A Surface-Functionalized Ionovoltaic Device for Probing Ion-Specific Adsorption at the Solid–Liquid Interface

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Aqueous ion–solid interfacial interactions at an electric double layer (EDL) are studied in various research fields. However, details of the interactions at the EDL are still not fully understood due to complexity induced from the specific conditions of the solid and liquid parts. Several technical tools for ion–solid interfacial probing are experimentally and practically proposed, but they still show limitations in applicability due to the complicated measurements. Recently, an energy conversion device based on ion dynamics (called ionovoltaic device) was also introduced as another monitoring tool for the EDL, showing applicability as a novel probing method for interfacial interactions. Herein, a monitoring technique for specific ion adsorption (Cu²⁺ and Pb²⁺ in the range of 5 × 10⁻⁶–1000 × 10⁻⁶ M) in the solid–liquid interface based on the ionovoltaic device is newly demonstrated. The specific ion adsorption and the corresponding interfacial potentials profiles are also investigated to elucidate a working mechanism of the device. The results give the insight of molecular-level ion adsorption through macroscopic water-motion-induced electricity generation. The simple and cost-effective detection of the device provides an innovative route for monitoring specific adsorption and expandability as a monitoring tool for various solid–liquid interfacial phenomena that are unrevealed.

Ion–solid surface interactions at electric double layers (EDLs) have been studied in diverse research fields including colloidal science, nanofluidics, and electrochemistry. Although the interfacial structure of EDLs was theoretically described with the Gouy–Chapman–Stern (GCS) model, the interfacial interactions at this region were not fully comprehended due to a complexity that depends on pH, ionic species and strength, and solvent. In particular, direct ion–surface interactions at an inner part of the Stern layer are still not clearly explained. These interactions, called specific adsorption, are differentiated from physical adsorption by Coulombic interactions. Furthermore, they are induced by non-Coulombic interactions such as chemical bonding, coordinating complexation, hydrophobic bonding, and hydrogen bonding. The specific adsorption can drastically change the electrical properties of the surface, and related phenomena such as charge inversion are still actively studied. There have been many experimental trials to observe the ion–surface interaction. These methods offered substantial information on the interfacial properties and the adsorption phenomena. However, the intricate equipment and demanding measurement conditions hindered their wide applications. In practical perspectives, ion-sensitive field-effect transistor (ISFET) and molecular controlled semiconductor resistor (MOCSER) were developed to monitor the interfacial adsorption, which extends to chemical and biological sensing platforms.

Recently, several studies carried out by various groups, including our own, reported on a water-motion-induced energy conversion device based on solid–liquid interfacial phenomena. In addition, an ion-on-dynamics-induced electricity generation (called an ionovoltaic device) was proposed as a working mechanism. In these studies, it was revealed that the electrical properties at the EDL can influence the device performance. Based on these observations of the interfacial properties like interfacial charge density, an EDL dependent on different ions (ion specificity), and an adsorption of protons, were demonstrated within the devices. Similarly, conventional electrokinetic methods have been studied to measure the interfacial properties. However, their complex measurements (nanofluidic channel or porous medium and prerequisites for pressure or ion concentration gradients) and low signal conversion efficiency remained as limitations. Compared with the electrokinetic methods and other probing
Here, we observed the chemical adsorption of biologically harmful heavy metal ions (Cu^{2+} and Pb^{2+}) at the solid–liquid interface by introducing an ion chelating group to the ionovoltaic device and newly proposed this system as an ion detection tool. The ion adsorptions and the corresponding chemical states of the molecular surface were confirmed with X-ray photoemission spectroscopy (XPS). The adsorption-induced interfacial potential variations were investigated by measuring zeta potentials and Kelvin probe force microscopy (KPFM). Through a proposal of potential profiles at an electrolyte–dielectric–electrode, a working mechanism of the device was elucidated. In addition, selective adsorption of target ions at the ligand surface was studied in terms of ion–ligand complexation. The suggested results provide insight into the adsorption at the molecular level and the corresponding interfacial properties by observing simple and macroscopic water-motion-induced electricity generation. An identification of electricity generation dependent on the interfacial phenomena is still in its infancy. The investigation of these adsorption phenomena will broaden the understanding of the solid–liquid interfacial phenomena and an applicability of the device as a novel interfacial probing tool.

Schematic images of the ionovoltaic device and its ion detection process are shown in Figure 1. The device is comprised of three layers: an indium tin oxide (ITO) glass, a polydimethoxysiloxane (PDMS) dielectric, and a mixed self-assembled monolayer (SAM). The mixed SAM is composed of two molecules: 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (PFOTS) and N^1-(3-trimethoxysilylpropyl)diethylenetriamine (T-DETA). PFOTS and T-DETA are treated to lower surface energy (Figure S1, Supporting Information) and induce a chemical adsorption by a chelation effect in the mixed SAM, respectively. To operate the device, a water droplet (200 µL of NaCl 0.01 M) is placed above the mixed SAM surface and then alternately pushed and released by mechanical upper plate motions. The voltages generated by the plate motions are shown in Figure S2 (Supporting Information). In the mixed SAM, a negative (positive) pole of voltage (≈0.8 V) are observed while in the pushing (releasing) motion. Compared to the mixed SAM, a surface without T-DETA displays reversed pole of voltages (≈0.7 V) during the droplet motions. The upper plate motion drives contact-area-dependent ion adsorption (desorption) and, simultaneously, capacitive charging (discharging) at the ITO electrode by contact-area variations between the droplet and the bottom plate.\([^{15,17}]\) The signals in the mixed SAM reflect how electrons are repelled (drawn) at the bottom plate by physical adsorption (desorption) of ions (Cl\(^{-}\)) during the pushing (releasing) motion due to a positive surface potential by protonated T-DETA (Figure 1a).\([^{19,20}]\) A reverse process can be induced under the absence of T-DETA due to a negative surface potential by PFOTS.\([^{21,22}]\) To assess ion detection performance, we measured the voltages of the device before and after chemical adsorption at the mixed SAM surface (Figure 1a–c). It was well-known that DETA can form a chelate complex with Cu^{2+} and Pb^{2+} ions.\([^{23–25}]\) First, we monitored the generated voltages of the mixed SAM device and then the bottom plate was exposed to a few milliliters of target ion (Cu^{2+} or Pb^{2+}) solutions. The target ion can be chemically adsorbed through a complexation with T-DETA. As shown in Figure 1c, we found that output voltages decreased after Cu^{2+} and Pb^{2+} exposures under the same measurement conditions as the initial state.

Figure 2 shows experimental results of target ion adsorption up to 1000 × 10^{-9} M on the device. The output voltages decreased after Cu^{2+} adsorption in both pushing and releasing motions (Figure 2a). In addition, the voltage variations were accomplished within 5 min after exposure to the target ion (Figure S3, Supporting Information). Relative variations of peak voltage (\((V – V_0)/V_0\)) depending on exposed Cu^{2+} and Pb^{2+} concentrations are presented in Figure 2b. Similar to the results of Cu^{2+}, the peak voltage was also gradually varied with Pb^{2+} exposure. The voltage changes for Cu^{2+} and Pb^{2+} reached

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Schematic images of the ion detection process with an ionovoltaic device. a) Voltage measurement with a droplet pushing and releasing motions under a mixed self-assembled monolayer (mixed SAM) surface. b) Target ion exposure to the mixed SAM surface. c) Voltage measurement after a chemical adsorption of target ions at the mixed SAM surface. An electrolyte solution used for working the ionovoltaic device (water droplets in (a) and (c)) was fixed for the 0.01 M NaCl solution (200 µL) throughout the experiments.
Based on the relative saturated.

A slope of each data was following: 4.07 × 10^{-3} (R^2 = 0.85) and 3.02 × 10^{-3} μm^{-1} (R^2 = 0.97) for Cu^{2+} and Pb^{2+}, respectively.

A selectivity for Cu^{2+} and Pb^{2+} against several cations was also investigated for 100 × 10^{-6} M of solutions. As shown in Figure 2c, the device displayed negligible voltage variations (less than 10%) for K^{+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}, and Ni^{2+}, whereas the peak voltages with the target ions (Cu^{2+} and Pb^{2+}) were largely changed. This distinctive variation was 3.3–18 times higher than for other ions. The output voltage curves in Figure 2a implies that the voltage reduction is not resulting from the mechanical modulation of the droplet motions due to the almost same voltage generated times (=0.12 s) with a top plate motion time (=0.1 s). In addition, the voltage reduction was not derived from the exposure of Na^{+} or Cl^{-} and water molecules (Figure S4, Supporting Information) or PFOTS.

Consequently, the peak voltage reduction in Figure 2 might come from selective Cu^{2+}/Pb^{2+}-DETA complexation.

To investigate chemical states of the mixed SAM, XPS was measured. As shown in Figures S5a,b and S6a (Supporting Information), C 1s, F 1s, and N 1s peaks present the mixed SAM above the PDMS layer, respectively.[22,25,26] XPS spectra of Cu 2p and Pb 4f at the mixed SAM surface (Figure S6c,d, Supporting Information) after the ion exposure indicates that each ion is chemically adsorbed at the surface.[27,28] To determine the surface state after Cu^{2+} adsorption, XPS spectra of N 1s in the mixed SAM were investigated based on three chemical states (neutral, protonated, and Cu^{2+}-coordinated amines, Figure S6, Supporting Information). The N 1s peaks of four different samples (0, 40 × 10^{-6}, 100 × 10^{-6}, and 1 × 10^{-3} M of Cu^{2+} exposures) were deconvoluted into the three chemical states and areal portions of protonated and Cu^{2+}-coordinated amines, as presented in Figure 3a. The portion of the Cu^{2+}-coordinated amine was increased by simultaneously lowering that of the protonated amine and then was saturated over 100 × 10^{-6} M. In addition, XPS results of Cu 2p peaks corresponding to adsorption states (40 × 10^{-6}, 100 × 10^{-6}, and 1 × 10^{-3} M of Cu^{2+} exposures) were mainly positioned near 932 eV and shifted from A (931.5 eV) to B (932.25 eV) by being prolonged in its shoulder (Figure 3b). Several points were obtained from the XPS results: First, Cu 2p_{3/2} of DETA-coordinated Cu^{2+} was less than the actual binding energy of Cu^{2+} (=934 eV), implying the chemical adsorption of Cu^{2+} with T-DETA (Figure 3b).[27] Second, an increase in adsorbed Cu^{2+} ion can drive the deprotonation of T-DETA (Figure 3a). In general, DETA forms three N-coordination bonds with Cu^{2+};[29] therefore, T-DETA in the mixed SAM can be fully deprotonated by Cu^{2+} adsorptions. However, at high Cu^{2+} concentrations (100 × 10^{-6} and 1 × 10^{-3} M Cu^{2+}), an increase of unbound Cu^{2+} ions (an elevation of Cu 2p_{3/2} shoulder at 933–934 eV, Figure 3b) implies that the chemical adsorption of Cu^{2+} was inhibited by a crowding of binding sites. Based on the XPS results, we can assume a Cu^{2+}-DETA complexation reaction as

\[ \text{[H}_n\text{(DETA)}\]^{n+} + Cu^{2+} \leftrightarrow [(\text{DETA})\text{Cu}]^{2+} + n\text{H}^+ \] (1)

Figure 2. a) Output voltages as a function of time under different Cu^{2+} concentrations. The curves at the top and bottom figures correspond to pushing and releasing motions, respectively. b) Relative peak voltages as a function of the exposed ion concentrations. Dashed lines in the graph and a data point at 0 × 10^{-6} M (a black dashed square) are presented for eye guidance. c) Relative peak voltage changes as a function of different ion species (100 × 10^{-6} M).

==0.4 and ≈0.34, respectively, at 100 × 10^{-6} M until they became saturated. However, there were negligible variations in the PFOTS–SAM (without T-DETA) device. Based on the relative peak voltage curves in Figure 2b, an ion sensitivity, which was defined by a change of the relative peak voltage over a change of the ion concentration (Δ(V – V_0)/V_0)/ΔC, where ΔC is the change of the ion concentration), was calculated from a linear fit of 0–100 × 10^{-6} M at the region of steep changing. Figure 3a presents the change of the ion concentration (Δ) was defined by a change of the relative peak voltage over a change of the ion concentration (Δ(V – V_0)/V_0)/ΔC, where ΔC is the change of the ion concentration), was calculated from a linear fit of 0–100 × 10^{-6} M at the region of steep changing.

A slope of each data was following: 4.07 × 10^{-3} (R^2 = 0.85) and 3.02 × 10^{-3} μm^{-1} (R^2 = 0.97) for Cu^{2+} and Pb^{2+}, respectively.
where \( n \) is the number of protonation in DETA (\( n = 0, 1, 2, \) or 3). A preference between the protonation of DETA and the Cu\(^{2+}\)–DETA complexation can be inferred from stability constants (equilibrium constant, \( \log K_a \)) by \( \log K_a(\text{H}^+) = 9.84, 9.02, \) and 4.23 for \( n = 1, 2, \) and 3, respectively, and \( \log K_a(\text{Cu}^{2+}) = 15.9. \) Therefore, Cu\(^{2+}\) can be more preferably adsorbed into the mixed SAM than the other protons as suggested in our XPS results.

Influential factors for the output voltage in our device are the contact-areal variation rate between the droplet and the bottom plate \( \frac{d}{dt} \) resistor–capacitor (RC) discharging, and the interfacial potential difference between the electrolyte (droplet) and the ITO electrode. Among them, the effect of the interfacial potential difference can outplay the influence of \( \frac{d}{dt} \) and the RC discharging. Therefore, the output voltage variations can be derived from a change in the interfacial potential difference by Cu\(^{2+}\) adsorption. The potential difference \( (\sum \psi) \) can be expressed by \( \text{(1)} \)

\[
\sum \psi = \psi_S + \psi_{\text{SAM}} + \psi_D
\]

In this equation, \( \sum \psi \) is composed of a potential drop across a Stern layer \( \psi_S \), the SAM \( \psi_{\text{SAM}} \), and the PDMS dielectric layer \( \psi_D \). In the solid–liquid interface, accurate and direct measurements of physical parameters like interfacial potentials and charge densities are almost impossible. Therefore, to investigate the variation in \( \sum \psi \) for Cu\(^{2+}\) and Pb\(^{2+}\) adsorption, zeta potentials \( (\zeta) \) and KPFM were measured (Figure 3c,d and Figures S7 and S8 (Supporting Information)). As shown in Figure 3c, the zeta potentials of the PFOTS–SAM, T-DETA–SAM, and mixed SAM surfaces before and after exposure of the Cu\(^{2+}\) ion solutions \( (40 \times 10^{-6} \) and \( 1 \times 10^{-3} \) \( \text{m} \)). The measurement was performed under 0.01 \( \text{m} \) of NaCl solution, which was used as the working solution of the devices. The values shown in (d) were obtained by subtracting the surface potential of neat Si/SiO\(_2\) as a reference.
T-DETA–SAM exhibited potentials of −401.33 and 246.05 mV, respectively,[21,31] and that of mixed SAM was observed between them (74.65 mV). After exposure to Cu²⁺ (1 × 10⁻⁵ M), both T-DETA– and the mixed SAM showed drastically lowered potentials. These potential shifts in SAM (ψSAM) can be expressed by[21,31]

\[ \psi_{\text{SAM}} = \frac{n_{\text{SAM}} \mu_{\text{SAM}}}{\varepsilon_{\text{SAM}}} \]  

(4)

where \( n_{\text{SAM}} \) and \( \mu_{\text{SAM}} \) denote surface density and net vertical dipole moment of a self-assembled molecule, respectively, while \( \varepsilon_{\text{SAM}} \) denotes permittivity of the SAM. Accordingly, a diminution of \( \psi_{\text{SAM}} \) can be induced by reducing \( \mu_{\text{SAM}} \) due to the deprotonation and Cu²⁺–DETA complexation.[31] Therefore, an interfacial potential between SAM and PDMS can be obtained (\( \psi_{\text{SD}} = \psi_i + \psi_{\text{SAM}} \)) and potential drops in the dielectric (\( \psi_D \)) are proportional to \( \psi_{\text{SD}} \). After Cu²⁺ adsorption, the magnitude of \( \psi_D \) and interfacial potential at ITO can be reduced. For simplicity, we assumed that \( \psi_D \) would decay similarly before and after Cu²⁺ adsorption; thus, it was neglected.

Consequently, schematic images across an electrolyte–dielectric (SAM and PDMS)–electrode (ITO) and the corresponding potential profiles are shown in Figure 4 (initial and Cu²⁺-adsorbed mixed SAM were denoted as I and Cu, respectively). \[ \sum \psi = \psi_{\text{SD}} - \zeta \]  

(5)

As Cu²⁺ is directly bound to DETA by chemical adsorption, it can be closer to the mixed SAM (specifically adsorbed) than the physically adsorbed anions in the electrolyte.[32] Therefore, \( \psi_{\text{SAM}} \) (from \( \psi_{\text{SD}} \) to \( \psi_{\text{SAM}} \)). Then, \( \sum \psi \) is decreased from \( \psi_{\text{SD}} - \zeta \) to \( \psi^{	ext{Cu}}_{\text{SAM}} - \zeta_{\text{Cu}} \) and decreases the output voltage of the device.

To investigate the ion selectivity further, we tested the device under heterogeneous ion solutions, as shown in Figure 5a. The solutions were prepared with an equimolar quantity (100 × 10⁻⁶ M) of the target ions (Cu²⁺ and Pb²⁺) and randomly chosen ions (Na⁺, Hg²⁺, Co²⁺, and Cd²⁺). Detailed constituents of the solutions were described in Table S1 (Supporting Information). The peak voltages were only varied in the solutions including Cu²⁺ and Pb²⁺ (Solutions 2, 3, and 4). They were reduced almost 32% compared to those in single ion solutions (33–40% in Figure 2c). This implies that there was a negligible ion interfering effect in heterogeneous solutions. To confirm the complexation preference between Cu²⁺ and Pb²⁺ ions, we investigated XPS spectra (Cu 2p and Pb 4f) of the mixed SAM exposed to Solution 4 (Figure S9, Supporting Information). The spectra display distinctive Cu 2p peaks without Pb 4f peaks. Therefore, we can infer that T-DETA in the mixed SAM had higher preference to Cu²⁺ than Pb²⁺.[23,24] As we mentioned in previous paragraph, the ion selectivity of Cu²⁺ among the other ions can be inferred from the stability constant of the complexation with DETA. Therefore, the high predominance of the Cu²⁺–DETA complexation in comparison with other ions are discussed in Note S1 and Table S2 (Supporting Information).

As exhibited in Equation (1), Cu²⁺ exposure drives the formation of the Cu²⁺–DETA complex. A reverse reaction, desorption of Cu²⁺, is also possible by an acidic solution.[25] As shown in Figure S10a (Supporting Information), decreased peak voltage (by 100 × 10⁻⁶ M Cu²⁺) was restored within 35 min by exposure to 0.01 M HCl. The peak voltage was recovered up to ≈71% of initially generated voltages. This signal recovery might come from desorption of Cu²⁺ at the mixed SAM and protonated amine formation. Compared to the Cu²⁺ adsorption time (less than 5 min, Figure S3, Supporting Information), a desorption of Cu²⁺ requires much larger time due to a lower affinity of protons with DETA than that of Cu²⁺ with DETA. Peak voltage recovery was confirmed under different HCl concentrations and was highest at 0.05 M HCl by reaching ≈86% of the initial voltages (Figure S10b, Supporting Information). In more than 0.05 M, the signal recovery was blunted (0.1 M HCl) or the voltage was rather decreased than that for the Cu²⁺ exposed state (0.5 and 1 M HCl). As shown in contact angle images (Figure S10c, Supporting Information), this deterioration can come from damage to mix SAM by the highly acidic condition. We repeated Cu²⁺ exposure and recovery by 0.05 M HCl to our device, as shown in Figure 5b. Consequently, the peak voltages recovered well for 3 cycles without any deteriorations.

Figure 4. Schematic images of the electrolyte (water droplet)–dielectric (SAM and PDMS)–ITO electrode interfaces and its potential profiles in the vertical direction. Anions (Cl⁻) in the working solution and holes at the ITO layer are schematically presented. A change of the SAM from an initial state to a Cu²⁺ ion adsorption state (left) and the corresponding variations of each potential value (right) are denoted by subscript letters of I and Cu in the schematic, respectively. The schematic images and potential profiles were presented based on the GCS model.
Accordingly, we confirmed that the mixed SAM can be recovered repeatedly and that our device has reusability for practical applications.

In summary, we proposed a simple and pragmatic interfacial probing tool through ion-specific adsorptions in the ionovoltaic device. The device selectively detects Cu\(^{2+}\) and Pb\(^{2+}\) in the \(10^{-6}\) to \(10^{-6}\) M range and shows reusability by ion desorption under acidic conditions. The ion-specific adsorption at the solid–liquid interface was investigated with XPS and surface potential measurements (the zeta potentials and KPFM). Detailed potential profiles at the electrolyte–dielectric-electrode structure were studied to elucidate the working mechanism of the device. Our results showed the influence of the ion–ligand interactions in the nanoscopic region to the solid–liquid interfacial potentials and on to the output voltage driven by the macroscopic water motion. At the molecular level, the ion selectivity of the device was explained by a preferential target ion–ligand complexation compared to other ions including protons. Therefore, these results imply a tunability of the ion selectivity through a modulation of the ion-chelating molecular layer. This work demonstrates that the ionovoltaic device has a high potentiality to probe not only the solid–liquid interfacial phenomena with simple technical tools, but also a practical platform to detect biologically hazardous heavy metal ions. As the adsorption phenomena is widely utilized in electrochemical sensors, ISFETs and water refinement technology, these findings can offer informative analysis about the specific adsorption and the corresponding influence of interfacial potentials. In addition, by introducing functional interfaces such as various ion chelating groups and bioreceptors, an applicability of the device can be expanded to chemical and biological monitoring tools for diverse interfacial phenomena that are unrevealed.

**Experimental Section**

**Preparations of Surface-Functionalized Ionovoltaic Device:** ITO glass (5 \(\times\) 5 cm\(^2\)) was sonicated sequently under detergent, acetone, and isopropyl alcohol (each for 15 min) and blown with \(N_2\) gas to clean. \(O_2\) plasma was then treated to the ITO glass for 30 s. To prevent leakage current across an ITO–NaCl solution interface, PDMS dielectric was spin-coated onto the glass and cured for 2 h in 80 °C hot plate. The thickness of the dielectric layer was \(\approx 2\) \(\mu\)m. Two organic molecules, which were PFOTS (Sigma-Aldrich) and T-DETA (Sigma-Aldrich), were treated to the PDMS-coated ITO glass to form mixed self-assembled monolayer (mixed SAM). Each molecule was treated in order of a following procedure; the PDMS-coated ITO glass was exposed to oxygen plasma for 30 s, and then dipped into T-DETA solution (10 vol%) in deionized (DI) water for 10 min in an ambient condition. The sample was washed with DI water to remove physically adsorbed molecules. After that, PFOTS (40 \(\mu\)L) was treated to the sample at a chamber for 30 min under 160 °C hot plate. To remove physically attached molecules, the sample was sonicated under DI water. PFOTS–SAM samples without a T-DETA treatment were prepared by omitting the T-DETA treatment process in the mixed SAM surface preparation. As shown in Figure S1 (Supporting Information), the mixed SAM surface presented same hydrophobic nature with a PFOTS-SAM surface and suggested that the dynamic droplet motions were possible. \(O_2\) plasma was treated under 0.6 Torr and 100 W condition in this experiment.

**Device Measurements:** A probe and a ground electrode of the oscilloscope (DPO-2024, Tektronix) were connected to the bottom and top plate, respectively, and a water droplet (200 \(\mu\)L) was placed between them. The top and bottom plates were composed of a neat and the mixed SAM–treated ITO glasses, respectively (Figure 1a). Alternating droplet pushing and releasing motions were induced constantly with a custom-built vertical motion controller with following conditions; the droplet was pushed and released by the top plate with a speed and a traveling distance of 2 cm s\(^{-1}\) and 2 mm, respectively. A gap between the two plates was 3 and 1 mm for a released and pressed state, respectively. To prevent an effect of external resistance, an external load was fixed throughout the experiment (Figure S11a, Supporting Information). While, the droplet motions, contact-area-dependent electric signals were measured with oscilloscope. As a salt concentration of the droplet could be an influential factor in the system (Figure S11b, Supporting Information), 0.01 M NaCl solution was fixed as working solution throughout the experiments. After an exposure of ion solutions (5 min, Figure S3, Supporting Information), the bottom plate was sonicated in DI water and dried enough to remove physically adsorbed ions and water residues. Acidity of all cation solutions were positioned in a range of pH 5–6 except for HCl solutions (pH 2.05 and 1.02 for 0.01 and 0.1 M, respectively) used in Figure S5b. Anions of all tested solutions were unified with Cl\(^-\) to exclude an anion effect in chemical adsorption of Cu\(^{2+}\) and Pb\(^{2+}\) ions.

**Surface Characterizations:** Chemical states of SAM were characterized by XPS. To characterize a potential above the mixed SAM surface, zeta potential measurement (ELSZ-2000, Otsuka Electronics Co.) was performed under a NaCl 0.01 M solution atmosphere (pH 5.47), which was the working solution in the experiments. The samples measured in XPS and zeta potential were prepared in the same manner with the preparation of
ionvoltaic device. The KPFM measurement was performed with an atomic force microscopy system (XE-100, Park systems). To perform a reliable measurement without subsidiary effects (for example, surface roughness and self-charging effect), Si/SiO2 substrate was used as a substrate instead of PDMS surface. Detailed explanations were described in Note S2 (Supporting Information). Surfaces of SAMs were prepared on the Si wafers with 100 nm SiO2 layer and measured under ambient condition. The measured potentials were subtracted by a potential of pure Si/SiO2 surface as a reference. The measurement was performed in a noncontact mode with a conductive tip (Pt/Ir-coated Si, work function = 4.836 eV) under AC 2 V and 17 kHz. A surface potential shift of each sample was obtained by an average value from potential mapping of a 5 × 5 μm2 area.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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