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Supporting Information

Biodegradable Naphthenic Acid Ionic Liquids: Synthesis, Characterization and QSBR Study

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Preparation and characterization of [BMIM]NA

Preparation of [BMIM]OH[1]

Solid potassium hydroxide (25.930 g, 0.462 mol) was added to a solution of [BMIM]Br (101.131 g, 0.462 mol) in dry methylene chloride (200 mL), and the mixture was stirred vigorously at room temperature for 24h. The precipitated KBr was filtered off, and the filtrate was evaporated to leave the crude [BMIM]OH as a viscous liquid that was washed with ether (3×50 mL) and dried at 90? for 10h to prepare the pure [BMIM]OH.

Preparation of [BMIM]NA: [BMIM][CHC], [BMIM][Sa], [BMIM][NOA]

To prepare [BMIM]NA, the equilimolar neutralization method similar to the procedure to synthesize [Ch]NA was adopted. [CHC] (5.962 g, about 0.047 mol) (6.420 g for [Sa], and 9.412 for [NOA], respectively) dissolved in ethanol (50 mL) was loaded into a flask (250 mL) with a magnetic stirrer, and then, under vigorous stirring, equimolar [BMIM]OH in 50 mL ethanol was added to the flask. The reaction lasted for 2 h at room temperature. The solvent was removed in vacuo at 50? in a rotary evaporator. The resultant residue was dried under vacuum over P_2O_5 for 48 h at 80? to afford desired products. They were characterized by spectroscopic data:

[BMIM][CHC]

^{1}H NMR, (400 MHz, DMSO, 25? , TMS): d= 8.88 (s, 1H; c1cnc*H*n1), 7.71 (d, 1H, ^3J (H,H) =3.6 Hz; c1*H*cncn1), 7.65 (d, 1H, ^3J (H,H) =3.2 Hz; c1c*H*ncn1), 4.35 (t, 2H, ^3J (H,H) =14.6 Hz; -NCH_2CH$_2$CH$_2$CH$_3$), 4.03 (s, 3H; -NCH_3), 2.09 (m, 1H, ^3J (H,H) =11.3 Hz; OC(=O)C1*H*CCCCC1), 1.94 (m, 2H, ^3J (H,H) =14.6 Hz; -NCH$_2$CH_2CH$_2$CH$_3$), 1.79 (m, 2H, ^3J (H,H) =10.1 Hz; OC(=O)C1CH_2CCCC1), 1.70 (m, 2H, ^3J (H,H) =3.8 Hz; OC(=O)C1CCCCC1H_2), 1.41 (m, 2H, ^3J (H,H) = 12.0 Hz; -NCH$_2$CH$_2$CH_2CH$_3$), 1.31 (m, 6H, ^3J (H,H) =12.2 Hz; OC(=O)C1CCH_2CH_2CH_2C1), 0.97 (t, 3H, ^3J (H,H) = 14.0 Hz; -NCH$_2$CH$_2$CH$_2$CH_3) ppm; ^{13}C NMR, (100 MHz, DMSO, 25? , TMS): d= 178.28 (O*C*(=O)C1CCCCC1), 137.53 (c1cn***c***n1),

124.67 (***c***1cncn1), 123.32 (c1***c***ncn1), 50.09 (-N*C*$H_2CH_2CH_2CH_3$), 47.86 (OC(=O)*C*1CCCCC1), 36.47 (-N*C*H_3), 32.69 (-NCH$_2$*C*$H_2CH_2CH_3$), 30.70 (OC(=O)C1*C*CCCC*C*1), 25.78 (OC(=O)C1CC*C*CC1), 19.91 (-NCH$_2$CH$_2$*C*H_2CH_3), 13.64 (-NCH$_2$CH$_2$CH$_2$*C*H_3) ppm; elemental analysis calcd (%) for $C_{15}H_{33}N_2O_2$: C 57.78, H 8.90, N 7.78; found: C 57.62, H 9.12, N 7.69.

[BMIM][Sa]

^{1}H NMR, (400 MHz, D_2O, 25? , TMS): d= 8.69 (s, 1H; c1cnc*H*n1), 7.77 (d, 1H, ^3J (H,H) =7.8 Hz; c1*H*cncn1), 7.62 (d, 1H, ^3J (H,H) =3.2 Hz; c1c*H*ncn1), 7.54 (d, 1H, ^3J (H,H) =2.3 Hz; OC(=O)c1c*H*cccc1O), 7.40 (t, 1H, ^3J (H,H) =8.4 Hz; OC(=O)c1cccc*H*c1O), 6.93 (m, 2H, ^3J (H,H) =25.5 Hz; OC(=O)c1cc*H*c*H*cc1O), 4.29 (t, 2H, ^3J (H,H) =8.9 Hz; -NCH_2CH$_2$CH$_2$CH$_3$), 4.00 (s, 3H; -NCH_3), 1.91 (m, 2H, ^3J (H,H) =12.0 Hz; -NCH$_2$CH_2CH$_2$CH$_3$), 1.46 (m, 2H, ^3J (H,H) = 9.6 Hz; -NCH$_2$CH$_2$CH_2CH$_3$), 0.92 (t, 3H, ^3J (H,H) = 16.7 Hz; -NCH$_2$CH$_2$CH$_2$CH_3) ppm; ^{13}C NMR, (100 MHz, DMSO, 25? , TMS): d= 171.21 (O*C*(=O)c1ccccc1O), 163.08 (OC(=O)c1cccc***c***1O), 137.76 (c1cn***c***n1), 132.79 (OC(=O)c1cc***c***cc1O), 131.14 (OC(=O)c1***c***cccc1O), 124.89 (***c***1cncn1), 123.56 (c1***c***ncn1), 120.73 (OC(=O)c1c***c***ccc1O), 116.34 (OC(=O)***c***1ccccc1O), 115.75 (OC(=O)c1ccc***c***c1O), 50.55 (-N*C*$H_2CH_2CH_2CH_3$), 36.20 (-N*C*H_3), 32.94 (-NCH$_2$*C*$H_2CH_2CH_3$), 20.27 (-NCH$_2$CH$_2$*C*H_2CH_3), 13.88 (-NCH$_2$CH$_2$CH$_2$*C*H_3) ppm; elemental analysis calcd (%) for $C_{15}H_{20}N_2O_3$: C 62.44, H 6.53, N 7.52; found: C 62.26, H 6.71, N 7.46.

[BMIM][NOA]

^{1}H NMR, (400 MHz, DMSO, 25? , TMS): d= 8.82 (s, 1H; c1cnc*H*n1), 7.78 (t, 2H, ^3J (H,H) =9.4 Hz; c1*H*cncn1), 7.69 (d, 2H, ^3J (H,H) =8.2 Hz; c1c*H*ncn1), 7.61 (d, 1H, ^3J (H,H) =7.2 Hz; OC(=O)COc1ccc2c*H*ccc*H*c2c1), 7.41 (t, 1H, ^3J (H,H) =16.1 Hz; OC(=O)COc1cc*H*c2ccccc2c1), 7.29 (t, 1H, ^3J (H,H) =15.0 Hz; OC(=O)COc1ccc2ccc*H*cc2c1), 7.11 (dd, 1H, ^3J (H,H) =11.2 Hz; OC(=O)COc1ccc2cc*H*ccc2c1; OC(=O)COc1ccc2ccccc2c1*H*), 7.07 (d, 1H, ^3J (H,H) =2.2 Hz; OC(=O)COc1c*H*cc2ccccc2c1), 4.29 (t, 2H, ^3J (H,H) =7.6 Hz; -NCH_2CH$_2$CH$_2$CH$_3$), 4.20 (s, 2H; OC(=O)CH_2Oc1ccc2ccccc2c1), 3.99 (s, 3H; -NCH_3), 1.87 (m, 2H, ^3J (H,H) =9.4 Hz; -NCH$_2$CH_2CH$_2$CH$_3$), 1.36 (m, 2H, ^3J (H,H) = 19.7 Hz; -NCH$_2$CH$_2$CH_2CH$_3$), 0.94 (t, 3H, ^3J (H,H) =

11.2 Hz; -$NCH_2CH_2CH_2CH_3$) ppm; ^{13}C NMR, (100 MHz, DMSO, 25?, TMS): d= 169.22 (O*C*(=O)COc1ccc2ccccc2c1), 157.18 (OC(=O)CO***c***1ccc2ccccc2c1), 137.69 (c1cn***c***n1), 134.32 (OC(=O)COc1c***c***c2ccccc2c1), 128.62 (OC(=O)COc1cc***c***2ccccc2c1), 128.00 (OC(=O)COc1ccc2cccc***c***2c1), 127.35 (OC(=O)COc1ccc2***c***cccc2c1), 126.38 (OC(=O)COc1ccc2ccc***c***c2c1), 126.00 (OC(=O)COc1ccc2cc***c***cc2c1), 124.74 (***c***1cncn1), 123.31 (c1***c***ncn1), 123.01 (OC(=O)COc1ccc2c***c***ccc2c1), 119.07 (OC(=O)COc1***c***cc2ccccc2c1), 106.62 (OC(=O)COc1ccc2ccccc2***c***1), 67.58 (OC(=O)*C*Oc1ccc2ccccc2c1), 50.39 (-N*C*$H_2CH_2CH_2CH_3$), 36.41 (-N*C*H_3), 32.63 (-NCH_2*C*$H_2CH_2CH_3$), 19.98 (-NCH_2CH_2*C*H_2CH_3), 13.45 (-$NCH_2CH_2CH_2$*C*H_3) ppm; elemental analysis calcd (%) for $C_{20}H_{24}N_2O_3$: C 56.34, H 6.67, N 5.84; found: C 56.17, H 6.82, N 5.76.

[1] B. C. Ranu, S. Banerjee, *Org. Lett.* **2005**, 7, 3049-3052.