Bandgap evolution in nanographene assemblies

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Recently cycloarene has been experimentally obtained in a self-assembled structure, forming graphene-like monoatomic layered systems. Here, we establish the bandgap engineering/prediction in cycloarene assemblies within a combination of density functional theory and tight-binding Hamiltonians. Our results show that the inter-molecule bond density rules the bandgap. The increase in such bond density increases the valence/conduction bandwidth decreasing the energy gap linearly. We derived an effective model that allows the interpretation of the arising energy gap for general particle-hole symmetric molecular arranges based on inter-molecular bond strength.

1 Introduction

The ability to predict and control the energy gap in 2D materials allows the rational design of nanodevices. Graphene, the first discovered 2D material, has emerged as a promise to different phenomena and device application. Its monoatomic layer has shown to be very resistant against tearing while retaining the flexibility inherent in 2D system. Together with these mechanical properties, the emerging Dirac cone makes its electronic mobility reach $10^3$ cm$^2$V$^{-1}$s$^{-1}$. The 2D structure, combined with interesting electronic properties, lead to the emerging field of vdW heterostructures of 2D systems for device designs. Graphene functionalization and interfacing have also brought a degree of freedom in tuning its properties. For instance, upon transition metal absorption/interfacing, graphene presents magnetic and topological phases ruled by the spin-orbit coupling. One lasting challenge in graphene systems is creating semiconducting phases with a wider gap to expand its application in nanoelectronics and photonics. However, finding ways to fine-tune the graphene energy gap around 0.5 eV, and higher is still an open problem. Inducing an energy gap in graphene has been proposed by applying an external field in graphene bilayers. Additionally, a small gap ($\sim 100$ meV) can be opened by interfacing graphene with boron-nitride and other substrates. Nano-technological applications could profit from a graphene system with an energy gap of the silicon order.

Recently nanoporous graphene has emerged as a solution to higher gap graphene (with $\sim 1$ eV gap). Such systems can be viewed as an assembly of carbon molecules forming graphene-like systems, usually presenting porous or distortions. Given the interest in those systems, they have suffered a rapid development with many molecule/structures synthesized. The variety of such molecular systems allows for many possible self-assembled structures, leading to rich nanoporous graphene structures. For instance, different coronoids structures were synthesized on Au(111), while cellulose acetates have shown to evolve to graphene monolayers on Cu surface. In recent work, Qiang et al. have identified the self-assembly of cycloarenes in Au(111) surface. Such graphene frameworks can host a semiconducting phase, envisioned for graphene electronics devices. Additionally, such structures can preserve graphene mechanical characteristics: (i) strong planar sp2 bond; (ii) weak interlayer vdW interaction for future heterostructures devices. Moreover, the nanoporous structure allows for further chemical functionalization.

In this paper, we correlate the cycloarene assemblies with their inherent energy gap. Here we show that the energy gap depends linearly on the inter-molecule bond density, being almost independent of the assembly structure. By using a density functional theory (DFT) fitted tight-binding (TB) model, we have tracked different assemblies’ electronic structure. We propose an effective model that allow to understand the gap variation phenomena while showing its generality to other molecular-based porous graphenes.

2 Methods

We have performed DFT calculations as implemented in the Quantum Espresso code [37]. The exchange-correlation was included within the PBE functional [38] in a plane-wave base with a cutoff energy of 30 Ry. We also performed HSE06 hybrid-functional calculations [40] to access a better estimation of the cycloarene energy gap. For the isolated molecule, a single k-point was considered for Brillouin zone integration, while for the assemblies, a k-mesh of $3 \times 3 \times 1$ special points. The electron-ion interaction was described within the projected augmented wave method (PAW) [43], where all atoms were relaxed until the forces...
In order to construct the assemblies, we are taking the cycloarene molecule as a building-block. Cycloarene is a coronoid nano-graphene, C108-molecule, as shown in Fig. 1(a). We have calculated an isolated molecule with the DFT approach, presenting a carbon-carbon mean distance of 1.43 Å and a non-magnetic ground state ruled by the molecule’s armchair termination. The non-magnetic ground state is 0.92 eV lower in energy than a doublet configuration (1 unpaired electron). Our converged isolated molecule follows the same carbon-carbon distance distribution observed experimentally. Our goal is to explore assemblies of C108 nano-graphenes, which have a large number of carbon atoms in the periodic cell.

To expand our DFT calculations for higher number of atoms, we derived a nearest-neighbors (NN) TB model. In this model, we considered the on-site energy of the carbons $p_z$ orbitals as zero. The Hamiltonian is described as

$$ H = \sum_{\langle ij \rangle} t \langle i | \langle j \rangle, \epsilon_g, \langle DFT \rangle, \langle TB \rangle \rangle $$.  

with the summation over NN sites. By taking $t = 2.7$ eV, the TB model could predict the DFT bandgap energy which we validate for three different assemblies band structure [Fig. 1(b)-(d)]. The TB model deviates from the DFT bandgap on average by only 0.08 eV. Such small variation, compared with the energy gap scale (~1 eV) does not alter the discussion presented below.

### 3 Results and Discussion

The isolated cycloarene molecule presents a calculated energy gap of 2.01 eV, on the PBE functional level. By assembling it in different structures, we found a gap reduction. The control of molecules' position on surfaces, by atomic force microscopy and scanning tunneling microscopy tips, and nano-patterning in graphene allows the precise generation of ordered structures. Additionally, by varying experimental growth degrees of freedom, highly ordered structures can self-assemble.

Here we explore different cycloarene assemblies by varying the number of bonds between neighboring molecules and the lattice geometry. For a hexagonal cell with perfect triangular geometry, only three possible structures can be constructed, with 1, 3, and 5 bonds between adjacent molecules, as shown in Fig. 1(b), (c), and (d), respectively. Such structures give rise to variations of the energy gap in the assembly, being 1.89, 1.22, and 0.44 eV [Fig. 1(b)-(d)]. Following the same inter-molecule bonding order, we can construct three molecular AB sublattice graphene-like structures, as shown in Fig. 1(e)-(g). In these graphene-like structures, the inter-molecule bond is equal to the perfect triangular...
structure, 1, 3, or 5. However, the inter-molecule bond density

\[ \eta = n_b/N, \]

with \( n_b \) inter-molecule bonds and \( N \) molecules in the unit cell, gets lower than the triangular systems by a factor of 2. This lowering of \( \eta \) weakens the coupling between neighboring molecules and leads to an increase in the energy gap of \( 1.85 \rightarrow 1.95, 1.22 \rightarrow 1.57, \) and \( 0.44 \rightarrow 1.26 \text{ eV} \) [Fig. 1(e)-(g)]. Comparing the band structures of Fig. 1 we see that the effective inter-molecule interaction, ruled by \( \eta \), alter the HOMO/LUMO molecular states dispersion, that is, alter its bandwidth. Such an effect lower the energy gap for high-dispersive bands [Fig. 1(b2)] while converges to the isolated molecular gap (2.01 eV) for low-dispersive bands [Fig. 1(e2)].

Linear assemblies between cycloarenes are present in its experimental realization. By studying different 1D periodic geometries, we see also a dependence of the energy gap with the different inter-molecular bond density. For a linear array of cycloarene with only one bond between molecules, we see an energy gap of 1.93 eV, Fig. 2(a). Such gap is lowered to 1.64 and 1.63 eV for linear and sinuous molecular arrays with three bonds (\( \eta = 3 \)) between neighboring molecules [Fig. 2(b1)-(b2)]; and to 1.39 and 1.35 eV for the five bonds case [Fig. 2(c1)-(c2)]. Here we can understand that (i) the gap has a weak dependence on the system structure (linear or sinuous), instead (ii) the inter-molecule bond density rules the energy gap.

From (i) and (ii), we are motivated to extend the cycloarene assemblies to other geometries and track the gap evolution of the system as a function of the inter-molecule bond, Fig. 3(a). We have explored 42 different assemblies based on 2D lattices ranging from one molecule per unit cell (108 atoms/unit cell) up to 13 molecules per unit cell (1404 atoms/unit cell), depicted in the supplemental material. The energy gap follows a linear tendency with the carbon bonding density \( (\eta) \) between adjacent cycloarenes, Fig. 3(b). As previously stated for the 1D assemblies, the energy gap's linear behavior is weakly dependent on the molecular assembly geometry. That is, taking different geometry assemblies but with the same \( \eta \) presents a low energy gap variation of \( \sigma = \sqrt{\langle \epsilon_g^2 \rangle - \langle \epsilon_g \rangle^2} \sim 0.05 \text{ eV} \). We could extrapolate such linearity to an energy gap curve evolution of \( \epsilon = \epsilon_g^0 - \alpha \eta = (2.07 - 0.11 \eta) \text{ eV} \). The \( \epsilon_g^0 \) value from the linear extrapolation (isolated molecule gap) deviates by only 0.06 eV from the calculated one. Although the energy gap underestimation in DFT calculations, the energy gap trend is correctly described. As we will show next, the linear factor \( \alpha \) originates from the inter-molecule interaction energy, to which DFT offers excellent estimations. To give a better estimation of the cycloarene assemblies energy gap, we have performed hybrid-functional cal-

![Figure 2](https://example.com/figure2.png)

**Fig. 2** 1D assemblies of cycloarene forming hole decorated graphene nanoribbons. The upper panels show the atomic configuration with red shaded regions indicating the inter-molecular bonds. (a) The lower inter-molecular bond density 1D assembly, (b)-(c) the second and third lowest inter-molecular bond density assembly with two configurations: (a1)-(b1) linear, and (b2)-(c2) sinuous.

![Figure 3](https://example.com/figure3.png)

**Fig. 3** (a) Examples of different cycloarene assemblies. All explored assemblies are described in the supplemental material. (b) Energy gap evolution with respect to the inter-molecule bond density \( \eta \).
culations for the isolated molecule and the three reference assemblies, Fig. 1(a1)-(d1). Here we found that the bandgap increases by 34% on average, 29% for the isolated molecule, giving an energy gap of $\varepsilon^g_0 = 2.48$ eV. These results are in accordance with the predicted linear gap evolution. By adjusting $\varepsilon^g_0$ to the experimental value, a realistic estimation of the assembly range of the bandgap is obtained. From voltage-dependent differential conductance measurements the experimental gap of cycloarene was estimated to be 2.97 eV, representing an increase of 19% in relation to the HSE calculations. Assuming such correction to the other structures, we can expect the cycloarene assemblies bandgap to evolve in the range of [2.97, 0.81] eV. Therefore, the cycloarene assemblies allow tuning porous graphene energy gap in an interval of energy close to the silicon values ($\sim$ 1 eV).

We can understand the linear behavior of the energy gap with a simple two-level interacting model with hamiltonian

$$H = \begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix},$$  \hspace{1cm} (3)

to which eigenvalues, for $\Delta$ real, is given by $\varepsilon_{\pm} = \pm|\Delta|$, and the energy gap between the two levels $\varepsilon_{\pm} = \varepsilon_+ - \varepsilon_- = 2|\Delta|$. This hamiltonian’s base $\{|\pm\rangle\}$ can always arise in semiconducting/insulating systems with particle-hole (chiral) symmetry. They relate with the HOMO, LUMO states by $|\pm\rangle = (|\text{HOMO}\rangle \pm |\text{LUMO}\rangle)/\sqrt{2}$. By forming an assembly of this molecular system, inter-cell interactions ($V$) will appear in the hamiltonian

$$H_A = \begin{pmatrix} 0 & \Delta + V \\ \Delta + V^* & 0 \end{pmatrix},$$  \hspace{1cm} (4)

which will modify the energy gap to $\varepsilon_\pm = 2\sqrt{(\Delta + V)(\Delta + V^*)}$. The inter-cell coupling ($V$) can be written generally as $V = \delta f(k)$. Here, $\delta \in \mathbb{R}$ is the coupling strength, and $f(k)$ is an oscillatory term given by the system periodicity. For simplicity taking a 1D system and $f(k) \in \mathbb{R}$, it assumes the form $f(k) = \cos(k)$. The energy gap at each k point is

$$\varepsilon_\pm = 2|\Delta + \delta \cos(k)|.$$  \hspace{1cm} (5)

The minimum gap will occur in the $f(k)$ minimum, $[f(k)]_{\text{min}} = -1$, $[\varepsilon_\pm]_{\text{min}} = 2|\Delta - \delta|$.  \hspace{1cm} (6)

Therefore, the energy gap behaves linearly with the inter-cell coupling strength. Similar arguments are possible for 2D assemblies, and a low coupling limit $\delta \ll \Delta$ is straightforwardly obtained for a general case (3D), all obeying the same linear equation.

The proposed model captures the gap evolution of the studied cycloarene system. Here the number of bonds between neighboring cycloarene rules the inter-molecule coupling, $\delta = (0.11 \eta) \text{ eV}$. The generality of this model can predict the gap evolution of other non-magnetic carbon-based molecules. For instance, we can exemplify by discussing two different TB models of graphene assembly. In Fig. 1(a1), we considered the graphene formed by C$_2$ molecules assembled towards increasing intermolecular interaction. The system gap evolves linearly with the intermolecular interaction, Fig. 1(a2). In this illustrative model, the $|\pm\rangle$ base states assume precisely the $|A\rangle$ and $|B\rangle$ sublattice states of the C$_2$ molecule. Additionally, we can consider graphene as the assembly of benzene molecules [Fig. 1(b1)], where the gap also evolves linearly with $\delta$ [Fig. 1(b2)]. This second case is a limit of the well-known Kekule distortion of graphene.

Besides the band gap, the mobility of a semiconductor is key for constructing efficient devices. Organic semiconductors present usually a mobility in the range of $10^{-1}$ to $10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ while values around $10^2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ are required for practical application [cite]. Graphene is predicted to have a phonon-limited ultrahigh-mobility of $210^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with its zero-gap Dirac bands. In order to estimate the electronic mobility in the semiconducting nanoporous graphene we have computed the phonon-limited mobility based on the deformation potential [57], which was successfully used to interpret mobility in 2D systems based on the Takagi model [58-60]. The mobility can be written as

$$\mu_j = \frac{e\hbar^2C_{2D}k_BTm_j^*m_d(E)}{k_BTm_j^*m_d(E)},$$  \hspace{1cm} (7)

with $\mu$, $\hbar$, and $k_B$, the electron charge, reduced plank constant and Boltzmann constant, respectively; $C_{2D}$ and $m_j^*$ are the elastic modulus and effective mass along the $j$ propagation direction, with $m_j = \sqrt{m_i^*m_j^*}$ being the average effective mass. The term $E$ is the deformation potential constant for the conduction band minimum (for electron mobility). We have computed $C_{2D}$ and $E$ considering a dilatation/compression with a step of 0.5% of the lattice constant. These DFT calculations were performed in the three systems used as reference, Fig 1(b1)-(d). Here we estimate the mobility along the zig-zag direction ($\mu_{zz}$) of each lattice, the values are presented in the Table 1.

The estimated values are in accordance with 3D nanoporous graphene systems [61] and show that for suitable assemblies with higher inter-molecular bond-density ($\eta$) the mobility can reach ultra-high values towards the graphene predicted mobility. Particularly, the system with higher $\mu$, which is the experimentally achieved assembly [23] of Fig 1(d1), present an estimated energy
gap of 0.8 eV.

4 Conclusions

In summary, we have explored cycloarene self-assemblies as a route to manipulation of the energy gap in graphene-like systems. We have established a rule for the energy gap engineering based on the inter-molecule bond density. The energy gap evolves linearly with the inter-molecule bond density. That leads to a possible variation of the bandgap from 2.9 eV (lower bond density) down to 0.8 eV (higher bond density) in cycloarene assemblies, estimated from the experimental energy gap. We explain the origin of such inter-molecule bond dependence of the energy gap as the π bandwidth variation in the assemblies. This interpretation allows us to define an effective model for the gap evolution. Our effective model can be generally applied to predict and understand the bandgap evolution in other non-magnetic carbon molecules, capturing the bandgap in Kekule distorted graphene. Within the cycloarene assemblies, we have shown that for the higher inter-molecular bond density systems (lower bandgap), the phonon-limited electron mobility can reach ultrahigh values up to $10^4 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$.

Conflicts of interest

There are no conflicts to declare.

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