



Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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P. Turek^{a b c}, P. Petit^{a b c}, J.-J. Andre^{a b c}, J. Simon^{a b c}, R. Even^{a b c}, B. Boudjema^{a b c}, G. Guillaud^{a b c} & M. Maitrot^{a b c}

^a Groupe de Recherches Interdisciplinaires sur les Matériaux Moléculaires (G.R.I.M.M.);, I.C.S., 67083, Strasbourg, France

^b E.S.P.C.I., 75231, Paris, Cédex, France

^c U.C.B., 69100, Villeurbanne, France

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TWO EXAMPLES OF MOLECULAR SEMICONDUCTORS : PHTHALOCYANINE COMPLEXES OF LITHIUM AND LUTETIUM

P. TUREK, P. PETIT, J.-J. ANDRE, J. SIMON,
R. EVEN, B. BOUDJEMA, G. GUILLAUD and
M. MAITROT

Groupe de Recherches Interdisciplinaires sur
les Matériaux Moléculaires (G.R.I.M.M.);
I.C.S., 67083 Strasbourg, France; E.S.P.C.I.,
75231 Paris Cédex, France, and U.C.B., 69100
Villeurbanne, France.

Abstract. The designation "molecular semi-conductor" has never received any clear cut definition. The following criteria are proposed : (i) it is a molecular material constituted of molecular units which can be individually synthesized (ii) its intrinsic conductivity is in the range 10^{-6} - $10^{-1} \Omega^{-1} \text{cm}^{-1}$ (iii) it can be doped with electron donors and/or electron acceptors to form n- or p-doped materials. This paper deals with the description of the electrical properties of lithium phthalocyanine PcLi and lutetium bisphthalocyanine Pc_2Lu , in the intrinsic and extrinsic conduction ranges.

The synthesis of both Pc_2Lu and PcLi has been previously described¹⁻⁴.

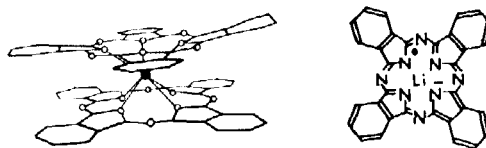


FIGURE 1. Chemical representation of bis-phthalocayninato-lutetium (Pc₂Lu) and lithium phthalocyanine (PcLi).

The electrical properties of Pc₂Nd, compressed pellets^{5,6} or doped with electron acceptors⁷ were described. The conduction found did not distinguish it from many other molecular derivatives doped, fortuitously or not, with impurities such as dioxygen⁸. Electrical properties of Pc₂Lu and PcLi have been determined for sublimed thin films and studied under vacuum (Table 1).

	solid state			solution		E_{calcd} , eV
	σ_{RT} , $\Omega^{-1} \text{ cm}^{-1}$	E , eV	μ_e , $\text{cm}^2/(\text{V}\cdot\text{s})$	$E_{1/2}^{\text{ox}}$, V	$E_{1/2}^{\text{red}}$, V	
PcH ₂	SC $<10^{-12}$ TF	2.00	1.2 $10^{-2}-10^{-3}$	+0.86	-0.58	
PcCu	SC $<10^{-12}$ TF $<10^{-10}$	2.00 1.98	7 10^{-2}	+0.98	-0.84	2.2
PcNi	SC $<10^{-12}$	2.28		+1.05	-0.85	2.6
Pc ₂ Lu	SC 6×10^{-5} TF $\sim 10^{-5}$	0.64 0.52	1.3	+0.03	-0.45	0.9
PcLi	SC 2×10^{-3} TF $10^{-4}-10^{-5}$	0.2		+1.0	+0.17	1.1

TABLE 1. Electrical properties of thin films (TF) and single crystals (SC) of metallo-phthalocyanines. σ_{RT} : room temperature conductivity; E : thermal activation energy; μ_e : electron mobility; $E_{1/2}$: redox potentials; E_{calcd} : activation energy calculated from redox potentials.¹⁵ (after ref. 9,10)

This procedure is known to avoid the presence of impurities even in minute amounts. The intrinsic conductivity is found to be 10^{-5} for thin films of Pc₂Lu and $10^{-4}-10^{-3}$ for PcLi. This is the first time that sublimed thin films of molecular materials have shown such high conductivity. The

value found for single crystals of Pc_2Lu is of the same order of magnitude ($\sim 6 \times 10^{-5}$). It is significantly higher in the case of PcLi (2×10^{-3}). This will be shown to be correlated with the interunit interaction energy leading to delocalized electronic states for PcLi and localized ones for Pc_2Lu . The possibility of p- and n-doping by the co-sublimation technique has been demonstrated for Pc_2Lu ¹¹.

Electron Spin Resonance studies were carried out on Pc_2Lu ¹² and PcLi ¹³ single crystals. For Pc_2Lu , a signal is observed at $g=2.0021$ with a linewidth $\Delta H_{pp}=0.7\text{G}$. The susceptibility shows a Curie Weiss^{pp} behavior with $\theta \sim 6\text{K}$. The magnetic behavior of PcLi is drastically different. At room temperature an extremely narrow line ($\Delta H_{pp}=25\text{mG}$) is observed at $g = 2.0020$. The temperature dependence demonstrates strong antiferromagnetic coupling in the stack direction. It is possible to estimate the interunit interaction energy by using a Hubbard model^{12,14}. The interaction energy is 12 meV for Pc_2Lu and more than 250meV for PcLi . A classical band model may therefore only be applied to the latter case. For conventional diamagnetic PcM , the conductivities are, in all cases, less than $10^{-10} \Omega^{-1} \text{cm}^{-1}$. The conductivity of single crystals of Pc_2Lu and PcLi are $6 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ and $2 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$, respectively. The thin film conductivity is unchanged for Pc_2Lu and lower by a factor of 100 in the case of PcLi . This is clearly related to the difference in the interunit interaction energy.

Pc_2Lu and PcLi are the first examples of intrinsic molecular semiconductors with localized or delocalized electronic states, respectively. The mobility of the charge carriers may be calculated from the thermal activation energy of conduction by assuming that the number of conduction states is equal to the number of molecular units¹⁶. For $E=0.5\text{eV}$, this leads to 10^{16} carriers per cm^3 ($10\text{ppm}^2\text{m:m}$) and to a mobility of the order of $6 \times 10^{-3} \text{cm}^2/\text{v.s.}$ for thin films of Pc_2Lu . The mobility may also be calculated from current-voltage curves in the space charge limited region¹⁷. In this case, a value of $1.3 \text{cm}^2/\text{v.s.}$ is found¹⁰. The apparent discrepancy is due to the different charge

migration processes involved in the two cases. In SCLC determinations, a charge is injected from the electrode into the molecular semiconductor and the mobility determined is correlated with interunit hopping energy:



In the second case, the generation of charge carriers involves, additionally, the dissociation of an ion pair:



An order of magnitude estimate of the ion pair binding energy, E_{ip} , may be calculated from classical electrostatic laws. A value of

0.2-0.3 eV is found^{8,18}. Since $\exp(-\frac{E_{ip}}{2kT}) = 10^{-2} - 10^{-3}$

at room temperature, this rationalizes the mobility difference previously noticed.

In conclusion, it has been shown that macrocyclic radicals can lead to intrinsic molecular semiconductors because of their peculiar redox properties. The charge carrier mobility observed in thin films is shown to be strongly dependent upon ion pair trapping. High speed electronics devices can be obtained however by diminishing the charge carrier migration path¹⁹.

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