Introduction.— Exotic electronic structures are a source of rich phenomena in solid-state physics. In particular, density of states (DOS) near the Fermi energy is one of the key quantities for the determination of physical properties, such as phase transitions and response to external electric and magnetic fields. In this regard, bands with constant energy in the entire Brillouin zone, called flat bands, are of particular interest because they provide diverging DOS, which implies instability. Indeed, when flat bands are present near the Fermi energy, various correlation-induced phases such as ferromagnet [1, 2] and superconductivity [3–7] are predicted to be realized. Also it may induce structural deformation (i.e., the Peierls instability).

Recently, a search for flat-band materials has become active [8–10]. Among various routes for realizing flat bands, electronic structure engineering in two-dimensional materials with π-electron networks, such as graphene [11–15] and silicene [16–18], has attracted considerable attention. One of the most prominent findings along this line is the emergence of strongly correlated physics and superconductivity in twisted bilayer graphene [19–22], which originates from the twist-induced flat bands, or the Moiré flat bands, appearing in designated twist angles called magic angles [23]. Another promising method for electronic structure engineering is fabricating superstructures [24] by making holes or chemical substitutions/adsorptions. π electrons do not have in-plane anisotropy, so their electronic structures are largely dominated by geometrical structures of lattices that the π electrons form. This fact leads to a clear guiding principle for realizing flat bands, namely, to arrange the π-electron network such that it is equivalent to the famous flat-band lattice models. For instance, the flat bands originating from the kagome-like network appear in graphene with periodic holes [25, 26] and hydrocarbon networks containing sp² and sp³ carbons [27–29] (i.e., the covalent organic framework).

In this Letter, we propose a characteristic π-electron network hosting a flat band, which we term an extended martini lattice [Fig. 1(a)]. The network consists of the corner sharing triangle network (solid and dashed red bonds), which is equivalent to the kagome lattice, and the Y-shaped units (blue bonds) centered at the downward triangles. Without downward triangles, (i.e., the dashed red bonds), the lattice is called the martini lattice [30–34], which belongs to a class of flat-band lattices called partial line graph [30, 31]. Hence, the extension we consider here refers to the existence of the downward triangles.

We first elucidate the characteristic band structures in the extended martini lattice by employing the minimal tight-binding model. We find that the electronic structure strongly depends on the ratio between two hopping parameters. In par-
ticular, when the ratio exceeds a critical value, the lattice system becomes an unconventional gapless semiconductor where a flat band is at the conduction band edge or the valence band edge. We further show, based on the density functional theory, that the extended martini lattice can be realized by partial chemisorption of graphene and silicene. In those materials, the flat bands acquire a finite dispersion, resulting in carrier doping to the flat bands accompanied by ferromagnetic ordering. Remarkably, the electronic structure near the band edge doping to the flat bands accompanied by ferromagnetic ordering.

**Robust flat band in extended martini lattice model.**—The main target of this Letter is the extended martini lattice model, shown in Fig. 1(a). There are four sublattices per unit cell. Thus, in the tight-binding model for spinless, single-orbital fermions, the Bloch Hamiltonian $H_k$ has a form of $4 \times 4$ matrix. The explicit form of $H_k$ is shown in Supplemental Materials [35]. There are four parameters: $t_1$, $t'_1$, $t_2$, and $V$. Note that the conventional martini lattice model, which belongs to the partial line graph [30], corresponds to the case of $t'_1 = V = 0$.

We elucidate that the exact flat band appears for any parameters, using the wisdom of linear algebra [36–41]. To begin with, we introduce three column vectors: $\psi_{k,1} = (0, 1, 1, 1)^T$ and $\psi_{k,2} = (0, 1, e^{-ik \cdot a_1}, e^{-ik \cdot a_2})^T$, and $\psi_{k,3} = (1, 0, 0, 0)^T$ [42]. We additionally introduce a $4 \times 3$ matrix, $\Psi_k = (\psi_{k,1} \; \psi_{k,2} \; \psi_{k,3})$. Its Hermitian conjugate, $\Psi_k^\dagger$, is the $3 \times 4$ matrix. It follows that, for any $k$, there exists a four-component vector $\varphi_k$ that satisfies $\Psi_k^\dagger \varphi_k = 0$. In other words, $\varphi_k$ belongs to the kernel of the linear map represented by $\Psi_k$. Its explicit form can easily be obtained for generic $k$:

$$\varphi_k = \frac{1}{N_k} \left( 0, e^{ik \cdot a_2} - e^{ik \cdot a_1}, 1 - e^{ik \cdot a_2}, e^{ik \cdot a_1} - 1 \right)^T,$$

where $N_k$ being the normalization constant. Note that $\varphi_k$ has a vanishing amplitude at sublattice 1. The remaining finite components on sublattices 2-4 are identical to those of the flat band wave functions of the kagome lattice. Note also that $\varphi_k$ becomes a zero vector at $k = (0, 0)$ (i.e., $\Gamma$ point), namely, $\varphi_k$ is singular at this point. We will address the implication of this fact later.

A key property for obtaining the flat band is that $H_k$ can be expressed by the matrices introduced above:

$$H_k = \Psi_k \begin{pmatrix} t_1 & 0 & 0 \\ 0 & t'_1 & t_2 \\ 0 & t_2 & V - \varepsilon_k \end{pmatrix} \Psi_k^\dagger + \varepsilon_k I_4,$$

where $\varepsilon_k = -(t_1 + t'_1)$. Recalling that $\Psi_k^\dagger \varphi_k = 0$ holds, we find $\varphi_k$ is the eigenvalue of $H_k$ with eigenenergy being the $k$-independent value, $\varepsilon_k$.

**Band structures of the tight-binding model.**—We discuss the characteristics of the entire band structure, including an exact flat bands. In what follows, we focus on the case where $t_1 = t'_1 = -1$ and $V = 0$, leaving analysis of generic parameters in Supplemental Materials [35]. In Fig. 2, we plot the band structures for several values of $t_2/t_1$. We see that, in all panels, the exact flat band with the energy being $\varepsilon_k$ indeed exists. At $\Gamma$ point, the quadratic band touching between

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**FIG. 2.** Band structure the for the tight-binding model along the high-symmetry lines in the Brillouin zone. The high-symmetry points are $\Gamma = (0, 0)$, $K = \left( \frac{2\pi}{\sqrt{3}a_0}, 0 \right)$, and $M = \left( \frac{\sqrt{3}t_1}{\sqrt{3}a_0}, \frac{\sqrt{3}t_1}{\sqrt{3}a_0} \right)$. We fix $t_1 = t'_1 = -1$, $V = 0$ and vary $t_2/t_1$ whose value is shown at the top of each panel.

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**FIG. 3.** Schematic figure of the band structure around the Fermi levels for $|t_2| \gg |t_1|$ for $t_1 < 0$ (i.e., the type-I) and $t_1 > 0$ (i.e., the type-II). The solid green (dashed orange) bands are filled (empty).
the flat band and the dispersive band occurs. Such a band touching is ubiquitous in various flat band models [38, 43–48]. The band touching can be accounted for by the singularity of \( \varphi_k \) which we have addressed before. In fact, at \( \Gamma \) point, \( \psi_{k,1} = \psi_{k,2} \) holds, which results in the increase of the dimension of the kernel of \( \psi_k^\dagger \) from 1 to 2. Hence, only at this specific point, there are two eigenstates with the same eigenenergy \( \varepsilon = \varepsilon_{FB} \), resulting in the quadratic band touching [38, 40, 41, 49–51].

Besides these parameter-independent features, we also see in Fig. 2 that varying \( t_2/t_1 \) causes the change of entire band structures. Since the target materials are half-filled, we will focus on this case in the following discussions. For \( 0 < t_2/t_1 < 2 \) [Fig. 2(a)-(c)], the system is a conventional band insulator, where two dispersive bands are completely filled. Interestingly, at fine-tuned parameter corresponding to Fig. 2(b), the flat band is doubly degenerate. At \( t_2/t_1 = 2 \) [Fig. 2(d)], the triple band touching occurs at \( \Gamma \) point, around which the dispersive bands exhibit linear dispersion. The analytic derivation of this critical value is shown in Supplemental Materials [35]. For \( t_2/t_1 > 2 \) [Fig. 2(e)], the system becomes an unconventional gapless semiconductor, where the top of the valence band touches the empty flat band. The Fermi level is right at the flat band, meaning that the DOS is divergingly large. This will be a source of exotic physical properties, as we will discuss later. Considering the fact that the blue bonds is shorter than the red bonds in Fig. 1(a), it is reasonable to assume that \( |t_2| \gg |t_1| = |t'_1| \) holds when implementing this structure by \( \pi \)-electron networks. We thus focus on the unconventional gapless state [Fig. 2(e)] in the following discussions.

**Two types of unconventional gapless semiconductor.**—Before proceeding to the material realizations, we note that the sign of \( t_1 \) is essential in determining actual electronic state [52]. The schematic figure of the electronic structures around the Fermi level for \( |t_2| > 2|t_1| \) is shown in Fig. 3. For \( t_1 < 0 \), which is the case of Fig. 2(e), the dispersive band touching the flat band is convex downward and is completely filled, whereas the flat band is completely empty. We refer to this case as the type-I [Fig. 3(a)]. Meanwhile for \( t_1 > 0 \), the entire band structure is obtained by flipping the sign of the eigenenergies of those for \( t_1 < 0 \). As a result, we find that the dispersive band touching the flat band is convex upward and is completely empty; instead, the flat band right below the dispersive band is completely filled. We refer to this case as the type-II [Fig. 3(b)]. In fact, both of these two types are feasible by the choice of mother materials and adatoms, as we shall discuss below.

**Material design of extended martini lattice.**—We now argue the materials realization of the extended martini model. Geometric and electronic structures of realistic martini structures derived from graphene and silicene are investigated using the density functional theory [53, 54]. See Supplemental Materials for details of the calculation methods.

Honeycomb covalent networks of C and Si are plausible starting materials to design the extended martini lattice because a corresponding network is obtained by partially thinning out the \( \pi \) electrons by adsorption or chemical substitution. Here, we focus on the adsorption on graphene, leaving the results for silicene in Supplemental Materials [35]. Figure 1(a) shows the schematic views of the possible structure of the extended martini lattice derived from the honeycomb C network. The extended martini lattice can be found in Fig. 1(a) as downward three-pointed stars comprising white circles by adsorbing or substituting four of eight atomic sites forming upward three-pointed-star in each 2×2 lateral unit cell by foreign atoms. The chemisorption of H onto graphene and silicene effectively removes \( \pi \) electrons on H terminated C atomic sites, leading to the extended martini lattice of \( \pi \) electrons on these partially H adsorbed graphene [C-H in Fig. 1(b)]. Partial fluorination of graphene also effectively causes the extended martini lattice [C-F in Fig. 1(c)]. The optimized lattice parameters of the extended martini networks of C-H and C-F are 5.04 and 5.04 Å, respectively, which are slightly longer than that of graphene, because the chemisorption on four of eight atomic sites per cell leads to sp³ bonds. In addition to the adsorption, the substitution of C by B and N atoms can substantially modulate the \( \pi \) electron environment on the honeycomb networks, so that the in-plane heterostructures of three-pointed stars of C and B/N are possible candidates for the extended martini lattice. We argue the details of this case in Supplemental Materials [35].

Figures 4(a) and 4(b) show the electronic band structure of
the extended martini lattice derived from the honeycomb networks of C. The extended martini systems of C-H and C-F are semiconductors where two branches just below and above the Fermi level in the majority and the minority spin states, respectively, possess characteristic dispersion relation: One of the two is less dispersive and the other has dispersion with substantially width. Furthermore, these two branches degenerate at the \( \Gamma \) point. These characteristic dispersion relations are the same as those obtained by the tight-binding approximation, indicating that these networks are the extended martini lattice derived from graphene by atom adsorption. The adsorbate species on graphene can control the band structure attributed to the extended martini lattice. The flat band emerges in the lower branches and upper branches of two branches for the extended martini of C-F and C-H, respectively. Comparing these with the tight-binding model, we find that C-F corresponds to the type-I in Fig. 3(a), while C-H corresponds to the type-II in Fig. 3(b). These facts imply that the constituent elements of honeycomb networks and the adsorbates can control a sign of the effective electron transfer between the next-nearest \( \pi \) electrons (i.e., \( t_1 \) and \( t_1' \)), allowing further band edge engineering in these graphene derivatives.

In the extended martini lattice derived from graphene, long-range wave function overlap and the incomplete \( \pi \) termination by adsorbates lead to the small but finite band dispersion in the flat band state. The calculated band widths of the flat band states are 0.46 and 0.23 eV for the extended martini lattices of C-H and C-F, respectively. This small but finite band width leads to the partial occupation that causes the large Fermi level instability. The extended martini networks of C-H and C-F exhibit spin polarization as shown in Figs. 4(a) and 4(b), respectively. The majority and minority bands associated with the martini flat band state shift downward and upward, respectively, owing to the spin polarization. The polarized spin is primarily distributed on the three edges of three-pointed star of bare C atoms [Figs. 4(c) for C-H and 4(d) for C-F]. The distribution corresponds to the wave function of the martini bands at \( \Gamma \) and the Fermi level. Namely, the flat band wave function of Eq. (1) has a vanishing amplitude at the sublattice 1. The number of polarized electrons is 2 per \( 2 \times 2 \) unit cell for both C-H and C-F, corresponding to 0.15 \( \mu_B/\text{Å}^2 \). Therefore, these facts indicate that the partial hydrogenation or fluorination of graphene, (as well as the partial hydrogenation of silicene [35]), are the magnetic materials whose magnetization is attributed to itinerant \( \pi \) electrons on atomic layer materials. In contrast, the C/BN heterostructures obtained by B/N substitution do not exhibit spin polarization, owing to the substantial band width of the flat band states. The calculated band widths of the flat band states are 1 eV or wider [35].

**Summary and discussions.**—We have investigated the characteristic electronic structures in the extended martini lattice model and its materialization in partially chemisorbed graphene and silicene. The analytic treatment of the tight-binding model reveals that the unconventional gapless semiconductor with the exact flat band at the Fermi level is realized when \( |t_2| > 2|t_1| \) (for \( t_1 = t_1' \)). Depending on the sign of \( t_1, t_1' \), the gapless semiconductor is classified into the type-I, with the completely empty flat band, and the type-II, with the completely filled flat band. In the actual materials, the types can be tuned by the species of the adsorbed atoms.

We close this Letter by addressing possible future problems and intriguing functionalities of the extended martini materials. Firstly, regarding the materials design, our scheme of electronic state engineering will applicable not only to layered materials but also to surfaces systems [55]. In addition, three-dimensional analog of the extended martini network, which corresponds to the pyrochlore lattice with one additional site per downward tetrahedron, will be pursued in metal organic frameworks and covalent organic frameworks.

Secondly, as for the functionality due to the spin polarization, it is expected that the electronic state like Figs. 4(a) and 4(b) can be utilized for spin-filtered transport. Furthermore, when the spin-polarization is weak such that the flat band of the majority spin is partially filled, the interplay between the flat-band state of majority spins and the mobile holes of the minority spins will give rise to exotic many-body states. Studying such situations will be an intriguing future problem.

Finally, if one can suppress the spin polarization and retain the nonmagnetic unconventional gapless semiconductor, the sharply-varying DOS around the Fermi level can be a source of large thermoelectric responses [56–58]. Further, very recent theoretical studies have revealed that the quadratic band touching between the flat and the dispersive bands gives rise to unconventional quantum geometric tensor, which anomalously affects various fundamental quantities such as a magnetic-field response [59, 60] and a superfluid weight [61–63]. The extended martini materials will serve as suitable platforms for studying these phenomena.

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S1. TIGHT-BINDING HAMILTONIAN AND ITS PROPERTY

The Hamiltonian matrix for Fig. 1(a) of the main text is given as

\[
H_k = \begin{pmatrix}
V & t_2 e^{i k \cdot a_1} & t_2 e^{i k \cdot a_2} \\
t_2 & t_1 + t'_1 e^{i k \cdot a_1} & t_1 + t'_1 e^{i k \cdot a_2} \\
t_2 e^{-i k \cdot a_1} & t_1 + t'_1 e^{-i k \cdot a_1} & 0 \\
t_2 e^{-i k \cdot a_2} & t_1 + t'_1 e^{-i k \cdot a_2} & t_1 + t'_1 e^{i k \cdot (a_2 - a_1)} & 0
\end{pmatrix}.
\]  

(S1)

We note that the eigenenergies of \(H_k\) do not depend on the sign of \(t_2\). To be concrete, \(H_k\) satisfies

\[
H_k(t_1, t'_1, -t_2, V) = \gamma H_k(t_1, t'_1, t_2, V)\gamma,
\]

where we explicitly write the hopping parameter dependence of the Hamiltonian, and \(\gamma = \text{diag}(-1, 1, 1, 1)\) is the unitary matrix. Note that \(\gamma\) satisfies \(\gamma^\dagger = \gamma\). Equation (S2) indicates that \(H_k(t_1, t'_1, -t_2, V)\) and \(H_k(t_1, t'_1, t_2, V)\) are unitary equivalent to each other, thus their eigenvalues are the same. Hence, the band structure is determined by the signs of \(t_1\) and \(t'_1\).

S2. ADDITIONAL NUMERICAL RESULTS FOR TIGHT-BINDING MODEL

In this section, we present additional numerical results for the tight-binding model.

A. Conventional martini lattice

The model includes the conventional martini lattice model as a special case with \(V = t'_1 = 0\). Here we show the band structures of the conventional martini lattice model [1]. In Fig. S1, we plot the band structures for several values of \(t_2\). We see that the flat band and the quadratic band touching at \(\Gamma\) point occurs for all case, as we have argued in the main text. Similarly to the case we have discussed in the main text, the transition from the band insulator to the unconventional gapless semiconductor occurs at \(t_2/t_1 = 1\); at \(t_2/t_1 = 1\), the triple band touching occurs [Fig. S1(b)].

![Figure S1](https://example.com/figure1.png)  

**FIG. S1.** Band structures for \(V = t'_1 = 0\). We set \(t_1 = -1\). The values of \(t_2/t_1\) are indicated at the top of each panel. The high-symmetry momenta are \(\Gamma = (0, 0)\), \(K = \left(\frac{4\pi}{3}, 0\right)\), and \(M = \left(\pi, \frac{\pi}{\sqrt{3}}\right)\).
FIG. S2. Band structures for $t_1 = t'_1 = t_2 = -1$ and finite $V$. The values of $V$ are indicated at the top of each panel.

FIG. S3. Band structures for $t_1 = t'_1 = -1$, $t_2 = -3$ and finite $V$. The values of $V$ are indicated at the top of each panel.

The analytical derivation of this value is shown in Sec. S3A. It is also worth noting that the Dirac cone formed by the first and the second lowest bands appears at $t_2/t_1 = \sqrt{2}$ [Fig. S1(c)].

B. Effect of on-site potential

Next, we investigate the effects of the on-site potential, $V$. We first consider the case with $t_1 = t'_1 = t_2 = -1$. The band structures for several values of $V$ are shown in Fig. S2. In this case, the transition point between the band insulator and the unconventional gapless semiconductor is at $V = 1.5$ [Fig. S2(d)]. Besides, at $V = 1$, the doubly degenerate flat band appears [Fig. S2(b)], similarly to Fig. 2(b) in the main text. The analytic derivation of this value is presented in Appendix S3B.

We also consider the case with $t_1 = t'_1 = -1$ and $t_2 = -3$. In this case, the transition from the band insulator to the conventional semiconductor occurs at $V = -2.5$ [Fig. S3(d)], whereas the doubly degenerate flat band occurs at $V = -7$ [Fig. S3(b)].

S3. ANALYTIC DERIVATIONS OF CHARACTERISTIC BAND STRUCTURES

In this section, we analytically investigate the origins of the characteristic band structures, namely the triple band touching at Γ point and the doubly degenerate flat band.

A. Triple band touching at Γ point

We first examine the condition of the triple band touching by explicitly solving the eigenvalue equation at Γ point with a certain ansatz. Specifically, as we have seen, two out of four eigenstates have the eigenvalue $\varepsilon^\text{BF} = -(t_1 + t'_1)$ at Γ point, so we investigate the remaining eigenvalues. Then, recalling that $\varphi_{k=\Gamma}$ is orthogonal to $(0,1,1,1)^T$, we...
assume the following form of the eigenvector (up to the normalization constant):

\[ \varphi'_{k=\Gamma} = \begin{pmatrix} \alpha \\ 1 \\ 1 \\ 1 \end{pmatrix} . \]  

(S3)

Acting the Hamiltonian to \( \varphi'_{\Gamma} \), we have

\[ H_{\Gamma} \varphi'_{\Gamma} = \begin{pmatrix} V & t_2 & t_2 & t_2 \\ t_2 & 0 & t_1 + t'_1 & t_1 + t'_1 \\ t_2 & t_1 + t'_1 & 0 & t_1 + t'_1 \\ t_2 & t_1 + t'_1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ 1 \\ 1 \\ 1 \end{pmatrix} = \begin{pmatrix} \alpha V + 3t_2 \\ \alpha t_2 + 2(t_1 + t'_1) \\ \alpha t_2 + 2(t_1 + t'_1) \\ \alpha t_2 + 2(t_1 + t'_1) \end{pmatrix} . \]  

(S4)

In order that the triple band touching occurs, it is sufficient that \( \varphi'_{\Gamma} \) is the eigenvector of \( H_{\Gamma} \) with the eigenvalue \(-(t_1 + t'_1)\). If it is the case, the following conditions have to be satisfied:

\[ \alpha V + 3t_2 = -\alpha(t_1 + t'_1), \]  

and

\[ \alpha t_2 + 2(t_1 + t'_1) = -(t_1 + t'_1). \]  

(S5)

(S6)

From Eq. (S5), we have \( \alpha = -\frac{3t_2}{V + t_1 + t'_1} \). Similarly, from Eq. (S6), we have \( \alpha = -\frac{3(t_1 + t'_1)}{t_2} \). Then, we can conclude that the triple band touching occurs for the fine-tuned parameters where the above two conditions are satisfied simultaneously. Specifically, the condition for the tight-binding parameters is

\[ t_2^2 = (t_1 + t'_1)(V + t_1 + t'_1). \]  

(S7)

The parameter sets for Figs. S1(b), S2(d), and S3(d), as well as Fig. 2(d) in the main text, indeed satisfy Eq. (S7).

**B. Doubly degenerate flat band**

Next, we elucidate the origin of doubly degenerate flat bands. Generically, the doubly degenerate flat band at \( \varepsilon^{FB} = -(t_1 + t'_1) \) appears when the Hamiltonian can be written as

\[ H_k = \Psi_k h_k' \Psi_k^\dagger - (t_1 + t'_1)I_4, \]  

(S8)

where \( \Psi_k \) is a \( 4 \times 2 \) matrix and \( h_k' \) is a \( 2 \times 2 \) Hermitian matrix.

Here, we make assumptions on the forms of \( h_k' \) and \( \Psi_k \). To be specific, we assume

\[ h_k' = \begin{pmatrix} t_1 & 0 \\ 0 & t'_1 \end{pmatrix}, \]  

(S9)

and

\[ \Psi' = \begin{pmatrix} 0 & \beta \\ 1 & 1 \\ 1 & e^{-ik \cdot a_1} \\ 1 & e^{-ik \cdot a_2} \end{pmatrix}, \]  

(S10)

where \( \beta \) is the variable to be determined. Substituting Eqs. (S9) and (S10) into Eq. (S8), we have

\[ H_k = \begin{pmatrix} \beta^2 t'_1 - (t_1 + t'_1) & \beta t'_1 & \beta t'_1 e^{ik \cdot a_1} & \beta t'_1 e^{ik \cdot a_2} \\ \beta t'_1 e^{-ik \cdot a_1} & t_1 + t'_1 e^{ik \cdot a_1} & t_1 + t'_1 e^{ik \cdot a_2} & t_1 + t'_1 e^{ik \cdot (a_2 - a_1)} \\ \beta t'_1 e^{-ik \cdot a_2} & t_1 + t'_1 e^{-ik \cdot a_2} & t_1 + t'_1 e^{ik \cdot (a_1 - a_2)} & t_1 + t'_1 e^{ik \cdot (a_2 - a_1)} \end{pmatrix}. \]  

(S11)
Comparing Eq. (S1) with Eq. (S11), we find that $\beta$ has to satisfy

$$\beta = \frac{t_2}{t_1^\prime}.$$  \hspace{1cm} (S12)

Substituting this into $(1,1)$-component of Eq. (S11) and comparing it with that of Eq. (S1) we have

$$V = \frac{t_2^2}{t_1^\prime} - (t_1 + t_1^\prime).$$  \hspace{1cm} (S13)

Therefore, the doubly degenerate flat band occurs for the parameter sets satisfying Eq. (S13). The parameter sets for Figs. S2(b) and S3(b), as well as Fig. 2(b) in the main text, indeed satisfy Eq. (S13). It is also worth pointing out that, for the conventional martini lattice (i.e., $t_1^\prime = 0$), the doubly degenerate flat band occurs only in the limit of $V \to \infty$ since Eq. (S12) requires $\beta \to \infty$.

\section*{S4. DFT CALCULATIONS}

We perform the density functional theory calculation by using STATE program package \cite{2, 3}. Exchange-correlation potential among interacting electrons is treated by generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) functional \cite{4}. An ultrasoft pseudopotential is adopted to described the interaction between valence electrons and ions \cite{5}. Valence wave functions and the deficit charge density were expanded in terms of plane-wave basis sets with cutoff energies of 25 and 225 Ry, respectively. A Brillouin-zone integration was carried out with a $1\times1\times1$ $k$-mesh for the self-consistent electronic structure calculations. Atomic coordinates of martini structures are optimized till the force less than $1.33\times10^{-3}$ hartree.

\section*{S5. PARTIALLY HYDROGENATED SILICENE}

The partially hydrogenated silicene has a type-I flat band arrangement as the case of fluorinated graphene (Fig. S4). Owing to the partial occupation of the flat band, the hydrogenated silicene exhibits spin polarization with the magnetic moment of 0.15 $\mu_B$/Å$^2$, where the polarized electron spin has the same spatial distribution as the flat-band wave function of the extended martini model at $\Gamma$ and the Fermi level.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig_s4.png}
\caption{Band structure of partially hydrogenated silicene. Red and blue curves denote the energy band for majority and minority states, respectively. Energies are measured from the vacuum level. The horizontal dotted line indicates the Fermi level.}
\end{figure}
In addition to the adsorption, the chemical substitution is another method of controlling the structure of the π-electron network. Here we show the results of graphene with B/N substitution. The electronic structure of BCN heterostructures with C-B and C-N borders are shown in Fig. S5. The heterostructures are obtained by substituting four of eight C atomic sites in 2×2 unit cell of graphene by B an N atoms. Both heterostructures are metals in which the Fermi level crosses parabolic and flat dispersion bands owing to the substantial band width of the flat bands. The heterostructures with C-B and C-N borders have type-I and type-II flat band arrangement, respectively. Therefore, a sign of electron transfer $t_1$ is tunable by controlling the border atomic arrangement. Furthermore, the band filling of the flat band may also be tunable by the atomic species which are substitutionally doped in graphene.

![Fig. S5. Electronic and geometric structures of BCN heterostructures with (a) C-B and (b) C-N borders. Energies are measured from the vacuum level. Red dotted horizontal lines denote the Fermi level. Red, gray, and green balls denote B, C, and N atoms, respectively. The rhombus denotes the unit cell of BCN heterostructures.](image)

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