

SUPPORTING INFORMATION

Tough ion gels composed of coordinatively crosslinked polymer networks using ZIF-8 nanoparticles as multifunctional crosslinkers

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(1) Synthesis of poly(DMAAm-co-NSA) and PDMAAm

The poly(DMAAm-co-NSA) and PDMAAm used in this study were synthesized using RAFT polymerization. First, a sealed three-necked flask was purged with N₂ for 10 min, five times. Subsequently, a certain amount of 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN) was dissolved in a certain amount of 1,4-dioxane. The solution was then injected into a three-necked flask using a syringe. A mixture of DMAAm, NSA, and cellulose triacetate (CTA) was prepared in another vessel. In the case of the PDMAAm synthesis, NSA was not added to the mixture. The amounts of reagents used for the syntheses of poly(DMAAm-co-NSA) and PDMAAm are listed in Tables S1 and S2, respectively.

The mixture was then injected into a three-necked flask using a syringe. The obtained solution was purged with N₂ for 30 min under magnetic stirring. Subsequently, the three-necked flask containing the solution was heated in an oil bath at 333 K and continuously stirred for 24 h. The reaction product was dissolved in 100 g of THF and transferred into a 300 mL egg-plant flask for evaporation at 333 K for 2 h. The white precipitate was purified 2 times by reprecipitation using THF and hexane as good and poor solvents, respectively. The synthesized polymer was obtained after drying for 24 h at 373 K in a vacuum oven.

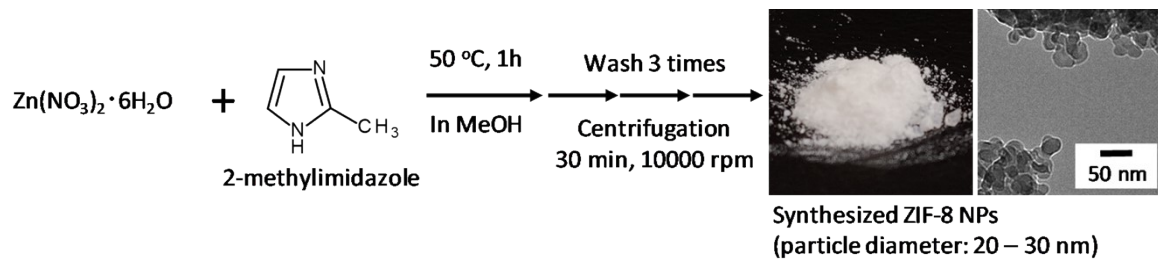
Table S1 Amounts of reagents used for the synthesis of poly(DMAAm-co-NSA).

Reagent	Amount (g)	Amount (mol)	Remarks (obtained polymer)
1,4-dioxane	40.0	4.5×10^{-1}	
DMAAm	20.0	2.0×10^{-1}	M_n 176 kg/mol, M_w 101 kg/mol, M_w/M_n 1.73
NSA	0.696	4.0×10^{-3}	Molar ratio of NSA was 2.0 mol%
ADVN	0.0020	8.0×10^{-6}	
CTA	0.0292	8.0×10^{-5}	

Table S2 Amounts of reagents used for the synthesis of PDMAAm.

Reagent	Amount (g)	Amount (mol)	Remarks (obtained polymer)
1,4-dioxane	10.0	1.1×10^{-1}	
DMAAm	5.0	0.5×10^{-1}	M_n 146 kg/mol, M_w 85 g/mol, M_w/M_n 1.70
ADVN	0.0050	2.0×10^{-6}	
CTA	0.0073	2.0×10^{-5}	

(2) Synthesis scheme of ZIF-8 NPs



Scheme S1 Synthesis procedure of ZIF-8 NPs at 323 K.

(3) FT-IR spectra of the amide I band of the PDMAAm/[Bmim][Tf₂N] solutions, with and without Zn(NO₃)₂·6H₂O

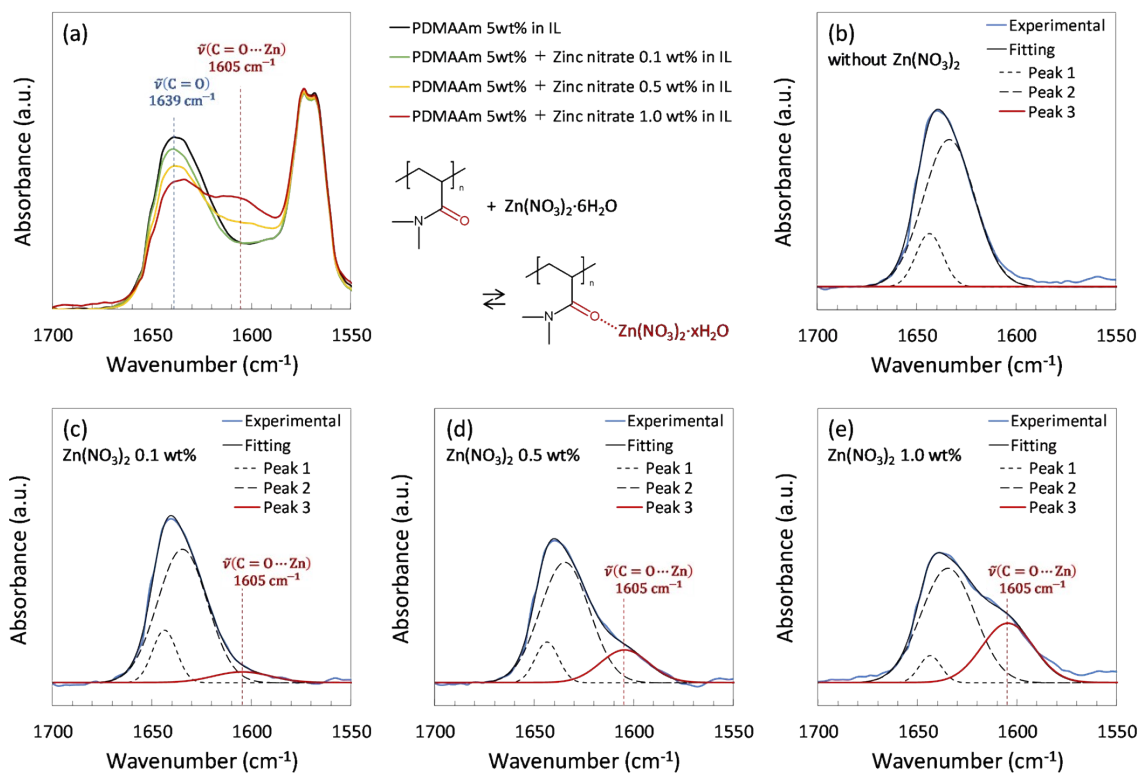


Figure S1 Normalized FTIR spectra of the Zn(NO₃)₂·6H₂O/PDMAAm/[Bmim][Tf₂N] solutions. (a) Zn(NO₃)₂·6H₂O concentration effect on the FT-IR spectra of the Zn(NO₃)₂·6H₂O/PDMAAm/[Bmim][Tf₂N] solution, (b) baseline-subtracted amide I band of the PDMAAm/[Bmim][Tf₂N] solution without Zn(NO₃)₂·6H₂O, and (c-e) baseline-subtracted amide I band of the Zn(NO₃)₂·6H₂O/PDMAAm/[Bmim][Tf₂N] solutions with different concentrations of Zn(NO₃)₂·6H₂O. The Peaks 1 and 2 shown in (b) - (e) could be assigned to the carbonyl groups that formed no hydrogen bonds and the carbonyl groups that are bounded to water molecule or IL molecule through a hydrogen bond, respectively.^{46,48} The Peak 3 in these figures is the carbonyl groups that are bounded to coordinatively unsaturated zinc on the surface of ZIF-8 NPs.

(4) Dispersion states of the ZIF-8 NPs in PDMAAm/[Bmim][Tf₂N]/EtOH and [Bmim][Tf₂N]/EtOH mixtures before and after EtOH removal

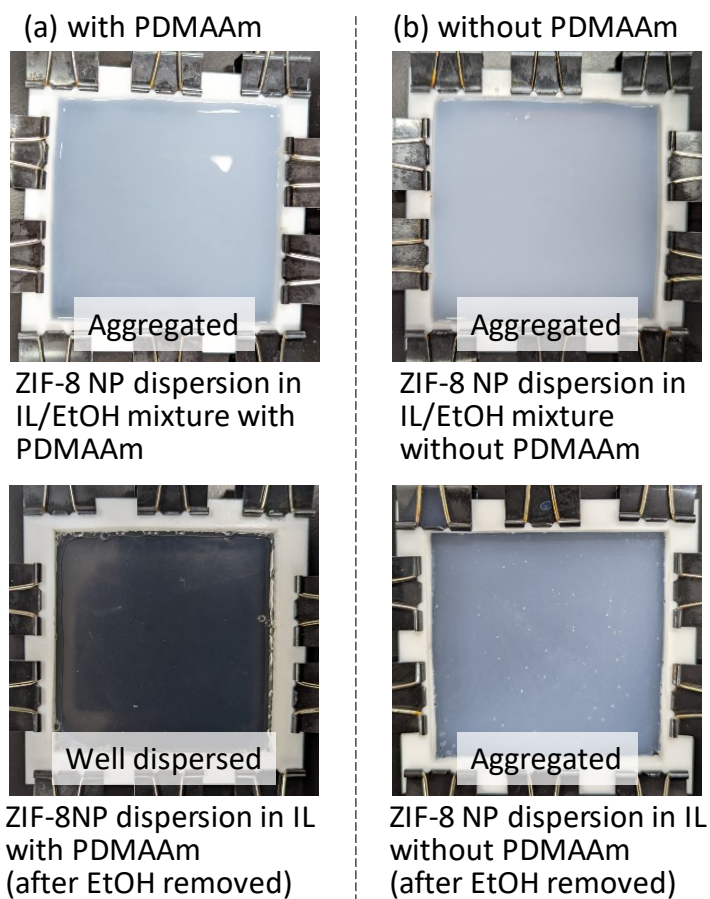


Figure S2 Dispersion states of the ZIF-8 NPs in (a) PDMAAm/[Bmim][Tf₂N]/EtOH mixture and (b) [Bmim][Tf₂N]/EtOH mixture before and after EtOH removal.

(5) Size distributions of the ZIF-8 NPs in [Bmim][Tf₂N], with and without PDMAAm

In this study, to evaluate the aggregated state of ZIF-8 nanoparticles in [Bmim][Tf₂N], the particle size distribution measurement was conducted by a static light scattering method using a nano particle size analyzer (SALD-7500nano, SHIMADZU Co., Japan). To evaluate the change in the size of ZIF-8 NPs caused by adding PDMAAm in the system, the particle size distributions of ZIF-8 NPs suspension in [Bmim][Tf₂N] with and without PDMAAm were measured. For the measurement, a high-concentration sample measurement system (SALD-HC75, optical path length: 50 μm, SHIMADZU Co. Japan) was used.

The ZIF-8 NP suspension in [Bmim][Tf₂N] without PDMAAm were prepared according to the following procedure. First, a ZIF-8/methanol suspension with a certain concentration of ZIF-8 NPs was added to [Bmim][Tf₂N]. Subsequently, the mixture was vigorously stirred at 60 °C for 1 hour. Then, it was heated at 60 °C for 12 hours under vacuum (less than 200 Pa) to remove methanol to obtain the ZIF-8 NP suspension in [Bmim][Tf₂N] without PDMAAm. The content of the ZIF-8 NPs was 5 wt%.

On the other hand, ZIF-8 NP suspension in [Bmim][Tf₂N] with PDMAAm was prepared according to the following procedure. First, the ZIF-8 NP suspension in [Bmim][Tf₂N] without PDMAAm was prepared in the same procedure shown above. It was added to a PDMAAm/ethanol solution and vigorously stirred. Then, ethanol was removed by heating the mixture at 60 °C for 24 hours under vacuum (less than 200 Pa) to obtain the ZIF-8 NP suspension in [Bmim][Tf₂N] with PDMAAm. The ZIF-8 NP content and PDMAAm concentration in the suspension were 5 wt% and 15 wt%, respectively.

The result shown in Figure S3 indicated that the size of ZIF-8 NPs decreased by adding PDMAAm. This would be due to the adsorption of PDMAAm on the surface of ZIF-8 NPs as a dispersion stabilizer.

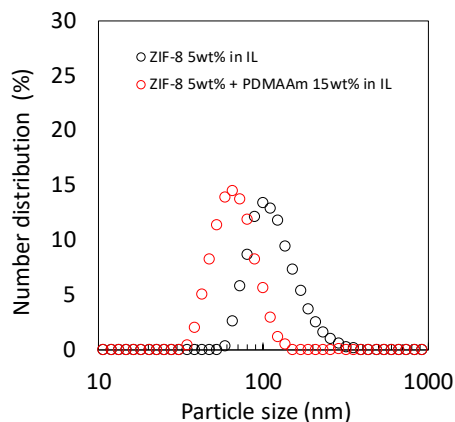


Figure S3 Size distributions of the ZIF-8 NPs in [Bmim][Tf₂N], with and without PDMAAm.

(6) XRD patterns of the ZIF-8 NP ion gel and ZIF-8 NPs synthesized at 333 K

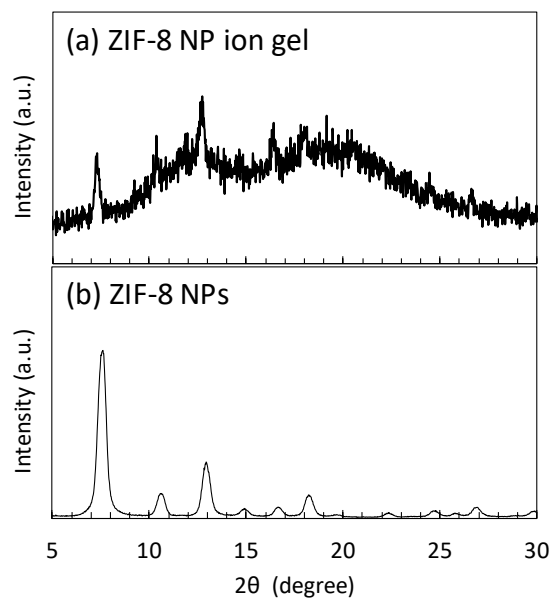


Figure S4 XRD patterns of the (a) ZIF-8 NP ion gel and (b) ZIF-8 NPs synthesized at 333 K, which was used to prepare the ZIF-8 NP ion gel.

(7) ZIF-8 NPs with different primary particle diameters synthesized at different temperatures

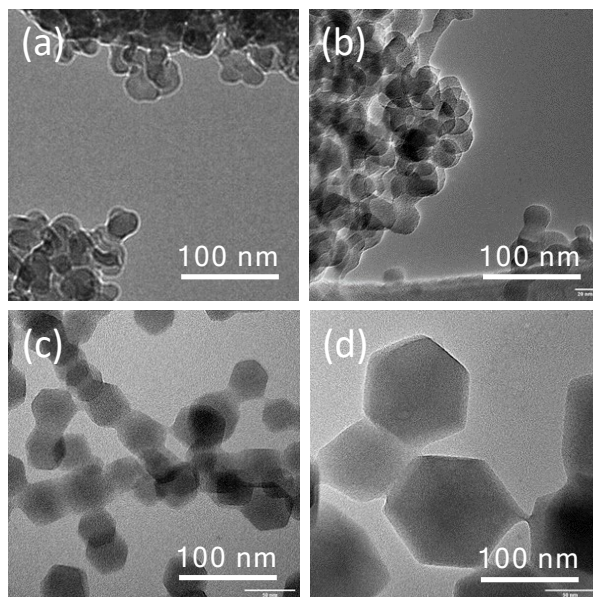


Figure S5 TEM images of the ZIF-8 NPs synthesized at different temperatures: (a) 323 K, (b) 303 K, (c) 273 K, and (d) 263 K. Primary particle diameters of the ZIF-8 NPs were (a) 17.5 nm, (b) 35.0 nm, (c) 47.5 nm, and (d) 120 nm.

(8) Uniaxial and cyclic tensile stress-strain curves of the ZIF-8 NP ion gels prepared using the ZIF-8 NPs with different primary particle sizes

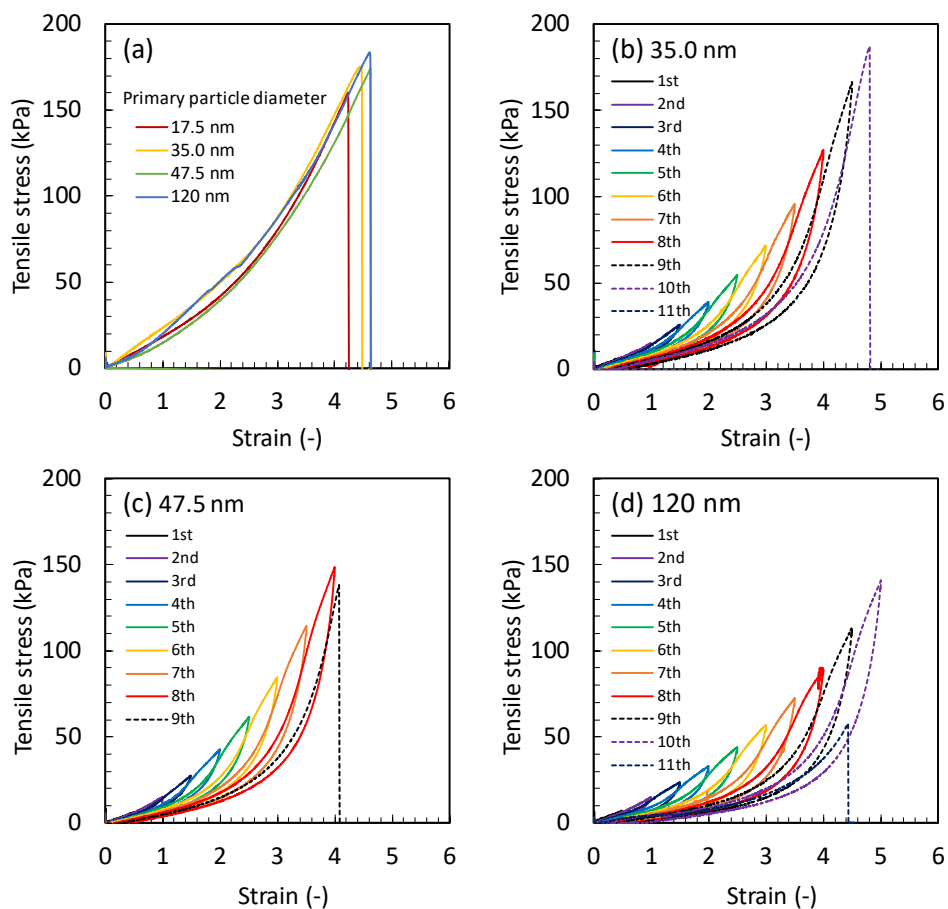


Figure S6 Mechanical properties of ZIF-8 NP ion gels prepared using ZIF-8 NPs with different primary particle diameters. (a) Uniaxial tensile stress-strain curves and (b-d) cyclic tensile stress-strain curves for the ion gels containing the ZIF-8 NPs with the primary particle diameter of 35.0 nm (b), 47.5 nm (c), and 120 nm (d).