Electronic Supplementary Material (ESI) for Soft Matter.

SUPPLEMENTARY INFORMATION

Poly(3-hexylthiophene) Nanowires in Porous Alumina: Internal structure under Confinement

Jaime Martín[1,], Mariano Campoy-Quiles[2], Aurora Nogales[3], Miquel Garriga[2], M Isabel Alonso[2], Alejandro R. Goñi[2,4], Marisol Martín-González[1,*]*

[1]Instituto de Microelectrónica de Madrid (IMM-CSIC), Calle de Isaac Newton 8, Tres Cantos, 28760 Madrid, Spain

[2]Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193 Bellaterra, Spain.

[3]Instituto de Estructura de la Materia (IEM- CSIC), Serrano 121, 28006 Madrid, Spain

Corresponding Authors

* Emails: jaimemartinp@imm.cnm.csic.es, marisol@imm.cnm.csic.es.

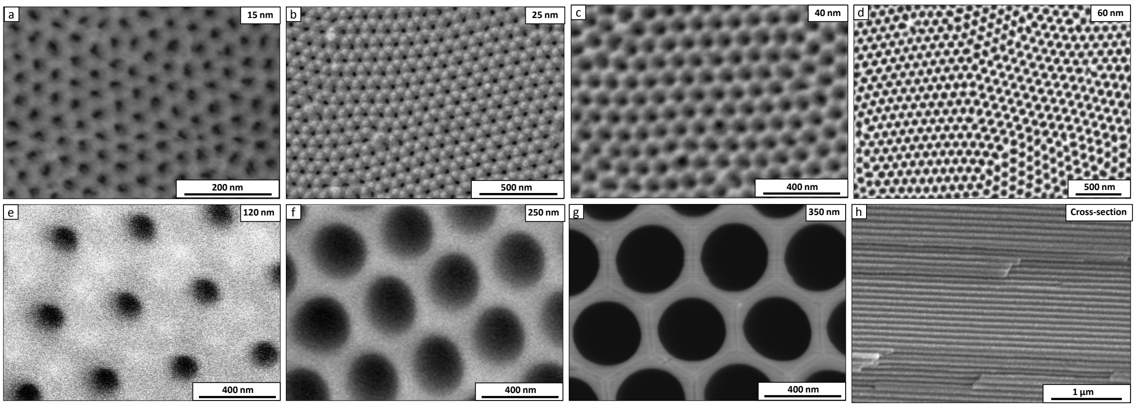

Figure S1. SEM images of the used AAO templates. Diameters: (a) 15 nm, (b) 25 nm, (c) 40 nm, (d) 60 nm, (e) 120 nm, (f) 250 nm, (g) 350. (h) cross section of a 40 nm in diameter template.

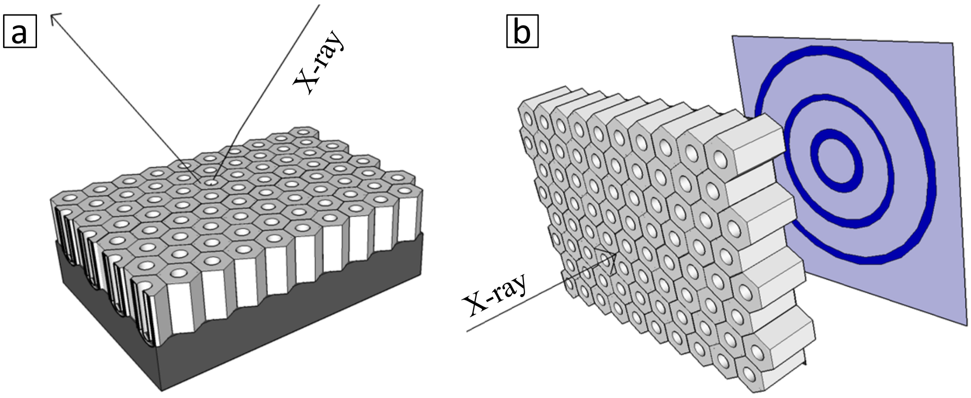

Figure S2. Schematic representations of WAXS experiments: (a) Experiment in reflection geometry in which the wave vector *Q* is parallel to pore long axis.(b) Experiment in transmission geometry. The X-ray beam travels along the direction perpendicular to the template surface, in such a way that *Q* is nearly perpendicular to the pore long axis.

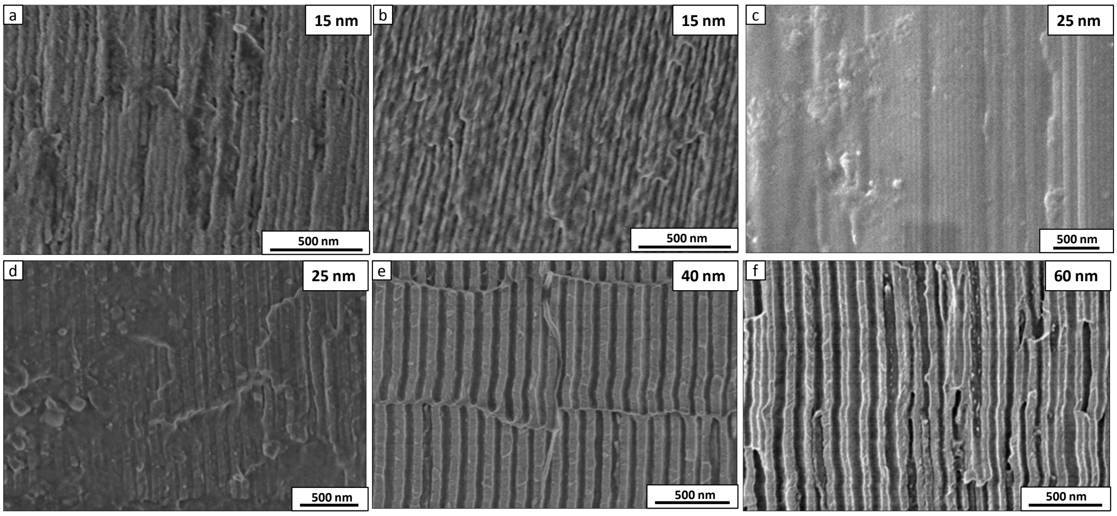

Figure S3. Cross sectional SEM micrographs of the AAO templates having the P3HT nanowires (a) melt-processed 15 nm nanowires s, (b) solution-processed 15 nm nanowires, (c) melt-processed 25 nm nanowires, (d) solution-processed 25 nm nanowires, (e) solution-processed 40 nm nanowires, and (f) solution-processed 60 nm nanowires. The appearance of empty pores is very likely related to the polymer being undesirably removed from the side during cleavage and handling of the samples.

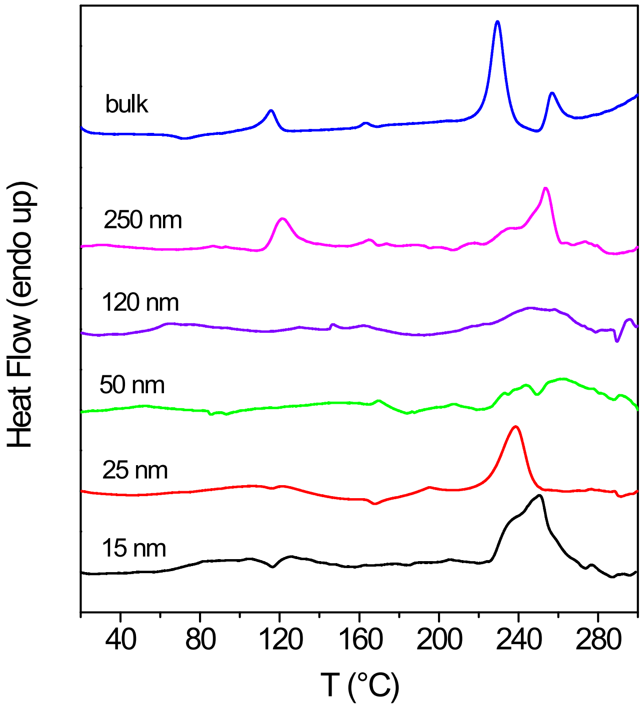

Figure S4. DSC second heating scans of bulk, and 250 nm, 120 nm, 50 nm, 25 nm, and 15 nm in diameter nanowires solidified from the melt. The measurements of nanowires were performed on samples comprised of nanowires embedded into the AAO templates. The heating rate was 40 °C/min.

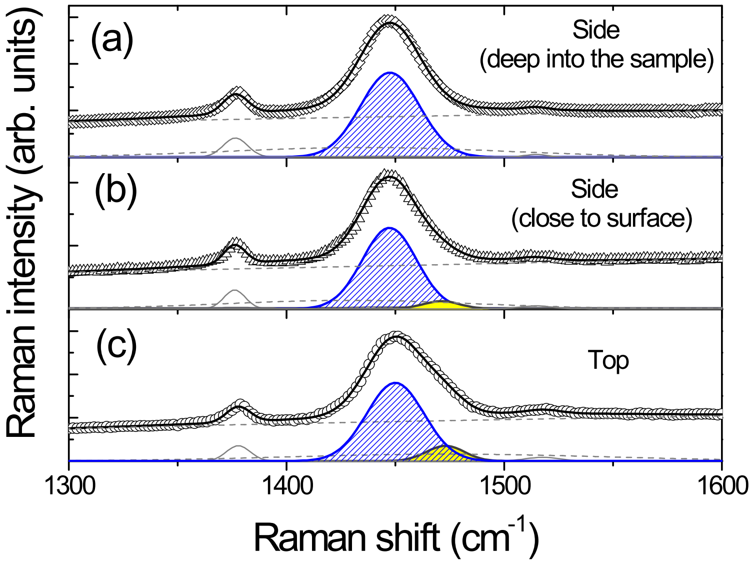

Figure S5. Experimental Raman spectra (open symbols) and fits (black lines) for a melt infiltrated nanowire sample with 25 nm diameter. The data was collected (c) from the top, (b) from the side but close to the surface and (a) from the side deep inside the sample. The blue (yellow) shadowed areas mark the ordered (amorphous) contributions. Dashed lines correspond to background, and grey lines to additional vibrations.

In order to understand in more detail the mechanisms behind this process, we have employed Raman spectroscopy. Raman scattering can offer important information about both degree of ordering and chain orientation. For the case of P3HT, it has been shown that the main stretching mode of the C-C bond, centered at around 1450 cm^{-1}, is in fact a band consisting of two components, one arising from the highly crystalline domains and the other from the amorphous regions.[1] By following the relative intensity of the two components, it is possible to assess the degree of ordering in different locations. We have used confocal micro-Raman to interrogate this degree of ordering across the depth of the nanowires with 25 nm in diameter. For this, a cleaved sample was scanned from the side. Figure S4 shows how the amorphous component is slightly higher at the surface than well inside the nanowires. Reassuringly, these results also support the view that crystallization starts within the nanowires, instead of propagating from the surface of the film.

1. W. C. Tsoi, D. T. James, J. S. Kim, P. G. Nicholson, C. E. Murphy, D. D. C. Bradley, J. Nelson and J.-S. Kim, *Journal of the American Chemical Society*, 2011, **133**, 9834-9843.