Synthesis of a New Class of Conductive Organic Compounds based on Phthalocyanines and Iodine

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The title compounds exhibit high electrical conductivity, thermal stability, and a wide range of continuous variation of stoicheiometry and are synthesized by doping phthalocyanines with iodine vapour.

The charge-transfer complexes formed from metallophthalocyanines MPc and iodine represent one of the interesting types of conductive organic solids obtained[1,2] *via* reaction (1) where in general $x < 4$. Regardless of the method of synthesis (codiffusion of the components in a solution[1] or doping by iodine vapour at $t \leq 200$ °C [2]) MPc was oxidized to MPc^+, iodine was reduced to I_2^- or I_3^-. In this work we have investigated doping of MPc by iodine at high temperatures of MPc ($t > 200$ °C). To this end MPc (M = Cu, Zn, Ni, Co, Fe, Mg, H_2) was heated together with iodine in a closed evacuated tube;[3] at t 200—480 °C no reactions, other than (1), were detected. We have found that at $t > 480$ °C a new irreversible reaction, equation (2), occurs, where x can be continuously varied from 0.2 to 1.7, as evidenced by elemental[3] and *X*-ray fluorescence analyses. Based on e.s.r. and optical absorption data we have shown[4] that the product of reaction (2) contains neutral MPc^0, doubly-charged MPc^{2+} molecules of MPc, and iodine anions I^-. Taking into account the charge distribution,

Table 1. Electrical conductivity σ (20 °C), S cm^{-1}, of CuPcI$_x$.

x	0	0.2	0.5	0.8	1.0	1.3	1.5	1.7
σ	*ca.* 10^{-13}	2×10^{-3}	7×10^{-5}	2×10^{-5}	9×10^{-5}	4×10^{-2}	6.5	40

$MPcI_x = (MPc^0)_{1-x/2}\ [(MPc^{2+})(I^-)_2]_{x/2}$, it is clear that the product of reaction (2) is quite different from the products of reaction (1).

$$MPc + x/2I_2 \rightleftharpoons MPcI_x \quad (1)$$

$$MPc + x/2I_2 \rightarrow MPcI_x \quad (2)$$

Since at $t > 480$ °C the saturated vapour pressure p_s of MPc is rather high ($p_s > 0.1$ Torr), reaction (2) is accompanied by a sublimation of MPc molecules. An appropriate choice of conditions for reaction (2) (*e.g.* high pressures of iodine vapour: up to 50 Torr) reduces this loss down to a few weight %.

The case when single crystals of MPc were used for doping is of especial interest. At $t \leq 200$ °C iodine vapour did not enter into the MPc single crystals even at iodine pressures up to 500 Torr.[5] We have found that at $t > 480$ °C where the thermal energy of MPc molecules is comparable with the bonding energy of the crystal lattice, the coefficient of diffusion of I_2 vapour into MPc single crystals increases sharply, making it possible to dope the entire volume of MPc crystals. Crystallinity is retained upon doping in most cases especially at $x < 1.2$, as supported by e.s.r.,[6] *X*-ray, and optical absorption[4] data. The homogeneously doped crystals can be obtained if doping is carried out in the range t 540—580 °C. The homogeneity of doping is deduced from the following: (i) the unusually high thermal stability of the samples (they neither melt nor decompose at heating up to 550—600 °C *in vacuo*[4]) cannot be reasonably explained if there are undoped parts in the crystals; (ii) the e.s.r.,[4,6] optical,[4] and electrical properties of the moderately doped samples do not correspond to a simple superposition of the undoped and heavily doped ($x = 1.7$) ones; (iii) unlike the apparently inhomogeneous crystals, obtained at 480—540 °C, no colour inhomogeneities were observed under an optical microscope, either on the surface or in cross-section for the ones obtained at 540—580 °C.

The ability to vary stoicheiometry within a wide range provides a unique opportunity to investigate and to monitor the evolution of electrical, magnetic, optical, and other solid-state properties of MPcI$_x$, *e.g.* the electrical conductivity of the thin amorphous films of CuPcI$_x$ can be gradually modified in the range from *ca.* 10^{-5} to 40 S cm^{-1} (see Table 1).[4]

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