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LETTER

Electrical conductivity of octakis(decyloxy)phthalocyaninato-copper(II)

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Metallophthalocyanines which are insulators become semi- or metallic-conductors when partially oxidized by means of oxidants such as iodine, nitrosyl tetrafluoroborate ($NOBF_4$) and nitrosyl hexafluorophosphate ($NOPF_6$) [1, 2].

To control the stacking layers of the complexes, polymer complexes of phthalocyaninatosilicon(IV) bridged by a halogen or an oxygen atom were prepared and showed good conductivities when partially oxidized [3, 4]. Furthermore, metallophthalocyanines with hydrocarbon chains were prepared, and the property of their discotic mesophase was investigated [5]. Recently, it has become apparent that the conductivity is significantly influenced by the degree of overlap of the phthalocyanine rings as well as the distance between the rings [6].

We report here the conductivity of a partially oxidized phthalocyanine copper(II) complex with long-chain decyloxy substituents the arrangement of which might be controlled by their fastener effect (Fig. 1).

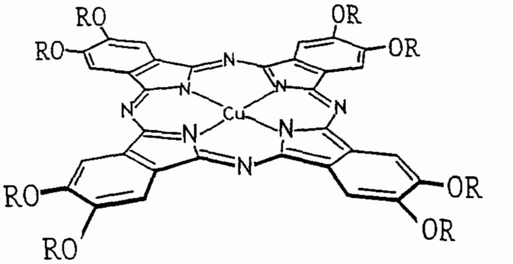

Fig. 1. The $CuPc(OC_{10}H_{21})_8$ complex; $R=C_{10}H_{21}$.

Experimental

Synthesis

4,5-Dicyano-1,2-bisdecyloxybenzene was prepared by a method similar to that described in the literature [7].

A mixture of 4,5-dicyano-1,2-bisdecyloxybenzene (2.0 g, 4.5 mmol), copper(II) chloride dihydrate (1.0 g, 5.9 mmol), ethylene glycol (4 ml) and 1,8-diazabicyclo[5.4.0]undec-7-ene (1 ml) was heated at 180 °C for 5 h. The precipitates obtained were washed with ethanol. Then, the chloroform solution of the precipitates was poured onto an alumina column. Using chloroform as an eluent, a green solution was eluted out (yield 20%). *Anal.* Found: C, 73.25; H, 9.65; N, 5.91. Calc. for $CuPc(OC_{10}H_{21})_8$: C, 73.66; H, 9.71; N, 6.31%.

Partial oxidation and conductivity measurements

To a chloroform solution of the complex, an acetonitrile solution containing adequate amounts of $NOBF_4$ was added dropwise under a nitrogen atmosphere, and then the mixture was stirred at room temperature for 1 h. The doped complex was filtered and dried at room temperature. The degree of doping was determined by means of elemental analyses.

Conductivity measurements of pressed pellets were carried out with a two-probe method.

Results and discussion

It has been reported that oxidation on the central metal slightly affects the Q band, while ring oxidation extensively decreases the intensity of the Q band [8, 9]. During oxidation of $CuPc(OC_{10}H_{21})_8$ by $NOBF_4$, absorbance for the Q band (681 nm) decreased, and a new band appeared at 580 nm (the color of the solution changed from green to reddish purple), showing partial oxidation of the phthalocyanine ring (Fig. 2).

The conductivity of $CuPc(OC_{10}H_{21})_8$ at room temperature increased with the doping rate, but decreased with excess doping: $\log \sigma/\mathrm{S\ cm^{-1}} < -13$ for $x=0$, -7.5 for $x=0.7$, and -8.8 for $x=1.0$, where x is the degree of oxidation, i.e., $CuPc(OC_{10}H_{21})_8(BF_4)_x$. This tendency is in agreement with that of the unsubstituted phthalocyanine complexes [10]. The conductivity of the doped copper(II) complexes increased with an increase of temperature, showing that they are semiconductors. The activation energy of the partially oxidized complex (e.g. $E_{act}=0.15$ eV for $x=0.7$) was lower than that of the undoped complex ($E_{act}=0.78$ eV for $x=0$).

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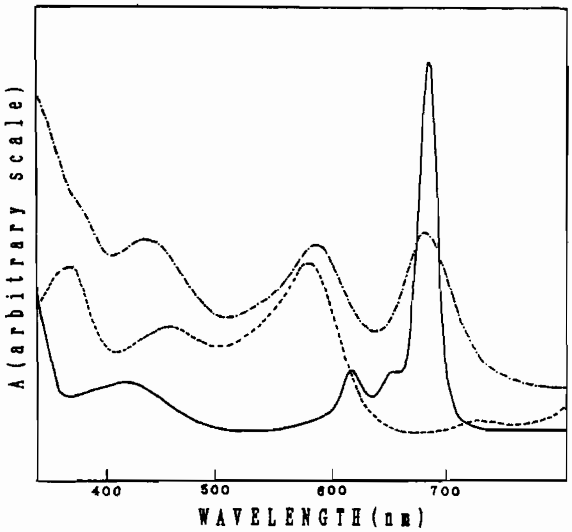

Fig. 2. Electronic spectra of $CuPc(OC_{10}H_{21})_8$ in dichloromethane: (——) $CuPc(OC_{10}H_{21})_8$; (- - -) $CuPc(OC_{10}H_{21})_8(BF_4)_{0.7}$, (· · · · ·) $CuPc(OC_{10}H_{21})_8(BF_4)_{1.0}$.

The conductivity of the powder samples of $CuPc(OC_{10}H_{21})_8$ in which the complex might be orderly stacked by the fastener effect of the long-chain substituents is less than that of the unsubstituted phthalocyanine complexes or the cofacially joined polymeric phthalocyanine complexes [3, 4]. However, by choosing the dopants or the peripheral substituents, this could become one of the methods used to control the stacking of macrocyclic complexes.

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