# Title: High Temperature Semiconducting Polymer Blends

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**Abstract:** Although high temperature operation (i.e., beyond 150 °C) is of great interest for many electronics applications, it is fundamentally challenging to achieve stable carrier mobilities for either inorganic or organic semiconductors at elevated temperatures. Here we report a general strategy to make thermally-stable high temperature semiconducting polymer blends, composed of interpenetrating semicrystalline conjugated polymers and high glass-transition temperature insulating matrices. We find that, when properly engineered, such polymer blends display a temperature-insensitive charge transport behavior across a wide temperature range from room temperature up to 220 °C in thin film transistors. This discovery opens new horizons for organic semiconductors and printed electronics.

**One Sentence Summary:** Polymer-based electronics are not afraid of extreme heat.

**Main Text:** It is in principle challenging to achieve thermally-stable operation for either inorganic or organic semiconductors at elevated temperatures. The ubiquitous crystalline inorganic semiconductors (i.e. silicon) usually operate below 85 °C in commercial-grade electronics. Their performance is sharply deteriorated at higher temperatures due to increased carrier densities, junction leakages, and reduced charge carrier mobility (*1-3*). To improve the device performance and lifetime in these harsh thermal conditions, wide-band gap materials as well as the use of increased amounts of insulating components have been utilized (*4, 5*). Active or passive cooling, as well as thermally-engineered packaging are needed to maintain the optimal electronic performance (*6*). In contrast, organic semiconductors commonly display thermally-activated charge transport features (*7, 8*). Charge transport is facilitated in organics with moderate temperature increases, leading to improved performance (*9*). However, this thermally-activated charge transport becomes counteracted by unstable morphologies and disrupted molecular packing at higher temperatures, especially in polymer thin films (*10, 11*). Although organic electronics is emerging as a new form of electronic devices (*12-14*), this frontier between charge transport and thermal operation stability has rarely been addressed in the design of organic semiconductors. A few notable examples employing small molecule organic semiconductors are only concerned with the high temperature annealing effect (*15-17*). But in all cases, charge carrier mobilities are temperature-dependent and start to decline at temperatures above 150 °C. Little work has been done on designing high temperature organic semiconductors that operate at elevated temperatures (*18*).

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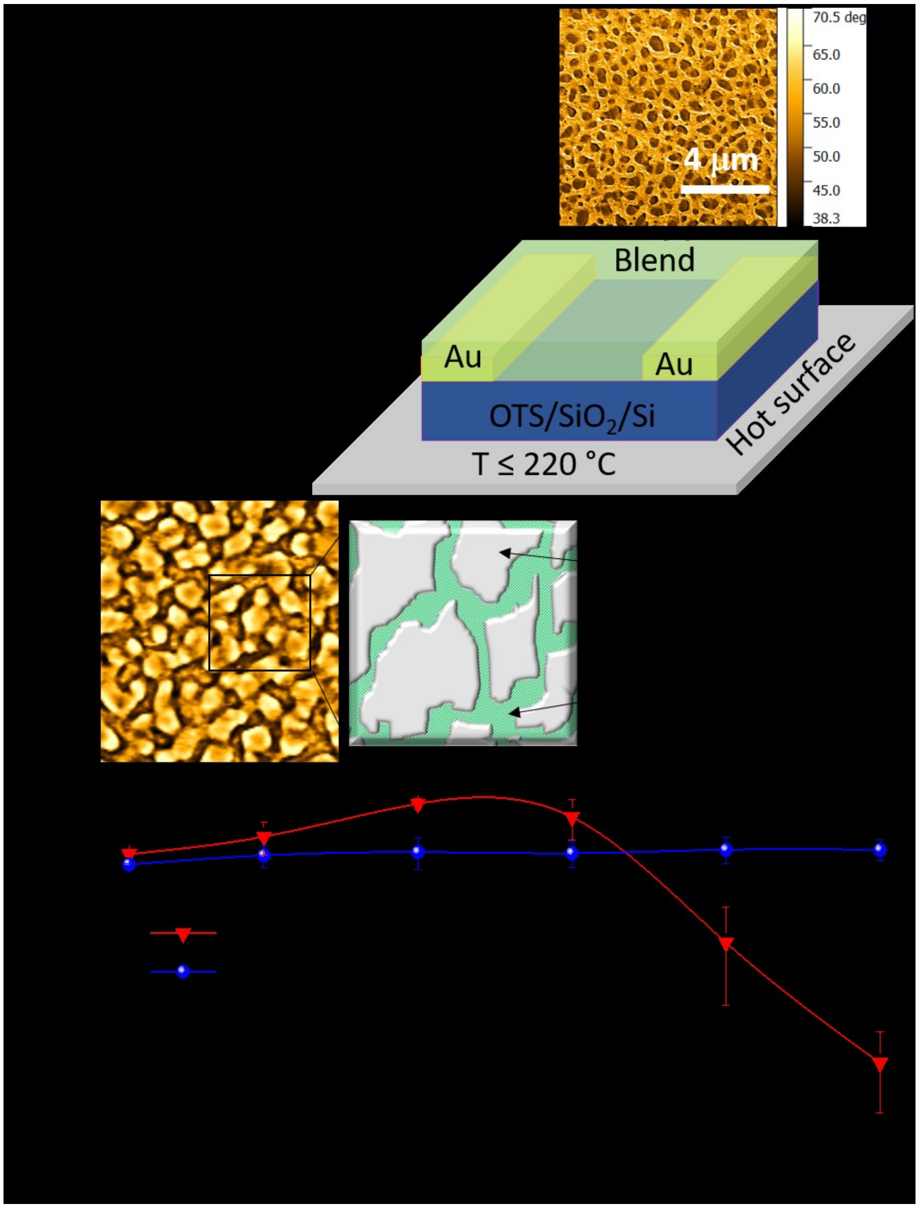

**Fig. 1 Blending design for high temperature semiconducting polymer blends.**

**A,** Chemical structures of the semiconducting polymer (P1) and the insulating matrix polymer (PVK). **B,** Device structure of the studied thermally-stable FET. The AFM phase morphology reveals the interpenetration of the semiconducting polymer within the insulating host. **C,** Illustration of the blending design with the semiconducting crystalline pathways dispersed within rigid host islands. **D,** Measured hole mobilities for FET devices based on P1/PVK (40/60, wt%) blends at different temperatures at ambient compared with pure P1. The data points represent average values from twenty different devices and the error bars represent the standard deviation from the average.

Blending semiconducting polymers with insulating hosts has been adopted for various purposes, such as improving electronic performance, processability, mechanical and environmental stability in electronic devices (*19, 20*). In this study, by recognizing that preserving close intermolecular interactions and packing motifs at elevated temperatures is the key challenge, especially for semiconducting polymers, to attain excellent thermal stability (*10, 18*), we hypothesize that the proper formation of semiconducting polymer blends can lead to the confinement of conformational changes of semiconducting polymer chains at elevated temperatures. Thus, we conceive high temperature semiconducting polymer blends — an interpenetrating network between semicrystalline conjugated polymers and high glass-transition ($T_g$) insulating polymer hosts. To test this concept, we first select diketopyrrolopyrrole-thiophene (P1), a high-performance conjugated polymer, and poly(vinyl carbazole) (PVK, $T_g$ ~220 ºC) as the high-Tg host (**Fig. 1A**). The blends with optimized ratios form interpenetrating channels between conjugated polymer P1 and the rigid host PVK, as observed from atomic force microscopy (AFM) images (**Fig. 1, B and C**). Testing the blend films in field-effect transistors (FETs) under ambient and inert conditions, we observe thermally-stable operations at high temperatures up to 220 °C with hole mobilities as high as 2.5 $cm^2/Vs$ (**Fig. 1D** & Fig. S1). Compared with the pristine semiconductor P1, our blends present unprecedented operational stability over a wide temperature range

To understand the significance of the interpenetrating morphology in thermally-stable thin films, we vary the blending ratio from 40 to 90 weight percentage (wt%) of PVK in spin-cast films (**Fig. 2, A and B** & Fig. S2). The thermal stability analyses of the electronic performance reveal that the optimal blending ratio is attained between 55-65% of PVK. In this blending range, the films exhibit interconnected domains of P1 that correlate with thermally-stable charge transport properties. With loadings outside this range, undesired vertical or large lateral phase segregation occurs, which leads to the loss of thermal stability. From the UV-Vis absorption spectra (**Fig. 2C**), an increase in the *0-0* vibronic peak intensities is observed upon approaching the optimal blending ratios, indicative of increasing ordering and π-π interactions between P1 chains in the confined domains (*21-23*). The bottom surface morphology analysis confirms that the interpenetrating structure is preserved at the gate interface in the thermally-stable high-performance blends (**Fig. 2D** & Fig. S3).

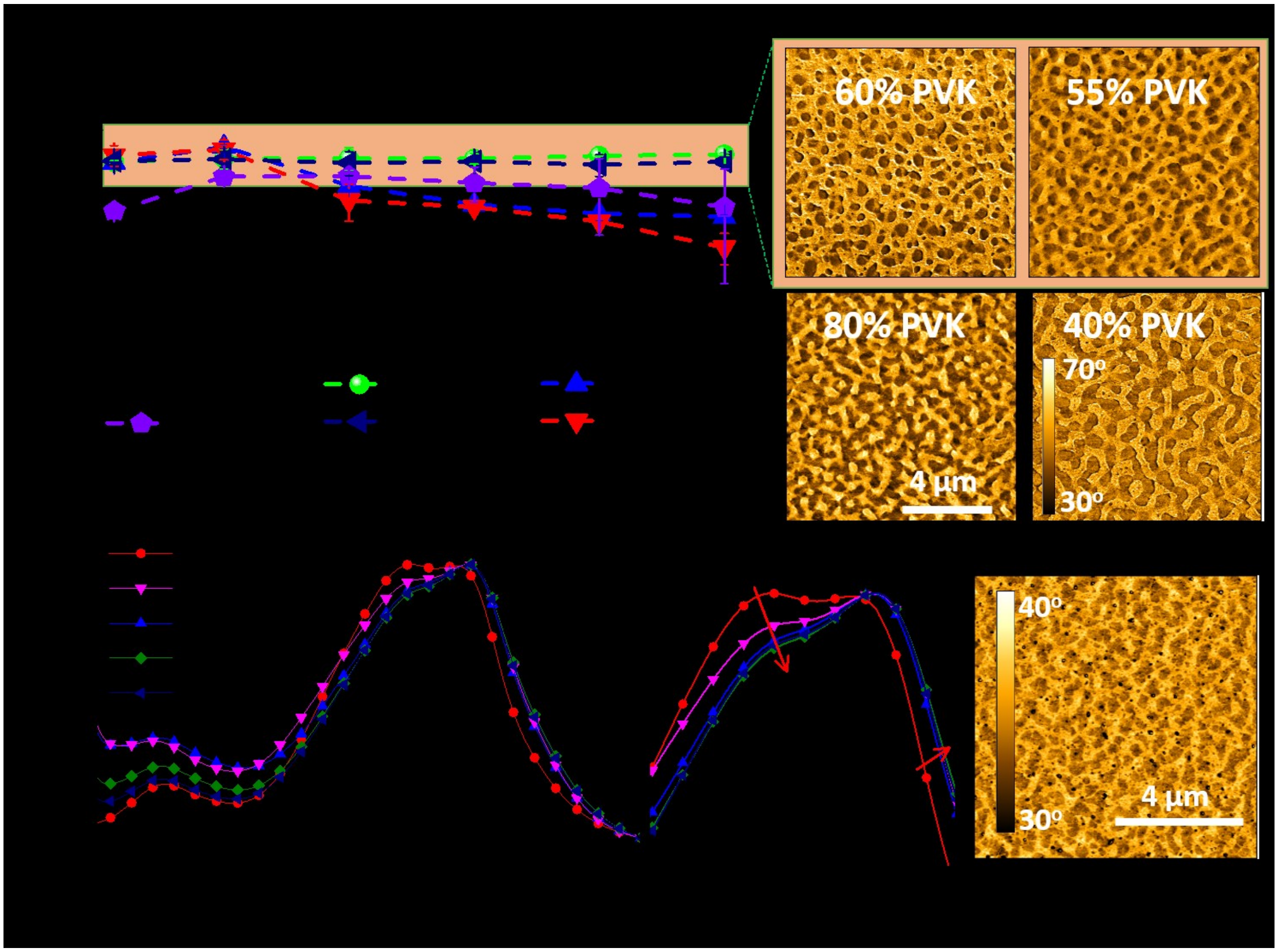

**Fig. 2 Morphology stabilization: the interdigitation and thermal stability can be tuned via blending ratio control.**

**A,** Temperature-dependent charge carrier mobility in FET devices based on P1 blends containing various ratios of PVK. The data points represent the average hole mobility measured from ten different devices for each blending ratio and the error bars represent the standard deviation from the average. **B,** AFM phase images of the spin-cast thin films of the polymer blends with various amounts of PVK. An optimal amount of the semiconductor is required to establish interpenetrated morphology. Beyond this threshold, lateral phase separation occurs, and the interconnectivity is lost. **C,** Normalized UV-Vis absorption spectra of P1/PVK blends with varying amounts of the matrix polymer. The confinement of the semiconductor within rigid domains of the host leads to increased ordering of the conjugated polymer chains. **D,** AFM phase image of the bottom surface of a delaminated film of the optimized blend revealing persistent interpenetrating morphology of semiconducting domains at the substrate interface.

To elucidate the observed thermal stability, we use in-situ temperature-dependent UV-Vis spectroscopy, AFM, grazing incidence x-ray diffraction (GIXD), as well as molecular dynamics (MD) simulations to study the effect of temperature on the intermolecular interactions of the semiconducting chains in the pristine P1 and the 60% PVK blend films. Upon heating, the UV-Vis absorption spectra of pristine P1 films reveal a significant blue shift, accompanied by a decrease in both the *0-0* and the *0-1* peaks (**Fig. 3A**). These phenomena are consistent with the polymer chains de-aggregating and reorganizing as the thermal energy disrupts the crystallites. For the blend films the chain ordering and interchain interactions are less affected upon heating, in comparison to pristine P1 films, as evidenced by the less pronounced decrease of the *0-0* vibronic peak intensity. More strikingly, the *0-0* vibronic peak that vanishes in the P1 films is retained in the blended films even at temperatures up to 220 °C (**Fig. 3B**). The temperature-dependent AFM analysis also reveals that the microscale morphology of the pristine P1 films changes upon heating while the P1/PVK blend film morphology is not affected by heating (Fig. S4). Together, these observations indicate that the matrix polymer effectively confines the semiconducting polymer and limits dihedral twisting and larger structural reorganizations that are responsible for the loss of the carrier mobility at high temperatures.

In-situ temperature-dependent GIXD studies provide further information on the intermolecular interactions upon heating. In the 60% PVK blend film the π-π stacking distance of P1 reduces from 3.70 Å to 3.64 Å, relative to the pristine P1 (**Fig. 3, C and D &** Fig. S5). In both cases, π-π stacking distance expands when the thin films are heated, reaching 3.79 Å and 3.73 Å at 200 °C for the pure P1 and the PVK blend films, respectively. To evaluate the effect of this π-π stacking confinement on the polymer dihedral distribution molecular dynamics modeling is performed. In these simulations, the π-π separation of the semiconducting polymer chains are restrained to model varying levels of confinement and the resulting dihedral distributions are compared to characterize the polymer reorganization dynamics (**Fig. 3E**). At π-π confinements of 3.0 Å we observe complete conservation of the dihedral distributions at all temperatures. Notably, the CCCN dihedral, corresponding to the diketopyrrolopyrrole-thiophene (DPP-T) conformations, exhibits interconversion between gauche conformers, but there is no evidence of gauche to trans interconversion (i.e., the onset of chain twisting) at any temperature. Likewise, the SCCC dihedral, corresponding to the thiophene-thiophene conformations, broadens with temperature but remains sharply peaked. In contrast, at π-π confinements of 5.0 Å, the SCCC dihedral distribution is broadened at all temperatures and the CCCN dihedral begins to exhibit gauche to trans interconversion at temperatures of 425 °C (**Fig. 3, F and G)**. Systematic studies of the dihedral distributions under confinements from 3 Å to 6 Å allow us to conclude that large-scale DPP-T reorganizations begin relatively abruptly once π-π fluctuations reach ~5 Å (Figs. S7-9). The simulation suggests that engineering of π-π stacking distance can lead to minimize dihedral twisting over a wide range of temperatures. It corresponds well with our finding that the blending strategy improves the initial molecular packing, minimizes the microscale morphological rearrangements of the blend film, and ultimately offers thermally-stable charge transport in the PVK blend films.

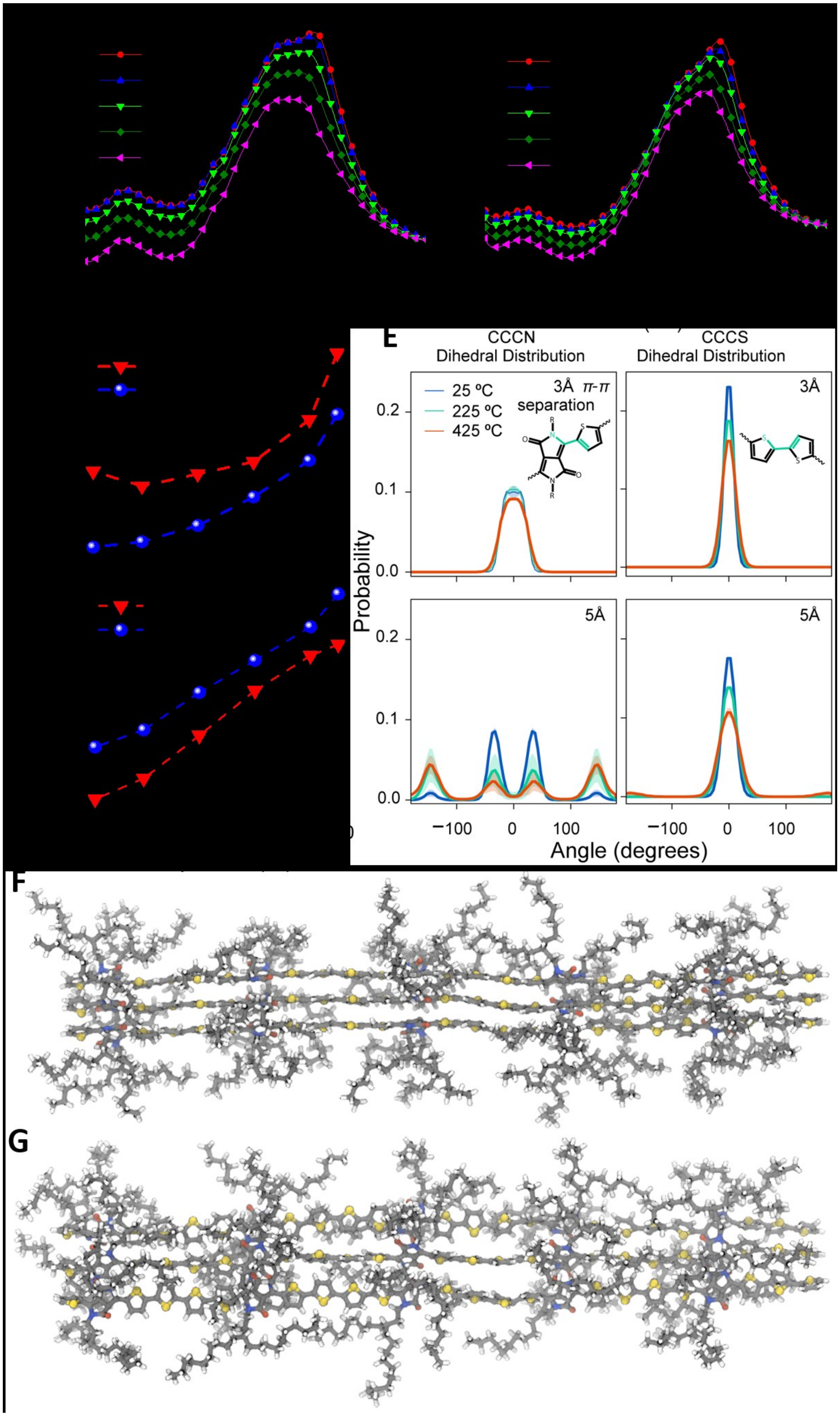
E
CCCN
Dihedral Distribution
CCCS
Dihedral Distribution
25 ºC
225 ºC
425 ºC
3Å π-π
separation
3Å
5Å
5Å
Probability
0.0
0.1
0.2
−100
0
100
Angle (degrees)
F
G

**Fig. 3 Thermally-stable packing behavior in PVK blends.**

**A**, **B**, Temperature dependent UV-Vis absorption spectra of pristine P1 films and the corresponding PVK blend. **C**, **D**, Evolution of π-π d-spacing and lamellar stacking in thin films treated at different temperatures. The presence of PVK in the films not only induces closer packing of the conjugated polymer chains, but it also reduces their freedom to thermally expand and rearrange. π-π stacking distance as close as 3.72 Å can be retained at 200 °C in the case of the PVK blend film. The peak position was extracted from Gaussian fits to the 1D I(q) vs. q plots. **E**, Simulated dihedral distributions at different temperatures when confined to both 3 Å and 5 Å. With the spatial constraint of 5 Å, the distribution broadens indicative of chains twisting at all temperatures. **F**, **G**, Packing behavior of DPP-T chains when confined to 3 Å and 5 Å, respectively.

To evaluate the stability of the blend films under prolonged thermal stress, the fabricated FET devices are subjected to the constant heating at 150 °C for six hours. For inorganic semiconductors, prolonged heating leads to increased charge carriers density and uncontrolled thermal doping (*24*). For organics, prolonged heating, especially above the glass-transition or the melting point of the semiconductors, leads to morphology changes and device performance degradation (*10, 11, 17*). We monitor FET device performance for six hours while heating at 150 °C in open air. In contrast with the pristine P1 devices under the same conditions, the devices based on the 60% PVK blends retain excellent electronic properties (as high as 95% of the original mobility) under thermal stress (**Fig. 4A**). The FET devices made from pristine P1 showed declining $I_{ON}/I_{OFF}$ and increased threshold voltages under constant heating, consistent with earlier observation of unstable morphologies at high temperatures. The thermally-stabilized blend-based FET devices retain $I_{ON}/I_{OFF}$ higher than $10^3$, and threshold voltages below 3V after six hours of heating in open air (**Fig. 4, B to D**).

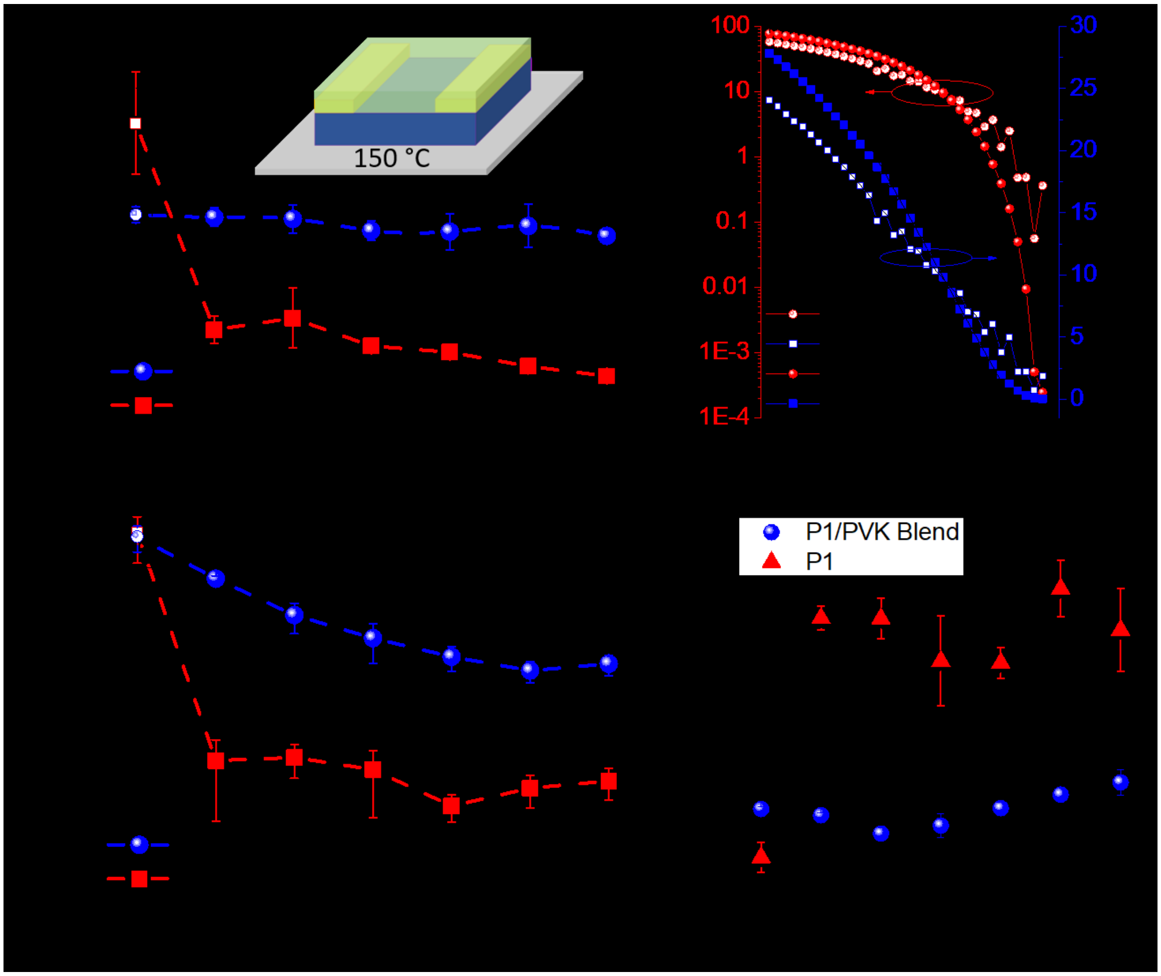

**Fig. 4 Effect of thermal stress on OFET devices and thermal stability of PVK blends.**

**A,** Measured hole mobilities under constant thermal stress for six hours. A sudden decline in mobility is observed for pure P1 when the FET device is heated. The blend can retain its original mobility after six hours. **B**, Characteristic transfer curves of FET devices based on P1 with and without PVK after 1 hour of heating. **C**, Impact of heating on the $I_{ON}/I_{OFF}$. After one hour of heating, the ratio falls to nearly 10 for the devices based on P1 while remaining > $10^4$ for the blend devices. **D**, Threshold voltages for FET devices based on the 60% PVK blends (below 3 V), and pure P1 (exceeding 20 V) upon prolonged heating. The data points represent the average values measured from ten different devices and the error bars represent the standard deviation from the average.

To demonstrate the generality of our blending strategy, we explore the FET thermal stability of P1 blended with four other high-$T_g$ matrices (**Fig. 5A**). We first optimize the blending ratios to attain interpenetrating morphologies (Fig. S10A). FET devices based on these optimized blends exhibit hole mobilities as high as 2.0 cm$^2$/Vs that are stable up to 220 °C in open air (**Fig.**

**5B**). It is noted that the optimized blend of P1 and polycarbonate (PC, $T_g$ ~182 ºC) only provides thermally-stable operation up to 180 ºC, which is near the $T_g$ of the host. We also test other high-performance diketopyrrolopyrrole (DPP) (P2)(*21*) and isoindigo (P3)(*25*) based donor-acceptor semiconductors (**Fig. 5C**), and study the thermal stability of their blend films with the champion high-Tg matrices, i.e. PVK and PAC. After optimizing the blend ratios to obtain an interpenetrating morphology (Fig. S10B), FET devices with excellent thermal stability up to 220 °C are also achieved (**Fig. 5D**). Temperature-dependent UV-Vis absorption analyses on the blend films of P2 and P3 confirm that those blend pairs with thermally-insensitive charge transport properties exhibit a similar behavior as the P1/PVK blend at high temperatures (Figs. S11-14). One exception is the P2/PVK pair, which does not present a thermally-stable charge transport behavior (**Fig. 5D**). Likewise, this pair does not preserve the characteristic intermolecular interaction vibronic peak upon heating, indicating that this is a necessary feature in stable blends (Fig. S12). We also notice that the pristine P3 film exhibits a nearly thermally-stable operation across the tested temperature range. Consistent with the thermally-stable blends previously discussed, the P3 film itself also exhibits strong intermolecular interactions even at high temperatures (Fig. S13), which suggests the organization of P3 is uniquely robust among the studied semiconductors and warrants a further investigation.

To design high temperature semiconducting polymer blends, a few requirements thus seem universal: 1) a host matrix with a glass transition temperature higher than the desired operating temperature; 2) a semicrystalline semiconducting polymer; 3) the interpenetration of the semiconducting component into the host matrix; and 4) improved intermolecular π- π stacking within semiconducting channels that can be retained at high temperature. The use of high-$T_g$ matrices is demonstrated to be a general strategy to attain these properties by minimizing spatial rearrangements within the polymer films at elevated temperatures. As far as the charge transport mechanism in the blends is concerned, we hypothesize that the superior ordering in the confined channels leads to reduced activation energy and trap density. Further studies on activated charge transport in confined environments is warranted.

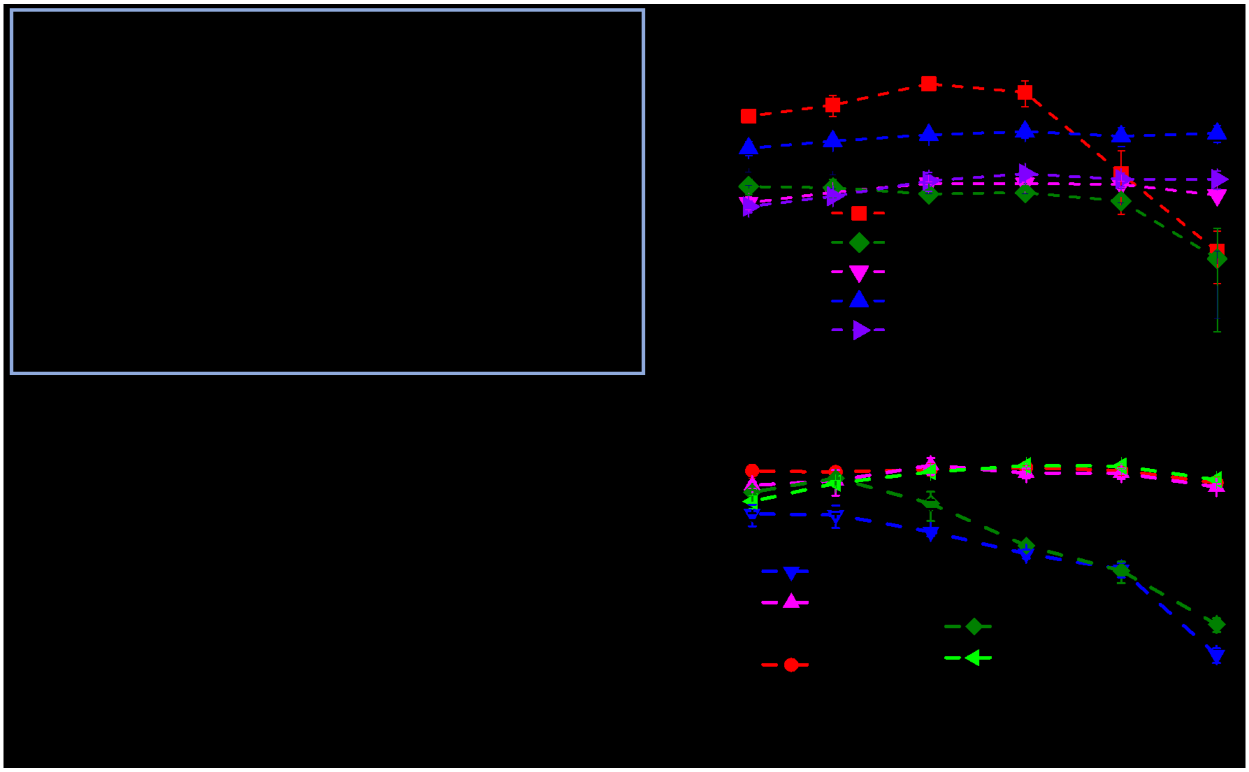

**Fig. 5 Attaining universal thermal stability in semiconducting polymer blends.**

**A,** Molecular structures of the representative matrix polymers tested for high-temperature charge transport. **B,** Hole mobilities of FET devices based on the optimized blends of P1 in four different matrices measured in open air. **C**, Molecular structures of additional semiconducting polymers studied for thermally-stable blends. **D**, Measured FET mobilities from the blend films of P2 and P3 with PVK and PAC used as the host matrices. The blend combinations that have stable close packing exhibit hole mobilities stable up to 220 °C. The data points represent the average mobility values measured from ten different devices and the error bars represent the standard deviation from the average**.**

With the demonstrated high OFET mobility, ON-OFF ratios, and high tolerance of thermal stress, the presented polymer blending strategy shows that organic semiconductors hold a significant promise in high-temperature electronics. Indeed, our results provide critical insight for the development of materials for existing and future needs where electronic performance under extreme heat conditions is necessary, such as in aerospace and automotive industries, the down-hole oil and gas drilling industry, as well as light-weight electronic textiles and equipment for military applications in a desert environment. Our results unequivocally demonstrate that carefully designed semiconducting polymer blends have great potential for meeting this important technological demand. Finally, we believe that fundamental investigations on charge transport mechanisms, which have been historically bounded to low temperature regimes in which the impact of morphological changes is negligible, could also exploit this blending design to cover wider temperature ranges.

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**Author contributions**: A.G. and J.M. designed the experiments; A.G. processed the thin films and did the morphology characterizations, fabricated and characterized the transistor devices; D.T.T. and Y.Z. helped with the measurements under nitrogen. X.L. synthesized the conjugated polymers; D.T.T. performed the DSC measurements; K.A.J. helped with the UV-Vis measurements. G.M.P., T.J.D, and A.L.A. designed and performed the GIXD measurements. B.M.S. designed and performed all the computational work. A.G., B.M.S., and J.M. organized the data and wrote the manuscript, and all authors contributed to the editing of the manuscript. J.M. conceived and directed the project.

**Data and materials availability**: All data needed to evaluate the conclusions in the manuscript are provided in the manuscript or the supplementary materials.

**Supplementary Materials:**

Materials and Methods

Tables S1-S3

Figures S1-S19

References *(26-33)*