Electronic Supplementary Information

Phase Behavior and Ionic Conductivity of Dendron-Coil-Dendron Block Copolymer/Ionic Liquid Electrolytes

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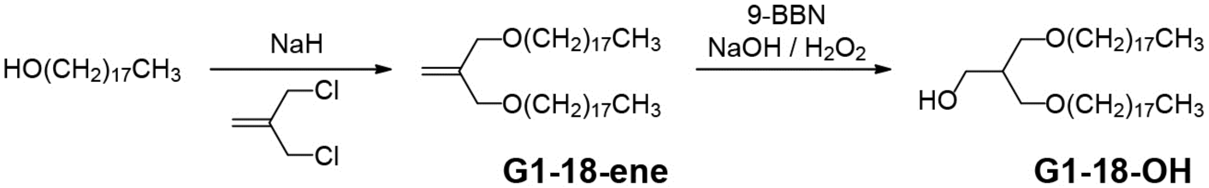
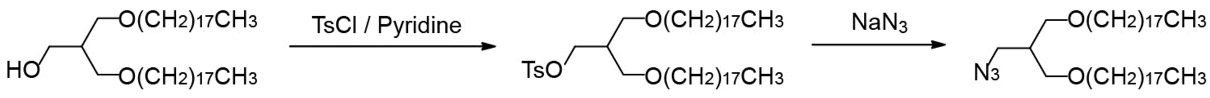
Synthesis of the intermediate compounds and ionic liquids.



G1-18-ene **G1-18-OH**

Synthesis of G1-18-ene. 1-Octadecaol (40.00 g, 147.88 mmol), NaH (8.80 g, 201.65 mmol), methallyl dichloride (8.10 mL, 67.22 mmol) were dissolved in 300 mL of THF and 100 mL of DMF. The reaction mixture was heated to reflux for 12 hours at 75 °C under N_2 atmosphere. After removing THF and DMF using a rotary evaporator, the mixture was extracted with deionized water and dichloromethane. The dichloromethane layer was washed with deionized water several times, and then dried over anhydrous $MgSO_4$. After removing dichloromethane using a rotary evaporator, the resulting mixture was washed with methyl alcohol. The resulting mixture was purified by silica-gel column chromatography using *n*-hexane:dichloromethane = 1:1 solvent mixture as the eluent, to yield 24.22 g (60.8%) of a white solid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 5.16 (s, 2H, $\mathrm{C}\mathit{H}_2\mathrm{{=}C(CH_2\text{-})_2}$), 3.96 (s, 4H, $\mathrm{CH_2{=}C(C}\mathit{H}_2\text{-})_2$), 3.40 (t, 4H, J = 6.0 Hz, $\mathrm{CH_2{=}C(CH_2OC}\mathit{H}_2\mathrm{CH_2}\text{-})_2$), 1.55 (m, 4H, $\text{-}\mathrm{CH_2CH(CH_2OCH_2C}\mathit{H}_2\text{-})_2$), 1.25 (m, 60H, $\text{-}\mathrm{OCH_2CH_2(C}\mathit{H}_2)_{15}\mathrm{CH_3}$), 0.88 (t, 6H, J = 6.2 Hz, $\text{-}\mathrm{O(CH_2)_{17}C}\mathit{H}_3$).

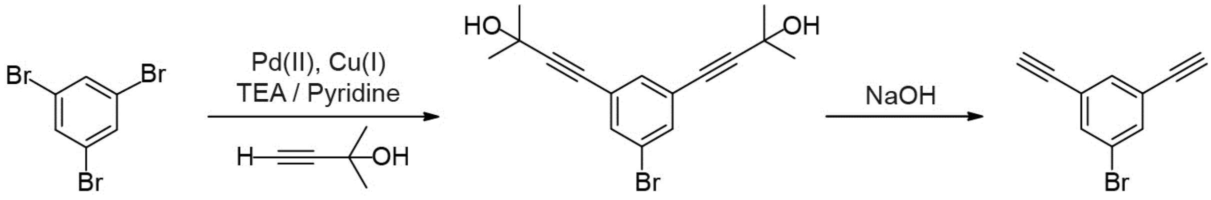
Synthesis of G1-18-OH. G1-18-ene (20.00 g, 33.75 mmol) was dissolved in 202.49 mL of 0.5 M 9-BBN solution in THF under N_2 atmosphere at room temperature. The reaction mixture was stirred for 24 hour at 40 °C. After cooling to 0 °C in an ice bath, 44.92 mL of 3 M NaOH aqueous solution was carefully added to the reaction mixture. After one hour, 44.92 mL of 34.50% H_2O_2 aqueous solution was subsequently added to the reaction mixture. The solution was stirred for another hour at room temperature. Then, organic solvent was removed using a rotary evaporator. The mixture was saturated with K_2CO_3 and extracted with chloroform. The chloroform layer was washed with deionized water several times, and then dried over anhydrous $MgSO_4$. After removing chloroform using a rotary evaporator, the resulting mixture was purified by silica-gel column chromatography using ethyl acetate as the eluent, to yield 15.38 g (74.63%) of a white solid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 3.76 (d, 2H, J = 5.2 Hz, $\mathrm{HOC}\mathit{H}_2\text{-}$), 3.55-3.38 (m, 8H, $\mathrm{HOCH_2CH(C}\mathit{H}_2\mathrm{OC}\mathit{H}_2\mathrm{CH_2}\text{-})_2$), 2.88 (t, 1H, J = 5.6 Hz, $\mathit{H}\mathrm{OCH_2}\text{-}$), 2.13-2.07 (m, 1H, $\mathrm{HOCH_2C}\mathit{H}\mathrm{(CH_2}\text{-})_2$), 1.55 (m, 4H, $\text{-}\mathrm{CH_2CH(CH_2OCH_2C}\mathit{H}_2\text{-})_2$), 1.25 (m, 60H, $\text{-}\mathrm{OCH_2CH_2(C}\mathit{H}_2)_{15}\mathrm{CH_3}$), 0.88 (t, 6H, J = 6.2 Hz, $\text{-}\mathrm{O(CH_2)_{17}C}\mathit{H}_3$).



G1-18-OH **G1-18-OTs** **b**

Synthesis of G1-18-OTs. **G1-18-OH** (10.00 g, 16.38 mmol) and *p*-toluenesulfonyl chloride (31.22 g, 163.77 mmol) were dissolved in 100 mL of dichloromethane and 20 mL of chloroform. To this mixture, pyridine (13.22 mL, 163.77 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 12 hours under N_2 atmosphere. The pyridine was removed by extraction with HCl solution and dichloromethane. The organic solvents were washed with deionized water several times, and then dried over anhydrous $MgSO_4$. After removing the organic solvents using a rotary evaporator, the resulting mixture was purified by silica-gel column chromatography using *n*-hexane:dichloromethane = 3:1 solvent mixture as the eluent, to yield 11.51 g (91.92%) of a white solid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.78 (d, 2H, J = 8.2 Hz, Ar-H), 7.33 (d, 2H, J = 8.0 Hz, Ar-H), 4.09 (d, 2H, J = 5.6 Hz, $sTO\text{-}C\mathit{H_2}CH(CH_2\text{-})_2$), 3.38-3.25 (m, 8H, $sTOCH_2CH(C\mathit{H_2}OC\mathit{H_2}CH_2\text{-})_2$), 2.44 (s, 3H, Ar-$C\mathit{H_3}$), 2.19 (m, 1H, $sTOCH_2C\mathit{H}(CH_2\text{-})_2$), 1.57 (m, 4H, $\text{-}CH_2CH(CH_2OCH_2C\mathit{H_2}\text{-})_2$), 1.25 (m, 60H, $\text{-}OCH_2CH_2(C\mathit{H_2})_{15}CH_3$), 0.88 (t, 6H, J = 6.4 Hz, $\text{-}O(CH_2)_{17}C\mathit{H_3}$).

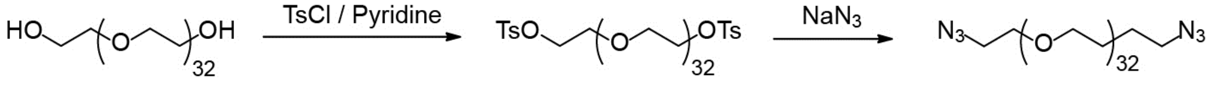
Synthesis of b. G1-18-OTs (10.00 g, 13.08 mmol) and sodium azide (8.50 g, 130.78 mmol) were dissolved in 100 mL of DMF. The reaction mixture was heated to reflux for 12 hours at 110 °C under N_2 atmosphere. After removing DMF using a rotary evaporator, the mixture was extracted with deionized water and chloroform. The chloroform layer was washed with deionized water several times, and then dried over anhydrous $MgSO_4$. After removing chloroform using a rotary evaporator, the resulting mixture was purified by silica-gel column chromatography using *n*-hexane:dichloromethane = 1:1 solvent mixture as the eluent, to yield 7.60 g (91.42%) of a white solid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 3.43-3.36 (m, 8H, $N_3CH_2CH(C\mathit{H_2}OC\mathit{H_2}\text{-})_2$), 2.12 (m, 1H, $N_3CH_2C\mathit{H}(CH_2\text{-})_2$), 1.56 (m, 4H, $\text{-}CH_2CH(CH_2OCH_2C\mathit{H_2}\text{-})_2$), 1.25 (m, 60H, $\text{-}OCH_2CH_2(C\mathit{H_2})_{15}CH_3$), 0.88 (t, 6H, J = 6.8 Hz, $\text{-}O(CH_2)_{17}C\mathit{H_3}$).



di-OH **a**

Synthesis of di-OH. 1,3,5-Tribromobenzene (10.00 g, 31.77 mmol), 2-methyl-3-butyn-2-ol (5.59 mL, 57.18 mmol), copper(I)iodide (0.05 g, 0.26 mmol), $PdCl_2(PPh_3)_2$ (0.08 g, 0.11 mmol) were dissolved in 150 mL of dry triethylamine and 50 mL of dry pyridine. The reaction mixture was heated to reflux for 12 hours at 80 °C under N_2 atmosphere. After removing triethylamine using a rotary evaporator, the pyridine was removed by extraction with a diluted HCl solution and dichloromethane. The dichloromethane layer was washed with deionized water several times, and then dried over anhydrous $MgSO_4$. After removing dichloromethane using a rotary evaporator, the resulting mixture was purified by silica-gel column chromatography using *n*-hexane:ethyl acetate = 3:1 solvent mixture as the eluent, to yield 5.02 g (49.22%) of a yellowish solid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.50 (s, 2H, Ar-*H*), 7.40 (s, 1H, Ar-*H*), 1.60 (s, 3H, $C(CH_3)_2OH$).

Synthesis of a. di-OH (5.02 g, 15.63 mmol) and sodium hydroxide (12.50 g, 312.57 mmol) were dissolved in 240 mL of toluene. The reaction mixture was heated to reflux for 24 hours at 80 °C under N_2 atmosphere. After removing toluene using a rotary evaporator, the mixture was extracted with deionized water and dichloromethane. The dichloromethane layer was washed with deionized water several times, and then dried over anhydrous $MgSO_4$. After removing dichloromethane using a rotary evaporator, the resulting mixture was purified by silica-gel column chromatography using *n*-hexane as the eluent, to yield 2.50 g (78.13%) of a white solid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.61 (s, 2H, Ar-*H*), 7.52 (s, 1H, Ar-*H*), 3.14 (s, 2H, Ar-C≡C*H*).

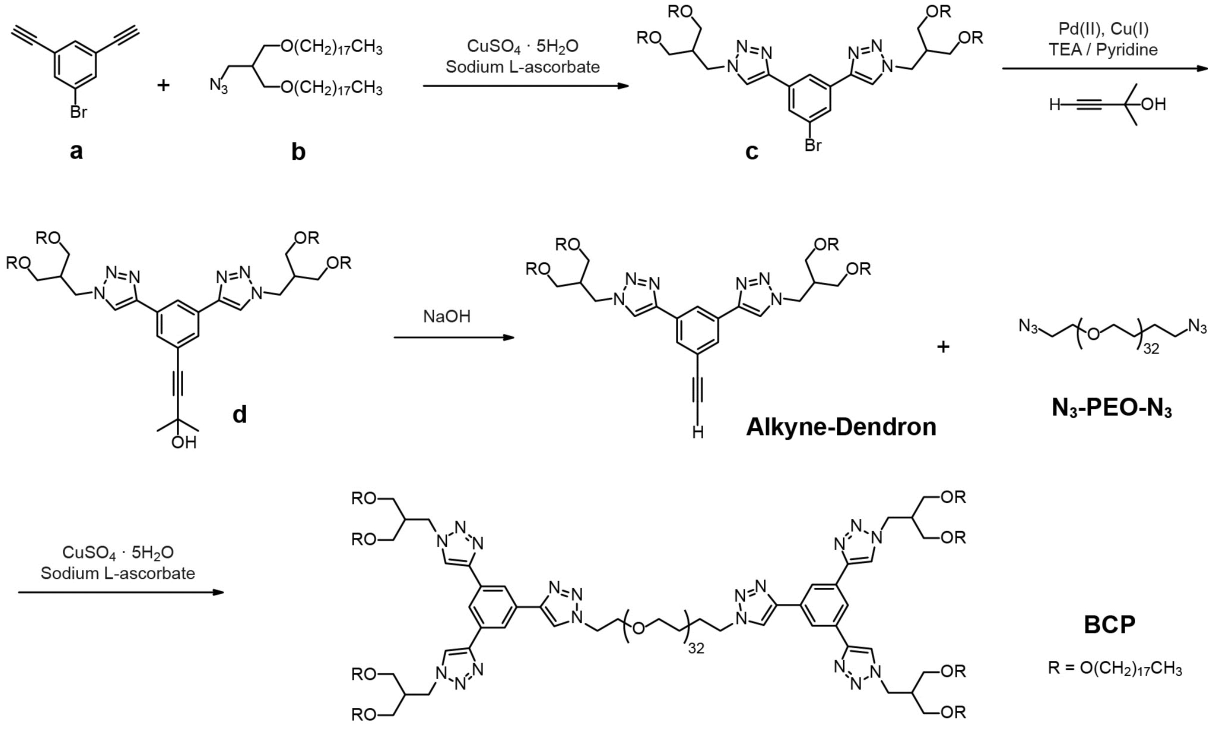


HO-PEO-OH **TsO-PEO-OTs** **N_3-PEO-N_3**

Synthesis of TsO-PEO-OTs. HO-PEO-OH (13.00 g, 8.67 mmol) and *p*-toluenesulfonyl chloride (33.05 g, 86.67 mmol) were dissolved in 130 mL of dichloromethane. To this mixture, pyridine (13.99 mL, 86.67 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 24 hours under N_2 atmosphere. The pyridine was removed by extraction with HCl solution and dichloromethane. The dichloromethane layer was washed with deionized water several times, and then dried over anhydrous $MgSO_4$. After removing dichloromethane using a rotary evaporator, the resulting mixture was purified by silica-gel column chromatography using dichloromethane:methyl alcohol = 10:1 solvent mixture as the eluent, to yield 9.35 g (59.66%) of a white solid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.83 (d, 4H, Ar-

H), 7.35 (d, 4H, Ar-*H*), 4.16 (t, 4H, *J* = 6.8 Hz, -CH$_2$C*H*$_2$OTs), 3.71-3.58 (br, -C*H*$_2$C*H*$_2$O-), 2.45 (s, 6H, Ar-C*H*$_3$).

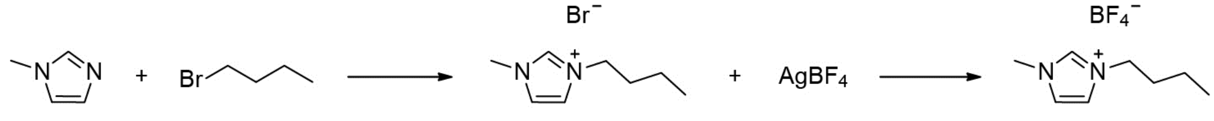
Synthesis of N$_3$-PEO-N$_3$. TsO-PEO-OTs (9.35 g, 5.17 mmol) and sodium azide (6.72 g, 51.71 mmol) were dissolved in 100 mL of DMF. The reaction mixture was heated to reflux for 24 hours at 120 °C under N_2 atmosphere. After removing DMF using a rotary evaporator, the mixture was extracted with deionized water and chloroform. The chloroform layer was washed with deionized water several times, and then dried over anhydrous $MgSO_4$. After removing chloroform using a rotary evaporator, the resulting mixture was purified by silica-gel column chromatography using dichloromethane:methyl alcohol = 10:1 solvent mixture as the eluent, to yield 7.02 g (87.57%) of a white solid. ^{1}H-NMR (CDCl$_3$, δ, ppm): 3.84-3.37 (br, -C*H*$_2$C*H*$_2$O- and –CH$_2$C*H*$_2$N$_3$).



Synthesis of c. Compound **a** (1.00 g, 4.88 mmol), compound **b** (7.45 g, 11.70 mmol), $CuSO_4 \cdot 5H_2O$ (1.22 g, 4.88 mmol) and (+)-sodium L-ascorbate (1.93 g, 9.75 mmol) were dissolved in 80 mL of THF and 8 mL of water. The reaction mixture was degassed three times by freeze-pump-thaw cycles. The mixture was stirred at room temperature for 12 hours under N_2 atmosphere. After removing THF using a rotary evaporator, the mixture was extracted with deionized water and chloroform. The dichloromethane layer was washed with deionized water several times, and then dried over anhydrous $MgSO_4$. After removing chloroform using a rotary evaporator, the resulting mixture was purified by silica-gel column chromatography using *n*-hexane:ethyl acetate = 10:1 solvent mixture as the eluent, to yield 5.55 g (77.14%) of a white solid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 8.24 (s, 1H, Ar-*H*), 7.95 (s, 2H, Ar-*H*), 7.86 (s, 2H, triazole-*H*), 4.53 (d, 4H, *J* = 6.4 Hz, $-CH_2CH(CH_2-)_2$), 3.44-3.37 (m, 16H, $-CH_2CH(CH_2OCH_2-)_2$), 2.53-2.47 (m, 2H, $-CH_2CH(CH_2OCH_2-)_2$), 1.55 (m, 8H, $-OCH_2CH_2(CH_2)_{15}CH_3$), 1.25 (m, 120H, $-OCH_2CH_2(CH_2)_{15}CH_3$), 0.91-0.84 (m, 12H, $-O(CH_2)_{17}CH_3$).

Synthesis of d. Compound **c** (5.55 g, 3.76 mmol), 2-methyl-3-butyn-2-ol (3.67 mL, 37.57 mmol), copper(I)iodide (0.30 g, 1.58 mmol), $PdCl_2(PPh_3)_2$ (0.50 g, 0.71 mmol) were dissolved in 50 mL of dry triethylamine. The reaction mixture was heated to reflux for 12 hours at 120 °C under N_2 atmosphere. After removing triethylamine using a rotary evaporator, the mixture was extracted with deionized water and chloroform. The chloroform layer was washed with deionized water several times, and then dried over anhydrous $MgSO_4$. After removing chloroform using a rotary evaporator, the resulting mixture was purified by the silica-gel column chromatography using *n*-hexane:ethyl acetate = 5:1 solvent mixture as the eluent, to yield 4.82 g (86.66%) of a yellow solid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 8.26 (s, 1H, Ar-*H*), 7.87-7.85 (m, 3H, Ar-*H* and triazole-*H*), 4.53 (d, 4H, *J* = 6.4 Hz, $-CH_2CH(CH_2-)_2$), 3.44-3.38 (m, 16H, $-CH_2CH(CH_2OCH_2-)_2$), 2.52-2.49 (m, 2H, $-CH_2CH(CH_2OCH_2-)_2$), 1.99 (s, 1H, $-C(CH_3)_2OH$), 1.55 (m, 14H, $-OCH_2CH_2(CH_2)_{15}CH_3$ and $-C(CH_3)_2OH$), 1.25 (m, 120H, $-OCH_2CH_2(CH_2)_{15}CH_3$), 0.91-0.84 (m, 12H, $-O(CH_2)_{17}CH_3$).

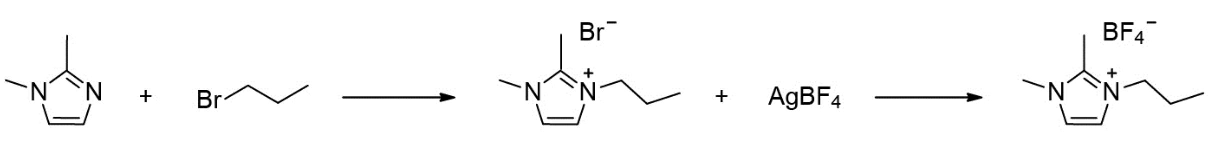
Synthesis of Alkyne-Dendron. Compound **d** (4.82 g, 3.26 mmol) and sodium hydroxide (1.30 g, 32.56 mmol) were dissolved in 50 mL of toluene. The reaction mixture was heated to reflux for 24 hours at 120 °C under N_2 atmosphere. After removing toluene using a rotary evaporator, the mixture was extracted with deionized water and dichloromethane. The dichloromethane layer was washed with deionized water several times, and then dried over anhydrous $MgSO_4$. After removing dichloromethane using a rotary evaporator, the resulting mixture was purified by silica-gel column chromatography using dichloromethane:ethyl acetate = 20:1 solvent mixture as the eluent, to yield 3.70 g (79.90%) of a yellowish solid. ^{1}H-NMR ($CDCl_3$, δ, ppm): 8.32 (s, 1H, Ar-*H*), 7.92 (s, 2H, Ar-*H*), 7.86 (s, 2H, triazole-*H*), 4.53 (d, 4H, *J* = 6.2 Hz, $-CH_2CH(CH_2-)_2$), 3.43-3.37 (m, 16H, $-CH_2CH(CH_2OCH_2-)_2$), 3.12 (s, 1H, $Ar-C\equiv CH$), 2.52-2.46 (m, 2H, $-CH_2CH(CH_2OCH_2-)_2$), 1.54 (m, 8H, $-OCH_2CH_2(CH_2)_{15}CH_3$), 1.25 (m, 120H, $-OCH_2CH_2(CH_2)_{15}CH_3$), 0.90-0.84 (m, 12H, $-O(CH_2)_{17}CH_3$).



[BMIM][Br] **[BMIM][BF$_4$]**

Synthesis of [BMIM][Br]. 1-Methylimidazole (15.00 g, 182.70 mmol) was dissolved in 50 mL of toluene. To this mixture, 1-bromobuthane (24.14 mL, 219.24 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 24 hours under N_2 atmosphere. The resulting mixture was washed with toluene and ethyl acetate, to yield 37.21 g (92.95%) of a colorless liquid. ^{1}H-NMR (CD_2Cl_2, δ, ppm): 10.51 (s, 1H, -$NC\mathit{H}N$-), 7.36 (s, 1H, $CH_3NCHC\mathit{H}N$-), 7.32 (s, 1H, $CH_3NC\mathit{H}CHN$-), 4.31 (t, 2H, J = 7.4 Hz, -$NC\mathit{H_2}CH_2CH_2CH_3$), 4.07 (s, 3H, -$NC\mathit{H_3}$), 1.97-1.82 (m, 2H, -$NCH_2C\mathit{H_2}CH_2CH_3$), 1.44-1.29 (m, 2H, -$NCH_2CH_2C\mathit{H_2}CH_3$), 0.97 (t, 3H, J = 7.2 Hz, -$NCH_2CH_2CH_2C\mathit{H_3}$).

Synthesis of [BMIM][BF$_4$]. [BMIM][Br] (5.00 g, 22.82 mmol) and silver tetrafluoroborate (4.44 g, 22.82 mmol) were dissolved in 50 mL of methanol. The reaction mixture was stirred at room temperature for 2 hours under N_2 atmosphere. After removing methanol using a rotary evaporator, the [BMIM][BF_4] solution was passed through an alumina column to remove impurities. A silver nitrate test indicated the complete anion exchange. The resulting mixture was washed with ethyl acetate and chloroform, to yield 3.51 g (68.06%) of a yellowish liquid. ^{1}H-NMR (CD_2Cl_2, δ, ppm): 8.76 (s, 1H, -$NC\mathit{H}N$-), 7.31 (s, 1H, $CH_3NCHC\mathit{H}N$-), 7.29 (s, 1H, $CH_3NC\mathit{H}CHN$-), 4.17 (t, 2H, J = 7.4 Hz, -$NC\mathit{H_2}CH_2CH_2CH_3$), 3.94 (s, 3H, -$NC\mathit{H_3}$), 1.90-1.82 (m, 2H, -$NCH_2C\mathit{H_2}CH_2CH_3$), 1.42-1.32 (m, 2H, -$NCH_2CH_2C\mathit{H_2}CH_3$), 0.96 (t, 3H, J = 7.4 Hz, -$NCH_2CH_2CH_2C\mathit{H_3}$). ^{13}C-NMR ($CD_2Cl_2$, δ, ppm): 136.93, 124.10, 122.66, 50.48, 36.86, 32.40, 19.89, 13.62.



[PMMIM][Br] **[PMMIM][BF$_4$]**

Synthesis of [PMMIM][Br]. 1-Methylimidazole (15.00 g, 182.70 mmol) was dissolved in 50 mL of toluene. To this mixture, 1-bromopropane (17.01 mL, 219.24 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 24 hours under N_2 atmosphere. The resulting mixture was washed with toluene and ethyl acetate, to yield 29.88 g (87.39%) of a colorless liquid. ^{1}H-NMR (CD_2Cl_2, δ, ppm): 7.64 (s, 1H, $CH_3NCHC\mathit{H}N$-), 7.46 (s, 1H, $CH_3NC\mathit{H}CHN$-), 4.14 (t, 2H, J = 7.2 Hz, -$NC\mathit{H_2}CH_2CH_3$), 3.97 (s, 3H, -$NC\mathit{H_3}$), 3.74 (s, 3H, -NC*H*$_3$N-), 1.89-1.82 (m, 2H, -NCH$_2$C*H*$_2$CH$_3$), 0.99 (t, 3H, *J* = 7 Hz, -NCH$_2$CH$_2$C*H*$_3$).

Synthesis of [PMMIM][BF$_4$]. [PMMIM][Br] (6.29 g, 28.69 mmol) and silver tetrafluoroborate (5.58 g, 28.69 mmol) were dissolved in 70 mL of methanol. The reaction mixture was stirred at room temperature for 2 hours under N_2 atmosphere. After removing methanol using a rotary evaporator, the [PMMIM][BF$_4$] solution was passed through an alumina column to remove impurities. A silver nitrate test indicated the complete anion exchange. The resulting mixture was washed with ethyl acetate and chloroform, to yield 4.66 g (71.82%) of a yellowish liquid. ^{1}H-NMR (CD$_2$Cl$_2$, δ, ppm): 7.28 (s, 1H, CH$_3$NCHC*H*N-), 7.24 (s, 1H, CH$_3$NC*H*CHN-), 4.03 (t, 2H, *J* = 7.4 Hz, -NC*H*$_2$CH$_2$CH$_3$), 3.80 (s, 3H, -NC*H*$_3$), 3.60 (s, 3H, -NC*H*$_3$N-), 1.87-1.83 (m, 2H, -NCH$_2$C*H*$_2$CH$_3$), 0.98 (t, 3H, *J* = 7.2 Hz, -NCH$_2$CH$_2$C*H*$_3$). ^{13}C-NMR (CD$_2$Cl$_2$, δ, ppm): 144.43, 123.09, 121.49, 50.70, 35.75, 23.57, 10.99, 9.93.

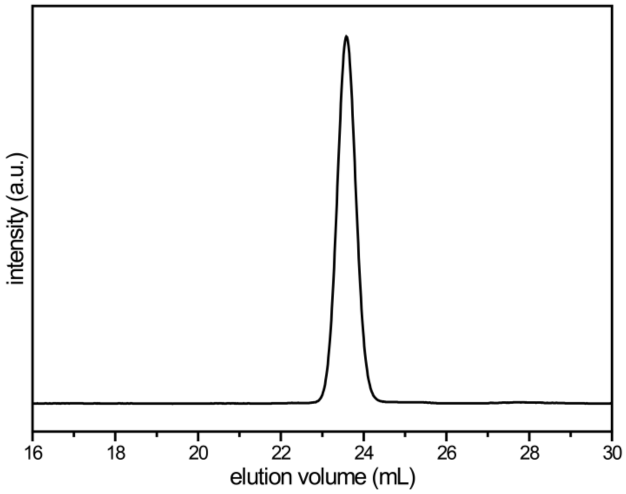


Fig. S1 GPC elugram of the final BCP.

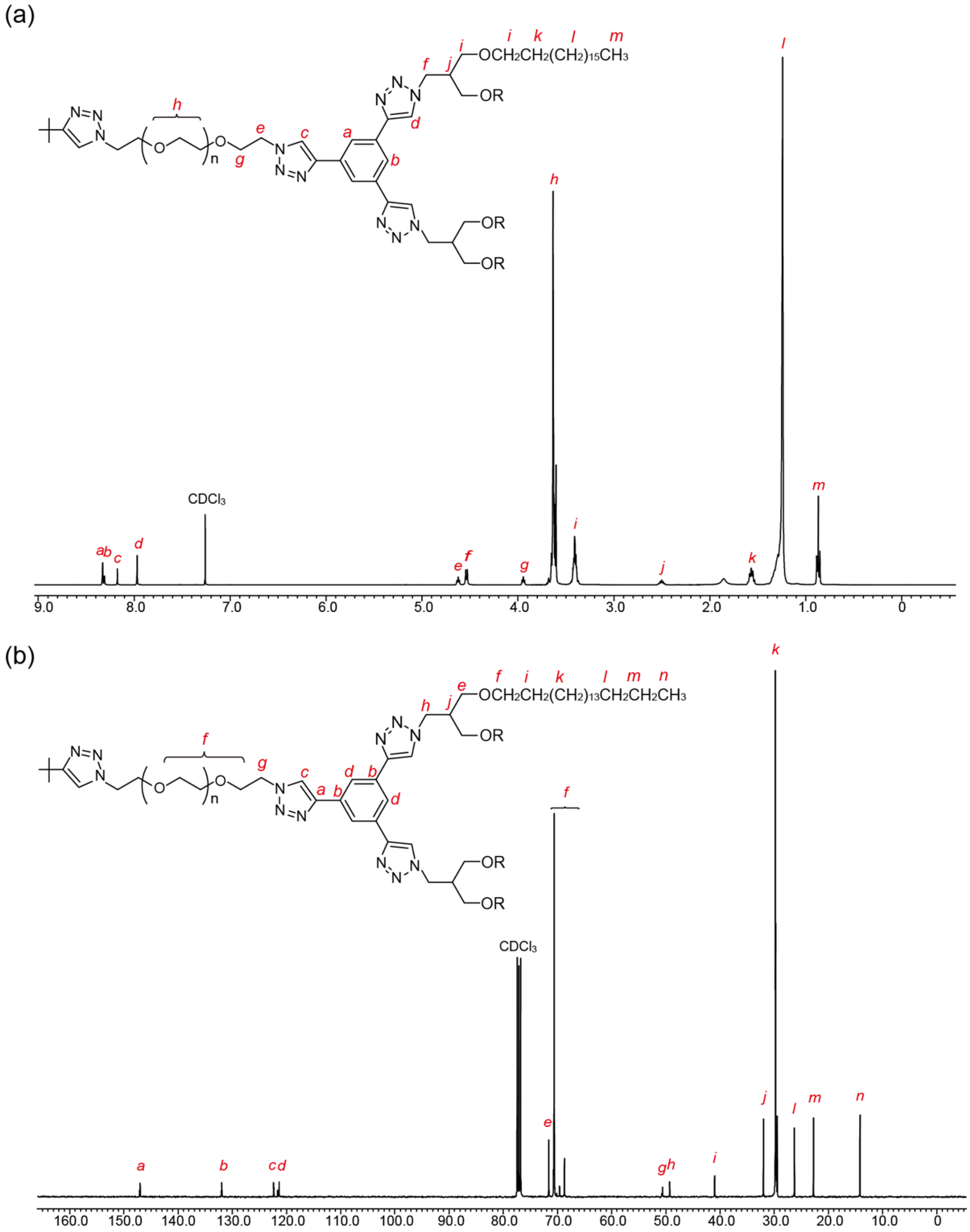


Fig. S2 (a) ^{1}H-NMR and (b) ^{13}C-NMR spectra of the pristine BCP.

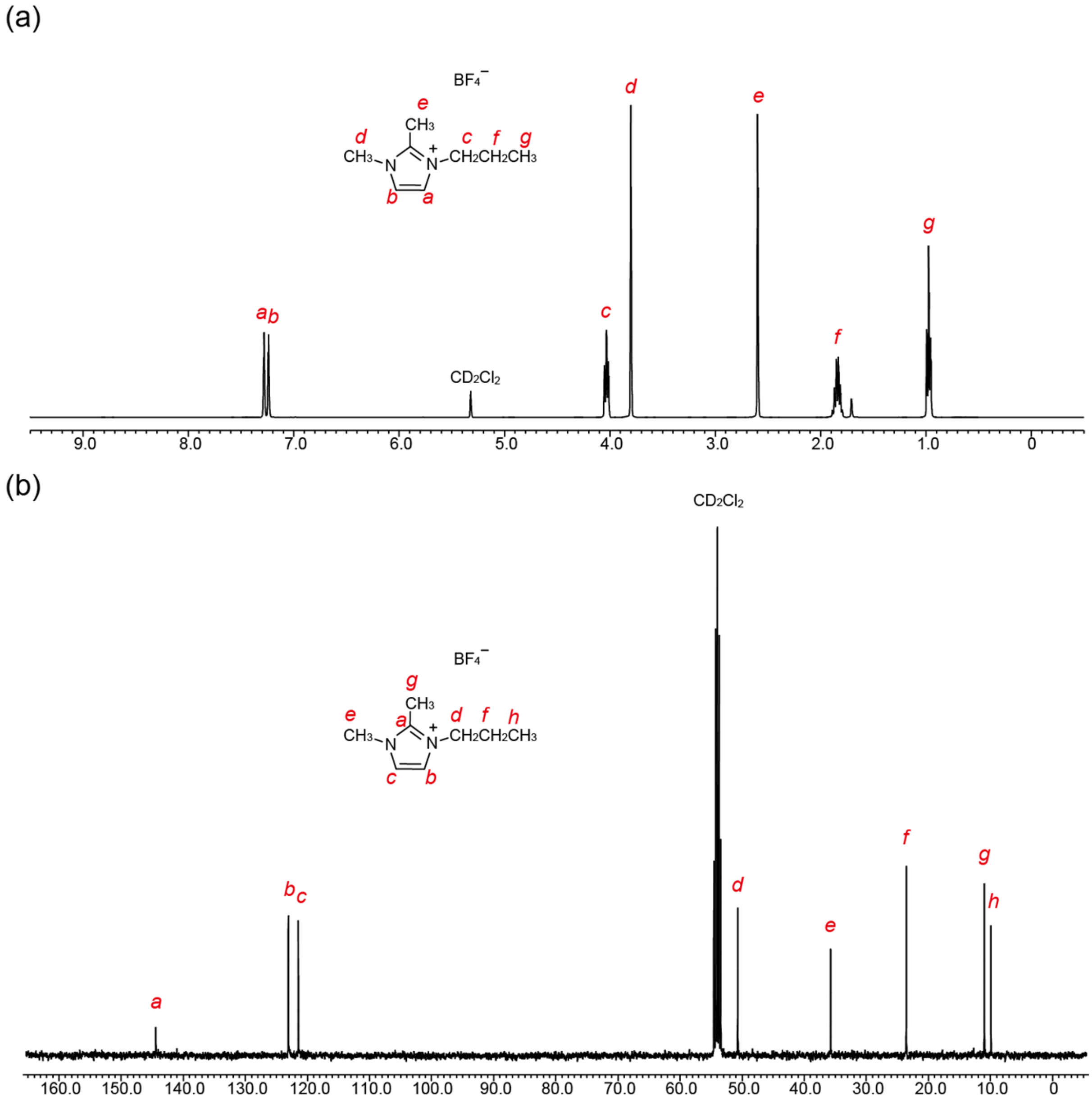


Fig. S3 (a) ^{1}H-NMR and (b) ^{13}C-NMR spectra of [PMMIM][BF_4].

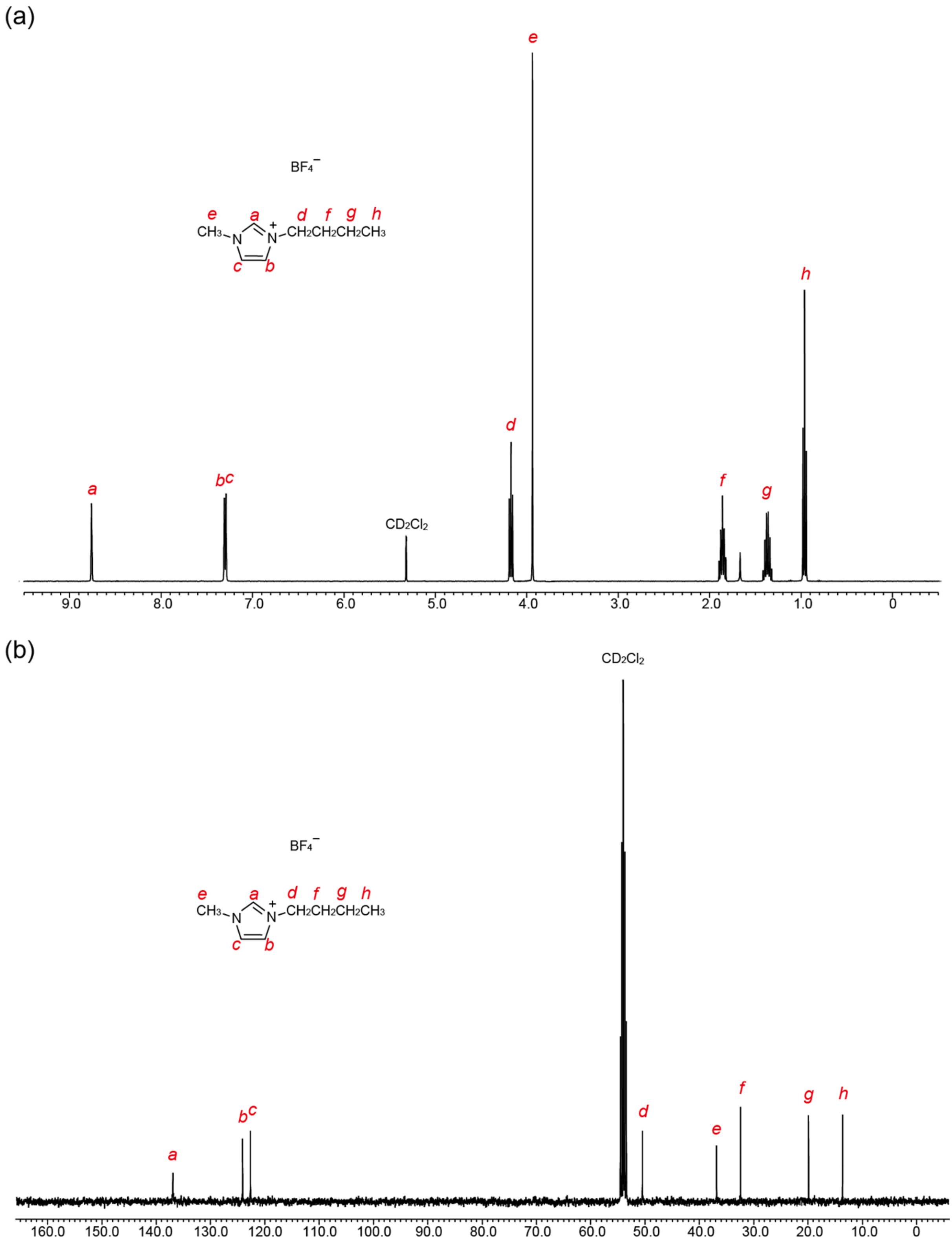


Fig. S4 (a) ^{1}H-NMR and (b) ^{13}C-NMR spectra of [BMIM][BF$_4$].

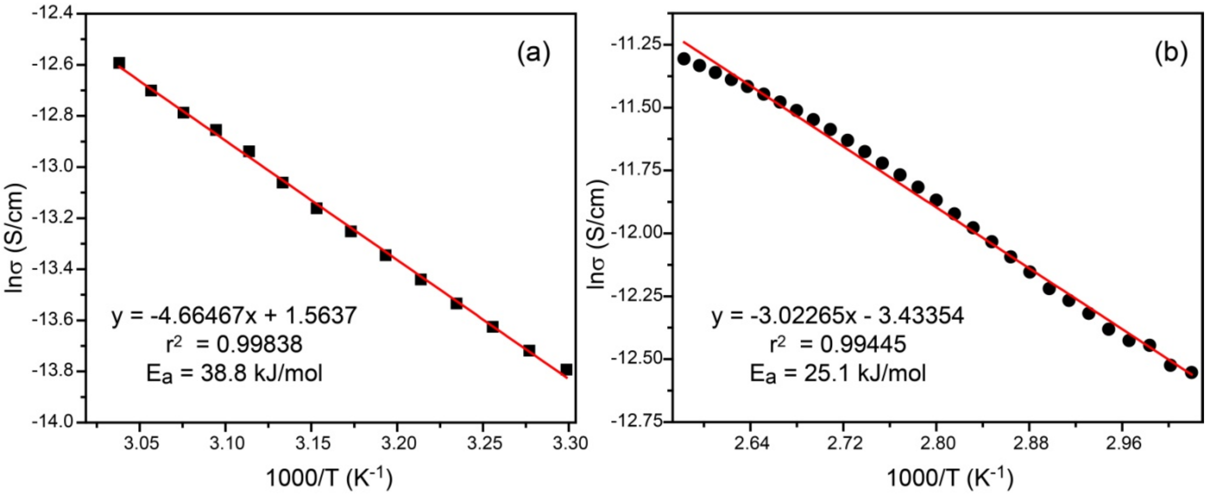


Fig. S5 Arrhenius plots of the conductivity curve of electrolyte **1** in (a) crystalline and (b) disordered micellar phases.

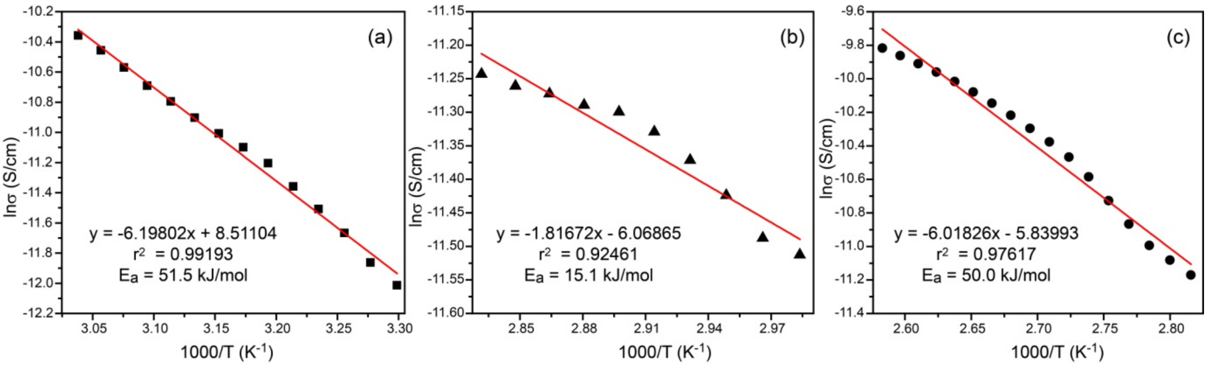


Fig. S6 Arrhenius plots of the conductivity curve of electrolyte **2** in (a) crystalline, (b) ordered LC (COL) and (c) disordered micellar (DIS) phases.