

Supporting Information for

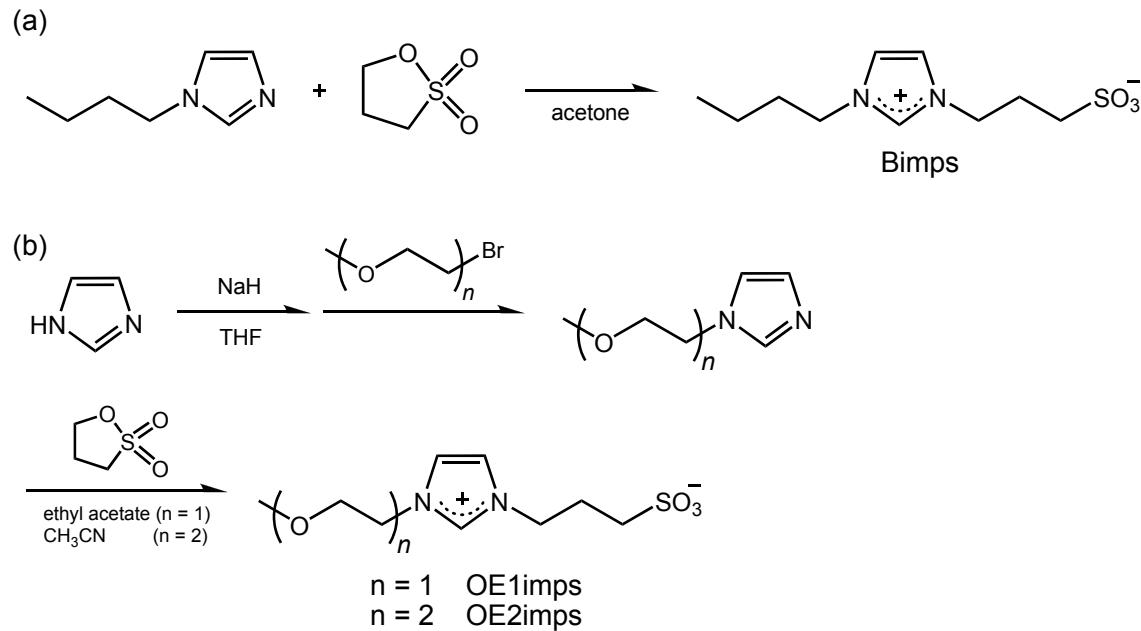
Low-melting zwitterion: effect of oxyethylene units on thermal properties and conductivity

Masahiro Yoshizawa-Fujita,* Tetsuya Tamura, Yuko Takeoka, and Masahiro Rikukawa

*Department of Materials & Life Sciences, Sophia University,
7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan.*

General. ^1H and ^{13}C NMR spectra were recorded on a JEOL 300 spectrometer. Mass spectra were obtained with a JMS-SX102A. Elemental analyses were carried out with a Perkin Elmer PE 2400-II. DSC measurements were performed on a DSC7020 at a scanning rate of $10\text{ }^\circ\text{C min}^{-1}$. TG-DTA measurements were performed on a TG-DTA7200 at a scanning rate of $10\text{ }^\circ\text{C min}^{-1}$ under a N_2 atmosphere. Ionic conductivities were measured using a Schlumberger Solartron 1260 impedance analyzer (frequency range: 5 Hz - 1 MHz, applied voltage: 10 mV).

Synthesis of zwitterions. All reagents and solvents were purchased from Aldrich or Wako, and appropriately purified, if necessary. The synthetic routes used to obtain zwitterions are shown in Scheme S1. Bimps was prepared according to the literature.^{1,2}



Scheme S1. Syntheses of (a) Bimps and (b) zwitterions with oxyethylene unit, OE1imps and OE2imps.

1-(2-Methoxyethyl)-1*H*-imidazole. Under an argon atmosphere sodium hydride (5.23 g, 218 mmol) was suspended in THF (20 mL). Imidazole (6.80 g, 99.9 mmol), which was dissolved in 30 mL THF, was dropwisely added to the solution. The mixture was stirred at room temperature for 24 h. Then, 1-bromo-2-methoxyethane (13.9 g, 100 mmol) was added to the solution. After stirring at 70 °C for 6 h, the resulted suspension was filtered to remove white precipitation. The solvent was removed by a rotary evaporator to give the crude product. The crude product was purified by distillation under reduced pressure. A fraction was collected at 105 °C under reduced pressure of 1 mmHg to obtain an imidazole derivative, 1-(2-methoxyethyl)-1*H*-imidazole (OE1im), as a colorless oil (yield = 4.53 g, 35.9%). ¹H NMR (300 MHz, CD₂Cl₂, Me₄Si): δ 7.46 (s, 1H), 6.98 (d, *J* = 3.8 Hz, 2H), 4.07 (t, *J* = 5.2 Hz, 2H), 3.61 (t, *J* = 5.2 Hz, 2H), 3.32 (s, 3H). MS (FAB): *m/z* 127.1 [M+H]⁺; calcd. 127.2.

3-(1-(2-Methoxyethyl)-1*H*-imidazol-3-iium-3-yl)propane-1-sulfonate (OE1imps). OE1im (4.03 g, 31.9 mmol) was dissolved in 40 mL ethyl acetate, and then 1,3-propanesultone (3.72 g, 30.5 mmol) was added dropwise to the solution under N₂ atmosphere. The mixture was refluxed for 20 h. The white precipitation was collected by filtration and was purified by recrystallization from ethanol twice to give the product as a white solid (yield = 3.00 g, 73.9%). ¹H NMR (300 MHz, DMSO-*d*₆, Me₄Si): δ 9.16 (s, 1H), 7.80 (t, *J* = 1.7 Hz, 1H), 7.74 (t, *J* = 1.7 Hz, 1H), 4.38-4.28 (m, 4H), 3.68 (t, *J* = 5.0 Hz, 2H), 3.27 (s, 3H), 2.39 (t, *J* = 7.2 Hz, 2H), 2.08 (m, *J* = 7.1 Hz, 2H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 136.6, 122.8, 122.4, 69.5, 58.1, 48.7, 47.9, 47.3, 26.2. MS (FAB): *m/z* 249.2 [M+H]⁺; calcd. 249.3. Anal. calcd. for C₉H₁₆N₂O₄S₁: C, 43.53; H, 6.49; N, 11.28; S, 12.91%; found: C, 43.51; H, 6.63; N, 11.57; S, 12.70%.

1-(2-Methoxyethoxyethyl)-1*H*-imidazole. An imidazole derivative, 1-(2-methoxyethoxyethyl)-1*H*-imidazole (OE2im), was synthesized with the same procedure as that of OE1im. The amounts of reagents were as follows; sodium hydride (15.7 g, 656 mmol), imidazole (21.1 g, 309 mmol), and 1-bromo-2-(2-methoxyethoxy)ethane (55.0 g, 300 mmol). The obtained yellow liquid was purified by distillation under reduced pressure. A fraction was collected at 136 °C under reduced pressure of 1 mmHg to obtain the imidazole derivative, OE2im, as a colorless oil. (yield = 21.7 g, 24.8%) ¹H NMR (300 MHz, CD₂Cl₂, Me₄Si): δ 7.48 (s, 1H), 6.98 (d, *J* = 10 Hz, 2H), 4.09 (t, *J* = 5.2 Hz, 2H), 3.71 (t, *J* = 5.1 Hz, 2H), 3.58-3.53 (m, 2H), 3.50-3.45 (m, 2H), 3.32 (s, 3H). MS (FAB): *m/z* 171.2 [M+H]⁺; calcd. 171.2.

3-(1-(2-Methoxyethoxyethyl)-1*H*-imidazol-3-iium-3-yl)propane-1-sulfonate

(OE2imps). OE2im (21.7 g, 128 mmol) was dissolved in 40 mL acetonitrile, and then 1,3-propanesultone (14.8 g, 122 mmol) was added dropwise to the solution under N₂ atmosphere. The mixture was refluxed for 40 h. The solvent was removed by a rotary evaporator. The residue was washed several times with diethyl ether by decantation. Then, the product was dried *in vacuo* at 50 °C for 24 h to provide OE2imps as a colorless viscous liquid (yield = 29.4 g, 82.7%). ¹H NMR (300 MHz, DMSO-*d*₆, Me₄Si): δ 9.11 (s, 1H), 7.78 (t, *J* = 1.7 Hz, 1H), 7.72 (t, *J* = 1.7 Hz, 1H), 4.30-4.20 (m, 4H), 3.77 (t, *J* = 5.0 Hz, 2H), 3.57-3.51 (m, 2H), 3.48-3.42 (m, 2H), 3.21 (s, 3H), 2.79 (t, *J* = 7.4 Hz, 2H), 2.19 (m, *J* = 7.3 Hz, 2H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 136.6, 122.8, 122.3, 71.1, 69.4, 68.1, 58.1, 48.8, 47.9, 47.3, 26.3. MS (FAB): *m/z* 292.5 [M]⁺; calcd. 292.1. Anal calcd. for C₁₁H₂₀N₂O₅S₁: C, 45.19; H, 6.90; N, 9.58; S, 10.97%; found: C, 44.70; H, 6.99; N, 9.33; S, 10.90%.

Thermal stability. TG curves of the zwitterions and the equimolar mixtures of the zwitterion and LiN(Tf)₂ are shown in Fig. S1 and Fig. S2.

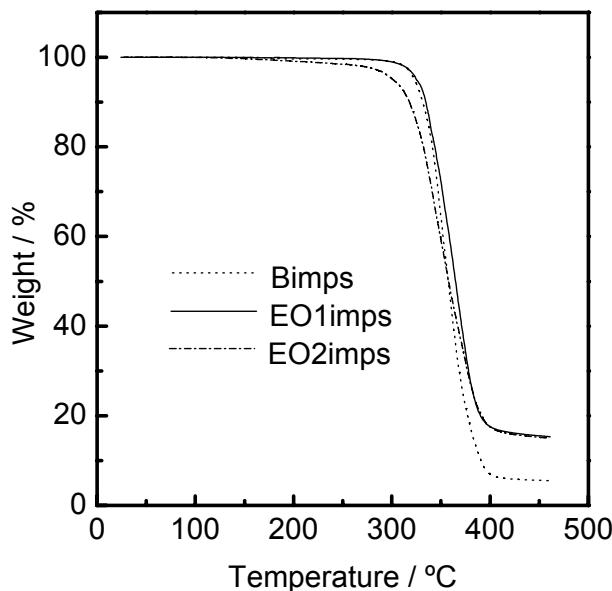


Fig. S1 TG curves of the zwitterions.

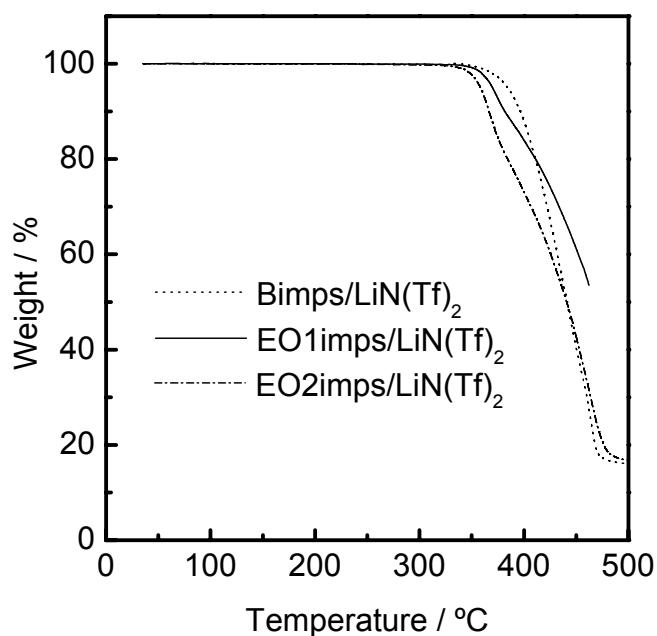


Fig. S2 TG curves of the equimolar mixtures of the zwitterions and LiN(Tf)₂.

References

1. M. Yoshizawa, M. Hirao, K. Ito-Akita and H. Ohno, *J. Mater. Chem.*, 2001, **11**, 1057
2. M. Yoshizawa, A. Narita and H. Ohno, *Aust. J. Chem.*, 2004, **57**, 139.