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Highly Conductive Crystals Prepared by Electrocrystallization of Potassium Dicyanophthalocyaninatoiron(III)

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Inherently conductive (0.4 $S\cdot cm^{-1}$) crystals of cyanophthalocyaninatoiron(III) were prepared by electrocrystallization of potassium dicyanophthalocyaninatoiron(III) in acetonitrile. This crystal was suggested to have a three-dimensional interplaner overlapping of π-orbitals by X-ray diffraction.

The inherently conductive single crystals of cyanophthalocyaninatocobalt(III) (PcCoCN) were firstly prepared by electrocrystallization of potassium dicyanophthalocyaninatocobalt(III).[1-3] The crystal showed conductivity of 57 $S\cdot cm^{-1}$. The same methodology was applied to prepare crystals of cyanophthalocyaninatoiron(III) to confirm the generality of this type of crystal growth. Dichlorophthalocyaninatoiron(III) was prepared by the reaction of phthalocyaninatoiron(II) with thionylchloride in nitrobenzene at 80 °C.[4] A brown product thus

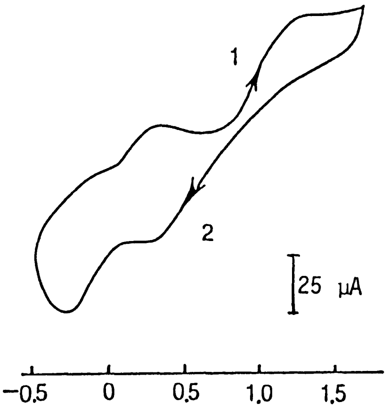

Fig. 1. Cyclic voltammogram for potassium dicyanophthalocyaninatoiron(III) in acetonitrile: scan rate, 50 $mV\cdot s^{-1}$, Pt electrode, surface area, 0.2 cm^2.

obtained was reacted with KCN in boiling ethanol to give purple products.[5] Recrystallization from dry acetone yielded blue-purple crystals. Elementary analysis showed that the crystal was composed of $K^+[PcFe(CN)_2]^-$, Calcd. for$C_{34}H_{16}N_{10}FeK$: C;61.9,H;2.4,N;21.2, Fe;8.5,K;6.0, Found: C;62.1,H;3.2,N;20.6, Fe;7.9,K;6.2%. A sharp absorption band appeared at 2112 cm^{-1} for the vibration of CN in an IR spectrum.[6]

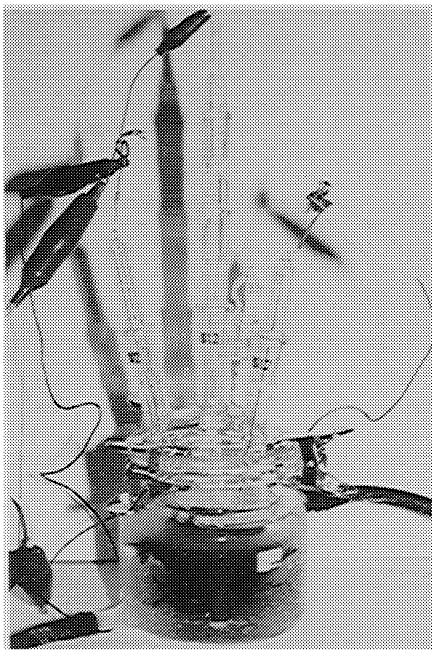

Fig. 2. Cell construction for electrocrystallization.

A cyclic voltammogram for potassium dicyanophthalocyaninatoiron(III) in acetonitrile solution showed the oxidation peak at +1.2 V vs. Ag/AgCl (Fig. 1). This corresponds to the oxidation of the phthalocyanine ring when the results on cobalt complexes and the redox behaviors of other phthalocyanines[7–9] are taking into account. In addition to the ring oxidation, this compound showed a reversible redox cycling of Fe(II)/Fe(III): the oxidation and reduction potential peaks were observed at +0.4 V and -0.2 V vs. Ag/AgCl, respectively.

Electrocrystallization was carried out with a double-walled Pylex glass cell to keep a solution temperature constant. Platinum wires having a surface area of 0.2 cm^2 were used as electrodes, and the distance between those two electrodes was set to be 1.0 cm. A typical cell construction was shown in Fig. 2. An acetonitrile solution containing $1.0x10^{-3}$–$1.0x10^{-1}$ $mol{\cdot}dm^{-3}$ phthalocyanine was set in the cell and constant potential of 1.2 V was applied for several hours. Under this condition, black-purple crystals were grown on the anode surface in a good yield. As has already been found for

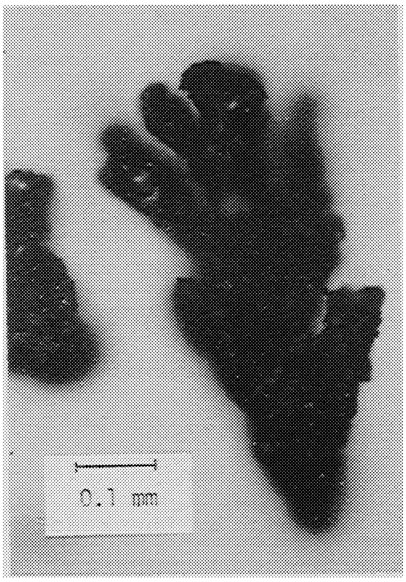

Fig. 3. Optical micrograph of cyanophthalocyaninatoiron(III).

PcCoCN, crystal growth was observed only when the potential for the oxidation of the phthalocyanine ring was applied. A typical optical micrograph for crystals is shown in Fig. 3. The crystals were microcrystalline state and soluble in polar solvents such as alcohols, acetone, and water.

The CN vibrational absorption appeared at 2100 cm^{-1} in the IR spectrum, indicating that a cyano group is bound to the metal ion directly. The existence of the phthalocyanine ring structure was also confirmed by IR and UV spectroscopies. The present crystals were composed of only cyanophthalocyaninatoiron(III) (PcFeCN) which was revealed by elementary analysis, Calcd for $C_{33}H_{16}N_9Fe$: C;66.7,H;2.7,N;21.2,Fe;9.4, Found: C;65.5,H;2.8,N;21.7,Fe;10.0% (Fe;11.9 by atomic absorption spectrum).

Larger crystal growth of cyanophthalocyaninatoiron(III) by electrocrystallization was difficult comparing with that of cobalt complex. Only tiny crystals with length of about 100 nm have been obtained so far.

The conductivity of a pressed disk of cyanophthalocyaninatoiron(III) was measured as 4.1×10^{-1} $S \cdot cm^{-1}$ at room temperature by van der Pauw four probe method. This conductivity was about 1.5 times smaller than that of a pressed disk of cyanophthalocyaninatocobalt(III) crystals. An activation energy was calculated as 0.23 eV from the temperature dependence of the conductivity. This crystal was as stable as that of cobalt complex, and no decay in the conductivity was found after keeping it under air for several months.

To understand the molecular arrangement of this crystal the X-ray powder diffraction analysis was applied, and the same patterns were obtained as those of cyanophthalocyaninatocobalt(III) as shown in Fig. 4. It means that both crystals are isomorphorus and the present crystal of cyanophthalocyaninatoiron(III) has also the three-dimensional

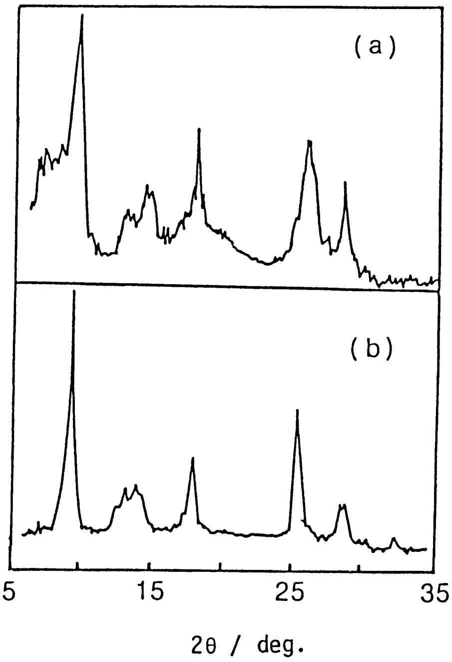

Fig. 4. X-Ray powder diffraction patterns: (a) PcFeCN, (b) PcCoCN.

π- orbital overlap as for cyanophthalocyaninatocobalt(III). Thus, the highly inherent conduction of the present crystal may also be concluded to be due to the three-dimensional π-orbital overlap. ESR measurements revealed that the present crystal had smaller amount of organic spins, compared with 0.83 spin per molecule for cyanophthalocyaninatocobalt(III), though the quantitative measurements have not been succeeded yet because of signal overlapping with that of iron(III). This smaller amounts of spin should be related to the lower conductivity.

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