Supporting Information

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Mechanical Properties of Organic Electronic Polymers on the Nanoscale

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SI Section 1: Calibration of PeakForce quantitative nanomechanical mapping using a PDMS reference sample

Before beginning a measurement of the nanomechanical properties of the three organic polymers studied in this work, we carried out a tip calibration and a reference measurement of a standard PDMS reference sample at Bruker UK. Results of this reference calibration are shown in Figure S1.

**Figure S1** (a) Topography, (b) Modulus, (c) Adhesion, and (d) Deformation together with quoted average values of each of the measured quantities. The average value is measured across the surface maps that contain 512 x 512 data points.

PDMS is a soft organic polymer commonly used to create molds for application in microfluidics. Its average modulus value is typically around 3 MPa but is known to show an aging effect that increases the average modulus to around 6 MPa (measured in this calibration routine). The material’s softness is also shown through much higher levels of adhesion and deformation compared to the other organic polymer materials with moduli in the GPa range studied in the main text. Once the PeakForce quantitative nanomechanical mapping measurement kit was used to validate the modulus of PDMS, we used the same calibration to carry out PeakForce quantitative nanomechanical mapping measurements on the semicrystalline, near-amorphous and amorphous organic polymers shown in the main text. These organic polymers are considered soft enough for measurements to be made with the chosen cantilever tip without the introduction of any measurement related errors.


SI Section 2: Deposition protocols of the organic polymers

Substrate cleaning

1. Si/SiO$_2$ substrates were diced using a Karl Suss automatic diamond scriber tool in the Microelectronics Research Center (MRC) Cambridge. The tool cut a few substrates to 10 mm x 10 mm, and some slightly smaller.
2. Several diced Si/SiO$_2$ substrates (700 µm thick Si with 300 nm SiO$_2$) of the size 10 mm x 10 mm were cleaned in Decon 90/Water (a cap full of Decon 90 in a beaker of DI Water) for 10 mins in an ultrasonicator at room temperature.
3. The next step was to clean the substrates for 10 mins in DI water alone in the sonicator.
4. This was followed by 10 mins in acetone in the sonicator.
5. The final subsequent cleaning step was to sonicate the substrates in IPA for 10 mins.
6. The substrates were blow-dried in nitrogen.
7. The substrates were placed in a TEGAL plasma asher and plasma-ashed for 10 minutes at 300 W to clean the substrate of any residues.
8. Plasma ashed substrates were stored in a DB12 box in the cleanroom in the MRC for a few days.
9. Just before the actual deposition of the organic polymer films, the substrates were cleaned again in acetone and IPA for 10 minutes each. They were plasma-ashed for 10 mins at 300 Watts just prior, and less than 30 minutes before the actual deposition of the films in the MBraun glovebox.

Deposition of organic polymer films in a nitrogen MBraun glovebox

1. Deposition of PBTTT films.
   a. PBTTT solution (10mg/ml DCB) was placed on a hotplate at 80° Celsius for two hours until its colour changed from dark turbid purple to fluid transparent purple.
   b. Glass pipettes were placed on the hot plate for about 30 minutes prior to spin coating the solution.
   c. The PBTTT solution was spin coated onto freshly cleaned oxygen plasma treated Si/SiO$_2$ from hot solution at 1000 rpm with a ramp of 3 seconds and for 60 seconds in total. Glass pipettes were used.
   d. The samples were then placed on a hot plate directly at 180° Celsius where the film formation was completed.
   e. The films were annealed at 180° Celsius, 10 minutes after which the hotplate was turned off, and the samples were let to cool slowly.
   f. Once the hotplate reached a temperature below 100° Celsius, the samples were removed and left on a cold metallic surface to quench.
   g. The samples were then placed in a DB12 box and prepared for shipping on the same day they were fabricated.
   h. The sample thickness was around 50 nm.

2. Deposition of Cytop films
   a. Cytop solution (3:1 Cytop:CT Solvent) was removed from the fridge and left to warm up to room temperature.
   b. Inside the glovebox, the solution was then spin onto the clean Si/SiO$_2$ substrates first for 3 seconds at 500 rpm and then for 20 seconds at 2000 rpm.
c. The samples were placed on a hotplate at 90° Celsius for 20 minutes to cure the Cytop films.
d. The samples were then removed from the glovebox and prepared for shipping.
e. The sample thickness was around 500 nm.

3. Deposition of IDTBT films
   a. We fabricated the IDTBT Pristine 10 g/l (75% 1,2-dichlorobenzene – 25% chloroform) solution using the following protocol:
      i. We weighed roughly 2 mg of IDTBT powder (Mn 69 kg/mol, Mw 116 kg/mol, PDI 1.68) in air.
      ii. We purged the glovebox during the entire procedure.
      iii. We pre-heated the hot plates for 20 minutes.
      iv. We used separate glass syringes and stainless-steel needles for the two solvents.
      v. The glass syringes and steel needles were cleaned using the following protocol:
         1. The steel needle was attached to the syringe.
         2. The plunger was removed and rinsed with acetone.
         3. The syringe body was filled with the acetone and the plunger pushed the acetone through the syringe and needle into the waste beaker.
         4. The above process was repeated for IPA.
         5. The syringes and needles were blow dried with the N2 gun.
         6. The syringes were plasma treated at 300 Watts for 10 minutes.
   b. Once the IDTBT was completely dissolved in the solution, 17 μL of solution was sufficient for a 1 cm x 1 cm substrate. The solution was fluid enough to coat the entire substrate.
   c. The IDTBT was spin coated at 1500 rpm for 60 seconds, again using an initial ramp of 3s in the glovebox.
   d. Three samples were annealed for 1 hour at 100° C, while purging the glovebox.
   e. The samples were removed from the hotplate and stored in a DB12 box.

The samples were shipped in air or in nitrogen to the laboratories where they were to be measured, and all measurements were completed within a week to eight weeks from the date of fabrication. Multiple such samples were fabricated over several months to cross validate the measurements.
SI Section 3: Nanomechanical characterisation of Cytop-M

Topography and modulus of the amorphous polymer Cytop-M showing a very smooth topographical map but greater structure in the modulus map and in its line scan along the white dotted line (Figure S2). The width of the modulus histogram is larger than that for C16-IDTBT, but smaller than that of C14-PBTBT. It should be re-iterated here that this Cytop-M sample was nearly ten times as thick as the C14-PBTBT and C16-IDTBT films investigated in greater detail in the main manuscript. This thickness however should not impact the comparison we draw in the manuscript since the surface deformation during modulus measurements is very low and on the order of a couple of nanometres at most.

Figure S2 (a), (b), (c) and (d) are the topography, modulus, modulus line scan along the dotted white line, and modulus histogram over 1 µm x 1 µm, in Cytop-M respectively.
SI Section 4: Reconfirmation of high homogeneity in the nanoscale modulus of C16-IDTBT thin films through additional measurements

In the main manuscript we demonstrated how C16-IDTBT is a near-amorphous organic semiconductor that shows high spatial homogeneity in its nanomechanical modulus. To show that this measurement is not a one-off, we show below another measurement of the topography, modulus, modulus line scan, and modulus histogram on a different region of the fabricated C16-IDTBT thin film having an area of 5 µm x 2.5 µm with 512 x 256 data points (Figure S3). This scan was done seven weeks after the fabrication of the film and upon storage in ambient air for this entire duration. The average modulus measured was 2.06 +/- 0.11 GPa. A systematic, time evolution study of potential ageing effects in C16-IDTBT goes beyond the scope of this manuscript and will be studied in a follow up work.

**Figure S3** (a), (b), (c) and (d) are the topography, modulus, modulus line scan along the dotted vertical white line, and modulus histogram over a 5 µm x 2.5 µm region, in C16-IDTBT respectively. This region of the film is different from the region shown in the main paper and was measured on a different day after recalibration.
SI Section 5: Doping C14-PBTTT to high carrier densities up to 1000 S/cm

C14-PBTTT (batch WZ-18/033, prepared by Prof Iain McCulloch’s research group) was dissolved in DCB (10 g/L) and dissolved at 120° Celsius, then cooled to 80° Celsius before use. Films were spun at 1500 rpm onto 90° Celsius preheated Si and Si/Au substrates using 90° Celsius preheated glass pipette tips. The samples were annealed at 180° Celsius for 20 mins after spin coating the polymer and allowed to cool slowly to room temperature.

Doping was performed using an ion exchange technique. Briefly, an anhydrous acetonitrile solution containing 100 mM BMP TFSI (Solvionic, 99.9%) and 1 mM FeCl₃ (Sigma-Aldrich, anhydrous) was pipetted onto the samples containing the polymer film, then spun off at 8000 rpm after a 100 second delay. While still spinning, the films were washed with 1 mL acetonitrile to remove any residual dopant solution. All preparation was performed in a nitrogen glovebox (<1 ppm H₂O, O₂). This recipe consistently gives high conductivities around 1000 S/cm. Samples were packed in nitrogen filled heat-sealed plastic bags for shipment.
SI Section 6: Evidence for charge carrier mobility enhancement (transistor device improvement) in the near-amorphous polymer IDTBT upon ambient air/oxygen exposure

Figure S4 shows the time evolution of the transfer characteristics of a C16-IDTBT based transistor with a Cytop-M dielectric showing significant improvement in device performance upon stabilisation of hole transport in ambient air/oxygen. In this device, the C16-IDTBT layer was patterned in an oxygen plasma asher during the processing of the transistor device. Despite any potential patterning process-induced degradation, the device heals over a month in ambient air to yield ideal transfer characteristics with high mobilities. Similar improvement in device characteristics is seen in C16-IDTBT devices that were not patterned in oxygen plasma.

In general, after device fabrication, the highest mobilities approaching 1 cm²/Vs in C16-IDTBT are observed only after a few days to a few weeks of curing the device in air. This was the reason we chose to probe the nanomechanical properties in C16-IDTBT several weeks after fabrication and after air-stabilisation to ensure that the state of the C16-IDTBT film is “trap-free”. The first documented evidence of this trap healing effect was shown earlier in the manuscript: M. Nikolka, I. Nasrallah et al., Nature Materials 16, 356–362 (2017).

**Figure S4** Time evolution of the charge current in a transistor made from C16-IDTBT, patterned using an oxygen plasma ashing process, and with a Cytop-M dielectric. The layers in the device had the same thicknesses as those probed in this manuscript. The channel length and width in this organic transistor was L = 50 μm and W = 1 mm, respectively. The thickness of the Cytop-M dielectric was 500 nm.
SI Section 7: Preliminary observation of modulus ageing effects in the semicrystalline polymer C14-PBTTT

Unlike C16-IDTBT, C14-PBTTT is known to be relatively less resilient to air exposure due to oxidative doping as shown in earlier work: Appl. Phys. Lett. 90, 123508 (2007); Adv. Funct. Mater. 25, 7038–7048 (2015); Adv. Mater. 21, 1091 (2009) and Nature Materials 5, 328-333 (2006).

We show here that the time evolution of the modulus in C14-PBTTT measured on two different films fabricated under the same conditions but probed seven weeks apart from each other, shows a slight difference (Figure S5). The origins of these aging effects go beyond the scope of the current manuscript and will be investigated in greater depth in a follow-on work.

![Modulus comparison](image)

**Figure S5** (a) Modulus of a C14-PBTTT film measured one week after fabrication having been stored in air since fabrication, (b) Modulus of a second C14-PBTTT film measured on the same equipment, under the same measurement conditions, seven weeks after fabrication having been stored in air for the entire duration. During storage in air, the samples were covered to mitigate any light induced modification to the films.
SI Section 8: Reconfirmation of the measured modulus in pristine C14-PBTSS through additional measurements at KTH Stockholm

Additional AFM measurements were carried out to verify the evaluated topography, elastic modulus, deformation, and adhesion parameters of pristine C14-PBTSS films. The nanomechanical measurements were carried out on areas of 5 µm x 5 µm, 1 µm x 1 µm and 0.3 µm x 0.3 µm for a new/freshly prepared C14-PBTSS sample, different from the ones we measured for the main paper. The measurements were conducted roughly 14-16 days after fabrication during which time it was stored in air. The topography, elastic modulus, adhesion, and deformation maps are shown below in Figure S6. In addition to using Gwydion’s Align Rows feature, the Plane Level feature was used on the topography only to remove image tilt and to enhance the images in this batch of measurements. Modulus, adhesion, and deformation channels show raw data. Similar local variations in topographical and elastic modulus maps, as reported in Figure 2 and Figure 3 of the main paper are observed as shown in Figure S6. Moreover, a higher-resolution image of 0.3 µm x 0.3 µm demonstrates single crystalline edges and clear variations in higher and lower elasticity at the single domain level.

The evaluated elastic moduli parameters are very similar to those reported in the main text, considering the error bars, and are 2.86 GPa ± 0.7 GPa for 5 µm x 5 µm area, 3.3 GPa ± 0.9 GPa for 1 µm x 1 µm area and 3.7 ± 1 GPa for 0.3 µm x 0.3 µm area. All evaluated parameters, such as RMS roughness, elastic moduli, adhesion, and deformation are summarized in Table S1 below. The deformation is a little higher in these measurements compared to those in the main text.
| Polymer PBTTT | RMS Roughness (nm) | DMT Modulus (GPa) | Adhesion (nN) | Deformation (nm) |
|---------------|-------------------|------------------|---------------|-----------------|
| 5 µm x 5 µm   | 3.33              | 2.86 ± 0.70      | 25.2 ± 3.70   | 2.20 ± 0.39     |
| 1 µm x 1 µm   | 3.00              | 3.3 ± 0.90       | 24.8 ± 4.20   | 2.30 ± 0.45     |
| 0.3 µm x 0.3 µm | 2.00           | 3.7 ± 1.00       | 14.0 ± 4.20   | 2.20 ± 0.50     |

**Table S1** Average values of roughness, modulus, adhesion and deformation in the organic polymer C14-PBTTT at different resolutions.
SI Section 9: Nanoindenter-based Scanning Probe Microscopy (SPM) mapping of semicrystalline C14-PBTTT

Despite the different instrumentation capabilities and the different nanomechanical regimes probed by the Nanoindenter and by the AFM, high-resolution scanning probe microscopy (SPM) mapping of the pristine C14-PBTTT polymer surface and of the doped C14-PBTTT polymer surface made using the nanoindenter shows remarkable agreement with the topography measured using the AFM. Figure S7 (a) and (b) show SPM maps taken over a 5 μm x 5 μm area in pristine C14-PBTTT and in doped C14-PBTTT, respectively. The AFM topography equivalent of the SPM image shown in Figure S7 (a) is the AFM scan of Figure 2 (a) in the main paper. The RMS roughness in these two films were measured to be 2.8 nm and 3.8 nm, respectively. These measured values of the RMS film roughness from nanoindentation compare favourably with those measured using the AFM which were 3.2 nm and 4.2 nm, respectively.

The imaging measurements were done in contact mode using Bruker’s MEMS-based xProbe transducer with an imaging set point of 30 nN. The xProbe transducer was originally designed to probe ultra-thin and ultra-soft films. With a 2 nN noise floor and high strain rate indentation down to 8 ms, it can apply AFM equivalent loads and displacements with direct and quantitative measurements. A cube corner tip was used, and the scan rate varied between 0.1 Hz and 1 Hz.

Figure S7 Nanoscale Scanning Probe Microscopy (SPM) over a 5 μm x 5 μm area in (a) pristine C14-PBTTT and (b) doped C14-PBTTT, measured using Bruker’s xProbe MEMS-based transducer mounted on a TI 980 Triboindenter.