

Imidazolium Ion-Terminated Self-Assembled Monolayers on Au: Effects of Counteranions on Surface Wettability

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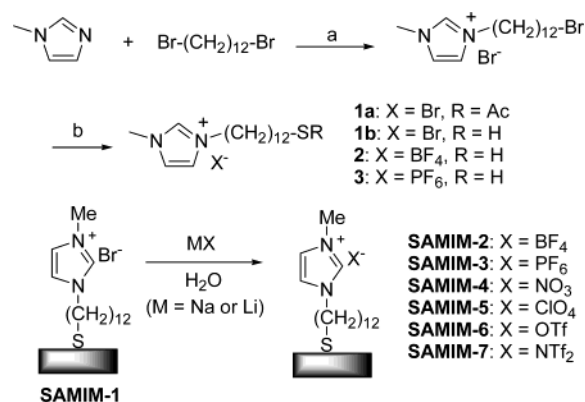
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Facile tunability of physicochemical properties of ionic liquids (ILs), particularly imidazolium ions bearing simple alkyl appendages as cations, has led to intense interest in ILs as an alternative to conventional organic solvents in a range of synthesis, catalysis, electrochemistry, and liquid–liquid extractions.¹ Recent developments include their use for biopolymers,² chemosensors for specific ions,³ determination of acidity scale,⁴ and formation of nanosized metal particles⁵ and hollow metal oxide microspheres.⁶ The availability of potentially hydrophobic and hydrophilic ILs attests to the ease in the manipulation of their physical properties.⁷ Especially, the choice of anions greatly effects the hydrophilicity and hydrophobicity. The only proven method currently available to quantify hydrophilicity and hydrophobicity of ILs is the comparison of IL–water partitioning with octanol–water. Therefore, the search for new methods for quantifying anion effects on hydrophilicity and hydrophobicity as well as for new applications of the tunable physicochemical properties of ILs is of importance in the burgeoning IL research field. During our studies on ILs⁸ and surface chemistry,⁹ we found that the combination of ILs with a technique of self-assembled monolayers (SAMs) could provide a simple method for quantifying the effects of anions on hydrophilicity and hydrophobicity of ILs. Herein we report for the first time the formation of SAMs presenting imidazolium ions at the tail ends (SAMIMs) on Au having different anions and the effects of counteranions on surface hydrophilicity and hydrophobicity, i.e., wettability, to demonstrate the possible applications of ILs in surface sciences.¹⁰

Modulation of surface properties such as wettability, adhesion, and biocompatibility has important implications in both fundamental and technological advances.¹¹ Various methods have been used to control the wettability of surfaces permanently¹² or dynamically.¹³ To the best of our knowledge, however, there is no report on controlling surface wettability by anion exchange. The success of our approach hinges upon the formation of SAMs presenting imidazolium ions to manifest the changes in wettability with change of the counteranions on surfaces. Three different SAMs of 1-methylimidazolium salts having different counteranions (Br, BF₄, and PF₆) (SAMIMs-1–3) were chosen as a model system. Measurements of water contact angles could provide quantitative information on the effects of counteranions on the surface wettability of the SAMIMs.¹⁴ For the preparation of SAMIMs on Au surfaces, the required thiol-terminated ILs **1b**, **2**, and **3** were synthesized as shown in Scheme 1. By reaction of 1-methylimidazole with 1,12-dibromododecane followed by substitution with potassium thioac-

Scheme 1^a



^a (a) CH₂Cl₂, reflux, 10 h, 85%. (b) (i) KSCoCH₃, THF, reflux, 6 h, 75%. (ii) For **1b**: EtOH/H₂O (3/1, v/v), NaOH, 0 °C, 1 h, then HBr, 83%. (iii) **1b**/Acetone, NaBF₄ for **2** (85%) and NaPF₆ for **3** (90%), rt, 35 h.

etate, the **1a** having a Br anion was obtained. Treatment of **1a** with NaOH followed by acidification with HBr provided **1b** in 83% yield. The anion exchange of **1b** with NaBF₄ and NaPF₆ in acetone provided the corresponding thiol-terminated ILs **2** (85%) and **3** (90%), respectively.

The well-ordered SAMs of **1b**, **2**, and **3** on Au surfaces were formed by submersing the Au substrates in 1 mM ethanolic solution of the corresponding thiol-terminated ILs for 3 h. Grazing-angle FTIR showed CH₂ stretching bands at 2919 and 2848 cm⁻¹, characteristic of a well-ordered, close-packed film.¹⁵ Ellipsometric measurement showed a thick film about 19 Å supporting the formation of monomolecular films. No sign of the formation of multilayers was observed even under longer incubation times or at higher concentrations. We found that the water contact angle of the SAMIM-1 (23 ± 1°) having a Br anion was increased by change of the counteranion to BF₄ (SAMIM-2: 35 ± 1°) and PF₆ anions (SAMIM-3: 52 ± 1°). These results clearly indicate that the wettability of SAMIM surface could be tailored by changing the anions.

Next, we examined the possibility of “direct” exchange of counteranions on SAMIM surfaces. For this purpose, we scrutinized various solvent systems such as acetone, EtOH, EtOH/water, or pure water and found that pure water was the most appropriate solvent for direct anion exchange on SAMIM surfaces. The SAMIM-1 was immersed in an aqueous solution of NaBF₄ and NaPF₆ without stirring for 6 h, rinsed extensively with H₂O followed by ethanol, and dried under an argon stream to give SAMIM-2 and SAMIM-3, respectively. The water contact angles of SAMIM-2 (34 ± 1°) and SAMIM-3 (53 ± 1°) were quite consistent with

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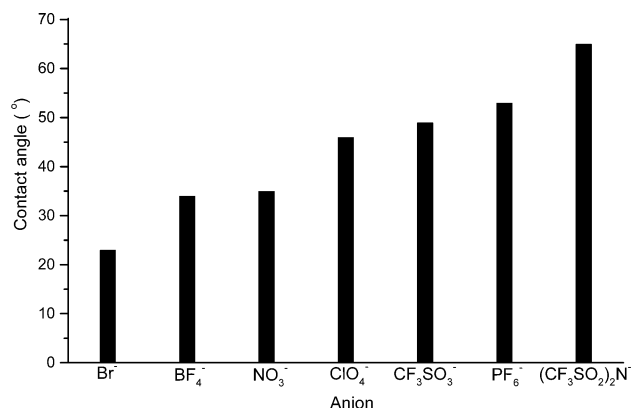


Figure 1. Effects of counteranions on water contact angles.

those of the SAMIM-2 and SAMIM-3 generated independently from the thiol-terminated ionic liquid 2 and 3. XPS analyses indicated the Br anion (3d_{3/2}, 70 eV and 3d_{5/2}, 69 eV) of SAMIM-1 was completely exchanged with BF₄ (B 1s, 188 eV and F 1s, 686 eV) and PF₆ (P 2p_{1/2}, 138 eV, 2p_{3/2}, 137 eV and F 1s, 687 eV) anions to form SAMIM-2 and SAMIM-3, respectively (see Supporting Information). Having established the direct anion exchange on SAMIM surfaces, we formed various SAMIMs (SAMIM-2–7) bearing different counteranions by direct anion exchange of SAMIM-1 and measured their contact angles, which provided information on quantitative effects of the counteranions on the surface wettability of the SAMIMs (Figure 1).

As shown in Figure 1, all of the anion-substituted SAMIM-2–7 showed higher contact angles than that of the SAMIM-1 having Br anion (23 ± 1°). Among them, the SAMIM-7 having the NTf₂ anion exhibited the highest contact angle (65 ± 1°). We also found that the SAMIMs bearing fluorinated anions such as PF₆⁻ (53 ± 1°) and CF₃SO₃⁻ (49 ± 1°) showed higher contact angles than those having other anions, such as ClO₄⁻ (46 ± 1°) and NO₃⁻ (35 ± 1°). The modulation of wettability of these SAMIMs is probably due to the solvation of the anion as observed in 1-alkyl-3-methylimidazolium-based ionic liquids where the ClO₄⁻ and NO₃⁻ anions had strong hydrogen-bonding interactions with water molecules.¹⁶ However, the surface of SAMIM-2 bearing an BF₄ anion (34 ± 1°) had relatively hydrophilic property.¹⁷ This result is quite consistent with that obtained from water-IL partitioning, in which 1-alkyl-3-methylimidazolium salts of PF₆ and NTf₂ are only sparingly miscible with water whereas BF₄ salts are water miscible at room temperature.^{2a,3} On the basis of the observed contact angles of the SAMIMs, it could be possible to quantify the effects of counteranions on hydrophobicity of the self-assembled monolayers of imidazolium-based ionic liquids in the following order: NTf₂ > PF₆ > CF₃SO₃ > ClO₄ > NO₃ > BF₄ > Br. It is worth noting that this report is the first quantitative determination of the effect of counteranions on the surface wettability of SAM, and it provides a simple and useful technique for the determination of quantitative counteranion effects on hydrophobicity of ILs.

In conclusion, this work demonstrates that the surface wettability of SAMs presenting imidazolium ions at the tail ends could be extrapolated to the water miscibility of the related ionic liquids. As a proof-of-principle, via direct ion exchange on a monolayer surface, changes in water contact angles of the SAM surfaces

presenting imidazolium ions have been observed. We believe that the anion effect on surface wettability demonstrated herein is of general significance to the adsorption on molecular surfaces. This effect could be advantageously incorporated into the design of monolayer-based technologies such as microfluidics and micro-devices used in anion sensing and in biomedical areas.

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Supporting Information Available: Synthetic procedures, ¹H and ¹³C NMR spectra of all new compounds 1a, b, 2, and 3, and IR and XPS spectra of SAMIM 1–3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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