄Pc)₂NO₃ bound to the surface of particle. The particle is electronic semiconductor and its surface is charged to the electrode potential if the oxidation current is low. Therefore, the oxidation of Lu(*t*-bu₄Pc)₂ may start all over the particle/solution interface, but its development requires the transport of anions through the solid film of ion pairs. The difference between oxidation and reduction peak potentials in Fig. 1a is 149 mV, which can be caused either

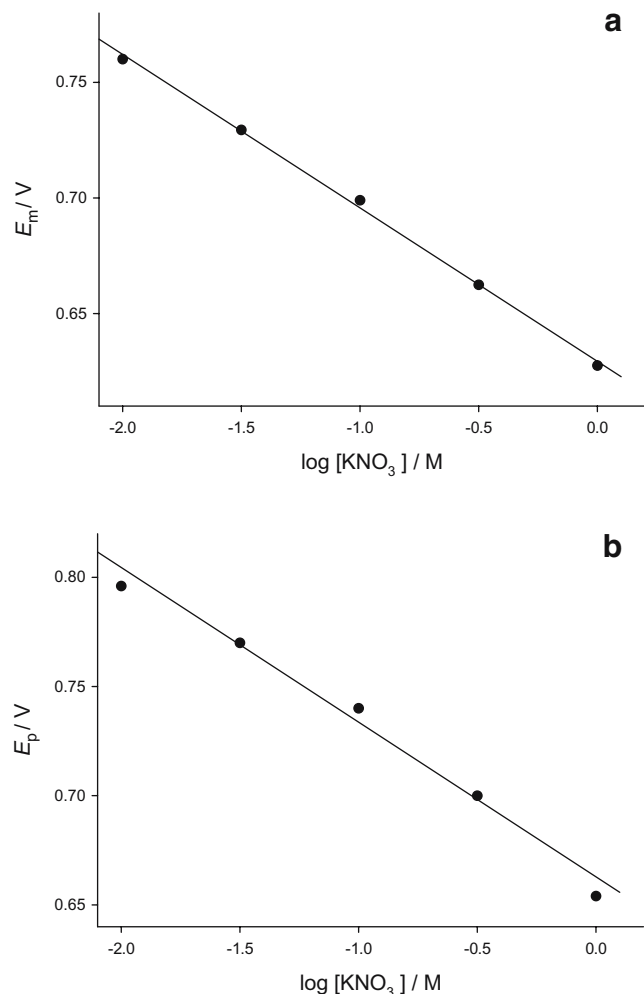


Fig. 3 Dependence of median potential in CV **a** and peak potential in SWV **b** on the logarithm of KNO₃ concentration. Experimental data are reported in Figs. 1 and 2

Table 1 Characteristic potentials of responses in 1 M electrolytes

Electrolyte	CV: E_m/V	SWV: E_p/V
NaClO ₄	0.471	0.494
KNO ₃	0.628	0.654
KCl	0.744	0.832

by the slow transfer of electrons across the electrode/particle interface or by the ohmic resistance of the particle.

The proposed mechanism is confirmed by the fact that median potentials in CV and peak potentials in SWV depend on the anion of electrolyte, which is reported in the Table 1. The difference is caused by the constant K in (2).

Figure 4 shows SWV of Lu(*t*-bu₄Pc)₂ microparticles immersed into 1 M NaClO₄ and 1 M KCl solutions. The responses appear less reversible than in KNO₃, but the net peak potentials are linear functions of the logarithms of anions concentrations. The slopes are -64 mV for NaClO₄

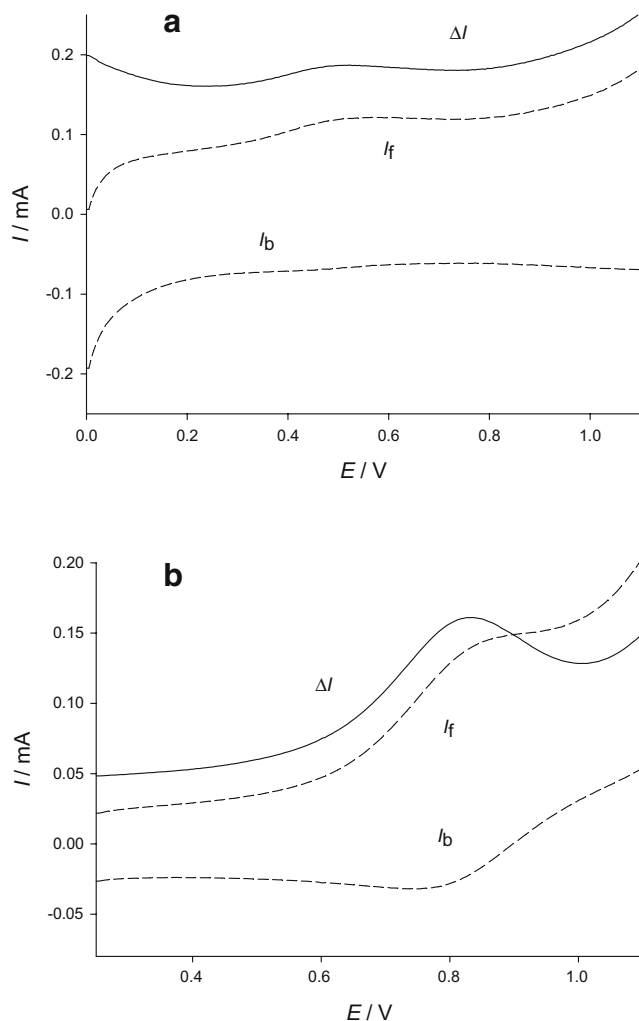


Fig. 4 Square wave voltammetry of solid Lu(*t*-bu₄Pc)₂ in 1 M NaClO₄ (a) and 1 M KCl (b). Experimental data are reported in Fig. 2

and -49 mV for KCl. The relationship between the median potential in CV and the logarithm of NaClO₄ concentration is also linear. The slope of this straight line is -56 mV. For KCl solutions, the corresponding slope is -47 mV. These results prove that ClO₄⁻ and Cl⁻ anions also form lutetium salts on the particle surface. Furthermore, in the contact with KBr and KSCN solutions, no oxidation of Lu(*t*-bu₄Pc)₂ was observed, which could mean that the solid oxidation products cannot be formed with these anions.

Finally, the critical potentials in CV and SWV do not depend on the pH of electrolytes, which indicates that no protons are involved in the electrode reaction.

The changes of the formal potentials for the redox process described by reaction (1) (see Table 1) go parallel to the changes of ion transfer energies of the same ions (perchlorate, nitrate, and chloride) for the system water–nitrobenzene [20] and also for the system water–*n*-octanol [21]. Figure 5 shows the dependence of median potentials in CV on the standard Galvani potential differences of anions on nitrobenzene/water interface. The slope of this linear relationship is equal to 1. This behavior suggests that the same factors are determining the thermodynamics of ion transfer from water to solid Lu(*t*-bu₄Pc)₂, i.e., that the free energy of solvation of the ions in water is decisive. This is not a trivial result because, in principle, it would have been also possible that the ionic radii and the free space in the solid compound would determine how easy the ions are transferred between water and the solid. However, the fact that bromide and thiocyanate ions are not intercalated cannot be understood on the basis of their hydrophobicity as they are more hydrophobic than chloride nor based on their ionic radii as they are smaller than perchlorate.

Our results are in agreement with voltammetric measurements of thin film of Lu(Pc)₂, in which the peak potentials

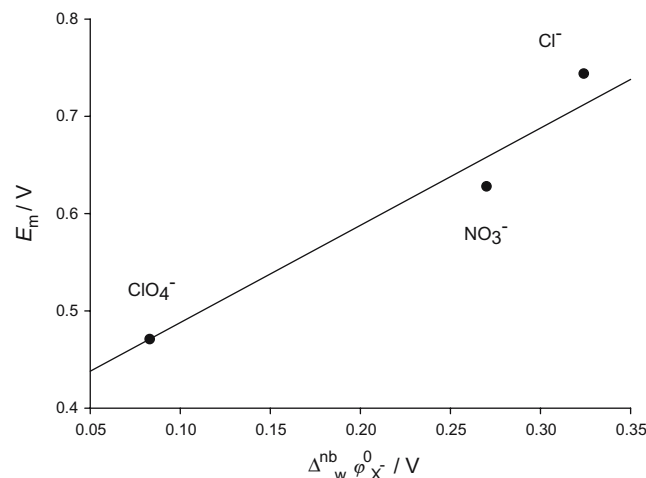


Fig. 5 Dependence of median potentials in CV (Table 1) on the standard Galvani potential differences of anions on nitrobenzene/water interface

were dependent on aqueous electrolytes and the brake-in phase preceded the oxidation in the first cycle [22]. In conclusion, the oxidation of Lu(*t*-bu₄Pc)₂ microparticles immobilized on the PIGE surface is reversible solid state process involving anions of aqueous electrolyte in the formation of solid product. This explains the reactivity of LuPc₂ microcrystals dispersed in carbon paste electrodes.

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