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SYNTHESIS AND ELECTRICAL PROPERTIES OF A NEW MOLECULAR SEMICONDUCTOR: THE UNSYMMETRICAL LUTETIUM PHTHALO-NAPHTHALOCYANINE*

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Abstract We propose a new synthetic method for the preparation of PcLuNPc. The electrochemical and electrical properties of thin films of this compound show it is a new molecular semiconductor.

Keywords: phthalocyanines, molecular semiconductors, naphthalocyanines, intrinsic semiconductors, lutetium

INTRODUCTION

In previous publications[1,2] lutetium bisphthalocyanine $LuPc_2$ and lithium phthalocyanine LiPc have been shown to be the first intrinsic molecular semiconductors. The demonstration of the intrinsic nature of the conduction has been thoroughly carried out in the case of $LuPc_2$ [3-6]. Recently the electrochemical and electrical properties of mixed phthalonaphthalocyanine of lutetium $LuPN_nNN_{8-n}$ have been described (PN = phthalonitrile, NN = 2,3-naphthalonitrile and n = number of phthalonitrile units per molecule)[4,5]. The synthesis of lutetium phthalonaphthalocyanine PcLuNPc and of lutetium bisnaphthalocyanine $LuNPc_2$ has been published

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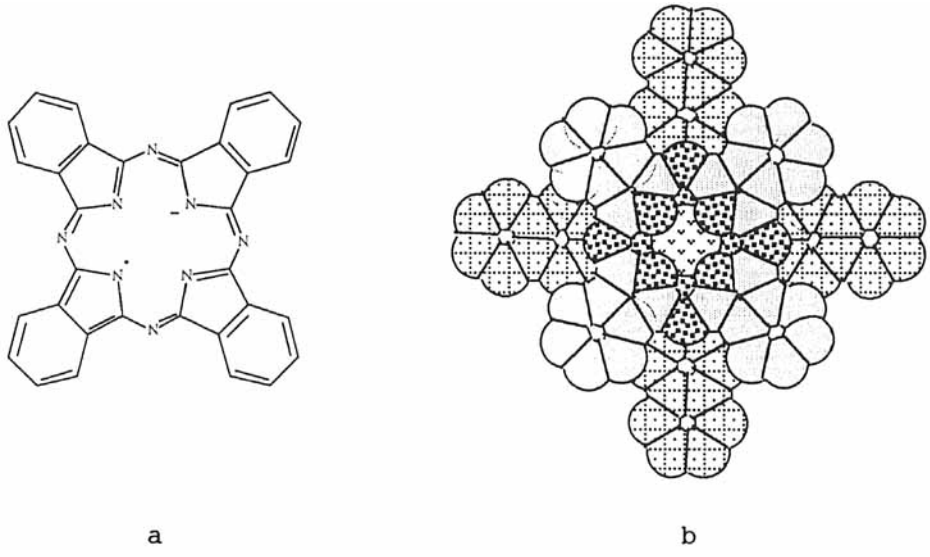
simultaneously to our work[7]. These two products were obtained from sodium mononaphthalocyanine Na_2NPc and lutetium monophthalocyanine LuPcOAc. We report here another synthetic method for the preparation of PcLuNPc. The electrochemical and electrical properties of thin films of this molecular unit are determined. The neutral, oxidized and reduced forms have been characterized by UV-visible spectroscopy. PcLuNPc crystallizes in the orthorhombic space group Pbcn with a = 22.8757 Å, b = 27.9551 Å, c = 22.6931 Å and Z = 8.



a b

FIGURE 1 Radical phthalocyanine $Pc^{\cdot -}$ (a) and top view along the C_4 axis of PcLuNPc (b).

EXPERIMENTAL

Synthesis

We prepared PcLuNPc by reacting 2,3-dicyanonaphthalene with lutetium monophthalocyanine LuPcOAc.

2,3-dicyanonaphthalene is prepared by reaction of fumaronitrile with α, α, α', α' -tetrabromo-o-xylene , in presence of NaI in dimethylformamide[8,9].

Lutetium monophthalocyanine LuPcOAc is obtained by reaction of 1,2-dicyanobenzene with lutetium acetate $Lu(OAc)_3$ in n-hexyl alcohol in the presence of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU). A related method was known[10] for the synthesis of lutetium bisphthalocyanine $LuPc_2$. The reaction time must not exceed 1.5 h to avoid the formation of $LuPc_2$. To obtain a quantitative transformation of $Lu(OAc)_3$, we used a ratio of 6 phthalonitrile molecules for one lutetium acetate, instead of the theoretical value (4:1). It is necessary to use a concentrated hexanolic solution of phthalonitrile (PN) ($c \geq 0.5$ mol PN/l). Under these conditions, LuPcOAc is obtained with a good yield and it can be easily purified by chromatography over deactivated silicagel (eluent: CH_2Cl_2 / CH_3OH).

The reaction of lutetium monophthalocyanine LuPcOAc with the 2,3-dicyanonaphthalene in n-hexyl alcohol in the presence of DBU leads to the unsymmetrical lutetium phthalonaphthalocyanine PcLuNPc. A large excess of 2,3-dicyanonaphthalene is necessary for a good transformation of LuPcOAc (8:1 instead of 4:1). A small quantity of LuPcOAc is transform into $LuPc_2$ showing that the lutetium ion can be released from the phthalocyanine complex.

2,3-dicyanonaphthalene

21.1 g (0.05 mol) of α, α, α', α' -tetrabromo-o-xylene and 3.9 g (0.05 mol) of fumaronitrile are heated in 0.35 l of dry dimethylformamide for 7 h at 75°C in the presence of 50 g of NaI previously dried (50°C, 5 Torr). The crude product is added dropwise at room temperature into a mixture of ice and water (0.5 l) and the solution is faded by addition of sodium bisulfite. The solid is filtered off, washed with distilled water and dried under vacuum (5 Torr) at 50°C. Recrystallisation from acetone at -30°C gives 7.8 g of beige

needles. The product is finally sublimed at 120°C (10^{-5} Torr) leading to small colorless needles. Yield = 88%.
m.p. 256°C (lit.[9]: 256°C); I.R. (KBr pellet): 2226 cm^{-1} (ν_{CN}); ^1H NMR ($CDCl_3$): δ 8.4 (s 1,4-H), 7.9 (m 5,6,7,8-H).
Anal. Calcd for $C_{12}H_6N_2$: C:80.88; H:3.40; N:15.75; found C:80.58; H:3.29; N:15.54.

LuPcOAc

1.55 g (12 mmol) of 1,2-dicyanobenzene, 0.7 g (2 mmol) of lutetium acetate previously dried at 100°C under vacuum (5 Torr), and 0.9 ml (6 mmol) of DBU in 15 ml of n-hexyl alcohol are heated under reflux for 75 mn. After cooling down at room temperature the blue solution is filtered. The precipitate is washed with acetic anhydride (10 ml), cold acetone (10 ml) and finally with pentane. The solid is extracted with dichloromethane. The soluble fraction (1.3 g) is purified by chromatography over deactivated silica gel (deactivation is achieved by addition of 20 ml of CH_3OH in 100 g of silica and stirring for 30 mn). A first fraction is collected with CH_2Cl_2 / CH_3OH 1% : it contains $LuPc_2$. 1.2 g of LuPcOAc is then obtained by elution with CH_2Cl_2 containing from 3 to 5 % of CH_3OH. Yield = 75%.
UV-Visible (CH_2Cl_2): 344 ($\log\varepsilon = 4.66$), 672 ($\log\varepsilon = 5.24$) nm.
^1H NMR ($CDCl_3$): δ 9.48 (m H_α), 8.11 (m H_β).
Anal. Calcd for $Lu(C_{32}H_{16}N_8)(CH_3CO_2)$: C: 45.70; H: 2.56; N: 15.01; Lu: 23.44 ; Calcd for $LuPc(CH_3CO_2)(2CH_3OH)$: C: 53.30; H: 3.40; N: 13.80; Lu: 21.60 ; Found C: 53.72; H: 3.24; N: 13.10; Lu: 20.88.

PcLuNPc

A mixture of 0.19 g (0.25 mmol) of LuPcOAc, 0.34 g (1.9 mmol) of sublimed 2,3-dicyanonaphthalene, 0.2 ml of DBU and 2 mg of ammonium molybdate ($(NH_4)_6Mo_7O_{24}$), in 15 ml of n-hexyl alcohol is refluxed under argon for 20 h. After cooling down to room temperature, the solid is filtered off and washed with 10 ml of acetic anhydride, 10 ml of cold acetone and a large quantity of pentane. The blue powder

(0.37 g) is extracted with toluene for one week in a soxhlet apparatus. The product is purified by chromatography over neutral alumina with a mixture toluene/CH_2Cl_2/CH_3OH (78/20/2) as eluent. The first green fraction contains mainly $LuPc_2$. A second fraction is composed of PcLuNPc and a small amount of $LuPc_2$. Further purification is achieved by dissolution of $LuPc_2$ in toluene and isolation of the solid by centrifugation. 89 mg of PcLuNPc are thus obtained as a blue powder. Yield 25%.

m/e (FAB) 1400 (MH^+). UV-Visible-NIR (CH_2Cl_2) 325, 697 (log ε = 5.0), 970, 1440 (log ε = 3.95) nm. I.R. (KBr pellet) 732, 764, 1114, 1326 cm^{-1}. EPR (powder under vacuum): signal at g = 2.0027, width: 1.6 G.

Anal. Calcd for $C_{80}H_{40}N_{16}Lu$: C:68.62; H: 2.88; N: 16.00; Lu: 12.49 ; Found C: 67.82; H: 3.06; N: 15.41; Lu: 11.35.

RESULTS AND DISCUSSION

Electrochemical potentials of PcLuNPc have been measured in a CH_2Cl_2/THF mixture (30/70) in the presence of Bu_4NClO_4 (0.05 M). Three monoelectronic reversible steps are observed (Fig. 2):

$$PcLuNPc^{2-} \underset{-1.46}{\overset{E^{red2}}{\rightleftharpoons}} PcLuNPc^{-} \underset{-0.43}{\overset{E^{red1}}{\rightleftharpoons}} PcLuNPc \underset{+0.05}{\overset{E^{ox1}}{\rightleftharpoons}} PcLuNPc^{+}$$

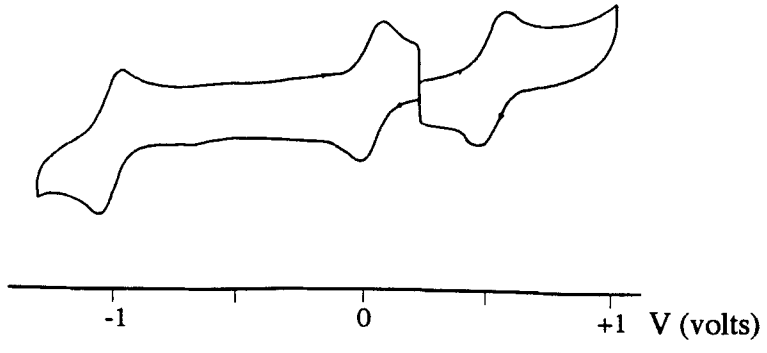


FIGURE 2 Cyclic voltammetry of PcLuNPc in CH_2Cl_2/THF mixture (in volts versus ferrocene / ferricinium).

A fourth step is observed in the mixture DMF/THF (50/50) at -1.82 volt.

The oxidized and reduced forms have also been obtained chemically in dichloromethane solutions by treating PcLuNPc with 1,2-dichloro 4,5-dicyanoquinone (DDQ) and aqueous hydrazine solution, respectively. The neutral, oxidized and reduced forms have been characterized by UV-visible spectrometry (Fig.3).

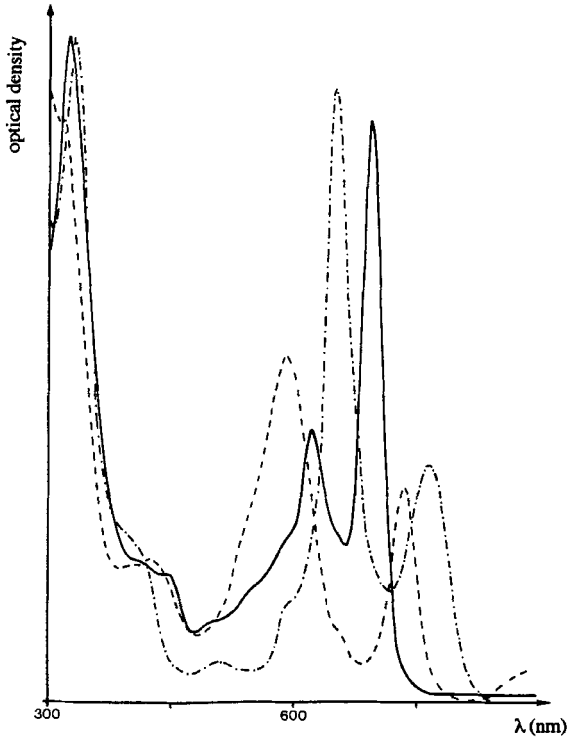


FIGURE 3 optical absorption spectra (U.V. and visible domains) of the reduced (-·-·), neutral (-) and oxidized forms (---) of PcLuNPc in CH_2Cl_2.

The radical nature of the neutral form has been checked by EPR spectroscopy. A signal centered at g = 2.0027 is noticed. The linewidth is 1.6 G for the powder in absence of oxygen and 11 G in a toluene solution. These values are of the same order of magnitude as those observed for $LuPc_2$ [1].

Single crystals have been obtained by a very slow evaporation of chloroformic solutions. PcLuNPc crystallizes in an orthorhombic system with a = 22.8757 Å, b = 27.9551 Å, c = 22.6931 Å and Z = 8 (space group Pbcn). Due to the small size of the crystals (≈ 0.15x0.15x0.03 mm) the structure could not be entirely resolved. Nevertheless the lutetium coordinates are determined and the electronic density distribution shows also that the macrocycles are parallel to the (010) plane.

The electrical properties of thin films of PcLuNPc have been measured between room temperature and 120°C, without breaking vacuum at any stage. The films are prepared by sublimation under vacuum (10^{-6} Torr) at about 600°C on a glass substrate with gold electrodes (film thickness: 500 Å). The conductivity is equal to 5 10^{-5} Ω^{-1} cm^{-1} at 25°C and the thermal activation energy E_{act} is 0.48 eV. This value is equal to the difference between the first oxidization and the first reduction potentials ($E^{ox1} - E^{red1} = 0.48$ volt). Other lutetium radical molecular semiconductors show the same property (Table I)[1,2,4].

TABLE I Electrical properties of thin films of lutetium compounds.

	σ_{RT} ($\Omega^{-1}cm^{-1}$)	E_{act} (eV)	$E^{ox1}_{o} - E^{red1}_{o}$ (V)
PcLuNPc	5 10^{-5}	0.48	0.48
Pc_2Lu	5 10^{-5}	0.52	0.48
$PN_nNN_{8-n}Lu$ ($\bar{n}\approx 4$)	6 10^{-5}	0.38	0.37

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