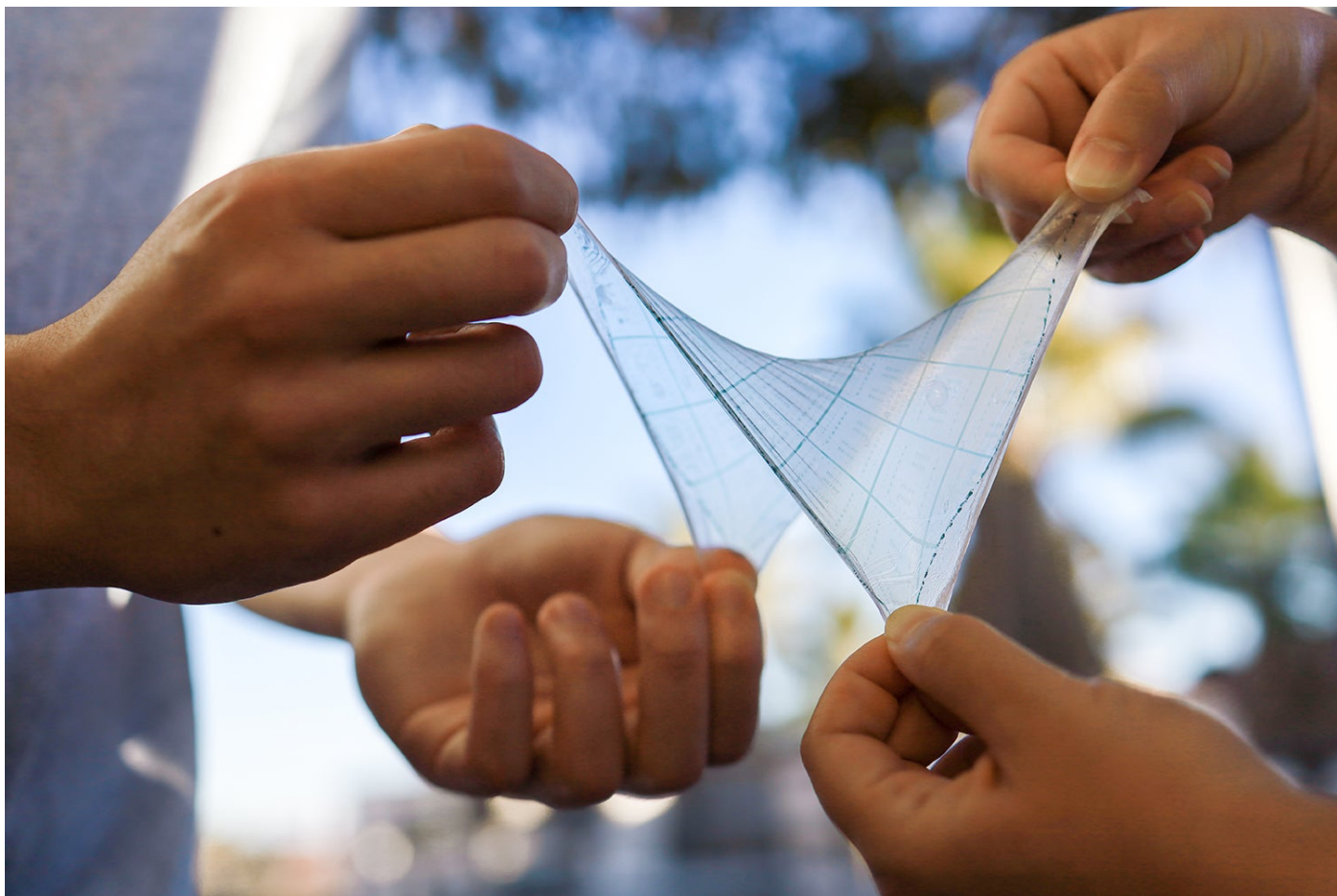


## Molecular Strategy Enables High Performance of Elastic Skin-inspired Electronics



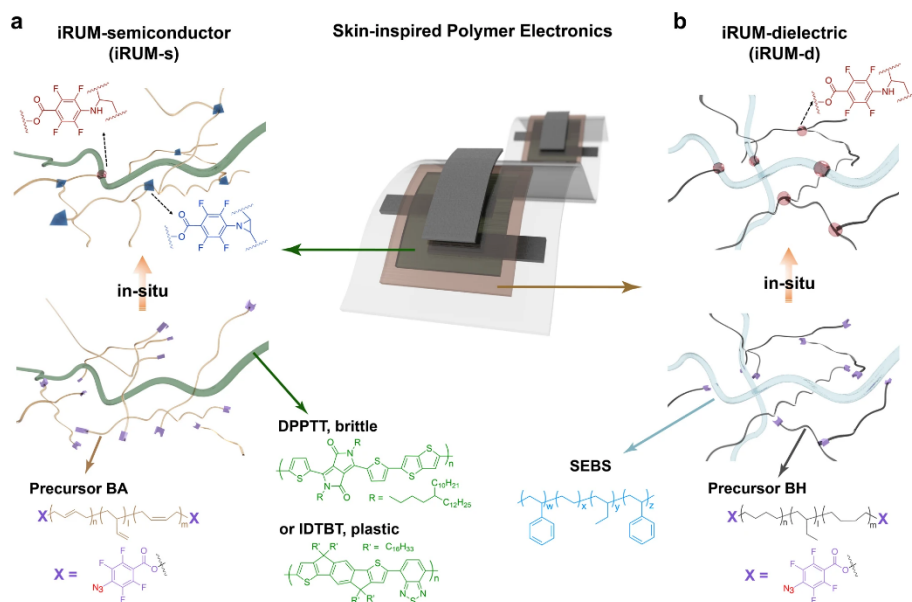
Researchers in the Bao Research Group at Stanford demonstrate the flexibility and stretchability of their artificial skin made using their newly created printing method. (Image credit: Yuqing Zheng)

by [Weilai Yu](#)

The human skin, research team at Stanford University led by **Prof. Zhenan Bao** ([Bao Group](#)) has been developing next-generation wearable electronics that are flexible, stretchable, self-healable and bio-degradable over the past decades. As state-of-art Si-based electronic devices are typically rigid and brittle, one innovative approach by the team is to design new polymeric materials, tailor their properties from the molecular level and finally assemble them into functional electronic devices under strain.

Field-effect transistor (FET) is an essential building block of electronic circuits consisting of semiconductor, dielectrics and metal. Building a stretchable circuit first requires elastic polymer semiconductors which are not only mechanically robust upon stretching, but which also exhibit high charge-carrier mobility under large strain (> 50 %). Also, the interface between polymer semiconductors and dielectrics should maintain intimate contact to ensure effective charge transport, after continuous cycles of stretching and releasing. Finally, these material components need to be compatible with facile and cost-effective fabrication process for mass production of FET arrays to assemble complex integrated circuits

Designing polymer semiconductors that can maintain high mobility under large strain (> 50 %) is a desired yet challenging task. One major obstacle is that the charge transport in polymer semiconductor occurs through semi-crystalline domains that may easily crack even at low strain (< 10 %), thus compromising charge mobility in FET. Previous reports on enhancing the mechanical properties of polymer semiconductors relied on reducing long-range crystalline order which may diminish upon continuous stretching over long term. In some cases, although fracture strain can be increased, polymers cannot reversibly return to their initial states after stretching causes hysteric behavior and thus form wrinkles or buckles in electronic devices. Further, solution processability of polymer electronic materials may simultaneously render their susceptibility to dissolution during layer-by-layer deposition into integrated architectures, adding the demand of solvent resistance for mass manufacturing.



**The iRUM strategy** of rationally tailored molecular precursors to in-situ form elastic rubber matrix with (a) DPPTT or IDTBT polymer semiconductors and (b) SEBS dielectrics. Image credit: Bao Group, Stanford U.

To address the above issues in stretchable electronics, **Yu Zheng** and **Zhiao Yu**, leading authors of this new report in [Nature Communications](#), introduced a strategy called covalently-embedded, in-situ rubber matrix (iRUM). This new molecular design concept simultaneously incorporates all the desired properties, including high electrical performance under large strain, reversible elasticity, solvent resistance as well as facile photo-patternability, into the resulting FET devices fabricated with polymer semiconductors and dielectrics.

In the beginning, the researchers rationally designed an iRUM precursor consisting of both perfluorophenyl azide (PFPA) end-capped polybutadiene (BA), which can be well mixed with polymer semiconductor (PSC) owing to the flexible backbone and compatible surface energy of BA. After mixing, BA can undergo self-crosslinking to generate a stretchable and elastic matrix through azide/C=C cycloaddition, resulting in a ‘semiconductor-in-rubber’ composite film. Besides self-crosslinking, the azide groups of BA can also react with and crosslink the alkyl side chains on PSC through azide/C–H insertion, which further ensures solvent resistance and photo-patternability.

Based on different reactivities of azide with C–H and C=C bonds, the researchers found that the self-crosslinking of BA occurred much faster relative to BA–PSC crosslinking, which beneficially preserved the original charge transport pathways *via* PSC aggregation. Importantly, the good miscibility between BA and PSC is key to ensure uniform mixing of the two crosslinked polymers even at high BA–PSC ratio, whereas the high covalent crosslinking density enables superior elasticity as well as solvent resistance of composite films. Due to the high elasticity of semiconductor composites, the fabricated FET retained its mobility after stretching to 100% strain and exhibited record-high mobility retention of  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  even after 1000 stretching releasing cycles at 50% strain, while the overall cycling life was stably extended to 5000 cycles.



Team leader, Prof. Zhenan Bao (left) and leading authors, Yu Zheng (mid) and Zhiao Yu (right).

To further expand the iRUM strategy to dielectrics, the team designed a different crosslinking precursor similarly endcapped with PFPA but composed of hydrogenated-polybutadiene (BH) backbone, a common ingredient used in the rubber industry for nearly a century. BH is selected to maximize crosslinking density with a widely used stretchable dielectric material, polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene (SEBS). The resulting BH-SEBS composite not only retains the original dielectric constant of SEBS but also exhibits solvent resistant, allowing multilayer device fabrication into stretchable FET.

Furthermore, the researchers successfully demonstrated the facile photo-patternability of the iRUM strategy to fabricate integrated stretchable circuit. Owing to their solvent resistance, both semiconductor and dielectrics polymer composites can survive multi-step solvent washing and UV exposure, guaranteeing the structural integrity of FET after layer-by-layer assembly. The photo-patternability of polymer building blocks represents a major advance towards conventional protection-etching process for patterning semiconductors that requires more supplicated fabrication process. Even after mass production of up to 36 FETs on a single substrate, a comparably high average charge carrier mobility of  $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was obtained, which again retained after 1000 stretching-releasing cycles at 50% strain.

Overall, the iRUM strategy developed by the Stanford team is a versatile and general strategy applicable to different functional components in FET. Notably, the full elasticity of polymer semiconductors allows mechanical integrity without sacrificing charge-carrier mobility even under large strain ( $>50\%$ ), addressing a major dilemma faced by all previous strategies. Applying iRUM to both polymer semiconductors and dielectrics creates robust stretchable circuits by facile photopatterning method, suitable for real-world, wearable applications. Importantly, this work constitutes a milestone in leveraging molecular-level design to construct elastic, multifunctional and robust skin-inspired electronics.

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