Electronic Supplementary Information

Origins of Dirac cones and pairity dependent electronic structures of α-graphyne derivatives and silagraphynes

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S1 First-principles molecular dynamics calculations of α-graphyne

We carried out first-principles molecular dynamics calculations at the NVT ensemble for α-graphyne at 600 K in a 32-atom cell (Fig. S1). The structure did not collapse in 3.5 ps. The atom structure of α-graphyne at 0 ps and 3.5 ps are shown in Fig. S1.
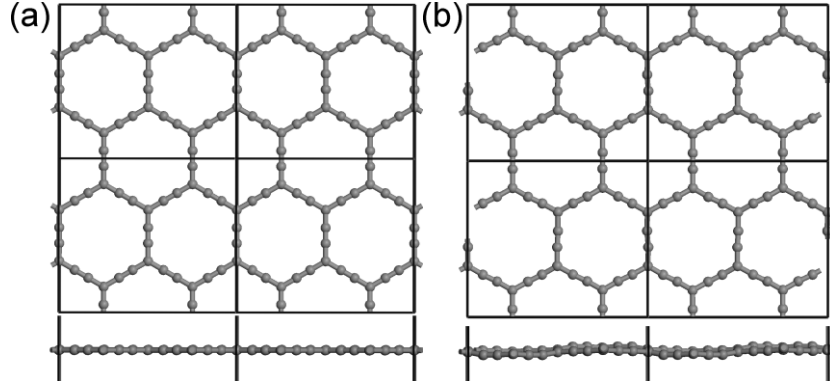

Fig. S1 Atom structure of α-graphyne at 0 ps (a) and 3.5 ps (b). The upper figures are top view, and the lower figures are side view.

S2 Derivations of the *H* matrix elements

For a periodic system, under Tight Binding frame, the Bloch wave functions generally are written as:

$$\psi_{\mathbf{k}}(r) = \frac{1}{\sqrt{N}} \sum_n [\sum_i C_i \varphi_i(\mathbf{r} - \mathbf{R}_n - \mathbf{r}_i) e^{i\mathbf{k}\cdot\mathbf{r}_i}] e^{i\mathbf{k}\cdot\mathbf{R}_n} \tag{1}$$

where, $\mathbf{R}_n$ is the vector of the origin of the *n*-th cell, $\mathbf{r}_i$ is the vector of the *i*-th atom in the *n*-th cell relative to $\mathbf{R}_n$, $\varphi_i(\mathbf{r} - \mathbf{R}_n - \mathbf{r}_i)$ is the wave function of the *i*-th atom in the *n*-th cell, and C_i are the coefficients required to be fixed further. The eq. (1) can be deduced further as:

$$\begin{aligned}
\psi_{\mathbf{k}}(\mathbf{r}) &= \frac{1}{\sqrt{N}} \sum_i C_i [\sum_n \varphi_i(\mathbf{r} - \mathbf{R}_n - \mathbf{r}_i) e^{i\mathbf{k}\cdot\mathbf{R}_n}] e^{i\mathbf{k}\cdot\mathbf{r}_i} \\
&= \sum_i C_i' [\frac{1}{\sqrt{N}} \sum_n \varphi_i(\mathbf{r} - \mathbf{R}_n - \mathbf{r}_i) e^{i\mathbf{k}\cdot\mathbf{R}_n}]
\end{aligned} \tag{2}$$

where $C_i' = C_i e^{i\mathbf{k}\cdot\mathbf{r}_i}$ still are the coefficients required to be fixed further. The derivation of eq. (2) is based on the fact that $\mathbf{r}_i$ and C_i are constants for various cells. Based on eq. (2), the basis Bloch wave functions can be written as

$$\varphi_{i\mathbf{k}}(r) = \frac{1}{\sqrt{N}}\sum_n \varphi_i(\mathbf{r} - \mathbf{R}_n - \mathbf{r}_i)e^{i\mathbf{k}\cdot\mathbf{R}_n} \tag{3}$$

In eq. (3), for the same cell, different atoms possess the same exponential factors $e^{i\mathbf{k}\cdot\mathbf{R}_n}$, which makes the further calculations easier.

Similarly, for α-graphyne, we chose basis Bloch wave functions as eq. (5) and (6) in the manuscript. Then the matrix elements of H (defined in the manuscript) can be obtained (the cells shown in Fig. 1(d) in the manuscript are adopted):

$$
\begin{aligned}
H_{2_b A} &=_{\mathbf{k}}\left\langle \varphi_{2_b}\left|\hat{H}\right|A\right\rangle_{\mathbf{k}} = (\frac{1}{\sqrt{N}}\sum_m {}_m\left\langle \phi_{2b}\left|e^{-i\mathbf{k}\cdot\mathbf{R}_m}\right.\right)\hat{H}(\frac{1}{\sqrt{N}}\sum_n |C_A\rangle_n\, e^{i\mathbf{k}\cdot\mathbf{R}_n}) \\
&= {}_0\left\langle \phi_{2b}\left|e^{-i\mathbf{k}\cdot 0}\hat{H}(\sum_n |C_A\rangle_n\, e^{i\mathbf{k}\cdot\mathbf{R}_n})\right.\right. \\
&= \frac{1}{\sqrt{2}}({}_0\langle C_3| + {}_0\langle C_4|)\hat{H}(\sum_n |C_A\rangle_n\, e^{i\mathbf{k}\cdot\mathbf{R}_n}) \\
&= \frac{1}{\sqrt{2}}{}_0\left\langle C_3\left|\hat{H}\right|C_A\right\rangle_0 e^{i\mathbf{k}\cdot 0} = \frac{-t}{\sqrt{2}}
\end{aligned}
\tag{4}
$$

$$
\begin{aligned}
H_{2_b B} &=_{\mathbf{k}}\left\langle \varphi_{2_b}\left|\hat{H}\right|B\right\rangle_{\mathbf{k}} = (\frac{1}{\sqrt{N}}\sum_m {}_m\left\langle \phi_{2b}\left|e^{-i\mathbf{k}\cdot\mathbf{R}_m}\right.\right)\hat{H}(\frac{1}{\sqrt{N}}\sum_n |C_B\rangle_n\, e^{i\mathbf{k}\cdot\mathbf{R}_n}) \\
&= {}_0\left\langle \phi_{2b}\left|e^{-i\mathbf{k}\cdot 0}\hat{H}(\sum_n |C_B\rangle_n\, e^{i\mathbf{k}\cdot\mathbf{R}_n})\right.\right. \\
&= \frac{1}{\sqrt{2}}({}_0\langle C_3| + {}_0\langle C_4|)\hat{H}(\sum_n |C_B\rangle_n\, e^{i\mathbf{k}\cdot\mathbf{R}_n}) \\
&= \frac{1}{\sqrt{2}}{}_0\left\langle C_4\left|\hat{H}\right|C_B\right\rangle_{\mathbf{b}} e^{i\mathbf{k}\cdot\mathbf{b}} = \frac{-t}{\sqrt{2}}e^{i\mathbf{k}\cdot\mathbf{b}}
\end{aligned}
\tag{5}
$$

The other matrix elements can be obtained similarly. The rules about the exponential factors are that the exponential factor is 1 when the two wave functions (used to form the corresponding matrix element) are in the same cell, or $e^{i\mathbf{k}\cdot(\mathbf{R}_n - \mathbf{R}_m)}$ when the two functions are different cells, where $\mathbf{R}_n$ and $\mathbf{R}_m$ are the vectors of the origins of the cells located in by the latter wave function

and the former wave function, respectively. (The latter wave function and the former wave function are the two wave functions to be used to form the corresponding matrix element.)

We found that if the basis Bloch wave functions like eq. (3) are adopted, the corresponding Hamilton matrix elements will be simple and the exact positions of the atoms are not required. The only required information is the neighbors of the atoms and the corresponding hopping energy. Our previous work[1] adopted the similar form for the basis Bloch wave functions.

S3 Atom structures of C$_2$Si$_6$-SGY, C$_2$C$_3$Si$_3$-SGY with lower energy

We constructed C$_2$Si$_6$-SGY and C$_2$C$_3$Si$_3$-SGY models by modifying the configuration of α-graphyne, and carried out geometry optimization. Atom structures with lower energy were obtained as shown in Fig. S2. The corresponding lattice parameters and formation energy are listed in in Table S1. The definitions of formation energy E_f and E'_f are in the manuscript (MS).
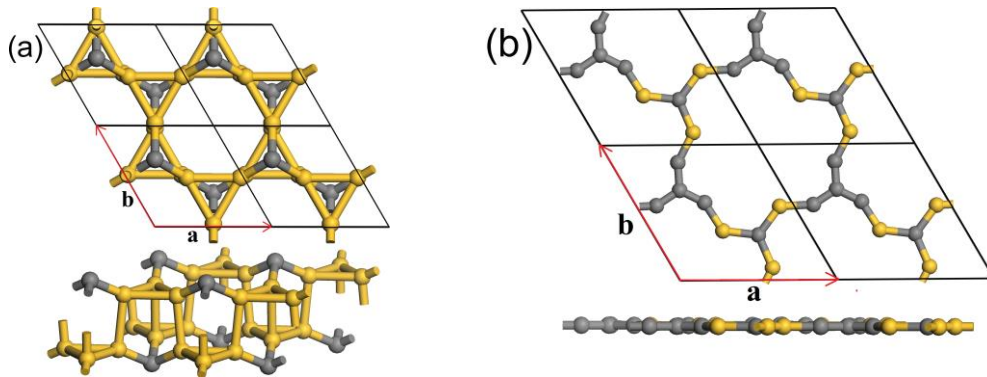

Fig. S2 (color online) Atom structures of C$_2$Si$_6$-SGY (a) and C$_2$C$_3$Si$_3$-SGY (b).

Table S1. Lattice parameters (a, b) and formation energy of C_2Si_6-SGY and $C_2C_3Si_3$-SGY.

	a (Å)	b (Å)	E_f (eV)	E_f' (eV)
C_2Si_6-SGY	5.22	5.22	5.52	-0.37
$C_2C_3Si_3$-SGY	7.88	7.88	6.22	-1.34

S4 Origin of electronic structures of $C_2R_3S_3$-SGY

If the chain atoms of α-graphyne are substituted by two different types of atoms –R–S–, the system dubbed $C_2R_3S_3$-SGY is acquired. Now we discuss whether $C_2R_3S_3$-SGY possesses DCs or not.

Regarding to equation (2-4) in the MS, as for one atom chain, the bonding states and anti-bonding states can be acquired by solving the eigenvectors and eigenvalues of the matrix

$$\begin{pmatrix} E_R & -t_{R-S} \\ -t_{R-S}^* & E_S \end{pmatrix} \tag{6}$$

where E_R and E_S are onsite energy of R and S atoms respectively, t_{R-S} is the hopping energy between R and S atoms.

The eigenvalues are

$$(E_R + E_S)/2 - \Delta, \quad (E_R + E_S)/2 + \Delta \tag{7}$$

where

$$\Delta = \frac{1}{2}\sqrt{(E_R - E_S)^2 + 4|t_{R-S}|^2} \tag{8}$$

The corresponding bonding states and anti-bonding states are

$$\left|\phi_{b}\right\rangle_{n}=c(a\left|R\right\rangle_{n}+b\left|S\right\rangle_{n}), \quad \left|\phi_{a}\right\rangle=c(b^{*}\left|R\right\rangle_{n}-a^{*}\left|S\right\rangle_{n}) \tag{9}$$

where

$$a=t_{R-S}, \quad b=(E_{R}-E_{S})/2+\Delta \tag{10}$$

c is a normalization factor.

From eq. (8) and (10), we obtain the following statement given that $t_{R-S}\neq0$:

$$E_{R}=E_{S}\Leftrightarrow|a|=|b| \tag{11}$$

Then, at K point, the corresponding H' matrix elements between $\left|A\right\rangle_{\mathbf{k}}$ and $\left|2_{b}\right\rangle_{\mathbf{k}}$ ($\left|2_{a}\right\rangle_{\mathbf{k}}$) as well as between $\left|B\right\rangle_{\mathbf{k}}$ and $\left|3_{b}\right\rangle_{\mathbf{k}}$ ($\left|3_{a}\right\rangle_{\mathbf{k}}$) listed in Table 3 of MS should change into

$$H'_{2_{b}A}=-\sqrt{3}c^{*}a^{*}t_{C-R}, \quad H'_{2_{a}A}=-\sqrt{3}c^{*}bt_{C-R},$$

$$H'_{3_{b}B}=-\sqrt{3}c^{*}b^{*}t_{C-S}, \quad H'_{3_{a}B}=\sqrt{3}c^{*}at_{C-S},$$

where t_{C-R}, t_{C-S} are the hopping energy between carbon atoms at A and R atoms as well as between carbon atoms at B and S atoms, respectively.

Then, the H' matrix of the first and second group at K point are

$$\begin{pmatrix} E_{A} & -\sqrt{3}cat_{C-R}^{*} & -\sqrt{3}cb^{*}t_{C-R}^{*} \\ -\sqrt{3}c^{*}a^{*}t_{C-R} & (E_{R}+E_{S})/2-\Delta & 0 \\ -\sqrt{3}c^{*}bt_{C-R} & 0 & (E_{R}+E_{S})/2+\Delta \end{pmatrix} \tag{12}$$

and

$$\begin{pmatrix} (E_{R}+E_{S})/2-\Delta & 0 & -\sqrt{3}c^{*}b^{*}t_{C-S} \\ 0 & (E_{R}+E_{S})/2+\Delta & \sqrt{3}c^{*}at_{C-S} \\ -\sqrt{3}cbt_{C-S}^{*} & \sqrt{3}ca^{*}t_{C-S}^{*} & E_{B} \end{pmatrix} \tag{13}$$

where E_{A} and E_{B} are the onsite energy of carbon atom at A and at B, respectively. The matrix (12) and (13) have 3 eigenvalues respectively, forming 3 pairs of eigenvalues similarly to the

analysis in MS. To form DC band structures, the middle pair of eigenvalues should be degenerated. This can be satisfied by two ways. The first way is that the two matrixes are the same except for phase. This requires the following equations

$$\begin{cases} E_A = E_B \\ \left|-\sqrt{3}c^*a^*t_{C-R}\right| = \left|-\sqrt{3}c^*b^*t_{C-S}\right| \\ \left|-\sqrt{3}c^*bt_{C-R}\right| = \left|\sqrt{3}c^*at_{C-S}\right| \end{cases} \tag{14}$$

The second way is that the two matrixes are not the same, but after diagonalization, E_A and E_B remain unchanged. Meanwhile, $E_A = E_B$, this requires the following equations

$$\begin{cases} E_A = E_B = (E_R + E_S)/2 \\ \left|-\sqrt{3}c^*a^*t_{C-R}\right| = \left|-\sqrt{3}c^*bt_{C-R}\right| \\ \left|-\sqrt{3}c^*b^*t_{C-S}\right| = \left|\sqrt{3}c^*at_{C-S}\right| \end{cases} \tag{15}$$

The equation (14) requires

$$\begin{cases} E_A = E_B \\ |t_{C-R}| = |t_{C-S}| \\ |a| = |b| \end{cases} \tag{16}$$

The equation (15) requires

$$\begin{cases} E_A = E_B = (E_R + E_S)/2 \\ |a| = |b| \end{cases} \tag{17}$$

From equation (11), the condition (16) is equivalent to

$$\begin{cases} E_A = E_B \\ E_R = E_S \\ |t_{C-R}| = |t_{C-S}| \end{cases} \tag{18}$$

and the condition (17) is equivalent to

$$E_A = E_B = E_R = E_S \qquad (19)$$

Because R and S are of different type, E_R and E_S are not the same, then the conditions (18) or (19) are not satisfied in general, and then $C_2R_3S_3$-SGY does not possess DC band structure generally.

S5 Positions of the Fermi surfaces of α-N graphyne derivatives

To determine which bands go through the Fermi surface, we make the following analysis:

(1) When N is even, there will be 3N+3 σ bonds in one cell, then 6N+6 electrons are filled in the σ bond states; Except for p_z orbitals, there still one π ($p_\perp$) orbital for each atom in the chains. The couplings of $p_\perp$ orbitals form N states for each chain, where N/2 states are bonding states and 3N/2 states are bonding states for three C chains filled by 3N electrons. Because there are 4(3N+2) electrons in one cell, there are 4(3N+2)-(6N+6)-3N=3N+2 electrons remained, which should be filled into the p_z orbitals. Because there are 3N+2 p_z orbitals in one cell, so the half of p_z orbitals are filled.

(2) When N is odd, the $p_\perp$ orbitals of each chain form N states, where (N-1)/2 states are bonding states, which should be filled by (N-1) electrons. Then there are 4(3N+2)-(6N+6)-3(N-1)=3N+5 electrons remained. The middle energy level of N states formed by the $p_\perp$ orbitals in one chains may be filled by electrons or empty. There are three such levels due to three C chains in a cell. These three levels ("3 $p_\perp$ middle levels") would split off and become deformed a little due to the couplings with vertex atoms. On the other hand, the 3N+2 p_z orbitals will form 3N+2 bands, where (3N+1)/2 bands are bonding states filled by (3N+1) electrons, and the middle band should be close to the "3 $p_\perp$ middle levels" because they are all the middle level from the π couplings of p orbitals. So far, the number of the remaining electrons is (3N+5)-(3N+1) = 4. These four remaining electrons can fill into the four bands (one is the middle band from p_z

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orbitals, and the other three are the "3 $p_\perp$ middle levels"). Because these 4 bands are close, the Fermi surface would be located near the middle band from p_z orbitals.

The DF calculations by Özcelik et al.[2], Longuinhos et al.[3], and Sun et al.[4] support our discussions described above.

References

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