

Supporting information

Supramolecular ionic networks with superior thermal and transport properties based on novel delocalized di-anionic compounds

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Experimental part

Materials

Cyanamide (99%, Aldrich) and silver nitrate ($\geq 99.0\%$, Aldrich) were used without further purification. Malononitrile (99%, Aldrich) was recrystallized before use. Trifluoromethanesulfonamide (98%, TCI Europe) was sublimed at $75^\circ\text{C}/10^{-2}$ mm Hg. Thionyl chloride ($>99\%$, Aldrich) was distilled over linseed oil, while 1,3-dibromopropane (99%, Aldrich), 1,5-dibromopentane (97%, Aldrich) and 1-methylimidazole (99%, Aldrich) were distilled over CaH_2 under inert atmosphere prior to use. Tetrahydrofuran (THF, 99+%, Aldrich) was dehydrated by distillation over sodium and benzophenone radical anion. Anhydrous grade triethylamine, acetonitrile, N,N-dimethylformamide (DMF), dichloromethane, ethyl acetate and diethyl ether were obtained from commercial sources and were used as received. 1,4-Butanedisulfonic acid disodium salt (98%, ABCR) and benzene-1,3-disulfonic acid disodium salt (97%, ABCR) were dried under vacuum (<1 mm Hg) at 70°C for 3 h prior to use. Lithium bis(trifluoromethanesulfonyl)imide (99%) was obtained from Aldrich and used as received.

Characterization

Prior any characterization, all samples (monomers and polymers thereof) were dried overnight at $55\div 70^\circ\text{C}/1$ mm Hg.

NMR spectra were obtained on Bruker AMX-300, Bruker AMX-400 and Bruker AC-500 spectrometers at 25°C in the indicated deuterated solvent and are listed in ppm. The signal corresponding to the residual protons of the deuterated solvent was used as an internal standard (^1H , ^{13}C relative to tetramethylsilane) and CHCl_2F was used as an internal standard for ^{19}F NMR. A Nicolet Magna-750 Fourier IR-spectrometer was used to record IR spectra at a resolution of 2 cm^{-1} and with the scan number equal to 128 (KBr pellets).

Powder X-ray diffraction (XRD) patterns were recorded at room temperature on a BRUKER (D8 Advance) diffractometer, working at 40 KV/30 mA, with $\text{CuK}\alpha$ wavelength ($\lambda = 1.54\text{ \AA}$). The experimental system was provided with a graphite monochromator and automatic slits.

Thermal transitions of the obtained ionic supramolecular polymers were investigated using Q1000 isothermal differential calorimeter (TA Instruments, USA) in the range of $-70 \div +180^\circ\text{C}$ at a heating rate of $10.0^\circ\text{C}/\text{min}$. While melting point (T_m) was determined from the first heating cycle, the glass transition temperature (T_g) was identified from the second heating trace and is reported as the midpoint of the thermal transition. Thermogravimetric analysis were carried out using a TGA 2950/Q500 analyzer. Samples were heated at a constant rate of $5^\circ\text{C}/\text{min}$, from room temperature to 500°C , under air atmosphere.

Small amplitude oscillatory flow experiments were carried out on a Thermo-Haake Rheostress I viscoelastometer, using a parallel plate geometry. Special care was taken during sample loading to exclude bubbles. Tests were repeated at least twice to insure good repeatability of the results. The testing protocol consisted of temperature sweeps to determine G' and G'' on heating cycles at an angular frequency of 6.28 rad/s and temperature intervals defined for each sample. The reversibility of the rheological process was checked by performing repeated cooling cycles. The temperature ramp rate was $1^\circ\text{C}/\text{min}$. The strain value $\gamma = 0.005\text{ s.u.}$ was low enough to ensure that both moduli G' and G'' were obtained in the linear viscoelastic regime. The transition temperature from network (solid) to liquid state (T_{nl}) was obtained from temperature scans at $\omega = 6.28\text{ rad/s}$ on heating cycles.

The ionic conductivity was evaluated via AC impedance spectroscopy using a Solartron potentiostat equipped with modulab MTS software. I. In case of solid samples, the Pellets with a thickness of $0.8 \div 1.0\text{ mm}$ and a diameter of 13 mm were prepared by pressing in a die under 3 tons of load for 5 minutes in inert atmosphere. The prepared pellets were sandwiched between two circular stainless steel electrodes in hermetically sealed conductivity cells (Advanced Industrial Services, Moorabbin, Australia). Data were collected over a frequency range of $100\text{ mHz} \div 1\text{ MHz}$ in a temperature range shown for each sample at 5°C intervals under single sine wave acquisition mode at 100 mV signal voltage amplitude and auto current mode. The temperature was controlled using a Eurotherm model 3504 controller and a $28\text{ V}/32\text{ W}$ heater (Helios Electroheat Pty Ltd, Cheltenham, Australia); II. In case of liquid samples a special conductivity cell was used, consisted of two platinum wires immobilized by a resin and embedded into a glass matrix. The cell was dipped into a glass vial containing the liquid sample while ensuring complete emersion of the wires and avoiding bubbles. The sample was excluded from environmental factors by using rubber seal and Teflon tape. Multiple measurements were carried out to check for stability and reproducibility in the Nyquist plots for each of the samples. Conductivity cell was calibrated prior each measurement with KCl standard solution (concentration: 0.01 mol/l , conductivity: $1,413\text{ }\mu\text{S}/\text{cm}$ at 25°C). An interval of 20 min was allotted between each measurement temperature (i.e., after each 5 or 10°C step).

Synthesis of the dianionic and dicationic compounds (numeration based on Scheme 1 in the manuscript):

Butane-1,4-disulfonyl dichloride (2)

Freshly dried 1,4-butanedisulfonic acid disodium salt (**1**) (10.0 g, 0.038 mol) was suspended in 60 mL of anhydrous THF under inert atmosphere and 2.1 mL of DMF was added as a catalyst. The reaction flask was cooled to 0-1°C in an ice bath and an excess of freshly distilled thionyl chloride (54.5 g, 0.458 mol) was added dropwise under stirring. The reaction proceeded at 0-1°C for 2 h, and then at room temperature for 24 h. The as obtained yellowish suspension was carefully poured onto the crashed ice (~200 mL). At this, the precipitation of white crystals was observed. The crystals were collected by filtration and quickly washed with cold deionized water (50 mL) on a glass filter, whereupon they were dissolved in dichloromethane (120 mL). The CH₂Cl₂ solution was washed with water (6 × 30 mL) and then dried over anhydrous magnesium sulfate. MgSO₄ was filtered off and the dichloromethane was gently evaporated under reduced pressure at 40°C. The residual white needle crystals were finally dried at 50°C/1 mm Hg for 5 h (hereinafter with a special flask filled with P₂O₅ and introduced into the vacuum line). Yield: 8.6 g (88%); m.p. = 79-80°C; Found: C, 19.01%; H, 3.35%; Calc. for C₄H₈Cl₂O₄S₂ (255.14): C, 18.83%; H, 3.16%; ¹H NMR (400 MHz, DMSO-d₆): δ = 2.63 (m, 4H, CH₂SO₂), 1.67 (m, 4H, CH₂CH₂SO₂); ¹³C NMR (100.6 MHz, DMSO-d₆): δ = 51.2 (CH₂SO₂), 23.8 (CH₂CH₂SO₂); IR (KBr pellet): 2991 (w, ν_{C-H}), 2974 (m, ν_{C-H}), 2960 (w, ν_{C-H}), 2925 (m, ν_{C-H}), 2886 (w, ν_{C-H}), 1456 (m, CH₂), 1369 (vs, ν_{as}SO₂), 1352 (m), 1331 (m), 1315 (m), 1266 (m), 1230 (w), 1157 (vs, ν_sSO₂), 1112 (w), 1040 (m), 879 (m), 775 (m), 760 (s), 732 (s), 536 (vs), 524 (vs), 420 (m) cm⁻¹.

Triethylammonium S,S'-(butane-1,4-diyl)bis(sulfonyl(trifluoromethylsulfonyl)imide) (3)

Trifluoromethanesulfonamide (9.7 g, 0.066 mol) and anhydrous triethylamine (14.5 g, 0.144 mol) were dissolved in 50 mL of anhydrous THF under inert atmosphere. The obtained colorless solution was cooled down to 0°C in an ice bath. Then the solution of **2** (8.3g, 0.033 mol) in 40 mL of anhydrous THF was added dropwise under inert atmosphere and an immediate precipitation of white powder was observed. The reaction proceeded at 0°C for 2 h and then it was left at rt overnight. The resultant precipitate, representing a mixture of product and trimethylammonium hydrochloride, was collected by filtration under inert atmosphere and dried at 50°C/12 mm Hg. Afterwards it was dissolved in anhydrous DMF and the byproduct, which is not soluble, was filtered off. The DMF was stripped off and the residue was washed with anhydrous diethyl ether. Monomer **3** in a form of a white solid was dried at 60°C/12 mm Hg for 1 h and additionally at 70°C/1 mm Hg for 5 h (hereinafter with a special flask filled with P₂O₅ and introduced into the vacuum line). Yield: 19.6 g (88%); m.p. = 73-74°C; Found: C, 32.11%; H, 5.96%; N, 8.26%; Calc. for

$C_{18}H_{40}F_6N_4O_8S_4$ (682.78): C, 31.66%; H, 5.90%; N, 8.21%; 1H NMR (400 MHz, D_2O): δ 3.35 (m, 4H, CH_2SO_2), 3.24 (q, 12H, $J = 7.3$ Hz, NCH_2CH_3), 2.03 (m, 4H, $CH_2CH_2SO_2$), 1.32 (t, 18H, $J = 7.3$ Hz, NCH_2CH_3); ^{13}C NMR (100 MHz, D_2O): $\delta = 119.65$ (q, CF_3 , $J = 324$ Hz), 54.50 (CH_2SO_2), 46.65 (NCH_2CH_3), 22.05 ($CH_2CH_2SO_2$), 8.24 (NCH_2CH_3); ^{19}F NMR (376 MHz, D_2O): $\delta = -78.59$; IR (KBr pellet): 3147 (m), 2977 (w, ν_{C-H}), 2942 (w, ν_{C-H}), 2739 (w, ν_{NH^+}), 2678 (m, ν_{NH^+}), 2604 (w, ν_{NH^+}), 2495 (w, ν_{NH^+}), 1472 (m, ν_{CH_2}), 1407 (w), 1314 (s), 1338 (vs, ν_{asSO_2}), 1192 (vs, ν_{CF}), 1122 (vs, ν_{sSO_2}), 1048 (s, ν_{CF}), 819 (m), 762 (m), 623 (s), 601 (s), 556 (w), 518 (s) cm^{-1} .

Triethylammonium S,S'-(butane-1,4-diyl)bis(sulfonyldicyanomethanide) (4)

The same procedure was used as for **3** with the substitution of trifluoromethanesulfonamide for malononitrile. Monomer **4** was obtained as yellow solid. Yield: 67 %; 1H NMR (500 MHz, D_2O): $\delta = 3.50$ (t, 4H, $J = 7.5$ Hz, CH_2SO_2), 3.23 (q, 12H, $J = 7.3$ Hz, NCH_2CH_3), 2.40 (m, 4H, $CH_2CH_2SO_2$), 1.32 (t, 18H, $J = 7.3$ Hz, NCH_2CH_3); ^{13}C NMR (125 MHz, D_2O): $\delta = 120.44$ (CN), 56.28 (CH_2SO_2), 46.69 (NCH_2CH_3), 21.79 ($CH_2CH_2SO_2$), 8.24 (NCH_2CH_3); IR (KBr pellet): 3106 (m), 2990 (w, ν_{C-H}), 2951 (w, ν_{C-H}), 2879 (w, ν_{NH^+}), 2825 (m, ν_{NH^+}), 2186 (vs, $\nu_{sC\equiv N}$), 2156 (vs, $\nu_{asC\equiv N}$), 1467 (m, ν_{CH_2}), 1426 (m), 1384 (w), 1325 (w), 1305 (s), 1297 (vs, ν_{asSO_2}), 1207 (m), 1121 (vs, ν_{sSO_2}), 1092 (s), 1072 (vs), 1031 (s), 887 (m), 832 (w), 777 (vs), 740 (m), 574 (vs), 524 (m), 506 (m), 413 (s) cm^{-1} .

Benzene-1,3-disulfonyl dichloride (6)

The same procedure was used as for **2** with the substitution of **1** for **5**. After sublimation at $50^\circ C/10^{-2}$ mm Hg the benzene-1,3-disulfonyl dichloride was obtained as white crystals. Yield: 86 %; m.p. = $62-64^\circ C$; Found: C, 26.20%; H, 1.48%; S, 23.19%; Calc. for $C_6H_4Cl_2O_4S_2$ (275.13): C, 26.19%; H, 1.47%; S, 23.31%; 1H NMR (400 MHz, $CDCl_3$): $\delta = 8.67$ (s, 1H, C^2H), 8.42 (d, 2H, $J = 7.9$, C^4H , C^6H), 7.98 (t, 1H, $J = 7.9$, C^5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 145.55$ (C^1 , C^3), 132.91 (C^4 , C^6), 131.78 (C^5), 125.52 (C^2); IR (KBr pellet): 3094 (m, ν_{C-H}), 3073 (m, ν_{C-H}), 3022 (w, ν_{C-H}), 1577 (m), 1470 (w), 1426 (m), 1418 (vs, ν_{asSO_2}), 1377 (vs, ν_{asSO_2}), 1299 (w), 1189 (vs, ν_{sSO_2}), 1167 (vs, ν_{asSO_2}), 1078 (m, Aryl CH), 996 (w), 907 (w), 799 (s, Aryl CH), 676 (s, Aryl CH), 615 (s), 676 (m), 667 (m), 615 (m), 589 (s), 560 (vs, Aryl CH), 544 (vs, Aryl CH), 507 (m), 449 (w), 429 (w) cm^{-1} .

Triethylammonium S,S'-(1,3-phenylene)bis(sulfonyl(trifluoromethylsulfonyl)imide) (7)

Monomer **7** was synthesized in analogous manner as **3** with the exception of utilization **6** as a starting compound and was obtained as light brown solid wax. Yield: 86 %; m.p. = $40-43^\circ C$; Found: C, 34.25%; H, 5.36%; N, 8.01%; Calc. for $C_{20}H_{36}F_6N_4O_8S_4$ (702.77): C, 34.18%; H, 5.16%; N, 7.97%; 1H NMR (400 MHz, $DMSO-d_6$): $\delta = 8.13$ (s, 1H, C^2H), 7.90 (d, 2H, $J = 7.9$, C^4H , C^6H), 7.63 (t, 1H, $J = 7.9$, C^5H); 3.07 (q, 12H, $J = 7.3$ Hz,

NCH_2CH_3), 1.16 (t, 18H, $J = 7.3\text{Hz}$, NCH_2CH_3); ^{13}C NMR (100 MHz, DMSO- d_6): $\delta = 145.11$ (C^1 , C^3), 128.67 (C^5), 128.53 (C^4 , C^6), 123.51 (C^2), 119.76 (q, $J = 324\text{ Hz}$, CF_3) 45.55 (NCH_2CH_3), 8.38 (NCH_2CH_3); ^{19}F NMR (376 MHz, DMSO- d_6): $\delta = -77.86$; IR (KBr pellet): 3099 (m, $\nu_{\text{C-H}}$), 2999 (m, $\nu_{\text{C-H}}$), 2954 (w, $\nu_{\text{C-H}}$), 2878 (w, $-\text{NH}^+$), 2828 (w, $-\text{NH}^+$), 2755 (w, $-\text{NH}^+$), 2679 (w, $-\text{NH}^+$), 2492 (w, $-\text{NH}^+$), 1475 (m, CH_2), 1413 (w), 1407 (w), 1330 (vs, ν_{asSO_2}), 1284 (s), 1194 (vs, ν_{CF}), 1120 (vs, ν_{sSO_2}), 1079 (s), 1053 (s, ν_{CF}), 827 (s, Aryl CH), 781 (m), 734 (m, Aryl CH), 688 (m), 650 (m), 605 (s), 585 (s, Aryl CH), 564 (s, Aryl CH), 521 (s) cm^{-1} .

Triethylammonium S,S'-(1,3-phenylene)bis(sulfonyl(cyano)imide) (8)

The same procedure was used as for **3**, except that the reaction was carried out with **6** and cyanamide was used instead of trifluoromethanesulfonamide. Monomer **8** was obtained in a form of light yellow oil. Yield: 74 %; Found: C, 48.80%; H, 7.41%; N, 16.94%; Calc. for $\text{C}_{20}\text{H}_{36}\text{F}_6\text{N}_6\text{O}_4\text{S}_2$ (488.67): C, 49.16%; H, 7.43%; N, 17.20%; ^1H NMR (400 MHz, DMSO- d_6): $\delta = 7.99$ (s, 1H, C^2H), 7.80 (d, 2H, $J = 7.9$, C^4H , C^6H), 7.60 (t, 1H, $J = 7.9$, C^5H); 3.07 (q, 12H, $J = 7.3\text{Hz}$, NCH_2CH_3), 1.15 (t, 18H, $J = 7.3\text{Hz}$, NCH_2CH_3); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 145.40$ (C^1 , C^3), 128.89 (C^5), 127.43 (C^4 , C^6), 122.29 (C^2), 45.55 (NCH_2CH_3), 8.43 (NCH_2CH_3); IR (KBr pellet): 3071 (w, $\nu_{\text{C-H}}$), 2990 (m, $\nu_{\text{C-H}}$), 2949 (w, $\nu_{\text{C-H}}$), 2783 (w, $-\text{NH}^+$), 2703 (m, $-\text{NH}^+$), 2507 (w, $-\text{NH}^+$), 2169 (vs, $\nu_{\text{C=N}}$), 1635 (w), 1558 (w), 1475 (s, CH_2), 1400 (m), 1359 (w), 1290 (vs, ν_{asSO_2}), 1223 (s), 1167 (m), 1135 (vs, ν_{sSO_2}), 1100 (m), 1076 (m), 1032 (m), 836 (vs, Aryl CH), 776 (w), 689 (s), 627 (s), 579 (vs, Aryl CH), 490 (m) cm^{-1} .

1,1'-(pentane-1,5-diyl)bis(3-methyl-1H-imidazol-3-ium) bromide (11)

The reaction route for the synthesis of **11** was chosen similarly to the procedure published in the reference 15 of the manuscript. However, it was conducted with some modification. To a solution of N-methylimidazole (13.8 g, 0.167 mol) in anhydrous methanol (40 mL) cooled to $0-1^\circ\text{C}$ in an ice bath, a solution of 1,5-dibromopentane (17.5 g, 0.076 mol) in methanol (30 mL) was slowly added dropwise under inert atmosphere. The reaction mixture was stirred for 4 h at $0-1^\circ\text{C}$, 24 h at 20°C , 12 h at 40°C , and 24 h at 55°C . Methanol was removed in vacuum at $50^\circ\text{C}/10\text{ mm Hg}$ and the residual solid was crystallized from acetonitrile-ethyl acetate mixture. The white crystalline product was dried for 5 h at $50^\circ\text{C}/1\text{ mm Hg}$. Yield: 27.0 g (90 %); m.p. = $141-142^\circ\text{C}$; Found: C, 39.63%; H, 5.64%; N, 14.27%; Calc. for $\text{C}_{13}\text{H}_{22}\text{Br}_2\text{N}_4$ (394.15): C, 39.61%; H, 5.63%; N, 14.21%; ^1H NMR (400 MHz, D_2O): $\delta = 8.77$ (s, 2H, Imidazole C^2H), 7.52, 7.47, 49 (s, s, 4H, Imidazole C^4H , C^5H), 4.24 (t, 4H, $J = 7.3\text{Hz}$, NCH_2), 3.93 (s, 6H, NCH_3), 1.97 (m, 4H, NCH_2CH_2), 1.37 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2$); ^{13}C NMR (100 MHz, D_2O): $\delta = 135.88$ (Imidazole C^2), 123.57, 122.15 (Imidazole C^4 , C^5), 49.18 (NCH_2), 35.77 (NCH_3), 28.73 (NCH_2CH_2), 22.20 ($\text{NCH}_2\text{CH}_2\text{CH}_2$); IR (KBr pellet): 3146 (m, $\nu_{\text{C-H}}$), 3085 (s, $\nu_{\text{C-H}}$), 2941 (m), 2862 (w), 1649 (m), 1634 (m), 1571 (vs, $\nu_{\text{C=N}}$), 1535 (w), 1512 (w), 1485 (m, CH_2), 1424 (w), 1376 (w), 1341 (w), 1168 (vs, $\nu_{\text{C-C}}$), 1088 (w), 1023 (w), 841 (m), 757 (s), 651 (m), 621 (s) cm^{-1} .

1,1'-(propane-1,3-diyl)bis(3-methyl-1H-imidazol-3-ium) bromide (10)

The same synthetic procedure was used as for **11**. The residual solid was purified by boiling in anhydrous acetonitrile. Monomer **10** was obtained as highly hydrophilic white crystalline solid. Yield: 98 %; m.p. = 155-156°C; Found: C, 36.18%; H, 4.99%; N, 15.37%; Calc. for C₁₁H₁₈Br₂N₄ (366.10): C, 36.09%; H, 4.96%; N, 15.30%; ¹H NMR (500 MHz, D₂O): δ = 8.81 (s, 2H, Imidazole C²H), 7.53, 7.49 (s, s, 4H, Imidazole C⁴H, C⁵H), 4.34 (t, 4H, J = 7.3Hz, NCH₂), 3.92 (s, 6H, NCH₃), 2.54 (m, 2H, NCH₂CH₂); ¹³C NMR (125 MHz, D₂O): 136.64 (Imidazole C²), 124.42, 123.17 (Imidazole C⁴, C⁵), 46.70 (NCH₂), 36.37 (NCH₃), 30.17 (NCH₂CH₂); IR (KBr pellet): 3142 (m, ν_{C-H}), 3075 (vs, ν_{C-H}), 3015 (m, ν_{C-H}), 2849 (w), 1632 (m), 1574 (vs, ν_{C=N}), 1563 (vs, ν_{C=N}), 1465 (m, ν_{CH₂}), 1388 (w), 1363 (w), 1324 (w), 1169 (vs, ν_{C-C}), 1188 (w), 1071 (w), 1020 (w), 856 (m), 770 (s), 639 (m), 622 (s) cm⁻¹.

Synthesis and characterization of supramolecular ionic networks

Hydrophobic supramolecular ionic networks **iNet-1**, **iNet-2** and **iNet-3** were prepared as follows: to the aq. solution of respective dianionic monomer (**3** or **7**) an aq. solution of di-imidazolium monomer (**10** or **11**) in equimolar ratio was added dropwise upon stirring at rt. The precipitation of desired product was immediately observed. Stirring was continued for 1 h, whereupon the upper layer was decanted and the residual oil was continuously washed with fresh portions of deionized water (4×40 mL). The obtained oil was diluted with dichloromethane (80 mL) and the CH₂Cl₂ solution was dried over anhydrous magnesium sulfate. MgSO₄ was filtered off and the dichloromethane was evaporated at 40°C/10 mm Hg. The residual solid product was finally dried at 50°C/1 mm Hg for 5 h.

Hydrophilic **iNet-2** and **iNet-5** were prepared through silver chemistry. To the aq. solution of respective dianionic monomer (**4** or **8**) a 2.1 molar excess of aq. solution of AgNO₃ was added dropwise under stirring at rt. The precipitated disilver salts of **4** or **8** were filtered and washed with deionized water on filter. Further on they were quantitatively transferred to the new flask and suspended in deionized water, whereupon an aq. solution of di-imidazolium monomer (**10** or **11**) in equimolar ratio was added dropwise and the precipitation of AgBr was immediately observed. After 2 h of stirring at rt the reaction mass was filtered and water was stripped off at 55°C/10 mm Hg from the collected filtrate. The residual solid was dried at 55°C/1 mm Hg for 8 h.

1,1'-(pentane-1,5-diyl)bis(3-methyl-1H-imidazol-3-ium) S,S'-(butane-1,4-diyl)bis(sulfonyl(trifluoromethylsulfonyl)imide) (iNet-1)

^1H NMR (400 MHz, D_2O): δ = 8.73 (s, 2H, Imidazole C^2H), 7.50, 7.47 (s, s, 4H, Imidazole C^4H , C^5H), 4.23 (t, 4H, J = 7.3Hz, NCH_2), 3.92 (s, 6H, NCH_3), 3.34 (m, 4H, CH_2SO_2), 2.02 (m, 4H, $\text{CH}_2\text{CH}_2\text{SO}_2$), 1.96 (m, 4H, NCH_2CH_2), 1.37 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2$); ^{13}C NMR (100 MHz, D_2O): δ = 135.86, 123.55, 122.09, 119.66 (q, J = 322Hz), 54.53, 49.12, 35.61, 28.71, 22.20, 22.06.

1,1'-(propane-1,3-diyl)bis(3-methyl-1H-imidazol-3-ium) S,S'-(1,3-phenylene)bis(sulfonyl(trifluoromethylsulfonyl)imide) (iNet-2)

^1H NMR (400 MHz, $\text{Me}_2\text{CO-d}_6$): δ = 9.04 (s, 2H, Imidazole C^2H), 8.29 (t, 1H, J = 2.0Hz, Benzene C^2H), 8.02 (dd, 2H, J = 7.8Hz, J = 2.0Hz, Benzene C^4H , C^6H), 7.73, 7.64 (t, t, 4H, J = 1.8Hz, Imidazole C^4H , C^5H), 7.61 (t, 1H, J = 7.8Hz, Benzene C^5H), 4.50 (t, 4H, J = 7.3Hz, NCH_2), 3.40 (s, 6H, NCH_3), 2.68 (m, 2H, NCH_2CH_2); ^{13}C NMR (100 MHz, $\text{Me}_2\text{CO-d}_6$): 146.91, 137.82, 129.65, 125.21, 123.39, 119.73, 47.34, 36.77, 31.13.

1,1'-(pentane-1,5-diyl)bis(3-methyl-1H-imidazol-3-ium) S,S'-(1,3-phenylene)bis(sulfonyl(trifluoromethylsulfonyl)imide) (iNet-3)

^1H NMR (400 MHz, $\text{Me}_2\text{CO-d}_6$): δ = 8.98 (s, 2H, Imidazole C^2H), 8.35 (t, 1H, J = 1.7Hz, Benzene C^2H), 8.02 (dd, 2H, J = 7.8Hz, J = 1.7Hz, Benzene C^4H , C^6H), 7.69, 7.61 (t, t, 4H, J = 1.8Hz, Imidazole C^4H , C^5H), 7.61 (t, 1H, J = 7.8Hz, Benzene C^5H), 4.32 (t, 4H, J = 7.3Hz, NCH_2), 3.97 (s, 6H, NCH_3), 1.99 (m, 4H, NCH_2CH_2), 1.45 (m, 2H, NCH_2CH_2); ^{13}C NMR (100 MHz, $\text{Me}_2\text{CO-d}_6$): 146.93, 137.46, 129.58, 125.22, 122.95, 119.74, 50.02, 36.64, 30.27, 23.20.

1,1'-(propane-1,3-diyl)bis(3-methyl-1H-imidazol-3-ium) S,S'-(butane-1,4-diyl)bis(sulfonyldicyanomethanide) (iNet-4)

^1H NMR (500 MHz, D_2O): δ = 8.79 (s, 2H, Imidazole C^2H), 7.60, 7.51 (s, s, 4H, Imidazole C^4H , C^5H), 4.33 (t, 4H, NCH_2), 3.92 (s, 6H, NCH_3), 3.35 (t, 4H, CH_2SO_2), 2.54 (m, 2H, NCH_2CH_2), 2.03 (m, 4H, $\text{CH}_2\text{CH}_2\text{SO}_2$); ^{13}C NMR (125 MHz, D_2O): 136.14 (Imidazole C^2), 123.95, 122.12 (Imidazole C^4 , C^5), 120.40 (CN), 56.24 (CH_2SO_2), 46.23 (NCH_2), 35.78 (NCH_3), 29.71 (NCH_2CH_2), 21.79 ($\text{CH}_2\text{CH}_2\text{SO}_2$)

1,1'-(propane-1,3-diyl)bis(3-methyl-1H-imidazol-3-ium) S,S'-(1,3-phenylene)bis(sulfonyl(cyano)imide) (iNet-5)

^1H NMR (400 MHz, D_2O): δ = 8.78 (s, 2H, Imidazole C^2H), 8.26 (t, 1H, J = 1.9Hz, Benzene C^2H), 8.15 (dd, 2H, J = 7.9Hz, J = 1.9Hz, Benzene C^4H , C^6H), 7.86 (t, 1H, J = 7.9Hz, Benzene C^5H), 7.50, 7.47 (s, s, 4H, Imidazole C^4H , C^5H), 4.32 (t, 4H, J = 7.3Hz, NCH_2), 3.92 (s, 6H, NCH_3), 2.51 (m, 2H, NCH_2CH_2); ^{13}C NMR (125 MHz, D_2O): 142.66, 136.08, 130.90, 129.59, 123.92, 122.87, 122.06, 46.19, 35.90, 29.74.

Synthesis of lithium doped supramolecular network

One supramolecular ionic networks (iNet-3) was used here as working substance. Doping was achieved by mixing iNet-3 with the required amounts of LiTFSI in a high purity argon environment glove box. Thereafter, the samples were allowed to completely dissolve LiTFSI for 1 hour at 110 °C using a stirrer. Composition of 10 mol% of LiTFSI was prepared.

Ionic conductivity

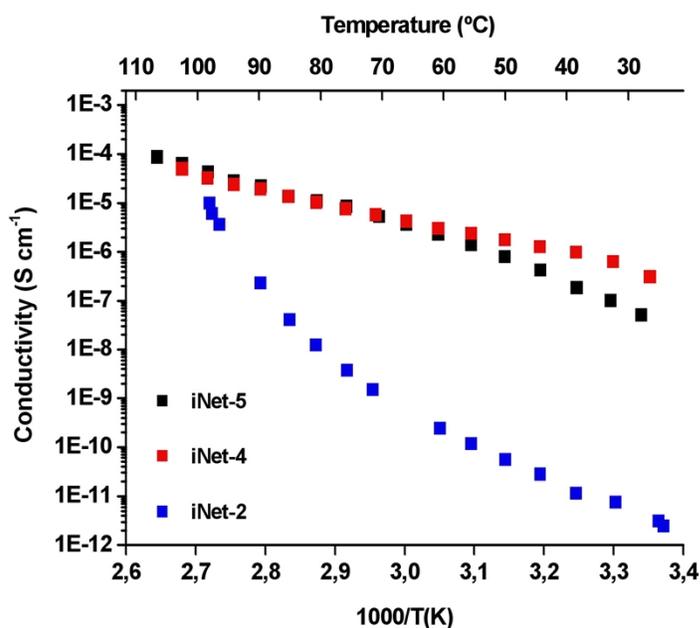


Fig.1 Temperature dependence of the ionic conductivity for iNet-2, iNet-4 and iNet-3

Powder X-ray diffraction (XRD)

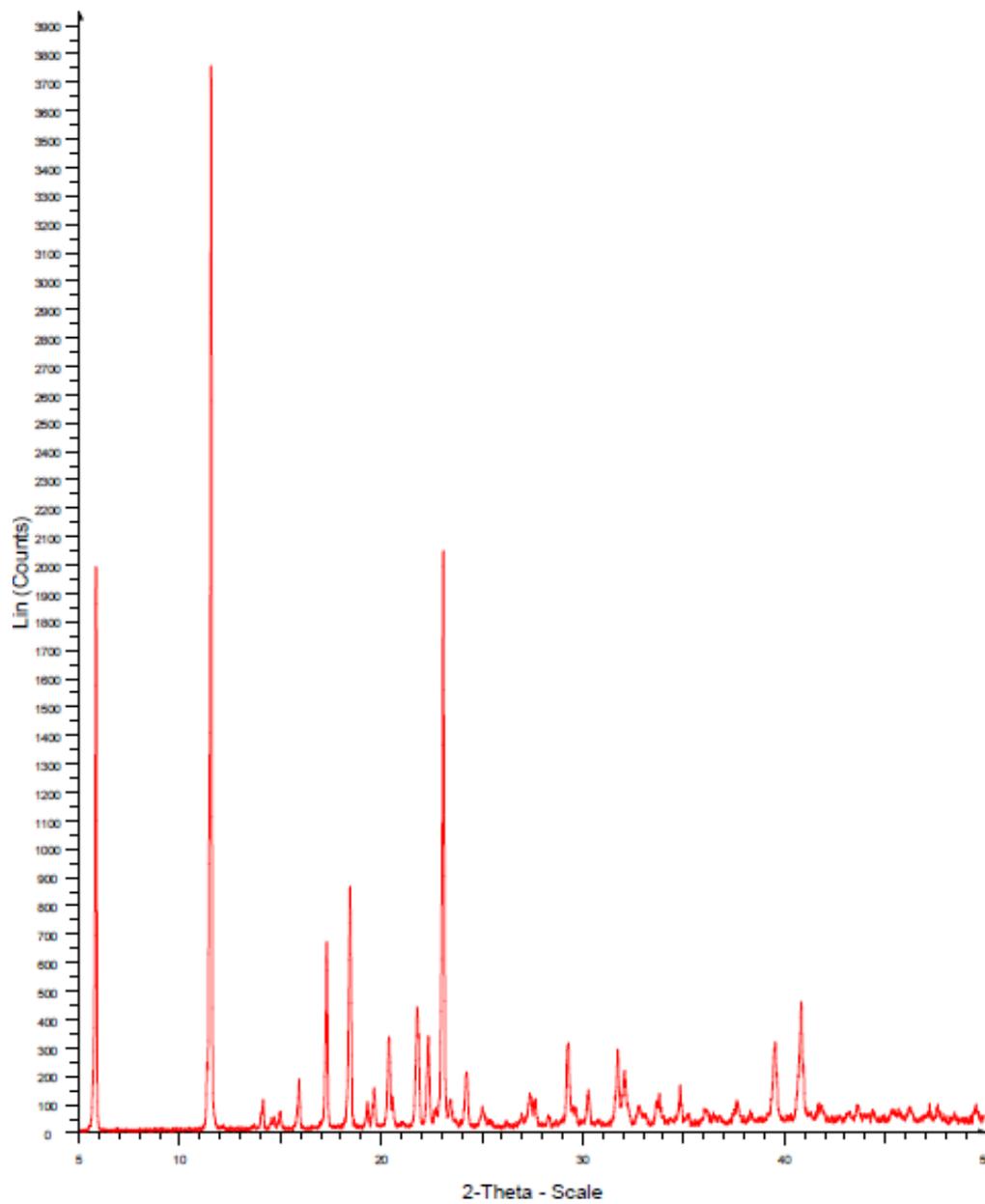


Fig.2 Powder X-ray diffraction (XRD) pattern of iNet-1

Rheological graphs

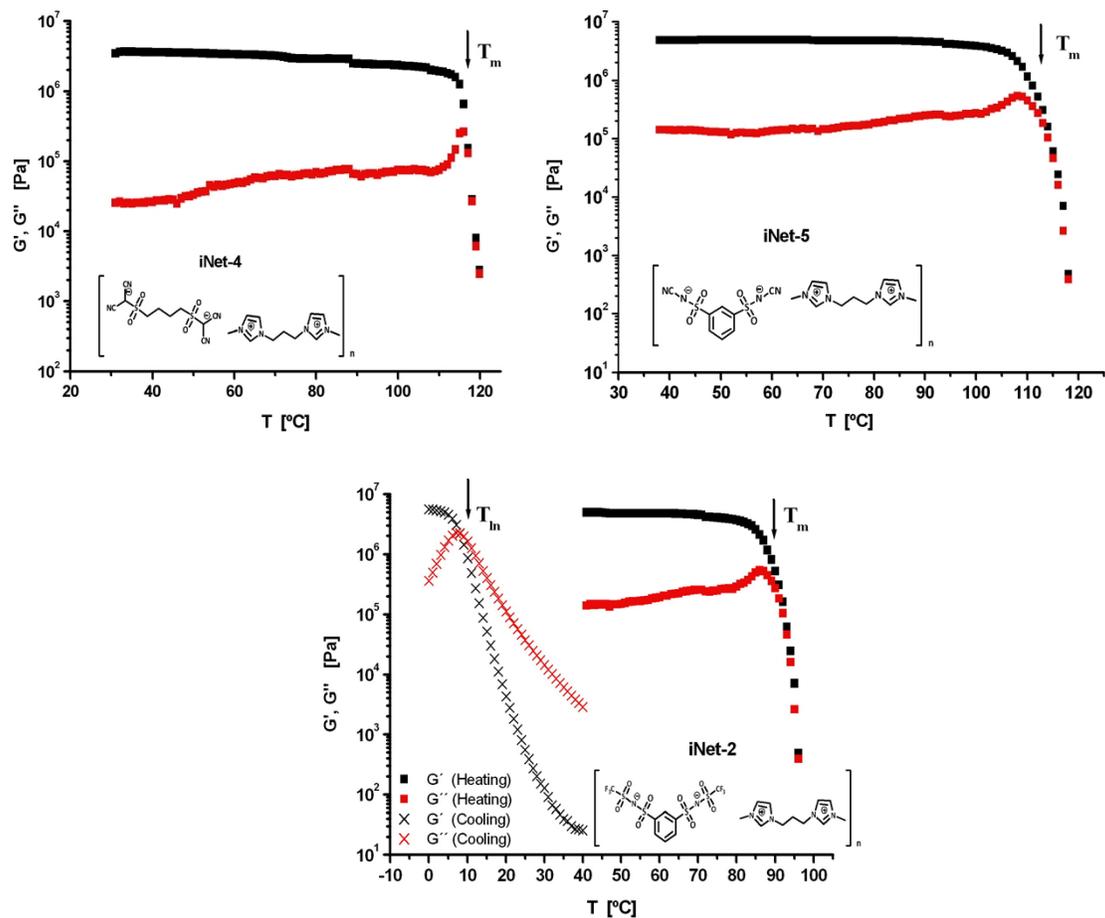


Fig.3 Temperature dependence of dynamic storage modulus G' (heating \blacksquare & cooling \times) and loss modulus G'' (heating \blacksquare & cooling \times) for iNet-4 and iNet-5 (top) and iNet-2 (down). Arrows in the figures indicate the melting point (T_m) and liquid to network transition (T_{ln}).