Preparation and characterisation of self-assembled monolayers of long-chain alkyl imidazolium-based ionic liquids on glass surface

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Self-assembled monolayers of long-chain alkyl imidazolium-based ionic liquid [C_{16}tespim]X (X = Br^-, BF_4^-, PF_6^-, Tf_2N^-) were grafted onto soda glass surfaces by –Si–O– covalent bonding. These monolayers transformed the wetting behaviour of the glass from hydrophilicity to hydrophobicity as investigated by water contact angle measurement. Exchange of the counteranion of the ionic liquids could tailor the surface wettability. It was found that the contact angle could be up to 112±4° on the glass surfaces when Tf_2N^- was the counteranion. The transmittance of glass-grafted ionic liquid monolayers was similar to that of the common glass.

Keywords: long-chain alkyl imidazolium-based ionic liquids, self-assembled monolayer, contact angle, wettability, glass

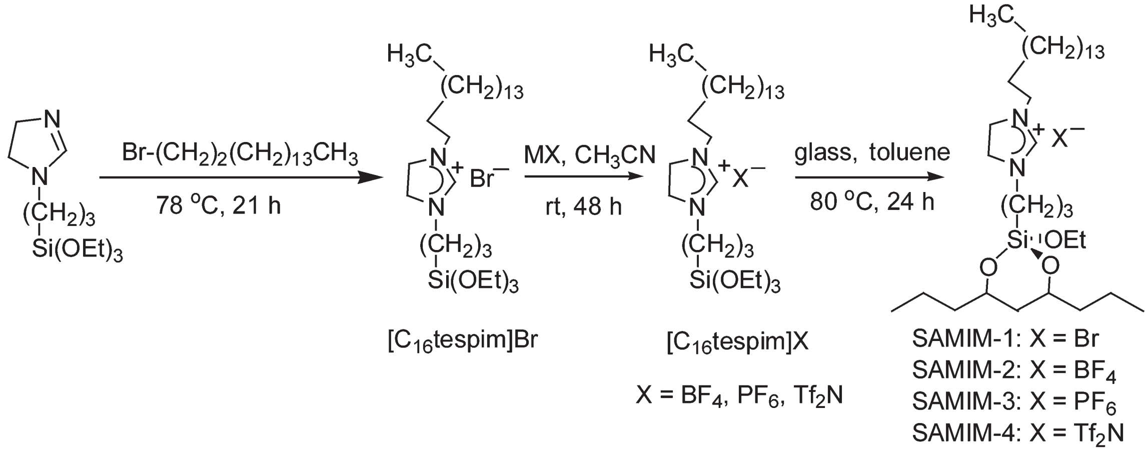
Recently, self-cleaning glass has been widely used in notable buildings and in the side mirrors of cars.[1,2] A number of materials have been used as hydrophobic films, including inorganic oxides and organic polymers. Among these, TiO_2-based surfaces can vary the transition from larger contact angles (CAs) to lower CAs upon UV illumination due to their intrinsic photocatalytic and photo-stimulated properties; they have been used as anti-fogging and self-cleaning films on the window glass of buildings. However, its shorter life-span limits its application.[3,4] More stable hydrophobic materials to modify glass surfaces have been researched.

As a new type of reaction medium and new function materials, room temperature ionic liquids (RTILs) have many important properties, such as negligible vapour pressure, relatively high ionic conductivity, good chemical and thermal stability, non-flammability, and a wide electrochemical potential window.[5–8] The physicochemical properties of imidazolium ion RTILs especially hydrophilicity and hydrophobicity, can easily be tuned by varying the alkyl appendages of the imidazolium cation and/or the counteranions. They then meet the demand of surface modification through transferring their tunable properties to the solid surfaces.[9] Therefore, utilisation of RTILs can provide a new strategy to control the properties of surfaces, and many papers in this area have been published.[10–19] The studies ranged from self-assembled monolayers (SAMs) of ionic liquids[10–15] to polyelectrolyte-functionalised ionic liquids (PFILs)[16] and poly(ionic liquid) brushes,[17] from linking by covalent bonding[10–17] to electrospinning[18] or spin-coating.[19] Among these, SAMs of ionic liquids have attracted interest due to their simple nature and practicability for surface modification. In 2004, Choi *et al.*[10,12] for the first time used SAMs of imidazolium ion-terminated ionic liquids (SAMIMs) to control the surface wettability of the gold and Si/SiO_2 surfaces. Subsequently, Lu *et al.*[13] modified negatively charged polyimide films using ionic liquids (ILs) based on electrostatic self-assembly and achieved the similar results. The tunable properties of ILs could also be extended to control the properties of carbon nanotube-based materials.[14,15] However, until now, the wettability of SAMs of ILs was limited from 21° to 95° because ILs used in these reports had short-chain alkyl groups bonded to the imidazolium ions.[10,12,17]

Many studies have indicated that ILs have a trend of increasing hydrophobicity with increasing chain length of the substituent. Therefore, long-chain imidazolium-based ILs should be more promised hydrophobic materials.[20–22] Here I have used the SAMs of long-chain alkyl substituted imidazolium ions to modify glass surfaces by –Si–O– covalent bonding by two fabrication routes. The wettability was monitored using water contact angle measurements. The results showed that long-chain imidazolium-based ILs could induce the glass to high hydrophobicity and hardly decreased the transmittance of the glass. Exchange of counteranions could tailor the wettability of the glass, and Tf_2N^- was an ideal counteranion.

Results and discussion

Two routes of fabricating the SAMs of ionic liquids on soda glass surfaces were designed for this report. Route 1 where the exchange of the anion has been done before grafting on the substrate surfaces is illustrated in Scheme 1. Firstly,



Scheme 1 Route 1 of fabrication of ionic liquid monolayers on glass surfaces.

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N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole reacted with *n*-hexadecyl bromide at 78 °C for 21 h to give a complex 1-hexadecyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium bromide ([C_{16}tespim]Br). The excess reactants and by-products were extracted with diethyl ether and pentane several times and the the residue was dried *in vacuo* to give the pure [C_{16}tespim]Br. Secondly, anion exchange of [C_{16}tespim]Br with MX ($NaBF_4$, KPF_6 and $LiTf_2N$) in acetonitrile was accomplished at room temperature for 48 h and provided the corresponding ILs, [C_{16}tespim]BF_4, [C_{16}tespim]PF_6 and [C_{16}tespim]Tf_2N, respectively. The main impurities were salts, including the excess MX and the MBr generated in the process of anion exchange and were difficult to remove. It was necessary to clean with deionised water many times, otherwise the impurities would influence the quality of the IL monolayers. Finally, the SAMIMs (see Scheme 1) with Br^-, BF_4^-, PF_6^-, Tf_2N^- were formed by covalent bonding onto glass surfaces by submersing freshly cleaned glass substrates into a 1% toluene solution of corresponding [C_{16}tespim]X at 80 °C for 24 h.

The SAMs of [C_{16}tespim]X grafted onto the glass surfaces could effectively change the wettability of the surfaces. By measuring the static contact angle (CA) by the sessile drop method, it was found that the water CA of glass substrates could increase from < 10 ° to 98±2 ° after grafting the SAM of [C_{16}tespim]Br, so the surface had been changed from a hydrophilic to a hydrophobic state (Fig. 1). As expected, the CA value was larger than that of the SAM of [C_4tespim]Cl (24 °) reported by Choi *et al.*,[10] indicating that the SAMs of longer-chain alkyl groups were more hydrophobic than those of shorter–chain alkyl groups.

Many studies have demonstrated that counteranions could determine the wettability of IL films. In order to evaluate the effect of the counteranions, Br^- was exchanged to BF_4^-, PF_6^- and Tf_2N^- in this work. Water CAs of the SAMs of [C_{16}tespim]BF_4, [C_{16}tespim]PF_6 and [C_{16}tespim]Tf_2N on glass were 102±3 °, 109±2 ° and 112±4 °, respectively (Table 1). Clearly, the counteranions could affect the wettability of ILs. The wetting rule was in the following order: $Br^- < BF_4^- < PF_6^- < Tf_2N^-$, which was in agreement with the trend of the solubility of ionic liquids in water.[9] Remarkably, Tf_2N^- as counteranion led to a CA of 112±4 °, which approached the limiting value 119 ° on the smooth surfaces.[24] This excellent hydrophobicity would make hydrophilic or oleophilic contaminants to be easily removed by rain.

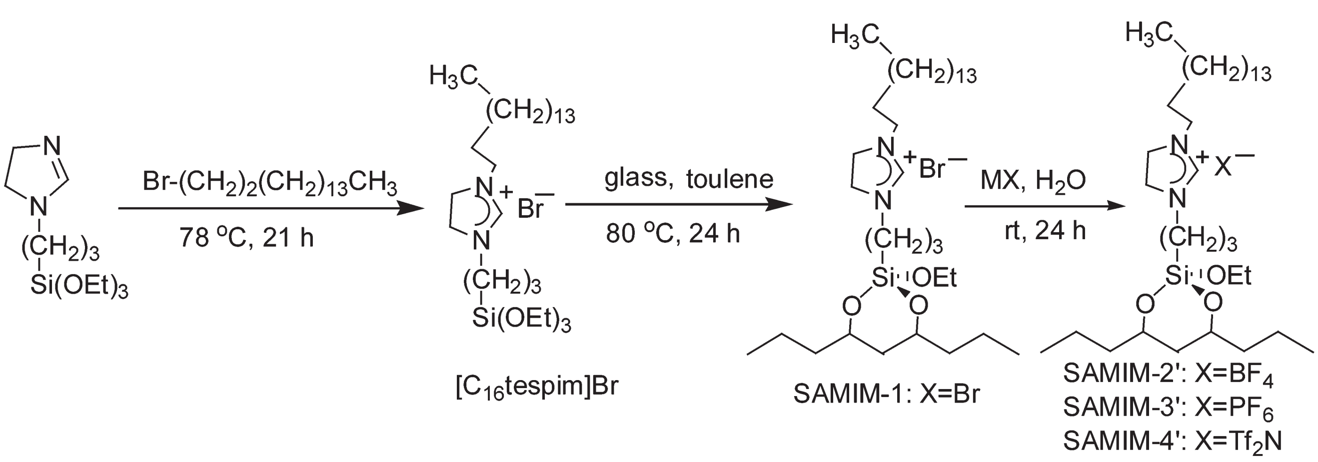
Fig. 1 Water counteranion (CA) of glass: (a) pure glass, CA < 10°, (b) glass coated with the SAM of [C_{16}tespim]Br, CA = 98±2°.

Table 1 The effect of counteranions on the water contact angle

Route	CA/°			
	Br^-	BF_4^-	PF_6^-	Tf_2N^-
1	 98±2°	 102±3	 109±2	 112±4
2		 103±2	 108±2	 112±2

However, the troublesome purification of [C_{16}tespim]X in Route 1 resulted in complexity in the preparation process as well as poor reproducibility of the IL monolayers. Therefore, Route 2 "direct" exchange of couteranions on the substrates was adopted according to the literature.[10,12] As shown in Scheme 2, SAMIM-1 having a Br anion was firstly grafted onto the glass surface, and then the anion was directly exchanged. Immersing the SAMIM-1 into an aqueous 50 mM solution of $NaBF_4$, KPF_6 or $LiTf_2N$ at room temperature for 24 h without stirring gave SAMIM-2′ having BF_4^-, SAMIM-3′ having PF_6^- and SAMIM-4' having Tf_2N^-, respectively. The water CAs of the SAMs of [C_{16}tespim]BF_4, [C_{16}tespim]PF_6 and [C_{16}tespim]Tf_2N on glass were 103±2 °, 108±2 ° and 112±2 °, respectively (Table 1). Clearly, the CA values were quite consistent with those of the SAMIM-2, SAMIM-3 and SAMIM-4 generated independently from the pure [C_{16}tespim]X (X = BF_4, PF_6 and Tf_2N). This indicated that the method of "direct anion exchange" could lead to the successful exchange of anion. In the meantime, the reproducibility of CA values were better than that of Route 1 because small amounts of salts formed during direct anion exchange were easy to remove by rinsing with deionised water followed by ethanol.

For window glass surfaces, optical transparency is important. The transmittance of the glass coated by SAMIMs was measured by UV-Vis spectroscopy. Using pure glass as standard material, light transmittance of the SAMIMs was >98% in the visible light at 400 nm. Table 2 clearly indicated that all of the samples were transparent to visible-light, no matter whether they were formed by Route 1 or Route 2.



Scheme 2 Route 2 of fabrication of ionic liquid monolayers on glass surfaces.

Table 2 The effect of the ionic liquid films on the transmittance of glass

SAM of Ionic liquid	Transmittance T/%	
	Route 1	Route 2
Pure glass	100	100
[C$_{16}$tespim]Br	98.7	98.9
[C$_{16}$tespim]BF$_4$	99.1	99.0
[C$_{16}$tespim]PF$_6$	98.7	98.6
[C$_{16}$tespim]Tf$_2$N	98.3	98.7

The mechanism

The wettability of ionic liquids can easily be tuned by varying the imidazolium cation and/or counteranions. For a fixed cation, in general, the effect of anions on hydrophobicity of the imidazolium-based ionic liquids was in the following order at the same temperature: $Tf_2N^- > PF_6^- > OTf^- > ClO_4^- > NO_3^- > BF_4^- > Br^-$, which is in agreement with the trend of solubility of RTILs.[9] In this report, the hydrophobicity follows this trend.

In addition to the anions, cations of ionic liquids are also used as wettability controlling agents to tailor the surface properties. Studies have indicated that increasing the alkyl chain length results in a decrease of solubility in water. Therefore, the longer-chain alkyl imidazolium-based ionic liquids have higher hydrophobicity than that of shorter-chain alkyl imidazolium ions.

Conclusion

SAMs of long-chain alkyl imidazolium-based ionic liquids were grafted onto glass, inducing a kind of high hydrophobic and transparent glass surface. Longer-chain alkyl imidazolium-based ionic liquids [C$_{16}$tespim]X has the advantage over shorter-chain ILs in improving the wettabilty of glass surfaces. Tf_2N^- as a promising counteranion could result in glass surfaces having the highest hydrophobicity. ILs' good chemical and thermal stability and the use of the SAM technique could provide a simple method to obtain self-cleaning glass.

Experimental

N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole, *n*-hexadecyl bromide, NaBF$_4$, KPF$_6$, LiTf$_2$N were of A.R. grade and were used without further purification. Toluene and acetonitrile were dried over 4 Å molecular sieves. All aqueous solutions were prepared with deionised water. ^{1}H NMR spectra were recorded at 400 MHz, using TMS as internal standard. FT-IR spectra were obtianed with a Nicolet IR200 spectrometer. Elemental analyses were performed on a Vario el Z III (Germany) instrument.

Soda glass substrates were cut into 1 cm × 1 cm pieces. The samples were sonicated in soapy water for 30 min, rinsed with deionised water, dried and were then cleaned using freshly prepared "piranha" solution (3:7 by volume of 30% H_2O_2 and H_2SO_4; at 90 °C for 1 h to generate -OH groups as well as to clean the surfaces, rinsed with deionised water, ethanol and dried under a stream of nitrogen.

CAUTION: Piranha solution reacts violently with most organic materials and must be handled with extreme care

Route 1

Preparation of [C$_{16}$tespim]Br:[23] A mixture of *N*-(3-triethoxysilylpropyl)-4,5- dihydroimidazole (1.37 g, 0.005 mol) and *n*-hexadecyl bromide (4.58 g, 0.015 mol) was refluxed at 78 °C for 21 h. The reaction mixture was cooled to room temperature and the volatiles evaporated under reduced pressure. The resulting material consisted of a brown coloured paste, which was washed with diethyl ether and pentane (6 x 50 mL) and dried *in vacuo*. Extraction of the material using dichloromethane (100 mL) gave a yellow solid after the removal of the volatile components under reduced pressure. ^{1}H NMR (400 MHz. CDCl$_3$): δ 0.63 (m, 3H), 1.22 (m, 9H),1.29–1.36 (m, 26H), 1.39 (t, J = 7.0 Hz, 2H), 2.30 (m, 4H), 3.60–3.82 (m, 8H), 4.08–4.27 (m, 6H), 8.48 (s, 1H); IR (cm^{-1}): 3359 (O–H), 2861 (–CH$_2$CH$_3$), 1637 (imidazolium), 1446–1076 (–C–C–), 956 (–C–C–). Anal. Calcd for $C_{28}H_{59}BrN_2O3Si$: C, 57.97; H, 10.21; Br, 13.80; N, 4.83; O, 8.27; Si, 4.86. Found: C, 58.10; H, 10.20; Br, 13.83; N, 4.84; O, 8.30; Si, 4.84%.

Preparation of [C$_{16}$tespim]X; general procedure: [C$_{16}$tespim]Br (2.90g, 0.005 mol) was dissolved in acetonitrile (20 mL) and treated with one equivalent of MX (NaBF$_4$, KPF$_6$ or LiTf$_2$N) (0.005 mol). The resulting slurry was stirred for 48 h at room temperature. After the removal of the precipitate by filtration through a bed of Celite, the volatiles were evaporated under reduced pressure to give a yellow liquid. The residue was dissolved in dichloromethane, and was extracted with deionised water (6 x 20 mL) to remove the salts completely. The removal of dichloromethane under reduced pressure gave a yellow liquid.

[C$_{16}$tespim]BF$_4$: Sodium tetrafluoroborate (NaBF$_4$) (0.55 g, 0.005 mol) was added into the acetonitrile solution of [C$_{16}$tespim]Br. After reaction and treatment, [C$_{16}$tespim]BF$_4$ was obtained. Yield: 2.35 g, 0.004 mol, 80%. ^{1}H NMR (400 MHz. CDCl$_3$): δ 0.65 (m, 3H), 1.21 (m, 9H), 1.30–1.37 (m, 26H), 1.40 (t, J = 6.7 Hz, 2H), 2.31 (m, 4H), 3.59–3.81 (m, 8H), 4.06–4.23 (m, 6H), 8.50 (s, 1H); IR (cm^{-1}): 3360 (–OH), 2861 (–CH$_2$CH$_3$), 1637 (Imidazolium), 1446–1077 (–C–C–), 957 (–C–C–). Anal. Calcd for $C_{28}H_{59}BF_4N_2O_3Si$: C, 57.27; H, 10.07; B, 1.87; F, 12.97; N, 4.77; O, 8.20; Si, 4.79. Found: C, 57.29; H, 10.06; B, 1.88; F, 12.96; N, 4.77; O, 8.18; Si, 4.77%.

*[C$_{16}$tespim]PF$_6$***:** Potassium hexafluorophosphate (KPF$_6$) (0.92 g, 0.005 mol) was added into the acetonitrile solution of [C$_{16}$tespim]Br. After reaction and treatment, [C$_{16}$tespim] PF$_6$ was obtained. Yield: 2.71 g, 0.0042 mol, 84%. ^{1}H NMR (400 MHz. CDCl$_3$): δ 0.66 (m, 3H), 1.20 (m, 9H),1.27–1.34 (m, 26H), 1.37 (t, J = 7.2 Hz, 2H), 2.28 (m, 4H), 3.59–3.80 (m, 8H), 4.04–4.31 (m, 6H), 8.41 (s, 1H); IR (cm^{-1}): 3360 (–OH), 2861 (–CH$_2$CH$_3$), 1638 (imidazolium), 1448–1077 (–C–C–), 958 (–C–C–). Anal. Calcd for $C_{28}H_{59}F_6N_2O_3PSi$: C, 52.17; H, 9.17; F, 17.67; N, 4.37; O, 7.47; P, 4.80; Si, 4.35. Found: C, 52.14; H, 9.16; F, 17.69; N, 4.35; O, 7.45; P, 4.81; Si, 4.35%.

*[C$_{16}$tespim]Tf$_2$N***:** Bistrifluoromethanesulfonimide lithium salt (LiTf$_2$N) (1.44 g, 0.005 mol) was added into the acetonitrile solution of [C$_{16}$tespim]Br. After reaction and treatment, [C$_{16}$tespim]Tf$_2$N was obtained. Yield: 3.00 g, 0.00385 mol, 77%. ^{1}H NMR (400 MHz. CDCl$_3$): δ 0.64 (m, 3H), 1.21 (m, 9H),1.30–1.34 (m, 26H), 1.40 (t, J = 6.5 Hz, 2H), 2.31 (m, 4H), 3.61–3.81 (m, 8H), 4.07–4.35 (m, 6H), 8.57 (s, 1H); IR (cm^{-1}): 3357 (–OH), 2862 (–CH$_2$CH$_3$), 1638 (imidazolium), 1448–1077 (–C–C–), 957 (–C–C–). Anal. Calcd for $C_{30}H_{59}F_6N_3O_7S_2Si$: C, 46.17; H, 7.56; F, 14.67; N, 5.41; O, 14.37; S, 8.21; Si, 3.60. Found: C, 46.19; H, 7.57; F, 14.63; N, 5.39; O, 14.37; S, 8.21; Si, 3.59%.

Preparation of SAMs of [C$_{16}$tespim]X on the glass surfaces; general procedure

In a 50 mL conical flask, 0.222 g [C$_{16}$tespim]X (X = Br, BF$_4$, PF$_6$ and Tf$_2$N) was added into 20 mL toluene to obtain a 1wt% toluene solution. Then the freshly cleaned glass substrates were immersed into the solution and reacted for 24 h at 80 °C. After the formation of SAMIM the substrates were rinsed with toluene, ethanol, and deionised water several times and then dried under a stream of N$_2$.

Route 2

(1) The preparation of [C$_{16}$tespim]Br and SAM of [C$_{16}$tespim]Br on the glass surfaces using the methods in Route 1.

(2) Exchanging the counteranion

In a 50 mL conical flask, the glass substrates coated with the SAM of [C$_{16}$tespim]Br were immersed in an aqueous 50 mM solution of MX (NaBF$_4$, NaPF$_6$ or LiTf$_2$N) at room temperature for 24 h, and the resulting glass substrates were thoroughly washed with water and ethanol and dried with a stream of N$_2$. Thus, the counteranion was completely exchanged directly on the glass substrates, and SAMs of [C$_{16}$tespim]BF$_4$, [C$_{16}$tespim]PF$_6$ or [C$_{16}$tespim]Tf$_2$N were formed.

Characterisation techniques

The static contact angle (CA) was measured by the sessile drop method with a deionised water droplet (3.5 μL) being placed on the surface using TRACKER (TECLIS Co., Ltd., France) instrument at room temperature. All measurements were repeated three times. UV–vis spectroscopy was performed using a UV–2450(SHIMADZU, Japan) instrument.

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