Substituted bis(phthalocyanines): electrochemical properties and probe beam deflection (mirage) studies

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Lutetium bis(phthalocyanine) has been shown to form intrinsic molecular semiconductors under the form of thin films. Unsubstituted and substituted lutetium complexes have been studied by electrochemistry to measure the number of charges exchanged during the redox processes together with the probe beam deflection (mirage) technique in order to determine the nature and the direction of the flux of ions coming in or out of the molecular thin film layer when oxidation or reduction occurs.

Introduction

Lutetium bis(phthalocyanine) (Pc_2Lu) is almost unique in the realm of molecular compounds since it possesses a π-conjugated macrocycle-centered radical as demonstrated by electron spin resonance studies.[1] The lutetium derivative can be sublimed under vacuum, treated with acidic media or exposed to air without degradation.

The synthesis and characterization of Pc_2Lu (and other rare earth complexes) were described in the early seventies by Russian researchers.[2–4] They deposited Pc_2Lu layers on semi-transparent conductive electrodes and noted that the initially green layer turns to red (or brownish red) by oxidation and to blue by reduction. These studies were, in most cases, carried out in aqueous neutral solution (0.1 M KCl). Further studies[5] in DMF demonstrated that it was possible to form electrochemically several redox products differing in their visible absorption spectra: violet, blue, green, yellow-red.

Nicholson *et al.* started studies in the seventies in order to elucidate the mechanisms involved in the electrochromic processes.[6] They confirmed that the conductivity of rare earth phthalocyanine materials is surprisingly high for molecular materials as previously reported by other authors for compressed pellets of Pc_2Nd[7] (formulated wrongly as Pc_2NdH: $\sigma = 4.3 \times 10^{-1}\ \Omega^{-1}\ cm^{-1}$).

However, at that time, it was almost impossible to make the distinction between (fortuitously or not) doped insulators and intrinsic molecular semiconductors. A clearcut separation has been proposed[8] and a detailed description of wide band (PcLi) and narrow band (Pc_2Lu) intrinsic molecular semiconductors has been given.[9] However, a few years before it was noted that "the lanthanide phthalocyanines show a high electrical conductivity probably related to the radical nature of some forms of $Lu(PC)_2$".[10]

Most of the studies concerning Pc_2Lu have been devoted to characterising its electrochromic properties and to understanding the chemical mechanisms involved during the redox processes. Two types of information can be obtained: (i) the measurement of the current involved in the redox process allows one to calculate the percentage of Pc_2Lu (or related molecular units) oxidized or reduced within the thin film. (ii) The probe beam deflection arising from a refractive index gradient (mirage) technique[11–13] permits one to know, at least in some cases, the direction of the flux of the cation or anion coming in or out the Pc_2Lu thin film.

Previous experiments are strongly influenced by whether or not the electrolyte can enter the Pc_2Lu layer prior to the redox processes (Fig. 1). In Fig. 1A, no electrolyte (M^+X^-) is present in the Pc_2Lu layer before oxidation. Electroneutrality is ensured by the entrance of an anion. In Fig. 1B, the oxidation to Pc_2Lu^+ is accompanied by the departure of the cation M^+ necessitating that some electrolyte was present prior to the oxidation process. In Fig. 1C, the two preceding mechanisms are both effective making it difficult to interpret the probe beam deflection (mirage) experiments.

In many cases, it was found that, during the voltammetric studies, the first scan differs from subsequent ones (see for instance ref. 10, 14) (Fig. 2). The first oxidation of the Pc_2Lu layer changes, in some way, the chemical nature of the molecular material. The incorporation of electrolyte and/or water within the thin film can be, for instance, envisaged.

The green/red transition could be cycled 10^4–10^5 times in neutral aqueous media containing NaF, KCl, LiCl, KBr.

The stability of the electrochromic devices based on Pc_2Ln (Ln = Lu, Er, Gd, Yb) was significantly increased in the presence of ethylene glycol instead of water.[15] The main degradation process seems to involve the attack of the hydroxide ion

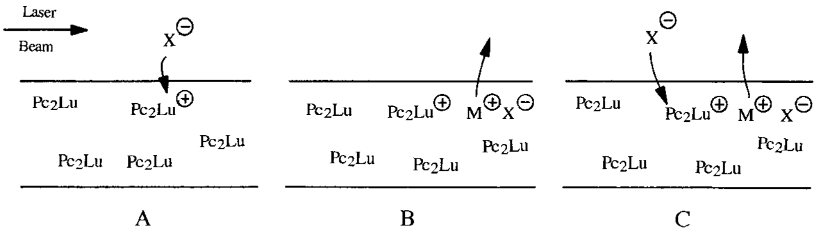


Fig. 1 Three of the possible ion exchanges which can arise when a Pc_2Lu layer is oxidized at the interface with an aqueous solution containing an electrolyte.

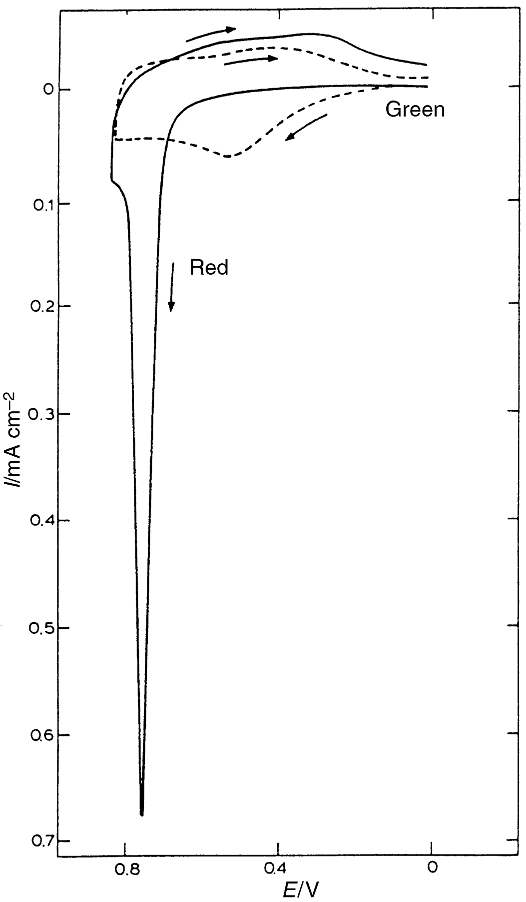


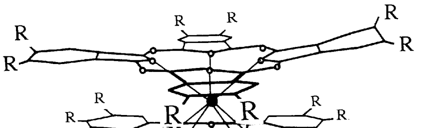
Fig. 2 Cyclic voltammetry of a virgin (full line) or cycled (dotted line) film of Pc_2Lu on platinum. Electrolyte 0.03 M KCl (potential *vs.* SCE) (after ref. 10). Green: Pc_2Lu (neutral); red: Pc_2Lu^+.

since better stabilities are obtained in acidic media. But, in this case, a disproportionation effect takes place:[16]

$$2\ Pc_2Lu + H^+ \leftrightharpoons Pc_2LuH + Pc_2Lu^+$$

In most cases, the green/blue transition corresponding to the reduction to Pc_2Lu^- can only be cycled a limited number of times.

Various compounds bearing side groups on the bis(macrocyclic) moieties have been synthesized and studied with *tert*-butyl or propoxy groups,[17–19] butoxy groups[20] and 4-phenyl moieties.[21] The first synthesis of bis[octa(alkyloxymethyl)phthalocyanine]lutetium complexes $[(H_{2n+1}C_nOCH_2)_8Pc]_2Lu$ (**2** in Fig. 3) was carried out in 1985[22] followed very shortly by electrochemical studies.[23,24] The compounds $[(H_{2n+1}C_nOCH_2)_8Pc]_2Lu$ ($n = 8$, 12, 18) demonstrated liquid crystalline properties both in the neutral and oxidized forms.[22] The electrical properties of the same derivatives were determined.[25] The synthesis of $[(H_{25}C_{12}O)_8Pc]_2Lu$ **3** and its oxidized form was described and their mesomorphic, electrical and magnetic properties determined.[26] The synthesis and electrochemical characterization of a crown-ether substituted phthalocyanine derivative, $[(15\text{-crown-}5)_4Pc]_2Lu$ **4**, were carried out in the following years.[27]



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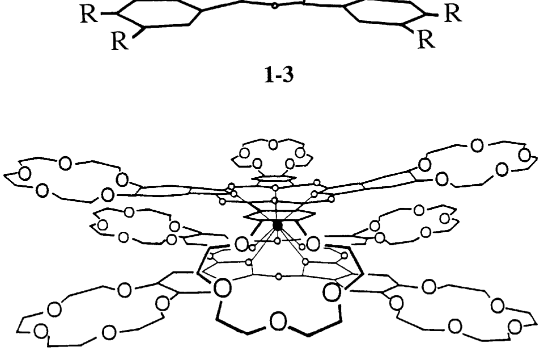

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Fig. 3 Lutetium bis(phthalocyanine) derivatives synthesized. **1** R = H (Pc_2Lu); **2** R = $CH_2OC_nH_{2n+1}$ (ref. 22) **a** $n = 8$, **b** $n = 12$, **c** $n = 18$; **3** R = OC_nH_{2n+1} (ref. 26); **4** $[(15\text{-crown-}5)_4Pc]_2Lu$ (ref. 27).

In the next sections, the comparative behavior of the bis(phthalocyanine) derivatives **1**–**4** (s-Pc_2Lu , s = substituted) will be examined.

Results and discussion

Oxidation of s-Pc_2Lu: green/red transition: $E^1_{G/R}$ (neutral media)

(a) Unsubstituted Pc_2Lu. The use of 15 different electrolytes demonstrates that the oxidation peak $E^1_{G/R}$ is independent of the nature of the cation when Cl^- anion is constantly used, but varies over about 0.2 V by varying the anion[28] (F^-, AcO^-, Cl^-, $NO_3{}^-$, I^-, $ClO_4{}^-$, $SO_4{}^{2-}$). The $E^1_{G/R}$ peak corresponds approximately to a one-electron process for the first scan. The number of electrons (n) exchanged per molecule of Pc_2Lu at this transition decreases at the second scan ($n \approx 0.4$–0.7) and then remains approximately constant (the thickness of the Pc_2Lu thin film is around 700 Å). This probably means that, at the first scan, the incorporation of the counter ion perturbs the Pc_2Lu thin film and that further cycling only involves part of the total Pc_2Lu molecular units.

The reverse transition (red to green) behaves differently: the redox potential does not depend on the nature of the cation and depends only slightly on the nature of the anion. Probe beam deflection (mirage) measurements showed an anion incorporation[13] at the molecular material/aqueous solution interface (KCl; neutral conditions).

(b) $[(H_{2n+1}C_nOCH_2)_8Pc]_2Lu$. Alkoxymethyl substituted and unsubstituted lutetium derivatives have unchanged redox properties in CH_2Cl_2 solution:[23] the $E_{G/R}$ is shifted by less than 0.07 V. The same thing was found for the reduction process ($\Delta V < 0.04$ V).

For a thin film of $[(H_{17}C_8OCH_2)_8Pc]_2Lu$, the electrochemical response is the same for the first and subsequent scans.[24] Ion diffusion within the thin film prior to oxidation of the molecular material is therefore probable. The nature of the anion intervenes, as previously, on the forward anodic peak (oxidation) (Table 1). The amount of oxidized s-Pc_2Lu, given by Q_{obs}/Q_{theo}, is around 0.5 (0.5 M $LiClO_4$) and does not depend on the thickness of the molecular material layer in the range 2000–4000 Å.[24]

Table 1 Oxidation potential (green/red) of $[(H_{17}C_8OCH_2)_8Pc]_2Lu$ on a gold–alumina electrode (*E vs.* SCE). Electrolyte (neutral): 0.5 M; film thickness 3000 Å; scan rate: 100 mV s^{-1} (ref. 24)

$ClO_4{}^-$	E_{ox}/mV	Na^+	E_{ox}/mV
Li^+	460	$ClO_4{}^-$	480
Na^+	480	Cl^- >	700
K^+	470	$BF_4{}^-$	490
$NH_4{}^+$	480	$NO_3{}^-$	680
$N(CH_3)_4{}^+$	470		

$[(H_{17}C_8OCH_2)_8Pc]_2Lu$ is far more stable under electrochemical cycling than its unsubstituted counterpart and in $NaClO_4$ (0.5 M) 10^6 cycles have been obtained with only a 5% decrease in the yield. $[(H_{17}C_8OCH_2)_8Pc]_2Lu$ has thus been cycled continuously for 94 days without apparent degradation.

When the length of the paraffinic side chain is increased ($n = 8$, 12, 18) in $LiClO_4$ (0.5 M) the oxidation $s\text{-}Pc_2Lu \rightarrow s\text{-}Pc_2Lu^+$ and the reverse reaction are both more difficult.

In the case of $[(H_{25}C_{12}OCH_2)_8Pc]_2Lu$ on a gold–alumina electrode (0.5 M $LiClO_4$), the number of cycles has been varied from one to 2×10^5 with a concomitant increase in the electrochemical signal (Fig. 4). This phenomenon is probably due to a slow diffusion of electrolyte and/or water molecules into the thin films during successive electrochemical cycles. Other causes are also possible such as a change in the morphology of the thin films.

(c) $[(15\text{-crown-}5)_4Pc]_2Lu$. As in the previous case, the crown-ether derivative does not show any anomaly for the first scan compared to the subsequent ones. The shape of the green/red peaks however depends strongly on the nature of the electrolyte (Fig. 5). Well shaped cyclovoltammetric curves are obtained for ClO_4^-, more perturbed ones are observed for Cl^- and SO_4^{2-}.[27] The effect of the cation is also important: Na^+ and K^+ yield similar results whereas Rb^+ and Cs^+ do not allow the easy oxidation of the $s\text{-}Pc_2Lu$ thin film. This demonstrates that both ions are incorporated within the molecular material thin film. It seems that the influence of Li^+ is mainly due to kinetic factors.

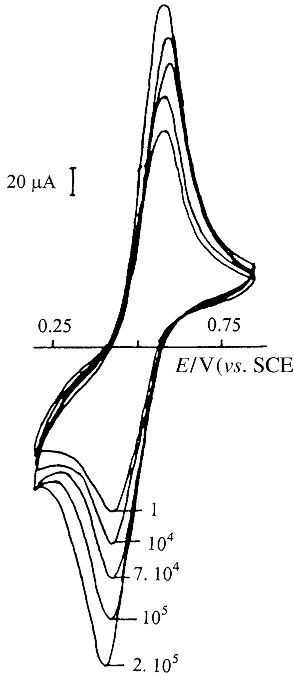

Fig. 4 Voltammogram of $[(H_{25}C_{12}OCH_2)_8Pc]_2Lu$ on a gold–alumina electrode (0.5 M $LiClO_4$); the scan is limited to the red/green process, (scan rate 100 mV s^{-1}; *E vs.* SCE).

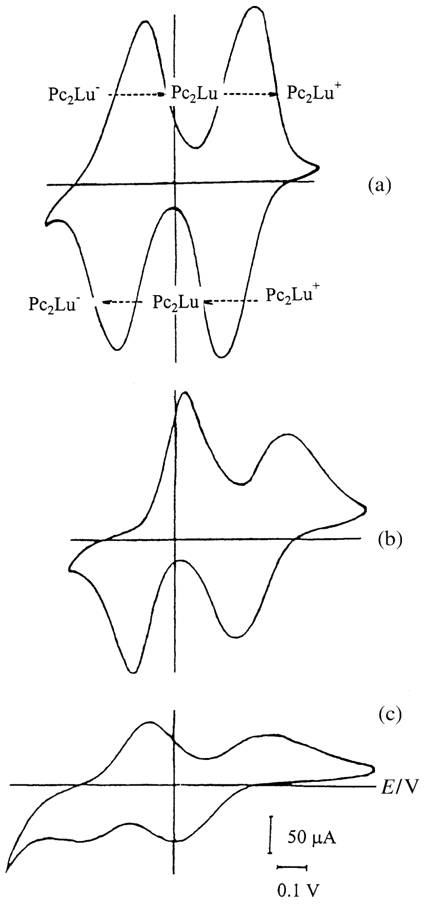

Fig. 5 Cyclic voltammetry of $[(15\text{-crown-}5)_4Pc]_2Lu$ on a SnO_2 electrode with a neutral solution of (a) saturated $KClO_4$ or 1 M $NaClO_4$ or 1 M KCl; (b) saturated Na_2SO_4 or K_2SO_4 or 1 M NaCl; (c) 1 M $LiClO_4$ (scan rate: 20 mV s^{-1}; *E vs.* SCE).

Mirage effect studies have been carried out in the presence of neutral KCl aqueous solutions. Contrary to what is observed for unsubstituted Pc_2Lu,[13] the laser beam is deflected towards the electrode during the forward scan ($Pc_2Lu \rightarrow Pc_2Lu^+$) indicating a more concentrated solution near the interface between the electrolyte and the molecular material. During the backward scan, the laser beam is deflected in the opposite direction. Since this effect arises at the very first scan and since it is constant whichever redox cycle follows, one can postulate the incorporation of electrolyte into the molecular film prior to the redox experiments.

Following a previously reported procedure,[29–31] it has been possible to determine the nature of the ions exchanged at the analyte/molecular material interface by measuring the ratio θ/i (θ = laser beam deflection angle; i = number of charges per second and per cm^2, or current density, electrochemically exchanged). The experimental results are gathered in Table 2. The θ/i ratio used as reference was determined from studies on Prussian blue.[29,30] Two mechanisms[31] may be postulated to rationalize the results shown in Table 2.

Prior to the redox processes, water molecules can occupy

Table 2 Experimental (scan rate 40 mV s^{-1}) and θ/i values in rad cm A^{-1} for different electrolytes. The sign of the ion mainly exchanged is given in parentheses

Electrolyte (1 M)	Medium	θ/i (green/red)	θ/i (reference)
LiCl	Neutral	<0.2 (+)	2–3[a]
NaCl	Neutral	0.55 (+)	2–3[a]
KCl	Neutral	0.65 (+)	2–3[a] and 1.8[b]
RbCl	Neutral	0.50 (+)	0.7[b]
KCl (Tris)	pH = 9.9	0.25 (+)	—

[a] According to ref. 29, 30 (scan rate < 20 mV s^{-1}). [b] Measured under the same conditions as previous ones, but at 40 mV s^{-1}.

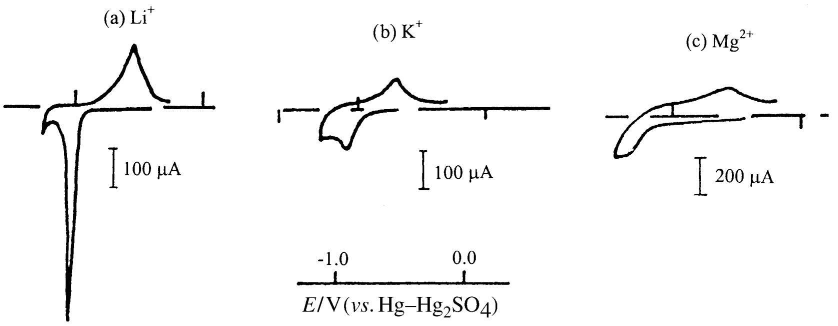

Fig. 6 Electrochemical behaviour (first scan) of the green/blue transition (reduction) (a) LiCl; (b) KCl; (c) $MgCl_2$ (0.5 M; neutral).

vacant sites within the molecular material layer. Oxidation of $[(15\text{-crown-}5)_4Pc]_2Lu$ to the corresponding cation could lead to the departure of H^+ from the thin film. This is in agreement with the known small θ/i ratios[29,30] associated with H^+. However, a comparable behavior is obtained in basic media.

The second process which can be envisaged involves the concomitant incorporation of an anion within the molecular layer (for instance Cl^-) and the departure of a cation. A double exchange of this type has been reported[32] for the couple $LiClO_4/WO_3$.

Reduction of s-Pc_2Lu: green/blue transition: $E^1_{G/B}$ (neutral media)

(a) Unsubstituted Pc_2Lu. Unsubstituted Pc_2Lu in dichloromethane solution affords three reversible monoelectronic processes:[33]

$$\mathrm{Pc_2Lu} \underset{-0.45}{\leftrightarrows} \mathrm{Pc_2Lu^-} \underset{-1.54}{\leftrightarrows} \mathrm{PC_2Lu^{2-}} \underset{-1.92}{\leftrightarrows} \mathrm{PC_2Lu^{3-}}$$

green *blue* *dark blue* *violet*

(*vs.* ferrocenium–ferrocene)

In the case of thin films, the first reduction process has been mainly studied.

It has been noticed (see for instance ref. 10) that in neutral aqueous media containing salts such as NaF, KCl, LiCl, *etc.* the green/blue transition leads to faster degradation than the one corresponding to the oxidation process.

For the first scan[28] the electrochemical behaviour is strongly influenced by the nature of the cation but only slightly by the nature of the anion, if at all (Fig. 6).

The presence of a strong cation complexing agent such as cryptand 222 in the solution prevents any electrochemical reduction process whereas the oxidation part remains unchanged.[28]

However, the cation no longer influences the reduction potential during the second transition from the green form to the blue one indicating a modification of the chemical composition of the molecular material layer during the first scan, probably the incorporation of electrolyte and/or water molecules.

Subsequent mirage effect studies[13] have shown that K^+ enters the molecular material layer during the reduction process.

(b) $[(H_{2n+1}C_nOCH_2)_8Pc]_2Lu$. The reduction of alkoxymethyl substituted lutetium bis(phthalocyanine) derivatives have also been studied. It has been found that the reduction process depends on the length of the side chains (Fig. 7). When the number of methylene groups in the side chains is increased, the reduction process seems more difficult.

(c) $[(15\text{-crown-}5)_4Pc]_2Lu$. Thin films of $[(15\text{-crown-}5)_4Pc]_2Lu$ afford in neutral aqueous media exceptionally well behaved electrochemical curves (see Fig. 5). The oxidation and reduction waves are both perfectly reversible. The stability of the thin film depends on the nature of the electrolyte: $KClO_4$, $NaClO_4$ and KCl yield stable redox systems whereas lithium salts decrease the stability for both oxidation and reduction cycling.[27]

Mirage effect experiments have been carried out to elucidate the nature of the ions involved in the process (Fig. 8). The mirage effect experiments indicate that cations are incorporated within the layer during reduction and that they are released during the backward reaction. The measured θ/i values roughly correspond to the exchange of one cation (Table 3). Similar θ/i ratios were measured for the first scan as well as for the others; the process can then simply be written as:

$$[(15\text{-crown-}5)_4Pc]_2Lu + e^- + M^+ \rightarrow [(15\text{-crown-}5)_4Pc]_2Lu^-, M^+$$

No significant difference has been noticed with $M^+ = Li^+$, Na^+, K^+, Rb^+.

In neutral aqueous solution, no degradation of the film could be noticed under cycling but no quantitative estimate has been made.

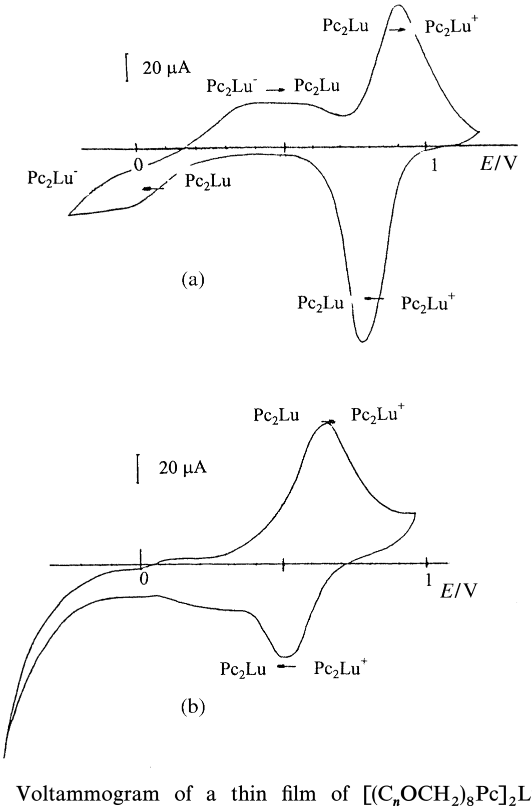

Fig. 7 Voltammogram of a thin film of $[(C_nOCH_2)_8Pc]_2Lu$ (a) $n = 8$; (b) $n = 12$ on gold deposited on glass electrodes (neutral 0.5 M $LiClO_4$; scan rate: 20 mV s^{-1}), *E vs.* SCE.

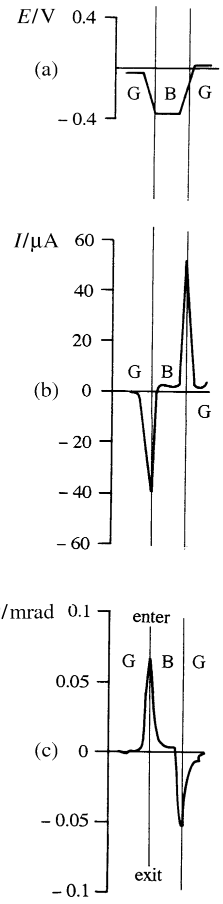

Fig. 8 Electrochemical measurements and mirage effect on thin films (300 Å) of $[(15\text{-crown-}5)_4Pc]_2Lu$ (electrolyte: neutral 1 M KCl). (a) Potential applied. (b) Corresponding current. (c) Mirage deflection angle θ, only the green/blue transition is shown as indicated by the letters G and B.

Transitions in acidic media

It has been seen that unsubstituted lutetium bis(phthalocyanine) cannot lead to many redox cycling processes in neutral media. The electrochemical stability is better in acidic media;[33] under such conditions 10^6 cycles may be attained with switching times of the order of a few milliseconds. Aqueous acidic solutions may protonate the reduced form of Pc_2Lu and then induce a disproportionation reaction. The electrochemical reaction is then:

$$Pc_2LuH \xrightarrow{-2e^-} Pc_2Lu^+ + H^+$$

We will study the $[(15\text{-crown-}5)_4Pc]_2Lu$ derivative as a protypical example:

$$2\ \text{s-}Pc_2Lu + H^+\ X^- \rightarrow \text{s-}Pc_2LuH + \text{s-}Pc_2Lu^+\ X^-$$

By varying the pH, the domains of stability of the different species can be determined (Fig. 9). When the pH is lower than approximately 3.5, s-Pc_2Lu is completely transformed into the protonated form and the conventional equilibria can only be found at pH > 4. The pK_A value of s-Pc_2Lu is around 3.8.

Table 3 Experimental θ/i values (rad cm A^{-1}) for different electrolytes (scan rate: 40 mV s^{-1}). The reference θ/i values are given in Table 2

Electrolyte	Medium	θ/i (green/blue)
LiCl	Neutral	1.10 (+)
NaCl	Neutral	1.20 (+)
KCl	Neutral	1.40 (+)
RbCl	Neutral	1.00 (+)
KCl (Tris)	pH = 9.9	0.9 (+)

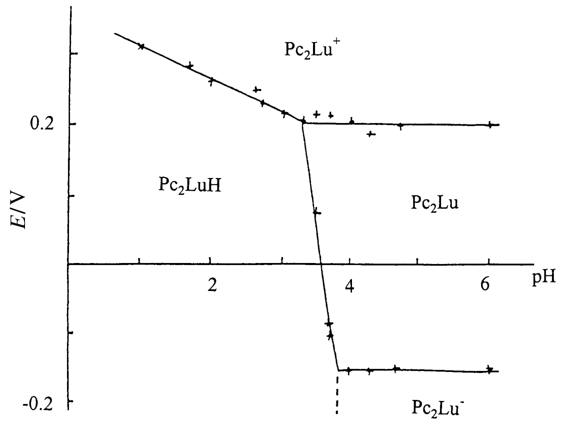

Fig. 9 E *vs.* pH diagram of $[(15\text{-crown-}5)_4Pc]_2Lu$ film in contact with a saturated $KClO_4$ with $HClO_4$ solution (E *vs.* SCE) (after ref. 27, 34).

Disproportionation can be easily demonstrated in CH_2Cl_2 in the presence of trifluoroacetic acid by measuring the UV-visible absorption spectra.

Conclusions

During the oxidation process (green/red transition), different results are obtained depending on the nature of the substituents on the lutetium bis(phthalocyanine) subunit.

Pc_2Lu: the first scan is different from the subsequent ones; it probably allows the incorporation of electrolyte within the molecular layer. For further cyclings, the green/red transition is independent of the cation but varies with the anion. 10^4 to 10^5 cycles are possible in neutral media (NaF, KCl, *etc.*).

$[(H_{2n+1}C_nOCH_2)_8Pc]_2Lu$: the electrochemical response is the same for the first scan as for the others. The oxidation peak is influenced by the nature of the anion as previously. An increase in the chain length ($n = 8$, 12, 18) decreases the facility of oxidation. For the octyl derivative 10^8 cycles have been obtained.

$[(15\text{-crown-}5)_4Pc]_2Lu$: the first scan is comparable to subsequent ones. Both the effect of the cation and the anion has been detected. Mirage effect studies indicate the incorporation of electrolyte prior to the first redox experiment.

During the reduction process (green/blue transition), the following results have been obtained depending on the compound studied.

Pc_2Lu: the first scan depends on the nature of the cation not that of the anion. The presence of the strong alkali ion complexing agent cryptand 222 prevents any reduction of the layer. However, the type of cation does not interfere further during subsequent cycles.

$[(15\text{-crown-}5)_4Pc]_2Lu$: the oxidation and reduction processes are both perfectly reversible in the presence of $KClO_4$, $NaClO_4$ or KCl. Mirage effects indicate that cations are incorporated within the molecular layer during the reduction.

Finally, electrochemical measurements have been carried out in acidic media and the disproportionation reaction:

$$2\ Pc_2Lu \rightleftharpoons Pc_2Lu^-, Pc_2Lu^+ \overset{H^+}{\rightleftharpoons} Pc_2LuH$$

has been clearly evidenced.

Experimental

The synthesis of the compounds has been previously described[22,26,27]

Unsubstituted Pc_2Lu **1** was deposited by evaporation under vacuum and the thickness was measured with a piezoelectric quartz crystal.

The deposition of octaalkoxymethyl-substituted lutetium bis(phthalocyanine) **2** on electrodes has been already described.[24] A technique derived from the Langmuir–Blodgett method was employed. The thickness was calculated by dissolving a known surface of the molecular film and by measuring its absorbance at 670 nm.[24]

The crown-ether derivative **4** was deposited by spin coating and the thickness was calculated by assuming the same molar absorption as for Pc_2Lu.

The electrochemical apparatus was fabricated by Tacussel. The mirage effect experiment was home-made (see ref. 29).

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