

Supporting Information

1. Synthesis of Protic salts based on N,N-Dimethylethylenediammonium (DMEDAH) cation

N,N-Dimethylethylenediamine (DMEDA), 99% and Triflic acid (99%) were obtained from Sigma-Aldrich (Austria) while bis(trifluoromethanesulfonyl) amide acid (HTFSA), 99% was purchased from Mortia Chemical Industries, Japan. The chemicals were used without purification. The synthesis and characterization of some of the salts based on DMEDA cation were given below.

1) 1-(N,N-Dimethylamino)-2-(ammonium)ethane triflate [DMEDAH][Tf]

DMEDAH Tf was made by neutralizing 1 mole of triflic acid with 1 mole of N,N-dimethylethylenediamine. Typically the synthesis involve a drop wise addition of aqueous solution of triflic acid (42 mmoles, 6.3g) to N,N-dimethylethylenediamine (42 mmoles, 3.7g) in an ice bath and the contents were stirred at room temperature. Then water was removed by distillation under reduced pressure at 70 °C and then dried in a vacuum chamber kept at room temperature for two days. The yield was found to be 98 %.

ESI-MS analysis

Electrospray mass spectroscopy analysis (Cone \pm 25 V): m/z (relative intensity, %), ES⁺, 89.1(CH₃)₂NCH₂CH₂NH₃); ES⁻, 148.9 (triflate, 100). The DMEDA cation undergoes fragmentation and so the positive electrospray has other fragmented ions.

NMR analysis

¹H NMR (600 MHz in CH₃CN d₃, δ , ppm relative to TMS): 2.48 (s, 6H), 2.74-2.76(m, 2H), 2.96-2.98(m, 2H), 5.01(s, 3H). The presence of NH₃⁺ appears as a broad peak due the presence of slight water in the solvent but the peak integrals of the number of protons of CH₃:CH₂:CH₂:NH₃ are obtained as 6.0:2.0:2.0:3.6 respectively and this shows that the sample is pure.

2) 1-(N,N-Dimethylammonium)-2-(ammonium)ethane-triflate [DMEDAH₂][Tf]₂

The compound was made by reacting 2 moles of triflic acid with 1 mole of N,N-dimethylethylenediamine. The synthesis involve a slow addition of aqueous solution of triflic acid (84 mmoles, 12.5g) to N,N-dimethylethylenediamine (42 mmoles, 3.7g) in an ice bath and the contents were stirred at room temperature. Water was removed by distillation and the final solid product was dried under vacuum for two days at room temperature and the yield was found to be 98 %. The pH of 0.1 M aqueous solution was found to be 2.1.

ESI-MS analysis

Electrospray mass spectroscopy analysis (Cone \pm 25 V): m/z (relative intensity, %), ES⁺, 89.1 (CH₃)₂NHCH₂CH₂NH₃); ES⁻, 148.9 (triflate, 100). The DMEDA cation undergoes fragmentation and so the positive electrospray has other fragmented ions.

NMR analysis

^1H NMR (600 MHz in CH_3CN d_3 , δ , ppm relative to TMS): 2.90 (s, 6H), 3.35-3.38(m, 2H), 3.42-3.45(m, 2H), 6.87(s, 3H), 7.75(s, 1H). The NH_3^+ (3 protons) and the proton on the tertiary nitrogen (1 proton) were clearly seen indicating that protonation occurred both at the primary and tertiary nitrogen of the DMEDA cation on treatment with 2 moles of triflic acid. The peak integrations of number of protons of $\text{CH}_3:\text{CH}_2:\text{CH}_2:\text{NH}_3:\text{NH}$ are obtained as 6.1:2.0:2.0:3.0:1.0 and this shows the sample is pure.

3) 1-(N,N-Dimethylamino)-2-(ammonium)ethane bis(trifluoromethanesulfonyl)amide [DMEDAH][TFSA]

The procedure is same as the case for triflate salt except the aqueous addition of bis(trifluoromethane sulfonyl)amide acid (HTFSA) was added in place of triflic acid. The addition of aqueous solution of HTFSA (27 mmol, 7.6 g) was made to N,N-dimethylethylenediamine (27 mmol, 2.38 g) kept in an ice bath. The contents were stirred and water was roto-evaporated at 70 °C under reduced pressure. The sample was further dried in a vacuum desiccator at room temperature and yield was found to be 99%.

ESI-MS analysis

Electrospray mass spectroscopy analysis (Cone \pm 25 V): m/z (relative intensity, %), ES^+ , 89.1($(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{NH}_3$); ES^- , 279.9 (TFSA, 100). The DMEDA cation undergoes fragmentation and so the positive electrospray has other fragmented ions.

NMR analysis

^1H NMR (600 MHz in CH_3CN d_3 , δ , ppm relative to TMS): 2.53 (s, 6H), 2.78-2.79(m, 2H), 2.94-2.96(m, 2H), 3.8-4.1(s, 4H). Here again NH_3^+ appears as a broad peak due the presence of water in the solvent.

4) 1-(N,N-Dimethylammonium)-2-(ammonium)ethane-bis(trifluoromethanesulfonyl)amide [DMEDAH₂][TFSA]₂

In this case 2 moles of aqueous solution of HTFSA was added to 1 mole of N,N-dimethylethylenediamine kept in an ice bath. Typically HTFSA (30.7 mmol, 8.64g) was added slowly to N,N-dimethylethylenediamine (15.3 mmol, 1.35g) kept in an ice bath. Water was roto-evaporated at 70 °C under reduced pressure and the product was further dried in a vacuum desiccator at room temperature. The yield was found to be 99%.

ESI-MS analysis

Electrospray mass spectroscopy analysis (Cone \pm 25 V): m/z (relative intensity, %), ES^+ , 89.1($(\text{CH}_3)_2\text{NHCH}_2\text{CH}_2\text{NH}_3$); ES^- , 279.9 (TFSA, 100). The DMEDA cation undergoes fragmentation and so the positive electrospray has other fragmented ions.

NMR analysis

^1H NMR (600 MHz in CH_3CN d_3 , δ , ppm relative to TMS): 2.88 (s, 6H), 3.26-3.34(m, 4H), 6.37-6.54(m, 3H), 6.88-7.05(m, 1H). In this case the two methylene protons were very close and integrated as one signal to get 4 protons. The NH_3^+ (3 protons) and the proton on the tertiary nitrogen (1 proton) were clearly seen indicating that protonation occurred both at the primary and tertiary nitrogen of the DMEDA cation on treatment with 2 moles of HTFSA.

5) 1-(N,N-Dimethylammonium)-2-(ammonium)ethane-TFSA-triflate [DMEDAH₂][TFSA][Tf]

Here 1 mole of aqueous solution of triflic acid was added to 1 mole of aqueous solution of DMEDAHTFSA. Typically triflic acid (19.3mmol, 2.9 g) was added slowly to DMEDAHTFSA (19.3mmol, 7.1g) kept in an ice bath. As described above, water was roto-evaporated at 70 °C under reduced pressure and the product was further dried in a vacuum desiccator at room temperature. The yield was found to be 99%.

ESI-MS analysis

Electrospray mass spectroscopy analysis (Cone \pm 25 V): m/z (relative intensity, %), ES⁺, 89.1(CH₃)₂NHCH₂CH₂NH₃); ES⁻, 279.9, 148.9 (TFSA, 100). The DMEDA cation undergoes fragmentation and so the positive electrospray has other fragmented ions.

NMR analysis

¹H NMR (600 MHz in CH₃CN d₃, δ , ppm relative to TMS): 2.89 (s, 6H), 3.33-3.39(m, 4H), 6.67-6.73(m, 3H), 7.42-7.49(m, 1H). Here again, the two methylene protons were very close and integrated as one signal to get 4 protons. The NH₃⁺ (3 protons) and the proton on the tertiary nitrogen (1 proton) were clearly seen indicating that protonation occurred both at the primary and tertiary nitrogen of the DMEDA cation on treatment with 1 mole of HTFSA and 1 mole of triflic acid.

Table. S1. The space group and unit cell parameters of [DMEDAH][Tf], [DMEDAH₂][Tf]₂, [DMEDAH₂][TfSA]₂, [DMEDAH₂][TfSA][Tf].

Materials	Space Group	a(Å)	b(Å)	c(Å)	alpha (°)	beta (°)	gamma (°)	Unit cell volume (Å ³)
[DMEDAH][Tf]	P1 (triclinic)	3.1	3.6	5.2	74.3	75.5	112.4	47.1
[DMEDAH ₂][Tf] ₂	P1 (triclinic)	3.8	4.4	7.3	77.7	83.7	65.6	108.9
[DMEDAH ₂][TfSA] ₂	P1 (triclinic)	4.0	4.4	8.5	77.6	99.0	98.3	145.0
[DMEDAH ₂][TfSA][Tf]	P1 (triclinic)	4.8	5.5	7.9	84.8	82.5	73.6	202.2