Synthesis of Thiol-Functionalized Ionic Liquids and Formation of Self-Assembled Monolayer on Gold Surfaces: Effects of Alkyl Group and Anion on the Surface Wettability

Bang Sook Lee and Sang-gi Lee*

Life Sciences Division, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea
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Twenty four thiol-functionalized ionic liquids based on imidazolium cation, 1-(12-mercaptododecyl)-3-alkylimidazolium salts, have been synthesized, and utilized to investigate the effects of alkyl-chain length and anion on the wettability of Au surfaces on the basis of self-assembled monolayers presenting [(CnSAMIM)X], where n = 1-6, X = Br, BF_4, PF_4 and NTf_2. Water wettabilities of the surfaces were measured as a water contact angle by contact angle goniometry. It was found that water wettability of the Au surfaces coated with imidazolium ions was largely dependent not only on counter anions but also on the length of alkyl chains. In the case of SAMs of *N*-alkylimidazolium ions having short length of *N*-alkyl chain (C_1-C_4), anions played great role in determining water wettability of the surfaces.

Key Words : Thiol-functionalized ionic liquids, Self-assembled monolayer, Surface wettability, Anion effect

Introduction

Recently, a new class of liquid has emerged that consists entirely of ions, so-called ionic liquids (ILs). They are made up of two components *i.e.* the anion and cation. As both anion and cation can be varied, these solvents can be designed for a particular set of properties such as solubility, density, refractive index, and viscosity. The favorable and readily tunable physicochemical properties of ILs, especially imidazolium cation-based ILs (Figure 1) have led to intense interest in these materials as alternatives to conventional organic solvents in a range of synthesis, catalysis, electrochemistry and liquid-liquid extractions.[1-6] The burgeoning field of IL research continues to demonstrate the potential for ILs in variety of applications such as biopolymers,[7,8] chemosensors for specific ions,[9] formation of nanosized metal particles etc.[10-12] Furthermore, their ionic nature makes them suitable for use as conductive media in lithium battery and solar cells.[13-15]

We reasoned that tunable physical properties of ILs could be transferred onto solid surfaces, whose properties, especially water wettability, could be adjusted by variation of the length of alkyl chain on cation and/or the anions. Controlling wettability of the solid surfaces by surface modification has intensively been studied due to many technologically important applications.[16-18] Among the surface modification methods, the formation of self-assembled monolayers (SAMs) proved to be a simple and practical technique for controlling wettability,[19-25] corrosion,[26-28] and (bio)adhesion[29-34] of solid surfaces. On the basis of SAMs, the wettability of solid surfaces could be controlled in various ways, *i.e.*, environmental changes (solvents,[35-37] pH,[38] temperature,[39-41] and surface pressure[42]) or external stimuli (*i.e.*, light,[23,24] charge,[25] and oxidation-reduction[43]). Our approach is a translation of the tunable water miscibility of ILs in solution onto surfaces to control surface wettability. Recently, we have demonstrated that the wettability of SAMs presenting *N*-methyl imidazolium ions at the tail ends on gold[44] or Si/SiO_2 surfaces[45] could be controlled by anion exchange on surfaces ("anion-directed control"). Thus, the water contact angles of the SAMs terminating *N*-methylimidazolium ions were increased as change the hydrophilic anions such as BF_4^- to hydrophobic anions such as NTf_2^-, which indicating clearly that the wettability of the surface can be tailored by changing the anion. Chujo *et al.* also documented the surface of Au nanoparticles modified with ionic liquids, which allowed the their phase transfer through the anion exchange.[46] The assortment of available and potential hydrophobic and hydrophilic ILs attests to their easily manipulated physical properties. Changing the length of alkyl groups and/or counter anions modulates the hydrophobicity of ILs, and consequently water miscibility can be varied. Therefore, the combination of two components, alkyl chain and anion, will provide more diverse surfaces, which may control the wettability more finely. In this report, we synthesized various thiol-functionalized ionic liquids and formed SAMs terminating imidazolium moiety bearing different length of alky chain (C_1-C_6) and anions (Br, BF_4, PF_6, NTf_2), and investigated the effects of alkyl-chain length and anion on surface wettability on Au surfaces.

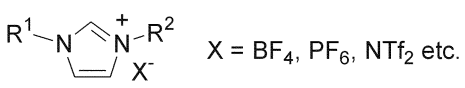


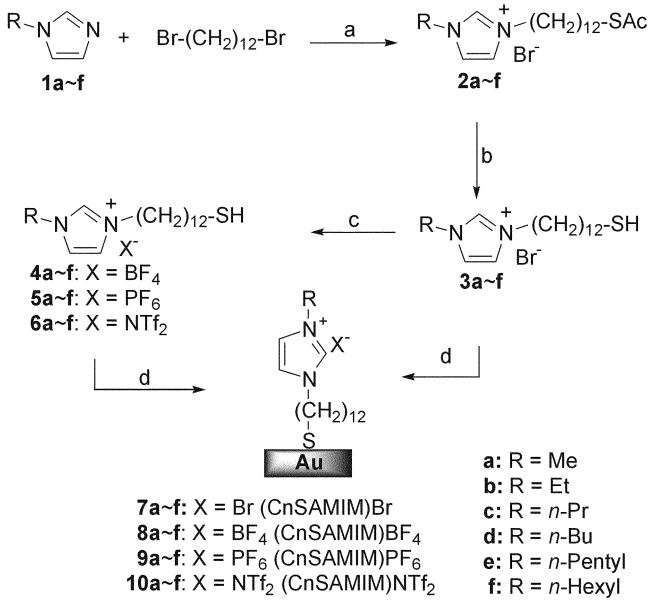
Figure 1. 1,3-Dialkylimidazolium Ionic Liquids.

*Corresponding Author. Tel: +82-2-958-5163; Fax: +82-2-958-5189; e-mail: sanggi@kist.re.kr

Results and Discussion

In order to investigate the effects of alkyl-chain length and anion on the wettability of Au surfaces coated with imidazolium ion, twenty four thiol-functionalized ionic liquids bearing different length of *N*-alkyl groups (methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl and *n*-hexyl) and counter anions (Br, BF_4, PF_6 and NTf_2) representing hydrophilic and hydrophobic anions have been synthesized. The synthetic scheme for the thiol-functionalized imidazolium cation-based ionic liquids (**3a-f**, **4a-f**, **5a-f** and **6a-f**) showed in Scheme1. Reaction of 1-alkyl imidazole **1a-f** with 1,12-dibromododecane in methylene chloride followed by nucleophilic substitution with potassium thioacetate could provide the imidazolium bromide **2a-f**. The thioacethyl group of **2a-f** was hydrolyzed with NaOH and acidified with HBr to give the corresponding thiol-functionalized imidazolium bromide salts **3a-f**. The anion exchange of **3a-f** with $NaBF_4$, $NaPF_6$ and $LiN(Tf)_2$ in acetone provided the corresponding thiol-functionalized ILs **4a-f**, **5a-f** and **6a-f**, respectively. The imidazolium ion-terminated SAMs [(CnSAMIM)X] [X = Br (**7**), BF_4 (**8**), PF_6 (**9**), NTf_2 (**10**)] having different alkyl groups and anions were formed by immersing freshly cleaned Au substrates in 1 mM solution of thiol-functionalized ionic liquids **3-6** in absolute ethanol for 3 h.

Figure 2 shows the IR spectra in the CH stretching region for [($C_{1\text{-}6}$SAMIM)Br]. The characteristic CH_2 asymmetric CH and symmetric CH stretching modes are observed at 2919-2922 and 2846-2851 cm^{-1}. The band at 2967-2985 cm^{-1} is assigned to CH_3 asymmetric in-plane CH stretching mode and the band at 2880-2894 cm^{-1} is assigned to the CH_3 symmetric CH stretching mode.[47] These IR spectral data indicate that the monolayered films are well-ordered and closed-packed. The ellipsometric thicknesses of the SAMs **7a-7f** (**7a**: 19 Å, **7b**: 21 Å, **7c**: 22 Å, **7d**: 23 Å, **7e**: 24 Å **7f**: 25 Å) presenting [(CnSAMIM)Br] also supported that the SAMs are packed densely.



Scheme 1. Syntheses of thiol-functionalized ionic liquids (**3a-f**, **4a-f**, **5a-f** and **6a-f**) having different alkyl chains and anions, and the formation of self-assembled monolayers on Au surfaces. (a) (i) CH_2Cl_2, reflux, 10 h. (ii) $KSCOCH_3$, THF, reflux, 6 h. (b) EtOH/H_2O (3/1, v/v), NaOH, 0 °C, 1 h, then HBr. (c) For **4**: $NaBF_4$; for **5**: $NaPF_6$; for **6**: $LiNTf_2$, acetone, rt, 35 h. (d) Au/1 mM solution of thiol terminated ionic liquids **3-6** in absolute ethanol for 3 h.

The water wettabilities of the SAM surfaces were measured as a water contact angle by contact angle goniometry at 22 °C and 30% humidity. The data for the water contact angles of the SAMs (**7-10**) were obtained from mean value of three times measurements. Figure 3 showed the effects of alkyl chain-length on the wettability for each anion. The water contact angles of the SAMs presenting [(C_nSAMIM)Br] **7a**-7**f** were increased as increase the length of alkyl chain (**7a**: 23 ± 1^o, **7b**: 39 ± 1^o, **7c**: 41 ± 1^o, **7d**: 43 ± 1^o, **7e**: 62 ± 1^o, **7f**: 63 ± 1^o). The relatively larger change (16°) in the contact angle was observed by change the *N*-methyl, [(C_1SAMIM)Br] (**7a**, 23 ± 1^o), to *N*-ethyl group, [(C_2SAMIM)Br] (**7b**, 39 ± 1^o). However, rather smaller changes in the contact angle (*ca.* 2°) have been observed between **7b-7d** having C_2-C_4 alkyl chains. Dramatic alkyl chain-length effect was observed in SAM **7e** [(C_5SAMIM) Br] having C_5-hexyl chain. Compare to **7d** (43 ± 1^o), about 20° of contact angle was increased in **7e** (62 ± 1^o). Whereas there is no changes in the water contact angles of surfaces presenting [(C_5SAMIM)Br] (**7e**: 62 ± 1^o) and [(C_6SAMIM)Br] (**7f**: 63 ± 1^o). Interest finding is relatively smaller changes in the contact angles of the surfaces bearing relatively hydrophobic counter anions. In the cases of the SAMs bearing relatively hydrophilic counter anion BF_4, **8a-f** (**8a**: 35 ± 1^o, **8b**: 43 ± 1^o, **8c**: 46 ± 1^o, **8d**: 57 ± 1^o, **8e**: 80 ± 1^o, **8f**: 84 ± 1^o), the effects of alkyl chain-length were quite similar with **7a-f** bearing a strong hydrophilic bromide anion. Thus, changing the length of alkyl chains from C_4 (**8d**) to C_5 (**8e**) increased about 20° of the contact angles. In contrast, the SAM **9a-f** bearing relatively hydrophobic counter anion PF_6 showed smaller changes in the contact angles as increased the length of alkyl chains (**9a**: 52 ± 1^o, **9b**: 59 ± 1^o, **9c**: 59 ± 1^o, **9d**: 69 ± 1^o, **9e**: 83 ± 1^o, **9f**: 84 ± 1^o). Among the examined counter anions, as increase the length of alkyl chains, the most hydrophobic anion NTf_2 showed the smallest changes in the water contact angles of surfaces presenting [(C_nSAMIM)NTf_2] (**10a-f**) (**10a**: 65 ± 1^o, **10b**: 66 ± 1^o, **10c**: 68 ± 1^o, **10d**: 78 ± 1^o, **10e**: 82 ± 1^o, **10f**: 85 ± 1^o). The different chain-length dependency of the surface wettability of the SAMs between the hydrophilic and hydrophobic anions may be related with the interactions between the anion, imidazolium cation and water molecules of the surface. The exact nature of the interactions remained to be solved. Nevertheless, these results clearly indicate that the wettability of the Au surfaces coated with alkylimidazolium ion is largely dependent on the length of alkyl chain attached onto the imidazolium moiety, *i.e.*, the water contact angles of the surfaces increased as increase the length of alkyl chain.

We also found that the effects of counter anion on surface wettability were also dependent on the length of alkyl

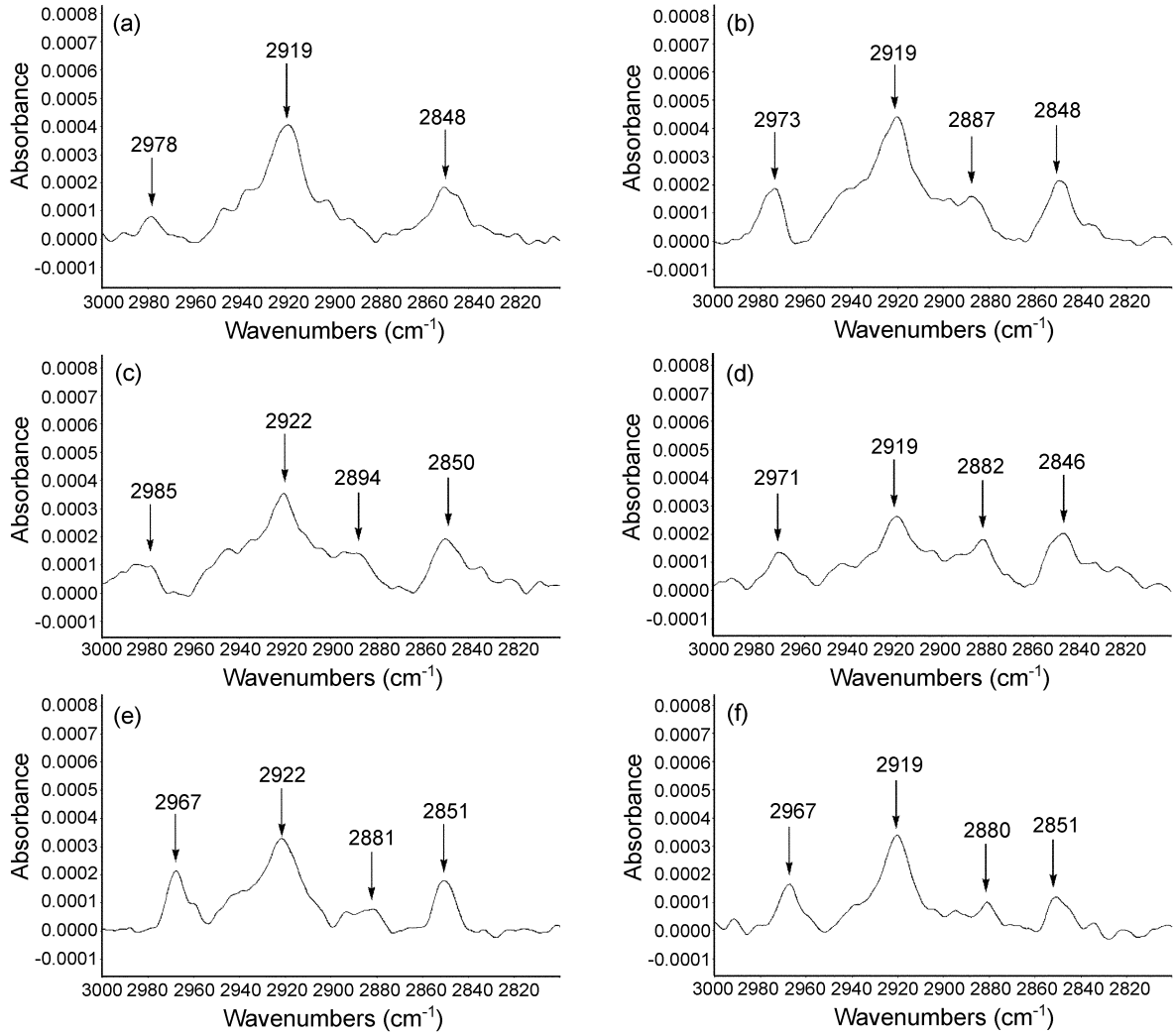


Figure 2. IR spectra for (a): [C_1(SAMIN)Br]; (b): [C_2(SAMIN)Br]; (c): [C_3(SAMIN)Br]; (d): [C_4(SAMIN)Br]; (e): [C_5(SAMIN)Br]; (f): [C_6(SAMIN)Br].

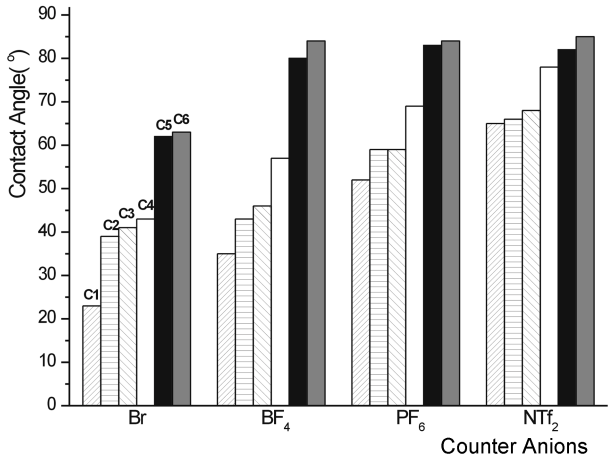


Figure 3. Graph of water contact angles versus length of alkyl chain for each counter anion.

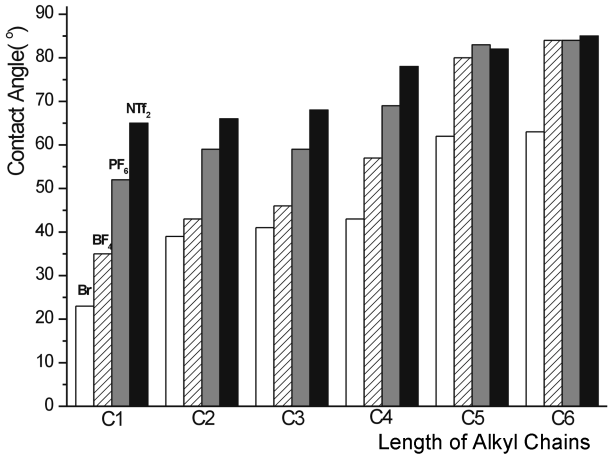


Figure 4. Graph of water contact angles versus counter anion for each alkyl chain.

chains. Figure 4 is another data graphic showing more clearly the effects of counter anion on the water contact angles for each SAMs having different alkyl chain length. As we observed previously, the water contact angles of the SAMs presenting [(C_1SAMIM)X] were systematically increased as change the counter anion from Br (**7a**: 23 ± 1^{o}) to BF_4 (**8a**:

35 ± 1^o), PF_6 (**9a**: 52 ± 1^o) and NTf_2 (**10a**: 65 ± 1^o).[44] However, in the cases of the SAMs bearing C_2 or C_3 alkyl chains, changes in contact angles were distinguished by the nature of the counter anions. Thus, relatively smaller changes in the contact angles of the surfaces bearing hydrophilic counter anions Br and BF_4 (**7b**: 39 ± 1^o *vs.* **8b**: 43 ± 1^o; **7c**: 41 ± 1^o *vs.* **8c**: 46 ± 1^o) were observed compared to those bearing hydrophobic counter anions PF_6 and NTf_2 (**9b**: 59 ± 1^o *vs.* **10b**: 66 ± 1^o; **9c**: 59 ± 1^o *vs.* **10c**: 68 ± 1^o). These results may suggest that the wettability of the SAM surfaces coated with C_1-C_3-alkylimidazolium ions controlled mainly by anion property. In case of the C_4-SAM presenting [(C_4SAMIM)X], both alkyl group and counter anion contributed almost equally to the wettability of the surfaces, and the contact angles were changed relatively regularly by changing the counter anions (**7d**: 43 ± 1^o, **8d**: 57 ± 1^o, **9d**: 69 ± 1^o, **10d**: 78 ± 1^o). However, the anions did not significantly affect the surface wettability of the C_5- and C_6-SAMs presenting [(C_5SAMIM)X] and [(C_6SAMIM)X], respectively, and the water wettabilities of the surfaces were mainly controlled by the alkyl groups. Little changes in contact angles of these surfaces imply that anions may be embedded in the relatively long pentyl or hexyl chains and in close contact with imidazolium cation. Therefore, effective "anion-directed" control of water wettability of Au surfaces coated with SAMs terminating in imidazolium ions could be possible only when the alkyl groups attached on the imidazolium moiety have less than four carbon atoms. Nevertheless, a strong hydrophilic bromide anion still affected the surface wettability, and thus, much smaller water contact angles were observed in [($C_{5\text{-}6}$SAMIM)Br] compared to those observed in [($C_{5\text{-}6}$SAMIM)X] (X = BF_4, PF_6 and NTf_2) bearing other counter anion. These anion effects are quite different with those observed on Si/SiO_2 surfaces, where counter anions did not effect at all the wettability of surfaces coated with *n*-butylimidazolium ions.[45] Unfortunately, it is hard to explain at present time why Au and Si/SiO_2 surfaces differently response to the alkyl-chain length and counter anion on the water wettability.

In summary, modulation of surface properties has important implications in both fundamental and technological advances. We reasoned that tunable water-miscibility of ILs could be transferred onto solid surface wettability, which could be adjusted by variation the length of alkyl chain on cation and/or anions. We designed and synthesized various kinds of thiol-functiolized ionic liquids having different length of alkyl chains and counter anions, and formed SAMs on Au surfaces with the aim of examining the effects of alkyl-chain length and counter anion on surface wettability. We found that the wettability of the Au surfaces coated with imidazolium ions were dependent not only on the length of alkyl-chain but also on counter anions.

Experimantal Section

General methods. NMR spectra were obtained on a Brüker 300 MHz. ^{1}H NMR spectra were referenced to tetramethylsilane in $CDCl_3$; ^{13}C NMR spectra were referenced to residual solvent. All reagents were used as received. 1-Methylimidazole and 1,12-dibromododecane, $NaBF_4$, $NaPF_6$, LiN (SO_2CF_3) were obtained from Sigma-Aldrich Korea or Acros Organics unless otherwise specified. All organic solvents were dried under standard purification conditions and distilled water was used. Polarized infrared external reflectance spectroscopy (PIERS) spectra were obtained in a single reflection mode using N_2-purged Thermo Nicolet Nexus Fourier Transform infrared spectrometer. The *p*-polarized light was incident at 80^o relative to surface normal of the substrate and a narrow band mercury-cadmium-telluride (MCT) detector was used. We averaged 1024 scans to yield the spectrum at a resolution of 2 cm^{-1}. The sample compartment was purged with dry and CO_2 free N_2. An ellipsometer (Gaertner L116s) equipped with a He-Ne Laser (632.8 nm) was used to determine the thickness of the monolayers. A contact angle instrument (Phoenix 300, Surface Electro Optics Co. Ltd., Korea) was used to determine the water contact angles of the monolayers and the water contact angles were measured at 22 ^{o}C and under 30% humidity. The Au substrates were prepared by thermal evaporation of 100 nm of Au onto polished Si(100) with a 20 nm Ti adhesion layer and cut into 1 cm^2 pieces.

General synthetic procedure for 1-[12-(thioacetyl) dodecyl]-3-alkylimidazolium bromide (2a-f). A solution of 1-alkylimidazole (25 mmol) in methylene chloride (10 mL) was added to a solution of 1,12-dibromododecane (25 g, 78 mmol) at room temperature. The reaction mixture was heated at reflux for 10 h. After evaporation of the solvent, the unreacted 1,12-dibromododecane was washed out thoroughly with hexane. The resulting solid was purified by silica column chromatography (CH_2Cl_2/MeOH = 7/1) to give 1-(12-bromododecyl)-3-alkylimidazolium bromide. To a solution of 1-(12-bromododecyl)-3-alkylimidazolium bromide (6.2 mmol) in dry THF (10 mL) was added potassium thioacetate (0.73 g, 6.2 mmol). After reflux for 6 h, the reaction mixture was cooled to room temperature, and the precipitate appeared was filtered off.s The filtrate was evaporated to remove solvent, and the residue was purified by silica column chromatography (CH_2Cl_2/MeOH = 7/1) to give 1-[12-(thioacetyl) dodecyl]-3-alkylimidazolium bromides **2a-f**.

2a: ^{1}H NMR ($CDCl_3$) δ 1.30-1.21 (m, 16H), 1.54 (m, 2H), 1.89 (m, 2H), 2.29 (s, 3H), 2.82 (t, J = 7.33 Hz, 2H), 4.11 (s, 3H), 4.29 (t, J = 7.42 Hz, 2H), 7.38 (s, 1H,), 7.54 (s, 1H), 10.36 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 26.1, 28.7, 28.9, 29.0, 29.2, 29.3, 29.4, 30.2, 30.5, 36.7, 50.1. 121.7, 122.8, 137.9. 196.1.

2b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, J = 7.38 Hz, 3H, CH_3), 1.29-1.20 (m, 16H, CH_2), 1.52 (m, 2H, CH_2), 1.95 (m, 2H, CH_2), 2.29 (s, 3H, CH_3), 2.82 (t, J = 7.29 Hz, 2H, CH_2), 4.32 (t, J = 7.29 Hz, 4H, CH_2), 7.44 (t, J = 1.77 Hz, 1H, Imid), 7.53 (t, J = 1.77 Hz, 1H, Imid), 10.50 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.2, 28.1, 28.6, 28.9, 29.2, 29.3, 30.2, 32.7, 34.1, 36.7, 50.2, 121.7, 123.4, 137.7. 196.1

2c: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, J = 7.32 Hz, 3H, CH_3), 1.43-1.24 (m, 18H, CH_2), 1.56 (m, 2H, CH_2), 2.32 (s, 3H, CH_3), 2.86 (t, J = 7.32 Hz, 2H, CH_2), 4.38 (m, J = 7.53 Hz, 4H, CH_3), 7.48 (s, 1H, Imid), 7.54 (s, 1H, Imid), 10.57 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 10.62, 24.60, 26.20, 28.85, 28.94, 29.01, 29.21, 29.28, 29.33, 29.35, 30.23, 30.53, 32.09, 49.71, 49.90, 121.50, 121.70, 137.11, 196.20.

2d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, J = 7.34 Hz, 3H, CH_3), 1.44-1.25 (m, 20H, CH_2), 1.56 (m, 2H, CH_2), 1.93 (m, 2H, CH_2), 2.32 (s, 3H, CH_3), 4.86 (t, J = 7.34 Hz, 2H, CH_3), 4.38 (q, J = 7.40 Hz, 2H, CH_2), 7.38 (s, 1H, Imid), 7.42 (s, 1H, Imid), 10.68 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.36, 19.36, 26.12, 28.66, 28.85, 28.94, 29.01, 29.21, 29.28, 29.33, 29.35, 30.23, 30.53, 32.09, 49.71, 29.99, 121.52, 122.02, 137.12, 195.97.

2e: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 6.63, 6.93 Hz, 3H, CH_3), 1.35-1.24 (m, 22H, CH_2), 1.54 (m, 2H, CH_2), 1.95 (m, 2H, CH_2), 2.32 (s, 3H, CH_3), 2.86 (t, J = 7.29, 7.35 Hz, 2H, CH_2), 4.38 (m, 4H, CH_2), 7.65 (t, J = 1.71 Hz, 1H, Imid), 7.61 (t, J = 1.71 Hz, 1H, Imid), 10.45 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.54, 21.75, 25.92, 27.92, 28.46, 28.68, 28.75, 28.81, 29.04, 29.08, 29.10, 29.14, 29.70, 30.05, 30.36, 49.68, 49.72, 121.96, 122.10, 136.51, 195.80.

2f: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, J = 6.90 Hz, 3H, CH_3), 1.31-1.24 (m, 24H, CH_2), 1.55 (m, 2H, CH_2), 1.92 (m, 4H, CH_2), 2.32 (s, 3H, CH_3), 2.86 (t, J = 7.32 Hz, 2H, CH_2) 4.37 (m, 4H, CH_2), 7.58 (t, J = 1.68 Hz, 1H, Imid), 7.61 (t, J = 1.63 Hz, 1H, Imid), 10.44 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.66, 22.10, 25.58, 25.96, 28.49, 28.71, 28.78, 28.84, 29.10, 29.11, 29.14, 29.17, 30.00, 30.07, 30.79, 49.75, 121.94, 122.02, 136.92, 195.90.

General synthetic procedure for 1-(12-mercaptododecyl)-3-alkylimidazolium bromide (3a-3f). To a solution of 1-[12-(*S*-acetyl)dodecyl]-3-alkylimidazolium bromide (0.247 mmol) in EtOH (3 mL) was added a solution of NaOH (0.01 g, 0.247 mmol) in H_2O (1.0 mL) at 0 °C. The reaction mixture was stirred at the same temperature, and then acidified with 2 N HBr until pH = 2. The organic materials were extracted with CH_2Cl_2, and dried with $MgSO_4$, evaporated to give product 1-(12-mercaptododecyl)-3-alkylimidazolium bromide 3a-f.

3a: ^{1}H NMR ($CDCl_3$) δ 1.34-1.25 (m, 17H), 1.36 (m, 2H), 1.58(m, 2H), 1.91 (m, 2H), 2.51 (q, J = 7.42 Hz, 2H), 4.13 (s, 3H), 4.32 (t, J = 7.49 Hz), 7.33 (s, 1H), 7.45 (s, 1H), 10.53(s, 1H); ^{13}C NMR ($CDCl_3$) δ 24.6, 26.2, 28.3, 28.9, 29.2, 29.4, 30.2, 33.9, 36.9, 50.1, 121.6, 123.4, 137.9.

3b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, J =7.38 Hz, 3H, CH_3), 1.31-1.24 (m, 16H, CH_2 and SH), 1.56 (m, 2H, CH_2), 1.88 (m, 2H, CH_2), 2.86 (t, J = 7.33 Hz, 2H, CH_2), 4.20 (m, J = 1.72 Hz, 1H, Imid), 7.38 (t, J = 1.72 Hz, 1H, Imid), 8.91 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 23.43, 26.15, 28.75, 28.89, 29.07, 29.10, 29.30, 29.37, 29.43, 29.45, 30.17, 30.62, 50.12, 51.52, 122.07, 122.23, 135.90.

3c: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (m, 19H, CH_2 and SH), 1.65-1.56 (m, 5H, CH_2 and CH_3), 1.93 (m, 2H, CH_2), 2.53 (q, J = 7.47 Hz, 2H, CH_2), 4.35 (m, J = 7.47 Hz, 2H, CH_3), 7.38 (t, J = 1.65 Hz, 1H, Imid), 7.54 (s, J = 1.65 Hz, 1H, Imid), 10.64 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 15.62, 24.59, 26.20, 28.26, 28.91, 28.96, 29.26, 29.36, 30.27, 33.94, 45.25, 50.10, 121.55, 121.69, 137.10.

3d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, J = 7.34 Hz, 3H, CH_3), 1.59-1.32 (m, 21H, CH_2 and SH), 1.60 (m, 2H, CH_2), 1.92 (m, 2H, CH_2), 2.57 (m, 2H, CH_2), 4.37 (q, J = 7.40 Hz, 2H, CH_2), 7.27 (s, 1H, Imid), 7.29 (s, 1H, Imid), 10.81 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.85, 22.31, 24.59, 25.81, 26.12, 28.27, 28.92, 28.96, 29.28, 29.35, 30.23, 30.53, 32.09, 49.71, 29.99, 121.70, 122.08, 137.10.

3e: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, J = 6.8 Hz, 3H, CH_3), 1.32-1.20 (m, 23H, CH_2 and SH), 1.55 (m, 2H, CH_2), 1.88 (m, 2H, CH_2), 2.46 (t, J = 7.32 Hz, 2H, CH_2), 4.30 (m, 4H, CH_2), 7.45 (s, J = 6.8 Hz, 1H, Imid), 7.47 (s, J = 1.62 Hz, 1H, Imid), 10.26 (s, 1H, Imid); ^{13}C NMR ($CDCl_3$) δ 13.67, 21.88, 24.46, 26.06, 28.06, 28.15, 28.81, 28.84, 29.17, 29.25, 29.28, 29.80, 30.15, 33.82, 49.87, 49.92, 50.16, 121.82, 122.01, 136.71.

3f: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.72 Hz, 3H, CH_3), 1.36-1.25 (m, 24H, CH_2 and SH), 1.61 (m, 2H, CH_2), 1.93 (m, 4H, CH_2), 2.52 (q, J = 7.32 Hz, 2H, CH_2), 4.37 (m, 4H, CH_2), 7.28 (s, 1H, Imid), 7.32 (s, 1H, Imid), 10.77 (s, 1H, Imid); ^{13}C NMR ($CDCl_3$) δ 15.60, 22.22, 25.40, 25.98, 28.55, 28.72, 28.80, 28.90, 29.22, 29.25, 29.15, 29.18, 23.10, 30.11, 30.80, 49.85, 121.85, 122.02, 136.59.

Synthesis of 1-(12-mercaptododecyl)-3-alkylimidazolium tetrafluoroborate (4a-4f), hexafluorophosphate (5a-5f) and bis(*N*-trifluoromethansulfonate) (6a-6f). To a suspension of 1-(12-mercaptododecyl)-3-alkylimidazolium bromide (**3**) (0.49 mmol) in acetone (7 mL) was added $NaBF_4$ (0.64 mmol) for **4** or $NaPF_6$ (0.64 mmol) for **5** and $Li(NTf_2)$ for **6**. The mixture was stirred at room temperature for 35 h. The solid was filtered off through Celite, and the filtrate was evaporated to remove solvent. The residue was purified by silica column chromatography to give the anion-exchanged products **4a**-**4f**, **5a**-**5f** and **6a**-**6f**.

4a: ^{1}H NMR ($CDCl_3$) δ 1.36-1.26 (m, 17H), 1.61 (m, 2H), 1.89 (m, 2H), 2.53 (q, J = 7.39, 2H), 3.96 (s, 3H), 4.17 (t, J = 7.44 Hz, 2H), 7.28 (s, 1H), 7.36 (s, 1H), 8.82 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 26.0, 28.7, 28.8, 29.6, 29.0, 29.2, 29.3, 29.4, 29.8, 30.5, 36.0, 50.0, 122.0, 123.6, 135.6.

4b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, J = 7.38 Hz, 3H, CH_3), 1.31-1.24 (m, 16H, CH_2 and SH), 1.56 (m, 2H, CH_2), 1.88 (m, 2H, CH_2), 2.86 (t, J = 7.33 Hz, 2H, CH_2), 4.20 (m, J = 1.72 Hz, 1H, Imid), 7.38 (t, J = 1.72 Hz, 1H, Imid), 8.91 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 23.43, 26.15, 28.75, 28.89, 29.07, 29.10, 29.30, 29.37, 29.43, 29.45, 30.17, 30.62, 50.12, 51.52, 122.07, 122.23, 135.90.

4c: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31-1.25 (m, 19H, CH_2 and SH), 1.65-1.43 (m, 5H, CH_2 and CH_3), 1.87 (m, 2H, CH_2), 2.52 (q, J = 7.38 Hz, 2H, CH_2), 4.19 (t, J = 7.50 Hz, 2H, CH_3), 4.28 (m, J = 7.35 Hz, 2H, CH_2), 7.34 (t, J = 1.71 Hz, 1H, Imid), 7.42 (t, J = 1.71 Hz, 1H, Imid), 8.90 (s, 1H,

Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 15.20, 26.18, 28.76, 28.89, 29.04, 29.10, 29.29, 29.38, 29.43, 29.45, 30.06, 30.64, 45.27, 50.14, 121.83, 122.01, 135.66.

4d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, J = 7.33 Hz, 3H, CH_3), 1.39-1.26 (m, 21H, CH_2 and SH), 1.58 (m, 2H, CH_2), 1.88 (m, 2H, CH_2), 2.52 (q, J = 7.31 Hz, 2H, CH_2), 4.22 (m, 4H, CH_2), 7.25 (s, 1H, Imid), 7.27 (s, 1H, Imid), 9.02 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.30, 26.11, 28.71, 28.85, 29.00, 29.06, 29.26, 29.34, 29.40, 30.06, 30.57, 31.91, 49.77, 50.05, 122.17, 122.32, 135.77.

4e: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 6.87 Hz, 3H, CH_3), 1.37-1.25 (m, 23H, CH_2 and SH), 1.54 (m, 2H, CH_2), 1.89 (m, 2H, CH_2), 2.60 (t, J = 7.32 Hz, 2H, CH_2), 4.24 (t, J = 7.32 Hz, 4H, CH_2), 7.40 (s, 1H, Imid), 7.42 (s, 1H, Imid), 9.26 (s, 1H, Imid); ^{13}C NMR ($CDCl_3$) δ 13.78, 21.98, 26.22, 28.19, 28.97, 29.02, 29.17, 29.23, 29.39, 29.48, 29.80, 30.03, 30.18, 31.00, 50.10, 55.73, 122.19, 122.25, 136.02.

4f: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.72 Hz, 3H, CH_3), 1.36-1.26 (m, 24H, CH_2 and SH), 1.60 (m, 2H, CH_2), 1.87 (m, 4H, CH_2), 2.52 (t, J = 7.30 Hz, 2H, CH_2), 4.22 (q, J = 7.42 Hz, 4H, CH_2), 7.27 (s, 1H, Imid), 7.28 (s, 1H, Imid), 9.03 (s, 1H, Imid); ^{13}C NMR ($CDCl_3$) δ 13.82, 22.60, 24.65, 25.74, 26.11, 28.31, 28.84, 29.03, 29.27, 29.44, 30.07, 30.93, 34.01, 50.27, 122.08, 135.24.

5a: ^{1}H NMR ($CDCl_3$) δ 1.38-1.25 (m, 17H), 1.60 (m, 2H), 1.86 (m, 2H), 2.52 (q, J = 7.37 Hz, 2H), 3.90 (s, 3H), 4.13 (t, J = 7.49 Hz, 2H), 7.24 (s, 1H), 7.28 (s, 1H), 8.49 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 24.6, 26.1, 28.3, 28.9, 29.0, 29.3, 29.4, 29.9, 34.0, 36.2, 50.1. 122.0, 123.6, 135.6.

5b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, J = 7.41 Hz, 3H, CH_3), 1.32-1.21 (m, 16H, CH_2 and SH), 1.64 (m, 2H, CH_2), 1.91 (m, 2H, CH_2), 2.68 (t, J = 7.32 Hz, 2H, CH_2), 4.20 (m, 4H, CH_2), 7.25 (s, 1H, Imid), 7.26 (s, 1H, Imid), 9.07 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 23.48, 26.07, 28.76, 28.80, 29.03, 29.11, 29.22, 29.36, 29.39, 29.46, 30.09, 30.61, 50.25, 51.62, 122.14, 122.20, 135.68.

5c: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36-1.26 (m, 19H, CH_2 and SH), 1.65-1.52 (m, 5H, CH_2 and CH_3), 1.87 (m, 2H, CH_2), 2.51 (q, J = 7.20 Hz, 2H, CH_2), 4.15 (t, J = 7.56 Hz, 2H, CH_3), 4.25 (q, J = 7.32 Hz, 2H, CH_2), 7.29 (s, 1H, Imid), 7.30 (s, 1H, Imid), 8.64 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 15.09, 24.64, 26.08, 28.20, 28.80, 28.90, 29.19, 29.34, 29.98, 34.67, 45.11, 49.98, 50.18, 121.88, 122.06, 135.60.

5d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, J = 7.34 Hz, 3H, CH_3), 1.39-1.24 (m, 21H, CH_2 and SH), 1.56 (m, 2H, CH_2), 1.84 (m, 2H, CH_2), 2.86 (t, J = 7.32 Hz, 2H, CH_2), 4.17 (m, 4H, CH_2), 7.33 (t, J = 1.65 Hz, 1H, Imid), 7.35 (t, J = 1.65 Hz, 1H, Imid), 8.57 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.26, 26.07, 28.71, 28.81, 29.00, 29.06, 29.23, 29.34, 29.40, 29.91, 30.58, 31.76, 49.81, 50.09, 122.20, 122.32, 135.0.

5e: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.87 Hz, 3H, CH_3), 1.41-1.26 (m, 23H, CH_2 and SH), 1.62 (m, 2H, CH_2), 1.88 (m, 2H, CH_2), 2.60 (t, J = 7.32 Hz, 2H, CH_2), 4.17 (m, 4H, CH_2), 7.30 (s, 1H, Imid), 7.36 (s, 1H, Imid), 8.65 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.84, 22.30, 24.62, 25.73, 26.10, 28.30, 28.85, 29.00, 29.21, 29.43, 29.80, 29.96, 30.82, 34.11, 50.17, 122.15, 135.25.

5f: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, J = 6.72 Hz, 3H, CH_3), 1.35-1.25 (m, 24H, CH_2 and SH), 1.60 (m, 2H, CH_2), 1.86 (m, 4H, CH_2), 2.52 (q, J = 7.35 Hz, 2H, CH_2), 4.17 (m, 4H, CH_2), 7.29 (s, 1H, Imid), 7.30 (s, 1H, Imid), 8.61 (s, 1H, Imid); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.84, 22.29, 24.62, 25.73, 26.13, 28.31, 28.86, 29.01, 29.29, 29.42, 29.88, 29.96, 30.82, 34.00, 50.17, 122.15, 135.27.

6a: ^{1}H NMR ($CDCl_3$) δ 1.38-1.25 (m, 17H), 1.60 (m, 2H), 1.86 (m, 2H), 2.52 (q, J = 7.37 Hz, 2H), 3.90 (s, 3H), 4.13 (t, J = 7.49 Hz, 2H), 7.27 (s, 1H), 7.26 (s, 1H), 8.81(s, 1H); ^{13}C NMR ($CDCl_3$) δ 24.6, 26.1, 28.3, 28.9, 29.0, 29.3, 29.4, 29.9, 34.0, 36.2, 50.1, 121.8, 123.5, 135.8.

6b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, J = 7.38 Hz, 3H, CH_3), 1.36-1.26 (m, 16H, CH_2 and SH), 1.60 (m, 2H, CH_2), 1.91 (m, 2H, CH_2), 2.52 (q, J = 7.26 Hz, 2H, CH_2), 4.18 (m, 4H, CH_3), 7.26 (s, 1H, Imid), 7.28 (s, 1H, Imid), 8.81 (s, 1H, Imid); ^{13}C NMR ($CDCl_3$) δ 19.23, 29.95, 28.64, 28.67, 29.03, 29.10, 29.20, 29.25, 29.39, 29.94, 30.09, 30.52, 50.25, 51.62, 177.31, 121.56, 122.31, 122.36, 134.94.

6c: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31-1.25 (m, 19H, CH_2 and SH), 1.62-1.53 (m, 5H, CH_2 and CH_3), 1.88 (m, 2H, CH_2), 2.52 (t, J = 7.20 Hz, 2H, CH_2), 4.20 (t, J = 7.35 Hz, 2H, CH_3), 4.28 (q, J = 7.41 Hz, 2H, CH_2), 7.36 (t, J = 1.89 Hz, 1H, Imid), 7.43 (t, J = 1.89 Hz, 1H, Imid), 8.64 (s, 1H, Imid); ^{13}C NMR ($CDCl_3$) δ 13.09, 19.24, 25.96, 28.64, 28.67, 28.91, 29.10, 29.20, 29.25, 29.94, 30.52, 31.84, 49.93, 50.20, 117.31, 121.51, 122.01, 134.94.

6d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, J = 7.34 Hz, 3H, CH_3), 1.39-1.24 (m, 21H, CH_2 and SH), 1.55 m, 2H, CH_2), 1.84 (m, 2H, CH_2), 2.86 (t, J = 7.32 Hz, 2H, CH_2), 4.14 (m, 4H, CH_2), 7.32 (s, 1H, Imid), 7.33 (s, 1H, Imid), 8.63 (s, 1H, Imid); ^{13}C NMR ($CDCl_3$) δ 18.24, 24.96, 28.64, 28.67, 29.10, 29.20, 29.21, 29.25, 29.94, 31.42, 31.85, 49.90, 50.10, 122.56, 122.31, 122.34, 134.64.

6e: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 6.95 Hz, 3H, CH_3), 1.34-1.26 (m, 23H, CH_2 and SH), 1.57 (m, 2H, CH_2), 1.88 (m, 4H, CH_2), 2.61(q, J = 7.34 Hz, 2H, CH_2), 4.17(m, 4H, CH_2), 7.23 (s, 1H, Imid), 7.24 (s, 1H, Imid), 8.60 (s, 1H, Imid); ^{13}C NMR ($CDCl_3$) δ 19.24, 25.96, 28.64, 28.67, 28.92, 29.10, 29.20, 29.21, 29.25, 29.94, 30.42, 31.85, 49.90, 50.10, 121.56, 122.31, 122.35, 134.94.

6f: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, J = 6.72 Hz, 3H, CH_3), 1.39-1.24 (m, 24H, CH_2 and SH), 1.55 (m, 2H, CH_2), 1.84 (m, 4H, CH_2), 2.86 (q, J = 7.34 Hz, 4H, CH_2), 4.14 (m, 4H, CH_2), 7.31 (s, 1H, Imid), 7.32 (s, 1H, Imid), 8.63 (s, 1H, Imid); ^{13}C NMR ($CDCl_3$) δ 13.09, 19.24, 25.96, 28.64, 28.67, 28.91, 29.10, 29.17, 29.20, 29.94, 30.52, 31.84, 49.93, 50.20, 117.31, 121.551, 122.31, 122.36, 134.94.

Preparation of imidazolium ion-terminated self-assembled monolayers (SAMIM-7-10) by spontaneous adsorption of thiol-functionalized ionic liqiuids 3-6. The Au substrates cleaned prior to adsorption in "*piranha*" solution (25% peroxide-75% sulfuric acid) for 1 min were immersed in 1 mM solution of thiol terminated ionic liquids **3-6** in absolute ethanol for 3 h. The modified Au surfaces

were rinsed with ethanol followed by distilled water, and were then dried by blowing with a rapid stream of nitrogen. The surfaces were then characterized by external reflection infrared spectroscopy and contact angle measurements.

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