

Quadruple H-Bonding Cross-Linked Supramolecular Polymeric Materials as Substrates for Stretchable, Antitearing, and Self-Healable Thin Film Electrodes

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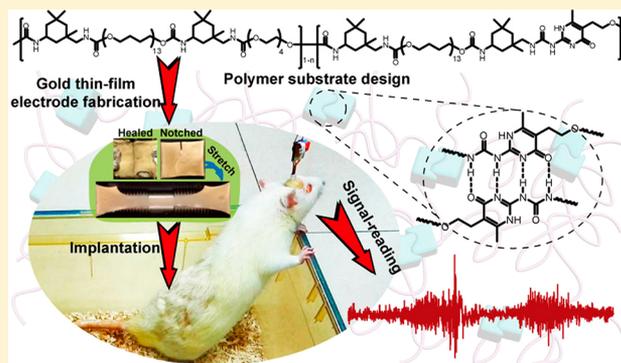
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Supporting Information

ABSTRACT: Herein, we report a de novo chemical design of supramolecular polymeric materials (SPMs-1–3) by condensation polymerization, consisting of (i) soft polymeric chains (polytetramethylene glycol and tetraethylene glycol) and (ii) strong and reversible quadruple H-bonding cross-linkers (from 0 to 30 mol %). The former contributes to the formation of the soft domain of the SPMs, and the latter furnishes the SPMs with desirable mechanical properties, thereby producing soft, stretchable, yet tough elastomers. The resulting SPM-2 was observed to be highly stretchable (up to 17 000% strain), tough (fracture energy $\sim 30\,000\text{ J/m}^2$), and self-healing, which are highly desirable properties and are superior to previously reported elastomers and tough hydrogels. Furthermore, a gold thin film electrode deposited on this SPM substrate retains its conductivity and combines high stretchability ($\sim 400\%$), fracture/notch insensitivity, self-healing, and good interfacial adhesion with the gold film. Again, these properties are all highly complementary to commonly used polydimethylsiloxane-based thin film metal electrodes. Last, we proceed to demonstrate the practical utility of our fabricated electrode via both in vivo and in vitro measurements of electromyography signals. This fundamental understanding obtained from the investigation of these SPMs will facilitate the progress of intelligent soft materials and flexible electronics.



INTRODUCTION

Demands for wearable and implantable electronics have boosted the development of various advanced materials, smart devices, and engineering methodologies.^{1–3} As such, skin-inspired mechanically compliant sensors and actuators have been extensively reported as well as their potential for applications in prosthetics,⁴ brain/machine interfaces,⁵ and soft robotics.⁶ Stretchable electrodes with high toughness play a crucial role in integrating various devices together to support functions under large mechanical deformations.² During the past few years, a variety of structural designs, such as wrinkled,⁷ serpentine,⁸ meshed,^{9,10} and microcracked,^{11,12} have been

used to reduce degradation of conductivity under mechanical strain. To date, stretchable thin film metal electrodes, particularly gold electrodes, are typically deposited on polydimethylsiloxane (PDMS) substrates. But they have several limitations, such as being sensitive to fracture/notch, poor interfacial adhesion, and lack of self-healing ability. Therefore, it is of interest to address these limitations in thin film stretchable gold electrodes.

Received: February 10, 2018

Published: March 29, 2018

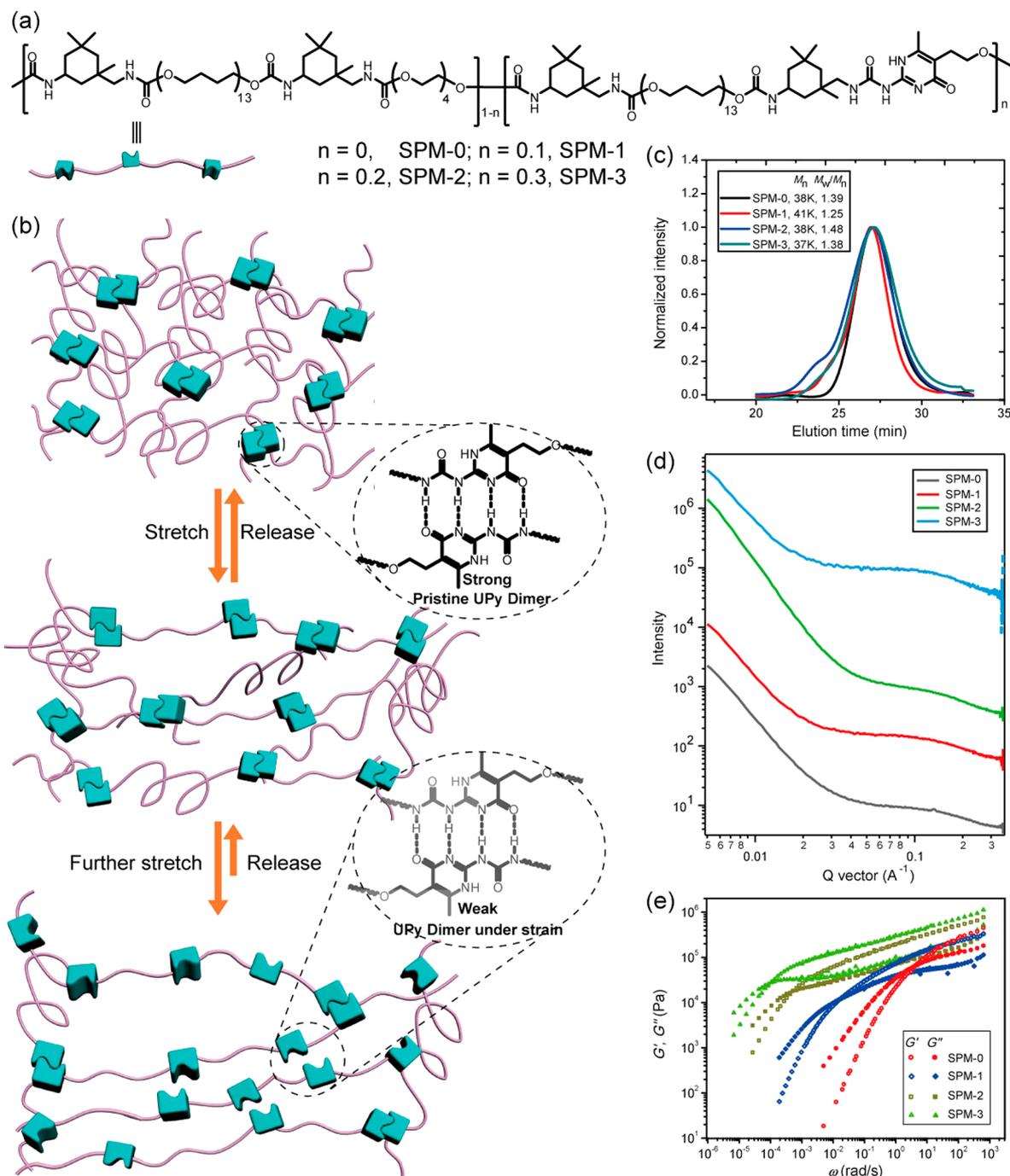


Figure 1. Schematic illustration of the design of stretchable supramolecular polymeric materials (SPMs) and general materials characterization. (a) Chemical structures of SPMs-0-3 with varying amounts of UPy cross-links to tune mechanical properties. (b) Cartoon representation of the proposed mechanism for highly stretchable SPMs. (c) GPC elution curves of SPMs-0-3 with DMF as the eluent and PMMA as the standard, showing that M_n and PDI of all polymers are comparable and relatively narrow, respectively. (d) SAXS profile plot for bulk SPMs that supports the presence of microphase separation on the order of 3.7 to 5.2 nm. (e) Master curves of SPMs shifted by time-temperature superposition (TTS). Frequency sweep of SPMs was performed from 100 to 20 °C with an interval of 20 °C over a span of three decades of frequency between 0.628 and 628 rad/s (reference temperature 20 °C, 1% strain).

Compared to self-healable composite electrodes (usually prepared by mixing a self-healing polymer matrix and a conductive material¹³⁻¹⁵), fabricating skin-inspired thin film gold electrodes that are stretchable, self-healing, and fracture insensitive, with good interfacial adhesion and with matched modulus between electrode and human tissue, is highly challenging.¹⁶ Here, we hypothesize that cross-linking through supramolecular chemistry will help to address the above

deficiencies because the cross-linkers are dynamic so that the supramolecular polymeric materials (SPMs) can be designed to possess both good mechanical strength and adaptability.¹⁷⁻²¹ Thus, this may be a promising direction for the design of desirable substrates for skin-inspired thin film gold electrodes.

Suo and co-workers previously reported a highly stretchable (tensile strain ~2000%) and tough (fracture energy ~9000 J/m²) supramolecular polymeric hydrogel by incorporating a

combination of ionically and covalently cross-linked networks.²² However, depositing gold film electrodes on a water-containing hydrogel substrate in a high-vacuum chamber is not practical. Furthermore, water vapor may result in the risk of electrical shorting. Guan et al. prepared a biomimetic supramolecular polymer using cyclic 2-ureido-4-pyrimidinone (UPy) cores as the repeating units, which showcased a rare combination of high strength, high toughness, self-healing, and shape memory.²³ However, its high Young's modulus (~ 200 MPa) and relatively low fracture onset strain ($\sim 100\%$) limit its use for skin-inspired stretchable substrates. Evidently, materials that meet a rigorous set of requirements associated with mechanical properties for skin-inspired thin film electrodes are rare.

Herein, we report the design and preparation of a series of supramolecular polymeric materials (SPMs) 0–3, wherein various amounts of stronger quadruple H-bonding UPy and weaker urethane cross-links are introduced into polymeric backbones to tune the mechanical properties of SPMs (Figure 1a). Based on their mechanical behaviors, SPM-2 is chosen as the polymeric substrate since it combines medium tensile stress (0.91 MPa), high stretchability ($\sim 17\,000\%$), high toughness (fracture energy $\sim 30\,000$ J/m²), human-tissue-compatible Young's modulus (~ 375 KPa), and efficient autonomous self-healing ability. Subsequently, we develop an SPM-2-supported high-performance thin film gold electrode, which exhibits a high stretchability of $\sim 400\%$. Even for the electrode containing a notch, a stretchability of $\sim 250\%$ was achieved, which could be useful for surgical and implantable medical applications. Unexpectedly, SPM-2 also lends the self-healing ability on its supported stretchable thin film gold electrode. The self-healed electrode recovered its original conductivity and showed a healed stretchability of $\sim 90\%$, which is comparable or even superior to previously reported composite self-healing electrodes. The interfacial adhesion between SPM-2 and thin film gold was enhanced by 6 times compared to a PDMS-supported thin film gold electrode. Finally, the superior electric and mechanical properties of the self-healing and stretchable gold electrode allow us to demonstrate its utility in detecting electromyography (EMG) on both skin and in vivo.

RESULTS AND DISCUSSION

Materials Design and Synthesis. Gold films usually were found to crack easily on most elastic materials.^{24,25} Additionally, the lack of either an antitearing feature or good adhesion is a big obstacle. To meet the requirements of skin-inspired film electrodes, i.e., stretchable, self-healing, and fracture toughness, we synthesized a series of supramolecular polymeric materials (SPMs-0–3) with increasing densities of the strong quadruple H-bonding UPy units as cross-linkers from 0 to 10 mol %, 20 mol %, and 30 mol % via condensation polymerization, in which a polytetramethylene glycol (PTMG, $M_n = 1000$ g/mol)-based prepolymer was first prepared in the presence of two equivalents of isophorone diisocyanate (IPDI) and catalytic amount of dibutyltin dilaurate (DBTDL), followed by chain extension using tetraethylene glycol (TEG) and 5-(2-hydroxyethyl)-6-methyl-2-aminouracil in a preset ratio (Scheme S1). Compared to methylenediphenyl 4,4'-diisocyanate (MDI) and hexamethylene diisocyanate (HDI), the combination of PTMG and the bulkier IPDI makes the resultant polymer soft, which is a key parameter for utilization in skin-inspired film electrodes. However, in view of the potential applications inside or in contact with organisms, it is

necessary to make polymeric materials with a Young's modulus of < 500 KPa.¹⁶ Therefore, we employ TEG as a chain extender, which also plays a role to make the polymeric backbone more flexible and less crystalline. To endow these polymers with good mechanical properties, noncovalent cross-linkers were designed to take advantage of strong hydrogen bonding. Specifically, the well-known quadruple hydrogen bonding UPy motif developed by Meijer and co-workers was chosen because it offers an appealing combination of high thermodynamic stability ($\Delta G = \sim 10$ kcal/mol; $k > 10^7$ M⁻¹ in chloroform) and rapid kinetic reversibility ($k_{\text{off}} = \sim 8$ s⁻¹),^{26,27} which are favorable parameters to furnish our new SPMs with satisfactory mechanical behaviors. Moreover, the presence of self-complementary UPy units was not expected to disrupt the PTMG-based soft domain, thus making SPMs soft, stretchable, self-healing, yet tough.

Materials Characterizations. ¹H NMR indicated the successful preparation of SPMs as indicated by the presence of characteristic peaks of IPDI, PTMG, and TEG segments in polymeric backbones (Figures S2, S4, S6, S8). For SPMs-1–3, the N–H signals on UPy units showed large downfield shifts (observed between 10.0 and 13.0 ppm) and low intensities (Figures S4, S6, S8), giving evidence for UPy dimerization, which is the driving force for the formation of cross-linked polymeric networks.^{28a} Furthermore, FTIR spectra and solid-state ¹H NMR were used to confirm the presence of the quadruple H-bonding in our prepared materials (Figures S8b and 10a). All polymers were obtained with comparable number-averaged molecular weights (M_n) in the range of 37 to 41 kDa and relatively narrow (≤ 1.48) polydispersity indexes (PDI, calculated by M_w/M_n) as measured by gel permeation chromatography (GPC) utilizing *N,N*-dimethylformamide (DMF) as the eluent and poly(methyl methacrylate) (PMMA) as the standard (Figure 1c). According to our obtained molecular weights, the average number of UPy units in the polymeric chains was calculated to be ~ 3.0 , 5.0, and 7.0 for SPMs-1–3, respectively. Also, differential scanning calorimetry (DSC) study conveyed that glass transition temperatures (T_g 's) are indeed present in SPMs-0–3. The T_g 's are in the range of -47.6 to -43.3 °C for the soft PTMG segments in the polymeric backbones (Figure S10), suggesting that the introduction of hard UPy cross-linkers in SPMs has no obvious influence on the T_g of the soft domain, which is a requirement for a low-modulus yet tough elastomer. Small-angle X-ray scattering (SAXS) of bulk SPMs displayed broad scattering peaks, indicative of the presence of microphase separation on the order of 3.7 to 5.2 nm (Figure 1d). To gain more insights into bulk material properties of SPMs, small-amplitude oscillatory shear (SAOS) experiments were carried out. In the master curves scaled by time temperature superposition (TTS), all SPMs have crossover frequencies (ω_c) between the storage modulus (G') and loss modulus (G''), at which $G'(\omega_c) = G''(\omega_c)$ (Figure 1e). At low frequency (ω), G'' is larger than G' , showing that the viscous property of SPMs is dominant. Upon increasing frequency, G' increases faster than G'' and the elastic property of SPMs is predominant at the region of $\omega > \omega_c$. Increasing the UPy amount of SPMs from 0 to 30% leads to a higher rubber plateau and longer terminal relaxation time, which is estimated as the reciprocal of ω_c . Accordingly, the crossover points of G' and G'' of SPMs move to lower frequency, which means the samples are more solid-like at lower frequency.

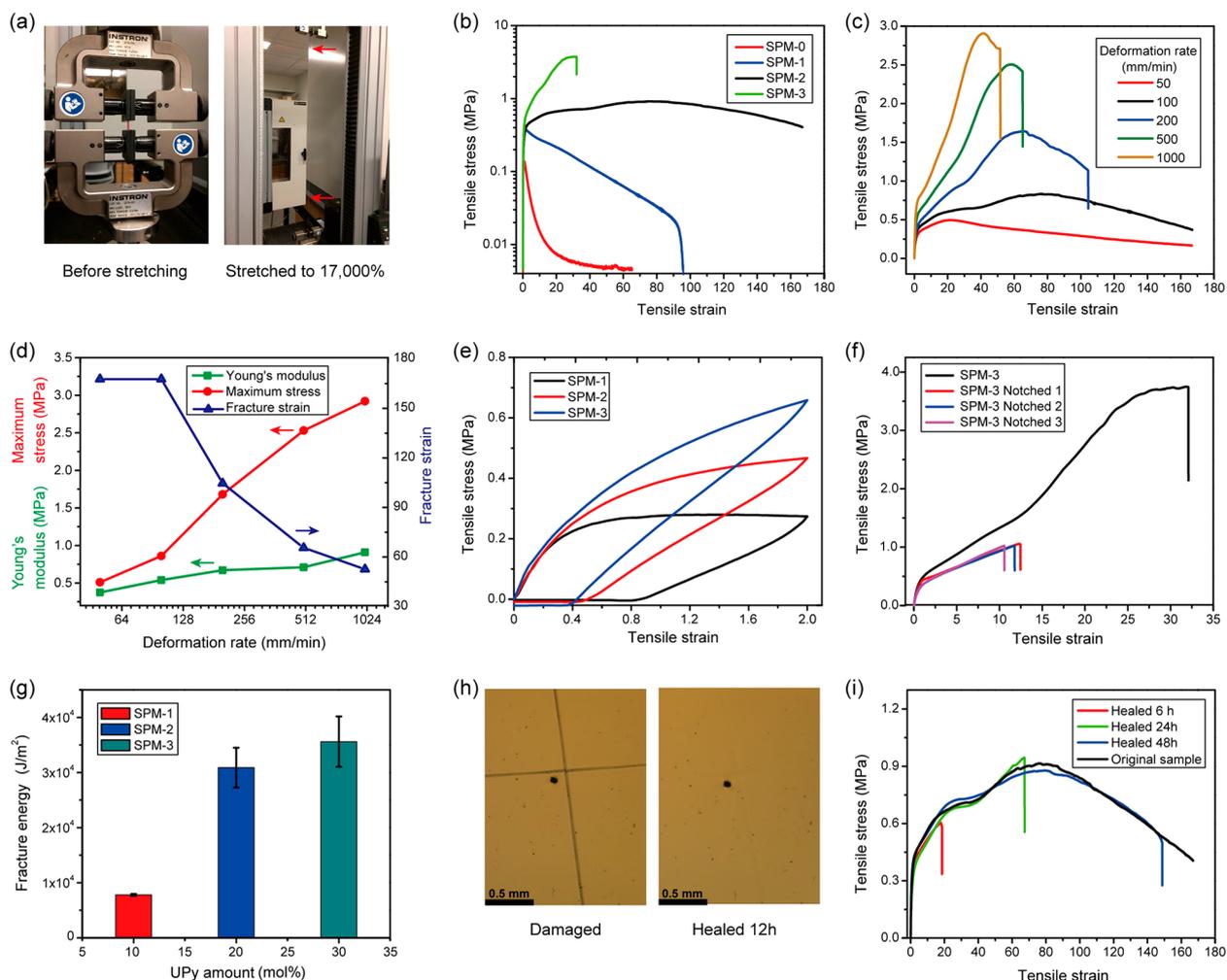


Figure 2. Mechanical properties of SPMs. (a) Photographs of an SPM-2 test specimen before and after stretching to 17 000%. Red arrows show where the stretched specimen is. (b) Stress–strain curves of SPMs-0–3 with different cross-linking densities, which have a pronounced impact on the mechanical properties. Maximum strain and stress reach 17 000% and 0.91 MPa for SPM-2 with a 20% UPy motif, respectively. Deformation rate: 100 mm/min. (c) Tensile behaviors of SPM-2 under different deformation rates in the range of 50 to 1000 mm/min. (d) Deformation rate dependence of SPM-2 on maximum stress, fracture strain, and Young’s modulus. (e) Cyclic tensile tests of SPMs-1–3 at a strain of 200% under the deformation rate of 100 mm/min. The pronounced hysteresis accounts for the great energy dissipation ability of SPMs, a pivotal characteristic for high toughness. (f) Stress–strain curves of the unnotched and notched samples of SPM-3. A notch of 1 mm in length was made in the middle of a rectangular specimen of about 1 mm in thickness and 5 mm in width. The specimen was fixed in the two clamps with a preset distance of 10 mm. Deformation rate: 100 mm/min. (g) Fracture energy as a function of UPy amount of SPMs. The fracture energy of $>30\,000\text{ J/m}^2$ is the highest value in the reported polymeric elastomers and tough hydrogels. (h) Optical microscope images of damaged and healed SPM-2 film. (i) Stress–strain curves of the original and self-healed SPM-2 specimens after three different healing times from 6 to 24 h and then to 48 h at room temperature. Deformation rate: 100 mm/min.

Mechanical Properties. The mechanical properties of SPMs-0–3 vary greatly depending on the different amounts of UPy cross-links embedded in the polymeric backbones (Figure 2). As shown in Figure 2b, tensile stress–strain curves of SPMs suggest that an increase in UPy content led to an improvement in mechanical performances, such as stretchability and tensile strength. SPM-0, i.e., without UPy cross-links, displays weak mechanical strength; for example, passing the yielding point at 75% strain, it behaves as a viscoelastic fluid (Figure 2b). Upon increasing the UPy units to 10 mol %, the mechanical behaviors such as tensile stress and strain of SPM-1 improve a lot. However, due to insufficient cross-linkers, an obvious necking phenomenon was observed when it was stretched to 90× its original length (Figure 2b). A further increase of UPy amount to 20 mol % clearly enhances the maximum strain and stress, respectively. It is worth mentioning that SPM-2 also possesses

remarkable mechanical strength so that it readily holds a weight 16 000× greater than its own without breaking (Figure S13). Finally, SPM-3, with a 30 mol % UPy motif, exhibits a maximum stress up to 3.74 MPa but markedly decreased stretchability of 3100%. Therefore, overall SPM-2 shows superior stretchability compared to most other self-healing polymers and tough hydrogels (Figure S14).^{22,29–31} These observations indicate that the incorporation of various amounts of UPy cross-linking units is effective in systematically tuning mechanical properties. Similar observations have also been reported previously,^{24,35b} in which both the strength and numbers of hydrogen bonds were observed to affect the mechanical properties of the resulting materials.

The high stretchability of our SPMs may originate from the cross-linking through the strong, highly directional quadruple H-bonding motif of UPy in the polymeric backbones. Previous

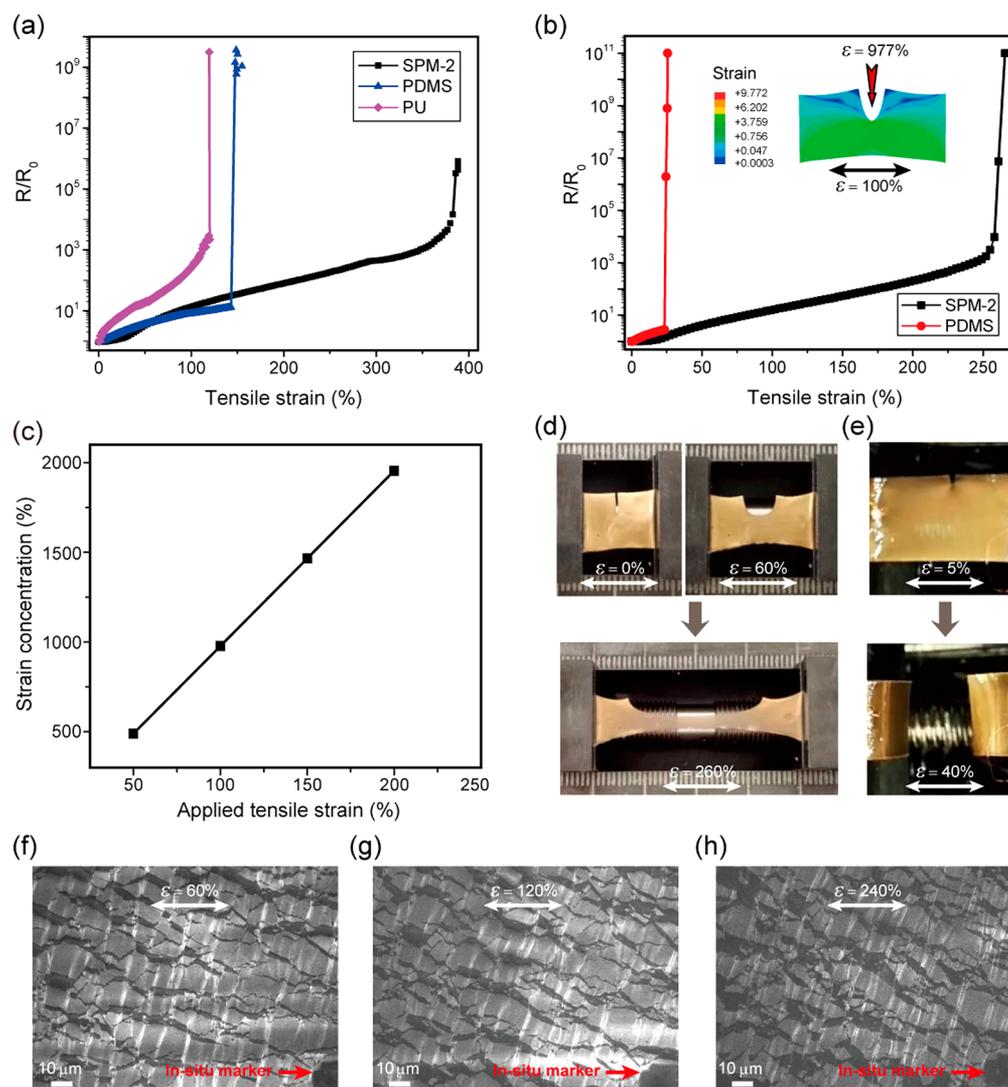


Figure 3. Highly stretchable thin film gold electrode with notch-insensitive property. (a) Stretchability comparison of the stretchable thin film gold electrode on different polymeric substrates. The thickness of the gold film deposition is 50 nm with the same deposition condition. The conductor is taken as breaking when the normalized resistance increases sharply to around $10^9 \Omega$. (b) Stretchability comparison of the notched SPM-2 electrode and PDMS electrode. Inset is the mechanical simulation by FEM to show the strain magnification effect induced by the notch. (c) Strain concentration at the tip of the notch calculated by FEM modeling. The strain concentration induced by the notch is much larger than the actual tensile strain applied. (d) Optical images to illustrate the stretching state of SPM-2-based stretchable thin film gold electrode with notch, and, as a comparison, the PDMS-based one is shown in (e). (f–h) In situ SEM images to reveal the mechanism of an SPM-2 stretchable thin film gold electrode. The randomly distributed microfractures assist the film to form a mesh structure under large mechanical deformation keeping the conductive path. The marker at the lower right corner indicates the same position.

work on a metal–ligand cross-linked polymer, in which ligands were incorporated into the polymer backbone, showed high stretchability. It was attributed to the reversible formation of intramolecular loops within the same chain and intermolecular loops between different polymeric chains.²⁵ A similar conformation is possible here via the UPy dimerization. In the unstrained state, the intrachain loops result in the folding of the polymeric backbone, which enables a considerable chain extension under deformation. Meanwhile, the interchain loops contribute to the formation of a cross-linked polymeric network, which further enhances the mechanical properties (Figure 1b). Due to the reversible nature of UPy moieties, the opening of intrachain or interchain loops by progressively disrupting the H-bonds upon stretching should bring about the unfolding and sliding of the polymeric networks, thereby enhancing the stretchability and toughness of SPMs. Moreover,

due to the high bonding strength of the UPy motif, we hypothesized that the UPy units may be only partially broken or have the chance to be close to other broken UPy units in adjacent chains, leading to dimerization and the formation of a weak temporary cross-link under strain (Figure 1b). These peculiar binding and exchanging modes of quadruple UPy H-bonding along with abundant H-bonding-directed intra- and interchain loops in polymeric networks cooperatively lead to our observed high stretchability in SPMs.

The stretching-speed-dependent tensile behavior (Figure 2c) is consistent with the proposed chain dynamics as shown in Figure 1b. The increase in both Young's modulus and maximum stress of SPM-2, along with increased deformation rate from 50 to 1000 mm/min (Figure 2d), indicated the dynamic characteristics of quadruple H-bonding. Similar phenomena were also observed for ionically and host/guest-

cross-linked hydrogel networks.^{32,33} The fracture strain of our material did not change at low deformation rate (50 and 100 mm/min). At higher rates (≥ 200 mm/min), the strain-at-break decreased gradually (Figure 2d). To our surprise, the specimen of SPM-2 can still be stretched up to 52 \times its original length with a maximum stress of 2.92 MPa at a high deformation rate of 1000 mm/min (Movie 1 in the Supporting Information (SI)). This ability to maintain high stretchability at high deformation rates is only observed with a few hydrogels³³ and rarely for other materials. These findings indicate the UPy H-bonding unit in SPM-2 is able to undergo rapid exchange and re-formation after dissociation under strain.

Our SPMs are also observed to dissipate mechanical energy during strain, as revealed by the large hysteresis in the cyclic stress–strain tests (Figure 2e). Even though only a 30% tensile strain is applied on the toughest sample (SPM-3), the hysteresis is still significant (Figure S15c). As shown in Figure S15d, a significant decrease of tensional stresses (by $\sim 9.0\%$) in the second cycle was recorded if the film was stretched and released in two consecutive cycles. However, after a resting period of 1 h, the film almost recovered its initial stress–strain behaviors, as seen by an overlap of the cyclic curves. These observations suggest that mechanical strain caused dissociation of UPy cross-links as a mechanism for strain energy dissipation.

Next, we performed crack propagation experiments on single-edged notched samples. Using SPM-3 as an example, the notch area became blunt and was stable up to an average elongation of $\sim 12\times$ (Figure 2f and Movie 2 in the SI). We observed that a crack initiated at the front of the notch and then propagated quickly to break apart the specimen under continuous strain. Based on the large-strain approximation of Greensmith (Supplementary eq 1),³⁴ we calculated the fracture energies of SPMs-1–3 to be 7798, 30 888, and 35 596 J/m², respectively (Figure 2g). In comparison, natural rubber^{35a} and a multistrength H-bonding elastomer based on a PDMS matrix reported previously by our group^{35b} have fracture energies of 10 000 and 12 000 J/m², respectively. The value of the toughest hydrogel²² based on an ionically and covalently cross-linked network was 9000 J/m², along with other well-known polymeric elastomers and hydrogels with noncovalent and covalent double networks possessing fracture energies in the range of 2000 to 5000 J/m² (Figure S16).^{32,33,36} The high fracture energy for the SPMs is interesting, considering that the polymeric network is purely cross-linked by quadruple H-bonding. We attribute the observed high toughness to the presence of intramolecular and intermolecular loops from the strong UPy H-bonding dimerization and its high thermodynamic stability and rapid kinetic reversibility.

On account of the dynamic bond and soft PTMG segment used in the materials design and preparation, we expect that the reversible UPy H-bonding ($k_{\text{off}} = \sim 8 \text{ s}^{-1}$)^{26,27} would likely confer the SPMs with self-healing capability at room temperature. As observed by optical microscopy, the scratches on the SPM-2 film almost totally disappeared after 12 h of healing at room temperature (Figure 2h), suggesting autonomous self-healing behavior. Subsequently, we cut the polymer specimen into two pieces with scissors and put them back into contact for different self-healing periods under ambient conditions. Upon increasing the healing time, higher healing efficiencies were observed based on recovered fracture strain ratio, which is defined as the ratio of fracture strain after healing divided by that before cutting (Figure 2i). For example, the healing efficiency was 12% after 6 h and went up to 88% after 48 h,

along with a large fracture strain of $\sim 15\ 000\%$. SPM-1 reached almost quantitative healing efficiency, while the self-healing efficiency of SPM-3 was only 45% after healing 48 h (Figure S17). This observed “weakening” trend of the self-healing efficiency is attributed to the gradual increase in mechanical strength from SPM-1 to SPM-3, as the availability of H-bonding as “molecular glues” for self-healing is decreased. Factoring in mechanical properties, SPM-2 showed a good balance of high fracture toughness and fast self-healing. Notably, the stress–strain curves of the self-healed SPM-2 samples overlapped well with the original sample (Figure 2i), indicating good recovery of the mechanical properties after healing.

Stretchable and Notch-Insensitive Thin Film Gold Electrodes. Using our new materials, stretchable thin-film gold electrodes are subsequently fabricated (see detailed fabrication procedures in the SI). No additional treatments were needed for the polymeric substrate prior to thin gold film deposition. Interestingly, upon applying a tensile strain, the film was still conductive even at $\sim 400\%$ strain, a value that is much larger than that deposited on other commonly used polymer substrates, e.g., PDMS and polyurethane (PU), on which the gold film becomes nonconductive typically at 150% and 120% strain, respectively (Figure 3a). This may be attributed to the molecular design of our polymers which include polar TEG groups. Aside from stretchability, a notch-insensitive property is also useful for practical applications of stretchable thin film electrodes. For example, notches and defects are frequently found in thin film electrodes either due to the repeated manipulations or by, for example, suturing during an operation. Therefore, we cut notches in the stretchable thin film electrodes to check whether they can still maintain both conductivity and stretchability. Indeed, the film remained conductive even after inducing notches in the film (Figure 3b) and subsequently loading a tensile strain of $\sim 260\%$ (Figure 3d and Movie 3 in the SI). Furthermore, we observed that our fabricated film did not break even after it was subjected to a $\sim 300\%$ tensile strain and then partially cut with scissors (Movie 4 in the SI). As a comparison, a stretchable thin film gold electrode on a PDMS substrate breaks into two parts at only $\sim 40\%$ applied strain (Figure 3b and e), even though the induced notch is shorter (Movie 5 in the SI).

When a notch is introduced, the strain is more concentrated at the tip of the notch than the two ends of the film (Figure 3c). This will more likely result in crack propagation from the tip of the notch both in the polymeric substrate and in the metal thin film deposited on top, resulting in the electrode losing its conductivity. However, our supramolecular polymer-based stretchable gold thin film electrodes with induced notches are still conductive when large tensile strains are applied, indicating that the electrode overcame the crack propagation both in the polymeric substrate and in the metal thin film. As a comparison, metal thin films are usually highly sensitive to the notch/defects during stretching, and throughout-cracks form readily for a PDMS or PU substrate due to crack propagation (Figure S18). It is unusual that the induced cracks did not propagate from the notch tip throughout the metal film on our polymer. First, the mechanism of the stretchability of our gold film was investigated. We observed that at initial state even without any strain applied, the gold thin film already possessed initial randomly distributed nanocracks (Figure S19). They were formed due to the mismatch in thermal expansion coefficient between gold and the elastic substrate. The radiation heat

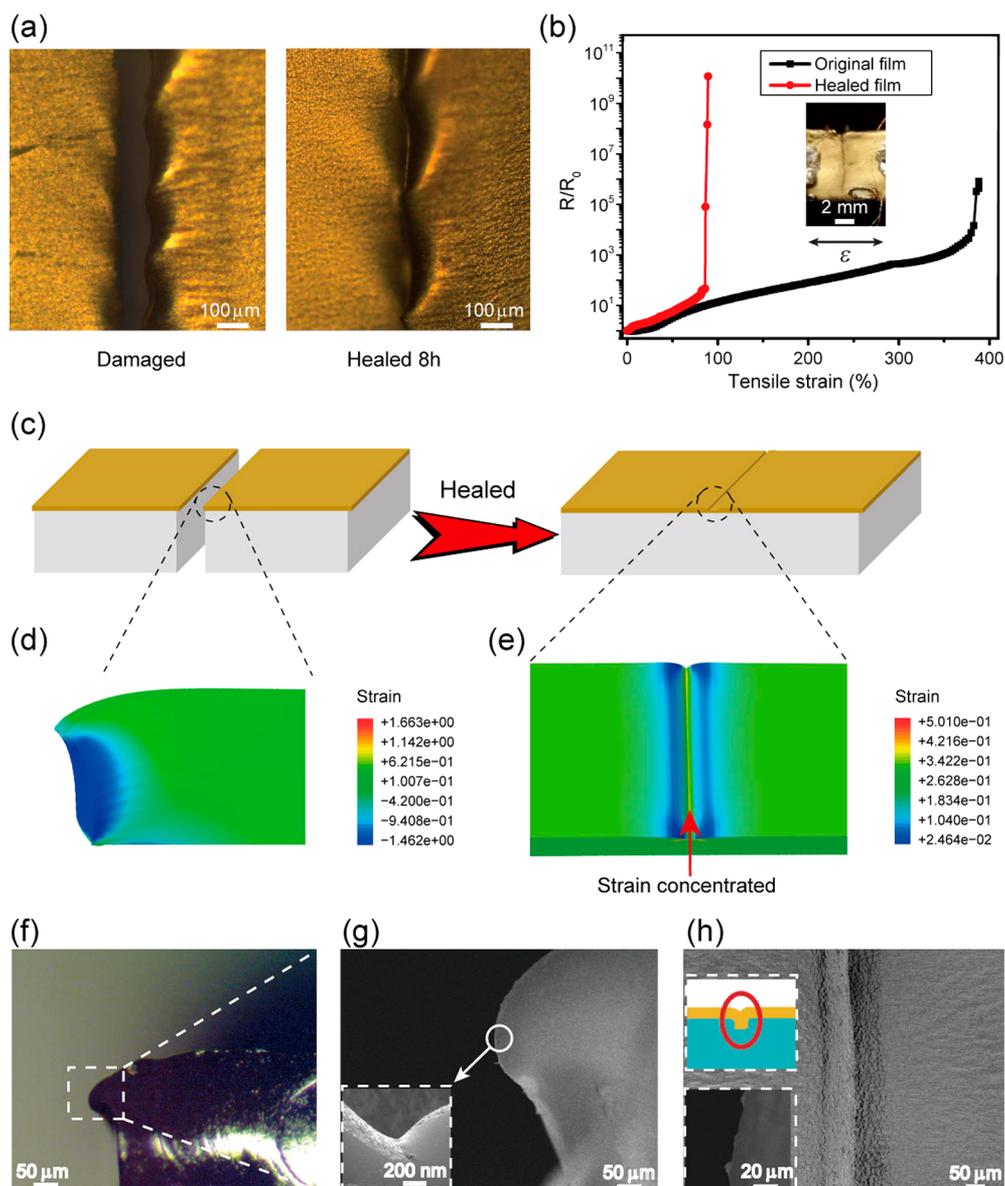


Figure 4. Self-healing property of the stretchable thin film gold electrode. (a) Optical microscope images of the cut gold films before and after healing. It can be observed that the edge of the cut film remains recurved even after healing. (b) Resistance change versus tensile strain to show the stretchability of the healed stretchable thin film gold electrode. (c) Illustration images to show the before and after healed state of the film, and the related mechanical simulation of the polymeric substrate by FEM is demonstrated in cross-section view in (d) to mechanically show the bending process at the cutting edge and in top view in (e) to illustrate the strain distribution after healing under 25% tensile strain. More strain is concentrated at the scar decreasing the stretchability of the metal film. (f) Optical image of the cross-section of the cut gold film and polymeric substrate. (g) SEM image of the same sample in (f). The inset shows the magnified SEM image. (h) SEM image of the top view of the healed electrode. The upper inset shows the cartoon model of the healed electrode, and the bottom inset displays the cross-section of the healed electrode.

during gold deposition causes greater thermal expansion of the elastomer and therefore generates nanocracks as reported previously for other elastomers.¹² Under strain, the nanocracks further developed into interconnected microislands of randomly distributed fractures. However, a conductive percolating network remained (Figure 3f–h). Such a morphology has previously been reported for gold thin film electrodes,^{11,37,38} but the notch-insensitive property was not observed. The numerous microfractures have previously been shown as a mechanism for preventing the further propagation of cracks under the strain. The applied strain energy to the gold film was assumed to be released by forming many microfractures, instead of large cracks, as shown in Figure S18. In the

case of our notch-tolerant substrate, since there is no tear of the substrate near the notch even at large strain, the notch only resulted in a higher density of microfractures near the notch, allowing the film to remain conductive through the network (Figure 3f–h). Thus, the high stretchability and notch-insensitivity of our SPM allowed stretchable and notch-insensitive gold thin film electrodes to be achieved.

Self-Healable Stretchable Thin Film Electrodes. Besides the high stretchability and notch insensitivity, we also observed a self-healing ability of the thin film gold electrode deposited on an SPM-2 substrate. We note that previously reported self-healing electrodes were mostly based on liquid metal^{35b} or composite materials.^{13,39,40} In those systems, the

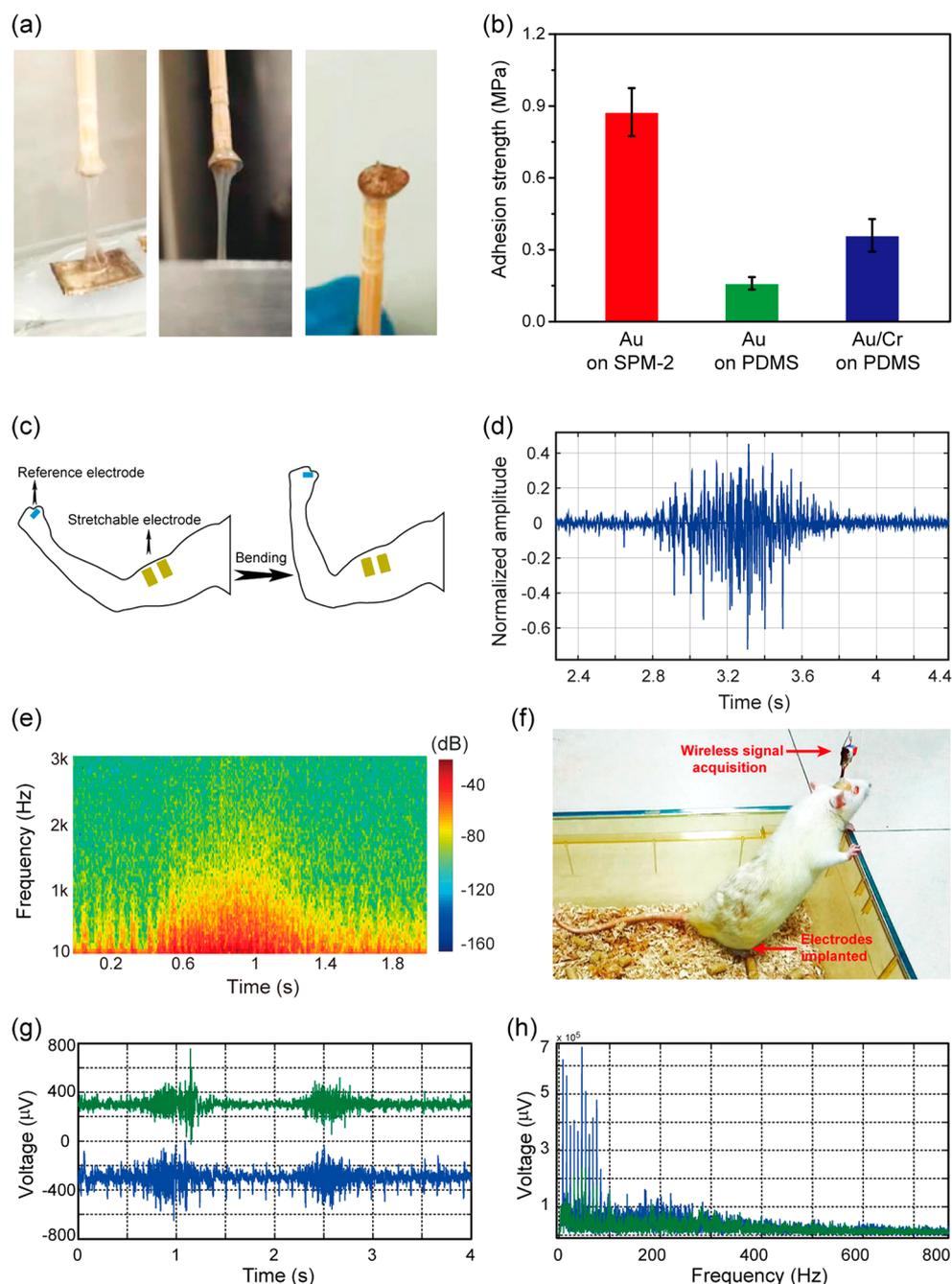


Figure 5. High-adhesion property of the electrode and on-skin and in vivo EMG detection. (a) Optical images of the adhesion testing process. The SPM-2 is stretched out from the electrode, indicating that the adhesion between the gold film and SPM-2 is quite good, and the adhesion strength is determined by the polymer substrate itself not by the interfacial adhesion between the gold film and the polymer. The right panel shows the final state at the bottom of the stick. The residual breaking polymer can be observed clearly, and the yellow gold film is underneath. (b) Adhesion strength of SPM-2-based electrode compared with that based on PDMS and nonstretchable electrode. (c) Sketch of the on-skin EMG detection. Two yellow parts illustrate the electrode position, and the blue part shows the reference electrode. (d) Typical EMG signal detected. (e) Energy spectrum analysis of the EMG signal in (d). (f) Side view of the rat implanted with SPM-2-based stretchable thin film gold electrode. See details of implantation process and electrode position in Figure S22. (g) Typical subcutaneous EMG signal. (h) Spectrum analysis of the EMG signal in (g).

conductive element was either a layer of liquid or conducting fillers dispersed in the thick self-healable polymer matrix. The conductive elements can easily recontact each other to recover conductivity. However, for stretchable thin film electrodes with a gold film of tens of nanometers in thickness, it is challenging to reconnect the gold film because their thicknesses are usually on the order of submicrometer. Here, a sharp blade was used to cut the electrode, with the gold thin film on the surface, into

two halves and subsequently joined back together by hand; that is, no special alignment machine was used in this process (Figures 4a and S20). After allowing the electrode to heal for 36 h at room temperature or 10 h at 45 °C, the cut trace visibly remains, but the conductivity of the gold film was recovered quantitatively (Figure 4a and b). Interestingly, we also observed that after the self-healing process of the polymeric substrate the film was conductive even under 90% tensile strain (Figure 4b).

We hypothesized that the mechanical deformation at the cutting edge induced by the blade played a key role in the stretchability. When the blade severed the electrode, we observed that the polymer adjacent to the cutting edge suffered plastic deformation and bent downward, which was also verified by the finite element modeling (FEM) (Figure 4c–e). Bending of the polymer's edge was estimated to be $\sim 50 \mu\text{m}$ by optical microscopy (Figure 4f), and the metal film was also covering the bent substrate surface (Figure 4g). Therefore, the gold film electrodes were able to reconnect, thus re-establishing connectivity, as the side walls of the substrates came in contact to begin to heal (Figure 4h).

On-Skin and Intramuscular EMG Detection. Interfacial adhesion between the metal film and polymeric substrate is important, as it was previously reported that a bad interfacial adhesion significantly affected the performance of the electrode; for example, interface friction may cause delamination.¹² Thus, we investigated the interfacial adhesion of the thin film metal electrode to various polymer substrates (Figure S21 and Movies 6–8 in the SI). We observed the adhesion of the gold film was strong enough to pull out the SPM-2 polymer underneath to cause cohesive failure (Figure 5a shows the back side of the gold film can be observed through the transparent residual polymer), indicating very strong bonding between gold and SPM-2. Next, we compared the adhesion strength with two types of gold films on PDMS, i.e., with and without a 3 nm chromium as the adhesive layer. Interestingly, the adhesion strength of gold film on SPM-2 is measured to be 3–4 \times higher than that of the other two (Figure 5b). The good adhesion is also important for reducing crack propagation in the gold film as shown in other reports.⁴¹

Last, we proceed to demonstrate two potential applications of the stretchable gold electrodes as *in vitro* and *in vivo* electrophysiological sensors. First, for *in vitro* measurements, we can reliably monitor electromyography signals (Figure 5c and d). Electrodes were attached to the skin surface of the muscle by medical tape, and due to the good conformability of our soft electrodes, no adhesion gel was required to enhance the conformability. The obtained on-skin EMG signal is clean and the signal-to-noise ratio is comparable to PDMS-supported gold electrodes (Figure 5d and e).^{12,38} Second, for *in vivo* measurements, we implanted the electrode into a rat to monitor the intramuscular myoelectric signal (Figures 5f and S22a). Briefly, the electrode was able to be sutured to the muscle to fix the detection position during the surgery (Figures S22b and S23). The signals obtained were both clear and stable (Figure 5g and h). So, here, we successfully demonstrated the potential of our novel stretchable thin film electrode for both *in vitro* and *in vivo* measurements.

CONCLUSION

In summary, we have described a molecular design approach to achieve stretchable, antitearing, and self-healing metal thin film electrodes. Our presented results indicated the functionalities of stretchable thin film electrodes can be significantly enhanced through the chemical design of the polymeric substrate. Specifically, we applied supramolecular polymer design principles to synthesize dynamically cross-linked SPMs via quadruple UPy H-bonding. The resulting SPM contained multiple intra- and interchain H-bonding in the polymeric networks to enable excellent mechanical properties. Subsequently, our fabricated thin film gold electrode from the SPM substrate possesses both excellent inherent conductivity

and unique mechanical behaviors. Our electrodes have many of the highly desirable parameters combined into a single thin film electrode, which include high stretchability, self-healing, notch insensitivity, and improved interfacial adhesion. Finally, this stretchable electrode was successfully shown to measure EMG signals both on human skin (*in vitro*) and implanted within live rats (*in vivo*). These demonstrations clearly indicate that our SPM-supported thin film gold electrodes are potentially promising toward the fabrication of next-generation wearable and implantable electronics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b01682.

Movie of a specimen of SPM-2 showing stretching up to 52 \times its original length with a maximum stress of 2.92 MPa at a deformation rate of 1000 mm/min (AVI)

Movie using SPM-3 as an example, showing the notch area becoming blunt and that it was stable up to an average elongation of $\sim 12\%$ (AVI)

Movie of the film showing that it remained conductive even after inducing notches in the film and subsequently loading a tensile strain of $\sim 260\%$ (AVI)

Movie showing that the fabricated film did not break even after it was subjected to a $\sim 300\%$ tensile strain and then partially cut with scissors (AVI)

Movie of a stretchable thin film gold electrode on a PDMS substrate breaking into two parts at only $\sim 40\%$ applied strain even though the induced notch is shorter (AVI)

Movie showing the interfacial adhesion of the thin film metal electrode to various polymer substrates (AVI)

Movie showing the interfacial adhesion of the thin film metal electrode to various polymer substrates (AVI)

Movie showing the interfacial adhesion of the thin film metal electrode to various polymer substrates (AVI)

Experimental details and additional data (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Z.B. acknowledges support from the Air Force Office of Scientific Research (grant no. FA9550-15-1-0106). X.C. thanks the financial support from the National Research Foundation, Prime Minister's Office, Singapore, under its NRF Investigatorship (NRF2016NRF-NRFI001-21) and Singapore Ministry of Education (MOE2015-T2-2-060). Q.Z. thanks the financial

support from the National Natural Science Foundation of China (21404056) and China Scholarship Council (201606195042). G.L. thanks the support from the National Natural Science Foundation of China under grant #U1613222. J.L. acknowledges support by the National Science Foundation Graduate Research Fellowship Program (grant no. DGE-114747). Part of this work was performed at the Stanford Nano Shared Facilities (SNSF), supported by the National Science Foundation under award ECCS-1542152. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-76SF00515. The SSRL Structural Molecular Biology Program is supported by the DOE Office of Biological and Environmental Research and by the National Institutes of Health, National Institute of General Medical Sciences (including P41GM103393). The contents of this publication are solely the responsibility of the authors and do not necessarily represent the official views of the NIGMS or NIH. We thank Ivan Rajkovic for the support at Beamline 4-2.

REFERENCES

- (1) Chen, D.; Pei, Q. *Chem. Rev.* **2017**, *117*, 11239–11268.
- (2) Someya, T.; Bao, Z.; Malliaras, G. G. *Nature* **2016**, *540*, 379–385.
- (3) Xu, S.; Zhang, Y.; Jia, L.; Mathewson, K. E.; Jang, K.-I.; Kim, J.; Fu, H.; Huang, X.; Chava, P.; Wang, R.; Bhole, S.; Wang, L.; Na, Y. J.; Guan, Y.; Flavin, M.; Han, Z.; Huang, Y.; Rogers, J. A. *Science* **2014**, *334*, 70–74.
- (4) Chortos, A.; Liu, J.; Bao, Z. *Nat. Mater.* **2016**, *15*, 937–950.
- (5) Liu, J.; Fu, T.-M.; Cheng, Z.; Hong, G.; Zhou, T.; Jin, L.; Duvvuri, M.; Jiang, Z.; Kruskal, P.; Xie, C.; Suo, Z.; Fang, Y.; Lieber, C. M. *Nat. Nanotechnol.* **2015**, *10*, 629–636.
- (6) Li, J.; de Ávila, B. E.-F.; Gao, W.; Zhang, L.; Wang, J. *Sci. Robot.* **2017**, *2*, eaam6431.
- (7) Xiao, J.; Carlson, A.; Liu, Z. J.; Huang, Y.; Jiang, H.; Rogers, J. A. *Appl. Phys. Lett.* **2008**, *93*, 013109.
- (8) Yeo, W. H.; Kim, Y.-S.; Lee, J.; Ameen, A.; Shi, L.; Li, M.; Wang, S.; Ma, R.; Jin, S. H.; Kang, Z.; Huang, Y.; Rogers, J. A. *Adv. Mater.* **2013**, *25*, 2773–2778.
- (9) Liang, J.; Li, L.; Tong, K.; Ren, Z.; Hu, W.; Niu, X.; Chen, Y.; Pei, Q. *ACS Nano* **2014**, *8*, 1590–1600.
- (10) Guo, C. F.; Sun, T.; Liu, Q.; Suo, Z.; Ren, Z. *Nat. Commun.* **2014**, *5*, 3121.
- (11) Lacour, S. P.; Chan, D.; Wagner, S.; Li, T.; Suo, Z. *Appl. Phys. Lett.* **2006**, *88*, 204103.
- (12) Liu, Z.; Wang, X.; Qi, D.; Xu, C.; Yu, J.; Liu, Y.; Jiang, Y.; Liedberg, B.; Chen, X. *Adv. Mater.* **2017**, *29*, 1603382.
- (13) (a) Tee, B. C.-K.; Wang, C.; Allen, R.; Bao, Z. *Nat. Nanotechnol.* **2012**, *7*, 825–832. (b) Gong, C.; Liang, J.; Hu, W.; Niu, X.; Ma, S.; Hahn, T.; Pei, Q. *Adv. Mater.* **2013**, *25*, 4186–4191.
- (14) (a) Huynh, T.-P.; Haick, H. *Adv. Mater.* **2016**, *28*, 138–143. (b) Ko, J.; Kim, Y.-J.; Kim, Y. S. *ACS Appl. Mater. Interfaces* **2016**, *8*, 23854–23861.
- (15) (a) Blaiszik, B. J.; Kramer, S. L. B.; Crady, M. E.; Mellroy, D. A.; Moore, J. S.; Sottos, N. R.; White, S. R. *Adv. Mater.* **2012**, *24*, 398–401. (b) Cai, G.; Wang, J.; Qian, K.; Chen, J.; Li, S.; Lee, P. S. *Adv. Mater.* **2017**, *4*, 1600190. (c) Kim, K.; Jung, M.; Kim, B.; Kim, J.; Shin, K.; Kwon, O.-S.; Jeon, S. *Nano Energy* **2017**, *41*, 301–307. (d) Kim, S.-M.; Jeon, H.; Shin, S.-H.; Park, S.-A.; Jegal, J.; Hwang, S. Y.; Oh, D. X.; Park, J. *Adv. Mater.* **2018**, *30*, 1705145.
- (16) Chen, X. *Small Methods* **2017**, *1*, 1600029.
- (17) Aida, T.; Meijer, E. W.; Stupp, S. I. *Science* **2012**, *335*, 813–817.
- (18) Greef, T. F. A. De; Smulders, M. M. J.; Wolfs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. *Chem. Rev.* **2009**, *109*, 5687–5754.
- (19) Yang, L.; Tan, X.; Wang, Z.; Zhang, X. *Chem. Rev.* **2015**, *115*, 7196–7239.
- (20) Yan, X.; Wang, F.; Zheng, B.; Huang, F. *Chem. Soc. Rev.* **2012**, *41*, 6042–6065.
- (21) Wojtecki, R. J.; Meador, M. A.; Rowan, S. J. *Nat. Mater.* **2011**, *10*, 14–27.
- (22) Sun, J.-Y.; Zhao, X.; Illeperuma, W. R. K.; Chaudhuri, O.; Oh, K. H.; Mooney, D. J.; Vlassak, J. J.; Suo, Z. *Nature* **2012**, *489*, 133–136.
- (23) Kushner, A. M.; Vossler, J. D.; Williams, G. A.; Guan, Z. *J. Am. Chem. Soc.* **2009**, *131*, 8766–8768.
- (24) Guan, Z.; Roland, J. T.; Bai, J. Z.; Ma, S. X.; McIntire, T. M.; Nguyen, M. J. *Am. Chem. Soc.* **2004**, *126*, 2058–2065.
- (25) Li, C.-H.; Wang, C.; Keplinger, C.; Zuo, J.-L.; Jin, L.; Sun, Y.; Zheng, P.; Cao, Y.; Lissel, F.; Linder, C.; You, X.-Z.; Bao, Z. *Nat. Chem.* **2016**, *8*, 618–624.
- (26) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. Ky; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601–1604.
- (27) Söntjens, S. H. M.; Sijbesma, R. P.; van Genderen, M. H. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 7487–7493.
- (28) (a) Yan, X.; Li, S.; Pollock, J. B.; Cook, T. R.; Chen, J.; Zhang, Y.; Ji, X.; Yu, Y.; Huang, F.; Stang, P. J. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 15585–15590. (b) Qin, B.; Zhang, S.; Song, Q.; Huang, Z.; Xu, J.-F.; Zhang, X. *Angew. Chem., Int. Ed.* **2017**, *56*, 7639–7643.
- (29) Jeon, L.; Cui, J.; Illeperuma, W. R. K.; Aizenberg, J.; Vlassak, J. J. *Adv. Mater.* **2016**, *28*, 4678–4683.
- (30) Chen, Y.; Kushner, A. M.; Williams, G. A.; Guan, Z. *Nat. Chem.* **2012**, *4*, 467–472.
- (31) Sun, G.; Li, Z.; Liang, R.; Weng, L.-T.; Zhang, L. *Nat. Commun.* **2016**, *7*, 12095.
- (32) Sun, T. L.; Kurokawa, T.; Kuroda, S.; Ihsan, A. B.; Akasaki, T.; Sato, K.; Haque, M. A.; Nakajima, T.; Gong, J. P. *Nat. Mater.* **2013**, *12*, 932–937.
- (33) Liu, J.; Tan, C. S. Y.; Yu, Z.; Lan, Y.; Abell, C.; Scherman, O. A. *Adv. Mater.* **2017**, *29*, 1604951.
- (34) Greensmith, H. W. *J. Appl. Polym. Sci.* **1963**, *7*, 993–1002.
- (35) (a) Sakulkaew, K.; Thomas, A. G.; Busfield, J. J. C. *Polym. Test.* **2011**, *30*, 163–172. (b) Kang, J.; Son, D.; Wang, G.-J. N.; Liu, Y.; Lopez, J.; Kim, Y.; Oh, J.-Y.; Katsumata, T.; Mun, J.; Lee, Y.; Jin, L.; Tok, J. B.-H.; Bao, Z. *Adv. Mater.* **2018**, *30*, 1706846.
- (36) Ducrot, E.; Chen, Y.; Bulter, M.; Sijbesma, R. P.; Creton, C. *Science* **2014**, *344*, 186–189.
- (37) Liu, Z.; Yu, M.; Lv, J.; Li, Y.; Yu, Z. *ACS Appl. Mater. Interfaces* **2014**, *6*, 13487–13495.
- (38) Liu, Z.; Qi, D.; Guo, P.; Liu, Y.; Zhu, B.; Yang, H.; Liu, Y.; Li, B.; Zhang, C.; Yu, J.; Liedberg, B.; Chen, X. *Adv. Mater.* **2015**, *27*, 6230–6237.
- (39) Benight, S. J.; Wang, C.; Tok, J. B.-H.; Bao, Z. *Prog. Polym. Sci.* **2013**, *38*, 1961–1977.
- (40) Wang, H.; Zhu, B.; Jiang, W.; Yang, Y.; Leow, W. R.; Wang, H.; Chen, X. *Adv. Mater.* **2014**, *26*, 3638–3643.
- (41) (a) Bitter, J. E.; Lardner, T. J.; Grayeski, W.; Prakash, G. C.; Lawrence, J. J. *Adhes.* **1997**, *63*, 265–284. (b) Potter, K. D.; Guild, F. J.; Harvey, H. J.; Wisnom, M. R.; Adams, R. D. *Int. J. Adhes. Adhes.* **2001**, *21*, 435–443. (c) Suo, Z.; Vlassak, J.; Wagner, S. *China Particuol.* **2005**, *3*, 321–328.