

Anion Exchange-Promoted Ru^{3+/2+} Redox Switch in Self-Assembled Monolayers of Imidazolium Ions on a Gold Electrode

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1,3-Dialkylimidazolium salts, known as one of the ionic liquids, are very attractive molecules because their physicochemical properties can easily be tuned by the variation of the alkyl appendages of the imidazolium cations and counteranions. In this paper we report that the self-assembled monolayers (SAMs) terminating in 1,3-dialkylimidazolium salts with various counteranions [except Fe(CN)₆³⁻] on a gold substrate exhibited a selective electron-transfer toward redox-probe molecules: the electron transfer occurred in the presence of Fe(CN)₆³⁻ (anionic redox-probe molecule) but did not occur in the presence of Ru(NH₃)₆³⁺ (cationic redox-probe molecule). The SAM having Fe(CN)₆³⁻ as an anion showed the electron-transfer toward Ru(NH₃)₆³⁺, and the Ru^{3+/2+} redox-switchable SAM was generated by reversible anion exchange between Fe(CN)₆³⁻ and SCN⁻ (or OCN⁻).

Electron transfer through nanometer-thick organic films is of fundamental importance to the development of nanometer-scale electronic materials.^{1–5} Knowledge of how chemical compositions and chemical structures affect the electron transfer between a solid substrate and a redox-active molecule is central in the study of molecular-level electron transfer. In particular, the concept of switching of molecular properties, “molecular switch”, is of relevance to the design and development of new electronic nano-devices.^{6–8} Self-assembled monolayers (SAMs) are commonly employed to study the influence of molecular-level modifications on the switching of molecular properties,^{9–14} and most of the modifications are based on either photo-

induced or electro-induced processes and are often associated with changes in molecular structure, for example, isomerization, proton transfer, or redox reactions.^{15–20}

Ionic liquids (ILs), especially 1,3-dialkylimidazolium salts, would be very attractive molecules because their physical and chemical properties can easily be tuned by the variation of the alkyl appendages of the imidazolium cations and counteranions and have received a great deal of attention in many fields of chemistry, such as catalysis, extraction, and organic synthesis.^{21–23} They are also functional as electrolytes in electrochemical systems with unprecedented electrochemical stability. Additionally, the combination of ILs with polymers and low-molecular-weight gelators can produce quasi-solid-state materials, which have been employed as electrolytes for electrochemical devices and highly selective separation membranes.^{24–29} Because of the increase in the potential of ILs as alternative materials in diverse electrochemical ap-

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(1) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148.

(2) Adams, D. M.; Brus, L.; Chidsey, C. E. D.; Creager, S.; Creutz, C.; Kagan, C. R.; Kamat, P. V.; Lieberman, M.; Lindsay, S.; Marcus, R. A.; Metzger, R. M.; Michel-Beyerle, M. E.; Miller, J. R.; Newton, M. D.; Rolison, D. R.; Sankey, O.; Schanze, K. S.; Yardley, J.; Zhu, X. *J. Phys. Chem. B* **2003**, *107*, 6668.

(3) Tour, J. M. *Molecular electronics: Commercial insights, Chemistry, Devices, Architecture and Programming*; World Scientific Publishing: River Edge, NJ, 2003.

(4) *Molecular electronics: Science and Technology*; Aviram, A., Ratner, M. A., Eds.; New York Academy of Sciences: New York, 1998.

(5) *An introduction to Molecular Electronics*; Petty, M. C., Bryce, M. R., Bloor, D., Eds.; Arnold: London, 1995.

(6) *Molecular Switches*; Feringa, B. L., Eds.; Wiley-VCH: Weinheim, 2001.

(7) Willner, I.; Katz, E. *Angew. Chem., Int. Ed.* **2002**, *39*, 1180.

(8) Irie, M. *Chem. Rev.* **2000**, *100*, 1683.

(9) Chidsey, C. E. D. *Science* **1991**, *251*, 919.

(10) Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T. M.; Mujcsce, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 4301.

(11) Sachs, S. B.; Dudek, S. P.; Hsung, R. P.; Sita, L. R.; Smalley, J. F.; Newton, M. D.; Feldberg, S. W.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1997**, *119*, 10563.

(12) Slowinski, K.; Slowinska, K. U.; Majda, M. *J. Phys. Chem. B* **1999**, *103*, 8544.

(13) Napper, A. M.; Liu, H.; Waldeck, D. H. *J. Phys. Chem. B* **2001**, *105*, 7699.

(14) Liu, B.; Bard, A. J.; Mirkin, M. V.; Creager, S. E. *J. Am. Chem. Soc.* **2004**, *126*, 1485.

(15) Luk, Y.-Y.; Abbott, N. L. *Science* **2003**, *301*, 623.

(16) Lahann, J.; Mitragotri, S.; Tran, T.-N.; Kaido, H.; Sundaram, J.; Choi, I. S.; Hoffer, S.; Somorjai, G. A.; Langer, R. *Science* **2003**, *299*, 371.

(17) Liu, Y.; Zhao, M.; Bergbreiter, D. E.; Crooks, R. M. *J. Am. Chem. Soc.* **1997**, *119*, 8720.

(18) Sortino, S.; Petralia, S.; Conoci, S.; Bella, S. D. *J. Am. Chem. Soc.* **2003**, *125*, 1122.

(19) Soto, E.; MacDonald, J. C.; Cooper, C. G. F.; McGimpsey, W. G. *J. Am. Chem. Soc.* **2003**, *125*, 2838.

(20) Cooper, C. G. F.; MacDonald, J. C.; Soto, E.; McGimpsey, W. G. *J. Am. Chem. Soc.* **2004**, *126*, 1032.

(21) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667.

(22) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH Verlag: Weinheim, Germany, 2003.

(23) *Ionic Liquids: Industrial Applications for Green Chemistry*; Roger, R. D., Seddon, K. R., Eds.; ACS Symposium Series 818; American Chemical Society: Washington, DC, 2002.

(24) Papageorgiou, N.; Athanassov, Y.; Armand, M.; Bonhôte, P.; Pettersson, H.; Azam, A.; Grätzel, M. *J. Electrochem. Soc.* **1996**, *143*, 3099.

(25) Matsumoto, H.; Matsuda, T.; Tsuda, T.; Hagiwara, R.; Ito, Y.; Miyazaki, Y. *Chem. Lett.* **2001**, 26.

(26) Kubo, W.; Kitamura, T.; Hanabusa, K.; Wada, Y.; Yanagida, S. *Chem. Commun.* **2002**, 374.

(27) Branco, L. C.; Crespo, J. G.; Afonso, C. A. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 2771.

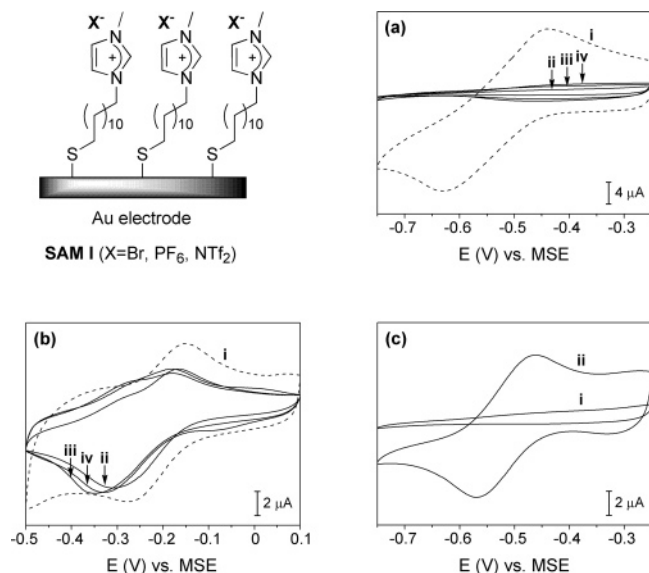


Figure 1. CVs of (a) (i) bare gold and SAM I having (ii) X = Br, (iii) X = PF₆, and (iv) X = NTf₂ with Ru(NH₃)₆Cl₃; (b) (i) bare gold and SAM I having (ii) X = Br, (iii) X = PF₆, and (iv) X = NTf₂ with K₃Fe(CN)₆; (c) SAM I (X = Br) with Ru(NH₃)₆Cl₃ (i) before and (ii) after pretreatment with K₃Fe(CN)₆. The active area of the gold electrode was 0.283 cm². The potential scan rate was 50 mV/s.

plications such as rechargeable batteries and molecular electronic devices,^{30–33} studies on the electrical properties of individual molecules and molecular assemblies of ILs are of great importance. In this paper, we incorporated the core moiety of the ILs, imidazolium cation, into SAMs on a gold surface and achieved the anion-directed switch of electron transfer.³⁴

To study the effect of the anion on electron transfer in the SAMs of imidazolium salts, the conductivity of SAM I, formed with 1-(12-mercaptododecyl)-3-methylimidazolium salts (X = Br, PF₆, and NTf₂)^{34a} on a gold electrode, was investigated using Ru(NH₃)₆Cl₃ and K₃Fe(CN)₆ as cationic and anionic redox probe molecules, respectively. Our previous study showed that the imidazolium ion-terminated thiol compounds formed well-ordered, close-packed SAMs on gold.^{34a} We observed that SAM I showed the selectivity toward redox probe molecules. The cyclic voltammogram (CV), obtained from SAM I (X = Br) in an aqueous solution of Ru(NH₃)₆Cl₃ (100 μM), showed that the conductivity (ii in Figure 1a) was attenuated significantly compared with that for the bare gold surface (i in Figure 1a) at an applied potential in the range from -0.75 to -0.25 V versus MSE (mercury sulfate electrode), which

suggests the formation of ordered insulating monolayers. In contrast, in the presence of K₃Fe(CN)₆ (100 μM) the CV of SAM I (X = Br) showed redox peaks of hexacyanoferrate(III) with slightly attenuated conductivity (ii in Figure 1b) compared with the bare gold surface (i in Figure 1b). Similar CV behaviors were observed with the SAMs of imidazolium salts bearing different counteranions such as PF₆⁻ (iii in Figure 1,b) and NTf₂⁻ (iv in Figure 1a,b). These results imply that SAM I has the selectivity toward redox probe molecules and hydrophobicity of the surfaces is not a key factor in the electron transfer.³⁵ When the electroactive probe molecule in the bulk solution was Fe(CN)₆³⁻, we always observed a sufficient electron transfer, no matter what the nature of the counteranion was. We believe that the observed electron transfer was caused by much stronger attraction between the imidazolium cation and Fe(CN)₆³⁻ compared with the cases of other anions. The strong attraction was proved by the experimental fact that the surface-immobilized Fe(CN)₆³⁻ could not easily be exchanged with other anions. Of interest, when we pretreated SAM I (X = Br) with an aqueous solution of K₃Fe(CN)₆ (10 mM, 10 min), the blocked electron transfer between Ru(NH₃)₆³⁺ and the gold surface that was previously blocked was now switched on. Figure 1c shows the CVs of the substrates containing Ru(NH₃)₆Cl₃ (i) before and (ii) after the treatment with K₃Fe(CN)₆. Although we have not yet determined the mode of the electron-transfer process of the SAM pretreated with Fe(CN)₆³⁻, the result suggests that the deposited Fe(CN)₆³⁻ promoted tunneling of electrons between the gold surface and Ru(NH₃)₆³⁺. Cooper and McGimpsey also recently reported the similar results on photoelectrochemistry where Cu(II) ion promoted the electron transfer of SAMs terminating in pyridin-2,6-dicarboxylic acid for K₃Fe(CN)₆ solution.^{19,20}

The X-ray photoelectron spectroscopy (XPS) spectra of the SAM I (X = Br) after CV experiments with K₃Fe(CN)₆ showed that some of the bromide anions (3d_{3/2}, 69 eV; 3d_{5/2}, 68 eV; compare i and ii in Figure 2b) of SAM I were exchanged with Fe(CN)₆³⁻ (Fe 2p_{1/2}, 721 eV; Fe 2p_{3/2}, 708 eV; compare i and ii in Figure 2a). The anion exchange was further confirmed by the independent treatment of the SAM I (X = Br) with aqueous K₃Fe(CN)₆ solution: the Br anion was completely exchanged with Fe(CN)₆³⁻ (compare i and iii in Figure 2a–c). The Br anion, however, remained as a counteranion after the CV experiments with Ru(NH₃)₆Cl₃. These results clearly indicate that the SAMs containing imidazolium salts at the terminal residue acted as insulating layers for the positively charged redox molecule, Ru(NH₃)₆³⁺, whereas the negatively charged redox probe molecule, Fe(CN)₆³⁻, was adsorbed onto the surface via anion exchange and then the resulting monolayer became electrically active.

We reasoned that anions capable of reversibly exchanging Fe(CN)₆³⁻ would result in the formation of insulating layers on the surface against Ru(NH₃)₆³⁺, and the formation of the anion-directed Ru^{3+/2+} redox-switchable surface could be achieved. After screening various counteranions, we found that the Fe(CN)₆³⁻ was reversibly exchanged with OCN⁻ and SCN⁻, resulting in the formation of insulating layers on the surface against Ru(NH₃)₆³⁺. For example, SAM I (X = Br) was exposed to an aqueous solution of KSCN (0.2 M, 10 min), yielding the anion-exchanged SAM II. The CV of SAM II with Ru(NH₃)₆³⁺

(28) Wang, P.; Zakeeruddin, S. M.; Comte, P.; Exnar, I.; Grätzel, M. *J. Am. Chem. Soc.* **2003**, *125*, 1166.

(29) Wang, P.; Zakeeruddin, S. M.; Moser, J.-E.; Humphry-Baker, R.; Grätzel, M. *J. Am. Chem. Soc.* **2004**, *126*, 7164.

(30) Lu, W.; Fadeev, A. G.; Qi, B.; Smela, E.; Mattes, B.; Ding, J.; Spinks, G. M.; Mazurkiewicz, J.; Zhou, D.; Wallace, G. G.; MacFarlane, D.; Forsyth, S. A.; Forsyth, M. *Science* **2002**, *297*, 983.

(31) Tiyapiboonchaiya, C.; Pringle, J. M.; MacFarlane, D. R.; Forsyth, M.; Sun, J. *Macromol. Chem. Phys.* **2003**, *204*, 2147.

(32) Stathatos, E.; Lianos, P.; Zakeeruddin, S. M.; Liska, P.; Grätzel, M. *Chem. Mater.* **2003**, *15*, 1825.

(33) Tiyapiboonchaiya, C.; Pringle, J. M.; Sun, J.; Byrne, N.; Howlett, P. C.; MacFarlane, D. R.; Forsyth, M. *Nat. Mater.* **2004**, *3*, 29.

(34) We and others have recently reported the surface modification of gold substrates, such as flat surfaces and nanoparticles, with the SAMs terminating in imidazolium salts to tailor the hydrophilicity/hydrophobicity of the substrates. See: (a) Lee, B. S.; Chi, Y. S.; Lee, J. K.; Choi, I. S.; Song, C. E.; Namgoong, S. K.; Lee, S.-g. *J. Am. Chem. Soc.* **2004**, *126*, 480. (b) Itoh, H.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **2004**, *126*, 3026. (c) Kim, K.-S.; Demberelynamba, D.; Lee, H. *Langmuir* **2004**, *20*, 556.

(35) Recently Gorman et al. reported that the rate and extent of electron hopping within the films composed of a redox-active dendrimer were increased with increasing the hydrophobicity of the counterion. See: Chasse, T. L.; Smith, J. C.; Carroll, R. L.; Gorman, C. B. *Langmuir* **2004**, *20*, 5501.

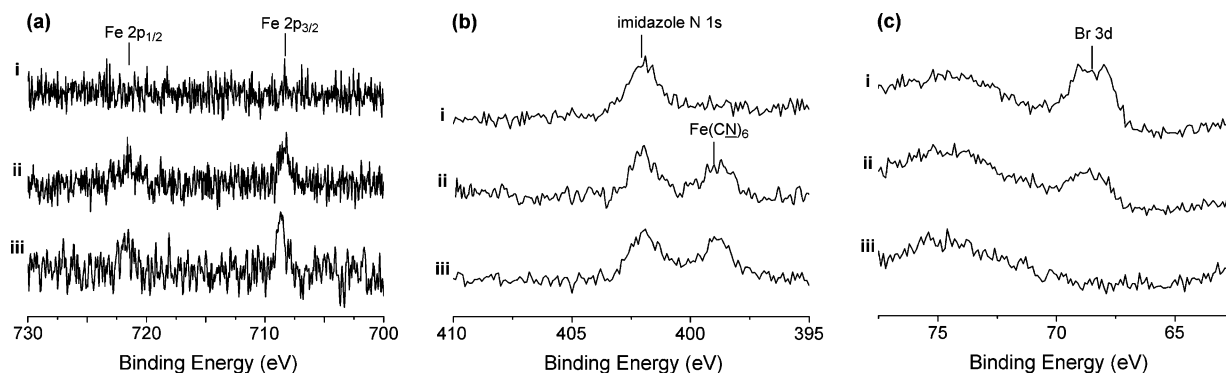


Figure 2. Narrow-scan XPS spectra of the (a) Fe 2p, (b) N 1s, and (c) Br 3d regions acquired from SAM I ($X = \text{Br}$). (i) Before the CV experiment with $\text{K}_3\text{Fe}(\text{CN})_6$; (ii) after the CV experiment with $\text{K}_3\text{Fe}(\text{CN})_6$; (iii) after the pretreatment with $\text{K}_3\text{Fe}(\text{CN})_6$.

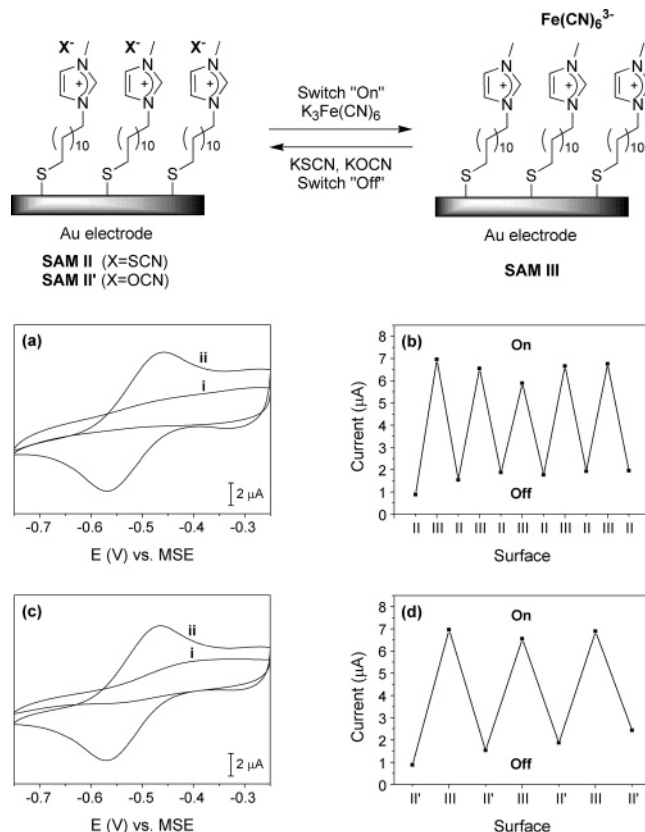


Figure 3. CVs of (a) (i) SAM II ($X = \text{SCN}$) and (ii) SAM III with $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$; (c) (i) SAM II' ($X = \text{OCN}$) and SAM III. The solutions contained 10 mM of KBr. The potential scan rate was 50 mV/s. $\text{Ru}^{3+/2+}$ redox switching of (b) SAM II and SAM III; (d) SAM II' and SAM III with 100 μM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$. The Y axis is the reduction current at -570 mV.

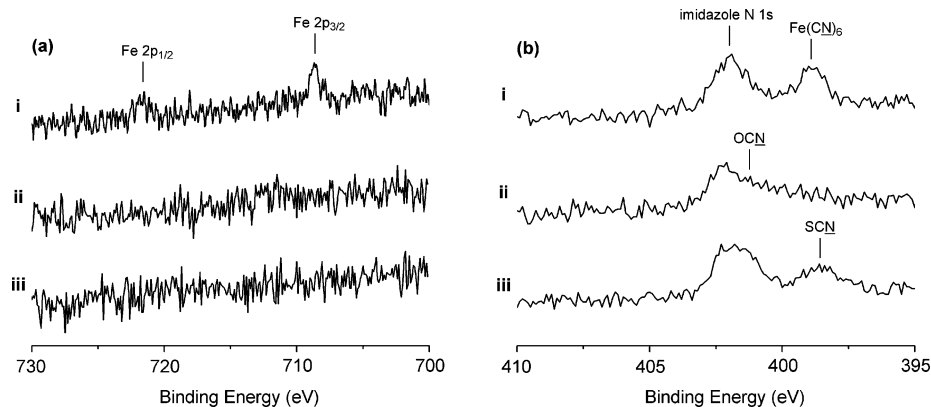


Figure 4. Narrow-scan XPS spectra of the (a) Fe 2p and (b) N 1s regions. (i) SAM III formed by the treatment of SAM I ($X = \text{Br}$) with $\text{K}_3\text{Fe}(\text{CN})_6$; (ii) after the treatment of SAM III with KOCCN; (iii) after the treatment of SAM III with KSCN.

showed the significantly attenuated conductivity (i in Figure 3a). When SAM II was exposed to an aqueous solution of $\text{K}_3\text{Fe}(\text{CN})_6$, resulting in SAM III, the CV of SAM III with $\text{Ru}(\text{NH}_3)_6^{3+}$ (ii in Figure 3a) was nearly identical to that of ii in Figure 1c. Re-exposure to an aqueous solution of KSCN resulted in the formation of insulating monolayers. The suitability of SAMs II and III as reversible molecular switches was tested by the alternating exposure of the substrates to aqueous solutions of KSCN and $\text{K}_3\text{Fe}(\text{CN})_6$. As a result, the five times $\text{Ru}^{3+/2+}$ redox cycles were achieved (Figure 3b). The reversible switching of electron transfer was also achieved when KOCCN (SAM II' in Figure 3) was used instead of KSCN (Figure 3c,d). In the XPS analysis, we confirmed that the $\text{Fe}(\text{CN})_6^{3-}$ of SAM III (i in Figure 4a,b) was exchanged with the OCN^- (ii in Figure 4a,b) and SCN^- (iii in Figure 4a,b). These findings provide clear and direct evidence that a reversible electron transfer of the imidazolium ion-terminated SAMs on gold occurred via the anion exchange of the imidazolium salt.

In conclusion, we showed the anion-directed $\text{Ru}^{3+/2+}$ redox-switchable SAM surfaces coated with imidazolium salts on a gold electrode. The SAMs on gold are highly ordered and well-defined structures, and, therefore, the SAMs have advantages over polymeric thin films in the precise design of surfaces and the molecule-level control of the physicochemical properties of surfaces. We believe that the anion effect on electron transfer demonstrated herein could advantageously be incorporated into the design of integrated molecular switch nanodevices.

Materials and Methods

The gold substrates were prepared by thermal evaporation of 5 nm of titanium and 100 nm of gold onto silicon wafers. Prior to use, gold substrates were cleaned for 1 min in piranha solution

(3:7 by volume of 30% H_2O_2 and H_2SO_4 , *Caution: piranha solution reacts violently with most organic materials and must be handled with extreme care*), rinsed with H_2O and ethanol, and dried under a stream of argon. SAM I ($\text{X} = \text{Br}$) was prepared by immersing the gold substrates in a 1 mM solution of 1-(12-mercaptododecyl)-3-methylimidazolium bromide in ethanol overnight, rinsing with ethanol several times, and then drying under a stream of argon. The SAM I having different counteranions ($\text{X} = \text{PF}_6$ and NTf_2) was prepared via direct anion exchange with the SAM I having a Br anion. The SAM I ($\text{X} = \text{Br}$) having a bromide anion was immersed in an aqueous solution of an aqueous 10 mM solution of salts (NaPF_6 , LiNTf_2) for 6 h. The surfaces were rinsed with water followed by ethanol and dried under an argon stream.

CVs were acquired using an Autolab potentiostat 10 (Ecochemie, Netherlands). The three-electrode electrochemical cell consisted of a modified Au electrode, a Pt wire counter electrode, and a $\text{Hg}/\text{Hg}_2\text{SO}_4$ (MSE, saturated K_2SO_4) reference electrode. Experiments were carried out in aqueous solution containing 10 mM KBr as a supporting electrolyte. The solution was deoxy-

genated with argon prior to use, and the active area of the electrode is 0.283 cm^2 . The XPS study was performed with a VG-Scientific ESCALAB 250 spectrometer (U.K.) with a monochromatized Al $\text{K}\alpha$ X-ray source. Emitted photoelectrons were detected by a multichannel detector at a take-off angle of 90° relative to the surface. During the measurements, the base pressure was 10^{-9} – 10^{-10} Torr. Survey spectra were obtained at a resolution of 1 eV from 3 scans, and high-resolution spectra were acquired at a resolution of 0.05 eV from 5 to 20 scans.

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