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Electrochemical synthesis of phthalocyanine–molecular mixed crystals in dilute solution

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ABSTRACT

We report the synthesis of a new phthalocyanine–molecular mixed crystal, $TPP[Cr_xCo_{1-x}(Pc)(CN)_2]_2$, by an electrochemical method using a dilute solution. For the whole range of x, the chemical composition of the obtained single crystals is homogeneous and nearly equal to the nominal one in the dilution solution, as revealed by energy-dispersive X-ray spectroscopy. We have found that the concentrations of the starting materials play a vital role in the homogeneous growth of mixed crystals.

1. Introduction

Molecular materials have attracted considerable attention in industry and basic science by virtue of their functional characteristics such as softness and self-organization. To further develop the functionality of these materials, it is crucial to control the physical parameters, such as lattice constant, carrier density, and local-moment density, by synthesizing mixed crystals [1–3]. In molecular mixed crystals, two or more kinds of molecules exist randomly in a crystallographically equivalent site. If different kinds of molecules form a superstructure, this regular arrangement will also modify the band structure. Thus, the random distribution of the molecules is essential for the discussion on only the dependence of the physical properties on the composition ratio. However, because of their unique stacking, in which molecules having an anisotropic shape stack in a particular pattern by van der Waals force in the crystal, it is difficult to stack different kinds of molecules in a regular manner. In fact, there have been few studies on mixed molecular crystals, e.g., $(TTF)_x(TSF)_{1-x}TCNQ$, made by a chemical reaction method [4].

The axially ligated metal–phthalocyanine molecular conductors $TPP[M(Pc)(CN)_2]_2$ (M = Fe and Cr) exhibit giant magnetoresistance [5,6]. Here, Pc and TPP denote phthalocyanine and tetraphenylphosphonium, respectively. The molecules of $Fe(Pc)(CN)_2$ and $Cr(Pc)(CN)_2$ have a local moment, while that of $Co(Pc)(CN)_2$ has no moment. Since these phthalocyanine–molecular crystals have a magnetic molecule and a nonmagnetic one in a crystallographically equivalent site, we can control the local-moment density by controlling the composition ratio between the above molecules. At low local-moment density, large magnetoresistance has been reported [7]. In order to investigate systematically the local-moment dependence of magnetoresistance and to realize larger magnetoresistance, it is necessary to synthesize homogeneous molecular mixed crystals and to control the molecular composition ratio accurately.

Electrochemical crystallization is a typical method to grow molecular conductors. In this method, one applies a current to the molecular solution and oxidizes (or reduces) the molecules. The starting materials in the solution decrease gradually with time [8]. To obtain large crystals, it is necessary to put excessive amounts of the starting materials in a solution. Thus, there remain precipitated starting materials that cannot dissolve perfectly in the solution. Here, the solution with sufficiently excessive starting materials is called "saturated solution". In the synthesis of mixed crystals, a current is applied to a solution that contains two kinds of molecules, for example, molecule A and molecule B. It is difficult to not only make a mixed crystal but also control the composition ratio between A and B to the target one. Mixed crystals may be

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obtained only in a narrow range of composition ratios. The difference in the solubility for the solvent between A and B might prevent adequate control of the composition ratio in the mixed crystals.

In this study, we synthesized a new phthalocyanine–molecular mixed crystal, $TPP[Cr_xCo_{1-x}(Pc)(CN)_2]_2$ ($TPP[\{Cr(Pc)(CN)_2\}_x\{Co(Pc)(CN)_2\}_{1-x}]_2$), by an electrochemical method, as described in Eqs. (1)–(4). Here, M denotes Cr or Co. In Eq. (1), the starting materials $TPP[M(Pc)(CN)_2]$ (M = Cr or Co) are dissolved in acetonitrile and change into the phthalocyanine-molecular ion $M(Pc)(CN)_2^-$ and the counter ion TPP^+. Eq. (2) indicates that the phthalocyanine-molecular ion is partially oxidized at the electrode. We assumed this intermediate reaction from the starting material $TPP[M(Pc)(CN)_2]$ and the obtained crystal $TPP[M(Pc)(CN)_2]_2$, which were confirmed in the previous study [9,11]. After these reactions, the TPP^+, $Cr(Pc)(CN)_2^{0.5-}$, and $Co(Pc)(CN)_2^{0.5-}$ in a molar ratio of $1{:}2x{:}2(1-x)$ aggregate into a crystal, as described in Eq. (3). Eqs. (1)–(3) are summarized in Eq. (4). The purpose of this paper is to clarify how the solution concentration of the molecules influences the variation in the composition ratio among the crystals synthesized in the same solution and their homogeneity in the saturated solution and the dilute solution.

Fig. 1(a) displays the molecular structure of the axially ligated phthalocyanine of $M(Pc)(CN)_2$ (M = Co, Fe, and Cr) [9–11]. Phthalocyanine is a large cyclic ligand, in which the π-electron orbital exists in the whole range of the molecule, and it can coordinate to various kinds of transition metals. Fig. 1(b) shows the crystal structure of a partially oxidized salt of $TPP[M(Pc)(CN)_2]_2$, which exhibits high electrical conductivity. The $M(Pc)(CN)_2$ is slipped-stacking along the c axis.

$$TPP[M(Pc)(CN)_2] \rightarrow TPP^+ + [M(Pc)(CN)_2]^- \quad (1)$$

$$2[M^{3+}(Pc^{2-})(CN^-)_2]^- \xrightarrow{\text{Electroox.}} 2[M^{3+}(Pc^{1.5-})(CN^-)_2]^{0.5-} + e^- \quad (2)$$

$$\begin{aligned} &TPP^+ 2x[Cr(Pc)(CN)_2]^{0.5-} + 2(1-x)[Co(Pc)(CN)_2]^{0.5-} \\ &\rightarrow TPP[Cr_xCo_{1-x}(Pc)(CN)_2]_2 \end{aligned} \quad (3)$$

$$\begin{aligned} &xTPP[Cr(Pc)(CN)_2] + (1-x)TPP[Co(Pc)(CN)_2] \\ &\times \xrightarrow{\text{Electroox.}} TPP[Cr_xCo_{1-x}(Pc)(CN)_2]_2 \end{aligned} \quad (4)$$

2. Experimental

The starting materials $TPP[M(Pc)(CN)_2]$ (M = Cr and Co) were prepared by a procedure described elsewhere [9,11]. Powders of $TPP[Cr(Pc)(CN)_2]$ and $TPP[Co(Pc)(CN)_2]$ were mixed at the target ratio x. In dilute solution, the mixed powder (10 mg) was dissolved in acetonitrile (100 ml, Wako, Special Grade). In the saturated solution, the mixed powder (50 mg) was put in acetonitrile (60 ml) and the solution was oscillated by ultrasonic waves to dissolve the powder. The solubility of starting materials $TPP[Cr(Pc)(CN)_2]$ and $TPP[Co(Pc)(CN)_2]$ in acetonitrile is 0.063 mg/ml and 0.11 mg/ml at room temperature, respectively. In our saturated solution in x = 50%, we added 24.9 mg of $TPP[Cr(Pc)(CN)_2]$ and 25.1 mg of $TPP[Co(Pc)(CN)_2]$ to the 60 ml acetonitrile. Then, an electrocrystallization glass cell equipped with a glass filter between the two compartments was filled with this solution in argon gas, as shown in Fig. 2(a). The glass filter allows interdiffusion of TPP^+ and $M(Pc)(CN)_2^-$ ions, but prevents the interdiffusion of the target crystals. We put silicone grease between the glass cell and the Teflon parts (valve and adaptors) which prevents the contamination of oxygen and water from the air, and the evaporation of the solvent. The glass cell was placed in the dark room whose temperature is kept at 23 °C by the air conditioner. We controlled the current applied between the two platinum electrodes (φ2 mm × 50 mm and φ1 mm × 50 mm) immersed in the solution of each compartment to keep the voltage between 1.0 V and 1.5 V by using a constant current power supply (Yazawa CS-12Z). This applied current was adjusted between 0.1 μA and 0.5 μA for about 2 months [8]. The obtained crystals were observed by a scanning electron microscope (SEM, JEOL JSM-7600F), which was operated at an acceleration voltage of 15 kV. Element analysis was performed by energy-dispersive X-ray spectrometry (EDS, ThermoFisher Scientific, Noran System 7 X-ray Microanalysis System) equipped with the SEM. We checked the ratio of Cr and Co atoms to reveal the ratio of $Cr(Pc)(CN)_2$ and $Co(Pc)(CN)_2$ in the crystal. The crystal structure was measured by an X-ray diffractometer (Rigaku VariMax RAPID FR-E).

3. Results and discussion

Fig. 2(b) and (c) show crystals grown on the anode in the saturated solution and the dilute solution, respectively. We obtained needle-shaped black crystals, whose typical size was 0.02 × 0.02 × 0.5 ~ 0.1 × 0.1 × 2 mm³. X-ray structural analysis indicated a tetragonal symmetry with the space group $P4_2/n$ for all of the mixed crystals, indicating that the obtained mixed crystals are isostructural to $TPP[M(Pc)(CN)_2]_2$ (M = Cr or Co) [9,11]. Since neither a superlattice nor diffuse scattering was discernible, we can infer that the $Cr(Pc)(CN)_2$ and $Co(Pc)(CN)_2$ molecules existed at random in the crystallographically equivalent site.

Fig. 3(a) shows the relationship between the composition ratio x_{EDS} evaluated from the EDS and the nominal ratio $x_{nominal}$ in the saturated solution. In the intermediate x range (20–50%), the com-

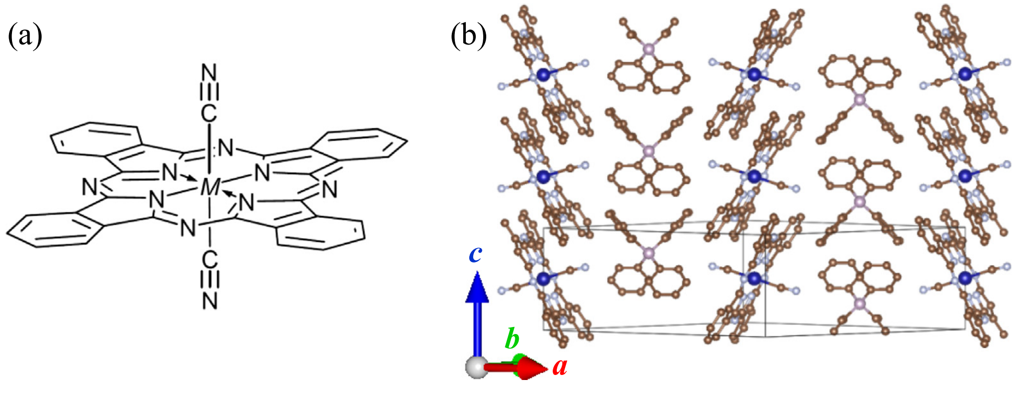

Fig. 1. (a) Molecular structure of $M(Pc)(CN)_2$. The M indicates the transition-metal atom. (b) Crystal structure of $TPP[M(Pc)(CN)_2]_2$ [9–11].