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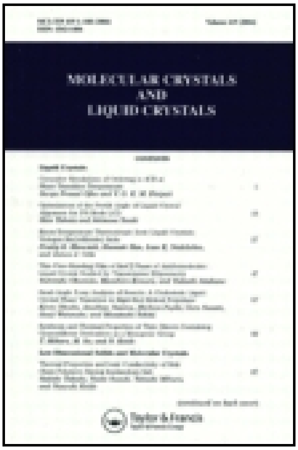

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Band-Filling Control in Organic-Inorganic Hybrid Molecular System

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BAND-FILLING CONTROL IN ORGANIC-INORGANIC HYBRID MOLECULAR SYSTEM

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ABSTRACT Charge control of 1-D energy band of TCNQ stack has been made in a charge-transfer salt using acid-base character of glyoximato-Pd-complex: $[Pd(H_2EDAG)_2]^{2+} \leftrightarrow [Pd(H_2EDAG)(HEDAG)]^{+} + H^{+} \leftrightarrow [Pd(HEDAG)_2]^{0} + 2H^{+}$ (HEDAG=hydro-etylenediaminoglyoxime). Deprotonation of $[Pd(H_2EDAG)(HEDAG)]^{+}$ leads to oxidation of $TCNQ^{-1}$ in a crystallization process. Three different band-fillings(-0.2,-0.7,-1.0) with iso-crystal structures were obtained.

INTRODUCTION

Control of a charge-carrier concentration in the Mott-Hubbard systems provides a unique chance to create the novel electronic states, such as SDW, CDW, the metallic state, or the high-Tc superconductivity as observed in layered-perovskite compounds of 3d transition metal oxides.[1] Various types of molecular metals have been extensively studied as a prototype of the Mott-Hubbard system.[2] However, successful results of band-filling control in the molecular metals have not been reported as yet.

$[M(H_2EDAG)(HEDAG)]TCNQ$(M=Ni, Pd, Pt) is the charge-transfer(CT) organic-inorganic hybrid system. These CT complexes consist of segregated regular stacks of two different chains. One of them is metal-complex chain which does not contribute to conductivity. The other one is TCNQ chain with metallic conductivity from R.T. to ca. 200K. The striking feature of this system is that the average charge of metal-complex chain varies continuously with a protonation-deprotonation process of its ligands. So

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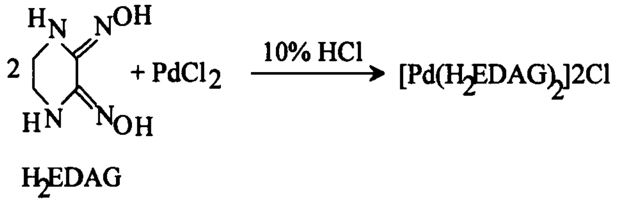
two functions of carrier-doping and carrier- transport coexist separately in [M(H_2EDAG)(HEDAG)] chains and TCNQ stacks, respectively. Taking advantage of this feature, carrier-doping into the TCNQ stacks has been made by protonation and deprotonation of the donor molecules, [Pd(H_2EDAG)(HEDAG)].

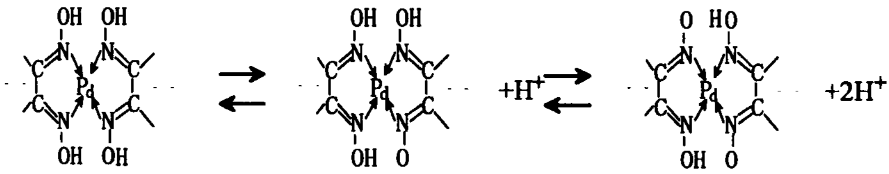
EXPERIMENTAL, RESULTS AND DISCUSSION

As a first step of preparation of filling-controlled samples, glyoximato-Pd-complex, [Pd(H_2EDAG)$_2$]2Cl, was prepared by reaction of H_2EDAG with $PdCl_2$ in 10% HCl



solution.[3] Single crystals of [Pd(H_2EDAG)(HEDAG)]TCNQ complexes were obtained by the method previously reported[3]. The carrier concentration of TCNQ is estimated to be ca. -0.7 from optical analyses of these samples discussed later. This indicates an occurrence of "deprotonation" in (H_2EDAG) molecules during the crystallization, in which glyoximato-Pd-complexes, [Pd(H_2EDAG)]$^{2+}$, are in the following equilibrium states.

(a)



(1) [Pd(H_2EDAG)$_2$]$^{2+}$ (2) [Pd(H_2EDAG)(HEDAG)]$^+$ (3) [Pd(HEDAG)$_2$]^0

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In basic solution, (3) is more stable than the other two states. Both of protonated and deprotonated glyoximato-Pd-complexes were obtained by using this character of equilibrium states, as follows.

(b) $2H_2EDAG + PdCl_2 \rightarrow [Pd(H_2EDAG)(HEDAG)]Cl + HCl$ (in H_2O)

(c) $2H_2EDAG + PdCl_2 \rightarrow [Pd(HEDAG)_2] + 2HCl$ (in NH_3 and NH_4Cl buffer solution)

In order to synthesize samples having an arbitrary degree of deprotonation, DMSO solvent with a mixing of four elements was used.

(d) $x[Pd(H_2EDAG)(HEDAG)]^+ + (1-x)[Pd(HEDAG)_2]^0 + xTCNQ^- + (1-x)TCNQ^0$

$\rightarrow [Pd(H_2EDAG)_x(HEDAG)_{2-x}]TCNQ$ (in DMSO;dimethylsulfoxide)

DMSO dissolves both of starting materials and final CT products. Accordingly a few drops of distilled water were added into the DMSO solution for extraction of powdered samples. The reaction (e) is rather suitable for crystallization of the CT complex with x=1.0.

(e)$[Pd(H_2EDAG)(HEDAG)]^+ + TCNQ^- \rightarrow [Pd(H_2EDAG)(HEDAG)]TCNQ$ (in H_2O)

From the reaction of (d), three kinds of CT complexes(x=0.2, 0.8 and 1.0) were successfully obtained. The crystal structures of obtained samples were examined by X-ray diffraction technique with Mac Science M18XHF-SRA diffractometer. X-ray powder diffraction patterns of these samples are shown in FIGURE 1. All of three samples are isostructural. Sample of x=0.2 seems to have some disordering.

A carrier concentration of the TCNQ stack of these samples was estimated by using Raman shifts of Ag-stretching mode (C=C) of TCNQ molecules[4]. Raman measurements were made by JASCO NR-1800 with an excitation at 514.5nm. The results are shown in FIGURE 2. The estimated values (ρ) are almost coincident with the mixing rate of x;

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The samples with ρ =-0.2, -0.7, -1.0 were obtained from x=0.2, 0.8, 1.0, respectively.

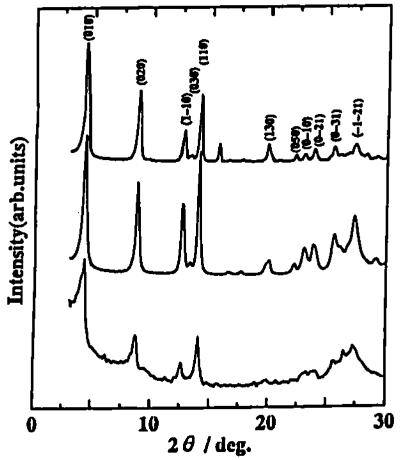

FIGURE 1 X-ray diffraction patterns of $[Pd(H_2EDAG)_x(HEDAG)_{2-x}]TCNQ$ (x=0.2, 0.8, 1.0)

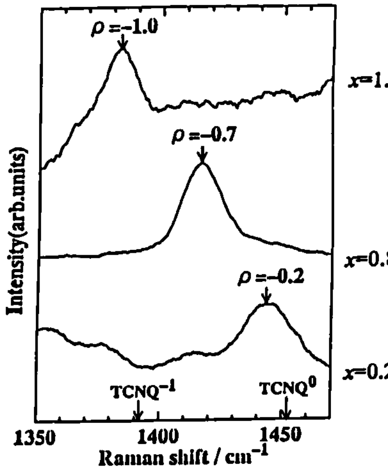

FIGURE 2 ρ estimation from Raman Shifts of Ag stretching mode(C=C) of TCNQ

As previously reported[5], the partial CT complexes (ρ =-0.7) shows the metal-to-insulator (M-I) transition around 200K with a large histeresis of ca. 50K. The driving force of the M-I transition is considered due to the localization of carriers in the TCNQ stacks accompanying with freezing of the motion of protons in intermolecular H-bonds. The band-filling control performed here is expected to provide a more detailed information about the mechanism of the M-I transition. As a microscopic probe of the electronic state of TCNQ molecules the vibration of C≡N stretching is quite useful because of its high sensitivity to the formal charge of TCNQ molecule. IR measurements were made on powdered samples by using a Nicolet FTIR 800. In FIGURE 3(a), the spectra above and below the M-I transition temperature for ρ =-0.7 are presented. The optical-active B_{1u} mode of the C≡N stretching (2196cm^{-1}) splits into two peaks at low temperature, indicating that the averaged valence state of TCNQ in the metallic state separates into the mixed-valence states of $TCNQ^0$ and $TCNQ^{-1}$.[6] This is corresponding to the localization of carriers in the insulating phase. On the other hand, for a fully ionic sample, ρ =-1.0, which is expected to be an insulator, the B_{1u} mode

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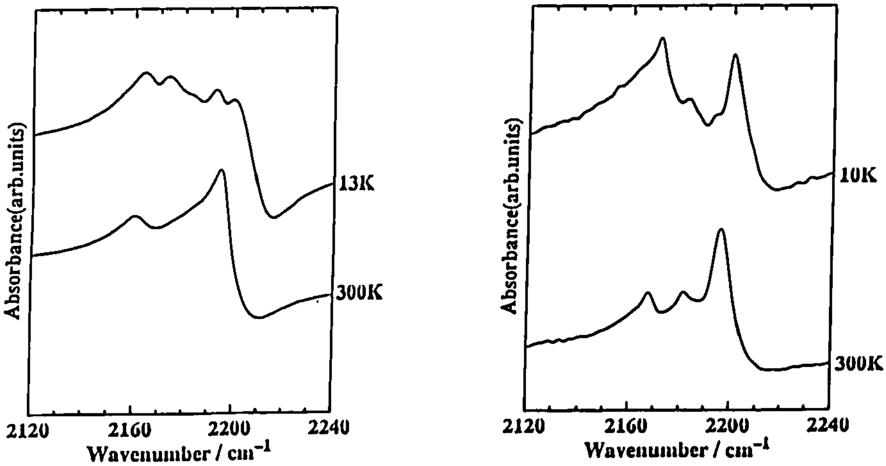
(2195cm^{-1}) does not split, as shown in FIGURE 3(b). This is consistent with the half-filled state. Furthermore, the Ag mode (2180cm^{-1}) of the C≡N stretching is more clearly observed compared with that for ρ =-0.7. Since the Ag mode is optically active under a dimerric distortion[7], this is attributable to the Spin-Peierls distortion in the half-filled Mott insulator. Further precise control of the band-filling is now in progress. The way of band-filling control performed in this study is expected to be applicable to other organic-inorganic hybrid systems.



(a) ρ=-0.7

(b) ρ=-1.0

FIGURE 3 IR spectra of [Pd(H$_2$EDAG)$_x$(HEDAG)$_{2-x}$]TCNQ

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