teractions. Very importantly, the derived qualitative conceptual scheme is not isolated from computational analysis. It can be tested, modified, and extended within the context of generalized valence bond theory as more accurate GVB calculations become available. For example, the full impact on bonding concepts of the strong orthogonality approximation (which is almost universally assumed) is yet to be thoroughly explored.

Summary. A generalization and extension of the classic valence bond ideas of Linus Pauling, first articulated nearly 60 years ago[1a] provide a natural framework to discuss hypervalent molecules. The valence bond method has been discredited as an approach to understanding hypervalent molecules because of too strict an adherance to the original concepts of atomic hybrid orbitals and resonance structures arising from various distributions of electrons among atomic orbitals. As seen here the use of GVB calculations (with SOPP restrictions) allows for a generalization of the original framework which achieves a consistent valence bond description. The extension to the full GVB method should retain much of what has been learned with GVB-SOPP; however, the orbitals will look less like atomic or hybrid orbitals and more like wave packets associated with one or more atomic cores. As the calculations for the full GVB method on hypervalent molecules do not exist yet, general arguments have been proferred which suggest the nature of the results. The resulting interpretational scheme has been used to discuss bonding in molecules for which calculations are not yet available.

Contrary to much previous discussion based on molecular orbital theory, generalized valence bond calculations exhibit *six bonds* to P and S atoms in the presence of electronegative ligands. One must conclude that this is strong evidence that such molecules violate the Lewis–Langmuir Octet rule.

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Electrochemistry and Electrochromic Behavior of Langmuir–Blodgett Films of Octakis-Substituted Rare-Earth Metal Diphthalocyanines

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Abstract: Heavy rare-earth metal diphthalocyanine complexes with alkoxy or alkyl substituents dissolved in common organic solvents formed stable Langmuir–Blodgett (L–B) films. The cyclic voltammogram of L–B films on indium–tin oxide Nesa glass electrodes showed smaller peak splitting and more symmetrical shape than those of corresponding solvent-cast films. The multicolor electrochromism was found both in L–B film and cast film systems in contact with an aqueous HCl–KCl electrolyte. For the completion of the color change, different potentials should be applied with different substituents. More than 1 V (versus SCE) was necesary for the *tert*-butyl-substituted complexes and less than 0.8 V for the propoxy-substituted ones. After about 7 h of repetitive cycling at 100 mV/s between 0 and 0.6$\sim$0.9 V, the relative Q-band intensity decreased by 2–5%, demonstrating good electrochemical stability.

Multicolor electrochromic devices have potential applications in man–machine interface and display systems. Heavy rare-earth metal diphthalocyanine complexes (Pc_2M, M = Lu, Yb, Er, Ho, Dy, Gd, etc.) exhibit green, red-brown, blue, and purple colors by changing the potential of Pc_2M-coated electrodes. Although many papers have been published in this area, most earlier reports[1–7] focused on the unsubstituted diphthalocyanine complexes.

Pc_2M is soluble in common organic solvents, such as chloroform and benzene, only in very low concentration, and therefore the preparation of homogeneous films on an electrode is difficult either by casting or the Langmuir–Blodgett (LB) technique. The resulting inhomogeneous film may exhibit rather slow response (of color change) to the potential change and also easier separation from the electrode surface. It seems to us that these may be the major reasons the lack of long-time reversibility and stability of Pc_2M films.

In addition, our previous work[8] showed that cast films of $R^2{}_8Pc_2M$ (where R^2 = *tert*-butyl, M = Er, Lu) on an indium–tin oxide glass exhibited better color change, but its redox wave II is too close to the chloride oxidation potential Cl^-/Cl. On the other hand, the second oxidation potential of $R^1{}_8Pc_2M$ (R^1 = propoxy) is far more negative than that of $R^2{}_8Pc_2M$, but its color change is not satisfactory.

The purpose of this report is 4-fold. First, to combine the better color change that appears in $R^2{}_8Pc_2M$ with the less positive oxidation potential possessed by $R^1{}_8Pc_2M$, new substituted diphthalocyanine complexes were prepared. Second, using the L–B technique, homogeneous films of these complexes were fabricated. Third, the electrochemical properties and electrochromic behavior in relation to the kinds of substitutents were examined. Lastly, the electrochemical stability under repetitive cycling was also investigated by measuring the relative Q-band intensity.

Experimental Section

Chemicals. 4-Nitrophthalonitrile with 96% purity was a donation from Toyo Ink Co. Ltd. Other chemicals were of reagent grade and used without further purification. Solvents were distilled twice and used immediately.

Octakis[propoxy(R^1)/*tert*-butyl(R^2)]diphthalocyanatoerbium/lutetium (R_8Pc_2M) was prepared using methods that have been described

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previously.[8] At least eight isomers were found by HPLC, but used without separation.

Complexes with different kinds of substituents incorporated randomly, *mix*-$R^1_4R^2_4Pc_2M$ were prepared by the reaction of equimolar mixtures of two different 4-substituted phthalonitriles (1 g of 4-propoxyphthalonitrile, 5.4 mmol; 0.99 g of 4-*tert*-butylphthalonitrile, 5.4 mmol) with lutetium acetate (0.47 g, 1.4 mmol) in an evacuated glass ampoule by steadily raising the temperature to 290 °C for 4 h. The crude product was milled, dissolved in chloroform and separated by column chromatography (silica gel, 100 mesh-up, $CHCl_3$). The first band contained a small amount of metal-free phthalocyanine, while the second main band with a green color is a mixture of diphthalocyanine and starting phthalonitrile. To eliminate phthalonitrile from diphthalocyanine, a precoated TLC plate (silica gel, 2-mm thickness) was used. Further purification by column chromatography ($CHCl_3$) gave 0.1 g of desired product in 4.6% yield. The product was also a mixture of many isomers, but no contamination by side products, such as *mix*-$R^1_3R^2_5Pc_2M$, *mix*-$R^1_5R^2_3Pc_2M$, or related compounds, was detected from the results of FD-mass spectroscopy; neither were such side products found in other elution bands.

Anal. Calcd for *mix*-$R^1_4R^2_4Pc_2Lu$ ($C_{92}H_{88}N_{16}O_4Lu$): C, 66.70; H, 5.35; N, 13.52. Found: C, 66.90; H, 5.47; N, 13.22. IR (KBr pellet, cm^{-1}) ν_{Pc-O} 1235–1220; UV [$CHCl_3$, λ_{max}, (log ϵ)] 673 (5.27), 608 (4.62), 465 (4.53), 350 (5.10), 325 (5.15), 286 (4.96).

Complexes with two different kinds of substituents incorporated asymmetrically (R^1_4 in one Pc ring, R^2_4 in another), *as*-$R^1_4R^2_4Pc_2M$, were synthesized as follows. A mixture of 0.43 g of 4-propoxyphthalonitrile (2.3 mmol), 0.0054 g of lithium metal, and 50 mL of freshly distilled amyl alcohol was stirred at 50 °C under an argon atmosphere until complete dissolution of Li, then refluxed for 2 h more. After addition of 0.2 g of $R^2_4PcLuOAc$, the green solution was further reacted for 15 h under reflux and finally evaporated to dryness. The purification, carried out as above for *mix*-$R^1_4R^2_4Pc_2Lu$, gave 0.1 g of desired product in 31.6% yield (calculated from the $R^2_4PcLuOAc$).

Anal. Calcd for *as*-$R^1_4R^2_4Pc_2Lu$ ($C_{92}H_{88}N_{16}O_4Lu$): C, 66.70; H, 5.35; N, 13.52. Found: C, 66.95; H, 5.65; N, 13.00. IR (KBr pellet, cm^{-1}) ν_{Pc-O} 1235–1220; ν_{CH_2-O} 1110; UV [$CHCl_3$, λ_{max} (log ϵ)] 674 (5.33), 607 (4.65), 465 (4.56), 350 (5.10), 325 (5.16), 288 (4.98).

Film Preparation. The L–B films were prepared with a home-made computer-controlled L–B apparatus. A given amount of R_8Pc_2M was dissolved in freshly distilled $CHCl_3$ (concentration ca. 0.15 mmol/L). The solutions of R_8Pc_2M were spread on the surface of twice-distilled water (ca. pH 6, 21 °C). After complete evaporation of the solvent, the surface pressure–area (*F*–*A*) isotherms were measured by compressing the mobile barrier at a speed of 20 mm/min. At a constant surface pressure of 20 dyn/cm, the Langmuir films were transferred to a substrate by the vertical dipping (VD) method with a substrate up–down speed of 5 mm/min. The substrates, either an indium–tin oxide (ITO) Nesa glass, quartz, or optical glass, were first washed with detergent, then with freshly distilled water, methanol, and chloroform in an ultrasonic bath for 30 min each, dried and immediately used.

In the case of cast films, they were prepared on an ITO electrode directly by a hand-casting method.

Measurements and Instruments. A Nicolet FT-IR 60SX spectrophotometer and a Hitachi 320 electronic spectrophotometer were used.

Electrochemical studies were carried out under bubbling argon in a conventional three-electrode cell unless otherwise stated. The working electrode was an ITO plate, on which the L–B film or cast film of R_8Pc_2M was deposited. A saturated calomel electrode was used as the reference electrode and a platinum sheet as the counter electrode. A Hokoto Denko potentiogalvanostat (HA-50), a NB-104 function generator, and a Model F-35 Riken Denshi X-Y recorder were used for the cyclic voltemmetry. The thickness of films was measured with a Sloan Dektak IIA surface profilometer.

Results and Discussion

Preparation. The preparation scheme of *mix*-$R^1_4R^2_4Pc_2Lu$ and *as*-$R^1_4R^2_4Pc_2Lu$ is shown in Figure 1. Although in the earlier literature,[9,10] activated alumina column chromatography was used for the purification of Pc_2M, this method was unsatisfactory in excluding impurities. Especially in the case of substituted diphthalocyanine complexes, the mononuclear side products, PcM–X, could not be eliminated because of their higher solubilities. The purification procedure described in the Experimental Section was necessary to obtain pure materials.

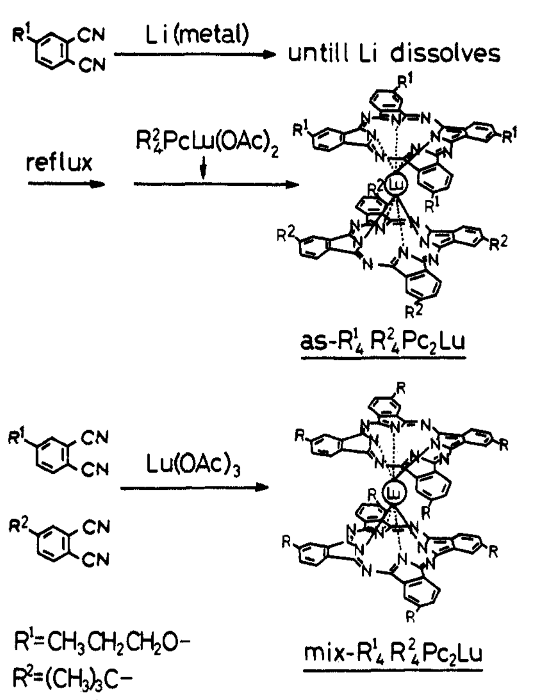

Figure 1. Synthesis of diphthalocyanine complexes with different kinds of substituents on the periphery of the benzo ring.

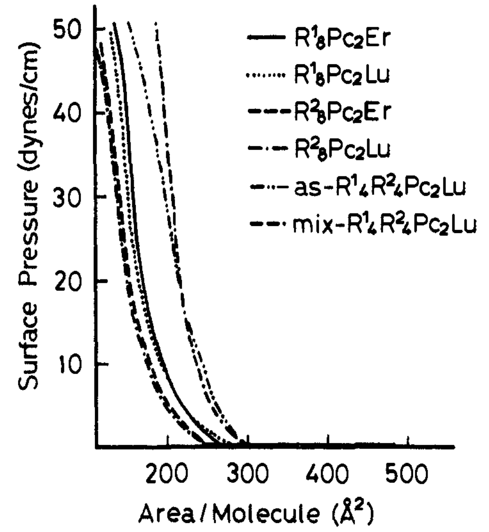

Figure 2. Surface pressure–area isotherms of R_8Pc_2M.

Table I. Limiting Molecular Areas (*A*) of R_8Pc_2M

compounds	*A* (Å^2)	compounds	*A* (Å^2)
$R^1_8Pc_2Er$	180	$R^2_8Pc_2Lu$	170
$R^1_8Pc_2Lu$	180	*as*-$R^1_4R^2_4Pc_2Lu$	250
$R^2_8Pc_2Er$	170	mix-$R^1_4R^2_4Pc_2Lu$	240

The high-temperature neat reaction usually yielded diphthalocyanine-rich products. In contrast to this, the cyclization of diiminoisoindolenine with one-quarter of the equivalent amount of rare-earth metal salt in refluxed solution gave only PcM–X compounds in high yield (typically 60%) without forming diphthalocyanine complexes. However, using PcM–X as the intermediate complex is very convenient not only for the preparation of asymmetrically substituted complexes (*as*-$R^1_4R^2_4Pc_2M$; see Figure 1) but also for the preparation of R_8Pc_2M because of the high total yield.

Langmuir–Blodgett Film Formation. The surface pressure–area (*F*–*A*) isotherms of R_8Pc_2M on pure water are shown in Figure

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2. Stable, reproducible Langmuir films of these complexes were formed with a high collapse pressure, up to 50 dyn/cm. The limiting molecular areas of R_8Pc_2M listed in Table I were determined by extrapolating the steeply rising part of the curves to zero surface pressure. There was no significant change in the *F–A* curves by adding inorganic base, acid, or neutral salts. The L–B films of R_8Pc_2M by the VD method were revealed to be Y-type films. The transfer ratio of the first 10 up–down strokes was smaller than unity (e.g., 0.9, especially in the case of down stroke), but reached unity after 10 strokes.

From Table I, two notable features follow. (a) The limiting molecular areas of R^1-substituted complexes are equal (180 Å^2) regardless of the central metal ions. The same phenomena are also observed in R^2-substituted complexes (170 Å), which indicate that the limiting molecular areas are independent of central metal ions and vary with the substituents. (b) The limiting molecular areas of *as*-$R^1_4R^2_4Pc_2Lu$ and *mix*-$R^1_4R^2_4Pc_2Lu$ are almost equal, but they are larger than those of other complexes. The limiting molecular area is useful in guessing a configuration of the phthalocyanine molecules at the air–water interface.[11] A full structure determination has not been carried our for R_8Pc_2M, and therefore it is difficult to be precise about the molecular dimensions. However, it is possible to make estimates. The diagonal distance across a molecule of *tert*-butyl-substituted monophthalocyanines is approximately 19.5 Å, as calculated by Hua et al.[11] An X-ray analysis of powder sample of unsubstituted lutetium diphthalocyanine showed three sharp reflections, at 2θ of 7.00°, 9.08°, and 10.48°, corresponding to spacing lengths of 12.63 Å, 9.74 Å, and 8.45 Å, respectively. Obviously one of these is the "thickness" of the diphthalocyanine molecules. If the molecules of $R^2_8Pc_2M$ are densely stacked in a face-to-face orientation and edge-on to the water surface, the average space per molecule would be approximately 164.8 Å^2 (19.5 Å × 8.45 Å), assuming that the "thickness" of the diphthalocyanine molecule is 8.45 Å. Since the calculated area (164.8 Å^2) per molecule is roughly consistent with the limiting molecular areas obtained by the experiment (170 Å^2), we suggest that the diphthalocyanine molecules are oriented face-to-face with the phthalocyanine plane perpendicular to the water surface. Moreover, that the limiting molecular areas of $R^1_8Pc_2M$ (180 Å) are larger than those of $R^2_8Pc_2M$ is also interpretable, because R^1 is longer than R^2. However the limiting molecular areas of *as*-$R^1_4R^2_4Pc_2Lu$ and *mix*-$R^1_4R^2_4Pc_2Lu$ are too large to be explained at present.

The L–B films of R_8Pc_2M were observed with a differential interference contrast optical microscope under polarized light at a magnification of 400. No grain formation larger than 0.01 μm was seen.

It is well-known that solubilities of unsubstituted metal monophthalocyanines in organic solvents are very poor, although a few unsubstituted metal diphthalocyanines can be fabricated into L–B films.[12] It is difficult to do so, and ultrasonic agitation must be used to ensure complete dissolution. During the deposition, a large amount of solution of these complexes had to be dropped on the aqueous subphase, owing to their comparatively low concentration. However, the substituents at the peripheral benzo ring make the phthalocyanine derivatives much easier to dissolve in common organic solvents. From this point of view, our substituted diphthalocyanine were found to be good L–B film-forming materials.

Cyclic Voltammetry. Figure 3 shows the cyclic voltammograms (CV) of L–B films (60 layers, full line) of R_8Pc_2M in pH 1 aqueous electrolyte, and for comparison cast films (thickness ca. 10^3 Å, dotted line) on ITO glass under same conditions. The results, formal potential, $E_p°$, separation of peak potential, ΔE_p, and difference of ΔE_p between L–B films and cast films, ΔE, are summarized in Table II. From these results four facts are ascertained. (a) In comparing the first cycle with cycles after repetitive scans at 100 mV/s for 5 min, with the L–B films, no significant change is observed, but for the cast films there is a slight change. (b) A smaller separation of peak potential and a more symmetrical shape of the oxidation–reduction peaks are seen for the L–B films as compared with those of corresponding cast films. (c) The L–B films exhibit a larger double layer capacitance. (d) For the completion of oxidation process, the applied potential for the R^2-substituted complexes (Figure 3, c and d) is over 1 V (versus SCE), while it is less than 0.8 V for the R^1-substituted complexes (Figure 3, a and b); in the case of *as*-$R^1_4R^2_4Pc_2Lu$ and *mix*-$R^1_4R^2_4Pc_2Lu$ (Figure 3, e and f), it is between those of the R^1- and R^2-substituted complexes.

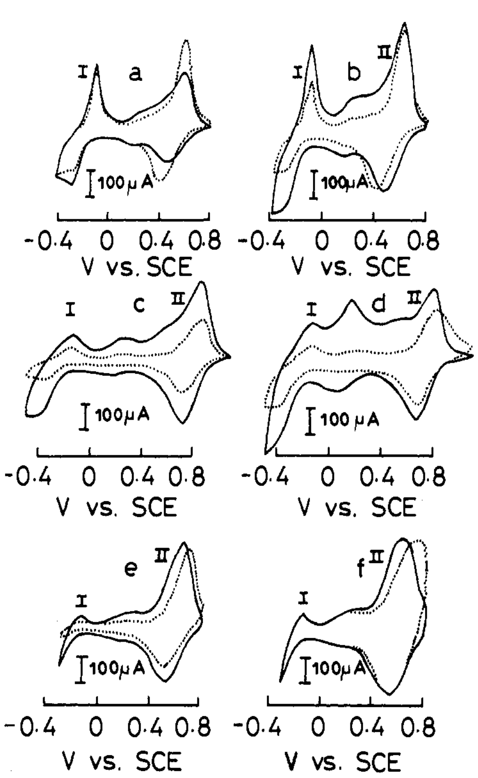

Figure 3. Cyclic voltammograms recorded on ITO glass electrode (ca. 3 cm^2) coated with R_8Pc_2M scanned at 100 mV/s in pH 1.0, 0.1 M HCl/0.1 M KCl electrolyte (full line, L–B films; dotted line, cast films): (a) M = Er, R = R^1; (b) M = Lu, R = R^1; (c) M = Er, R = R^2; (d) M = Lu, R = R^2; (e) M = Lu, R = *as*-$R^1_4R^2_4$; (f) M = Lu, R = *mix*-$R^1_4R^2_4$.

Table II. Comparison of Electrochemical Parameters of R_8Pc_2M between L–B Films and Cast Films

	$E_p°$, (V)		$\Delta E_p = E_{pa} - E_{pc}$ (V)		
samples	L–B films	cast films	L–B films	cast films	$\Delta E = \Delta E_p^{cast} - \Delta E_p^{L-B}$ (V)
$R^1_8Pc_2Er$	0.525	0.500	0.13	0.19	0.06
$R^1_8Pc_2Lu$	0.548	0.505	0.145	0.21	0.065
$R^2_8Pc_2Er$	0.78	0.785	0.13	0.16	0.03
$R^2_8Pc_2Lu$	0.735	0.77	0.12	0.15	0.03
as-$R^1_4R^2_4Pc_2Lu$	0.585	0.605	0.13	0.17	0.04
mix-$R^1_4R^2_4Pc_2Lu$	0.585	0.627	0.09	0.195	0.105

The mechanism of charge transport through redox films has been thoroughly discussed by Daum[13] and Collins.[3] Charge transprot across a redox film occurs by a flow of electrons, which migrate through the film by successive electron self-exchange between adjacent oxidized and reduced sites, and a flow of counter-ions, which enter or leave the film for charge compensation. These flows are accompanied by solvent flow and, eventually, film reorganization. Because of the regular layer structure of L–B films, they may have enough "space" for counter-ion

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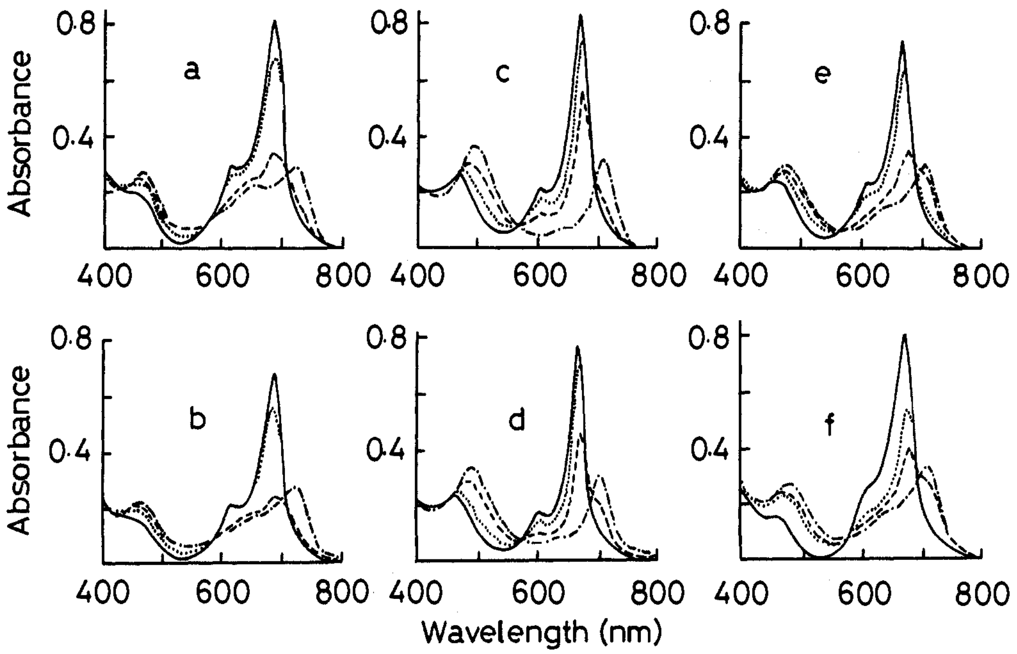

Figure 4. Absorption spectra of R_8Pc_2M in pH 1.0, 0.1 M HCl/0.1 M KCl electrolyte. (a) M = Er, R = R^1; (—) 0 V; (···) 0.9 V; (- - -) 1.1 V; (–·–) 1.3 V. (b) M = Lu, R = R^1; (—) 0 V; (···) 0.9 V; (- - -) 1.1 V; (–·–) 1.3 V. (c) M = Er, R = R^2; (—) 0 V; (···) 1 V; (- - -) 1.2 V; (–·–) 1.4 V. (d) M = Lu, R = R^2; (—) 0 V; (···) 1 V; (- - -) 1.2 V; (–·–) 1.4 V. (e) M = Lu, R = *as*-$R^1{}_4R^2{}_4$; (—) 0 V; (···) 0.9 V; (- - -) 1.1 V; (–·–) 1.3 V. (f) M = Lu, R = *mix*-$R^1{}_4R^2{}_4$; (—) 0 V; (···) 0.9 V; (- - -) 1.1 V; (–·–) 1.3 V.

migration and thus assist electron (or hole) propagation through the diphthalocyanine films. On the contrary, the inhomogeneous cast films consist of a few domains, which may cause rather slow response to the potential change. The reversibility and electrochemical stability of L–B film system is better than that of the cast film system. The R^1-substituted complexes have smaller oxidation potentials due to the electron-donating properties of alkoxy groups.

A linear dependence of the anodic peak current of peak II on the scan rate, ν, for a L–B film could be observed until the scan rate reached 0.3 V/s. The same relationship held for the cathodic peak, which indicates that the redox reaction is diffusion limited.

Electrochromism. The electrochromic behavior of either the L–B films or the cast films of R_8Pc_2M was determined with a two-electrode cell. The working electrode was ITO glass, and the counter electrode was an ITO plate. The gap between the two electrodes, 1 mm in width, contained an aqueous electrolyte (pH 1.0; 0.1 M HCl–0.1 M KCl).

Figure 4 shows the electronic spectra of L–B films of R_8Pc_2M recorded in situ at a series of controlled potentials. The electronic spectrum changes of the L–B films were similar to those of cast films.[8] When a positive voltage was applied to the film through the ITO electrode (oxidation), the Q-band of R_8Pc_2M became smaller and shifted to longer wavelengths with an increase of applied potential. At same time, the band at 460–490 nm became larger, indicating a color change. Note that the increment of the 470–490-nm band of R^2 complexes (Figure 4, c and d) is larger than that of R^1 complexes (Figure 4, a and b), which is the major reason why the R^2 complexes show a better color change than do the R^1 complexes. Although the band at 480–490 nm of *as*-$R^1{}_4R^2{}_4Pc_2Lu$ and *mix*-$R^1{}_4R^2{}_4Pc_2Lu$ is not as high as that of the R^2 complexes, they still demonstrated a better color change.

The color changes were also confirmed by taking photographs at given potentials. Four distinct colors, green, brown-red, blue and purple, were seen.

Electrochemical Stability. The electrochemical stability of the L–B films (60 layers) was investigated by measuring the electronic spectra recorded in situ after a given period of repetitive cyclic scanning at 100 mV/s between 0 V and 0.6~0.9 V. The relative Q-band intensity was calculated by taking the initial intensity of the Q band as unity.

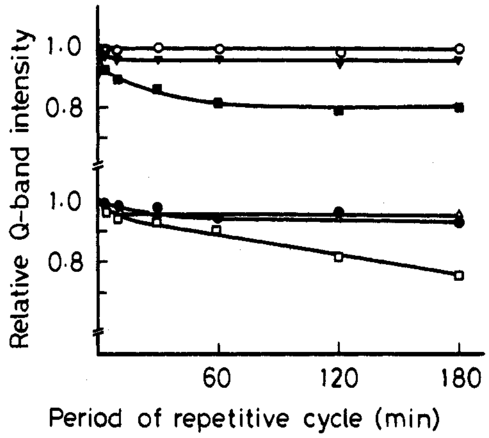

Figure 5. Decay of Q-band absorption maxima of R_8Pc_2M at 0 V on repetitive potential cycling between 0 and +0.8 V at 100 mV/s: (■) M = Er, R = R^1; (●) M = Lu, R = R^1; (△) M = Er, R = R^2; (▼) M = Lu, R = R^2; (□) M = Lu, R = *as*-$R^1{}_4R^2{}_4$; (○) M = Lu, R = *mix*-$R^1{}_4R^2{}_4$.

Collins and Schffrin studied the stability of evaporated films of unsubstituted diphthalocyanines.[3] When the Pc_2Lu film electrodes were cycled between the different color states, the color intensity decreased gradually until no color change was seen. For the green-red transition, this occurred after 10^4–10^5 reversals, whereas for the green-blue transition, the color loss was more rapid and the film tended to fracture. In our L–B films with the substituted diphthalocyanine system, after about 7 h of repetitive scans (ca. 1.5 × 10^3 cycles), the relative Q-band intensity decreased by 2–24% (Figure 5). The best one was the *mix*-$R^1{}_4R^2{}_4Pc_2Lu$ complex (2%), which exhibited excellent electrochemical stability.

Conclusions

Substituted rare-earth metal diphthalocyanine complexes with higher solublity in common organic solvents were found to be good L–B materials. Their Lanmguir films were densely stacked in a face-to-face orientation and edge-on to the water surface. The electrochemical reversibility and stability of the L–B film system was better than that of the corresponding cast film system. Multicolor electrochromism, i.e., green, brown-red, blue, and purple, were observed both in L–B and cast film system in contact with an aqueous electrolyte. The *mix*-$R^1{}_4R^2{}_4Pc_2Lu$ complex exhibited a smaller formal potential, a better color change, and the best electrochemical stability.