Direct Evidence of Interfacial Hydrogen Bonding in Proton-Electron Concerted 2D Organic Bilayer on Au Substrate

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Recent advances in the molecular design of organic materials have uncovered various novel functional properties. One of them is the coupling of proton dynamics and electrical conductivity, which can only be achieved in 3D organic crystals. However, reduction of dimensionality to two dimensions is essential in organic electronics application. In this study, we prepared and characterized a 2D organic bilayer with “proton-electron” concerted functionality on a solid surface. It consisted of catechol-fused bis(methylthio)tetrathiafulvalene (H2Cat-BMT-TTF) deposited onto an imidazole-terminated alkanethiolate self-assembled monolayer (Im-SAM) on a Au surface. Direct evidence of interfacial hydrogen bonding (H-bonding) was obtained by scanning tunneling microscopy (STM), infrared reflection absorption spectroscopy (IRAS), and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. STM images showed the deposited H2Cat-BMT-TTF molecules as grains with the thickness of a single molecular layer. The OH stretching vibrational modes of H2Cat-BMT-TTF in the IRAS spectra showed a large red shift and substantial broadening upon adsorption on Im-SAM, indicating that the OH groups of H2Cat-BMT-TTF act as the H+ donor sites. The counterpart H+ acceptor sites were pinpointed by N K-edge NEXAFS. The π* peak of the imino N atoms of the imidazole rings in Im-SAM shifted to higher energy upon the adsorption of H2Cat-BMT-TTF. Therefore, H-bonds form between the imino N atoms (H+ acceptor sites) of Im-SAM and the OH groups (H+ donor sites) of H2Cat-BMT-TTF. The present work is a steady step toward the realization of 2D organic functional materials, and the experimental methods adopted herein will serve as powerful tools for the detection of their functions.

Keywords Self-assembled monolayer; Hydrogen bond; Near edge X-ray absorption fine structure spectroscopy; Scanning tunneling microscopy; Infrared reflection absorption spectroscopy

I. INTRODUCTION

In recent years, organic materials have found increasing importance as organic electronics [1]. For example, organic light-emitting diodes are now widely used in commercial applications such as displays of televisions and mobile phones.

In addition, the development of organic solar cells and organic field-effect transistors for practical use has been actively performed [2–4]. Organic materials have the following advantages: (1) lightweight quality and flexibility, (2) ease of processing, and (3) diversity of molecular design. The last allows organic materials to exhibit various functional proper-
ties such as conductivity, magnetism, dielectricity, and response to external stimuli such as light, electric field, magnetic field, temperature, and pressure [5, 6]. Novel functionalities of organic materials are strongly required to further the development of organic electronics.

Recently, new organic functional materials that exhibit coupled proton dynamics and electrical conductivity have been reported by some of our co-authors [7−9]. For example, in the partially deprotonated molecular crystals of catechol-fused ethylenedithiotetrathiafulvalene (H₂Cat-EDT-TTF), hydrogen bonds (H-bonds) are formed between the molecules [7−9]. Generally, the H₂Cat-TTF molecules consist of two functional moieties: catechol and tetrathiafulvalene (TTF) [Figure 1(a)]. Catechol forms H-bonds, while TTF possesses π electrons that contribute to electrical conductivity. The change in the position of the proton in these H-bonds (proton dynamics) induces charge redistribution of the π electrons, which results in the switching of electrical conductivity [7−9].

Although the novel “proton-electron” concerted functionality of H₂Cat-TTF has only been achieved in 3D crystals [7−9], it is necessary to reduce the dimensionality to two dimensions when one considers its application in organic electronic devices. In the 2D state, organic molecules at surfaces and interfaces can be easily patterned and applied by external fields such as electric field and light.

In this study, we aimed to create the 2D state of H₂Cat-TTF in an organic bilayer on a solid surface by using the H-bonding between H⁺ donor and acceptor molecules. As the H⁺ donor molecular layer, we chose catechol-fused bis(methylthio)tetrathiafulvalene (H₂Cat-BMT-TTF) [Figure 1(a)]. Catechol forms H-bonds, while TTF possesses π electrons that contribute to electrical conductivity. The change in the position of the proton in these H-bonds (proton dynamics) induces charge redistribution of the π electrons, which results in the switching of electrical conductivity [7−9].

Secondly, the Im-SAM/Au surface was immersed in a deoxygenated ethanol solution containing 1 mM of 1-(11-mercaptoundecyl)-imidazole (Im-C₁₁SH; 96%, Sigma-Aldrich) for more than 20 h. This produced a well-packed imidazole-terminated undecanethiolate self-assembled monolayer on the Au substrate (Im-SAM/Au). Secondly, the Im-SAM/Au surface was immersed in a deoxygenated chloroform solution containing 1 mM of the synthesized H₂Cat-BMT-TTF [11] for more than 20 h. This produced a well-packed imidazole-terminated decanethiolate self-assembled monolayer on the Au substrate (Im-SAM/Au).

The adsorbed state and molecular interactions in the organic bilayer were studied by IRAS. The IRAS spectra of the sample were recorded in ultrahigh vacuum (UHV) (base pressure = 2.4 × 10⁻⁸ Pa). The sample was cooled down to ~80 K by liquid N₂. The adsorbed state and molecular interactions in the organic bilayer were studied by IRAS. The IRAS spectra of the samples were recorded in UHV (base pressure = 3.0 × 10⁻⁸ Pa) at 300 K using a Fourier-transform IR spectrometer (FT/IR-6100FV, Jasco) with a mercury cadmium telluride detector (KMPV11-1-J1, Kolmar Technologies). All IRAS spectra were obtained at 4-cm⁻¹ resolution using 2000 scans. In addition, the attenuated total reflection IR (ATR-IR) spectrum of a reference powder sample was recorded.

The prepared organic bilayer on Au was then examined by three different experimental techniques: STM, IRAS, and NEXAFS. The sample was transferred to the individual measurement systems using N₂-filled capsules of microtubes or a homemade load-lock cylinder to avoid exposure to air.

The morphology of the organic bilayer was investigated by STM (CreaTec Fischer & Co.). STM images of the sample were taken in ultrahigh vacuum (UHV) (base pressure = 2.4 × 10⁻⁸ Pa). The sample was cooled down to ~80 K by liquid N₂.

II. EXPERIMENTAL

The organic bilayer on a Au surface was prepared by sequential two-step immersion of the Au substrate in individual solutions of the organic compounds. For the Au substrate, epitaxial Au thin films grown on cleaved mica plates (Au thickness = 200 nm, Phasis) were used. The Au thin films were cleaned by annealing in a butane burner flame, which resulted in the formation of large flat (111)-faced grains more than several hundred nanometers in diameter. First, the clean Au substrate was immersed in a deoxygenated ethanol solution containing 1 mM of 1-(11-mercaptoundecyl)-imidazole (Im-C₁₁SH; 96%, Sigma-Aldrich) for more than 20 h. This produced a well-packed imidazole-terminated decanethiolate self-assembled monolayer on the Au substrate (Im-SAM/Au). The adsorbed state and molecular interactions in the organic bilayer were studied by IRAS. The IRAS spectra of the samples were recorded in UHV (base pressure = 3.0 × 10⁻⁸ Pa) at 300 K using a Fourier-transform IR spectrometer (FT/IR-6100FV, Jasco) with a mercury cadmium telluride detector (KMPV11-1-J1, Kolmar Technologies). All IRAS spectra were obtained at 4-cm⁻¹ resolution using 2000 scans. In addition, the attenuated total reflection IR (ATR-IR) spectrum of a reference powder sample was recorded.

The element- and site-specific molecular interactions in the organic bilayer were studied by IRAS. The IRAS spectra of the samples were recorded in UHV (base pressure = 3.0 × 10⁻⁸ Pa) at 300 K using a Fourier-transform IR spectrometer (FT/IR-6100FV, Jasco) with a mercury cadmium telluride detector (KMPV11-1-J1, Kolmar Technologies). All IRAS spectra were obtained at 4-cm⁻¹ resolution using 2000 scans. In addition, the attenuated total reflection IR (ATR-IR) spectrum of a reference powder sample was recorded.

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NEXAFS spectra were recorded in total electron yield (TEY) by measuring the sample drain current. The incidence angle of the p-polarized soft X-ray was set to 54.7° from the sample surface (i.e., “magic angle”). The energy resolving power of the incident soft X-ray was better than $E/\Delta E = 5000$. The incident soft X-ray beam was defocused to $\sim 60 \mu m (H) \times \sim 30 \mu m (V)$ to avoid beam damage of the organic molecules. All NEXAFS spectra were measured in UHV (base pressure $\sim 5 \times 10^{-6}$ Pa) at 300 K. The NEXAFS spectra were normalized with the incident photon flux measured by the drain current of the Au mesh and then, a linear background determined by the slope at the pre-edge region ($396 \sim 399$ eV) was subtracted. The NEXAFS spectra were fit by up to six Gaussian peaks for the excitation of a core electron to $\pi^*$ and $\sigma^*$ states, and two step functions for the excitation of a core electron to a continuum. Two step functions originate from two different N atoms in Im-SAM; imino N (N3) and amino N (N1) atoms [Figure 1(b)] [13, 14]. The step function was given by the product of the error function and an exponential decay [15].

III. RESULTS AND DISCUSSION

A. STM measurements

First, the morphology of the H2Cat-BMT-TTF layer adsorbed on the Im-SAM/Au surface was investigated by STM. Figure 2(a) shows a topographic STM image of the adsorbed H2Cat-BMT-TTF molecules. Small grains with diameters of 10–20 nm are observed in the H2Cat-BMT-TTF layer. The line profile in Figure 2(b) shows that the height of the small grains is less than 1.5 nm, which is close to the length of the molecular long axis of a single H2Cat-BMT-TTF molecule (~1.2 nm). This indicates that the H2Cat-BMT-TTF grain consists of a single molecular layer. Note that small grains of similar diameter were also observed by AFM at room temperature in our previous study [10]. In this study, the high-resolution STM image at liquid N2 temperature further reveals that the small grains contain fine protrusions, which are separated by 1–2 nm [Figure 2(b)]. The fine protrusions can be assigned to individual H2Cat-BMT-TTF molecules.

It should be noted that H2Cat-BMT-TTF molecules do not cover the whole Im-SAM/Au surface. The coverage of H2Cat-BMT-TTF was estimated to be approximately 0.4 ML using XPS in our previous study [10]; 1 ML was defined as the saturation coverage of Im-SAM. The formation of 2D grains of H2Cat-BMT-TTF with the limited coverage is probably due to a steric hindrance among H2Cat-BMT-TTF molecules.

B. IRAS measurements

The interaction between H2Cat-BMT-TTF and Im-SAM molecules was then studied by IRAS. Figure 3 shows the IRAS spectra of Im-SAM/Au and H2Cat-BMT-TTF adsorbed on the Im-SAM/Au surface. For comparison, the IR spectrum of the H2Cat-BMT-TTF powder recorded by ATR-IR is also included in the figure. The IRAS spectrum of Im-SAM on the Au surface consists of strong peaks around 2900 cm$^{-1}$ originating from the CH$_2$ stretching modes and complex vibrational features at 1700–1000 cm$^{-1}$ due to the CC and CN stretching modes and...
in-plane CH bending mode [10, 16, 17].

After the adsorption of H₂Cat-BMT-TTF on Im-SAM, strong peaks at 1483 cm⁻¹ and 1273 cm⁻¹ and a very broad peak between 3600–2300 cm⁻¹ appear in the IRAS spectrum. The strong peaks are ascribed to the CO stretching modes of the catechol moiety of H₂Cat-BMT-TTF [10, 18]. Note that these peaks are also observed in the IR spectrum of the reference H₂Cat-BMT-TTF powder. This confirms the successful adsorption of H₂Cat-BMT-TTF on the Im-SAM/Au surface.

On the other hand, the very broad peak is assigned to the OH stretching modes of H₂Cat-BMT-TTF [10, 18]. In comparison, the same modes of the reference H₂Cat-BMT-TTF powder are observed as a sharp peak at 3535 cm⁻¹ and broad peak at ~3430 cm⁻¹. Therefore, the OH stretching modes of H₂Cat-BMT-TTF show a large red shift and substantial broadening upon adsorption on Im-SAM. This indicates the H-bonding of H₂Cat-BMT-TTF with Im-SAM; more specifically, the OH group of the catechol moiety of H₂Cat-BMT-TTF acts as the H⁺ donor site in H-bonding.

The very broad peak of the OH stretching mode, extending to low frequencies below 3000 cm⁻¹, was often observed for the strongly H-bonded systems such as carboxylic acid dimers [19–21]. The broadening of the OH stretching peak was explained by a large anharmonic coupling of the OH stretching mode to other vibrational modes at lower frequencies such as the COH bending mode and the intermolecular H-bond stretching mode [19–21]. The inhomogeneous broadening due to H-bonds with different strength might also contribute to the peak width.

One would also expect spectral changes in the vibrational features of Im-SAM, which acts as the H⁺ acceptor site in H-bonding. However, the CN stretching modes of Im-SAM at 1700–1000 cm⁻¹ overlap with the strong absorption peaks of H₂Cat-BMT-TTF at 1483 cm⁻¹ and 1273 cm⁻¹. Thus, it is difficult to establish a complete picture of H-bonding in the bilayer of H₂Cat-BMT-TTF and Im-SAM on the Au surface based solely on IRAS data.

We note that the quality of the ATR-IR spectrum of the reference H₂Cat-BMT-TTF powder is better than that in our previous study [10]; particularly, the sharp OH stretching mode at 3535 cm⁻¹ was not previously observed probably owing to the absorption of moisture from air. In addition, the IRAS spectra of Im-SAM and H₂Cat-BMT-TTF adsorbed on the Im-SAM/Au surface in this study reproduced those in our previous study [10]. A Au thin film on mica was used as the substrate in this study, whereas a Au(111) single crystal was used in our previous study [10]. The reproducibility of the IRAS spectra of the organic layers justifies the use of Au/mica as the Au substrate.

C. NEXAFS measurements

For a complete picture of H-bonding in the bilayer of H₂Cat-BMT-TTF and Im-SAM on a Au surface, the N K-edge NEXAFS spectra were obtained. The element specificity of NEXAFS allows elucidation of the nature of H-bonding at the H⁺ acceptor side (i.e., Im-SAM) because N atoms exist only in the Im-SAM layer.

Figure 4 shows the N K-edge NEXAFS spectra of Im-SAM and H₂Cat-BMT-TTF adsorbed on Im-SAM. The NEXAFS spectra were measured in total electron yield. The incidence angle θ of the X-ray was 54.7° from the surface. (a) Whole absorption, (b) enlarged π* peak regions (raw data), and (c) enlarged π* peak regions (raw data and fit data). N K-edge NEXAFS spectra were fit by up to six Gaussian peaks and two step functions. Blue, green, and gray lines correspond to the N 1s → 1π* transition of N3 atom [denoted as N 1s → 1π* (N3)], N 1s → 1π* (N1), N 1s → 2π* (N3), respectively. Red line is the energy-shifted component of N 1s → 1π* (N3), N 1s → 1π* (N3'), which appeared after adsorption of H₂Cat-BMT-TTF. Orange and purple lines correspond to the N 1s → C–N σ* transitions of both N3 and N1 atoms. Black dashed lines represent step functions for N3 and N1 atoms. Light blue (pink) and black lines are the raw and fit data, respectively.

Figure 4: N K-edge NEXAFS spectra of Im-SAM and H₂Cat-BMT-TTF adsorbed on Im-SAM. The NEXAFS spectra were measured in total electron yield. The incidence angle θ of the X-ray was 54.7° from the surface. (a) Whole absorption, (b) enlarged π* peak regions (raw data), and (c) enlarged π* peak regions (raw data and fit data). N K-edge NEXAFS spectra were fit by up to six Gaussian peaks and two step functions. Blue, green, and gray lines correspond to the N 1s → 1π* transition of N3 atom [denoted as N 1s → 1π* (N3)], N 1s → 1π* (N1), N 1s → 2π* (N3), respectively. Red line is the energy-shifted component of N 1s → 1π* (N3), N 1s → 1π* (N3'), which appeared after adsorption of H₂Cat-BMT-TTF. Orange and purple lines correspond to the N 1s → C–N σ* transitions of both N3 and N1 atoms. Black dashed lines represent step functions for N3 and N1 atoms. Light blue (pink) and black lines are the raw and fit data, respectively.
400.0 eV and 401.8 eV are ascribed to the N 1s → 1π* transition of the imino N (N3) and amino N (N1) atoms, respectively, of the imidazole ring in Im-SAM [Figure 1(b)] [13, 14, 22]. The small component at 400.8 eV between two N 1s → 1π* peaks is attributed to the N 1s → 2π* transition of imino N. Similar peak between two 1π* peaks was observed for imidazole monomer in gas phase [13, 14]. Note that the N 1s → 2π* transition of amino N is not present because the 2π* orbital has no density of states at the amino N [14]. On the other hand, the broad peaks at 407.1 eV and 414.0 eV are assigned to the N 1s → C=N π* resonance transition of both imino N and amino N [13, 14].

Figure 4(b) shows the enlarged π* region of the N K-edge NEXAFS spectra of Im-SAM before and after the adsorption of H2Cat-BMT-TTF. The π* peak of imino N (N3) shifts from 400.0 eV to 403.3 eV, while that of amino N (N1) remains at the same energy. This shows that the adsorption of H2Cat-BMT-TTF changes the chemical environment of imino N. The peak fitting in Figure 4(c) reveals that only a part of the π* peak of imino N shifts from 400.0 eV to 403.3 eV. The ratio of the shifted component to the total imino N is determined to be 0.41 by the fit peak area.

Notably, beam damage effects on the present N K-edge NEXAFS spectra are negligible. An X-ray-damaged imidazolium-based ionic liquid was reported to show two characteristic peaks at 398.9 eV and 400.0 eV, which originate from the cleavage of the C=N bond between the alkyl groups and imidazole ring [23]. In the case of Im-SAM, an additional peak was observed at 398.6 eV for a sample intentionally damaged by higher X-ray photon flux density (not shown). The absence of such peak in the N K-edge NEXAFS spectra in Figure 4 demonstrates the insignificant effects of beam damage.

### D. Discussion

In this subsection, we discuss the origin of the change in the N K-edge NEXAFS spectra of Im-SAM upon the adsorption of H2Cat-BMT-TTF, specifically, the shift in the energy of the π* peak of imino N (N3), but not of amino N (N1).

Table 1 summarizes the N K-edge NEXAFS peak positions for imidazole in different chemical environments (gas, solid, and aqueous solution), Im-SAM, and H2Cat-BMT-TTF adsorbed on Im-SAM. In imidazole, the hydrocarbon chain in Im-SAM is substituted by a hydrogen atom.

The positions of the π* peaks of the N3 and N1 atoms of imidazole, as well as the energy splitting between these peaks, are sensitive to the chemical environment. From the gas phase monomer to the solid crystal, the N3 π* peak shifts by 0.4 eV to higher energy, while the N1 π* peak shifts by 0.5 eV to lower energy, and the energy splitting decreases from 2.4 eV to 1.5 eV. These changes are explained by intermolecular H-bonding between imidazole molecules; in aqueous solution, both imidazole and water molecules are involved in H-bonding [13, 14].

For Im-SAM, the N3 and N1 π* peaks appear at 400.0 eV and 401.8 eV, respectively. Compared with gas-phase imidazole (399.9 eV and 402.3 eV for the N3 and N1 π* peaks, respectively), the N3 π* peak of Im-SAM shifts slightly by 0.1 eV to higher energy, while the N1 π* peak shifts by as large as 0.5 eV to lower energy. The large peak shift is attributed to the change in the chemical environment of the N1 atom, which is covalently bonded to hydrogen in imidazole, but to a hydrocarbon chain in Im-SAM.

Upon the adsorption of H2Cat-BMT-TTF, the π* peak of imino N (N3) in Im-SAM shifts by 0.3 eV to higher energy, which would also be caused by intermolecular H-bonding with H2Cat-BMT-TTF. The IRAS data show that the OH groups in the catechol moiety of H2Cat-BMT-TTF form H-bonds. Therefore, a complete picture of the H-bonding in the 2D organic bilayer can now be drawn. H-bonds are formed between the imino N (N3) atoms in Im-SAM (the H+ acceptor layer) and OH groups in H2Cat-BMT-TTF (the H+ donor layer) (Figure 5). In contrast, the amino N (N1) does not show any shift in the π* peak upon the adsorption of H2Cat-BMT-TTF because it already forms covalent bonds with the three neighboring C atoms.

The H-bonding configuration between H2Cat-BMT-TTF and Im-SAM is discussed based on the quantitative analysis of the coverage of each molecule. The coverage of H-bonded Im-SAM is 0.41 ML, as revealed by N K-edge NEXAFS spectra. This matches the coverage of H2Cat-BMT-TTF (0.4 ML), which was estimated by XPS in our previous study [10]. This indicates that H2Cat-BMT-TTF and Im-SAM forms H-bonds in one to one fashion (Figure 5). Here it should be pointed out that one H2Cat-BMT-TTF molecule has two OH groups, which can form two H-bonds with two imino N atoms in Im-SAM. The following H-bonding configuration cannot be fully excluded; 0.2 ML H2Cat-BMT-TTF form two H-

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**Table 1**: N K-edge NEXAFS peak positions for imidazole in different environments (gas, solid, and aqueous solution), Im-SAM, and H2Cat-BMT-TTF adsorbed on Im-SAM.

| Sample | N 1s → 1π* (N3) | N 1s → 1π* (N1) | ΔE (N1–N3) | Ref. |
|--------|----------------|----------------|------------|------|
| Imidazole (gas) | 399.9 | 402.3 | 2.4 | [13] |
| Imidazole (solid) | 400.3 | 401.8 | 1.5 | [13] |
| Imidazole (aqueous solution) | 400.2 | 401.9 | 1.7 | [14] |
| Im-SAM | 400.0 | 401.8 | 1.8 | This study |
| H2Cat-BMT-TTF + Im-SAM | 400.3 | 401.8 | 1.5 | This study |
bonds with Im-SAM per molecule, and the rest 0.2 ML H$_2$Cat-BMT-TTF do not form H-bonds with Im-SAM but form H-bonds between H$_2$Cat-BMT-TTF molecules. The theoretical simulation of N K-edge NEXAFS spectra and the experimental O K-edge NEXAFS spectra in the future will provide the further details of the H-bonding configuration in the present 2D organic bilayer.

IV. CONCLUSIONS

In conclusion, we studied the organic bilayer of H$_2$Cat-BMT-TTF and Im-SAM on a Au surface by STM, IRAS, and NEXAFS. H$_2$Cat-BMT-TTF molecules on the Im-SAM/Au surface were imaged by STM as grains with the thickness of a single molecular layer. The large red shift and substantial broadening of the OH stretching vibrational modes of H$_2$Cat-BMT-TTF upon adsorption on Im-SAM revealed that the OH groups act as the H$^+$ donor sites. The H$^+$ acceptor site was revealed by element- and site-specific characterization using N K-edge NEXAFS. The $\pi^*$ peak of imino N shifted by 0.3 eV to higher energy, which can be explained by intramolecular H-bonding. Therefore, the present study confirmed the H-bonding between the OH group of the catechol moiety of H$_2$Cat-BMT-TTF and imino N of Im-SAM in the 2D organic bilayer.

The next step after successful characterization of the 2D organic bilayer is the exploration of its “proton-electron” concerted functionality. The experimental methodologies adopted in this work (i.e., STM, IRAS, and NEXAFS) will serve as powerful tools for that purpose. STM gives information on the electrical conductivity of the 2D organic bilayer, while IRAS and NEXAFS enable the evaluation of H-bonding at the H$^+$ donor and acceptor sites, respectively.

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