Effects of Organic Linkers on Energy Gaps of Covalent Based Triazine Frameworks

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Abstract

The Covalent Triazine Frameworks (CTFs) were successfully synthesized from the experiments. They usually consist of triazine ring covalently bonded with organic linkers. CTF-Benzene was defined in case of the organic linker be benzene ring. Moreover, 5 different types of organic linkers, namely, Napthalene, Quinoline, Quinoxaline, Anthracene and Acridine were chosen to connect to the boroxine ring and these structures are abbreviated as CTF-Naphthalene, CTF-Quinoline, CTF-Quinoxaline, CTF-Anthracene and CTF-Acridine, respectively. In the present study, the structural parameters, the density of states and energy bands of these structures were investigated by means of the first-principles calculations. For the CTF-Benzene structure, it shows an indirect band gap structure with energy gap of 1.86 eV. By considering the electron density at the states of valence band maximum and conduction band minimum, it was found that the electrons are only localized on the benzene ring. Hence, the optical property of this structure directly related to type of organic linker. This leads us to calculate the optical property of various types of the organic linker in order to adjust the optical property in the Covalent based Triazine Frameworks. According to CTF- Naphthalene, CTF-Quinoline and CTF-Quinoxaline structures, we found that the energy gap ranges from 1.0 to 1.5 eV. Moreover, our calculations revealed that the energy gaps of CTF- Anthracene CTF-Acridine are 0.40 and 0.75 eV, respectively. Based on these results, it is clearly seen that the optical band gaps of these CTF structures can be adjustable in range of 0.4 - 2.5 eV depending on the type of organic linker. Finally, we believed that these newly generated structures might be useful for both photovoltaic and solarcell applications.

Keywords: Covalent Triazine Frameworks, organic linkers, optical bandgaps, first-principles calculations, electron density

Introduction

Two dimensional nanostructures such as Graphene [1,2], Covalent Organic Frameworks [3,4] and so on were shown to be appropriate materials for various applications [5,6]. The promising layered materials successfully synthesized in the experiment are the Covalent Triazine Frameworks or CTFs [7,8]. The CTF usually consists of boroxine ring (B_3O_3 ring) strongly bonded with the organic linker, benzene ring for this case, forming as a periodic framework. It consists of light elements such as N, C and H. This structure is very stable due to rather strong bonding between boroxine ring and the benzene ring.

According to thermogravimetric analysis (TGA) experiments, this structure decomposes at 690 °C under oxidative atmosphere. Moreover, pore volume and Brunauer Emmett-Teller (BET) surface area of this material are 0.52 cm^3/g and 2011 m^2/g, respectively [7]. Owing to rather high surface area, it can be used as gas storage applications. For hydrogen storage purpose, Chen *et al.* [9] decorated alkali and alkaline earth metals into the surface of the CTF-1. They found that Li is the best metals giving the highest hydrogen capacity. Moreover, the hydrogen uptake for Li decorated CTF-1 is very high, namely about 12 H_2 wt%. For CO_2 storage purpose, Gomes *et al.* [10] used the triazine functionalized hexagonally ordered covalent organic polymer (TRITER-1) to trap CO_2 gas, and they found that it can store CO_2 for 58.9 wt% at 273 K and 5 bar pressure. Moreover, this material can also be used as ammonia sensing [11] and it also acts as a host to trap various organic dyes in the solarcell application [12]. Due to these promising properties, the CTFs show as a potential materials for energy storage application. For instance, Sakaushi e*t al.* [13] used the disordered CTF-1 as an electrode in sodium ion battery. They found that the specific energy (~ 500 wh/kg) and specific power (~ 10 kW/Kg) are rather high. Based on the first-principles studies, the boroxine ring of the CTF is acted as electron acceptor (with electron affinity of +0.46). On the other hands, benzine rings are shown as an electron donor with electron affinity -1.15 eV [14]. Consequently, this material has a potential for organic semiconductors with variety of electronic and optical properties.

Crystal structure of the CTF-0 possesses space group P$\bar{6}$ (space group no. 174) with the lattice constant a = b = 7.3 Å and c = 3.3 Å [7]. Each B_3O_3 ring connects to the C_6H_4 or benzene rings as a periodic structure. Its stacking sequence is AAA. In one unit cell, there are total 15 atoms, consisting of 9 atoms of C, 3 atoms of O and 3 atoms of H. In the present study, we abbreviated the CTF-0 as the CTF-Benzene. The crystal structure of the CTF-Benzene is clearly presented in Figure 1. In order to obtain the diversity of electronic and optical properties of the CTF structure, we modified this structure by changing the organic linkers. In the present study, 6 different CTF-0 systems are considered, namely CTF-0 or CTF-benzene, CTF-Naphthalene, CTF-Quinoline, CTF-Quinoxaline, CTF-Anthracene and CTF-Acridine. Calculation details are clearly mentioned in Section 2. The structural parameters, charge density at the valence band maximum (VBM) and conduction band minimum (CBM), band structure and density of states of these structures were investigated by means of the density functional theory as discussed in Section 3. Lastly, Conclusions were described in Section 4.
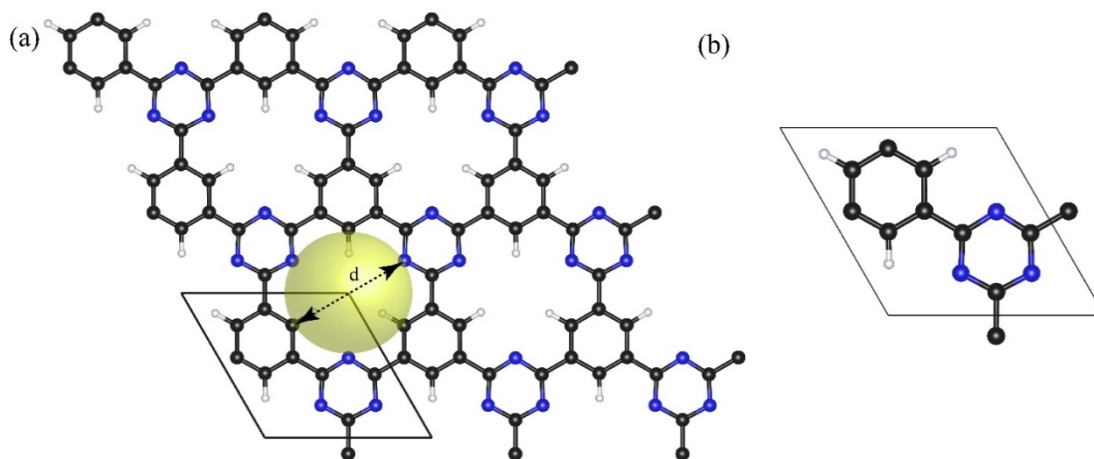

Figure 1 (a) Crystal structure of the CTF-0 or CTF-Benzene. Diameter (d) of yellow sphere stands for pore size of the CTF-0 structure. Nitrogen, carbon, and hydrogen atoms are shown as blue, black, and grey spheres, respectively. Black line represents unit cell of the CTF-0. (b) The unit cell of the CTF-0.

Computational methods

The electronic and optical properties of 6 different structures were computed by means of the density functional theory with the Vienna *Ab initio* Simulation Package (VASP) [15]. According to pseudopotential, the projector augmented wave approach [16] with Heyd-Scuseria-Ernzerhof 06 (HSE06) hybrid functional [17,18] was chosen. In the present work, the 650 eV of plane wave energy cutoff was successfully tested for total energy convergence. Under Monkhorst-Pack scheme [19], the $2\times2\times5$ and $3\times3\times7$ k-point samplings of the reciprocal lattice space were used for relaxed and static calculations, respectively. Lastly, the force acting to each ion was calculated by using the Hellman-Feynman theorem [20].

Results and discussion

Firstly, we determined the structural parameters of the CTF-Benzene by performing optimization this structure without any symmetry constraint. Moreover, we also relaxed other considered structures e.g. CTF-Naphthalene, CTF-Quinoline, CTF-Quinoxaline, CTF-Anthracene and CTF-Acridine as well. The structural parameters of these structures are summarized in **Table 1**. According to **Table 1**, it is clearly seen that our results are in excellent agreement to the experimental data [7]. Hence these results shown that our calculations give rather accurate results. Moreover, our study also revealed that the structural parameters of the boroxine ring of all considered structures seem to be constant. As a result, there is no change in boroxine ring when various organic linkers were inserted into the structures. In addition, our results shown that changing the organic linkers leads to varying the pore size of these materials. In other words, diameter (d) of yellow sphere in **Figure 1** is changed when we change the organic linker of the material. Experimentally, pore size of material can be measured by the BET technique. According to experimental results of Katekomol *et al.* [7], pore size of the CTF-0 is 5.6 Å. In the present study, we found that the pore size after performing the structural optimization of the CTF-0 is 5.66 Å. Hence, our calculated parameters used in the present work were appropriate because it gives very accurate results. In addition, the pore size of all considered structures ranges from 3 - 10 Å in the present study.

Table 1 Structural parameters of CTF-Benzene, CTF-Naphthalene, CTF-Quinoline, CTF-Quinoxaline, CTF-Anthracene and CTF-Acridine.

Systems	a	b	c	Boroxine ring		Organic linker		
	(Å)	(Å)	(Å)	N-C (Å)	N-C-N (Deg.)	C-C (Å)	C-H (Å)	C-C-C (Deg.)
CTF-Benzene	7.32	7.32	3.30	1.35	115.85	1.40	1.09	119.99
CTF-Benzene (exp) [7]	7.31	7.31	3.30	1.35	120.30	1.39	-	119.99
CTF-Napthalene	7.35	9.84	3.32	1.35	123.57	1.42	1.09	119.93
CTF-Quinoline	7.29	9.72	4.14	1.35	124.32	1.42	1.09	119.45
CTF-Quinoxaline	7.29	9.58	4.13	1.35	124.39	1.41	1.09	120.22
CTF-Anthracene	7.35	12.29	3.32	1.35	123.66	1.41	1.09	120.01
CTF-Acridine	7.33	12.15	4.24	1.35	124.12	1.42	1.09	120.16

Next, we investigated the band structure and the density of states of the CTF-Benzene. The calculated results are shown in **Figure 2a**. In addition, the density of states of the boroxine and benzene rings in the CTF-Benzene is represented in **Figure 2b**. As clearly shown in **Figure 2a**, the highest energy of the valence band is at point K and the lowest energy of the conduction band is at point H. Hence, the CTF-Benzene structure shows an indirect bandgap. According to **Figure 2**, we also determined the band

gap of this structure and we found that it is 1.86 eV. From **Figure 2b**, it was found that the major contribution of the states near the fermi level comes from the p-orbitals of the benzene ring. This result leads us to plot the electron density near the Fermi level. In the present work, the electron density of VBM and CBM was plotted. The first peak (about 0-0.5 eV below Fermi level in **Figure 2b**) was chosen as the VBM, and the first peak above the Fermi level was defined as the CBM (about 0 - 2.15 eV above Fermi level in **Figure 2b**).
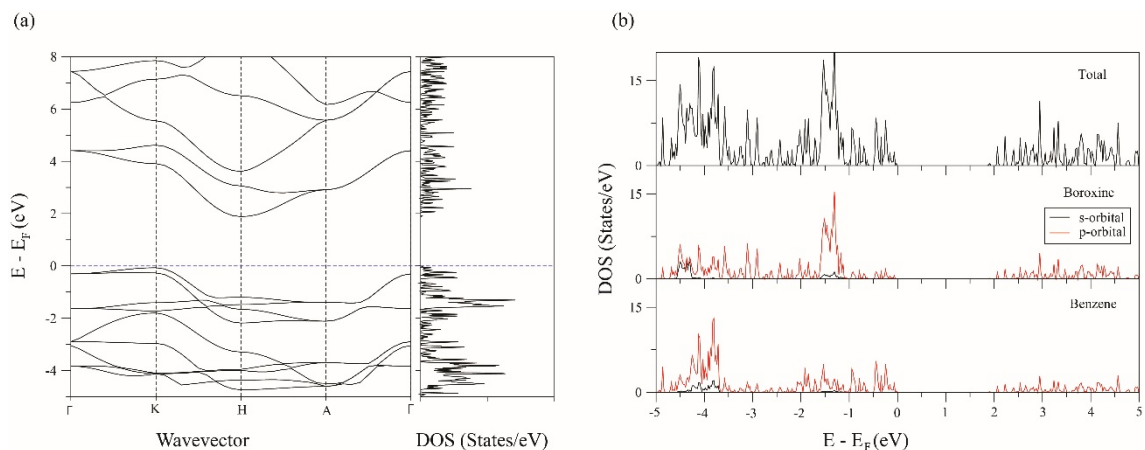

Figure 2 (a) Band structure and the density of states (DOS) of the CTF-Benzene. (b) Total density of states and the partial density of states of the boroxine and benzine rings. Γ, K, H and A points denote the high symmetry points in the Brillouin Zone.

The electron density of both VBM and CBM was presented in **Figure 3**. According to **Figure 3**, we found that electrons at the VBM and CBM are mainly contributed from the benzene ring. As a consequence, the organic linker (benzene ring) plays a crucial role for the electron excitations. Owing to these results, the optical property of this structure can be altered by changing the organic linker in this structure. In the current study, other 5 different types of the organic linkers, namely Napthalene, Quinoline, Quinoxaline, Anthracene and Acridine were replaced by the benzene ring of the CTF-0 and we defined these structures as CTF- Naphthalene, CTF-Quinoline, CTF-Quinoxaline, CTF-Anthracene and CTF-Acridine, respectively.
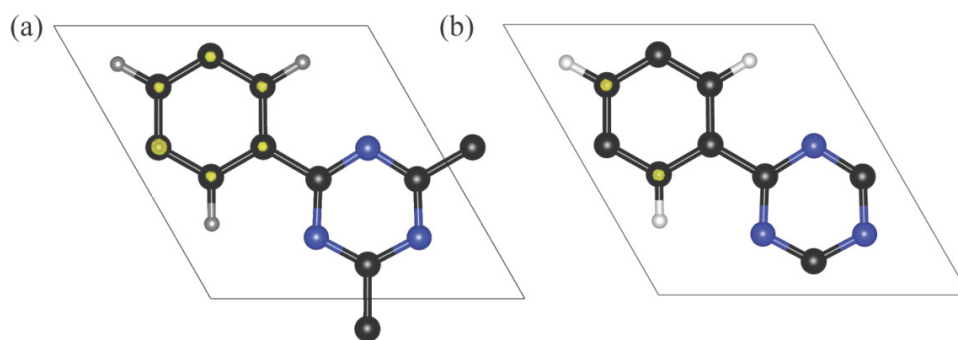

Figure 3 Electron density of (a) the VBM peaks (0 - 0.5 eV below Fermi level in **Figure 2b**) and (b) CBM peaks (0 - 2.15 eV above Fermi level in **Figure 2b**) of CTF-Benzene. Electron density of both VBM and CBM states is denoted by yellow shape.

Again, to investigate the optical property of these newly generated structures, the electronic density of states of the CTF-Napthalene was plotted as displayed in **Figure 4**. For other considered systems, the partial density of states (PDOS) of boroxine and organic linker rings is presented in the Supporting Information. According to CTF-Napthalene, its unit cell is represented in **Figure 4a**. By analyzing the PDOS in **Figure 4b**, we found that the states below the Fermi levels come mainly from p-orbitals of the Napthalene ring.
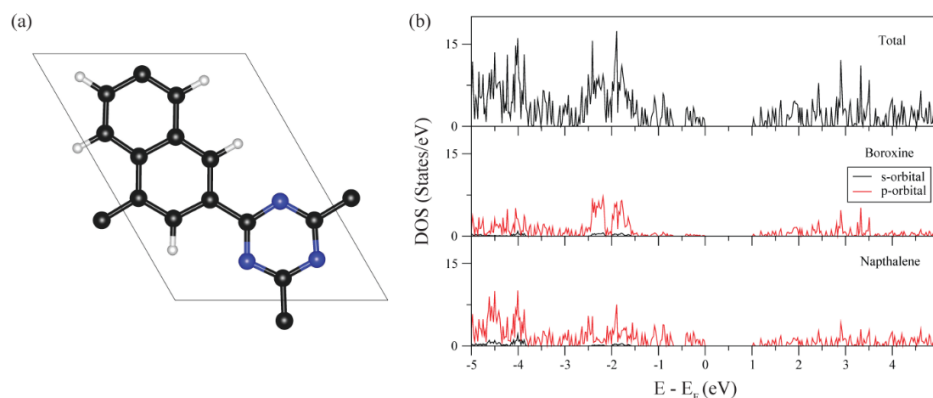

Figure 4 (a) Unit cell of the CTF-Napthalene. (b) The total and partial densities of states of the CTF-Napthalene.

Therefore, electrons from C atoms of naphthalene linker are excited to the conduction band when it absorbed light. As displayed in **Figure 5**, the band gap can be altered by changing the organic linker. Our results revealed that the energy gaps of these structures are 1.00, 2.60, 2.40, 0.37 and 2.10 eV for CTF-Naphthalene, CTF-Quinoline, CTF-Quinoxaline, CTF-Anthracene and CTF-Acridine, respectively. By considering the PDOS of the CTF-Quinoline, CTF-Quinoxaline, CTF-Anthracene and CTF-Acridine, we also found the same results as discussed in the case of CTF-Benzene and CTF-Napthalene. The major contribution to the states near the Fermi level comes mainly from the p-obitals of N and C atoms of the organic linker. In addition, distortion of crystal structure (from the structural optimization process) is also another factor related to the existence of the electron states near the Fermi level.
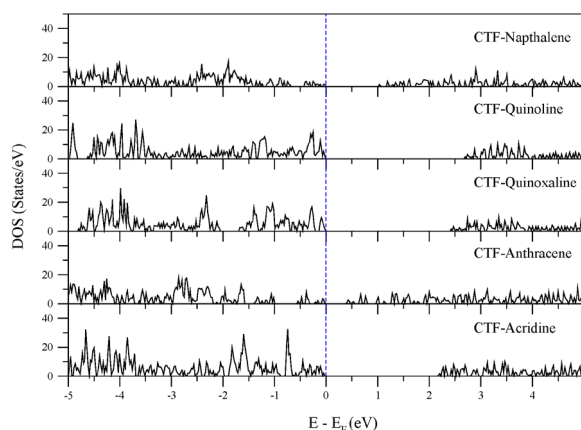

Figure 5 The total density of states of the CTF-Napthalene, CTF-Quinoline, CTF-Quinoxaline, CTF-Anthracene and CTF-Acridine. The dotted vertical line represents the Fermi level.

Based on all results, the relationship between optical bandgap of all considered structures and the number of rings in organic linker is presented in Figure 6. Moreover, it was found that the optical band gap can be tuned by changing the electronic structure of the organic linkers. In addition, the changing of the optical gap in these structures comes from the p-orbitals of the atoms in the organic linkers. Finally, we believed that these findings can stimulate both theorists and experimentalists to investigate the appropriate materials which can tune the optical properties for using in various optical related applications.
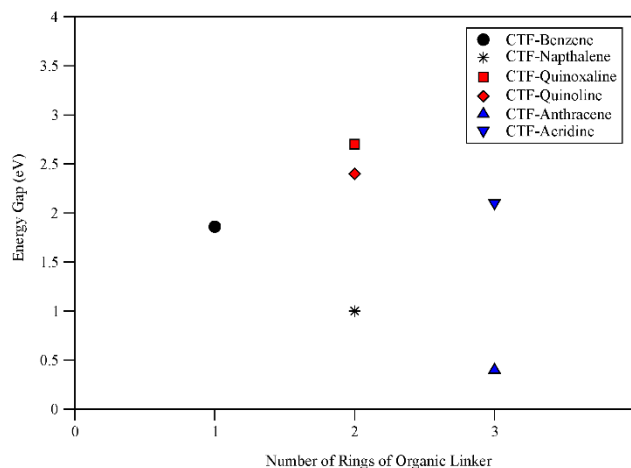

Figure 6 The energy gap of the six different types of the CTFs, namely CTF-Benzene, CTF- Napthalene, CTF-Quinoline, CTF-Quinoxaline, CTF-Anthracene and CTF-Acridine.

Conclusions

The electronic and optical properties of the covalent triazine based frameworks were carried out by using the density functional theory implemented in the Vienna Ab initio Simulation Package. In the present work, we firstly investigated the optical band gap of CTF-Benzene. We found that it is an indirect band gap structure with energy gap of about 1.86 eV. In addition, we also found that the electron states of valence band maximum come mostly from the organic linkers. This leads us to investigate the energy gap of the Covalent Triazine Frameworks with other five organic linkers. Our results showed that the energy gap ranges from 0.4 to 2.5 eV for these structures.

Acknowledgements

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