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Interplay between the Kagome flat band and the Dirac cone in porous graphitic networks



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ABSTRACT

We have investigated the geometric and electronic structures of porous graphene consisting of triangular hydrocarbon molecules polymerized by oligoacene interconnects by density functional theory. The networks possess both Dirac cones and Kagome flat bands near the Fermi level of which electron filling is controllable by selecting appropriate oligoacene interconnects because the triangular units and interconnects are arranged in honeycomb and Kagome lattices, respectively. The partially filled Kagome band in the network with the shortest interconnects induces ferromagnetic spin ordering throughout the porous graphitic network with a magnetic moment of $1.00 \mu_B/\text{cell}$. For networks with longer interconnects, the sheet is a zero gap semiconductor with a Dirac cone at the Fermi level of which band width decreases with increasing length of the interconnect despite the network containing pentagonal rings.

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1. Introduction

The electronic structures of graphitic sp^2 C networks are sensitive to both the local and global network topologies of the π electrons [1–15]. Graphene is the starting material to consider such nanoscale sp^2 C materials [16,17]. Open boundary condition on graphene cause graphene nanoflakes which possess either closed-shell or open-shell electronic structures depending on their molecular shapes [8,9,18]. For instance, phenalenyl and triangulene, which are triangular molecular shapes, have radical spins of $S = 1/2$ and $S = 1$, respectively, corresponding to the sublattice imbalance [8,9,18,19,20,21]. For the molecules with hexagonal shape, (e.g. benzene and coronene), the band gap monotonically decreases with increasing molecular sizes [8,9]. For the case of one-dimensional boundary conditions, tubular and striped graphitic network materials can be synthesized under periodic and open boundary conditions, respectively. The tubes can be metals or semiconductors which are determined by the chirality of the hexagonal network along their circumference [1,2,10,11,22]. In the case of graphene nanoribbons, a peculiar edge localized state is induced by the delicate balance among the electron transfer at the zigzag edges, in addition to the metallic and semiconducting electronic

structures of ribbons with armchair edges [12–15,23–26]. In addition to these boundary conditions, topological defects in sp^2 C networks, such as pentagonal and heptagonal rings, cause further versatile electronic structures: Flat band states and Kagome bands are induced at or near the Fermi level leading to spin polarization around them or throughout the networks [4–7,27,28].

In our previous work, we investigated a sp^2 C network composed of hexagonally arranged phenalenyls units with phenyl interconnects that exhibits unusual electronic structures around the Fermi level [29]. The radical spin state of phenalenyl causes the Dirac cone with extremely narrow band width, leading to the ferromagnetic and antiferromagnetic spin ordering in the radical spin localized on the phenalenyl units. In addition to the Dirac cone associated with the radical spin on the phenalenyl unit, the electron states associated with the phenyl interconnects cause Kagome flat bands just below and above the Dirac cone, because the phenyl interconnects form a Kagome network by phenalenyl units [30,31]. This result raises the question whether the Kagome flat band and Dirac cone coexists at the Fermi level by selecting appropriate hydrocarbon interconnects between the phenalenyl units.

In this study, we theoretically investigated the geometric and electronic structures of a two-dimensional (2D) network of sp^2 C atoms composed of phenalenyl units connected by oligoacene interconnects as a potential candidate for a porous graphitic network with an unusual electronic structure. Our first-principles total-energy calculations show that the porous graphitic networks

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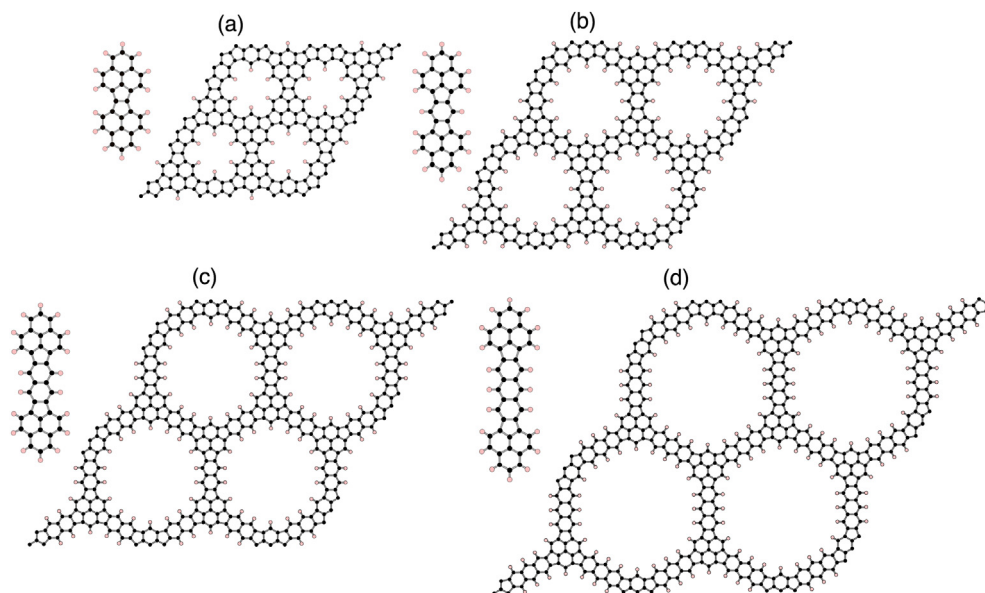


Fig. 1. Optimized structures of porous hydrocarbon sheets consisting of phenalenyl connected by (a) C₂, (b) benzene, (c) naphthalene, and (d) anthracene. Black and pink balls denote carbon and hydrogen atoms, respectively.

simultaneously possess a Dirac cone and a Kagome flat band at the Fermi level for a particular oligoacene interconnect. The partially filled Kagome flat band at the Fermi level induces spin polarization with ferromagnetic ordering throughout the network. Furthermore, although the networks contain pentagonal rings between phenalenyl units and oligoacene interconnects that deviate from a bipartite network, the networks possess a Dirac cone that has a wave function that exhibits a nonbonding nature as the edge state of the graphene nanoribbon with zigzag edges [12,13]. As the length of the oligoacene interconnect increases, the width of the Kagome band monotonically decreases, so that the flat band state associated with the Kagome band shifts downward and is filled by electrons, and thus spin ordering disappears. This indicates that the electronic and magnetic properties of the porous graphitic network can be controlled by the size of the pores.

2. Calculation method

All of the calculations were performed within the framework of the density functional theory [32,33] using the simulation tool of atom technology (STATE) code [34]. To calculate the exchange–correlation energy among the interacting electrons, we used the generalized gradient approximation with the Perdew–Burke–Ernzerhof functional [35]. To investigate the spin-polarized states of the porous hydrocarbon sheets, the spin degree of freedom was taken into account in all of the calculations. Vanderbilt ultrasoft pseudopotentials were used to describe the electron–ion interactions [36]. The valence wave functions and deficit charge density were expanded in terms of plane waves with cutoff energies of 25 and 225 Ry, respectively, which sufficiently describe the electronic structure and energetics of hydrocarbon molecules and graphene-related materials [37]. To simulate an isolated porous hydrocarbon sheet, the sheet was separated by a vacuum spacing of 10.58 Å. The atomic structures of the sheets were fully optimized until the force acting on each atom was less than 1.33×10^{-3} HR/au. Integration over the Brillouin zone was carried out using an equidistance mesh of $2 \times 2 \times 1$ \mathbf{k} points. To ensure the thermal stability of the networks, we performed an ab initio molecular dynamics (MD) simulation using the velocity scaling method to keep the temperature constant during the

simulation.

3. Results and discussions

Fig. 1 shows the optimized structures of porous hydrocarbon sheets consisting of phenalenyl units and oligoacene interconnects. They contain not only hexagonal rings but also pentagonal rings between phenalenyl units and oligoacene interconnects. C₂, benzene, naphthalene, and anthracene are representative interconnects, which characterize the size of the pores of the networks. By focusing on the phenalenyl units, the network can be regarded as a honeycomb network with structural hierarchy or an internal degree of freedom arising from the hexagonally arranged phenalenyl units. The network can also be regarded as a Kagome lattice in terms of the oligoacene interconnects. Under the equilibrium lateral lattice constant of each network, these networks retain a planar conformation. The optimized bond lengths belonging of the phenalenyl units is range from 1.36 to 1.42 Å, irrespective to of the oligoacene length, which are similar values to those of an isolated phenalenyl molecule. For the oligoacene interconnects, the optimum bond lengths are 1.43–1.47 and 1.36–1.42 Å for the atoms without and with H atoms, respectively.

The calculated total energies, ϵ , of the networks consisting of phenalenyl units and oligoacenes are given in Table 1. The total energy, ϵ , was determined by the following equation:

$$\epsilon = \frac{E_{\text{total}} - \mu_{\text{C}} \times N_{\text{C}} - \mu_{\text{H}} \times N_{\text{H}}}{N_{\text{C}}},$$

where E_{total} , N_{C} , N_{H} , μ_{C} , and μ_{H} are the total energy of the network, number of C atoms, number of H atoms, chemical potential of the C

Table 1
Total energy of networks consisting of phenalenyl units and oligoacene interconnect (ϵ).

Interconnects	Total energy (ϵ) [meV]
C ₂	250
Benzene	172
Naphthalene	143
Anthracene	129

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