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ACCESSORY PUBLICATION

A facile strategy to tune chiral recognition capability of chiral ionic liquids by changing achiral alkyl chain

Wei Yu[A], Haibo Zhang[A], Long Zhang[A], Xiaohai Zhou[A, B]

[A] College of Chemstry, Wuhan University, Wuhan, Hubei 430072, P. R. China.

[B] Corresponding author. Email: zxh7954@hotmail.com

Experimental Section

General Information.

All the solvents used were reagent grade and were used as received.

^{1}H NMR spectra were conducted on a Mercury VX-300 (Varian, 300 MHz) spectrometer. ^{13}C NMR spectra were conducted on a Mercury VX-300 (Varian, 75 MHz) spectrometer. ^{19}F NMR spectra were conducted on a Unity-Inova 600 (Varian, 564.37 MHz) spectrometer. ESI-MS was recorded on Finigan LCQ Advantage instrument. Optical rotation value of ILs were obtained as a solution in ethanol with a PerkinElmer 341 polarimeter. Decomposition temperature (T_{dec}) was determined with an instrument of SETSYS TG-DTA/DSC in N_2 with a heating rate of 10 □ min^{-1}. DSC measurements were collected on a Mettler Toledo DSC 822e calorimeter. Heating and cooling rates of 10□ min^{-1} were typically employed. The viscosity measurements were carried out in a rotational controlled-stress rheometer (Rheostress 600, HAAKE) in plate-plate configuration at 25ºC.

All the L-proline derived CILs were obtained by column chromatography of the crude product on silica gel using chloroform/ethanol (20:1) as eluent. And they are characterized by spectroscopic analysis of ^{1}H NMR, ^{13}C NMR and ESI-MS (electrospray ionization mass spectroscopy).

Synthesis and data of Ionic Liquids

General procedure for ionic liquid synthesis

L-proline (0.1mol), 1-bromoalkane (0.3mol) and potassium carbonate (0.05mol) were mixed in a 100 mL round bottom flask with acetonitrile as solvent at 70℃ for 2 days in an inert atmosphere.

The reaction was monitored by flash chromatography (silica; 1/20 ethanol/chloroform elution, the product has R_F 0.6). After filtering, the solvent was removed by distillation and the raw product was washed by ether for several times. After purified by column chromatography, the product was dried under vacuum for 5 hours to afford the CILs **1a-f** (over 90% isolated yields).

1a-f (0.02mol) and silver nitrate (or tetrafluoroborate ammonium) (0.02mol) were stirred at room temperature for 4 hours with ethanol as solvent. After filtering, the solvent was distilled off and the desired CILs **2a-f** (over 70% isolated yields) and **3a-f** (over 50% isolated yields) were obtained.

1a $[\alpha]_D^{20}$ -46.9° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 1.26-1.57(m, 6H, CH_3), 2.25-2.68(m, 4H, CH_2), 3.34-3.78(m, 3H, NCH_2), 3.79(d, 1H, *J*=6.9Hz, NCH_2), 4.30(q, 2H, *J*=6.9Hz, NCH_2), 4.62(s, 1H, CH), 8.87(br s, 1H, OH); δ_C(75 MHz; $CDCl_3$; TMS) 11.69, 14.48, 22.61, 28.83, 54.76, 58.29, 63.29, 66.54, 168.19. MS (ESI): m/z = 172.2 (M^+).
2a $[\alpha]_D^{20}$ -48.8° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 1.08-1.37(m, 6H, CH_3), 2.09-2.52(m, 4H, CH_2), 3.17-3.53(m, 3H, NCH_2), 3.79(s, 1H, NCH_2), 4.04-4.17(m, 3H, NCH_2, CH), 8.83(br s, 1H, OH); δ_C(75 MHz; $CDCl_3$; TMS) 11.19, 14.10, 22.43, 28.34, 50.79, 54.38, 63.0, 66.44, 168.01. MS (ESI): m/z = 172.2 (M^+).
3a $[\alpha]_D^{20}$ -47.8° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 1.24-1.43(m, 6H, CH_3), 1.94-2.71(m, 4H, CH_2), 3.19-3.46(m, 3H, NCH_2), 3.93(s, 1H, NCH_2), 4.17-4.27(m, 3H, NCH_2, CH), 6.48(br s, 1H, OH); δ_C(75 MHz; $CDCl_3$; TMS) 11.25, 14.10, 22.91, 28.67, 51.65, 55.53, 63.75, 66.74, 168.66. MS (ESI): m/z = 172.2 (M^+).
1b $[\alpha]_D^{20}$ -38.8° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.70-0.83(m, 6H, CH_3), 1.24-1.42(m, 4H, CH_2), 1.44-1.64(m, 4H, CH_2), 1.82-2.24(m, 3H, CH_2), 2.38-2.54(m, 1H, CH_2), 3.02-3.28(m, 3H, NCH_2), 3.63-3.74(m, 1H, NCH_2), 4.08-4.22(m, 2H, NCH_2), 4.29 (t, 1H, *J*=8.4 Hz, CH); δ_C(75 MHz; $CDCl_3$; TMS) 13.0, 13.2, 18.7, 19.4, 22.6, 27.3, 28.3, 29.9, 55.4, 55.8, 67.1, 67.1, 169.. MS (ESI): m/z = 228.2 (M^+).
2b $[\alpha]_D^{20}$ -43.9° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.78-0.92(m, 6H, CH_3), 1.22-1.38(m, 4H, CH_2), 1.48-1.78(m, 4H, CH_2), 2.02-2.26(m, 3H, CH_2), 2.42-2.56(m, 1H, CH_2), 3.14-3.46(m, 3H, NCH_2), 3.84(s, 1H, NCH_2), 4.14(t, 2H, *J*=6 Hz, NCH_2), 4.29 (t, 1H, *J*=8.4 Hz, CH); δ_C(75 MHz; $CDCl_3$; TMS) 13.7, 13.8, 19.2, 20.2, 22.5, 28.2, 30.5, 30.5, 55.3, 56.4, 66.9, 67.6, 167.5. MS (ESI): m/z = 228.2 (M^+).
3b $[\alpha]_D^{20}$ -42.7°(*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.68-0.94(m, 6H, CH_3), 1.14-1.40(m, 4H, CH_2), 1.42-1.80(m, 4H, CH_2), 1.97-2.24(m, 3H, CH_2), 2.36-2.52(m, 1H, CH_2), 3.06-3.40(m, 3H, NCH_2), 3.79(d, 1H, *J*=4.5Hz, NCH_2), 4.12(t, 2H, *J*=6.6 Hz, NCH_2), 4.20-4.32 (m, 1H, CH), 7.78(s, 1H, OH); δ_C(75 MHz; $CDCl_3$; TMS) 13.5, 13.7, 19.1, 19.7, 22.9, 27.9, 28.7, 30.4, 56.1, 56.4, 67.3, 67.4, 168.8. MS (ESI): m/z = 228.2 (M^+).
1c $[\alpha]_D^{20}$ -30.2° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.68-0.84(m, 6H, CH_3), 1.08-1.36(m, 12H, CH_2), 1.44-1.88(m, 4H, CH_2), 2.02-2.21(m, 3H, CH_2), 2.42-2.62(m, 1H, CH_2), 3.13-3.40(m, 3H, NCH_2), 3.71(s, 1H, NCH_2), 4.10(t, 2H, *J*=6.6 Hz, NCH_2), 4.26-4.38 (m, 1H, CH), 7.44(br s, 1H, OH); δ_C(75 MHz; $CDCl_3$; TMS) 14.0, 14.0, 22.1, 22.5, 22.6, 25.6, 25.9, 26.7, 28.5, 28.6, 31.3, 31.5, 53.7, 53.7, 64.9, 67.0, 168.1. MS (ESI): m/z = 284.3 (M^+).
2c $[\alpha]_D^{20}$ -33.6° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.70-0.90(m, 6H, CH_3), 1.10-1.38(m, 12H, CH_2), 1.52-1.82(m, 4H, CH_2), 2.04-2.32(m, 3H, CH_2), 2.40-2.58(m, 1H, CH_2), 3.10-3.44(m, 3H, NCH_2), 3.82(s, 1H, NCH_2), 4.13(t, 2H, *J*=6.3 Hz, NCH_2), 4.27 (t, 1H, *J*=6.6 Hz, CH); δ_C(75 MHz; $CDCl_3$; TMS) 14.1, 14.2, 22.5, 22.7, 22.7, 25.5, 26.0, 26.2, 28.4, 28.6, 31.3, 31.5, 53.6, 53.6, 67.1, 67.1, 167.6. MS (ESI): m/z = 284.3 (M^+).
3c $[\alpha]_D^{20}$ -34.0° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.78-0.94(m, 6H, CH_3), 1.18-1.44(m, 12H, CH_2), 1.60-1.78(m, 4H, CH_2), 2.05-2.28(m, 3H, CH_2), 2.53-2.68(m, 1H, CH_2), 3.20-3.39(m,

3H, NCH_2), 3.88-4.04(m, 1H, NCH_2), 4.16-4.30(m, 3H, NCH_2, CH), 5.22(br s, 1H, OH); δ_C(75 MHz; $CDCl_3$; TMS) 14.1, 14.2, 22.5, 22.7, 22.7, 25.5, 26.0, 26.2, 28.4, 28.6, 31.3, 31.5, 56.1, 56.4, 67.8, 67.8, 168.3. MS (ESI): m/z = 284.3 (M^+).

1d $[\alpha]_D^{20}$ -26.5° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.72-0.88(m, 6H, CH_3), 1.05-1.38(m, 20H, CH_2), 1.52-1.94(m, 4H, CH_2), 2.15(d, 3H, *J*=3.9Hz, CH_2), 2.47-2.63(m, 1H, CH_2), 3.13-3.50(m, 3H, NCH_2), 3.52-3.74(m, 1H, NCH_2), 4.14(t, 2H, *J*=6.9 Hz, NCH_2), 4.23-4.38 (m, 1H, CH); δ_C(75 MHz; $CDCl_3$; TMS) 14.2, 14.2, 22.1, 22.7, 22.7, 25.9, 25.9, 27.0, 28.5, 28.5, 29.3, 29.3, 29.3, 29.3, 31.8, 31.9, 53.9, 53.9, 66.9, 66.9, 168.1. MS (ESI): m/z = 340.4 (M^+).

2d $[\alpha]_D^{20}$ -28.1° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.73-0.85(m, 6H, CH_3), 1.06-1.39(m, 20H, CH_2), 1.52-1.82(m, 4H, CH_2), 2.02-2.32(m, 3H, CH_2), 2.40-2.60(m, 1H, CH_2), 3.14-3.45(m, 3H, NCH_2), 3.96(d, 1H, *J*=5.1Hz, NCH_2), 4.15(t, 3H, *J*=6 Hz, NCH_2, CH); δ_C(75 MHz; $CDCl_3$; TMS) 14.2, 14.2, 22.5, 22.8, 22.8, 25.9, 25.9, 26.9, 28.5, 28.5, 29.3, 29.3, 29.3, 29.3, 31.8, 31.9, 55.2, 56.5, 67.1, 67.4, 167.9. MS (ESI): m/z = 340.4 (M^+).

3d $[\alpha]_D^{20}$ -28.4° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.85-0.94(m, 6H, CH_3), 1.15-1.40(m, 20H, CH_2), 1.58-1.79(m, 4H, CH_2), 2.05-2.35(m, 3H, CH_2), 2.63(d, 1H, *J*=9 Hz, CH_2), 3.30(d, 3H, *J*=11.1 Hz, NCH_2), 4.00(d, 1H, *J*=4.5 Hz, NCH_2), 4.23(t, 3H, *J*=6.6 Hz, NCH_2, CH), 7.85(s, 1H, OH); δ_C(75 MHz; $CDCl_3$; TMS) 11.5, 11.5, 20.0, 20.2, 20.2, 23.1, 23.3, 23.8, 25.7, 25.9, 26.5, 26.5, 26.6, 26.6, 29.1, 29.2, 53.3, 54.0, 64.6, 65.1, 165.8. MS (ESI): m/z = 340.4 (M^+).

1e $[\alpha]_D^{20}$ -26.2° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.61-0.74(m, 6H, CH_3), 0.96-1.22(m, 28H, CH_2), 1.40-1.80(m, 4H, CH_2), 2.03(d, 3H, *J*=5.4 Hz, CH_2), 2.45(d, 1H, *J*=8.1 Hz, CH_2), 3.18-3.39(m, 3H, NCH_2), 3.70(s, 1H, NCH_2), 4.00(t, 2H, *J*=6.6 Hz, NCH_2), 4.34-4.42(m, 1H, CH); δ_C(75 MHz; $CDCl_3$; TMS) 14.3, 14.3, 22.0, 22.8, 22.8, 26.0, 26.0, 27.1, 28.6, 28.6, 29.2, 29.2, 29.4, 29.4, 29.7, 29.7, 29.7, 29.7, 32.0, 32.0, 53.3, 53.3, 67.0, 67.0, 167.9. MS (ESI): m/z = 396.4 (M^+).

2e $[\alpha]_D^{20}$ -27.0° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.81-0.90(m, 6H, CH_3), 1.20-1.39(m, 28H, CH_2), 1.54-1.81(m, 4H, CH_2), 2.11-2.25(m, 3H, CH_2), 2.45-2.49(m, 1H, CH_2), 3.15-3.36(m, 3H, NCH_2), 3.76(s, 1H, NCH_2), 4.12-4.25(m, 3H, NCH_2, CH); δ_C(75 MHz; $CDCl_3$; TMS) 14.2, 14.2, 22.3, 22.8, 25.9, 26.0, 26.9, 28.3, 28.5, 28.5, 29.3, 29.3, 29.4, 29.4, 29.7, 29.7, 29.7, 29.7, 32.0, 32.0, 54.5, 55.2, 66.2, 66.9, 168.1. MS (ESI): m/z = 396.4 (M^+).

3e $[\alpha]_D^{20}$ -27.2° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.63-0.84(m, 6H, CH_3), 0.98-1.42(m, 28H, CH_2), 1.42-1.90(m, 4H, CH_2), 1.93-2.22(m, 3H, CH_2), 2.51(s, 1H, CH_2), 3.06-3.40(m, 3H, NCH_2), 3.84(s, 1H, NCH_2), 3.97-4.18(m, 2H, NCH_2), 4.20-4.29(m, 1H, CH); δ_C(75 MHz; $CDCl_3$; TMS) 14.3, 14.3, 22.3, 22.8, 22.8, 26.0, 26.0, 26.9, 29.2, 29.2, 29.4, 29.4, 29.4, 29.4, 29.7, 29.7, 29.7, 29.7, 32.0, 32.0, 54.4, 54.4, 67.2, 67.2, 168.1. MS (ESI): m/z = 396.5 (M^+).

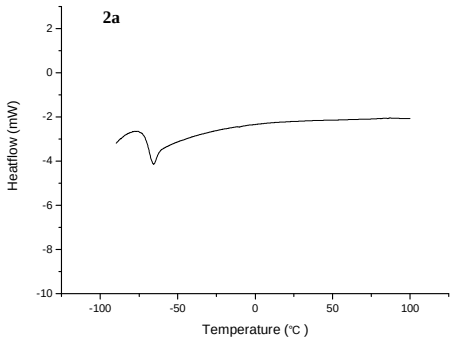
1f $[\alpha]_D^{20}$ -25.9° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.78-0.97(m, 6H, CH_3), 1.05-1.40(m, 36H, CH_2), 1.48-1.98(m, 4H, CH_2), 1.98-2.42(s, 3H, CH_2), 2.60(s, 1H, CH_2), 3.06-3.38(m, 3H, NCH_2), 3.64(s, 1H, NCH_2), 4.04-4.18(m, 2H, NCH_2), 4.20-4.29(m, 1H, CH); δ_C(75 MHz; $CDCl_3$; TMS) 14.3, 14.3, 22.3, 22.8, 22.8, 26.0, 26.0, 26.9, 29.2, 29.2, 29.4, 29.4, 29.4, 29.4, 29.7, 29.7, 29.7, 29.7, 32.0, 32.0, 54.4, 54.4, 67.2, 67.2, 168.1. MS (ESI): m/z = 452.5 (M^+).

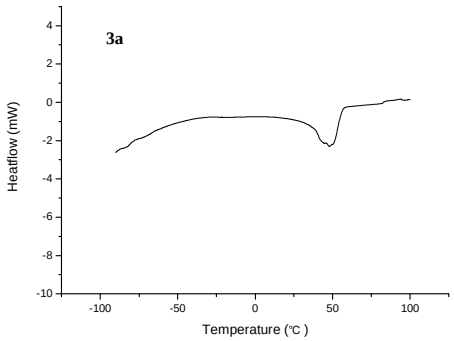
2f $[\alpha]_D^{20}$ -26.6° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.82-0.91(m, 6H, CH_3), 1.16-1.39(m, 36H, CH_2), 1.40-1.68(m, 4H, CH_2), 1.69-1.98(m, 3H, CH_2), 2.02-2.17(m, 1H, CH_2), 2.24-2.71(m, 3H, NCH_2), 3.04-3.23(m, 2H, NCH_2), 4.08-4.16(m, 2H, NCH_2, CH); δ_C(75 MHz; $CDCl_3$; TMS) 14.38, 14.38, 22.94, 22.94, 23.30, 26.15, 27.85, 28.88, 28.99, 29.60, 29.60, 29.60, 29.90, 29.90, 29.90, 29.90, 29.90, 29.90, 29.90, 29.90, 29.90, 29.90, 32.16, 32.16, 53.82, 55.51, 64.95, 66.52,

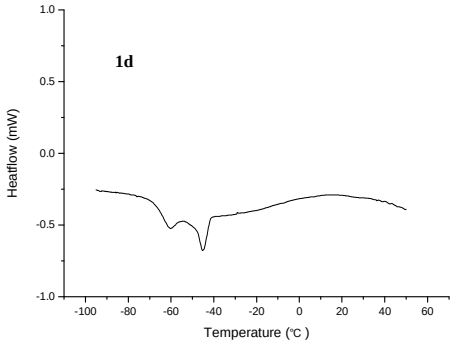
174.74. MS (ESI): m/z = 452.5 (M^+).

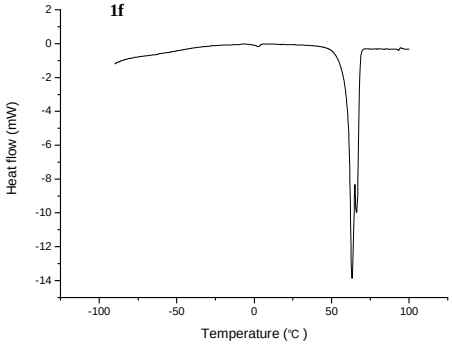
3f $[\alpha]_D^{20}$ -26.3° (*c* 1 in ethanol) δ_H(300 MHz; $CDCl_3$; TMS) 0.78-0.91(t, 6H, *J*=6.6Hz, CH_3), 1.16-1.38(m, 36H, CH_2), 1.64(t, 4H, *J*=6.6Hz, CH_2), 2.04-2.13(m, 3H, CH_2), 2.40-2.51(m, 1H, CH_2), 2.94-3.18(m, 3H, NCH_2), 3.74(s, 1H, NCH_2), 3.93(s, 1H, NCH_2), 4.18(t, 2H, *J*=6.6Hz, NCH_2, CH), 6.45(s, 1H, OH); δ_C(75 MHz; $CDCl_3$; TMS) 14.32, 14.37, 22.91, 22.91, 22.91, 25.96, 25.96, 26.87, 26.93, 28.6, 28.60, 28.60, 29.41, 29.41, 29.57, 29.57, 29.67, 29.67, 29.85, 29.85, 29.85, 29.85, 32.13, 32.13, 55.23, 55.99, 66.78, 66.96, 170.00. MS (ESI): m/z = 452.5 (M^+).

Typical DSC curves:








1f
Heat flow (mW)
2
0
-2
-4
-6
-8
-10
-12
-14
-100
-50
0
50
100
Temperature (℃)