Electronic Supplementary Information (ESI) for

Preparation of tough, thermally stable, and water-resistant double-network ion gels consisting of silica nanoparticles/poly(ionic liquid)s through photopolymerisation of ionic monomer and subsequent solvent removal

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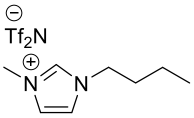
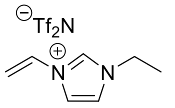


[Bmim][Tf_2N]



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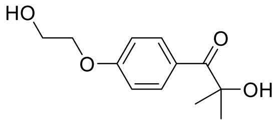

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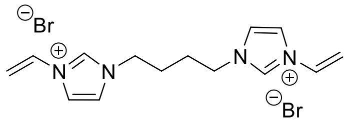
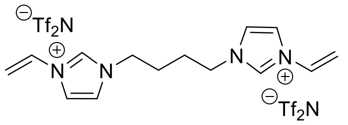
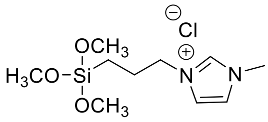


[$(VIM)_2C_4$]Br_2



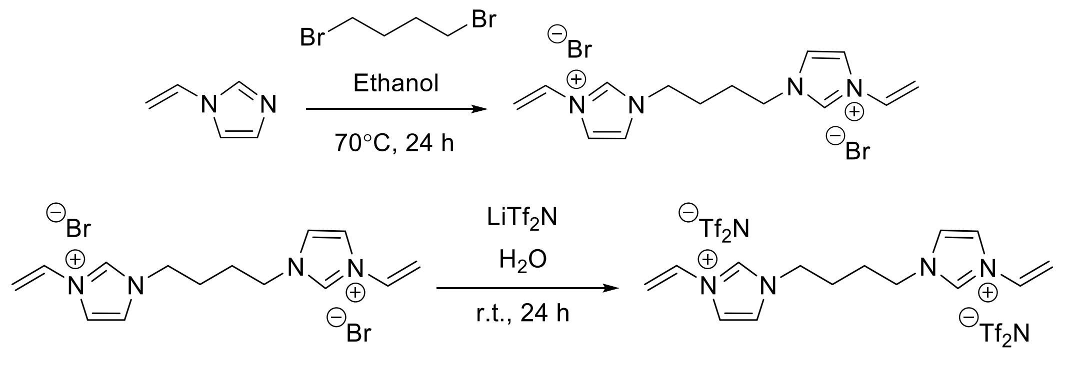
[$(VIM)_2C_4$] [Tf_2N]$_2$



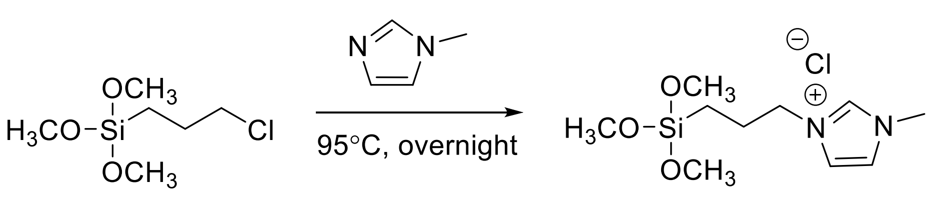
Cl^-ILSC

Figure S1. Chemical structures of reagents used to prepare PILs DN ion gels.

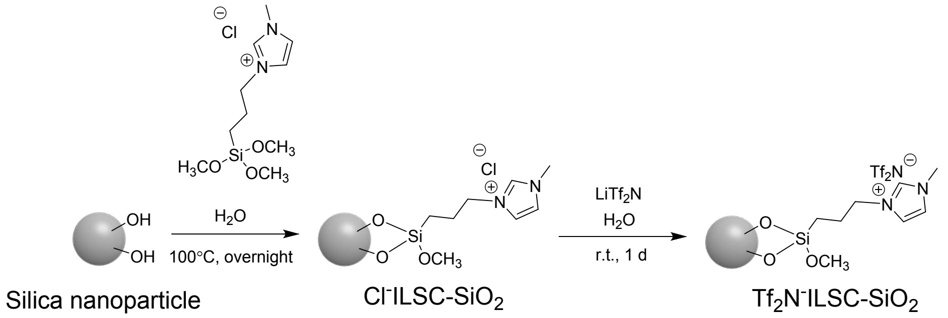
Scheme S1. Synthesis of [$(VIM)_2C_4$]Br_2 and [$(VIM)_2C_4$] [Tf_2N]$_2$.



Scheme S2. Synthesis of Cl^-ILSC.



Scheme S3. Preparation of Cl^-ILSC-SiO_2 and Tf_2N^-ILSC-SiO_2.



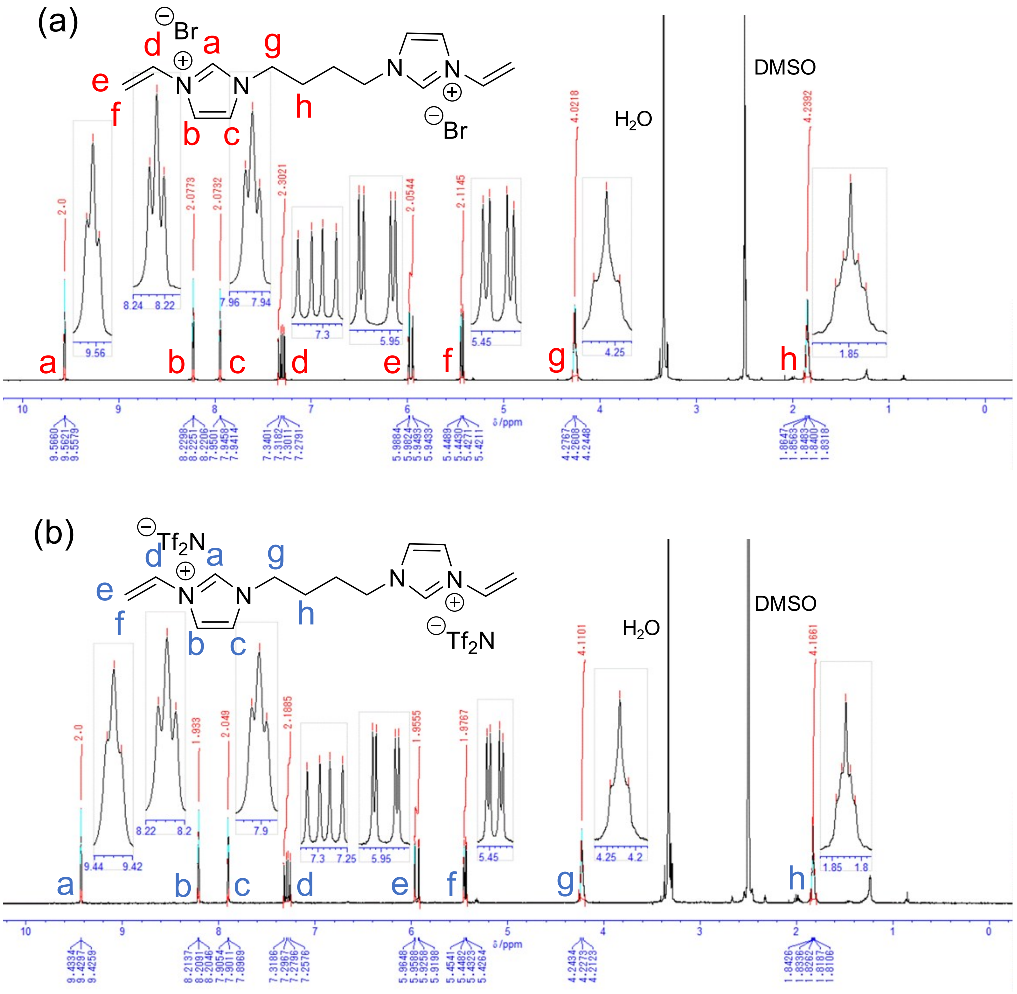


Figure S2. ^{1}H NMR spectra of **(a)** $[(VIM)_2C_4]Br_2$ and **(b)** $[(VIM)_2C_4]$ $[Tf_2N]_2$. (Solvent: DMSO-d_6).

$[(VIM)_2C_4]Br_2$: ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.56 (t, J =1.6 Hz, 2H), 8.23 (t, J =1.8 Hz, 2H), 7.95 (t, J = 1.7 Hz, 2H), 7.31 (dd, J = 15.6, 8.1 Hz, 2H), 5.97 (dd, J = 15.6, 2.4 Hz, 2H), 5.44 (dd, J = 8.7, 2.4 Hz, 2H), 4.26 (t, J = 6.3 Hz, 4H), 1.85 (q, J = 3.3 Hz, 4H). **$[(VIM)_2C_4]$ $[Tf_2N]_2$:** ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 9.43 (t, J = 1.5 Hz, 2H), 8.21 (t, J = 1.8 Hz, 2H), 7.90 (t, J = 1.7 Hz, 2H), 7.29 (dd, J = 15.6, 8.1 Hz, 2H), 5.94 (dd, J = 15.6, 2.4 Hz, 2H), 5.44 (dd, J = 8.7, 2.4 Hz, 2H), 4.23 (t, J = 6.3 Hz, 4H), 1.83 (q, J = 3.3 Hz, 4H).

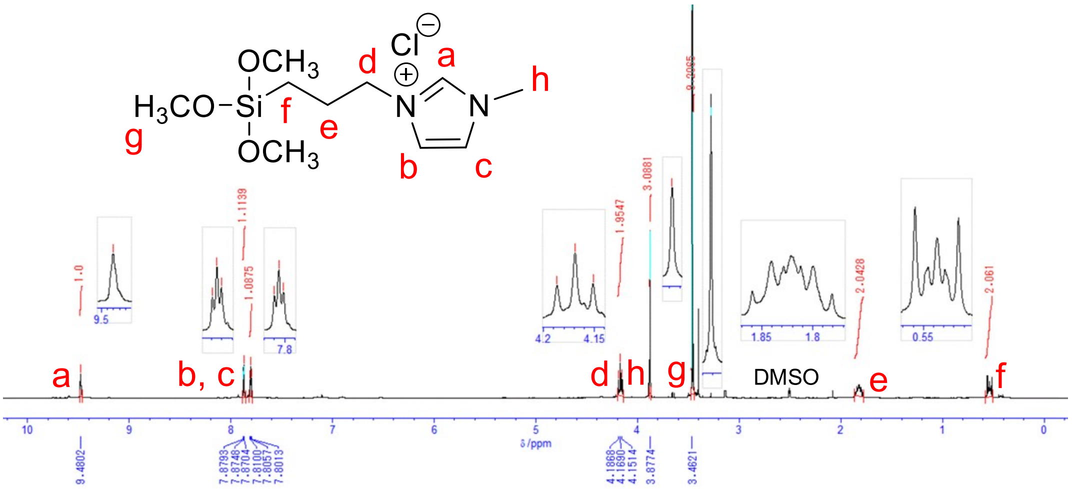


Figure S3. ^{1}H NMR spectrum of Cl$^-$ILSC. (Solvent: DMSO-d_6).

Cl$^-$ILSC: ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.48 (s, 1H), 7.87 (t, J = 1.7 Hz, 1H), 7.81 (t, J = 1.7 Hz, 1H), 4.17 (t, J = 7.1 Hz, 2H), 3.87 (s, 3H), 3.46 (s, 9H), 1.87-1.77 (m, 2H), 0.57-0.50 (m, 2H).

Characterisation of IL-modified silica nanoparticles.

To confirm the synthesis of IL-modified silica nanoparticles, we carried out FT-IR measurement and thermal gravimetric analysis of the products. **Figure S4** shows FT-IR spectra of silica nanoparticles, Cl$^-$ILSC-SiO$_2$, and Tf$_2$N$^-$ILSC-SiO$_2$. As shown in **Figure S4**, incorporation of Cl$^-$ILSC moiety into silica nanoparticles were confirmed by the presence of the bands at 1570 cm^{-1} assigned to a carbon-carbon double bond. Incorporation of Tf$_2$N$^-$ILSC moiety into silica nanoparticles were also confirmed by the presence of the bands at 1350 cm^{-1} assigned to S-N-S bond. **Figure S5** shows thermal gravimetric curves of silica nanoparticles, Cl$^-$ILSC-SiO$_2$, Tf$_2$N$^-$ILSC-SiO$_2$, Cl$^-$ILSC, and Tf$_2$N$^-$ILSC. As shown in **Figure S5**, all samples showed the first decomposition step below

200 °C. This decomposition step is assigned to the adsorbed water and other volatile compounds present in the systems. In the case of silica nanoparticles, the second decomposition step was shown in the range of 200−600 °C, which is due to dehydroxylation of internal and surface OH silanol group.[1] In the case of Cl^-ILSC-SiO_2, the second and third decomposition peaks at around 250 °C and 500 °C were detected, which corresponded to the IL moiety attached to the silica nanoparticle. Regarding Tf_2N^-ILSC-SiO_2, the second decomposition peak at around 400 °C was detected, which corresponded to the IL moiety attached to the silica nanoparticle. These results clearly showed that Cl^-ILSC-SiO_2 and Tf_2N^-ILSC-SiO_2 were successfully obtained.

Based on the thermal analysis results, we then estimated the proportion of the IL contents incorporated into silica nanoparticles. Specifically, we calculated the mass losses at 600 °C in the IL-modified silica nanoparticles and original silica nanoparticles and compared the difference between them (**Table S1**). We found that the amounts of incorporated IL in Cl^-ILSC-SiO_2 and Tf_2N^-ILSC-SiO_2 were approximately 8.5 and 16.0 wt%, respectively.

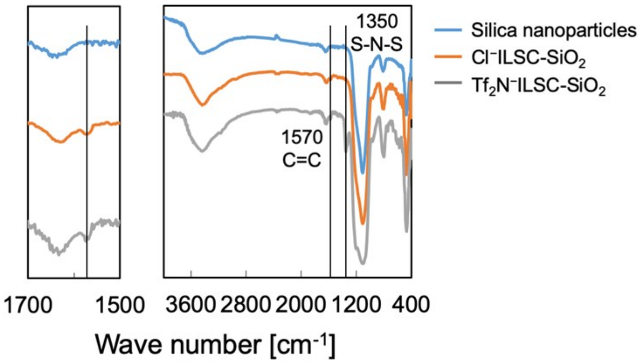


Figure S4. FT-IR spectra of silica nanoparticles, Cl^-ILSC-SiO_2, and Tf_2N^-ILSC-SiO_2.

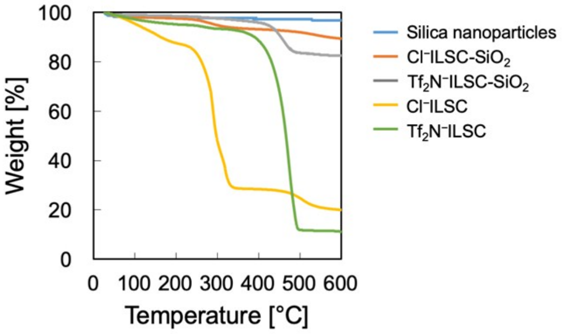


Figure S5. Thermal gravimetric curves of silica nanoparticles, Cl^-ILSC-SiO_2, Tf_2N^-ILSC-SiO_2, Cl^-ILSC, and Tf_2N^-ILSC.

Table S1. Results of thermal gravimetric analysis for silica nanoparticles, Cl^-ILSC-SiO_2, Tf_2N^-ILSC-SiO_2, Cl^-ILSC, and Tf_2N^-ILSC.

Sample	Weight loss at 600 °C [wt%]	IL content [wt%]	Decomposition temperature [°C]
Silica nanoparticles	3.2	0	–
Cl^-ILSC-SiO_2	11.7	8.5	–
Tf_2N^-ILSC-SiO_2	19.2	16.0	–
Cl^-ILSC	80.5	–	250 and 500
Tf_2N^-ILSC	89.4	–	400

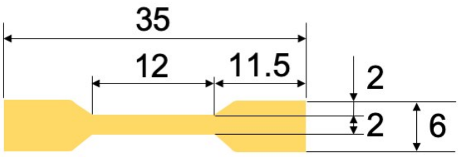


Figure S6. Geometry of a dumbbell-shaped specimen for mechanical property measurement of ion gels. The unit is millimeter.

Effect of the amount of ethyl acetate on the viscosity of silica nanoparticles/[Bmim][Tf_2N] dispersion.

To evaluate the effect of the amount of ethyl acetate on the fluidity of silica nanoparticles/[Bmim][Tf_2N] dispersion, we prepared silica nanoparticles/[Bmim][Tf_2N] dispersions containing different amount of ethyl acetate (0, 6, 11, 16, 20, 24, 28 wt%) and observed their bulk fluidity by the sample tube tilting method.[2] We found that when the amount of ethyl acetate was equal and larger than 16 wt% in the system, the silica nanoparticles/[Bmim][Tf_2N] dispersion kept sol state. Based on this result, we fixed the typical amount of ethyl acetate in the system at 20 wt%.

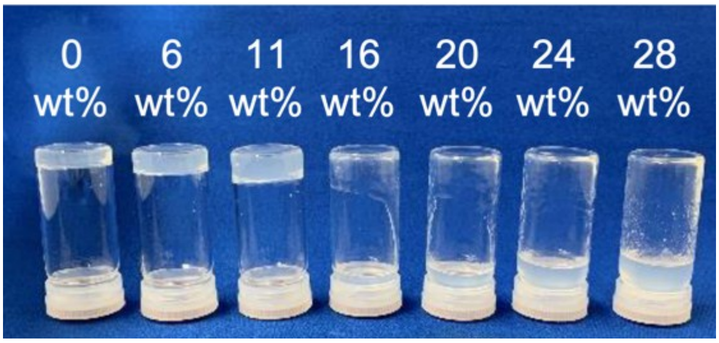


Figure S7. Photograph of silica nanoparticles/[Bmim][Tf_2N] dispersions containing different amounts of ethyl acetate.

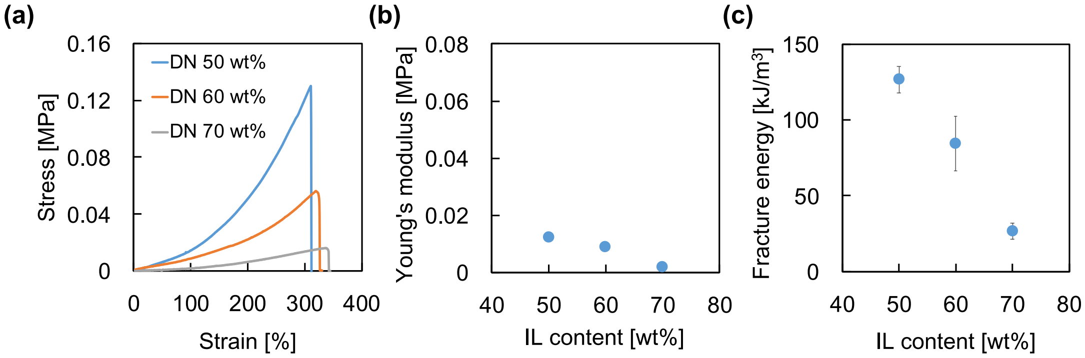


Figure S8. (a) Tensile stress-strain curves of the silica nanoparticles/PILs DN ion gels with different content of incorporated [Bmim][Tf_2N]. Changes in **(b)** the Young's modulus and **(c)** the fracture energy of silica nanoparticles/PILs DN ion gels as a function of incorporated content of [Bmim][Tf_2N]. In all ion gels, the cross-linker concentration was 0.5 mol% on monomer basis.

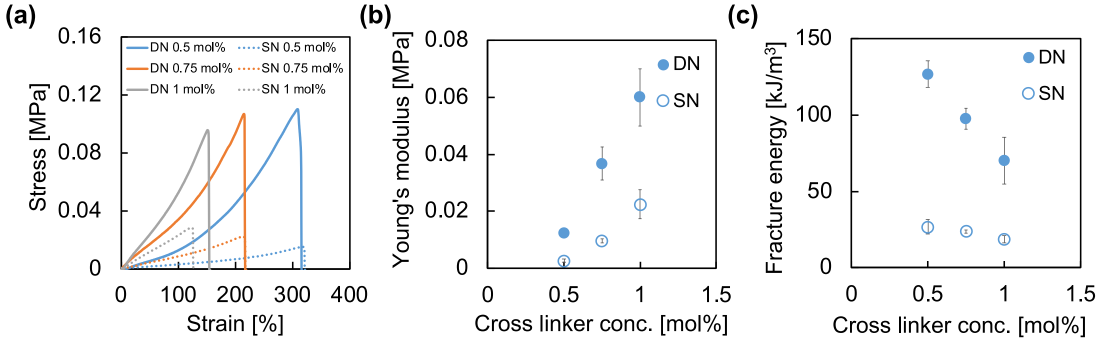
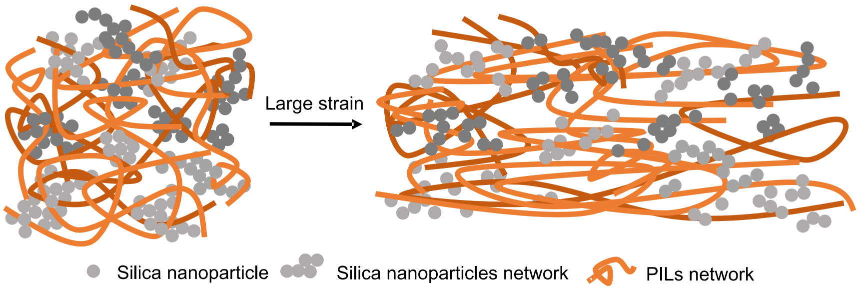


Figure S9. (a) Tensile stress-strain curves of the silica nanoparticles/PILs DN ion gels with different cross-linker concentrations. Changes in **(b)** the Young's modulus and **(c)** the fracture energy of silica nanoparticles/PILs DN ion gels as a function of cross-linker concentration. In all ion gels, the IL content was fixed at approximately 50 wt%.

Scheme S4. Schematic illustration of a toughening mechanism of silica nanoparticles/PILs DN ion gels when a large strain is induced.



References

[1] A. Bertora, M. Castellano, E. Marsano, M. Alessi, L. Conzatti, P. Stagnaro, G. Colucci, A. Priola, A. Turturro, *Macromol. Mater. Eng.* 2011, **296**, 455-464

[2] S. Malik, T. Jana, A. K. Nandi, *Macromolecules,* 2001, **34**, 275-282.