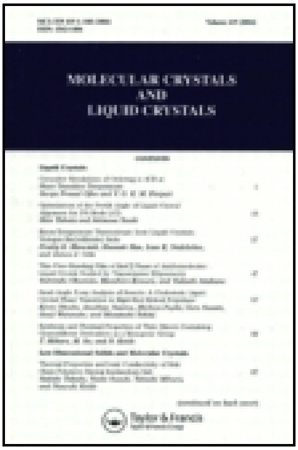

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ELECTRON-PROTON CO-OPERATION IN 1-D d-π ELECTRONIC STATE -BASIC STUDY OF PROTONO-ELECTRONICS-

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Abstract The electron-proton co-operation in organic-inorganic hybrid systems, [Pd(H_{2-x}EDAG) (HEDAG)] · TCNQ and [Pt(H_{2-x} DAG) (HDAG)] · TCNQ complexes, leads to two different types of the metal-insulator transition, which originate in the instability of the 1-D π electronic state of the TCNQ stacks. Here, HDAG or HEDAG stands for hydro- or hydroethylene-diaminoglyoxime. Their driving forces are attributable to freezing of the fluctuation of protons in the interchain H-bonds and the charge transfer from the [Pt(H_{2-x} DAG) (HDAG)] metal complex to TCNQ stacks, respectively.

INTRODUCTION

"Protono-electronics" previously proposed[1] means a generation of molecular functions by competition or co-operation of proton and electron having independent degrees of freedom in solids. There are many possibility to create new functions if we consider the characteristic properties of the proton, such as light mass, quantum fluctuation, and the strong proton-electron correlation. Among them, the fluctuation of protons in the intermolecular H-bonds has been demonstrated to be significantly useful for design and construction of new molecular functions using the organic-inorganic hybrid systems[1] Fig. 1 shows a schematic model of these systems, which has been realised in[Pd(H_{2-x}EDAG) (HEDAG)] · TCNQ and [M(H_{2-x}DAG) (HDAG)] · TCNQ complexes. Here, M=Ni, Pd, Pt, and HEDAG or H_2EDAG stands for hydro- or dihydro-ethylene-diaminoglyoxime, respectively.[1-4]

This system has three basic functions required for construction of quantum molecular devices,[1] namely "transport", "storage or supply", and "control" of electrons, as shown in Figure 1: a) The "electron transport" in the 1-D π-electronic state is constructed by a segregated stack of TCNQ molecules. b)The "storage or supply" of electrons is achieved by control of the valence instability of M ions or by hole-doping into the TCNQ stack through deprotonation from the ligand of M, i. e. change of $(H_2EDAG)^0$ into $(HEDAG)^{-1}$. c) The third is the "control" of the 1-D π-electronic state, which can be made by using the " quantum switching" character of H-bond between (H_2EDAG) (or (H_2DAG)) and TCNQ molecules. Since the system as a whole is the charge-transfer (CT) complex composed of the donor molecules of $[M(H_{2-x}DAG)(HDAG)]$ chain and the acceptor molecules of TCNQ stack, the character of the three functions becomes active when the system is electrostatically balanced. Particulaly, the dynamics of electron and proton are essentially influenced by a degree of the CT and/or a concentration of the doping.

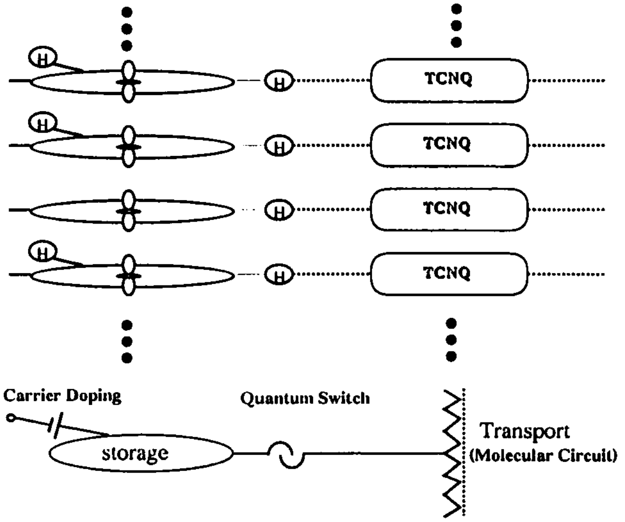

FIGURE 1 A Schematic crystal structure of $[M(H_{2-x}EDAG)(HEDAG)] \cdot TCNQ$, M=Ni, Pd, or Pt.

Thus, the co-operation of these three functions is expected to form a new molecular functions as a whole system. In this report, on the basis of semi-empirical calculations of the co-operation and the experimental results of the temperature-dependent X-ray analysis, we will characterise two different types of the metal-insulator (M-I) phase transition observed in [Pd(H_{2-x}EDAG) (HEDAG)] · TCNQ and [M(H_{2-x}DAG) (HDAG)] · TCNQ complexes. The experimental results of the conductivity, the IR vibration, ESR, and XPS measurements provide clear concepts for these new M-I transitions.

THE FLUCTUATION OF PROTON

The crystal structures of [Pd(H_{2-x}EDAG) (HEDAG)] · TCNQ and [Pt(H_{2-x}DAG)(HDAG)] · TCNQ are presented in Figure 2 a) and b).

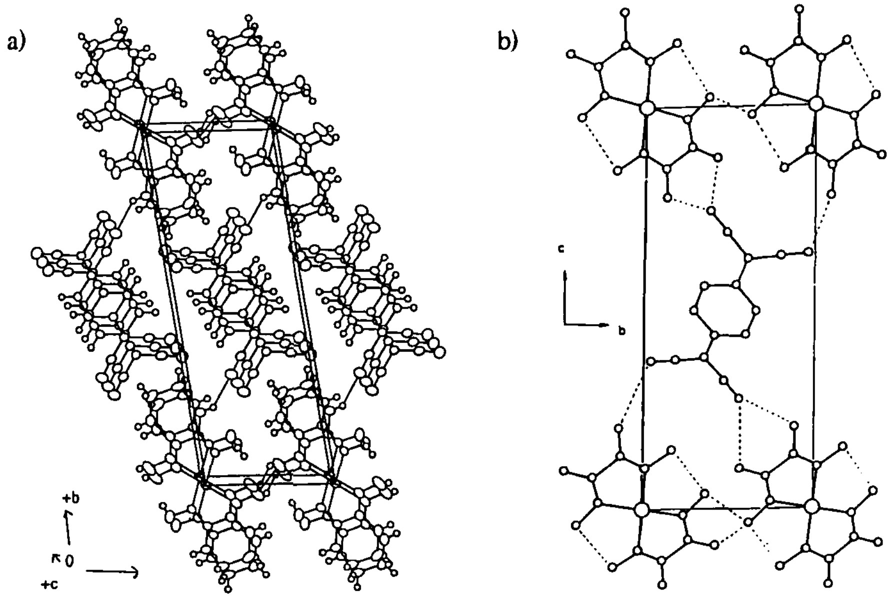

FIGURE 2 The crystal structures of a) [Pd(H_{2-x} EDAG) (HEDAG)] · TCNQ and b) [Pt(H_{2-x} DAG)(HDAG)] · TCNQ.

In the both crystals,[2] the M chain is not expected to contribute to an electric conduction due to a considerably large M-M distance of ca. 3.9 Å but it has a function of carrier-doping in the system as discussed later. On the other hand, TCNQ segregated stacks have a large π-overlap integral due to a small plenary distance of ca. 3.2 Å. Since the π orbitals of TCNQ is perpendicular to the inter-molecular H-bonds, there is no mixing between them and the electron fluctuation along the 1-D stack co-operates with the motion of protons purely through the electrostatic interaction. Accordingly, the motion of proton is sensitively influenced by the charge distribution of TCNQ molecules and by a total amount of the CT. In order to investigate the doping effect on the motion of proton, the semi-empirical unrestricted-Hartree-Fock calculations (MOPAC) were made on a pair-molecular model of $[M(H_2DAG)(HDAG)] \cdot TCNQ$, in which M=Pd was replaced by Zn for simplisity and the crystal parameters of M=Pd obtained at room temperature was used. The results are shown in Figure 3. a) When the system is neutral, the potential for the proton coodinate in the inter-molecular N-H ··· N bond shows a double-well structure, which has a minimum on a side of the $[M(H_2DAG)(HDAG)]$ molecule. b) With doping of an electron into the system, excess electrons distributes almost upon TCNQ molecule and the potential minimum transfer to a side of TCNQ molecule. This result indicates an occurrence of a proton transfer from $[Pd^{2+}(H_2EDAG)^0(HEDAG)^{1-}]^{1+}$ to $TCNQ^{1-}$. In this case, the H-bond should be treated in a strong coupling regime,[5] and the N-H N stretching mode might be unobservable due to a shift of the frequency to a lower energy and a considerable broadening of the structure with an increase of fluctuation of proton motion.[6] c) With further doping of $2e^-$, the potential becomes almost same as the neutral one.

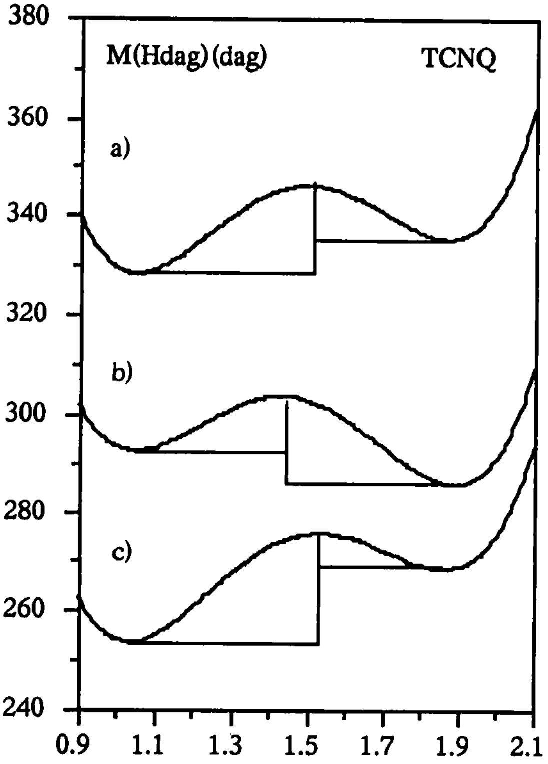

FIGURE 3 The doping effect on Heat formation energies of $[Zn(H_2EDAG)(HEDAG)] \cdot TCNQ$ as a function of proton reaction co-ordinate, a) neutral, b) e^-, and c) $2e^-$.

Although these calculated results could not be dirrectrly applied to the experimental results, it has been confirmed that thare is a close correlation between the motion of proton and the electron density in the TCNQ stack and a possibility of the proton transfer accompaning with the doping.

EXPERIMENTAL RESULTS AND DISCUSSIONS

a) [Pd(H_{2-x} EDAG) (HEDAG)] · TCNQ

In preparation of metallic samples, we employed a new carrier-doping method utilising deprotonation of the ligand of (H_2EDAG): [7] The control of carries was made by crystallisation in the solvent of DIMSO (+ H_2O) with a mixture of

(x) $[P^{2+}(HEDAG)_2{}^{1-}]^0$, (1-x) $[Pd^{2+}(H_2EDAG)^0\ (HEDAG)^{1-}]^{1+}$, and LiTCNQ.

Accordingly, holes with a concentration of x are doped in a half-filled band of $TCNQ^{1-}$stack, leaving an incomensulation of protons in the [Pt(H2-xDAG) (HDAG)] chain as shown Figure 1. By the Raman spectroscopy of the samples, it was confirmed

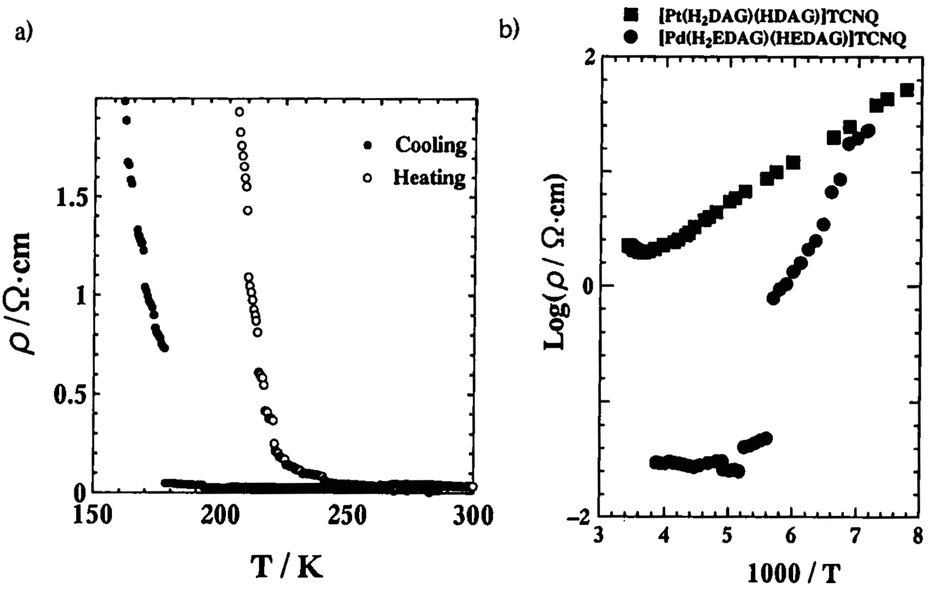

FIGURE 4 Temperature dependences of the conductivity of [Pd(H_{2-x}EDAG) (HEDAG)] · TCNQ a) as a function of T and b) comparison with [Pt(H_{2-x}DAG) (HDAG)] · TCNQ complexe in a logarithmic scale against 1/T.

that an averaged-valence of TCNQ $^{\rho}$ is stable for ρ = - 1, - 0.7, or - 0.2. The details is reported in other paper.[7] For x=0, the crystal is completely ionic and semiconducting. In a partially deprotonated crystal of x = 0.7, a metallic phase appears around room temperature and the metal-insulator (M-I) phase transition occurs at ca. 160 K with a large hysteresis of more than 50K upon a heating process, as shown in Figure 4 a).

A similar hysteresis was observed in the vibration spectra of N-H stretching mode of the inter-molecular H-bonds in coincidence with the M-I transition shown in Figure 4 (a). It was a quite interesting that the N-H stretching band observed in the insulation phase disappears in the metallic phase.[3] These behaviours indicate that electron-carriers in the 1-D TCNQ stack transport above under the influence of the fluctuation of protons and presumably they are localised accompanying with the freezing of the protons in the H-bond network, which provides an observation of the N-H mode below the M-I transition.

While, the sharp ESR signals were observable at low temperatures considerably lower than the M-I transition point. Their g values of 2.00248 and 2.00268 at room temperature are coincident with those of TCNQ ions. Decreasing temperature, its intensity reduces monotonically without any spectral chamge around the M-I transition point. A concentration of spins is ca. 0.05 spin/mol at room temperature. This indicates that almost

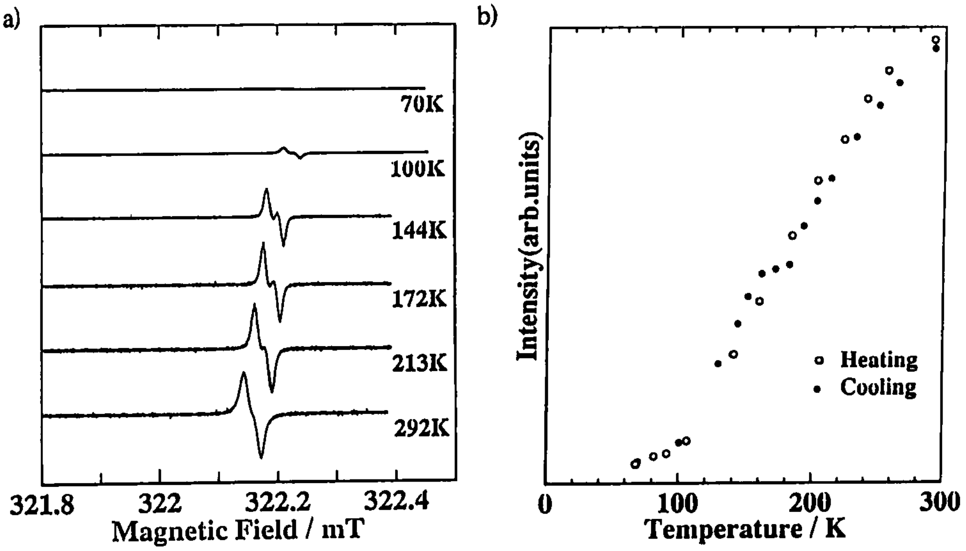

FIGURE 5 Temperature dependencies of a) ESR signals and b) their intensities of [Pd(H_{2-x} EDAG)(HEDAG)] · TCNQ for x=0.7.

electron-spins in the TCNQ stack form a singlet spin-pair and spins detected by the ESR measurements are thermally excited from the spin-pairs. In addition, it is noticed that a half-width is extremely small less than 0.2 mT and almost temperature-independent. This is attributable to a small spin-lattice relaxation rate in the 1-D electronic state highly isolated by the proton network.

These spin-charge-separated phenomena in 1-D system require a new model for an interpretation of the metallic state. Considering the singlet ground state stabilised by the dimmeric-lattice modulation along the stacking axis, a bipolaron (S=0) carrying a charge ($2e^-$) provides a suitable interpretation to the spin-charge separation including the close correlation of charge-fluctution and motion of protons mentioned above.

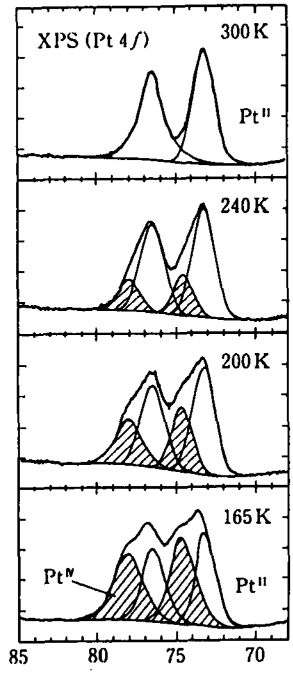

FIGURE 6
Temperature dependence of XPS spectra of [Pt(H_{2-x} DAG)(HDAG)] · TCNQ.

b) [Pt(H_{2-x}DAG) (HDAG)] · TCNQ

The essential difference of the crystal structure between [Pt(H_{2-x}DAG) (HDAG)] · TCNQ complex and [Pd(H_{2-x} EDAG) (HEDAG)] · TCNQ complex is in the interchain H-bonds, in which many H-bonds are contributing to the inter-chain coupling, as shown in Figure 2 b). This might induce a large fluctuation of proton and suppress the freezing of the proton motion observed in [Pd(H_{2-x} EDAG) (HEDAG)] · TCNQ at the M-I phase transition around 200 K. In fact, there were observed no distinguishable changes of the IR spectra corresponding to the freezing. Instead, by the XPS measurements, it was found that the mono-to-mixed valence transfomation in Pt atoms takes place gradually below the transition temperature as shown in Figure 6. This indicates the occurrence of the CT from Pt atoms to TCNQ molecules, which has been confirmed by the X-ray analysis of temperature-dependent crystal structure.[8] These analysis also indicates that the π - electronic state of the TCNQ stacks is no more orthogonal to the H-bonds but there seems to occur a considerable mixing between them accompanying with the CT. In this cense, the M-I transition observed in this complex is essentially different from that of the [Pd(H$_{2-x}$EDAG) (HEDAG)] · TCNQ complex mentioned before. Thus, it is note that the moophology of the H-bond network plays an essential role in the co-operation of the moleculare functions. The more detailed investigation of the proton motion by the temperatute-dependent X-ray analysis is now in progress.

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