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Synthesis of Chiral *Geminal* Dicationic Ionic Liquid from Amino Acids

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Chiral imidazolium ionic liquids (**3**) from amino acid were synthesized when reacted with 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,6-dibromohexane and 1,9-dibromononane, respectively, to obtain a series of chiral *geminal* dicationic ionic liquid (**5**), The structures of the synthesized compouds were determined by IR, ^{1}H and ^{13}C NMR, this method for the synthesis of chiral *geminal* dicationic ionic liquid is simple and rapid with high yield and the study for their application is under way.

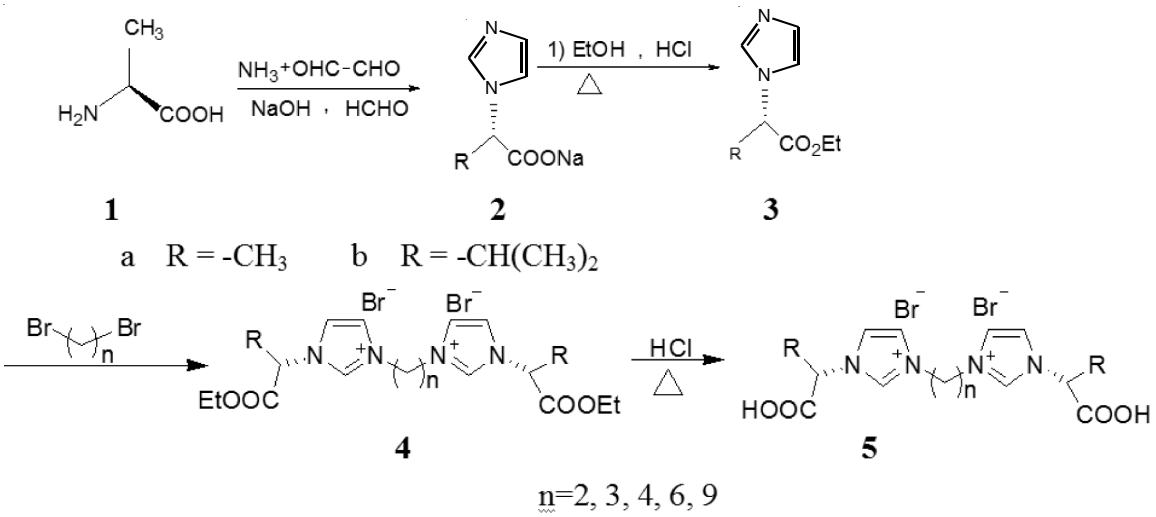
Key Words: Chiral imidazolium ionic liquids, Chiral *geminal* dicationic ionic liquid, Synthesize, Characterization.

INTRODUCTION

Since the first report of *geminal* dicationic ionic liquids in 2003[1], much effort has been devoted to the *geminal* dicationic ionic liquids because their superior physical properties compared to traditional monocationic ionic liquids[2]. The application as solvents in high-temperature reactions[3], novel high-temperature lubricants[4,5], ultrastable separation phases[6] and dye sensitized solar cells[7,8] have been reported.

It is well known that the chiral monocationic ionic liquids are attractive due to their potential for asymmetric synthesis[9,10], gas chromatography[11], optical resolution of racemates[12], stereo selective polymerization[13]. But there is no report on the synthesis and application of chiral *geminal* dicationic ionic liquids.

In this work, chiral imidazolium ionic liquids were designed from the natural amino acid, then reacted with 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,6-dibromohexane and1,9-dibromononane, respectively, to obtain a series of chiral *geminal* dicationic ionic liquid (**Scheme-I**), the structures of the synthesized compouds were determined by IR, ^{1}H NMR, ^{13}C NMR and the study for their application research in synthesis and separation is under way.



Scheme-I: Synthetic route of chiral *geminal* dicationic ionic liquid

EXPERIMENTAL

All the chemical reagents used are of analytical pure grade,1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,6-dibromohexane and 1,9-dibromononane was distilled again. Chiral imidazolium ionic liquids **3** from amino acid were synthesized according to the literature procedures[14] and the products were determined by IR, ^{1}H NMR.

Melting points were recorded on a digital microscope are uncorrected. IR (KBr) spectra (ν cm^{-1}) were obtained on Nicolet AVATAR 370 spectrometer, ^{1}H and ^{13}C NMR spectra were taken on a Avance 400 NMR spectrometer, using TMS as internal standard. The specific rotations were measured on an Optical Instrument Ltd. WZZ-ZS polarimeter made in Shanghai Jinke.

Procedure for the synthesis of chiral geminal dicationic ionic liquid (5): 0.25 molar of 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,6-dibromohexane and 1,9-dibromononane, resprctively, reacted with 0.5 molar **3** under the protection of N_2 at room temperature then all the products were purified by extraction by 200 mL ethyl acetate four times when reaction solution changed into viscous and vacuum drying 72 h to get product **4**, which on refluxing in 20 mL concentrated hydrochloric acid for 4 h, evaporated solvent under reduced pressure to obtain crude products and then recrystallized to afford the products **5**.

RESULTS AND DISCUSSION

Melting points and optical activity of chiral *geminal* dicationic ionic liquid: Generally speaking, most ionic liquid are low melting, called room temperature ionic liquids, but the synthesized chiral *geminal* dicationic ionic liquid **5** have high melting (Table-1) and with the linkage chains increase, the melting pionts decrease.

TABLE-1
MELTING POINTS AND OPTICAL ACTIVITY OF **5**

Compound	T (ºC)	$[\alpha]_D^{25}$
5a$_2$	218	+7.4(C2.0 %, CH_3OH)
5a$_3$	211	+7.8(C2.0 %, CH_3OH)
5a$_4$	205	+8.3(C2.0 %, CH_3OH)
5a$_6$	197	+9.4(C2.0 %, CH_3OH)
5a$_9$	164	+10.6(C2.0 %, CH_3OH)
5b$_2$	224	-18.4 (C2.0 %, CH_3OH)
5b$_3$	216	-18.9(C2.0 %, CH_3OH)
5b$_4$	208	-19.4(C2.0 %, CH_3OH)
5b$_6$	201	-20.3(C2.0 %, CH_3OH)
5b$_9$	171	-22.8(C2.0 %, CH_3OH)

[a]Melting points were recorded on a digital microscope and are uncorrected.

Synthesis of chiral *geminal* dicationic ionic liquid: The synthesis for chiral *geminal* dicationic ionic liquid **5** is easy to purify and have high yields and the products were determined by IR, ^{1}H NMR (Table-2), ^{13}C NMR (Table-3). Compounds **5** in IR showed absroption at 3424 cm^{-1} (-OH), 1736 (C=O), 1629, 1579 ((imidazole).

Solubility of chiral *geminal* dicationic ionic liquid: Great attention has been paid to the ionic liquid as a new type of green solvent. The solubility of the synthesized chiral *geminal* dicationic ionic liquid in different solvent were investigated (Table-4). It was found that all the chiral *geminal* dicationic ionic liquid synthesized were dissolved in water and methanol and insoluble in ethyl acetate, acetone, chloroform, which is quite similar to the monocationic ionic liquids with Br^- as anion.

TABLE-2
^{1}H NMR SPECTRA OF COMPOUNDS **5**

Compound	^{1}H NMR, δ (ppm)
5a$_2$	8.76 (s, 2H), 7.40(s, 2H), 7.34(s, 2H), 4.82(q, 2H), 3.72 (t, 4H), 1.60(d, 6H).
5a$_3$	8.77(s, 2H), 7.43(s, 2H), 7.34(s, 2H), 4.80, (q, 2H), 3.80 (t, 4H), 1.71 (m, 2H), 1.62(d, 6H).
5a$_4$	8.84(s, 2H), 7.46(s, 2H), 7.41(s, 2H), 4.78 (d, 2H), 3.76 (t, 4H), 1.75 (m, 4H),1.61(d, 6H).
5a$_6$	8.89(s, 2H), 7.48(s, 2H),7.37(s, 2H), 4.87(q, 2H), 3.78 (t, 4H), 1.86(m, 4H), 1.56(d, 6H), 1.30(m, 4H).
5a$_9$	8.85(s, 2H), 7.44(s, 2H), 7.35(s, 2H), 4.88(q, 2H), 3.79 (t, 4H), 1.88(m, 4H), 1.58(d, 6H), 1.33-1.40(m, 10H).
5b$_2$	8.76(s, 2H), 7.40(s, 2H), 7.36(s, 2H), 4.82(q, 2H), 3.72 (t, 4H), 2.22(m, 2H), 1.01 (d, 6H), 0.80 (d, 6H).
5b$_3$	8.76(s, 2H), 7.42(s, 2H), 7.38(s, 2H), 4.81, (q, 2H), 3.79 (t, 4H), 2.22(m, 2H), 1.73 (m, 2H), 1.02 (d, 6H), 0.84 (d, 6H).
5b$_4$	8.87(s, 2H), 7.48(s, 2H), 7.42(s, 2H), 4.80 (d, 2H), 3.78 (t, 4H), 2.22(m, 2H), 1.76 (m, 4H), 1.04 (d, 6H), 0.87 (d, 6H).
5b$_6$	9.01(s, 2H), 7.68(s, 2H), 7.67(s, 2H), 4.80 (br, 2H), 3.73 (m, 4H), 2.21 (m, 2H), 1.87 (m, 4H), 1.32 (m, 4H), 1.06 (d, 6H), 0.80 (d, 6H).
5b$_9$	8.89(s, 2H), 7.62(s, 2H), 7.58(s, 2H), 4.80(q, 2H), 3.81(t, 4H), 1.86(m, 4H), 2.24(m, 2H), 1.32-1.39(m, 10H), 1.01 (d, 6H), 0.85 (d, 6H).

^{1}H NMR spectra were taken in D_2O (**5**), using TMS as internal standard.

TABLE-3
^{13}C NMR SPECTRA OF COMPOUNDS **5**

Compound	^{13}C NMR, δ (ppm)
5a$_2$	14.6, 25.4, 58.6, 122.4, 123.6, 138.7, 172.2
5a$_3$	14.8, 25.2, 34.8, 58.9, 122.3, 123.4, 137.4, 172.2
5a$_4$	14.8, 25.6, 38.6, 64.6, 122.8, 123.0, 137.4, 172.2
5a$_6$	15.0, 27.3, 30.3, 54.8, 72.4, 122.8, 123.6, 137.3, 172.2
5a$_9$	15.1, 26.3, 28.3, 30.4, 32.5, 54.8, 72.2, 122.7, 123.6, 137.2, 172.1
5b$_2$	17.3, 25.3, 28.9,53.1, 70.7, 122.4, 123.5, 138.7, 172.2
5b$_3$	17.4, 25.2, 28.3, 52.3,71.7, 122.3, 123.4, 137.4, 172.2
5b$_4$	17.9, 25.3, 30.4, 52.1, 72.5, 122.5, 123.7, 137.4, 172.1
5b$_6$	18.2, 25.2, 27.6, 30.5, 55.0, 73.2, 120.3, 123.4, 137.0, 172.2
5b$_9$	17.8, 25.2, 26.1, 28.3, 30.0, 32.5, 52.5, 70.2, 122.3,123.5, 137.1, 172.3

Conclusion

A synthetic route toward a novel chiral *geminal* dicationic ionic liquid from amino acids has been described. The solubility and other physical properties have been preliminary studied, further investigations for their application is under way.

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TABLE-4
SOLUBILITIES OF THE CHIRAL GEMINAL DICATIONIC IONIC LIQUID

Chiral geminal dicationic ionic liquid	Solubility				
	Water	Methanol	Ethyl acetate	Acetone	Chloroform
$5a_2$	s	s	ins	ins	ins
$5a_3$	s	s	ins	ins	ins
$5a_4$	s	s	ins	ins	ins
$5a_6$	s	s	ins	ins	ins
$5a_9$	s	s	ins	ins	ins
$5b_2$	s	s	ins	ins	ins
$5b_3$	s	s	ins	ins	ins
$5b_4$	s	s	ins	ins	ins
$5b_6$	s	s	ins	ins	ins
$5b_9$	s	s	ins	ins	ins

[a]s = soluble, ins = insoluble.

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