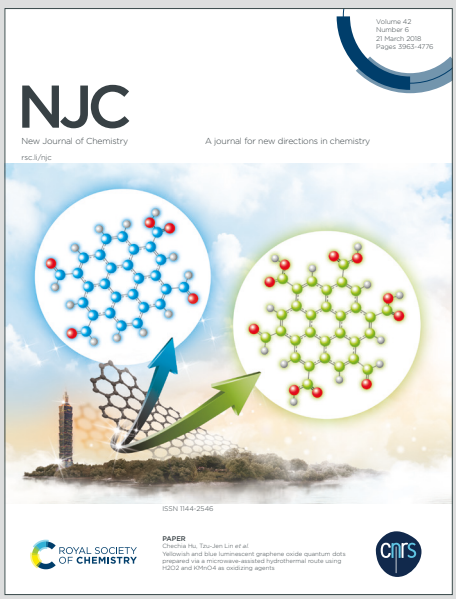
NJC

New Journal of Chemistry

A journal for new directions in chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: L. Rose, F. Motaghedi, N. Vanier, M. J. Ahamed and S. Rondeau-Gagné, *New J. Chem.*, 2026, DOI: 10.1039/D6NJ00535G.



ROYAL SOCIETY OF CHEMISTRY

rsc.li/njc

View Article Online
DOI: 10.1039/D6NJ00535G

Tuning Metal-Ligand Crosslinking for Shape-Stable, Self-Healing Capacitive Pressure Sensors

Lina Rose,[1,2,∇] Fatemeh Motaghedi,[1,∇] Nicole Vanier,[1] Mohammed Jalal Ahamed,[2 **] and Simon Rondeau-Gagné [1**]

[1] Department of Chemistry and Biochemistry, University of Windsor, Windsor, Canada
[2] Department of Mechanical, Automotive Materials Engineering, University of Windsor, Windsor, Canada
[∇] These authors contributed equally to this work

Corresponding Authors **E-mail: srondeau@uwindsor.ca (SRG); jahamed@uwindsor.ca (MJA)

ABSTRACT

Self-healing polymers inspired by biological tissue regeneration pave the way for developing robust, flexible wearable electronic devices. In this work, we report a self-healing capacitive pressure sensor composed of an imine- and metal-ligand crosslinked polymer as the dielectric layer, integrated with carbon nanotube (CNT) electrodes. Through fine-tuning of the dynamic crosslinking ratios, a clear structural property relationship was established, yielding a dielectric with improved geometric stability, mechanical rigidity, and efficient autonomous self-healing. The fabricated sensor demonstrated stable performance under pressures ranging from 60 kPa to 1 MPa, with minimal hysteresis, high cyclic durability, and good fatigue resistance. Crack width and healing time were quantitatively analysed, and the device showed stable operation after consecutive cut-and-healing cycles, while the CNT electrodes retained conductivity with only minor resistance drift. The optimized material was subsequently incorporated into Mesoamerican pyramidal (MAP) microstructured devices to enhance pressure-sensing performance. This work highlights a scalable, intrinsically self-healing pressure sensor with potential for long-term use in wearable electronics, biomedical devices, and harsh industrial environments.

DOI: 10.1039/D6NJ00535G

INTRODUCTION

The remarkable ability of human skin to rejuvenate and repair itself is inspiring scientists worldwide to design artificial tissue-like materials that incorporate dynamic covalent bonds and supramolecular interactions capable of autonomous healing.[1–3] Self-healing is particularly fascinating phenomenon because it enables materials to recover functionality after damage, opening the door to devices that are safer, longer lasting, and far more resilient than conventional systems.[4,5] These properties are especially promising for applications where mechanical flexibility and durability are critical, including wearable electronics, soft robotics, and biomedical device engineering.[6–8] Such polymeric materials with self-healing capabilities could ultimately play a vital role in enabling devices that can autonomously repair damage and sustain prolonged used.[9–11] Self-healing materials can be categorized by various characteristics. For instance, self-healing can be intrinsic when it relies on reversible interactions such as hydrogen bonding and metal-ligand coordination to repair damage without external input, or extrinsic, when the materials need healing agents or triggers such as heat or light to achieve healibility [12]. Furthermore, these systems can also be further described as autonomous or non-autonomous depending on whether external stimulation is necessary.[13] Over the years, researchers have explored a wide range of self-healing mechanisms and material architectures. In extrinsic systems, mechanical damage ruptures embedded microcapsules or vascular networks, releasing healing agents that initiate repair [14]. Although effective, these systems typically depend on external stimuli and often offer only one-time healing, limiting their long-term applicability.[5,15,16] In contrast, intrinsic systems often incorporate reversible interactions directly within the materials matrix, such as hydrogen bonding and metal- ligand coordination, allowing repeated healing cycles without external intervention.[17–21] These materials provide high durability and re-processability, making them particularly suitable for flexible electronic devices that inevitably experience mechanical stress.[22–24]

View Article Online
DOI: 10.1039/D6NJ00535G

Recent progress in self-healing polymers has enabled materials with enhanced functionality across multiple fields. Self-healing behaviour has been incorporated into flexible sensors,[25–28] pressure and force sensors,[29–35] organic field-effect transistors,[36–39] dielectric materials[40] and stretchable conductors,[41–46] where mechanical damage would otherwise compromise electrical performance. For example, self-healing e-skins and tactile sensors can maintain mechanical integrity and stable signals after repeated deformation, supporting their use in (bio)signal monitoring and human-machine interfaces.[47–50] Beyond wearable and biomedical systems, self-healing materials are also being explored in industrial and aerospace environments, where they can mitigate mechanical, chemical, and thermal degradation.[51,52]

Among the various self-healing mechanisms, metal-ligand coordination has emerged as a particularly effective strategy for designing soft, functional materials with tunable mechanical and dynamic properties.[53,54] By controlling the density and geometry of coordination bonds within a polymer network, the viscoelastic response can be precisely adjusted to balance efficient healing with sufficient rigidity and structural stability.[47,55–57] Within the broad landscape of self-healable polymeric systems, our group has developed a platform based on an aminopropyl-terminated oligosiloxane that, upon reaction with 2-pyridinecarboxaldehyde, yields an *N*-ligand-terminated prepolymer. Subsequent coordination with selected divalent metal cations (M^{2+}) produces dynamically crosslinked networks with tailorable properties.[58,59] Systematic investigation of this material family revealed high stretchability, efficient self-healing behavior, and straightforward fine-tuning of thermomechanical properties through judicious choice of the metal crosslinker.[58] In recent years, we have extended this class of materials toward practical applications, including microfluidic components and plastic-based capacitive sensors.[59,60] Despite their promising material-level performance, metal-ligand coordinated self-healing polymers remain relatively underexplored for bulk sensing applications. To date, most demonstrations have focused on

thin-film or low-pressure sensing configurations, with comparatively few studies addressing shape stability or high-load pressure sensing. This limited adoption largely stems from the intrinsically soft and viscoelastic nature of these materials, which can compromise shape retention and dimensional stability under sustained or repeated mechanical loading. As a result, deformation-induced drift and structural relaxation may lead to inconsistent sensor outputs, posing a significant barrier to their implementation in robust, bulk sensing platforms.

In this work, we addressed these limitations by systematically correlating metal-ligand crosslinking density with geometric stability, self-healing efficiency, and device-level pressure-sensing performance. This structure-property framework enabled the identification of an optimal crosslinking regime that balanced structural rigidity with dynamic bond exchange, yielding shape-stable dielectric networks suitable for capacitive pressure sensing. The optimized self-healing dielectric was subsequently integrated between carbon nanotube (CNT) electrodes to fabricate capacitive sensors capable of repeated cut-heal cycles and reliable operation across a broad pressure range of 60 kPa to approximately 1 MPa. Device-level characterization before damage and after autonomous healing confirmed both mechanical resilience and electrical stability. The sensors retained over 90% of their original performance following damage and repair, with pressure sensitivity reaching 64.1 kPa^{-1} prior to cutting and remaining at 47.8 kPa^{-1} after healing. Collectively, these results established a direct link between molecular network design, and device functionality, demonstrating a practical pathway for translating soft self-healing polymers into shape-stable, microstructured capacitive pressure sensors capable of durable operation.

Experimental Methods

Materials preparation. The pre-polymer used to access the self-healing dielectric materials was prepared following previously reported procedures [58]. Briefly, a 500 ml round bottom

View Article Online
DOI: 10.1039/D6NJ00535G

flask, equipped with a stir bar, was first purged with nitrogen gas. Subsequently, aminopropyl-terminated siloxane (50 g, 0.01 mmol) and pyridine-2-carboxaldehyde (3.213 g, 0.03 mmol) were added and dissolved in chloroform (20 mL). The solution stirred for 48 hours at room temperature. Subsequently, the solvent was removed under reduced pressure, resulting in the formation of a gel. The gel was dissolved in hexanes and subjected to three extractions using a mixture of hexane and acetonitrile. The hexane fraction was collected, and dried under vacuum, resulting in the formation of the prepolymer as a waxy solid. Molecular weight was determined via DOSY-NMR, found M_W = 5480 g/mol. Molecular weight was also measured by high-temperature GPC in 1,2,4-trichlorobenzene (180°C) and found to be M_W = 5994 g/mol. To crosslink the pre-polymer and access the self-healing materials, cobalt (II) tetrafluoroborate hexahydrate ($Co(BF_4)_2 \cdot 6H_2O$) was used at a 1:1 molar ratio with pre-polymer, following previously reported procedures.[58]

Polymer crosslinking and molding. The resulting crosslinked polymer was drop casted into a PTFE mold and degassed under a vacuum chamber for 2 hours to eliminate trapped air and volatile residues. This step was repeated in layers until the desired film thickness for sensor fabrication was achieved. The mold was then left to dry at room temperature for 3 hours before carefully demolding the self-healing elastomeric film. Similarly, the polymer was cast on to inverse molding of PDMS- MAP- Ecoflex mold to fabricate MAP like microstructures following previously reported procedures.[61] MAP micropatterns with a height of 1250 µm, a top length of 850 µm, a base length of 2100 µm, and an inter-structural spacing of 400 µm were employed.

Device fabrication. The demoulded crosslinked polymer film, serving as the dielectric layer, was subsequently coated with conductive carbon nanotube (CNT) electrodes on both sides to fabricate the capacitive pressure sensor. CNT dispersion was prepared following a previously reported procedure and spray-coated uniformly onto the polymer surface (both sides) using a

precision airbrush system under ambient conditions.[62] The coated films were then dried at room temperature for 1 hour to remove residual solvent and stabilize the electrode layers. The fabrication sequence of the self-healing capacitive pressure sensor consisting of a CNT-polymer-CNT structure based on the metal- ligand crosslinked dielectric is ready for electrical and mechanical characterization, as shown in **Figure 1.**

RESULTS AND DISCUSSIONS

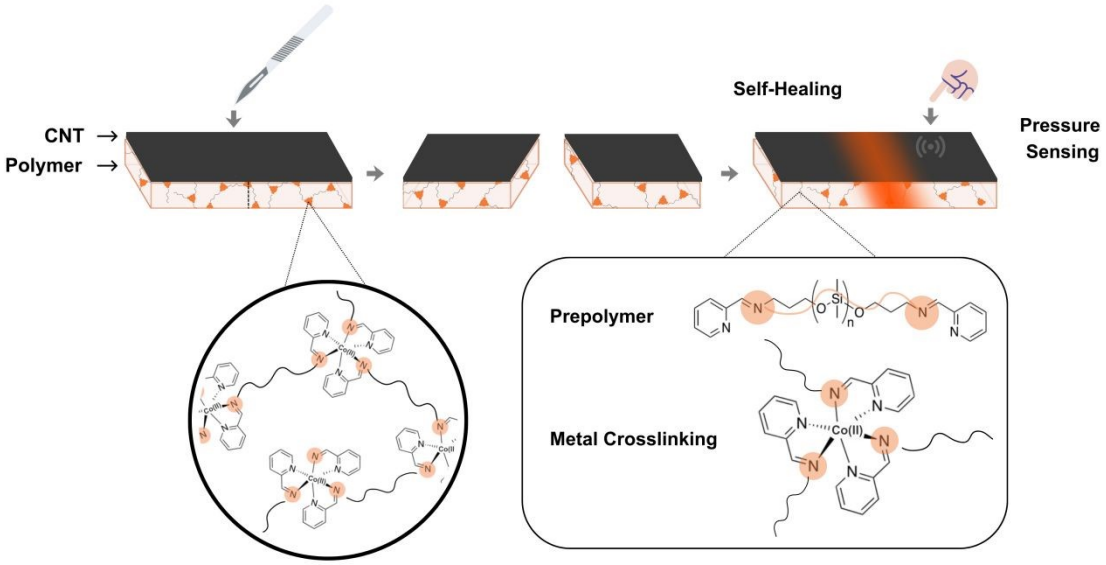


Figure 1. Self-healing capacitive pressure sensors based on *N*-ligand-terminated oligosiloxanes and their crosslinking with Co $^{(II)}$.

Guided by the material design principles outlined previously, we first investigated how metal-ligand crosslinking density governs geometric stability during processing and operation in order to identify formulations that maintain mechanical compliance while preventing brittle failure. Because the metal-ligand to prepolymer ratio directly dictates network connectivity and viscoelastic response, it plays a central role in determining device robustness. Initially, crosslinking of the prepolymer with Co^{2+} cations were investigated (**Figure 1**). Cobalt was

View Article Online
DOI: 10.1039/D6NJ00535G

selected as the metal crosslinker based on previous studies showing that Co^{2+}-coordinated networks exhibit slightly higher Young's moduli (8.10 MPa) than other crosslinked systems while retaining excellent stretchability and self-healing efficiency (61%), as determined by tensile pull tests.[58] Detailed synthetic procedures are provided in the Experimental section and in prior reports [58,59]. To achieve an optimal balance between autonomous self-healing and shape stability upon molding, a series of metal- ligand crosslinking ratios was systematically examined, as shown in **Figure S1**. At low prepolymer to metal-ligand ratios (1:0.5), the polymers, although capable of self-healing, displayed excessive viscoelasticity that led to pronounced deformation over time. Although initially stable, these polymers underwent geometric deformation even at room temperature and, under applied stress, failed to preserve structural consistency, ultimately compromising their functionality as capacitive pressure sensors. Increasing the metal-ligand ratio to 1: 0.75 resulted in partial deformation (approximately 80%), indicating improved structural integrity while preserving a degree of viscoelastic response. Notably, at a 1:1 metal-ligand ratio, the polymer exhibited excellent geometric stability, remaining dimensionally intact after demolding while preserving efficient autonomous self-healing. For this difunctional *N*-ligand-terminated polymer forming octahedral Co^{2+} complexes, this stoichiometry best balances coordination saturation and network connectivity. At this stoichiometry, the formation of dynamic coordination crosslinks promotes efficient intermolecular network percolation while limiting intrachain coordination and avoiding excessive network constraint. This balance enables the material to maintain robust shape stability while preserving sufficient segmental mobility for dynamic bond exchange, which is essential for effective self-healing. When the metal-ligand content is increased beyond this ratio (e.g., 1:2), the higher density of crosslinks can lead to an over constrained network. This results in reduced chain mobility, increased stiffness, and a transition toward more brittle mechanical behavior. Under these conditions, the restricted segmental dynamics hinder bond

View Article Online
DOI: 10.1039/D6NJ00535G

rearrangement across damaged interfaces, leading to incomplete or suppressed self-healing. To further probe for the mechanical properties of the self-healing materials, tensile pull testing by dynamic mechanical analysis (DMA) was performed on the self-healing materials crosslinked at a 1:1 metal-ligand ratio, as shown in **Figure S2.** A Young's modulus of 0.512 MPa was determined from the initial linear region of the tensile stress-strain curves for the pristine materials. The self-healing efficiency, calculated based on the recovery of strain at break, was found to be approximately 68%.

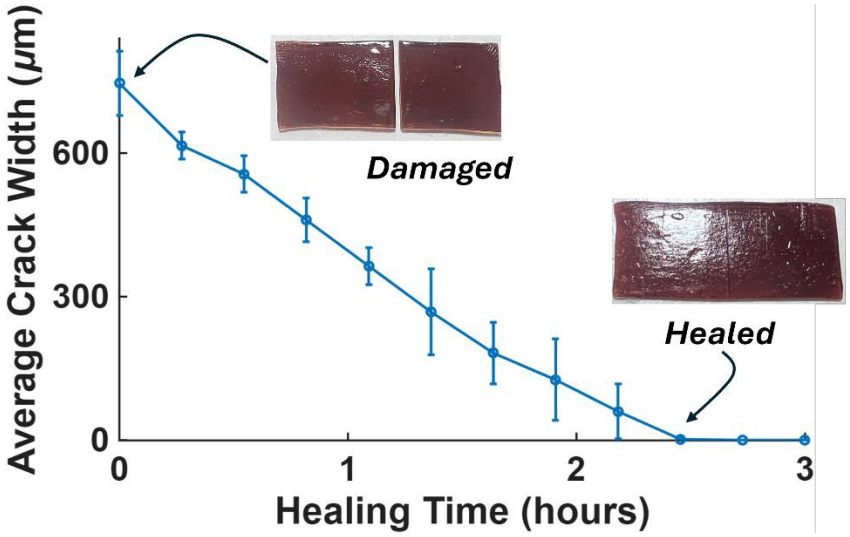


Figure 2. Average crack width upon mechanical damage in function of time. Inserts represent photographs of self-healing materials upon damage and after self-healing.

To assess the autonomous repair capability of the dynamically crosslinked network, the self-healing behavior of the system was evaluated by monitoring the time required to close cracks of varying widths through optical microscopy, as shown in **Figure 2** and **Figure S3**. As expected, narrow cracks (between 100 to 300 μm) were found to healed rapidly, typically within a couple of hours at room temperature, whereas wider cracks (around 500 to 600 μm) required 3-4 hours to heal. This trend reflects the increased time needed for polymer chain diffusion and redistribution across larger damaged interfaces. In addition, brittle samples

View Article Online
DOI: 10.1039/D6NJ00535G

resulting from an increased crosslinking density due excessively high metal-ligand content (2:1 ratio) displayed minimal or no self-healing, indicating that over-crosslinking severely restricts polymer chain mobility and suppresses the dynamic bond exchange required for healing. These results confirm that self-healing efficiency is governed by a delicate interplay between crosslinking density, crack width, and healing time, underscoring the importance of optimizing network dynamics for practical device applications.

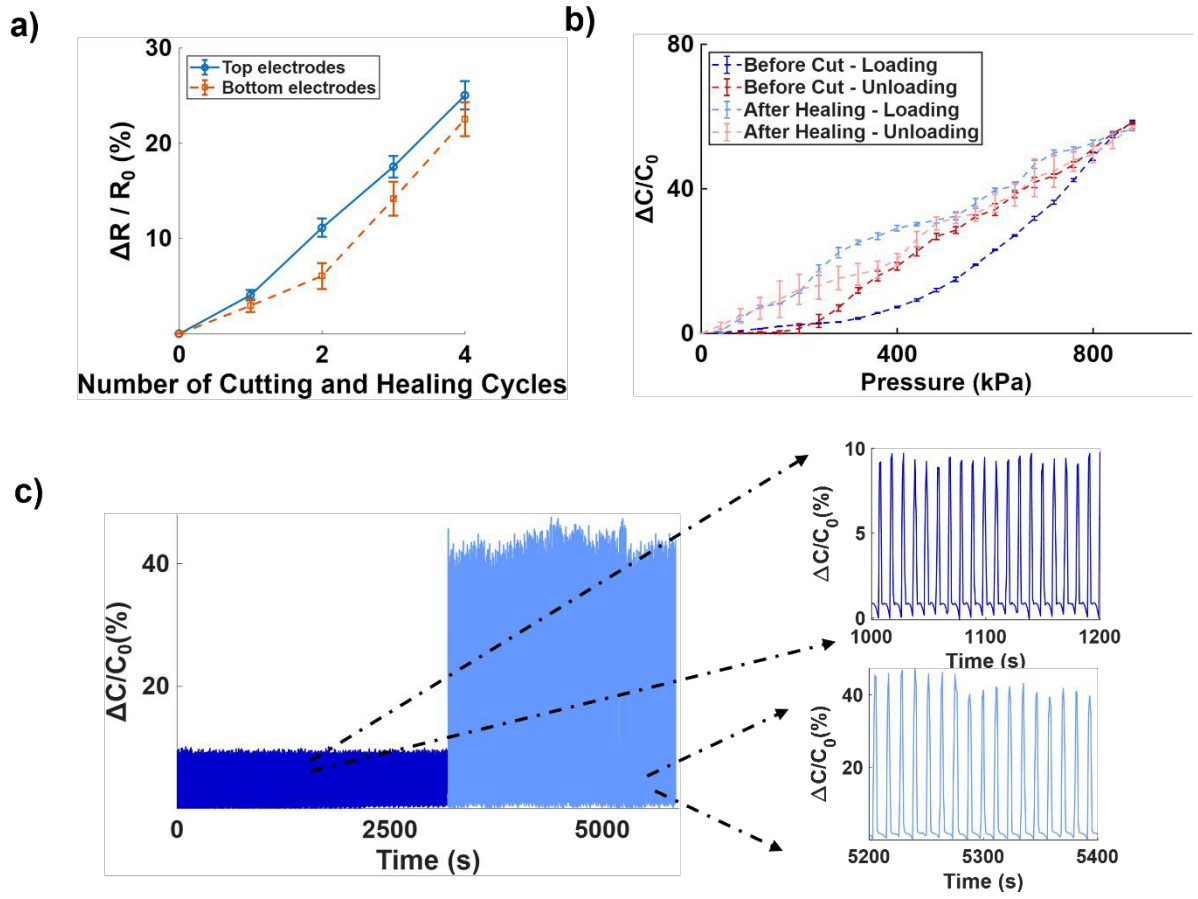


Figure 3. a) Relative resistance change ($\Delta R/R_0$) of the CNT electrode layers for multiple sensors subjected to successive cutting and self-healing cycles; b) Hysteresis behaviour of the capacitive pressure sensor during loading and unloading cycles measured before cutting and after self-healing for pressure less than 1MPa; c) Relative capacitance change ($\Delta C/C_0$) of the self-healing polymer under cyclic loading at 60 kPa and 840 kPa.

View Article Online
DOI: 10.1039/D6NJ00535G

To evaluate device-level electrical stability, we investigated the self-healing polymer in conjunction with carbon nanotube (CNT) electrodes. While CNT-based electrodes and conductive networks have been widely used in flexible and self-healing sensors, many reported systems rely on composite-based conductive layers and require external stimuli such as heat, light, or electrical input to restore conductivity.[63,64] Moreover, only limited studies have combined CNT electrodes with autonomously self-healing dielectrics for room-temperature, capacitive pressure sensing.[65,66] In contrast, the present device was designed to operate with the autonomously self-healing metal-ligand dielectric at room temperature, enabling repeated cut-heal cycles without external activation. CNTs were selected as conductive electrodes here due to their high electrical conductivity, mechanical flexibility, and proven compatibility with soft, deformable substrates. Notably, compared to metallic thin films or brittle conductive fillers, CNT networks can better accommodate large strains and damage events while maintaining conductive pathways, making them particularly well-suited for self-healing and flexible pressure-sensing applications where repeated deformation and cutting are expected.

To confirm the suitability of the CNT electrodes for self-healing pressure sensors, their electrical robustness under repeated damage and repair was first evaluated by monitoring the relative resistance change ($\Delta R/R_0$) over 4 cut-heal cycles, as shown in **Figure 3a**. Multiple samples were used for the study, and undergone subsequent damage- heal cycles, and electrical conductivity was measured at the top and bottom of the polymer to confirm uniformity. After the first damage-healing cycle, the resistance remains close to the initial value. In contrast, a gradual increase in resistance was observed following the second and third cutting-healing events. Importantly, even after four consecutive damage-healing cycles, which cumulatively lead to an increase in overall resistance, the electrodes remain within an operational range suitable for pressure sensing. The observed resistance increase can be attributed to localized

View Article Online
DOI: 10.1039/D6NJ00535G

defects, junction loss, and slight CNT misalignment induced during repeated damage and repair cycles. Nevertheless, the electrode network retained sufficient connectivity to preserve sensing functionality.

In parallel with the evaluation of electrode stability, the pressure-sensing performance of the capacitive devices was assessed through cyclic loading and unloading tests conducted before and after cutting and self-healing. As shown in **Figure 3b**, the sensors exhibited a largely comparable capacitive response following damage and repair for pressures less than 1 MPa, indicating that the self-healing process effectively restores both the mechanical integrity of the dielectric layer and the electrical functionality of the device. Notably, a modest increase in the separation between the loading and unloading curves was observed after healing. The difference between the loading and unloading capacitance responses can be attributed to structural and interfacial changes induced by cutting and healing cycles. In addition, the viscoelastic nature of the polymer matrix can introduce a mechanical lag, further contributing to the observed behaviour. Nevertheless, the sensors maintained stable and reproducible responses under applied pressures of up to approximately 1 MPa, demonstrating their suitability for moderate-to-high-pressure sensing applications. Overall, these results confirmed that autonomous self-healing does not significantly compromise sensor performance, reinforcing the potential of self-healing polymer-based capacitive sensors for long-term, durable operation in applications requiring mechanical resilience and reliable pressure detection.

Building on these findings, the capacitive response of the self-healing polymer was evaluated under cyclic loading at low to moderate (60 kPa) and high (840 kPa) pressures, as shown in **Figure 3c** and **Figure S4**. These regimes were chosen to represent wearable and tactile sensing conditions as well as higher-pressure scenarios such as robotic gripping and industrial handling.[67,68] The relative capacitance change ($\Delta C/C_0$) showed stable and

View Article Online
DOI: 10.1039/D6NJ00535G

reproducible behaviour, with consistent pressure sensitivity maintained for up to 2000 cycles. At 60 kPa, the sensor exhibited a largely linear response with minimal hysteresis, indicating excellent mechanical recovery. At 840 kPa, slight deviations from linearity and increased hysteresis were observed, attributed to viscoelastic deformation and minor structural relaxation under repeated stress. Despite this, reliable functionality was retained across the entire pressure range. Sensitivities of 26.4 kPa^{-1} and 71.3 kPa^{-1} were obtained in the low- and high-pressure regimes, respectively. Fatigue testing at ~860 kPa revealed wear and tear beyond 10,000 cycles, indicating the upper operational limits of the device. Prior to failure, $\Delta C/C_0$ remained stable and reproducible, confirming reliable performance within the intended pressure range.

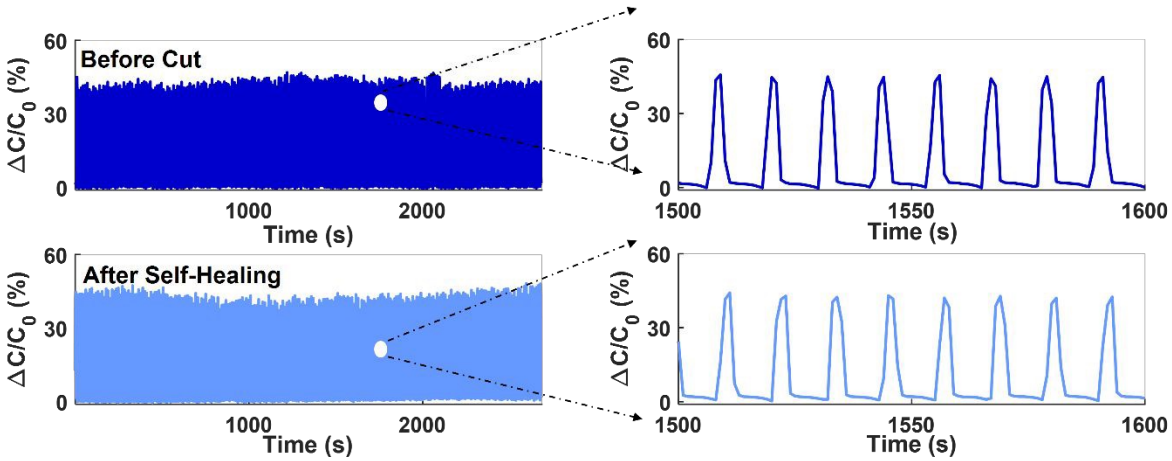


Figure 4. Relative change in capacitance for self-healing polymer sensor cyclic response for 500 kPa a) before cut and b) after healing.

To further assess the long-term durability of the self-healing capacitive pressure sensors under realistic operating conditions, fatigue testing was performed before and after self-healing under cyclic loading at 500 kPa for 2000 cycles, as shown in **Figure 4**. This pressure level was selected as a representative moderate-to-high load relevant to practical sensing scenarios, while also providing a demanding condition to evaluate the mechanical robustness and stability of the self-healing sensor. Following cutting and autonomous self-healing, the sensor displayed

View Article Online
DOI: 10.1039/D6NJ00535G

only minor deviations from the pre-damage capacitance response, indicating that the healing process effectively restores device functionality. Quantitatively, the self-healed polymer retained over 90% of its original sensing performance, demonstrating recovery of both structural integrity and electrical characteristics. The pressure sensitivity at moderate-to-high pressures decreased from 64.1 kPa^{-1} before cutting to 47.8 kPa^{-1} after healing. However, the healed sensor maintained a stable and repeatable response under identical loading conditions, comparable to its pre-damage behavior. This resilience supports the suitability of the sensor for long-term operation under continuous mechanical stress.

For better contextualization, a comparison between the performance of the present sensor and other reported pressure sensors is provided in **Table 1**, highlighting the competitive balance between sensitivity, durability, and self-healing capability achieved by the current sensing platform. Notably, while **Table 1** focuses on piezoresistive and capacitive sensors, which represent the most widely studied and technologically relevant platforms for stretchable and self-healable pressure sensing, other sensing mechanisms have also been explored in this field. These include piezoelectric, triboelectric, and optical (e.g., mechanochromic or photonic) sensors.[69–71] Piezoelectric and triboelectric devices can generate self-powered signals and exhibit high sensitivity, particularly under dynamic stimuli.[72,73] However, they are generally less effective for static pressure detection and can be more challenging to integrate with self-healing polymer systems. Optical-based sensors offer advantages in terms of signal decoupling and noise, but often require more complex instrumentation and are less compatible with scalable, flexible device architectures.[74,75] Given these considerations, piezoresistive and capacitive platforms remain the most practical and widely adopted approaches for self-healable pressure sensors, which motivated their focus in **Table 1**.

View Article Online
DOI: 10.1039/D6NJ00535G

Table 1. Comparison of previously reported self-healing pressure sensors with the current work.

Self-healing Material	Electrode materials	Sensor type	Pressure range (kPa)	Sensitivity (kPa^{-1})	Ref.
Polystyrene microsphere	LIG-PU, Cu	Piezoresistive	< 1	7.21	35
			1-10	130	
			10-100	157	
MXene-based polyurethane composite	MXene-based	Piezoresistive	0.20–1.70	281.5	29
			1.70–5.70	509.8	
			5.70–20.3	66.7	
PHAE	PET-Cu	Capacitive	< 0.5	2.45	30
FPU	rGO	Piezoresistive	0−300	9.45	34
IPNPUA	-	Capacitive	700	0.125	76
Disulfide-crosslinked polyurethane	PI-Ag	Piezoresistive	100 Pa−50kPa	197	32
Imine-based PDMS	CNTs	Capacitive	< 1MPa	71	**This work**

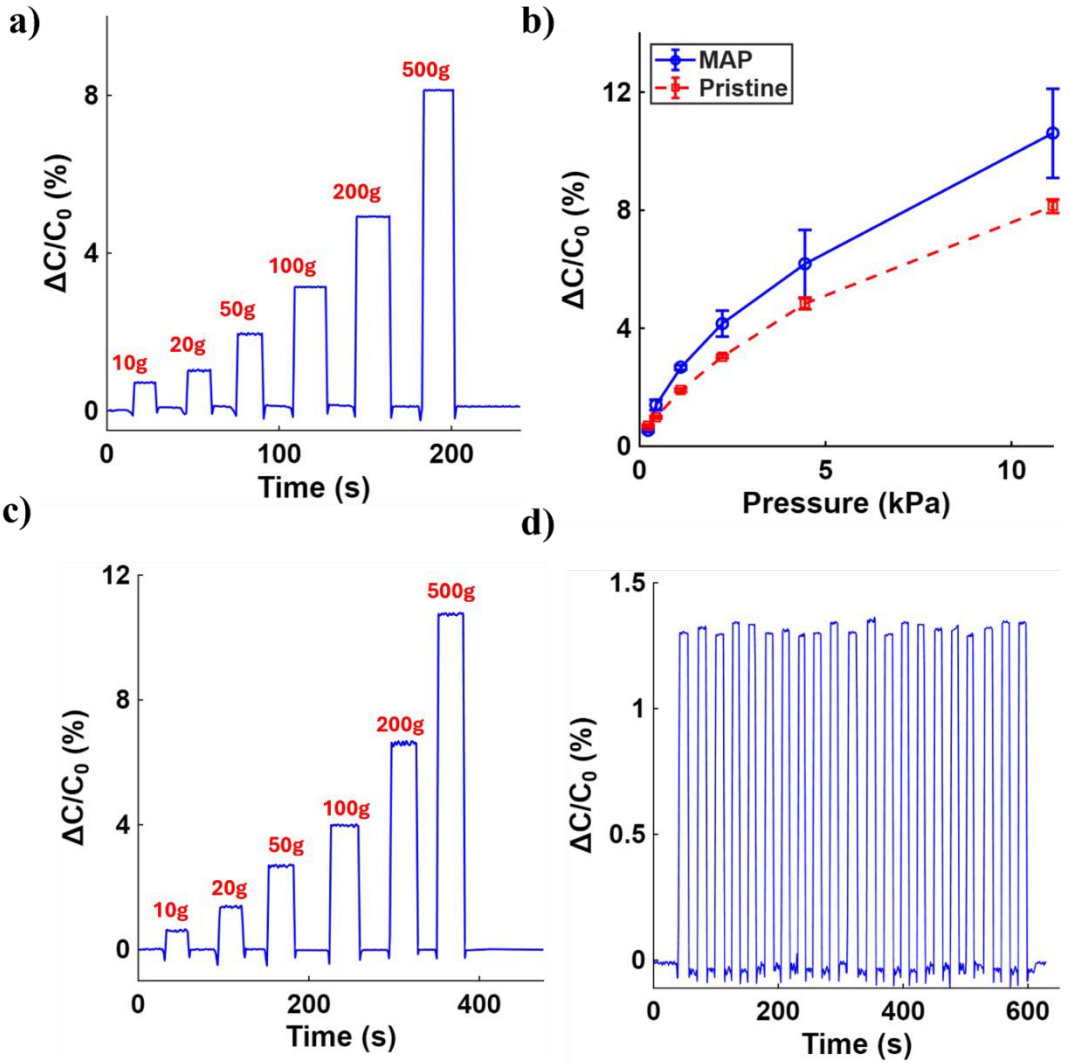


Figure 5. a) Relative change of pressure of the pristine pressure sensor for pressure less than 10 kPa; b) Pressure response comparison between MAP and pristine sensors in the low-pressure range; c) Relative change of capacitance of the microstructured (MAP) pressure at pressures below 10 kPa (using weights); d) Cyclic response under 20 g loading for 20 cycles for MAP microstructures.

In order to further increase the performance of the capacitive sensors, the self-healing behaviour and sensing performance of microstructured dielectric sensors were then investigated. Notably, our initial focus on unstructured self-healing polymer dielectrics was intended to establish baseline material performance and healing efficiency in capacitive pressure sensors. Building on this foundation, we introduced microstructured architectures to enhance pressure sensitivity, particularly in the low-pressure regime relevant to wearable and human-interfacing applications.[77] Among the available micro structuring strategies to improve device sensitivity to pressure change, Meso-American Pyramidal (MAP) geometries were selected due to their well-established ability to amplify pressure-induced deformation through progressive collapse mechanisms, thereby increasing effective dielectric compressibility.[61,78] A detailed analysis of MAP geometrical parameters, their impact on device performance, and comparisons with alternative microstructures (e.g., micropillars) can be found in our previous work.[61] Integrating MAP structures into a dynamic, self-healing dielectric further enabled us to assess whether such sensitivity enhancing architectures remain compatible with reversible metal-ligand networks. To this end, the MAP-based sensors were systematically evaluated under controlled loading conditions to probe pressure sensitivity, mechanical stability, and structural durability. The MAP structures were subjected to a cut and heal cycle to analyse the self-healing capacity without deformation of microstructures as shown in **Figure S5** and the

View Article Online
DOI: 10.1039/D6NJ00535G

relative change in capacitance response was also studied before cut and after healing for a 20 g weight as depicted in **Figure S6**.

Incorporation of MAP markedly increased the effective compressibility of the dielectric layer, resulting in a pronounced enhancement of the pressure capacitance response. Stepwise loading experiments were first conducted using incrementally increasing weights (**Figure 5a,c**). The MAP-based sensor exhibited a clear and reproducible stepwise increase in the normalized capacitance change ($\Delta C/C_0$) with increasing applied load, confirming stable and reliable electromechanical coupling. When compared to the pristine (flat) self-healing sensor, the MAP device consistently displayed a larger capacitance change at equivalent pressures, directly demonstrating the pressure-amplification effect imparted by the microstructured architecture. This enhancement is particularly evident in the low-pressure regime (**Figure 5b**), where the MAP sensor achieved a sensitivity of 0.135 kPa^{-1}, nearly twice that of the pristine device (0.07 kPa^{-1}). The sensitivity enhancement arises from the progressive deformation of the micro-pyramids, which increases the effective electrode contact area while simultaneously reducing the dielectric thickness under small, applied loads. To assess durability and operational stability, cyclic loading tests were performed under a constant load of 20 g (≈ 0.4 kPa), for 20 consecutive cycles (**Figure 5d**). The MAP sensor maintained a repeatable and reversible capacitance response throughout cycling, indicating robust electromechanical behavior. However, slightly increased signal fluctuations were observed relative to the pristine sensor. These variations can be attributed to microstructural deformation and partial viscoelastic relaxation of the self-healing polymer's MAP features under repeated compression. MAP structures remain stable during single loading and unloading (<10 kPa) as shown in **Figure 5c,** but under repeated cycling they permanently deformed. Notably, the magnitude of signal variation increased with applied pressure. At pressures at higher loading of weights (≈0.6 kPa), permanent deformation of the micro- pyramids was observed (**Figure**

View Article Online
DOI: 10.1039/D6NJ00535G

S7), signalling the onset of structural collapse. Beyond this threshold, the MAP dielectric layer effectively transitions toward a flattened, pristine- like configuration, thereby diminishing the microstructure-induced sensitivity enhancement. Overall, these results demonstrate that MAP micro structuring is an effective strategy for significantly improving low-pressure sensitivity in self- healing capacitive sensors, while also defining a clear upper operating pressure limit governed by microstructural mechanical stability. This balance between enhanced sensitivity and structural robustness provides important design guidelines for integrating dynamic, self-healing polymers into pressure amplifying microarchitectures.

CONCLUSIONS

In summary, this work establishes a structural property relationship for capacitive pressure sensors based on metal-ligand coordinated self-healing polymers. By correlating metal- ligand crosslinking density with viscoelastic behavior, geometric stability, and healing efficiency, an optimal 1:1 metal-ligand ratio was identified. These conditions afforded shape-stable dielectrics that remained dimensionally intact after molding while preserving rapid, room-temperature autonomous self-healing. The optimized material was successfully integrated into Mesoamerican pyramidal (MAP) microstructured capacitive sensors with compliant CNT electrodes, enabling repeated cut and heal cycles and stable operation across a wide pressure range from approximately 60 kPa to 1 MPa. At the device level, this structure exhibited robust electrical and mechanical performance, retaining over 90% of its original sensing performance after healing. Pressure sensitivities of 64.1 kPa^{-1} before damage and 47.8 kPa^{-1} after healing were measured, with stable and repeatable responses under identical loading conditions. Fatigue testing at 500 kPa over 2000 cycles further confirmed long-term durability. Collectively, these results establish a clear structure and property performance relationship, where insufficient crosslinking leads to excessive viscoelastic flow and poor shape retention,

while over-crosslinking suppresses chain mobility and healing efficiency. The optimized self-healing materials enabled a unique combination of mechanical resilience, autonomous healing, and device-level reliability, advancing metal-ligand based self- healing polymers from material level demonstrations to practical capacitive pressure sensors.

Author Contributions

All authors contributed to the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Acknowledgments

This work was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC) through a Discovery Grant (RGPIN-2022-04428). N.V thanks NSERC for financial support through an Undergraduate Student Research Award.

REFERENCES

1 N. T. P. Vo, T. U. Nam, M. W. Jeong, J. S. Kim, K. H. Jung, Y. Lee, G. Ma, X. Gu, J. B.-H. Tok, T. Il Lee, Z. Bao and J. Y. Oh, Autonomous self-healing supramolecular polymer transistors for skin electronics, *Nat. Commun.*, 2024, **15**, 3433.

2 Y. Zhou, X. Jiang, X. Yang, H. Liang, X. Xie and W. Fu, Self-Lubricating and Self-Healing Polyurethane Elastomer as a Meniscal Prosthesis to Delay Osteoarthritis Progression, *Adv. Funct. Mater.*,2025, **38**, 2420344.

3 W. Li, J. Guo and W. Tian, Polyurea/hydrogen-bonded reduced graphene oxide composite coating with self-repairing functions for applications of anti-cavitation and anti-corrosion, *Prog. Org. Coat.*, 2025, **200**, 108979.

4 S. Wang and M. W. Urban, Self-healing polymers, *Nat. Rev. Mater.*, 2020, **5**, 562–583.

5 S. Jadoun, Synthesis, Mechanism, and Applications of Self-healing Materials, *Biomater. Devices*, 2024, **2**, 225–240.

6 C. Liu, S. O. Kelley and Z. Wang, Self-Healing Materials for Bioelectronic Devices, *Adv. Mater.*, 2024, **36**, 2401219.

7 S. Chen, S. Fan, Z. Qiao, Z. Wu, B. Lin, Z. Li, M. A. Riegler, M. Y. H. Wong, A. Opheim, O. Korostynska, K. M. Nielsen, T. Glott, A. C. T. Martinsen, V. H. Telle-Hansen and C. T. Lim, Transforming Healthcare: Intelligent Wearable Sensors Empowered by Smart Materials and Artificial Intelligence, *Adv. Mater.*, 2025, **37**, 2500412.

8 Z. Li, J. Lu, T. Ji, Y. Xue, L. Zhao, K. Zhao, B. Jia, B. Wang, J. Wang, S. Zhang and Z. Jiang, Self-Healing Hydrogel Bioelectronics, *Adv. Mater.*, 2024, **36**, 2306350.

9 J. Jung, S. Lee, H. Kim, W. Lee, J. Chong, I. You and J. Kang, Self-healing electronic skin with high fracture strength and toughness, *Nat. Commun.*, 2024, **15**, 9763.

10 C. Jiao, J. Liu, S. Yan, Z. Xu, Z. Hou and W. Xu, Hydrogel-based soft bioelectronic interfaces and their applications, *J. Mater. Chem. C*, 2025, **13**, 2620–2645.

11 S. Bin Choi, J. S. Meena, J. Joo and J.-W. Kim, Autonomous self-healing wearable flexible heaters enabled by innovative MXene/polycaprolactone composite fibrous networks and silver nanowires, *Adv. Compos. Hybrid Mater.*, 2023, **6**, 227.

12 R. Shanker. Srivastav and A. P. More, A Comprehensive Review of Self-Healing Polymers: Mechanisms, Types, and Industry Implications, *Polym. Adv. Technol.*, 2025, **36**, e70092.

13 Electronics, heal thyself, *Nat. Electron.*, 2019, **2**, 133.

14 S. An, M. W. Lee, A. L. Yarin and S. S. Yoon, A review on corrosion-protective extrinsic self-healing: Comparison of microcapsule-based systems and those based on core-shell vascular networks, *Chem. Eng. J.*, 2018, **344**, 206–220.

15 P. Wan, S. Wu, Q. Liu, H. Wang, X. Gong, Z. Zhao, S. Xu, J. Jiang, L. Fan and L. Tu, Extrinsic self-healing asphalt materials: A mini review, *J. Clean. Prod.*, 2023, **425**, 138910.

16 A. Verma, K. Bhushan and H. Singh, Nanocomposites for extrinsic self-healing polymer Materials: A comprehensive review of their repair behaviour, *Results Chem.*, 2025, **13**, 101973.

17 S.-M. Yang, S. Zhou and J.-Y. Yuan, Self-Healing Elastomers and Coatings via Metal Coordination Bonds, *Chem. Eur. J.*, 2025, **31**, e202404038.

18 C. Chen, T. Shen, J. Yang, W. Cao, J. Wei and W. Li, Room-Temperature Intrinsic Self-Healing Materials: A review, *Chem. Eng. J.*, 2024, **498**, 155158.

19 S. Zhou, N. Qi, Z. Zhang, P. Jiang, A. Li, Y. Lu and X. Su, Recent progress in intrinsic self-healing polymer materials: Mechanisms, challenges and potential applications in oil and gas development, *Chem. Eng. J.*,, 2025, **511**, 161906.

20 Z. Xie, B.-L. Hu, R.-W. Li and Q. Zhang, Hydrogen Bonding in Self-Healing Elastomers, *ACS Omega*, 2021, **6**, 9319–9333.

21 C. Wang, N. Liu, R. Allen, J. B.-H. Tok, Y. Wu, F. Zhang, Y. Chen and Z. Bao, A Rapid and Efficient Self-Healing Thermo-Reversible Elastomer Crosslinked with Graphene Oxide, *Adv. Mater.*, 2013, **25**, 5785–5790.

22 H. Park, T. Kang, H. Kim, J.-C. Kim, Z. Bao and J. Kang, Toughening self-healing elastomer crosslinked by metal–ligand coordination through mixed counter anion dynamics, *Nat. Commun.*, 2023, **14**, 5026.

23 L. Cao, Z. Gong, C. Liu, J. Fan and Y. Chen, Design and fabrication of mechanically strong and self-healing rubbers via metal-ligand coordination bonds as dynamic crosslinks, *Compos. Sci. Technol.*, 2021, **207**, 108750.

24 X. You, H. Xu, C. Li, J. Wei, N. Liu and D. Fang, Synthesis of room-temperature self-healing network polymers based on multiple metal–ligand coordination interactions, *J. Polym. Res.*, 2025, **32**, 24.

25 H. Zheng, N. Lin, Y. He and B. Zuo, Self-Healing, Self-Adhesive Silk Fibroin Conductive Hydrogel as a Flexible Strain Sensor, *ACS Appl. Mater. Interfaces*, 2021, **13**, 40013–40031.

26 Y. Liu, F. Wang, Z. Hu, M. Li, S. Ouyang, Y. Wu, S. Wang, Z. Li, J. Qian, L. Wang and S. Ma, Applications of cellulose-based flexible self-healing sensors for human health monitoring, *Nano Energy*, 2024, **127**, 109790.

27 Y. Zhang, Q. Lei, R. Liu, L. Zhang, B. Lyu, L. Liu and J. Ma, Self-healing cellulose-based flexible sensor: A review, *Ind. Crops Prod.*, 2023, **206**, 117724.

28 R. Abouzeid, M. Shayan, T. Wu, J. Gwon, T. A. Kärki and Q. Wu, Highly Flexible, Self-Bonding, Self-Healing, and Conductive Soft Pressure Sensors Based on Dicarboxylic Cellulose Nanofiber Hydrogels, *ACS Appl. Polym. Mater.*, 2023, **5**, 7009–7021.

29 M. Yang, Y. Cheng, Y. Yue, Y. Chen, H. Gao, L. Li, B. Cai, W. Liu, Z. Wang, H. Guo, N. Liu and Y. Gao, High-Performance Flexible Pressure Sensor with a Self-Healing Function for Tactile Feedback, *Adv. Sci.*, 2022, **9**, 2200507.

30 G. Ma, F. Guo, Y. Li, X. Luo, C. Luo, Q. Jin, H. Wu, J. Fu, M. Zhang and Y. Long, A novel 3D-Printed self-healing, touchless, and tactile multifunctional flexible sensor inspired by cutaneous sensory organs, *Compos. Commun.*, 2025, **54**, 102287.

31 S. Bin Choi and J.-W. Kim, Dual-responsive fully self-healing triboelectric pressure sensor: Integrating truncated sphere morphology with deep learning-enhanced signal, *Nano Energy*, 2024, **128**, 109833.

32 X. Sun, Q. He, Y. Hou, X. Zheng, P. Bi, Y. Xu, X. Zhang, Y. Liu, R. Xiong, Y. Yang and Z. Wang, Self-Healing Flexible Pressure Sensor for Human Motion Detection Based on Silver-Nanoparticle-Modified Polyimide Membranes, *ACS Appl. Polym. Mater.*, 2023, **5**, 5951–5960.

33 Y. Li, D. Yang, Z. Wu, F.-L. Gao, X.-Z. Gao, H.-Y. Zhao, X. Li and Z.-Z. Yu, Self-adhesive, self-healing, biocompatible and conductive polyacrylamide nanocomposite hydrogels for reliable strain and pressure sensors, *Nano Energy*, 2023, **109**, 108324.

34 H. Zhu, D. Dong, Y. Wei, H. Lu, Y. Zhong, M. Wei, X. Lai, H. Li and X. Zeng, Self-Healing, Degradable, and Biobased Polyurethane Elastomer for High-Performance Piezoresistive Pressure Sensors with a Hump-like Microstructure, *Langmuir*, 2025, **41**, 5603–5613.

35 Q. Tian, W. Yan, Y. Li and D. Ho, Bean Pod-Inspired Ultrasensitive and Self-Healing Pressure Sensor Based on Laser-Induced Graphene and Polystyrene Microsphere Sandwiched Structure, *ACS Appl. Mater. Interfaces*, 2020, **12**, 9710–9717.

36 S. J. Benight, C. Wang, J. B. H. Tok and Z. Bao, Stretchable and self-healing polymers and devices for electronic skin, *Prog. Polym. Sci.*, 2013, **38**, 1961–1977.

37 H. Yue, Z. Wang and Y. Zhen, Recent Advances of Self-Healing Electronic Materials Applied in Organic Field-Effect Transistors, *ACS Omega*, 2022, **7**, 18197–18205.

38 K. Liu, B. Ouyang, X. Guo, Y. Guo and Y. Liu, Advances in flexible organic field-effect transistors and their applications for flexible electronics, *npj Flex. Electron.*, 2022, **6**, 1.

39 W. Wang, Z. He, C. Di and D. Zhu, Advances in organic transistors for artificial perception applications, *Mater. Today Electron.*, 2023, **3**, 100028.

40 N. A. Andreeva and V. V Chaban, Self-healing in dielectric capacitors: a universal method to computationally rate newly introduced energy storage designs, *Phys. Chem. Chem. Phys.*, 2024, **26**, 29393–29405.

41 K. Li, Z. Xu, S. Zhao, X. Meng, R. Zhang, J. Li, J. Leng, G. Zhang, D. Cao and R. Sun, Biomimetic, recyclable, highly stretchable and self-healing conductors enabled by dual reversible bonds, *Chem. Eng. J.*, 2019, **371**, 203–212.

42 H. Gao, J. Xu, S. Liu, Z. Song, M. Zhou, S. Liu, F. Li, F. Li, X. Wang, Z. Wang and Q. Zhang, Stretchable, self-healable integrated conductor based on mechanical reinforced graphene/polyurethane composites, *J. Colloid Interface Sci.*, 2021, **597**, 393–400.

43 T.-M. Jang, W. B. Han, S. Han, A. Dutta, J. H. Lim, T. Kim, B. H. Lim, G.-J. Ko, J.-W. Shin, R. Kaveti, H. Kang, C.-H. Eom, S. J. Choi, A. J. Bandodkar, K.-S. Lee, E. Park, H. Cheng, W.-H. Yeo and S.-W. Hwang, Stretchable and biodegradable self-healing conductors for multifunctional electronics, *Sci. Adv.*, 2024, **10**, eadp9818.

44 Y. Lin, T. Fang, C. Bai, Y. Sun, C. Yang, G. Hu, H. Guo, W. Qiu, W. Huang, L. Wang, Z. Tao, Y. Lu and D. Kong, Ultrastretchable Electrically Self-Healing Conductors Based on Silver Nanowire/Liquid Metal Microcapsule Nanocomposites, *Nano Lett.*, 2023, **23**, 11174–11183.

45 T. D. Khanh, J. Joo and J.-W. Kim, Autonomous self-healing in a stretchable polybutadiene-based urethane and eutectic gallium indium conductive composite, *npj Flex. Electron.*, 2024, **8**, 79.

46 K. Parida, G. Thangavel, G. Cai, X. Zhou, S. Park, J. Xiong and P. S. Lee, Extremely stretchable and self-healing conductor based on thermoplastic elastomer for all-three-dimensional printed triboelectric nanogenerator, *Nat. Commun.*, 2019, **10**, 2158.

47 Y. Lee, X. Tian, J. Park, D. H. Nam, Z. Wu, H. Choi, J. Kim, D.-W. Park, K. Zhou, S. W. Lee, T. A. Tabish, X. Cheng, S. Emaminejad, T.-W. Lee, H. Kim, A. Khademhosseini and Y. Zhu, Rapidly self-healing electronic skin for machine learning–assisted physiological and movement evaluation, *Sci. Adv.*, 2025, **11**, eads1301.

48 X. Dai, Q. Liang, Z.-H. Zhao, Y. Wu, J. Yang, J. Han, Y. Cao, Y. Wang, C.-H. Li, A. Zhong and L.-B. Huang, Self-powered sensors for flexible electronic skins capable of self-healing under multiple extreme environments, *Nano Energy*, 2024, **121**, 109239.

49 J.-S. Benas, F.-C. Liang, M. Venkatesan, Z.-L. Yan, W.-C. Chen, S.-T. Han, Y. Zhou and C.-C. Kuo, Recent development of sustainable self-healable electronic skin applications, a review with insight, *Chem. Eng. J.*, 2023, **466**, 142945.

50 Z. Lu, W. Li, L. Zhu, Y. Zhang, Z. Ming, Y. Zhang, X. Zhou and J. Xiong, Self-healing electro-optical skin for dual-mode human-machine interaction, *Nano Energy*, 2025, **135**, 110617.

51 A. Kausar, I. Ahmad, M. Maaza and P. Bocchetta, Self-Healing Nanocomposites—Advancements and Aerospace Applications, *J. Compos. Sci.*, 2023, **7**, 148.

52 L. Pernigoni, U. Lafont and A. M. Grande, Self-healing polymers for space: A study on autonomous repair performance and response to space radiation, *Acta Astronaut.*, 2023, **210**, 627–634.

53 N. Sun, X. Ma, B. Wang, J. Zheng, X. Wang, Z. Li, Z. Chen and Y. Liu, A novel strategy for designing high-performance self-healing polysiloxane-polyurea

composites enhanced by dopamine-grafted cellulose nanofibers and Zn2+, *Compos. Sci. Technol.*, 2025, **266**, 111159.

54 G. Thangavel, M. W. M. Tan and P. S. Lee, Advances in self-healing supramolecular soft materials and nanocomposites, *Nano Converg.*, 2019, **6**, 29.

55 H. Wen, J. Sun, K. Yu, X. Yang, X. Dai and Z. Zhang, A self-healing and energy-dissipating impact-hardening polymer based on a variety of reversible dynamic bonds, *Mater. Des.*, 2023, **231**, 112057.

56 T. Hayashi and A. Shimojima, Self-healing materials based on dynamic properties of siloxane networks, *J. Solgel Sci. Technol.*,2025, **116**, 1995-2009

57 M. Ahmadi, G. Pareras, M. Bin Yeamin, K. Amann-Winkel, A. Rimola, A. Poater and S. Seiffert, Coordination Geometry and Mineralization in Self-Healing Mussel-Inspired Hydrogels, *Chem. Mater.*, 2024, **36**, 3345–3358.

58 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.

59 J. Pignanelli, B. Billet, M. Straeten, M. Prado, K. Schlingman, M. J. 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.

60 S. Vu, G. Nagesh, N. Yousefi, J. F. Trant, D. S.-K. Ting, M. J. Ahamed and S. Rondeau-Gagné, Fabrication of an autonomously self-healing flexible thin-film capacitor by slot-die coating, *Mater. Adv.*, 2021, **2**, 6676–6683.

61 L. Rose, G. Nagesh, P. Das, D. Skaf, F. Motaghedi, S. Rondeau-Gagné and M. J. Ahamed, Exploring mesoamerican pyramidal micro-structures in soft capacitors for positive and negative pressure sensing, *Flex. Print. Electron.*, 2025, **10**, 25003.

62 Z. Li, F. Sun, L. Rose, G. Nagesh, N. K. Shekar, P. R. Pedapati, A. Ansar, R. Kumar, V. Damodaran, D. Skaf, S. Rondeau-Gagné and M. J. Ahamed, Multilayered Single-Walled Carbon Nanotube-Based Flexible Temperature Sensor, *IEEE Sens. J.*, 2025, **25**, 193–204.

63 X. Meng, H. Tang, X. Lü, J. Zhang, Y. Shi, Y. He and W. Bao, Biomimetic cell in-situ self-healing PCL/CNT conductive composites for flexible pressure sensors with high sensitivity and wide linear measurement range, *Sci. China Inf. Sci.*, 2026, **69**, 122404.

64 L. Kong, Y. Yang, Z. Lin, B. Huang, L. Liao, Y. Wang and C. Xu, A ENR-based conductive film integrating electricity-triggered self-healing, damage detection and high sensitivity for flexible sensors, *Chem. Eng. J.*, 2024, **479**, 147624.

65 Y. Chen, X. Pu, M. Liu, S. Kuang, P. Zhang, Q. Hua, Z. Cong, W. Guo, W. Hu and Z. L. Wang, Shape-Adaptive, Self-Healable Triboelectric Nanogenerator with Enhanced Performances by Soft Solid–Solid Contact Electrification, *ACS Nano*, 2019, **13**, 8936–8945.

66 A. Narayanan, T. M. Bhagyasree, A. Torris and S. S. Babu, A functionalized CNT-azobenzene-PVA-based self-healing aqueous gel as a conductive photo-responsive actuator, *J. Mater. Chem. C*, 2023, **11**, 16571–16577.

67 X. Wang, Y. Li, Y. Wang, W. Huang, X. Zhao, K. Chen, F. Luo and Y. Qin, Fabrication method and various application scenarios of flexible capacitive pressure sensor based on direct formation of conical structure, *Chem. Eng. J.*, 2024, **496**, 153957.

68 Z. Zhan, Y. Yang, W. Zuo, M. Xie and M. Ning, Recent advances and challenges of tactile sensing for robotics: from fundamentals to applications, *Mater. Today Phys.*, 2025, **54**, 101740.

69 B. Cheng, C. Li, T. Ji, Y. Zhao, K. Gao, J. Hao and W. Xu, A triboelectric sensing array integrating material identification and self-healing enabled by a healable polyamide-based device unit, *Nano Energy*, 2024, **127**, 109718.

70 Y. Jeong, C. Majidi and S. H. Ko, Self-Healing Soft Robots: Materials, Sensors and Integrated Systems, *Int. J. Precis. Eng. Manuf.*, 2025, **26**, 2781–2801.

71 H. Bai, Y. S. Kim and R. F. Shepherd, Autonomous self-healing optical sensors for damage intelligent soft-bodied systems, *Sci. Adv.*, 2026, **8**, eabq2104.

72 X. Dai, Q. Liang, Z.-H. Zhao, Y. Wu, J. Yang, J. Han, Y. Cao, Y. Wang, C.-H. Li, A. Zhong and L.-B. Huang, Self-powered sensors for flexible electronic skins capable of self-healing under multiple extreme environments, *Nano Energy*, 2024, **121**, 109239.

73 G. Chen, Y. Zhu, D. Huang and S. Zhou, Self-powered and self-sensing devices based on piezoelectric energy harvesting, *Sci. China Technol. Sci.*, 2024, **67**, 1631–1667.

74 X. Wang, G. Chen, K. Zhang, R. Li, Z. Jiang, H. Zhou, J. Gan and M. He, Self-Healing Multimodal Flexible Optoelectronic Fiber Sensors, *Chem. Mater.*, 2023, **35**, 1345–1354.

75 J. Zheng, Z. Wang, G. Chen, K. Hou and M. Zhu, Self-healing hydrogel optical fibers with programmable functions for multi-signal sensing and decoupling, *Sci. China Mater.*, 2025, **68**, 4107–4114.

76 H. Wu, X. Luo, C. Wang, Q. Jin, Y. Li, F. Guo, W. Guo and Y. Long, 3D printing of robust, self-healing, and highly sensitive pressure sensor based on an interpenetrating polymer network elastomer, *Colloids Surf. A Physicochem. Eng. Asp.*, 2024, **685**, 133248.

77 S. R. A. Ruth, L. Beker, H. Tran, V. R. Feig, N. Matsuhisa and Z. Bao, Rational Design of Capacitive Pressure Sensors Based on Pyramidal Microstructures for Specialized Monitoring of Biosignals, *Adv. Funct. Mater.*, 2020, **30**, 1903100.

78 F. Motaghedi, L. Rose, M. J. Ahamed, T. B. Carmichael and S. Rondeau-Gagné, A multifunctional thermochromic–elastomeric composite for integrated pressure and temperature sensing, *RSC Appl. Polym.*, 2026, **4**, 422–431.

View Article Online
DOI: 10.1039/D6NJ00535G

Data availability

The data supporting this article have been included as part of the Supplementary Information.