# Three-dimensional covalent networks of $sp^2$ and $sp^3$ C atoms: Energetics and electronic properties of polymerized diphenylmethane and tetraphenylmethane

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Based on the density functional theory with the generalized gradient approximation, we investigate geometric and electronic structures of three-dimensional covalent organic frameworks of polymerized diphenylmethane and tetraphenylmethane in which phenyl and biphenyl are arranged in tetrahedral manner connected via methane vartexes. These three-dimensional covalent networks are energetically stable with the total energy of 90 and 65 meV/atom for diphenylmethane and tetraphenylmethane polymers, respectively, with respect to that of diamond. Polymerization reactions of diphenylmethane and tetraphenylmethane are endothermic with the reaction energy of 1.62 and 0.68 eV, respectively. These polymers have peculiar electronic band structures in their valence and conduction states, which consist of the combination of the doubly degenerate flat band and two dispersive states forming a Dirac cone at the W point. The wavefunction analysis and the simple tight-binding calculation reveal that the peculiar electron states are ascribed to the delicate balance between inter- and intra-phenyl/biphenyl π electron transfers, indicating that these polymers could be regarded as the three-dimensional kagome pyrocroa networks with the internal degree of freedom.

# 1. Introduction

Carbon and hydrocarbon molecules consisting of $sp^2$ C atoms show rich variation in their geometries, depending on their size, shape, local network topology, and boundary condition[1,2]. Hexagonal rings of C cause planar hydrocarbon molecules which basically and approximately possess symmetric $\pi$ electron states with respect to the Fermi level, when they satisfy the bipartite topology in their C network[1]. The energy gap between the lowest unoccupied and the highest occupied states inversely proportional to the molecular size and asymptotically approaches zero corresponding to the zero-gap semiconducting property of graphene[3-5] which is an infinite limit of the hydrocarbons[6,7]. By imposing the asymmetries in their bipartite networks, the hydrocarbon molecules possess half-filled non-bonding states at the Fermi level, of which number corresponds with the sublattice imbalance[1,8-13]. Accordingly, by arranging and connecting these hydrocarbons in appropriate manner, resultant one-dimensional and two-dimensional networks exhibit unusual electronic structures[14-20], known to be nanographenes or covalent organic frameworks. It has been theoretically and experimentally established that graphene nanoribbons with hydrogenated zigzag edges possess peculiar edge localized states leading to half-filled flat dispersion bands around the Brillouin zone boundary because of the delicate balance among the electron transfer around the edge atomic sites[15,16,18]. Porous graphene consisting of phenalenyl (a hydrocarbon molecule with a triangular shape consisting of three hexagonal rings) and phenyl possess kagome bands above and below the Dirac band at the Fermi level[19,20].

In addition to the planar hydrocarbon, non-planar hydrocarbons are also attracting much attention, because of their structural flexibility to design two- or three-dimensional molecular architectures which may possess unique physical properties. Triptycene is one of the representative non-planar hydrocarbon with $D_{3h}$ symmetry and a Y-shaped ridged structure consisting of three benzene rings connected via bridgehead C atoms with fourfold coordination ($sp^3$ hybridization) situated at the molecular axis[21]. In addition to triptycene, the molecules possessing acene panels with $sp^3$ C bridgeheads have been synthesized experimentally and known as iptycene, which is characterized by the size and shape of three acene planes[22-24]. According to mixing of $sp^2$ and $sp^3$ C atoms, iptycene possess non-planar covalent organic frameworks of which electronic structure is characterized by two-different π electron transfer within the acene panel and that between them. The ridged three-dimensional structure of iptycene/triptycene allow them constituent units of covalent organic frameworks for atoms and molecular storages, supermolecules for a hybrid structure with other molecules[25-30], and molecular machines[31-34]. Among them, the covalent organic frameworks consisting of triptycene and other hydrocarbons had unusual electronic structure near the Fermi level: They have the kagome bands in valence and conduction states because the π electron network is characterized by the kagome lattice with the internal degree of freedom[35,36].

Adequate choices of such non-planar hydrocarbon allow us to design three-dimensional covalent C networks. The different π electron transfers between and within $sp^2$ moieties in such networks the unusual electronic structure, which is absent in the conventional covalent organic framework or the other carbon allotropes. Tetraphenylmethane[37], which consists of a methane core with four phenyl substituents, and diphenylmethane[38], which consists of a methane with two phenyl substituents, are the simplest possible candidates for construing three-dimensional covalent networks, because of their tetrahedrally arranged phenyl substituents. Thus, in this work, we aim to theoretically design three-dimensional covalent networks of C assembling and polymerizing diphenylmethane or tetraphenylmethane as constituents and to explore their electronic properties, using the density functional theory (DFT) with the generalized gradient approximation (GGA). Our calculations showed three-dimensional networks consisting of phenyl and biphenyl connected via methane vertexes are semiconductors with the peculiar electronic structures near the Fermi level, which consist of flat dispersion bands and a Dirac cone. These networks energetically and thermally stable, indicating the possible three-dimensional covalent organic frameworks consisting of both $sp^2$ and $sp^3$ C atoms. Wave function analyses indicate that the electron states associated with the flat band as well as the Dirac cone exhibit extended nature. Furthermore, the simple tight-binding analysis clarifies that the flat bands and a Dirac cone is ascribed to their network topology classified as the three-dimensional kagome pyrocroa network with the internal degree of freedom.

## 2. Calculation method and structural model

All calculations were conducted on the basis of the DFT[39,40] as implemented in the program package STATE[41]. We used GGA with the Perdew-Burke-Ernzerhof functional to describe the exchange-correlation potential energy among interacting electrons[42]. An ultrasoft pseudopotential generated using the Vanderbilt scheme was adopted for describing the interaction between electrons and ions[43]. Valence wave functions and deficit charge densities were expanded in terms of plane-wave basis sets with cutoff energies of 25 and 225 Ry, respectively, which give sufficient convergence in the total energy and electronic structures of covalent networks consisting of both $sp^2$ and $sp^3$ C atoms[44]. Ab initio molecular dynamics simulations were conducted using the velocity scaling method to keep the temperature constant during the simulation to insure the thermal stability of the three-dimensional covalent networks. Integration over the first Brillouin zone was carried out using an equidistant $2\times2\times2$ k-mesh for the network phenyl and biphenyl interconnects, respectively. Lattice parameters and internal atomic structures were fully optimized until the force acting on each atom became less than 5 mRy/Å.

## 3. Results and discussion

Figure 1 shows optimized structures of three-dimensional covalent networks consisting of phenyl and methane. Here we consider two representative networks of the polymerized non-planar HC, polymerized diphenylmethane [Fig. 1(a)], in which tetrahedrally arranged $sp^3$ C atoms are connected via phenyl, and of the polymerized tetraphenylmethane [Fig. 1(b)], in which $sp^3$ C atoms are connected via biphenyl. According to the choice of the constituents and their arrangements, they could be regarded as the extended diamond networks in which the methane and phenyl or biphenyl mimic the atom and bonds, respectively.

The optimized lattice parameters of three-dimensional porous carbon networks are 9.74 and 16.93 Å for the polymerized diphenylmethane and tetraphenylmethane, respectively. Under the optimum lattice parameters, the optimized bond lengths of the networks are summarized in Table 1. The optimized length of the bond associated with methane is about 1.55 and 1.56 Å for the polymerized diphenylmethane and tetraphenylmethane, respectively, indicating their $sp^3$ bond nature. For the covalent bonds belonging to phenyl ring, an optimized length is approximately 1.4 Å, indicating their $sp^2$ nature. For the case of the polymerized tetraphenylmethane, the optimized length of the bond adjoining two phenyls is 1.49 Å, showing its single bond nature as an isolated biphenyl. As far as $\pi$ electrons are concerned, thus, these networks are regarded as the tetrahedral networks of phenyl or biphenyl which are connected to methane vertexes.

To investigate the energetic stability of these hydrocarbon polymers, we calculated the total energy per C atom of them. The total energy is evaluated by a formula,

$$\varepsilon = (E - \mu_C N_C - \mu_H N_H)/N_c$$

where $E$, $\mu_C$, $\mu_H$, $N_C$, and $N_H$ are the total energy of polymers, a chemical potential of C evaluated by diamond, a chemical potential of H in benzene form, the number of C, and the number of H, respectively. Calculated total energy of the polymerized diphenylmethane and tetraphenylmethane are 90 and 65 meV/atom, respectively. Therefore, the polymers are energetically stable. Furthermore, the energy is independent to the size of the $\pi$ electron network or the phenyl length, as the case of the polyphenyl owing to the single bond nature of covalent bond between phenyl rings.

To give further insight into the thermal stability of the polymers, we performed ab initio molecular dynamics simulations under the temperature of 1500 K for simulation times of about 0.8 ps or longer. Figure 2 shows snap shots of geometric structures of the polymerized diphenylmethane and tetraphenylmethane at the temperature of 1500K and simulation times of about 0.8 ps. As depicted in figures, these polymers retains their initial covalent network topologies at this temperature and after the above simulation times. Therefore, these polymers are energetically and thermally stable under the ambient condition, rotating their covalent networks, once they are synthesized using appropriate experimental procedures. Note that the MD calculations are conducted under the primitive cell, so that the further investigations under extended cell are mandatory to give rigorous conclusion of the dynamical stability.

It is worth to estimate the formation energy $\Delta E$ of these polymers from the polymeric reaction of diphenylmethane or tetraphenylmethane as

$$2 \times diphenylmethane \; = \; poly - diphenylmethane \; + \; 8 \times H_2 \; + \; \Delta E$$
$$2 \times tetraphenylmethane \; = \; poly - tetraphenylmethane \; + \; 8 \times H_2 \; + \; \Delta E.$$

The calculated formation energies are 1.62 and 0.68 eV/molecule for the polymerized diphenylmethane and tetraphenylmethane, respectively. Although these reactions are endothermic, the formation energies are small enough to overcome the polymerization reaction, leading to the three-dimensional covalent networks of $sp^2$ and $sp^3$ C atoms. Small $\Delta E$ of poly-diphenylmethane and poly-tetraphenylmethane is ascribed to the phenyl arrangement around $sp^3$ C atom. Mutual angles of phenyls in poly-diphenylmethane and poly-tetraphenylmethane are almost same as those of an asolated tetraphenylmethane (Table 2). As for the phenyl-phenyl arrangement for the poly-tetraphenylmethane, the angle is about 8.3°- 13.2° which is slightly shallower than the ideal angle of biphenyl.

Because of the covalent networks of phenyl or biphenyl with methane vertexes, these polymers could be a low density materials with nanometer scale pores. Indeed, the densities of the polymerized diphenylmethane and tetraphenylmethane are 0.31 and 0.83 g/cm$^3$, respectively, which are lower by one- to two-tenth than that of diamond. The estimated pore radii are 6.9 and 14.7 Å for the diphenylmethane and tetraphenylmethane polymers, respectively. Therefore, the polymers can incorporate atoms and molecules so that they are possible materials for designing the molecular capacitors. It should be noted that these polymers can accommodate $C_{60}$ or other fullerene molecules in their interstitial pores, leading to the interesting complexes with mixed network dimensionality as the case of $C_{60}$ intercalated graphite45). On the other hand, these nanoscale pores decrease the mechanical strength of the networks, even though they consist of strong covalent bonds of $sp^2$ and $sp^3$ C atoms. Indeed, they have small bulk moduli of 39 and 9 GPa/cm$^3$ for diphenylmethane and tetraphenylmethane polymers, respectively, which are extremely smaller than that of diamond.

Figures 3(a) and 3(b) show the electronic structure of the polymerized diphenylmethane and tetraphenylmethane, respectively. Covalent networks are semiconductors with an indirect band gap of 3.38 and a direct gap of 3.02 eV for diphenylmethane and tetraphenylmethane polymers, respectively. Furthermore, they have peculiar band structures in both valence and conduction states: Each energy band consists of four branches, two of which have finite dispersion of about 0.5 eV forming a Dirac cone at the W point while the remaining two show flat band or less dispersive natures throughout the Brillouin zone. For both cases, the highest branches of the valence band and the third lowest branches of the conduction band show flat band nature. Thus, the polymers may exhibit the strong absorption or emission between these states in UV region. Moreover, by tuning the Fermi level to these flat band states using appropriate doping techniques, they also may exhibit unusual physical properties, such as magnetism and superconductivity, because of the large Fermi level density of states associated with these state, leading to the Fermi level instability. In addition to the flat band states, although the $\pi$ electron networks are segmented in each phenyl or biphenyl and are terminated by $sp^3$ C atoms situated at the network vertexes, the Dirac cone with the band width of 0.5 eV indicates that $\pi$ electrons could itinerate through the covalent network with different hopping probabilities between and within $sp^2$ moieties.

We investigate the effective mass of electron and hole of these polymers. For the conduction band edge of diphenylmethane and tetraphenylmethane polymers at the $\Gamma$ point, the effective masses of electron are 2 and 7, respectively, irrespective of the $\boldsymbol{k}$ direction, indicating that the electrons possess relatively large effective masses. In contrast, as for the hole masses of the diphenylmethane polymer, the hole masses around the L point are 8, and 4 $\Gamma$ alongand Q lines, respectively. For the case of tetraphenylmethane polymer, the hole mass around the $\Gamma$ point is 142, owing to the flat band nature of the states. Therefore, hole masses of these polymers are heavier than the electron masses. In particular, the holes injected into the valence band edge of the tetraphenylmethane may exhibit unusual phenomena attributed by the partially filled flat dispersion band.

To provide further insight into the electronic structure of these porous three-dimensional covalent networks, we show squared wave function of the highest three branches at the valence band edge and the lowest branch in the conduction band at the $\Gamma$ point of the polymerized diphenylmethane and tetraphenylmethane [Fig. 4]. Note that the flat dispersion bands are doubly degenerated become of their pyrocroa symmetry. All wave functions exhibit their extended nature throughout the network except the methane sites. Three states in the valence band show a nature of the highest occupied molecular orbital of an isolated phenyl or biphenyl, despite they are connected to methane vertexes, while the lowest branch exhibits the lowest unoccupied molecular orbital nature of the isolated phenyl or biphenyl. Therefore, the substantial band dispersions of the valence and conduction bands are ascribed to the wave function overlap between adjacent $sp^2$ moieties. By focusing the electron state associated with the flat band states which are doubly degenerate at the $\Gamma$ point, the wave function also exhibits its extended nature similar to the other dispersive states. Therefore, the flat band at the valence band edge is not caused by the segmentation of the phenyl or biphenyl by the methane, but the delicate balance of wavefunction overlap among the highest occupied states of $sp^2$ moieties, as the case of the flat band associated with the edge states of graphene nanoribbons with zigzag edges[14,15)].

## 4. Discussion

Characteristic band dispersion relation, which consists of the flat band and a Dirac band, seems to be the similar to that of the kagome band for two- and three-dimensional kagome networks. From the topological views, phenyl and biphenyl are arranged in the tetrahedral symmetry with sharing their vertexes, which could be regarded as the three-dimensional kagome networks with internal degree of freedom, because $\pi$ electron is extended through the $sp^2$ constituents. To ensure the qualitative mechanism of the flat band state in these polymers, we perform the single orbital tight-binding calculation on the three-dimensional networks consisting of dimers which are arranged in tetrahedral manner with the inter- and intra-dimer electron transfers of $t$ and $t'$ (=1), respectively, as the simplest model of the three-dimensional kagome network with the internal degree of freedom to simulate the diphenylmethane and tetraphenylmethane polymers [Fig. 5(a)]. With increasing the inter-dimer transfer $-t$ from 0, quadruply degenerate bonding and antibonding states of the dimer form valence and conduction bands with characteristic band dispersion relation [Fig. 5(b)]. The valence and conduction bands consist of two flat dispersion bands and two dispersive band with the Dirac cone at the W point up to the $t = -0.5$, which is qualitatively the same as the band structure of the diphenylmethane and tetraphenylmethane polymers.

As in the case of these polymers, the electron transfer among adjacent $sp^2$ moieties is smaller than that within the $sp^2$ moiety, because the inter-phenyl/inter-biphenyl spacing is longer than C-C bond length. Therefore, the unusual electronic structures in these polymers are ascribed to the $\pi$ constituent units arranged in tetrahedral manner, being regarded as the three-dimensional kagome networks with the internal degree of freedom. Note that the further increase of the inter-dimer transfer ($t > -0.5$) leads to the fascinating electronic structure, in which the half-filled flat band emerges at the Fermi level. Thus, the diphenylmethane and tetraphenylmethane polymers may have such unusual electronic structure at the Fermi level with the enhancement of the inter-phenyl or inter-biphenyl $\pi$ electron transfer by controlling geometric structures around the methane vertexes.

## 5. Conclusions

We studied geometric and electronic structures of three-dimensional porous hydrocarbon covalent network consisting of diphenylmethane or tetraphenylmethane which is polymerized each other, using the DFT with GGA. According to the choice of the constituent non-planar hydrocarbon with the three-dimensional covalent networks, both diphenylmethane and tetraphenylmethane polymers are regarded as the three-dimensional kagome network with the internal degree of freedom characterized by phenyl and biphenyl, respectively, as far as the $\pi$ electron states are concerned. Owing to the covalent networks without the substantial distortions from ideal $sp^2$ and $sp^3$ C atoms, these polymers have relatively small total energy of 90 and 65 meV/atoms, indicating that the polymers are energetically stable. Furthermore, the thermal stability and possible polymerization reaction have been confirmed by ab initio molecular dynamics simulation under the elevated temperature and by the evaluation of the formation energy, respectively. The electronic structure analysis clarified that the polymers are semiconductors with the moderate band gap of 3.4 and 3.0 eV for the diphenylmethane or tetraphenylmethane polymers, respectively. More interestingly, these polymers possess peculiar band structures, which consist of a doubly degenerate flat band states and two dispersive bands forming a Dirac cone around the W point. These peculiar geometric and electronic properties make these polymers constituent materials for wide area of modern technology. The wavefunction analysis and the simple tight-binding calculation on the model system reveals that the peculiar electron states is ascribed to the delicate balance between inter- and intra-phenyl/biphenyl π electron transfer, indicating that these polymers could be regarded as the three-dimensional kagome networks with the internal degree of freedom.

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# Figure Captions

**Fig. 1.** (Color Online) Optimized geometric structures of the (a) diphenylmethane and (b) tetraphenylmethane polymers. The black, gray and white ball indicate the $sp^3$ C, $sp^2$ C, and H atom, respectively. (c) A schematic view of phenyl arrangement around $sp^3$ C atom. $\vec{n}_i$ indicates the normal vector of each phenyl.

**Fig. 2.** Snap shots of the geometric structures of the (a) diphenylmethane and (b) tetraphenylmethane polymers under the temperature of 1500K for 0.5ps simulation times. The black, gray and white ball indicate the $sp^3$ C, $sp^2$ C, and H atom, respectively.

**Fig. 3.** (Color Online) Electronic energy band of (a) the diphenylmethane and (b) tetraphenylmethane polymers along the high symmetries points in the fcc Brillouin zone. The energies are measured from that of the valence band top. An index I is the lowest branch of the conduction band. Index Ⅱ and Ⅲ indicalte the highest and the second highest branches of the valence band. An indexes Ⅳ indicates the top of second kagome band and the third highest branch in valence band for poly-diphenylmethane and poly-tetraphenylmethane, respectively.

**Fig. 4.** (Color Online) Isosurfaces of the squared wavefunction at the Γ point of (a) the diphenylmethane and (b) tetraphenylmethane. The indexes in each panel correspond those in Fig. 3. The isosurfaces correspond with the electron density of 2.0 e/(a.u.)$^3$.

**Fig. 5.** (Color Online) (a) Geometric and (b) electronic structures of the three-dimensional kagome network consisting of dimers. t and t' indicate the inter- and intra-dimer electron transfers, respectively.

**Table I** Optimized bond length of the diphenylmethane and tetraphenylmethane polymers. The bond labels defined in Figure 1.

| | bond length | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | d1 | d2 | d3 | d4 | d5 | d6 | d7 | d8 |
| p-diphenylmethane | 1.55 | 1.40 | 1.40 | 1.39 | - | - | - | - |
| p-tetraphenylmethane | 1.56 | 1.41 | 1.40 | 1.39 | 1.39 | 1.41 | 1.41 | 1.49 |

**Table II** Phenyl arrangement around $sp^3$ C atom of the poly-diphenylmethane, poly-tetraphenylmethane, and tetraphenylmethane. The angles labels defined in Figure 1.

| | $\theta_{12}$ | $\theta_{13}$ | $\theta_{14}$ | $\theta_{23}$ | $\theta_{24}$ | $\theta_{34}$ |
|---|---|---|---|---|---|---|
| tetraphenylmethane | 100.2 | 78.7 | 128.2 | 52.8 | 102.3 | 79.0 |
| poly-diphenylmethane | 99.7 | 80.4 | 131.7 | 48.2 | 99.5 | 80.4 |
| poly-tetraphenylmethane | 109.6 | 81.6 | 117.1 | 48.9 | 94.8 | 72.8 |

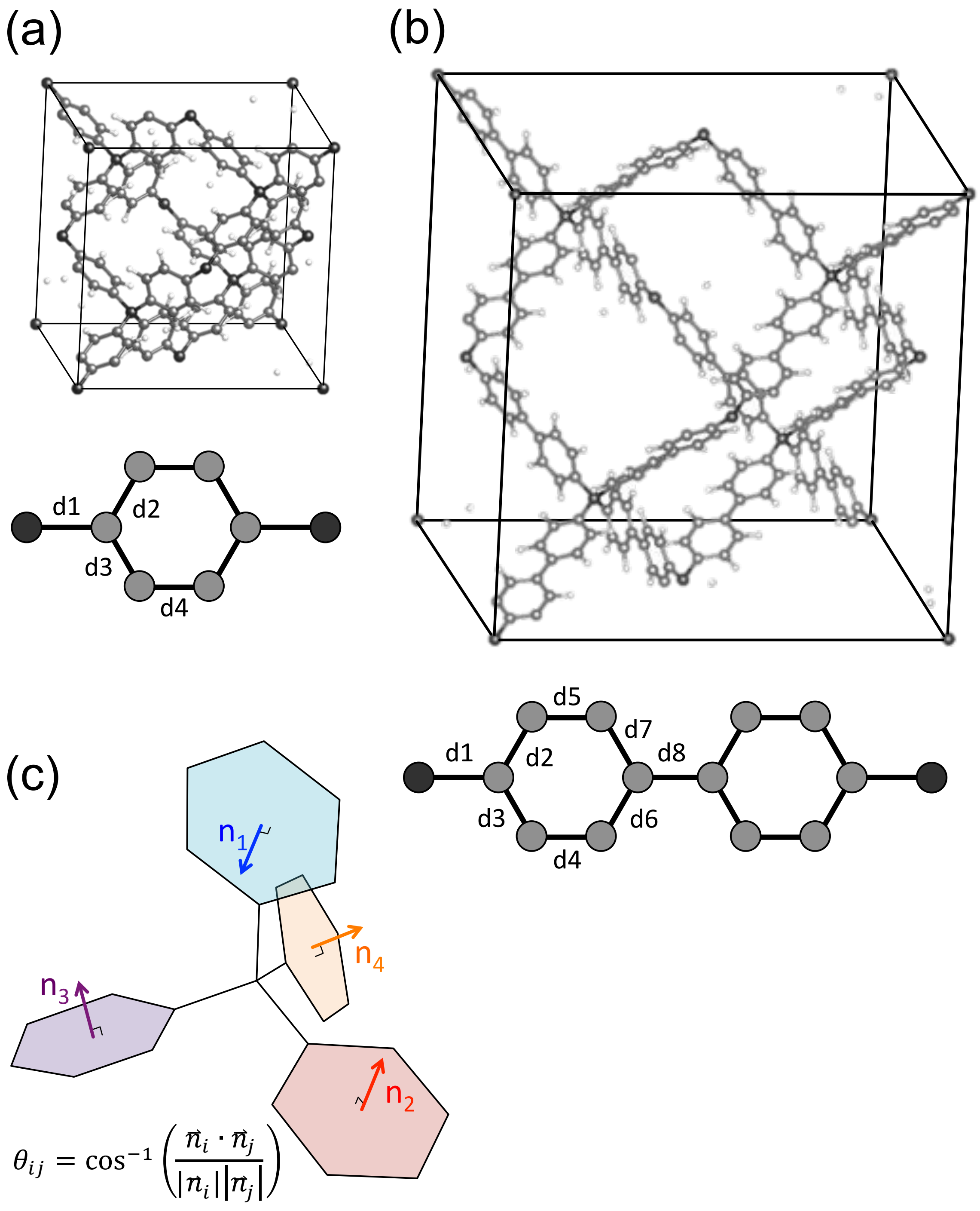

Fig. 1. (Color online)

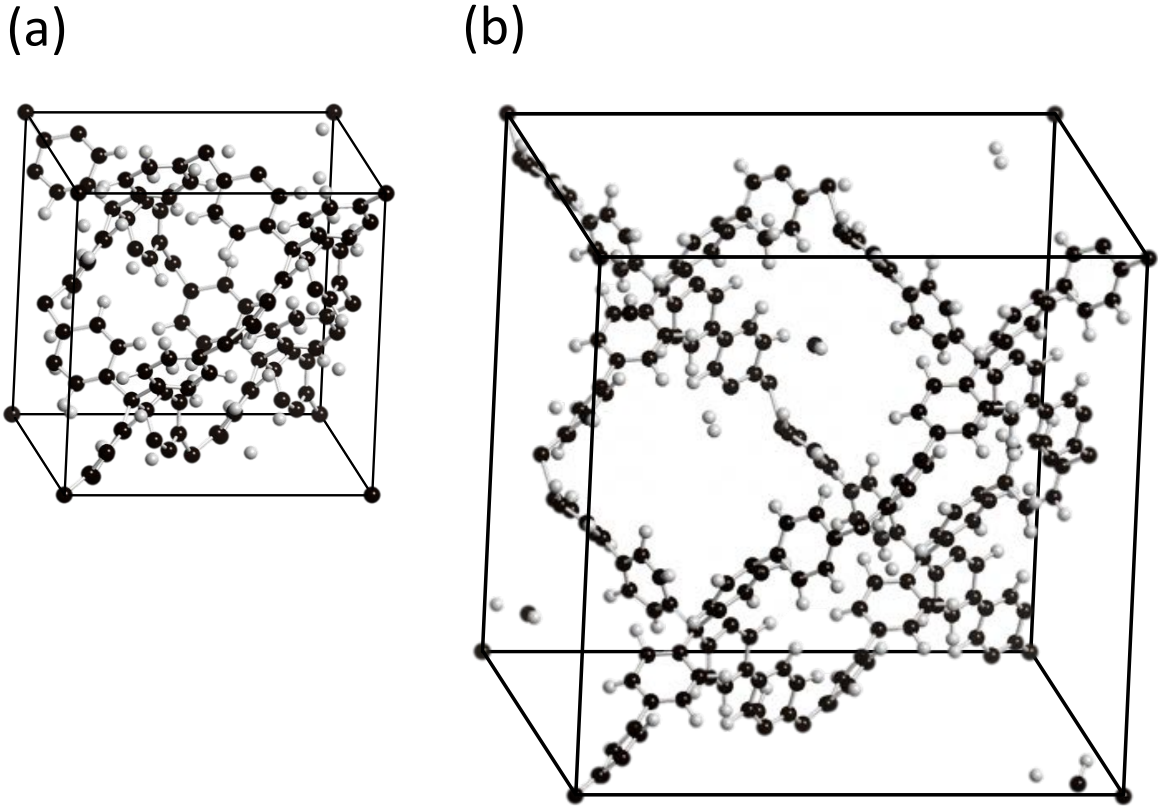

Fig. 2. (Black and white)

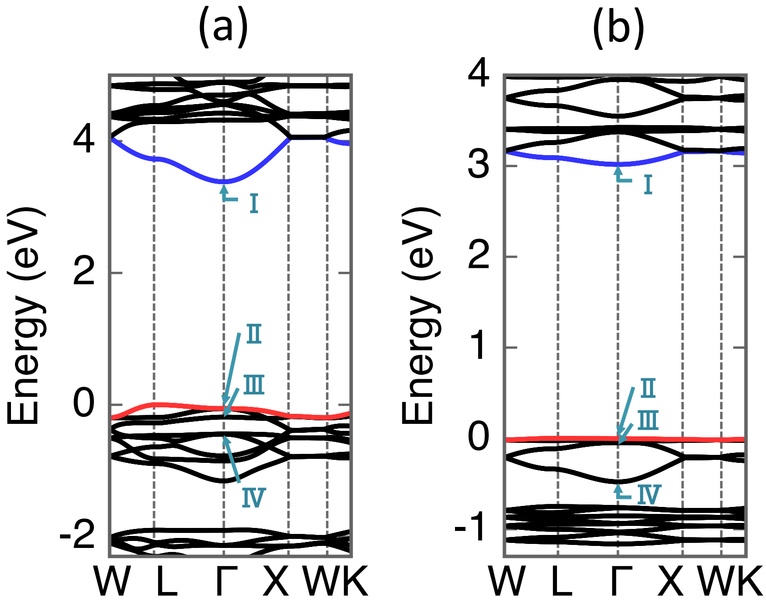

Fig. 3. (Color Online)

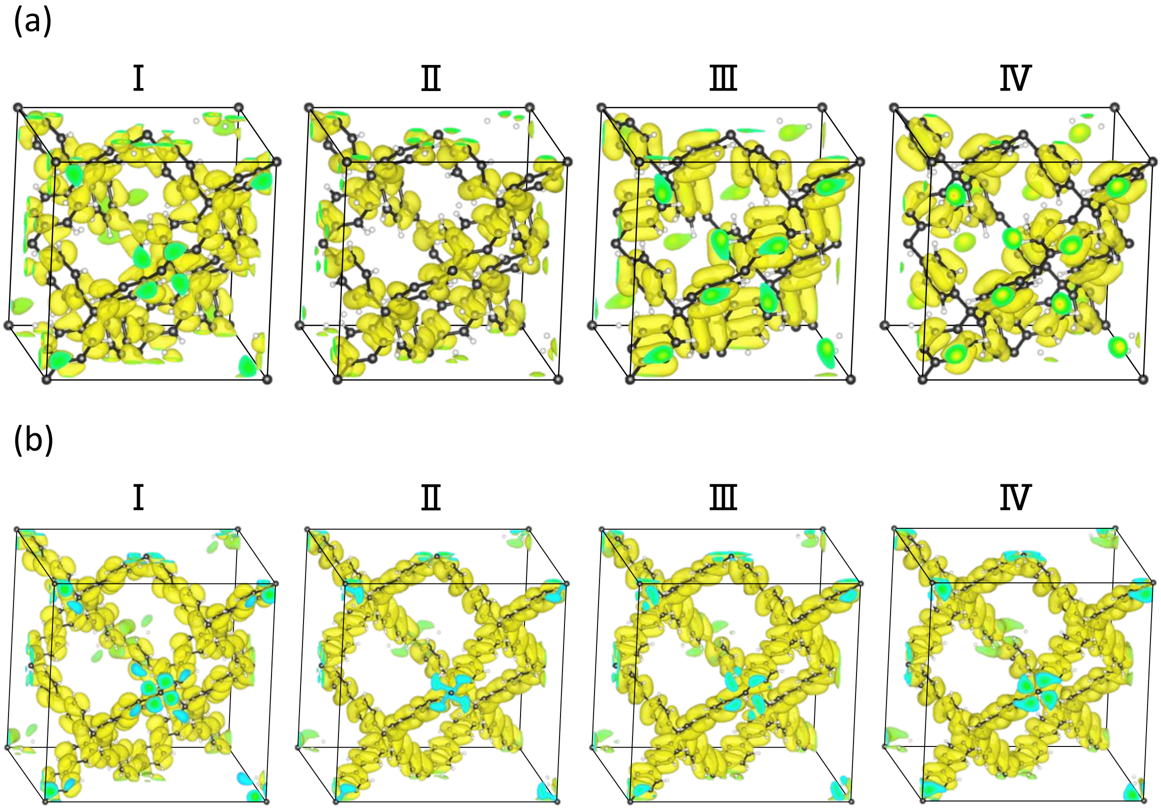

Fig. 4. (Color Online)

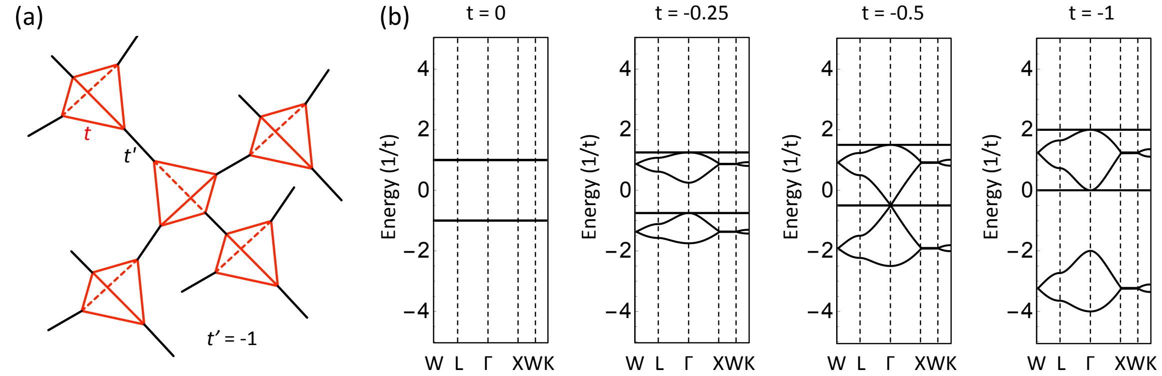

Fig. 5. (Color Online)