

Synthesis and Characterization of some Lanthanide Phthalocyanines

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Abstract

The study of lanthanide phthalocyanine synthesis shows increasing difficulty in obtaining the diphthalocyanine from lutetium to lanthanum. Mono- and diphthalocyanine complexes have been characterized by spectroscopic methods. The rare earth effect on the phthalocyanine radical character has been detected.

Introduction

The discovery that electrochromic materials may be utilized in visual displays has generated great interest in the field of lanthanide diphthalocyanine (LnPc_2) (Pc = the phthalocyaninato group $\text{C}_{32}\text{H}_{16}\text{N}_8$) [1–3]. Deposited as a thin film on an electrode dipped in an electrolyte, rare-earth diphthalocyanines exhibit different colors according to the applied potential: the green starting material turns yellow/orange when oxidized, and blue and purple when reduced [4, 5]. For a long time rare earth diphthalocyanines have not satisfactorily been characterized due to the lack of a reliable synthesis method. Kirin *et al.* [6] found that the neodymium diphthalocyanine complex was a blue compound; MacKay *et al.* [7] concluded that under different conditions gadolinium diphthalocyanine could be green or blue, and Yamana [8] found for the dysprosium that the blue form was a diphthalocyanine complex and the green one a monophthalocyanine complex. The first characterization of lutetium diphthalocyanine was reported by Chang and Marchon [9], who obtained a pure green product after purification by liquid chromatography.

The main purpose of this work was to perfect a reliable synthesis method leading, after washing out the by-products, to pure diphthalocyanine thin films by standard vacuum sublimation. In this paper we report on the synthesis of several mono- and diphthalocyanines with the lanthanides Lu, Yb, Dy, Tb, Gd and Nd, and their characterization by elemental analysis, electron spin resonance (ESR), infrared, far infrared and UV–Vis spectroscopy.

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Experimental

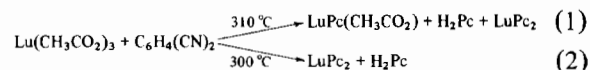
The various complexes were synthesized according to the method of Moskalev and Kirin [10]. Dry rare earth acetate (Johnson Matthey, 4 N purity) and *o*-phthalonitrile (Fluka AG), recrystallized twice in methanol, were mixed (molar ratio 1/10) and heated under stirring in an open glass tube dipped in a vertical tube furnace. The temperature regulation system was a Eurotherm 919 PID ($\Delta T = \pm 1^\circ\text{C}$). The synthesis parameters studied are detailed below.

The crude product was washed successively with analytical grade solvents, ethanol, dimethylformamide and ethanol; every washing included stirring with ultrasonic waves followed by centrifugation. The final product was dried overnight at 110°C and finely ground. The purification of the different diphthalocyanines was carried out in a train sublimation system under a purified nitrogen flow [11].

Infrared spectra (KBr disks) and far infrared spectra (polyethylene disks) were recorded on a FTIR spectrophotometer BRUKER IFS 113. UV–Vis spectra were recorded on a CARY 2300 spectrometer connected to a DS 15 data station.

Results and Discussion

Temperature and reaction times were determined to be the most important parameters to study [12]. At 310°C a mixture of lutetium monophthalocyanine (LuPcA , with $\text{A}^- = \text{anion}$) and metal free phthalocyanine (H_2Pc) was obtained, while at 300°C LuPc_2 was mainly found mixed with a small amount of H_2Pc . Thus it is to be noted that for a temperature difference of 10°C , LuPc_2 may or may not be the main product, according to the following reaction:



In the preparation of thin films by vacuum sublimation, the presence of H_2Pc was avoided because of its lower sublimation temperature, therefore there was no risk of film contamination. On the contrary, a small amount of LuPcA will prevent one

TABLE I. Rare Earth Diphthalocyanine Synthesis: Yield and Amount of Metal-Free Phthalocyanine Present in the End Product

	LnPc ₂ (%) ^a	H ₂ Pc (%) ^b
LuPc ₂	60	2
YbPc ₂	60	2
DyPc ₂	40	30
GdPc ₂	20	45
NdPc ₂	5	75

^aCalculated from the rare earth salt. ^bCalculated from the washed end product.

from obtaining pure LuPc₂ thin films: although this complex is not sublimable, it is swept along with LuPc₂ during the sublimation process.

The temperature difference between reactions (1) and (2) becomes smaller and smaller as the rare earth

atom is changed from Lu to Nd and reaction (2) gets more and more difficult to control. Furthermore the H₂Pc amount increases sharply from Gd (Table I). Trials are in progress to limit the formation of H₂Pc.

The synthesis time was varied from 30 min to 5 h. The LuPc₂ amount rises to a maximum after 3 h reaction time and then levels off.

Characterization

The phthalocyanine complexes were characterized by elemental analysis, ESR, infrared, far infrared and UV-Vis spectroscopy.

Elemental analysis of the green compounds were consistent with the formula LnPc₂ as confirmed for Ln = lutetium [13]. The blue compounds correspond to the monophthalocyanine, formula (LuPc)⁺A⁻ with A⁻ = acetate, as found by Weiss [14] (see Table II).

We have already reported on LuPc₂ ESR spectroscopy [13]; this complex shows an intense signal with a linewidth of 11.9 G and a g factor close to the free

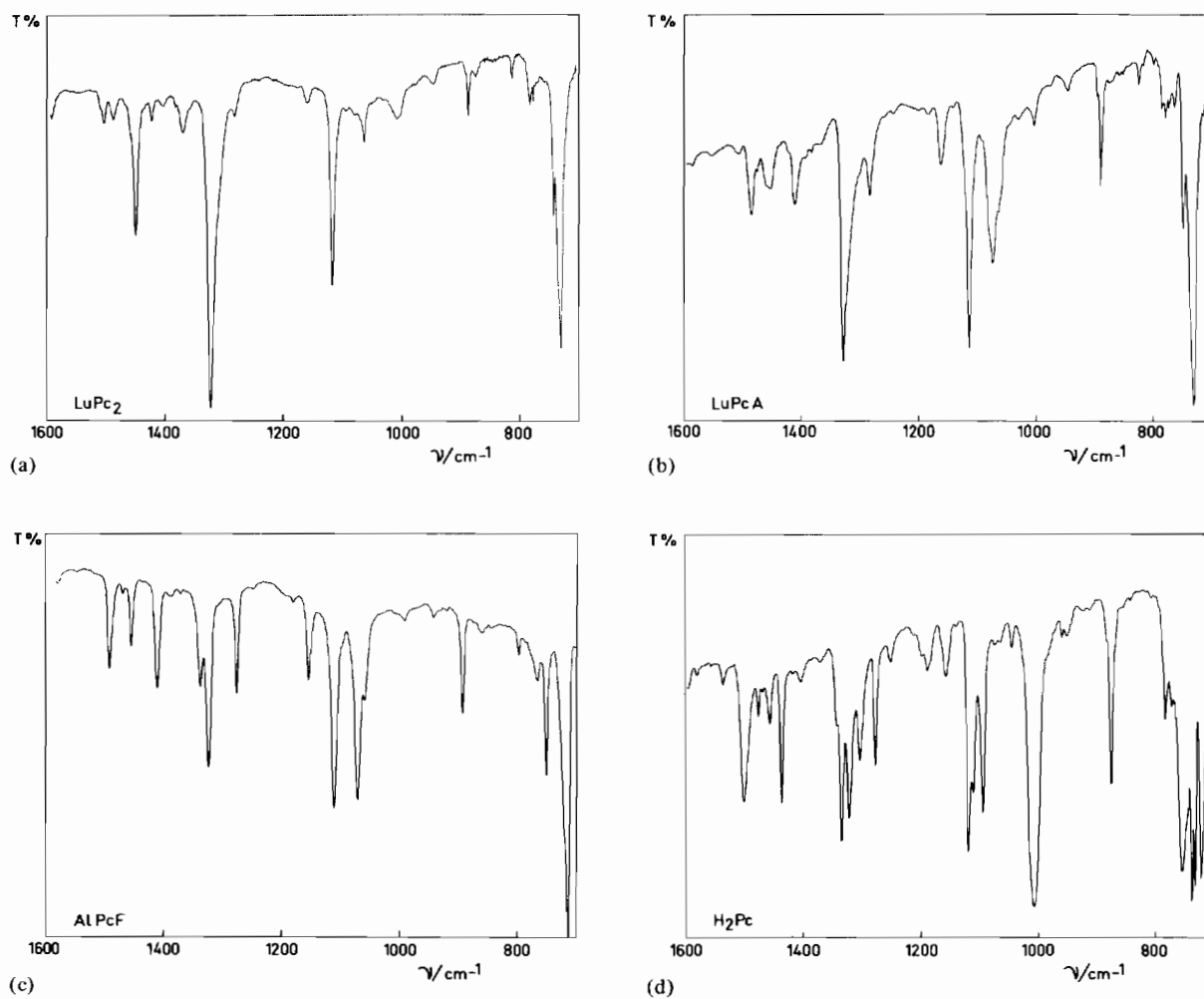


Fig. 1. Infrared spectra of (a) lutetium diphthalocyanine, (b) lutetium monophthalocyanine, (c) aluminum phthalocyanine, and (d) metal-free phthalocyanine.

TABLE II. Elemental Analyses of Various Rare Earth Phthalocyanine Complexes

	Anal. Calc. (found)		
	C	H	N
LuPc ₂	64.05 (63.68)	2.67 (2.54)	18.68 (18.32)
YbPc ₂	64.16 (64.05)	2.67 (2.56)	18.71 (18.73)
DyPc ₂	64.73 (64.26)	2.70 (2.95)	18.88 (18.67)
GdPc ₂	65.00 (65.57)	2.71 (2.83)	18.96 (19.30)
NdPc ₂	65.75 (65.97)	2.74 (2.87)	19.18 (19.32)
LuPc(CH ₃ CO ₂)	54.69 (54.86)	2.55 (2.42)	15.01 (14.82)

TABLE III. Main Infrared Bands (cm⁻¹) for Lutetium Mono- and Diphthalocyanines, Aluminum and Metal-Free Phthalocyanines

LuPc ₂	LuPcA	AlPcF	H ₂ Pc
725	725	725	720–750
740	740	760	780
811	821	808	
886	886	904	874
			1008
1063	1063		
	1073	1071	1093
		1083	
1115	1115	1124	1111
			1119
1323	1331	1336	1335
1452	1413	1424	1437
	1460	1468	
	1487	1505	1502

electron value $g = 2.002$. Recently we have carried out some experiments on Yb, Dy, Tb and Nd diphthalocyanines and Ln monophthalocyanines that show no signal.

Infrared spectroscopy has been generally used to check the purity of phthalocyanine complexes [7, 15], especially to detect H₂Pc, which shows as a characteristic band at 1008 cm⁻¹. We have compared lutetium mono- and diphthalocyanines with mono-metallic phthalocyanine (AlPcF) and H₂Pc (Fig. 1); the data are gathered in Table III. In the region between 1550 and 1385 cm⁻¹ – where the pyrrole moiety possesses three absorption bands – we observe for LuPc₂ one band at 1452 cm⁻¹ much more intense than the two others at 1493 and 1507 cm⁻¹, instead of three bands of the same intensity for

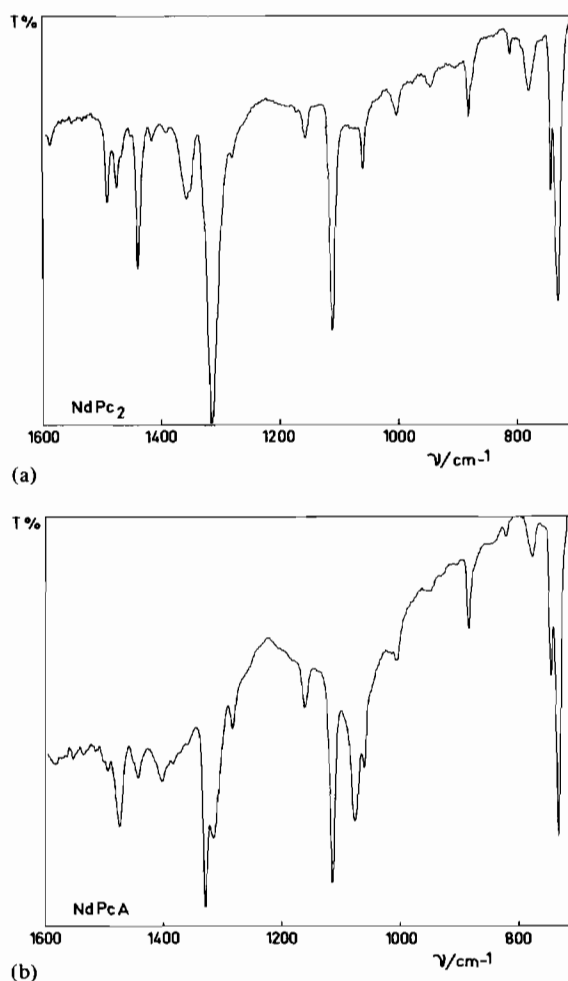


Fig. 2. Infrared spectra of (a) neodymium diphthalocyanine, and (b) neodymium monophthalocyanine.

LuPcA at 1413, 1460 and 1487 cm⁻¹. Between 1300 and 1150 cm⁻¹, LuPc₂ presents a very strong band at 1323 cm⁻¹ and LuPcA one at 1331 cm⁻¹, while for H₂Pc these two bands appear with the same strong intensity. In the last region up to 700 cm⁻¹, LuPc₂ shows a very strong band at 1115 cm⁻¹ and a weak and sharp one at 1063 cm⁻¹; these two bands are also present in the LuPcA spectrum but the 1063 cm⁻¹ band is changed into a shoulder on the main absorption at 1073 cm⁻¹. One can find this band shifted to higher frequency in the AlPcF spectrum. LuPc₂ and LuPcA show a weak band at 811 and 820 cm⁻¹ respectively which will be discussed later; the bands at 886 and 725 cm⁻¹ are common to the two phthalocyanine complexes.

In conclusion, we suggest that the characteristic bands for LuPc₂ are at 1452, 1323 and 811 cm⁻¹, and for LuPcA at 1331, 1073 and 821 cm⁻¹. The lack of the 1008 cm⁻¹ peak in the two spectra confirms the absence of H₂Pc. The assignment to a metal ligand vibration of the band at 886 cm⁻¹ seems to be

TABLE IV. Characteristic Infrared Bands for Various Rare Earth Phthalocyanines

Compound	Bands (cm^{-1})		
LuPc ₂	811	1323	1452
YbPc ₂	811	1321	1451
DyPc ₂	809	1320	1448
TbPc ₂	809	1319	1447
GdPc ₂	809	1319	1445
NdPc ₂	808	1314	1442
LuPcA	821	1073	1331
NdPcA	817	1076	1329

TABLE V. Far Infrared Metal–Ligand Vibrations for Various Rare Earth Phthalocyanines (cm^{-1})

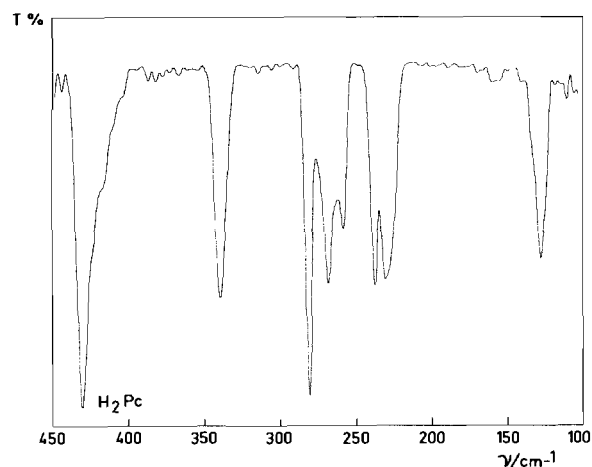
	LnPc ₂	LnPcA
Lu	188	177
Yb	188	
Dy	190	180
Gd	182	191
Nd	186	

unclear as we can observe a band at 874 cm^{-1} in the H₂Pc spectrum [16]; therefore we prefer, as proposed by Pinzutti [16], to attribute the band near $810\text{--}820 \text{ cm}^{-1}$, absent in the H₂Pc spectrum, to a possible metal–ligand vibration.

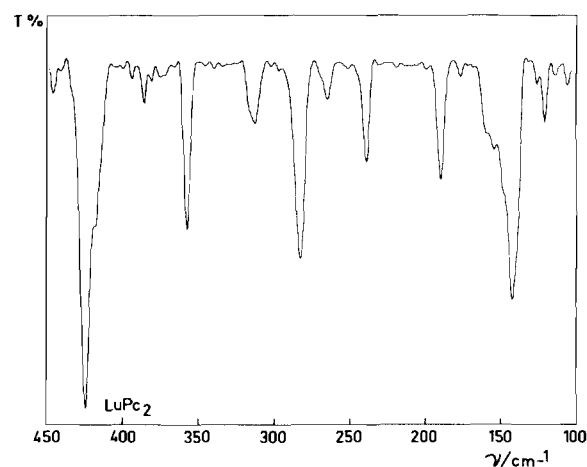
The other lanthanide phthalocyanine spectra are similar to the lutetium ones; we only observe a small shift to lower frequency when going from Lu to Nd (Fig. 2), especially for diphthalocyanine complexes (Table IV).

These results complete those already obtained with Lu and Yb diphthalocyanines by Walton *et al.* [15] who wrongly attributed the bands at 720 and 1115 cm^{-1} as characteristic bands, due to the lack of well-characterized rare earth monophthalocyanines.

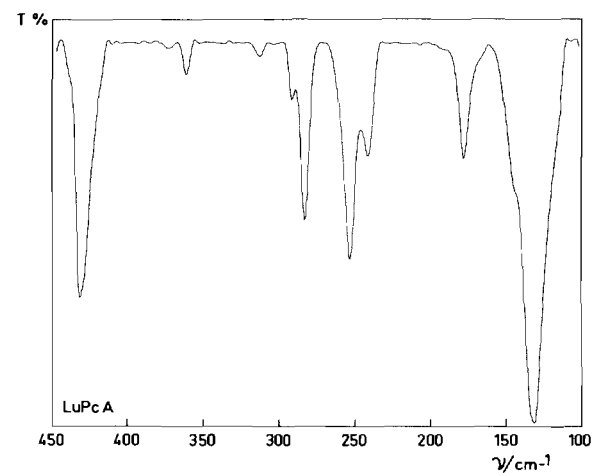
The far infrared spectra of several metal phthalocyanines have been studied by Kobayashi [17], especially for the assignment of metal dependent bands. We can observe in each spectrum (Fig. 3) two out-of-plane vibrations associated with the isoindole ring dependent on the metal nature (also observed in H₂Pc around 350 and 255 cm^{-1}) and a third one in the region between 130 and 230 cm^{-1} , attributed to a metal ligand vibration that we particularly studied. In this region the H₂Pc spectrum shows no absorption band while rare earth mono- and diphthalocyanines present a peak with high intensity. Going from Lu to Nd the absorption band is shifted to higher frequencies in the case of monophthalocyanines (Table V): first investigations show that we cannot easily correlate the band frequency with rare earth physical parameters, as obtained by Kobayashi



(a)

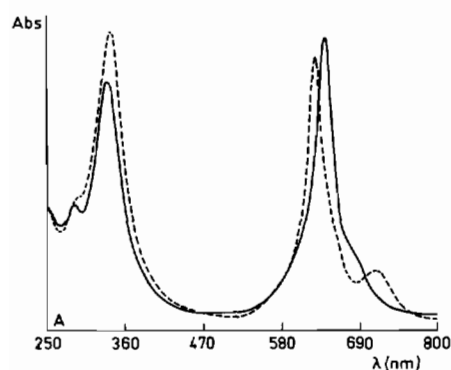


(b)

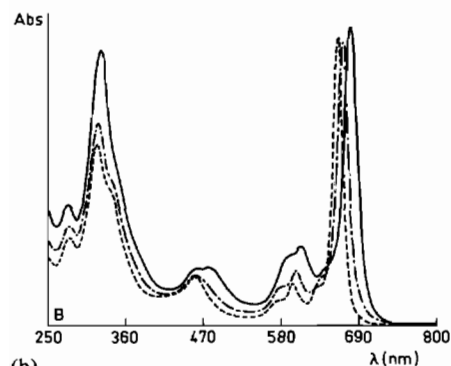


(c)

Fig. 3. Far infrared spectra of (a) metal-free phthalocyanine, (b) lutetium diphthalocyanine, and (c) lutetium monophthalocyanine.



(a)



(b)

Fig. 4. UV-Vis spectra of rare earth phthalocyanines in dichloromethane solution. (a) Monophthalocyanines; (b) diphthalocyanines; —, Lu; —, Nd; - · -, Tb.

with the transition metals. This can be explained by the fact that the trivalent rare earth atom is bound with both the phthalocyanine ring and the acetate anion. So we propose that this metal-ligand vibration might be regarded as a rare earth characteristic band. The case of diphthalocyanines is more confused as the frequency seems independent of the rare earth metal (Table V); we can suppose that in a diphthalocyanine complex, the rare earth effect is weak and the nature of the bands metal/ring is first affected by the overlap of the two phthalocyanine rings. According to experimental results, one ring is rotated by 45° with respect to the other for Lu [14] and Nd [18], which corresponds to the most stable position of the complex. Thus the position of the two rings, independent of the rare earth metal, can explain the FIR results.

The LuPcA visible spectrum shows (Fig. 4a) a Soret band at 335 nm and a Q band at 626 nm. From Lu to Nd we observe a bathochromic shift of the Q band and the disappearance of the secondary peak at 712 nm. The NdPcA spectrum is similar to the AlPcF one [19]. The above-mentioned LnPcA and the reduced form of LnPc₂, which are both blue colored, have often been confused [8]; however we note that in the reduced form of LuPc₂ the secondary peak is

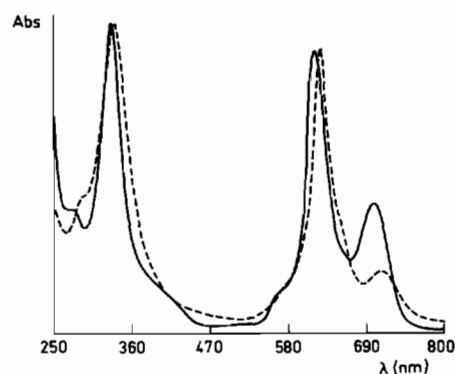


Fig. 5. UV-Vis spectra of LuPc₂ reduced form (—) and LuPcA (---) in dichloromethane solution.

TABLE VI. Visible Absorption Maxima for Various Rare Earth Phthalocyanines in Dichloromethane Solution ($\epsilon_{\text{LuPc}_2} = 2.0 \times 10^5$, $\epsilon_{\text{GdPc}_2} = 1.7 \times 10^5$, $\epsilon_{\text{NdPc}_2} = 1.4 \times 10^5$ l mol⁻¹ cm⁻¹)

Compound	Absorption maxima (nm)	
LuPc ₂	659	457
YbPc ₂	659	457
DyPc ₂	664	459
TbPc ₂	665	459
GdPc ₂	668	459
NdPc ₂	676	455-485
LuPcA	626	712
NdPcA	639	680

more intense and shifted to lower frequency, which enables us to distinguish these two phthalocyanines (Fig. 5).

The LuPc₂ spectrum (Fig. 4b) shows a Soret band at 320 nm with a shoulder near 340 nm, a Q band near 660 nm and a weak and broad band near 460 nm. From Lu to Nd (Table VI) we observe a small bathochromic shift of the visible band [20] and a broadening of the band near 460 nm; furthermore, with NdPc₂ this band is split into two bands at 455 and 485 nm (Fig. 6). In their studies on lithium and rare earth monophthalocyanine radicals, Sugimoto *et al.* [21, 22] noted the constant presence of a broad band at about 500 nm and inferred that it can be regarded as evidence for the existence of a phthalocyanine radical. They mentioned the band splitting for LiPc and suggested it would be expected assuming a much weaker metal-ligand coordination. Taking into account this result, we can apply the same argument to the rare earth diphthalocyanines; the ionic radius increases from Lu to Nd, so we can expect a coordination weakness between the two phthalocyanine rings and the central metal that modifies the radical nature revealed by the broadening and the splitting of the band. This suggestion is confirmed by the synthesis results which show how

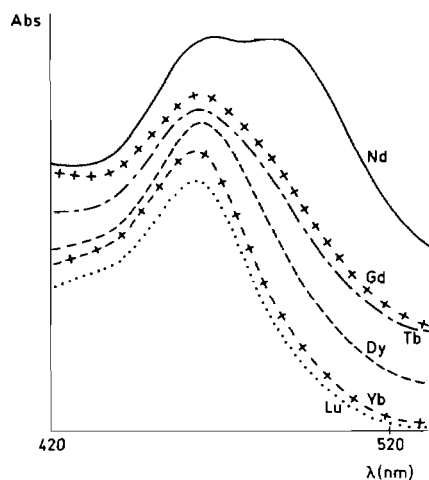


Fig. 6. Modification of the diphthalocyanine visible radical band related to the rare earth atom.

difficult it is to obtain neodymium diphthalocyanine as opposed to the monophthalocyanine.

In conclusion to this paper, the study of LnPc_2 synthesis parameters has enabled us to optimize the process and to obtain end products directly available for sublimation. Trials are in progress to determine the experimental conditions of pure LnPc_2 thin film formation and to correlate the nature of the rare earth metal with electrochemical properties [23].

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