Supplementary Information

Fabrication of an Autonomously Self-Healing Flexible Thin-Film Capacitor by Slot-Die Coating

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General Procedure

Materials. Commercial reactants were used without further purification unless stated otherwise. All the solvents used in these reactions were distilled prior to use. Aminopropyl-terminated polydimethylsiloxane with molecular weight of 1000 Da, and dispersity of 1.33 was purchased from Gelest (Pennsylvania, USA). Pyridine-2-carboxaldehyde and Iron (II) tetrafluoroborate hexahydrate were purchased from Sigma-Aldrich and used as received. PEDOT:PSS (Clevios PEDOT:PSS) was purchased from Heraeus (Ohio, USA).

Measurements and Characterization. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 MHz. Chemical shifts are given in parts per million (ppm). UV-Visible spectroscopy was performed on a Varian UV/Visible Cary 50 spectrophotometer. Slot die-coating was performed with a FOM Technologies Nano Roll Coater equipped with a World Precision Instruments high pressure syringe pump. Optical microscope images were obtained with a Keyence Digital Microscope VHX-950F. For film thickness measurements, WiTec Alpha 300 R AFM/Raman equipped with a True Surface (TM) surface profilometer was used. An area was scanned around the scratch with the profilometer and transects drawn across the scratch to determine the depth profile of the scratch using ControlFour Analysis Software on the WiTec Equipment. The scratch was made with a scalpel and light pressure.

Evaluation of self-healing properties. The printed films were damaged by submersion in liquid N_2 for 30 seconds to generate an array of cracks. In analyzing the self-healing efficiency of the film, the cracks were observed under an optical microscope periodically every hour for 24 hours, when the cracks became fully healed. In examining the self-healing film at body temperature, the cracked film was placed on a temperature controlled microscope stage heated to 37°C. The film was observed every hour for 5 hours, whereby damage on the film was restored.

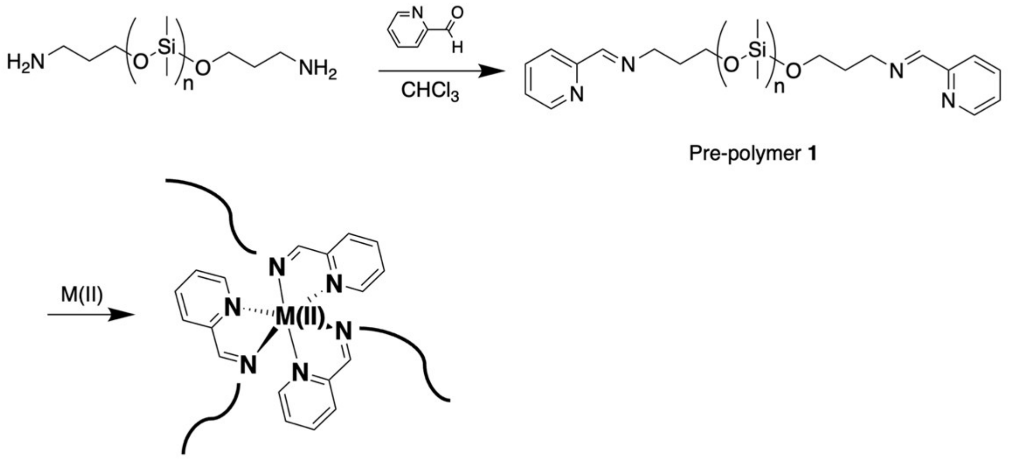
PET Platform: The platform used to deposit the self-healing dielectric was prepared from silver (Ag) nanoparticles ink deposited onto a 125 μm-thick polyethylene terephthalate (PET). Briefly, samples were printed by an industrial roll-to-roll press with flexography printing units (OMET Varyflex V2) using a silver nano-silver water-based ink (NovaCentrix, PFI500) with adjusted viscosity and drying retardant. The ink was put in contact with a micro-engraved cylinder (anilox), filling its cells, and was scraped with a doctor blade to assure that the cells were filled with a constant, controlled volume of ink at a rate of 2.2 bcm (billion cubic microns per square inch). The ink was then transferred onto a printing form, which defined the pattern information. The inked pattern was then pressed against the PET substrate in the nip zone between the printing form and an impression cylinder. The ink transfer onto the substrate was performed with the lowest possible pressure at a printing speed of 15 m/min. The printed substrates have been dried in-line with the hot air at the temperature of 100 °C. The produced sample showed a conductivity of 4.40 x 10^6 S/m and a thickness of 352 nm. Patterns with circular-shape bottom electrodes with areas of 1.0, 1.5, and 2.0 cm^2 were used.

Device Fabrication. The dielectric layer was printed on top of the PET with electrodes using slot-die coating. A PEDOT:PSS solution was then printed over the dielectric layer to act as the top electrode using the same slot-die coater. The details of the deposition parameters can be found in the following section. The device was allowed to dry in a fume hood for 12 hours to ensure excess solvent was no longer present in the films, then the device was ready for measurements.

Slot die coating. Slot-die coating was carried out with a commercial table slot coater (FOM Technologies Nano Roll Coater) connected to a syringe pump system under ambient conditions. The dielectric layer was printed with the flow rate of 0.02 mL/min as the roller moved at the speed of 0.1 m/min at 35 °C. The dielectric layer consisted of 4 coatings to achieve a film with the sufficient thickness. The PEDOT:PSS layer was printed with the flow rate of 0.04 mL/min as the roller moved at the speed of 0.1 m/min at 50 °C. A single layer of the PEDOT:PSS solution was printed over each electrode to attain the device.

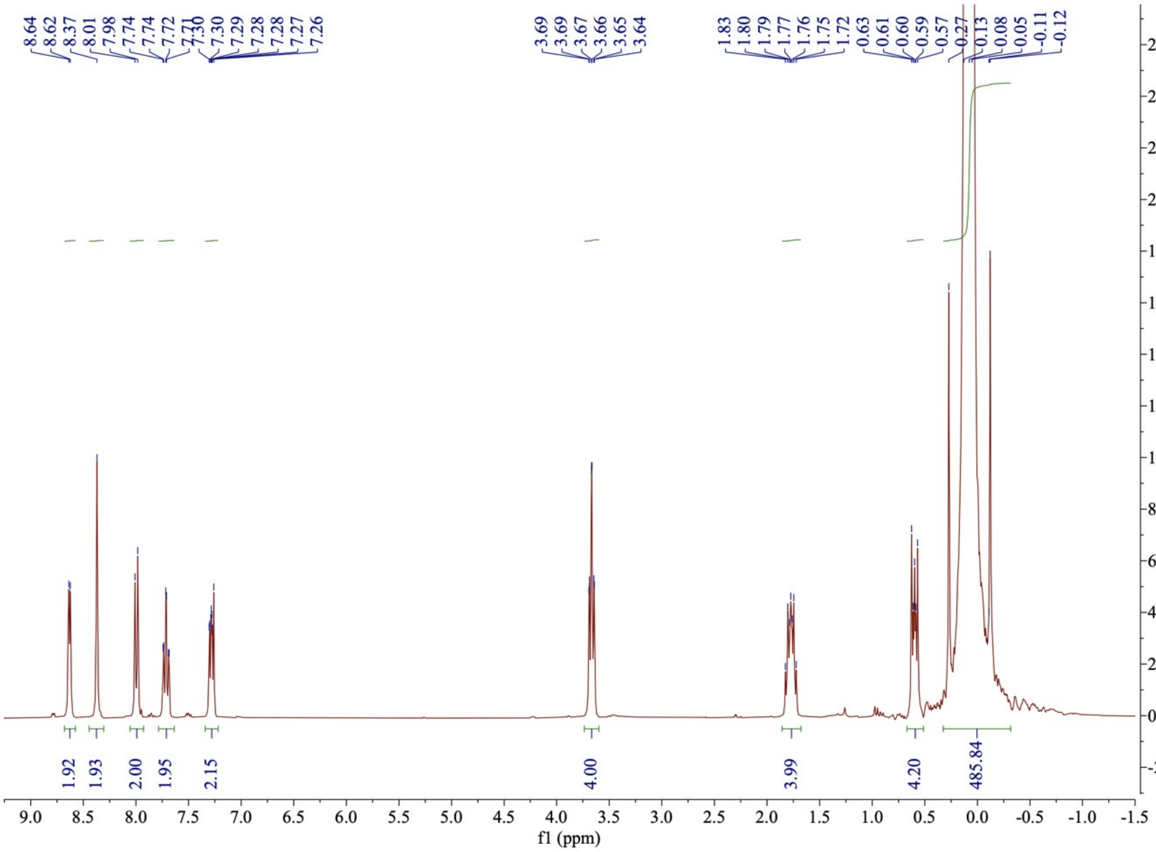
Device Characterization. Fabricated and assembled capacitive sensing pressure sensor devices were connected to an Agilent E4980A 2MHz Precision LCR meter for capacitance measurements. To understand the sensitivities in low skin-like pressure region we applied 12 different weights ranging from 1 to 20 g (0.37 to 1.91 kPa) on the pressure and measured the capacitance for pressure in this experiment from pressure 0 to 2kPa. The devices were tested at various pressures within this range in order to construct a sensitivity curve. Sensors were also characterized for loading and unloading during a bending of the device. A test fixture was designed and used to test bending and unbending of the sensors. As shown in Figure S4, bending of the samples (concave) was performed while capacitance values were recorded simultaneously. Same loading and unloading experiment were performed for healed samples after damage.

Experimental Procedure

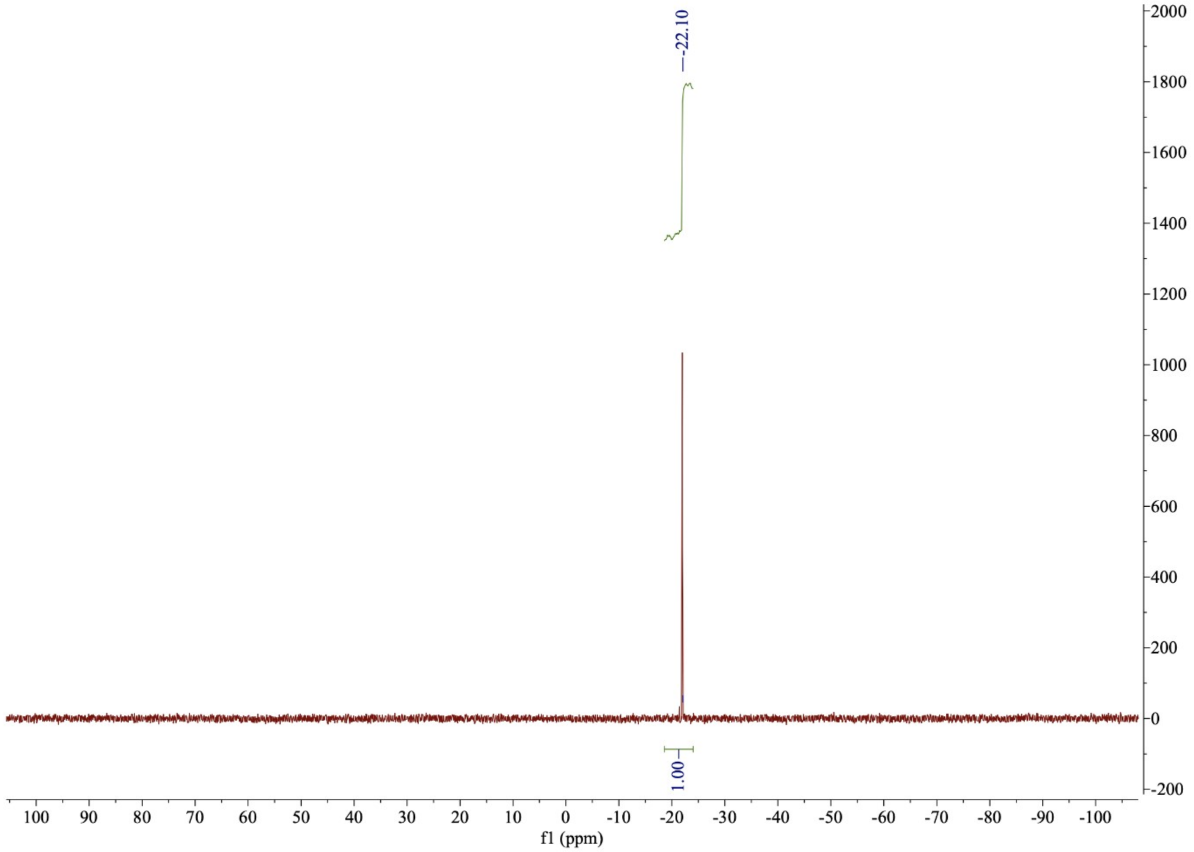


Scheme S1. Synthesis of pre-polymer **1** followed by chemical crosslinking with metal (II)-based salts.

Pre-polymer 1. The procedure to prepare **pre-polymer 1** has been described elsewhere.[1,2] A round bottom flask equipped with a magnetic stir bar was charged with aminopropyl-terminated PDMS (20 g, 0.020 mol), pyrimidine-2-carboxaldehyde (4.28 g, 0.042 mol) and $CHCl_3$ (20 mL). The reaction was left stirring for 48 hours at room temperature and $CHCl_3$ was removed under reduced pressure. The resulting materials was diluted in hexanes and was extracted with MeCN to remove unreacted monomer and dried under vacuum to afford **pre-polymer 1** as a viscous thick oil. ^{1}H NMR (300MHz, $CDCl_3$, 298 K): 8.62 (d, J = 4.2 Hz, 2H), 8.35 (s, 2H), 7.98 (dd, J = 7.8 Hz, 2H), 7.72 (t, 2H), 7.29 (t, J = 15 Hz, 2H), 3.67 (t, J = 14 Hz, 4H), 1.79 (m, 4H), 0.58 (t, J = 7.5 Hz, 4H), 0.13 (br s, 486 H). Molecular weight, M_n = 5994 Da, was estimated from ^{1}H NMR using a previously described procedure.[3]



^{1}H NMR spectrum of pre-polymer **1** in $CDCl_3$



^{29}Si NMR spectrum of pre-polymer **1** in $CDCl_3$

General procedure for the preparation of Fe-coordinated polymer: The crosslinking of pre-polymer 1 was performed by dissolving 10 g of the pre-polymer in chloroform (0.1 g/mL) and stirring for 5 minutes at room temperature. 0.09 g of Fe(II) tetrafluoroborate hexahydrate was dissolved in a minimal amount of methanol and then added to the solution. The solvents were removed under reduced pressure and then redissolved in chloroform. The solution was left to stir for 1 hour and the resulting gel-like materials was directly used for printing.

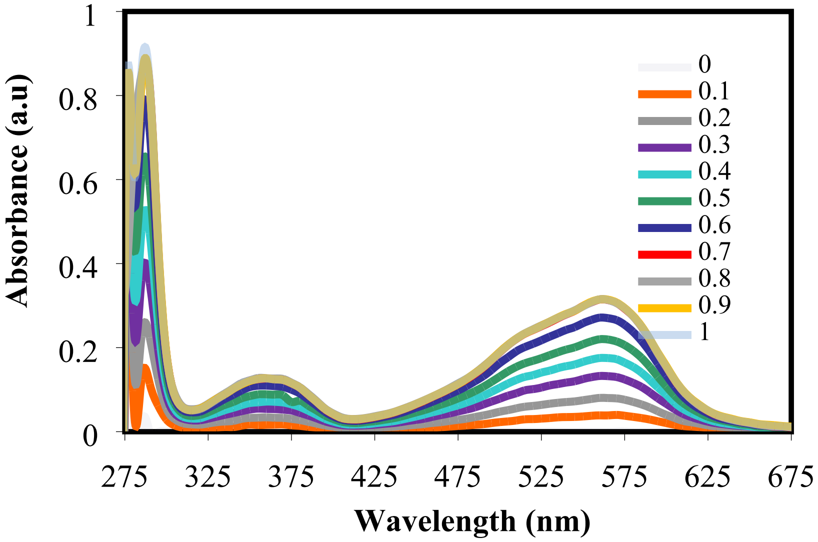


Figure S1. UV-vis absorption spectra of pre-polymer **1** upon progressive addition of $Fe(BF_4)_2$ x 6 H_2O in $CHCl_3$ (increments of 0.1 equivalent, from 0 to 1 equivalent).

Materials and Devices Characterization

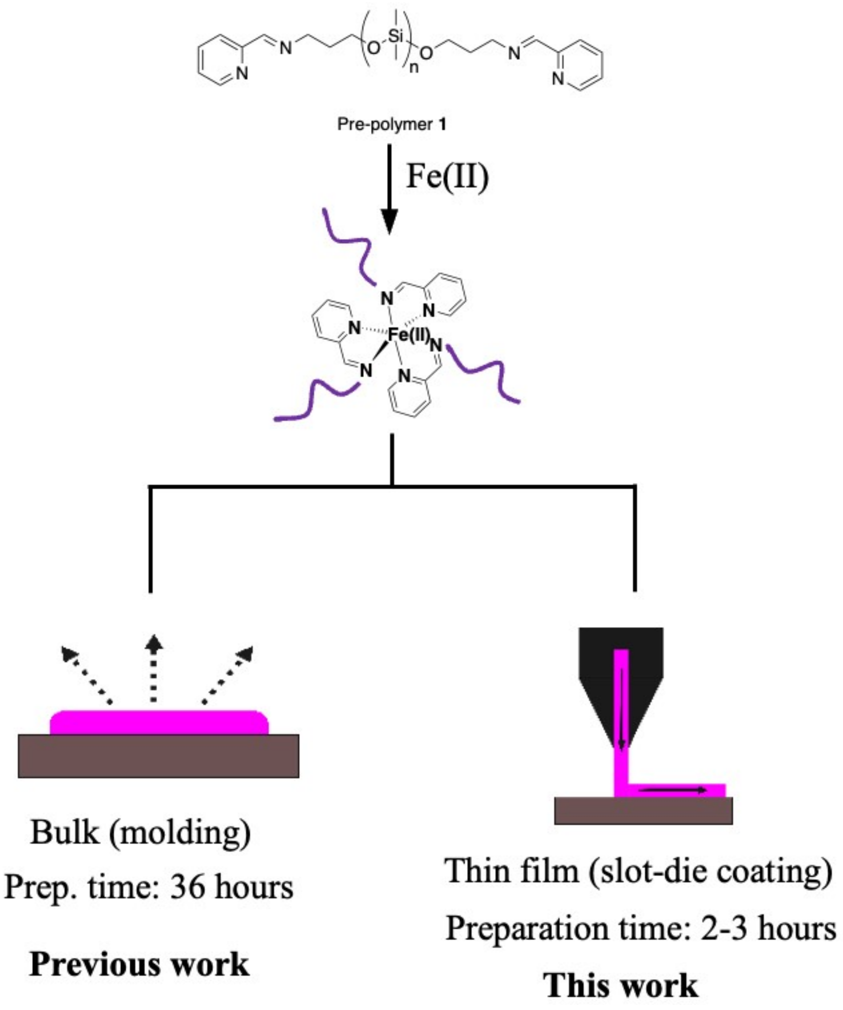


Figure S2. Comparison between previous and current work on the slot-die coating of the self-healing dielectric and the fabrication of flexible thin film capacitive sensors.

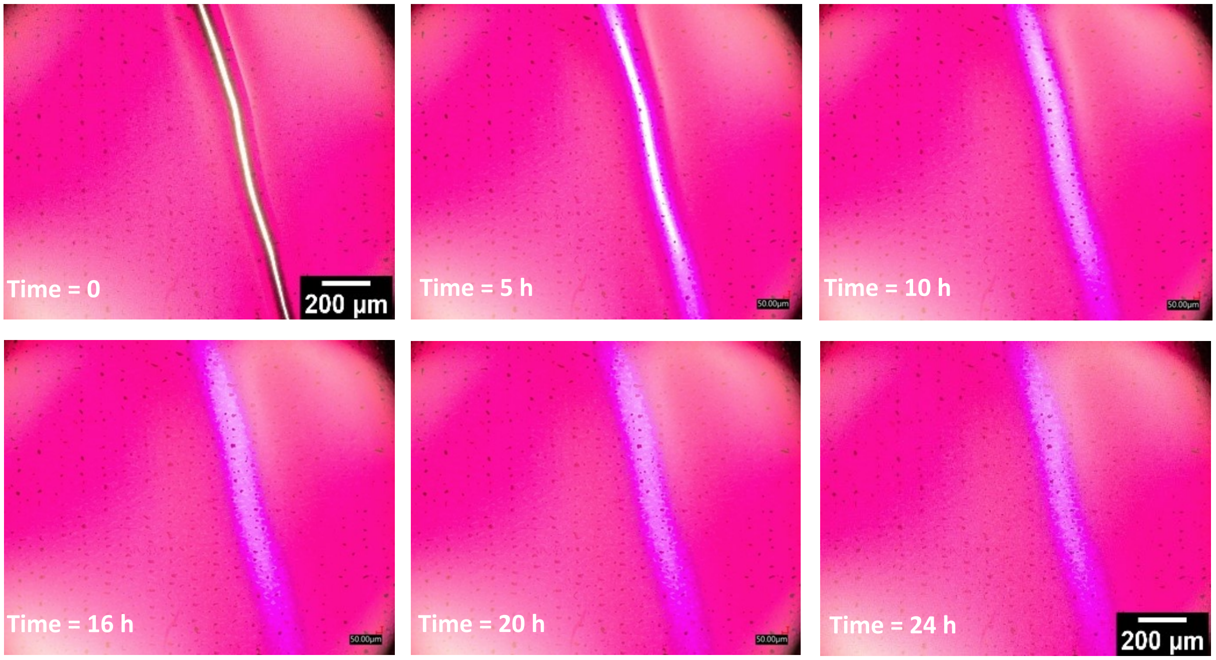


Figure S3. Optical microscope images of the damaged dielectric film and its autonomous healing at room temperature.

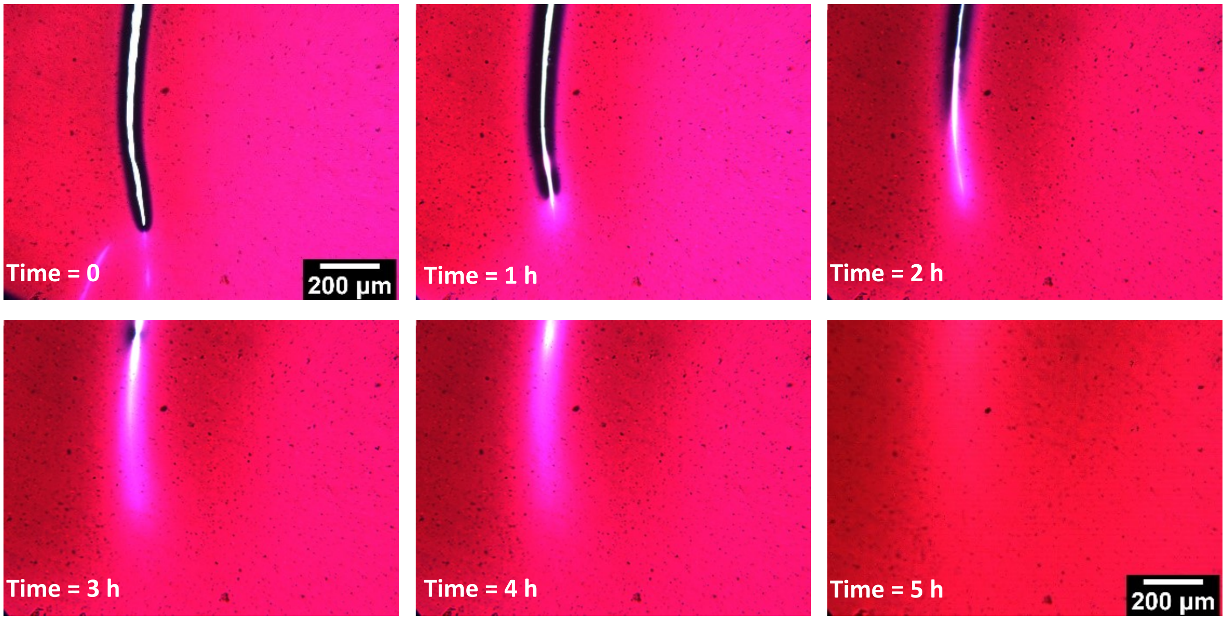


Figure S4. Optical microscope images of the damaged dielectric film and its autonomous healing at 37 °C.

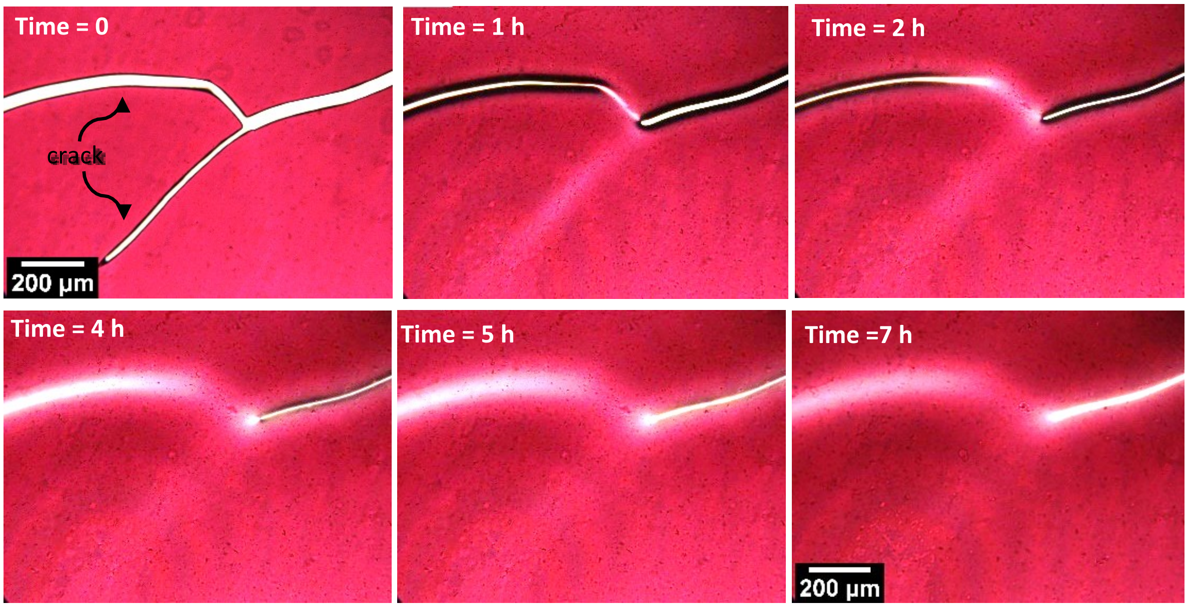


Figure S5. Optical microscope images of the damaged dielectric film and its autonomous healing at 50 °C.

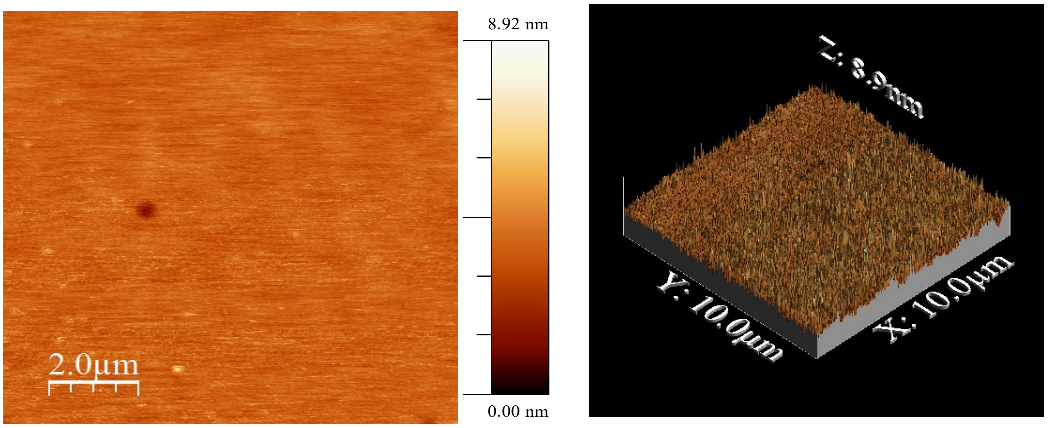


Figure S6. Atomic force microscopy (AFM) height image (left) and three-dimensional height image (right) of the dielectric film. Scale bar is 2 μm.

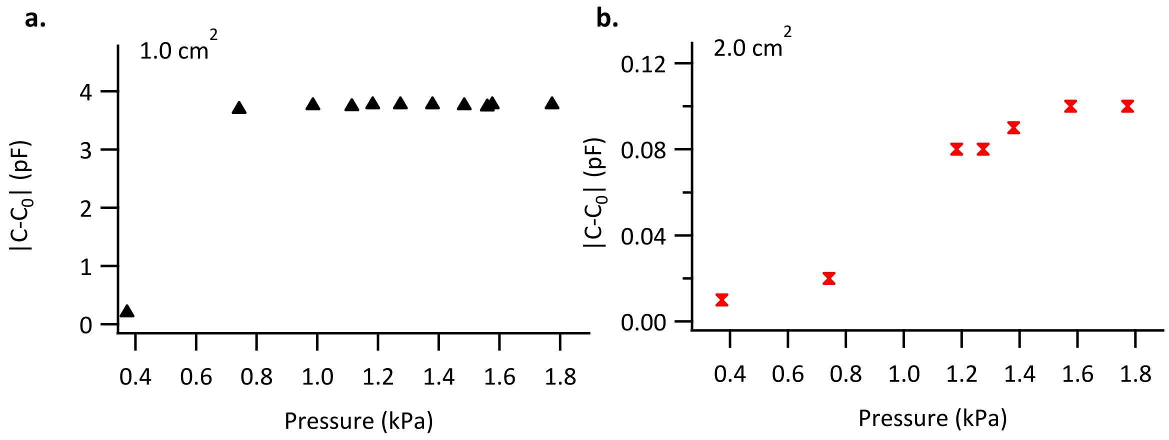


Figure S7. The capacitance changes as a function of applied pressure for 1.0 cm^2 (a) and 2.0 cm^2 (b) capacitor area.

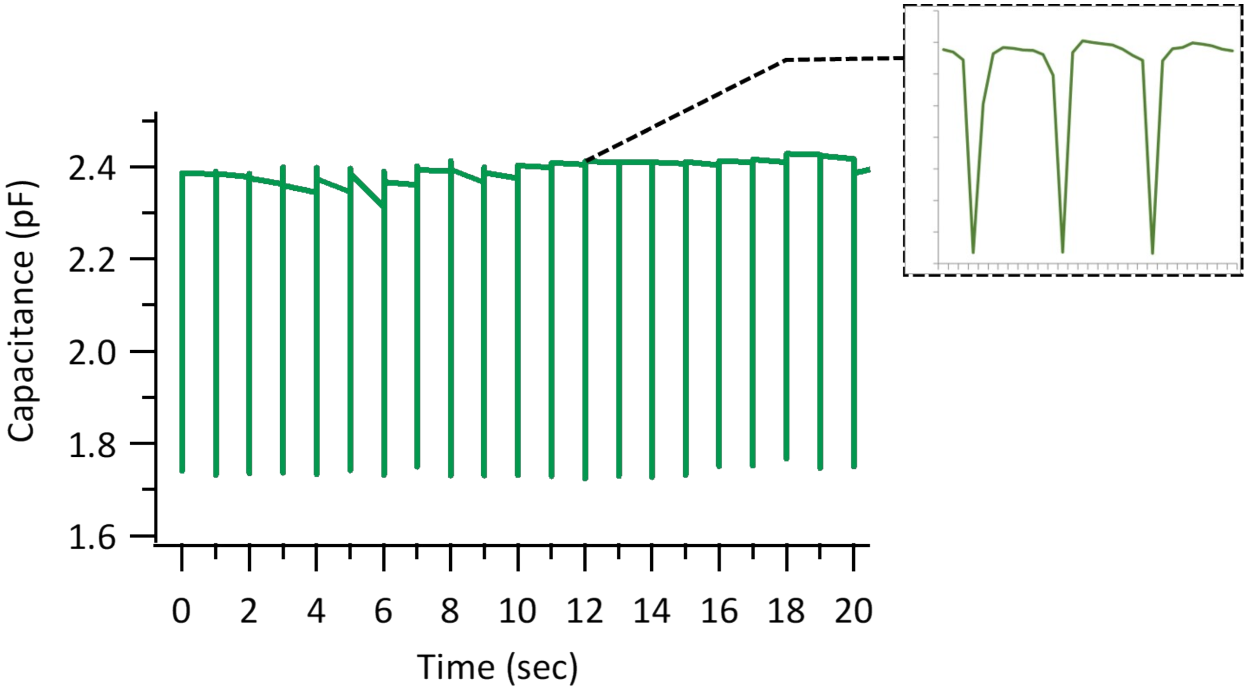


Figure S8. Dynamic capacitance testing. A random pressure was applied on the sensor (1.5 cm^2 capacitor area) with a fingertip and removed from the sensor with capacitance recorded.

References

1 J. Pignanelli, B. Billet, M. Straeten, M. Prado, K. Schlingman, M. Jalal Ahamed and S. Rondeau-Gagné, Imine and metal–ligand dynamic bonds in soft polymers for autonomous self-healing capacitive-based pressure sensors, *Soft Matter*, 2019, **15**, 7654–7662.

2 J. Pignanelli, Z. Qian, X. Gu, M. J. Ahamed and S. Rondeau-Gagné, Modulating the thermomechanical properties and self-healing efficiency of siloxane-based soft polymers through metal–ligand coordination, *New J. Chem.*, 2020, **44**, 8977–8985.

3 J. U. Izunobi and C. L. Higginbotham, Polymer Molecular Weight Analysis by ^{1} H NMR Spectroscopy, *J. Chem. Educ.*, 2011, **88**, 1098–1104.