Supporting Information for

Growth of polythiophene nano-walls and their unique electrochemical and optical properties

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Organic thiophene-based nano-walls

In order to differentiate the wall from monomer crystals, three separate experiments were performed i.e. soaking the sample in thiophene, or in acetonitrile or keeping the sample at 110 °C for many hours. The experiments were designed base on the fact that both terthiophene and bithiophene are very soluble in thiophene (Th) and acetonitrile and the melting point of terthiophene which is 93-95°C. Nano-walls were shown to beclearly polymeric as SEM images of samples after the three treatments show no degradation in the walls. Acetonitrile breaks and removes some of the walls rather than dissolving them (Figure S1 (d)). Acetonitrile is a strong solvent and possibly removed some oligomers or short chain polymer around the wall hence the wall broke off in some areas.

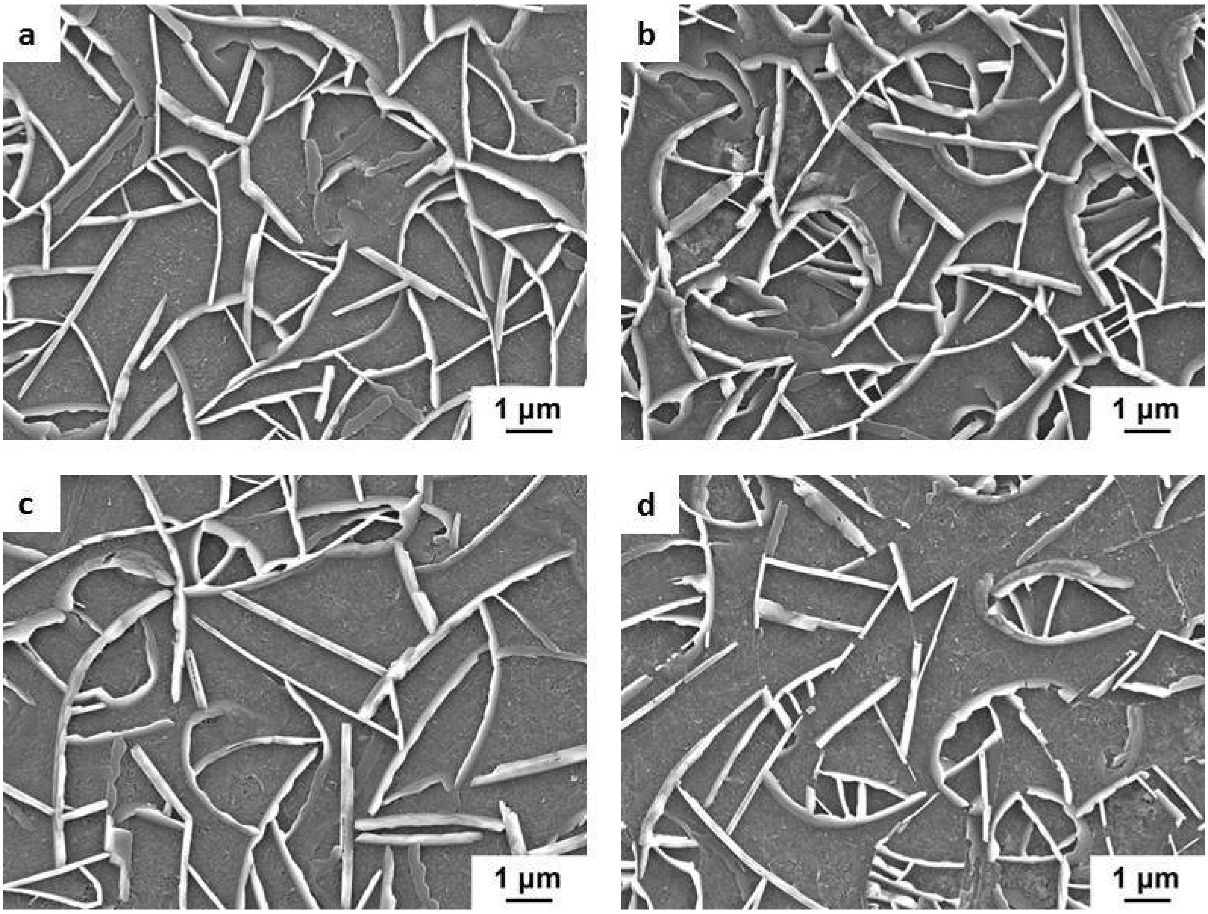

Figure S1 SEM images of the surface for the sample polymerized for 3 hours, where (**a**) is the control sample, (**b**) sample was rinsed and washed in thiophene for 24 hours, (**c**), sample was kept in the oven at 110°C for 120 hours (**d**) sample was rinsed and washed in acetonitrile for 24 hours.

Wall growth over time – SEM cross sectional images

Please note that since wall density calculation is a good quantification and provides realistic values, total area calculation is only a good estimation. Both values can differ even for the same sample depending on the SEM image, as wall distributions are not totally uniform. Area coverage and total area values for samples polymerized for different time periods are shown in table S1.

Table S1 Area coverage of the walls, total area caused by the walls and thickness of the film.

Polymerization time (min.)	**Wall coverage (%)**	**Total area (%)***	**Film thickness (nm)**	**Wall height (nm)**	**Wall thickness (nm)**
30	-	-	593 ± 7	-	-
60	-	-	602 ± 4	-	-
90	11 ± 0.3	138 ± 2	593 ± 9	101 ± 4	120 ± 1
120	13 ± 1	272 ± 16	725 ± 13	384 ± 34	143 ± 3
180	19 ± 0.2	335 ± 96	711 ± 21	632 ± 252	184 ± 4
360	20 ± 2	402 ± 201	713 ± 27	669 ± 350	216 ± 44

*Calculated for 100 μm geometrical area of the sample.

Order of film formation

Figure S3 presents a control experiment, where the same amount of Fe(III)PTS oxidant was used, but polymers were polymerized separately, one after another, instead of mixing the monomers. The oxidant coated substrate was first exposed to (only) bithiophene for one hour and thereafter transferred to a chamber with only terthiophene where the polymerisation process was continued (figure S3 (a) and (b)). The resulting material showed the same kind of “nano-wall on porous film” structure as seen with mixed monomers. This strongly indicates that bi- and terthiophene have their particular role in the process i.e. bithiophene being the main component of the porous film and terthiophene being the main building-block of the nano-walls.

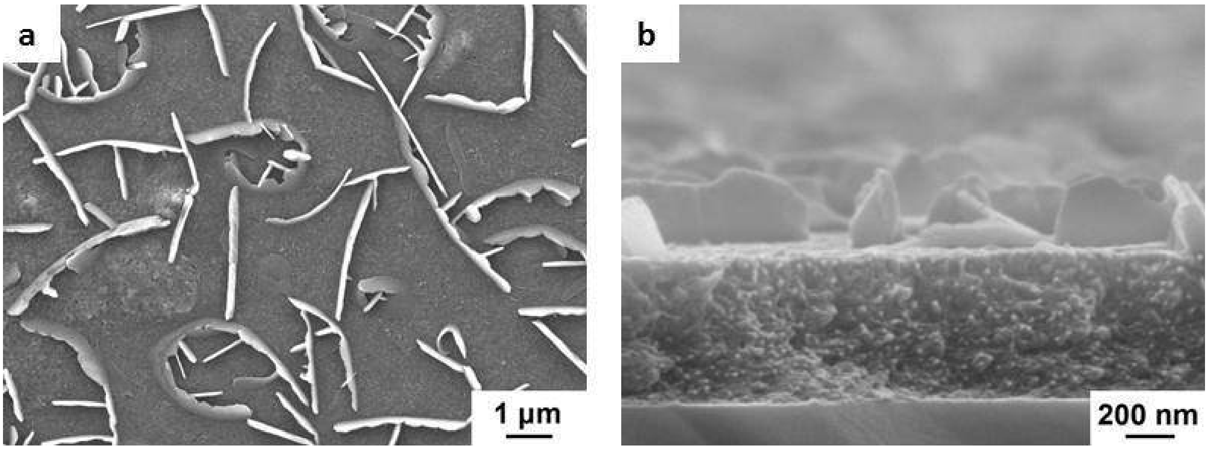

Figure S2 SEM images for poly(bi- terthiophene) polymerized separately, (**a**) and (**b**) Poly(bithiophene) polymerized for 1 hour at 70°C firstly, and next poly(terthiophne) polymerized for 3 hours at 105°C.

Poly(therthiophene) nano-walls can be produced using terthiophene only, this however requires much longer polymerization time. Since terthiophene has a much lower vapour pressure than bithiophene at the same temperature, it takes longer for terthiophene to form the polymer film and the nano-walls on top of it. The Raman spectra of these films/wall are similar to those produced with mixed monomer composition.

It is also possible to produce nano-walls using only bithiophene monomer, however this requires certain conditions. We have noticed poly(bithiophene) nano-wall formation around the steel clip used as a sample holder. We believe this is related to different heat capacity and heat exchange between steel clip and the glass and polymer film.

Image processing details

Estimation of the area coverage of the walls and increase in total surface area was done using Matlab software and Image Processing Toolbox. SEM images of the surface was converted to a binary image using Otsu's method, which computes a global threshold that can be used to convert an intensity image to a binary image. Otsu's method chooses the threshold to minimize the intraclass variance of the thresholded black and white pixels. All white pixels corresponding to the walls, was counted using a Matlab algorithm. Knowing height and width in pixels of the SEM image, percentage of the wall coverage of the area was calculated using formula below.

$$\text{wall coverage} = (\text{number of wall pixels}/(\text{image width in pixels} * \text{image height in pixels})) * 100$$

To calculate the increase in the area caused by walls, the binary image described above was further processed using morphological operations. The final image shows the contours of the walls. All the contour pixels have been counted by the Matlab algorithm and was used to calculate the wall area.

$$\text{wall area in pixels} = \text{number of the contour pixels} * \text{average wall height in pixels}$$

Average wall height was read from the corresponding cross section image. The total percentage area increase caused by the walls has been calculated using below equation.

*total area = ((image width in pixels*image height in pixels + wall area in pixels)/ (image width in pixels*image height in pixels))*100*

Above calculations can be converted to micrometres or nanometres, using the scale bar from SEM images. Image processing is shown below.

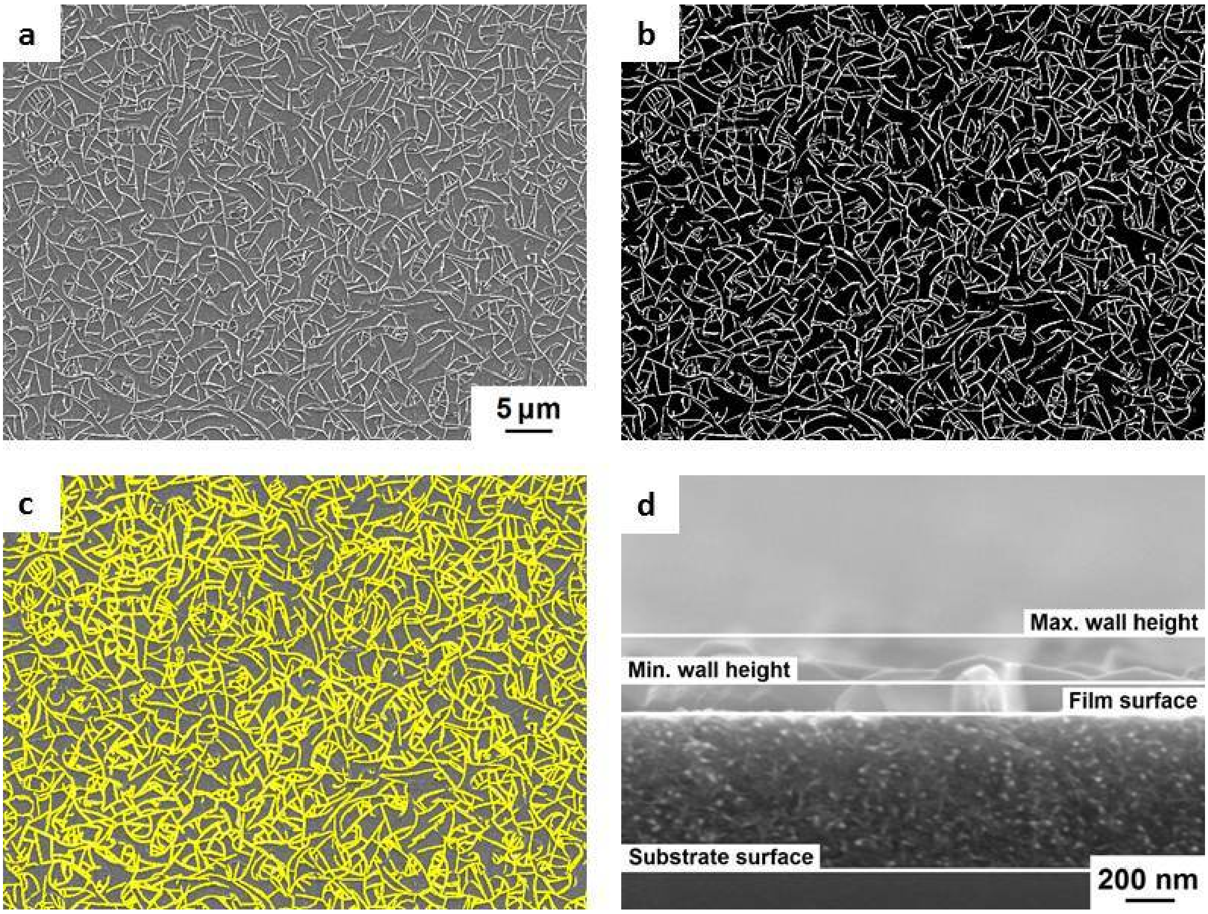

Figure S3 Image processing of the SEM images, (**a**) starting SEM image, (**b**) binary image converted using Otsu's method, (**c**) original image with wall boundaries visible (yellow), (**d**) cross section image with measured wall height.

Vapour phase polymerisation set-up

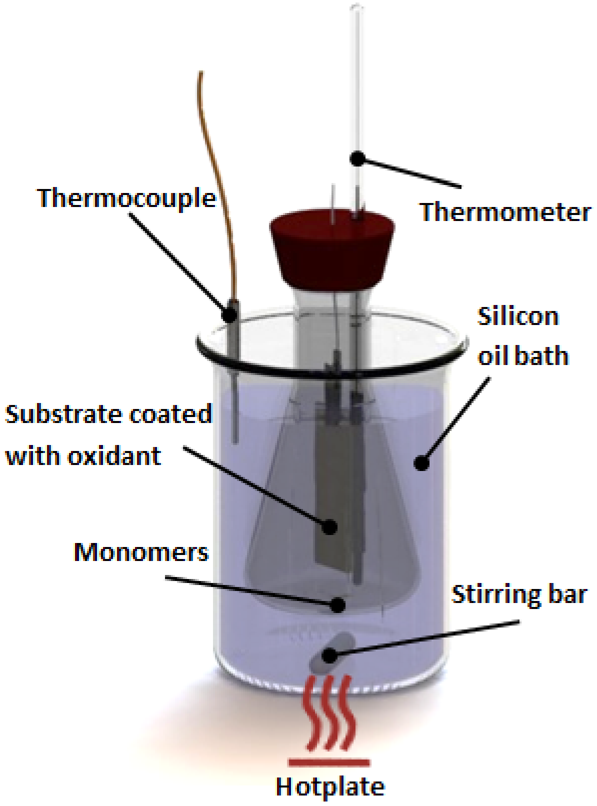

Figure S4 The VPP setup used for polymerization of the polymer films.

Nano-walls waveguide

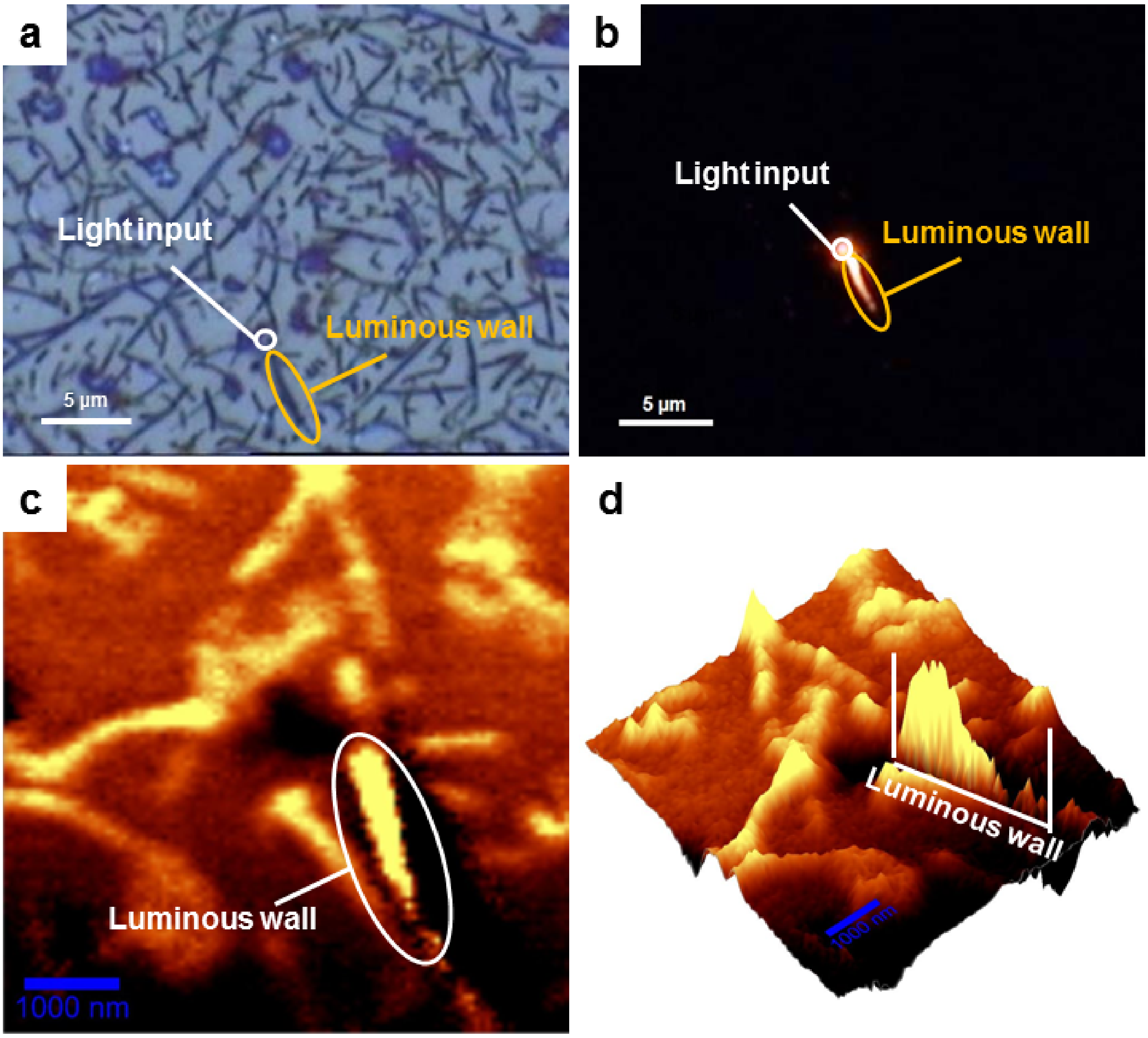

Figure S5 (a) Microscopic image of excitation spot. **(b)** Dark field image with visible excitation spot and light leak along the wall. Both images have the same scale. **(c)** 2D image of Raman mapping and **(d)** 3D image of Raman mapping of excited nano-wall, brighter areas represent nano-walls while darker areas are polymer film.

The wave guide experiment has been described in the manuscript. Please note that luminosity comes from external light which travels through the wall, not from fluorescence of the material.

Contact angle measurement

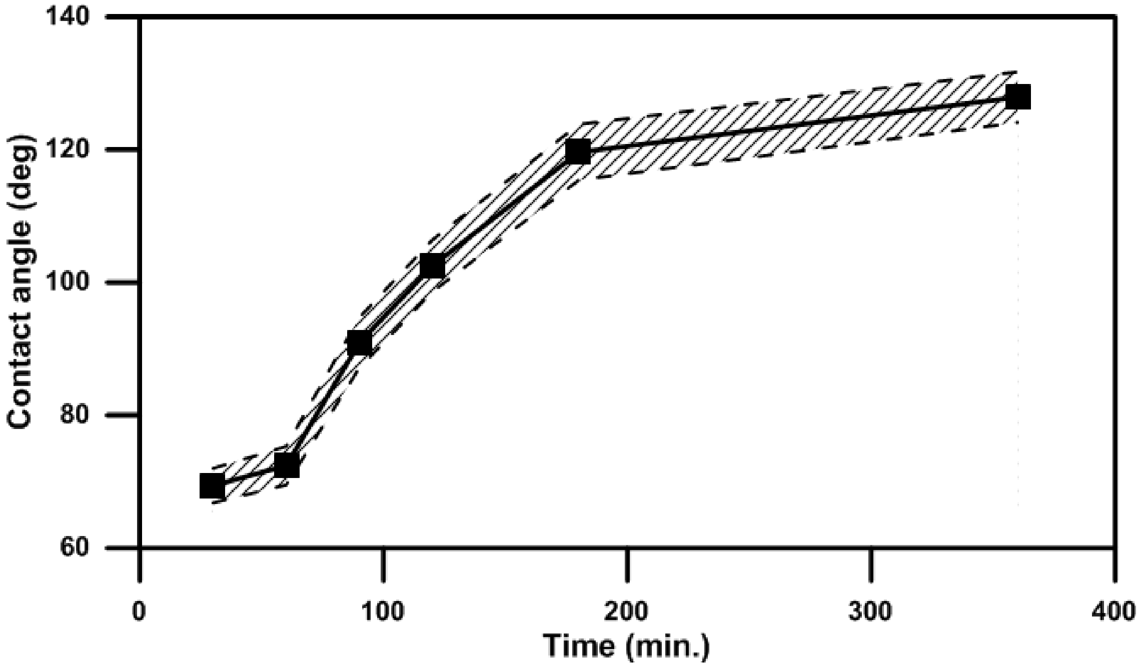

Figure S6 Contact angle dependence versus polymerization time. The average taken over several measurements is shown by the continuous black line. The shaded slashed background is the deviation calculated from several measurements.

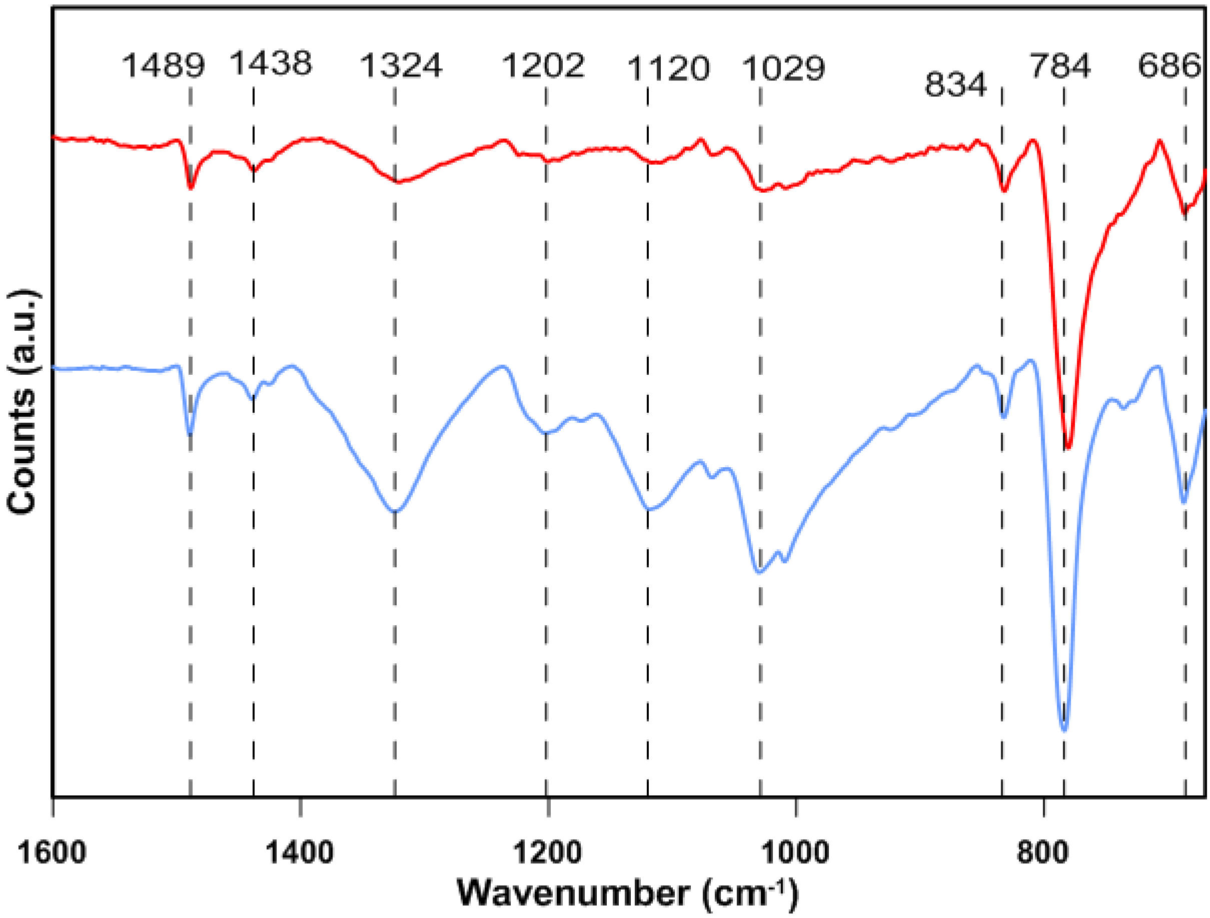

Figure S7 FT-IR spectra of polymeric film (red) and polymeric film with nano-walls (blue).

Above FT-IR spectra are similar to polythiophene spectra reported elsewhere[1,2]. The only distinguished difference between the polymeric film with and without nano-walls is that the film with nano-walls has higher doping level. Doping level is related to the amplitude of the four peaks at around ~ 1324, 1202, 1120, 1029 cm^{-1}, which are contributed from C=C (1320 cm^{-1}) and C-C (1202, 1120 and 1029 cm^{-1}) ring stretching vibrations[2]. The vibrations at 686 and 784 cm^{-1} are assigned as C_β-H out-of-plane deformations[2], 834 cm^{-1} is assigned for in-plane ring deformation[1], 1438 cm^{-1} is contributed to C_α=C_β symmetric stretching vibration and 1489 cm^{-1} is from C_α=C_β asymmetric stretching vibration[1].

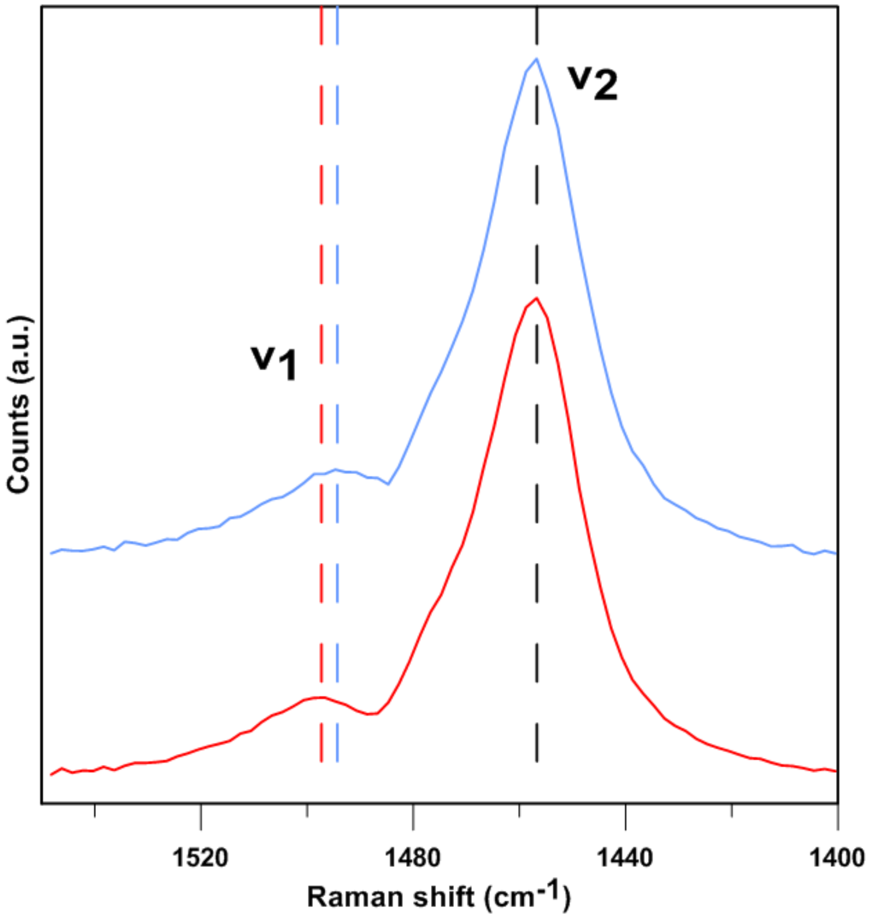

Figure S8 Enlarged Raman spectra showing area around v_1 and v_2 modes, where nano-wall (blue) and polymer film (red).

References

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