Supplementary Information for:

"Nanoscale Functionalization of Surfaces by Graft-Through Sonogashira Polymerization"

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1.Materials

3-chloropropyltrimethoxysilane, sodium azide, CuI, diisopropylamine, N,N-dimethylformamide, 2-bromo-5-(5-bromothiophen-2-yl)thiophene, hydroquinone, bromohexane, bromine were purchased from Sigma-Aldrich. 3-Azidopropyltrimethoxysilane was prepared from 3-(chloropropyl)trimethoxysilane and sodium azide using literature procedure.[1] 2-ethynyl-5-(5-ethynylthiophen-2-yl)thiophene (1) was freshly prepared from 2-bromo-5-(5-bromothiophen-2-yl)thiophene using the method described by Wong and others. 1,4-dibromo-2,5-bis(hexyloxy)benzene was prepared from hydroquinone using the literature procedure and used immediately.

2. Imaging and spectroscopy

UV-vis spectra were recorded on Cary 50 Bio spectrometer. Cyclic voltammetry was performed on CHI600D electrochemical workstations with ITO substrate as working electrode, Ag/AgCl as reference electrode and support electrolyte used was tetrabutylammonium hexafluorophosphate. Atomic force micrographs were obtained from Nova 1.026 RCI atomic force microscope with NT-MDT solver software analysis. Contact angle measurement was done using Holmarc HO-IAD-CAM-01 instrument. Thickness measurement was performed using Filmetric F20-UV thin film analyzer. XPS measurements were done in Omicron Nanotechnology, GmBH XPS (ESCA).

3. Formation of azide functionalized ITO, Si surface

The ITO plate was sequentially washed with toluene, water, acetone, ethanol (each one 10 minutes), followed by plasma cleaning for 10 minutes. The ITO, Si plate was placed in (H_2O:H_2O_2:NH_3)

in the ratio of (5:1:1) at 70 °C for 3h. After 3h, the ITO, Si plate was washed with distilled water for 3 times.

The ITO or Si plate was placed into 10 ml hot and cleaned round bottom flask and added 0.1 ml of 3-azido propyl (trimethoxysilane) and 5 ml of dry toluene in N_2 atm at room temperature. It was then heated at 100 °C for 2 h. After the completion of reaction, the ITO or Si plates were washed and used further.

4. Formation of triazole and end alkyne functionalized ITO, Si surface.

We took 10 ml 2 neck round bottom flask degassed with N_2 gas, and we added end azide functionalized ITO or silicon plate and 5 ml of dry toluene under N_2 atm at 0 ˚C. Then, we added N_2 purged solution of [DMF 4ml+CuI-16mg + freshly distilled diisopropylamine -16 microliter] and 2-ethynyl-5-(5-ethynylthiophen-2-yl)thiophene [35mg, 0.163 m.mol] at 0 ˚C. After that the reaction mixture was heated at 60 °C for 24h. After the completion of reaction the ITO, Si plate was washed with toluene, $CHCl_3$, water, acetone and ethanol by sonication method and kept under N_2 atm.

5. Sonogashira polymerization on ITO surface

We took hot and cleaned 10 ml 2 neck round bottom flask, degassed with N_2 gas and added alkyne-functionalized ITO surface, freshly distilled 10 ml diisopropylamine. After that, we added 2-ethynyl-5-(5-ethynylthiophen-2-yl)thiophene [25mg, 0.116 m.mol], 1,4-dibromo-2,5-bis(hexyloxy)benzene [43mg, 0.10 m.mol], CuI [5 mg, 0.026 m.mol], palladium (II) acetate [5mg, 0.022 mmol] and triphenylphosphine [15mg, 0.057 m.mol]. After that the reaction mixture was heated at 75 °C for 12h. After the completion of 12h, we added 0.1 ml of ethynyltrimethylsilane, and refluxed for another 12 h. The ITO plate was taken out and washed with $CHCl_3$, toluene, H_2O, acetone, ethanol [each one 15 minutes] in a sonicator, dried over by N_2 atm. Fig. S1 represents the AFM pictures of ITO surface before polymerization (A) and after polymerization (B and C).

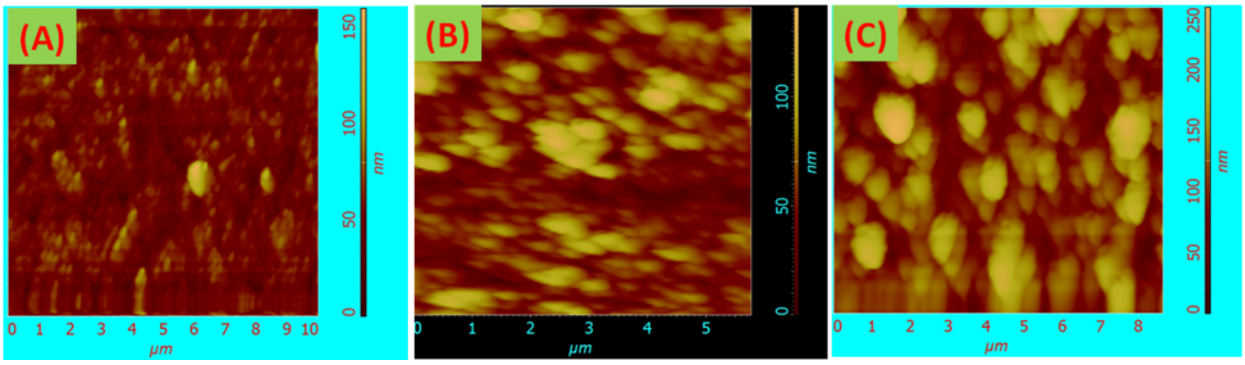

Fig. S1 AFM images of (A) alkyne-functionalized ITO plate, (B) ITO plate after the polymerization reaction for 12 h (C) ITO plate after the reaction for 24h.

6. Study of polymerization by NMR spectroscopy in residual solution

After the "graft through" polymerization on surface, the residual solution was studied by ^{1}H and ^{13}C NMR (Fig. S2). In ^{1}H NMR, the peak at 3.4 ppm (Inset, R1) disappeared while new peak at 0.26 ppm appeared. In ^{13}C NMR, peak characteristic at ~88 ppm Inset, R2) was changed.

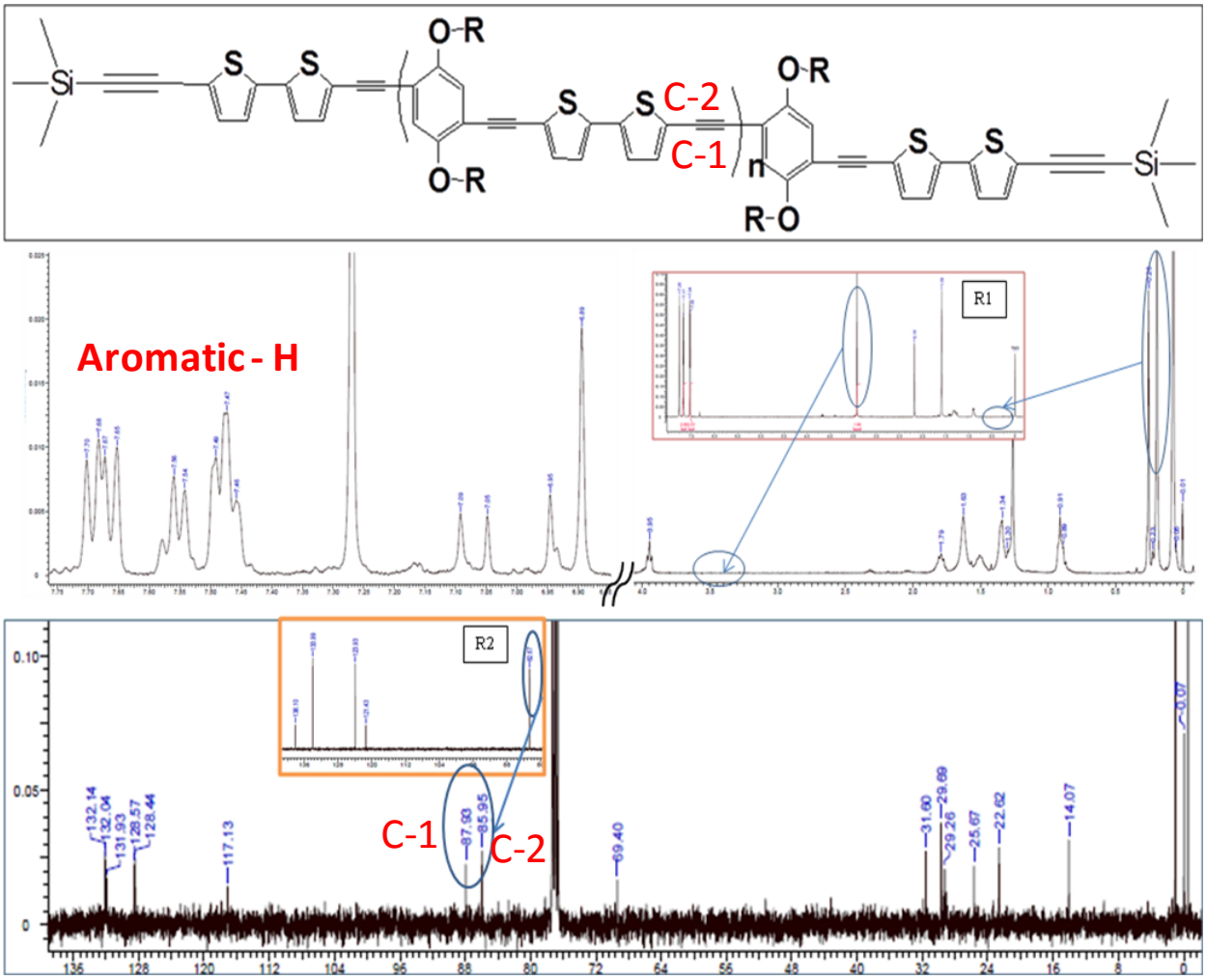

Fig. S2. ^{1}H (top) and ^{13}C NMR (bottom) of the Sonogashira polymer from the solution after "graft through" polymerization. Inset (R1) and (R2): NMR of the starting material (2-ethynyl-5-(5-ethynylthiophen-2-yl)thiophene).

7. Device studies

The device was fabricated as a sandwiched structure to measure I-V characteristics with eight sets of experiments. Measurements were carried out in ambience with the thickness of 100 to 150 nm and the area of 0.6 cm^2 (0.3cmx2.0 cm). The charge carrier mobility of polymer functionalized layer was determined under space charge limited current (SCLC) condition.

It is clear from the band structure of the device (Fig S3) that the hole and electron injection barriers are 0.52 and 0.56 eV respectively. Hence, the mobility value corresponds to ambipolar mobility.

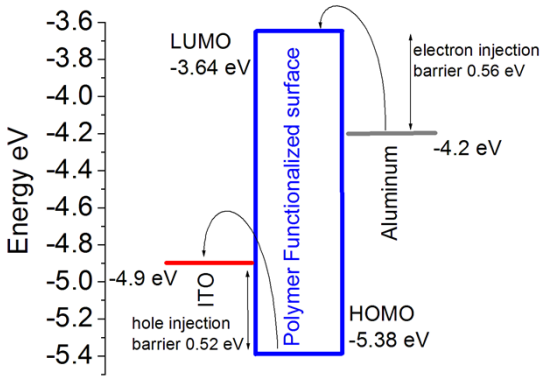

Fig. S3. Energy level diagram of polymer functionalized layer in the device configuration of ITO/grafted polymer/Al

8. AFM study of the polymer functionalized silicon surface

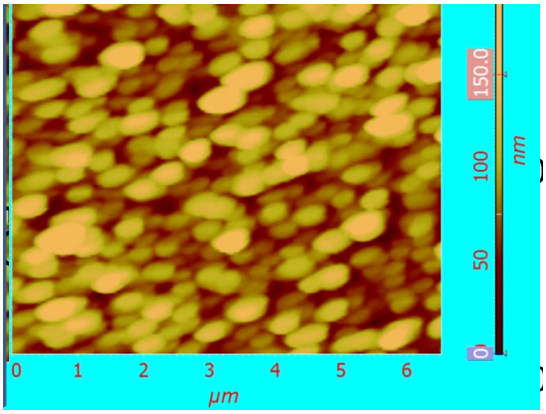

Fig. S4. AFM image of polymer functionalized silicon surface after performing the polymerization reaction for 24h

9. Study of distribution profile of surface by AFM

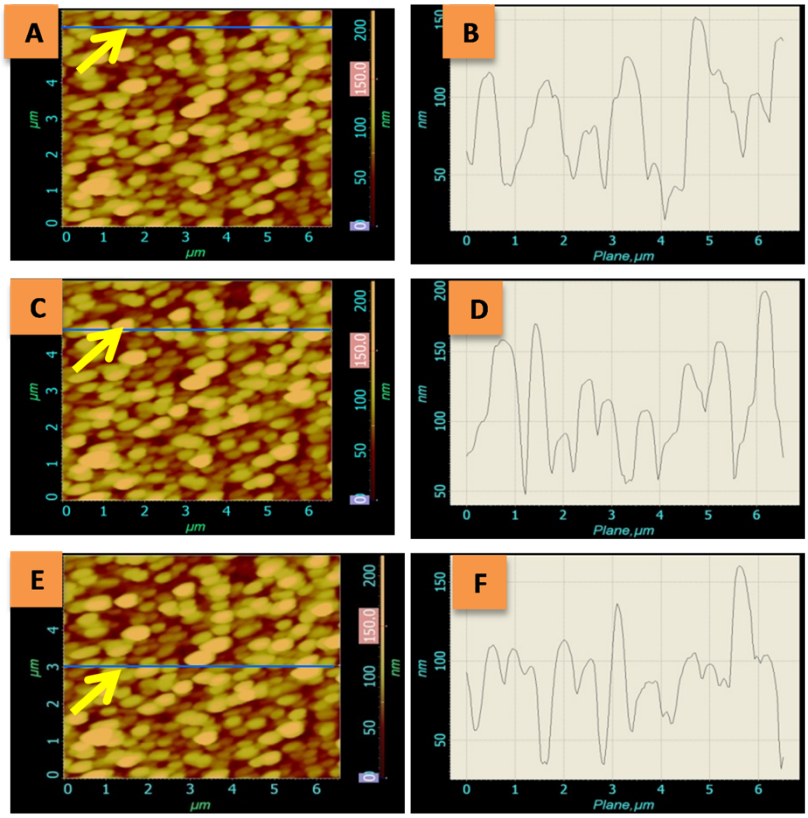

Fig. S5. Distribution profiles of grafted polymer across the polymer functionalized silicon surface studied by AFM using NOVA software when the polymerization reaction was performed for 24h

10. XPS studies on silicon surface

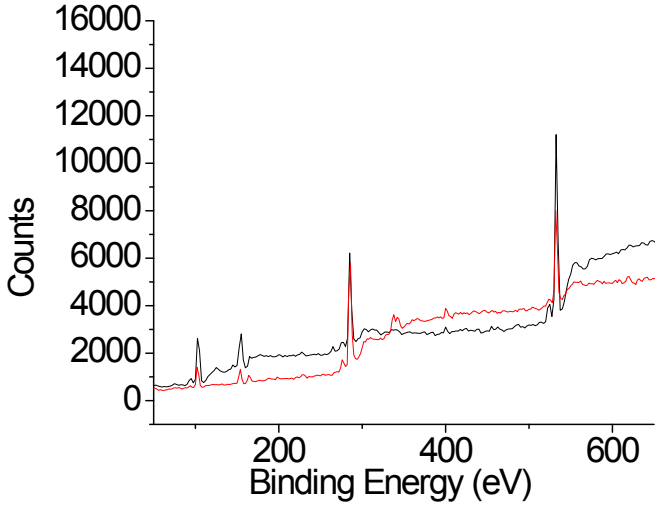

Fig. S6. XPS spectra of alkyne-functionalized (black curve) and polymer grafted (red curve) silicon surfaces (polymerization time 24 h).

11. TAUC plot

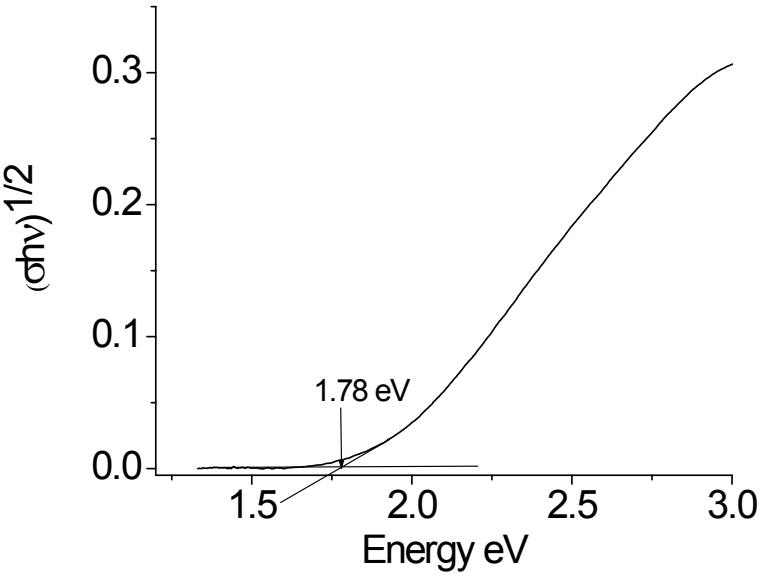

Fig. S7. TAUC plot for the calculation of band gap for polymer functionalized surface

12. Control experiments for I-V characterization on ITO plate

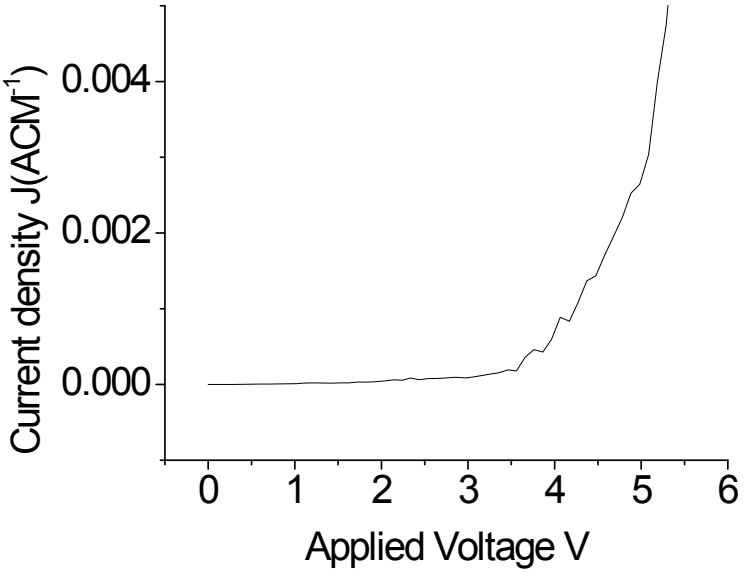

Fig. S8. Current Voltage characteristics of the ITO surface spin coated with polymer in the fabricated device using aluminium as cathode in a sandwich structure.

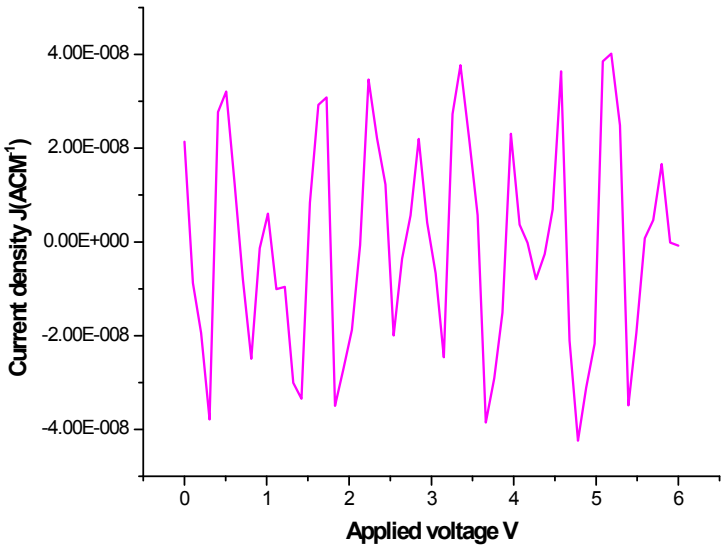

Fig. S9. Control experiment: Current-Voltage characteristics of the ITO surface (without polymer) in the fabricated device using aluminium as cathode in a sandwich structure.

1 P. Paoprasert, J. W. Spalenka, D. L. Peterson, R. E. Ruther, R. J. Hamers, P. G. Evans, P. Gopalan, *J. Mater. Chem.,* 2010, **20**, 2651.