Supplementary Figure 1 | Experimental setup for crystal growth. Schematic drawing of the experimental setup for C₈-BTBT crystal growth.

Supplementary Figure 2 | AFM study of the C₈-BTBT crystal growth process on exfoliated graphene and BN. AFM images of C₈-BTBT layers grown on BN, along with the thickness measurement of (a) IL, (b) 1L, (c) 2L. The number of layers is marked on each figure. The thickness of the IL, 1L and 2L sample is ~0.53nm, 1.68nm and 2.85nm, respectively. The heights are similar to those on graphene, suggesting that the molecular packing is the same (Supplementary Figure 24).
Supplementary Figure 3 | Sequential AFM images of the growth process of C₈-BTBT on BN. The growth nucleates at certain points and proceeds nearly isotropically in a layer-by-layer manner, similar to the growth on graphene.
Supplementary Figure 4 | Sequential AFM snapshots of a graphene sample at different stages during a 95-minute growth. The scale bars are 2μm. The number of layers, nucleation sites, and the total growth time are marked on each image. (a) is the AFM image of the graphene sample before growth, showing defects such as cracks and wrinkles.
Supplementary Figure 5 | Thickness measurements of each layer for the first three layers. AFM images of (a) (b) IL, (c) (d) 1L and (e) (f) 2L C$_8$-BTBT grown on graphene along with the thickness measurements. The number of layers is marked in each image.
Supplementary Figure 6 | Sequential AFM images of the growth process of a 2L C$_8$-BTBT on graphene. (a) is the AFM image of the graphene substrate prior to growth. (b)-(f) are the AFM images taken after growing for 25, 35 55, 100, and 110 minutes, respectively. At stage (b), uniform and complete coverage of 1L is achieved. From (c)-(f), 2L starts to grow from the edges of graphene and proceed uniformly towards the inside. Only one extra nucleation site is observed in (d) during the growth of 2L. (g) and (h) are cross-polarized optical microscopy images of the sample in (f). The uniform color change clearly shows that the whole film is a single crystal. (i)-(l) are high-resolution AFM images taken at the marked positions in (f), where (i) and (j)
are close to one nucleation sites while (k) and (l) are close to the other. The unit cell vectors are marked in (i). α is defined as the angle between a and horizontal axis and is marked in every image. The four images show very close lattice orientation, consistent with the cross-polarized microscopy images in (g) and (h). The small difference in lattice orientation could be due to thermal drift of the samples during high-resolution AFM scan. Inset is the Fast Fourier Transform of the AFM image. The scale bars are 2nm.

**Supplementary Figure 7 | AFM images of IL C₈-BTBT grown on graphene.** The growths are terminated just before the completion of IL to characterize the thickness. Excellent uniformity is achieved in all the samples.
Supplementary Figure 8 | AFM images of 1L C₈-BTBT grown on graphene. The samples in (a) and (b) are completely covered by 1L of C₈-BTBT as determined from the total thickness of the sample. The sample in (c) is partially (but uniformly) covered by 1L of C₈-BTBT. The clear boundary between the 1L and IL implies that the growth is epitaxial in nature. Good reproducibility allows us to frequently obtain IL and 1L C₈-BTBT (nearly) completely covering graphene by controlling the growth time.

Supplementary Figure 9 | Characterizations of 1L C₈-BTBT grown on exfoliated graphene with size of ~80μm. (a) Optical microscopy and (b) AFM images of the sample. (c) and (d) are cross-polarized optical microscopy images of the sample. (e)-(i) are the high-resolution AFM images of 1L taken from different spots marked in (a). The unit cell vectors are marked in (e). α is defined as the angle between a and horizontal axis and is marked in every image. Inset is the Fast Fourier Transform of the AFM image. The scale bars are 1nm. (j) Zoom-in AFM image from the blue rectangle in (b). The step height of 1.69nm suggests that the whole sample is covered.
by 1L C₈-BTBT. From the AFM and cross-polarized microscopy images, we can confirm single-crystalline 1L C₈-BTBT over the entire sample.

Supplementary Figure 10 | High-resolution AFM images of the IL C₈-BTBT crystal on the same graphene sample in Supplementary Figure 9. (a) Optical microscopy image of the sample. (b)-(g) High-resolution AFM phase images of the IL C₈-BTBT crystal taken at different spots marked in (a). The scale bars are 2nm. Compared to the high-resolution images in Supplementary Figure 9, these images are taken with increased drive amplitude of the cantilever to obtain the information of IL. The crystal orientations match very well for different spots, indicating the single-crystalline nature of IL. The measured periods of two orthogonal directions are 2.72nm and 0.73nm respectively, close to the STM results in the main text.
Supplementary Figure 11 | Characterizations of 1L C₈-BTBT grown on exfoliated graphene with size of ~50μm. (a) Optical microscopy and (b) AFM images of the sample. (c) (d) Cross-polarized optical microscopy images of the sample. The scale bars are 4μm. (e)-(j) are the high-resolution AFM images of 1L taken from different spots in (a). The unit cell vectors are marked in (e). α is defined as the angle between a and horizontal axis and is marked in every image. Inset is the Fast Fourier Transform of the AFM image. The scale bars are 2nm. From the AFM and cross-polarized microscopy images, we can confirm single-crystalline 1L C₈-BTBT over the entire sample.
Supplementary Figure 12 | Root mean square roughness measurements. Root mean square roughness ($R_q$) analyses of SiO$_2$ substrate (a) and (b), exfoliated monolayer graphene on SiO$_2$ (c) and (d), and BN substrate (e) and (f) used in this work. The $R_q$ values are shown in each figure. The scale bars are 1μm. The $R_q$ of SiO$_2$ and graphene is similar (~0.14-0.17nm) while that of BN is the smallest (~0.09nm), consistent with literature. All the substrates have very small $R_q$, which is important for the high quality epitaxial growth.
Supplementary Figure 13 | Raman spectroscopy study of C₈-BTBT crystals. (a) Raman spectrum of C₈-BTBT crystals on graphene. The peak near 1470cm⁻¹ is from C₈-BTBT, consistent with Supplementary Reference 1. Another peak at 1550cm⁻¹ overlaps with graphene G peak and is difficult to observe. Left inset shows the optical image of the sample. The green dot marks the position where the spectrum is taken. Right inset shows the AFM image of the C₈-BTBT crystal grown on graphene. The 1.6nm step height suggests that the area on the left is 1L. (b) Raman spectrum of the same C₈-BTBT crystal in Fig. 1g. The C₈-BTBT peak at 1470cm⁻¹ is clearly visible, although the intensity is low due to the monolayer thickness of the sample. Fig. 1h shows the Raman mapping of C₈-BTBT peak at 1470cm⁻¹.
Supplementary Figure 14 | DFT calculations of the structure of C₈-BTBT IL on graphene. Different configurations of C₈-BTBT molecule adsorbed on graphene (side view) considered in DFT calculations (a-f) and their binding energies (g). Structure A, “stand-up” configuration in which the benzothiophene is parallel to graphene while the carbon chains “stand” up on graphene with the height of 1.04nm. Structures B-D, the C₈-BTBT molecule leans gradually on graphene with the angle of 8, 16, and 24 degrees respectively. Structure E, C₈-BTBT molecule completely lay down on top of graphene, the alkly chains are almost parallel with the graphene layer. The leaning angle is ~35 degree compared to A. Structure F, from Structure E, the benzothiophene plane is rotated until it is also parallel with the graphene layer. The
grey thick lines in (a)-(f) represent the graphene layer. The binding energy $E_b$ is calculated from the formula $E_b = E(C_8\text{-BTBT}) + E(\text{graphene}) - E(C_8\text{-BTBT@graphene})$, where the three terms on the right hand side are the total energy of C$_8$-BTBT molecule, graphene and a single C$_8$-BTBT molecule on graphene, respectively. As expected, Structure F is much more stable than any other configurations because of the strongest $CH-\pi$ interactions and the $\pi-\pi$ interactions.

Supplementary Figure 15 | The binding energy per molecule of C$_8$-BTBT IL crystals on graphene as a function of lattice constant along (a) $d_1$ direction and (b) $d_2$ direction. The structure is the fully relaxed structure shown in Fig. 2b of main text.
Supplementary Figure 16 | DFT calculations of the structure of C₈-BTBT IL on graphene. (a)-(e): Five different configurations of two C₈-BTBT molecules on top of graphene. (f) Binding energy per molecule for the different configurations. The configuration in (a) is the most stable one.
Supplementary Figure 17 | DFT calculations of the structure of C₈-BTBT IL on graphene. (a)-(c): Three different configurations of two C₈-BTBT dimers on top of graphene. (d) Binding energy per molecule for the different configurations. The configuration in (c) is the most stable one.
Supplementary Figure 18 | DFT calculations of the structure of C₈-BTBT IL on graphene. (a) and (b): Different configurations for 8 C₈-BTBT molecules on graphene. (c) and (d): Different configurations for 12 C₈-BTBT molecules on graphene. Eₘ represents binding energies per molecule. For the 12-molecule cluster, 2D growth in (c) is more stable.
Supplementary Figure 19 | DFT calculations of the structure of C₈-BTBT IL on graphene. (a)-(c) Different configurations of an 8-C₈-BTBT cluster adsorbed on graphene. In (b) and (c), the cluster is rotated clockwise by 12 degrees and 32 degrees respectively with respect to the origin direction in (a), where the benzothiophene align with the armchair direction of graphene layer. (d) Relative energy of the system as a function of the rotation angle between the cluster and graphene. A global energy minimum is observed for the configuration in (b).
Supplementary Figure 20 | 1L C₈-BTBT molecule adsorbed on IL@graphene and IL@BN. An 1L C₈-BTBT molecule adsorbed on IL@graphene (a) and IL@BN (c). Two 1L C₈-BTBT molecules adsorbed on IL@graphene (b) and IL@BN (d). The binding energy is 0.069eV (0.048eV) between the single 1L C₈-BTBT molecule and IL@graphene substrate (IL@BN substrate). The binding energy between two 1L C₈-BTBT molecules is 0.651eV and 0.704eV for graphene and BN substrate respectively. The fact that interlayer interaction is much weaker than the intralayer interaction suggests the effective decoupling of 1L from the underlying substrate.
Supplementary Figure 21 | Large-area STM image of graphene monolayer grown on Cu foils. (a) is taken at $V_{\text{sample}} = -1.00\, \text{V}$ and $I = 20.6\, \text{pA}$. (b) is taken at $V_{\text{sample}} = 1.20\, \text{V}$ and $I = 12.7\, \text{pA}$.

Supplementary Figure 20 | A topographic STM image of a C$_8$-BTBT IL on graphene/Cu foil recorded at $V_{\text{sample}} = -1.36\, \text{V}$ and $I = 4.2\, \text{pA}$. The periodic structure of the C$_8$-BTBT IL is clearly observed. The single-crystalline structure of the C$_8$-BTBT sheet can maintain over the steps and grain boundaries of the substrate.
Supplementary Figure 23 | (a) A typical high-resolution topographic STM image of a C$_8$-BTBT IL on CVD graphene recorded at $V_{\text{sample}} = -0.91$ V and $I = 11.6$ pA. It is easy to observe large-area uniform IL in our samples. The angle between the alkyl chains and the benzothiophene is measured to be $140^\circ$, which agrees well with the result $\sim 134^\circ$ obtained from DFT calculation. The atomic structure of the C$_8$-BTBT monolayer is overlaid on the STM image. (b) The section scans along the color lines in panel (a). In (b), we can see a $\pi/2$ phase shift between line a/c and line b. (c) Calculated height profile from the structure in Fig. 2b along the same lines in (b). The phase shift was consistent with experimental results in (b).
**Supplementary Figure 24 | High resolution AFM studied of C₈-BTBT crystals.** (a) High-resolution AFM image of 1L C₈-BTBT on graphene. The unit cell is marked. Inset is the Fast Fourier Transform of the AFM image. (b) AFM image of C₈-BTBT grown on BN. The number of layers is marked on the image, together with the height of each layer. (c) High-resolution AFM image of 1L C₈-BTBT on BN. The unit cell is marked. Inset is the Fast Fourier Transform of the AFM image. (d) High-resolution AFM image of 2L C₈-BTBT on BN. The unit cell is marked. Inset is the Fast Fourier Transform of the AFM image. (e) High-resolution AFM image of bare BN substrate. Inset is the Fast Fourier Transform of the AFM image. The lattice is hexagonal as expected, in clear contrast to the C₈-BTBT crystals.
Supplementary Figure 25 | Transport of graphene before and after deposition of C$_8$-BTBT. Transfer characteristics of two graphene devices before (black line) and after (red line) deposition of few-layer C$_8$-BTBT. $V_{ds}=10$mV in all cases. Blue lines are theoretical fittings to extract the mobility. The mobility values for electron and hole are listed in the Supplementary Table 1.

Supplementary Figure 26 | Optical microscopy images of large-area 1L C$_8$-BTBT grown on CVD graphene. The coverage of C$_8$-BTBT is marked on every image. The scale bars are 35$\mu$m.
Supplementary Figure 27 | AFM images of C₈-BTBT grown on CVD graphene.

(a)-(f) Large area AFM images of C₈-BTBT grown on CVD graphene. The C₈-BTBT are predominantly 1L, with small amount of 2L and voids. The scale bars are 5μm. (g) and (h) are high resolution AFM images of 1L C₈-BTBT on CVD graphene taken at two different positions. The unit cell vectors are marked in (g). The molecular packing is the same as 1L C₈-BTBT on exfoliated graphene. The scale bars are 1nm.
Supplementary Figure 28 | Cross-polarized optical microscopy images of C$_8$-BTBT film on CVD graphene. The C$_8$-BTBT is poly-crystalline with average domain size of tens of micrometers. The green dashed lines represent a graphene wrinkle, which strongly affects the growth. Many grain boundaries fall on the wrinkle. The scale bars are 25μm.

Supplementary Figure 29 | Energy band diagram of vertical FETs. Energy band diagram of the vertical FETs under $V_{ds}=0$ and $V_s=0$. 
**Supplementary Figure 30 | More data on vertical C$_8$-BTBT OFETs.** Double sweep $J_{ds}$-$V_g$ characteristics of the device in Fig. 3a. From top to bottom, $V_{ds}$=2V and 1V, respectively. We observe small but finite hysteresis in this device. Since the top Au electrodes were transferred on top of C$_8$-BTBT layers in ambient conditions, the hysteresis is likely due to the trapped molecules in the C$_8$-BTBT/Au interface. These molecules can be minimized by shortening the exposure time in ambient, or performing the transfer in a glove box.
Supplementary Figure 31 | More data on vertical C$_8$-BTBT OFETs

(a) (b) $J_{ds}$-$V_g$ characteristics of the same device in Fig. 3a at 260K and 160K, respectively. The current is very sensitive to temperature under forward bias but does not change much under reverse bias. From top to bottom, $V_g$=-100V, -90V, -80V, -70V and 0V, respectively. (c) $J_{ds}$ as a function of $1/T$ of the device under $V_{ds}$=-2V and $V_g$=-100V. (d) Room temperature $J_{ds}$-$V_{ds}$ characteristics of another device with 19-layer thick C$_8$-BTBT. From top to bottom, $V_g$=-100V, -90V, -80V, -70V, -60V, -50V and -10V, respectively. (e) Room temperature $J_{ds}$-$V_g$ characteristics of the same device in (d). From top to bottom, $V_{ds}$=2V and 1V, respectively. The $J_{ds}$ at on-state was slightly higher than the thinner device in Fig. 3a, likely due to the difference in contact resistance.
Supplementary Figure 32 | More data on planar C$_8$-BTBT OFETs. (a) Room temperature $I_{ds}$-$V_g$ characteristics ($V_{ds}$=-1V) of a planar monolayer C$_8$-BTBT FET on BN. Black and blue lines are drawn in linear and log scales, respectively. Inset shows the optical microscopy image of the device. (b) $I_{ds}$-$V_{ds}$ characteristics of the device. From top to bottom, $V_g$=-10V, -25V, -30V, -35V and -40V, respectively. (c) The extracted $\mu$-$V_g$ relationship at room temperature. The peak mobility is over 5cm$^2$V$^{-1}$s$^{-1}$ for this device. (d) AFM image in the channel of the device after C$_8$-BTBT crystal growth. There exists a small hole with a step height of ~2.2nm (IL+1L), which confirms that the top layer is 1L. The inset shows the height profile along the dashed line.
Supplementary Figure 33 | More data on planar C₈-BTBT OFETs. (a) Room temperature double-sweep $I_{ds}$-$V_g$ characteristics ($V_{ds}$=−0.2V), with little hysteresis. Black and blue lines are drawn in linear and log scales respectively. Inset shows the extracted $\mu$-$V_g$ relationship, the peak mobility is 4.3cm²V⁻¹s⁻¹. (b) $I_{ds}$-$V_{ds}$ characteristics of the device in (a). From top to bottom, $V_g$=−10V, -25V, -30V, -35V and -40V, respectively. Inset shows the optical microscopy image of the device. Scale bar, 30μm. (c) Variable-temperature $I_{ds}$-$V_g$ characteristics ($V_{ds}$=−0.2V) of the device in (a) at 300K, 290K, 270K and 250K, respectively (from top to bottom). Inset shows $\mu$ as a function of temperature.

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Supplementary Table 1 | The mobility values for electron and hole. The high mobility values after deposition strongly suggest the weak coupling between graphene and C₈-BTBT layers.
**Supplementary note 1: Molecular structure of C₈-BTBT molecules on graphene.**

In order to understand the growth process of IL, we first need to find the most stable configuration of C₈-BTBT dimers as the building block. In Supplementary Figure 16 we calculate the energy of five different configurations, and find that the most stable configuration appears when the two molecules are closely packed. This is expected because the interaction between the two molecules is strongest in this configuration.

Next, using the most stable dimer as the building block, we can build the quadrumer. Supplementary Figure 17 shows three different configurations, and the most stable one is (c) where the interaction between the dimers is the strongest. At this stage, 1D growth is still favorable.

Similarly, we can build larger clusters with the building blocks. However, as we increased the size of the cluster to some point, 1D growth starts to become less favorable because interaction only occurs between one pair of C₈-BTBT molecules. At this point, 2D growth happens. In Supplementary Figure 18 we calculate the clusters with 8 and 12 C₈-BTBT molecules. For the 8-molecule cluster, 1D and 2D configuration have very similar binding energies (2D growth is slightly more stable). For the 12-molecule cluster, the preference of 2D growth becomes more evident. Therefore, we conclude that the 2D growth of IL C₈-BTBT molecules is a natural result of the interactions between the molecules.

**Supplementary note 2: large-area single crystals of C₈-BTBT epitaxially grow on graphene**

To understand why large-area single crystals of C₈-BTBT can epitaxially grow on graphene, we further calculate the total energy of a C₈-BTBT cluster and graphene as a function of the rotation angle between them (Supplementary Figure 19). We find that there exists a global energy minimum, where the IL C₈-BTBT is the most stable. This explains why IL C₈-BTBT can form a large single crystal on graphene (Supplementary Figure 10), even with multiple nucleation sites. However, we note that the energy difference is on the order of 0.2eV, which is not very large. So it is still possible to have multiple domains on the same exfoliated graphene, as shown in Fig.
Supplementary note 3: STM study of C₈-BTBT crystals on graphene

In our STM experiment, we use monolayer CVD graphene grown on Cu foil as the substrate. Before the growth of the C₈-BTBT films, the graphene on Cu foil was studied carefully by STM. Supplementary Figure 21 shows two typical large-area STM images recorded at different positions of the as-grown sample. The sample is overall very flat with small corrugated areas and with some steps on the copper surface. Our STM studies indicate that the graphene sheet can cross over the copper steps and maintain a continuous structure. Since high resolution STM scans are usually recorded in small areas like 10nm × 10nm, the substrate roughness is very small and does not affect the STM measurement. Supplementary Figure 22 shows a large-area STM image of the IL C₈-BTBT film on CVD graphene. The periodic structure in the C₈-BTBT film can clearly be observed. The C₈-BTBT over-layer can maintain a continuous single-crystalline structure over the grain boundaries and steps of the graphene surface. This result also implies that the interaction between graphene and the C₈-BTBT is very weak, consistent with the vdW epitaxy.

Supplementary note 4: C₈-BTBT crystal growth on CVD graphene

The growth on CVD graphene has two major challenges compared to exfoliated graphene. 1. Our CVD graphene samples are poly-crystalline with average domain size on the order of tens of micrometers. 2. After transfer, there are unavoidable wrinkles, cracks and small amount of PMMA residue on graphene samples, which strongly affect the growth of C₈-BTBT crystals (see Fig. 1 of main text and related discussions). Despite these challenges, we are able to grow large-area C₈-BTBT films on CVD graphene, with over 90% coverage. Supplementary Figure 26 and 27 show the optical and AFM images of typical C₈-BTBT films on CVD graphene. The C₈-BTBT films are predominantly 1L, with small areas of voids and 2L.

To further characterize the C₈-BTBT films on CVD graphene, we carry out cross-polarized microscopy (Supplementary Figure 28). The films are poly-crystalline, with similar domain size as the graphene substrate. This is not surprising considering
the epitaxial nature of the growth. Therefore, we attribute the poly-crystalline nature mainly to the underlying graphene substrate. But other impurities such as winkle and cracks also affect the growth and are expect to make the C₈-BTBT domain even smaller (Supplementary Figure 28).

**Supplementary References:**
