## Supplementary material

## I. Band structures of atomic layer-stacked superlattices

For each proposed superlattice, energy bands are calculated along  $\Gamma$ -A-L-M-K-H-A- $\Gamma$  direction in reciprocal space as shown in Fig. S1. Two methods are used to identify the band lines of different materials: referring to PDOS and comparing the shape of band lines between superlattices and free standing component materials along M- $\Gamma$ -K-M direction.

In Fig. S2, the band lines of  $(\text{graphene})_2(\text{BN})_2$  superlattices are distinguished by comparing the energy levels with the peaks of PDOS. For instance, two  $E_{L-M}$  energy levels occur at M point around 1.8 eV, corresponding to the two peaks at PDOS of carbon atoms and zero state of boron or nitrogen atoms. Therefore, these two energy levels should belong to graphene, identified by blue lines (BN by red lines).

In contrast, for some superlattices such as  $(C_4F)_2(CH)_2$  in Fig. S3, we cannot identify the band lines by PDOS, because both the component materials have carbon atoms. Thus, the band structures of isolated  $C_4F$  and CH along M- $\Gamma$ -K-M direction are compared with that of  $(C_4F)_2(CH)_2$  superlattices. The shape of CH band lines (blue lines in the left sub-plot) is very different with that of  $C_4F$  (red lines), making their own band lines easy to distinguish in the band structure of layer-stacked superlattice.



Fig. S1: The schematic of Brillouin zone for the layer-stacked superlattices based on graphene and graphene-like materials.



Fig. S2: Band structures of  $(graphene)_2(BN)_2$  superlattices and PDOS of different atoms.



Fig. S3: Band structures of isolated  $C_4F$  and CH along M- $\Gamma$ -K-M direction on the left, band structure of  $(C_4F)_2(CH)_2$  superlattices in the middle and its corresponding PDOS on the right. The red and blue band lines belong to  $C_4F$  and CH, respectively.

## II. Dependence of layer-stacked superlattices on well width

Figs. S4-S8 show the band structures of graphene/CF, graphene/CH, BN/CF, BN/CH, and CF/CH superlattices in conditions of different barrier/well widths. In electron/hole potential wells, the continuous subbands ( $B_{L-M}$ ) or quantized energy levels ( $E_{L-M}$ ) along L-M direction are consistent with the number of well layers while those along K-H direction ( $E_{K-H}$ ) are not. For example, Fig. S4 shows that the number of  $E_{L-M}$  levels or  $B_{L-M}$  subbands in (graphene)<sub>n</sub>(CF)<sub>m</sub> superlattices is equal to the number of graphene layers in one period. However, it is not true for  $E_{K-H}$  levels or  $B_{K-H}$  subbands. Other proposed layer-stacked superlattices abide by the same rule as shown in Figs. S5-S8.



Fig. S4: Energy bands of graphene/CF superlattices with different barrier/well width. The number of  $E_{L-M}$  levels ( $B_{L-M}$  subbands) in hole potential wells is consistent with the number of graphene layers in one period.



Fig. S5: Energy band structures of graphene/CH superlattices with different barrier/well width. The number of  $E_{L-M}$  levels ( $B_{L-M}$  subbands) in electron potential wells is equal to the number of graphene layers in one period.



Fig. S6: Energy band structures of BN/CF superlattices with different barrier/well width. The number of  $E_{L-M}$  levels in the hole potential wells is equal to the number of BN layers in one period.



Fig. S7: Energy band structures of BN/CH superlattices with different barrier/well width. The number of  $E_{L-M}$  levels ( $B_{L-M}$  subbands) in electron potential wells is consistent with that of BN layers in one period.



Fig. S8: Energy band structures of CH/CF superlattices with different barrier/well width. The number of  $E_{L-M}$  levels in electron potential wells is equal to the number of CF layers in one period.