Iodine-doped "crowned" phthalocyanines

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Abstract. In this paper, we describe the effect of iodine doping on the structure and electrical properties of crown-ether-substituted phthalocyanines. For the doped phthalocyanines, a layered two-dimensional structure was found. A.c. impedance spectroscopy revealed that doping strongly increases the bulk electronic conductivity of the "crowned" phthalocyanines and their alkali-metal picrate complexes. The intermolecular barriers for conductivity were not affected by the iodine dopant.

Introduction

Phthalocyanines (Pc's) are known to exhibit semiconducting properties. An important constraint for achieving these properties is a face-to-face-stacked arrangement of the phthalocyanines with small interplanar distances. This stacking provides an extended pathway for electronic charge migration. A second requisite is the presence of free charge carriers, that is, the molecules must have either a fractionally occupied valence or a conductance band. This can be achieved by partially oxidizing the Pc molecules, e.g. with iodine.

\[
Pc + \frac{x}{2} I_2 \rightarrow (Pc)I_x
\]

Iodine is a commonly used reagent because it easily forms charge-transfer complexes with phthalocyanines. These complexes consist of segregated parallel arrays of partially oxidized \(Pc^{+0.33}\) ions and polyiodine \(I_3^-\) ions. In the arrays the Pc units have been reported to have staggering angles of \(\approx 40^\circ\). Semiconducting properties have also been observed with partially oxidized ligand bridged Pc's. Outstanding results have been obtained with iodine-doped single crystals of phthalocyanines. These systems exhibit a temperature dependence of the electrical conductivity usually found for metals.Room-temperature conductivities of \(10^2-10^5\) S/m have been reported. Powdered polycrystalline samples, however, show lower room-temperature conductivities of \(10^{-1}-10^{-4}\) S/m. Studies have revealed the site of oxidation in Cu(Pc)I and Ni(Pc)I to be the ligand \(\pi\) system. On the contrary, in Co(Pc)I it is the metal center which is oxidized. In all systems the conduction pathway leads exclusively through the macrocyclic stacks and not through the polyiodide chains, the principal charge carriers being electron holes.

In earlier publications we have reported on the synthesis and properties of phthalocyanines (1) to which four 18-crown-6 rings are attached.

These molecules can be aggregated with the help of alkali-metal ions which coordinate to the crowns. Ions with large diameters are sandwiched between the crown ethers and induce a face-to-face stacking of the phthalocyanines and the formation of columnar aggregates. The stacking distance in the columns depends on the type of alkali-metal ion and decreases in the series \(K^+ > Cs^+ > Rb^+\). The columnar aggregates display increased electronic conductivities as compared to the non-aggregated systems. The highest conductivity has been measured for the phthalo-
cyanine–rubidium-picrate complex. A.c. impedance studies have revealed that the conduction pathway involves intra-columnar charge migration steps as well as inter-columnar hopping steps. The barriers of the latter steps are lower when alkali-metal ions act as cross-linking agents between the columns. The most efficient cross-linkers are Rb⁺ and Cs⁺ since for these ions the lowest barriers have been measured, viz. ~0.45 eV.

As an extension of these studies we now report on the behaviour of iodine-doped crowned phthalocyanines and their metal picrate complexes.

Experimental

Phthalocyanines substituted with 18-crown-6 and 21-crown-7 rings were synthesized as previously described. The K⁺, Rb⁺ and Cs⁺ picrate complexes of 18-crown-6-substituted copper–phthalocyanine, 1 • K⁺, 1 • Rb⁺ and 1 • Cs⁺, respectively, were prepared as in our previous paper. The phthalocyanine compounds were doped with iodine by keeping them in closed vessels containing elemental-iodine vapour, for two weeks at room temperature. The phthalocyanines-to-iodine molar ratios were calculated from the increase in weight after the doping process and by elemental analyses. A I₂/Pc molar ratio of 2.3 could be reached. Exposing the samples for a shorter time to iodine vapour resulted in lower ratios.

X-ray powder-diffraction patterns of the studied compounds were recorded on Guinier Johannson FR552 and Kiessig powder diffractometers (100- and 400-mm sample to film distances). DSC thermograms were taken on Setaram and Perkin-Elmer DSC-2 differential-scanning calorimeters with a heating rate of 10 K/min. Phase transitions were studied with an Olympus polarizing microscope in combination with a hot stage.

Alternating-current (a.c.) impedance spectra were recorded in the temperature range of 20 to 80 °C on samples which were doped under identical conditions. The analyses of the impedance spectra have been previously reported.

Results and discussion

The iodine dopant appeared to be weakly bound to the investigated materials. TGA measurements showed that the doped compounds are thermally stable up to 90 °C. Above this temperature loss of iodine occurred. The doping process was reversible. The starting phthalocyanines could be recovered by extraction with toluene or by keeping the doped samples under vacuum at elevated temperatures. All doped compounds were air stable. Storage in open bottles at room temperature for extended periods of time, did not lead to a loss of iodine or to a change in physical properties. Undoped 1 is soluble in chloroform and slightly soluble in DMF. After doping with iodine, compound 1 appeared to be soluble in DMF and only slightly soluble in chloroform. UV/Vis revealed that doping had little effect on the solution spectra of 1 and of its free-base derivative. Many examples of donor–acceptor systems are known to show stronger charge transfer in the solid state than in solution. In solution charge transfer is determined by the relative donor and acceptor strength of the solvated components. For instance the TTF/TCNQ system has a strong solvent-dependent charge transfer, which is always weaker in solution than in the solid state.

The X-ray powder-diffraction patterns of the iodine-doped phthalocyanines showed less sharp lines than those of the undoped samples. This indicates that the crystalline structures are distorted when introducing iodine. When doped, compound 1 and its free-base derivative revealed variations in diffraction patterns. The patterns have great similarities with those described by Simon and co-workers for an undoped phthalocyanine similar to 1 but with 15-crown-5 subunits. They have proposed for this compound an orthorhombic structure with a unit cell a = 20.5, b = 18, c = 4.5 Å as shown in Figure 1. The diffraction patterns of the present doped compounds with the larger 18-crown-6 rings could be fitted into a similar structure. Two very intense reflections at 23.8 and 19.6 Å in our samples could be related to a two-dimensional ordered structure in the ab plane as indicated in Figure 1. CPK models showed that the center-to-center distance of the Pc molecules along a two-dimensional square lattice is approximately 22 Å. To fit the crown ethers into the orthorhombic lattice, Simon and co-workers suggested a deformation of the crown ethers out of the plane of the lattice, as shown in Figure 1B.

In our doped samples of 1 two diffuse halos were observed between 4.2–4.1 and 3.4–3.3 Å. These halos have also been reported for liquid–crystalline phthalocyanines substituted with eight aliphatic side chains. These phthalocyanines are surrounded by a paraffinic zone. In the mesophase the Pc molecules are stacked in columns which are organized in two-dimensional hexagonal arrays. Our diffraction patterns showed similarities with this columnar mesophase, but the symmetry of the reciprocal spacings did not fit into a hexagonal ordered structure. Presumably, the reason is that the crown-ether subunits can not fill the voids in the same way as the paraffinic side chains. The diffuse halo at 4.2–4.1 Å can be assigned to inter-crown-ether distance in the crystalline phases. This distance is slightly smaller than that found by Simon et al. for the undoped compounds. The second halo at 3.4–3.3 Å, can be related to the interplanar Pc distance. This distance is slightly smaller than the 3.5 Å found for undoped 1. These data suggest that with doping the interplanar Pc distance decreases. This observation is in accordance with literature data on unsubstituted Pc's where also a decrease of the Pc spacing has been observed when doping with iodine. Since our halos at 4.1 and 3.3 Å were diffuse, they did not correspond to a periodicity of the lattice but only to mean values. This indicates that some disorder is present along the c axis. The doped compounds, therefore, seem to have a two-dimensional layered structure (Figure 1) in which the successive layers are poorly correlated. Some stacking order of the Pc molecules, however, is still present. Similar layered structures have been reported for charge-transfer complexes between π donors substituted with long aliphatic chains, and TCNQ. These complexes have been found to exhibit smectic and nematic mesophases.
calculated from conventional Arrhenius plots of the temperature dependence of the electronic conductivity, \( \sigma = \sigma_0 \exp \left( - \frac{E_a}{k \cdot T} \right) \). A substantial increase of the electronic conductivity by several powers of ten occurs when crowned phthalocyanine 1 and its metal picrate complexes are partially oxidized by iodine. Values of \( 10^{-3} \) to \( 10^{-4} \) S/m (at room temperature) are obtained and must be compared to the values of \( 10^{-4} \) to \( 10^{-7} \) (at 180°C) for the undoped compounds.

### Table II

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \sigma/(S \cdot m^{-1})^a )</th>
<th>( E_a/\text{eV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Doped</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 1 \cdot \text{I}^+ )</td>
<td>( 7.10^{-3} )</td>
<td>0.12</td>
</tr>
<tr>
<td>( 1 \cdot \text{K}^+ \cdot \text{I}^+ )</td>
<td>( 2.10^{-4} )</td>
<td>0.18</td>
</tr>
<tr>
<td>( 1 \cdot \text{Rb}^+ \cdot \text{I}^+ )</td>
<td>( 5.10^{-4} )</td>
<td>0.15</td>
</tr>
<tr>
<td>( 1 \cdot \text{Cs}^+ \cdot \text{I}^+ )</td>
<td>( 2.10^{-4} )</td>
<td>0.15</td>
</tr>
<tr>
<td><strong>Undoped</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 1 )</td>
<td>( 5.10^{-7} ) ( (180^\circ \text{C}) )</td>
<td>1.18</td>
</tr>
<tr>
<td>( 1 \cdot \text{K}^+ )</td>
<td>( 1.10^{-2} ) ( (180^\circ \text{C}) )</td>
<td>1.33</td>
</tr>
<tr>
<td>( 1 \cdot \text{Rb}^+ )</td>
<td>( 3.10^{-4} ) ( (180^\circ \text{C}) )</td>
<td>1.02</td>
</tr>
<tr>
<td>( 1 \cdot \text{Cs}^+ )</td>
<td>( 7.10^{-5} ) ( (180^\circ \text{C}) )</td>
<td>1.09</td>
</tr>
</tbody>
</table>

\( ^a \) It should be noted that these values are dependent on the microstructures of the samples.

**Fig. 5.** Microstructures of samples densified after chemical synthesis (A) and after melting (B).
The increase in the electronic conductivity is larger for 1 than for its metal picrate complexes (Table II). Doped 1 exhibits the highest conductivity. It is difficult to relate the electronic properties of doped materials to crystal structures, since it is not known how many charge carriers are actually generated in each compound when doped with iodine. It is striking, however, that doped 1 is a better conductor than the doped metal picrate complexes of 1. Doping leads to a structural reorganisation, resulting in a smaller interplanar Pc distance for 1 than for its metal picrate complexes. As mentioned above, the structures of metal picrate complexes of 1 do not significantly change upon doping. Apparently, the metal salts prevent any reorganisation and the increase in conductivity seems only to be dependent on the generation of free charge carriers. Therefore, the sequence in conductivity is more or less similar to that of the undoped samples (Table I).

The parallel $R_i Q_i p$ unit in the equivalent circuit (Figure 4) can be explained by the existence of grain boundaries in the samples, or may result from interstack crossing of the charge carriers. To resolve this ambiguity, impedance spectra of samples having different micro-structures were studied. In order to obtain these different micro-structures, samples were densified either after chemical synthesis, or after extensive grinding. In addition, melting the samples provided a third type of micro-structure. Scanning electron micrographs revealed distinct differences in micro-structures (Figure 5).

It appeared that $R_i$ was not influenced. However, $R_p$, was affected, in the sense that the lowest values of $R_p$ were obtained for samples with the smallest grain size. Decreasing the dopant level resulted in increased values for $R_p$. $R_i$ was not affected. At $I_2/P_c$ ratios between 0.5 and 0.9 ($\sigma < 10^{-5} \text{S/m}$), the impedance spectra were similar to those of the undoped samples and could be fitted into the equivalent circuit $R_p C_p p Q_i R_i R_s$. $R_i$ values did not vary on decreasing the dopant ratio. At dopant ratios lower than 0.5, impedance spectra could not be measured accurately at room temperature. $Q$ has values for $\sigma$ of 0.5 and may, therefore, be related to a contribution of iodine diffusion. These data suggest that $R_i$ in Figure 4 represents the barrier between the stacks which charge carriers have to cross. The activation energies, $E_a(R_i)$, for this intercolumnar hopping process are listed in Table III.

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the metal picrate complexes. The rationale is that in the latter complexes the intercolumnar distance is shorter, since the alkali-metal ions act as cross-linking agents. The barrier is dependent upon the size of the metal ion is smaller for the Rb⁺ complex than for the Cs⁺ complex. This can be explained from the fact that Rb⁺ is a more efficient cross-linker than Cs⁺. The barrier for the K⁺ complexes is relatively large, since in this compound the picrate ions are intercalated between the Pc macrocycles.

The present experiments with iodine-doped compounds, clearly reveal that the bulk electronic conductivity is dramatically enhanced when increasing the number of free charge carriers by partial oxidation. The electronic conductivity dominates any ionic contribution of iodine and metal ions. It is of interest to note that the crossing of the charge carriers between the stacks is likely to be the bottleneck of the electronic conductivity in the iodine-doped compounds.

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References

1a J. L. Petersen, C. S. Schramm, D. R. Stojakovic, B. M. Hoffman and T. J. Marks, J. Am. Chem. Soc. 99, 286 (1977);
1b E. Canadell and S. Alvarez, Inorg. Chem. 23, 573 (1984);
1c T. J. Marks, Science 227, 881 (1985);
1h C. J. Schramm, R. P. Scaringe, D. R. Stojakovic, B. M. Hoffman, J. A. Ibers and T. J. Marks, J. Am. Chem. Soc. 102, 6702 (1980);
1k O. Schneider and M. Hanack, Angew. Chem. Suppl. 41 (1982);
1m M. Hanack, U. Keppeler and H. J. Schulze, Synthetic Metals 20, 347 (1987);
1r Y. Tomkiewicz, J. B. Torrance, B. A. Scott and D. C. Green, J. Chem. Phys. 60, 5111 (1974);
1v J. Simon, J. J. André and A. Skoulios, Nouv. J. Chim. 10, 295 (1986);
1w C. Piechocki and J. Simon, Nouv. J. Chim. 9, 159 (1985);
1x D. Musarel, C. Sirlin and J. Simon, New J. Chem. 11, 455 (1987);
1y M. Hanack, A. Beck and H. Lehmann, Synthesis 703 (1987);