Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information for:

1,2-Bis[N-(N'-alkylimidazolium)]ethane Salts: a New Class of Organic Ionic Plastic Crystals

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Experimental

1-Heptylimidaozle.[S1] To a solution of imidazole (2.40, 30 mmol) in NaOH (50%) solution (2.86 g, 35 mmol), 1-bromoheptane (5.36 g, 30 mmol) and THF (15 mL) were added. The mixture was refluxed for 3 days. After the mixture had cooled to room temperature, THF was removed by a rotoevaporator. The residue was extracted with dichloromethane/water 3 times. The combined organic layer was washed with water and then dried over Na_2SO_4. The drying agent was filtered off and the filtrate solution was concentrated. Drying in a vacuum oven gave a yellow oily product, 4.71 g (94%). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ 0.88 (t, J=7, 3H), 1.28 (m, 8H), 1.76 (m, 2H), 3.91 (t, J=7, 2H), 6.90 (s, 1H), 7.04 (s, 1H), 7.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): 14.0, 22.5, 26.4, 28.7, 31.0, 31.6, 47.0, 118.7, 129.3, 137.0.

1-Octylimidazole.[S1] To a solution of imidazole (2.40, 30 mmol) in NaOH (50%) solution (2.86 g, 35 mmol), 1-bromooctane (5.79 g, 30 mmol) and THF (15 mL) were added. The mixture was refluxed for 3 days. After the mixture had cooled to room temperature, THF was removed by a rotoevaporator. The residue was extracted with dichloromethane/water 3 times. The combined organic layer was washed with water and then dried over Na_2SO_4. The drying agent was filtered off and the filtrate solution was concentrated. Drying in a vacuum oven gave a yellow oily product, 4.70 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ 0.88 (t, J=7, 3H), 1.28 (m, 10H), 1.76 (m, 2H), 3.91 (t, J=7, 2H), 6.90 (s, 1H), 7.04 (s, 1H), 7.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ 13.0, 21.6, 15.5, 28.0, 28.1, 30.1, 30.8, 46.0, 117.7, 128.3, 136.0.

1-Decylimidzole. [S1] To a solution of imidazole (2.40 g, 30 mmol) in NaOH (50%) solution (2.86 g, 35 mmol), 1-bromodecane (6.63 g, 30 mmol) and THF (15 mL) were added. The mixture was refluxed for 3 days. After the mixture had cooled to room temperature, THF was removed by a rotoevaporator. The residue was extracted with dichloromethane/water 3 times. The combined organic layer was washed with water and then dried over Na_2SO_4. The drying agent was filtered off and the filtrate solution was concentrated. Drying in a vacuum oven gave a yellow oily product, 6.31 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ 0.88 (t, *J*=7, 3H), 1.28 (m (br), 14H), 1.76 (m, 2H), 3.91 (t, *J*=7, 2H), 6.90 (s, 1H), 7.04 (s, 1H), 7.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ 14.0, 22.6, 26.4, 29.0, 29.3, 29.4, 31.0, 31.7, 46.9, 118.7, 129.2, 136.9.

NMR Spectra

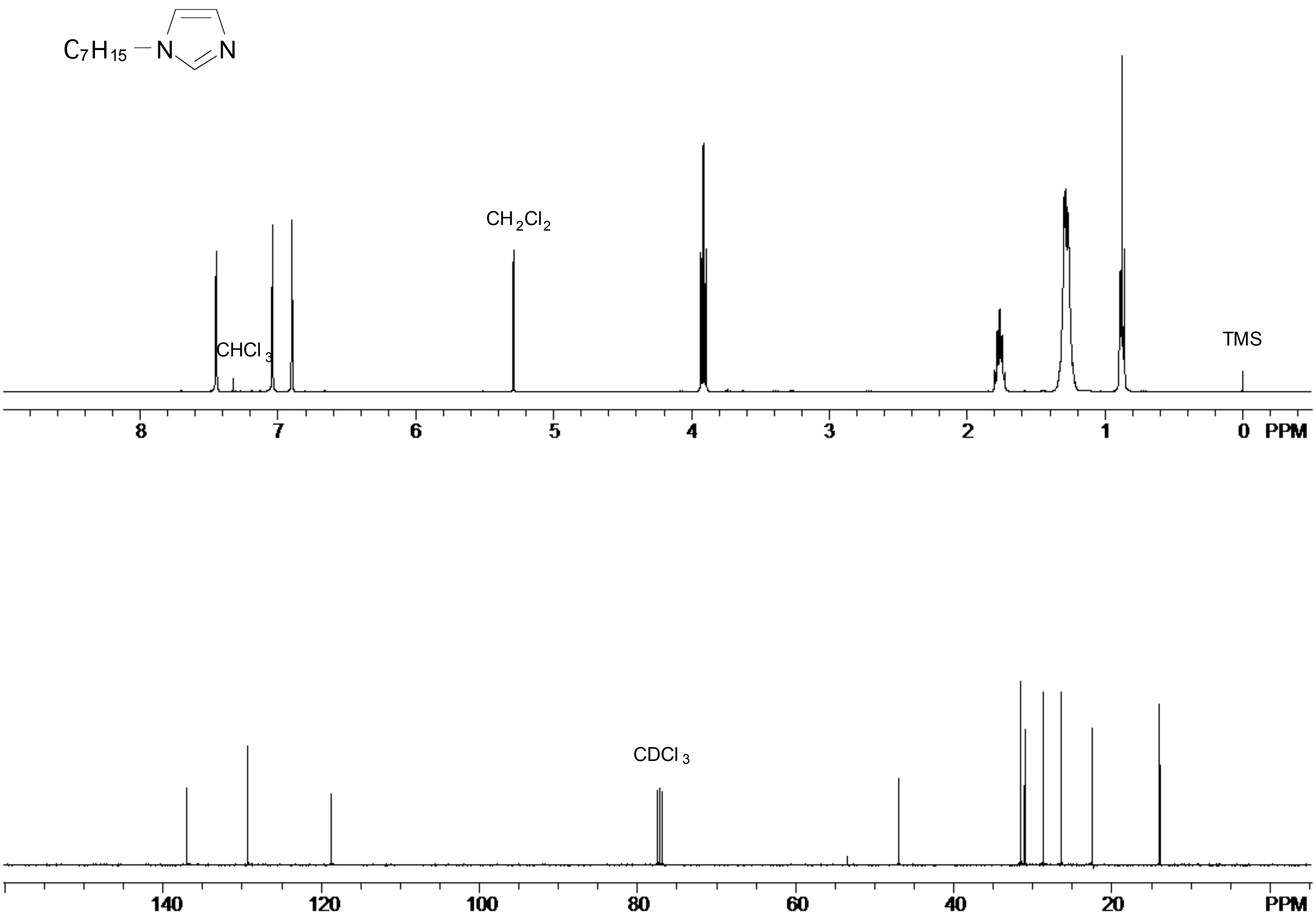
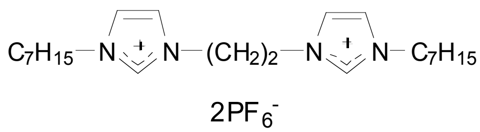


Figure S1. 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectrum of 1-heptylimidazole ($CDCl_3$, 22 °C).



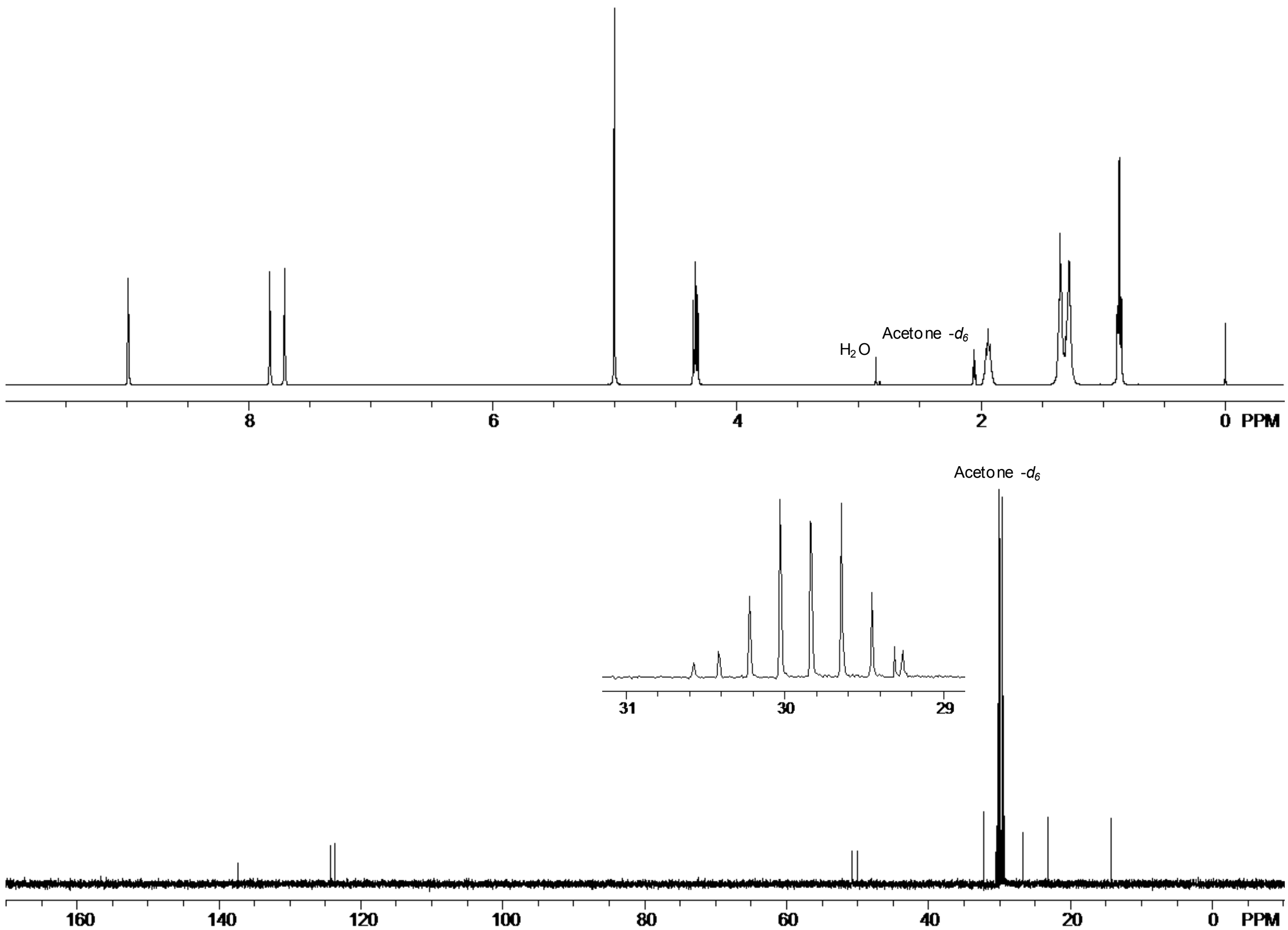


Figure S2. 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectrum of 1,2-bis[N-(N'-heptylimidazolium)]ethane $2PF_6^-$ (**$8PF_6$**) (CD_3CN, 23 °C).

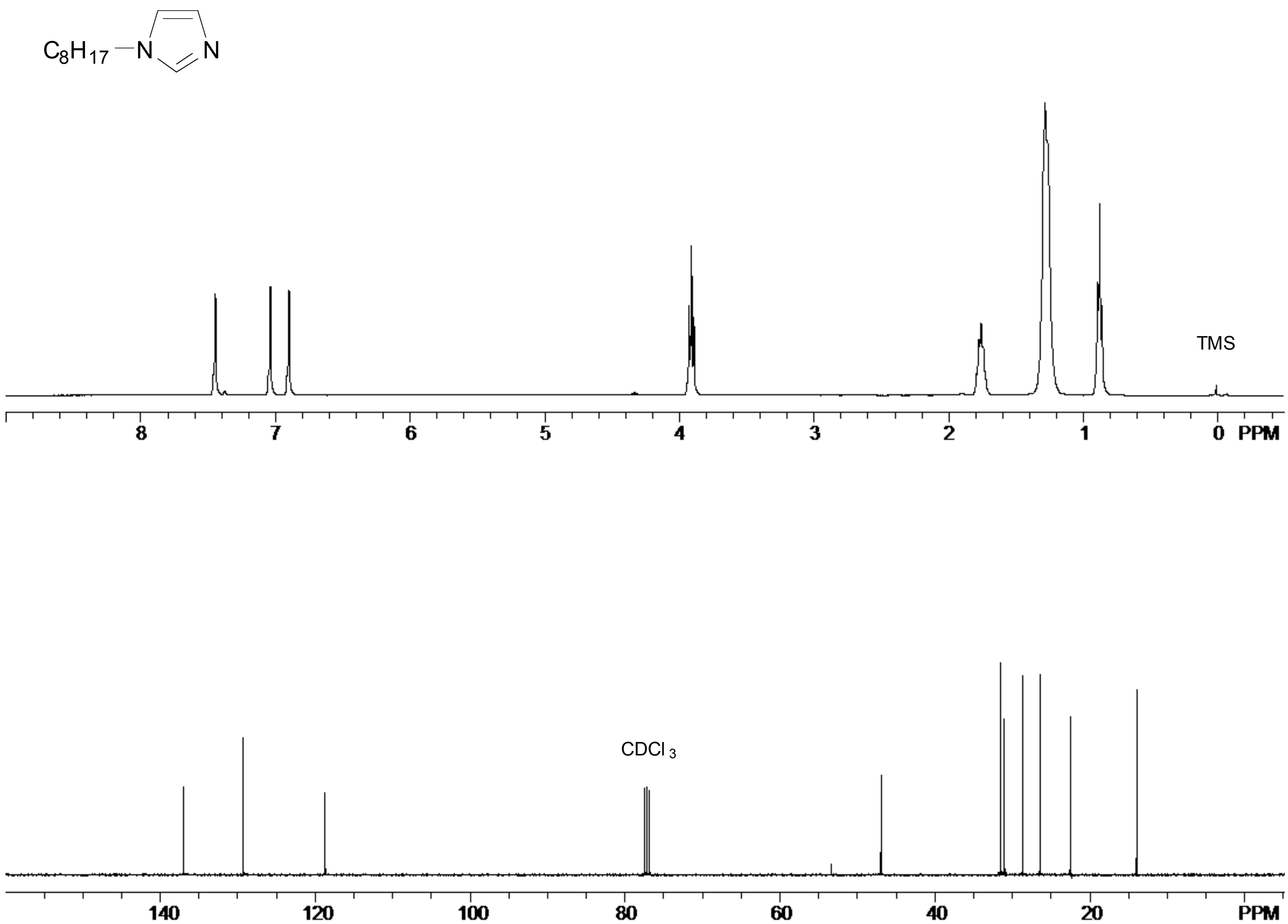


Figure S3. 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectrum of 1-octylimidazole ($CDCl_3$, 22 °C).

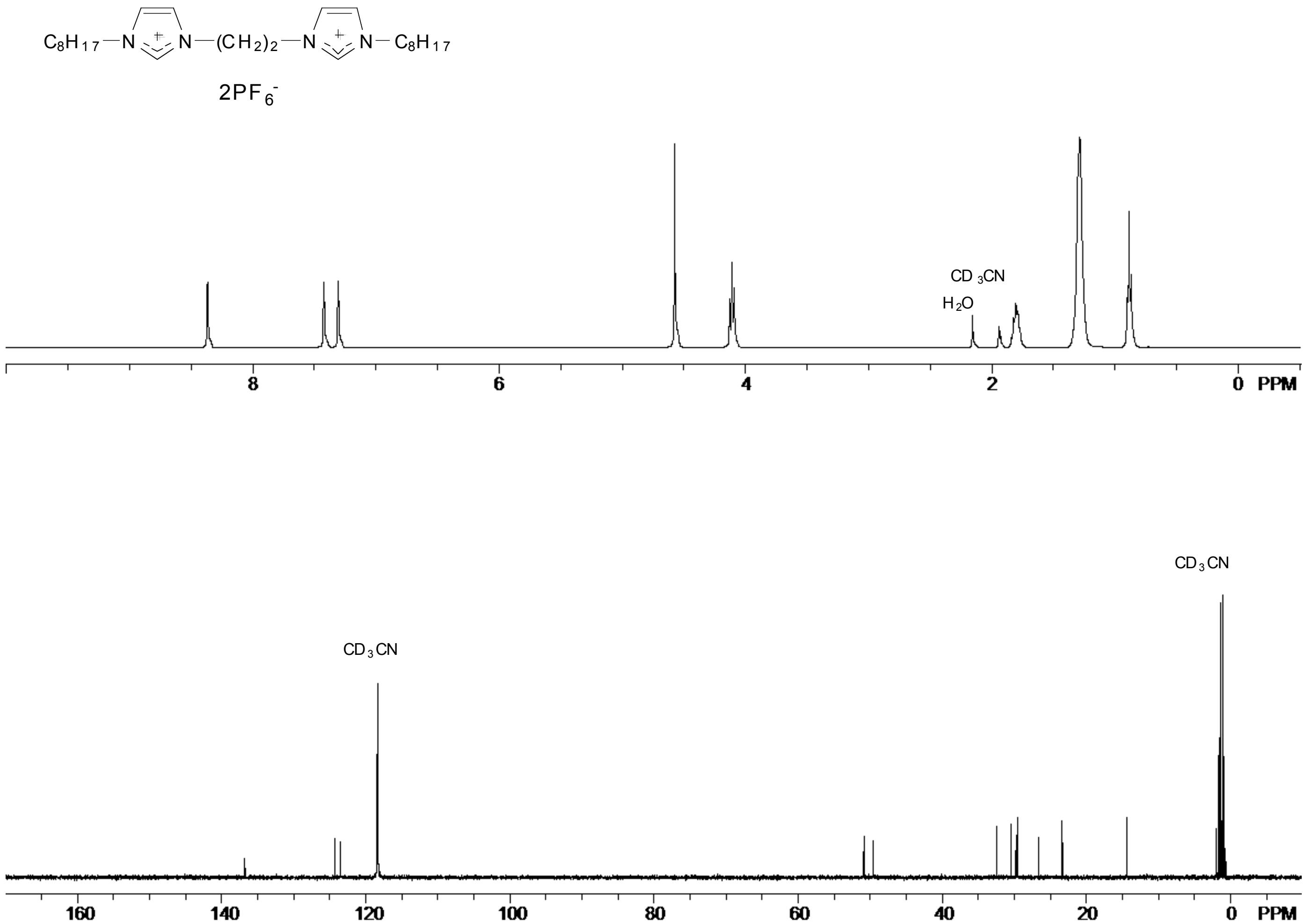


Figure S4. 400 MHz ^{1}H NMR spectrum of 1,2-bis[N-(N'-octylimidazolium)]ethane $2PF_6^-$ (**$9PF_6$**) (CD_3CN, 23 °C).

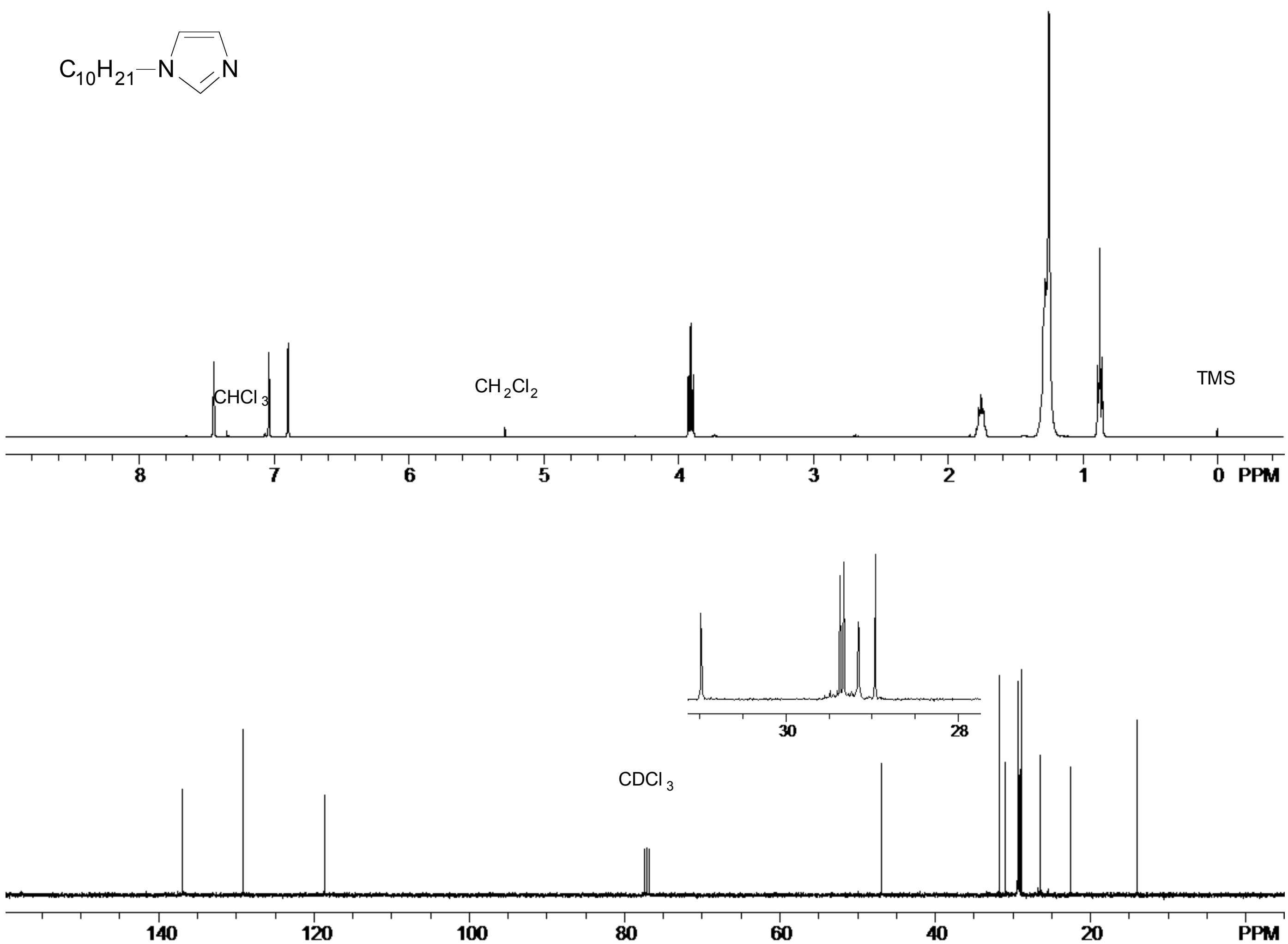


Figure S5. 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectrum of 1-decylimidazole ($CDCl_3$, 22 °C).

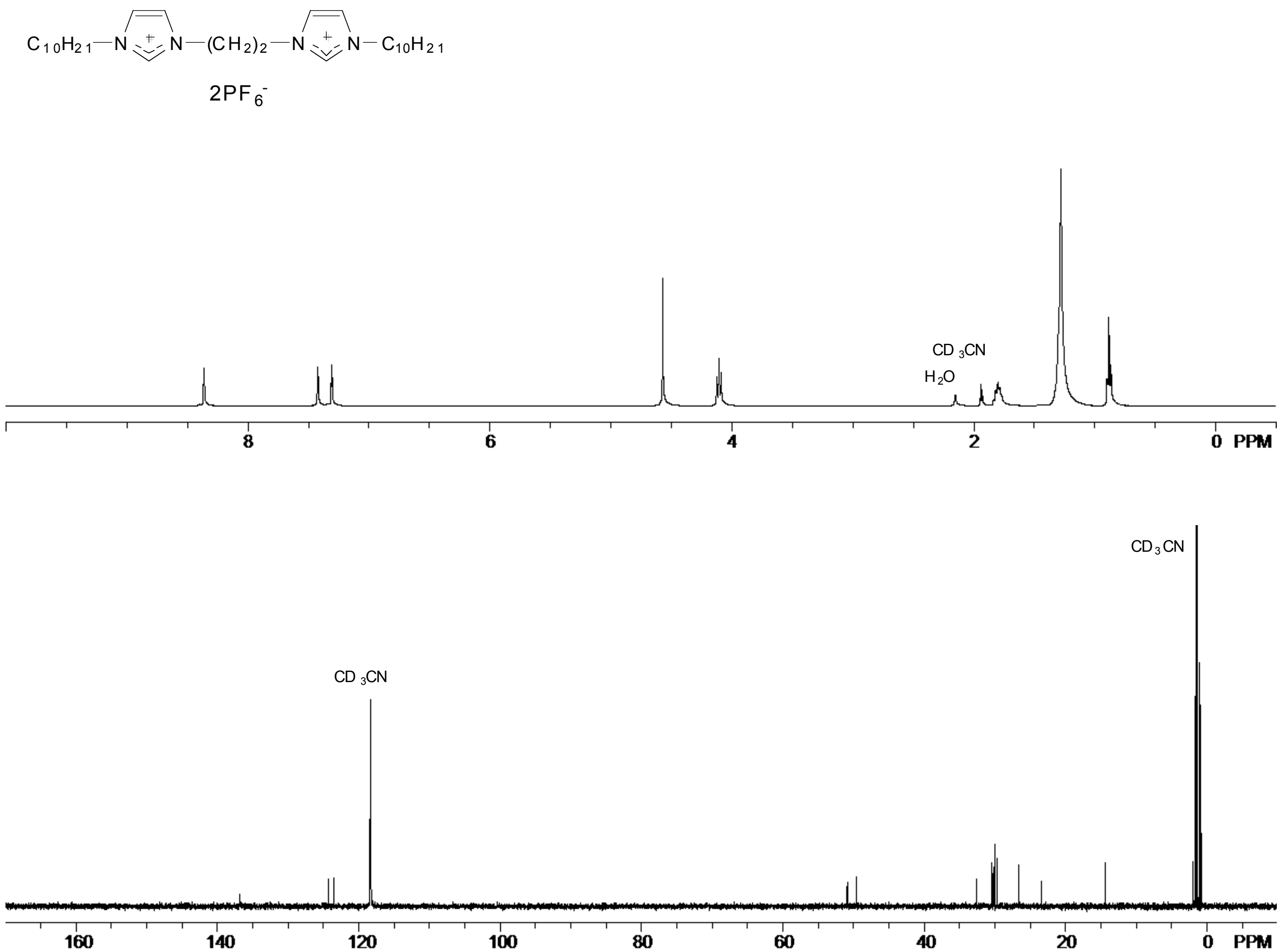


Figure S6. 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectrum of 1,2-bis[N-(N'-decylimidazolium)]ethane $2PF_6^-$ (**$10PF_6$**) (CD_3CN, 23 °C).

MS Spectra of the Dications

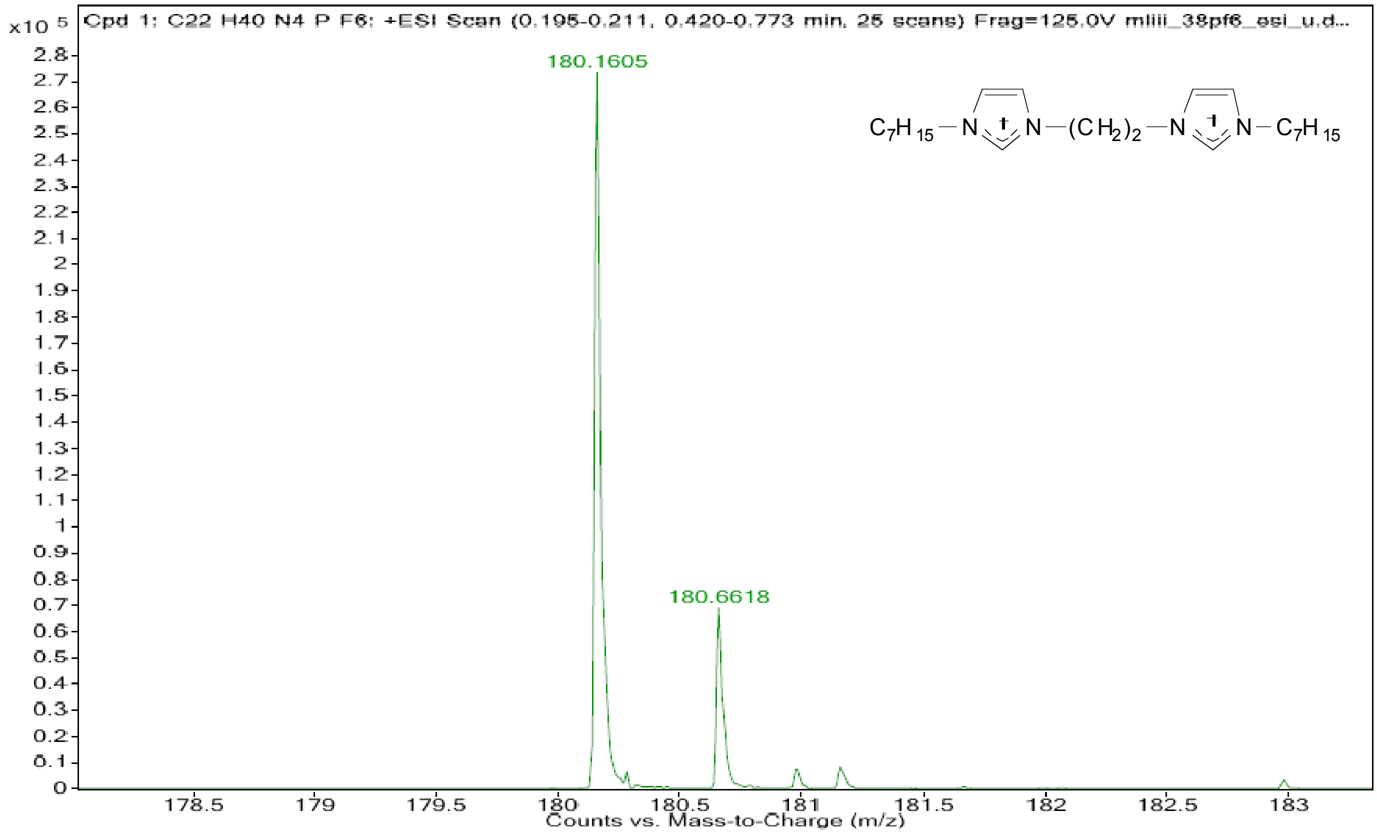


Figure S7. Partial HR ESI MS spectrum of **$8PF_6$**. $[M-2PF_6]^{2+}$ at m/z 180.1605 (calcd. m/z 180.1621) proves the formation of the imidazolium dication. The peak at m/z 180.6618 is the M+1 isotopic peak; 25% intensity relative to M, theory: 24%.

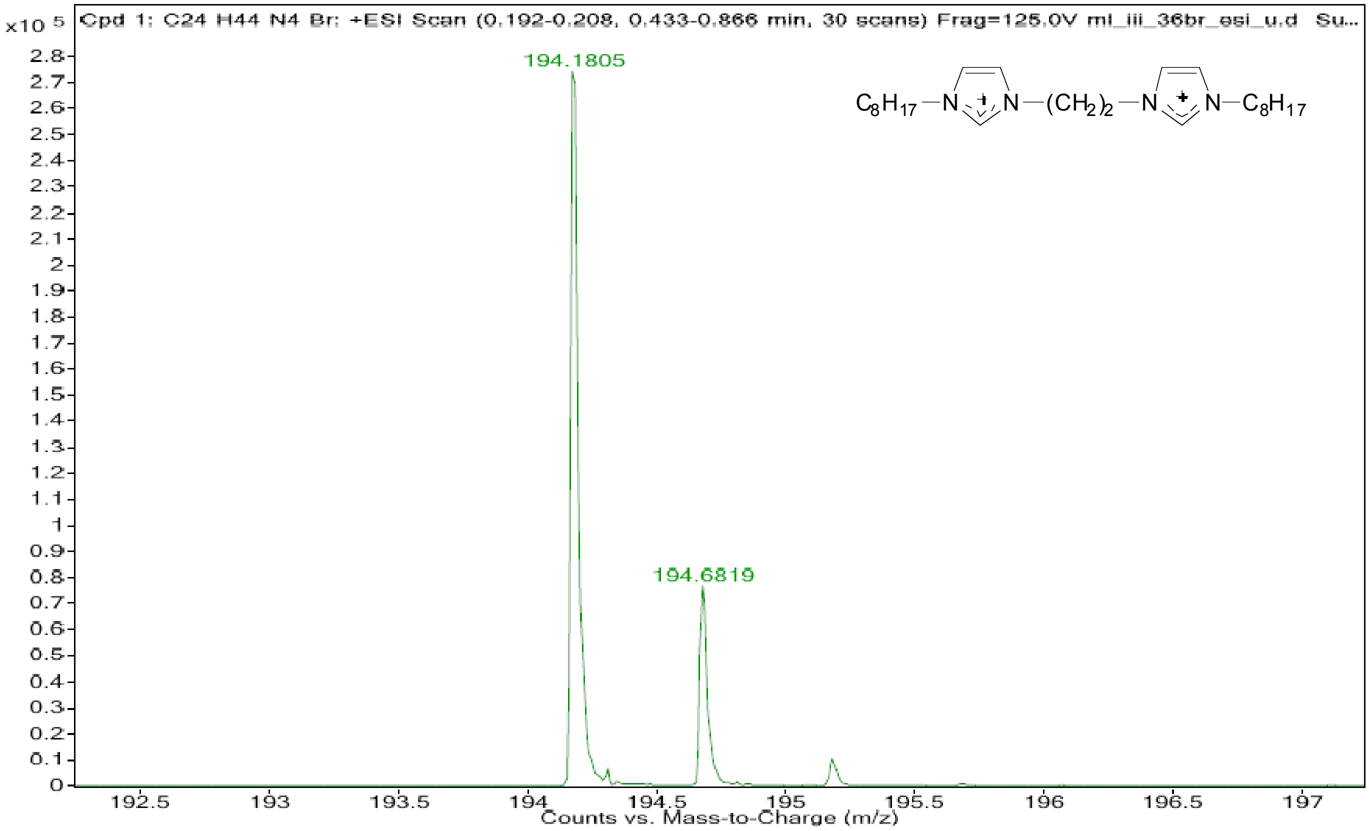


Figure S8. Partial HR ESI MS spectrum of **$9PF_6$**. $[M\text{-}2PF_6]^{2+}$ at m/z 194.1805 (calcd. m/z 194.1778) proves the formation of the imidazolium dication. The peak at m/z 194.6819 is the M+1 isotopic peak; 28% intensity relative to M, theory: 27%.

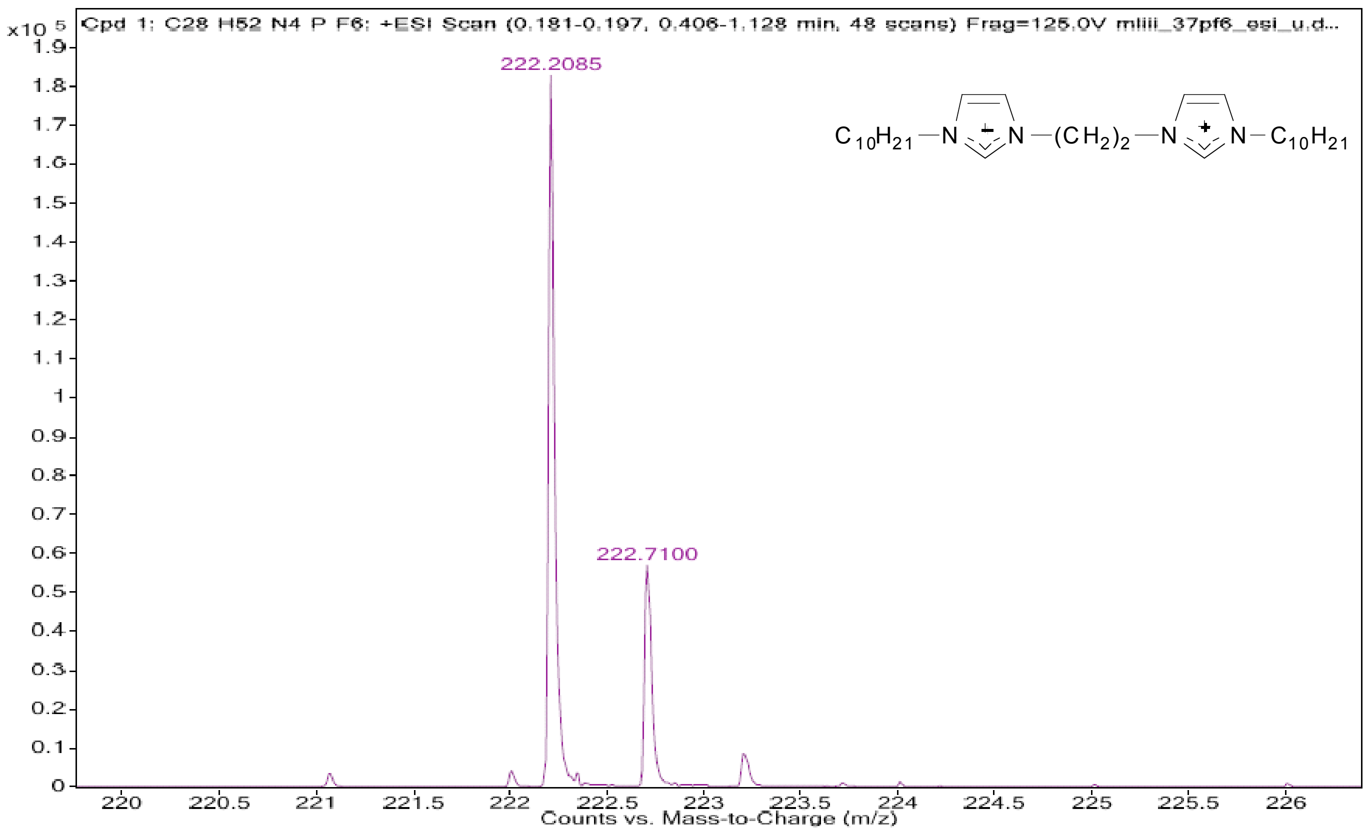


Figure S9. Partial HR ESI MS spectrum of **$10PF_6$**. $[M\text{-}2PF_6]^{2+}$ at m/z 222.2085 (calcd. m/z 222.2093) proves the formation of the imidazolium dication. The peak at m/z 222.7100 is the M+1 isotopic peak; 31% intensity relative to M, theory: 31%.

DSC Diagrams

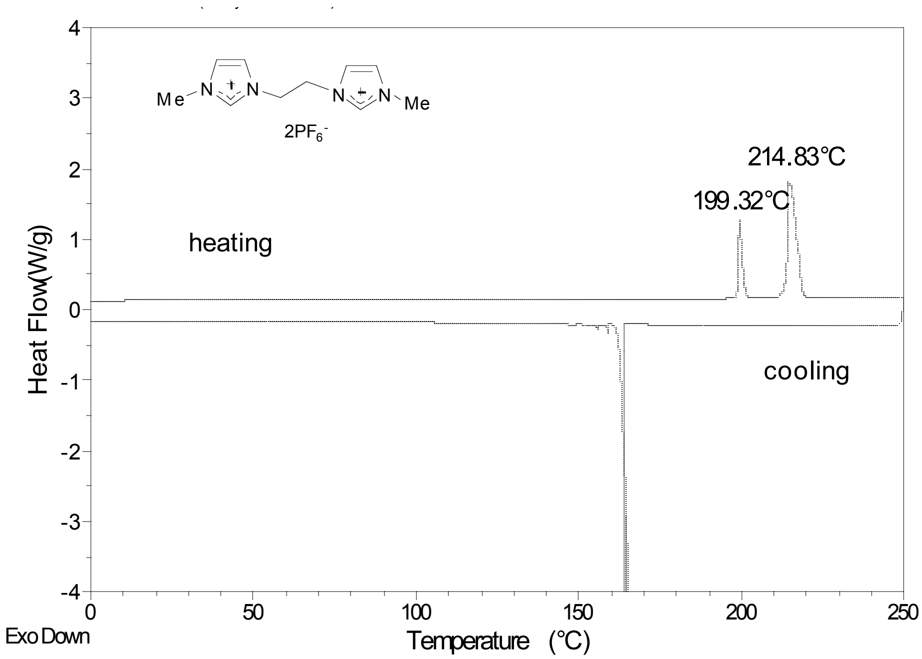


Figure 10. DSC diagram of **$1PF_6$** (heating and cooling rate 5 K/min, N_2). Only the second heating and cooling traces are shown in this figure.

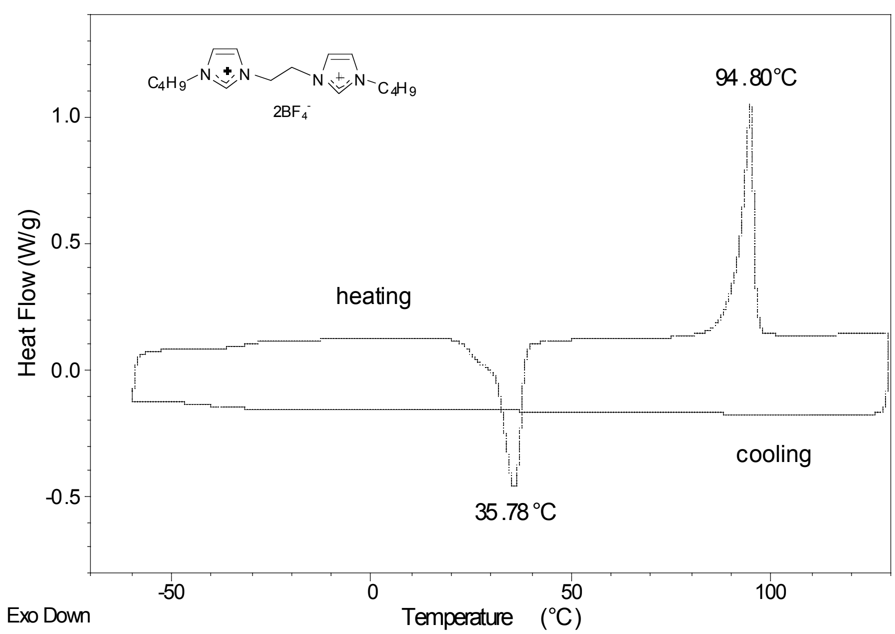


Figure 11. DSC diagram of **$3BF_4$** (heating and cooling rate 5 K/min, N_2). Only the second heating and cooling traces are shown in this figure.

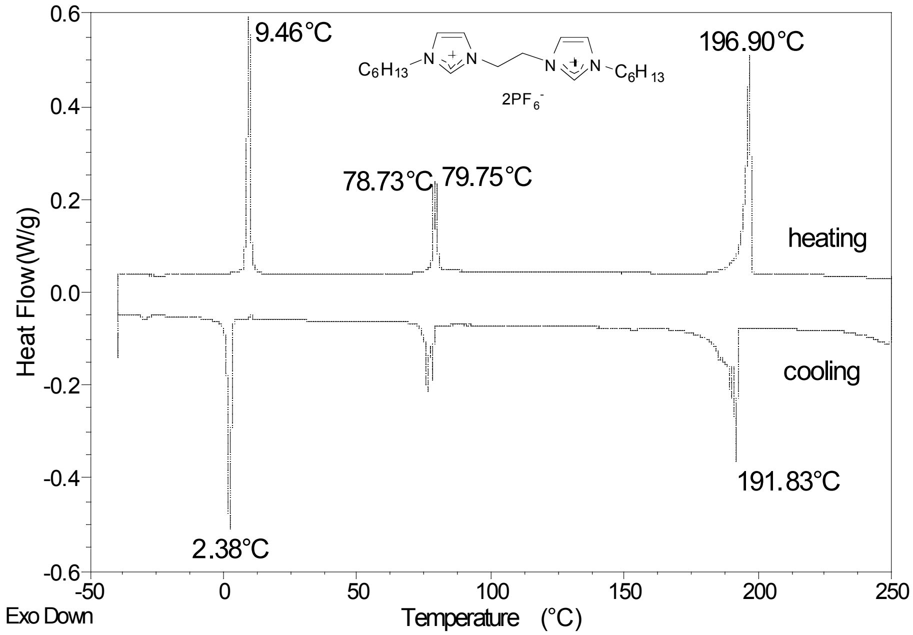


Figure 12. DSC diagram of **$6PF_6$** (heating and cooling rate 5 K/min, N_2). Only the second heating and cooling traces are shown in this figure.

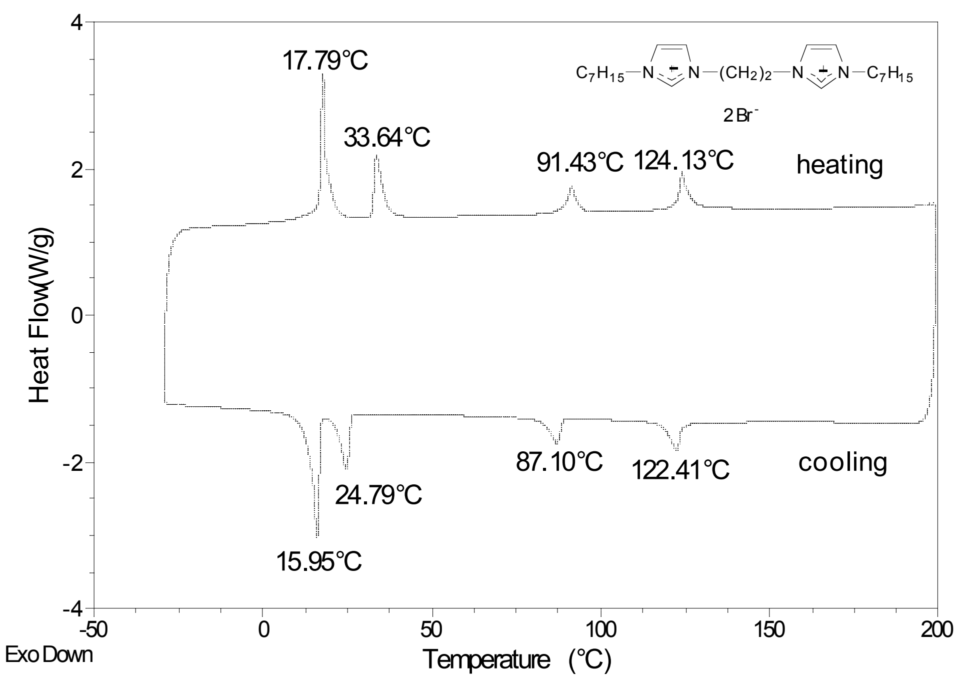


Figure 13. DSC diagram of **8Br** (heating and cooling rate 5 K/min, N_2). Only the second heating and cooling traces are shown in this figure.

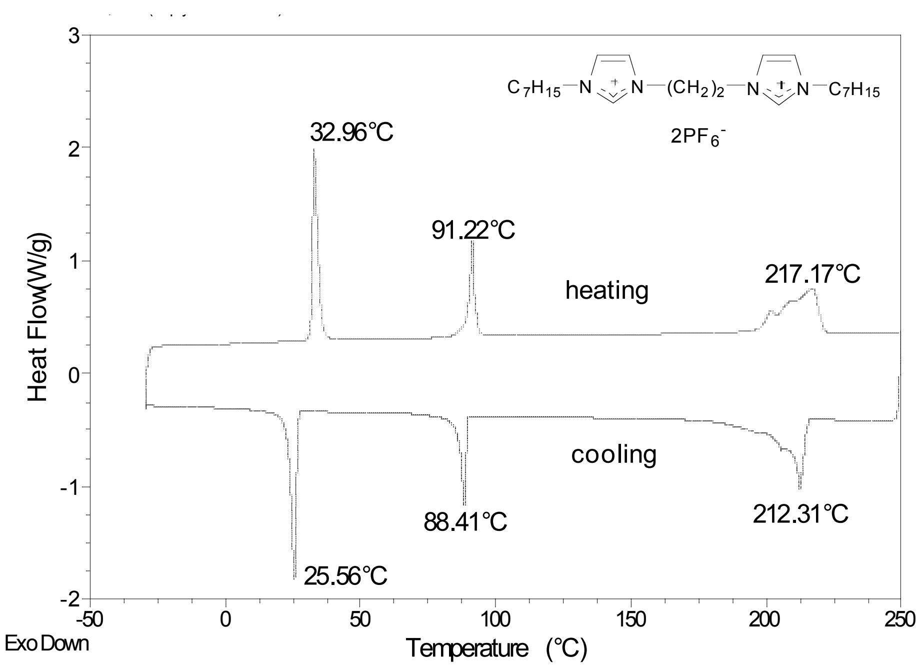


Figure 14. DSC diagram of **8PF$_6$** (heating and cooling rate 5 K/min, N_2). Only the second heating and cooling traces are shown in this figure.

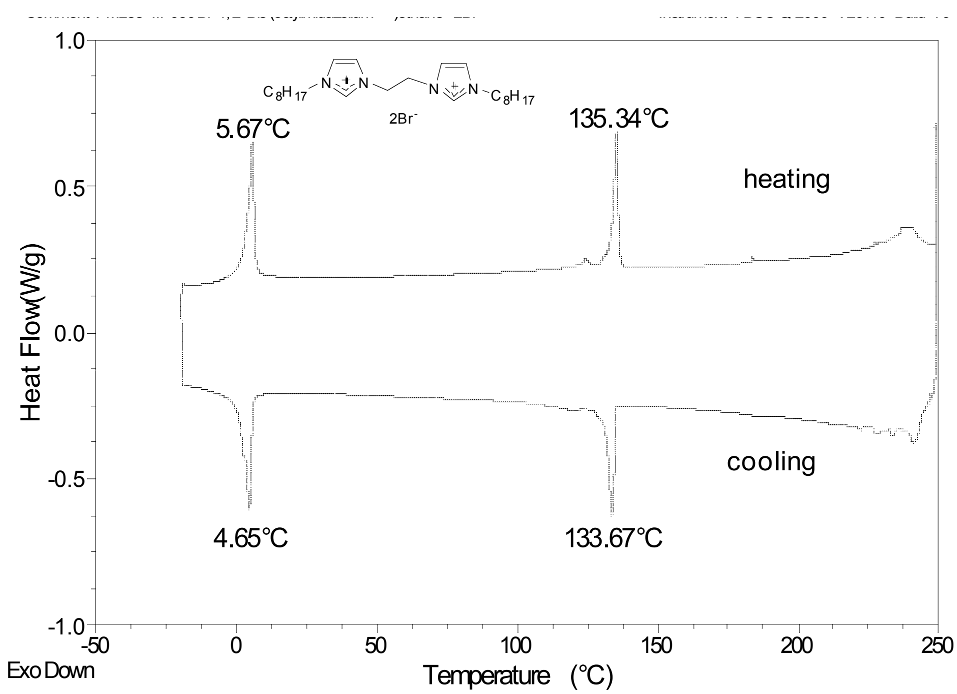


Figure 15. DSC diagram of **9Br** (heating and cooling rate 5 K/min, N_2). Only the second heating and cooling traces are shown in this figure.

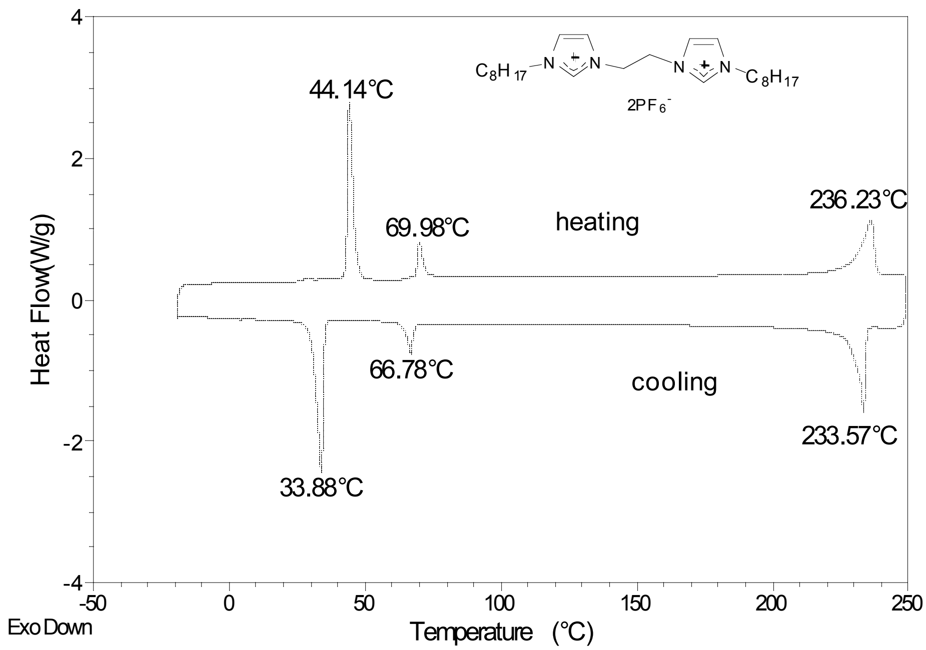


Figure 16. DSC diagram of **$9PF_6$** (heating and cooling rate 5 K/min, N_2). Only the second heating and cooling traces are shown in this figure.

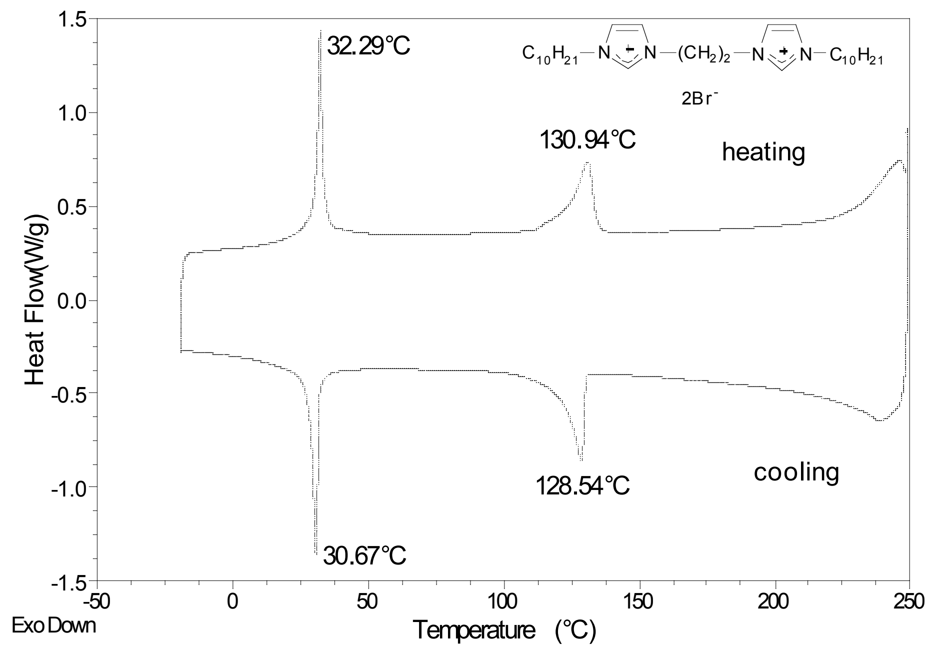


Figure 17. DSC diagram of **10Br** (heating and cooling rate 5 K/min, N_2). Only the second heating and cooling traces are shown in this figure.

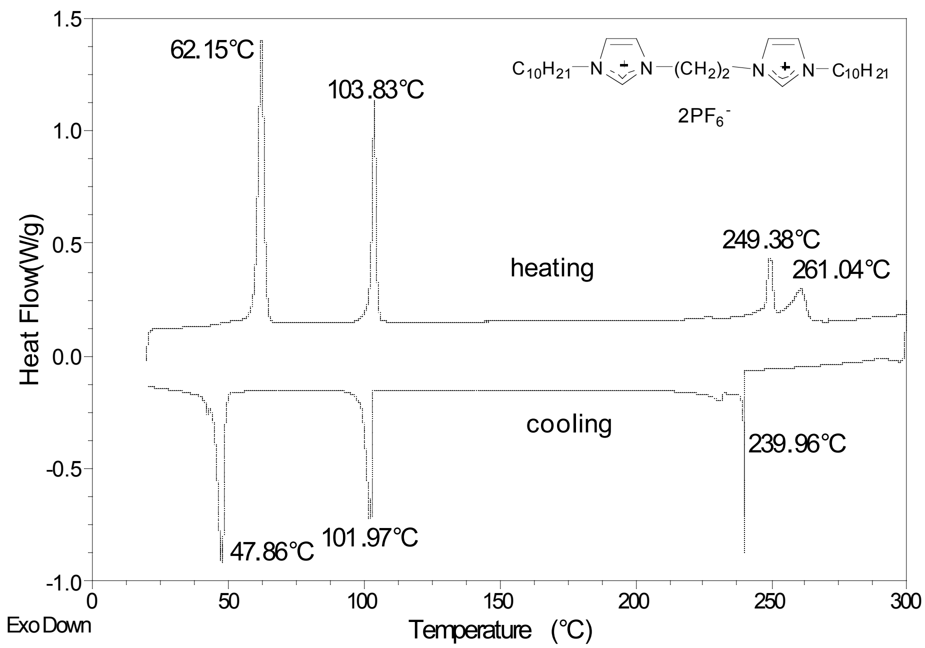


Figure 18. DSC diagram of **10PF$_6$** (heating and cooling rate 5 K/min, N_2). Only the second heating and cooling traces are shown in this figure.

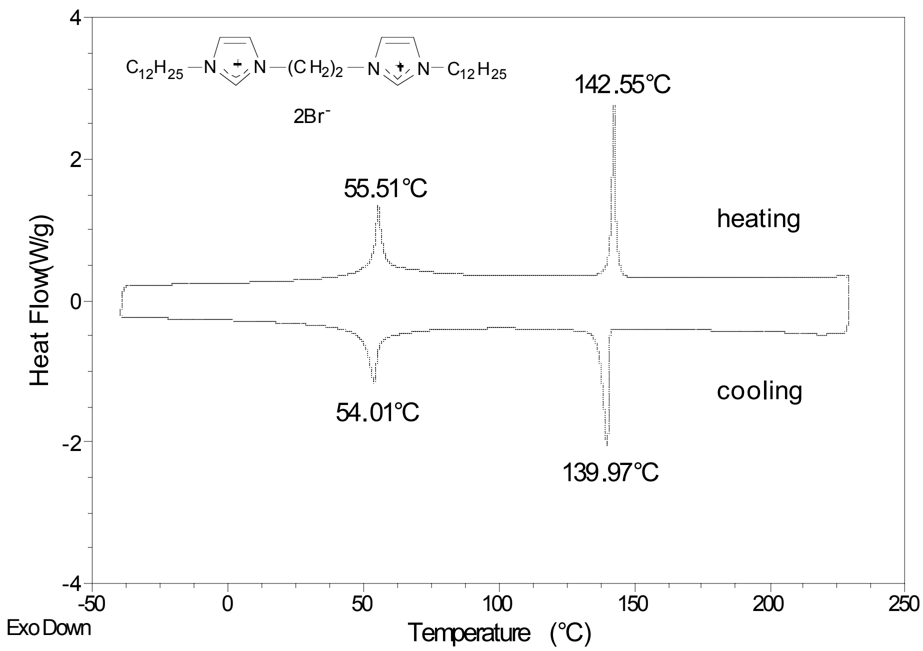


Figure 19. DSC diagram of **11Br** (heating and cooling rate 5 K/min, N_2). Only the second heating and cooling traces are shown in this figure.

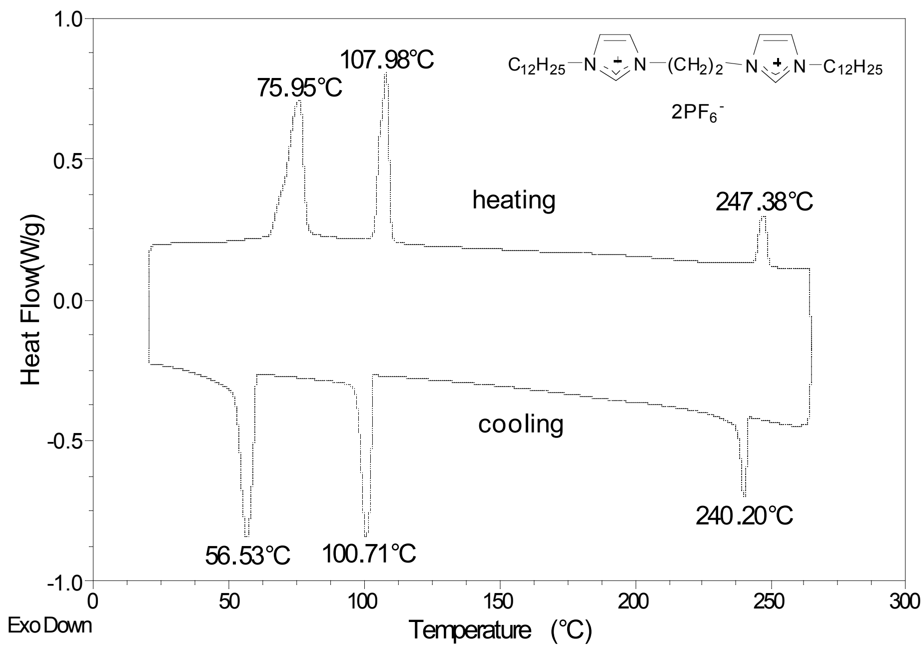


Figure 20. DSC diagram of **11PF$_6$** (heating and cooling rate 5 K/min, N_2). Only the second heating and cooling traces are shown in this figure.

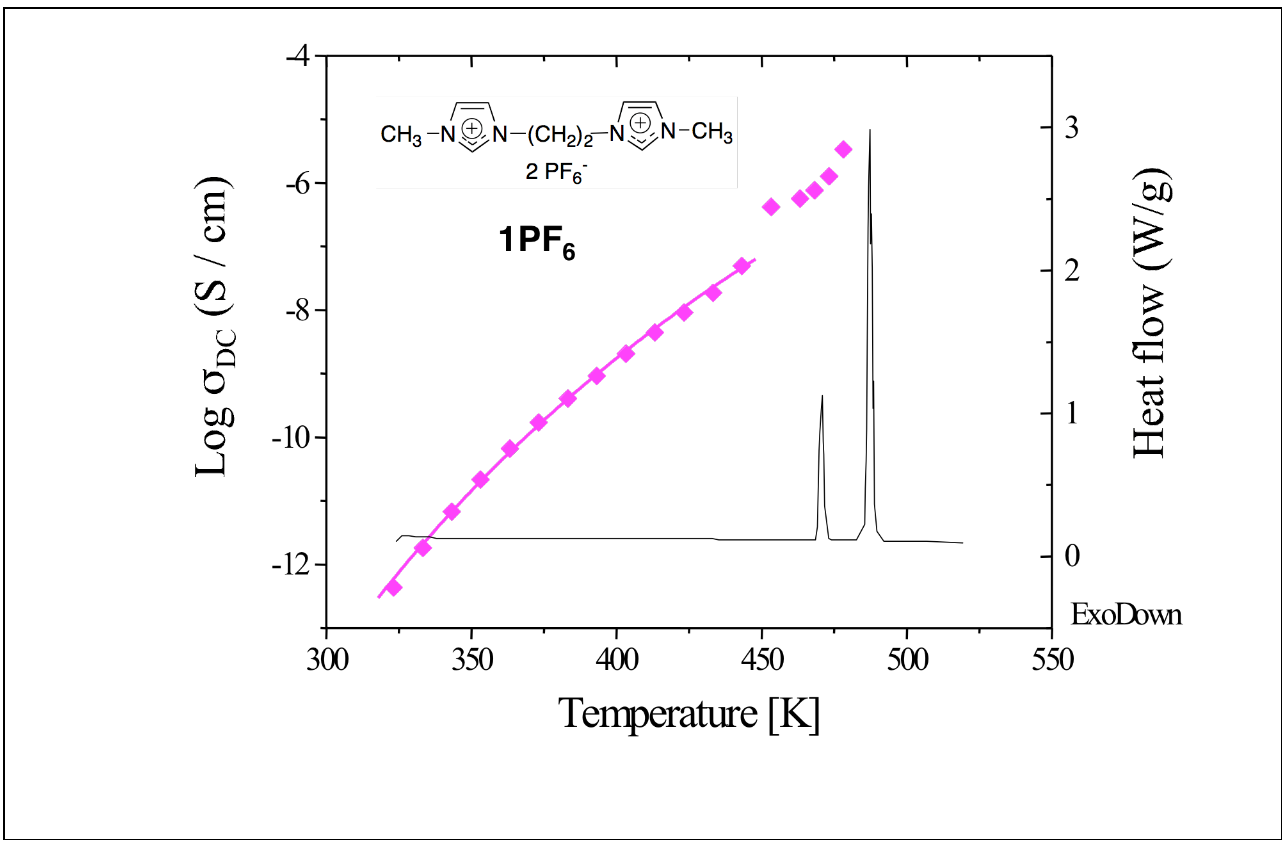


Figure 21. Temperature dependence of the ionic DC conductivity of **1PF$_6$**. The DSC heating trace is superimposed on the plot.

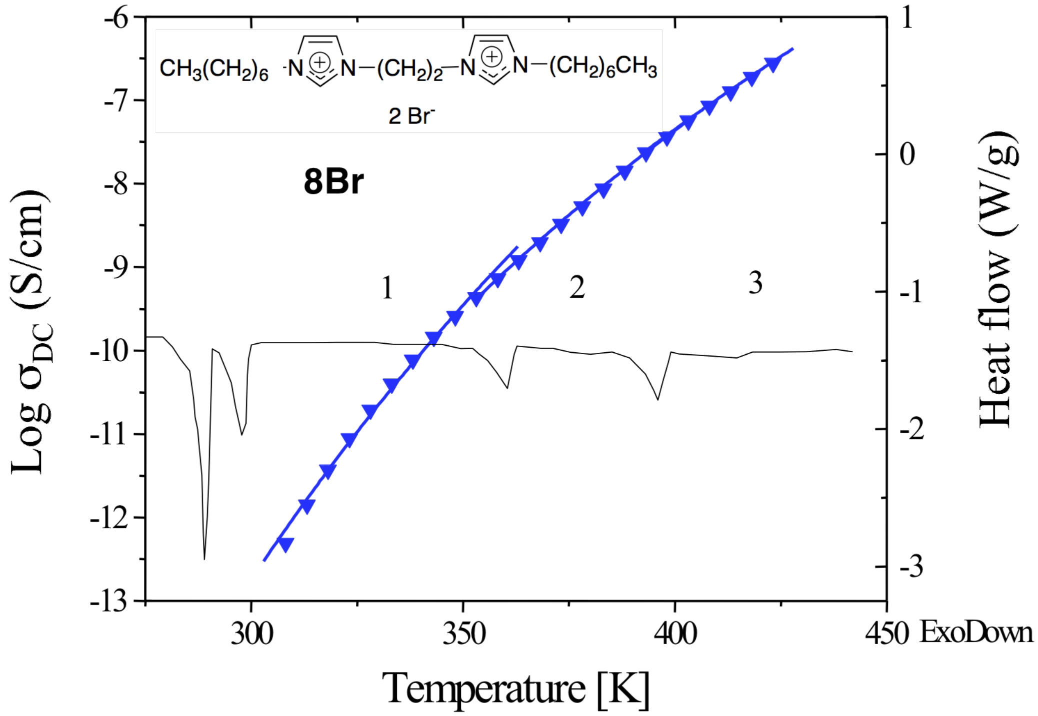


Figure 22. Temperature dependence of the ionic DC conductivity of **8Br**. The DSC cooling trace is superimposed on the plot.

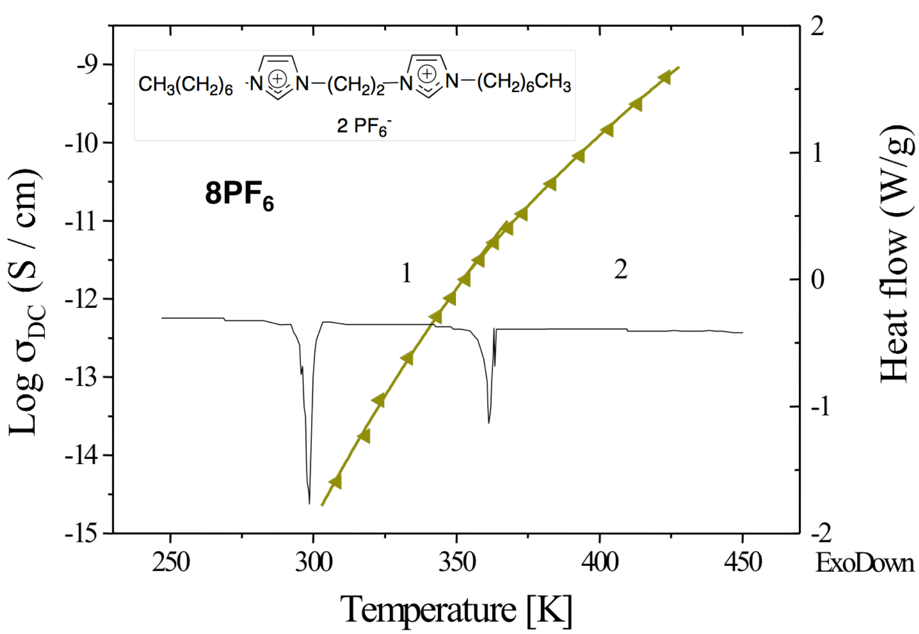


Figure 23. Temperature dependence of the ionic DC conductivity of **$8PF_6$**. The DSC cooling trace is superimposed on the plot.

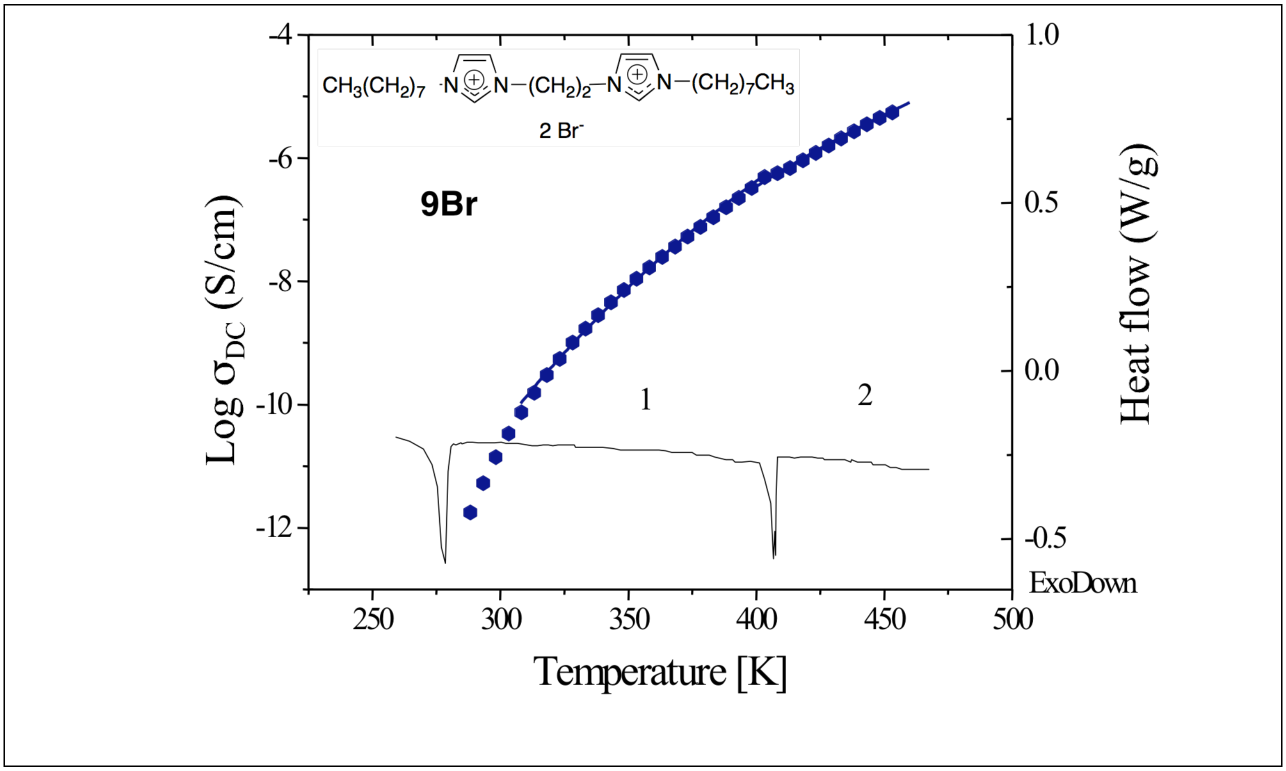


Figure 24. Temperature dependence of the ionic DC conductivity of **9Br**. The DSC cooling trace is superimposed on the plot.

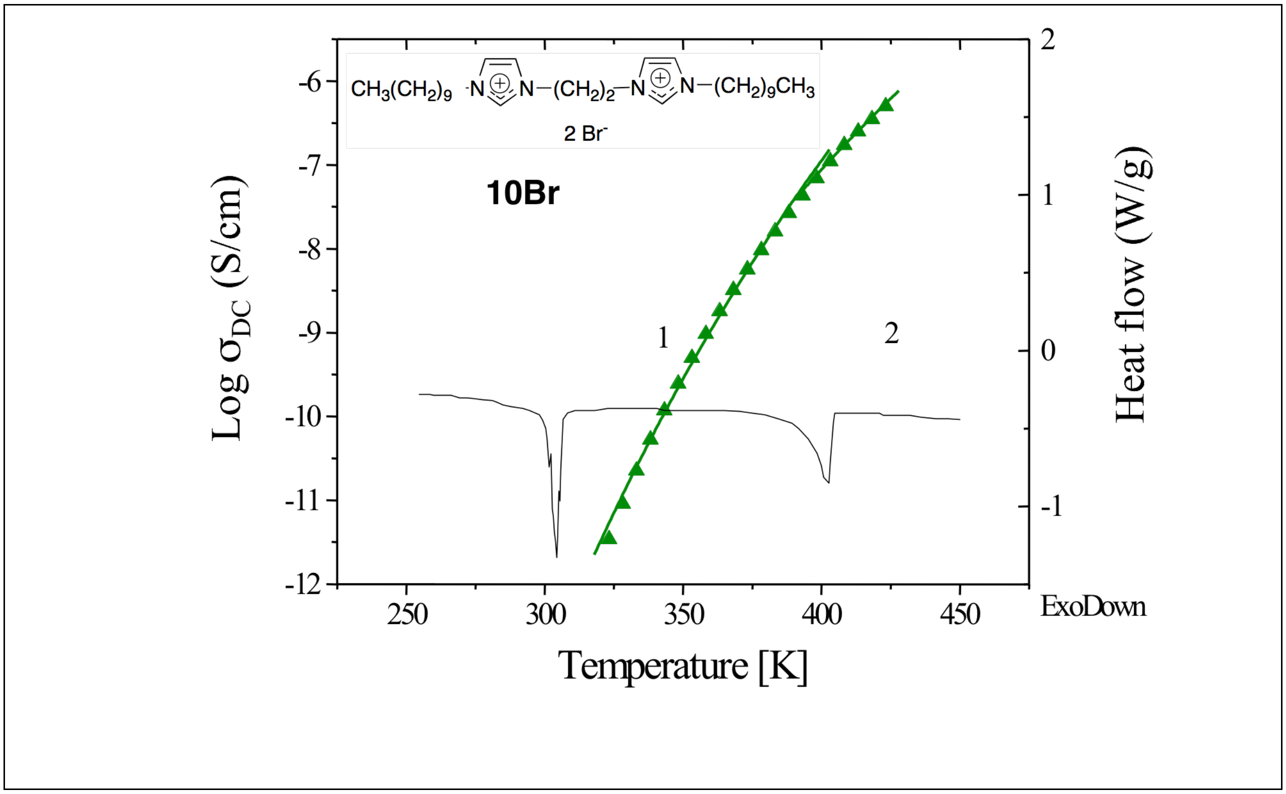


Figure 25. Temperature dependence of the ionic DC conductivity of **10Br**. The DSC cooling trace is superimposed on the plot.

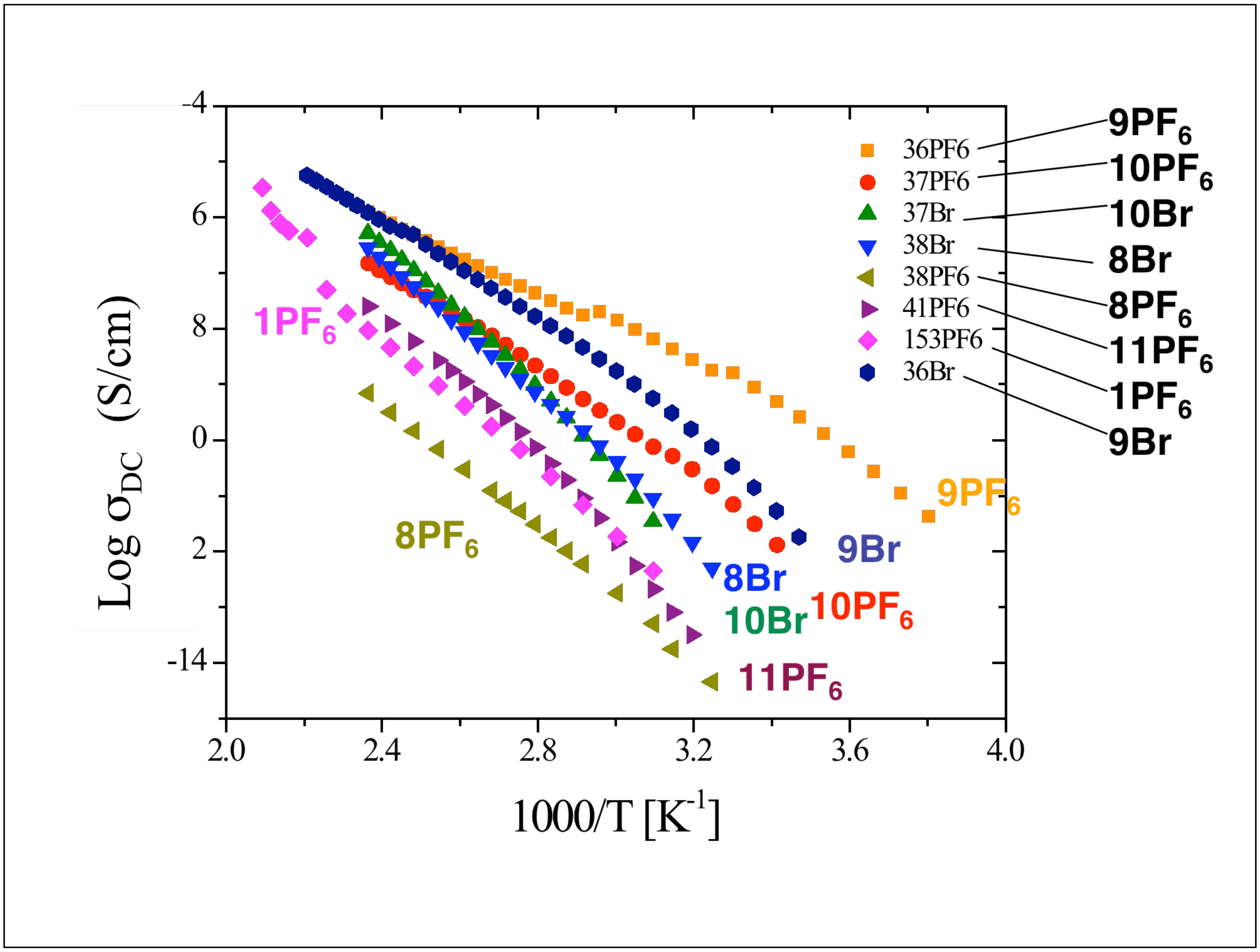


Figure 26. Arrhenius plots: logarithm of ionic DC conductivity vs. inverse absolute temperature for **$1PF_6$**, **8Br**, **$8PF_6$**, **9Br**, **$9PF_6$**, **10Br**, **$10PF_6$**, and **$11PF_6$**.

Reference:

S1. S. Khabnadideh, Z. Reazei, A. Khalafi-Nezhad, R. Bahrinajafi, R. Mohamadi, A. A. Farrokhroz, *Bioorg. Med. Chem. Lett.* 2003, **13**, 2863.