



# Excited-state properties of a blue luminescent covalent organic framework by the time-dependent density-functional tight-binding method



Guo-Hong Fan, Xing Li, Jian-Yong Liu\*, Guo-Zhong He

State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian 116023, Liaoning, China

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## ABSTRACT

Excited-state properties of a blue luminescent two-dimensional (2D) layered covalent organic framework (COF) have been studied by the time-dependent density-functional tight-binding (TD-DFTB) method and compared with available experimental data. For single layer fragment, signatures in absorption and emission spectra are revealed, which show the typical  $\pi$ - $\pi^*$  transitions and intramolecular charge transfer (ICT) character. The influence of interlayer stacking has also been considered. Our calculations on the interlayer spacing of the COF suggest that adjacent layers are considerably more stable if their stacking arrangement is horizontally offset by  $\approx 1.4$  Å compared with the eclipsed AA stacking structure. Excited-states calculations of high-symmetry eclipsed AA stacking and low-symmetry offset stacking are also considered. The low-symmetry offset stacking shows higher luminescence intensity but lower carrier transport ability. These calculations will be helpful for understanding interlayer excitation and carrier mobility, and the balance of the two processes is essential to the designing of the COF-based optoelectronic devices.

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## 1. Introduction

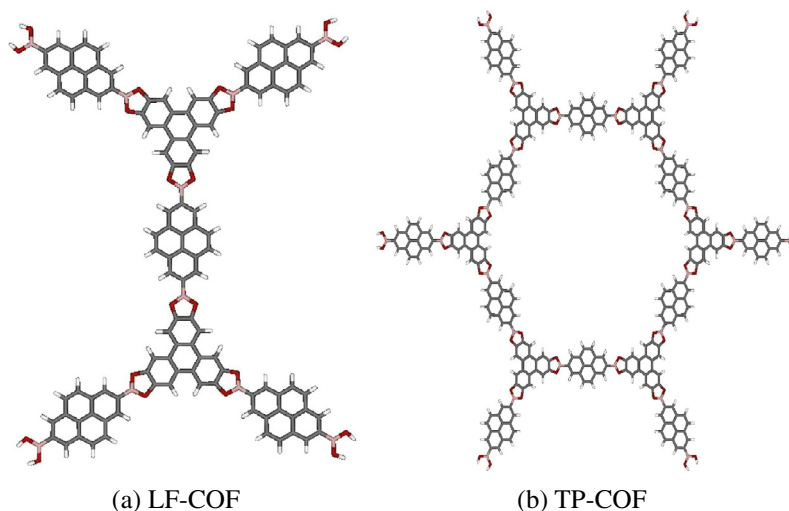
Covalent organic frameworks (COFs) are porous and crystalline macromolecules organized by well defined building blocks into layered two-dimensional (2D) [1–7] or three-dimensional (3D) [8–10] periodic crystalline networks. These materials have the advantage that all framework bonds represent strong covalent interactions and they are made from light elements. This means that COFs have lower mass density due to the absence of heavy atoms and therefore might be important for many applications. These materials are composed of inexpensive and non-toxic building blocks and can be synthesized solvothermally in a condensation reaction, allowing their large-scale industrial production to be possible. Most studies to date are focused on the development of synthetic methodologies with the aim to optimize the pore size and surface area [2–4,8–10]. However, the functions of COFs, apart from gas storage [11], have not yet been well explored. The layered 2D variants stack functional  $\pi$ -electron systems contact with maximal  $\pi$ -orbital overlap. Such a large  $\pi$ -conjugated system with stacking alignment provides a pathway for optoelectronic applications. These properties, in addition to the predictable nature of COF design, have attracted great interest such as the structurally precise optoelectronic materials [12–16].

From a topological viewpoint, we distinguish 2D and 3D COFs. In 2D COFs, the covalently bond framework is restricted to 2D layers. The crystal is similar to graphite or hexagonal boron nitride, composed by a stack of layers, which are not connected by covalent bonds but held together primarily by dispersion interactions [17]. Nearly all 2D layered COFs have been described as fully eclipsed structures based on their powder X-ray diffraction (PXRD) patterns [12,13]. This geometrical arrangement maximizes the proximity of the molecular entities and results in straight channels to the COF layers, which are known from the literature [1–4,12,13]. However, the fact that relatively broad peaks of PXRD do not rule out small horizontal offsets between layers have been proved by recent theoretical research [6,18,19]. They have performed a detailed theoretical analysis of the interlayer potential energies of various stacking conformations of COFs. These studies suggest that adjacent layers of COFs are slightly offset from the true AA eclipsed packing structure, which is in contrast to experimental observation for most of the COFs.

Recently, Jiang and coworkers [12] reported the first example of a blue luminescent and semiconducting COF (TP-COF), which adopts a belt shape and consists of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and pyrene-2,7-diboronic acid (PDBA) functionalities alternately linked in a mesoporous hexagonal skeleton (TP-COF, Fig. 1). The TP-COF becomes an excellent candidate for optoelectronic application due to the ease of synthesis and high luminescent. However, scanning tunneling microscope (STM)

\* Corresponding author. Tel.: +86 0411 84379293.

E-mail address: [beam@dicp.ac.cn](mailto:beam@dicp.ac.cn) (J.-Y. Liu).



**Fig. 1.** Optimized structures of LF-COF and TP-COF in the ground state. Carbon – black, oxygen – red, boron – pink, hydrogen – white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

image and PXRD pattern used for COF characterization are unable to distinguish between eclipsed and slightly offset structures. The effect of optical properties due to small changes in slight offset need be discussed, and an efficient computational method is important to understand their properties and performance. In experiment, it has been found that TP-COF can harvest photons over a wide wavelength range and the blue fluorescence is related to intramolecular energy transfer from the triphenylene unit to pyrene unit. But for such a large conjugated system, the excited-state behavior is very complicated. The physical mechanisms and chemical nature of the optically activated  $\pi$ -conjugated system need further investigation.

In this work, a detailed theoretical study of such COF-based material is presented to understand the structure, electronic and optical properties. The self-consistent charge density functional-based tight-binding method (SCC-DFTB) and time-dependent density-functional tight-binding (TD-DFTB) method is applied to these systems, including monomers and molecular dimer in a geometry compatible with the crystalline phase. It is assumed that the structure and properties of the whole system can be represented by a finite part of the infinite crystal structure in our calculations. The structures for calculating the spectra have been relaxed to the closest local-energy minimum as a first step and all atoms are allowed to move. Our theoretical simulation and studies are expected to provide understanding at the atomic level of the interaction and to promote molecular design for such COF-based materials with improved performance. In Section 2, the methods used for the study of the COF material are briefly explained and the detailed results and discussions are present in Section 3. Conclusions are made in the last section about the significance of the study on the designing of COF-based optoelectronic devices.

## 2. Computational methods

In the present work, all calculations are carried out by the SCC-DFTB method for structural optimizations and the TD-DFTB method for absorption and emission processes. The SCC-DFTB [20,21] method is based on a second-order expansion of the Kohn-Sham total energy in the Density-Functional Theory (DFT) with respect to charge density fluctuations around a given reference density. The main idea behind this method is to describe the Hamiltonian with a parameterized Hamiltonian matrix elements depending only on the inter-nuclear distances and orbital symmetries. Several

approximations including a  $\gamma$ -approximation and Hamiltonian matrix element with a two-center approximation are used to derive the total energy [22]:

$$E_{GS} = \sum_i \sum_{\mu\nu}^{occ} C_{\mu}^i H_{\mu\nu}^0 C_{\nu}^i + \frac{1}{2} \sum_{\alpha\beta} \Delta q_{\alpha} \gamma_{\alpha\beta} \Delta q_{\beta} + E_{rep} \quad (1)$$

In the equation,  $\Delta q_{\alpha}$  and  $\Delta q_{\beta}$  represent the Mulliken net charge on atom  $\alpha$  and  $\beta$  respectively. The above total energy can be written in the simplified form [23]:

$$E_{tot} = E_{BS} + E_{coul} + E_{rep} \quad (2)$$

where  $E_{BS}$  is the sum over the occupied orbital energies derived from the diagonalization of the electronic Hamiltonian,  $E_{coul}$  is mainly Coulomb interaction but containing also  $xc$ -contributions. The  $E_{rep}$ , including the ionic repulsion and corrections due to approximations made in the first term, is approximated as a sum of short-range repulsive potentials.

The TD-DFTB [22] method following the TD-DFT route of Casida [24,25] is capable of efficiently handling the excited-state calculations of large systems. In excited-state calculations, a self-consistent field (SCF) calculation is firstly conducted to obtain the single-particle Kohn–Sham (KS) orbital and the corresponding KS energies. Then, a coupling matrix which gives the response of the SCF potential with respect to a change in the electronic density is obtained. The excitation energies ( $\Omega_i$ ) are obtained by solving the following equation [22]:

$$\sum_{ij\sigma} (\omega_{ij}^2 \delta_{ik} \delta_{jl} \delta_{\sigma\tau} + 2\sqrt{\omega_{ij}\omega_{kl}} K_{ij\sigma,kl\tau} \sqrt{\omega_{kl}}) F_{ij\sigma}^l = \Omega_i^2 F_{kl\tau}^l \quad (3)$$

$$\omega_{ij} = \epsilon_j - \epsilon_i \quad (4)$$

$K_{ij\sigma,kl\tau}$  is the coupling matrix which is then approximated by the  $\gamma$ -approximation into a simple form [22]:

$$K_{ij\sigma,kl\tau} = \sum_{\alpha\beta} q_{\alpha}^{ij} \gamma_{\alpha\beta} q_{\beta}^{kl} \quad (4)$$

In our previous paper we have presented the efficient implementation and application of the TD-DFTB method in large systems [26]. The implementation of the TD-DFTB method on a series of large systems shows that it can obtain excited energy of better accuracy than CIS and a reasonable result close to that of TD-B3LYP with much less computational requirement. To describe the interaction between two separated interlayer fragments, a

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