**CHEMISTRY**

**Ionic liquid–based click-ionogels**

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Gels that are freeze-resistant and heat-resistant and have high ultimate tensile strength are desirable in practical applications owing to their potential in designing flexible energy storage devices, actuators, and sensors. Here, a simple method for fabricating ionic liquid (IL)–based click-ionogels using thiol–ene click chemistry under mild condition is reported. These click-ionogels continue to exhibit excellent mechanical properties and resilience after 10,000 fatigue cycles. Moreover, due to several unique properties of ILs, these click-ionogels exhibit high ionic conductivity, transparency, and nonflammability performance over a wide temperature range (−75° to 340°C). Click-ionogel–based triboelectric nanogenerators exhibit excellent mechanical, freeze-thaw, and heat stability. These promising features of click-ionogels will promote innovative applications in flexible and safe device design.

**INTRODUCTION**

Stretchable conductive materials can be used as stretchable components in resistive circuits or capacitive elements and have attracted extensive attention (1, 2) because of their potential uses in flexible energy storage devices, actuators, and sensors (3, 4). Extant stretchable conductive materials include conducting polymers (5), inorganic/organic compounds (6), and quasi-solid conductive gels (7). Among these materials, conductive hydrogels offer notable potential because of their tunable mechanical properties, relatively high electrical conductivity, and low interfacial resistance (8—10).

Hydrogels with outstanding strength and broad thermal compatibility are desirable for practical applications, and great progress in preparing tough hydrogels using a variety of strategies has occurred in the past decade (11—14). Among them, double-network (DN) hydrogels, which comprise a brittle initial sacrificial network and a tough and covalently cross-linked second network, show extraordinarily high elasticity and toughness (15, 16). Li et al. reported the preparation of alginate-polyacrylamide–based DN hydrogels, consisting of both ionic and covalently cross-linked polymeric networks. The prepared DN gel exhibited high elastic modulus and fracture energy (17). However, covalently cross-linked networks are typically obtained using free radical polymerization of vinyl monomers, which requires heating or ultraviolet (UV) light and anaerobic conditions (18). Moreover, Kami et al. reported that most DN gels are prepared using a two-step process, which forms inhomogeneous spatial network clusters within their respective parent gels, limiting the improvement of mechanical properties (19). Li et al. further pointed out that it is conducive to form a more homogeneous sacrificial network one-step process via controllable gelation, which improves the resilience and fracture energy of DN gels (20). Therefore, it is desirable to develop a one-step, controllable polymerization method to prepare DN gels under ambient conditions. In addition, most previously reported hydrogels freeze at subzero temperatures and dehydrate at high temperatures, and each of these behaviors severely limits their practical applications (21, 22). The use of an organic solvent system has enabled the fabrication of anti-freezing and nondrying hydrogels for long-term applications (23). However, the introduction of flammable organic solvent will bring potential fire and explosion hazards, especially at high temperatures. Therefore, freeze- and heat-resistant safe gels are desirable for practical applications.

Ionic liquids (ILs) are composed of cation-anion pairings of an organic ion and inorganic counterion (24—26). They have attracted a great deal of interest in academic research because of their unique physicochemical properties, such as high ionic conductivity, nonflammability, and thermal, electrochemical, and chemical stabilities (27, 28). Moreover, their freezing points can be tuned by adjusting the respective structures of these paired cations and anions. Poly(ionic liquid)s (PILs) are polymers whose backbones comprise IL monomers (repeat units) (19, 29). PILs combine polymer chain durability with small-molecule IL functionality and have received a considerable amount of attention in polymer and materials sciences.

Here, based on the concept of DN, we prepared IL click-ionogels under mild conditions. Ionic interactions between poly(1-butyl-3-vinyl imidazolium fluoroborate) (PIL-BF₄) and benzene tetracarboxylic acid (BTC) were selected to form a sacrificial network. Due to high reactivity, mild reaction conditions, and good selectivity, we demonstrate click chemistry to form a covalent network. Because of different gelation mechanisms, our synthesis of an ionic cross-linked network and a thiol-ene click network can be conducted simultaneously in a one-pot reaction scheme. These click-ionogels exhibit excellent mechanical properties and resilience even after 10,000 fatigue cycles. Moreover, due to several unique properties of ILs, these click-ionogels show excellent performance over a wide temperature range (−75° to 340°C), high ionic conductivity, transparency, and nonflammability. These attractive features suggest that click-ionogels will make good candidates for safe stretchable conductive materials.

**RESULTS AND DISCUSSION**

**Preparation of click-ionogels**

Figure 1 shows our preferred preparation method of click-ionogels based on a thiol-ene click reaction. Because many compounds are poorly soluble in ILs, methanol was used as the first solvent in this process. First, poly(ethylene glycol) diacrylate (PEGDA), pentaerythritol tetraacrylate (PETA; cross-linker for covalent network), and anionic BTC (cross-linker for the ionic bond network) were dissolved in methanol to obtain a homogeneous and transparent solution (solution A). Similarly, a mixture containing PIL-BF₄, triethylamine (TEA; a catalyst for the thiol-ene click reaction), and 1,2-ethanediol (ED) in methanol (solution B) was also prepared. When solutions A and...
B were mixed at room temperature, a gel formed, which was pre-conditioned by soaking in a room temperature IL at 80°C under vacuum for 24 hours. Here, a room temperature IL, 1-propyl-3-methylimidazolium fluoborate [IL-BF₄; melting point (m.p.) = −79°C, boiling point (b.p.) >300°C], was selected for the preparation of ionogels (table S1). The methanol (b.p. = 65.4°C) in the gel was removed (evaporated) and replaced by IL-BF₄ to form a tough and transparent click-ionogel (fig. S1). Varying the catalyst amount allowed the speed of the thiol-ene reaction to be adjusted from 240 min to 40 s, as shown in table S2. A very fast reaction speed inhibits any formation of a uniformly distributed ion-paired network and ultimately results in deteriorated mechanical properties. Hence, minimal amounts of catalysts (m<sub>TEA</sub>:m<sub>ED</sub> = 0.1) were used to control the click reaction rate and covalent network gelation time.

The TEA-catalyzed thiol-ene Michael addition reaction was monitored via Fourier transform infrared (FT-IR) spectroscopy and solid-state nuclear magnetic resonance (SSNMR). As shown in fig. S7, the peak at 1630 cm⁻¹ corresponding to the C=≡C bonds of PEGDA nearly disappeared after the click reaction (30). Similar results were observed in the SSNMR spectra. The peak of the C=≡C bonds disappeared after gelation, while the S—CH₂ bond at around...
2.5 parts per million (ppm) was observed (fig. S8). These results indicate that these click-ionogels had successfully formed. Considering that both FT-IR and SSNMR spectra are qualitative tests, a more accurate reaction conversion is further calculated on the basis of Wijs titration, following the Association of Official Analytical Chemists (AOAC) methods. As shown in fig. S9, iodine chloride was used for C=C bond saturation analysis and the consumed iodine was measured by titration with 0.1 M standard sodium thiosulfate solution. On the basis of the titration results and formulas, the conversion and cross-linking density (Mc) can be determined to be 99.3% and 6940 g mol⁻¹, respectively. These mild click gelation conditions give our click-ionogels outstanding processability and wide shape designability. Figure 1C shows that the click-ionogels can be readily designed to form different shapes, such as circles, butterfly, fish, flowers, and leaves, illustrating this latitude, and simple processing consisting of blending solutions A and B at room temperature.

**Mechanical properties of click-ionogels**

To meet the higher requirements of flexible devices, it is not only important but also challenging to accommodate large and reversible deformations of conductive gels. Superior mechanical properties of DN hydrogels have been attributed to both ionic bonds and covalent bond cross-linking that form such hybrid networks. To determine the role of each component in click-ionogels, ionic cross-linked gels (IC gels) and covalently cross-linked gels (CC gels) were prepared for comparison. As shown in Fig. 2 (B and C), the CC gels display high tensile stress but poor compressive strain behavior, with a failure tensile strain of 83% and a failure compressive strain of 28%. This is because there was no sacrificial network present to dissipate energy during deformation. In contrast, the IC gels, which lacked covalent cross-linking, showed soft and unrecoverable deformation with a failure tensile stress of 0.2 MPa and a failure compressive stress of 0.08 MPa. Click-ionogels combine the advantages of both IC and CC gels and exhibit enhanced mechanical properties with a failure tensile stress of 2.28 MPa at a strain of 1390% and a failure compressive stress of 23.7 MPa at a strain of 92%.

It should be noted that an ionic cross-linking network can be formed even if IL-BF₄ is used as a solvent. Although the storage modulus (G’) and loss modulus (G″) of IC gels decreased slightly after replacing methanol with IL-BF₄, G’ is dominant over G″ from 0.1 to 10 Hz, suggesting that the gelled state is maintained (fig. S10). Moreover, the interaction energy between polyacid-based BTCA and PIL-BF₄ (or IL-BF₄) was calculated via density functional theory (DFT), which showed that the interaction energy between BTCA
and PIL-BF₄ is higher than that between BTCA and IL-BF₄ (fig. S11). The higher BTCA/PIL-BF₄ interaction prevents IL-BF₄ from destroying the ionic cross-linking network via robust quadruple ionic cross-linking.

In addition, the optimal mechanical properties of ionogels were attained by tuning the contents of the IC network and the covalent cross-linking density of the CC network. Because of the existence of sacrificial bonds in the IC network, the stretchability and toughness of ionogels increase with the increase of the IC network content. However, an excessive amount of BTCA cannot be fully dissolved in methanol, which seriously diminished the mechanical properties and transparency of ionogels. Moreover, the covalent cross-linking density of the CC network, the molar ratio of PETA (cross-linker) to PEGDA (monomer), also significantly affected the mechanical properties of ionogels. As shown in table S3, smaller or higher cross-linking density is not conducive to improving the mechanical properties of the ionogels. When the molar ratio of PETA to PEGDA is lowered to 0.05, the obtained ionogels are soft and show poor fracture stress, while the ionogels become brittle at a molar ratio exceeding 0.2. The ionogels with optimal mechanical properties can be obtained at the molar ratio of 0.1. The IC network content is 78 mg/ml.

The resilience and cycling stability of these gels highly determine the durability of flexible devices. Here, the cyclic compressive tests of the click-ionogels showed that these gels are compressed with 70% strain without fracture and then recover nearly their original state after the force is removed (Fig. 2, A and D). Moreover, a small residual strain (approximately 3%) is observed, indicating the occurrence of an internal rupture of the IC network in ionogels. The IC network plays an indispensable role in improving resilience and durability of ionogels. When the ionogels undergo deformation, the ionic bonds between PIL-BF₄ and BTCA dissipate energy and quickly reform during unloading, which avoids the damage to the ionogel caused by external forces. Because of this coupled energy dissipation system, these click-ionogels also show excellent resilience even after being subjected to 10,000 compressive fatigue cycles (Fig. 2E).

### Anti-freezing properties of click-ionogels

Considering that all solvents have a freezing point, the elasticity of the gels will inevitably be influenced by temperature. Hydrogels tend to lose their elasticity at subzero temperatures since water freezes, which greatly limits their practical application at subzero temperatures. In this work, gels were formulated with low–freezing point IL-BF₄ as an antifreeze solution, and our click-ionogels showed an expected stable mechanical strength and elasticity at subzero temperatures. This behavior is illustrated in Fig. 3A and movie S1, where the click-ionogels can be stretched over the surface of liquid nitrogen (about −50°C). Figure 3(B and C) shows that when temperature decreased below −40°C, the click-ionogels still had more than 1000% stretching elasticity and 85% compressive strain. Figure 3D shows the storage moduli (G′) and loss moduli (G″) of these click-ionogels and hydrogels. When hydrogel temperature is decreased to the range of 0°C to −30°C, its storage modulus and loss modulus abruptly show an approximately 1000-fold increase, which indicates that the hydrogel froze. In contrast, the click-ionogels exhibited stable storage and loss moduli from −70°C to 200°C because IL-BF₄ has a low freezing point.

To more accurately determine thermal limits of low temperature freezing in these click-ionogels, differential scanning calorimetry (DSC) was done from −100°C to −20°C. For (water-based) hydrogels, a sharp peak was observed at 0°C, the melting point of bulk water. In contrast, these DSC results show that neat IL-BF₄ has a freezing point of −79°C, which is nearly consistent with that reported previously (31), and a glass transition temperature (Tg) of the dry (un-solvated) polymer occurs at −62°C. The thermogram of IL-BF₄ in the click-ionogels does not display a freezing peak and only showed a peak similar to a glass transition at −75°C.

This disappearance of a freezing point is consistent with IL-BF₄ being an effective solvent for similarly structured units in the PIL-BTCA network, which prevents any formation of a crystalline IL-BF₄ phase. In addition, a confinement effect on the IL in polymer networks has been observed in IL/poly(propylene oxide) composites and explained by a Gibbs-Thomson model and hydrogen-bonding interactions (32, 33). Because of their high electropositivity, the critical “active” hydrogens in the imidazolium cation (e.g., sites C-2, C-4, and C-5) can serve as hydrogen bond donors, while the electronegative oxygens in the PEGDA segments act as acceptors (Fig. 3F). As shown in Fig. 3G, the intensity of active hydrogens on imidazole decreases with the addition of PEGDA, and a new C−O−H bond peak is observed at about 3.1 ppm, indicating the formation of hydrogen bonds between IL-BF₄ and PEGDA segments. Because of the interaction, IL-BF₄ tends to form composite aggregates within a polymer network, which causes a transition temperature of the click-ionogel to lie between the freezing point of IL-BF₄ and the Tg of the polymer network. Therefore, our click-ionogels have not only good elasticity and high toughness but also outstanding anti-freezing properties down to −75°C.

### Thermal stability of click-ionogels

In addition to their anti-freezing properties, another important property of gels is their long-term thermal stability. Because the water in typical water-based hydrogels continuously evaporates, even at room temperature (22), their solvation under ambient conditions is a limiting design feature. The very low partial vapor pressure of IL-BF₄ allows these click-ionogels to exhibit long-term stability at temperatures above 100°C. With a further increase in temperature, the elastic modulus of these click-ionogels shows a slight decrease because the polymer chains have more mobility. However, these click-ionogels still have notable toughness and strength, with more than 1.5-MPa tensile strength and 15-MPa compressive strength, as shown in Fig. 4 (A and B) at 120°C. Figure 4C shows a long-term thermal stability of a hydrogel and a click-ionogels at 50° and 250°C, respectively. This hydrogel lost about 75 weight % (wt %) within half an hour at 50°C. In contrast, even after 5 days at 250°C, the weight of this click-ionogel remained constant, which indicates that click-ionogels have excellent high-temperature stability. The excellent mechanical properties of ionogels at high temperature come not only from the high–boiling point IL-BF₄ but also from a very strong interaction force between ILs and polymer chains. High temperature stimulates and activates random thermal motions of solvent molecules in the gel. In this case, the solvent will leach out of the polymer network and ultimately affect the mechanical properties of the gel, if there is a lack of interaction between the solvent molecule and the polymer chain. In addition, IL-BF₄ used in this work can form strong multiple hydrogen bonds with the polymer chains (Fig. 3G), providing the high-temperature thermal stability of the ionogels. Thermogravimetric analysis was used to further study the thermal stability of the click-ionogels. As shown in Fig. 4D, these click-ionogels have very
Fig. 3. Mechanical properties of anti-freezing click-ionogels at low temperatures. (A) Photographs of a click-ionogel stretched above liquid nitrogen (about −50°C). (B) Tensile stress-strain and (C) compressive stress-strain curves for the click-ionogels from −40° to 0°C. (D) Storage moduli ($G'$) and loss moduli ($G''$) of hydrogels from −30°C to 100° and the click-ionogels from −80° to 180°C. (E) Dynamic scanning calorimetry (DSC) results of neat IL-BF$_4$, dry polymer (drying the click-ionogel when the solvent is methanol), click-ionogel, and hydrogel between −100° and 20°C. The inset is the spectra enlargement of the dry polymer and click-ionogels. (F) Schematic hydrogen bonds between IL-BF$_4$ and PEGDA segments. (G)$^1$H NMR spectra of IL-BF$_4$, PEGDA, and IL-BF$_4$/PEGDA. Photo credit: Yongyuan Ren, Soochow University.
high decomposition temperatures, up to 343°C in air, which indicates that these click-ionogels could be used in service temperature applications greater than 250°C. On the basis of the results discussed above, it can be concluded that the prepared click-ionogels exhibit excellent performance over a wide temperature range (from −75°C to 340°C). Compared with the reported freeze/heat-resistant gels (listed in table S4), it is clear that our click-ionogel is a highly competitive candidate for freeze/heat-resistant conductive material.

In addition to this high-temperature stability, the nonflammability of IL/PIL further ensures thermal safety features of click-ionogels in practical applications. Flammable organogels [such as propylene carbonate (PC)– and ethylene glycol (EG)–based gels] are often used as electrolytes in electronic devices, which brings potential safety hazards such as fire and explosion. As shown in fig. S12 and movie S2, the PC- and EG-based organogels were ignited in only a few seconds, followed by a slight burst and a lot of smoke. However, even after being exposed to flames for 30 s, these click-ionogels could not be ignited, and only some charring was observed, likely due to the decomposition of the click-ionogels at high temperatures. Therefore, these heat-resistant and nonflammable click-ionogels show both excellent mechanical performance and flame retardancy over a wide temperature range.

Applications in triboelectric nanogenerator devices
In addition to having excellent mechanical properties at both low and high temperatures, it is important in some applications for these click-ionogels to have high electrical conductivities. Here, the conductivity \( \sigma = L/(SR) \); \( L, S, \) and \( R \) correspond to the thickness, effective overlap area, and resistance of click-ionogels, respectively] of these click-ionogels was investigated between −60°C and 200°C. As shown in fig. S13, abundant pores were formed after drying-out treatment, while the pores disappeared completely after soaking in IL-BF\(_4\). A porous structure facilitates the filling of more IL-BF\(_4\) in polymer networks, and the smooth surface of ionogel indicates that IL-BF\(_4\) has a good affinity with polymer networks. Both of them are conducive for improving the conductivity of ionogels. As shown in Fig. 5A, the conductivity of the click-ionogels designed in this study is about 0.83 S m\(^{-1}\) at room temperature. This conductivity increases as temperature increases because the viscosity of ILs decreases at higher temperatures (163 cP at 10°C and 24 cP at 70°C), which leads to more rapid ion transport and higher conductivity.

In addition to electrical conductivity, it is also important for gels to have a stable and wide electrochemical window. For example, aqueous supercapacitors and zinc-ion batteries have relatively small electrochemical windows (usually <1.0 V), which severely limits their output voltage and energy density. To measure a decomposition voltage of these click-ionogels, linear sweep voltammetry was performed at a scan rate of 0.5 mV/s from 0 to 5.0 V. Figure 5B shows that the measured hydrogel current increased sharply when an applied voltage exceeds ~1.5 V, accompanied by bubble generation on the interfaces of the electrodes. Such bubble formation indicates electrolysis of water in the hydrogel. In contrast, the click-ionogels exhibit a much higher decomposition voltage at about 3.5 V due to well-known high electrochemical stability of IL-BF\(_4\), which meets the voltage requirements for most electronic devices (e.g., lithium-sulfur batteries, zinc-ion batteries, and supercapacitors).

Recently developed triboelectric nanogenerators (TENGs), which convert mechanical energy to electricity by exploiting a coupling
effect of contact electrification and electrostatic induction (Fig. 5C), have advantages of simple structures, low cost, and many material design choices (34–37). To further explore an application of click-ionogels in electronic devices, a flexible TENG was prepared by using an elastomer (Very High Bond, VHB) and click-ionogels as an electrification layer and electrode, respectively (Fig. 5C). Because of the excellent stretchability and flexibility of click-ionogels and VHB, the prepared TENG exhibited outstanding mechanical properties when stretched and...
bent (Fig. 5, D and E) and corresponding electrical outputs were recorded when polyamides experienced contact-separation motion relative to the VHB. Energy harvesting and stability of a resulting TENG were evaluated under extreme conditions, such as large deformations, low temperature, and high temperature. An instantaneous peak value of an ac current was about 0.1 μA/cm² at room temperature, which is close to the value reported in a previous study that used a hydrogel as an electrode (38). Compared with the original state without strain, the output current of the TENG (Fig. 5F) is greatly improved from ~0.05 to ~0.2 μA after being stretched to 500%, which was attributed to an increase in the contact area for the electriication as the surface area of the device increased under tension. In contrast, because the effective contact area between polyamides and VHB did not change, the device exhibited a stable output current even when it was bent and twisted, as shown in Fig. 5G.

In addition, operating temperature ranges of previously reported TENGs that use hydrogels, such as polyvinyl alcohol and alginate gels as the electrodes, are seriously limited by water freezing and evaporation. Although hydrogels are encapsulated in VHB tape to reduce water evaporation, water vapor bubbles inside the TENG have been observed when polyamides experienced contact-separation motion relative to the VHB. Energy harvesting and stability of a resulting TENG were evaluated under extreme conditions, such as large deformations, low temperature, and high temperature. An instantaneous peak value of an ac current was about 0.1 μA/cm² at room temperature, which is close to the value reported in a previous study that used a hydrogel as an electrode (38). Compared with the original state without strain, the output current of the TENG (Fig. 5F) is greatly improved from ~0.05 to ~0.2 μA after being stretched to 500%, which was attributed to an increase in the contact area for the electriication as the surface area of the device increased under tension. In contrast, because the effective contact area between polyamides and VHB did not change, the device exhibited a stable output current even when it was bent and twisted, as shown in Fig. 5G.

CONCLUSION
A click-reaction process that introduces click-ionogels prepared under ambient conditions in a single step has been demonstrated. Because thiol-ene click chemistry is highly efficient under mild conditions, the click-ionogels can be readily prepared by simply blending two solutions, without additional oxygen, humidity, or heating requirements. This simplicity will enable shape-design and large-scale production. The prepared click-ionogels continue to exhibit excellent mechanical properties and resilience after 10,000 fatigue cycles. Moreover, due to several unique properties of ILS and the formation of a hydrogen bond between IL-BF₄ and polymer network, the click-ionogels show high electrical conductivity, broad thermal compatibility (~75°C to 340°C), good optical transparency, and non-flammability. Because of these properties, these click-ionogels have promising applications in various electrical devices, including flexible sensors, energy storage, and electronic skin.

MATERIALS AND METHODS
Synthesis of IL monomer
A mixture containing 1-vinyl imidazole (10.34 g, 0.11 mol) and 1-bromobutane (13.7 g, 0.10 mol) was stirred at room temperature for 3 days. The synthesized 1-butyl-3-vinyl imidazolium bromide (BVIm-Br) was washed with diethyl ether three times and then dried under vacuum at 25°C for 12 hours to give a colorless transparent liquid (16.78 g, yield: 72.6%).

A solution of BVIm-Br (3.47 g, 1.50 mmol) in water was added to NH₄BF₄ (1.78 g, 1.70 mmol) solution and stirred for 5 hours at room temperature. Then, the solution was extracted with dichloromethane three times. The combined organic phase was washed with water and then dried by MgSO₄ and spin evaporation to give the yellowish transparent liquid 1-butyl-3-vinyl imidazolium fluoborate (BVIm-BF₄) (0.32 g, yield: 32.4%).¹H NMR (400 MHz, DMSO-d₆ (ppm)): 9.5 (s, 1H, N═CH═N), 8.2 (s, 1H, CH═CH═N), 7.8 (s, 1H, CH═CH═N), 7.2 (m, 1H, N─CH═CH₂), 5.9 (d, 1H, N─CH═CH), 5.3 (d, 1H, N─CH═CH), 4.2 (m, 2H, N─CH₂─CH₂), 1.7 (m, 2H, CH₂─CH₂─CH₂), 1.3 (m, 2H, CH₂─CH₂─CH₂), 0.7 (m, 3H, CH₃─CH₃) (fig. S2).

The similar procedure was used for synthesizing 1-propyl-3-methylimidazolium fluoborate (IL-BF₄).¹H NMR (400 MHz, DMSO-d₆ (ppm)): 9.2 (s, 1H, CH═CH═N), 7.8 (d, 1H, CH═CH═N), 4.2 (m, 2H, N─CH₂─CH₂), 3.7 (m, 3H, N─CH₃), 1.8 (m, 2H, CH₂─CH₂─CH₂), 0.8 (m, 3H, CH₃─CH₃) (fig. S3).

Synthesis of poly(BVIm fluoborate)
A mixture containing BVIm-BF₄ (0.223 g, 1.0 mmol) and 2,2-azobisisobutyronitrile (AIBN) (8.7 mg, 0.05 mmol) was stirred in dried dimethyl formamide (DMF) at 60°C for 24 hours. The resultant raw product was purified by precipitating into dichloromethane three times to remove unreacted BVIm-BF₄, and then dried in a vacuum oven at 60°C for 12 hours.¹H NMR (400 MHz, DMSO-d₆ (ppm)): 9.5 (s, 1H, N═CH═N), 7.8 (d, 1H, CH═CH═N), 4.1 (m, 2H, N─CH₂─CH₂), 1.7 (m, 2H, CH₂─CH₂─CH₂), 1.3 (m, 2H, CH₂─CH₂─CH₂), 0.7 (m, 3H, CH₃─CH₃) (fig. S4).

Preparation of ionic cross-linked gels
The ionic bond cross-linked gels were prepared according to the following procedure: 100 mg of PIL-BF₄ was dissolved in 2 ml of IL-BF₄, and then BTCA (25.4 mg, 0.11 mmol) was added to the solution under vigorous stirring to form the IC gels through electrostatic interactions between the cationic PIL-BF₄ and the anionic BTCA (fig. S5).

Preparation of covalently cross-linked gels (CC gels)
For the synthesis of covalent cross-linked gels, PEGDA (0.6 g, 1 mmol), PETA (43.8 mg, 0.1 mmol), and TEA (11.0 mg, 0.11 mmol) were dissolved in 0.65 ml of methanol. Then, ED (112.8 mg, 1.2 mmol) was added to the mixture under vigorous stirring, and the gelation time was checked by tube inversion method (fig. S6). In this system, the gelation time can be controlled from 40 s to 240 min, depending on the amount of catalyst added (table S1). Subsequently, the obtained gel was soaked in IL-BF₄ and then dried at 80°C under vacuum for 24 hours to displace methanol with IL-BF₄ to obtain CC gels. A similar procedure was used for preparing PC organogels and EG organogels.

Preparation of click-ionogels
The preparation method of click-ionogels is similar to AB glue. First, PEGDA (0.6 g, 1 mmol), PETA (43.8 g, 0.1 mmol), and BTCA (12.7 g, 0.05 mmol) were thoroughly dissolved in 0.4 ml of methanol to obtain a homogeneous and transparent solution, namely, precursor solution A. Similarly, 50 mg of PIL-BF₄, TEA (11 mg, 0.11 mmol), and ED (112.8 mg, 1.2 mmol) were dissolved in 0.4 ml of methanol to obtain a homogeneous transparent solution, namely,
precursor solution B. Then, the mixture of precursor solutions A and B \((V_A/V_B = 1)\) was poured into the mold and the gelation reaction was conducted at room temperature for 3 hours. Subsequently, the obtained gel was soaked in IL-BF\(_4\) and then dried at 80°C under vacuum for 24 hours to displace methanol with IL-BF\(_4\). The IL content of the click-ionogel is about 53 wt %.

**Preparation of hydrogels**

Polyacrylamide (PAAm) hydrogels were used as references. PAAM hydrogels were prepared by being mixed with the mixture of 1 mmol acrylamide (Aam), 0.01 mmol N-methylene bisacrylamide, and 0.01 mmol ammonium peroxodisulfate to 1.4 mL of water and by heating at 70°C for 6 hours.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/8/eaax0648/DC1

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