



Supplementary Materials for
**Semiconducting polymer blends
that exhibit stable charge transport
at high temperatures**

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Published 7 December 2018, *Science* **362**, 1131 (2018)
DOI: 10.1126/science.aau0759

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Materials and Methods

Materials

P1, P2, P3 were synthesized and the corresponding molecular weights were evaluated by gel permeation chromatography (GPC) as previously reported (25-27). Poly(9-vinylcarbazole) (PVK, average Mw 25,000-50,000), polyacenaphthylene (PAC, average Mw 5,000-10,000) were purchased from Sigma Aldrich and used as received. Polycarbonate (PC), polyetherimide (PEI), and Matrimid® 5218 (MI) were purchased from PolyK Technologies and purified by precipitation and filtration in methanol before use. All polymer solutions for thin film formation were obtained in chloroform (10 mg/ml) and allowed to stir for 10 hours. The blends were obtained by mixing the appropriate volume percentages for at least 1 hour.

Poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning) was prepared at ratio of 10:1 (base/cross-linker, w/w) and cured at 80 °C for 4 hours and used for film delamination.

Octadecyltrichlorosilane used for surface modification was purchased from Sigma Aldrich and used as received.

Thermal transition measurements

The glass transitions of the studied matrix polymers were verified by dynamic scanning calorimetry (DSC). The DSC thermograms were measured using a TA Q5000 calorimeter. The polymer sample was sealed in a hermetic aluminum pan and measured under nitrogen purge (50 mL / min). The sample was heated and cooled in two cycles between -30 to 400 °C (or otherwise as indicated), with the first cycle removing any thermal history of the sample. The heating and cooling rates for all measurements were 10 °C / min.

OFET devices fabrication and characterization

A heavily n-doped Si wafer with a 300 nm SiO₂ surface layer (capacitance of 11 nF/cm²) was employed as the substrate with Si wafer serving as the gate electrode and SiO₂ as the dielectric. The gold source/drain electrodes were sputtered and patterned by photolithography technique. The device channel width was 1400 μm and the channel length was 50 μm. For the octadecyltrichlorosilane surface modification, the silicon wafer (with Au bottom contact) was first cleaned with hot piranha solution (H₂SO₄ (98%):H₂O₂ (30% water solution) = 7:3) followed by a copious rinsing with water. It was then further subjected to sonication sequentially in water and acetone for 5 minutes each. After drying at 80 °C inside an oven, the silicon wafer was then put in a clean and dried Petri dish with a small drop of OTS in the center. The dish was then covered and heated in a vacuum oven at 120 °C for 3 hours, resulting in the formation of an OTS self-assembled monolayer on the surface. The OTS-modified substrates were rinsed with hexane, ethanol, and chloroform and blow-dried by nitrogen. During the temperature-dependent analyses, the contribution from the thermal expansion of the substrate was assumed to be negligible for the studied temperature range. The semiconductor layer was deposited on the OTS-treated Si/SiO₂ substrates by spin-coating with speed of 2000 rpm for 30 seconds. The solvent used is chloroform. The concentrations of the solutions used for spin coating were 10 mg/mL. The devices were annealed in a N₂ glovebox up to 200 °C then slowly cooled to 25 °C prior to electrical measurements.

OFET devices characterizations were carried out using a Keithley 4200 both in ambient and under N₂ environment. The field-effect mobility was calculated in the saturation regime by using the equation $I_{DS} = (WC_i / 2L)\mu(V_G - V_T)^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer, V_G is the gate voltage, and V_T is the threshold voltage. OFET performances were obtained by applying a gate bias from -60 V to 6 V, with the potential gradient between the source and drain contacts kept at -60 V. To control the thermal conditions, the HFS600E-PB4 Linkam stage was used, and for the measurement carried under inert environment, the stage chamber was first purged for 10 minutes and hermetically filled with N₂ gas prior to measurement. The heating and cooling rates were maintained at 10 °C/ min and OFET devices were allowed to reach thermal equilibrium for 30 minutes at each temperature before measuring.

Morphology analysis

Polymer thin films were spin cast on cleaned and OTS-modified Si/SiO₂ substrates. The film thickness was measured to be around 170 nm when chloroform was used as a solvent. AFM images were taken using Cypher Asylum AFM and processed through Gwyddion Software. For the in-situ temperature dependent morphology study, the films annealed at 50 °C for solvent removal were first imaged with the temperature on the sample stage maintained to 25 °C. The sample stage temperature was then increased to 120 °C (the instrument limitation), and the films were re-imaged for comparison. The same samples were further heated to 220 °C in open air and re-imaged.

In-situ temperature-dependent Grazing Incidence X-ray Diffraction (GIXD)

GIXD measurements were performed at the Stanford Synchrotron Radiation Lightsource (SSRL), generated with a 24-pole, 2-Tesla wiggler insertion device. Beamline 11-3 utilizes a beam of energy of 12.7 keV with a 2×10^{12} photons/s flux. The beam grazed the sample at an incidence angle of 0.12 for 180 seconds, and the resulting diffraction pattern was collected onto a 2D area detector 315 mm away. Lanthanum hexaborate; a polycrystalline material, was used to calibrate the sample-to- detector distance as well as the scattering vector. The beam footprint is 3.0 x 0.15 mm and was shaped with adjustable slit widths. TIFF files were generated at beamline 11-3 and were processed in WxDiff. Prior to collecting any GIXD measurements, the film on Si/SiO₂ substrates was annealed thermally at 200 °C in a He atmosphere. The sample was allowed to “equilibrate” at a given temperature for 5 minutes prior to collecting the respective diffraction pattern.

UV-Vis spectroscopy

Samples were prepared by spin casting the chloroform polymer solutions onto cleaned glass substrates. All absorption spectra were collected using a UV/Visible/NIR Cary 3000i spectrophotometer. To compare aggregation behavior between films of pure P1 and its PVK blends, and to probe the effect of temperature on the formed aggregates, all films were annealed to 200 °C and slowly cooled down to room temperature inside a N₂ glovebox before each measurement. In-situ absorption spectra were recorded at different temperatures using the HFS600E-PB4 Linkam stage. Each sample was first carefully mounted inside the stage and hermetically encapsulated in the N₂-purged chamber. The stage was then brought into the light path of the UV/Visible/NIR Cary 3000i spectrophotometer. Prior to each measurement, each sample was allowed to reach thermal equilibrium for 30 minutes. The HFS600E-PB4 Linkam stage with a clean glass slide hermetically mounted in the chamber was used as the baseline and the

background spectra were obtained after heating the blank sample for 10 minutes for each temperature. Temperature-dependent spectra were then obtained with corresponding baseline correction.

Semiconducting Polymer	M _n (kDa) ^a	<i>Đ</i>
P1	30.7	3.6
P2	26.5	1.7
P3	28.0	4.0

Table S1. Summarized molecular weight values of the studied semiconducting polymer materials. Low molecular weight extracts were used in this study as they could be easily solution processed into thin films from the blend solutions with the matrices.

^aTrichlorobenzene was used as the eluent at 150 °C.

Matrix Polymer	T _g (°C)	M _n (kDa)
PVK	210	23.7
PAC	265	67.0
PC	182	23.4
PEI	263	37.8
MI	325	7.2

Table S2. Summarized glass transition temperatures (T_g) of the studied host matrices. Shown in parentheses for T_g values are the commercially reported values.

^bDynamic scanning calorimetry (DSC) scans were taken at 10 °C/min heating/cooling rates.

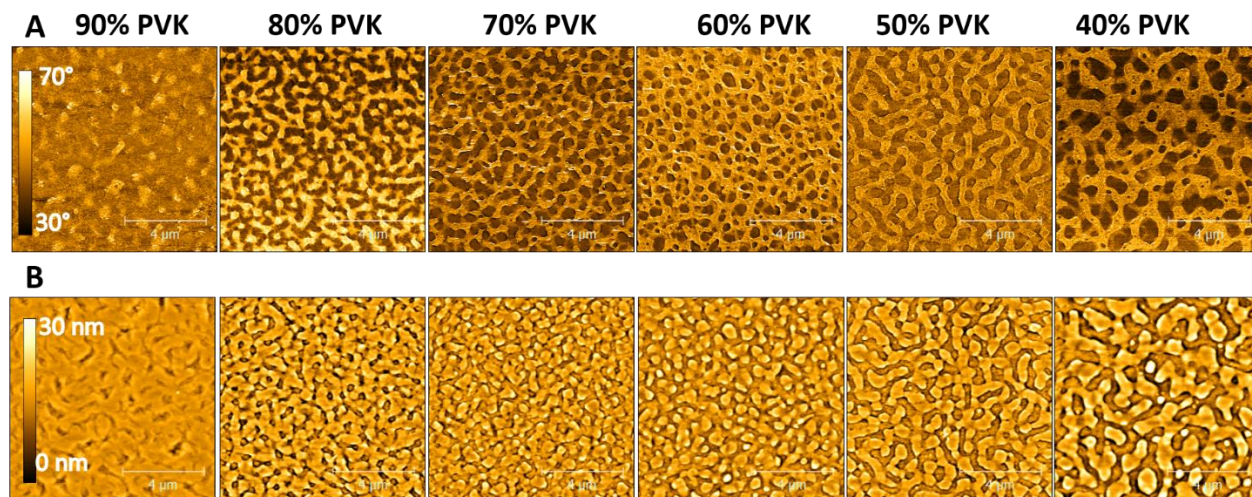


Fig. S1. Morphology control via blending of P1 and PVK. The thin films were fabricated by spin casting on Si/SiO₂ substrates and the AFM **A**, phase and **B**, height images were scanned after annealing. Domains of P1 start to interpenetrate when as high as 30 % P1 is present in the blend. After reaching the interpenetrating morphology, further addition of the conjugated polymer leads to an increase in lateral phase separation.

OFET device characterization under inert conditions

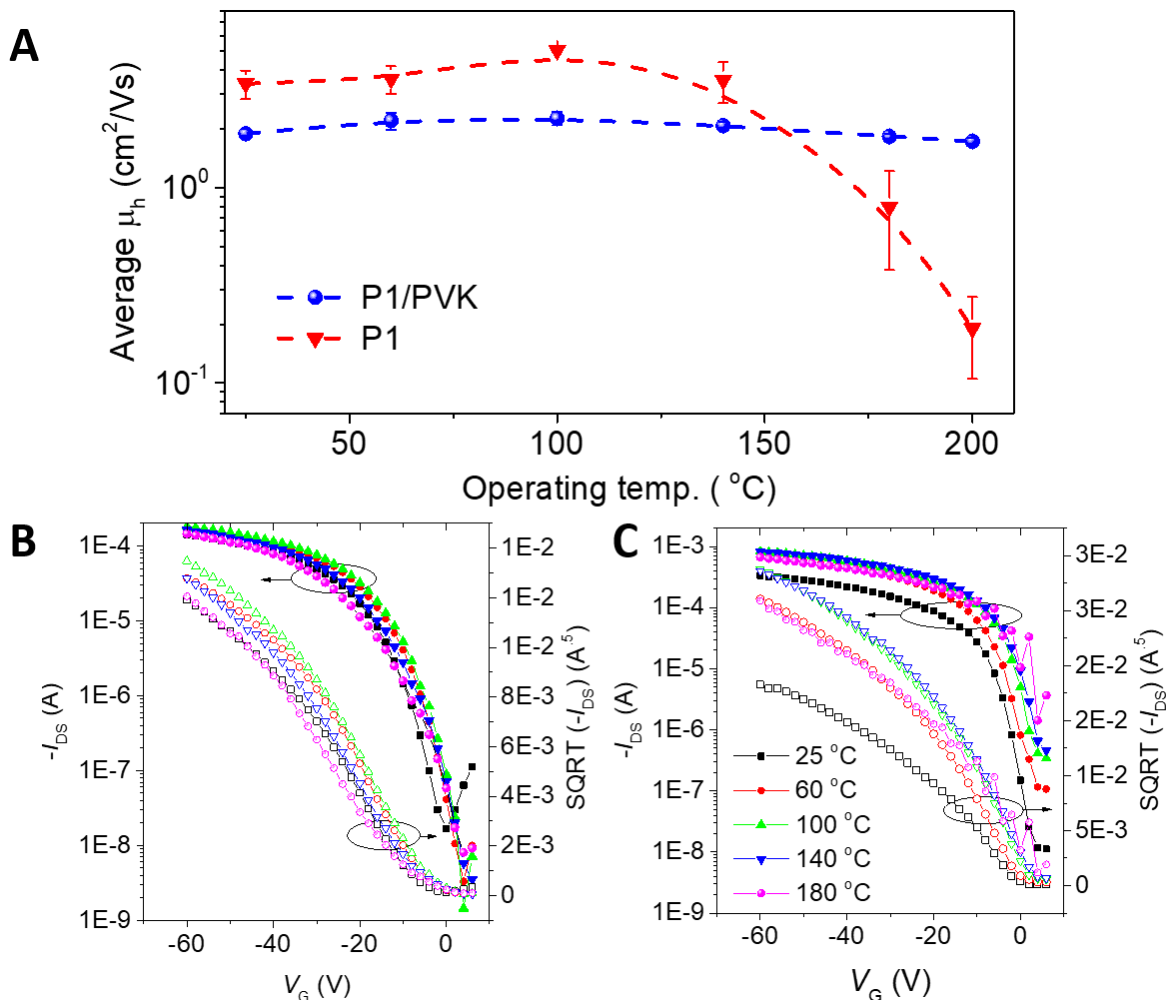


Fig. S2. A, Measured hole mobilities for OFET-devices measured under N₂. The devices based on 60% PVK blends outperform the ones based on pure P1 at temperatures above 150 $^{\circ}\text{C}$. Due to thermal limitation inside the N₂ glovebox, the device measurements were only taken up to 200 $^{\circ}\text{C}$. The data points represent the average mobility from ten different devices measured at each temperature and the error bars represent the standard deviation of the average. **B**, **C**, Representative transfer curves for OFET devices based on P1/PVK blend and pure P1, respectively.

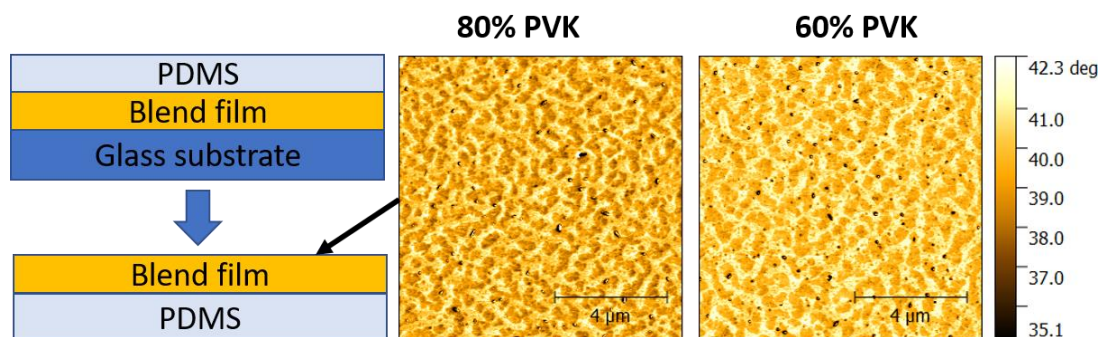


Fig. S3. Bottom morphology analysis of the blend films of P1 and PVK. The thin films were first spin cast and annealed onto Si/SiO₂ substrates and transferred onto PDMS slabs. After delamination, the bottom surface phase images were obtained. The interface shows enrichment in the conjugated polymer (bright yellow domains) with interpenetrating morphology at the optimized blending ratio (60% PVK).

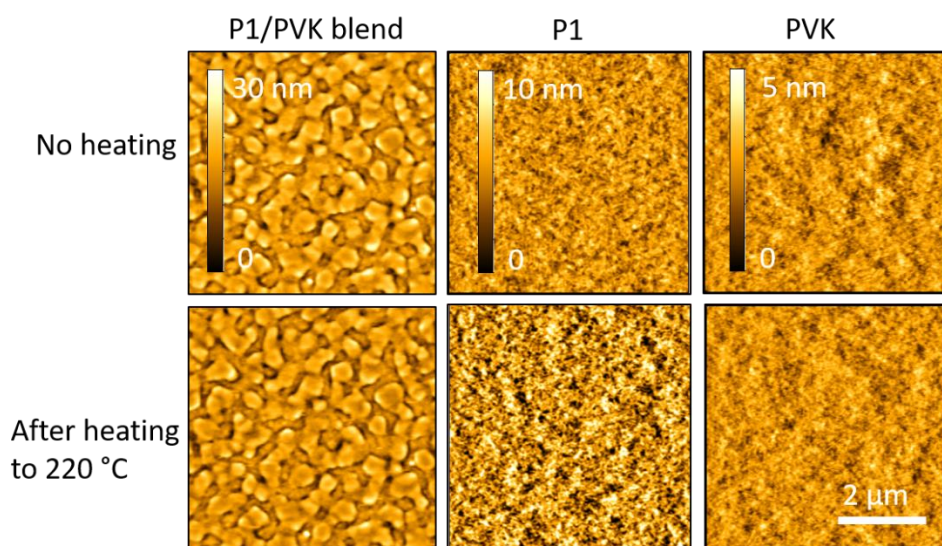
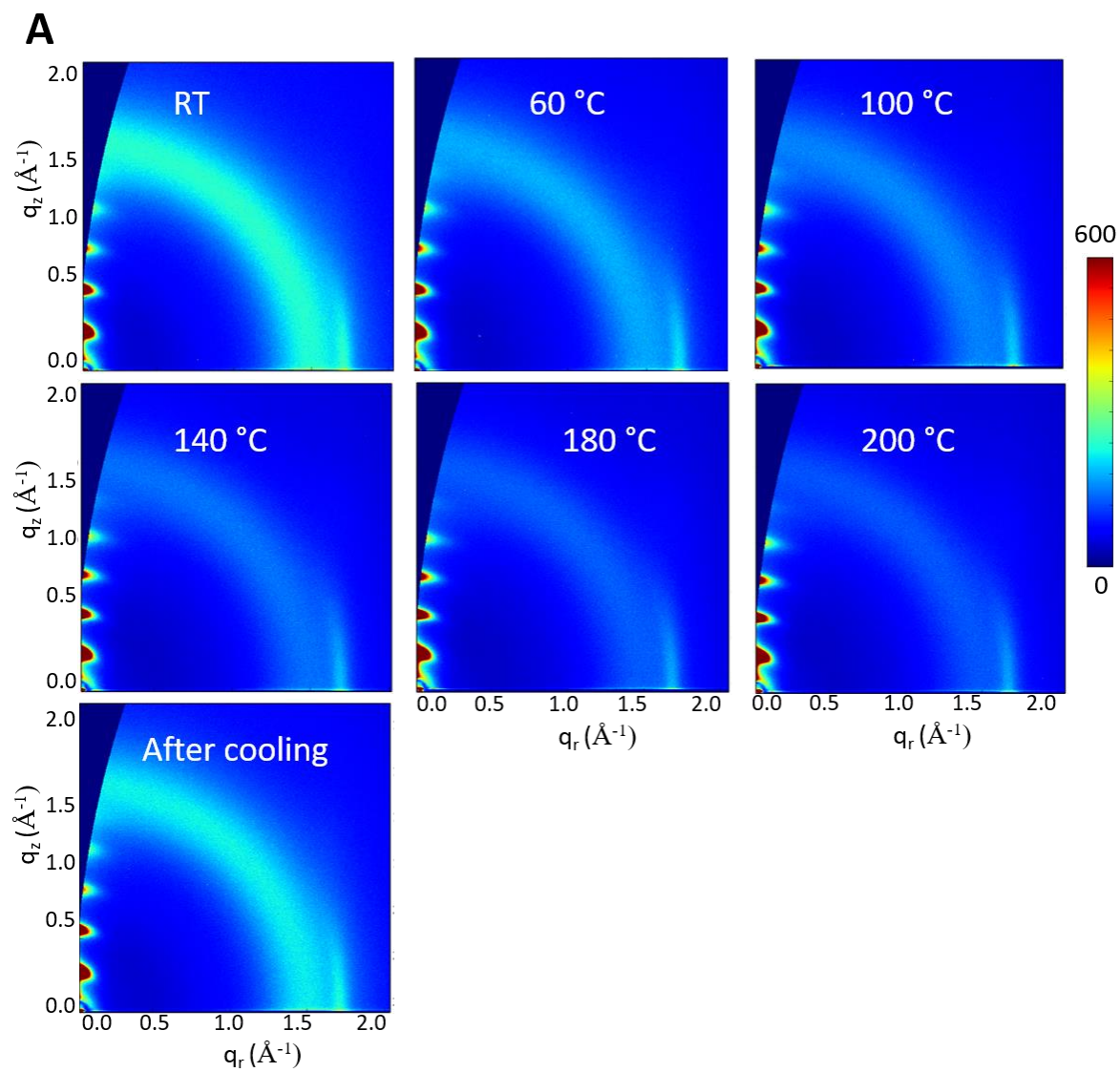
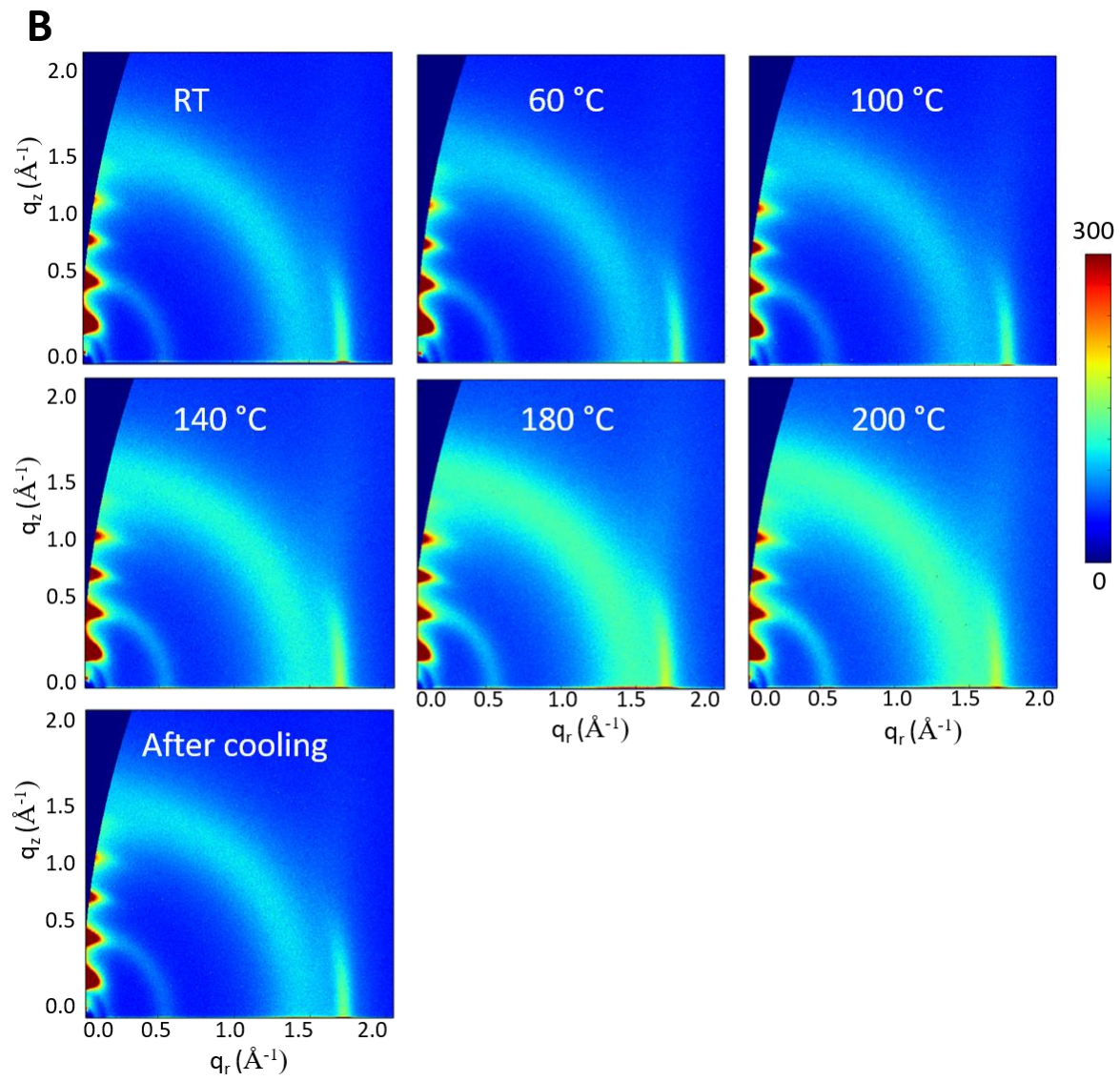


Fig. S4. The impact of heating on thin film morphology. Shown are the AFM height images demonstrating thermally stable morphology for films of both pure PVK and its 60% blend in P1, while the films of pure P1 demonstrate significant morphology changes when heated to 220 °C and directly imaged.

Temperature-dependent GIXD analysis





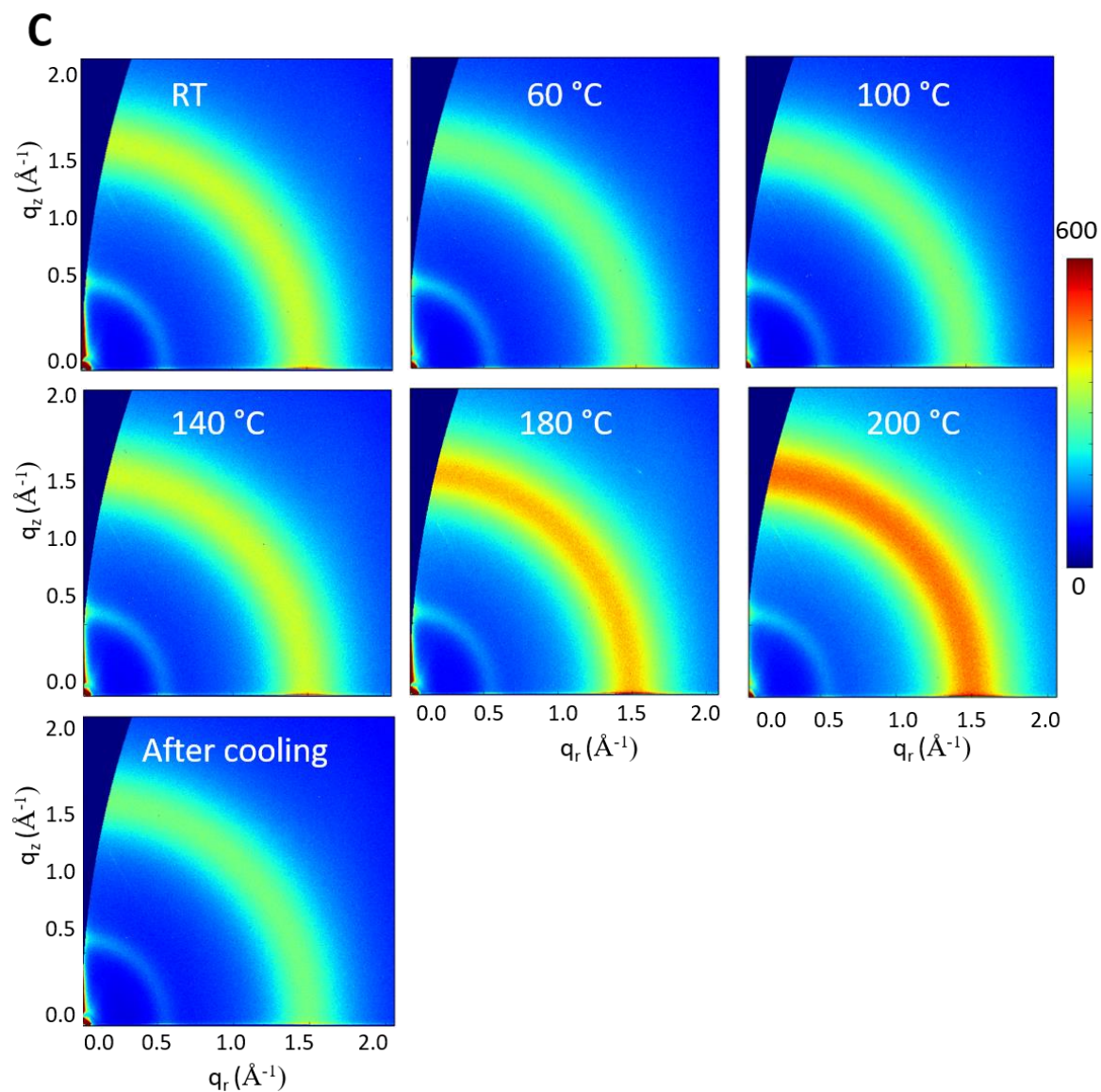
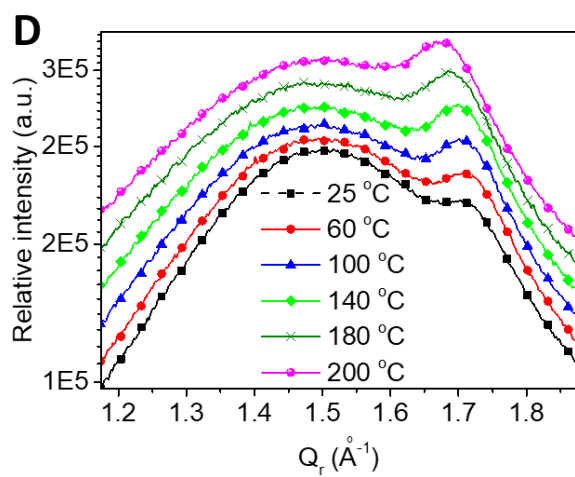
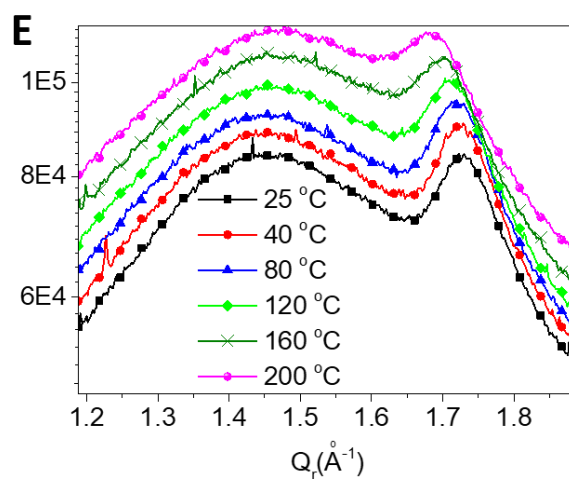


Fig. S5. Temperature dependent GIXD patterns of thin films based on **A**, pristine P1; **B**, 60% PVK blend; and **C**, pure PVK. The films were cast on Si/SiO₂ and annealed to 200 °C; in-situ measurements were taken in inert conditions. All thin films show to recover the original diffraction patterns after cooling back to room temperature. **D**, **E**, Temperature dependent 1D linecuts along the in-plane direction from the 2D diffraction patterns of P1 film and P1/PVK blend film, respectively.

Molecular dynamics (MD) simulations

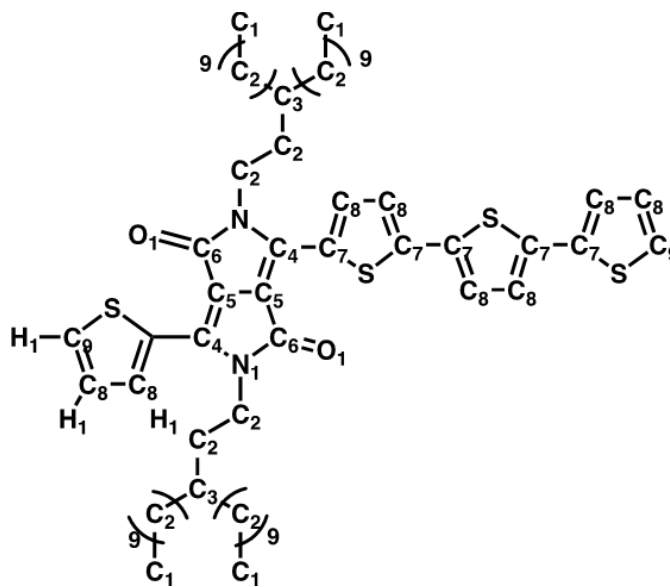


Fig. S6. Atom type assignment for the partial charges used in the molecular dynamics simulations.

All simulations were performed on atomistic models of the P1 polymer, using the GAFF force-field to describe bond, angle, dihedral, and Lennard-Jones terms (28). The partial charges were parameterized based on density function theory (DFT) calculations of the monomer unit with ethyl substituted side-chains. The monomer was geometry optimized at the ω B97X-D/def2-TVZP level of theory (29-30) and the electrostatic potential was calculated using the CHELPG methodology as implemented in Orca (31). The partial charges were fit using a least-squares optimization to minimize the deviation between the monopole-based and quantum-chemically calculated electrostatic potential on the surface of the molecule. During the fit, the point charges of identical atom types were constrained to be identical. The partial charges of the side chain carbons were set to achieve charge neutrality based on the number of bonded hydrogens. Improper dihedral terms were added to all three-coordinate atoms to promote planarity using harmonic potentials centered at 0° with a force constant of 100 kcal/mol. All partial charges are shown in Table S3.

LAMMPS was used to perform the MD simulations (32). All simulations used a one fs integration timestep and shrink-wrapped conditions. Electrostatics and LJ interactions were truncated at 14 Å. The initial polymer geometry was generated in an extended all-trans configuration for the backbone and side-chains. The dynamics were integrated using the Velocity-Verlet algorithm and temperature was fixed using a Langevin thermostat with 100 fs damping coefficient. The simulations were first relaxed in the NVE ensemble with restrained atomic displacements of 0.01 Å per timestep for 10 ps, followed by 100 ps of further equilibration with the Langevin thermostat

and 3 ns of production simulations. To avoid chain-folding and mimic the condensed-phase packing, a harmonic restraint was applied between the terminal hydrogen atoms on each polymer backbone with a 10 kcal/mol force constant and minima corresponding to the displacement of the terminal hydrogen atoms in the initial all-trans structure. All results and errors are reported as the average and standard deviation, respectively, of the reported quantities over five independent trajectories.

Atom Type	Partial Charge
C1	-0.439660
C2	-0.298968
C3	-0.149484
C4	0.039690
C5	0.111411
C6	0.038846
C7	-0.007710
C8	-0.157400
C9	-0.144707
O1	-0.311233
N1	0.000374
S1	0.036663
H1	0.149484

Table S3. Summarized partial charges of each atom type parameterized based on ω B97X-D/def2-TVZP calculations of the minimized geometry. The atom type labels can be compared with Fig. S6.

The “unconfined” simulations consisted of a pentamer of P1 (MW of ~5kD) with a single harmonic restraint on the terminal hydrogens as described above. The “confined” simulations consisted of three pentamers of P1 with individual harmonic restraints on the terminal hydrogens as described above. These simulations were initialized to avoid overlaps by aligning a single extended chain so that its long axis and π -system were maximally aligned in the x-y plane, making two replicas of this geometry, then displacing the replicas +/- 10 Å along the z-axis from the original structure. To systematically investigate π - π confinement, additional harmonic potentials were applied between subsets of the flexible dihedral atoms in each chain to restrain the chain separations and lateral registration (Fig. S7A). These restraints were grown during the equilibration phase of the simulations (from a force constant of 0 kcal/mol to 10 kcal/mol) to avoid forming kinetically-trapped structures. The confinement lengthscale in the reported results corresponds to the harmonic minima in the applied restraints. The effect of lateral registry, or slip, between the π -stacked chains was also investigated by performing simulations with restraints between subsequent pairs of flexible dihedrals (Fig. S7B). In all confined simulations the dihedral statistics of the central (confined) chain were calculated and reported. In the main text, the confined simulations correspond to restraints of 3 Å in the π - π separation with full lateral registry between the chains. We observe qualitatively identical behavior for the slipped simulations.

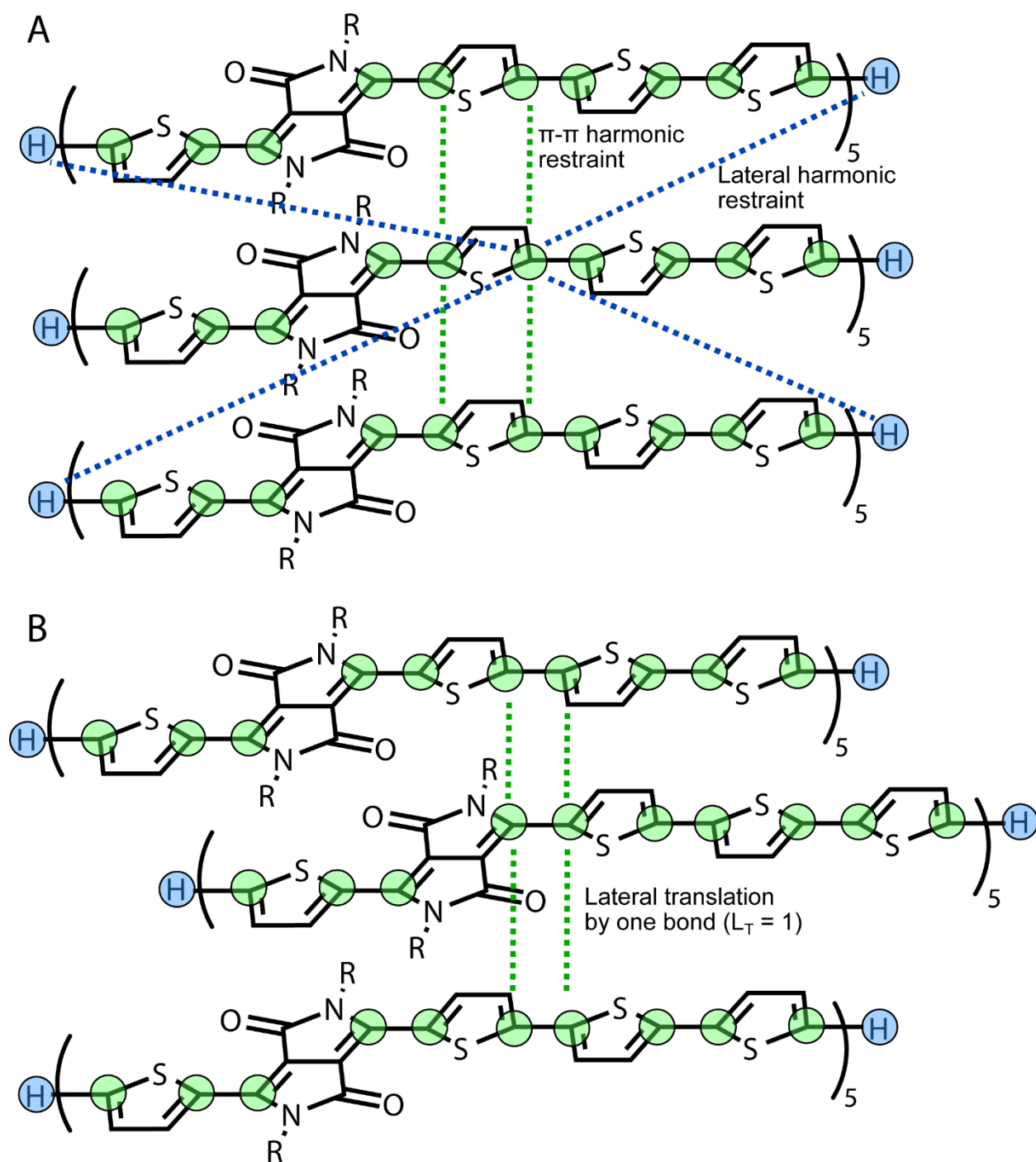


Fig. S7. Description of the restraints used to confine polymers during the MD simulations. **A**, Atoms show in green correspond to the 1-2 atoms in flexible dihedrals. Harmonic restraints were used between identical atoms on each chain to maintain a prescribed separation (green-dotted), while lateral restraints were used (blue-dotted) between the terminal hydrogens and the backbone atoms of the central chain to avoid slip. **B**, Definition of lateral translation unit (L_T) whereby the π - π constraints are shifted by L_T bond(s) to simulate slipped configurations.

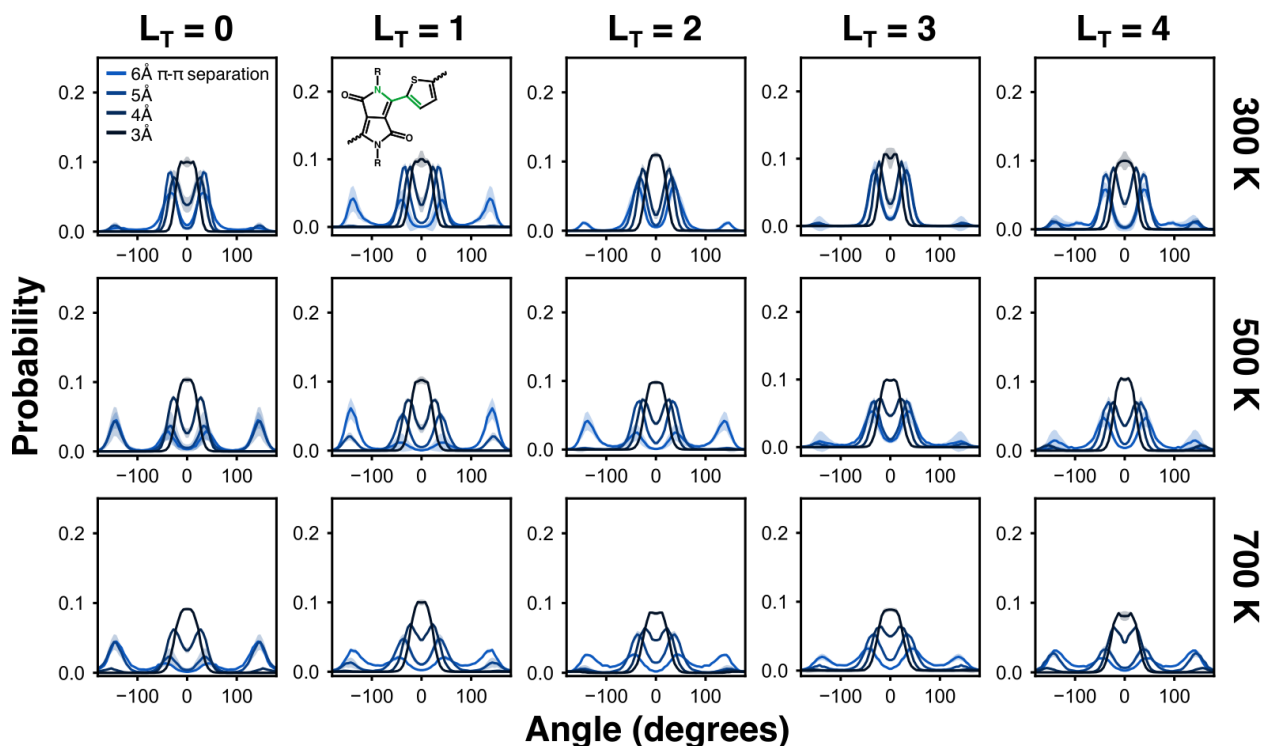


Fig. S8. A systematic investigation of the dihedral distributions for the CCCN dihedral in P1 (inset) under varying levels of confinement (color), temperature (row), and lateral displacement of the chains (column). The curves shown in the main text correspond to confinements of 3 Å and 5 Å with $L_t = 0$, respectively.

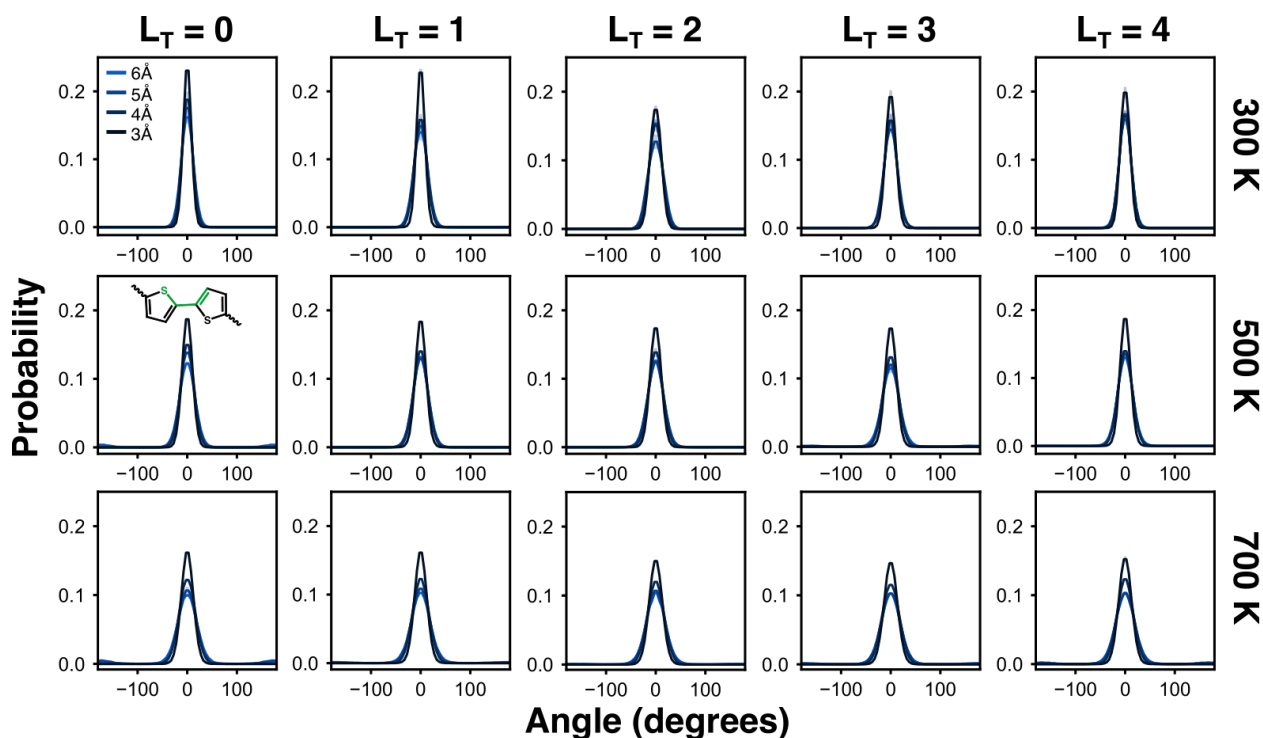
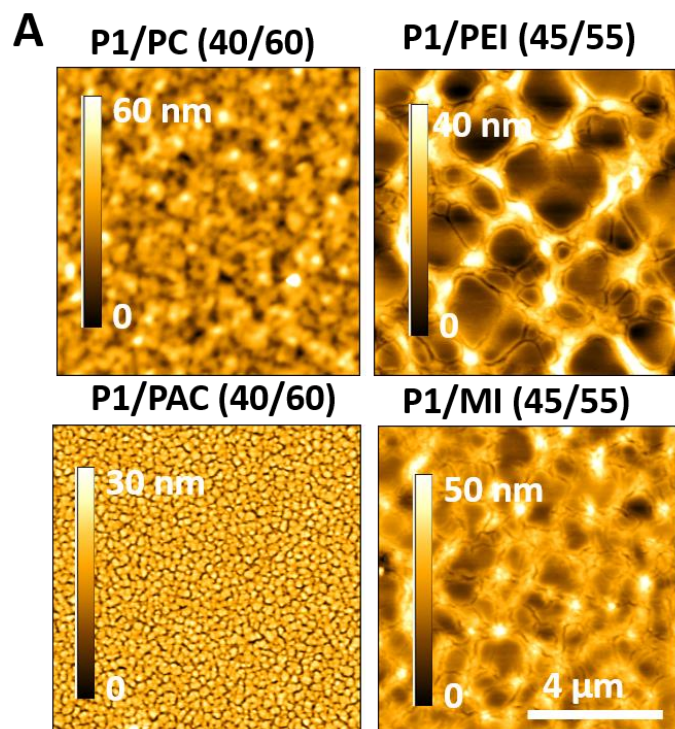


Fig. S9. A systematic investigation of the dihedral distributions for the SCCC dihedral in P1 (inset) under varying levels of confinement (color), temperature (row), and lateral displacement of the chains (column). The curves shown in the main text correspond to confinements of 3Å and 5Å with $L_t = 0$, respectively.

Blending scope



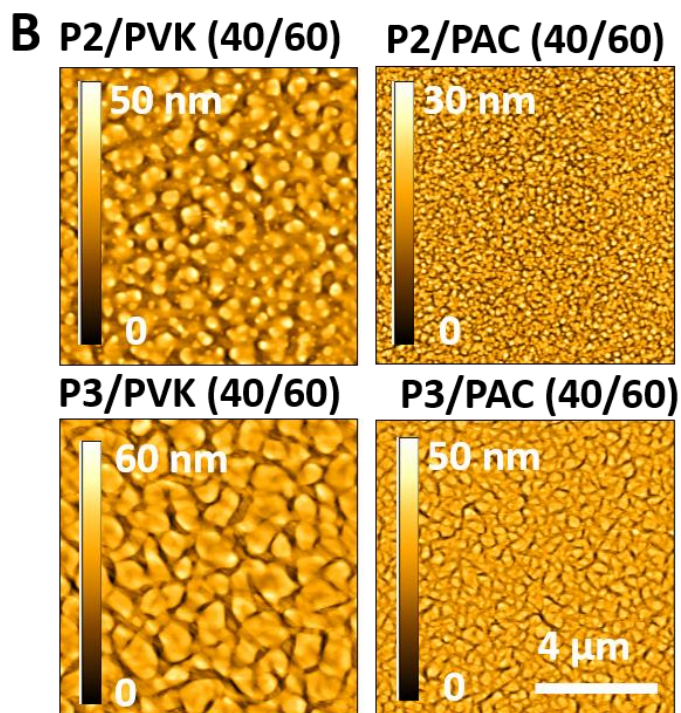


Fig. S10. AFM height images of blend films based on **A**, P1 and the optimized blend contents of four different insulating hosts studied for thermal stability; **B**, P2 and P3 blend films with the champion hosts.

Temperature-dependent UV-Vis absorption spectra

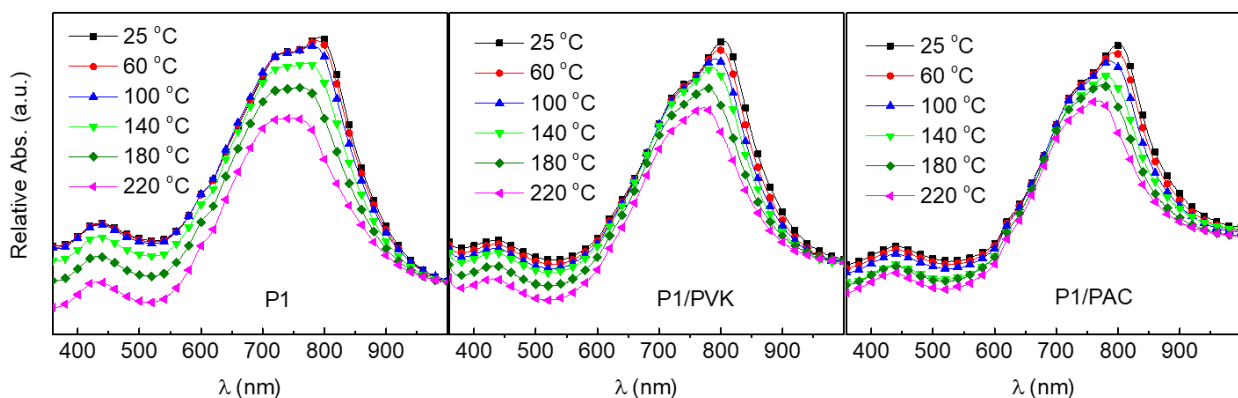


Fig. S11. Temperature-dependent UV-Vis absorption spectra of P1 films compared to P1/PVK and P1/PAC blends. The *0-0* vibronic peak intensity is significantly increased upon blending and can be retained even when the samples are heated to 220 °C. This shows that in the blends, the conjugated polymer chains can remain tightly packed even at elevated temperatures.

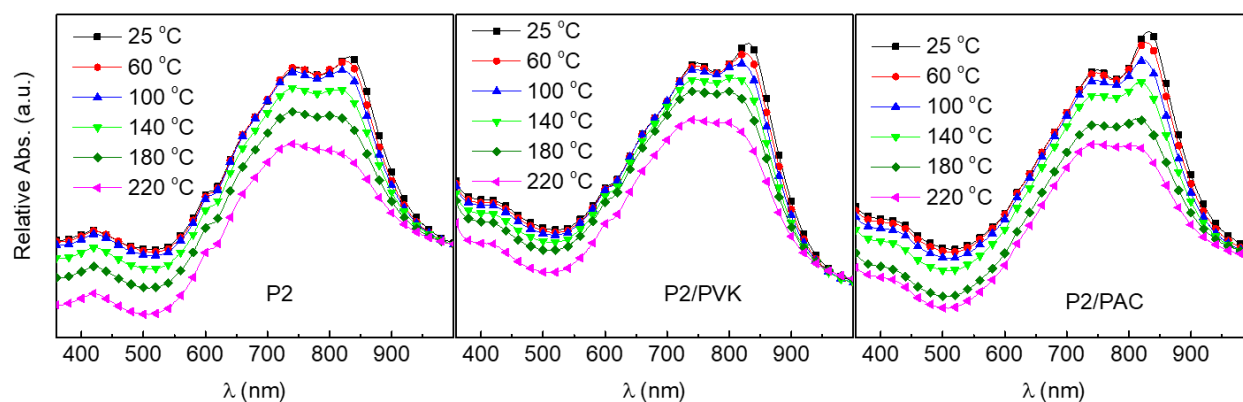


Fig. S12. Temperature-dependent UV-Vis absorption spectra of P2 films as well as its blend films in the studied champion matrices. Beyond 100 °C, the *0-0* vibronic peak starts to decrease in intensity for both pure P1 films and the PVK blend films. The PAC blend films could maintain a much higher *0-0* vibronic peak intensity indicative of retained intermolecular interactions even at temperatures as high as 220 °C.

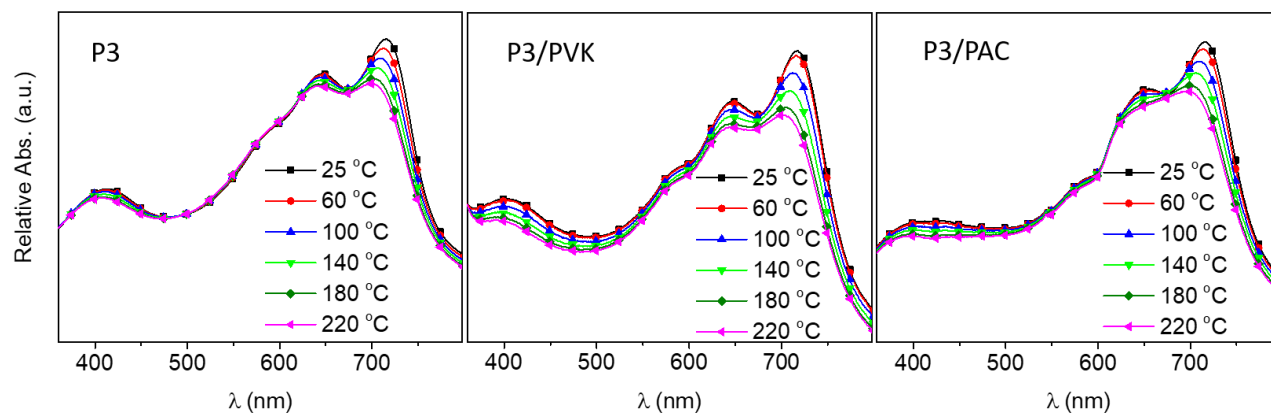


Fig. S13. Temperature-dependent UV-Vis absorption spectra of P3 films and its blend films during the heating cycle. The *0-0* vibronic remains persistent at the studied temperatures in all cases.

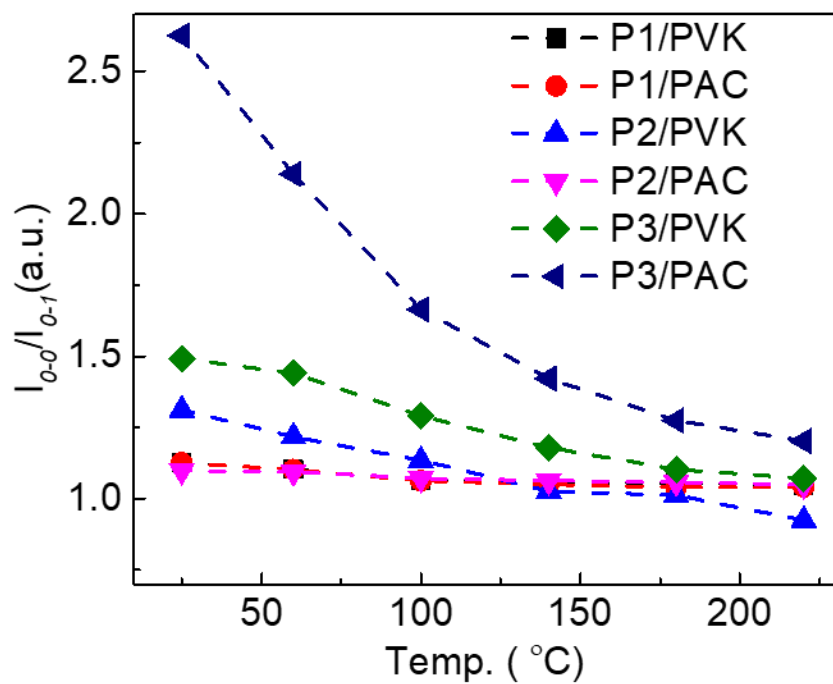


Fig. S14. Extracted ratios between the $0-0$ and $0-1$ vibronic peaks from the UV-Vis absorption spectra of the representative studied blend films at different temperatures. The blend films with thermally-stable electronic properties show the I_{0-0}/I_{0-1} higher than 1 at all temperatures indicative of retained ordering and π - π interactions upon heating.

Characteristic transfer curves

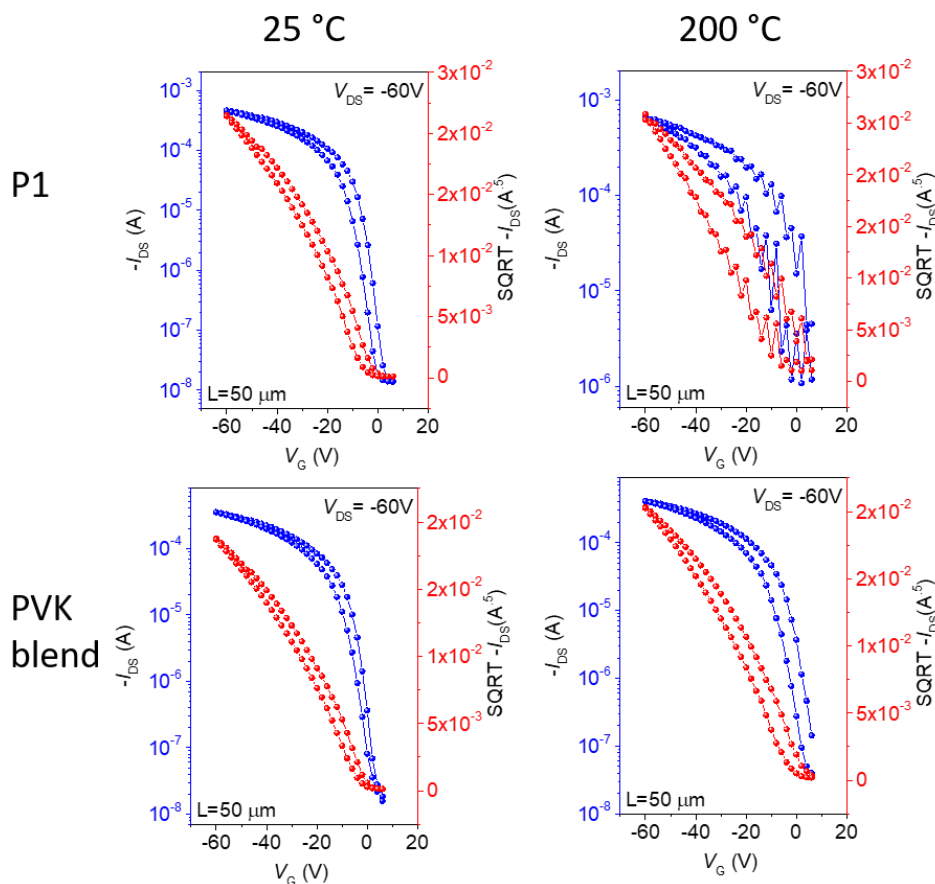


Fig. S15. Hysteresis analysis on OFET devices under thermal stress in open air. The forward and backward sweep of the transfer measurements (where the gate voltage is swept from positive to negative for the forward scan and subsequently swept negative to positive for the backward scan) is used as one indication of how thermal stress affects the OFET device performance. Upon heating, the devices based on pure P1 lose their original transfer characteristics, especially as seen from the shift in threshold voltage. In contrast, little to no change could be seen for the counterparts based on PVK blends.

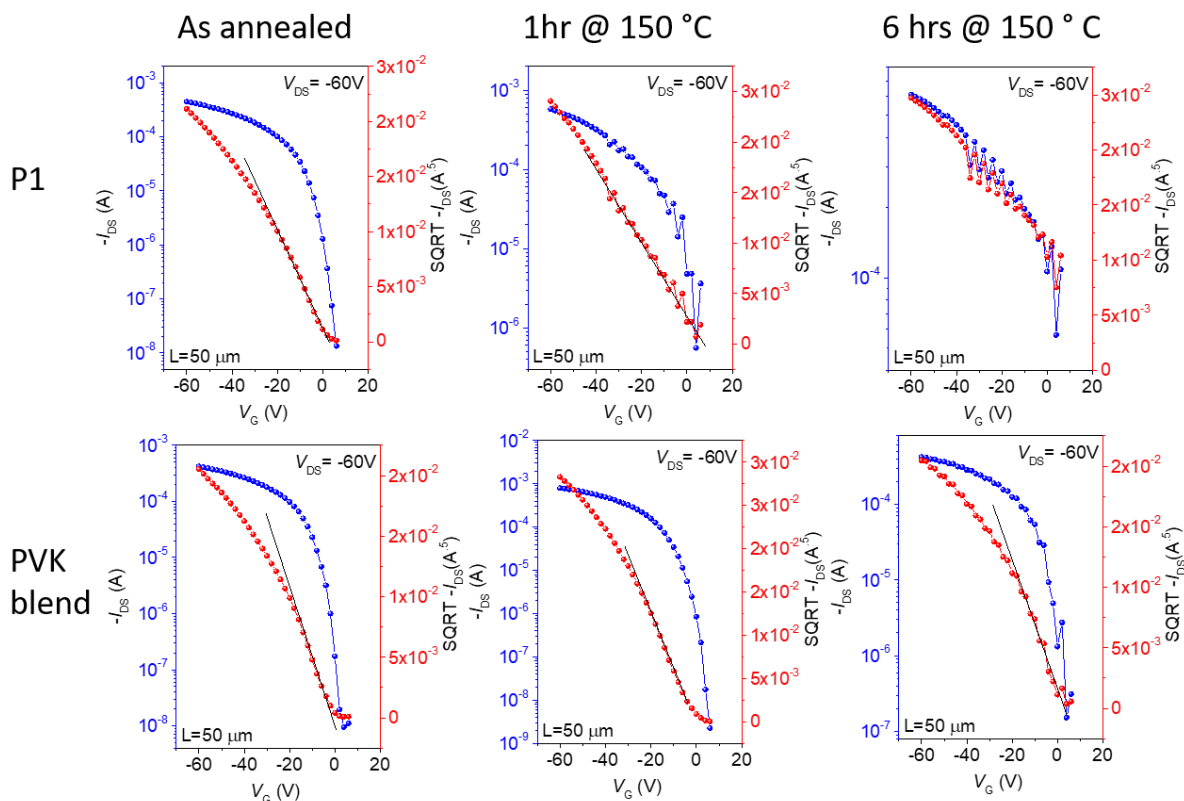
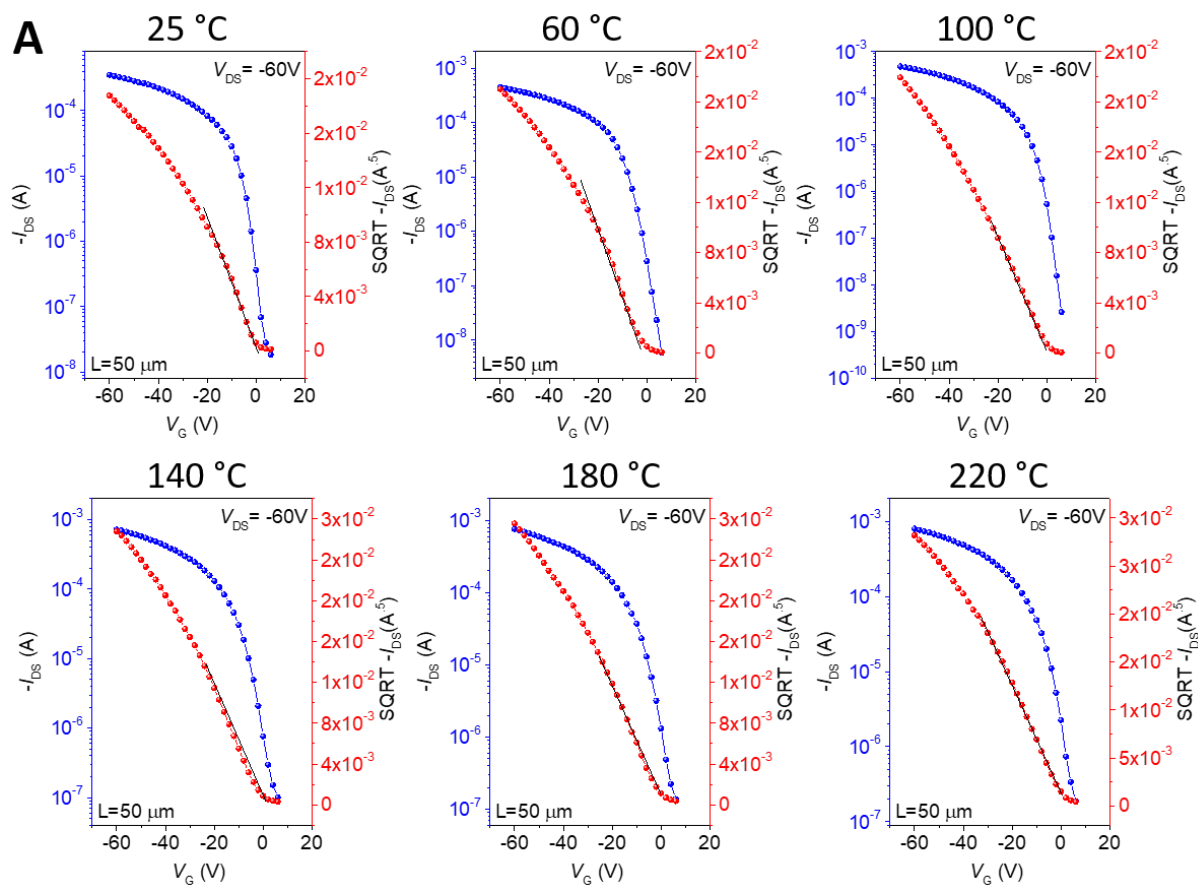


Fig. S16. Effect of constant thermal stress on OFET device performance. Characteristic transfer curves of OFET devices based on both pure P1 and its PVK blend when heated at 150 °C in open air. After six hours of heating, P1-based devices become thermally unstable and lose their semiconducting abilities.



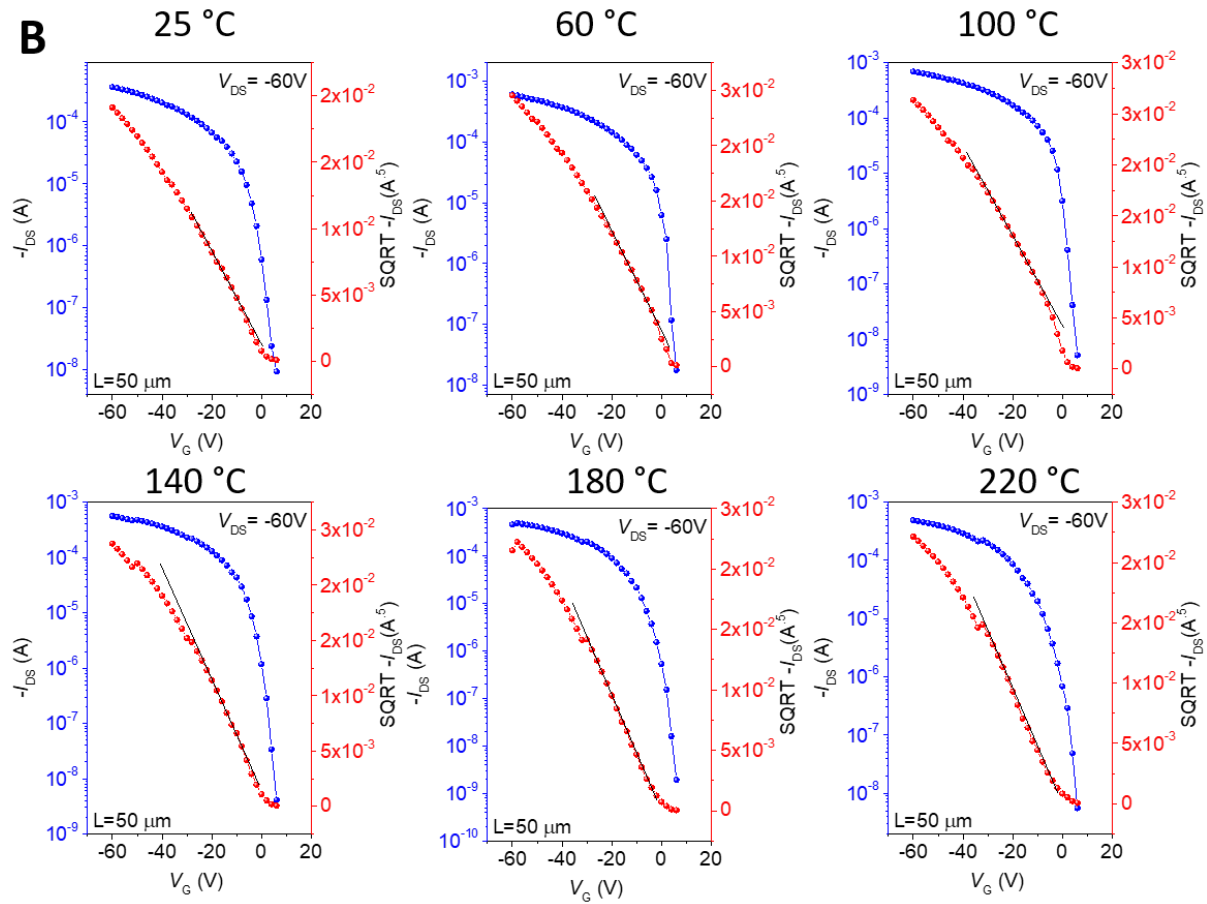
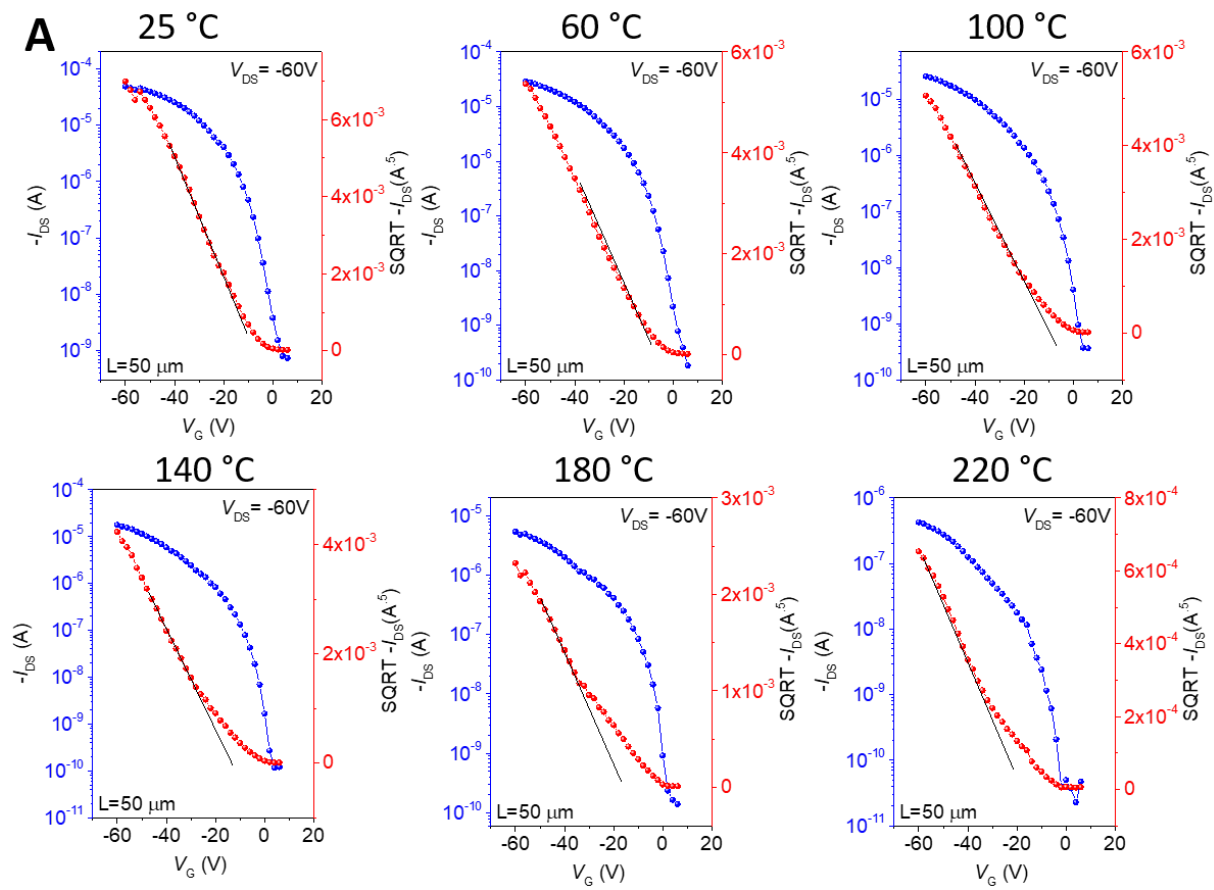


Fig. S17. Characteristic transfer curves of OFET devices fabricated from **A**, P1/PVK and **B**, P1/PAC. With increasing temperature, the blend devices are able to retain the original characteristics.



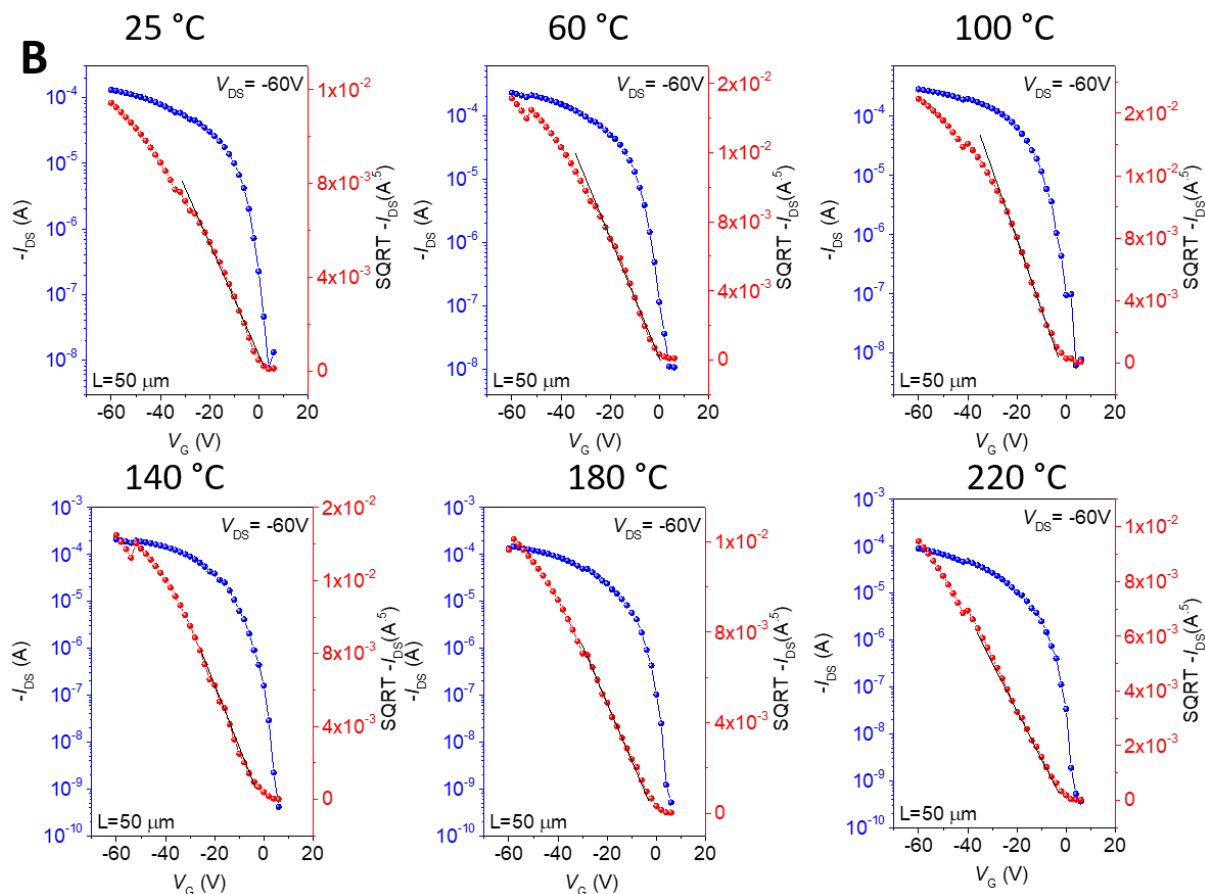
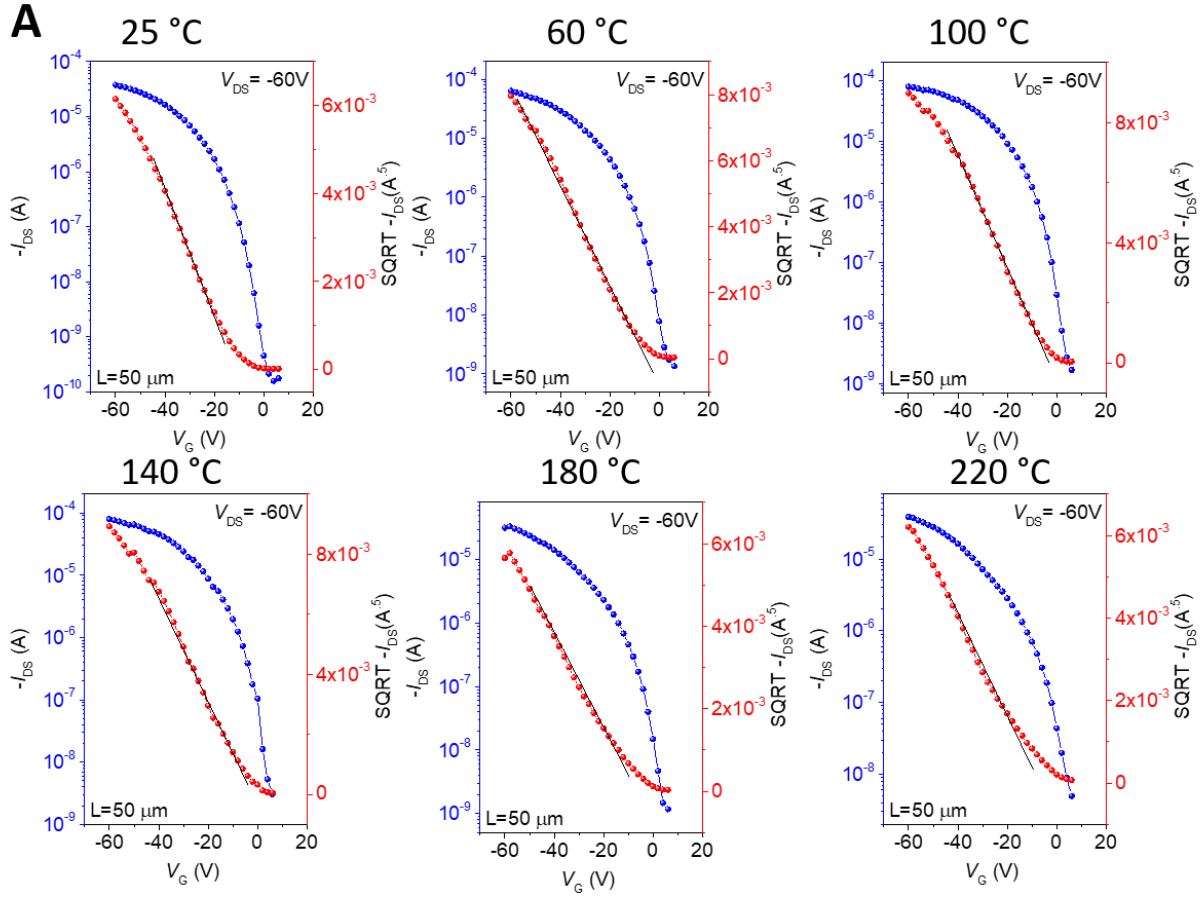


Fig. S18. Characteristic transfer curves of OFET devices fabricated from **A**, P2/PVK and **B**, P2/PAC blends. With increasing temperature, the PVK blend devices start to lose the original characteristics while the PAC blends can retain excellent semiconducting curves. The original slopes (black lines) are inserted in all cases to highlight the shift in the threshold voltage with increasing temperature specifically in the case of P2/PVK blends.



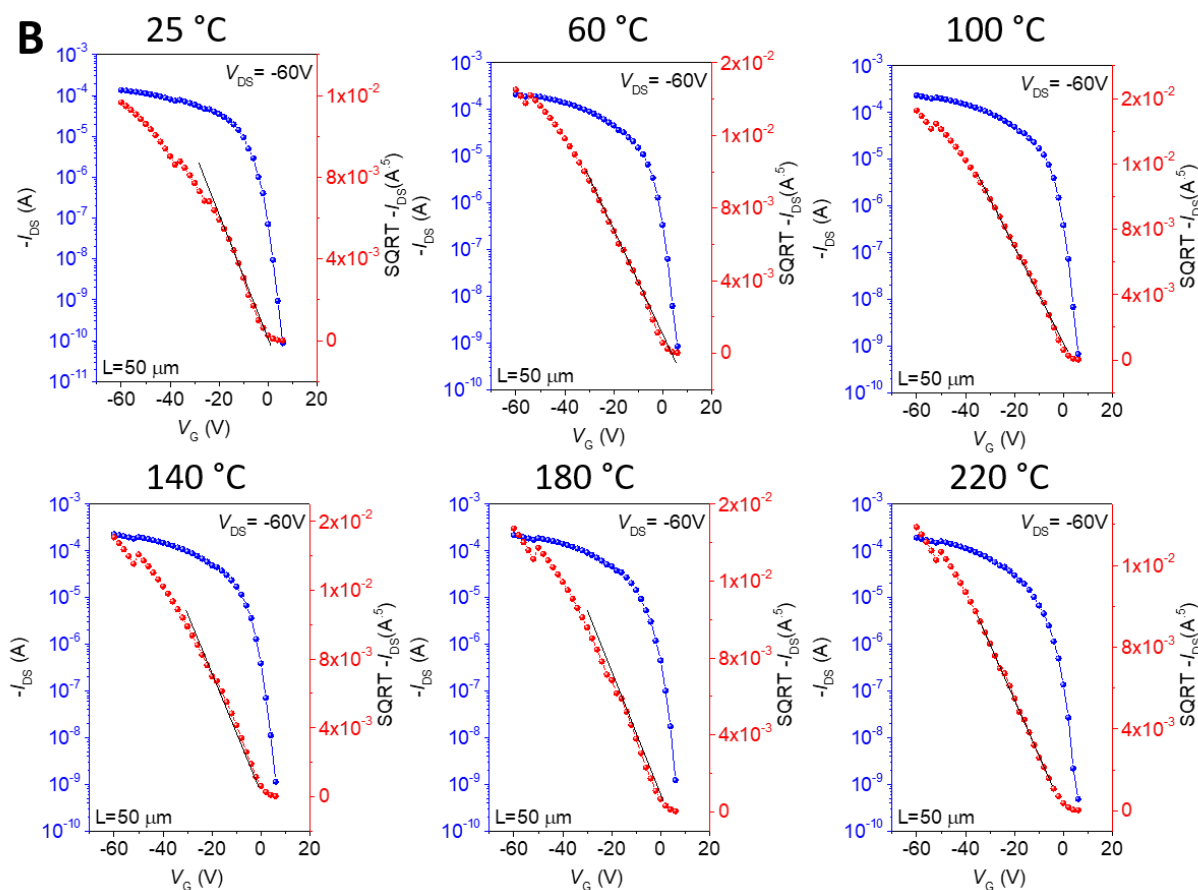
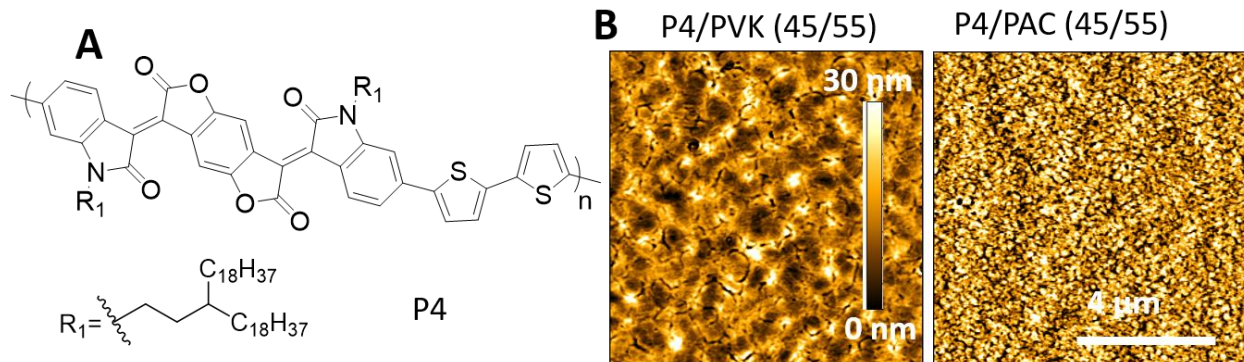
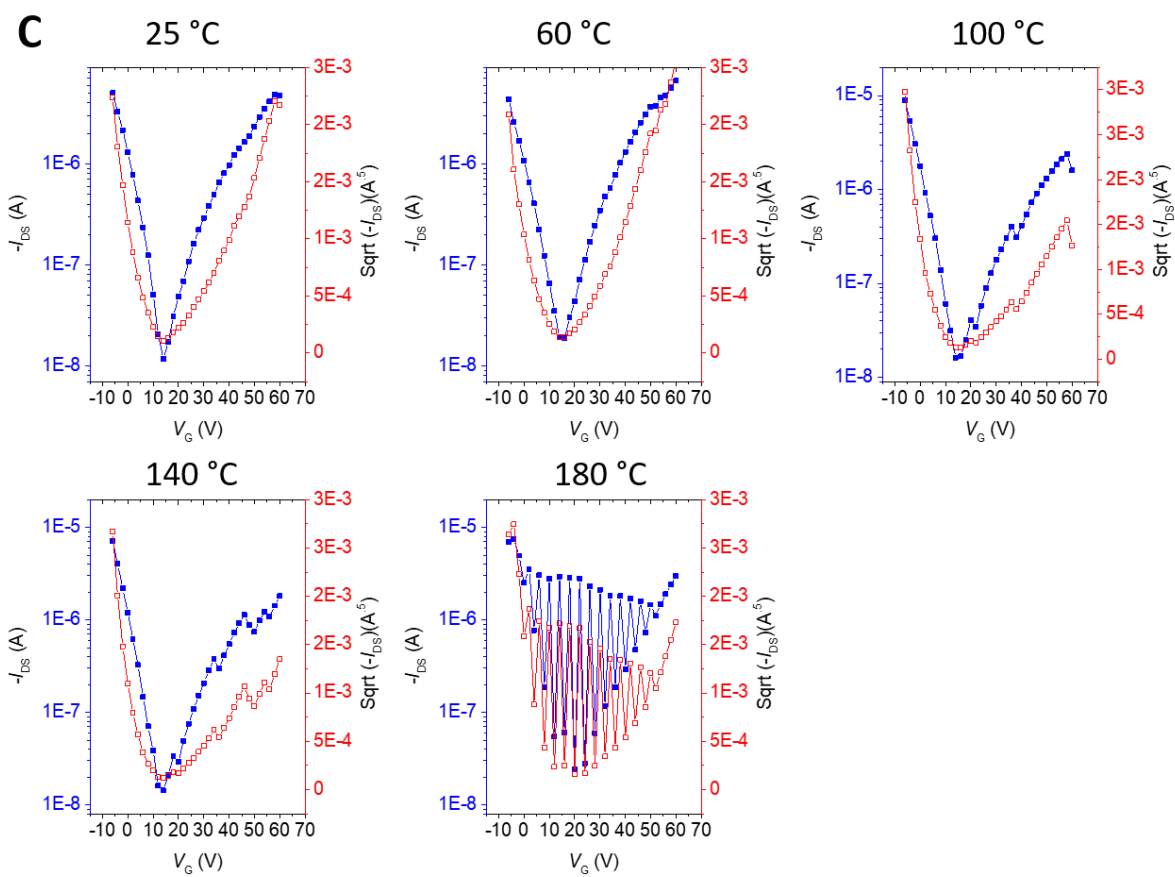
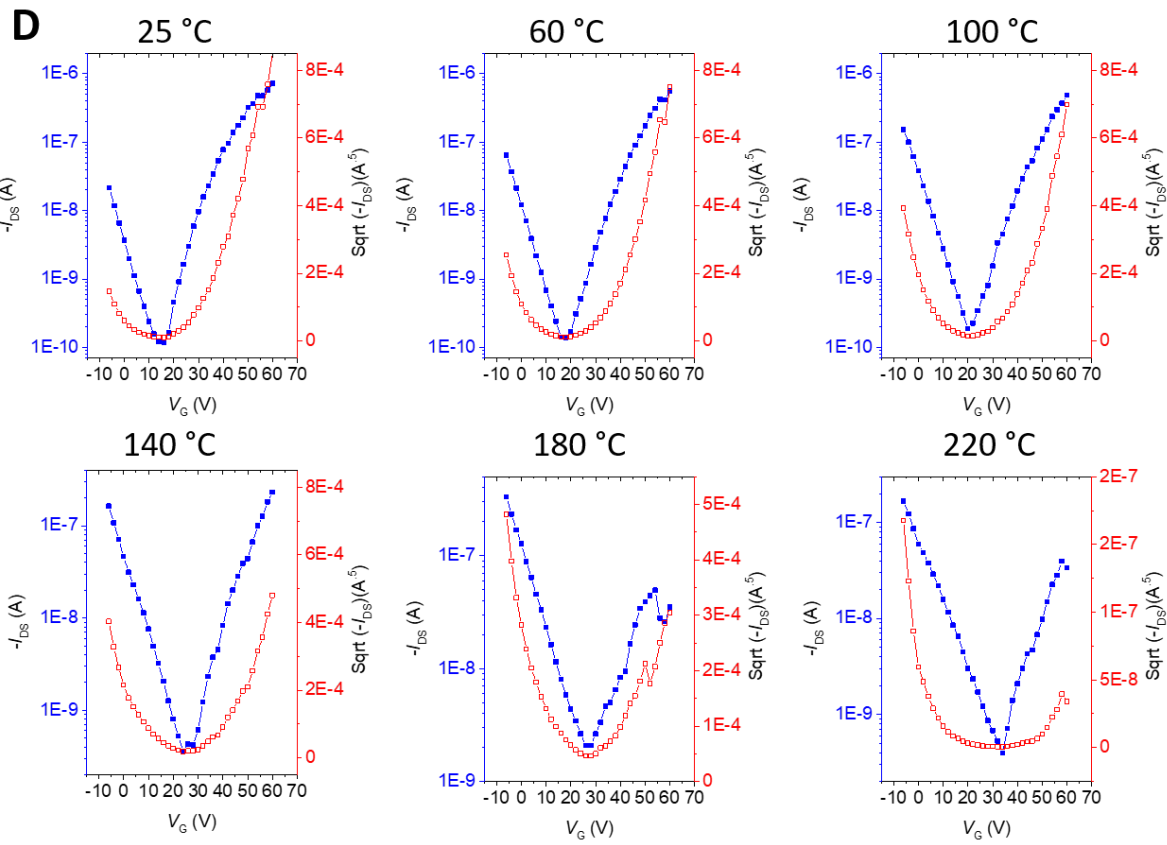


Fig. S19. Characteristic transfer curves of OFET devices fabricated from **A**, P3/PVK and **B**, P3/PAC. With increasing temperature, the blend devices are able to retain the original characteristics.

OFETs Characterization for N-type Semiconducting Blends

To further test the generality of the blending design, we select a previously reported air-stable electron transporting semiconducting polymer, P4 (33) (Figure S20A), and we process its blends with both PVK and PAC. The film morphology analysis reveals that P4 forms a bi-continuous morphology within the high-T_g matrices, with a more pronounced interpenetration in the case of PAC than PVK (Fig. S20B). We then fabricated FET devices analogous to the p-type blends and probed the thermal stability of the blends compared to pristine P4 in open air. The blend films show improved device stability up to 220 °C while to the pristine P4 films show to lose their electronic properties when heated beyond 140 °C.





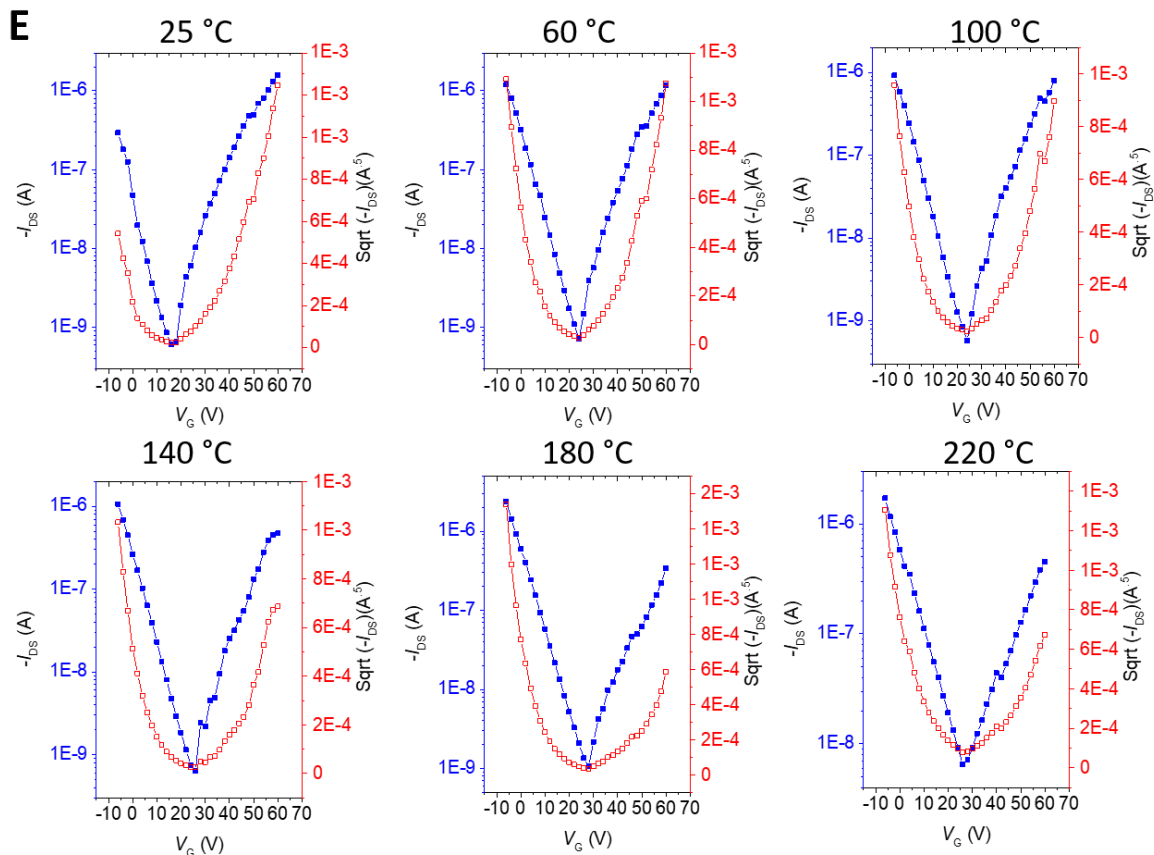


Fig. S20. A, Molecular structure of the n-type semiconducting polymer tested for thermal stability. **B,** AFM height images of blend films of P4 and the studied matrices. **C, D, E,** Characteristic transfer curves of OFET devices fabricated pristine films of P4, PVK blends, and PAC blends, respectively.

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