

## 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 stoichiometry and are synthesized by doping phthalocyanines with iodine vapour.

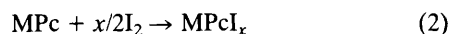
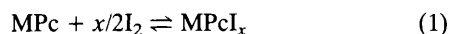
The charge-transfer complexes formed from metallophthalocyanines MPc and iodine represent one of the interesting types of conductive organic solids obtained<sup>1,2</sup> via reaction (1) where in general  $x < 4$ . Regardless of the method of synthesis (codiffusion of the components in a solution<sup>1</sup> or doping by iodine vapour at  $t \leq 200$  °C<sup>2</sup>) MPc was oxidized to MPc<sup>+</sup>, iodine was reduced to I<sub>2</sub><sup>-</sup> or I<sub>3</sub><sup>-</sup>. 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<sub>2</sub>) was heated together with iodine in a closed evacuated tube;<sup>3</sup> 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<sup>3</sup> and X-ray fluorescence analyses. Based on e.s.r. and optical absorption data we have shown<sup>4</sup> that the product of reaction (2) contains neutral MPc<sup>0</sup>, doubly-charged MPc<sup>2+</sup> molecules of MPc, and iodine anions I<sup>-</sup>. Taking into account the charge distribution,

**Table 1.** Electrical conductivity  $\sigma$  (20 °C), S cm<sup>-1</sup>, of CuPcI<sub>x</sub>.

$x$	0	0.2	0.5	0.8	1.0	1.3	1.5	1.7
$\sigma$	ca. 10 <sup>-13</sup>	2 × 10 <sup>-3</sup>	7 × 10 <sup>-5</sup>	2 × 10 <sup>-5</sup>	9 × 10 <sup>-5</sup>	4 × 10 <sup>-2</sup>	6.5	40

MPcI<sub>x</sub> = (MPc<sup>0</sup>)<sub>1-x/2</sub> [(MPc<sup>2+</sup>)(I<sup>-</sup>)<sub>2</sub>]<sub>x/2</sub>, it is clear that the product of reaction (2) is quite different from the products of reaction (1).



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.<sup>5</sup> 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<sub>2</sub> 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.,<sup>6</sup> X-ray, and optical absorption<sup>4</sup> 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*<sup>4</sup>) cannot be reasonably explained if there are undoped parts in the crystals;

(ii) the e.s.r.,<sup>4,6</sup> optical,<sup>4</sup> 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 stoichiometry 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<sub>x</sub>, e.g. the electrical conductivity of the thin amorphous films of CuPcI<sub>x</sub> can be gradually modified in the range from ca. 10<sup>-5</sup> to 40 S cm<sup>-1</sup> (see Table 1).<sup>4</sup>

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