Alkylimidazolium-Based Ionic Liquids with Tailored Anions and Cations for CO_2 Capture

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Supplementary Materials

1. NMR results:

The nuclear magnetic resonance (NMR), elemental analysis (actual vs. theoretical percent), mass fraction of water, mass fraction of halide (bromide), and purity data for all the prepared ILs are shown as follows:

[C_2CN Bim][[DOSS]; δ_H(300 MHz; $CDCl_3$): = 9.95 (s, 1 H, NC*H*N), 7.80 (s, 1 H, *CH*N), 7.34 (1 H, s, *CH*N), 4.71 (t, 1 H, *CH*SO_3), 4.28 (t, 2 H, NCH_2), 4.05 (d, 4 H, OCH_2CH), 3.98 (t, 2 H, CNCH_2), 3.19 (t, 2 H, CH_2CH_2CN), 1.91 (d, 2 H, COCH_2CH), 1.62 (t, 2 H, CH_2CH_2N), 1.38 (d, 4 H, OCH_2CH), 1.24 (br m, 16 H, CH_2), 0.84 (t, 15 H, CH_3CH_2). ^{13}C NMR (75 MHz; $CDCl_3$) = 171.26, 168.56, 136.68, 122.64, 116.67, 67.53, 66.92, 62.06, 48.21, 48.00, 47.78, 47.57, 47.36, 30.21, 28.81, 22.75, 19.15, 13.24, 13.20. Elemental analysis: % actual C, 59.89; H, 9.15; N, 6.90; S, 5.41. $C_{30}H_{54}N_3O_7S$ % theoretical C, 59.97; H, 9.06; N, 6.99; S, 5.34; mass fraction of water 198×10^{-6}, mass fraction of bromide 78×10^{-6}, purity 98.1.

[CNC_2Him][DOSS]: δ_H(300 MHz; $CDCl_3$): = 9.83 (s, 1 H, NC*H*N), 7.80 (s, 1 H, *CH*N), 7.30 (s, 1 H, *CH*N), 4.71 (t, 1 H, *CH*SO_3), 4.25 (t, 2 H, NCH_2), 4.16 (d, 4 H, OCH_2CH), 4.01 (t, 2 H, CNCH_2), 3.17 (t, 2 H, CH_2CH_2CN), 2.30 (d, 2 H, COCH_2CH), 1.92 (t, 2 H, CH_2CH_2N), 1.59 (d, 4 H, OCH_2CH), 1. 28 (br m, 24 H, CH_2), 0.88(t, 15 H, CH_3CH_2). ^{13}C NMR (75 MHz; $CDCl_3$) = 171.44, 169.22, 137.68, 123.22, 121.78, 116.96, 76.70, 67.23, 62.05, 50.27, 45.39, 38.56, 34.24, 31.03, 28.88, 25.87, 22.93, 19.62, 14.00, 10.93, 10.78.

Elemental analysis: % actual C, 61.03; H, 9.41; N, 6.52; S, 5.13. $C_{32}H_{58}N_3O_7S$

% theoretical C, 61.12; H, 9.30; N, 6.52; S, 5.10; mass fraction of water 219×10^{-6}, mass fraction of bromide 65×10^{-6}, purity 96.9 %.

[C_2CN Oim][DOSS]: δ_H(300 MHz; $CDCl_3$): = 9.72 (s, 1 H, N*CH*N), 7.86 (s, 1 H, *CH*N), 7.33 (s, 1 H, *CH*N), 4.73 (t, 1 H, *CH*SO_3), 4.24 (t, 2 H, N*CH* $_2$), 4.13 (d, 4 H, O*CH_2*CH), 3.98 (t, 2 H, CN*CH_2*), 3.19 (t, 2 H, *CH_2*CH_2CN), 3.11 (d, 2 H, CO*CH_2*CH), 1.89 (t, 2 H, *CH_2*CH_2N), 1.62 (d, 4 H, O*CH_2*CH), 1. 27 (br m, 24 H, *CH_2*), 0.89 (15 H, t, *CH_3*CH_2). ^{13}C NMR (75 MHz; $CDCl_3$) = 171.41, 169.31, 137.44, 123.30, 121.88, 117.01, 77.35, 67.95, 61.98, 50.25, 45.34, 38.67, 34.09, 31.65, 28.99, 26.25, 23.63, 22.93, 19.66, 14.03, 10.91, 10.85.

Elemental analysis: % actual C, 62.18; H, 9.44; N, 6.47; S, 4.82. $C_{34}H_{62}N_3O_7S$

% theoretical C, 62.10; H, 9.51; N, 6.47; S, 4.88; mass fraction of water 152×10^{-6}, mass fraction of bromide 67×10^{-6}, purity 97.6 %.

[C_2CN Dim][DOSS]: δ_H(300 MHz; $CDCl_3$): = 9.62 (s, 1 H, N*CH*N), 7.88(s, 1 H, *CH*N), 7.34 (s, 1 H, *CH*N), 4.72 (t, 1 H, *CH*SO_3), 4.24 (t, 2 H, N*CH_2*), 4.17 (d, 4 H, O*CH_2*CH), 3.96 (t, 2 H, CN*CH_2*), 3.21 (t, 2 H, *CH_2*CH_2CN), 2.83 (d, 2 H, CO*CH_2*CH), 1.87 (t, 2 H, *CH_2*CH_2N), 1.55 (d, 4 H, O*CH_2*CH), 1.32 (br m, 28 H, *CH_2*), 0.88 (15 H, t, *CH_3*CH_2). ^{13}C NMR (75 MHz; $CDCl_3$) = 171.40, 169.37, 137.32, 123.31, 121.93, 117.05, 68.01, 50.23, 45.32, 38.58, 31.82, 30.03, 29.22, 28.84, 26.26, 23.39, 22.90, 19.67, 13.99, 10.83.

Elemental analysis: % actual C, 63.03; H, 9.65; N, 6.04; S, 4.73. $C_{36}H_{66}N_3O_7S$

% theoretical C, 63.12; H, 9.71; N, 6.13; S, 4.68; mass fraction of water 184×10^{-6}, mass fraction of bromide 83×10^{-6}, purity 96.9 %.

[CNC_2Him][DDS]: δ_H(300 MHz; D_2O): = 9.92 (s, 1 H, N*CH*N), 7.75 (s, 2 H, *CH*N), 7.51 (t, 2 H, N*CH_2*CH_2), 4.57 (t, 2 H, O*CH_2*CH_2), 4.63 (t, 2 H, CN*CH_2*), 4.19 (t, 2 H, *CH_2*CH_2CN), 3.18 (t, 2 H, *CH_2*CH_2N), 1.93 (t, 2 H, *CH_2*CH_2O), 1.81 (br m, 4 H, *CH_2*), 1.30 (br m, 20 H, *CH_2*), 0.87 (t, 6 H, *CH_3*CH_2).

Elemental analysis: % actual C, 61.09; H, 9.92; N, 8.81; S, 6.73. $C_{24}H_{46}N_3O_4S$

% theoretical C, 60.98; H, 9.81; N, 8.89; S, 6.78; mass fraction of water 198×10^{-6}, mass fraction of bromide 83×10^{-6}, purity 96.9 %.

[C_2CN Oim][DDS]: δ_H(300 MHz; D_2O): = 7.77 (s, 1 H, N*CH*N), 7.75 (s, 2 H, *CH*N), 4.81 (t, 2 H, N*CH_2*CH_2), 4.57 (t, 2 H, O*CH_2*CH_2), 4.27 (t, 2 H, CN*CH_2*), 3.98 (t, 2 H, *CH_2*CH_2CN), 3.18 (t, 2 H,

CH$_2$CH$_2$N), 1.93 (t, 2 H, *CH*$_2$CH$_2$O), 1.63 (br m, 8 H, *CH*$_2$), 1.32 (br m, 20 H, *CH*$_2$), 0.89 (t, 6 H, *CH*$_3$CH$_2$).

Elemental analysis: % actual C, 62.45; H, 10.05; N, 8.35; S, 6.36. $C_{26}H_{50}N_3O_4S$

% theoretical C, 62.36; H, 10.06; N, 8.39; S, 6.40; mass fraction of water 137×10^{-6}, mass fraction of bromide 53×10^{-6}, purity 97.9 %.

[CNC$_2$Him][SBA]: δ_H(300 MHz; D_2O): = = 9.93 (s, 1 H, N*CH*N), 8.27 (br, 2 H, C(*CH*)$_2$SO$_3$), 8.06 (s, 1 H, OH), 7.96 (d, 2 H, C(*CH*)$_2$COOH), 7.59 (s, 1 H, N*CH*CHN), 7.53 (s, 1 H, NCH*CH*N), 4.53 (t, 2 H, N*CH*$_2$(CH$_2$)$_4$), 4.16 (t, 2 H, CN*CH*$_2$CH$_2$), 3.13 (t, 2 H, *CH*$_2$CH$_2$CN), 1.80, (t, 2 H, NCH$_2$*CH*$_2$(CH$_2$)$_3$), 1.21 (br m, 6H, *CH*$_2$), 0.77 (t, 3 H, *CH*$_3$CH$_2$). ^{13}C NMR (75 MHz; D_2O) = 135.79, 132.08, 129.63, 129.46, 126.31, 123.14, 122.46, 117.88, 49.99, 44.84, 30.34, 29.08, 25.00, 21.81, 19.33, 13.30.

Elemental analysis: % actual C, 55.93, H, 6.45; N, 10.35; S, 7.89. $C_{19}H_{26}N_3O_5S$

% theoretical C, 56.00; H, 6.18; N, 10.31; S, 7.87; mass fraction of water 233×10^{-6}, mass fraction of bromide 74×10^{-6}, purity 96.9 %.

[C$_2$CN Oim][SBA]: δ_H(300 MHz; D_2O): = 9.02 (s, 1 H, N*CH*N), 7.64 (br, 2 H, C(*CH*)$_2$SO$_3$), 7.85 (s, 1 H, OH), 4.70 (d, 2 H, C(*CH*)$_2$COOH), 4.57 (s, 1 H, N*CH*CHN), 3.16 (s, 1 H, NCH*CH*N), 2.19 (t, 2 H, N*CH*$_2$(CH$_2$)$_4$), 1.86 (t, 2 H, CN*CH*$_2$CH$_2$), 1.25 (t, 2 H, *CH*$_2$CH$_2$CN), 1.21, (t, 2 H, NCH$_2$*CH*$_2$(CH$_2$)$_3$), 1.19 (br m, 6H, *CH*$_2$), 0.79 (t, 3 H, *CH*$_3$CH$_2$). ^{13}C NMR (75 MHz; D_2O) = 135.90, 123.12, 122.55, 117.86, 50.00, 44.89, 31.17, 29.25, 28.40, 25.44, 22.14, 19.42, 13.57.

Elemental analysis: % actual C, 57.72; H, 6.99; N, 9.57; S, 7.30. $C_{21}H_{30}N_3O_5S$ % theoretical C, 57.91; H, 6.71; N, 9.65; S, 7.36; mass fraction of water 145×10^{-6}, mass fraction of bromide 59×10^{-6}, purity 97.7 %.

[CNC$_2$Him][BS]: δ_H(300 MHz; D_2O): = 8.96 (br, 2 H, CHCSO$_3$), 7.75 (s, 1 H, N*CH*N), 7.61 (s, 1 H, *CH*N), 7.57 (s, 1 H, *CH*N), 7.50 (d, 3 H, *CH*CHCH), 4.56 (t, 2 H, N*CH*$_2$CH$_2$), 4.19 (t, 2 H, CN*CH*$_2$CH$_2$), 3.15 (t, 2 H, *CH*$_2$CH$_2$CN), 1.84 (t, 2 H, *CH*$_2$CH$_2$N), 1.26 (br m, 6H, *CH*$_2$), 0.81 (t, 3 H, *CH*$_3$CH$_2$). ^{13}C NMR (75 MHz; D_2O) = 135.83, 129.03, 125.40, 123.17, 123.11, 122.48, 122.43, 117.92, 50.02, 49.99, 44.86, 44.83, 30.35, 29.10, 25.01, 21.81, 19.36, 13.31.

Elemental analysis: % actual C, 51.35, H, 7.14; N, 11.57; S, 8.72. $C_{18}H_{26}N_3O_3S$

% theoretical C, 59.31; H, 7.19; N, 11.53; S, 8.80; mass fraction of water 206×10^{-6}, mass fraction of bromide 52×10^{-6}, purity 97.3 %.

[C_2CN Oim][BS]: δ_H(300 MHz; D_2O): = 9.01 (br, 2 H, $CHCSO_3$), 7.77 (s, 1 H, N*CH*N), 7.62 (s, 1 H, *CH*N), 7.39 (s, 1 H, *CH*N), 7.54 (d, 3 H, *CH*CHCH), 4.54 (t, 2 H, N*CH_2*CH_2), 4.20 (t, 2 H, CN*CH_2*CH_2), 3.13 (t, 2 H, *CH_2*CH_2CN), 1.86 (t, 2 H, *CH_2*CH_2N), 1.22 (br m, 6H, *CH_2*), 0.77 (t, 3 H, *CH_3*CH_2). ^{13}C NMR (75 MHz; D_2O) = 135.92, 128.74, 125.60, 123.06, 122.54, 117.85, 49.96, 44.89, 31.25, 29.31, 28.49, 28.33, 25.52, 22.20, 19.43, 13.62.

Elemental analysis: % actual C, C 61.12; H, 7.78; N, 10.61; S, 8.20. $C_{20}H_{30}N_3O_3S$

% theoretical C, 61.20; H, 7.70; N, 10.70; S, 8.17; mass fraction of water 184×10^{-6}, mass fraction of bromide 71×10^{-6}, purity 97.2 %.

[CNC_2Him][TFMS]: δ_H(300 MHz; D_2O): = 7.92 (s, 1 H, N*CH*N), 7.60 (s, 1 H, *CH*N), 7.56 (s, 1 H, *CH*N), 4.55 (t, 2 H, N*CH_2*CH_2), 4.21 (t, 2 H, CN*CH_2*CH_2), 3.14 (t, 2 H, *CH_2*CH_2CN), 1.84 (m, 6H, *CH_2*), 1.26 (t, 2 H, *CH_2*CH_3), 0.81 (t, 3 H, *CH_3*CH_2). ^{13}C NMR (75 MHz; D_2O) = 181.60, 169.11, 161.62, 137.72, 135.79, 127.34, 123.11, 120.29, 117.89, 115.00, 106.15, 49.98, 44.80, 42.59, 30.33, 24.98, 21.78, 9.27, 13.26, 11.93.

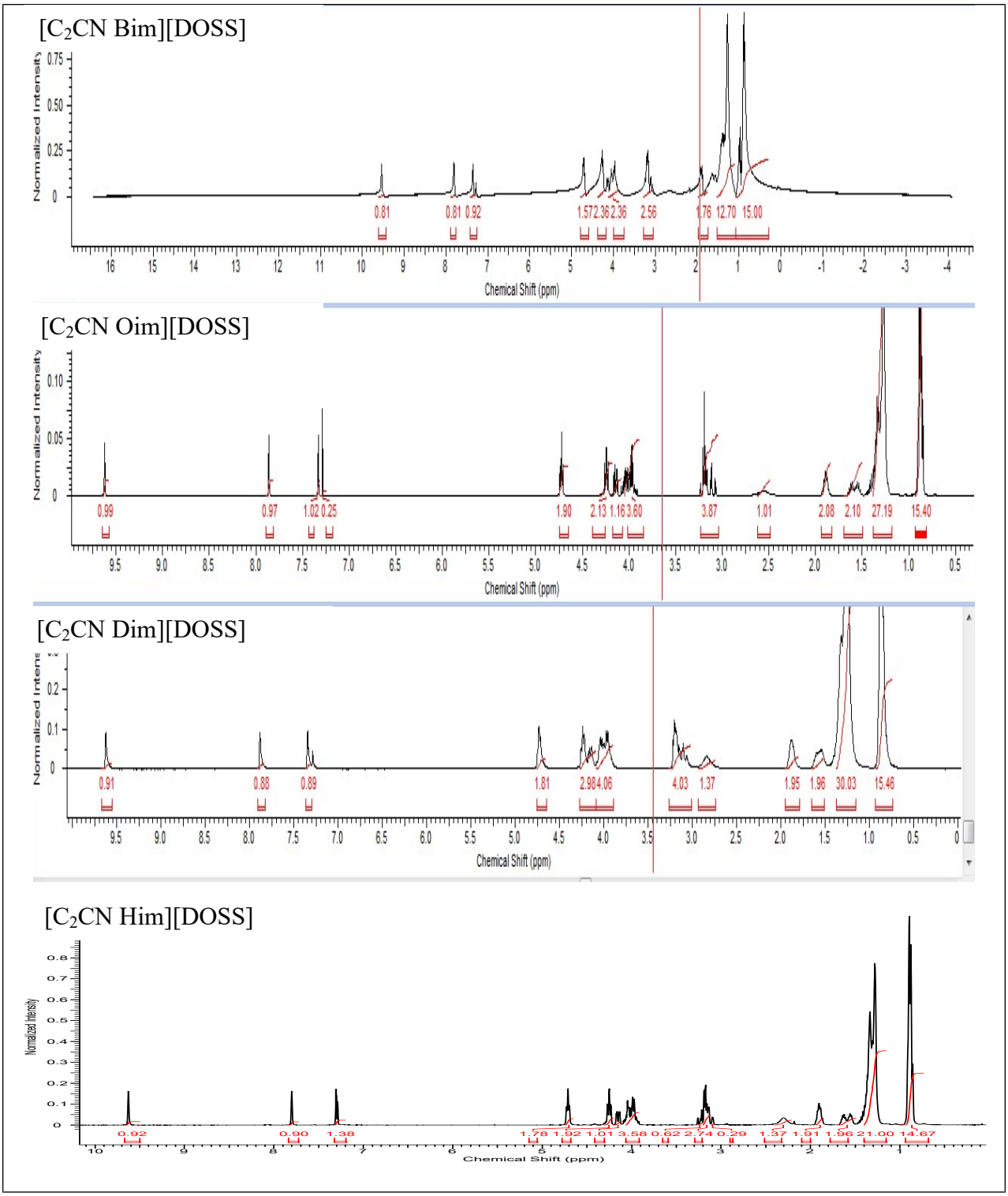
Elemental analysis: % actual C, 43.98, H, 5.78; N, 11.70; S, 9.13. $C_{13}H_{20}F_3N_3O_3S$

% theoretical C, 43.94; H, 5.67; N, 11.82; S, 9.02; mass fraction of water 243×10^{-6}, mass fraction of bromide 91×10^{-6}, purity 96.5 %.

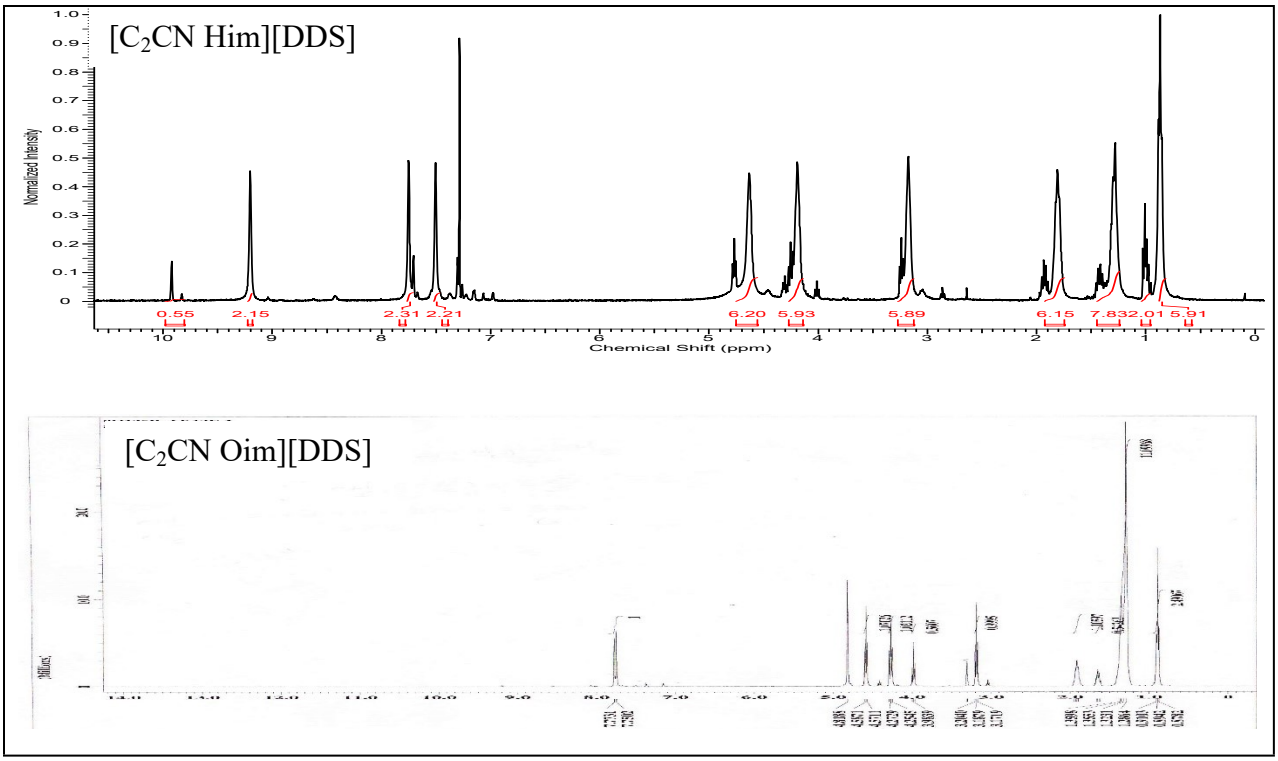
[C_2CN Oim][TFMS]: δ_H(300 MHz; D_2O): = 8.06 (s, 1 H, N*CH*N), 7.67 (s, 1 H, *CH*N), 7.55 (s, 1 H, *CH*N), 4.42 (t, 2 H, N*CH_2*CH_2), 4.18 (t, 2 H, CN*CH_2*CH_2), 3.12 (t, 2 H, *CH_2*CH_2CN), 1.85 (m, 10H, *CH_2*), 1.21 (m, 2 H, *CH_2*CH_3), 0.81 (t, 3 H, *CH_3*CH_2). ^{13}C NMR (75 MHz; D_2O) = 172.00, 165.62, 157.89, 154.98, 137.03, 135.63, 125.94, 122.79, 120.21, 118.43, 114.67, 106.72, 99.17, 91.88, 77.63, 67.27, 49.68, 44.65, 31.28, 28.74, 24.96, 22.11, 19.40, 13.30.

Elemental analysis: % actual C, 47.01; H, 6.43; N, 10.89; S, 8.42. $C_{15}H_{24}F_3N_3O_3S$

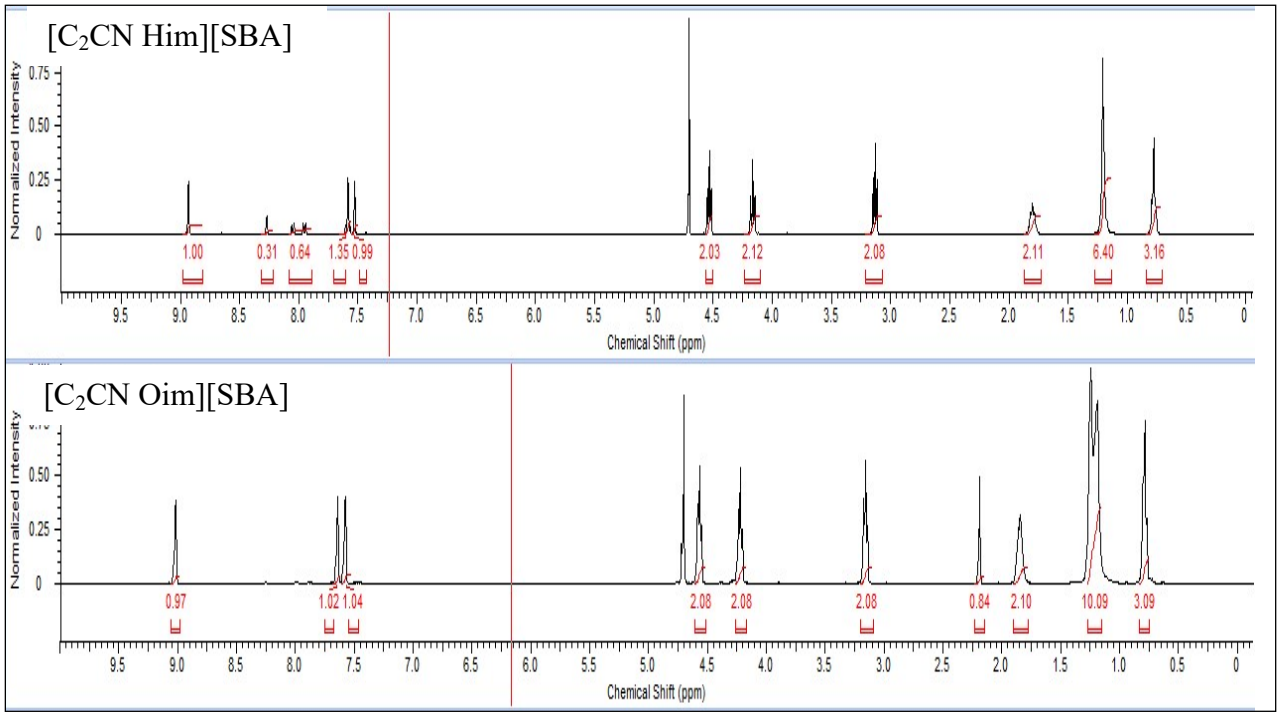
% theoretical C, 46.99; H, 6.31; N, 10.96; S, 8.36; mass fraction of water 197×10^{-6}, mass fraction of bromide 62×10^{-6}, 97.3.



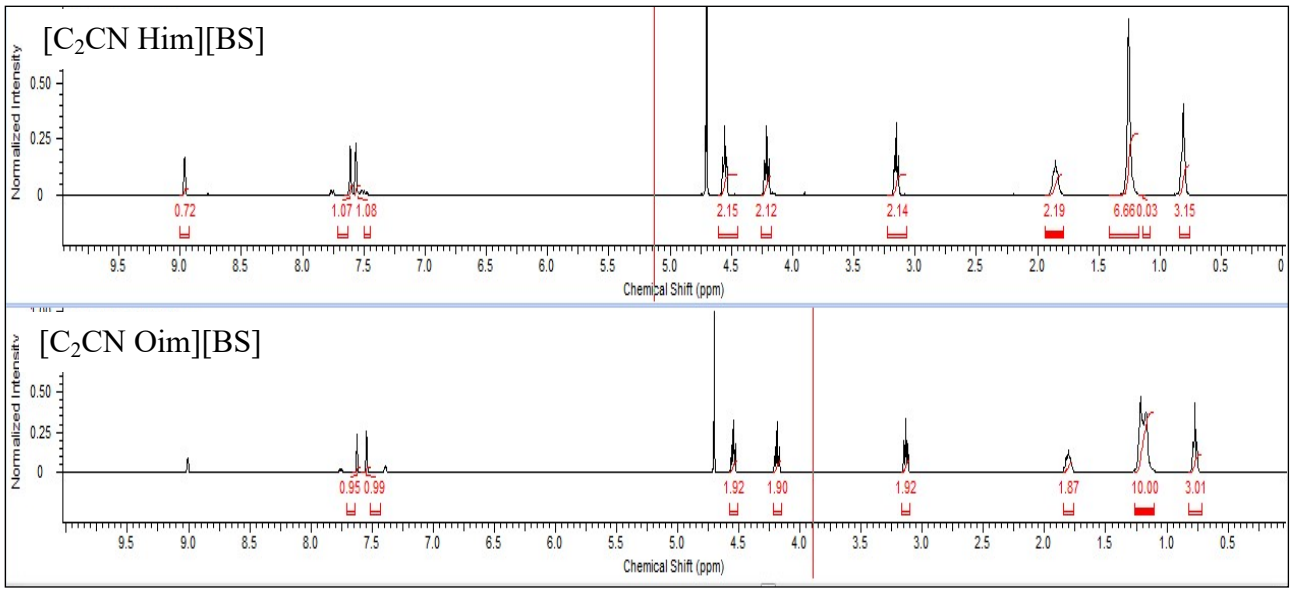
Fiqure SI. 1. ^{1}H NMR spectra for [C_2CN $C_n$im][DOSS] ILs



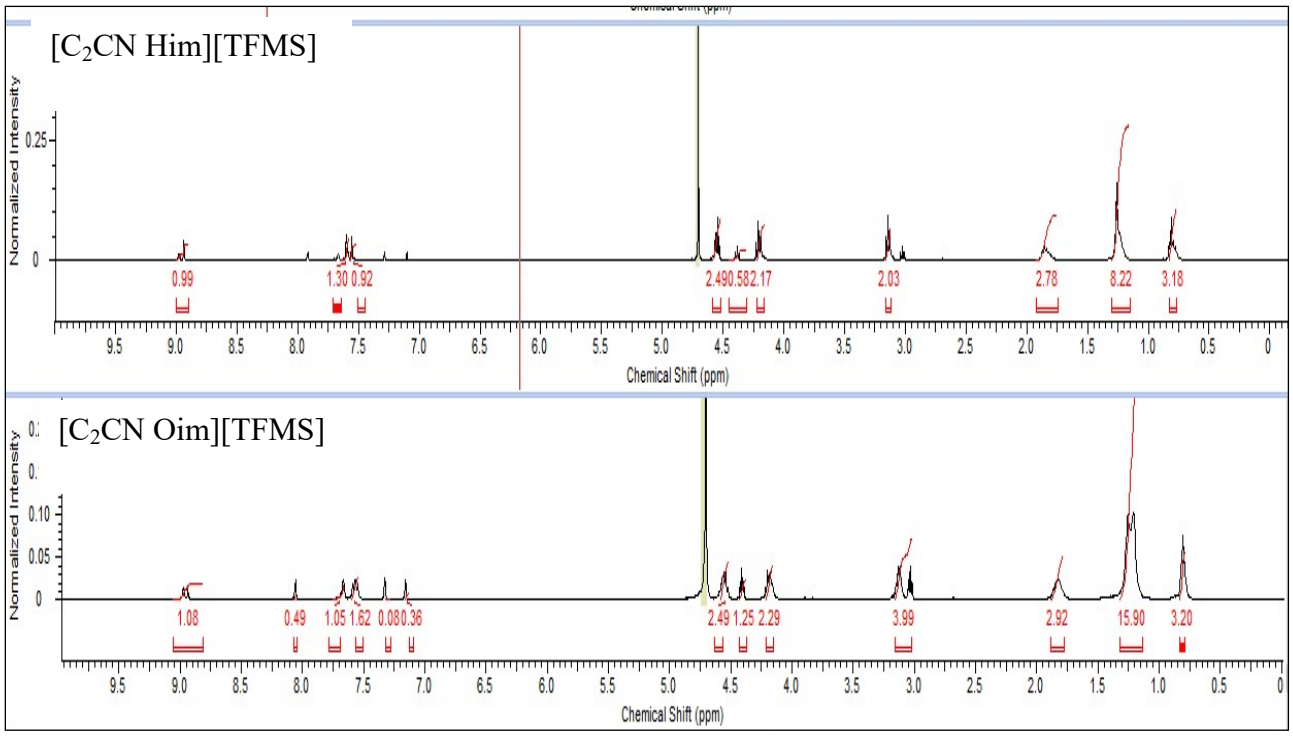
Fiqure SI. 2. ^{1}H NMR spectra for [C_2CN $C_n$im][DDS] ILs



Fiqure SI. 3. ^{1}H NMR spectra for [C_2CN $C_n$im][SBA] ILs

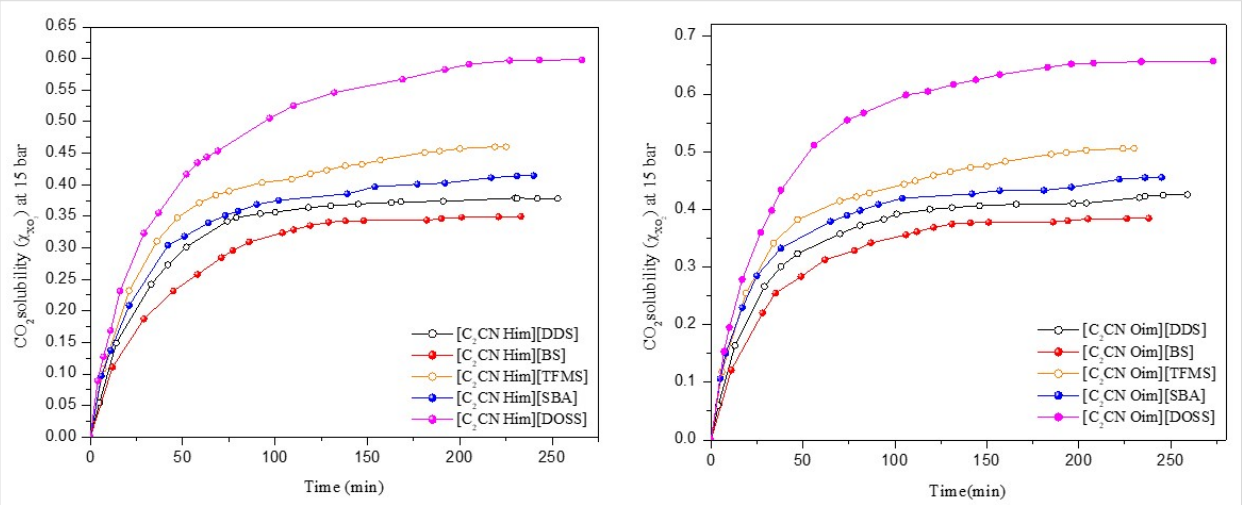


Fiqure SI. 4. ^{1}H NMR spectra for [C_2CN $C_n$im][BS] ILs

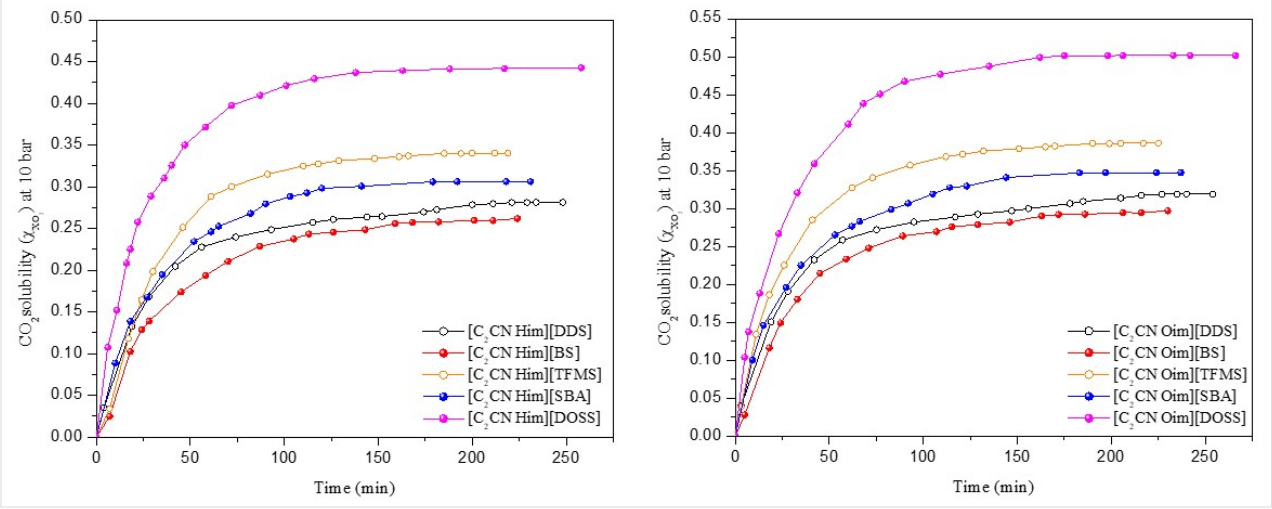


Fiqure SI. 5. NMR spectra for [C_2CN $C_n$im][TFMS] ILs

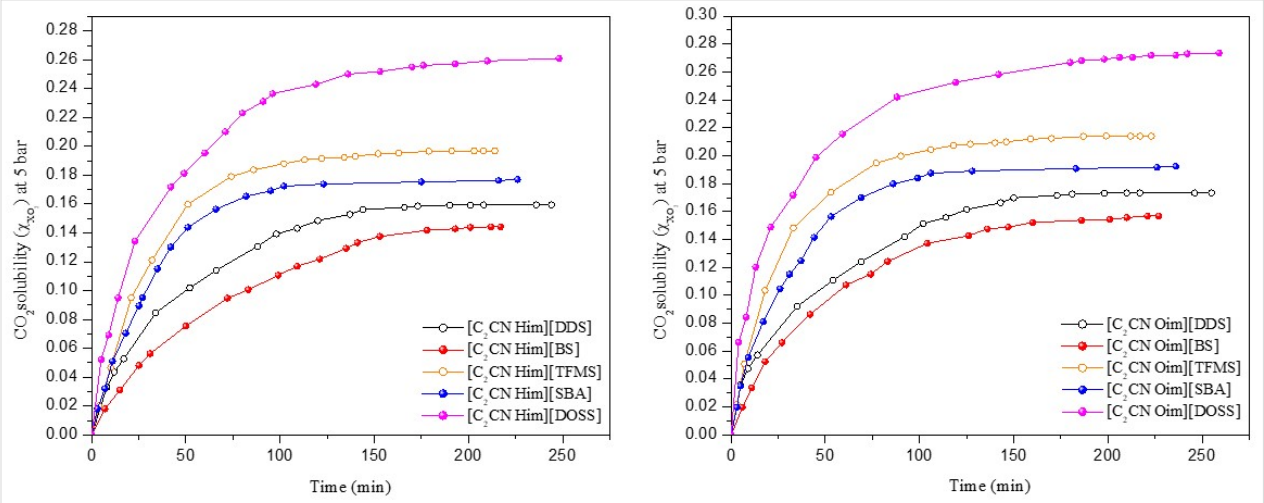
2. Influence of anions on the CO_2 solubility



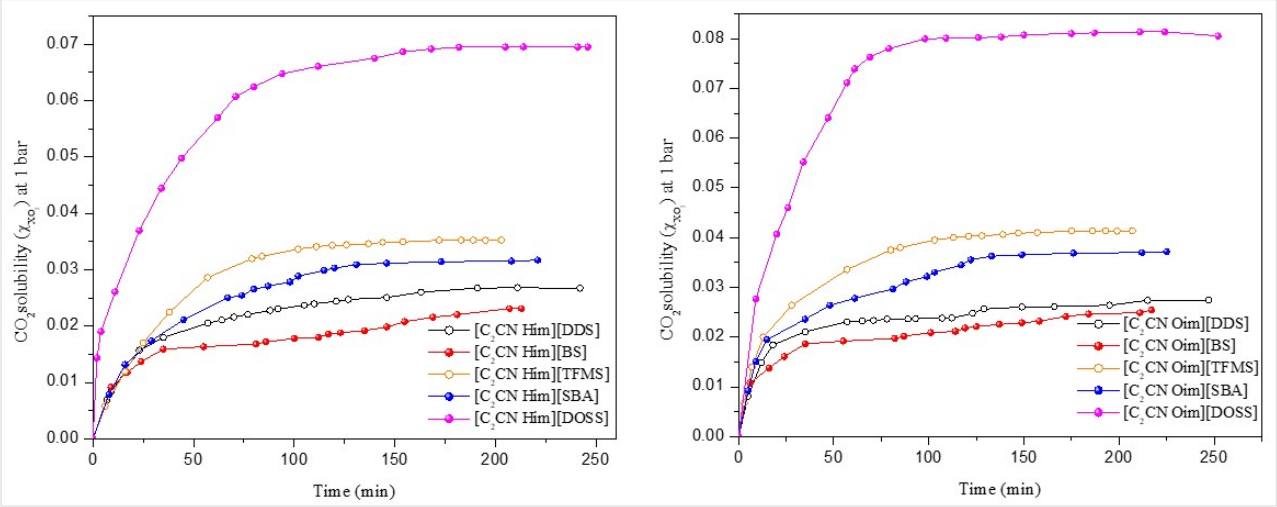
Fiqure SI. 6. CO_2 solubility in the [C_2CN Him] and [C_2CN Oim]-based ILs incorporated with [DDS], [BS], [TFMS], [SBA] and [DOSS] anions at 298.15 K at 15 bar.



Fiqure SI. 7. CO_2 solubility in the [C_2CN Him] and [C_2CN Oim]-based ILs incorporated with [DDS], [BS], [TFMS], [SBA] and [DOSS] anions at 298.15 K at 10 bar.



Fiqure SI. 8. CO_2 solubility in the [C_2CN Him] and [C_2CN Oim]-based ILs incorporated with [DDS], [BS], [TFMS], [SBA] and [DOSS] anions at 298.15 K at 5 bar.



Fiqure SI. 9. CO_2 solubility in the [C_2CN Him] and [C_2CN Oim]-based ILs incorporated with [DDS], [BS], [TFMS], [SBA] and [DOSS] anions at 298.15 K at 1 bar.