Electrosynthesis of a New Molecular Semiconductor: Lithium Naphthalocyanine Radical

Michel A. Petit,* Marcel Bouvet and Didier Nakache

Laboratoire de Chimie et Electrochimie des Matériaux Moléculaires, UA 429 CNRS-ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France

An electrochemical procedure is used to reduce 2,3-dicyanonaphthalene into the lithium naphthalocyanine radical (NPcLi$^\cdot$): a new material with semiconducting properties.

The lithium complex of the phthalocyanine radical PcLi$^\cdot$ is a molecular material with unusual magnetic[1] and intrinsic semiconducting properties.[2] To the best of our knowledge, the related naphthalo compound (NPcLi$^\cdot$) has never been described though it may be interesting to see if the substitution of benzene rings by naphthalene units induces substantial changes in the electrical properties of the macrocyclic material, *i.e.* gap, redox potentials, carrier densities and mobility. An earlier study has already reported on such changes observed in a mixed bis(naphthalo-phthalocyanine)

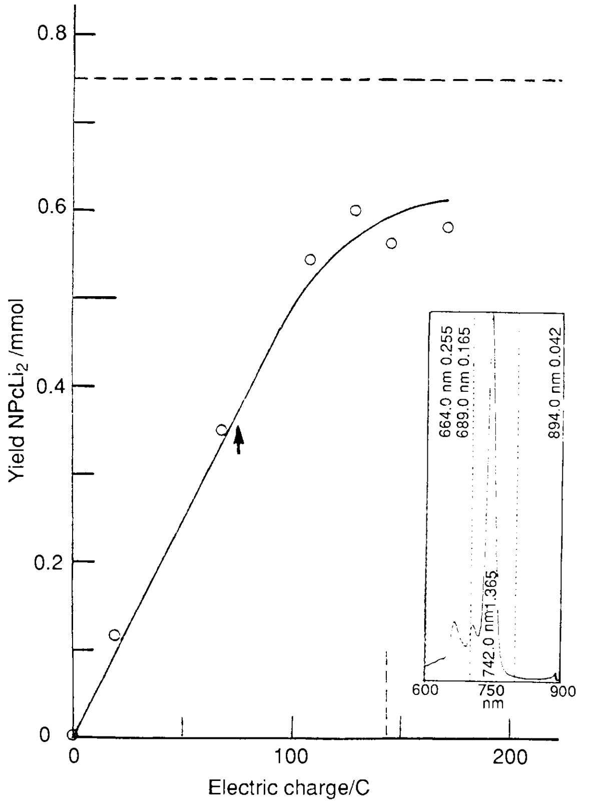

Fig. 1 Yield (calculated from the maximum optical density at 742 nm and an $\epsilon_{742\ \text{nm}}$ value of 2×10^5 dm^3 mol^{-1}) of electrosynthesized $NPcLi_2$ *vs.* electric charge. Insert: visible spectrum of $NPcLi_2$ in a 0.3 mol dm^{-3} lithium ethoxide solution.

complex of lutetium.[3] We describe here a convenient preparation of NPcLi$^\bullet$ by the electroreduction of 2,3-dicyanonaphthalene (DCNP) following a procedure similar to the efficient one that we used for the synthesis of lithium phthalocyanine radicals.[4,5] The starting dinitrile DCNP was prepared according to a known method[6,7] and then sublimed. A 6 mA current was used for the electroreduction of DCNP (3 mmol) in a divided cell[5] kept at 70°C under argon, the solvent being a mixture of ethanol and dimethylacetamide (1 : 1) containing lithium chloride. Electrochemical reduction occurs as shown in eqn. (1). The soluble $NPcLi_2$ species was found and quantified in the catholyte from visible absorption spectra (Fig. 1); λ_{max} (EtOLi, 0.3 mol dm^{-3} in EtOH) 742 nm (ϵ 2× 10^5 dm^3 mol^{-1} cm^{-1}).

$$4\text{DCNP} + 2e^- + 2\text{Li}^+ \longrightarrow \text{NPcLi}_2 \qquad (1)$$

The best preparation of NPcLi$^\bullet$ was obtained by stopping the electroreduction at mid-electrolysis (*ca.* 75 C) and then leaving the catholyte stirring for 15 h at 70 °C under argon. A blue powder was obtained by filtration of the catholyte, washed in a Soxhlet apparatus with ethanol and acetone and dried to give 0.22 g of NPcLi$^\bullet$ (40% yield). A sample of $NPcH_2$ was also prepared, in 35% yield, by exhaustive electrolysis of DCNP and subsequent transfer of the catholyte into an aqueous HCl solution. Stirring the resulting solution for 24 h, leads to a green suspension which was filtered to give $NPcH_2$.

Both compounds gave satisfactory chemical analyses. Fig. 2 shows the IR absorptions of NPcLi$^\bullet$ and $NPcH_2$. An EPR spectrum of an NPcLi$^\bullet$ powder was run in air at room temperature, showing a single line with a peak-to-peak width of 0.55 mT in agreement with a free-radical structure of the compound. NPcLi$^\bullet$ was vacuum vapour deposited onto a transparent support in order to run a visible–near IR spectrum from 400 to 2700 nm, giving absorption maxima at 616, 787, 904 and 1190 nm. Coatings of NPcLi$^\bullet$ were also deposited onto gold electrodes and used as previously described[8] for the measurements of the electrical conductivity (σ) and activation energy (ΔE), the NPcLi$^\bullet$ film always being kept under high vacuum (10^{-6}–10^{-7} Torr) at each stage of the experiment. Stable semiconducting behaviour was observed during several cycles of temperature between 25 and 125 °C: $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ with $\sigma_{25\,°\text{C}} = 1.1\ 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$ and $\Delta E = 1.05$ eV.

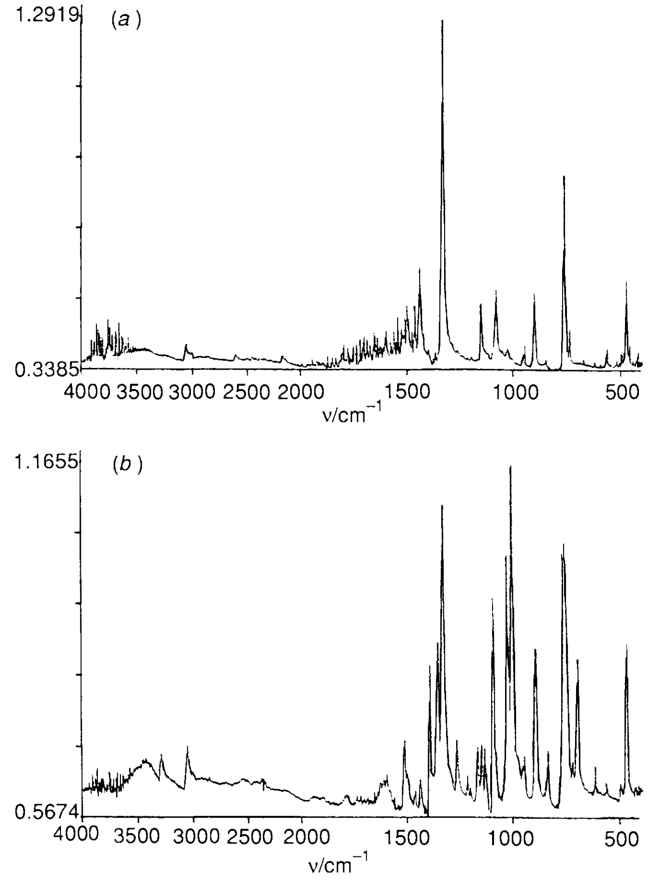

Fig. 2 IR spectra of (*a*) NPcLi$^\bullet$ and (*b*) $NPcH_2$. v/cm^{-1} NPcLi: 472, 762, 898, 1078, 1147, 1330 and 1437.

It is worth pointing out that the thermal activation energy for conduction is well correlated to the absorption maximum at 1190 nm (0.95 eV), which we therefore attribute to an intermolecular charge transfer transition.[1,9]

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