Theoretical predictions of two-dimensional covalent organic frameworks (COF) with triangular topologies

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Abstract. In the last decades, covalent organic frameworks (COFs) – the class of highly ordered organic crystalline porous, have attracted huge research interest because of their unique structures and potential applications in gas separation/storage, catalysis, energy storage and optoelectronic materials device. In this works, we proposed several series of triangular topologies to study the applicability of the formation of two-dimensional (2D) COFs from various pre-defined individual building blocks using Density Functional based tight-binding (DFTB) method. Different high-symmetry stacking, e.g. AA and AB stacking sequence are also designed and investigated. The designed series band gaps are found to be ranging from 0 eV to 2.93 eV. Furthermore, the COF series, revealing a variety of promising mechanical and electronic properties, which can potentially find future realistic applications.

Keywords: Covalent organic frameworks (COF), Density Functional based tight-binding (DFTB), structure prediction.

1. Introduction  
In a past decade, the covalent organic framework (COF) has emerged as a novel class of high ordered crystalline organic polymers, attracting a huge research interest due to its potential applications in gas storage and/or separation, energy storage, catalysis and optoelectronics. Since 2005, when Yaghi et.al. have reported the synthesis of the first crystalline COF [1], many COFs with various configurations have been produced using reticular chemistry. The strong covalent framework bonded and the very low mass density due to the inclusion of the light-weight elements only is the main advantage of COF over the metal organic framework (MOF) [2]. Crystalline COF networks, especially the 2D COFs of predefined ordered structures with diverse stability, functionality and porosity can be obtained just starting from designed secondary building blocks and their arrangement of closed shapes to completely cover a plane [3-5].  
From a topological viewpoint, to form 2D COFs by connecting chosen secondary building blocks into a high symmetry periodical skeletons and ordered nanoporous using only one type of monomer as vertices and edges, only a few polygon pattern have satisfy the critical mathematical requirement of such combination as triangular, tetragonal and hexagonal lattice and pore’s shape, see the review [4-7].
and reference there in. That is the construction principle of COF’s frameworks, which is to direct the
topological evolution with controlled geometry [8].
In this work, we extend our previous design approach [9, 10], to examine one of the possible
geometries of the 2D COF’s pore – triangular topology. The two series of 2D COF have been
identified and studied by computations at the levels of density functional by the suitable DFTB+
method. Their structural and thermodynamical stability, mechanical properties and electronic
structures are examined and characterized.

2. Computational details

Density-Functional-Based Tight-Binding Plus (DFTB+) method

Our calculations were performed within the spin-polarized, charge self-consistent, density functional
based tight binding plus (DFTB+) approach, which is described in details in Refs [11-15]. Briefly, the
DFTB+ method is based on a second-order expansion of the spin-dependent Kohn-Sham total energy
functional with respect to a given reference charge and magnetization density. Deriving all matrix
elements and orbitals from fully density functional theory calculations, DFTB relies on a small basis
set of atomic orbitals, which reduce the matrix dimension and two-center non-orthogonal Hamiltonian,
allowing use of extensive look-up table. By such DFTB+ is semi-empirical method, which is different
from empirical one by its explicit calculation of the wave function, which allows deeper physics
insight and better control of the approximation used. Using self-consistent Mulliken charge projection,
this approach has demonstrated to give transferable, accurate interaction potential and numerical
efficiency for molecular dynamic simulation of supercell containing up to a thousand atoms. The
DFTB+ parameterization advantage is that only a few, possibly well chosen systems are needed to
create the parameters. Then this well tested parameter in an attention for solid state systems and defect
physics as in the current case, can be used for much larger systems due to its transferability. More
details on DFTB can be found in the review [13] and [14]. In our calculations, the parameter and its
transferability have been successfully applied in several previous DFTB works [3, 16-18]

3. Results and discussion

3.1. Structure design

In this section we briefly describe our approach for theoretical design the crystal structure of 2D
covalent organic frameworks (COF) with triangular topologies. For the systematic design our COF
crystal structure, we use the two monomer types which are commonly called as the secondary building
blocks as the node and the linker, the former is similarly as crystal site and the later as connectivity.
Traditionally, the linear, trigonal and hexagonal building blocks have been selected for designing 2D
COF. In this work to study the COF’s family with the triangular topology we choose the two kinds of
node (I–II) (see the first row in Fig.1) with 6/mmm and 6m2 point symmetry, i.e. belong to hexagonal
group, accordingly and two series of the linkers (III-IV), where III is a chain consist of n number of
single linker unit (n =1, 2, 3, 4, 5) (see left 2nd row in Fig.1) whereas the (IV) linker type is a series of
similar triangles also with 6m2 point symmetry the side’s length from one to five. At a results we can
create two series of COF crystal structure (named as A, B), each have five members and can be seen
as a series COF with same node and different linker of common kind. With that 2D layer the total of
20 studied structures of two series. Some of the COF of A-series are already well known in the
literature [7, 8] however most of them with more than one linker units are still hypothetical.

(I) (II)
Fig1. The two type of the nodes (1st row) and the two series of the linkers (2nd row) numbered to the linear length and side length $n$ ($n = 1, 2, 3, 4, 5$), used as the secondary building blocks in this work, (the “…” denotes a series sequence). Here Hydrogen, Carbon, Oxygen, Boron atoms are shown in purple, gray, red and green accordingly. All graphics illustrations in this work is prepared by VESTA [18].

Starting from the hexagonal point symmetry we construct the 2D COF of triangular pore’s shape (triangular topology) by connecting 3 identical nodes with 3 identical linker of various length from a sets of nodes and linkers shown in Fig.1. Our COF was chosen as the highest possible symmetry configurations of design (see Fig.2). Note that different from the linker series III that is linear chain of a linker units, the linker IV can also be treated as a node so that the B-series can also seen as a series of same linker, i.e. II, and different node with similar kind (see Fig.2 (right)). Further when these 2D mono-layers are stacked each on other, there are various stacking sequences. We used only the two highest-symmetry stacking sequences commonly named as AA and AB. In AA stacking, the atom’s layer lie directly on the top of the adjacent layers, while in the AB stacking, the nodes staggered directly on the geometric centre of triangular-rings of neighbouring layer (see Fig.2 column 3).

Fig2. From left to right the relaxed structure of some representative of series A (in the first row as: (A-1, A-2 … A-2-AB)), B (in second row B-1, B-2, … B-2-AB), with increasing linker length with AA stacking is assumed if not specified, i.e. A-1, B-1 …). The black box shows the 2D unit cell.

3.2. Cohesive energy, phase stability and Equation of State (EOS).

After designing, we have performed careful structural relaxation and calculated binding energy of the COF’s structures. Then we compare the energetic stability of our 2D COF by considering the dependence of their total energy vs structural strain. To compare the total energy of different structures with different number of atoms, here we used the relative binding energy, which is the binding energy of the strained structure relative to the its minimum, i.e. to the binding energy of the relaxed structure.
Fig. 3 shows the dependence of calculated relative total binding energy per atom vs. volume strain, in which the solid curves derive from third-order Birch–Murnaghan EOS fitting [19].

[Graph showing relative binding energy vs. volume strain]

The analysis of the dependence of relative binding energy vs. volume strain, leads to the following conclusions on COF energetic stability as: (1) all the designed COF are energetically stable phase, which can exist against the volume deformation (at reasonable range) (2) structures A-1, B-1 show different reaction against stressed strain, structure A-1 is more stable (iii) Within one series the smaller pore, i.e. A-1 in the series, is more stable.

[Graph showing calculated bulk modulus vs. effective core radius] [Graph showing bulk modulus vs. COF porosity]

From the fitting the binding energy results vs volume strain to the third order Birch–Murnaghan isothermal equation of state (EOS), as performed in Ref. [19] we can derive a value of the bulk modulus with respect to pressure. The bulk modulus, quantity shows the material’s ability to resist to uniform strain, is important quantity to estimate the mechanical stability of the solid composition and crystal structure. Noted that, for the COF’s pore effective radius we use the radius of inscribed circle of a triangle. i.e. the circle tangent to all its sides. So that as the pore’s effective radius increases, the bulk modulus falls off rapidly before having a tendency to saturate to a certain value at radius larger than 10 Å. In Fig. 4 (right), there is another show for the bulk modulus in a function of the porosity. Here porosity is the effective parameter that we defined as...
the ratio between the occupied volume and the total volume of the COF, which reflects the porosity of the structures. For the occupied volume we defined as the volume confined by the Connolly surface or solvent-excluded surface (also known as the molecular surface) inside the COF’s pore region. Tentatively, the porosity and the effective pore radius are inversely dependent, so thus the trend of the bulk modulus in Fig.4 (right) is somewhat opposite to that in Fig.4 (left). So that the arrow in Fig.4 (right) show the pore’s radius increases with the decrease of the porosity. Noted that although the bulk modulus depends on radius similarly with the series A and B, as the bulk modulus decreases when the radius increase then having a tendency to saturate, it depend differently on the porosity. That is with a series A the porosity is reduced and approaching a certain value at smaller porosity whereas with a series B the bulk modulus decreases nearly linearly (see Fig.4 (right)) with the porosity. It may due to the different type of the linker in series A and B (as shown in Fig.1). Finally the series B shows more mechanically stable than the series A.

3.3. Electronic band structure
To determine whether our designed COF’s series, if synthesized, would possess novel electronic properties, one should explore their electronic structures. The comparing benchmark between the DFTB theoretical calculated gap and the experimental optical band gap (received from the electronic adsorption spectra) for double-stage COFs, was done by X. Chen et.al [6], which shows that DFTB gives fairly good result, e.g. for HTTP Triphenylene-based COFs the DFTB gap is overestimated the experimental gap for only 10-15%. To compare the DFTB gap result with standard DFT one, we have carried out an additional calculation for our A-1 structure within dispersion-corrected density functional theory (DFT-D3) with the projector-augmented wave (PAW) method as implemented in Vienna Ab Initio Simulation Package (VASP) using the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional. The DFT’s gap for our A-1 is 0.998eV. Comparing to our DFTB 2.038 eV, it is shown that the standard DFT calculation grossly underestimate the COF’s band gaps. Figure 5 shows the calculated band gap vs. pore’s effective radius. The calculated parameters of the electronic band structure are also shown in Table 1. Our calculations show that the band gap of series A weakly changed varies from 2.04 eV to 2.2 eV among the series while the gap of series B fall off fast and reached a zero value at larger linker.

![Fig5. The band gap vs. COF’s pore effective radius](image)
It may due to the fact that as mentioned on the structural design part, the series B can consider as a series of same linker (II) and different node (IV) and due to the structure of IV, that can see as a graphene fragment with zero HOMO-LUMO gap. The inset image in the Fig.5 show how we define the effective radius as of the radius of the gray region, i.e. pore’s inner circle.

3.4. Thermodynamical stability
In this part, we continue our stability discussion extends to finite temperatures by performing the DFTB+ ab-initio Molecular dynamics (AIMD) simulation within NPT ensemble and Andersen thermostat for two representatives of our A family of structures as A-1 and A-5. We choose the MD time step of 1-2 fs and the run is over 5000 steps, equivalent 5 ps time). The MD results show that our structures, i.e. A-1 and A-5, can be stable against temperature at the temperature of 300K with the volume via density nearly unchanged (see the Fig.6 (left)). It also preserves the cell parameter, i.e. lattice parameters – cell size and cell angles as well as topology.

![Graph of temperature and density over time for A-1 and A-5 structures.](image1)

![Graph of cell parameters over time for A-1 and A-5 structures.](image2)

**Fig6.** DFTB+ AIMD simulation the employs the Andersen thermostat and NPT ensemble for the representative structure of A-1 (1st row) and A-5 (2nd row)
3.5. Effect of layer’s stacking

Fig 7. The relative binding energy vs. the number of the linker units (or vs. different linker in a series) (left) and the stacking energy of three series with stacking scheme AA (solid lines) and difference in binding energy per layer of the AA and AB stacking schemes (dash lines) of each series (right).

Our 2D COF structures are truly 2D structure since it can exist in 2D or mono layer form. Fig. 7 (right) show the binding energy of the two series depend on the linker. While the binding energy of series A increase (more negative) linearly with the linker unit increases, since its linker itself is linear chain of the linker unit III (see Fig. 1 second row), the binding energy of the series B depend not linearly to the linker unit, in fact a rather quadratic one. That because the B-series linker are not simple chain of the first linker unit (IV). The B-series linker have scaled over the area of the triangle, which side scaled as integral number of the linker unit. (see Fig. 1 second row).

In order to estimate the effect of layer’s stacking as well as the stability that the staging of layers could bring, we have calculated the stacking energy, which is defined here as:

\[ E_{\text{stack}} = E_{\text{mono}} - \frac{E_{n\text{-layer}}}{n_{\text{layer}}} \]

Where \( E_{\text{stack}} \) is a stacking energy, \( E_{n\text{-layer}} \) is total energy of \( n \)-layer number of layers stacked in a COF, \( E_{\text{mono}} \) is total energy of monolayer stand alone.

The results in Fig. 7 (right), show similar behaviour to the Fig. 7 (left). That the stacking energy and the difference in binding energy between AA and AB of the series A depend linearly to the linker’s unit due to the linearly inclusion of the linker unit to the linker chain. Whereas the non-linearly inclusion to the linker’s chain causes the non-linear dependence of the stacking energy.

In Fig. 7 (right) the dashed line show the energy difference between the binding energy per layer between the AA and the AB stacking. The difference in binding energy with different stacking shows for both the series A and B (red and blue dashed line) the AB stacking is energy favourable than AA only in the case of two first linker unit, then further while the pore’s radius is enlarge the AA stacking is more favourable.

For completeness, we also show the estimations of unit cell (UC) internal specific pore surface toward the application COF in catalytic application (see Table 1), which also somehow reflect the porosity of their framework. The other essential structural parameters, such as the lattice contents, particle density, mass density, crystal structure together with the symmetry space group, which shows that all the COF phases are high symmetry. i.e. come with high stabilities, are also listed in characteristic.
### Table 1. Calculated characteristics of most of studied phase of triangular COF.

| Structures | A-1 | A-2 | A-3 | A-4 | A-5 | A1-AB |
|------------|-----|-----|-----|-----|-----|-------|
| Mass Density (gcm⁻³) | 1.392 | 1.158 | 0.989 | 0.862 | 0.764 | 1.431 |
| V/at Å³ | 12.818 | 14.087 | 15.649 | 17.333 | 19.087 | 12.467 |
| Part.density (10²³ cm⁻³) | 576.78 | 816.71 | 1056.639 | 1296.577 | 1536.524 | 2304.802 |
| Crystall symmetry | P6/MMM (IT191) | P6/MMM (IT191) | P6/MMM (IT191) | P6/MMM (IT191) | P6/MMM (IT191) | P6/MMM (IT191) |
| Unit cell (atoms) | 72 | 102 | 132 | 162 | 192 | 144 |
| Lattice param. Å (a-c) | 3.48 | 3.48 | 3.48 | 3.48 | 3.48 | 3.48 |
| Band gap eV | 2.038 | 2.039 | 2.046 | 2.044 | 2.043 | 2.222 |
| UC specific surface area Å² | 132.82 | 275.14 | 383.13 | 492.37 | 603.87 | 378.13 |
| UC occupied volume Å³ | 683.84 | 920.27 | 1175.73 | 1424.89 | 1668.66 | 2884.04 |
| UC free volume Å³ | 239.05 | 516.65 | 890.37 | 1383.13 | 1996.15 | 706.42 |

| B-1 | B-2 | B-3 | B-4 | B-5 | B-1-AB |
|-----|-----|-----|-----|-----|-------|
| Mass Density (gcm⁻³) | 1.029 | 0.926 | 0.872 | 0.845 | 0.832 | 1.098 |
| V/at Å³ | 16.360 | 17.695 | 18.568 | 19.133 | 19.502 | 15.329 |
| Part.density (10²³ cm⁻³) | 336.611 | 416.565 | 512.539 | 624.523 | 752.513 | 672.652 |
| Crystall symmetry | P-6M2 (IT187) | P-6M2 (IT187) | P-6M2 (IT187) | P-6M2 (IT187) | P-6M2 (IT187) |
| Unit cell (atoms) | 42 | 52 | 64 | 78 | 94 | 84 |
| Lattice param. Å (a-c) | 3.49 | 3.44 | 3.41 | 3.39 | 3.38 | 6.53 |
| Band gap eV | 2.912 | 1.277 | 0.177 | 0.00 | 0.0 | 3.058 |
| UC specific surface area Å² | 301.58 | 548.56 | 795.01 | 1044.48 | 1289.97 | 813.29 |
| UC occupied volume Å³ | 143.52 | 173.72 | 204.56 | 236.1 | 267.51 | 425.85 |
| UC free volume Å³ | 304.46 | 457.83 | 630.53 | 805.03 | 1007.6 | 526.21 |

### 4. Conclusions
The COF’s materials, especially 2D COF’s with topological pore of hexagonal symmetry, i.e. triangular and hexagonal form, have now been increasingly important because of the ability to control their pore sizes and shapes, which, in turn, tailors their physical and chemical properties for particular applications. The main interest on these COF’s is due to their capability to interact with ions or atoms throughout both their pore channel and their internal surface areas, making them attractive for application as catalysts or as membranes. Thus our theoretical work enables the predictions of properties and/or tendency are useful for technological application. The analysis on structural, mechanical, electronic and thermodynamic properties clearly reveals that the COF series phases may describe the real 2D COF.
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