

Supporting Information

Effects of Substituents and Substitution Positions on Alkaline Stability of Imidazolium Cations and Their Resulting Anion-Exchange Membranes

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1. The Synthesis of Imidazolium Salts

Synthesis of 1-Butyl-2,3-dimethylimidazolium Bromide ([N1-BDMI][Br]).

[N1-BDMI][Br] was synthesized by stirring a mixture containing 1, 2-dimethylimidazole and an equivalent molar amount of 1-bromobutane at room temperature under nitrogen atmosphere for 24 h. The resultant white solid was washed with ethyl ether three times and then dried in dynamic vacuum at room temperature for 24 h (yield: 90%). ¹H NMR (400 MHz, D₂O): 7.28 (d, 1H), 7.29 (d, 1H), 4.09 (t, 2H), 3.75 (s, 3H), 2.57 (s, 3H), 1.77 (m, 2H), 1.31 (m, 2H), 0.91 (t, 3H).

Synthesis of 2-Butyl-1,3-dimethylimidazolium Iodide ([C2-BDIm][I]).

[C2-BDIm][I] was synthesized as documented in previous literature:¹ NaH (60% in mineral oil, 0.45 g, 11.72 mmol) and 1,3-dimethylimidazolium iodide ([DMIm][I], 2.00 g, 8.93 mmol) were dissolved in 50 ml acetonitrile. The mixture was stirred for 4 h, and chlorobutane (2.48 g, 26.79 mmol) was added in and then stirred at room temperature for 16 h. The precipitated NaCl was removed by filtration and the solvent was removed under dynamic vacuum. The resultant oil was washed with ethyl ether three times and then dried in dynamic vacuum at room temperature (yield: 88%). ¹H NMR (400 MHz, D₂O): 7.22 (d, 1H), 7.19 (d, 1H), 3.72 (ds, 6H), 2.80 (t, 2H), 1.72 (m, 2H), 1.27 (m, 2H), 0.87 (t, 3H).

Synthesis of 3-Butyl-1,2-dimethylimidazolium Iodide ([N3-BDIm][I]).

[N3-BDIm][I] was synthesized by stirring a mixture containing 1-butyl-2-methylimidazole and an equivalent molar amount of iodomethane at room temperature under nitrogen atmosphere. The resultant white solid was washed with ethyl ether three times and then dried in dynamic vacuum at room temperature for 24 h (yield: 92%). ¹H NMR (400 MHz, D₂O): 7.27 (d, 1H), 7.25(d, 1H), 4.05 (t, 2H), 3.70 (s, 3H), 2.52 (s, 3H), 1.72 (m, 2H), 1.27 (m, 2H), 0.87 (t, 3H).

Synthesis of 2-Ethyl-1-butyl-3-methylimidazolium Bromide ([C2-EBMIm][Br]).

[C2-EBMIm][Br] was synthesized as follows: NaH (60% in mineral oil, 0.45 g, 11.7 mmol) and 1-butyl-3-methylimidazolium bromide ([BMIm][Br], 2.00 g, 9.13 mmol) were first dissolved in 50 ml acetonitrile. The mixture was stirred for 4 h, and bromoethane (4.02 g, 36.89 mmol) was added and stirred for 16 h. The precipitated

NaCl was removed by filtration and the solvent was removed under dynamic vacuum. The resultant oil was washed with ether three times and then dried in dynamic vacuum at room temperature (yield: 76%). ¹H NMR (400 MHz, D₂O): 7.41 (d, 1H), 7.36 (d, 1H), 4.09 (t, 2H), 3.85 (s, 3H), 3.04 (m, 2H), 1.76 (m, 2H), 1.26 (m, 5H), 0.88 (t, 3H).

Synthesis of 2,1-Dibutyl-3-methylimidazolium Bromide ([C2-BBMIm][Br]). [C2-BBMIm][Br] was synthesized as follows: NaH (60% in mineral oil, 0.45 g, 11.7 mmol) and 1-butyl-3-methylimidazolium bromide ([BMIm][Br], 2.00 g, 9.13 mmol) were first dissolved in 50 ml acetonitrile. After allowing the mixture to stir for 4 h, chlorobutane (2.54 g, 27.44 mmol) was added and stirred for 16 h. The precipitated NaCl was removed by filtration and the solvent was removed under dynamic vacuum. The resultant oil was washed with ether three times and then dried in dynamic vacuum at room temperature (yield: 90%). ¹H NMR (400 MHz, D₂O): 7.31 (d, 1H), 7.28 (d, 1H), 4.08 (t, 2H), 3.75 (s, 3H), 2.95 (t, 2H), 1.76 (m, 2H), 1.59 (m, 2H), 1.22 (m, 4H), 0.81 (dt, 6H).

Synthesis of 2-Hydroxymethyl-1-butyl-3-methylimidazolium Bromide ([C2-HMBMIm][Br]). [C2-HMBMIm][Br] was synthesized according to the described procedure:² a mixture containing 1-butyl-3-methylimidazolium bromide ([BMIm][Br], 2.00 g, 9.13 mmol) and paraformaldehyde (0.5 g, 16.74 mmol with respect to CH₂O units) was stirred in a sealed flask at 80 °C for 48 h. The resultant liquid was separated and then analyzed without further purification (yield: 95%). ¹H NMR (400 MHz, D₂O): 7.36 (d, 1H), 7.41 (d, 1H), 4.75 (s, 2H), 4.19 (t, 2H), 3.88 (s,

3H), 1.80 (m, 2H), 1.27 (m, 2H), 0.86 (t, 3H).

Synthesis of 1-Butyl-3-methylimidazolium Bromide ([BMIm][Br]): [BMIm][Br] was synthesized by stirring a mixture containing N-methylimidazole and an equivalent molar amount of 1-bromobutane at room temperature under nitrogen atmosphere. The resultant white solid was washed with ethyl ether three times and then dried in dynamic vacuum at room temperature for 24 h (yield: 90%). ¹H NMR (400 MHz, D₂O): 8.70 (s, 1H), 7.44 (d, 1H), 7.42 (d, 1H), 4.18 (t, 2H), 3.87 (s, 3H), 1.84 (m, 2H), 1.30 (m, 2H), 0.91 (t, 3H).

Synthesis of 1-Vinyl-3-butylimidazolium Bromide ([VBIm][Br]): [VBIm][Br] was synthesized by stirring a mixture containing N-vinylimidazole and an equivalent molar amount of 1-bromobutane at room temperature under nitrogen atmosphere. The resultant white solid was washed with ethyl ether three times and then dried in dynamic vacuum at room temperature for 24 h (yield: 87%). ¹H NMR (400 MHz, D₂O): 8.91 (s, 1H), 7.84 (d, 1H), 7.60 (d, 1H), 7.14 (m, 1H), 5.82 (m, 1H), 5.46 (m, 1H), 4.26 (t, 2H), 1.90 (m, 2H), 1.36 (m, 2H), 0.95 (t, 3H).

Synthesis of 1-Vinyl-2,3-dibutylimidazolium Bromide ([VDBIm][Br]): [VDBIm][Br] was synthesized as follows: NaH (60% in mineral oil, 0.45 g, 11.7 mmol) and 1-vinyl-3-butylimidazolium bromide ([VBIm][Br], 2.00 g, 8.65 mmol) were first dissolved in 50 ml acetonitrile. After allowing the mixture to stir for 4 h, chlorobutane (2.41 g, 26.03 mmol) was added into it and stirred for 16 h. The precipitated NaCl was removed by filtration and the solvent was removed under dynamic vacuum. The resultant oil was washed with ether three times and then dried

in dynamic vacuum at room temperature (yield: 85%). ^1H NMR (400 MHz, D_2O): 7.34 (d, 1H), 7.30 (d, 1H), 7.14 (m, 1H), 5.82 (m, 1H), 5.46 (m, 1H), 4.26 (t, 2H), 2.57 (t, 2H), 1.76 (m, 2H), 1.26 (m, 6H), 0.90 (dt, 6H).

2. The Calculation of Degradation Degree

The detailed analysis of ^1H NMR spectra was used to estimate the degradation degree of the imidazolium cations. Here, we take [N1-BDMIm][Br] as an example, as shown in Figure 1A (^1H NMR spectra of the cations in 4 M KOH solution at 80 °C at various times). The degradation degree could be calculated by the relative integrated intensities of the indicated ^1H resonances. For example, the quantity $(\Lambda_8 \times \Lambda_{3'}) / (\Lambda_3 \times \Lambda_{8'})$ can provide the degradation degree. Where Λ_8 , $\Lambda_{3'}$, Λ_3 , and $\Lambda_{8'}$ indicate the relative integrated intensity of the peaks marked with 8, 3', 3, and 8', respectively.

References

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