

Hierarchically Crosslinked Gels Containing Hydrophobic Ionic Liquids towards Reliable Sensing Applications

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Electronic Supplementary Information

Abstract Human skin can function steadily regardless of surrounding circumstances (dry or wet), while it is still a challenge for artificial ionic skins, which tend to release solvents in dry air and leach electrolytes in wetted state. Herein, a series of hierarchically crosslinked ionogels containing hydrophobic ionic liquids (ILs) is fabricated by combining a crystalline fluorinated copolymer with hydrophobic ILs. With a reasonable combination of nonvolatility, transparency, stretchability, and sensitivity, such ionogels can work as reliable sensors for real-time monitoring human motions and operate steadily in complex environments as human skin does, which can contribute to the development of durable sensing devices with a simple design.

Keywords Ionogels; Conductivity; Hydrophobicity; Strain sensors

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INTRODUCTION

Human skin is a soft and stretchable natural tissue with distributed sensors toward external stimuli. The properties of our skin have inspired people to develop various flexible and wearable devices for on-body sensing, healthcare monitoring, and human-machine interaction.^[1–3] Existing sensing devices are mostly based on electronic conductors (e.g., metals, graphene sheets, and carbon nanotubes) or semiconductors (e.g., silicon), which meet the essential requirements of conductivity and sensitivity, but struggle to satisfy additional demands like stretchability and transparency.^[4] Recently, ionic conductors have been adapted as a new type of sensing materials.^[4–7] In particular, hydrogels containing electrolytes allow long-distance ionic migration and offer a unique combination of conductivity, transparency, softness, and stretchability.^[8–10] They have exhibited great promise in wearable skin-like sensors, including strain sensors, pressure sensors, and touch panels.^[6,11,12] When being used, nevertheless, these ionic conductors tend to dehydrate in open air and leach electrolytes once in contact with an aqueous phase (e.g., human sweat and rainwater), leading to an irrevers-

ible recession in their composition and performance.^[13–15] Although these problems can be alleviated by wrapping the ionic conductors with a barrier layer, it may cause other problems like interfacial mismatches and complicated structures.^[16,17]

Rather than surface modification, enhancing the intrinsic stability of an ionic conductor is more convenient and it can contribute to the manufacture of a reliable sensing device with a simple design. To achieve an ionic conductor capable of tolerating both dry and wet conditions, two criteria must be satisfied: (i) solvent evaporation should be minimized; (ii) all components including electrolytes must be hydrophobic. Whereas hydrogel-based ionic conductors hardly meet these requirements, ionogels may have an opportunity to do so. An ionogel is a three-dimensional polymeric network that hosts an ionic liquid (IL) as both solvent and electrolyte.^[18,19] Unlike conventional solvents, ILs are nearly non-volatile even in vacuum.^[19,20] Besides, the affinity of an IL to water is highly tunable through choosing the pairing of cation and anion.^[21,22] Hydrophobic ILs derived in this manner have been applied in a series of electronic applications, such as moisture-tolerant lithium-air batteries.^[23]

Herein, we utilize a hierarchically crosslinked hydrophobic ionogels composed of poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) and 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_nMIm][NTf₂]) (Fig. 1a) towards reliable sensing applications. PVDF-HFP is a fluorinated copolymer containing two monomer units and its crystallin-

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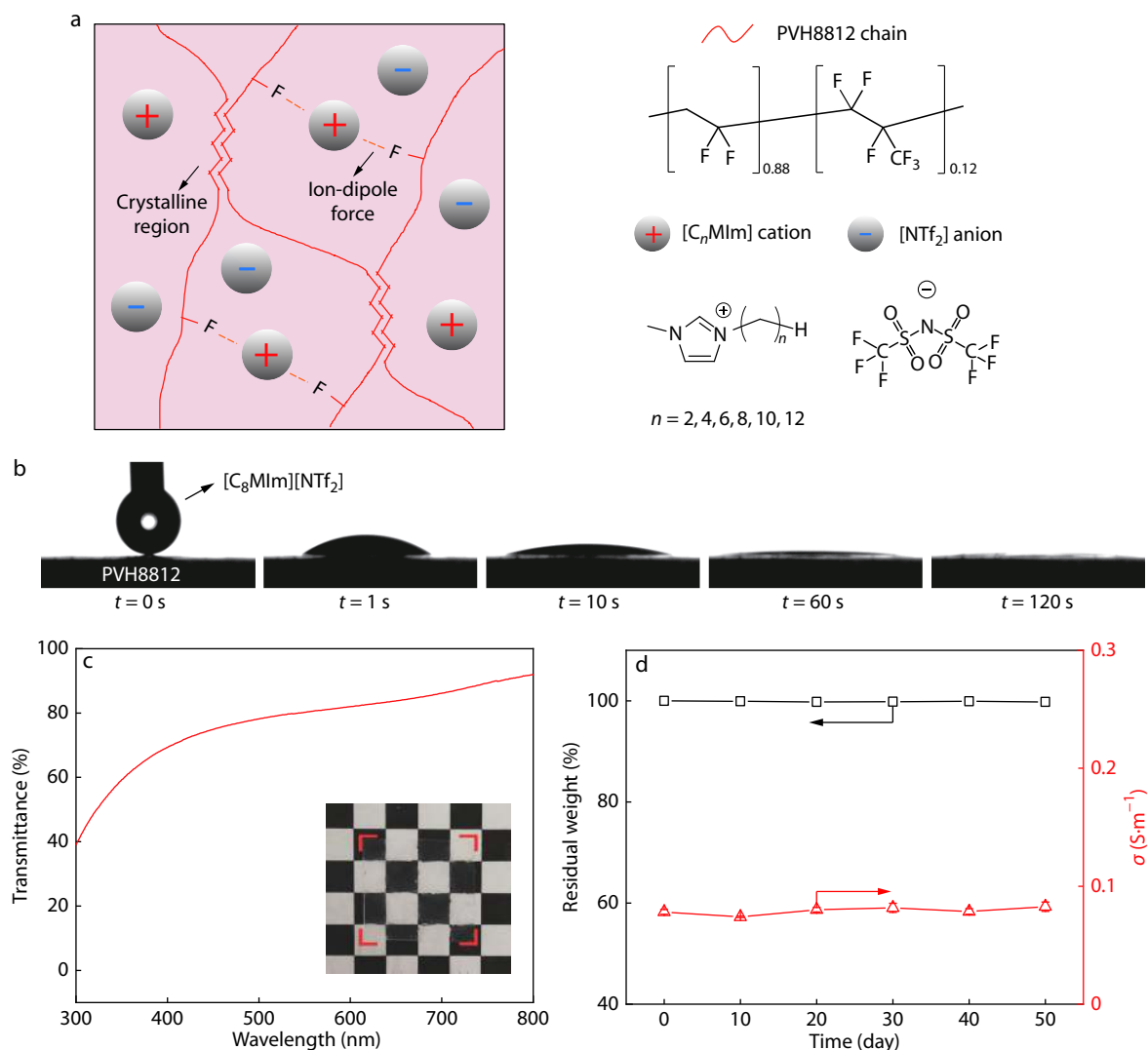


Fig. 1 (a) Schematic illustration of the intermolecular interactions within a PVH8812/[C_nMIm][NTf₂] ionogel. The regional crystalline structures of PVH8812 can form strong interchain interactions within ionogels and provide essential mechanical strength. The polar groups along its main chain can interact with cation *via* ion-dipole interaction, making this polymer compatible with [C_nMIm][NTf₂] and forming relatively weak interchain interactions. (b) A droplet of 0.5 μL [C₈MIm][NTf₂] quickly spreading on a PVH8812 film, indicating the strong affinity between PVH8812 and [C_nMIm][NTf₂]. (c) Transmittance spectrum and photograph of a 200-μm-thick PVH8812/[C₈MIm][NTf₂] ionogel. (d) The weight and ionic conductivity of a PVH8812/[C₈MIm][NTf₂] ionogel keeping almost invariant for at least 50 days, indicating an excellent long-term stability.

ity can be regulated through the ratio of HFP monomer.^[24,25] With a HFP ratio of 12%, PVDF-HFP copolymer (PVH8812) is highly crystalline in bulk state and remains partially crystalline in the presence of ILs. The crystallization effect of PVH8812 can form strong interchain interactions within ionogels and provide essential mechanical strength (Fig. 1a). On the other hand, the polar fluoride groups along its main chains can interact with [C_nMIm]⁺ cation *via* ion-dipole interaction, making this polymer compatible with [C_nMIm][NTf₂] (Fig. 1a). The conductivity of such ionogels can be highly tunable and exhibit an excellent long-term stability. Owing to the hydrophobic property of these ionogels, the effect of water on their sensing performance can be negligible, even when coming into direct contact. To the best of our knowledge, this is the first report of applying hydrophobic

ionogels as strain sensors. Such sensing materials can be made into a wearable form and monitor human motions steadily in both dry and wet conditions. These properties make them usable directly in an open environment and contribute to building a simple but durable sensing device.

EXPERIMENTAL

Materials

PVH8812 (M_w 4.0×10^5) was purchased from Sigma-Aldrich. PVH5545 (Dyneon FC 2230) was purchased from 3M. The ILs used in this study were obtained from Lanzhou Yulu Fine Chemical Co., Ltd. (China). Anhydrous acetone was purchased from Beijing Chemical Works (China). All materials were used as received.

Fabrication of Ionogels

Polymer solution was prepared by dissolving 0.5 g of PVDF-HFP in 50 mL of acetone at 50 °C. Then, a certain amount of IL was added into the polymer solution under stirring to give a clear solution. Subsequently, the mixture was poured onto a precleaned glass plate. After evaporating the solvent at room temperature for 3 h, the sample was placed in a drying oven at 80 °C for 1 h to further remove the residual solvent. Subsequently, the resulting ionogel was detached from the substrate and cut into required sizes for further characterizations.

Characterization

Scanning electron microscopy (SEM, Hitachi SU8010, Japan) was performed to reveal the surface morphologies of samples as needed. Mechanical properties of samples were tested using a single-column force tester (Mark-10 ESM301, USA) equipped with a 250 N load cell. The conductivity of pure ILs was measured by a conductivity meter (INESA DDS-11A, China). The conductivity of ionogels was determined by using a four-probe resistivity measurement system (Probes tech Co., Ltd. China). Differential scanning calorimetry (DSC, TA Instruments Q2000, USA) was carried out under a nitrogen atmosphere. The samples were cooled to −120 °C followed by heating to 200 °C at a constant rate of 10 °C·min^{−1}. A stepper machine (Thorlabs LTS150/M, USA) was used to stretch or bend samples with one end fixed and the other end travelling at a certain speed. An electrochemical analyzer (Chenhua CHI660E, China) was connected to the samples through two wires and record the changes of electric current during the stretching or bending experiments. The transmittance of samples was recorded using an UV-Vis spectrophotometer (Shimadzu UV-2600, Japan). The intermolecular interactions within various samples were studied by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Varian Excalibur 3100, USA) and X-ray diffraction (XRD, Bruker D8 focus, Germany).

RESULTS AND DISCUSSION

PVH8812/[C_nMIm][NTf₂] ionogels were prepared by a casting method with a transparent solution of PVH8812 and [C_nMIm][NTf₂] in acetone. After removing acetone *via* evaporation, gel-like materials without microscale phase separations formed spontaneously (Fig. S1 in the electronic supplementary information, ESI). This is ascribed to the strong affinity between PVH8812 and [C_nMIm][NTf₂], which is intuitively demonstrated by the spontaneous spreading of a [C₈MIm][NTf₂] droplet on a PVH8812 film (Fig. 1b). When a [C₈MIm][NTf₂] content of 1.0 mmol·g^{−1} (the molar number of IL per gram of polymer, n_{IL}/m_p) was adopted, the optical transmittance of a 200-μm-thick ionogel reached up to 80.5% at 554 nm (Fig. 1c). Unlike hydrogels, these ionogels were nearly non-volatile and exhibited an excellent long-term stability. As shown in Fig. 1(d), a PVH8812/[C₈MIm][NTf₂] ionogel could maintain its weight and ionic conductivity for over 50 days without any protective packaging. The addition of ILs can plasticize the polymer matrix and make the resulting compound soft and flexible. Meanwhile, there was no visible leakage of IL out of the ionogel even when the concentration of [C₈MIm][NTf₂] was as high as 82.6 wt%, indicating a benign compatibility between PVH8812 and [C_nMIm][NTf₂]. These materials can be quite useful for building

wearable electroluminescent devices, where flexible, transparent conductors are essential to apply voltage and let light out.

The physical properties of imidazolium-based ILs can be tuned by selecting anion and substituents.^[21,22] Choosing different ILs, the affinity of ionogels to water can be effectively regulated.^[24,26] As shown in Fig. 2(a), water droplets were pinned to the surfaces of ionogels containing hydrophilic [C₂MIm][BF₄]. At the same tilting angle (30°), a water droplet could slide off from an ionogel with hydrophobic [C₂MIm][NTf₂]. Quantitative analysis of the water affinities of these materials is shown in Figs. 2(b) and 2(c). With the same n_{IL}/m_p value of 0.6 mmol·g^{−1}, the water contact angle of an ionogel with hydrophilic [C₂MIm][BF₄] was much lower than those of ionogels with hydrophobic [C_nMIm][NTf₂] (Fig. 2b). Water droplets (10 μL) did not slide off from the samples with a hydrophilic IL ($n_{IL}/m_p = 0.6$ mmol·g^{−1}), even they were vertically positioned, while the sliding angle of water on a PVH8812/[C₂MIm][NTf₂] ionogel ($n_{IL}/m_p = 0.6$ mmol·g^{−1}) was only 26.6° (Fig. 2c). The water affinity of hydrophobic ionogels could be further reduced by using [C_nMIm][NTf₂] with a longer alkyl chain length as well as a weaker affinity to water (Figs. 2b and 2c). In this study, [C₈MIm][NTf₂] was chosen as the default IL for ease of further investigation. The content of hydrophobic IL also strongly affected the water affinity of samples (Fig. S2 in ESI). With a n_{IL}/m_p value of 0.1 mmol·g^{−1}, the PVH8812/[C₈MIm][NTf₂] ionogel showed an adhesive surface to water droplets, just as the same as pristine PVDF-HFP. Nevertheless, increasing the content of [C₈MIm][NTf₂] to 0.2 mmol·g^{−1} or above would make the surface of ionogels slippery and water-repellent.

The sheet resistance of PVH8812/[C_nMIm][NTf₂] ionogels was determined by using a four-probe resistivity measurement system at the temperature of 298.15 K. Then, the conductivity of the ionogels can be calculated according to the following equation:^[19]

$$\sigma = \frac{1}{R_s T}$$

where R_s is the sheet resistance of the ionogels and T is the thickness of the ionogels. The conductivity of a PVH8812/[C_nMIm][NTf₂] ionogel can be adjusted by selecting the type of IL and tuning its content. For [C_nMIm][NTf₂], its intrinsic conductivity is negatively correlated with the size of the [C_nMIm] cation and the latter can be tuned by its alkyl chain length (Fig. S3 in ESI). As shown in Fig. 3(a), using an IL with a smaller cation is favorable to increasing the conductivity of ionogels. This is primarily because ions with a smaller size tend to migrate more easily.^[26] Raising the content of IL is another way to increase the conductivity of these ionogels (Fig. 3b). It is quite understandable since this can effectively enhance the density of charge carriers (which are ions in this case) within the samples. However, compared with pure ILs, the conductivity of these ionogels was much lower. The ionic conductivity of pure [C₈MIm][NTf₂] was 1.36×10^{-1} S·m^{−1}, while a PVH8812/[C₈MIm][NTf₂] ionogel with an IL amount of 82.6 wt% ($n_{IL}/m_p = 1.0$ mmol·g^{−1}) had a conductivity of 7.96×10^{-2} S·m^{−1}, only 58.5% of that of pure IL. Such reduction in ionic conductivity can be attributed to the impact of PVH8812 networks. On the one hand, the polymeric networks generate a steric hindrance to the

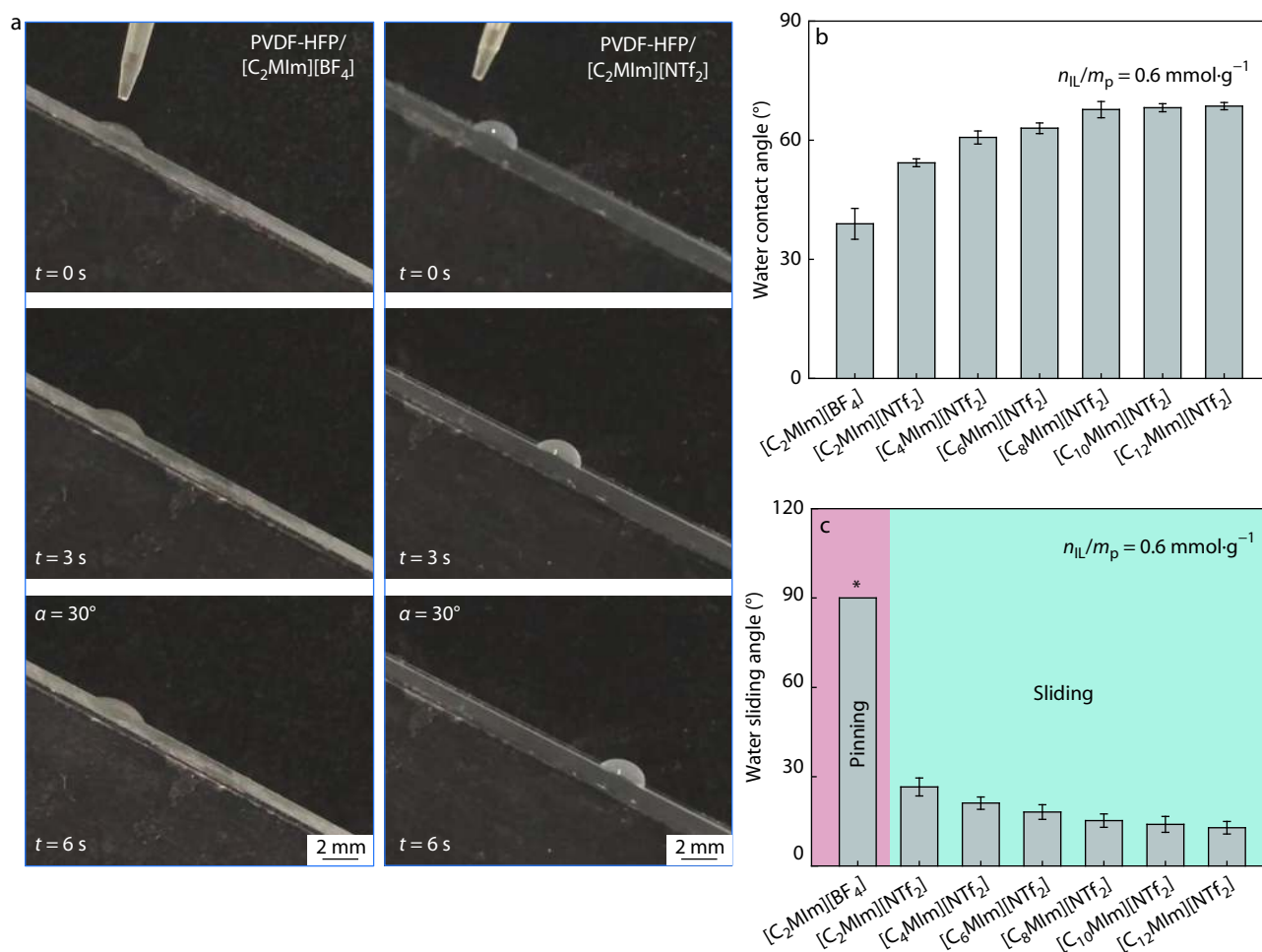


Fig. 2 (a) Time-lapsed photographs showing the affinities of different ionogels to 10 μL water droplets. The left panel and the right panel are PVH8812/[C₂MIm][BF₄] and PVH8812/[C₂MIm][NTf₂] ionogels, respectively, both of which have the same IL content of 0.6 $\text{mmol}\cdot\text{g}^{-1}$. (b) Contact angles and (c) sliding angles of water droplets (10 μL) on different ionogels with a $n_{\text{IL}}/m_{\text{p}}$ value of 0.6 $\text{mmol}\cdot\text{g}^{-1}$. “*” indicates the situation where water droplets were pinned on the surface of samples.

migration of ions. This effect is relatively small in some ionogels, especially when the concentration of polymeric networks is pretty low ($< 6 \text{ wt}\%$).^[27] On the other hand, ions can bind to the polar groups along the main chain of PVH8812 *via* ion-dipole interaction^[28–30] and lose their original mobility, leading to the decrease of valid charge carriers within ionogels.

Unlike electronic conductors or semiconductors which are stiff or brittle,^[10,12,31] the mechanical properties of a PVH8812/[C_{*n*}MIm][NTf₂] ionogel can be regulated over a large range. The ionogels with a $n_{\text{IL}}/m_{\text{p}}$ value of 0.6 $\text{mmol}\cdot\text{g}^{-1}$ exhibited a Young’s modulus of 1.99–2.64 MPa (Fig. 3c) and a maximum strain of 70%–360% (Fig. S4 in ESI). It is found that an IL with a larger [C_{*n*}MIm] cation tends to work as a slightly better plasticizer, which may increase the interchain distance of PVH8812 and weaken the intermolecular interaction. Compared to that, the content of IL has a greater impact on the mechanical properties of ionogels (Fig. 3d). The Young’s modulus of a PVH8812/[C₈MIm][NTf₂] ionogel was 70.5 MPa with a [C₈MIm][NTf₂] content of 0.1 $\text{mmol}\cdot\text{g}^{-1}$, and could be further reduced to 0.75 MPa with increasing [C₈MIm][NTf₂] content to 1.0 $\text{mmol}\cdot\text{g}^{-1}$, which is even lower than the Young’s modulus

of human skin.^[31,32] Such soft conductor can achieve “mechanical invisibility” required for flexible sensors, which monitor human tissues without constraining them. When increasing [C₈MIm][NTf₂] up to 0.2 $\text{mmol}\cdot\text{g}^{-1}$, the ionogels exhibited the highest stretchability with a maximum strain exceeding 300% (Fig. S5 in ESI). However, a further increase of [C₈MIm][NTf₂] content decreased the stretchability of the materials (Fig. S5 in ESI). Just as natural skin is soft and stretchable, these ionogels can undergo various forms of deformation—bending, twisting, and stretching (Fig. 3e)—making these materials mechanically compatible with human motions and applicable as wearable forms.

In order to understand the intermolecular interactions within PVH8812/[C_{*n*}MIm][NTf₂] ionogels, attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), differential scanning calorimetry (DSC), and X-ray diffraction (XRD) were carried out. Fig. 4(a) and Fig. S6 (in ESI) show the ATR-FTIR spectra of various samples. With the existence of ion-dipole interaction, the strength of C—F bond is expected to be changed due to the interaction between [C_{*n*}MIm] cation and C—F dipole along the PVH8812 chain. This is verified

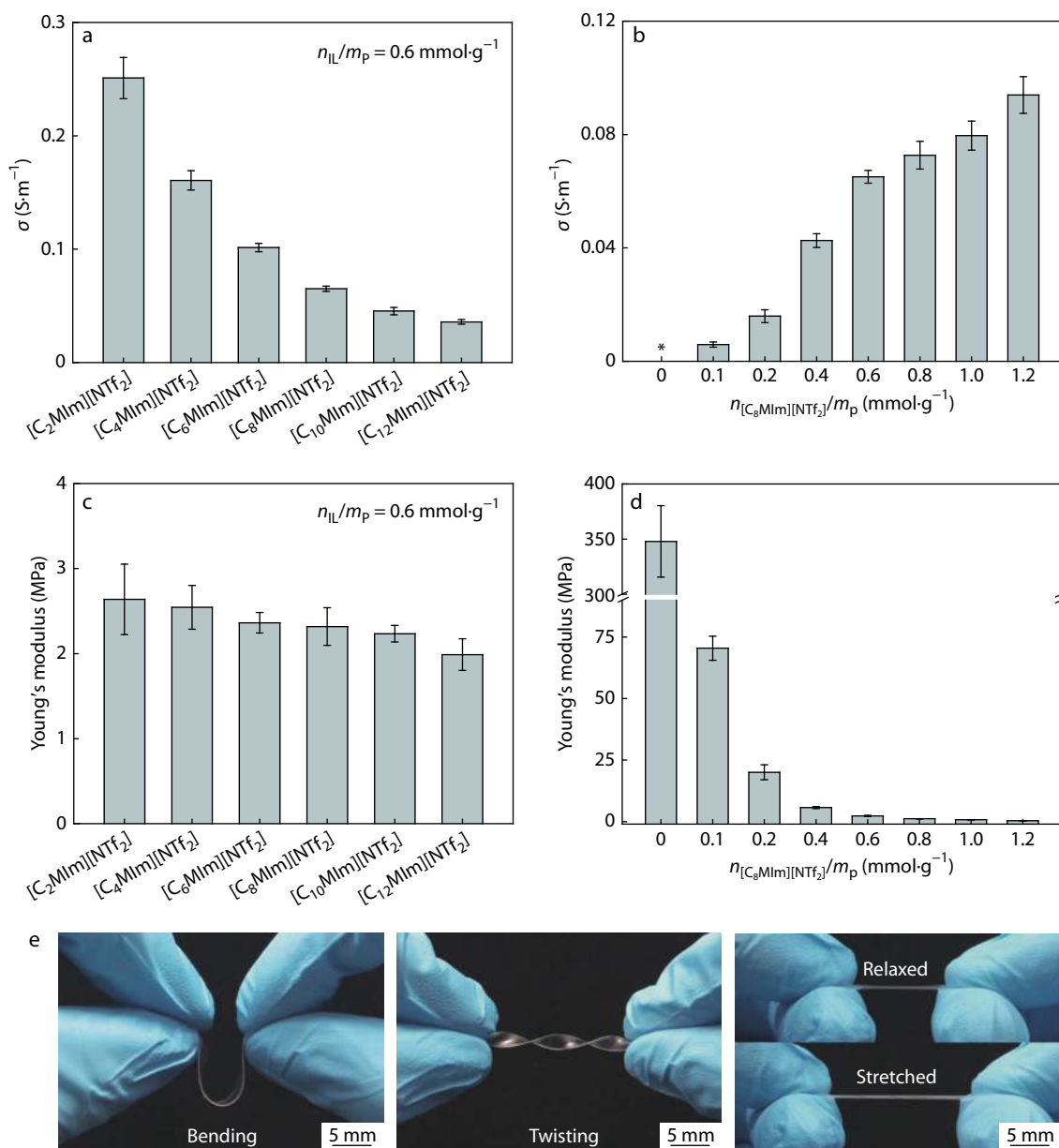


Fig. 3 (a) The influence of cations in $[C_nMIm][NTf_2]$ on the conductivity of ionogels ($n_{IL}/m_p = 0.6 \text{ mmol}\cdot\text{g}^{-1}$). (b) Conductivity of ionogels as a function of the content of $[C_8MIm][NTf_2]$. The conductivity of pristine PVH8812 was too low to be detected and is represented by “*”. (c) The effect of cations in $[C_nMIm][NTf_2]$ on the Young's modulus of ionogels ($n_{IL}/m_p = 0.6 \text{ mmol}\cdot\text{g}^{-1}$). (d) Young's modulus of ionogels as a function of the content of $[C_8MIm][NTf_2]$. (e) Mechanical flexibility of a PVH8812/ $[C_8MIm][NTf_2]$ ionogel ($n_{IL}/m_p = 1.0 \text{ mmol}\cdot\text{g}^{-1}$).

by the shift of C—F stretching band^[33] from 1400 cm^{-1} to 1407 cm^{-1} (Fig. 4a). DSC results provided more evidence on the intermolecular interaction (Fig. 4b). The bulk PVDF-HFP did not exhibit any transition behaviour in the temperature range from -100°C to -50°C , while pure $[C_8MIm][NTf_2]$ displayed a distinct change of heat capacity at -82°C , corresponding to its glass transition temperature (T_g).^[34] For ionogels with a $[C_8MIm][NTf_2]$ content of $0.2 \text{ mmol}\cdot\text{g}^{-1}$ or above, a glass transition was detected around -82°C , indicating the presence of free IL^[34,35] within polymeric networks. However, when the $[C_8MIm][NTf_2]$ content was decreased to $0.1 \text{ mmol}\cdot\text{g}^{-1}$, the change of heat capacity could be hardly detected around -82°C . This demonstrates the existence of in-

teraction between the polymer and IL, which could restrict the mobility of most IL molecules when their content was relatively low. Fig. 4(c) shows the XRD profiles of bulk PVH8812 and ionogels with different contents of $[C_8MIm][NTf_2]$. The diffraction peaks observed around 18.2° , 20.0° , 27.1° , and 39.1° are assigned to the crystalline phases of PVDF-HFP.^[28,36] Upon addition of $[C_8MIm][NTf_2]$, the crystallinity of PVH8812 decreased accompanied by obvious phase transformations. With increasing $[C_8MIm][NTf_2]$ content, the crystallinity of PVH8812 was further decreased and this led to a more amorphous polymeric network.

Both crystallization effect and ion-dipole interaction can be involved in the formation of a crosslinked network

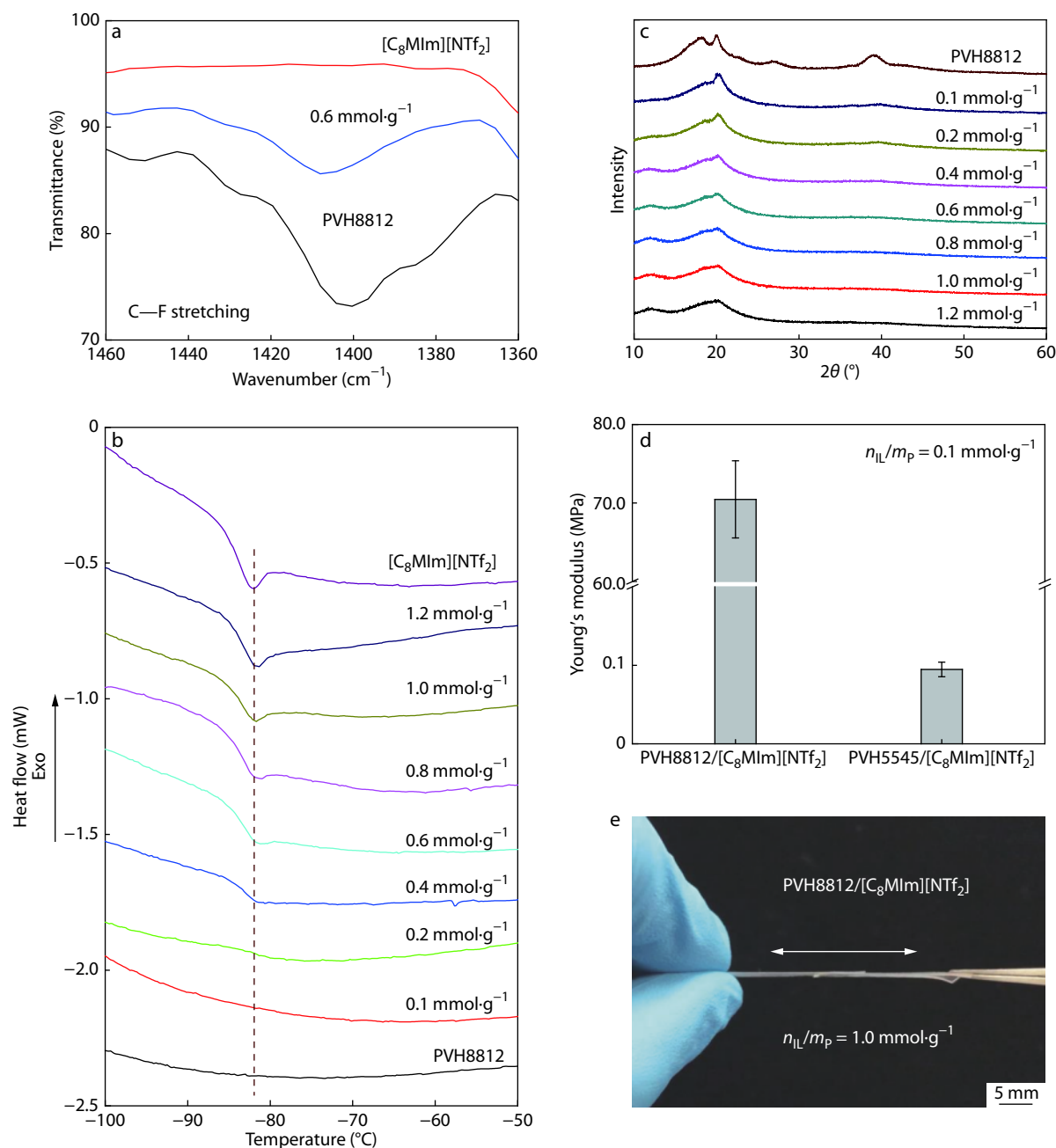


Fig. 4 (a) ATR-FTIR spectra of bulk PVH8812, pure $[\text{C}_8\text{MIm}][\text{NTf}_2]$, and PVH8812/ $[\text{C}_8\text{MIm}][\text{NTf}_2]$ ionogel ($n_{\text{IL}}/m_{\text{p}} = 0.6 \text{ mmol}\cdot\text{g}^{-1}$). 1460–1360 cm^{-1} were chosen for analyzing the ion-dipole interaction between PVH8812 and IL. (b) DSC thermograms of bulk PVH8812, pure $[\text{C}_8\text{MIm}][\text{NTf}_2]$, and ionogels with different $[\text{C}_8\text{MIm}][\text{NTf}_2]$ contents. When the content of $[\text{C}_8\text{MIm}][\text{NTf}_2]$ reaches $0.2 \text{ mmol}\cdot\text{g}^{-1}$ or above, the glass transition of free IL within the samples can be detected around -82°C . (c) XRD patterns of bulk PVH8812 and ionogels with different contents of $[\text{C}_8\text{MIm}][\text{NTf}_2]$. (d) Young's modulus of semicrystalline PVH8812/ $[\text{C}_8\text{MIm}][\text{NTf}_2]$ ionogel and amorphous PVH5545/ $[\text{C}_8\text{MIm}][\text{NTf}_2]$ ionogel. Both of them have a $n_{\text{IL}}/m_{\text{p}}$ value of $0.1 \text{ mmol}\cdot\text{g}^{-1}$. (e) Two PVH8812/ $[\text{C}_8\text{MIm}][\text{NTf}_2]$ ionogels had a tendency to stick together due to the formation of ion-dipole interactions on their interface. A horizontal stretching (indicated by an arrow) was applied to qualitatively display the interfacial adhesion between two ionogels.

(Fig. 1a), but they may have difference in their contribution to the mechanical properties of ionogels. To learn more information on this aspect, an ionogel without crystalline structures was constructed using a PVDF-HFP with an HFP ratio of 45% (PVH5545). According to previous studies,^[2,24] the crystalline properties of PVDF-HFP can be highly regulated through the

ratio of HFP monomer. Similar to PVH8812, PVH5545 could also interact with $[\text{C}_n\text{MIm}]$ cations *via* ion-dipole interaction, owing to the polar groups along main chains (Fig. S7 in ESI). In the ATR-FTIR spectra of PVH5545 and its corresponding ionogels (Fig. S8 in ESI), we did not observe vibrational bands related to crystalline phase, indicating their amorphous

nature. With the same $[C_8MIm][NTf_2]$ content of $0.1 \text{ mmol}\cdot\text{g}^{-1}$, an ionogel based on PVH8812 exhibited a Young's modulus 700 times higher than the amorphous one based on PVH5545 (Fig. 4d). It implies that the crystalline structures are much stronger than the ion-dipole interactions and play a dominant role in providing the mechanical strength of ionogels. Although the ion-dipole interaction is relatively weak and susceptible to mechanical stimulation, it has some features not typically offered by crystalline structures, such as reversibility. Self-healing materials harnessing ion-dipole interactions as dynamic bonds have been demonstrated previously.^[29] In this study, two PVH8812/ $[C_8MIm][NTf_2]$ ionogels had a tendency to stick together (Fig. 4e) and this can be ascribed to the formation of ion-dipole interactions in their interface.

We further investigated the potentials of PVH8812/ $[C_nMIm][NTf_2]$ ionogels as sensing materials. A PVH8812/ $[C_8MIm][NTf_2]$ ionogel ($n_{IL}/m_p = 1.0 \text{ mmol}\cdot\text{g}^{-1}$) with a thickness of $200 \mu\text{m}$ was gradually stretched to different tensile strains and its electrical resistance was measured in real time. The change of its electrical resistance was calculated ($\Delta R/R_0 = (R - R_0)/R_0$, where R_0 denotes the original resistance in a relaxed state and R is the real-time resistance during testing) and plotted with respect to applied strain (ϵ). As shown in Fig. 5(a), $\Delta R/R_0$ increased linearly with the increase of tensile strain up to 50%,

which is sufficient for a sensing material to be used on the surface of human skin for personal healthcare (primary sensing target: $< 55\%$ strain).^[37,38] In order to evaluate the strain sensitivity of the ionogel, $\Delta R/R_0$ was related to ϵ by a gauge factor (GF):^[39]

$$GF = \frac{\Delta R/R_0}{\epsilon}$$

Upon applying a tensile strain from 0% to 50%, the GF value of the PVDF-HFP/ $[C_8MIm][NTf_2]$ ionogel maintained stable at around 2 (Fig. 5b). The cycling stability of the ionogel was also tested. As shown in Fig. 5(c), a steady fluctuation in resistance could be maintained during 1000 cycles of tensile stretching and releasing between 0% and 10% strain, implying the long durability and high reliability of this material as strain sensors. In addition to the sensing of stretching movement, such ionogel also showed a capacity of detecting bending movement (Fig. 5d). It is quite meaningful since bending is another common form of motion in human activities. This ionogel can be quite useful in many cases, like sensing the bending motion at the inner margin of articular portions.

For hydrogel-based ionic conductors, gain of water or loss of salt driven by osmotic pressure differences may occur when wearable devices come into contact with an aqueous

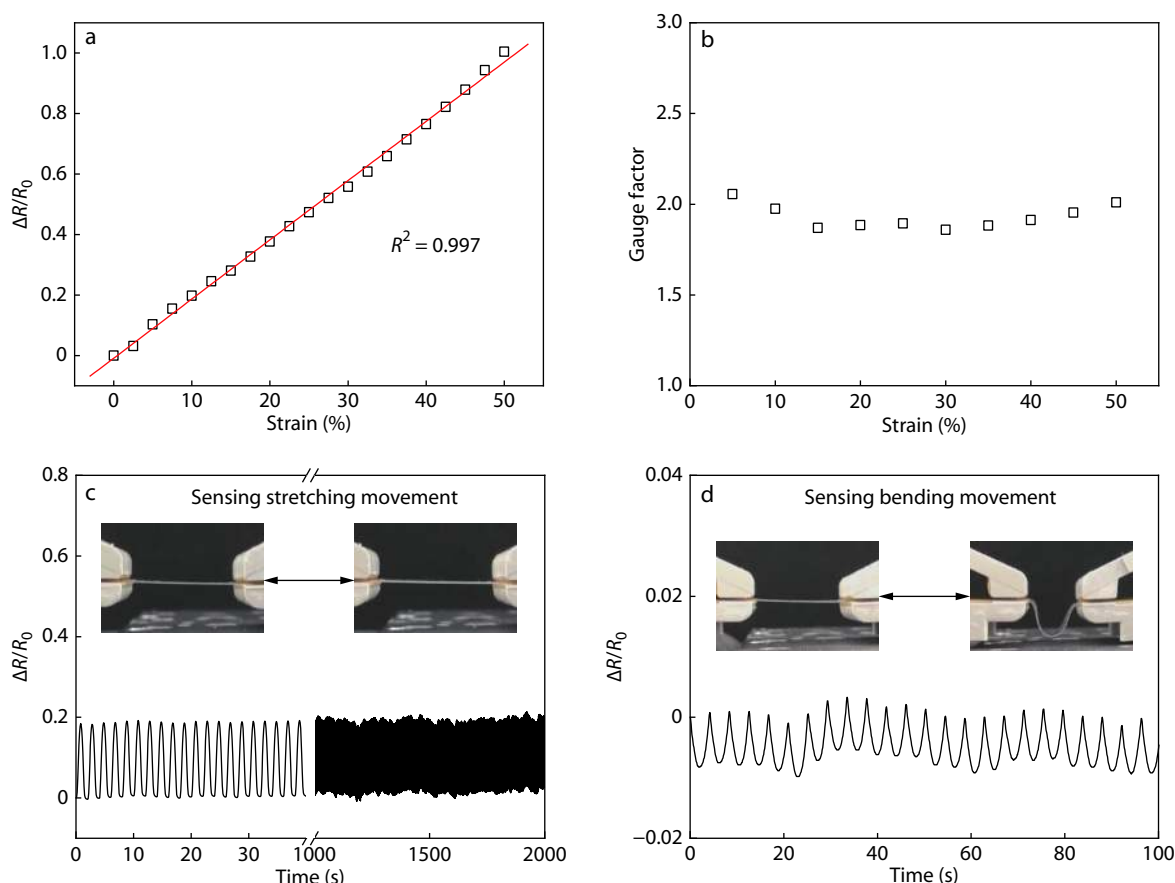


Fig. 5 Sensing performance of PVH8812/ $[C_8MIm][NTf_2]$ ionogels ($200 \mu\text{m}$ thick, $n_{IL}/m_p = 1.0 \text{ mmol}\cdot\text{g}^{-1}$). Change of (a) electrical resistance and (b) gauge factor as a function of strain. (c) Resistive response during 1000 cycles of tensile stretching and releasing between 0% and 10% strain. (d) Variation in electrical resistance for repetitive bending cycles. Insets in c and d are optical photographs showing the stretching and bending movement of the samples.

phase (e.g., human sweat and rainwater), leading to an undesired fluctuation of material composition and performance.^[10,13,40] The affinity of an ionogel to water is highly dependent on the type of IL contained. In the inset of Fig. 6(a), an ionogel hosting a hydrophilic IL ($[\text{C}_2\text{MIm}][\text{BF}_4]$, $n_{\text{IL}}/m_{\text{p}} = 1.0 \text{ mmol}\cdot\text{g}^{-1}$) was stretched cyclically and a water droplet ($10 \mu\text{L}$) was placed on its upper surface after the first 30 s. Immediately after adding the water droplet, the $\Delta R/R_0$ value of the sample experienced a dramatic drop. In this case, the hydrophilic IL and water penetrated mutually and this could change the internal environment of the ionogel and subsequently the mobility of charge carriers. As a result, the electric performance of the material was seriously disturbed. The effect of water on an ionogel containing a hydrophobic IL ($[\text{C}_8\text{MIm}][\text{NTf}_2]$, $n_{\text{IL}}/m_{\text{p}} = 1.0 \text{ mmol}\cdot\text{g}^{-1}$) was also tested by placing a water droplet ($10 \mu\text{L}$) on its upper surface. Since the sample was stretched horizontally, the water droplet could rest on its surface without draining off. After 270 s, only a slight change happened to the fluctuation behavior of its $\Delta R/R_0$ value (Fig. 6b), indicating a stable sensing performance in wetted state. Such benign tolerance to water can be

mainly ascribed to the hydrophobic properties of PVH8812 and $[\text{C}_8\text{MIm}][\text{NTf}_2]$, which significantly suppress the permeation of water as well as the loss of IL. Apparently, using hydrophobic ILs instead of hydrophilic ones is favorable to obtaining stable sensing ionogels when used in environments where moisture can be almost inevitable.

Fig. 6(c) shows the schematic design of a wearable strain sensor based on a PVH8812/ $[\text{C}_8\text{MIm}][\text{NTf}_2]$ ionogel. The ionogel was connected between two metallic electrodes for ease of applying a voltage and attached onto the surface of human skin via a stretchable adhesive tape (VHB 4905, 3M). Such wearable strain sensor can deform along with the movement of human body and output electric signals correspondingly. For the purpose of demonstration, this wearable strain sensor was used to real-time monitor the bending movement of an index finger. As shown in the insets of Fig. 6(d), the strain sensor could follow the finger movement and be stretched repeatedly. At the same time, a stable $\Delta R/R_0$ fluctuation was output (Fig. 6d). Water droplets were dropped discontinuously onto the strain sensor for 30 s during this experiment to test its sensing stability against wet condition. It can

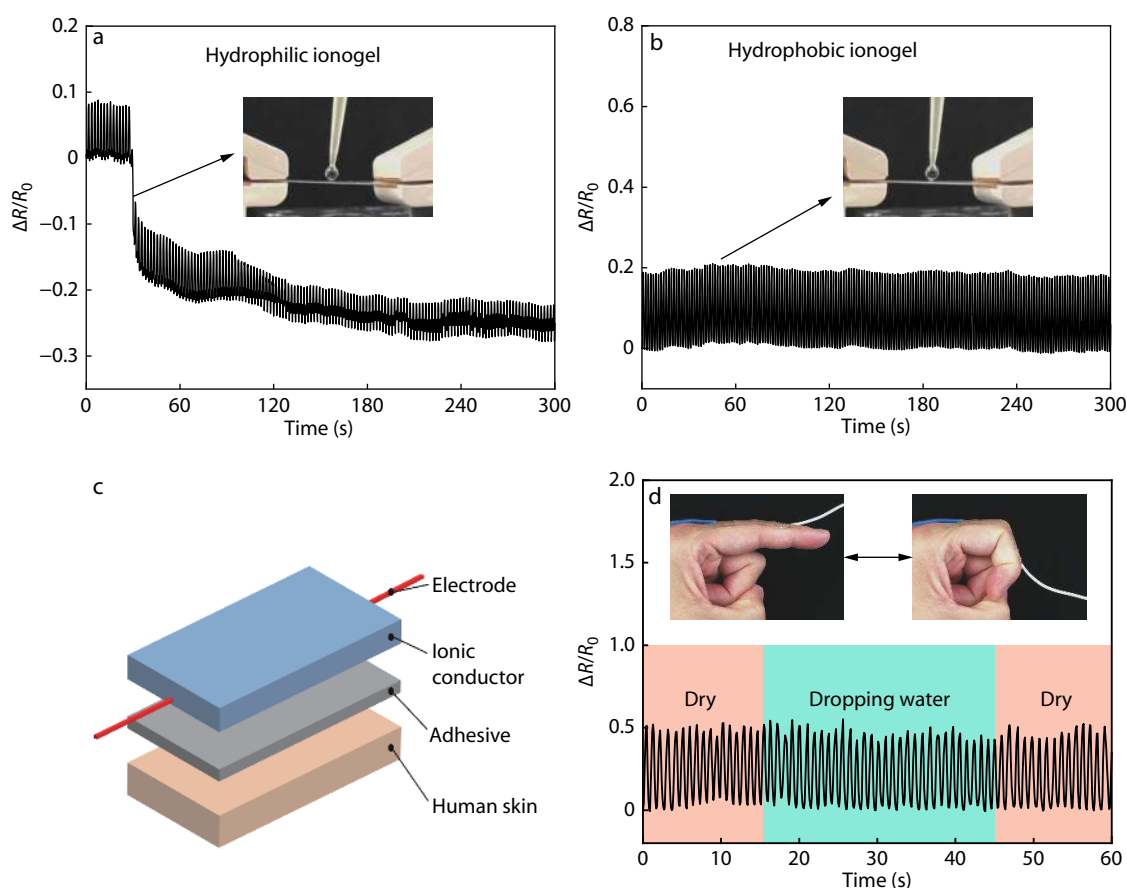


Fig. 6 The effect of water droplets on the sensing stability of ionogels. (a, b) One water droplet ($10 \mu\text{L}$) placed on the surfaces of (a) a hydrophilic PVH8812/ $[\text{C}_2\text{MIm}][\text{BF}_4]$ ionogel and (b) a hydrophobic PVH8812/ $[\text{C}_8\text{MIm}][\text{NTf}_2]$ ionogel when they were stretched cyclically between 0% and 10% strain. Black arrows are applied to indicate the point in time when the water droplet was released. (c) Schematic design of a wearable strain sensor based on a PVH8812/ $[\text{C}_8\text{MIm}][\text{NTf}_2]$ ionogel. The ionogel was connected between two metallic electrodes for ease of applying a voltage and attached onto the surface of human skin via a stretchable adhesive tape. (d) Real-time monitoring of the bending movement of an index finger using the wearable strain sensor. Insets present the repetitive stretching of the sensor in response to finger movement. The sensing stability of the sensor was tested by dropping water discontinuously onto its surface for 30 s (from the 15th to the 45th second).

be found that the sensing performance of the device was not affected by water droplets, indicating that such wearable sensor can function under wet or rainy conditions.

CONCLUSIONS

The work reported here addresses challenges related to the search of environmentally tolerant ionic conductors for reliable sensing applications. A series of hierarchically crosslinked ionogels containing hydrophobic ILs were tested. With a reasonable combination of nonvolatility, transparency, stretchability, and sensitivity, such ionogels can work as reliable sensors for real-time monitoring human motions and operate steadily in both dry and wet conditions. We anticipate that this work will boost the designing of advanced and multifunctional ionic conductors for novel wearable devices.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-020-2357-2>.

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