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Electrochemistry of a Double-Decker Lutetium(III) Phthalocyanine in Aqueous Media. The First Evidence for Five Reductions

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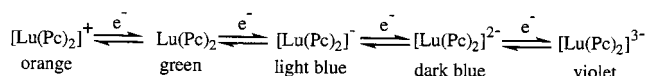
The double-decker lutetium(III) phthalocyanine, Lu[(RS)₄Pc]₂, where R = C₁₂H₂₅, was synthesized and electrochemically characterized under several solution conditions. The neutral complex undergoes a single reversible one-electron oxidation and up to four reversible one-electron reductions in nonaqueous solutions of CH₂Cl₂ or benzonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP), while one oxidation and five reductions are seen in aqueous 0.5 M KCl for a gel-like cast film membrane of Lu[(RS)₄Pc]₂ in a tetraoctylphosphonium bromide (4C₈P⁺Br[−]) matrix at a basal plane pyrolytic graphite electrode. The half-wave potentials for reduction of Lu[(RS)₄Pc]₂ in CH₂Cl₂, 0.1 M TBAP are located at $E_{1/2}$ = 0.04, −1.03, −1.36 and −1.73 V, while the single oxidation is located at $E_{1/2}$ = 0.43 V vs SCE. These potentials, when measured vs Fc/Fc⁺, are negatively shifted by 0.20–0.46 V from the $E_{1/2}$ values obtained in the 0.5 M KCl solution where the electrogenerated anions of the double-decker complex are stabilized by the cations of the 4C₈P⁺Br[−] matrix and five reductions are seen at $E_{1/2}$ = 0.29, −0.66, −0.94, −1.22, and −1.41 V vs SCE. The fifth reduction has been theoretically predicted but had never before been observed for any double-decker lutetium(III) phthalocyanine or related complex. A cast film of Lu[(RS)₄Pc]₂ displays only one oxidation in the 0.5 M KCl solution (at $E_{1/2}$ = 0.78 V vs SCE), and no reductions at all are seen in the absence of a matrix. An almost identical oxidation potential of $E_{1/2}$ = 0.80 V is seen for oxidation of Lu[(RS)₄Pc]₂ in KCl when dissolved in the cationic matrix. These half-wave potentials for oxidation in the cationic film, when measured vs Fc/Fc⁺, are thus more positive by more than 0.27–0.32 V than $E_{1/2}$ values measured in CH₂Cl₂ or PhCN and this is consistent with a decreased degree of solvent or anion binding to {Lu[(RS)₄Pc]₂}⁺ in the 4C₈P⁺Br[−] matrix, as compared to what is observed in solution.

Introduction

Double-decker phthalocyanines and especially the lutetium derivatives have been the subject of extensive investigations as to their electrochromic properties,¹ their intrinsic semiconductivity,² and their third-order optical nonlinearity.³ Lu(Pc)₂, where Pc represents the dianion of phthalocyanine, has been shown to undergo up to seven redox processes, five of which have been characterized with respect to the color changes shown in Chart 1.

The solution⁴ and film⁵ electrochemical behavior of double-decker lutetium(III) phthalocyanines have also been extensively investigated under different experimental conditions. Some electrochemical studies were carried out in solutions of methylene chloride (CH₂Cl₂) or benzonitrile (PhCN) containing tetra-*n*-butylammonium perchlorate (TBAP) or tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆),⁴ while others were carried out in aqueous LiClO₄, KClO₄, or KCl solutions on cast, Langmuir–Blodgett, or spin-coated films of Lu(Pc)₂,^{1g,a,c,f} Lu-(R₄Pc)₂, or Lu(R₈Pc)₂, where R = 15-crown-5,^{5d,f} C_nH_{2n+1}-OCH₂,^{5b,f} or C₃H₇O.^{5e}

CHART 1



The present paper reports the synthesis and electrochemical characterization of Lu[(RS)₄Pc]₂ (1), where R = C₁₂H₂₅ (see Chart 2), under several different solution and experimental conditions. These were (1) in solutions of CH₂Cl₂ or PhCN containing 0.1 M TBAP and (2) in solutions of 0.5 M KCl as a cast film of Lu[(RS)₄Pc]₂ on a bare pyrolytic graphite electrode (BPG) and as a cast film of the same compound incorporated into a cationic matrix of 4C₈P⁺Br[−]. The latter measurements provide the first data for the multiple reduction of any double-decker phthalocyanine in aqueous media.

Organic gels,⁶ a gel-like membrane of a tetraoctylphosphonium bromide (4C₈P⁺Br[−]) lipid analogue,⁷ and a multilayer of synthetic ammonium lipids^{8–10} are all known to provide suitable microenvironments for examining the electrochemistry of redox active molecules, and this has recently been utilized for measuring the reduction potentials and ion-pairing reactions of easily reducible C₆₀ at an electrode surface in an aqueous medium.^{7,9} The same methodology is used in the present paper for examining the multiple reductions of Lu[(RS)₄Pc]₂ and enabled, for the first time, an experimental determination of

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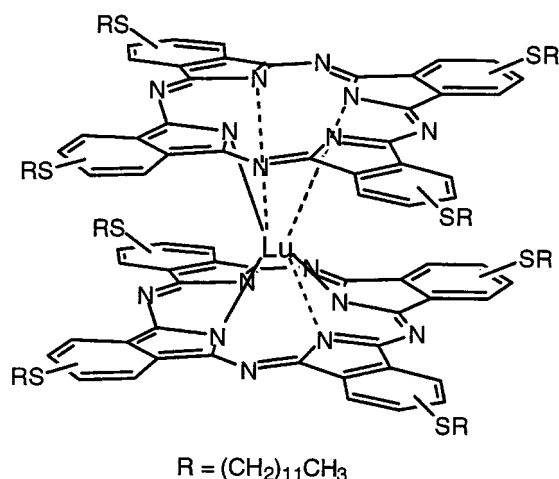
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CHART 2



$E_{1/2}$ for the theoretically predicted¹¹ fifth consecutive one-electron-transfer reduction of a double-decker phthalocyanine complex.

One goal of our current study was to determine the maximum number of reductions and oxidations that could be observed at a film electrode in aqueous media for a highly soluble double-decker lutetium(III) phthalocyanine complex containing eight $SC_{12}H_{25}$ substituents,¹² while another was to compare the solution and film redox behavior of a double-decker lutetium(III) phthalocyanine complex, the latter measurement being carried out in a cationic matrix known to stabilize the electro-generated anions.

Experimental Section

Chemicals and Reagents. Dodecane-1-thiol (Merck Chemical Co.) and tetraoctylphosphonium bromide ($4C_8P^+Br^-$, Aldrich Chemical Co.) were used as received. Benzonitrile (PhCN) was distilled over P_2O_5 under vacuum, while dichloromethane (CH_2Cl_2) was treated three times with H_2SO_4 and distilled over P_2O_5 and CaH_2 prior to use. Tetra-*n*-butylammonium perchlorate (TBAP, Fluka Chemical Co.) was recrystallized from ethyl alcohol and dried in a vacuum oven at 40 °C for at least 1 week prior to use. 4-Nitro-1,2-dicyanobenzene¹³ and 1-(dodecylthio)-4,5-dicyanobenzene¹⁴ were synthesized according to published procedures.

Instrumentation. Infrared (IR) spectra were recorded as KBr pellets on a Perkin-Elmer 983 spectrophotometer. Fast atom bombardment (FAB) mass spectra were obtained on a VG-ZAB-SPEC spectrometer using *m*-nitrobenzyl alcohol as the matrix. Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) were carried out using an IBM model EC 225 voltammetric analyzer. Current-voltage curves were recorded with a Zenith Data system model Z-386 SX/20 computer coupled with a Hewlett-Packard Deskjet 600 plotter. A three electrode system was used for CV measurements in CH_2Cl_2 or PhCN and consisted of a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture. The ferrocene/ferrocenium couple (Fc/Fc^+) was used as an internal standard, but all potentials in the paper are referenced to the SCE. Solutions containing **1** were deoxygenated by a stream of high-purity nitrogen for at least 5 min prior to running the experiment, and the solution was protected from air by a blanket of nitrogen

during the experiment. A three electrode system was also used for voltammetric measurements of **1** as a cast film on a homemade basal plane pyrolytic graphite (BPG) with and without the gel-like membrane of $4C_8P^+Br^-$.

Preparation of Cast Film. Typical procedures for preparation of a gel-like membrane of $1/4C_8P^+Br^-$ (molar ratio, 1/19) on the BPG electrode are as described in the literature.⁷ A 28 μL portion of $1/4C_8P^+Br^-$ in chloroform ($[1] = 0.27$ mM, $[4C_8P^+Br^-] = 5.15$ mM) was placed on a BPG electrode surface (geometric area, 0.36 cm^2) and then air-dried. A **1**-modified BPG electrode was prepared in a similar manner. A 75 μL portion of **1** in chloroform ($[1] = 0.10$ mM) was placed on a BPG electrode surface and then air-dried. Both modified electrodes were immersed in a 0.5 M KCl aqueous solution, followed by measurements of the electrochemistry at 25 °C under a nitrogen atmosphere.

Synthesis of Bis[tetrakis(dodecylthio)phthalocyaninato]-lutetium. A round-bottom flask with a condenser was degassed and flame-dried under dry argon. The flask was charged under argon with 1-(dodecylthio)-4,5-dicyanobenzene (2.48 g, 7.54 mmol), $Lu(OAc)_3 \cdot 3H_2O$ (0.34 g, 0.96 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (565 μL , 3.76 mmol), and 15.8 mL of hexan-1-ol. The mixture was refluxed for 20 h. Evaporation of the hexan-1-ol under reduced pressure left a green waxy product. The product was refluxed in methanol (50 mL) and the methanol was then decanted. The reflux was repeated three times using about 50 mL of methanol. Purification was achieved by column chromatography over silica gel (CH_2Cl_2/n -hexane, 5:3 (v/v)) followed by two successive preparative thin-layer chromatographies (silica gel; eluent CH_2Cl_2/n -hexane, 1:1 (v/v)). Precipitation from methanol led to 215 mg (yield: 8.1%) of a viscous paste **1**: IR (cm^{-1}): 2960, 2860, 2820, 1600, 1450, 1305, 1260, 1070, 1035, 910, 820, 750. Anal. Calcd for $C_{160}H_{224}LuN_{16}S_8$ (M_w : 2803): C, 68.56; H, 8.05; N, 8.00. Found: C, 69.00; H, 7.98; N, 7.95. MS (FAB, matrix: *m*-NBA), m/z (%): 2802.4 (100) $[M - 1]^+$, 2634.3 (35) $[M - C_{12}H_{25}]^+$, 2469.3 (8) $[M - 2(C_{12}H_{25})]^+$, 1401.6 (5) $[M/2]^+$, 985.9 (5), 285.8 (3).

Results and Discussion

Synthesis. Synthesis of the desired double-decker lutetium(III) compound was accomplished by reaction of 1-(dodecylthio)-4,5-dicyanobenzene with lutetium acetate in hexanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base. Purification was achieved by column chromatography over silica gel and two successive preparative thin-layer chromatographies. The desired compound, which is substituted by four dodecylthio groups on the periphery of each phthalocyanine macrocycle (eight $C_{12}H_{25}S$ groups in total) is isolated as a mixture of isomers, all of which appear to have the same electrochemical properties. The same is true for other octa-substituted double-decker lutetium(III) phthalocyanine complexes.¹⁵ Infrared spectra were used only to identify substituents on the periphery of each phthalocyanine core. Characteristic IR stretching vibrations attributable to the C-H (aliphatic) and Ar-S groups of the thio alkyl chains are observed at 2960–2820 and 1260 cm^{-1} , respectively. Fragments for **1** were observed by FAB-MS at 2802.4 $[M - 1]^+$, 2634.3 $[M - C_{12}H_{25}]^+$, and 2469.3 $[M - 2(C_{12}H_{25})]^+$, all of which match the theoretical values.

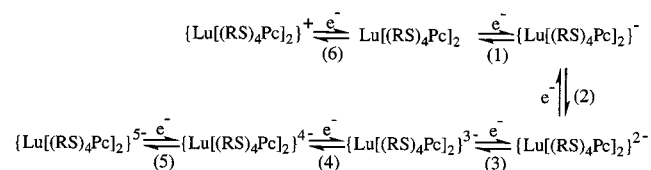
Electrochemistry. All lanthanide bis(phthalocyanines) and related double-deckers can undergo multiple reductions of the π -orbitals of the conjugated macrocycle and only the cerium derivatives show a metal-centered redox process in this series of compounds.^{4a} The lowest unoccupied molecular orbital

TABLE 1: Electrochemical Half-Wave Potentials of Lu[(C₁₂H₂₅S)₄Pc]₂ and Selected Double-Decker Lutetium(III) Phthalocyanines

compound	solvent/condition	supporting electrolyte	RE	Ox(1) (6)	Red(1) (1)	Red(2) (2)	Red(3) (3)	Red(4) (4)	Red(5) (5)	ref ^d
Lu[(C ₁₂ H ₂₅ S) ₄ Pc] ₂	CH ₂ Cl ₂	TBAP	SCE	0.43	0.04	−1.03	−1.36	−1.73		tw
			Fc/Fc ⁺ ^a	−0.06	−0.45	−1.52	−1.85	−2.22		tw
	PhCN	TBAP	SCE	0.46	0.10	−1.00	−1.33			tw
			Fc/Fc ⁺ ^b	−0.01	−0.37	−1.47	−1.80			tw
	H ₂ O/4C ₈ P ⁺ Br [−]	KCl	SCE	0.80	0.29	−0.66	−0.94	−1.22	−1.41	tw
			Fc/Fc ⁺ ^c	0.26	−0.25	−1.20	−1.48	−1.76	−1.95	tw
	H ₂ O/cast film	KCl	SCE	0.78						tw
			Fc/Fc ⁺	0.00	−0.45	−1.54	−1.92			4b,4 ^e
Lu(Pc) ₂	CH ₂ Cl ₂	TBAPF ₆	Fc/Fc ⁺	−0.05	−0.46	−1.54	−1.92	−2.40		4f ^f
	PhCN	TBAPF ₆	Fc/Fc ⁺							
Lu[(C ₈ H ₁₇ OCH ₂) ₈ Pc] ₂	CH ₂ Cl ₂	TBAPF ₆	Fc/Fc ⁺	−0.04	−0.41					4c
Lu[(C ₁₂ H ₂₅ OCH ₂) ₈ Pc] ₂	CH ₂ Cl ₂	TBAPF ₆	Fc/Fc ⁺	0.01	−0.42					4c
Lu[(C ₄ H ₉ O) ₈ Pc] ₂	CH ₂ Cl ₂	TBAP	SCE	0.25	−0.19	−1.29				4e
Lu(Pc) ₂	H ₂ O/cast film	LiClO ₄	SCE	0.60	−0.30					5c,5f
Lu[(15-crown-5) ₄ Pc] ₂	H ₂ O/spin coated	KClO ₄	SCE	0.20	−0.16					5d,5f
Lu[(C ₈ H ₁₇ OCH ₂) ₈ Pc] ₂	H ₂ O/LB film	LiClO ₄	SCE	0.44						5b,5f
Lu[(C ₁₂ H ₂₅ OCH ₂) ₈ Pc] ₂	H ₂ O/LB film	LiClO ₄	SCE	0.50						5b,5f
Lu[(C ₃ H ₇ O) ₄ Pc] ₂	H ₂ O/LB film	KCl	SCE	0.55						5e

^a The value vs Fc/Fc⁺ in CH₂Cl₂ can be calculated from the values vs SCE by subtracting 0.49 V. ^b The value vs Fc/Fc⁺ in PhCN can be calculated from the values vs SCE by subtracting 0.47 V. ^c The value vs Fc/Fc⁺ in H₂O for Fc/4C₈P⁺Br⁻ (molar ratio, 1/19) composite modified electrode can be calculated from the values vs SCE by subtracting 0.54 V. ^d tw = this work. ^e The second oxidation is seen at 1.19 V vs Fc/Fc⁺. ^f The second and third oxidations are seen at 1.05 and 1.43 V vs Fc/Fc⁺, respectively.

CHART 3



(LUMO) of mono-metallophthalocyanines has doubly degenerate e_g symmetry and can therefore accept up to four electrons.¹⁶ In contrast, the HOMO level of double-decker or bis-phthalocyanines results from a splitting of the $4a_u$ π -HOMO of the monophthalocyanine due to interactions between both rings and leads to a complex whose HOMO is occupied by only one electron, giving a radical character to the compound.¹¹ These types of compounds should be reducible by a total of five electrons although this number of redox processes had not in the past been experimentally observed.

The investigated compound undergoes a single reversible oxidation and up to four reversible reductions when dissolved in nonaqueous media, while five reductions and one oxidation are seen in aqueous 0.5 M KCl solutions when measurements are made using a gel-like membrane of $1/4C_8P^+Br^-$ on a BPG electrode. Typical cyclic voltammograms are shown in Figure 1a,b and the electrode reactions are schematically illustrated in Chart 3, where the reductions are labeled as (1)–(5) and the single oxidation as (6). The reduction process 5 has not previously been observed for any double-decker lutetium(III) phthalocyanine or related complex.

The redox processes of **1** and $1/4\text{C}_8\text{P}^+\text{Br}^-$ were examined as a function of potential scan rate in order to ascertain the mode of mass transport. The cathodic and anodic currents for the oxidation and reduction couples in CH_2Cl_2 and PhCN each increased in the direct proportion to the square root of the scan rate between 0.05 and 0.25 V/s, thus suggesting that the redox reactions in solution are controlled by diffusion.^{17a} The cathodic and anodic currents for the redox processes of (1), (2), and (6) for a cast film of $1/4\text{C}_8\text{P}^+\text{Br}^-$ on a BPG electrode also increased in proportion to the square root of scan rate in a range of scans between 0.1 and 0.4 V/s, thus suggesting that the electrochemistry in the film is also controlled by diffusion at the measured

scan rates. This is not the case in the film at scan rates below 0.03 V/s, where the peak currents are directly proportional to the scan rate, consistent with thin-layer electrochemical behavior.^{17b}

The electrochemistry of **1** in CH_2Cl_2 differs from that of previously investigated double-decker lutetium(III) phthalocyanines⁴ in that additional reductions are seen under our experimental conditions. For example, only three reductions had previously been reported for $\text{Lu}(\text{Pc})_2$ and related complexes in CH_2Cl_2 ⁴ containing TBAPF_6 but we clearly see four reductions for **1** in this solvent containing TBAP. The neutral form of **1** exhibits one reversible oxidation and three reversible reductions in PhCN, while the unsubstituted complex, $\text{Lu}(\text{Pc})_2$, has been shown to undergo three oxidations and four reductions in PhCN containing TBAPF_6 .^{4f} The measured potentials for **1** in solution and as a film are listed in Table 1 which also includes selected data from the literature for related compounds.

Differential pulse voltammetry also showed $1/4\text{C}_8\text{P}^+\text{Br}^-$ to undergo five reductions and one oxidation in aqueous solutions containing 0.5 M KCl. The half-wave potentials for reductions in the film are located at $E_{1/2} = 0.29, -0.66, -0.94, -1.22$, and -1.41 V while the single oxidation is seen at $E_{1/2} = 0.80$ V vs SCE. The half-wave potentials of $1/4\text{C}_8\text{P}^+\text{Br}^-$, when measured vs Fc/Fc^+ , are all more positive by 0.20–0.46 V than the measured $E_{1/2}$ values in CH_2Cl_2 , with the larger differences being seen for the trianionic and tetranionic species. The positive shift in $E_{1/2}$ upon going from CH_2Cl_2 or PhCN to the film is larger for the first oxidation than for the first reduction (see Table 1), and this results in an increased $\Delta E_{1/2}$ value of 0.51 V for $1/4\text{C}_8\text{P}^+\text{Br}^-$ as compared to 0.39 V for both **1** and $\text{Lu}(\text{Pc})_2$ in solution.

Simon and co-workers^{5b,f} have studied the film electrochemical properties of double-decker lutetium(III) phthalocyanines in aqueous media under three experimental conditions, none of which utilized an accompanying membrane. These were (i) at a cast film, (ii) at a LB film, and (iii) as a spin-coated film on an electrode, conditions under which the redox potentials of the double-decker lutetium(III) phthalocyanines depended greatly upon the type of utilized supporting electrolyte. The reduced anionic forms of double-decker lutetium(III) phthalocyanines have been shown to associate with mono- and divalent alkali

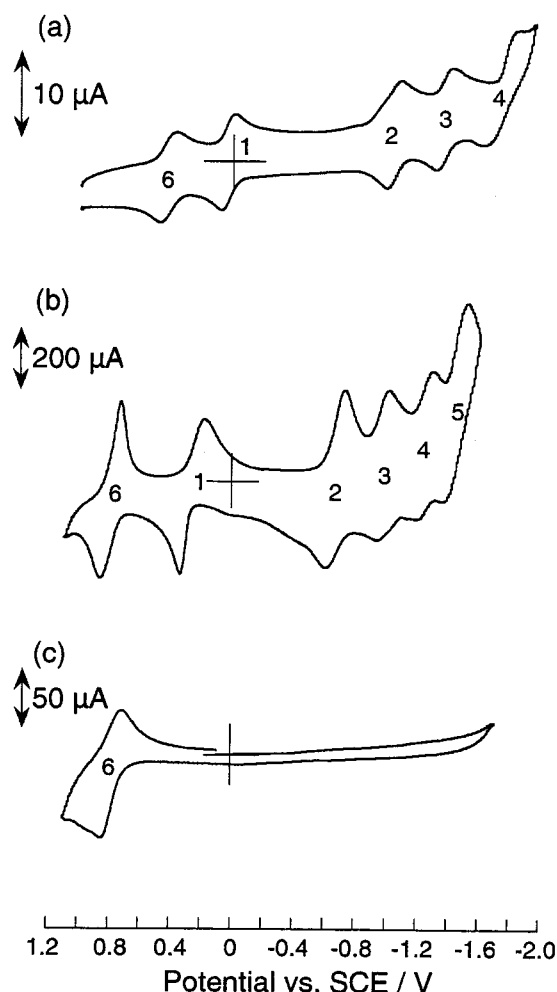


Figure 1. Cyclic voltammograms (a) for **1** (1.05 mM) in a 0.1 M TBAP, CH_2Cl_2 solution, (b) a cast film of $1/4\text{C}_8\text{P}^+\text{Br}^-$ (molar ratio, 1/19), and (c) **1** only on a BPG electrode in a 0.5 M KCl aqueous solution at 25 °C. Scan rate = 0.1 V/s.

metal cations,^{5b,c,f} and this association also occurs with cations in our $4\text{C}_8\text{P}^+\text{Br}^-$ matrix, thus leading to a larger stabilization of the electroreduced forms of **1** in the film and a positive shift in the $E_{1/2}$ for each redox couple (an easier reduction) as compared to what is observed for the same compound in nonaqueous media.

Nakashima et al.^{7,9} have recently studied the film electrochemistry of C_{60} and found that the first three reduction steps to give mono-, di-, and trianions could be clearly observed in aqueous media by incorporating C_{60} onto a cast film of a synthetic ammonium lipid,⁹ a tetraalkylammonium lipid analogue,⁷ or a gel-like membrane of $4\text{C}_8\text{P}^+\text{Br}^-$.⁷ The binding of ammonium or phosphonium ions from the matrix to the first three forms of electroreduced C_{60} resulted in a shift of all $E_{1/2}$ values to positive potentials as compared to half-wave potentials that had previously been recorded for the same fullerene in a variety of nonaqueous solvents.¹⁸ The binding of the electro-generated C_{60} anions to the ammonium ions in the supporting electrolyte also resulted in a shift of $E_{1/2}$ to more positive potentials.¹⁹ Thus, such an interaction with the cations of the matrix is not specific to the C_{60} anions but is general for a π -conjugated system such as hypericine.¹⁰

As indicated in Table 1, only potentials for the first reduction and first oxidation of $\text{Lu}(\text{Pc})_2$ have been reported in a cast film in aqueous media, and this may be due to the inability to observe higher reduced forms of the compound under these experimental

conditions. A cast film of **1** displays only one redox couple (at $E_{1/2} = 0.78$ V vs SCE) when examined in the absence of a matrix (Figure 1c). No reductions at all can be observed under our experimental conditions, and this result is similar to behavior reported by Simon and co-workers^{5b,f} for $\text{Lu}[(\text{C}_n\text{H}_{2n+1}\text{OCH}_2)_8\text{Pc}]_2$, where it was difficult to obtain a well-defined first reduction peak in a LB film of the compound. This behavior contrasts significantly with what is observed in the present study for **1**, where up to five well-defined reductions are seen in a cationic matrix film. Finally, it should be noted from Table 1 that almost identical values of $E_{1/2}$ are seen for oxidation of $\text{Lu}[(\text{RS})_4\text{Pc}]_2$ as a cast film at the bare electrode in 0.5 M KCl (0.80V) and as a film in the cationic matrix ($1/4\text{C}_8\text{P}^+\text{Br}^-$, 0.78 V). Both of these oxidation half-wave potentials are more positive than $E_{1/2}$ values in solution by 0.26–0.32 V, when measured vs Fc/Fc^+ , and this is consistent with a decreased degree of solvent or anion binding to $\{\text{Lu}[(\text{RS})_4\text{Pc}]_2\}^+$ in the film as compared to what is observed in solution.

Concluding Remarks

In summary, the results of our present study provide the first experimental verification for a fifth reduction of any substituted or unsubstituted double-decker lutetium(III) phthalocyanine. It also provides the first example where any reduced double-decker lutetium(III) phthalocyanine complex above its monoanionic form has been examined as a film in aqueous media. Spectroscopic studies of the di-, tri-, tetra-, and the pentaanionic forms of $\text{Lu}[(\text{RS})_4\text{Pc}]_2$ should be of interest and are now in progress.

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