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Preparation of Bis(phthalocyaninato)lutetium with Various Substituents and Their Electrochemical Properties

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A series of bis(phthalocyaninato)lutetium complexes with substituents on each benzoring [Lu(pc$_2$R$_8$)] was prepared and the electrochromic behavior investigated by means of cyclic voltammetry of coated electrodes. Although the unsubstituted complex, Lu(pc)$_2$, showed multistep electrochromism, its stability was quite unsatisfactory due to a falling-off of films from the electrode surface upon repetitive potential scanning. In the case of R=*t*-butyl, the improved solubility in organic solvents brought about an easier filming process and better adhesion to the electrode surface, though its high oxidation potential caused a cleavage of bi-peripheral complex. In contrast, complexes with electron-donating groups, such as R=propoxy or neopentyloxy, showed a lower oxidation potential and better stability upon repetitive potential scans, though the oxidized color was brownish rather than bright red. Complexes with 4 groups each of tetra-*t*-butyl and tetra propoxy had the oxidation potential close to that of octapropoxy or octakis(neopentyloxy) complexes and showed much improved stability and electrochromic behavior.

It has been well-known that the modified electrodes of bis(phthalocyaninato)lantanum complexes [La(pc)$_2$] exhibit a reversible multicolor electrochromic behavior as a result of multistep redox reactions.[1-3] With an aqueous HCl–KCl supporting electrolyte, the film color generally turns from original green to blue in a reduction process and to red through yellow in an oxidation process. However, the solubility of these M(pc)$_2$ complexes is not quite sufficient to make homogeneous coatings on the electrode materials by (for instance) spin-coating. The subsequently occuring inhomogeneous, brittle films with sputtered microcrystalline multiphases may cause an interuption of counter ion migration through the films. Therefore, cyclic voltammograms with large tailing and peak splitting, corresponding to slow electrochemistry, may be seen. Futhermore, the complex film may change its volume due to counter ion compensation upon redox reactions, while the complex is driven between the uncharged and charged states. Such a volume change is easier in the thinner area, resulting in a falling-off of films. Even in the case of macroscopically homogeneous vacuum-deposited films, the film stability is unsatisfactory and sometimes the majority of deposited films occur suddenly to leave from the electrode surface.

In the present study, the *t*-butyl and/or alkoxyl-substituted bis(phthalocyaninato)lutetium [Lu(pc$_2$R$_8$)] were synthesized in the hope of improving the solubility of materials, as well as the brittleness and electrochemical properties of the resulting films. Especially, the electron-donating effect of alkoxyl substituents is discussed in accordance with a decrease in the oxidation potential and an improvement of the stability.

Experimental

Chemicals: All chemicals of reagent grade were used without further purification. Solvents and water were distilled twice and used immediately.

Preparation: The 6 lutetium complexes employed in the present work are summarized in Table 1 (also see Eq. 1), where "mix-" denotes the statistical substitution of each 4 groups of R^1 and R^2 in two phthalocyanine rings; "un-" means that one phthalocyanine ring is substituted by 4 groups of R^1 and another by 4 groups of R^2. Hereafter, we abbreviate phthalocyaninato-ring as pc, and unsubstituted and substituted lutetium complexes as Lu(pc)$_2$ and Lu(pc$_2$R$_8$).

The preparation of Lu(pc)$_2$, Lu(pc$_2$R$^1_8$), Lu(pc$_2$R$^2_8$), Lu(pc$_2$R$^3_8$), and mix-Lu(pc)$_2$ was carried out according to methods described in the literature[4] by reacting the corresponding (equimolar mixture of) phthalonitriles and 1/8 equivalent amount of lutetium triacetate in bulk at 250—350 °C. The purification was carried out by using silica gel (in lit, alumina eluted with DMF–methanol) column chromatography (100 mesh-up, chloroform), followed silica-gel thin-layer chromatography (200 mesh, chloroform/acetone=50/1) and HPLC (inversed phase, silica-gel 200 mesh, chloroform). The literature-method using alumina did not completely exclude the impurities by one passage of the column, and the purity did not reach more than 90%.

In the case of un-Lu(pc)$_2$, it was first necessary to prepare an acetato(phthalocyaninato)lutetium complex [Lu(pc)(OAc)]. 4-propoxyphthalonitrile was converted into the corresponding

Table 1. Abbreviation of Bis(phthalocyaninato)-lutetium Complexes

Abbreviation	Substituents	
	On 1st pc ring	On 2nd pc ring
Lu(pc)$_2$	H	H
Lu(pc$_2$R$^1_8$)	R^1=*t*-butyl	R^1
Lu(pc$_2$R$^2_8$)	R^2=propoxy	R^2
Lu(pc$_2$R$^3_8$)	R^3=neopentyloxy	R^3
mix-Lu(pc)$_2$	Statistical substitution of each 4 of R^1 and R^2	
un-Lu(pc)$_2$	R^1	R^2

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2*H*-isoindole-1,3(2*H*)dimine by passing dry ammonia for 2.5 h to the refluxing dry saturated methanolic solution in the presence of a catalytic amount of sodium methoxide. After being collected by filtration, a hygroscopic white powder was dried in vacuo, then reacted with 1/4 equivalent amount of lutetium triacetate in refluxing 2-(dimethylamino)ethanol for 5 h. The resulting solution with a greenish precipitate was poured into a large amount of methanol. The green powder was collected, and then chromatographed on a silica-gel column as described above. The greenish second elution band (first, was metal-free phthalocyanine) was collected and dried to obtain $Lu(pcR^2_4)(OAc)$. Meanwhile, 4-*t*-butylphthalonitrile and a 1/2 equivalent amount of lithium pentyloxide were refluxed in pentyl alcohol for 5 h. To the resulting phthalocyaninatodilithium solution, a supposed equimolar amount of $Lu(pcR^2_4)(OAc)$ was added and refluxed for another 5 h. After being cooled, the mixture was poured into a large amount of water. The green precipitate was collected, dried, and purified as described above to obtain un-$Lu(pc)_2$ in ca. 10% yield (nitrile standard).

The structures of the complexes were confirmed by IR, UV-Vis, FD-Mass spectra, and elementary analyses.

Measurements: For the spectroscopies, a JASC IRA-2 infrared spectrophtometer and a Hitachi 320 electronic spectrophotometer were used.

Cyclic voltammetry and potential-step chronocoulometry were carried out using a Hokuto Denko HA-501G potentio/galvanostat and an HB-105B function generator. A saturated calomel reference electrode (SCE), a platinum sheet (ca. 4 cm^2) as a counter electrode, a basal plane pyrolytic graphite working electrode [5 mm-dia. (ca. 0.2 cm^2) of which the sidewall was insulated by a heat shrinkable tubing] and a conventional three-chamber cell were employed. For *in situ* spectroscopic measurements of electrochromism, an indium-tin oxide Nesa glass (ITO, 10 Ω/sq., ca. 230 nm-thick) cut into a 1 cm width and processing of ca. 3.5 cm^2 working area was used. The complex films of about 150 nm on freshly cleaved graphite or ITO were prepared by hand-casting from milimolar chloroform or DMF solutions through a microsyringe. The typical supporting electrolytes were as follows: pH 1—3 0.1 M KCl+HCl, pH 4—6 0.1 M KCl+0.05 M acetate buffer, pH 7—9 0.1 M KCl+0.05 M phosphate buffer (1 M=1 mol dm^{-3}). All measurements were conducted under an argon atmosphere at room temperature (21±3 °C).

Special Notes

Before entering the Results and Discussion, we wish to explain the abbreviation of complexes used here in order to avoid any misunderstanding by the readers, since there are many opinions concerning the structures of bis(phthalocyaninato)lanthanide complexes, as is discussed later. Since rare earth metal ions are trivalent, the abbreviations such $LuH(pc_2)$ [see Eq. 1(A)] were used in most of the literatures without any distinct evidence. We simply use the abbreviations $Lu(pc)_2$ and $Lu(pc_2R_8)$ for unsubstituted and octasubstituted complexes, respectively. Hereafter, $Lu(pc)_2$, for instance, denotes any kind of unsubstituted bis(phthalocyaninato)lutetium complexes, such as $LuH(pc_2)$ (protonated/neutral), $Lu(pc)_2^-$ (deprotonated/anion), $Lu(pc)_2*$ (deprotonated/radical), etc. If it is necessary to discriminate these structures, we also use $LuH(pc)_2$, $Lu(pc)_2^-$, $Lu(pc)_2*$, etc.

Results and Discussion

Preparation and Structure. The high-temperature bulk reaction of phthalonitrile and lutetium triacetate, according to the literature,[4)] usually provides $Lu(pc_2R_8)$ as a major product in 5—10% yield. On the contrary, we find that the mononuclear complex, $Lu(pcR_4)(OAc)$, can be prepared in high yields, such as 40—70% with no formation of binuclear complexes. Because the yield of phthalocyaninatodilithium [$Li_2(pc)$] is also satisfactorily high, 60—70%, and the combination reaction between $Lu(pcR_4)(OAc)$ and $Li_2(pc)$ is easily carried out, a reaction once passing the mononulcear complex is very convenient not only for the preparation of the unsymmetrical complex un-$Lu(pc)_2$, but also the usual $Lu(pc)_2$ complex.

For instance, if the unsubstituted phthalonitrile is used, the highest yields of $Lu(pc)_2$ are 7% and 20% (nitrile standard) by a bulk one-step reaction and the present two-step method, respectively.

Although the solubility of $Lu(pc)_2$ is rather low in chloroform, that of $Lu(pc_2R_8)$ is improved to milimolar or higher by the existence of peripheral substituents.

It is reported that there are "green" and "blue" types of $Lu(pc)_2$ complexes, and arguments are presented concerning the structure of ground-state complexes, as follows, including the unspecified structures:

i) Uncharged, protonated (structure A in Eq. 1) =$LuH(pc)_2$.

ii) Radical cation, protonated=$LuH(pc)_2^{+}*$.

iii) Negatively charged, deprotonated=$Lu(pc)_2^-$.

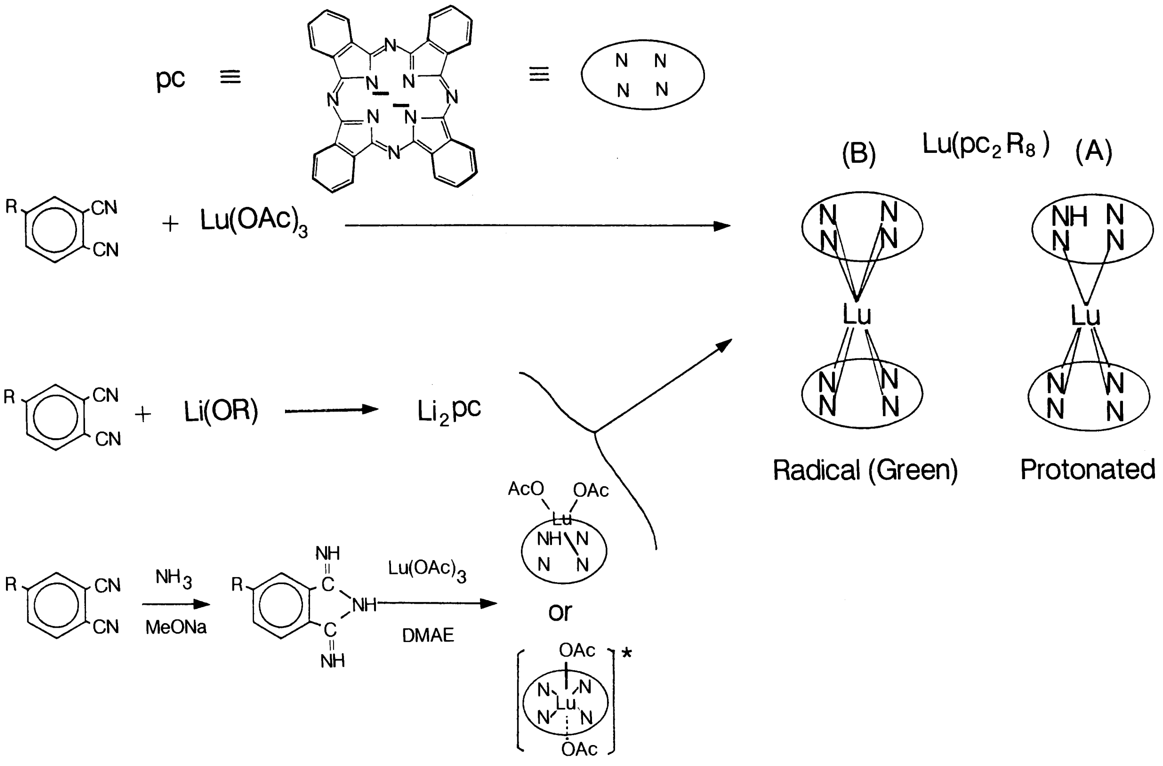
iv) Radical, deprotonated (structure B in Eq. 1) =$Lu(pc)_2*$.

Here, the radical cation species are believed to correspond to the "green" form, and the others to the "blue" form. The green form is usually obtained when the complex is separated using the silica-gel/chloroform chromatographic technique, or by sublimation; the blue form is obtained only by using a method described in the literature, involving alumina/DMF–methanol chromatography.[5—7)] We found, however, that a green–blue conversion occurs very easily:

From green to blue: Passing alumina column eluted with DMF–methanol or standing the deaerated green DMF solution.

From blue to green: Passing silica-gel column eluted with chloroform, or sublimation in vacuuo.

As is well-known, DMF is a rather basic solvent with any reducing power due to the existence of unavoidable amine impurities; chloroform is a rather acidic solvent due to photodecomposed impurities. The green–blue change of $Lu(pc)_2$ is thus attributed to acid–base



Equation 1.

and/or oxidation–reduction equilibrium. The acid–base equilibrium seems not to be a predominant factor, since the change from green to blue does not occur instantaneously in deaerated DMF, nor does it occur at all in a deaerated toluene–tributylamine solution.

Kasuga et al.[8] reported on the XPS spectrum of the green complex. The results of an XPS analysis suggested that the eight inner nitrogen atoms of the two phthalocyanine rings in $Lu(pc)_2$ coordinate equally to the central metal ion. From this result and the fact that no extra axial ligand, such as acetato ligand, is found from the FD-Mass spectra, the structure of the green complex must be $Lu(pc)_2{}^*$, in order to satisfy the valency. It is rather curious to consider the neutral radical as being of the stable form, though evidence has been found in the ESR spectrum. The green form complex of $Lu(pc_2R^2{}_8)$ showed a distinct ESR signal assignable to an organic radical in the toluene solution (Fig. 1). All other green form complexes employed in the present article gave similar ESR spectra. The lack of a super hyperfine structure of the ESR spectrum suggests that the radical is strongly delocalized, and possibly interacting with the central metal ion. The poor solubility of the green form $Lu(pc)_2$ in toluene gave a similar, but more diffused, ESR spectrum.[9,10]

Since the solubility of the green $Lu(pc)_2$ complex is lower than that of the blue form, the NMR spectrum was obtained only for the blue complex.[8] In Fig. 2 the NMR spectrum (in $CDCl_3$) of green $Lu(pc_2R^2{}_8)$ is compared with that of tetrapropoxyphthalocyanine ($H_2pcR^2{}_4$). The substituent methylene proton of $Lu(pc_2R^2{}_8)$ is shifted to a higher magnetic field, compared with that of $H_2pcR^2{}_4$, due to the paramagnetic properties, as seen in the ESR spectrum. The benzoproton diffused very much, and plausibly existed between +40 and +300 ppm; it was not, however, clearly distinguishable, due to baseline drifting. The most important information here is the lack of an N-H proton down to −160 ppm in the case of $Lu(pc_2R^2{}_8)$, although it is clearly seen in $H_2pcR^2{}_4$ at −6 ppm.

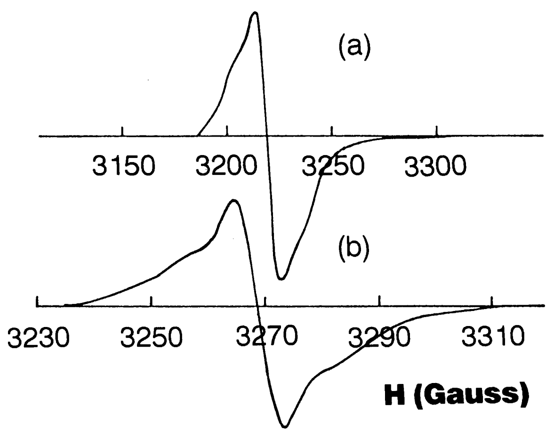


Fig. 1. ESR spectra of $Lu(pc_2R^2{}_8)$ at (a) room temperature and (b) 77K in toluene.

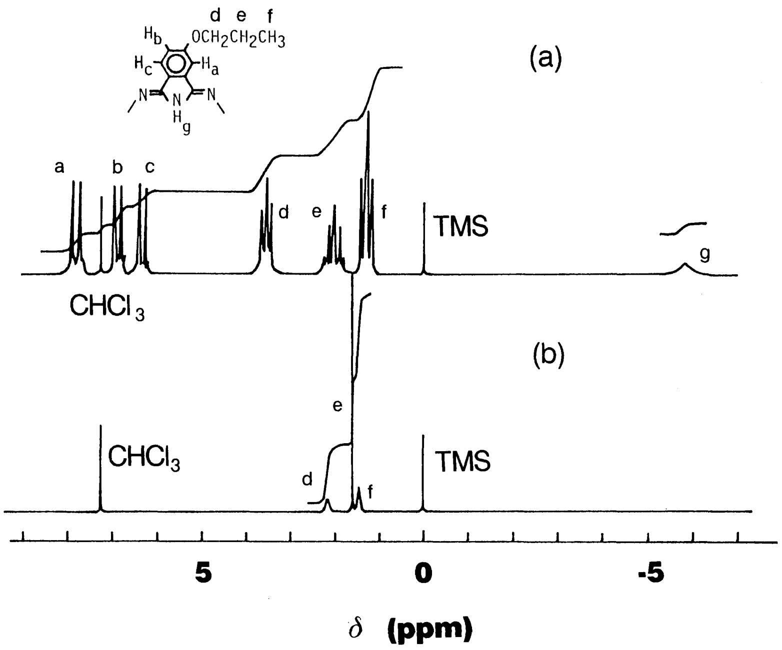


Fig. 2. NMR spectra of (a) $H_2(pcR^2_4)$ and (b) $Lu(pc_2R^2_8)$ in $CDCl_3$. Scanned between −160 and +360, but only −10 to +10 ppm region is shown.

From the NMR spectrum of the blue $Lu(pc)_2$ complex in DMSO-d_6, no N-H proton and 2 kinds of benzo-protons at 6—20 ppm were reported.[8] However, the labile N-H proton may disappear in such a strong proton-acceptor solvent, even if it exists. We also tried to observe the NMR spectrum of blue $Lu(pc_2R^2_8)$ in $CDCl_3$ and found 3 kinds of benzo-protons at 6—18 ppm, but no clear data could be obtained due to purification difficulties.

Electrochemical Properties. Figure 3 illustrates a set of cyclic voltammograms of $Lu(pc_2R_8)$ coated graphite electrodes in a pH 1 aqueous supporting electrolyte. There is one reduction wave near 0 volt (wave I) and another larger oxidation wave near +0.5 volt (wave II). The formal potential of wave I ($E^{O'}_I$) is apparently dependent on the pH with an almost 60 mV/pH slope, for instance 62 mV/pH in $Lu(pc_2R^1_8)$, as shown in Fig. 4. The $E^{O'}_I$ values are not affected by changing the concentration and the kind of anions in supporting electrolyte. The number of electrons involved in redox wave I (n_I) was found to be very close to unity from a comparison between the involved charge and the surface coverage of the complex. From this evidence, redox wave I is likely to be a $1e^-/1H^+$-consuming reaction. The other substituted $Lu(pc_2R_8)$ complexes gave similar results.

A negative potential scan beyond redox wave I turns the film color from the original green to blue. Since redox wave I exists very close to 0 volt, most of the organic or inorganic reductants such as DMF, ascorbic acid, $FeCl_2$, etc. can proceed the reduction of the original green complexes. From an electronic spectral study for $Lu(pc)_2$ or $Lu(pc_2R^1_8)$, the blue complexes were found to originate from a) preparation according to the literature, b) conversion from the green form by rechromatography on alumina eluted with DMF–methanol, and c) conversion from the green form by an electrochemical reduction, are coincident with each other. We thus can conclude that the green and blue complexes are the original and one-electron reduced species, respectively, as shown in Eq. 2. The structure of the blue complex is still controversial, whether the protonated base-type $Lu(Hpc_2R^1_8)$ or the salt type $H^+[Lu(pc_2R^1_8)]^-$. With changing the concentration of alkali metal

$$\underset{\text{(green)}}{\mathrm{Lu(pc_2R^1_8)^*}} \xleftrightarrow[-1e^-,\ -1H^+]{+1e^-,\ +1H^+} \underset{\text{(blue)}}{\mathrm{Lu(Hpc_2R^1_8)}}\ \{\text{or } \mathrm{H^+[Lu(pc_2R^1_8)]^-}\} \tag{2}$$

neutral salts or the kind of the cation in the supporting electrolyte *at neutral pH*, no shift of $E^{O'}_I$ is observed, while $E^{O'}_I$ is strongly dependent on the pH. This result suggests that the protonated base type is the better possibility. Other substituted lutetium complexes give similar electrochemistry at redox wave I. In the case of unsubstituted $Lu(pc)_2$, that more complicated phenomena, such as the $3e^-$-redox reaction, may occur at this potential was reported.[4] A successive $3e^-$-redox reaction in $Lu(pc)_2$ seemed to split into 2 separated redox processes in the case of substituted lutetium complexes, i.e., the $1e^-$-redox process at near 0 volt (wave I); the other reduction was shifted to a far negative potential due to

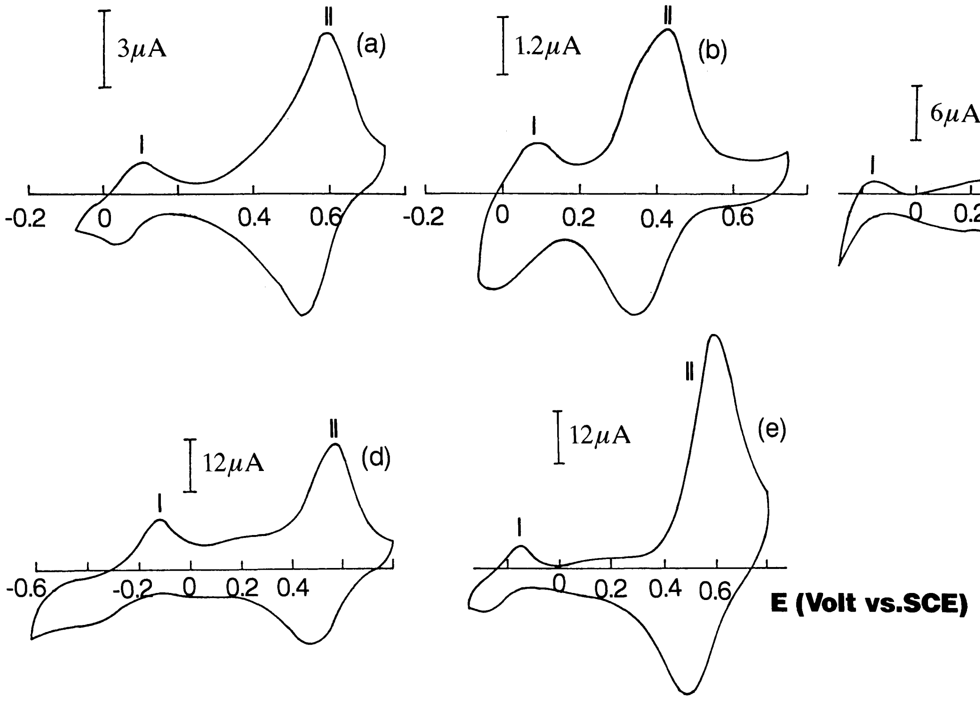


Fig. 3. Cyclic voltammograms of Lu(pc_2R_8) coated on graphite electrodes recorded at 100 mV s^{-1} in pH1 HCl-KCl (0.1+0.1 M). (a) Lu($pc_2R^1_8$), (b) Lu($pc_2R^2_8$), (c) Lu($pc_2R^3_8$), (d) mix-Lu(pc)$_2$, (e) un-Lu(pc)$_2$.

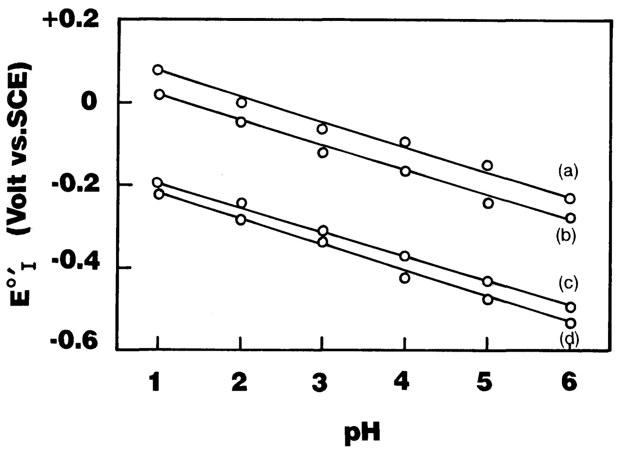


Fig. 4. pH dependence of $E^{\circ\prime}_{I}$. The alphabetical symbols are same as in Fig. 3.

the electron-donating properties of substituents at about −0.8 volt. Unfortunately, the second reduction wave is irreversible and overlaps with hydrogen evolution; it is thus difficult to present exact discussions.

The apparent formal potential of wave II ($E^{\circ\prime}_{II}$) is independent of the pH up to pH 4, beyond which the redox response becomes irreversible and some follow-up reaction occurs. Also, the reversibility and $E^{\circ\prime}_{II}$ values are very sensitive to the concentration and kind of major anion in the electrolyte solution. The chloride anion gave the best results,[11] with sharp peaks and a smaller peak splitting in the cyclic voltammograms. If its concentration is lower than 0.01 M, redox wave II becomes quasi-reversible with large peak splitting, or even becoming irreversible. If n_I is unity, the number of electrons involved in redox wave II is calculated to be 3 (i.e., between 2.5 and 3.6) for the case of Lu($pc_2R^1_8$). Thus, one can note that redox wave II is a $3e^-/Cl^-$-consuming reaction. A similar redox behavior is observed for other substituted lutetium complexes.

In electrochromic displays it is necessary to exhibit three fundamental colors by one substance; bis(phthalocyaninato)lutetium complexes are one of the best candidates in this meaning. As discussed later, the redox reactions through wave I and II are essential to exhibit three colors, as follows:

wave I ($1e^-/1H^+$) ⟷ Lu(pc_2R_8)* ⟷ wave II ($3e^-/Cl^-$)
(at near 0 Volt) (at near +0.5 Volt)
blue ⟷ green ⟷ yellow ⟷ red
(3)

The reduced blue-colored complex is stable, since redox wave I exists near 0 volt, and the total stability of the present electrochromic material is dominated by an oxidation reaction in which the color turns to red. Although the apparent formal potential of redox wave II ($E^{\circ\prime}_{II}$) of unsubstituted Lu(pc)$_2$ is about +0.6 volt,[4] completion of a color change to red usually requires an

Table 2. Characteristic Potentials of Bis(phthalocyaninato)lutetium Complexes (volt vs. SCE)

Complex	E_r	$E^{\circ\prime}_{\mathrm{I}}$	E_e	$E^{\circ\prime}_{\mathrm{II}}$	E_o
$Lu(pc)_2$	a)	b)	+0.02	+0.6	+0.8
$Lu(pc_2R^1{}_8)$	−0.08	+0.08	+0.21	+0.57	+1.0
$Lu(pc_2R^2{}_8)$	−0.08	+0.02	+0.18	+0.39	+0.70
$Lu(pc_2R^3{}_8)$	−0.25	−0.20	+0.02	+0.59	+0.75
mix-$Lu(pc)_2$	−0.35	−0.22	+0.05	+0.53	+0.75
un-$Lu(pc)_2$	−0.32	−0.21	+0.01	+0.54	+0.80

E_r: The reduction edge potential where blue color completely develops. $E^{\circ\prime}_{\mathrm{I}}$: The apparent formal potential of redox wave I. E_e: The potential where the coated electrodes are equilibrated before and after the potential scan (corresponding to open-circuit potential). $E^{\circ\prime}_{\mathrm{II}}$: The apparent formal potential of redox wave II. E_o: The oxidation edge potential where red(dish) color completely develops. a) Difficult to determine, ca. −0.3 Volt. b) Difficult to determine due to overlapping of next reduction wave.

oxidation potential of +0.8 volt, or even more positive, where many side reactions, such as $2Cl^-/Cl_2$ or H_2O/H_2O_2, occur in a pH 1 HCl–KCl supporting electrolyte. The evolution of such side products occuring at the electrode/film interface accelerates not only the falling-off of the complex film, but also the decomposition of $Lu(pc)_2$. Therefore, in order to elongate the lifetime of the bis(phthalocyaninato)lutetium complex, it is necessary to decrease the oxidation potential by the a chemical modification.

In Table 2 $E^{\circ\prime}_{\mathrm{II}}$ and E_o are summarized at which the color change to red completes. The $E^{\circ\prime}_{\mathrm{II}}$ values decrease in accordance with the strength of the electron-donating properties of the substituents, i.e., $R=H\approx R^1 \gg R^3 > R^2$. These results can be interpreted that $E^{\circ\prime}_{\mathrm{II}}$ is arbitrarily controllable between +0.8 and +0.5 or less by changing the kind and number of incorporation of alkoxyl substituents. The $E^{\circ\prime}_{\mathrm{II}}$ values of mix-$Lu(pc)_2$ and un-$Lu(pc)_2$ are not between those of [$Lu(pc)_2$, $Lu(pc_2R^1{}_8)$] and [$Lu(pc_2R^2{}_8)$, $Lu(pc_2R^3{}_8)$], but are very close to that of $Lu(pc_2R^2{}_8)$.

When films with a few μm to 0.5 μm tickness were prepared in order to observe the color change by naked eye, the electrochemically active sites in the coatings of $Lu(pc)_2$ or $Lu(pc_2R^1{}_8)$ were only 60—70% from that of a coulometric analysis. The amount of electrochemically inactive portions decreases in the thinner, but still 20—10% remains inactive at the thickness employed for the spectroscopic study. Because the solubility of $Lu(pc)_2$ is poor in chloroform, its coatings on an electrode surface are carried out from the DMF solution. Inhomogeneous coagulation of $Lu(pc)_2$ during the slow evaporation of the solvent is unavoidable. Although $Lu(pc_2R^1{}_8)$ is much more soluble in common organic solvents, it also forms coagulated, rather brittle films from the chloroform solution. From an observation using a differential interference contrast optical microscope, these films have been revealed to comprise many domes with ca. 10 μm dia. These domes seem to be the assemblies of microcrystals with different crystalline states, as many kinds of unidentified sharp peaks are seen in the X-ray diffraction patterns. Since counter-ion migration through the film is necessary in order to maintain electroneutrality during the redox reaction, only the thinner part of the film gives a quick electrochemical response, and most of thicker part becomes electrochemically inactive. In fact, there are rapid and slow stages in the charge-time response of the potential-step chronocoulometry across redox wave II. The rapid stage corresponding to the electrochemistry of the thinner part terminates within 0.5 s and is the majority (more than 70%) of the total charge. The remaining slow stage corresponding to the thicker part redox reaction takes more than 1 min for completion. The result obtained in such inhomogeneous films implies that, 1) not only is the sharp color change unexpected, 2) but also the applied potential and the flowing current may concentrate to the thinner area, thus causing side reactions or an electrostatic break-down of the film.

Other substituted complexes, being soluble in chloroform in milimolar or higher concentrations, from homogeneous and amorphous cast films. The electrochemically active units in these complex films are more than 95% at a film thickness of a few μm to sub-μm. They also give a rapid, one-stage chronocoulometric response which terminates within 0.3 s.

Electrochromism. The change of in the working electrode from graphite to ITO (indium-tin oxide Nesa glass), in order to observe the electrochromism *in situ*, does not affect $E^{\circ\prime}_{\mathrm{II}}$, the shape of cyclic voltammogram and the chronocoulometric response. Figure 5 illustrates the electrochromic behavior of $Lu(pc_2R_8)$, when the electrode potential is scanned to the positive side. The typical color changes of these complexes are, as reported earlier,[11] from green to blue/purple by a negative potential scan beyond wave I and from green to orange/red through yellow by a positive potential scan across wave II. Because the positive edge potential, E_o (see Table 2), of $Lu(pc)_2$ and $Lu(pc_2R^1{}_8)$ is higher than the potential where the oxidation of either water or Cl^- occurs, it is very important to decrease E_o by attaching the electron-donating group to the complex nuclei in order to minimize the decomposition of the complexes. Although the E_o values of $Lu(pc_2R^2{}_8)$ or $Lu(pc_2R^3{}_8)$ are satisfactorily low, their electrochromism does not reach to bright red, but stops at a brownish color upon oxidation, owing to a smaller growth of the 500 nm region. On the contrary, the mix-$Lu(pc)_2$ and un-$Lu(pc)_2$ possessing similar E_o values as $Lu(pc_2R^2{}_8)$, give better electrochromism; the magnitude of growth of the 500 nm region is sufficiently good to represent red color upon oxidation. Especially, the electrochromism of mix-$Lu(pc)_2$ is superior to other low-E_o complexes for observations with the naked eyes.

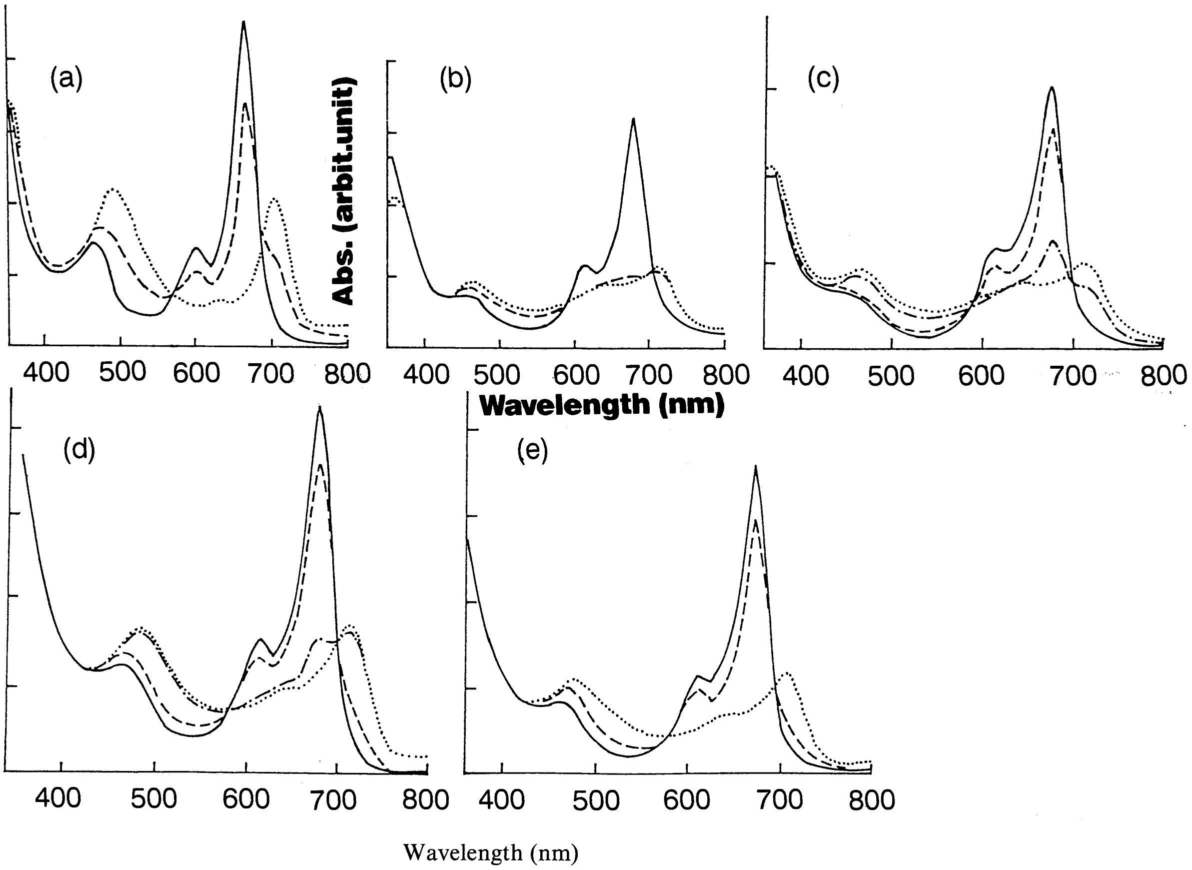


Fig. 5. Spectral change at given electrode potentials in pH1 HCl–KCl (0.1+0.1 M). The alphabetical symbols are same as in Fig. 3.

The reason of such a difference, i.e., why mix-Lu(pc)$_2$ is superior to other complexes, is plausibly related to the stereochemistry, such as the pc–Lu–pc distance, and will be reported elsewhere.

Stability upon Oxidation. After the coated electrodes were equilibrated at the potential, E_e (between $E^{O'}_{I}$ and $E^{O'}_{II}$, corresponding to the open-circuit potential, see Table 2), where the original green color is maintained, their electrochromism was investigated in situ by scanning the potential between E_o and E_r (the reduction edge potential is sufficiently good to develop a blue color, see Table 2). When the electrode potential is repetitively scanned for many hours at 100 mV s^{-1} between E_e and E_r, and again set to E_e, no decomposition or spectral change is found in all of the complexes, except for Lu(pc$_2$R$^2_8$), which seems to gradually dissolve into the aqueous phase upon reduction. On the other hand, if the potential is scanned either between E_r and E_o or E_e and E_o for a given period, and then set to E_e, the Q-band absorbances of complexes apparently decrease and new peaks appear with isosbestic points. In Fig. 6, the decay of the Q-band maximum, thus determined, is shown as a function of the period of the repetitive potential scan between E_r and E_o. Since a major portion of the Lu(pc)$_2$ film fell off from the ITO surface, such a repetitive scan was not carried out. A similar falling-off also occurs in the Lu(pc$_2$R$^1_8$) films. It is noted that the stability of the mix-Lu(pc)$_2$ complex is much improved due to the smaller E_o value.

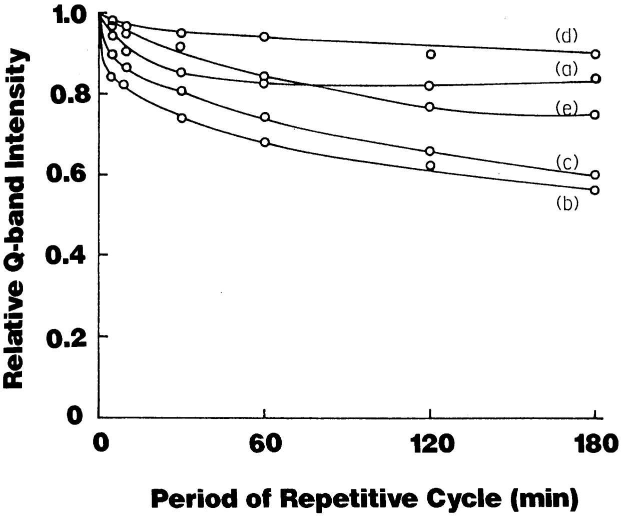


Fig. 6. Decay of Q-band absorption maxima at E_e after repetitive potential scan between E_r and E_o at 100 mV s^{-1}. The alphabetical symbols are same as in Fig. 3.

Degradation is mainly brought about by a cleavage of the Lu–pc bond, as the initial decomposition materials are assigned to be the corresponding metal-free phthalocyanine and mononuclear LuX(pcR_8) from the FD-mass spectroscopy and the shape of electronic spectra [here, X denotes an apical ligands]. It is therefore reasonable that Lu($pc_2R^3{}_8$) with bulky neopentyloxy substituents enforce the cleavage reaction rather rapidly, although it has a moderately small E_o value.

No significant difference between cast and spin-coat films has been found in the electrochemistry and electrochromic properties, except for $Lu(pc)_2$. However, we can observe outstanding improvements of film structure and, therefore, the electrochemical properties by using the Langmuir–Blodgett technique. This fact suggests that a coherent propagation of electrons and/or counter ions through the film layers is necessary for an improvement of the electrochemical properties in such coated electrodes, which will be reported elsewhere.

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