

Supporting Information

Controlling Microarray Feature Spreading and Response Stability on Porous Silicon Platforms by Using Alkene-Terminal Ionic Liquids and UV Hydrosilation

Shruti Trivedi,^{*,[a]} Sudhir Ravula,^[b] Gary A. Baker,^{*,[c]} Siddharth Pandey,^{*,[d]} and Frank V. Bright^{*,[a]}

^[a]Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY 14260-3000, USA

^[b]Department of Comprehensive Dentistry and Biomaterials, Louisiana State University Health Science Center, School of Dentistry, 1100 Florida Avenue, New Orleans, LA 70119, USA

^[c]Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, USA

^[d]Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India

*Corresponding Author: E-mail: chefvb@buffalo.edu; Fax: (716) 645-6963;

Tel: +1(716) 645-4180

Synthesis of Alkene-Terminal Ionic Liquids.

1-Butyl-3-vinylimidazolium bis(trifluoromethylsulfonyl)imide, [BVIm][Tf₂N]: 1-Vinylimidazole (4.08 g, 43.35 mmol) and 1-bromobutane (5.94 g, 43.35 mmol, 1.0 equiv) were combined together (solvent-free) in a 50 mL round bottom flask and stirred at room temperature for 2 days. The resulting yellow viscous liquid was washed with ethyl acetate (3 × 100 mL) to remove unreacted starting materials and white solid material slowly precipitated. The precipitated material was filtered, washed again with cold ethyl acetate (2 × 20 mL) and then dried under vacuum to yield the titular bromide salt as a white solid. To remove traces of color from the bromide salt, decolorizing charcoal (1.0 g) was added to the solid material dissolved in 50 mL of water and stirred for 24 h. Carbon was removed via filter flask followed by water removal on a rotary evaporator under reduced pressure. The bromide salt was dried under vacuum at 50 °C for 12 h to yield [BVIm]Br as a white solid in 51% yield. To initiate ion exchange, [BVIm]Br was dissolved in 50 mL of Ultrapure water followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (1.02 equiv, pre-dissolved in a minimal amount of water). All water used for ionic liquid synthesis consisted of freshly-drawn Ultrapure water having a measured resistivity of 18.2 MΩcm with TOC < 10 ppb and a bacterial count <10 CFUml⁻¹. The resulting solution was stirred for a few hours and then allowed to separate into two phases. The aqueous phase was decanted and the IL phase was washed with water (6 × 100 mL) until no residual halide could be detected in the aqueous phase using silver nitrate test. The resulting liquid was dried on a Schlenk line under vacuum at 45 °C for two days to yield a free-flowing, light-yellow fluid ([BVIm][Tf₂N]) with a 76% yield for the metathesis step. ¹H-NMR (300MHz, DMSO-*d*₆): δ = 9.47 (s, 1H), 8.18 (t, *J* = 1.8 Hz, 1H), 7.91 (t, *J* = 1.5 Hz, 1H), 7.27 (dd, *J* = 8.7, 15.6 Hz, 1H), 5.94

(dd, $J = 2.4, 15.9$ Hz, 1H), 5.42 (dd, $J = 2.4, 9.0$ Hz, 1H), 4.19 (t, $J = 7.5$ Hz, 2H), 1.91–1.70 (m, 2H), 1.42–1.28 (m, 2H), 0.91 (d, $J = 7.2$ Hz, 3H).

1-Allyl-3-vinylimidazolium bis(trifluoromethylsulfonyl)imide, [AVIm][Tf₂N]: 1-Vinylimidazole (13.24 g, 140.7 mmol, 1.0 equiv) and allyl bromide (34.04 g, 281.4 mmol, 2.0 equiv) were combined in 65 mL of ethyl acetate and stirred at room temperature for 2 days. The obtained solid white material was filtered, washed with ethyl acetate (3×50 mL) and then dried under vacuum to yield the desired bromide salt in 85% yield. Decolorizing and metathesis steps were performed in the same manner as for [BVIm][Tf₂N] above, to yield [AVIm][Tf₂N] as a colorless fluid (77% yield). ¹H-NMR (300 MHz, DMSO-*d*₆): $\delta = 9.45$ (s, 1H), 8.21 (t, $J = 1.8$ Hz, 1H), 7.85 (t, $J = 1.5$ Hz, 1H), 7.30 (dd, $J = 8.7, 15.6$ Hz, 1H), 6.06 (ddt, $J = 6.0, 10.2, 17.1$ Hz, 1H), 5.96 (dd, $J = 2.4, 15.6$ Hz, 1H), 5.53–5.28 (m, 3H), 4.87 (d, $J = 6.0$ Hz, 2H).

1-Allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [AMIm][Tf₂N]: 1-Methylimidazole (9.06 g, 110.4 mmol, 1.0 equiv) and allyl bromide (26.7 g, 220.7 mmol, 2.0 equiv) were combined in 50 mL of ethyl acetate and stirred at room temperature for 2 days in a round bottom flask. The resulting yellow viscous liquid was washed with ethyl acetate (3×100 mL) to remove unreacted starting materials and then dried *in vacuo* to yield the desired bromide salt in 99% yield. Decolorizing and metathesis steps were carried out as above to yield [AMIm][Tf₂N], a slightly yellow fluid, in 70% overall yield. ¹H-NMR (300 MHz, DMSO-*d*₆): $\delta = 9.09$ (s, 1H), 7.70 (dt, $J = 1.8, 6.0$ Hz, 2H), 6.03 (ddt, $J = 6.0, 10.2, 16.2$ Hz, 1H), 5.46–5.24 (m, 2H), 4.83 (d, $J = 6.0$ Hz, 2H), 3.86 (s, 3H).

1-(Oct-9-en-yl)-3-methylimidazolium bromide, [DeMIm]Br. The preparation of this monomer followed literature procedures, with slight modifications.¹ In a dry 100 ml flask, 1.75 g of 1-methylimidazole (98%, 21.3 mmol) and 4.67 g of 10-bromo-1-decene (97%, 21.3 mmol, 1.0 equiv) were refluxed in 40 mL of toluene for 24 h. A dark brown liquid phase separated during the progress of the reaction. The excess solvent was decanted and the viscous liquid then washed with cold ethyl ether (Et₂O; 2 × 20 mL) and ethyl acetate (EtOAc; 2 × 20 mL) to remove unreacted starting materials, followed by drying on a rotary evaporator at 60 °C for 4 h to yield a brownish viscous liquid in high yield (6.29 g, 98% yield). ¹H-NMR (300 MHz, D₂O): δ = 8.74 (s, 1H), 7.51 (t, *J* = 1.8 Hz, 1H), 7.47 (t, *J* = 1.8 Hz, 1H), 5.95 (ddt, *J* = 6.6, 10.2, 17.1 Hz, 1H), 5.08 (dm, *J* = 17.1, 1.5 Hz, 1H), 5.01 (dm, *J* = 10.2, 1.2 Hz, 1H), 4.22 (t, *J* = 6.9 Hz, 2H), 3.92 (s, 3H), 2.08 (q, *J* = 6.9 Hz, 2H), 1.98–1.80 (m, 2H), 1.50–1.22 (m, 10H).

1-(Oct-9-en-yl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [DeMIm][Tf₂N]. To remove the brown color from the bromide salt, decolorizing charcoal (1.58 g) was added to 6.29 g of [DeMIm]Br (20.9 mmol) pre-dissolved in 50 mL of water and then stirred for 24 h. The resulting solution was vacuum filtered through a medium ceramic frit to remove carbon and 5.99 g of lithium bis(trifluoromethylsulfonyl)imide [LiTf₂N] (20.9 mmol, 1.0 equiv) in 10 mL of water added to the filtrate. The cloudy mixture was stirred for several hours and then allowed to separate into two distinct phases. The aqueous phase was decanted and the dense, lower phase washed iteratively with Ultrapure water (6 × 30 mL) past the point where residual halide could no longer be detected in the aqueous extracting phase using a silver nitrate test. The resultant liquid was dried under high vacuum at 60 °C for two days, to isolate [DeMIm][Tf₂N] as a dark yellow fluid in 75% yield (7.83 g). ¹H-NMR (300 MHz, DMSO-*d*₆): δ = 9.09 (s, 1H), 7.75 (dd, *J* = 1.8, 3.6 Hz, 1H), 7.69 (dd, *J* =

1.8, 3.6 Hz, 1H), 5.79 (ddt, $J = 6.6, 10.2, 16.8$ Hz, 1H), 5.05–4.85 (m, 2H), 4.14 (t, $J = 7.2$ Hz, 2H), 3.84 (s, 3H), 2.01 (qt, $J = 6.9, 1.2$ Hz, 2H), 1.77 (m, $J = 6.9$ Hz, 2H), 1.45–1.10 (m, 10H).

1-(Hex-5-en-yl)-3-methylimidazolium bromide, [HeMIm]Br. The preparation of this monomer followed literature procedures, with slight modifications.¹ To a dry 100 ml flask, 3.05 g of 1-methylimidazole (98%, 37.1 mmol) and 6.05 g of 6-bromo-1-hexene (95%, 37.1 mmol, 1.0 equiv) were refluxed in 40 mL of toluene for 24 h. A dark brown liquid separated during the progress of the reaction. After decanting excess solvent, the viscous liquid was washed with cold ethyl ether (Et₂O; 2 × 20 mL) followed by ethyl acetate (EtOAc; 2 × 20 mL) to remove unreacted reagent and dried at 60 °C for 4 h on a rotovap to yield 8.59 g of a dark brownish viscous liquid (94% isolated yield). ¹H-NMR (300 MHz, D₂O): $\delta = 8.74$ (s, 1H), 7.51 (t, $J = 1.8$ Hz, 1H), 7.46 (t, $J = 1.8$ Hz, 1H), 5.90 (ddt, $J = 6.6, 10.2, 17.1$ Hz, 1H), 5.21–4.96 (m, 2H), 4.24 (t, $J = 7.2$ Hz, 2H), 3.92 (s, 3H), 2.14 (qt, $J = 1.2, 7.2$ Hz, 2H), 2.01–1.81 (m, 2H), 1.53–1.32 (m, 2H).

1-(Hex-5-en-yl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [HeMIm][Tf₂N]. Carbon-decolorization and ion exchange were performed using the same procedures as described earlier for the [DeMIm]Br salt to recover the light-yellow [HeMIm][Tf₂N] in 78% yield. ¹H-NMR (300 MHz, DMSO-*d*₆): $\delta = 9.09$ (s, 1H), 7.75 (t, $J = 1.8$ Hz, 1H), 7.69 (t, $J = 1.8$ Hz, 1H), 5.79 (ddt, $J = 6.6, 10.5, 17.1$ Hz, 1H), 5.12–4.88 (m, 2H), 4.17 (t, $J = 7.2$ Hz, 2H), 3.84 (s, 3H), 2.05 (qt, $J = 1.2, 7.2$ Hz, 2H), 1.89–1.69 (m, 2H), 1.43–1.23 (m, 2H).

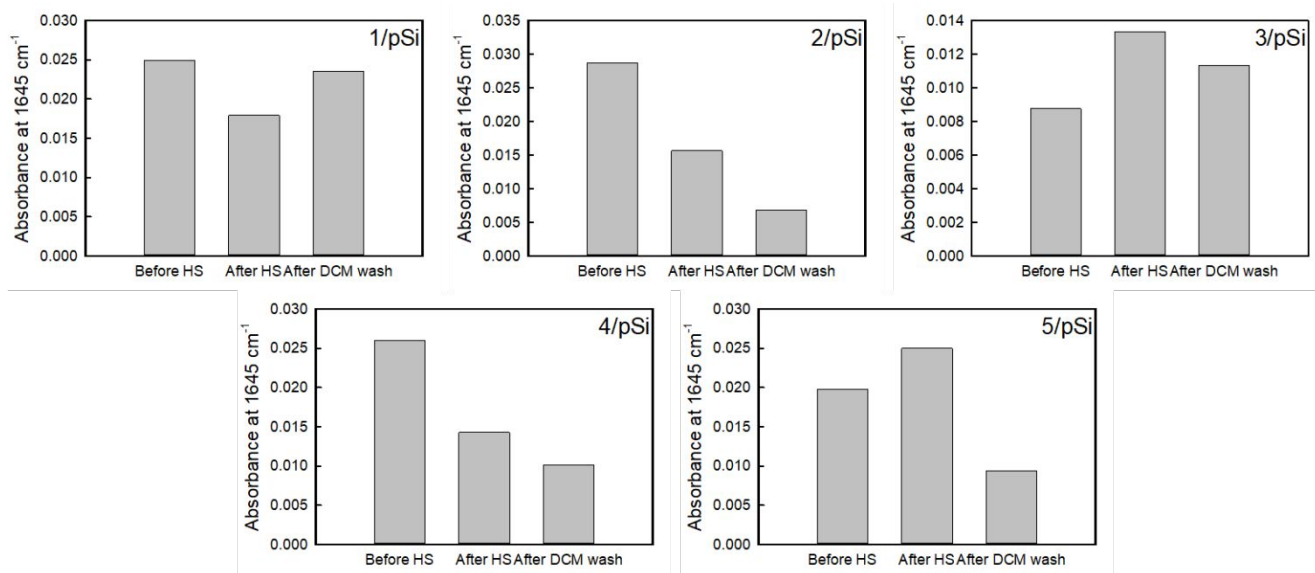


Figure S1. Absorbance plots at 1645 cm⁻¹ accounted for alkene absorption from individual AT-IL (numbered 1-5) on pSi at several points along the CPP-hydrosilation-washing time line. (HS: Hydrosilation)

References:

1. Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R. Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. Comparative investigation of ruthenium-based metathesis catalysts bearing N-heterocyclic carbene (NHC) ligands. *Chem. Eur. J.* **2001**, 7, 3236–3253.