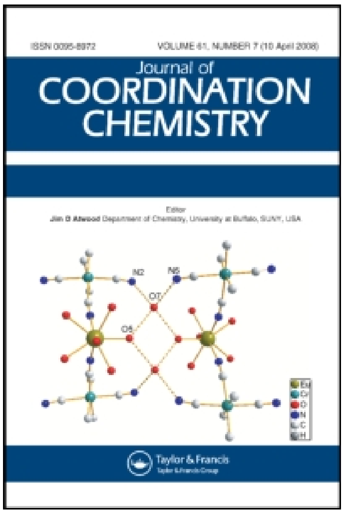


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE ELECTROCHROMIC BEHAVIOUR OF LANTHANIDE BISPHTHALOCYANINES: THE ACID-BASE NATURE OF THE MECHANISM

Roderick B. Daniels[a]; Gregory L. Payne[b]; Jim Peterson[a]
[a] Department of Chemistry, The University of Alabama, Tuscaloosa, AL, U.S.A. [b] Chemistry Department, Southeast Missouri State University, Cape Girardeau, MO, U.S.A.

To cite this Article Daniels, Roderick B. , Payne, Gregory L. and Peterson, Jim(1993) 'THE ELECTROCHROMIC BEHAVIOUR OF LANTHANIDE BISPHTHALOCYANINES: THE ACID-BASE NATURE OF THE MECHANISM', Journal of Coordination Chemistry, 28: 1, 23 — 31

To link to this Article: DOI: 10.1080/00958979308035141

URL: http://dx.doi.org/10.1080/00958979308035141

J. Coord. Chem., 1993, Vol. 28, pp. 23–31
Reprints available directly from the publisher
Photocopying permitted by licence only

THE ELECTROCHROMIC BEHAVIOUR OF LANTHANIDE BISPHTHALOCYANINES: THE ACID-BASE NATURE OF THE MECHANISM

RODERICK B. DANIELS,[1] GREGORY L. PAYNE[2]
and JIM PETERSON[1]*

[1] *Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487-0336, U.S.A.*
[2] *Chemistry Department, Southeast Missouri State University, Cape Girardeau, MO 63701, U.S.A.*

(*Received October 10, 1991*)

Lanthanide bisphthalocyanines are shown to exist in at least three different coloured forms in acetonitrile solution: blue, green and red. The conversion of the blue to green and the green to red species can be achieved by the addition of trifluoromethanesulfonic acid. These processes can be quantitatively reversed by the addition of base. The results are discussed in relation to various proposed mechanisms for the observed electrochromism of lanthanide bisphthalocyanine films.

Keywords: Bisphthalocyanine, electrochromism, lanthanides

INTRODUCTION

Lanthanide bisphthalocyanines ($LnPc_2H$) are an intriguing class of compounds which show some considerable promise for applications in the area of visual displays. These materials, either in solution, or deposited as thin films, have the interesting property of reversibly changing colour in response to applied voltages. This electrochromic behaviour, first reported by Kirin *et al.*[1] and since confirmed by a number of other groups,[2–5] can be summarized as follows:

SCHEME I

$$\begin{array}{ccccc} \text{Red} & \rightleftharpoons & \text{Green} & \rightleftharpoons & \text{Blue} \\ +1.0\text{ V} & & 0.0\text{ V} & & -0.8\text{ V} \end{array}$$

where the applied potentials are with reference to a saturated calomel electrode. Scheme I does, of course, imply that mechanistically the electrochromism involves oxidation-reduction chemistry. Indeed, based on the disappearance of a radical EPR signal associated with the green form of lutetium bisphthalocyanine, a mechanism has been proposed[6] where the red and blue compounds are respectively oxidation and reduction products of the green material. This explanation has found some additional support.[7] However, other groups have reported that they can find no

---

* Author for correspondence.

radical EPR signals associated with the green forms of either the gadolinium[8] or ytterbium[9] bisphthalocyanines.

Working with aqueous media and using sulfonated lanthanide phthalocyanine derivatives, Moskalev and Kirin[10] proposed some twenty years ago an acid-base mechanism to explain the green/blue interconversion. Extending their arguments to include the red species, the electrochromic process may alternatively and plausibly be described as follows:

SCHEME II

$$\text{Red} \underset{+\text{H}^+}{\overset{-\text{H}^+}{\rightleftharpoons}} \text{Green} \underset{+\text{H}^+}{\overset{-\text{H}^+}{\rightleftharpoons}} \text{Blue}$$

At least some rudimentary understanding of the molecular basis for the observed colour changes in the lanthanide bisphthalocyanines is desirable if prototype visual display devices employing these materials are to be improved. The present state of confusion in the literature is clearly unsatisfactory. In an effort to address this problem, we report here the results of experiments employing the "superacid" trifluoromethanesulfonic (triflic) acid in solvent acetonitrile to effect the colour changes blue → green → red in solutions of various lanthanide bisphthalocyanines and in the absence of any applied electrical potential.

EXPERIMENTAL

Liquid secondary ion mass spectra (LSIMS) were obtained using a VG AutoSpec high resolution instrument. DMF solutions of samples were diluted in an equal volume of 15% (v/v) trifluoroacetic acid in 3:1 (v/v) dithiothreitol:dithioerythritol for introduction to the mass spectrometer. Electronic absorption spectra were recorded on a Perkin-Elmer λ5 spectrophotometer. Concentrations of dysprosium bisphthalocyanine solutions were determined spectrophotometrically by diluting samples into acidified dichloromethane and using the value 1.8×10^5 M^{-1} cm^{-1} for the extinction coefficient of the green form absorption maximum.[7]

Certified ACS grade solvents acetonitrile, dichloromethane, dimethylformamide (DMF) and methanol were purchased from Fisher Scientific. Unless stated to the contrary, all other reagents were obtained from Aldrich Chemical Company and used as supplied. Acetonitrile was maintained nominally dry for use in these experiments by storage over 4A molecular sieve. Lanthanide bisphthalocyanines were prepared and purified following a modification of the method originally reported by Kirin *et al.* for the neodymium complex.[1] The synthesis of dysprosium bisphthalocyanine, as described below, represents a typical preparation. While this procedure starts with dysprosium acetate, we found that chlorides (e.g., holmium chloride) and finely divided oxides (e.g., thulium oxide) were also suitable sources of the required lanthanide.

1.0 g (3.0 mmol) dysprosium (III) acetate hydrate was ground and intimately mixed with 3.5 g (27 mmol) 1,2-dicyanobenzene. This was heated at 200°C for 3 hours in a crucible with a lid. After cooling, the solidified melt was ground to a powder, then Soxhlet extracted with 100 cm^3 of DMF for 2 hours. The entire DMF extract was applied to a 45 × 5 cm column of silica (Kieselgel 60 F_{254}, E. Merck) slurried in DMF. The column was developed with 20 cm^3 methanol and then elution continued with DMF. The entire (ca 400 cm^3) dark blue/green band was collected. After rotary evaporation to ca 50 cm^3, the sample was applied to a second 45 × 5 cm silica/DMF column, developed with methanol, then elution continued with DMF. The main band was collected in 50 cm^3 fractions, aliquots of which were diluted in DMF in order to record electronic absorption spectra. Only those fractions in which the ratio A_{332}/A_{621} was less than 1.4, i.e., the azure blue head of the band, were retained. The distinctly turquoise/green fractions representing the tail of the band were discarded [N.B. Based on the ratio A_{332}/A_{621}, subjecting samples to additional and varied chromatographic procedures did not lead to further purification]. The combined azure blue fractions were rotary evaporated to less than 10 cm^3 and stored at room temperature, sometimes for weeks, prior to use. The stability of the DMF solutions proved to be important, since we found it impossible to isolate solid materials from these preparations of the blue form without substantial decomposition occurring. If the product was dried by further rotary evaporation and heating to 150°C, the solid material obtained could only be partially redissolved in DMF to yield solutions which did not exhibit any "electrochromic" behaviour and had absorption characteristics unlike the spectra of Figures 3 and 4. Yields of chromatographically pure dysprosium bisphthalocyanine were always less than 10% based on starting dysprosium acetate.

RESULTS

In Figure 1 we present the mass spectrum of thulium bisphthalocyanine in the range *m*/*z* 600 to *m*/*z* 2000. There is nothing evident at *m*/*z* 1874 which would be indicative of the Ln_2Pc_3 complex suggested by others to be formed in some circumstances.[11] The signal at *m*/*z* 681 corresponds to $[TmPc]^+$, either a minor contaminant in samples, or a fragment of the parent ion. The most abundant species occurs in the region of *m*/*z* 1195, which is expanded in Figure 2*A* to show the mass distribution pattern of this signal. The isotope distribution pattern calculated for a molecular ion

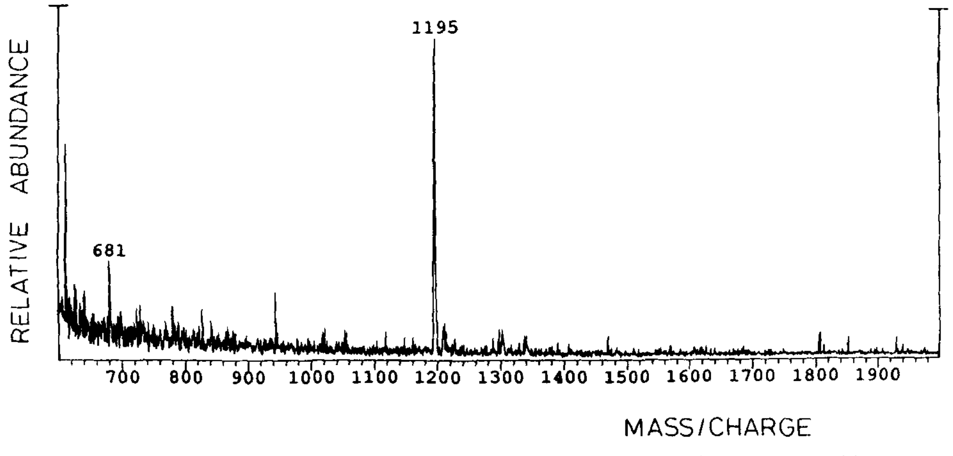


FIGURE 1 LSIMS of thulium bisphthalocyanine dissolved in 7% (v) trifluoroacetic acid, 11% (v) dithioerythritol, 32% (v) dithiothreitol, 50% (v) DMF.

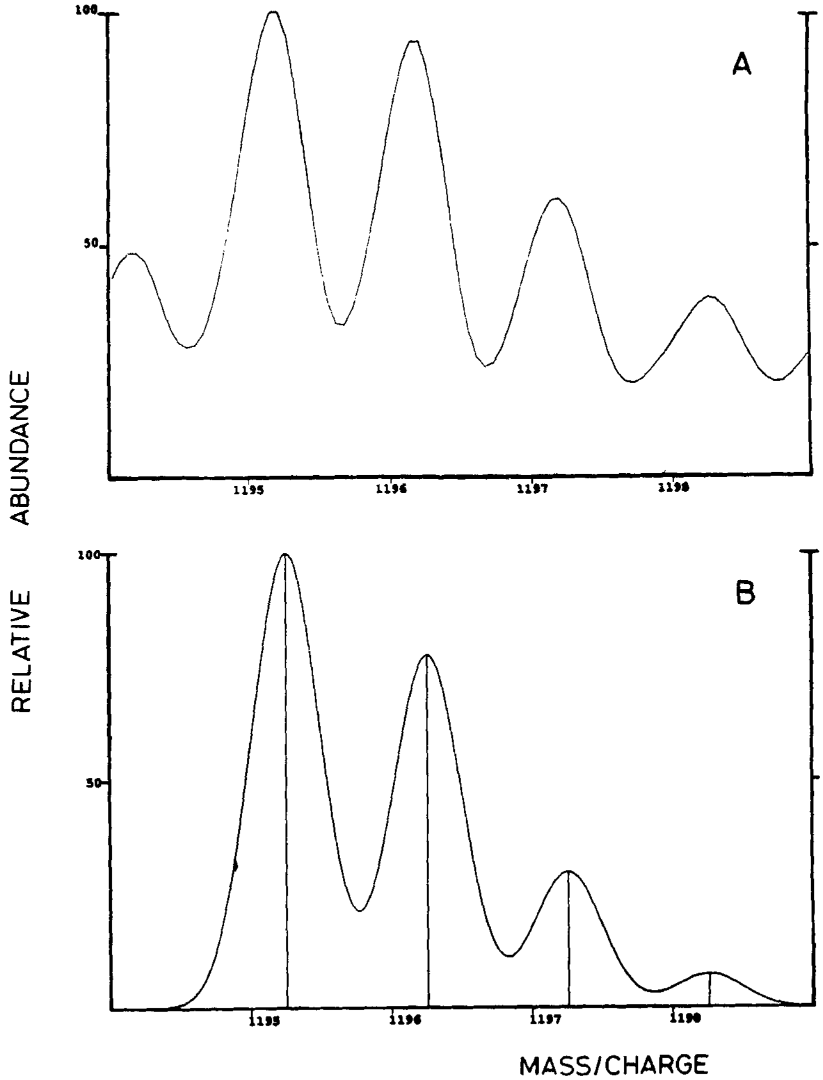


FIGURE 2 LSIMS of thulium bisphthalocyanine, sample as in Figure 1. *A*: Data. *B*: Isotope distribution calculated for $[TmPc_2H_2]^+$.

with the formula $[TmPc_2H_2]^+$ is given in Figure 2*B*. There is clearly good agreement between the data of Figures 2*A* and 2*B*, suggesting that the main thulium phthalocyanine species in solution is $TmPc_2H$, since the $[M + H]^+$ molecular ion is most likely to be obtained by LSIMS.[12] The existence of the small signal at m/z 1194 in the data of Figure 2*A* is presumably due to the parent ion $[TmPc_2H]^+$.

The other lanthanides give rise to more complicated isotope distribution patterns than thulium. However, so far as we were able to ascertain, the results we obtained for neodymium and dysprosium phthalocyanines were in good agreement with the data presented in Figures 1 and 2 for the thulium complex.

In Figure 3 are shown the visible/near-infrared electronic absorption spectra of some dysprosium bisphthalocyanine derivatives in solvent acetonitrile. Following the addition of 5% (v/v) triflic acid in acetonitrile (a single drop from a Pasteur pipette into 3 cm^3 of starting solution) the red species was quantitatively obtained. Subsequently, addition of undiluted *n*-butylamine (two drops from a Pasteur pipette) resulted in conversion of the red to the green species. Further addition of *n*-butylamine resulted in regeneration of the blue species. In other experiments (data not shown) using more dilute triflic acid solutions, it was found to be possible to convert the blue species to the green without first generating the red. Taking into account the dilution of the chromophore, these reactions were found to be fully reversible.

The blue to green conversion is quite readily achieved using almost any acid. For example, the addition of acetic acid to a solution of dysprosium bisphthalocyanine in dichloromethane leads to slow formation of the green species from the blue with reasonably well maintained isosbestic points.[11] In fact, the details of this reaction in

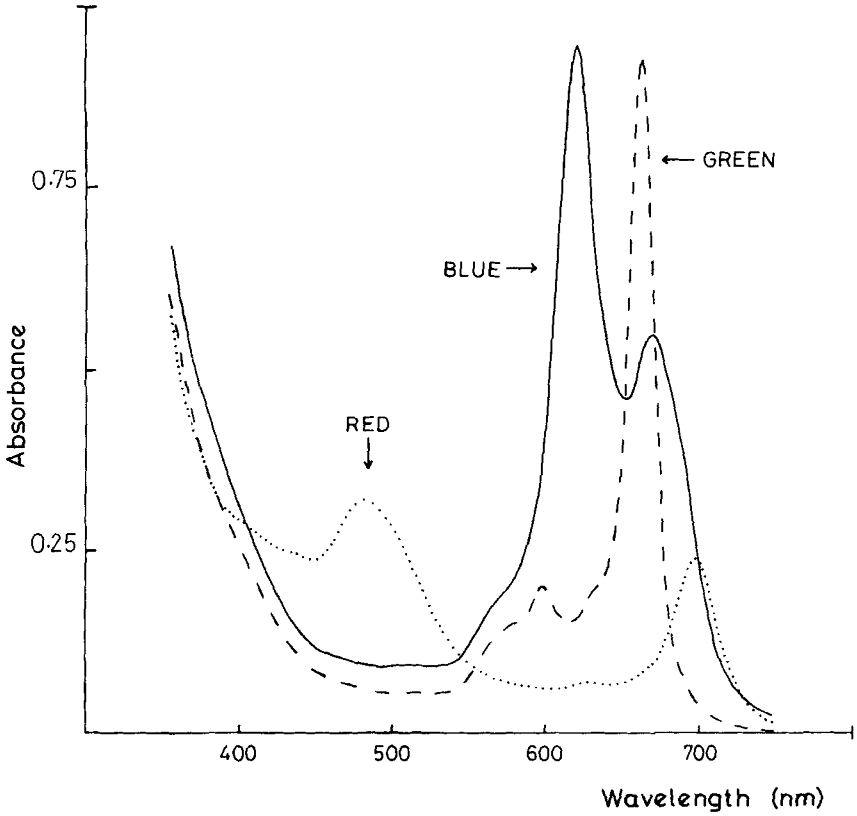


FIGURE 3 Electronic absorption spectra of dysprosium bisphthalocyanine in acetonitrile solution, 1 cm pathlength, 20°C. Initially 3 cm^3 of 6 μM blue form (———), + one drop 5% (v) triflic acid (·····), + two drops *n*-butylamine (– – –).

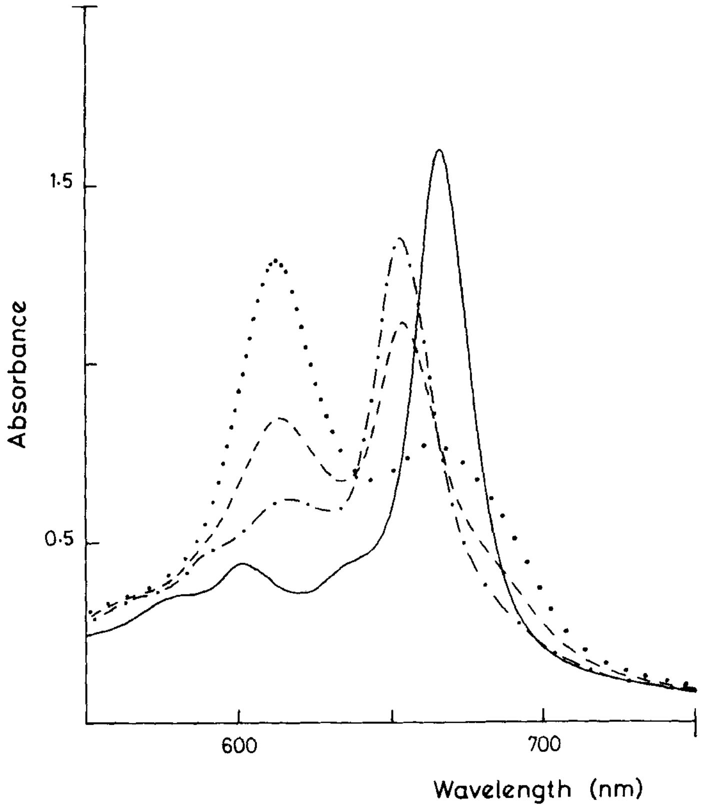


FIGURE 4 Electronic absorption spectra of dysprosium bisphthalocyanine in dichloromethane solution, 1 cm pathlength, 20°C, 9 μM sample concentration, 5% (v) acetic anhydride. Initial spectrum (·····), 5 min (– – – –), 30 min (–·–·–) and 2 hours (———) elapsed time.

solution are a little more complicated than the earlier study would lead us to believe. If the experiment is repeated using acetic anhydride, formation of the green species from the blue is initially observed, with isosbestic points at 638 nm and 666 nm as seen in Figure 4 (broken lines). However, the spectrum of the green species ultimately becomes red shifted by some 12 nm (Figure 4, solid line). Given the known tendency of lanthanide ions to adopt a variable coordination number, often in excess of eight,[13] it seems entirely likely that this indicates the slow loss of bound water molecules from the coordination sphere of the dysprosium ion. The processes represented in Figure 4 are readily reversible. Bases such as triethylamine and tributylamine may be used in place of *n*-butylamine and many solvent systems are suitable for use, including DMF.

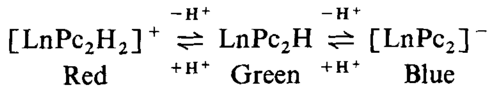
The green to red conversion is much more difficult to accomplish. To date, triflic acid is the only acid with which we have been able to perform this reaction. In addition, it should be noted that the solvent is important. The red species does not form in protic solvents such as methanol, nor basic solvents such as DMF, at least not by the action of triflic acid.

Similar results to those depicted in Figures 3 and 4 were obtained for the bisphthalocyanines of all lanthanides from gadolinium to ytterbium. Surprisingly, the same was not true for lutetium bisphthalocyanine. Conversion of the blue form of the lutetium complex to the green in DMF solution led to an absorption spectrum of about half the expected intensity, based on the relative intensities of the blue and green lutetium species in solid films.[5] That is, some decomposition of the bisphthalocyanine complex occurred. Concomitantly, a radical EPR signal appeared in these solutions of the green species, very like that previously observed by others in an electrochemical cell.[6] In our experiments the intensity of this EPR signal was variable. The other lanthanide bisphthalocyanines, which exhibit very little tendency to decompose during the blue to green conversion, did not produce a radical EPR signal.

DISCUSSION

The data presented in Figure 3 clearly demonstrate that the interconversion of the blue, green and red forms of dysprosium bisphthalocyanine in acetonitrile solution can be effected simply by acids and bases, without the addition of oxidants or reductants and in the absence of applied electrical potentials. We did not take any particular precautions to exclude molecular oxygen from these reactions, but the 100% reversibility of the colour changes observed for all save the lutetium complex argues strongly against the involvement of oxygen-derived species. The electronic absorption spectra in acetonitrile solution of the three forms of dysprosium bisphthalocyanine (Figure 3) and those of the other disphthalocyanines gadolinium through lutetium (data not shown) are strikingly similar to the spectra obtained for the analogous forms in solid films.[5,9] Barring some possible differences in the degree of hydration of the coordinated lanthanide ion, this represents convincing evidence that the similarly coloured species in solution and films are chemically identical. It follows therefore, that both in solution and in solid films, the observed colour changes are mediated by acid-base chemistry, not oxidation-reduction processes, and consequently, the mechanism is like that in Scheme II.

The available elemental analysis data give the composition of the green forms of the ytterbium and lutetium complexes as $YbPc_2H$ and $LuPc_2H$,[9] where the odd proton is required for overall charge neutrality. It is noteworthy regarding this point that sublimation of lanthanide bisphthalocyanine preparations results in deposition of a green film on a nearby substrate,[5] irrespective of the colour of the starting material. This appears to be consistent with the green species having no net electrical charge. Furthermore, the mass spectra in Figures 1 and 2 are for the green form of the thulium complex, the trifluoroacetic acid added to samples effecting the conversion prior to introduction to the spectrometer. Consequently, since LSIMS tends to yield the $[M + H]^+$ ion, we find the composition of the green solution form of the thulium complex to be $TmPc_2H$, in good agreement with the earlier findings. A crystal structure of the neodymium complex has been published, in which the position of the odd proton could not positively be identified; nevertheless, one of the phthalocyanine rings did appear distorted, indicating its possible location.[14] While there is presently no unambiguous evidence concerning the composition of the blue and red forms of the lanthanide bisphthalocyanines, a reasonable working hypothesis for the species involved is shown below.



$$\underset{\text{Red}}{[\mathrm{LnPc_2H_2}]^+} \underset{+\mathrm{H}^+}{\overset{-\mathrm{H}^+}{\rightleftharpoons}} \underset{\text{Green}}{\mathrm{LnPc_2H}} \underset{+\mathrm{H}^+}{\overset{-\mathrm{H}^+}{\rightleftharpoons}} \underset{\text{Blue}}{[\mathrm{LnPc_2}]^-}$$

This kind of reaction for the green to blue interconversion has previously been proposed by Moskalev and Kirin[10] and by MacKay *et al.*[8] What is new in the present study is the extension of this acid-base theme to include the red species, plus some experimental verification of the idea. Other (oxidation-reduction) mechanisms proposed in the literature seem to be based on the erroneous suggestion that the green form of lutetium bisphthalocyanine is a radical species, while the blue form is not.[6] We are currently attempting to address this matter further by a study of the blue and green solution forms of ytterbium and lutetium bisphthalocyanines by combined EPR and magnetic circular dichroism (MCD) spectroscopies.[15] Preliminary findings are that the blue and green forms of lutetium bisphthalocyanine are both diamagnetic, confirming that their interconversion does not involve an oxidation-reduction reaction.

There is no doubt whatsoever that solid films of lanthanide bisphthalocyanines change colour in response to an applied electrical potential and in this sense they certainly may reasonably be called "electrochromic". However, it has been noted that results of cyclic voltammetric studies on such preparations are inconsistent with a rate controlled by electron transfer and depend in a complicated manner on the composition of the supporting electrolyte.[16] Since the colour changes probably depend upon proton fluxes (presumably counter-ions) this should no longer seem surprising. In addition, lanthanide bisphthalocyanine-based devices prepared as Langmuir-Blodgett films have been reported to display enhanced colour changes and improved electrochemical stability.[17] Again, these observations appear consistent with the present results. Langmuir-Blodgett films are likely to be much thinner than sublimed ones, allowing protons (and perhaps other ionic species) to more easily move in and out of the chromophore-containing layer with minimal disruption. A detailed explanation of the electrochemical processes will probably require further studies. However, in light of our current findings, at least some reappraisal of the literature concerning the electrochemistry of lanthanide bisphthalocyanine films would seem to be appropriate.

ACKNOWLEDGEMENTS

R.B.D. is the holder of a Future Faculty Fellows scholarship at The University of Alabama. G.L.P. was a participant in the 1989 NSF-REU program at The University of Alabama. Wee-Khuan Loo performed some of the control experiments as part of an undergraduate course option. We are grateful to Russell Timkovich and S. Ley Hathcock for help in obtaining the mass spectra.

REFERENCES

1. I.S. Kirin, P.N. Moskalev and Y.A. Makashev. *Zh. Neorg. Khim.*, **10**, 1951–1953 (1965).
2. M.M. Nicholson and F.A. Pizzarello. *J. Electrochem. Soc.*, **128**, 1740–1743 (1981).
3. G.C.S. Collins and D.J. Schiffrin. *J. Electroanal. Chem.*, **139**, 335–369 (1982).
4. M.-T. Riou, M. Auregan and C. Clarisse. *J. Electroanal. Chem.*, **187**, 349–354 (1985).
5. C.S. Frampton, J.M. O'Connor, J. Peterson and J. Silver. *Displays*, **9**, 174–178 (1988).
6. G.A. Corker, B. Grant and N.J. Clecak. *J. Electrochem. Soc.*, **126**, 1339–1343 (1979).

7. D. Markovitsi, T.-H. Tran-Thi, R. Even and J. Simon. *Chem. Phys. Lett.*, **137**, 107–112 (1987).
8. A.G. MacKay, J.F. Boas and G.J. Troup. *Aust. J. Chem.*, **27**, 955–964 (1974).
9. D. Walton, B. Ely and G. Elliott. *J. Electrochem. Soc.*, **128**, 2479–2484 (1981).
10. P.N. Moskalev and I.S. Kirin. *Zh. Neorg. Khim.*, **16**, 110–115 (1971).
11. M. M'Sadak, J. Roncali and F. Garnier. *J. Chim. Phys.*, **83**, 211–216 (1986).
12. J.R. Chapman, in "Practical Organic Mass Spectrometry", pp. 111–112 (John Wiley & Sons, New York, 1985).
13. F.A. Cotton and G. Wilkinson, in "Advanced Inorganic Chemistry" (5th Ed.), pp. 959–961 (John Wiley & Sons, New York, 1988).
14. K. Kasuga, M. Tsutsui, R.C. Petterson, K. Tasumi, N. Van Opdenbosch, G. Pepe and E.F. Meyer, Jr. *J. Am. Chem. Soc.*, **102**, 4835–4836 (1980).
15. R.B. Daniels, W.C. Porter and J. Peterson. Unpublished observations.
16. F. Castaneda and V. Plichon. *J. Electroanal. Chem.*, **236**, 163–175 (1987).
17. Y. Liu, K. Shigehara, M. Hara and A. Yamada. *J. Am. Chem. Soc.*, **113**, 440–443 (1991).