Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

In this work, three typical stacking patterns with 90° twisted are taken into consideration. As stated in the main content, the supercell of the twisted α-PC bilayer is composed of two layers of 1×3 unit cell of monolayer with an interlayer rotation of 90°. Using the bottom layer as a reference, in configuration I (Figs. S1(a)-(b)), the top layer only rotate 90° and then stack vertically on the bottom layer. In configuration II (Figs. S1(c)-(d)) or III (Figs. S1(e)-(f)), the top layer move $0.5d_x$ or $0.5d_y$ along the *x* or *y* direction after 90° rotation and then stack vertically on the upper layer, where d_x and d_y are the length of the six-membered ring in the corresponding direction. As shown in the table R1, the binding energies of the three configurations are calculated respectively. Configuration I shows lowest binding energy, which is the structure used in this paper. To further verify the dynamic stability of the 90° twisted α-phosphorus carbide (α-PC) bilayer, the phonon spectrum (Fig. S2) of configuration I is calculated, and no imaginary frequency appears.

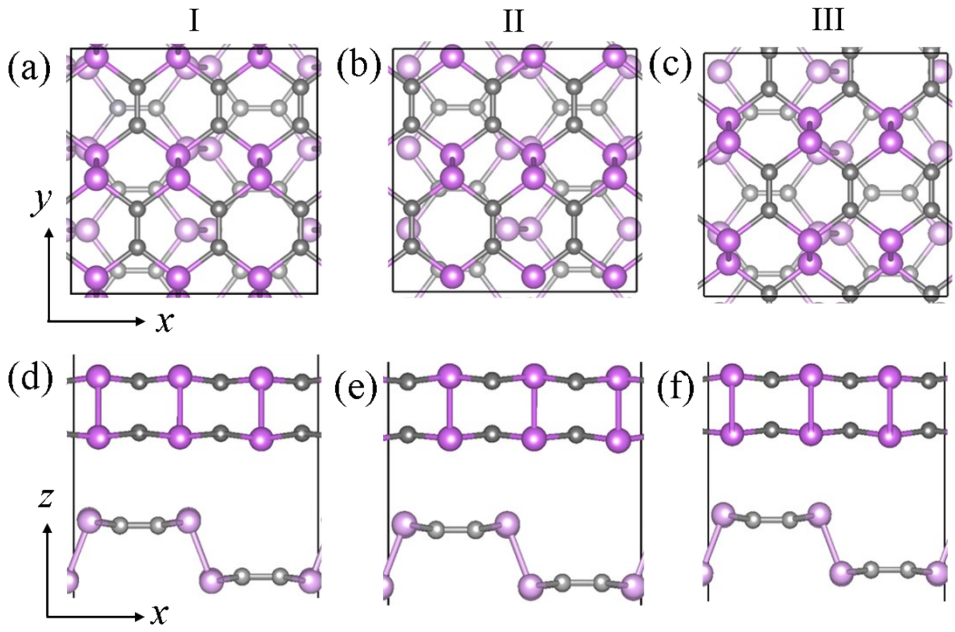

Figure S1. The top and side views of three different stacked patterns of 90° twisted α-phosphorus carbide bilayer. (a) and (b) are configuration I, (c) and (d) are configuration II, (e) and (f) are configuration III. The purple and gray balls denote P and C atoms, respectively.

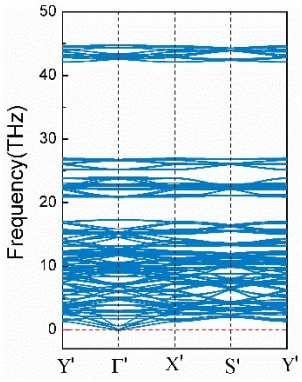

Figure S2. The phonon spectrum band diagram of 90° twisted α-PC bilayer (configuration I).

Table S1. The binding energies of different configurations

	monolayer	AB stacked	90° twisted		
			I	II	III
E_{TOT}(eV)	-56.29	-113.15	-339.18	-338.98	-338.99
E_b (eV/unit cell)	/	-0.29	-0.24	-0.21	-0.21

Calculations using hybrid functional methods[1] have been taken to evaluate the band gap and optical properties of 90° twisted α-PC bilayer. As shown in Fig. S3, the band structure calculated by HSE06 hybrid functional method shows generally similar characters with that obtained by PBE, only the band gap increased from 0.39 eV to 0.99 eV. The carrier effective mass calculated by HSE06 are slightly larger than the corresponding ones based on PBE method, as listed in Table S2. Therefore, the PBE method is used to calculate the subsequent band diagrams of 90° twisted α-PC bilayer.

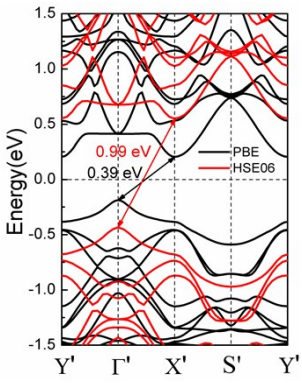

Figure S3. (a)The band diagram by PBE (black) and HSE06 (red).

Table S2. The carrier effective mass of 90° twisted α-PC bilayer by PBE and HSE06 methods.

	$m_e^*(m_0)$		$m_h^*(m_0)$	
	Γ′-X′	Γ′-Y′	Γ′-X′	Γ′-Y′
PBE	0.25	0.25	-0.29	-0.29
HSE06	0.28	0.29	-0.40	-0.40

When the electric field intensity (D) increases to 0.8 eV/Å, the band structure (PBE) of 90° twisted α-PC bilayer changes from indirect to direct (Fig. S4). Their CBM are both located in Γ', and the flat energy dispersions near Γ' point disappear.

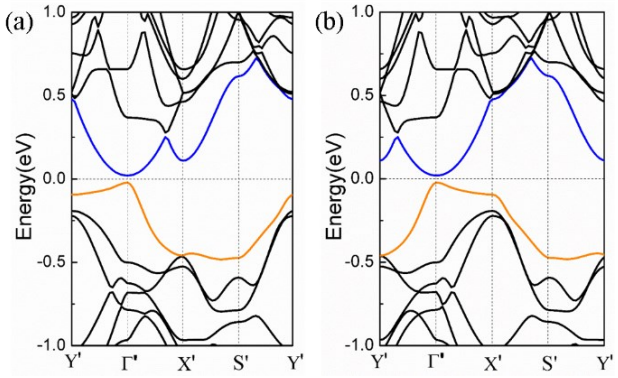

Figure S4. The band diagram of 90° twisted α-PC bilayer under the electric field. (a) 0.8 eV/Å and (b) -0.8 eV/Å.

Reference

[1] Heyd J, Scuseria G E, Ernzerhof M. Hybrid functionals based on a screened Coulomb potential[J]. Journal of Chemical Physics, 2003, 118(18): 8207–8215.