Supplementary Information for

Effect of Alkyl and Aryl Substitutions on 1,2,4-triazolium-Based Ionic Liquids For Carbon Dioxide Separation and Capture

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1. Synthesis of ionic liquids

4-ethyl-1-methyl-1H-1,2,4-triazol-4-ium bis((trifluoromethyl)sulfonyl)amide (**1a**)
To a round bottom flask containing 1 eq of 1-methyl-1,2,4-triazole, cooled in an ice bath, was added 1.2 eq of 1-bromoethane. After the addition was complete, the ice bath was removed, the flask sealed, and the reaction stirred at room temperature for 72 hours. Diethylether (30 ml) was added to the reaction and the mixture stirred for 10 minutes and subsequently filtered. The resultant white solid, 4-ethyl-1-methyl-1H-1,2,4-triazol-4-ium bromide, was washed with ethyl acetate (3 x 50 ml) followed by ether (3 x 50 ml) and dried under vacuum for 1 hour. A 5.0g (0.026 mol) aliquot of 4-ethyl-1-methyl-1H-1,2,4-triazol-4-ium bromide was dissolved in 150 ml of deionized water and activated carbon added. The mixture was stirred overnight at 50°C. The reaction was cooled and filtered, followed by addition of Lithium bis(trifluoromethanesulfonimide) (1 eq). The mixture was stirred overnight after which the biphasic mixture was allowed to settle. The aqueous layer was decanted and the remaining layer was dissolved in dicholoromethane, washed with water (6 x 100 ml), the solvent removed in vacuo, and the resultant clear liquid dried under high vacuum for 4 days. Compound **1a** was isolated as a liquid which solidified after standing for several weeks at room temperature. Yield: 5.91g (57.7 %) ^{1}H NMR (Acetone-d_6 ,400MHz): δ = 9.96 (s, 1 H), 9.09 (s, 1 H), 4.54 (q, *J*=7.3 Hz, 2 H), 4.25 (s, 3 H), 1.63 ppm (t, *J*=7.3 Hz, 3 H) ^{13}C NMR (Acetone-d_6 ,101MHz): δ = 145.2, 143.5, 125.8, 122.6, 119.4, 116.2, 44.7, 39.6, 15.2 ppm. ESI-MS: (+ve) 112.09 *m/z* $[C_5H_{10}N_3]^+$; ESI-MS: (-ve) 279.92 *m/z* $[C_2F_6NO_4S_2]^-$.

4-isopropyl-1-methyl-1H-1,2,4-triazol-4-ium bis((trifluoromethyl)sulfonyl)amide (**1b**)
Compound **1b** was synthesized using 2-bromopropane following the same procedure as for **1a**. Yield: 17.03g (56.3%)
^{1}H NMR (Acetone-d_6 ,400MHz): δ = 9.98 (s, 1 H), 9.16 (s, 1 H), 4.98 (dt, *J*=13.5, 6.7 Hz, 1 H), 4.23 (s, 3 H), 1.69 ppm (d, *J*=6.8 Hz, 6 H) ^{13}C NMR (Acetone-d_6 ,101MHz): δ = 144.0, 142.6, 125.8, 122.6, 119.4, 116.2, 53.8, 39.6, 22.6 ppm. ESI-MS: (+ve) 126.11 *m/z* $[C_6H_{12}N_3]^+$; ESI-MS: (-ve) 279.92 *m/z* $[C_2F_6NO_4S_2]^-$.

1-methyl-4-propyl-1H-1,2,4-triazol-4-ium bis((trifluoromethyl)sulfonyl)amide (**1c**)
Compound **1c** was synthesized using 1-bromopropane following the same procedure as for **1a**. Yield: 19.37g (63.8%)
^{1}H NMR (Acetone-d_6 ,400MHz): δ = 9.97 (s, 1 H), 9.10 (s, 1 H), 4.48 (t, *J*=7.3 Hz, 2 H), 4.26 (s, 3 H), 1.99 - 2.10 (m, 2 H), 1.01 ppm (t, *J*=7.4 Hz, 3 H) ^{13}C NMR (Acetone-d_6 ,101MHz): δ =

145.5, 143.7, 125.8, 122.6, 119.5, 116.2, 50.7, 39.7, 23.9, 10.8 ppm. ESI-MS: (+ve) 126.11 *m/z* $[C_6H_{12}N_3]^+$; ESI-MS: (-ve) 279.92 *m/z* $[C_2F_6NO_4S_2]^-$.

1-methyl-4-butyl-1H-1,2,4-triazol-4-ium bis((trifluoromethyl)sulfonyl)amide (**1d**)
Compound **1d** was synthesized using 1-bromobutane following the same procedure as for **1a**. Yield: 12.03g (63.2%)
1H NMR (Acetone-d_6 ,400MHz): δ = 9.97 (s, 1 H), 9.10 (s, 1 H), 4.51 (t, J=7.4 Hz, 2 H), 4.25 (s, 3 H), 2.00 (s, 2 H), 1.43 (dq, J=15.1, 7.5 Hz, 2 H), 0.95 ppm (t, J=7.3 Hz, 3 H) ^{13}C NMR (Acetone-d_6 ,101MHz): δ = 145.4, 143.7, 125.8, 122.6, 119.4, 116.3, 49.0, 39.7, 32.4, 20.0, 13.7 ppm. ESI-MS: (+ve) 140.12 *m/z* $[C_7H_{14}N_3]^+$; ESI-MS: (-ve) 279.92 *m/z* $[C_2F_6NO_4S_2]^-$.

1-methyl-4-hexyl-1H-1,2,4-triazol-4-ium bis((trifluoromethyl)sulfonyl)amide (**1e**)
Compound **1e** was synthesized using 1-bromohexane following the same procedure as for 1a. Yield: 22.61g (81.9%)
^{1}H NMR (Acetone-d_6 ,400MHz): δ = 9.97 (s, 1 H), 9.10 (s, 1 H), 4.50 (t, *J*=7.4 Hz, 2 H), 4.25 (s, 3 H), 1.96 - 2.07 (m, 2 H), 1.36 - 1.47 (m, 2 H), 1.25 - 1.36 (m, 4 H), 0.82 - 0.92 ppm (m, 3 H) ^{13}C NMR (Acetone-d_6 ,101MHz): δ = 145.4, 143.7, 125.8, 122.6, 119.4, 116.1, 49.2, 39.7, 31.8, 30.5, 26.4, 23.0, 14.2 ppm. ESI-MS: (+ve) 168.16 *m/z* $[C_9H_{18}N_3]^+$; ESI-MS: (-ve) 279.93 *m/z* $[C_2F_6NO_4S_2]^-$.

1-methyl-4-octyl-1H-1,2,4-triazol-4-ium bis((trifluoromethyl)sulfonyl)amide (**1f**)
Compound **1f** was synthesized using 1-bromooctane following the same procedure as for **1a**. Yield: 17.39 (77.6%)
^{1}H NMR (Acetone-d_6 ,400MHz): δ = 9.99 (s, 1 H), 9.12 (s, 1 H), 4.52 (t, *J*=7.4 Hz, 2 H), 4.27 (s, 3 H), 1.99 - 2.08 (m, 2 H), 1.22 - 1.48 (m, 10 H), 0.88 ppm (t, *J*=6.6 Hz, 3 H) ^{13}C NMR (Acetone-d_6 ,101MHz): δ = 145.4, 143.7, 125.7, 122.6, 119.4, 116.2, 49.2, 39.7, 32.5, 30.5, 29.8, 29.6, 29.4, 26.8, 23.3, 14.4 ppm. ESI-MS: (+ve) 196.19 *m/z* $[C_{11}H_{22}N_3]^+$; ESI-MS: (-ve) 279.93 *m/z* $[C_2F_6NO_4S_2]^-$.

4-butyl-1-methyl-1H-1,2,4-triazol-4-ium hexafluorophosphate (**1g**)
4-butyl-1-methyl-1H-1,2,4-triazol-4-ium bromide was prepared following the procedure for **1a**. A 3.0g (0.014 mol) aliquot was dissolved in 50ml of dry acetonitrile. A 2.58g (0.014 mol) aliquot of KPF_6 was added and the mixture stirred overnight. The reaction was filtered and the solvent removed in vacuo yielding a white solid. Yield: 2.91g (75.1%) ^{1}H NMR (Acetone-d_6 ,400MHz): δ = 9.87 (s, 1 H), 9.06 (s, 1 H), 4.48 (t, *J*=7.4 Hz, 2 H), 4.23 (s, 3 H), 1.92 - 2.03 (m, 2 H), 1.43 (dq, *J*=15.1, 7.4 Hz, 2 H), 0.95 ppm (t, *J*=7.3 Hz, 3 H) ^{31}P NMR (Acetone-d_6 ,162MHz): δ = -143.3 ppm. ESI-MS: (+ve) 140.12 *m/z* $[C_7H_{14}N_3]^+$; ESI-MS: (-ve) 144.96 *m/z* $[PF_6]^-$.

4-benzyl-1-methyl-1H-1,2,4-triazol-4-ium bis((trifluoromethyl)sulfonyl)amide (**2a**)
Compound **2a** was synthesized using benzylbromide following the same procedure as for **1a**. Yield: 12.4g (69.2%)
^{1}H NMR (Acetone-d_6,400MHz): δ = 9.97 (s, 1 H), 9.15 (s, 1 H), 7.53 - 7.59 (m, 2 H), 7.43 - 7.51 (m, 3 H), 5.72 (s, 2 H), 4.25 ppm (s, 3 H)

^{13}C NMR (Acetone-d_6,101MHz): δ = 145.3, 143.7, 133.9, 130.4, 130.2, 129.9, 125.8, 122.6, 119.4, 116.2, 52.4, 39.8 ppm. ESI-MS: (+ve) 174.11 *m/z* $[C_{10}H_{12}N_3]^+$; ESI-MS: (-ve) 279.92 *m/z* $[C_2F_6NO_4S_2]^-$.

1-methyl-4-(4-(trifluoromethoxy)benzyl)-1H-1,2,4-triazol-4-ium bis((trifluoromethyl)sulfonyl)amide (**2b**)
Compound **2b** was synthesized using 4-(trifluoromethoxy)benzyl bromide following the same procedure as for **1a**. Yield: 5.7g (71.8%)
^{1}H NMR (Acetone-d_6 ,400MHz): δ = 10.06 (s, 1 H), 9.20 (s, 1 H), 7.73 (d, *J*=8.7 Hz, 2 H), 7.43 (d, *J*=8.2 Hz, 2 H), 5.81 (s, 2 H), 4.26 ppm (s, 3 H) ^{13}C NMR (Acetone-d_6 ,101MHz): δ = 150.8, 145.7, 144.2, 133.5, 132.4, 126.1, 125.5, 123.0, 122.9, 120.4, 119.7, 117.8, 116.5, 51.8, 40.1 ppm. ESI-MS: (+ve) 258.10 *m/z* $[C_{11}H_{11}N_3F_3O]^+$; ESI-MS: (-ve) 279.93 *m/z* $[C_2F_6NO_4S_2]^-$.

1-methyl-4-(2-(trifluoromethoxy)benzyl)-1H-1,2,4-triazol-4-ium bis((trifluoromethyl)sulfonyl)amide (**2c**)
Compound **2c** was synthesized using 2-(trifluoromethoxy)benzyl bromide following the same procedure as for **1a**. Yield: 6.0g (75.5%)
^{1}H NMR (Acetone-d_6 ,400MHz): δ = 10.05 (s, 1 H), 9.20 (s, 1 H), 7.61 - 7.73 (m, 2 H), 7.46 - 7.53 (m, 2 H), 5.86 (s, 2 H), 4.26 ppm (s, 3 H)
^{13}C NMR (Acetone-d_6 ,101MHz): δ = 148.3, 145.6, 144.0, 132.8, 132.6, 128.9, 126.1, 125.8, 125.2, 122.6, 121.4, 120.1, 119.5, 117.5, 116.3, 47.4, 39.9 ppm. ESI-MS: (+ve) 258.10 *m/z* $[C_{11}H_{11}N_3F_3O]^+$; ESI-MS: (-ve) 279.93 *m/z* $[C_2F_6NO_4S_2]^-$.

4-(3,5-dimethylbenzyl)-1-methyl-1H-1,2,4-triazol-4-ium bis((trifluoromethyl)sulfonyl)amide (**2d**)
Compound **2d** was synthesized using 3,5-dimethylbenzyl bromide following the same procedure as for **1a**. Yield: 10.8g (62.9%)
^{1}H NMR (Acetone-d_6 ,400MHz): δ = 9.95 (s, 1 H), 9.13 (s, 1 H), 7.17 (s, 2 H), 7.10 (s, 1 H), 5.61 (s, 2 H), 4.24 (s, 3 H), 2.29 ppm (s, 6 H)
^{13}C NMR (Acetone-d_6 ,101MHz): δ = 145.3, 143.6, 139.9, 133.7, 131.8, 127.7, 125.8, 122.6, 119.4, 116.1, 52.4, 39.8, 21.2 ppm. ESI-MS: (+ve) 202.15 *m/z* $[C_{12}H_{16}N_3]^+$; ESI-MS: (-ve) 279.93 *m/z* $[C_2F_6NO_4S_2]^-$.

1-methyl-4-(2,3,5,6-tetrafluoro-4-(trifluoromethoxy)benzyl)-1H-1,2,4-triazol-4-ium bis((trifluoromethyl)sulfonyl)amide (**2e**)
Compound **2e** was synthesized using 4-methoxytetrafluorobenzyl bromide following the same procedure as for **1a**. Yield: 2.46g (31.5%)
^{1}H NMR (Acetone-d_6 ,400MHz): δ = 10.14 (s, 1 H), 9.24 (s, 1 H), 5.93 (s, 2 H), 4.27 (s, 3 H), 4.14 ppm (s, 3 H) ^{13}C NMR (Acetone-d_6 ,101MHz): δ = 148.2, 145.7, 145.5, 144.1, 143.2, 141.1, 140.6, 125.8, 122.6, 119.4, 116.2, 105.8, 105.6, 105.4, 62.9, 40.1, 39.9 ppm. ESI-MS: (+ve) 276.09 *m/z* $[C_{11}H_{10}N_3F_4O]^+$; ESI-MS: (-ve) 279.93 *m/z* $[C_2F_6NO_4S_2]^-$.

2. TGA Curves for compounds under ambient atmosphere.

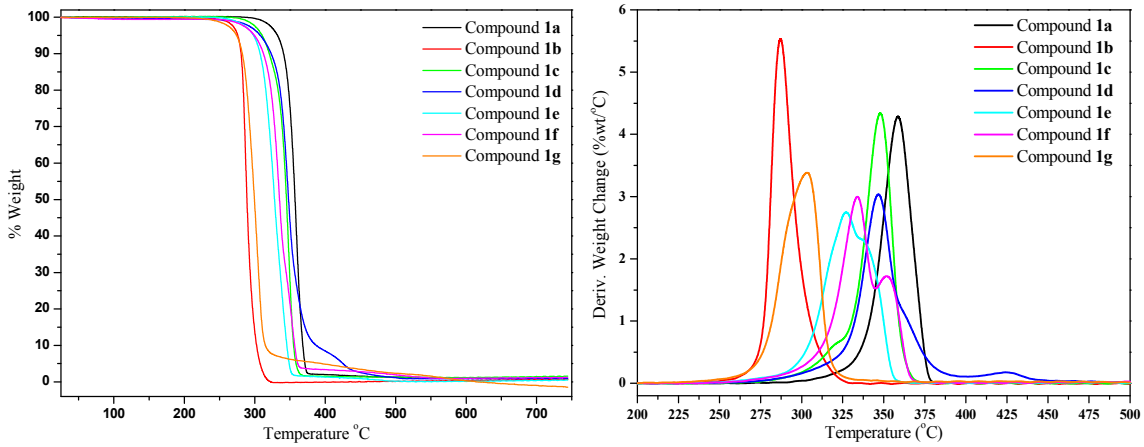

Figure S1. TGA (left) and DTG (right) traces for alkyl bearing triazolium ILs (**1a-1f**) under ambient atmosphere.

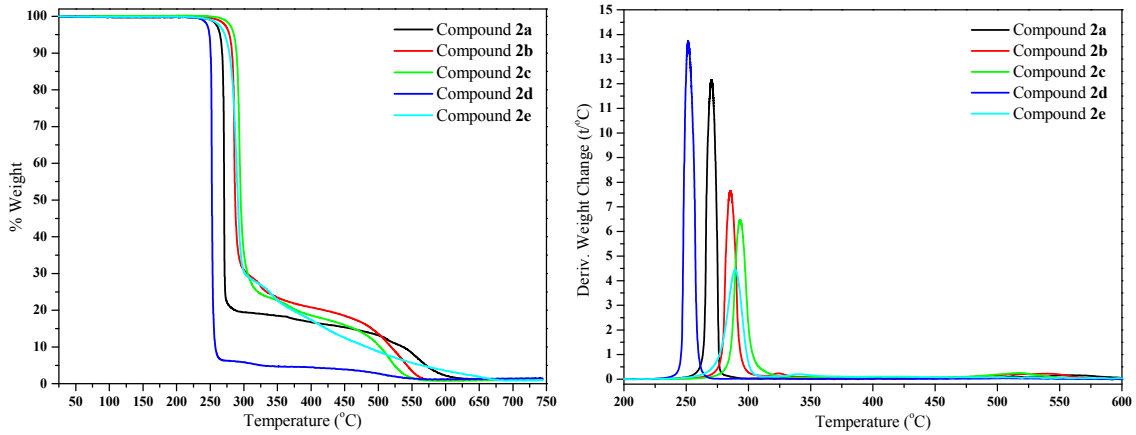

Figure S2. TGA (left) and DTG (right) traces for benzyl bearing triazolium ILs (**2a-2e**) under ambient atmosphere.

3. DSC Traces for triazolium-based ionic liquids

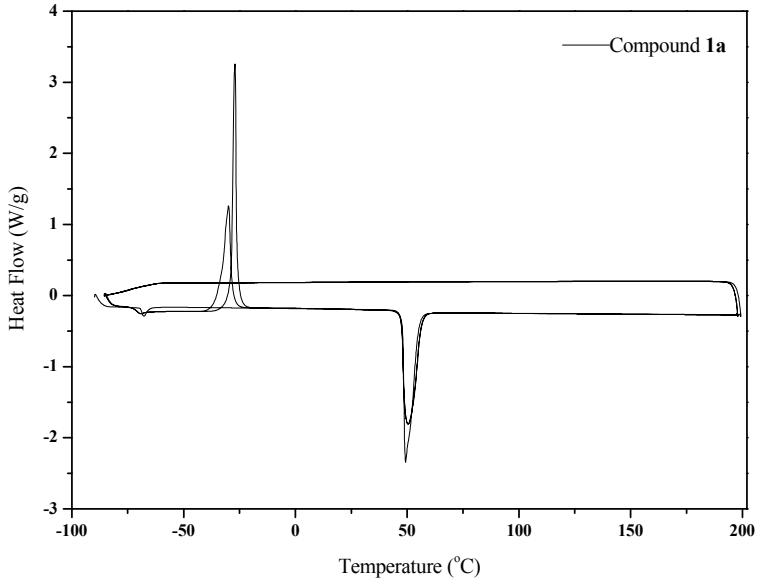

Figure S3. DSC trace of compound **1a**

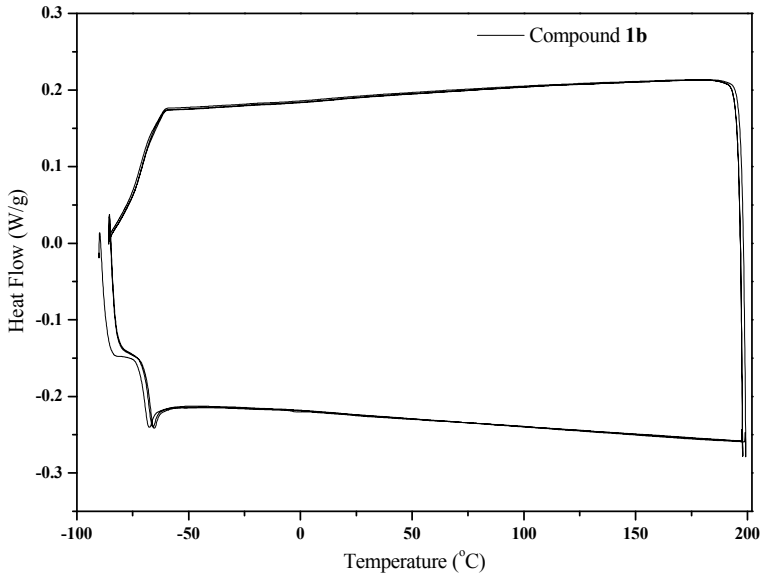

Figure S4. DSC trace of compound **1b**

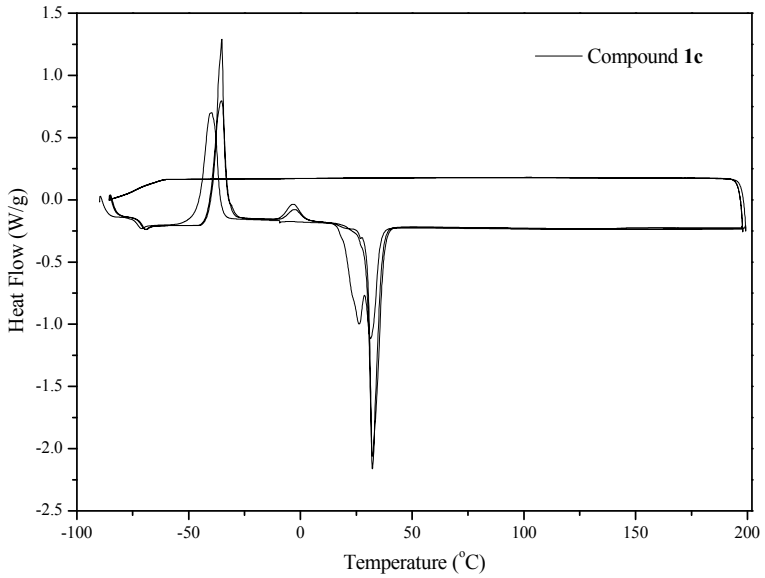

Figure S5. DSC trace of compound **1c**

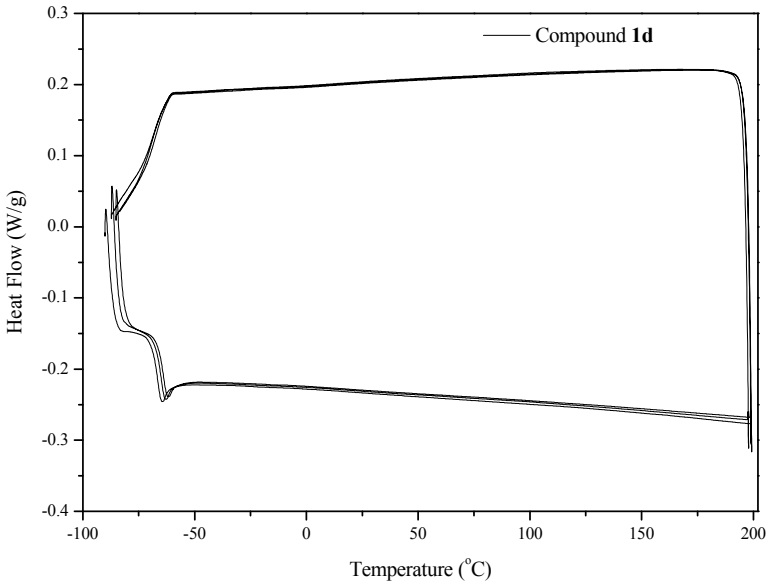

Figure S6. DSC trace of compound **1d**

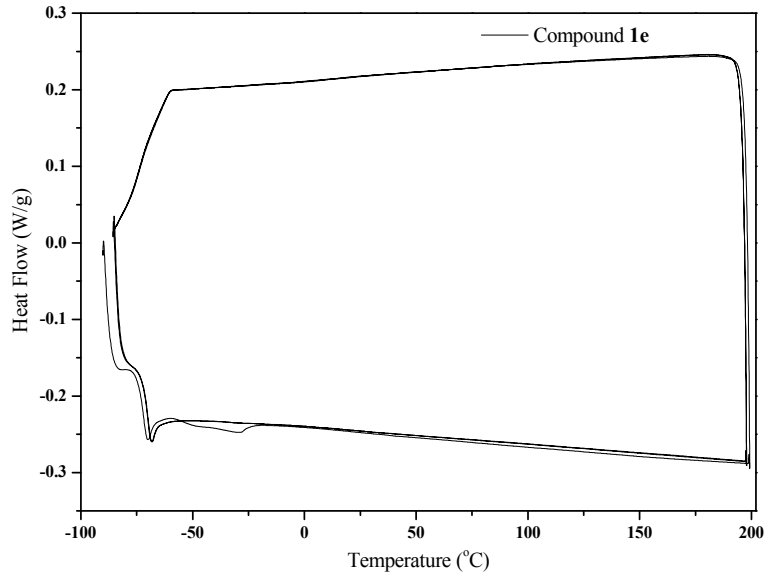

Figure S7. DSC trace of compound **1e**

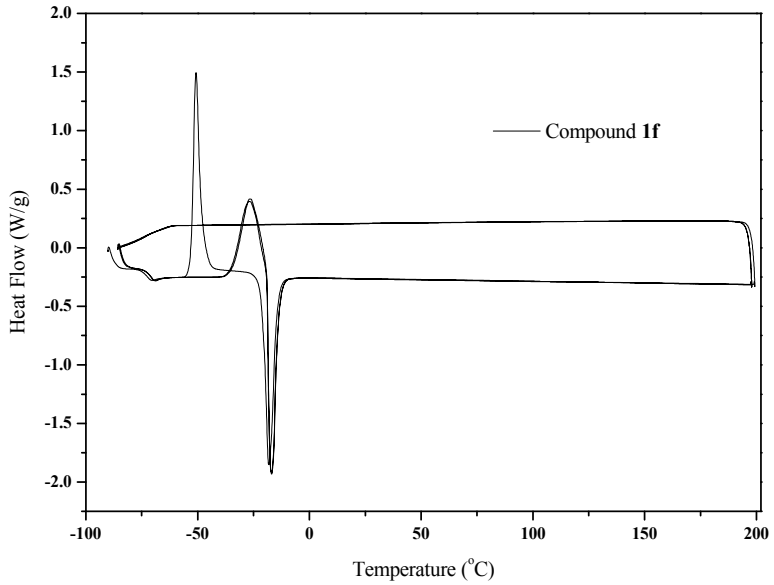

Figure S8. DSC trace of compound **1f**

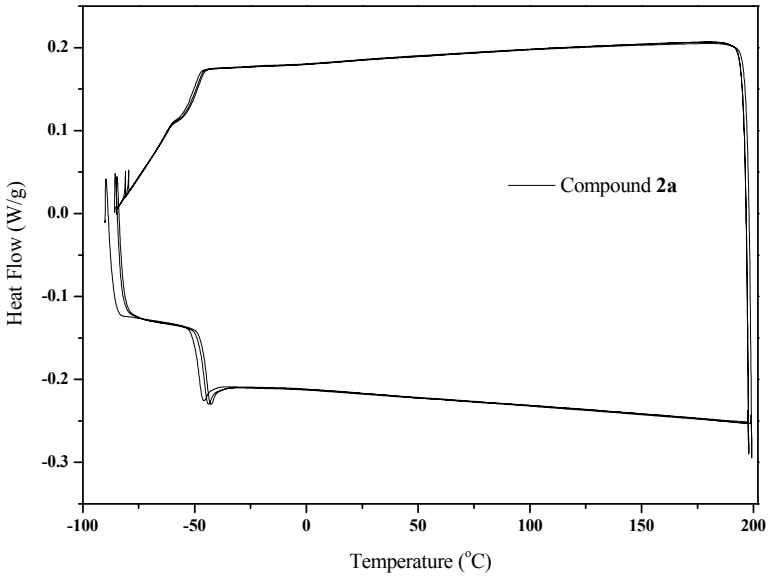

Figure S9. DSC trace of compound **2a**

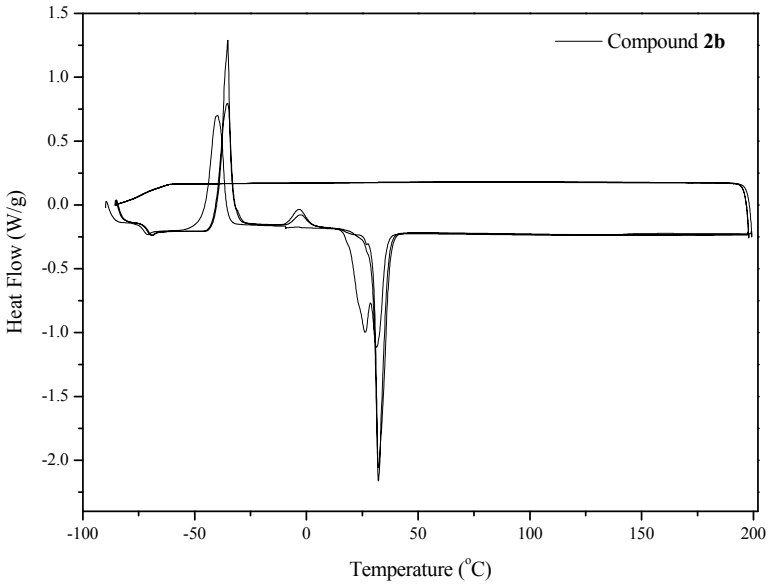

Figure S10. DSC trace of compound **2b**

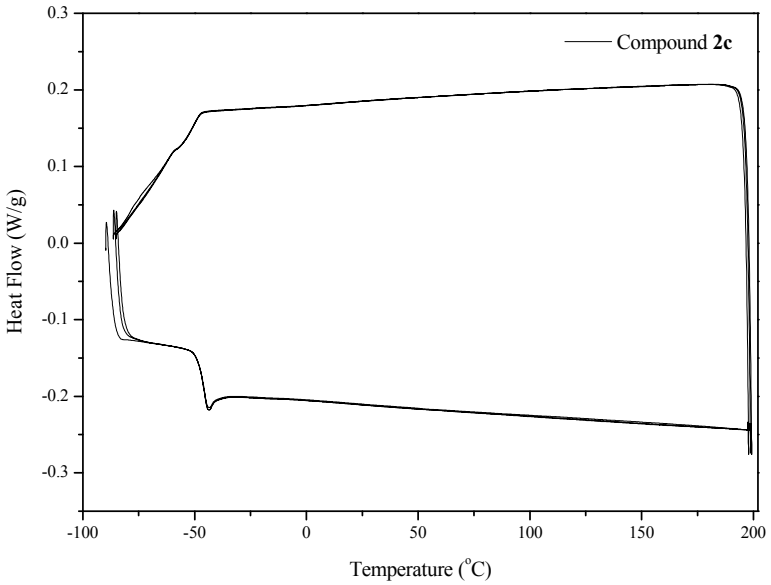

Figure S11. DSC trace of compound **2c**

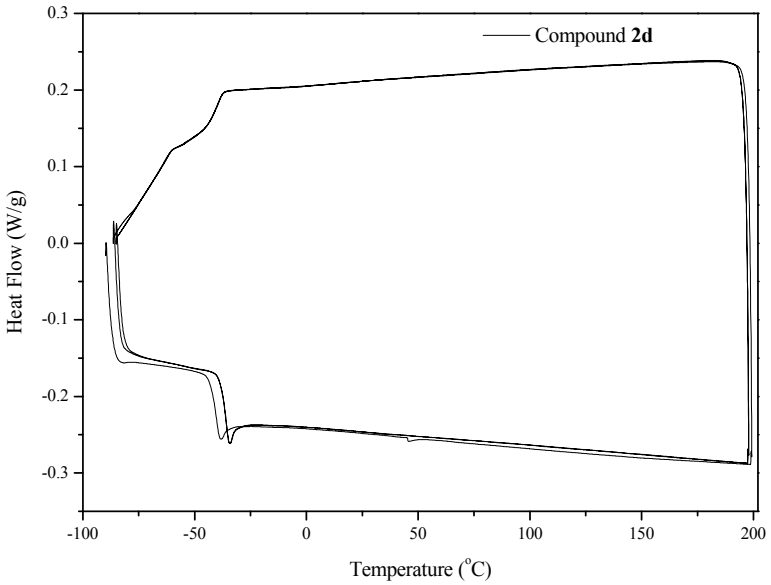

Figure S12. DSC trace of compound **2d**

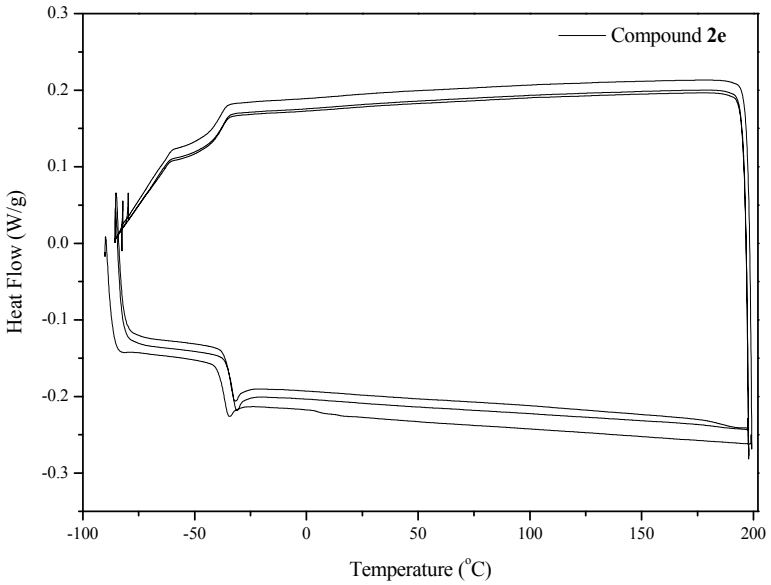

Figure S13. DSC trace of compound **2e**