実験報告書様式（一般利用課題・成果公開利用）

（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。）

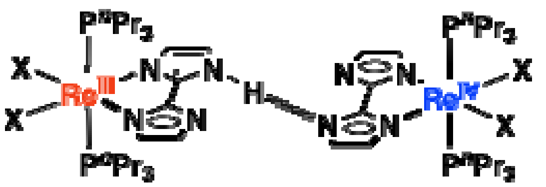
CROSS TOKAI **Experimental Report** J-PARC	承認日 Date of Approval 2014/11/07 承認者 Approver Takashi OHHARA 提出日 Date of Report
課題番号 Project No. 2013A0022 実験課題名 Neutron Structure Analysis of Molecular Dielectric Material by Proton-Electron Co-transfer System 実験責任者名 Makoto Tadokoro 所属 Tokyo University of Science	装置責任者 Takashi Ohhara 装置名 SENJU/（BL No.18） 実施日 2013/5/8-5/17

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Name of Sample: $[Re^{III}Cl_2(PPr_3)_2(Hbim)]$ $[Re^{IV}Cl_2(PPr_3)_2(bim)]$

Cheical formula: $Re_2C_{48}H_{93}N_8Cl_4$



$[Re^{III}X_2(Hbim)(^nPr_3P)_2][Re^{IV}X_2(bim)(^nPr_3P)_2]$(1)

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）

Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

A 3.0 x 3.0 x 1.0 mm^3 size crystal of $[Re^{III}Cl_2(PPr_3)_2(Hbim)]$ $[Re^{IV}Cl_2(PPr_3)_2(bim)]$ (1) H-bonding mixed valence complex was covered with an Al foil and mounted on the 4 K cryostat which has two axes goniometer, and then installed in the vacuum chamber of SENJU. The temperature of the sample crystal was set to 4 K and 233 K. Single crystal neutron diffraction measurements was carried out by using 0.4 ~ 4.0 A (first frame) and 4.0 ~8.0 A (second frame) wavelength neutron. For both first and second frames, 10 data set (10 settings of goniometer angle) were measured. Diffraction data was processed by using a data reduction program STARGazer to obtain a HKLF list for structure analysis. Structure analysis is done by using program SHELXL. The obtained crystal data was indicated as follows: $C_{48}H_{93}N_8Re_2Cl_4P_4$; *triclinic*, *P*1 (#2), T = 4 K, a = 19.039(1) Å, b = 10.2558(5) Å, c = 16.5984(8) Å, α = 75.148(4)°, β = 86.169(5)°, γ = 75.154(5)°, V = 3028.1(3) Å^3, Z = 2, R_1 = 13.52%, wR_2 = 16.01%.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

The purpose of this study is to create a self-organized molecular system that makes it possible to transfer electrons in the ground state without the need for a charge-splitting state. This will be achieved by simultaneously transferring a H-bonding proton and an intermolecular electron via a proton-coupled electron transfer (PCET) reaction. A proton has 1840 times the mass of an electron and cannot exist by itself. It is a small elemental particle that exhibits a quantum effect next to an electron and is the smallest particle capable of being used in chemical applications. The H-bond is an electromagnetic interaction involving protons. It is often found in natural biomolecules as a constituent factor and as a proton-binding bond between the atoms of O and N, elements with high electronegativity. As shown in Fig. 1, when a proton or an electron is removed from a neutral substance, a negative or positive charge is induced in the substance, respectively. The substance thus achieves an unstable charge-splitting state while having a high level of excitation energy. (Figs. 1a and 1b)

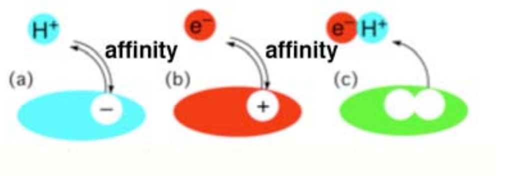


Fig. 1 Charge-splitting states for proton and electron transfers

Providing an electron results in the transfer of a small amount of energy to another substance, thereby the recombination of the excited electron results in the return of the substance to the initial state by a reverse reaction. As the result, a proton or an electron cannot be transferred to other positions, if each has no energy over the excitation state. However, if an electron is simultaneously transferred with a proton, it can freely move into the substance like a neutron with a large transmittance, owing to work done as a neutral particle without a charge. (Fig. 1c) When two elemental particles that exhibit a quantum effect and possess mutually opposite charges, such as an electron and a proton, are fused, unprecedented functional molecules can be achieved. For example, this fusion can lead to the development of a new dielectric material that has tan δ almost equal to zero and that operates only at high frequencies such that an electron and proton are exchanged with each other. It can also result in a novel molecular electron conductor that is controlled by the quantum tunnel effect resulting from the proton transfer.

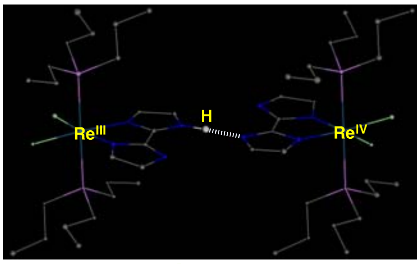


Fig. 2 The result of neutron crystal analysis of [Re^{III}Cl$_2$(Hbim)(PPr$_3$)$_2$] [Re^{IV}Cl$_2$(bim)(PPr$_3$)$_2$]: the proton was localized into one site of a double-well energy potential of the H-bond.

The H-bonding mixed-valence complex [Re^{III}Cl$_2$(PPr$_3$)$_2$(Hbim)] [Re^{IV}Cl$_2$(PPr$_3$)$_2$(bim)] (1), which exhibits paraelectricity (ε_1 = ~50), works even at 4 K owing to a PCET reaction. It is likely that this complex 1 also works at high frequencies, i.e., in the terahertz (THz) region. At room temperature, the broadening of the electron density for the H-bonding proton can be observed by X-ray-based structural analysis, as shown in Fig. 3. On the basis of the results of a tentative neutron crystal analysis at room temperature, it was found that the transferring proton moves through an almost single-welled potential energy surface with the distance between H-bonding N···N atoms being 2.786 (3) Å. In the result of this study, we performed a neutron crystal structure analysis that is based on temperature at ~4K. As shown in Fig. 2, the proton was localized into one side of the bottom of a double-well potential at 4 K. By the neutron structure analysis, we have observed a localized nuclear density for the H-bonding proton for the complex 1 with a proton-assisted electron transfer. Further, it was evidence that the transferring proton was localized by a phase transition at 5 K, which was really the lowest temperature to localize a transferring proton and an electron, and communicate a phonon like a proton.

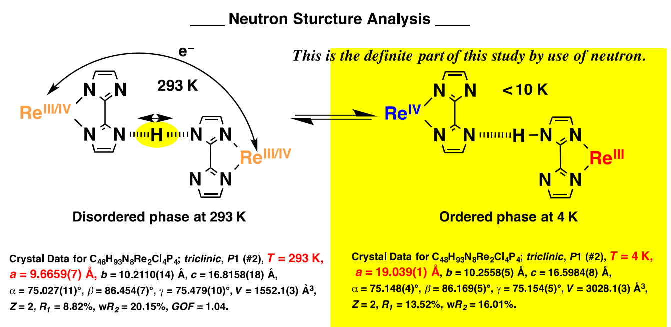


Fig. 3 Order-Disorder transition of complex 1 at ~5K