Supplementary Information

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Experimental Section

Oligo(p-phenylenevinylene)s (OPV4) and OPV4-C5 were home-synthesized. 1-bromooctadecane ($C_{18}H_{37}Br$), octadecane ($C_{18}H_{38}$), and 1-octadecanol ($C_{18}H_{37}OH$) were from Aldrich. A drop of acetone solution containing OPV4 molecule ($<10^{-4}$ M), and an OPV4/$C_{18}H_{37}X$ (X = Br, H, OH) mixture (1:3) was directly deposited onto a freshly cleaved, atomically flat HOPG surface, respectively. The former was used for the preparation of oligomer chiral assembly, and the latter for the coadsorption assembly. Besides acetone, toluene, alcohol, octylbenzene and octanol were also used to dissolve OPV4. STM experiments were carried out under ambient conditions on a Nanoscope IIIa STM with mechanically cut Pt/Ir tips.

Theoretical calculations were conducted using density functional theory (DFT) as implemented in the DMol3 package. All of the computations were all-electron, spin restricted.

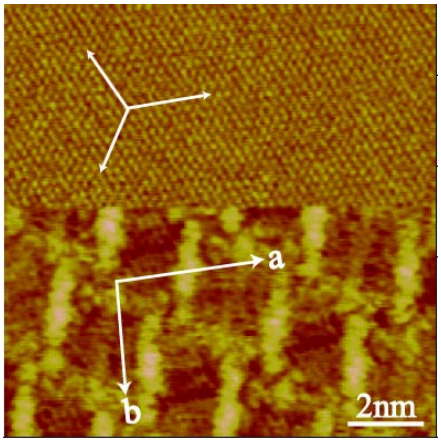

Fig. S1. A composite STM image showing the underlying HOPG lattice and the windmill structure. The imaging conditions are V_{bias} = 658mV, I_t = 667pA for the molecular adlayer (*Lower*) and V_{bias} = 50mV, I_t = 667pA for HOPG lattice (*Upper*). The image was recorded by switching the bias during the STM scan from the bottom to the upper frame.

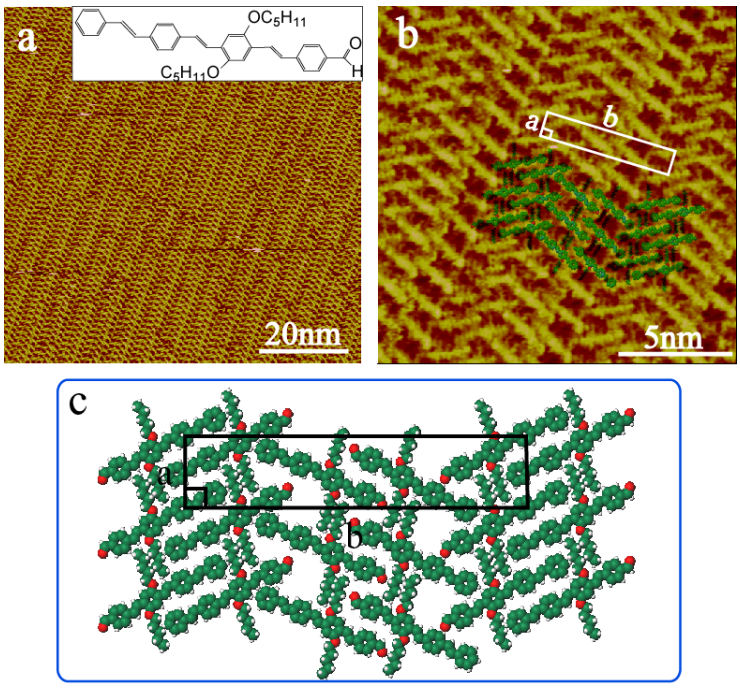

Fig. S2. Self-assembly of OPV4-C5. (a) Large-scale STM image. V_{bias} = 680 mV; I_t = 653 pA. The inset is OPV4-C5 molecular structure. (b) High-resolution STM image. V_{bias} = 680 mV; I_t = 647 pA. (c) Structural model for the adlayer with a rectangular unit cell, and a = 1.2nm, b = 7.9nm.