

## **Supplementary Information**

### **Molecular-Level Periodic Arrays of Long-Chain Poly (3-hexylthiophene-2,5-diyl) Driven by Electric Field**

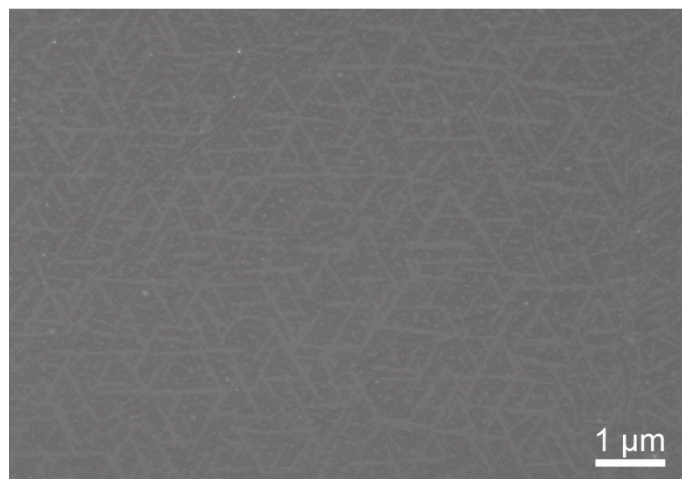
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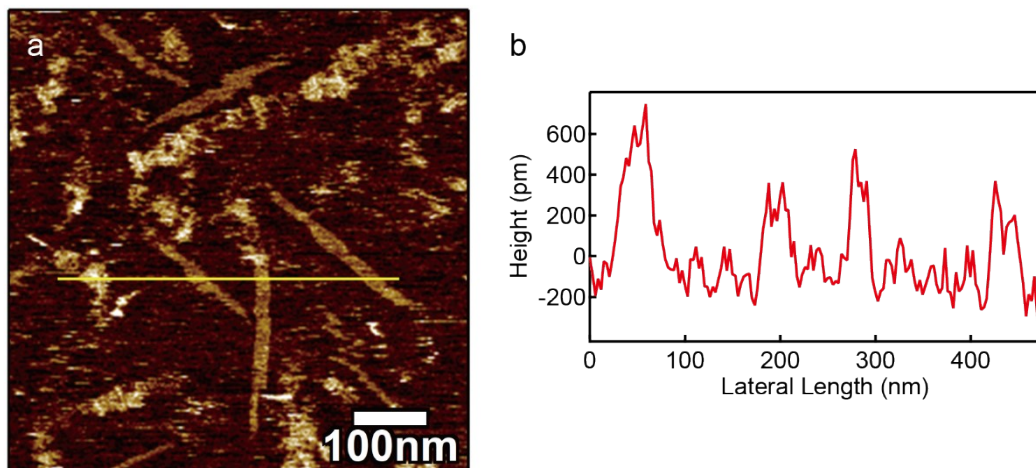
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E-mail: songyu16@jlu.edu.cn (Y.S.) and zhangwk@jlu.edu.cn (W.Z.)

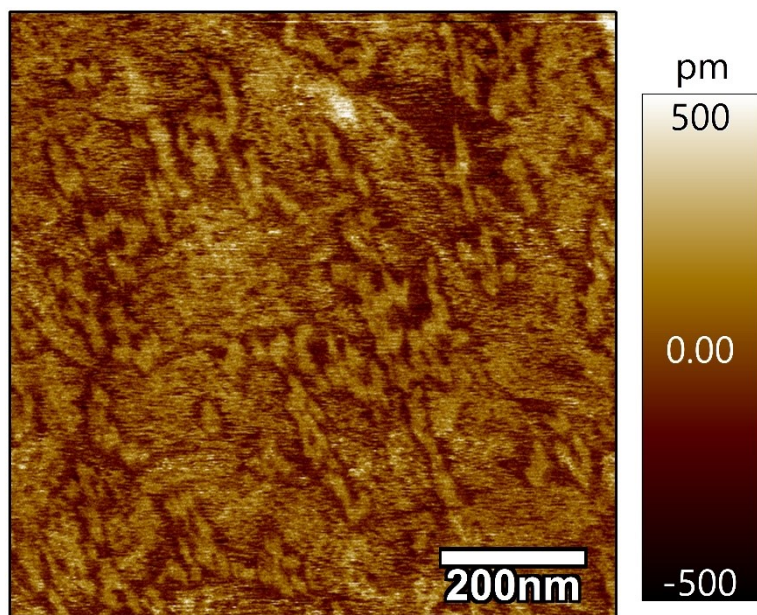
## Supporting Figures



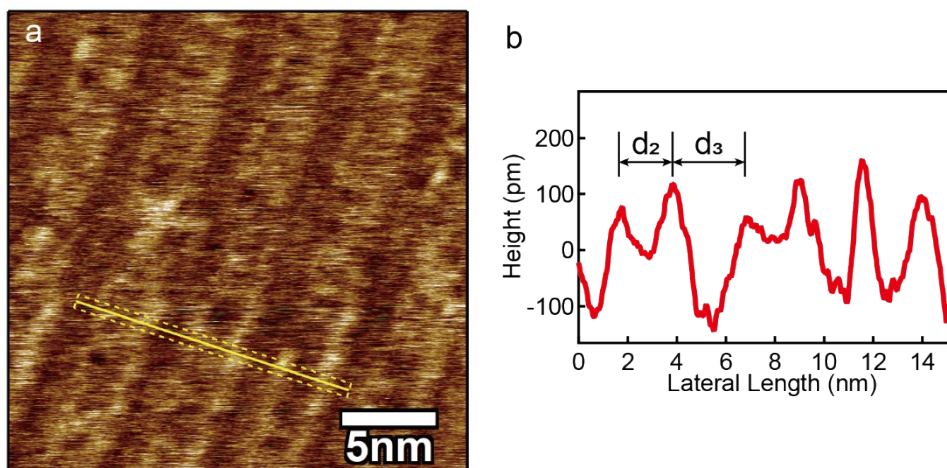
**Fig. S1.** SEM images of P3HT assembly on HOPG under  $-30$  V at 90 min. P3HT nanosheets aligned along three equivalent directions on HOPG.



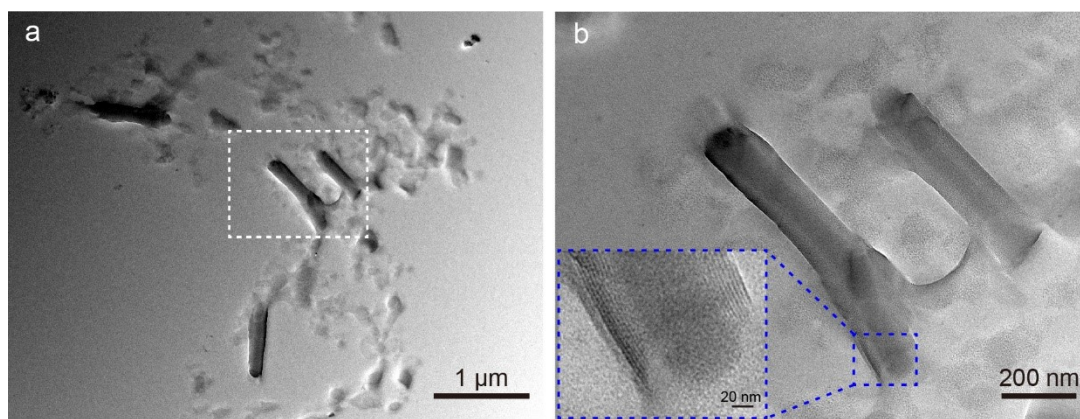
**Fig. S2.** The morphology of self-assembled P3HT characterized by AFM. (a) The AFM height image of clusters and nanosheets on HOPG. (b) A cross-sectional height profile from different clusters and nanosheets by the yellow line in (a). The height of nanosheets is around 0.36 nm and the height of clusters is 0.56 nm.



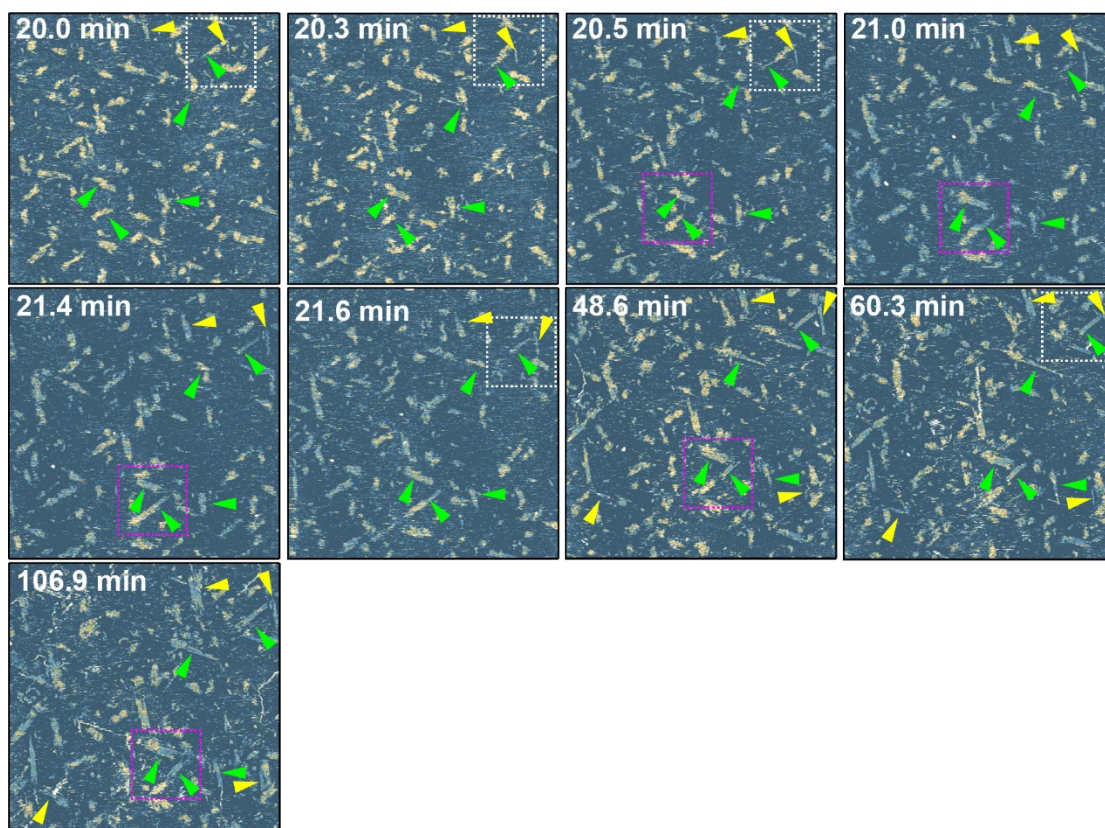
**Fig. S3.** AFM images of the P3HT clusters deposited on HOPG within 120 min at 0 V.



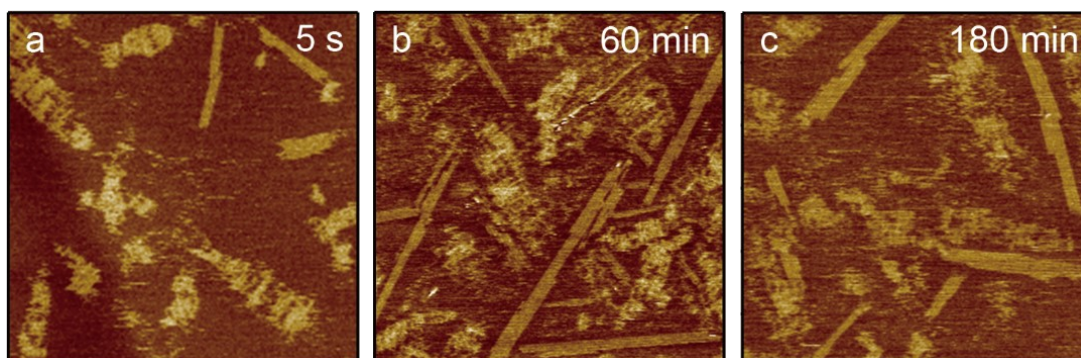
**Fig. S4.** The high-resolution AFM image of P3HT assembly on HOPG. (a) High-resolution AFM height imaging of P3HT chains using the second eigenmode of SNL probe oscillating at 0.93 MHz and a setpoint of 19.8 mV. Scan rate 9.8 Hz,  $1024 \times 1024$  px. (b) Cross-sectional height averaged along a path perpendicular to the section path to a width as specified by the yellow box in (a). The values of  $d_2$  and  $d_3$  were averaged by multiple measurements.



**Fig. S5.** TEM images of (a) P3HT assembly on graphene under  $-30$  V at 90 min and (b) enlarged view of the area indicated by the white dotted square on (a). The TEM images observed that the repeating period of nanosheets on graphene corresponds with  $d_1$  as shown in Fig. 1e.

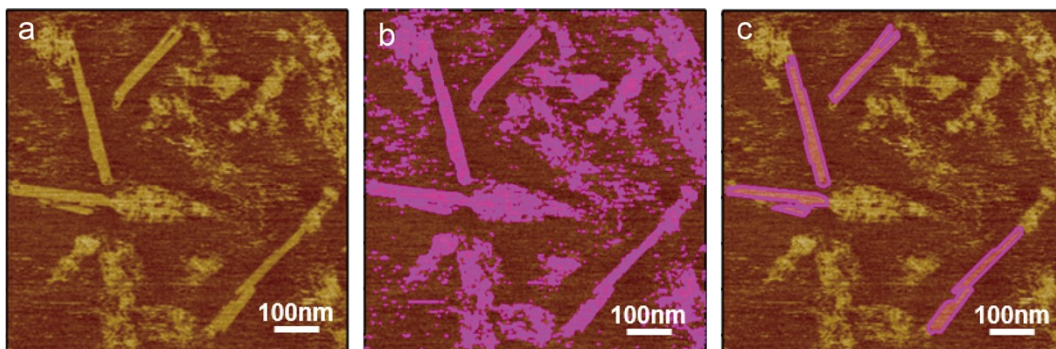


**Fig. S6.** In situ large-scale AFM images of nucleation and growth process of clusters. The green and yellow triangles are used to denote the nucleation of smaller and larger clusters, respectively. Enlarged views of the areas indicated by the white boxes in upper row and the pink boxes in lower row of Fig. 3 in main text. Image size: 1670 nm  $\times$  1670 nm.

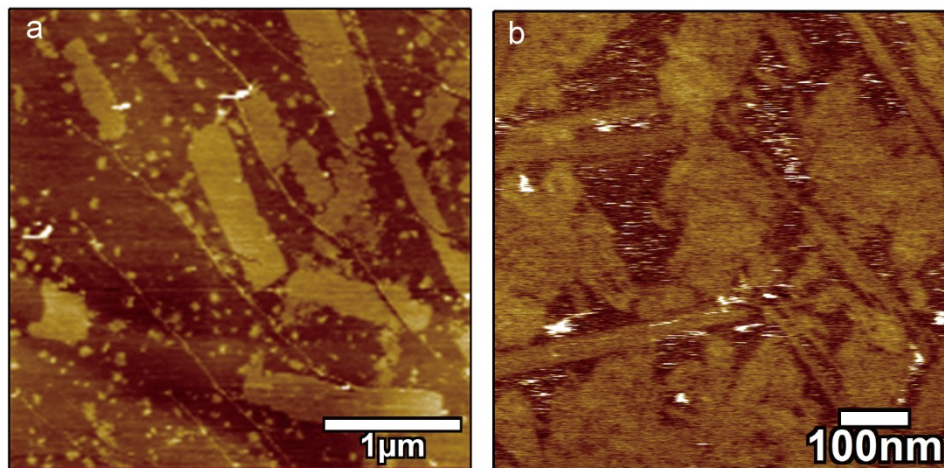


**Fig. S7.** AFM height images of P3HT assembly on HOPG under  $-30$  V at (a)  $t = 5$  s, (b) 60 min and (c) 180 min. Image size:  $550$  nm  $\times$   $550$  nm.

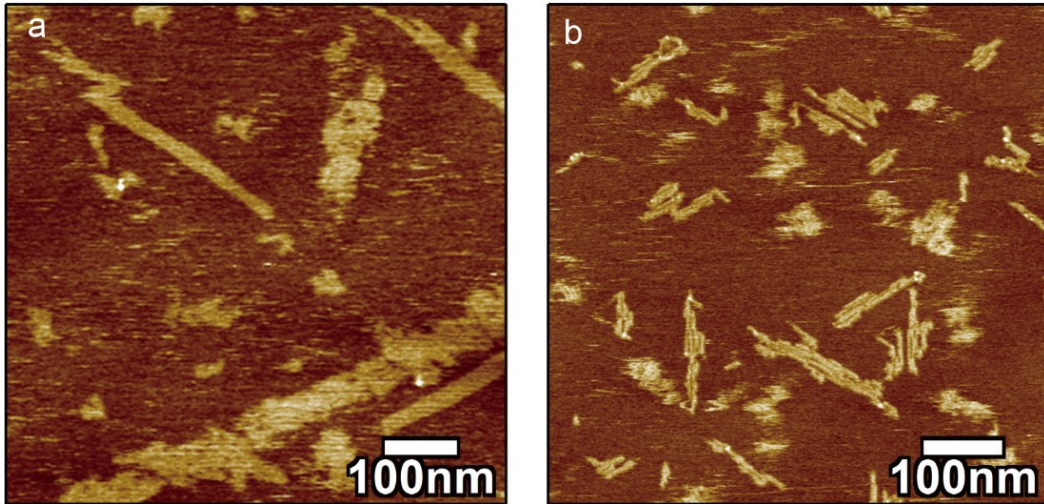




**Fig. S8.** Calculation of assembly proportion by making masks. (a) The height image of P3HT assembly by AFM. (b) Polymers were discriminated from substrate by applying a threshold to those pixels based on the sample height, thus obtaining the fraction of nanosheets and clusters onto the surface of the full image. (c) Polygon masks were drawn to segregate the nanosheets from the surface, including points within the mask to obtain the nanosheets fraction of the full image.



**Fig. S9.** AFM height images of the P3HT periodic arrays persisted for (a) twenty days in air and (b) four days in octyl benzene following the removal of the electric field.



**Fig. S10.** AFM height images of periodic arrays of poly(3-alkylthiophene)s on HOPG. (a) Poly(3-butylthiophene-2,5-diyl) (P3BT) periodic arrays prepared under  $-15$  V for 2 h. (b) Poly(3-dodecylthiophene-2,5-diyl) (P3DDT) periodic arrays prepared under  $-30$  V for 1 h.