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

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Abstract. Recently, covalent organic frameworks (COFs) - a new class of highly ordered organic crystalline porous polymers, have attracted huge research interest because of their unique structures and potential applications in gas separation/storage, catalysis, energy storage and optoelectronic materials development. We have studied several structure's series of hexagonal shapes to explore 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 stackings, e.g. AA and AB stacking sequence are also designed and investigated. The designed series's band gaps are found to be ranging from 1.7 to 4.0 eV. Further, 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
Recent advances in materials science have reached the capability of producing highly ordered open-framework materials with precise control of the crystalline structures. Since the work of Yaghi et.al. In 2005, where they reported the first crystalline covalent organic frameworks (COFs) [1], many COFs with various porous tessellations have been synthesized using reticular chemistry. In COF’s structure the organic linker molecules are connected together by covalent elements, e.g. nitrogen, boron and oxygen atoms to form a regular framework. Thus the advantage of COF is that all framework bonded by the strong covalent bonding, and they are composed of light-weight elements only comparing to the metal organic framework (MOF), leading to a very low mass density [2]. That open an approach to use various possible building block and related geometry to the design and synthesis of such reticular structures [3].

From a topological viewpoint, one may distinguish two- and three-dimensional COFs. For two-dimensional (2D) COFs, the covalently bound frameworks are within a mono-layer. Then the crystal is build up, like the graphite, by stacking mono-layers, that are connected by weak Van der Waal (VdW) bonds, i.e. not covalent. Its highly ordered columnar periodic arrays, low densities, low gravimetric, permanent porosity and high thermal stabilities have attracted considerable attention for applications related to gas storage and/or separations, optoelectronics and catalysis, see Ref and reference there in...
Its modular nature has permitted integration of various conjugated molecular building blocks into predictable design enabled the creation of many distinctive COFs with tunable pore sizes and shapes [5, 6]. At a given relative density, it is well known that the shape-dependent strength of cellular micro-lattice shows higher relative strength with the triangular and hexagonal pore’s topologies [7]. Therefore, in this work, we extend our previous approach [8], examining the possible geometries of the 2D COF’s pore, i.e., hexagonal. A number of series of 2D COF have been identified and summarized in Table 1, and studied by computations at the levels of density functional based tight binding. Their structural stabilities, mechanical properties, and electronic structures of these 2D COFs are examined, and the implications of the results on COFs materials engineering are discussed.

2. Bottom-up structure design approach
In this section we briefly describe our “bottom up” approach for theoretical design the crystal structure of 2D covalent organic frameworks (COF) with hexagonal topologies.

For the systematic design our COF crystal structure, we have considered 2 type of the secondary building blocks as the node and the linker, the former formally stayed similarly as crystal site and the later as connectivity, so that each COF was built from one type of the node and one type of the linker. Our 2 kind of node (I–II) (see Fig.1 1st row) and two series of the linkers (I-II) consist of n single linker unit (n = 1, 2, 3, 4, 5) (see Fig.1 2nd row) to create three series of COF crystal structure (named as A, B and C), each have five member. Moreover, we have considered two type of the most table according to B. Lukose et.al. [3] stacking configurations as AA and AB resulting on the total of 30 studied structures. Some of the COF are already well known in the literature [3, 5, 6] however most of them with more than one linker units are still hypothetical.

The possibility of the formation of different low-density COF framework materials based on highly stable the node and linker, which are were systematically investigated in [3, 5, 6]. Generally, the preferred COF are chosen as the high symmetries with HOMO–LUMO gaps, that are supposed to be most energetically stable. Via the covalent coalescence or linking scheme from these secondary building units, many interesting design of COF of varying crystal structure and porosity can be proposed.

Starting from the hexagonal symmetry we construct the 2D COF of hexagonal pore’s shape (hexagonal topology) by connecting 6 identical nodes with 6 identical linker of various length from our sets of nodes and linkers as shown in Fig.1. The COF was chosen as with the higher-symmetry configurations of possible design (see Fig.2). The three series of COF’s design was specific that the A and B series have the same node and different type of the linker whereas the A and C series have the same linker type but are different in the node form. Further when these 2D structure are stacked each other one can find various stacking sequence. Here we used only the two stacking sequence with the highest crystal symmetry as AA and AB. In the AA stacking, the atom’s layer stacked directly on the...
top of the adjacent layers, while in the AB stacking, three-connected nodes staggered directly on the
geometric centre of six-membered rings of neighbouring layers (see Fig.2 column 3).

Fig2. From left to right the relaxed structure of some representative of series A (1\textsuperscript{st} row), B (2\textsuperscript{nd} row), C (3\textsuperscript{rd} row) with one linker unit (1\textsuperscript{st} column), two linker units (2\textsuperscript{nd} column) with AA stacking scheme and two-linker units with AB stacking scheme. The 1\textsuperscript{st} row also show the view of A-2-AB COF along the c-axes (upper right). The black box show the unit cell.

3. Computational details

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

The spin-polarized, charge self-consistent, DFTB approach 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. The method has been extensively discussed elsewhere [10-13]. With matrix
elements and orbitals are derived from Density Functional Theory calculation, the advantage of DFTB
method relies on the small basic set of atomic orbitals to reduce the matrix dimension for
diagonalization speed-up and the restriction to two center non-orthogonal Hamiltonian with extensive
using of look-up table. It distinguishes from semi-empirical methods by the explicitly calculation of
the basic wave function allowing deeper physics insight and better control of the approximation used.
DFTB method solved Kohn-Sham equation self-consistently using Mulliken charge projection. The
approach have proved to give transferable and accurate interaction potential as well as numerical
efficiency allowing Molecular Dynamic (MD) simulation of supercell containing several hundreds to a
thousand atoms. Thus DFTB is particular suitable to study the electronics proper and dynamics of
large mesoscopic system and organic molecule such as Nano-wire, CNT’s, DNA stands or absorbate
on surface, semiconductor hetero-structure etc. see review in [11-12] and references there in. In our
calculation the parameter and its transferability have been successfully applied in several DFTB works
[3, 8, 14-17]. Moreover, the DFTB have inclusion the COF Van der Waals interlayer interaction via
dispersion correction, which is suitable to modelling the specific 2D layered COF as for this work.
4. Results and discussion

4.1. Corhersive energy, phase stability and Equation of State (EOS).

To compare the stability of our 2D COF, we have calculated total binding energy per atom vs. volume for every studied structures. The results are presented in Figure 3, in which the solid curves derive from third-order Birch–Murnaghan EOS fitting. Note to compare the binding 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 minimum corresponding to the binding energy of the relaxed structure.

![Fig3](image)

**Fig3.** The curve for the dependences of the relative binding energies vs volume strain for the representative structures of different series (A-1, B-1, C-1) (left) and the different structures within a series (right).

On the basis of these fitted curves, we may draw some conclusions on their energetic stabilities. As shown in the Figure 3, we can derive that (i) all our COF are energetically stable phase, which can be exist again collapse by reasonable volume deformation (ii) structures A-1, B-1, C-1 show different reaction against compressed and stressed strain (iii) Within one series the smallest pore, i.e. A-1 in the

![Fig4](image)

**Fig4.** Calculated bulk modulus vs. effective core radius (left) and bulk modulus vs. COF porosity (right).

Fig.4 right is the most stable against strain. From the fitting the above binding energy results vs volume strain to the third order Birch–Murnaghan isothermal equation of state (EOS), as performed in Ref. [18] we can have a value of the bulk modulus with respect to pressure. The bulk modulus which
measures material's resistance to uniform compression, and is important quantity to estimate the mechanical stability of the chemical composition and crystal structure. This is the macroscopic mechanical property and to estimate is we can make an efforts to establish direct correlations between the macroscopic properties and the microscopic parameters of crystal, related to the bonding nature of materials. Noted that, as the COF’s pore effective radius increases, the bulk modulus falls off rapidly before having a tendency to saturate to a certain value. In Fig. 4 (right), the bulk modulus is shown as a function of the porosity, the quantity we define here as the ratio between the occupied volume and the total volume of the COF, i.e. the porosity will vary on the range from 0 to 1. For the occupied volume we measured the volume confined by the connolly surface within the COF’s pore internal surface. Its characterizes the density of the COF phase and somehow reflects the porosity of the structures. 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). We note that although the bulk modulus depends on the COF’s structure and the COF’s pore radius (as shown in Fig. 4 (left)), the bulk modulus decreases when the porosity is reduced and approaching a certain value regardless the structure of the COF or the radius of the pore, ~11 GPa for all series with the porosity ~0.16. It mean as low-density range, the COF’s bulk modulus depends solely on density and very weakly depend on structure or pore radius and the tendency may be a common for the hexagonal topology. Where as in the larger region (~0.3-0.6) of the porosity the series A shows less stable than the series B and then the series C.

4.2. Electronic band structure
Exploring the electronic structure of the designed COF’s structures for determining to what extend they can be used for promising potentially electronic-related applications. Direct benchmark comparison between the DFTB+ calculated electronic gap and the experimental optical band gap (using the electronic adsorption spectra) of double-stage COFs, was done by X. Chen et.al [5], shows that DFTB gives fairly good gaps, e.g. for HTTP Triphenylene-based COFs the DFTB+ gap is about 10-15% overestimated the experimental gap. To benchmark the DFTB+ with standard DFT, we have performed 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 A-1 is 0.435eV. Thus, comparing to our DFTB 1.338eV, it shows that the standard DFT calculation grossly underestimate the COF’s band gaps. We show in Fig. 4 the curves of band gap depend on the COF’s pore radius. So that with the purpose of gas separation application for the pore’s effective radius here we defined as the radius of the pore’s inner circle. The inset image in the Fig.5 show how we define the effective radius as of the radius of the gray region.
The first observation is that the band gap of the COF’s structures is generally fall in the region of the visible light and it depend on the pore’s size. Given a pore’s effective radius $r$, the gap is different for the different series, i.e. depend on the node and linker compound. Similarly, by increasing $r$, the gap in general be reduced having a tendency to saturate to a certain value at large pore.

4.3. Thermodynamical stability
In order to testify our COF’s design structure are thermodynamical stable we have performed the DFTB+ ab-initio Molecular dynamics (AIMD) simulation within NPT ensemble and Andersen thermostat for the 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 5-10 ps. The MD run’s results show that our structures, i.e. A-1 and A-5, can be stable against temperature of 300K with the volume via density nearly unchanged (see the Fig.6 (left-1st row)), more over it preserves the cell parameter (via lattice parameters), i.e. the cell symmetry as well as topology.
Fig. 6. 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)

4.4. Effect of the 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 (right) 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.

Our 2D COF structures are truly 2D structure since it can be exist in 2D or mono layer form. Fig. 7 (left) show the binding energy of all 3 series with reference to binding energy of the series B. As reference to the series B, the two series A and C, which have the same linker type in common and different only in the nodes type show the linear dependences on the number of the linker’s unit so resulted in the parallel lines because of their common difference is the difference in node’s energy only. The linearity also shows that the binding energy linearly increase with the number of linker’s unit. It is resulted from the 2D bonding nature of the structures. Fig. 7 (left) also show that the type II of linker are more stable than the type I if we compare the binding energy of the series A and B, which have the same node but different in linker type, since the A series have higher binding energy.

In order to estimate the effect of layer’s stacking as well as the stability that the staging layer could bring, we have calculated the stacking energy, which is defined [3] as:

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

Where \(E_{\text{stack}}\) is a stacking energy, \(E_{\text{total}}\) is the total energy of \(n\)-layer number of layers stacked in a COF, \(E_{\text{mono}}\) is total energy of monolayer stand alone.
Our results in Fig 7 (right), show that all three series can gain an additional energy by stacking together compare to the mono layer case. Furthermore, to estimate the stability of the two stacking regime AA and AB sequence. We also calculate the energy difference between the binding energy per layer of the AA and the AB stacking, which show in Fig. 7 (right) by the dashed lines, It shows that stacking energy increase with the linker’s unit increases, i.e. gain more energy from the stacking. Again the linearity show the number node increases linearly and the short range of the bonding (2D). Further the difference in binding energy with different stacking show for the series A (red dashed line) the AB stacking is energy favourable than AA only in the case of one linker unit, whereas for the case of series B and C the AA is the more energy stable in all linkers. Hereby, 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 does reflect the porosity of their framework to a certain extent.

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.

**Table 1.** Calculated characteristics of most of studied phase of Hexagonal COF.

| Structures | A-1 | A-2 | A-3 | A-4 | A-5 | A-1-AB |
|------------|-----|-----|-----|-----|-----|--------|
| Mass Density (g/cm³) | 1.022 | 0.667 | 0.514 | 0.418 | 0.352 | 1.096 |
| V/Å³ | 15.062 | 21.345 | 26.784 | 32.343 | 37.956 | 14.036 |
| Part. density (10²³ cm³) | 336.66 | 576.47 | 816.37 | 1056.31 | 1296.26 | 672.71 |
| Crystall symmetry | P6/MMM (IT191) | P6/MMM (IT191) | P6/MMM (IT191) | P6/MMM (IT191) | P6/MMM (IT191) | P63/MMC (IT194) |
| Unit cell (atoms) | 42 | 72 | 102 | 132 | 162 | 84 |
| Lattice param. Å (a-c) | 14.53 | 22.53 | 30.06 | 37.60 | 45.14 | 14.53 |
| Band gap eV | 1.338 | 2.630 | 2.423 | 2.314 | 2.249 | 1.6 |
| UC specific surface area Å² | 132.82 | 275.14 | 383.13 | 492.37 | 603.87 | 378.13 |
| UC occupied volume Å³ | 386.43 | 648.18 | 889.6 | 1139.37 | 1389.26 | 784.79 |
| UC free volume Å³ | 246.15 | 898.66 | 1842.42 | 3130.84 | 4759.66 | 480/88 |

| Structures | B-1 | B-2 | B-3 | B-4 | B-5 | B-1-AB |
|------------|-----|-----|-----|-----|-----|--------|
| Mass Density (g/cm³) | 0.834 | 0.537 | 0.395 | 0.312 | 0.258 | 0.977 |
| V/Å³ | 18.059 | 26.988 | 36.185 | 45.461 | 54.766 | 15.411 |
| Part. density (10²³ cm³) | 672.554 | 1248.371 | 1824.276 | 2400.22 | 2976.183 | 1344.649 |
| Crystall symmetry | P6/MMM (IT191) | P6/MMM (IT191) | P6/MMM (IT191) | P6/MMM (IT191) | P6/MMM (IT191) | P63/MMC (IT194) |
| Unit cell (atoms) | 84 | 156 | 228 | 300 | 372 | 168 |
| Lattice param. Å (a-c) | 22.42 | 37.39 | 52.35 | 67.32 | 82.30 | 22.42 |
| Band gap eV | 2.230 | 2.334 | 2.340 | 2.331 | 2.327 | 2.494 |
| UC specific surface area Å² | 301.58 | 548.56 | 799.01 | 1044.48 | 1289.97 | 813.29 |
| UC occupied volume Å³ | 749.36 | 1358.65 | 1968.25 | 2579.01 | 3189.03 | 15.1398 |
| UC free volume Å³ | 767.59 | 2851.5 | 6281.83 | 11059.35 | 17183.75 | 1519.93 |
|                  | C-1     | C-2     | C-3     | C-4     | C-5     | C-1-AB  |
|------------------|---------|---------|---------|---------|---------|---------|
| Mass Density (gcm\(^{-3}\)) | 0.558   | 0.446   | 0.371   | 0.318   | 0.278   | 0.595   |
| V/at Å\(^3\)     | 28.817  | 34.210  | 39.728  | 45.302  | 50.916  | 27.007  |
| Part. density (10\(^{23}\) cm\(^{-3}\)) | 768.347 | 1008.292| 1248.252| 1488.221| 1728.196| 1536.37 |
| Crystall symmetry | P6/MMM  (IT191) | P6/MMM  (IT191) | P6/MMM  (IT191) | P6/MMM  (IT191) | FMMM    (IT69) |
| Unit cell (atoms) | 96      | 126     | 156     | 186     | 216     | 192     |
| Lattice param. Å (a-c) | 30.24   | 37.76   | 45.30   | 52.84   | 60.37   | 30.25   |
| Band gap eV       | 2.650   | 2.537   | 2.445   | 2.368   | 2.306   | 2.940   |
| UC specific surface area Å\(^2\) | 367.09  | 476.81  | 586.49  | 694.91  | 806.95  | 1222.21 |
| UC occupied volume Å\(^3\) | 868.51  | 1181.21 | 1368.27 | 1617.70 | 1867.63 | 2887.82 |
| UC free volume Å\(^3\) | 1897.57 | 3192.27 | 4829.27 | 6808.48 | 9130.28 | 803.72  |

From the above table 1, the symmetry of the hollow phases also confirm that in various structures different stacking and/or linking orders, resulted from mixing the hcp- and the fcc-type stacking, would produce different polytypes.

5. Conclusions

The stability of studied COF structures evident that, it is reasonable to believe that these phases would be the attractive synthesis targets. Our theoretical design on the three series of 2D COF with hexagonal topology follow by the bottom up approach from different types of secondary building unit with different stacking order of the monolayer show that, the COF’s series could survive in periodic systems without structural collapse, leading to many promising application in electronics, catalyst and gas separation.

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