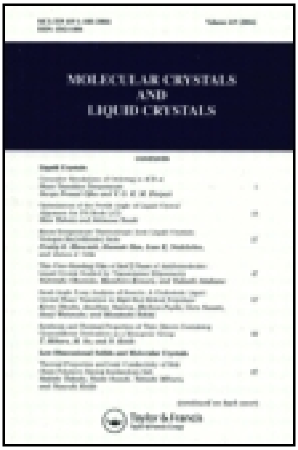

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A New Molecular System: Cooperation of Transition Metal Chain and Ct Stack via Inter-Molecular H-Bonds

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A NEW MOLECULAR SYSTEM:COOPERATION OF TRANSITION METAL CHAIN AND CT STACK *via* INTER-MOLECULAR H-BONDS

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Abstract A new aspect for design and construction of a electron-proton hybrid system using the elements of 1-dimensional metal chains, acceptor (or donor) molecules, and interchain H-bonds is proposed. As the first demonstration of this system, the experimental results of the optical and transport measurements on [M(H_2DAG)(HDAG)]TCNQ (M = Ni, Pd, Pt, and H_2DAG:diaminoglyoxime) single crystals are presented.

INTRODUCTION

The formation of the 2-dimensional (2-D) H-bond network in solids provides a unique opportunity for construction of a novel molecular assembly, which is a combination of the 1-D electronic systems coupled each other through the intermolecular H-bonds.[1] A typical model of this system is shown in Figure 1, where M stands for a 1-D metal chain containing ligands, L. A (or D) for a acceptor (or a donor) molecule, and H for a proton in the H-bond. A new molecular functions is expected to be produced in this system, if the motion of proton is closely correlated with the dynamics of the 1-D electronic states. This situation might be realized in a valancing condition of the redox potential and the electrostatic energy of the system.[1] In such a case, a partial charge-transfer (CT) will take place

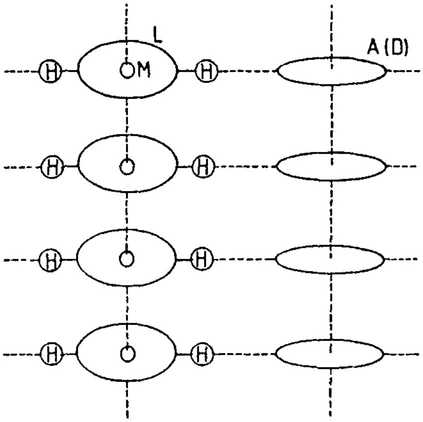

FIGURE 1 A model of a hybrid system of the electron and proton systems using 1-D metal chains, A (or D) molecular stacks and inter-system H-bonds.

between the components in a similar way of the segregated-stacked charge-transfer complexes.[2] In addition, the proton lattice will be disordered or melt quantum-mechanically through the electron-proton interaction.[1] Conversely, conduction electrons will moves under the influence of the quantum-mechanical motion of protons. Thus, the electron-proton hybrid system includes many fundamental problems in solid state physics, such as the order-disorder transition, the metal-insulator transition, and the CDW-SDW transition induced by cooperative electron and proton transfers.

The essential aspects of the proposal in this paper are based on our experimental results associated with H-bonds in solids as followed.

i) The interchain H-bond has a unique ability to control of the mixed-valence state of the 1-D halogen-bridged metal complexes as demonstrated by the H-bond effect on the CT exciton in figure 2.[3,4] Strengthening the interchain H-bonds between the ligands and the counter anions, the CT exciton shifts to a lower energy due to the decreasing of the Peierls distortion of the chain. In an aid of increase of the on-site electron-electron repulsive energy, i. e. the replacement of M = Pt or Pd by Ni, the mixed-valenced state is transferred into the mono-valenced state. This can be characterized by the CDW-SDW phase transition in the quasi-1-D system. Near this phase boundary, the soliton interacting with the interchain H-bonds has been observed, and a new type of the quasi-1-D transport mechanism of the soliton has been proposed.

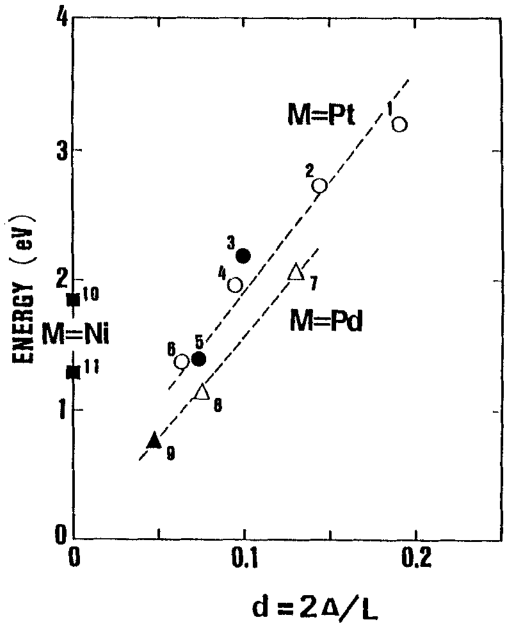

FIGURE 2 The H-bond effect on the CT exciton in 1-D halogen-bridged charge transfer crystals. (The complex having the strong H-bond is represented by closed characters.)

1: $\{Pt(chxn)_2Cl\}(ClO_4)_2$
2: $\{Pt(en)_2Cl\}(ClO_4)_2$
3: $\{Pt(chxn)_2Cl\}Cl_2$
4: $\{Pt(en)_2Br\}(ClO_4)_2$
5: $\{Pt(chxn)_2Br\}Br_2$
6: $\{Pt(en)_2I\}(ClO_4)_2$
7: $\{Pd(en)_2Cl\}(ClO_4)_2$
8: $\{Pd(chxn)_2Br\}(ClO_4)_2$
9: $\{Pd(chxn)_2Br\}Br_2$
10: $\{Ni(chxn)_2Cl\}Cl_2$
11: $\{Pt(chxn)_2Br\}Br_2$

ii) The presence of the cooperative proton-electron transfer (PET) state (see Figure 3) in the H-bonded CT crystals was demonstrated by the IR spectroscopy of quinhydrone charge-transfer complexes under high pressures.[5] This was followed by chemical modification of quinhydrone, which provided an additional information for the exploration of new electron-proton cooperation in charge-transfer crystals.[6]

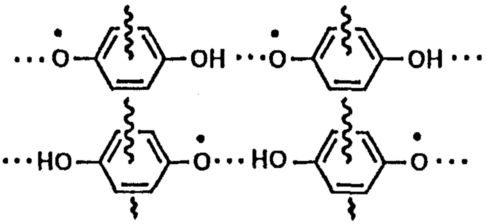

FIGURE 3 Schematic structure of the proton-electron transfer (PET) state of quinhydrone single crystals.

iii) Very recently, it has been experimentally confirmed that the quantum mechanical motion of protons in H-bonded linear chain is enhanced by doping electrons using the acetylenedicarboxylic acid crystals. By detailed investigation of the isotope effect on the IR spectra, it has been found that the quantum motion of proton is sensitive to change of the charge distribution (or the electronic bonds) surrounding the H-bonds.[7]

As suggested in these experimental results, the hybrid system is expected to show a novel type of electric transport coupled with the proton motion. If the proton lattice is quantumly melt, the system becomes exceptionally unique. There might be a possibility of observation of a high T_c superconductivity due to strong coupling with a high vibrational frequency of the H-bond.[1]

As well-known, the Little's model has been proposed about 30 years ago in order to realize a 1-D high T_c superconductivity on the basis of an excitonic mechanism.[8] Endres has been synthesized a new type of a charge transfer crystal, $[Ni(H_2DAG)(HDAG)]TCNQ$, where H_2DAG presents diaminoglyoxime, as an extension of the Little's model.[9] It is interesting to note that the structure of this complex includes essential aspects of the hybrid system proposed here, although the inter-molecular H-bond seems to be used only for an electronic isolation between metallic and excitonic systems in his reports. While, in the present model, the H-bond has a fundamental role to provide an additional freedom of the quantum motion in the system. Namely, the quantum-mechanical coupling between the electron and proton systems is supposed to be essential to create a new function in our model. Thus, the $[M(H_2DAG)(HDAG)]TCNQ$ complexes can be recognized as one of model materials for test of our proposal. As the first step of our research project of this system, we have made an effort to obtain good single crystals of the M = Ni, Pd, and Pt complexes and examined their optical and transport properties.

EXPERIMENTAL

In Figure 4, the absorption spectra of the complexes on powders at room temperature are presented. The structures assigned to the intermolecular (A and B) and intramolecular (C and D) transitions of the TCNQ stack are clearly distinguished, as usually observed in the metallic compounds such as NMP-TCNQ.[10] The appearance of the A band, which has been assigned to the CT transition within the partially filled band, suggests the occurrence of a similar partial CT from the M chain to the TCNQ stack in all of the M(H_2DAG)(HDAG)]TCNQ compounds.

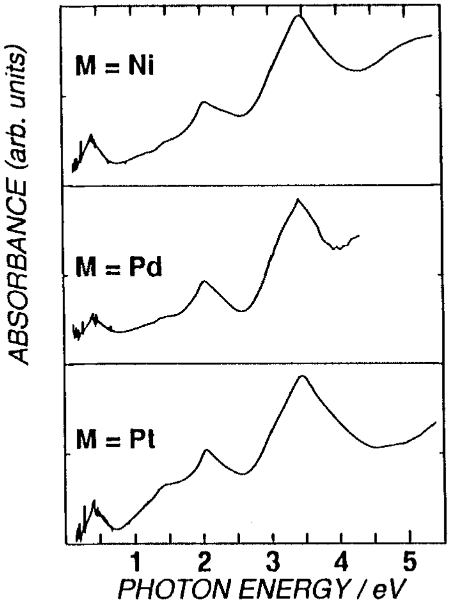

FIGURE 4 The absorbance of the powder samples of M(H_2DAG)(HDAG)]TCNQ (M = Ni, Pd, and Pt).

As expected from these optical spectra, all of these complexes have considerably high conductivities at room temperature as shown in Figure 5, in which the conductivities of the single crystals are plotted as a function of 1/T in a logarithmic scale. Among these crystals, the [Pd(H_2DAG)(HDAG)]-TCNQ crystal has an extremely high room-temperature conductivity of ca. 10 Scm^{-1}, which is almost comparable to values of several metallic organic compounds.[2] For the case of M = Ni, the conductivity has shown a metallic behavior around room temperature. However, the essential feature of the conductivities presented in Figure 5 is a semiconductor in a whole temperature region with a small activation energy of 0.05 - 0.1 eV. It should be noted that the data of the conductivities including the metal-to-insulator transition in [Ni(H_2DAG)(HDAG)]TCNQ showed a strong sample-dependency. Rather, it may be worthwhile to mention that these complexes are remarkably sensitive to the condition of the preparation.

Judging from the optical and transport properties, the partial CT from the 1-D metal chain to the 1-D TCNQ stack most likely takes place in all of these crystals. The semiconducting character may arise from the strong electron-lattice (or -proton) interaction; the CN stretching vibrational mode showed a characteristic temperature dependence. More detailed investigations including the spectral change by chemical modifications are in progress.

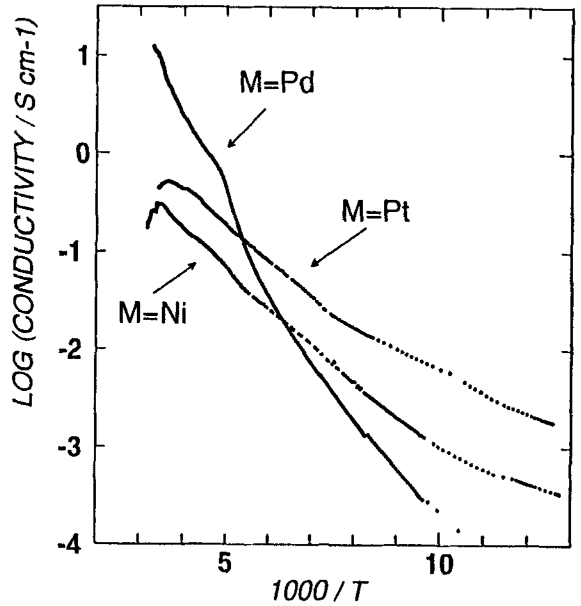

FIGURE 5 Temperature dependence of the conductivity of $[M(H_2DAG)(HDAG)]TCNQ$ single crystals of M = Ni, Pd, and Pt.

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