Title: Highly Stretchable Polymer Semiconductor Films through Nanoconfinement Effect

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Abstract: Soft and conformable wearable electronics require stretchable semiconductors but existing ones typically sacrifice charge-transport mobility to achieve stretchability. We explore a concept based on the nanoconfinement of polymers to significantly improve the stretchability of polymer semiconductors, without affecting charge transport mobility. The increased polymer chain dynamics under nanoconfinement significantly reduces the modulus of the conjugated polymer and largely delays the onset of crack formation under strain. As a result, our fabricated semiconducting film can be stretched up to 100% strain without affecting mobility, retaining values comparable to that of amorphous-Si. The fully-stretchable transistors exhibit high bi-axial stretchability with minimal change in on-current even when poked with a sharp object. We demonstrate a skin-like finger-wearable driver for a light emitting diode.

One Sentence Summary: Nanoconfined semiconducting polymers have increased ductility and retain original electrical performance under large strains.

Main Text:

Electronics for biomedical applications, such as physiological monitoring (*1*), implanted treatment (*2*), electronic skins (*3*) and human-machine interface (*4*), need to be mechanically compatible with biological tissues, with characteristics of low modulus, flexibility, and stretchability. Several approaches based on geometric designs, such as buckles (*5*), wavy patterns (*1, 2*) and kirigami (*6*), impart stretchability to electronics and have the potential for a variety of wearable applications. Stretchable electronics based on intrinsically stretchable materials may enable scalable fabrication, higher device density and better strain tolerance,but remain scarce due to the lack of high-performance stretchable semiconductors that possess both high mechanical ductility and high carrier mobility at large strains. Although some nano-material systems (such as two-dimensional materials) possess moderate stretchability (below 20% strain) with good electrical performance (*7*), their rigid nature has limited device density, mechanical robustness and wide applicability.

Conjugated polymers have been developed as a softer semiconductor with high charge carrier mobilities rivaling that of poly-Si (*8-10*) but they still have poor stretchability. Molecular design rules (*11-13*) that are effective in improving stretchability often results in decrease in mobility. Nanowire/nanofibril networks (*14, 15*) and micro-cracked films (*16*) improved strain tolerance, but the materials used were already known to be ductile (*17*) and had low mobilities. More recently, high-performance but brittle conjugated polymers have been afforded improved stretchability through blending with a ductile lower performance conjugated polymer (*18*). However, the films still has limited ductility due to the unchanged polymer chain packing and dynamics.

Nanoconfinement can alter many polymer physical properties including lowering the mechanical modulus (*19*) and glass transition temperature (*20*) and increasing the mechanical ductility (*21*). These changes have been attributed to the enhanced polymer chain dynamics in the amorphous regions (*22*, *23*) and the restricted growth of large crystallites (*24*), and these are all. desirable for stretchable materials. Therefore, we hypothesized that the effects caused by nanoconfinement may increase the mechanical stretchability of high-mobility less ductile polymer semiconductors.

This is achieved by creating the morphology of nanoscale semiconducting polymer network with increased chain dynamics and low crystallinity to reduce modulus and increase ductility, and fiber-like large aggregates to allow good charge transport, at the meanwhile they are interfaced with a soft deformable elastomer to prevent crack propagation (Fig. 1A). Possible fabrication techniques include photolithographic-patterning (*26*), nanostructure-templating (*27*) and phase separation (*28*), but only the latter method can simultaneously introduce all desirable features in one step, and is more scalable and low cost., We describe a CONjugated-polymer/elastomer PHase-separation INduced Elasticity (termed CONPHINE) methodology to achieve the desired morphology.

We first investigate poly(2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)diketopyrrolo[3,4-c]pyrrole-1,4-dione-alt-thieno[3,2-b]thiophen) (DPPT-TT; **1**) (*29*) as the high-mobility semiconducting polymer and polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS) as the soft elastomer (Fig. 1B). Their comparable surface energies should ensure a nanoscale mixed morphology (Fig. S1, Table S2). The improvement in mechanical ductility is investigated on three model films of **1**: (i) thick neat film (~135 nm), (ii) thin neat film (~35 nm) with the nanoconfinement effect, and (iii) thin film/SEBS bilayer film with both the nanoconfinement effect and a deformable interface (Fig. 1C), and together with the DPPT-TT nanofiber film with SEBS removed from the CONPHINE film. As an important parameter representing the polymer chain dynamics, the glass transition temperatures (T_g) obtained by differential AC chip calorimetric method show a decreasing trend from the thick, to the thin and finally to the nanofiber films (Figs. 1D and S2). This trend confirms increased chain dynamics due to nanoconfinement (*20, 22, 23*). Suppressed crystallization in thinner films (24) was also observed (Figs. 1E and S3). These two effects, together, result in a decrease in the measured elastic modulus, and significant increase in the onset strains of plasticity and cracks from thick to thin film (Figs. 1F and S4-6) (*19, 21, 30*). Under 2-dimensional nanoconfinement, the simulated modulus of the DPPT-TT nanofiber is two times lower than the bilayer film and almost six times lower than the thick film (Fig. 1F and Fig. S7). On the other hand, the introduction of the SEBS deformable interface further decreases the crystallinity and reduces crack propagation, which makes the bi-layer film further softened and more ductile (Figs. 1F and S4-6). The improvement in the stretchability from these effects is shown by both the dichroic ratios (from UV/Vis spectroscopy) (Fig. S8) and significantly different crack size of these films under strain (Fig. S9).

As observed by the atomic force microscopy (AFM) phase images, the CONPHINE-**1** film showed the desired fiber network with smaller nanofiber diameters at higher SEBS concentrations (Fig. S10). At 70 wt% of SEBS, the nanofiber diameter became small enough (<50 nm) to give a strong nanoconfinement effect at both the top and bottom surfaces (Fig. 1G). As revealed by X-ray photoelectron spectroscopy (XPS, Fig. S11), the layer between the top and bottom surfaces is primarily occupied by SEBS, containing a small amount of DPPT-TT. This morphology is depicted in Fig. 1H. Unlike the pre-grown nanowires/nanofibers (*14, 15*), the nanofibers formed from phase separation have reduced crystallinity but still high aggregation (Fig. S12), which ensures both enhanced stretchability and good charge transport. The CONPHINE-**1** film can be stretched up to 100% strain when supported on a rubbery substrate without any visible cracks (Fig. 1I). The additional benefit of the CONPHINE method is the reduced consumption of conjugated polymers and transparent film.

The stretchability of the CONPHINE-**1** film is studied by applying 100% strain on a polydimethylsiloxane (PDMS)-supported film (Fig. 2A), then transferring to a Si substrate for morphology characterization. The CONPHINE-**1** film with 70% SEBS can be effectively stretched to 100% strain without resulting in any cracks even at the nanoscale as characterized by AFM (Figs. 2B and Fig. S13A), despite inhomogeneity in film thickness after deformation (Fig. S13B). In comparison, the neat-**1** film at 100% strain developed cracks with widths around 20 μm (Fig. 2B).

The electrical performance of the CONPHINE-**1** film functioning as a stretchable semiconductor was measured in a thin-film transistor (TFT) by soft contact lamination (*13*) on a bottom-gate-bottom-contact stack: octadecyltrimethoxysilane (OTS)-assembled SiO_2 (gate dielectric) coated highly-doped Si (gate), with Au contacts on the top (Figs. 2C & S14). Since the DPPT-TT nanofibers on the bottom surface of the CONPHINE film are exposed, good ohmic contacts can be formed with the Au electrodes (Figs. S15). The CONPHINE film can be prepared on a wafer-scale with good uniformity in electrical performance (Figs. S16). By comparing the mobility from the CONPHINE-**1** film with different SEBS contents, it was determined that 70 wt% SEBS provides the optimum condition to enable the highest mobility at 100% strain (Figs. S17). As shown in Fig. 2D(i), the CONPHINE-**1** film (i.e. 70 wt% SEBS) gives similar transfer property as the neat-**1** film (i.e. 0% SEBS), which demonstrates that this approach does not sacrifice the semiconductor's electrical performance. When both films were stretched to 100% strain parallel to charge transport, the transfer curve of the CONPHINE film remained unaffected, with its on-current ~3 orders higher than that of the severely degraded neat-**1** film (Figs. 2D(ii) & S18A-B). In addition, the CONPHINE-**1** film showed no decrease in mobility during the entire stretching process (Fig. 2E), in which its mobility at 100% strain reached a maximum value of 1.32 cm^2/Vs, and 1.08 cm^2/Vs on average, which is ~3-order improvement compared to the neat-**1** film. On the other hand, when the stretching is perpendicular to the charge transport direction, we observed that there is only a very small decrease in both the on-current and the mobility from the CONPHINE-**1** film at 100% strain (Figs. 2D(iii) & 2F). This too is a significant improvement compared to the ~2 orders decrease in the neat film. To further probe the film's stretchability, we observed that the CONPHINE-**1** film can be even stretched to 200% strain, with its mobility maintained at 0.33 cm^2/Vs (Figs. 2G & S19).

For the CONPHINE-**1** film, the on-current only changes moderately after 100 cycles with 100% strain (Figs. S17E-H), and the mobility is still high at 0.2 cm^2/Vs (Figs. 2H and S20). There are no visible cracks in the film after 100 cycles (Fig. S21); however, we do observe that there is a slight increase in film roughness (Fig. S22), which is known to contribute to decreased mobility (*15*). In comparison, for the neat-**1** film, both the on-current and mobility greatly decreased by >3 orders after the 100 cycles (Figs. 2H, S17I-K and S20). Compared to the literature-reported cyclability for semiconductor films (*13, 15, 16*), the mobility of our CONPHINE film after cycled stretching is over ten times higher even with twice the strain. For the long-term usage of the CONPHINE film in practical applications, although the chain conformation under nanoconfinement has a metastable nature (*32*), the relatively long chain relaxation time allows the film to maintain the similar nanoscale morphology, electrical performance and stretchability, as was confirmed with a CONPHINE-**1** film after being stored for one year (Fig. S23).

We fabricated fully stretchable transistors in bottom-gate-bottom-contact structure, with carbon nanotube (CNT) network as the electrodes, SEBS as the dielectric layer, the stretchable substrate and the encapsulation layer (Figs. 3A & S24). The obtained TFT device has good transparency and excellent conformability for constructing e-skins on human epidermis (Fig. 3B). As shown via a representative transfer curve (Fig. 3C) and output characteristics (Fig. S25A), the fully stretchable TFT gives ideal transistor performance and an average mobility of 0.59 cm^2/Vs obtained from 20 devices with minimal variations (Fig. 3D). The lower mobility compared to that from the earlier soft contact lamination method is attributed to a higher contact resistance from CNT electrodes compared to Au (Fig. S26). When the device is stretched to 100% strain along the charge transport direction, there is only a very slight drop in the on-current due to the increase of channel length from stretching, with the mobility stably maintaining a value of 0.55 cm^2/Vs even to 100% strain (Figs. 3E & S25B and Table S3). Along the perpendicular direction, the combined effect of the slight decrease in mobility and the device geometric change makes the transfer curve highly stable under strain up to 100% (Figs. 3E & S25C). Moreover, this fully stretchable TFT is highly robust over 1000 repeated stretching cycles to 25% strain (the general range for applied strains in most wearable electronic applications), as shown in Figs. 3F & S25D-E. The high stretchablity and robustness of the TFT is also revealed by its stable drain-current under sequential stretching, twisting and even poking by a sharp object, as shown in Fig. 3G and Movie S1.

We attached our transistor, serving as a LED driver, conformably to a human finger to demonstrate its potential use for wearable electronics. During the repeated bending of the finger that created a large strain (>50%) on the device, the intensity of the light from the LED remains unaffected (Fig. 3H & Movie S2).

We applied our CONPHINE method to four other high-performance semiconducting polymers (**2-5)**, with their chemical structures shown in Figs. 4A-D (*10, 13, 33*) (Table S1 and Fig. S27). All neat films of these polymers severely crack when subjected to 100% strain (middle column in Figs. 4A-D), leading to degraded mobilities as shown. Upon using our CONPHINE method, nanoconfined morphologies with deformable interfaces are again obtained (Fig. S28). The stretchability of all these films (CONPHINE-**2** to CONPHINE-**5**) is significantly improved, only with inhomogeneous deformations at 100% strain (right column images in Figs. 4A-D & S29). As a result, both the on-currents and mobilities (values are indicated in their respective images) from these films at 100% strain are all much higher than their neat counterparts by one to four orders of magnitude (Figs. 4E & F). Significantly, four different conjugated polymers (including **1**) are imparted with mobilities >1.0 cm^2/Vs at 100% strain.

In summary, polymer nanoconfinement enables high stretchablity in semiconducting materials. We introduce the CONPHINE method to create conjugated-polymer nanostructures with increased chain dynamics and decreased crystallinity embedded in an elastomer matrix to maintain the mobility during stretching. We anticipate this general approach to advance the development of stretchable semiconductors for stretchable electronic-skin applications.

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Supplementary Materials:

Materials and Methods
Table S1 – S3
Fig S1 – S29
References (34 – 48)
Movie S1 and S2

Figure Legends:

Fig. 1. Nanoconfinement effect for enhancing the stretchability of polymer semiconducting film through CONPHINE method. (**A**) 3D schematic of the desired morphology comprised of embedded nanoscale networks of polymer semiconductor to achieve high stretchability, which can be used to construct highly stretchable and wearable thin-film transistor. (**B**) Chemical structures of semiconducting polymer DPPT-TT (labeled as **1**) and SEBS elastomer. (**C**) Three model films of DPPT-TT for investigation of the nanoconfinement effect (i.e. increased chain dynamics and suppressed crystallization). (**D**) Glass transition temperatures of the thick, thin and nanofiber films. (**E**) XRD line cuts for three model films and the CONPHINE-**1** with 70% SEBS film along the q_{xy} axes, normalized by the exposure time and volume of DPPT-TT layer, and offset for clarity. (**F**) Elastic moduli, onset strains of plasticity, and onset strains of crack of the model films, with the simulated modulus of the nanofiber film. (**G**) AFM phase images of the top and bottom interfaces of the CONPHINE-**1** film with 70 wt% SEBS. (**H**) 3-D illustration of the morphology of the CONPHINE-**1** film. (**I**) Photographs of a CONPHINE-**1** film (the blue area) at 0% strain and stretched to 100% strain on a rubber substrate.

Fig. 2. Characterization of the semiconducting film stretchability and electrical performance under different strains. (**A**) Schematic illustration of the stretching of the semiconducting film supported on PDMS substrate. (**B**) Optical microscope images of a neat-**1** film (left, top) and a CONPHINE-**1** film (left, bottom) under 100% strain, with AFM phase image showing the color variation in CONPHINE-**1** film is not due to cracks. (**C**) Schematic of the soft contact lamination method for characterizing the electrical performance of a semiconducting layer upon stretching. (**D**) Transfer curves ($V_D = -80$ V) obtained from the CONPHINE-**1** film and the neat-**1** film in its original condition (i), under 100% strain parallel to the charge transport direction (ii), and under 100% strain perpendicular to the charge transport direction (iii). (**E**, **F**) Mobilities from the CONPHINE-**1** film (blue) and the neat-**1** film (black) at different strains (**E**) parallel and (**F**) perpendicular to the charge transport direction. (**G**) Comparison of the obtained mobilities at stretched strains in this paper to the previously reported results in literature. (**H**) Mobilities of the CONPHINE-**1** film (green) and the neat-**1** film (black) as a function of 100%-strain stretching cycles parallel to the charge transport direction.

Fig. 3. Fully stretchable transistor fabricated from the CONPHINE-1 film. (**A**) Device structure (channel length: 200 μm; channel width: 4 mm; dielectric capacitance: 15 μF/m^2). (**B**) Pictures showing the transistor's transparency, the skin-like nature when attached on the back of hand (middle), with the conformability shown in the SEM image (right). (**C**) A typical transfer curve ($V_D = -30$ V) at 0% strain. (**D**) Distribution of the mobility from 20 devices in the arrays of fully stretchable transistors (shown with increased contrast in the inset). (**E**) Changes of the

on-current and mobility with strains up to 100%, both parallel to (solid points) and perpendicular to (hollow points) the charge transport direction. (**F**) Changes of the on-current, off-current and mobility with strain along the charge transport direction, and perpendicular to the charge transport direction (**F**). Changes of the on-current, off-current and mobility after multiple stretching-releasing cycles (up to 1000 cycles) at 25% strain along the charge transport direction. (**G**) Drain-current and gate-current of a fully stretchable TFT under sequential stretching, twisting and poking on a sharp object. (**H**) Demonstration of the fully stretchable transistor as a finger-wearable driver for an LED.

Fig. 4. Applying the CONPHINE method on four distinct conjugated semiconducting polymers to improve their stretchability. (**A–D**) Optical micrographs of neat conjugated polymer films (left) and corresponding CONPHINE films (right) at 100% strain, for polymers of (**A**) P-29-DPPDTSE; **2**, (**B**) PffBT4T-2DT; **3**, (**C**) P(DPP2TTVT); **4,** and (**D**) PTDPPTFT4; **5**, with the chemical structures shown on the right side. Scale bar = 20 μm. The CONPHINE films at 100% strain exhibited un-even thickness (Fig. S29), but no cracks due to plastic deformation. (**E**) Transfer curves ($V_D = -80$ V) of these neat polymer films (in the left plot) and corresponding CONPHINE films (in the right plot) at 100% strain, with the same vertical axis in the two diagrams. (**F**) Normalized mobilities of neat films (grey) and corresponding CONPHINE films (green) of these conjugated polymers, under 100% strain.