

Thermodynamic Study of Ion-Pairing Effects between Reduced Double-Decker Lutetium(III) Phthalocyanines and a Cationic Matrix

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Received: May 29, 2003; In Final Form: September 9, 2003

The thermodynamics of ion pairing between electrochemically reduced $[(C_6H_{13}S)_8Pc]_2Lu$ or $[(C_{12}H_{25}S)_4Pc]_2Lu$ and a cationic tetra-*n*-octylphosphonium bromide ($4C_8P^+Br^-$) matrix that was deposited in a gel-like cast film on a basal plane pyrolytic graphite electrode was investigated in an aqueous KCl solution that varied in concentration from 0.005 to 1.0 M. The purpose of this study was to elucidate ion-pairing effects between reduced double-decker lutetium(III) phthalocyanines with charges of -1 to -5 and cationic sites of the $4C_8P^+Br^-$ matrix. Both phthalocyanines undergo five one-electron reductions in the film, and a linear relationship was observed between the measured half-wave potentials ($E_{1/2}$) for these processes and the Cl^- concentration of the electrolyte in the film. The apparent number of electrons transferred in each reduction step was obtained from plots of $E_{1/2}$ versus $\ln[Cl^-]$, which gave Nernstian slopes of -23.5 ± 2.3 mV (or -54.1 ± 5.3 mV from plots of $E_{1/2}$ vs $\log[Cl^-]$) over a chloride concentration range of 0.005 to 1.0 M. The $E_{1/2}$ versus $\ln[Cl^-]$ plots indicate that the stepwise addition of electrons to the phthalocyanines in the film is accompanied by a stepwise unit increase in the number of associated $4C_8P^+$ cations. Thus, the ratio of phthalocyanine molecules to monocations increases from 1:1 for the singly reduced derivative to 1:5 in the case of $\{[(C_6H_{13}S)_8Pc]_2Lu\}^{5-}$ or $\{[(C_{12}H_{25}S)_4Pc]_2Lu\}^{5-}$. This result leads to the conclusion that a binding of reduced $[(C_6H_{13}S)_8Pc]_2Lu$ or $[(C_{12}H_{25}S)_4Pc]_2Lu$ to the cationic sites of the $4C_8P^+$ matrix is responsible for the experimentally observed positive shift of the measured half-wave potentials as compared to $E_{1/2}$ values for the same electrode reactions in nonaqueous media. The changes in $E_{1/2}$ upon changing the electrolyte counter cation and/or the charge of the matrix are also described, and these results further support the observed ion-pairing effects that were examined by means of electrochemical and spectroscopic techniques.

Introduction

The chemistry and physics of double-decker phthalocyanines and especially the lutetium derivatives have received increasing attention over the last 5 years.¹ A number of early studies concerning double-decker lutetium(III) phthalocyanines have had as their main focus a characterization of the compound's electrochromic properties.² In this regard, the electrochemistry of these types of compounds, both in solution³ and as films on electrode surfaces,⁴ has been the subject of an intense research focus.

Recently, Simon and co-workers^{4f} used the probe-beam deflection mirage technique to determine the nature and direction of the flux of ions coming into or going out of a molecular thin film layer of lutetium(III) phthalocyanines when oxidation or reduction occurred. The oxidation and reduction potentials of lutetium(III) phthalocyanine films are known to depend on the type of supporting electrolyte utilized. The reduced complexes will associate with mono- and divalent alkali metal cations, and the oxidized forms of the same double-decker phthalocyanines have been shown to associate with anions of the electro-

lytes.^{4b,c,f} Our own group has reported that the reversible redox potentials of a gel-like cast film membrane containing a lutetium(III) phthalocyanine in a tetra-*n*-octylphosphonium bromide ($4C_8P^+Br^-$) matrix at a basal plane pyrolytic graphite (BPG) electrode are positively shifted by up to 510 mV versus half-wave potentials for the same redox couples measured in dichloromethane (CH_2Cl_2) containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP).⁵ This result is most likely due to the strong Coulomb-coupled binding⁶ of the phthalocyanine reduction product in the film with the cationic sites of the matrix. A similar association between porphyrin double-decker anions and large organic cations is known to occur in organic solvents.⁷

Metal phthalocyanine tetrasulfonates,⁸ hemin,⁹ fullerenes,¹⁰ hypericin,¹¹ and proteins¹² have also been investigated as to their electrochemistry in aqueous solutions when incorporated into cast films of a cationic lipid matrix on an electrode surface. Nakashima and co-workers¹⁰ have reported that cationic matrix modified electrodes can be utilized for measuring reduction potentials and ion-pairing reactions of easily reducible fullerene anions. The binding of electrogenerated fullerene anions to the ammonium or phosphonium ion of an electrolyte on an electrode leads to a positive potential shift of the redox potential, which was described by a recent thermodynamic study.¹³

In this paper, we utilize a thermodynamic approach to analyze the film electrochemistry of $[(C_6H_{13}S)_8Pc]_2Lu$ and $[(C_{12}H_{25}S)_4Pc]_2Lu$ in a $4C_8P^+Br^-$ matrix film containing different types

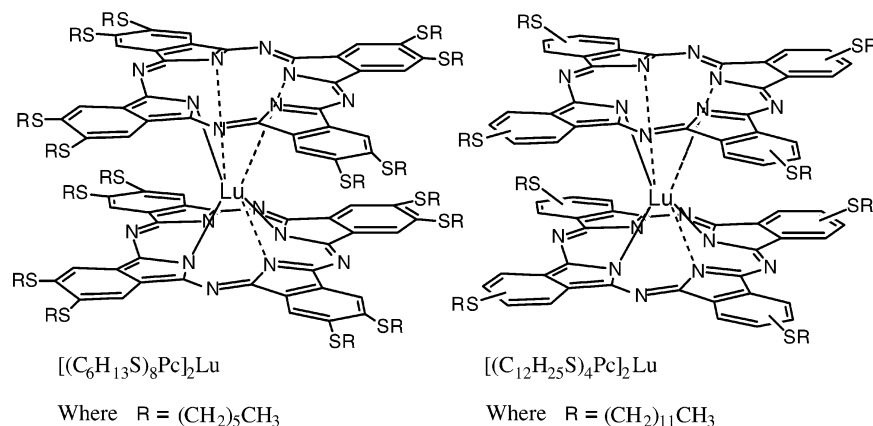
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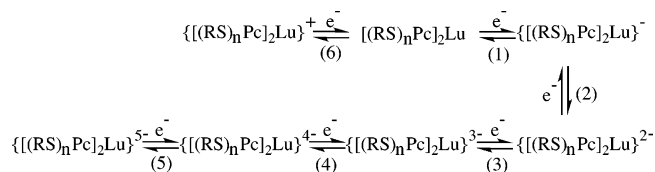
CHART 1



and different concentrations of supporting electrolytes in aqueous media that is in contact with the film. The alkyl thio-substituted double-decker lutetium(III) phthalocyanines that were examined in this study are shown in Chart 1 and are of interest from both a chemical and physical point of view.¹⁴

Figure 1 shows multiple-step cyclic voltammograms of $[(C_6H_{13}S)_8Pc]_2Lu$ and $[(C_{12}H_{25}S)_4Pc]_2Lu$ in the $4C_8P^+Br^-$ matrix film. The prevailing electrode reactions of the compounds have been elucidated in previous papers⁵ and are schematically summarized in Chart 2 where $n = 4$ ($R = C_{12}H_{25}$) or 8 ($R =$

CHART 2



C_6H_{13}) in the case of the macrocycle-substituted derivatives. The five reductions are labeled 1–5 in the Chart, and the single oxidation of the two compounds is labeled 6.

$[(C_6H_{13}S)_8Pc]_2Lu/4C_8P^+Br^-$ and $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8P^+Br^-$ undergo five reductions under the described experimental conditions. Half-wave potentials for the reduction of $[(C_6H_{13}S)_8Pc]_2Lu/4C_8P^+Br^-$ in the film are located at $E_{1/2} = 0.26, -0.58, -0.88, -1.19$ and -1.41 V, and the single oxidation of the complex is located at $E_{1/2} = 0.88$ V versus SCE. These potentials in the film are more positive by 210 to 490 mV than the measured $E_{1/2}$ values for the same compound in CH_2Cl_2 , 0.1 M TBAP.^{5b} Half-wave potentials for the reduction of $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8P^+Br^-$ in the film are located at $E_{1/2} = 0.29, -0.66, -0.94, -1.22$ and -1.41 V, and the single oxidation of the compound is located at $E_{1/2} = 0.80$ V versus SCE. These potentials are more positive by 250 to 510 mV than half-wave potentials for the same compound in solutions of CH_2Cl_2 .^{5a} The measured half-wave potentials for $[(C_6H_{13}S)_8Pc]_2Lu$ or $[(C_{12}H_{25}S)_4Pc]_2Lu$ in the $4C_8P^+Br^-$ film are listed in Table 1, which also includes half-wave potentials for the same compounds under different experimental conditions.

The large positive potential shifts in $E_{1/2}$ for reduction in the film are qualitatively consistent with an association between the electroreduced forms of the phthalocyanines and the cations in the $4C_8P^+Br^-$ matrix. However, a quantitative measure of

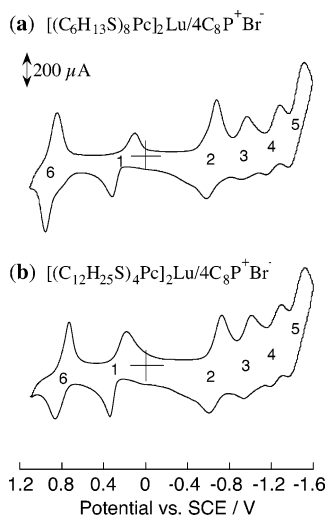


Figure 1. Cyclic voltammograms for (a) a cast film of $[(C_6H_{13}S)_8Pc]_2Lu/4C_8P^+Br^-$ (molar ratio 1:19) and (b) $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8P^+Br^-$ (molar ratio 1:19) on a BPG electrode in a 0.5 M KCl aqueous solution. Scan rate = 0.1 V/s.

TABLE 1: Half-Wave Potentials versus SCE for $[(C_6H_{13}S)_8Pc]_2Lu$ and $[(C_{12}H_{25}S)_4Pc]_2Lu$ under Different Experimental Conditions

compound	solvent/conditions	supporting electrolyte	Ox ₁ (6)	Red ₁ (1)	Red ₂ (2)	Red ₃ (3)	Red ₄ (4)	Red ₅ (5)
$[(C_6H_{13}S)_8Pc]_2Lu$	$H_2O/4C_8P^+Br^-$ ^a	KCl	0.88	0.26	-0.58	-0.88	-1.19	-1.41
	$H_2O/4C_8N^+Br^-$	KCl	0.89	0.23	-0.60	-0.92	-1.20	-1.43
	$H_2O/2C_{12}PO_4H$	KCl ^c	0.83					
	$H_2O/cast\ film^d$	KCl	0.88					
	$CH_2Cl_2^d$	TBAP ^d	0.46	0.05	-0.97	-1.25	-1.68 ^e	
$[(C_{12}H_{25}S)_4Pc]_2Lu$	$H_2O/4C_8P^+Br^-$ ^b	KCl	0.80	0.29	-0.66	-0.94	-1.22	-1.41
	$H_2O/4C_8N^+Br^-$	KCl	0.81	0.26	-0.66	-0.97	-1.21	-1.45
	$H_2O/2C_{12}PO_4H$	KCl ^c	0.68					
	$H_2O/cast\ film^b$	KCl	0.78					
	$CH_2Cl_2^b$	TBAP ^d	0.43	0.04	-1.03	-1.36	-1.73	

^a See ref 5. ^b See ref 5b. ^c Aqueous potassium hydroxide solution was used to adjust the pH. ^d 0.2 M tetra-*n*-butylammonium perchlorate (TBAP) was used as an electrolyte in CH_2Cl_2 . ^e Process was obtained at -50 °C.

how the type and concentration of counterions in the aqueous media will effect the reversible redox potentials had not been reported.

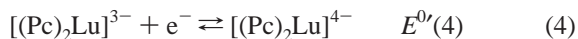
This is the subject of the present paper, which examines ion-pairing between the five electroreduced forms of $[(C_6H_{13}S)_8Pc]_2Lu$ or $[(C_{12}H_{25}S)_4Pc]_2Lu$ and cationic $4C_8P^+Br^-$ as a matrix. The interaction that occurs between the singly oxidized form of the two phthalocyanines and Cl^- was also examined in this study, which utilizes a thermodynamic approach that involves relating the measured $E_{1/2}$ values in the film to the type and concentration of supporting electrolytes in the aqueous solution.

Cast films of $[(C_6H_{13}S)_8Pc]_2Lu$ and $[(C_{12}H_{25}S)_4Pc]_2Lu$ provide excellent systems to use in quantitating the binding with $4C_8P^+Br^-$ for the following reasons: (i) the oxidized and reduced forms of the lutetium(III) phthalocyanines in the matrix film are quite stable in aqueous solutions, (ii) the electrolytes present in the aqueous media are permeable in the film, and (iii) the total concentration of the phthalocyanine in the film can be maintained at a much smaller value than the concentration of the cation or anion in the aqueous media, which can itself be varied over a wide concentration range, in this case from 0.005 to 1.0 M.

The film electrochemistry of the lutetium(III) phthalocyanines was also examined using di-*n*-dodecyl phosphate ($2C_{12}PO_4H$) as an anionic matrix, and these data are compared to results observed with tetra-*n*-octylammonium bromide ($4C_8N^+Br^-$) as a cationic matrix. Thus, the effect of changing the charge of the matrix could also be determined. Finally, the chemically reduced forms of the lutetium(III) phthalocyanines were obtained in a matrix film on a quartz substrate in water using $Na_2S_2O_4$ as a reducing agent, and the resulting ion-paired product was then characterized by vis-near-IR spectroscopy.

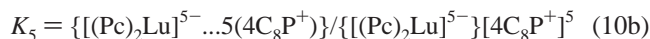
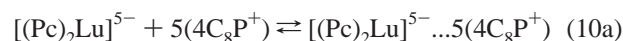
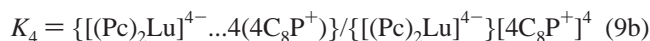
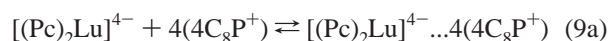
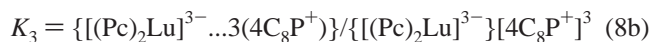
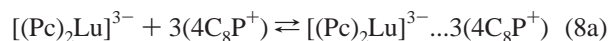
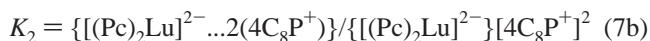
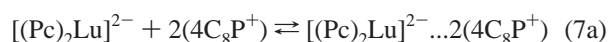
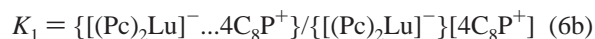
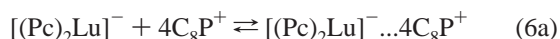
Model and Theory

In the absence of cation binding to electroreduced $(Pc)_2Lu$, the five consecutive one-electron-transfer reactions of $(Pc)_2Lu$ can be written as

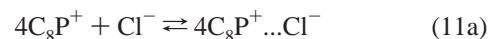


where $E^{0'}(1)$, $E^{0'}(2)$, $E^{0'}(3)$, $E^{0'}(4)$, and $E^{0'}(5)$ are the standard potentials for the five redox processes examined.

Binding of the tetraoctylphosphonium ion, $4C_8P^+$, to the five stepwise reduced forms of $(Pc)_2Lu$ in the matrix can be expressed by the equilibria and formation constants K_1 to K_5 given in eqs 6–10:



An equilibrium between $4C_8P^+$ and Cl^- also occurs in the film, and this process can be expressed as shown in eq 11:



The total cationic sites, $[4C_8P^+]_t$, are expressed as shown in eq 12.

$$[4C_8P^+]_t = [4C_8P^+] + [4C_8P^+ \dots Cl^-] + \{[(Pc)_2Lu]^- \dots 4C_8P^+\} + \{[(Pc)_2Lu]^{2-} \dots 2(4C_8P^+)\} + \{[(Pc)_2Lu]^{3-} \dots 3(4C_8P^+)\} + \{[(Pc)_2Lu]^{4-} \dots 4(4C_8P^+)\} + \{[(Pc)_2Lu]^{5-} \dots 5(4C_8P^+)\} \quad (12)$$

Because the quantity of Pc_2Lu in the film is only 5% of the total cationic sites, eq 12 can then be approximated by eq 13.

$$[4C_8P^+] = [4C_8P^+]_t / (1 + K_6[Cl^-]) \quad (13)$$

The Nernst equation that describes the $[(Pc)_2Lu]^{0/-}$ redox couple is given by eq 14.

$$E_{eq}(1) = E^{0'}(1) + (RT/nF) \ln \{[(Pc)_2Lu] / \{[(Pc)_2Lu]^- \}\} \quad (14)$$

where $E_{eq}(1)$ is the equilibrium potential, R is the gas constant, T is the temperature, and F is the Faraday constant. $[(Pc)_2Lu]$ and $\{[(Pc)_2Lu]^- \}$ represent the concentrations of the neutral and singly reduced phthalocyanines in the film. Combining eqs 6 and 14 leads to eq 15.

$$E_{eq}(1) = E^{0'}(1) + (RT/nF) \ln K_1 + (RT/nF) \ln [4C_8P^+] + (RT/nF) \ln \{[(Pc)_2Lu] / \{[(Pc)_2Lu]^- \dots 4C_8P^+\} \} \quad (15)$$

When $E_{eq}(1) = E_{1/2}(1)$, then $[(Pc)_2Lu] = \{[(Pc)_2Lu]^- \} + \{[(Pc)_2Lu]^- \dots 4C_8P^+\}$, where $E_{1/2}(1)$ is the reversible half-wave potential of redox reaction 1 in the $4C_8P^+$ film. Using this relationship, one can rewrite eq 15 as

$$E_{1/2}(1) = E^{0'}(1) + (RT/nF) \ln(1 + K_1[4C_8P^+]) \quad (16)$$

Under conditions where there is strong binding between $[(Pc)_2Lu]^-$ and $4C_8P^+$, the concentration of $4C_8P^+$ in the film will be high so that $K_1[4C_8P^+] \gg 1$ and the apparent number of electrons involved in the equilibrium relationship is given by $n_{app}(1)$; under these conditions, eq 16 can then be approximated as shown in eq 17.

$$E_{1/2}(1) = E^{0'}(1) + (RT/n_{\text{app}}(1)F) \ln K_1 + (RT/n_{\text{app}}(1)F) \ln [4\text{C}_8\text{P}^+] \quad (17)$$

Using the relationship of eq 13 and the approximation of $K_6[\text{Cl}^-] \gg 1$ allows eq 17 to be rewritten as

$$E_{1/2}(1) = E^{0'}(1) + (RT/n_{\text{app}}(1)F) \ln(K_1/K_6) - (RT/n_{\text{app}}(1)F) \ln [\text{Cl}^-] + (RT/n_{\text{app}}(1)F) \ln [4\text{C}_8\text{P}^+]_{\text{t}} \quad (18)$$

For example, $E^{0'}(1) = E(1)$ when the total concentration of the cationic sites is 1 M in the film, and one can then rewrite eq 18 as shown in eq 19.

$$E_{1/2}(1) = E(1) + (RT/n_{\text{app}}(1)F) \ln(K_1/K_6) - (RT/n_{\text{app}}(1)F) \ln [\text{Cl}^-] \quad (19)$$

The Nernst equations describing the redox couples of the second to fifth reductions of $(\text{Pc})_2\text{Lu}$, eqs 2–5, can then be written as shown in eqs 20–23:

$$E_{\text{eq}}(2) = E^{0'}(2) + (RT/nF) \ln \{[(\text{Pc})_2\text{Lu}]^- / [(\text{Pc})_2\text{Lu}]^{2-}\} \quad (20)$$

$$E_{\text{eq}}(3) = E^{0'}(3) + (RT/nF) \ln \{[(\text{Pc})_2\text{Lu}]^{2-} / [(\text{Pc})_2\text{Lu}]^{3-}\} \quad (21)$$

$$E_{\text{eq}}(4) = E^{0'}(4) + (RT/nF) \ln \{[(\text{Pc})_2\text{Lu}]^{3-} / [(\text{Pc})_2\text{Lu}]^{4-}\} \quad (22)$$

$$E_{\text{eq}}(5) = E^{0'}(5) + (RT/nF) \ln \{[(\text{Pc})_2\text{Lu}]^{4-} / [(\text{Pc})_2\text{Lu}]^{5-}\} \quad (23)$$

When $E_{\text{eq}}(2) = E_{1/2}(2)$, $E_{\text{eq}}(3) = E_{1/2}(3)$, $E_{\text{eq}}(4) = E_{1/2}(4)$, and $E_{\text{eq}}(5) = E_{1/2}(5)$, $\{[(\text{Pc})_2\text{Lu}]^- + \{[(\text{Pc})_2\text{Lu}]^- \dots 4\text{C}_8\text{P}^+\} = \{[(\text{Pc})_2\text{Lu}]^{2-} + \{[(\text{Pc})_2\text{Lu}]^{2-} \dots 2(4\text{C}_8\text{P}^+)\} = \{[(\text{Pc})_2\text{Lu}]^{3-} + \{[(\text{Pc})_2\text{Lu}]^{3-} \dots 3(4\text{C}_8\text{P}^+)\} = \{[(\text{Pc})_2\text{Lu}]^{4-} + \{[(\text{Pc})_2\text{Lu}]^{4-} \dots 4(4\text{C}_8\text{P}^+)\} = \{[(\text{Pc})_2\text{Lu}]^{5-} + \{[(\text{Pc})_2\text{Lu}]^{5-} \dots 5(4\text{C}_8\text{P}^+)\}$, where $E_{1/2}(2)$, $E_{1/2}(3)$, $E_{1/2}(4)$, and $E_{1/2}(5)$ are the half-wave potentials for redox reactions 2–5, respectively, in the film containing $4\text{C}_8\text{P}^+$ under electrochemically reversible conditions. Then eqs 19–23 can be approximated by eqs 24–27.

$$E_{1/2}(2) = E^{0'}(2) + (RT/nF) \ln \{1 + K_2[4\text{C}_8\text{P}^+]^2 / \{1 + K_1[4\text{C}_8\text{P}^+]\} \} \quad (24)$$

$$E_{1/2}(3) = E^{0'}(3) + (RT/nF) \ln \{1 + K_3[4\text{C}_8\text{P}^+]^3 / \{1 + K_2[4\text{C}_8\text{P}^+]^2\} \} \quad (25)$$

$$E_{1/2}(4) = E^{0'}(4) + (RT/nF) \ln \{1 + K_4[4\text{C}_8\text{P}^+]^4 / \{1 + K_3[4\text{C}_8\text{P}^+]^3\} \} \quad (26)$$

$$E_{1/2}(5) = E^{0'}(5) + (RT/nF) \ln \{1 + K_5[4\text{C}_8\text{P}^+]^5 / \{1 + K_4[4\text{C}_8\text{P}^+]^4\} \} \quad (27)$$

When the concentration of $4\text{C}_8\text{P}^+$ in the film is high and strong binding exists so that $K_2[4\text{C}_8\text{P}^+]^2 \gg 1$, $K_3[4\text{C}_8\text{P}^+]^3 \gg 1$, $K_4[4\text{C}_8\text{P}^+]^4 \gg 1$, $K_5[4\text{C}_8\text{P}^+]^5 \gg 1$, and $K_6[\text{Cl}^-] \gg 1$, the apparent number of electrons involved in the equilibrium relationships is given by $n_{\text{app}}(2)$, $n_{\text{app}}(3)$, $n_{\text{app}}(4)$, and $n_{\text{app}}(5)$ for each redox reaction, respectively, and eqs 24–27 can then be approximated as

$$E_{1/2}(2) = E(2) + (RT/n_{\text{app}}(2)F) \ln(K_2/K_1K_6) - (RT/n_{\text{app}}(2)F) \ln [\text{Cl}^-] \quad (28)$$

$$E_{1/2}(3) = E(3) + (RT/n_{\text{app}}(3)F) \ln(K_3/K_2K_6) - (RT/n_{\text{app}}(3)F) \ln [\text{Cl}^-] \quad (29)$$

$$E_{1/2}(4) = E(4) + (RT/n_{\text{app}}(4)F) \ln(K_4/K_3K_6) - (RT/n_{\text{app}}(4)F) \ln [\text{Cl}^-] \quad (30)$$

$$E_{1/2}(5) = E(5) + (RT/n_{\text{app}}(5)F) \ln(K_5/K_4K_6) - (RT/n_{\text{app}}(5)F) \ln [\text{Cl}^-] \quad (31)$$

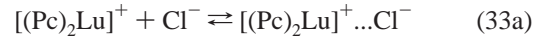
where $E(2)$, $E(3)$, $E(4)$, and $E(5)$ are the redox potentials when the concentration of the total cationic sites is 1 M. The apparent number of electrons, n_{app} , can then be obtained from the slope of the plot of $E_{1/2}$ versus $\ln[\text{Cl}^-]$.

On the other hand, in the absence of anion binding to the singly oxidized form of $(\text{Pc})_2\text{Lu}$, the one-electron-transfer oxidation of $(\text{Pc})_2\text{Lu}$ can be written as



where $E^{0'}(6)$ is the standard redox potential for the process.

When Cl^- is bound to the singly oxidized form of $(\text{Pc})_2\text{Lu}$, the binding equilibrium can be expressed as shown in eq 33.



The Nernst equation for the $[(\text{Pc})_2\text{Lu}]^{0/+}$ redox couple is written as

$$E_{\text{eq}}(6) = E^{0'}(6) + (RT/nF) \ln \{[(\text{Pc})_2\text{Lu}]^+ / [(\text{Pc})_2\text{Lu}]\} \quad (35)$$

When $E_{\text{eq}}(6) = E_{1/2}(6)$, $[(\text{Pc})_2\text{Lu}] = \{[(\text{Pc})_2\text{Lu}]^+ + \{[(\text{Pc})_2\text{Lu}]^+ \dots \text{Cl}^-\}$, where $E_{1/2}(6)$ is the half-wave potential of redox reaction 32 in the presence of Cl^- in the film under electrochemically reversible conditions. Using this relationship, one can rewrite eq 35 as

$$E_{1/2}(6) = E^{0'}(6) + (RT/nF) \ln(1 + K_7[\text{Cl}^-]) \quad (36)$$

When strong binding exists between $[(\text{Pc})_2\text{Lu}]^+$ and Cl^- and the concentration of Cl^- in the film is high such that $K_7[\text{Cl}^-] \gg 1$, the apparent number of electrons involved in the equilibrium relationship is given by $n_{\text{app}}(6)$, and eq 36 can be approximated as shown in eq 37.

$$E_{1/2}(6) = E^{0'}(6) - (RT/n_{\text{app}}(6)F) \ln K_7 - (RT/n_{\text{app}}(6)F) \ln [\text{Cl}^-] \quad (37)$$

The binding of Cl^- to $4\text{C}_8\text{P}^+$ in the matrix should also be considered. The equilibrium and binding constant for this reaction can be expressed as shown in eq 11. Under our experimental conditions, $[\text{Cl}^-]$ is in excess as compared to $[4\text{C}_8\text{P}^+]$, and the equilibrium in eq 11a can be neglected. The apparent number of electrons involved in the equilibrium relationship, $n_{\text{app}}(6)$, can then be obtained from the slope of a plot of $E_{1/2}(6)$ versus $\ln[\text{Cl}^-]$.

Similar thermodynamic relationships with the consideration of electrolyte anion binding to the matrix cation sites have also

been deduced by Sagara and co-workers for the case of hypericin in a cationic matrix.¹⁵

Experimental Section

Chemicals and Reagents. Tetra-*n*-octylphosphonium bromide ($4C_8P^+Br^-$, Aldrich Chemical Co.), tetra-*n*-octylammonium bromide ($4C_8N^+Br^-$, Tokyo Kasei), di-*n*-dodecyl phosphate ($2C_{12}PO_4H$, Sogo Pharmaceutical Co., Ltd), potassium chloride (KCl, Wako Pure Chemical Industries, Ltd.), lithium chloride (LiCl, Wako Pure Chemical Industries, Ltd.), sodium chloride (NaCl, Kishida Chemicals Co.), tetramethylammonium chloride ($Me_4N^+Cl^-$, Tokyo Kasei Co.), tetra-*n*-butylammonium chloride ($n-Bu_4N^+Cl^-$, Tokyo Kasei Co.), and sodium hydrosulfite ($Na_2S_2O_4$, Kishida Research Chemicals) were used as received. Bis[octakis(hexylthio)phthalocyaninato]lutetium(III)^{14b} and bis[tetrakis(dodecylthio)phthalocyaninato]lutetium(III)^{5a} were synthesized using reported procedures.

Instrumentation. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were carried out using an IBM model EC 225 voltammetric analyzer or a BAS-100BW electrochemical analyzer (Bioanalytical Systems). 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 voltammetric measurements of the double-decker lutetium(III) phthalocyanine compounds as a cast film on a homemade basal plane pyrolytic graphite (BPG) electrode¹⁶ with the matrices in aqueous media at 25 ± 1 °C under a nitrogen or an argon atmosphere. A saturated calomel electrode (SCE) and a Pt plate electrode were used as the reference electrode and the counter electrode, respectively.

Vis–near-IR absorption spectral measurements (JASCO V-570 UV–vis–near-IR spectrophotometer with a JASCO ISN-470 integrating sphere) for the modified quartz substrate were examined in Milli-Q water (Millipore Corp. > 18 MΩ cm) for the double-decker lutetium(III) phthalocyanine compounds in the absence or the presence of $Na_2S_2O_4$ as a reducing agent at 25 ± 1 °C under an argon atmosphere. The wavelength scan rate was 200 nm min^{−1}. The modified quartz substrate was vertically inserted into a quartz cuvette with a light path length of 10.0 mm. The cuvette was filled with Milli-Q water and then deoxygenated by argon gas. Five hundred micrograms of $Na_2S_2O_4$ was put into a disposable syringe and then dissolved in argon-degassed water in the syringe, after which the aqueous $Na_2S_2O_4$ solution was injected into the cuvette.

Preparation of Cast Film. Typical procedures for the preparation of a gel-like membrane of $[(C_6H_{13}S)_8Pc]_2Lu/4C_8P^+Br^-$ and $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8P^+Br^-$ (molar ratio 1:19) on the BPG electrode are as described in the literature.⁵ A 30-μL portion of $[(C_6H_{13}S)_8Pc]_2Lu/4C_8P^+Br^-$ or $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8P^+Br^-$ in chloroform ($[(C_6H_{13}S)_8Pc]_2Lu = [(C_{12}H_{25}S)_4Pc]_2Lu = 0.25$ mM and $[4C_8P^+Br^-] = 4.75$ mM) was placed on a BPG electrode surface (geometric area 0.36 cm²) and then air dried. The modified electrodes were immersed in aqueous electrolyte solutions containing concentrations of KCl between 1.0 and 0.005 M, followed by measurements of the electrochemistry at 25 °C under a nitrogen or an argon atmosphere. Modified electrodes containing the double-decker lutetium(III) phthalocyanines with $4C_8N^+Br^-$ or $2C_{12}PO_4H$ were prepared in a similar manner. A 30-μL portion of the double-decker lutetium(III) phthalocyanine/matrix ($4C_8N^+Br^-$ or $2C_{12}PO_4H$) (molar ratio 1:19) in chloroform ($[(C_6H_{13}S)_8Pc]_2Lu = [(C_{12}H_{25}S)_4Pc]_2Lu = 0.25$ mM and $[4C_8N^+Br^-] = [2C_{12}PO_4H] = 4.75$ mM) was placed on a BPG electrode surface

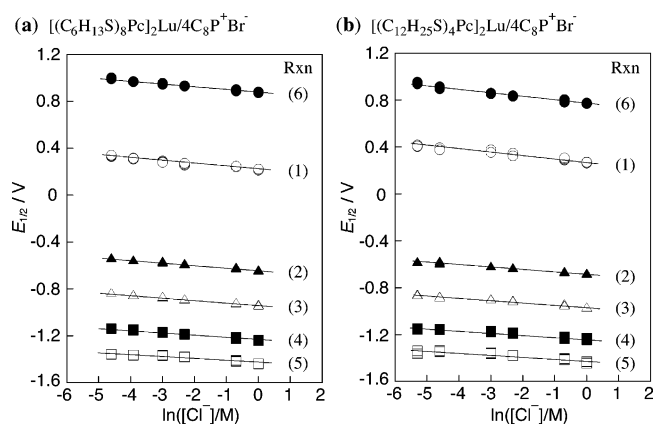


Figure 2. Plots of $E_{1/2}$ for each redox couple of (a) a cast film of $[(C_6H_{13}S)_8Pc]_2Lu/4C_8P^+Br^-$ (molar ratio 1:19) and (b) $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8P^+Br^-$ (molar ratio 1:19) on a BPG electrode vs $\ln[Cl^-]$. Closed circles denote the data for the first oxidation process in KCl aqueous solutions. Open circles, closed triangles, open triangles, closed squares, and open squares denote the data for the first through fifth reduction process, respectively, in KCl aqueous solution.

and then air dried. Each modified electrode was immersed in a 0.5 M KCl aqueous solution and then followed by the electrochemical measurements.

Results and Discussion

Thermodynamic Study. The values of $E_{1/2}$ obtained from differential pulse voltammograms were plotted versus the logarithm of the Cl^- concentration using KCl as a supporting electrolyte. Examples of these plots are shown in Figure 2. The results presented in Figure 2 were analyzed and interpreted in light of the model described in the above equations (eqs 1 to 37). It is evident that the $E_{1/2}$ versus $\ln[Cl^-]$ plots for the modified electrodes show a linear relationship. This fact confirms the validity of our thermodynamic treatment. In the case of the $[(C_6H_{13}S)_8Pc]_2Lu/4C_8P^+Br^-$ modified electrode, the apparent number of electrons involved in the equilibrium relationship were calculated as follows: $n_{app}(1) = 1.10$, $n_{app}(2) = 1.16$, $n_{app}(3) = 1.15$, $n_{app}(4) = 1.18$, $n_{app}(5) = 1.14$, and $n_{app}(6) = 1.04$. These values were obtained from the slopes of the $E_{1/2}$ versus $\ln[Cl^-]$ plots (Figure 2a) and give n_{app} values close to the expected integers. The apparent numbers of electrons involved in the equilibrium relationship for the $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8P^+Br^-$ modified electrode are as follows: $n_{app}(1) = 0.90$, $n_{app}(2) = 1.18$, $n_{app}(3) = 1.17$, $n_{app}(4) = 1.17$, $n_{app}(5) = 1.11$, and $n_{app}(6) = 0.93$. These values were obtained from the slopes of the $E_{1/2}$ versus $\ln[Cl^-]$ plots (Figure 2b). These results reveal that each stepwise one-electron addition to the two phthalocyanines is accompanied by a stepwise increase in the number of associated $4C_8P^+$ cations such that the ratio of phthalocyanine to monocations increases from 1:1 for the singly reduced derivative to 1:5 in the case of $\{[(C_6H_{13}S)_8Pc]_2Lu\}^{5-}$ or $\{[(C_{12}H_{25}S)_4Pc]_2Lu\}^{5-}$. In addition, the two singly oxidized phthalocyanine species form 1:1 complexes with Cl^- . The overall results lead to the conclusion that binding of the reduced forms of $[(C_6H_{13}S)_8Pc]_2Lu$ and $[(C_{12}H_{25}S)_4Pc]_2Lu$ with the cationic sites of the $4C_8P^+$ matrix is responsible for the positive shift of the formal potentials. However, the fact that each experimentally determined number of electrons transferred from the data in Figure 2 is not an integer leads to the conclusion that binding of the reduced forms of $[(C_6H_{13}S)_8Pc]_2Lu$ and $[(C_{12}H_{25}S)_4Pc]_2Lu$ with the $4C_8P^+$ cations must also compete with the binding of Cl^- , although this equilibrium is not predominant.

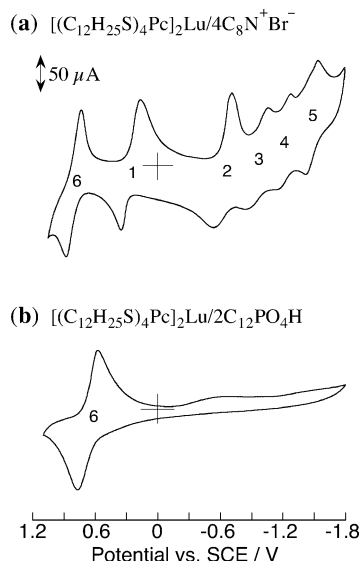


Figure 3. Cyclic voltammograms for (a) a cast film of $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8N^+Br^-$ (molar ratio 1:19) on a BPG electrode in a 0.5 M KCl aqueous solution at 25 °C and (b) a cast film of $[(C_{12}H_{25}S)_4Pc]_2Lu/2C_{12}PO_4H$ (molar ratio 1:19) on a BPG electrode in 0.5 M KCl at pH 10 in aqueous media. Scan rate = 0.1 V/s.

Dependence of $E_{1/2}$ on the Electrolyte. Additional electrochemical experiments were carried out on $[(C_6H_{13}S)_8Pc]_2Lu/4C_8P^+Br^-$ and $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8P^+Br^-$ modified electrodes in aqueous media containing five different types of electrolyte cations. Supporting electrolytes are known to influence the voltammograms for cast films of double-decker lutetium(III) phthalocyanines because the electrode reactions are accompanied by an incorporation of electrolyte ions from the bulk solution.^{4b,c,f} In the present system, however, cyclic and differential pulse voltammograms for cast films of $[(C_6H_{13}S)_8Pc]_2Lu/4C_8P^+Br^-$ and $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8P^+Br^-$ on the BPG electrodes were essentially the same in KCl, LiCl, NaCl, $Me_4N^+Cl^-$, or $n-Bu_4N^+Cl^-$ aqueous solutions (data not shown). In other words, the oxidation potentials for the investigated compounds remained invariant with changes in the type of cation of the supporting electrolyte as long as chloride was the associated anion. The reduction potentials were also invariant with changes in the type of supporting electrolyte cation. This result suggests that the cation of the matrix film is the counterion on the multiple reduced forms of $[(C_6H_{13}S)_8Pc]_2Lu$ and $[(C_{12}H_{25}S)_4Pc]_2Lu$ and also that the chloride of the supporting electrolyte is the counterion on the singly oxidized form of the investigated phthalocyanines.

Charge Dependence of the Matrix Films. To better understand the importance of the charge on the matrix for the electron-transfer reaction, we also investigated the use of cationic and anionic matrices, $4C_8N^+Br^-$ and $2C_{12}PO_4H$, instead of using $4C_8P^+Br^-$. The resulting cyclic and differential pulse voltammograms under these conditions indicate that the $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8N^+Br^-$ modified BPG electrode undergoes five reductions and one oxidation in 0.5 M KCl aqueous solution (Figure 3a), as was observed when the matrix was $4C_8P^+Br^-$. Half-wave potentials for the reduction of $[(C_{12}H_{25}S)_4Pc]_2Lu$ in the $4C_8N^+Br^-$ film are located at $E_{1/2} = 0.26, -0.66, -0.97, -1.21$ and -1.45 V, and the single oxidation is located at $E_{1/2} = 0.81$ V versus SCE. The half-wave potentials of $[(C_{12}H_{25}S)_4Pc]_2Lu$ in the $4C_8N^+Br^-$ film are more positive by up to 520 mV than the measured $E_{1/2}$ values in CH_2Cl_2 , 0.1 M TBAP (Table 1). This behavior is similar to what was seen in our previous electrochemical study of $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8P^+Br^-$ at

a modified BPG electrode⁵ and indicates strong Coulomb-coupled binding of the double-decker lutetium(III) phthalocyanine reduction products with cationic sites of the $4C_8N^+Br^-$ matrix. However, $[(C_{12}H_{25}S)_4Pc]_2Lu/2C_{12}PO_4H$ at a modified BPG electrode displays only one redox couple (at $E_{1/2} = 0.68$ V versus SCE) when examined in a 0.5 M KCl aqueous solution at pH 10 (Figure 3b). No reduction at all can be observed under these experimental conditions, and this behavior is similar to what was found in the absence of a matrix where no well-defined reduction peaks of this compound were observed.⁵ In the same way, $[(C_6H_{13}S)_8Pc]_2Lu/4C_8N^+Br^-$ undergoes five reductions and one oxidation at a $4C_8N^+Br^-$ modified BPG electrode, and $[(C_6H_{13}S)_8Pc]_2Lu/2C_{12}PO_4H$ displays only one redox couple at a $2C_{12}PO_4H$ modified BPG electrode (Table 1). The behavior at the modified electrode containing $2C_{12}PO_4H$ contrasts significantly with what is observed for the same double-decker lutetium(III) phthalocyanines at the modified electrode with cationic matrices where up to five well-defined reductions are seen in the films. However, it should be noted from Table 1 that oxidation potentials at the modified electrodes containing $2C_{12}PO_4H$ are up to 130 mV more negative than $E_{1/2}$ values observed for the compounds at the electrode with cationic matrices or in the absence of a matrix. This may be due to a strong Coulomb-coupled binding of the double-decker lutetium(III) phthalocyanines oxidation product with anionic sites of the $2C_{12}PO_4H$ matrix.

Chemical Reduction. As mentioned earlier, solutions or thin films of lutetium(III) phthalocyanines and their derivatives exhibit electrochromism.^{2,3} Moreover, when some of these lutetium(III) phthalocyanines are exposed to electron-donor or electron-acceptor molecules such as NO_x , $NaBH_4$, N_2H_4 , dichlorodicyanoquinone, or Br_2 , they undergo changes in their spectroscopic properties.^{2f,h,14b,17} In our previous study of $[(C_6H_{13}S)_8Pc]_2Lu$ and $[(C_{12}H_{25}S)_4Pc]_2Lu$ in organic solutions,^{5b} the spectroscopic and the electrochromic behavior were discussed. Similar spectral changes of $[(C_6H_{13}S)_8Pc]_2Lu$ are seen in this current study after generation of the chemically oxidized or chemically reduced phthalocyanines using Br_2 or $NaBH_4$ in organic media.^{14b}

To better understand ion-pairing interactions between reduced forms of the lutetium(III) phthalocyanines and the cationic sites of the matrix, we also examined the chemically reduced complexes using $Na_2S_2O_4$ as a reducing agent in aqueous solutions. The lutetium(III) phthalocyanine modified quartz substrates with cationic matrices of $4C_8P^+Br^-$ and $4C_8N^+Br^-$ or an anionic matrix of $2C_{12}PO_4H$ were characterized by vis–near-IR spectroscopy. A summary of the spectroscopic data in CH_2Cl_2 solutions and in cast films of $[(C_6H_{13}S)_8Pc]_2Lu$ or $[(C_{12}H_{25}S)_4Pc]_2Lu$ with $4C_8P^+Br^-$, $4C_8N^+Br^-$, or $2C_{12}PO_4H$ as well as in the absence of a matrix is listed in Table 2. Figure 4 shows vis–near-IR spectra for films of $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8N^+Br^-$, $[(C_{12}H_{25}S)_4Pc]_2Lu/2C_{12}PO_4H$, and $[(C_{12}H_{25}S)_4Pc]_2Lu$ on a quartz substrate in aqueous media in the absence (—) and presence (---) of $Na_2S_2O_4$ under an argon atmosphere. The characteristic Q bands of neutral $[(C_6H_{13}S)_8Pc]_2Lu$ and $[(C_{12}H_{25}S)_4Pc]_2Lu$ of the films, either in the presence of $4C_8P^+Br^-$, $4C_8N^+Br^-$, or $2C_{12}PO_4H$ or in the absence of a matrix are red-shifted (Table 2) and broadened with respect to what is seen in CH_2Cl_2 , and this is due to a strong aggregation of the phthalocyanines in the films. The bands at 935–967 nm are associated with the radical character of the phthalocyanine macrocycle,^{17a} and these bands, along with the phthalocyanine Q bands, both decreased in intensity upon reduction. This is seen, for example, in the case of $[(C_{12}H_{25}S)_4Pc]_2Lu$, where there

TABLE 2: Vis–Near-IR Spectral Data of [(C₆H₁₃S)₈Pc]₂Lu and [(C₁₂H₂₅S)₄Pc]₂Lu under Different Experimental Conditions

compound	condition	$\lambda_{\text{max}}/\text{nm}$			
[(C ₆ H ₁₃ S) ₈ Pc] ₂ Lu	H ₂ O/4C ₈ P ⁺ Br [−]	543	663 (sh) ^d	708	954
	Na ₂ S ₂ O ₄ /4C ₈ P ⁺ Br [−]	592	658	740	835
	H ₂ O/4C ₈ N ⁺ Br [−]	541	664 (sh)	709	967
	Na ₂ S ₂ O ₄ /4C ₈ N ⁺ Br [−]	591	663	740	834
	H ₂ O/2C ₁₂ PO ₄ H ^b	546	642 (sh)	708	957
	H ₂ O/cast film	542	642 (sh)	707	955
	CH ₂ Cl ₂ ^c	386	550	700	
{[(C ₆ H ₁₃ S) ₈ Pc] ₂ Lu} ^{−a}	CH ₂ Cl ₂ ^c	381	657	739	
{[(C ₆ H ₁₃ S) ₈ Pc] ₂ Lu} ^{2−a}	CH ₂ Cl ₂ ^c	371	657	816	
[(C ₁₂ H ₂₅ S) ₄ Pc] ₂ Lu	H ₂ O/4C ₈ P ⁺ Br [−]	638 (sh)	706	940	
	Na ₂ S ₂ O ₄ /4C ₈ P ⁺ Br [−]	575	636	720	820
	H ₂ O/4C ₈ N ⁺ Br [−]	636 (sh)	702	938	
	Na ₂ S ₂ O ₄ /4C ₈ N ⁺ Br [−]	579	640	715	815
	H ₂ O/2C ₁₂ PO ₄ H ^b	627 (sh)	690	935	
	H ₂ O/cast film	633 (sh)	700	937	
	CH ₂ Cl ₂ ^c	372	481	684	
{[(C ₁₂ H ₂₅ S) ₄ Pc] ₂ Lu} ^{−a}	CH ₂ Cl ₂ ^c	367	640	718	
{[(C ₁₂ H ₂₅ S) ₄ Pc] ₂ Lu} ^{2−a}	CH ₂ Cl ₂ ^c	360	636	793	

^a Electrochemically generated. ^b The pH of the aqueous solution was adjusted to 10 by a KOH aqueous solution. ^c CH₂Cl₂ solution containing 0.2 M tetra-*n*-butylammonium perchlorate (TBAP) as an electrolyte. See ref 5b. UV–vis spectroscopy was used. ^d (sh) means shoulder.

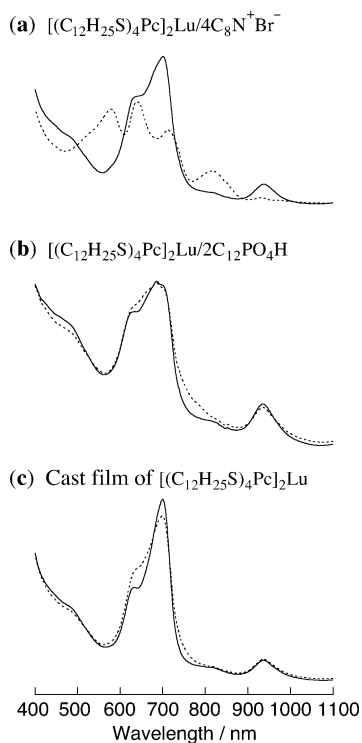


Figure 4. Vis–near-IR absorption spectra for (a) a cast film of [(C₁₂H₂₅S)₄Pc]₂Lu/4C₈N⁺Br[−] (molar ratio 1:19), (b) [(C₁₂H₂₅S)₄Pc]₂Lu/2C₁₂PO₄H (molar ratio 1:19), and (c) [(C₁₂H₂₅S)₄Pc]₂Lu only on a quartz substrate in water. The spectrum of the cast film of [(C₁₂H₂₅S)₄Pc]₂Lu/2C₁₂PO₄H was measured in water at pH 10. Solid lines denote spectra in the absence of Na₂S₂O₄, and dashed lines denote spectra in the cuvette containing the Na₂S₂O₄ reducing agent.

was a disappearance of the Q and radical bands and the appearance of four new bands at 580, 640, 715, and 815 nm within 10 min of adding Na₂S₂O₄ to a cuvette containing the phthalocyanine in the cast film with 4C₈N⁺Br[−] (Figure 4a). The absorption spectrum of chemically reduced [(C₁₂H₂₅S)₄Pc]₂Lu/4C₈N⁺Br[−] is similar to the electrogenerated spectrum for a solution containing a mixture of the mono- and dianionic forms

of [(C₁₂H₂₅S)₄Pc]₂Lu in CH₂Cl₂.^{5b} In contrast, cast films of [(C₁₂H₂₅S)₄Pc]₂Lu in a matrix containing 2C₁₂PO₄H or in the absence of a matrix show no significant spectral changes in aqueous media at pH 10 or in pure water even 30 min after adding Na₂S₂O₄ to the cuvette (Figure 4b,c).

Similar types of spectral changes were obtained upon adding Na₂S₂O₄ to cast films of [(C₆H₁₃S)₈Pc]₂Lu with the same series of matrices on a quartz substrate (Table 2). These results indicate that the cationic site of the matrix film plays the role of a counter cation for the chemically reduced lutetium(III) phthalocyanines. In other words, the effect of changing the charge of the matrix upon either electrochemical or chemical reduction supports the finding that the binding of the reduced forms of [(C₆H₁₃S)₈Pc]₂Lu and [(C₁₂H₂₅S)₄Pc]₂Lu to cationic sites of the matrix films is responsible for the positive shift of the measured half-wave potentials.

Concluding Remarks

In summary, the results of the present study provide the first experimental verification for ion-pairing effects of 4C₈P⁺Br[−] with reduced double-decker lutetium(III) phthalocyanines in several oxidation states when embedded in a gel-like cast film composite cationic matrix on a BPG electrode in aqueous media. We have determined from slopes of $E_{1/2}$ versus $\ln[\text{Cl}^-]$ (Cl^- = the anion in the aqueous media) the apparent number of electrons involved in the single oxidation and the five one-electron reductions. Our thermodynamic treatment enables a quantitative analysis of the interaction that occurs between multi-anions of the investigated double-decker lutetium(III) phthalocyanines and the matrix cations. The presently described thermodynamic treatment should be applicable not only to reduced double-decker lutetium(III) phthalocyanines but also to other highly reduced compounds such as porphyrins and fullerenes. The effect of changing the counter cations of the electrolyte or the charge of the matrix films was also examined and supports the observed ion-pairing effects in the matrix.

Acknowledgment. The support of the Robert A. Welch Foundation (K.M.K., grant E-680) is gratefully acknowledged. T.N. thanks the Japan Society for the Promotion of Science for a fellowship. I.Y. is grateful for a Grant-in Aid from TUBITAK (The Scientific and Technical Research Council of Turkey) with a NATO Scientific Fellowship and the Technical University of Istanbul for a fellowship. We are grateful to Professor T. Sagara at Nagasaki University for helpful discussions on the thermodynamic study.

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