

外电场调控二维共价有机框架的能带结构

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摘要: 基于第一性原理密度泛函理论, 研究了加不同方向电场对 NiPc-COF 能带结构的影响。结果显示: 沿[100]晶向的电场能够有效影响 NiPc-COF 的电子结构, 在 $3.09 \text{ V} \cdot \text{nm}^{-1}$ 的电场下 NiPc-COF 的能带降到了 0.22 eV 。此外, 分别从电子结构、前线轨道和 Mulliken 电荷方面的分析进一步研究了电场对 NiPc-COF 的作用, 结果表明沿[100]方向电荷密度的极化导致一些简并轨道的分裂从而降低了 NiPc-COF 的能带。

关键词: 共价有机框架结构; 电场; 密度泛函理论

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Tunable Band Gap of 2D Covalent Organic Framework by External Electric Field

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Abstract: The effect of directional electric field on the band gap of NiPc-COF was studied based on Density Functional Theory (DFT) calculations. The results indicate that electric field along [100] can effectively affect the electronic structure of NiPc-COF and result in the band gap of 0.22 eV at the electric field (EF) of $3.09 \text{ V} \cdot \text{nm}^{-1}$. Furthermore, both electronic structure and frontier orbits, coupled with Mulliken charge population, reveal that the polarization of charge density along [100] direction leads to the split of some degenerate orbits resulting in the decrease of band gap.

Key words: COFs; electric field; density functional theory

0 Introduction

Since the most revealing discovery reported by Yaghi in 2005^[1], Covalent Organic Frameworks (COFs), where the organic building units are held together by strong covalent bonds (such as C-C, C-O, B-O, and Si-C), have aroused enormous interest, largely stimulated by aesthetically interesting structures and unique properties, e. g. π -electronic skeletons, high surface areas ($4210 \text{ m}^2 \cdot \text{g}^{-1}$ for COF-103)^[2] and low crystal

densities ($0.17 \text{ g} \cdot \text{cm}^{-3}$ for COF-108)^[3]. Currently, efforts made by a number of chemists in the past decade have resulted in a large number of COFs, including various dimensionalities and doped modifications, such as COF-5 and Li-doped COF-102^[4]. These studies effectively facilitate the development of COFs in the fields of gas storage^[5-13].

In this field, one particular COFs and two-dimensional COFs (2D-COFs) have been attracting increasing attention because they feature a unique

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single-atom thickness and π -electronic 2D nanosheet with eclipsed stacking of aromatic components. It is these special features that make 2D-COFs particularly attractive in terms of physical properties, such as high-mobility electron-transporting property and prominent photoconductivity. Motivated by the fact, particular attentions are drawn on the studies regarding 2D-COFs either experimentally or theoretically.^[14-20] For instance, Jiang et al.^[21] reported that 2D-COFs feature excellent electron mobility. Sun et al.^[22] utilizing first-principles DFT calculations presented that TMPc-COFs based on different transition-metals display distinct magnetic properties. Moreover, via external physical field, such as electric field and force field, manipulating the electronic structures of those 2D atomic sheets (*e. g.* graphene) for practical applications has been an important and challenging topic^[23-34]. Especially for the system of NiPc-COF, Jiang et al.^[35] also reported that it features highly photoconductive property and suggested the feasibility for the applications of novel optoelectronics apparatus. However, for the 2D-COFs, featuring the similar π -electronic configuration with graphene, can EF with the absence of light affect the electronic structure? To the best of our knowledge, so far, it is still unclear.

Thus, via the first-principles DFT calculations, the electronic properties of NiPc-COF were studied and the effect of external EF along different directions on the electronic structure was the focus of the study. Under the EF of $3.09 \text{ V} \cdot \text{nm}^{-1}$ along $[100]$, the band gap can reduce from 1.44 to 0.22 eV, while obvious changes never appear in the EF along $[001]$. Furthermore, the polarization of charge density along $[100]$ direction plays an important role in the decrease of band gap. Generally, via the detailed analysis we can conclude that EF along $[100]$ direction can effectively manipulate band gap of NiPc-COF.

1 Computation details

All of the DFT calculations were performed by using the DMol³ module in Materials Studio^[36-37]. The generalized gradient approximation (GGA)^[38] with Revised Perdew Burke Ernzerhof (RPBE)^[39] correlation

was applied to describe the exchange-correlation (XC) effects. The double numerical basis sets plus polarization functional (DNP), which has a computational precision being comparable with split-valence basis set 6-31 g**, were applied in the expanded electronic wave function. All structures with and without electric field were optimized with the convergence of 10^{-5} eV and $2 \times 10^{-2} \text{ eV} \cdot \text{nm}^{-1}$. The initial NiPc-COF geometry was derived from the simulation by powder X-ray diffraction (PXRD) measurements. The Brillouin zone for all calculations is sampled by $8 \times 8 \times 1$ special k-points according to the Monkhorst-Pack scheme^[36].

2 Results and discussion

As shown in Fig.1, the resulting lattice parameters of NiPc-COF are respectively $a=b=2.319 \text{ \AA}$ and $c=0.4137 \text{ nm}$, in agreement with that obtained by PXRD measurements ($a=b=2.312 \text{ \AA}$, and $c=0.336 \text{ nm}$)^[35]. The difference between theoretical and experimental results may be due to that no dispersion correction was used by the calculation method. It is found that NiPc-COF features 2D sheet structures, which can be viewed simply as being constructed by phthalocyanine units via the linker of 1, 4-benzenediboronic acid (H_4BDBA).

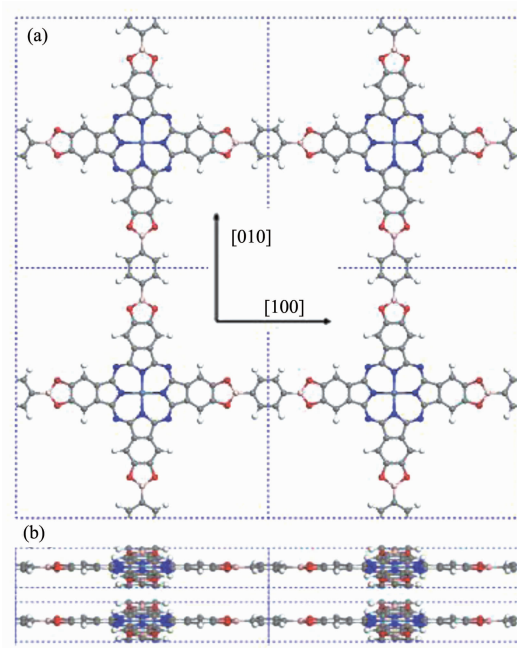


Fig.1 Geometry of NiPc-COF along $[001]$ (a) and $[010]$ (b) direction

The Ni atom is enveloped by phthalocyanine and coordinated by four nitrogen atoms with the Ni-N bond length of 0.193 nm, consistent with that obtained by Sun. et al^[22]. Moreover, the center-to-center distance between neighboring pores was 2.32 nm, approximating the experimental result (2.36 nm)^[35].

To investigate electronic properties of NiPc-COF, band structure and the density of states (DOS) were calculated. As shown in Fig.2(b), both valence bands (VBs) and conduction bands (CBs) can not well disperse over the first brillouin zone, suggesting that valent orbits have never generated stronger hybridizations. This phenomenon is different from other 2D NiPc-COF systems^[22], owing to that BDBA⁴⁻ can not effectively serve as an electron-transferring bridge. By referring to Fig.2(b), NiPc-COF attains the band gap of 1.42 eV,

slightly smaller than that of isolated NiPc molecule (1.46 eV), based on the Vosko-Wolk-Nusair (VWN) local spin-density potential plus Beckes gradient correction for exchange and Perdews gradient correction for correlation^[41]. Inspection of the DOS (see Fig.2 (g)) reveals that the states in the vicinity of Fermi level (−1 to 1 eV) are mainly comprised of 2p states, while 3d states of Ni atoms are located from −3.5 to −0.5 eV below Fermi level, which can be ascribed to two degenerate bands (d_{xz} and d_{yz}). The 3d peaks at 1.80 eV above Fermi level also hail from those degenerate bands. Furthermore, at −0.5 eV below Fermi level, 3d states of Ni overlap with 2p states of Pc, which may lead to partial delocalization of electrons of 2p bands of Pc to 3d bands.. Generally, NiPc-COF exhibits a semiconductor characteristic.

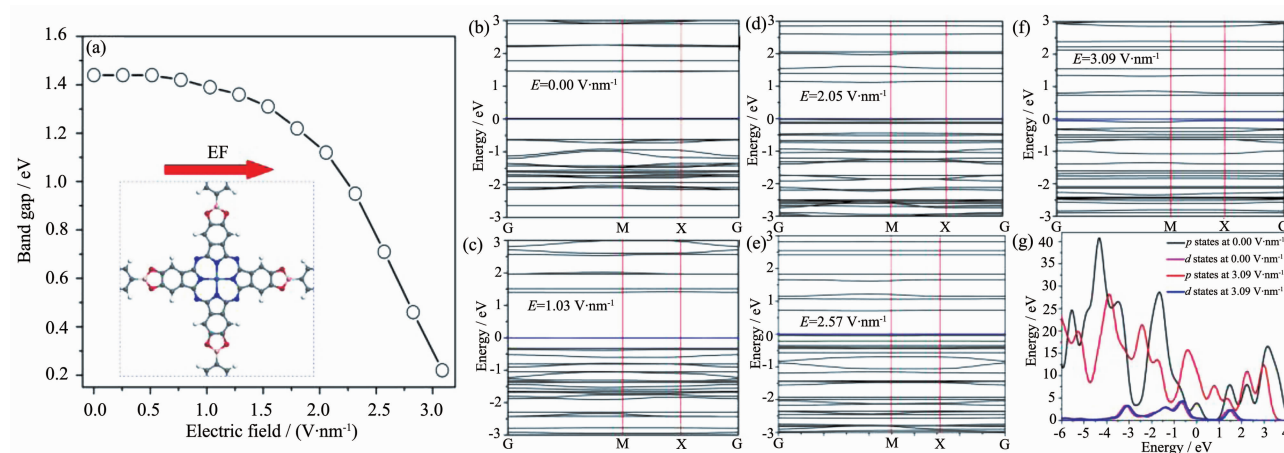


Fig.2 (a) Band gap of NiPc-COF under different EF along [100] direction; (b)-(f) the band structures at the selected EF with the Fermi level of 0.0 eV (blue line); (g) PDOS of NiPc-COF at the EF of 0.00 and 3.09 V · nm⁻¹

Inspired by the experimental results reported by Jiang et al.^[35], we further investigated whether the EF affects the band gap of NiPc-COF. Via the calculation under different EFs along [100] and [001] ([010] is equal to [100] for the space group of P4/mmm), it is obtained that under the [001] EF the band gap has no obvious change even though the intensity is up to 100 V · nm⁻¹, while it decreases with the increase of [100] EF. As shown in Fig.2(c), over the EF range of 0.00~1.03 V · nm⁻¹, the band gap of NiPc-COF is almost unchanged, indicating that such magnitude of EF is inadequate to alter the band structure. As the EF increasing, the value of the band gap gradually

decreases and reaches 1.12 eV at the EF of 2.05 V · nm⁻¹, as depicted in Fig.2(d). Upon further enhancing EF, the band gap abruptly reduces to 0.22 eV at the EF of 3.09 V · nm⁻¹. Scrutinizing the distinction of band structures under different EFs can help us understand how band structures are influenced by external EF. As shown in Fig.2(b)~(f), the bands below Fermi level with the EF are almost unchanged, while those empty bands move downward with the EF increasing. Specifically, as the EF enhancing, the bands at 1.46 eV above Fermi level as displayed in Fig.2 (a), which come from collective contribution of p and d states, transfer to 1.40 eV (1.03 V · nm⁻¹), 1.15 eV (2.05 V · nm⁻¹), 0.73 eV (2.57

$\text{V} \cdot \text{nm}^{-1}$) and 0.22 eV ($3.09 \text{ V} \cdot \text{nm}^{-1}$). Thus, the reason underlying the decrease of band gap can be mainly related to the transfer of empty bands. Furthermore, inspecting the PDOS of NiPc-COF at the EF of 0.00 and $3.09 \text{ V} \cdot \text{nm}^{-1}$, it can be seen that (1) no obvious change is found on the distribution of d states; (2) under the EF the peaks of p states move from high energy level to low energy level, resulting in a large peak appearing in the vicinity of Fermi level. Additionally, geometry optimized results under the EF of $[100]$ direction show that all geometries of NiPc-COF are robust. Consequently, the essential change of electronic structure under the EF can be attributed to the shift of p states for NiPc-COF.

To elucidate the nature of the decrease of band gap, we further perform frontier orbitals analysis at Gamma point under the EF of 0.00 and $3.09 \text{ V} \cdot \text{nm}^{-1}$, as shown in Fig.3. In the absence of EF, as displayed in Fig.3(a)~(c) both LUMO and LUMO+1 exhibit a set of degenerate orbits with E_u symmetry, consisting of localized π orbits of Pc and d_{xz} or d_{yz} orbit of Ni atom. Similarly, HOMO-1 and HOMO-2 are also E_u symmetry degenerate orbits, involving also similar components with that of LUMO and LUMO+1. Moreover, HOMO featuring A_{2u} symmetry mainly comes from localized π orbits of Pc and p-type dangling orbits of four N atoms with bonding to Ni. However, under the EF of $3.09 \text{ V} \cdot \text{nm}^{-1}$, three corresponding orbits exhibit different distributions though no changes occur in the geometry of NiPc-COF. Firstly, it is observed that the electron density of Pc along $[010]$ direction are polarized,

leading to that an inversion (i) symmetry for LUMO and HOMO and reflection (σ_v) symmetry along $[010]$ direction for HOMO-1 are removed as shown in Fig.3(d)~(f), and thereby induce that two sets of degenerate orbits with E_u symmetry (LUMO and LUMO+1, HOMO-1 and HOMO-2) are divided into four orbits, respectively, as shown in Fig.3(g). Therefore, it may be explained that under the EF of $3.09 \text{ V} \cdot \text{nm}^{-1}$ the band gap of NiPc-COF reduces from 1.44 eV to 0.22 eV . Secondly, three orbits still keep the σ_v symmetry along $[100]$ for LUMO and C_2 rotation symmetry along $[100]$ for HOMO and HOMO-1 despite the transfer of charges. Additionally, Mulliken charge population analysis reveals that the charge of two group atoms, locating at both sides along $[010]$ crystal axis as displayed in Fig.4 (a), show different variations as the EF increasing. As is clear from charge difference between two sides (see Fig. 4(b)~(c)), the electronic charges of left atoms (e. g. B1, C1-C11, N1-N2 and O1-O2) gradually lose with the value of EF increasing, while that of right atoms (e. g. B1, C1-C11, N1-N2 and O1-O2) attain more and more electronic charge with the EF enhancing. Consequently, it is evident that under the EF the electrons transfer from left side to right side, and further demonstrates that EF along $[100]$ direction facilitates the polarization of charge density along $[100]$ direction so as to induce degenerate orbits to split, leading to the decrease of the band gap. Similarly, it can be also obtained that the EF along $[001]$ direction has no capability of charge density to be polarized, and results in no obvious decrease of the band gap.

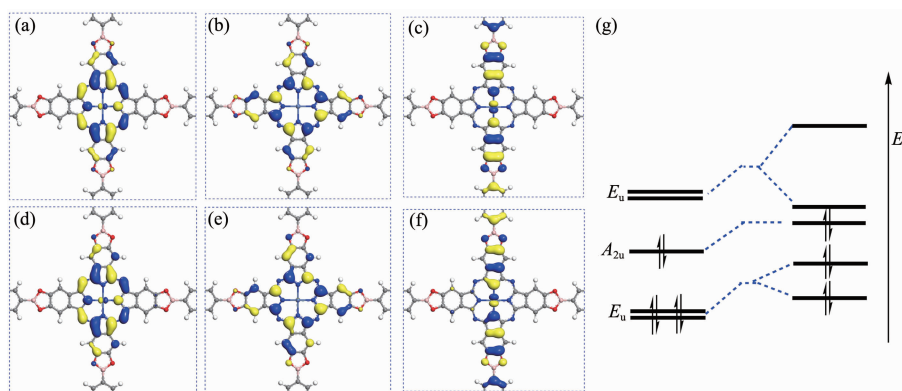


Fig.3 (a)~(c) and (d)~(f) LUMO, HOMO and HOMO-1 at the EF of 0.00 and $3.09 \text{ V} \cdot \text{nm}^{-1}$, respectively; (g) Illustration of frontier orbitals at the EF of 0.00 (left) and $3.09 \text{ V} \cdot \text{nm}^{-1}$ (right)

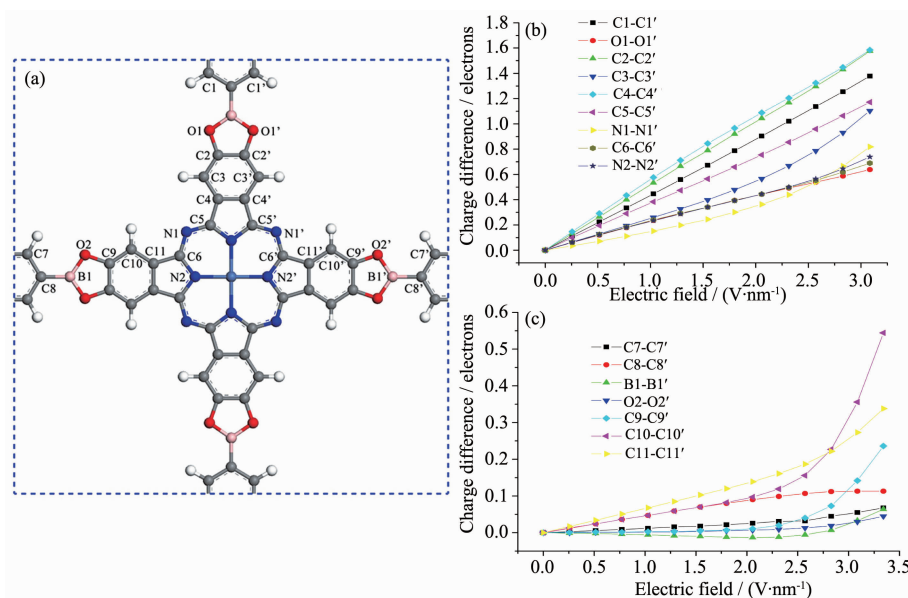


Fig.4 (a) Illustration of different atoms NiPc-COF along [010] direction; (b) and (c) Mulliken charge difference of the atoms at two sides along [010] in the range of 0.00~3.09 $\text{V} \cdot \text{nm}^{-1}$

Herein, it is worth emphasizing that only with the bias EF, NiPc-COF never indicates a good conductive characteristic experimentally^[35]. This may be due to two reasons: (1) Experimentally, the EF is unable to accurately lie on the [100] or [010] direction, which is incapable of inducing the polarization of charge density; (2) The intensity of EF is not adequate to polarize charge density.

3 Conclusions

In summary, utilizing the first-principles DFT calculations, our studies demonstrate that EF along [100] direction can effectively manipulate the band gap of NiPc-COF from 1.44 eV to 0.22 eV. Both electronic structure and frontier orbitals, coupled with Mulliken charge population, reveal that the polarization of charge density along [100] direction induces degenerate orbitals to split, resulting in the decrease of band gap. Therefore, our studies may be beneficial to the realizations regarding the effect of EF on the band gap of 2D-COFs.

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