Supporting information

Oligothiophenes on CVD Graphene Grown on Multi-crystalline Copper Foil: Supramolecular Assembling and Defect Impact

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1. Experimental details

The solvent, octanoic acid (≥99%) was purchased from Aldrich, and used without further treatment. The graphene was prepared with 25 μm thick copper foils as substrate.

The graphene used here was synthesized by ambient pressure chemical vapor deposition reported elsewhere.[1] Typically, the copper strips (Alfa Aesar 99.95% purity) were soaked in 1 M acetic acid at 42 ^{o}C for 10 min to remove the native oxide and rinsed with deionized water. Then, loaded into fused silica tube and heated to 1035 ^{o}C under the H_2:Ar = 50:450 sccm (standard-state cubic centimetre per minute), followed by annealing for 20 min. Subsequently, 0.1 sccm methane was introduced into the system for 20 min. At last, the furnace was cooled to room temperature under the same gas flow. For STM substrate the G-copper was used as prepared, while for Raman characterization, a PMMA supported transfer method was utilized to transfer graphene to the Si-SiO_2 substrate.[2]

Samples for STM investigation were prepared by depositing a droplet (~5μL) of the solution of oligothiophenes (in octanoic acid, 0.78mg/mL) on G-copper. STM measurements were performed under room temperature at the liquid-solid interface with a constant current mode (Agilent 5100, USA). Detailed imaging conditions are given in the figure captions. Mechanically cut Pt/Ir (80/20) tips were used. The STM images of the adlayers were corrected for XY drift against G-copper lattice.

2. Extra STM images of QT and QTDA on graphene

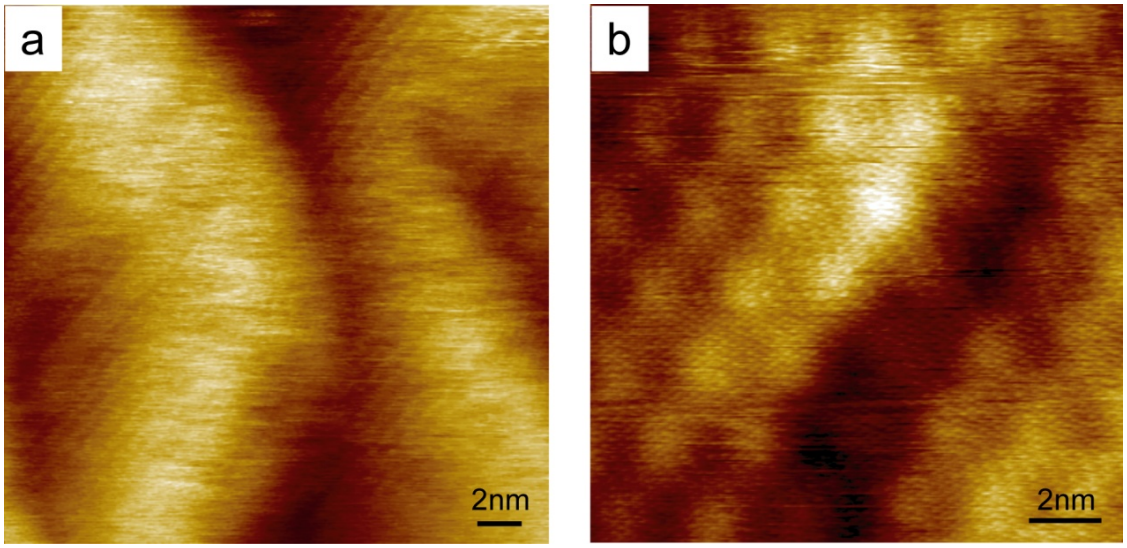


Figure S1: Formation of Moiré patterns of graphene on Cu(100) and Cu(111) terraces. Due to the weak coupling of graphene with copper substrate, Moiré patterns are not always seen. Imaging conditions: V_{bias} = 20 mV, I_{set} = 670 pA.

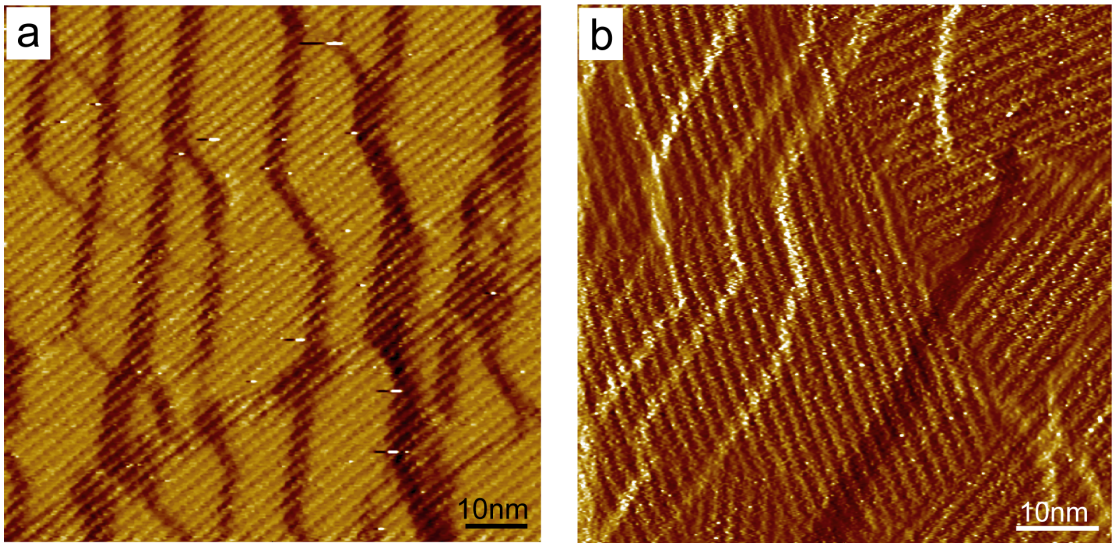


Figure S2. Coresponding current images of Figure 1a and 1d. Imaging conditions: V_{bias} = 800 mV, I_{set} = 35 pA.

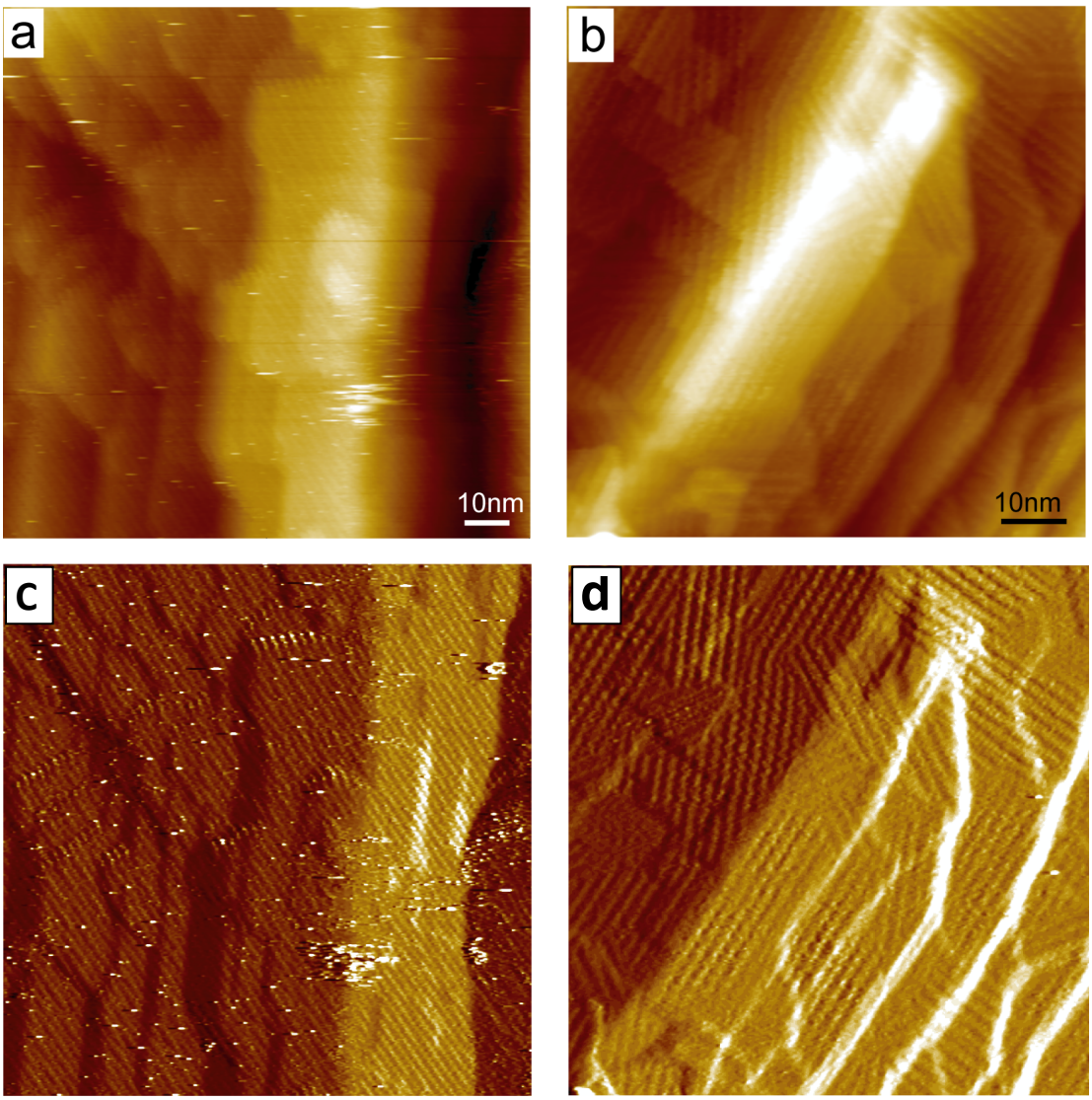


Figure S3. Assembling structures formed by QT (a) and QTDA (b) on graphene grown on Cu(100) terraces, the STM images underneath are the corresponding current images of the same area. The good continuity of the lamellae of these two molecules can be clearly seen both from the height and current images. Imaging conditions: V_{bias} = 800 mV, I_{set} = 30 pA.

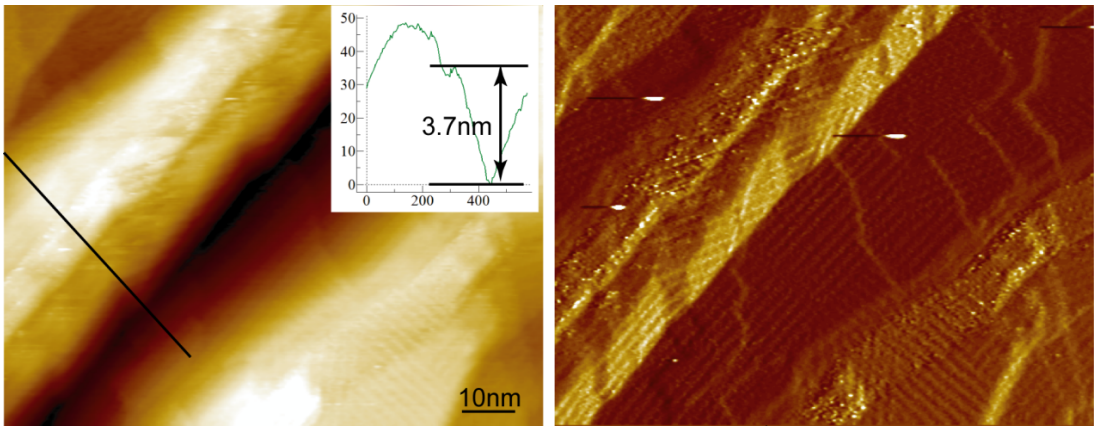


Figure S4. Height and current images show that the lamellae assembly of QTDA molecules grow continuously across step terraces more than 3.7 nm different in height. Imaging conditions: V_{bias} = 860 mV, I_{set} = 35 pA.

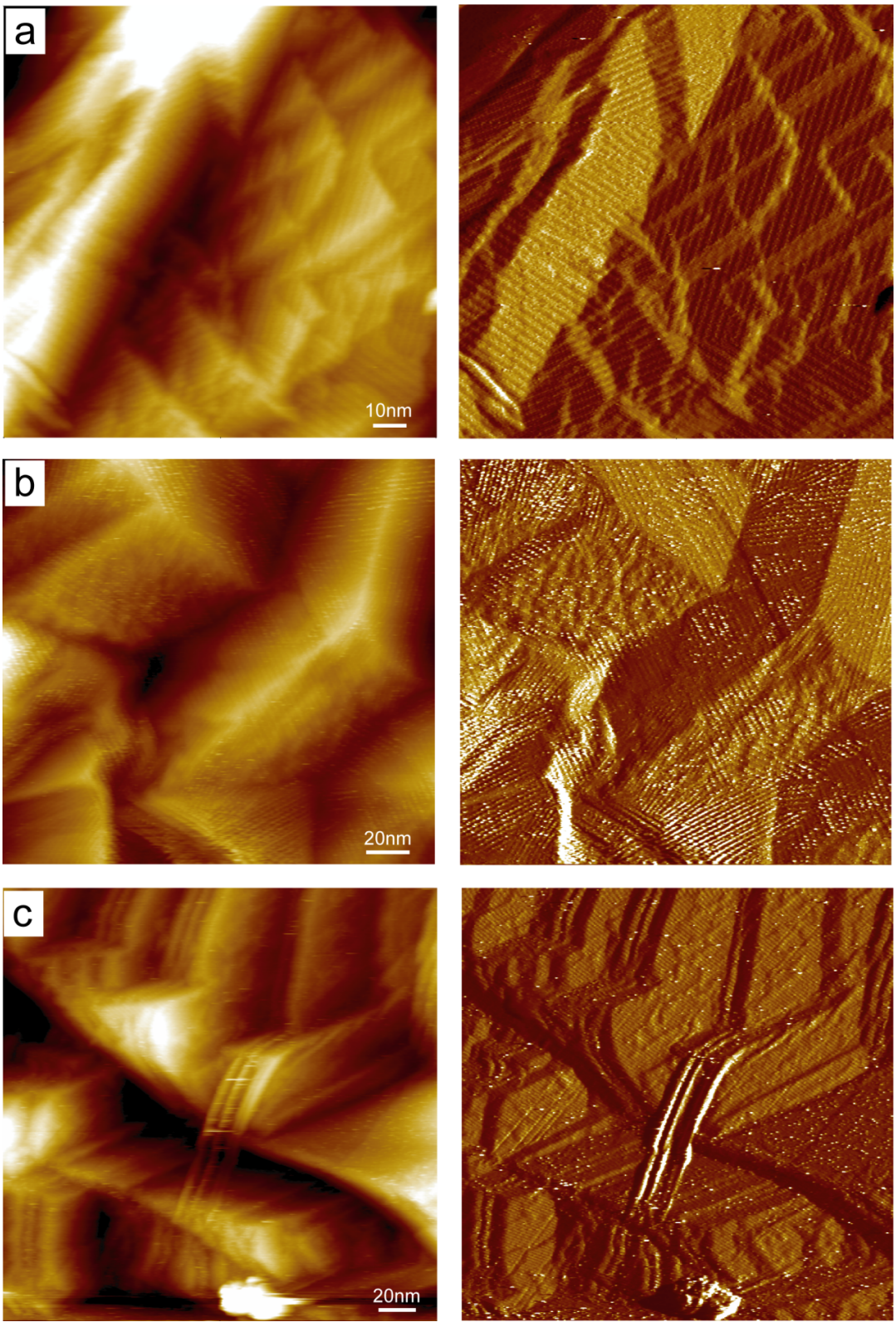


Figure S5. Large scale STM height and current images show the good continuity of assemblies of QTDA (a and b) and QT (c) growing in areas with large corrugations. Imaging conditions: V_{bias} = 800 mV, I_{set} = 35 pA.

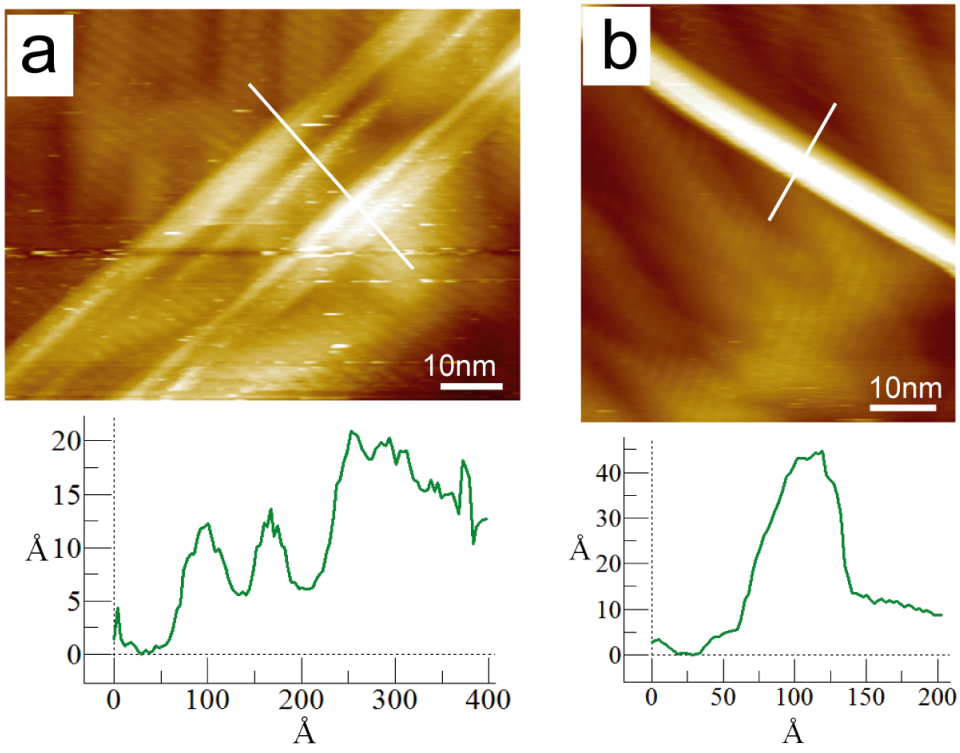


Figure S6. STM images show that there is no stable adsorption of QT on ripples and wrinkles with height ranging from ~0.6 to 3.2 nm. The section profiles corresponding to the site marked by the white lines are shown under the STM images. Imaging conditions: V_{bias} = 985 mV, I_{set} = 35 pA.

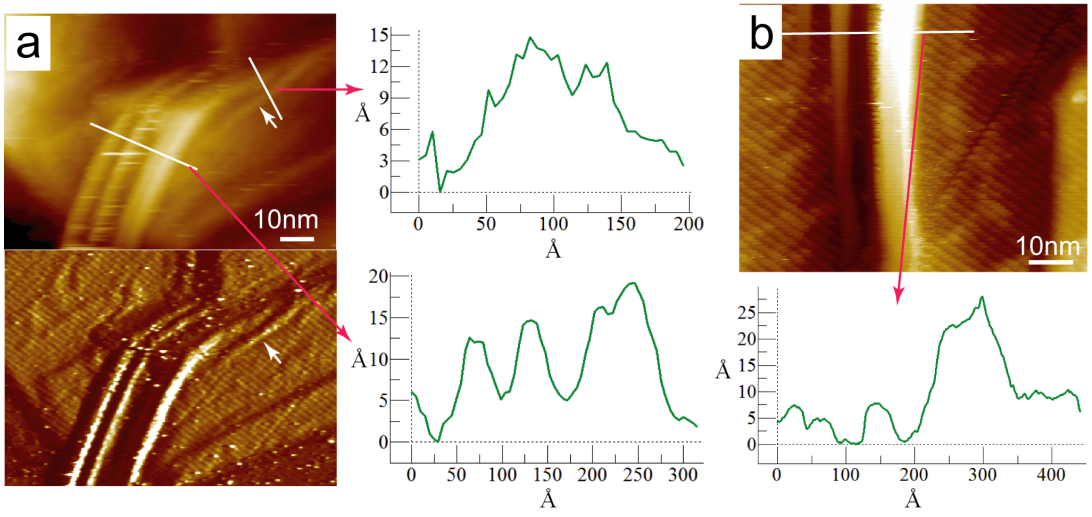


Figure S7. STM images revealing the adsorption of QT on ripples and wrinkles. In (a) stable adsorption of QT can be clearly seen in the small ripple indicated by the white arrow with height of 0.3 nm. While on other larger ripples and wrinkles no stable adsorption can be detected. Imaging conditions: V_{bias} = 800 mV, I_{set} = 34 pA.

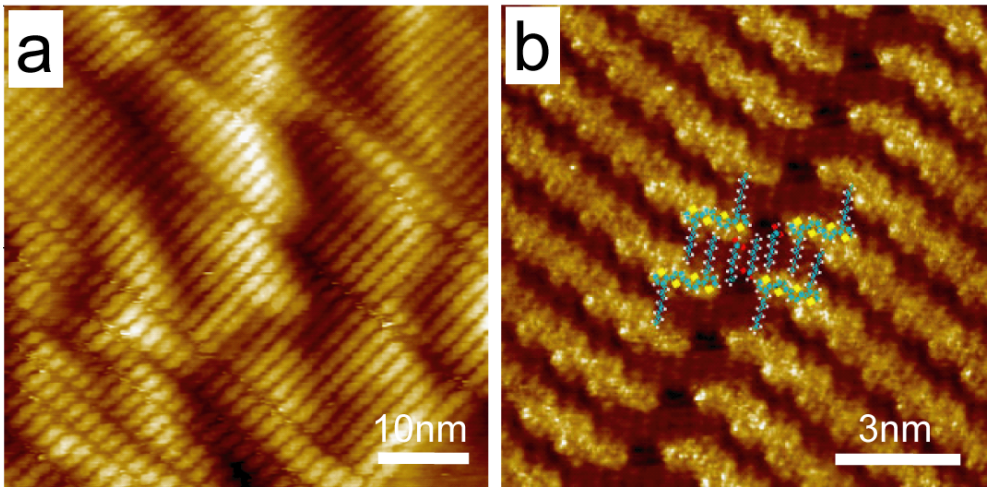


Figure S8. Due to coadsorption of octanoic acid molecules some dark troughs can be observed in the assembly of QT molecules, interrupting the lamellae. According to high resolution STM images, three octanoic acid molecules are supposed to be inserted between two QT molecules in each lamellae to form the dark trough. Imaging conditions: V_{bias} = 800 mV, I_{set} = 35 pA.

Raman mapping of graphene

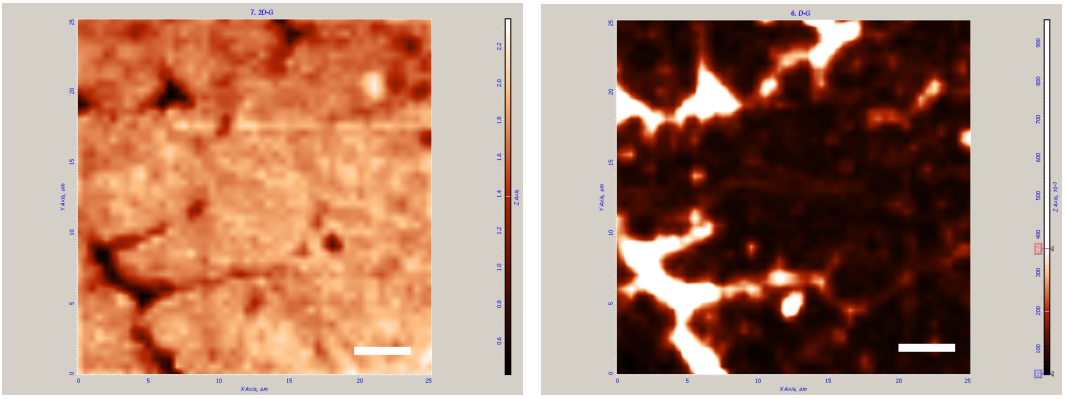


Figure S9. 2D/G (left) and D/G (right) Raman mapping of the graphene after transferring to SiO_2 substrate over 25 μm by 25 μm area. The results indicate the graphene obtained is dominantly monolayer. The scale bars are 4 μm.

3. Synthesis and characterization of QT and QTDA

Synthesis of 3, 3```-dioctyl-2,2`:5`,5``;2``,2```-quaterthiophene (QT)

The synthesis of QT was reported previously.[3] Yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.87 (t, J = 7.2 Hz, 6H), 1.28 (m, 16H), 1.37 (m, 4H), 1.64 (m, 4H), 2.77 (t, J = 7.8 Hz, 2H), 6.93 (d, J = 5.4 Hz, 2H), 7.01 (d, J = 3.6 Hz, 2H), 7.11 (d, J = 4.2 Hz, 2H), 7.16 (d, J = 4.8 Hz, 2H).

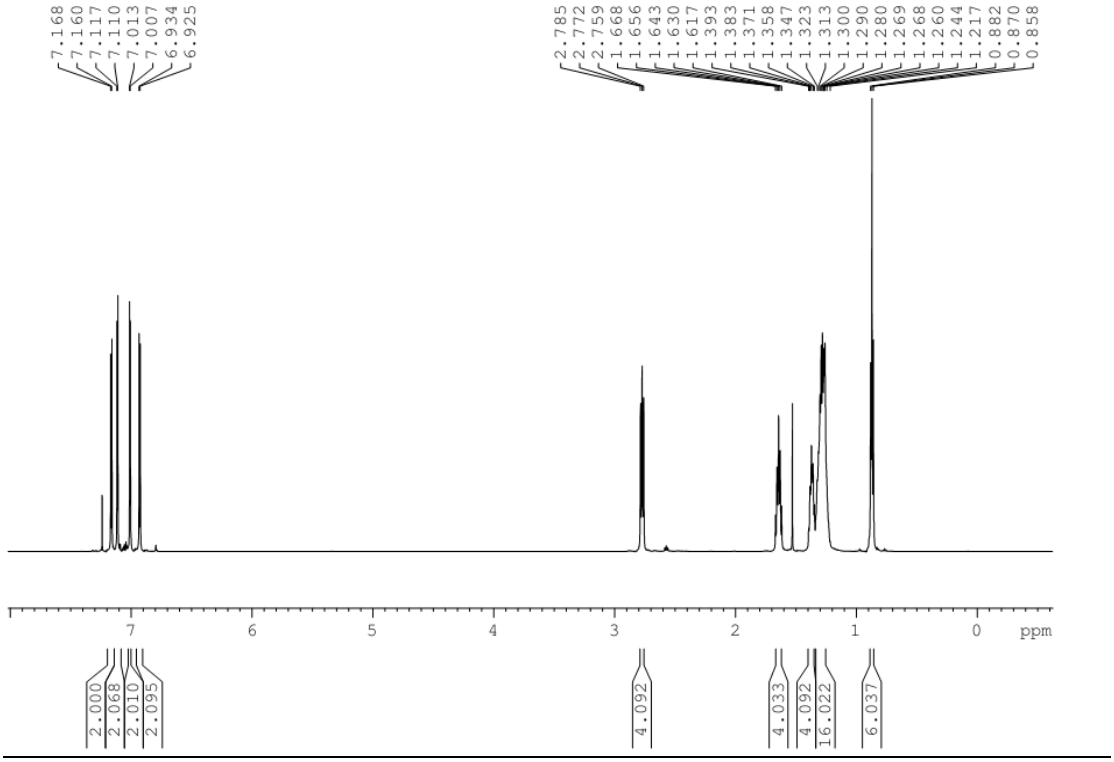
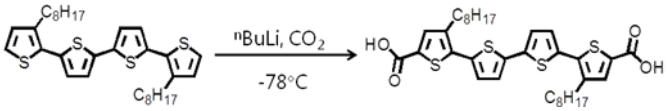


Figure S11 ^{1}H NMR (600 MHz, $CDCl_3$) of QT.

Synthesis of 3, 3```-dioctyl-2,2`;5`,5``:2``,2```-quaterthiophene-5,5'''-dicarboxy lic acid (QTDA)



QTDA was synthesized according to reported method.[4] 0.75 g (1.35 mmol) of QT was added to a flame dried two-neck round bottom flask (50mL) and the flask was evacuated and refilled with Ar (3x). 6.25 mL of dry THF was then added and reaction degassed with Ar for 10 minutes. The reaction mixture was cooled to - 78°C and 2.2 mL of ^{n}BuLi in hexane (1.60 M, 3.52 mmol) was added dropwise. The reaction mixture was allowed to warm to 0°C and stirred for 40 min. The reaction was then cooled down to -78°C and solid carbon dioxide was added and stirring was continued for 20 min at -78 °C and then 40 min at room temperature. 1M HCl was then added to terminate the reaction. The mixture was extracted with $CHCl_3$ and dried under vacuum after removing the solvent. The product was obtained as an orange-red solid (0.55 g, 0.86 mmol, 63%) and used without further purification. ^{1}H NMR (600 MHz, d_6-DMSO) δ = 0.82 (t, J = 7.00Hz, 6H), 1.23 (m, 20H), 1.61 (m, J = 5.2 Hz, 4H), 2.77 (t, J = 7.76 Hz, 4H), 7.33 (d, J = 3.87 Hz, 2H), 7.45 (d, J = 3.84 Hz, 2H), 7.63 (s, 2H), 13.18 (s, 2H); ^{13}C NMR (600 MHz, d_6-DMSO) δ = 14.39, 22.57, 29.01, 29.08, 29.13, 29.2, 30.11, 31.75, 125.87, 128.88, 132.39, 134.07, 136.39, 137.07, 140.75, 163.00. FT-IR 3400-2500 cm^{-1}, 2925 cm^{-1}, 2856 cm^{-1}, 1660 cm^{-1}, 1434 cm^{-1}, 1299 cm^{-1}, 932 cm^{-1}, 792 cm^{-1}. Melting point: 239-242°C. HRMS (EI): calcd for $[M+H]^+$ $C_{34}H_{42}O_4S_4$: 643.2039, found:643.2042.

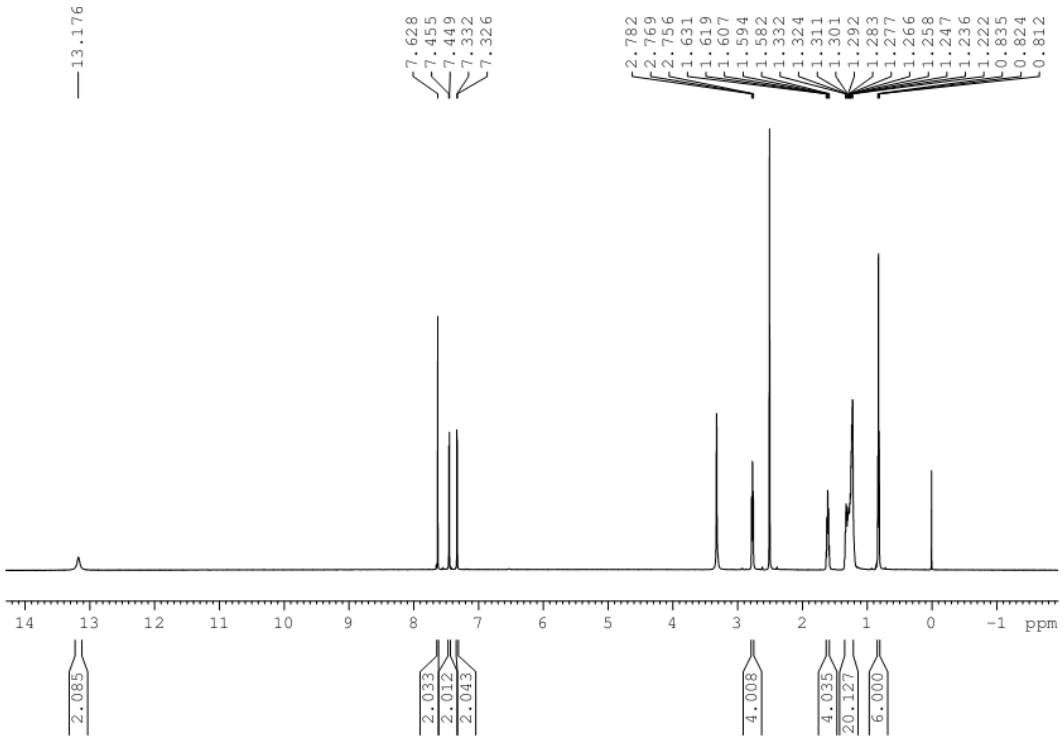


Figure S12 ^{1}H NMR (600 MHz, d_6-DMSO) of QTDA.

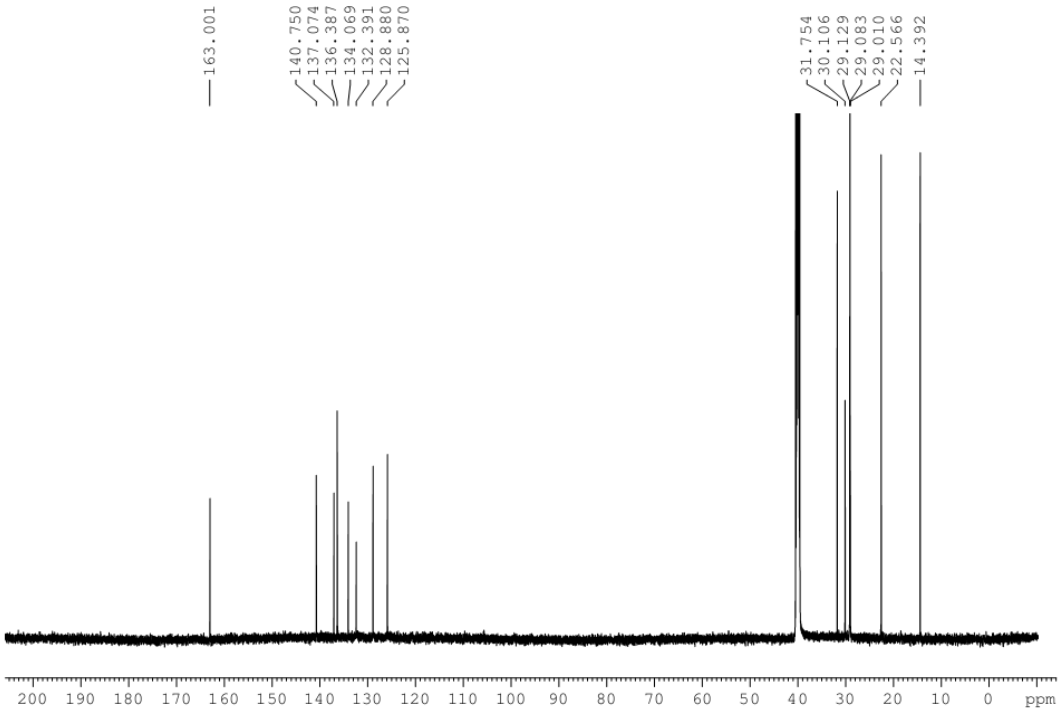


Figure S13. ^{13}C NMR (600 MHz, d_6-DMSO) of QTDA.

References:

（1）Zhang, J.; Hu, P. A.; Wang, X. N.; Wang, Z. L.; Liu, D. Q.; Yang, B.; Cao, W. W. *J. Mater. Chem.* **2012**, *22*, 18283.

（2）Li, X. S.; Cai, W. W.; An, J. H.; Kim, S. Y. ; Nah, J.; Yang, D. X.; Piner, R.; Velamakanni, A.;

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（3） Inouchi, K.; Kobashi, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *Org. Lett.* **2002**, *4*, 2533.

（4）Vadehra, G. S.; Wall, B. D.; Diegelmann, S. R.; Tovar, J. D. *Chem. Commun.* **2010**, *46*, 3947.