Supporting Information

Microfluidic supercritical antisolvent continuous processing and direct spray-coating of poly(3-hexylthiophene) nanoparticles for OFET devices

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Microreactor fabrication and set-up details

The microreactor was fabricated using standard silicon wafer micromachining techniques (photolithography followed by silicon wet etching), subsequently anodically bonded to a Schott Borofloat 33 wafer. The main channel has a trapezoidal shape with dimensions: top width: 350 µm, bottom width: 115 µm and depth: 165 µm and was functionalized with perfluorooctyltrichlorosilane using a Self-Assembly Monolayer (SAM) method described elsewhere[i] to reduce NPs interaction with the walls. The P3HT solution was injected through a fused silica capillary (156 µm O.D., 75 µm I.D.) inserted and further epoxy glued inside the microchannel creating a full 3-D coaxial injection. A heating element (DBK Enclosures, FG14745.4) contacts the bottom of the heated section of the device to control the temperature at 40 or 50°C, while pressure (8 or 10 MPa) is regulated with a back pressure regulator (Jasco, BP-2080) placed downstream the microreactor.
Figure S1-a shows the general packaged microsystem, while Figure S1-b displays a picture of the microreactor.

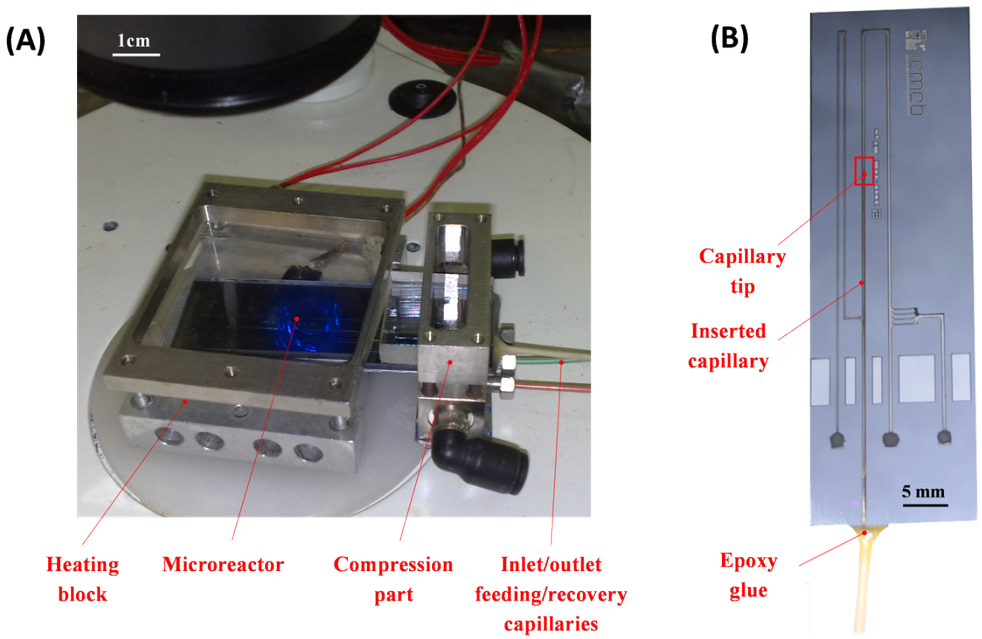

Figure S1: *(a) General set-up used in this study and (b) enlargement of the microreactor.*

XRD Analysis on P3HT film

The XRD patterns were recorded on a PANalytical X'Pert MPD powder diffractometer (θ–θ Bragg–Brentano geometry using Cu $K_{\alpha1,\alpha2}$ radiation (λ_1 = 1.54060 Å, λ_2 = 1.54441 Å), equipped with a secondary monochromator and a X'Celerator detector, in the range of 4–40°, in continuous scan mode at 3.5×10^{-3}°.s^{-1}.
The P3HT films were directly sprayed on a silicon substrate before being subjected to XRD.

P3HT SEM characterization

For SEM characterization, P3HT nanoparticles were directly sprayed into octane solvent to generate a colloidal solution. A drop of this latter was then deposited onto a copper-carbon grid before being analyzed with a JEOL 2000FX Scanning Electron Microscope (Figure S2).
A seen from the AFM characterization, the P3HT NPs are in the range 25 to 40 nm in diameter. However, the recovery method (in solution) leads to a certain degree of agglomeration compared to direct spray coating on substrate.

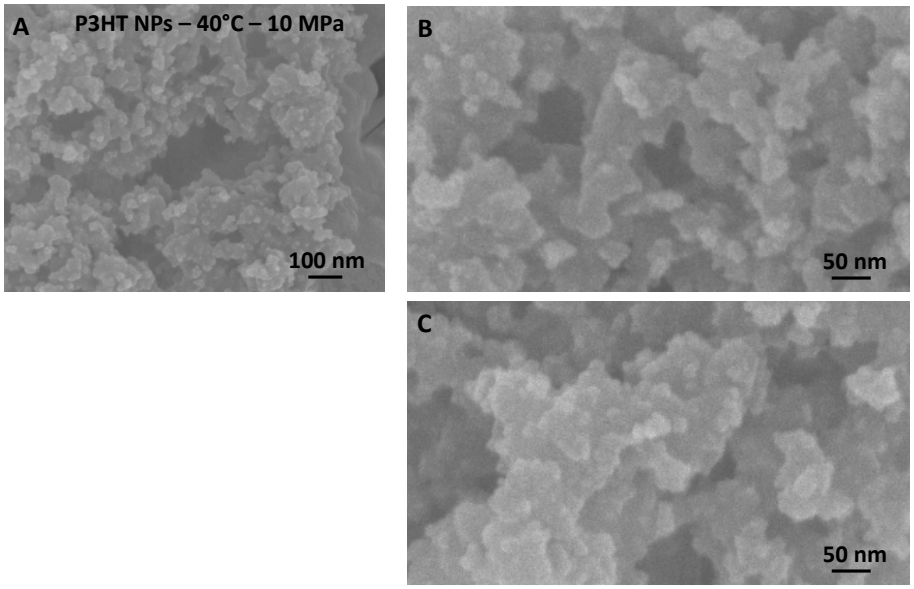

Figure S2: (A) *SEM snapshot of P3HT nanoparticles obtained from µSAS at 40°C and 10 MPa with additional enlargements (B) and (C).*

P3HT Size distributions

Size measurements were performed over more than 200 nanoparticles per sample using the ImageJ software, based on the AFM images.
As mentioned in the article, narrow particle size distributions are obtained, as shown in Figure S3:

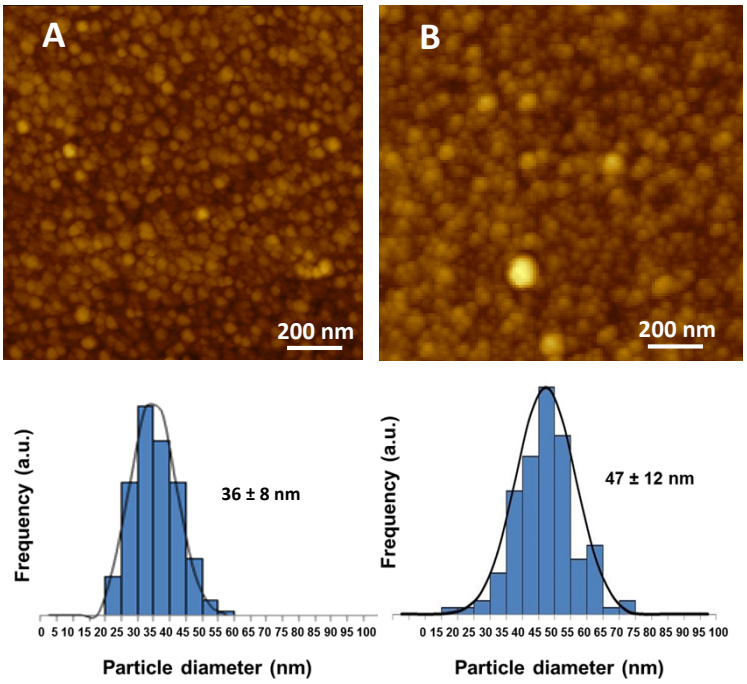

Figure S3: *P3HT nanoparticles size distribution measured from substrate spray-coated sample characterization by AFM. (A) 40°C, 10 MPa and (B) 50°C, 8 MPa.*

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[i] U. Srinivasan, M. R. Houston, R. T. Howe, R. Maboudian, J. *Microelectromech. Syst.,* 1998, **7**, 252–260.