

A One-step Electrosynthesis of a Molecular Semiconductor: Lithium Phthalocyanine Radical (PcLi^\cdot)

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The lithium complex of the phthalocyanine radical (PcLi^\cdot) is prepared in 70% yield by electrochemical reduction of phthalonitrile.

The phthalocyanine radical complex of lithium (PcLi^\cdot)¹ is a member of the class of intrinsic molecular semiconductors.² In spite of its remarkable electric² and magnetic³ properties, its synthesis has been little reported.⁴⁻⁶ We present here a convenient and efficient electrochemical process which directly converts phthalonitrile (PN) into pure PcLi^\cdot in high yield.

The electroynthesis is carried out at 70 °C under inert gas in a divided cell with two electrodes and two compartments separated by a glass-sintered disk (porosity 4). The cathode is

a gold grid and the anode a coiled platinum wire. The electrolysed medium is a stirred absolute ethanol solution (0.1 dm³) containing lithium chloride (3 g, 70 mmol). In a typical example, PN (2.56 g, 20 mmol) is added to the catholyte (0.08 dm³) and a constant current of 66 mA is applied. The catholyte rapidly darkens and the reaction is monitored using the u.v.-vis. spectra of solutions prepared by diluting aliquots withdrawn from the cathodic compartment into an absolute ethanol solution of EtOLi (0.3 mol dm⁻³). We found that the electrolysis produces PcLi_2 according to equation (1).

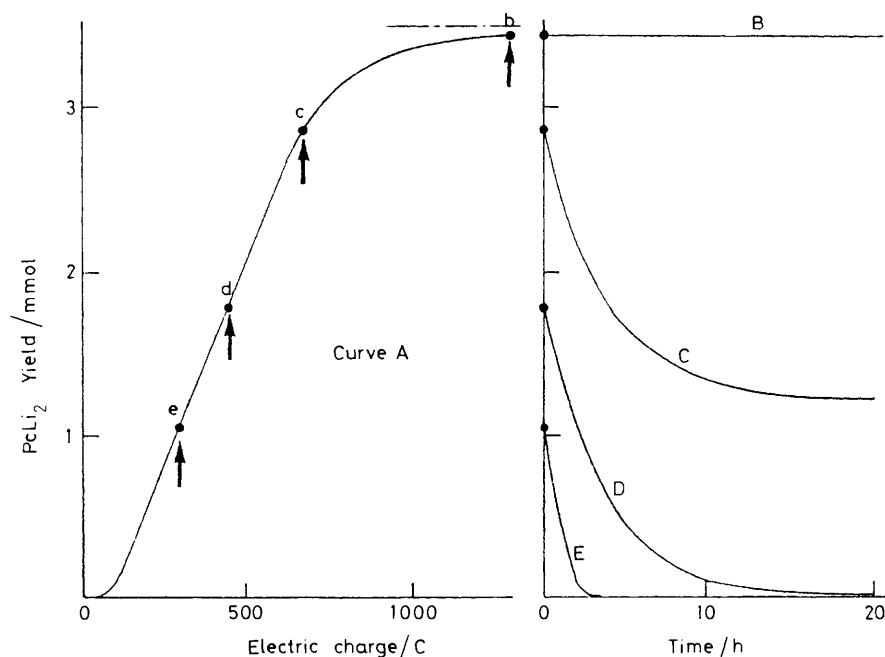
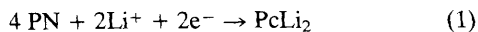


Figure 1. Curve A: yield of electrosynthesized PcLi_2 /mmol versus electric charge. Curves B, C, D, and E: yield of PcLi_2 /mmol versus time in catholytes obtained by electrolysis up to points b, c, d, and e of curve A.



PcLi_2 : λ_{max} . (EtOH, EtOLi 0.3 mol dm⁻³) 664 nm ($\epsilon = 2.5 \cdot 10^5$ dm³ mol⁻¹ cm⁻¹).

Curve A of Figure 1 represents the yield of PcLi_2 in the catholyte *versus* the charge. The curve is divided into three parts. Firstly an induction time, then a linear part with the theoretical slope (1 mole/2F) corresponding to equation (1). The last part shows that the yield of PcLi_2 reaches a plateau value of about 3.5 mmol (chemical yield of 70%) after the passage of the theoretical charge calculated from equation (1).

The stability of the catholyte was tested after stopping the electrolysis at various points on curve A. Each catholyte was left for several hours under inert gas at 70 °C and the amount of PcLi_2 monitored by u.v.-vis. spectroscopy. The changes of the PcLi_2 yields *versus* time in catholytes electrolysed up to points b, c, d, and e of curve A are represented on Figure 1 by curves B, C, D, and E respectively. Three types of behaviour were observed:

— the PcLi_2 amount remains unchanged (curve B) in catholytes obtained after electrolysis up to point b.

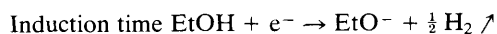
— the PcLi_2 amount decreases and then levels to a constant value (curve C) while a black powder precipitates in the solution.

— the PcLi_2 amount in the catholyte decreases to a zero value (curve E), meanwhile the initially deep blue-green solution turns into a colourless solution with a black material in suspension.

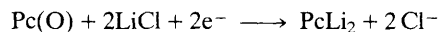
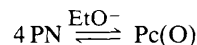
A particular behaviour was observed when the electrolysis was stopped at point d (curve D) corresponding to the passage of half the theoretical charge required by equation (1). In this case, the PcLi_2 amount in the catholyte falls to zero after several hours. We found that if electrolysis is started again, the suspended black material disappears while the PcLi_2 amount increases from zero to the maximum value at point b according to a slope of 1 mole/1F.

The black precipitate is isolated by filtration of the catholyte, purified with hot absolute ethanol in a Soxhlet apparatus and then dried. The material was identified as PcLi^\cdot from elemental analysis, u.v.-vis. spectroscopy⁶ in chloronaphthalene, and i.r. spectroscopy^{4b} in KBr matrix. The best chemical yield is found with catholytes obtained at mid-electrolysis (point d) and left overnight. Under these conditions, PcLi^\cdot is produced with a yield of about 70% (1.80 g, 3.5 mmol).

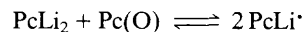
It is worth remarking that 1 mole of PcLi_2 produces two moles of PcLi^\cdot in catholytes isolated at point d. Our results may be rationalized by postulating that PcLi_2 reacts with a precursor Pc(O) of the phthalocyanine macrocycle,⁷ as shown in Scheme 1. A similar intermediate has been proposed in the synthesis of porphyrin derivatives.⁸



then according to Baumann⁹



and finally



Scheme 1

The reaction shown in Scheme 1 seems to be general since we found that various substituted phthalonitriles behave as phthalonitrile and, in the same way, yield the corresponding lithium phthalocyanine radical.

Received, 9th January 1988; Com. 9/00194H

References

- 1 H. Sugimoto, M. Mori, H. Masuda, and T. Taga, *J. Chem. Soc., Chem. Commun.*, 1986, 962.
- 2 P. Turek, P. Petit, J. J. André, J. Simon, R. Even, B. Boudjema, G. Guillaud, and M. Maitrot, *J. Am. Chem. Soc.*, 1987, **109**, 5119.
- 3 P. Turek, J. J. André, and J. Simon, *Solid State Comm.*, 1987, **63**, 741.
- 4 P. A. Barrett, D. A. Frye, and R. P. Linstead, *J. Chem. Soc.*, 1938, 1157; H. Homborg and C. L. Teske, *Z. Anorg. Allg. Chem.*, 1985, **527**, 45.
- 5 H. Sugimoto, T. Higashi, and M. Mori, *J. Chem. Soc., Chem. Commun.*, 1983, 622; P. Turek, J. J. André, A. Giraudeau, and J. Simon, *Chem. Phys. Lett.*, 1987, **134**, 471.
- 6 H. Homborg and W. Kalz, *Z. Naturforsch., B*, 1978, **33**, 1067.
- 7 M. A. Petit, V. Plichon, and H. Belkacemi, *New J. Chem.*, 1989, **52**, 827.
- 8 J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney, and A. M. Marguerettaz, *J. Org. Chem.*, 1987, **52**, 827.
- 9 F. Baumann, B. Bienert, G. Rösch, H. Vollmann, and W. Wolf, *Angew. Chem.*, 1956, **68**, 133.