SUPPORTING INFORMATION

Physical Supercritical Fluid Deposition: Patterning Solution Processable Materials on Curved and Flexible Surfaces

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1. Gravimetric Analysis of PBTNT-C\textsubscript{14} Saturated Solutions

The concentration of PBTNT-C\textsubscript{14} in pentane was measured using volatilization gravimetry at 7.0 MPa for several different temperatures and compared with in situ UV-vis measurements. The results are presented in Figure S1. In more detail, a crucible containing PBTNT-C\textsubscript{14} was placed at the bottom of the custom pressure cell (described in the main text). The cell was overfilled with deoxygenated pentane before being sealed and pressurized. Before heating, a reference UV-vis absorption spectrum was collected at room temperature. PBTNT-C\textsubscript{14} appears to be negligibly soluble under these conditions. The temperature of the cell was then set using cartridge heaters arranged around the corners of the cell and the pressure was set via a manual pressure generator. The system was allowed to equilibrate for 30 minutes before a UV-vis spectrum was collected through sapphire windows on the pressure cell. Spectra were integrated as described in the results and discussion section of the manuscript; the results are displayed in Figure S1. To perform the gravimetric analysis, the contents of the cell were collected by opening a valve and exhausting the solution into a collection vessel open to atmospheric pressure. The rapid expansion cooled the solution enough to allow it to be collected as a liquid. Pentane was evaporated and the mass of PBTNT-C\textsubscript{14} was determined. The concentration of the solution was estimated using the volume of our pressure cell.

![Figure S1](image)

**Figure S1.** Total integrated absorbance (Left Axis, a.u.) and concentration (Right Axis, mg/ml) as a function of temperature at 7.0 MPa.

Figure S1 demonstrates the qualitative correspondence between the concentration as measured spectroscopically and the solution concentration as determined gravimetrically. Of primary importance is the peak in solubility as a function of temperature. This solubility curve allows us to collect material onto a heated substrate by precipitation from a supercritical fluid. The use of pressures above the critical pressure is important for the technique. As a side note, we were largely unsuccessful at forming PBTNT-C\textsubscript{14} films using lower pressures. When lower pressures were used, pentane began to boil at the substrate surface forming films that appeared thin and inhomogeneous.
2. Optical Images of PBTTT-C_{14} Films

Figure S2 illustrates PBTTT-C_{14} films grown onto an ITO substrate with holding T_{wall} \approx 130 \degree C and T_{sub} \approx 160 \degree C for 90 minutes. The thickness of the films is estimated on the basis of ex situ UV-vis absorption measurements. Results are as follows: 11.0 nm for 7.0 MPa, 42.8 nm for 10.4 MPa, 452.5 nm for 17.2 MPa, and 30.0 nm for spin-coated film. The thicker films were visibly darker. The brightness of the images was adjusted in this figure to allow film uniformity and microscale morphology to be examined.

![Optical Images of PBTTT-C_{14} Films](image)

**Figure S2.** Optical microscope images of PBTTT-C_{14} films grown under several pressure conditions (100× magnification).
3. Chemical Characterization of PBTTT-C14 Using Raman Spectroscopy

Raman spectra were collected using a Reinshaw inVia Raman microscope (50× objective) with an excitation wavelength of (785 nm/50 mW) and acquisition time of 10 seconds. The laser power was set to 1% of its maximum power for as-received PBTTT-C14 and 50% for the PBTTT-C14 thin film grown in the supercritical fluid chamber at a pressure of 17.2 MPa. All spectra were background corrected, including a removal of signals from ITO in the case of the film deposited from supercritical fluids. Spectra were normalized to the peak intensity at 1390 cm$^{-1}$.

![Figure S3. Raman spectra of PBTTT-C14 as received from the supplier and PBTTT-C14 thin film deposited on ITO coated glass after 90 minutes deposition at 17.2 MPa.](image)

As illustrated in Figure S3, both collected Raman spectra share common features associated with the diagnostic peaks in the range of 1300-1600 cm$^{-1}$. The thienothiophene core and thiophene rings are known to possess three main modes. According to previous reports, the C-C intra-ring stretching peak position is located at 1380 cm$^{-1}$, the symmetric C=C stretching peak position is at 1445 cm$^{-1}$, and the and C=C/C-C stretching is at ~1488 cm$^{-1}$. These modes are known to be sensitive to π-electron delocalization (conjugation length) in polythiophene.$^1$

For both materials, we observed three main peaks, which are consistent between the two samples. The appearance of our spectra corresponds well with previous reports.$^{1,2}$ We observe a strong peak at 1395 cm$^{-1}$ (labeled A), another at 1415 cm$^{-1}$ (labeled B) and the highest energy mode is observed at 1490 cm$^{-1}$ (labeled C). We interpret the consistency between the peak positions of the two samples to demonstrate that the material deposited under supercritical conditions remained chemically unchanged during the deposition process.

Differences in the peak intensities were observed. To better visualize these differences, the spectra were normalized to the strongest mode, 1390 cm$^{-1}$. The main difference is attributed to the intensity decrease of C=C/C-C stretching mode for PBTTT-C14 thin film at ~1488 cm$^{-1}$. As a result, the height ratio of mode $A$ to mode $C$ ($I_A / I_C$) is observed to increase which has been previously related to the conjugation length.$^{2,3}$
4. References

(1) Paternò, G. M.; Robbiano, V.; Fraser, K. J.; Frost, C.; García Sakai, V.; Cacialli, F. Neutron Radiation Tolerance of Two Benchmark Thiophene-based Conjugated Polymers: the Importance of Crystallinity for Organic Avionics. *Scientific reports* 2017, 7 (1), 41013.
