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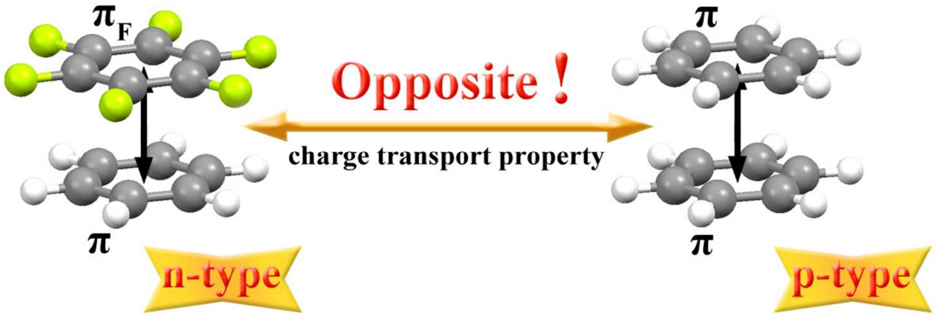

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The finding of phenyl–perfluorophenyl interaction for electron transport in crystals of fluorine substituted dibenzalacetones

Ling Liu, Guochun Yang*, Yun Geng, Yong Wu, and Zhongmin Su*

Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun, 130024 Jilin, China.

E-mail: yanggc468@nenu.edu.cn

Abstract：

Fluorine is considered to be one of the potential substitutions that can solve the instability problem in organic electronic materials and affect the molecular packing in their crystals, which can significantly affect the charge transport properties of the materials. Being one of the intermolecular interactions that involved fluorine, the phenyl–perfluorophenyl（π-π_F）interaction is a unique intermolecular interaction formed between the electropositive perfluorophenyl and electronegative non-flourinated phenyl, of which charge transport might be different from π-π interaction formed between ordinary phenyl rings. Three crystals with both π-π_F interaction and intermolecular hydrogen-bonding interaction are chosen to study the relationship between intermolecular interactions and their charge transport properties in both band-like model and hopping model. It is interesting to find that in contrast to ordinary π-π interaction, which is reported mainly responsible for hole transport, the π-π_F interaction turns out to be mainly responsible for electron transport. Thus, intermolecular π-π_F interaction is an effective packing style to realize n-type charge carrier. In the main time, C-H···F interactions is mainly responsible for electron transport while the C-H···O interaction for hole transport.

Keywords: phenyl–perfluorophenyl interaction, charge transport, intermolecular interaction, band model, hopping model

1 Introduction

Since organic electronic materials were first discovered in the last 50’s, the development of organic electronic materials has always been an active area of research. Back to the mid 70's, when highly conducting polyacetylene, which have attracted a lot of attention, was discovered by Shirakawa, MacDiarmid and Heeger [1, 2], rapid development started in the following decades and the achievements are remarkable. Various organic materials with outstanding properties were either designed or synthetized. They are low cost, light weight, large-area, with good flexibility, and can be widely used in a variety of applications such as organic light emitting diodes (OLEDs) [3, 4], organic field effect transistors (OFETs) [5, 6], organic photovoltaic cells (OPVs) [7], and sensors[8]. However, despite the advantages, comparing with traditional semiconductor materials, there are still several disadvantages such as low mobility and instability due to the complexity of their molecular structures, varied packing motifs of their crystal structures, uncontrollable intermolecular interactions and lack of knowledge in structure-property relationships, which always have been the main challenges in this field [9]. Thus, a fully understanding of the fundamental chemical and physical aspects behind the structural design to achieve better charge transport properties and stability is desired.

Fluorine as an important element has attracted more attention year by year. It has been involved in many parts of our daily life, from health care to alternative energy sector [10, 11]. Due to its electron-withdrawing characteristic, it is considered to be one of the potential substitutions that can solve the instability problem in organic electronic materials and affect the molecular packing in their crystals, which can significantly affect the charge transport properties of the materials [9-13]. A number of fluorine substituted compounds with different intermolecular interactions have been synthesized. However, they are turned out to have different charge transport properties. For example, perflouropentacene is a n-type semiconductor with its electron mobility of 0.11 $cm^2/(V \cdot s)$ [14]. The compound 2,2'-bis(4-trifluoromethylphenyl)-5,5'-bithiazole which synthesized by Yamashita and coworkers with electron mobility as high as 1.83 $cm^2/(V{\cdot}s)$ is considered to be the one compound of the highest value reported for halogen n-type semiconductors [9, 15]. And the α polymorph of the p-$CF_3C_6H_4$-substituted 2,6’-bi(thieno[2,3-c]thiophene), synthesized by Yamaguchi and coworkers, is reported to have hole mobility up to 4.0 $cm^2/(V{\cdot}s)$ along its longer axis and mobility of 1.3 $cm^2/(V{\cdot}s)$ as an isotropic value [16].

When considering to understand microscopic structures and behaviors that each molecular or supramolecular systems would take in certain conditions, the rules behind weak intermolecular interactions such as hydrogen bonding and π-π interactions is crucial. As many studies have shown, intermolecular interaction plays a significant role in photophysics, photochemistry and photobiology, as well as photoinduced electron transfer and charge transportation [17-22]. Generally, fluorine interactions of compound with fluorine substituents tend to be classified into π-π_F, C–F···H, F···F and C–F··· π_F interactions. The π-π_F interaction is a unique intermolecular interaction, stabilized by coulombic and dispersion forces, with stabilization energy about 20-25 kJ·mol^{-1} [23]. Unlike π-π interactions formed between non-flourinated phenyls, this kind of interaction is formed between the electropositive perfluorophenyl and electronegative non-flourinated phenyl [24-26]. With centre to centre separation of 3.4-4.8 Å [23, 27] and inter-ring angles up to 20° [11], the interaction offers considerable flexibility in forming crystal structures. There is evidence that this kind of interaction could, to some extent, affect packing motifs, since the 1:1 mixture co-crystal of benzene/hexafluorobenzene forms a face-to-face structure in contrast to the edge-to-face strucure formed by either of the molecule alone [28, 29]. The angles of C-H···F interaction can range from 70° to 180° with distance mostly around 2.67 Å and up to 2.9 Å [10]. It is not a strong kind of intermolecular interaction. In fact, it is much weaker compared to typical H-bonds with acceptors such as oxygen or nitrogen, since the different energy of the competing orbitals can be influenced by the electron delocalization of the molecules, suggested by Dunitz and Taylor [30]. Yet such weak interaction still can have influence on structure and properties of organic fluorine compounds in the same way as the C-H···O and C-H···N interactions [31-33]. As to the F···F interaction, whether this contacts have a steady nature or they are just a consequence as the molecules packed so closely in the crystal is still reported to be under controversy [11, 34-39], since they are rare and weak. But it have been reported that in some cases the F···F contacts could either driving or at least affect to crystal packing [38, 39]. Finding C-F···π_F interaction in perflourinated compounds is not rare, such as in fluorinated benzophenones or N-phenylmaleimides and phthalimides[35, 36]. Since the electron density distribution in a perflourinated aromatic ring is inversed to a common aromatic system, it can form contacts of more stability with C-F group. But this interaction also considered to be mostly determined by close packing [10, 11].

In this work, we have chosen three molecules **1**, **2**, and **3** and their corresponding crystals **a**, **b** and **c**, synthesized by Anke Schwarzer and Edwin Weber [40], to study the relationship between charge transport and intermolecular interactions especially for π-π_F interaction. Molecules **1**, **2**, and **3** are decafluoro (*1,5-Bis-(2,3,4,5,6pentafluorophenyl)penta-1,4-dien-3-one*), pentafluoro (*1-Phenyl-5-(2,3,4,5,6-pentafluorophenyl)penta-1,4-dien-3-one*), and nonfluoro (*1,5-Diphenyl-1,4-pentadien-3-one*) substituted dibenzalacetone, respectively. Crystal **a** and **b** each contains only one kind of molecule, which are molecule **1** for crystal **a** and molecule **2** for crystal **b**, while crystal **c** is the 1:1 mixture of the decafluorinated derivative **1** and the nonfluorinated parent **3**. These crystals contain some of the intermolecular interactions introduced above, especially two of the three have π-π_F interaction between molecules, which offer us a good opportunity to study the relationship between these intermolecular π-π_F interactions and their charge transport properties. And hopefully, the results will be helpful for further understanding the charge transport property of this kind of compounds and give some hints for material design.

2 Theoretical methodology

In general, band-like model and hopping model are widely used in calculations of the charge transport mechanism of organic semiconductor materials. In a standard band-theory model, given by the gradient of the band energy in *k*-space, the group velocity $v(k)$ of the delocalized electron or hole wave can be expressed as,

$$\vec{v}(k) = \nabla_k E(k)/h \qquad (1)$$

where $E(k)$ is the band structure of the system, k is the wave vector, and h is the Planck constant with $\hbar = h/2\pi$. As presented in Eq (1), the charge velocity $\vec{v}(k)$ is in proportion to the slope of $E(k)$. Generally, the larger the band dispersion is, the higher the mobility is.

The charge transport mechanism of the hopping model can be described as a nonadiabatic electron-transfer reaction from a charged molecule to an adjacent neutral one involving the self-exchange charge. The rate, k, of charge transfer between neighboring molecules can be expressed by the standard Marcus equation [41, 42],

$$k = \frac{4\pi^2}{h}\frac{1}{\sqrt{4\pi\lambda k_B T}}V^2 \exp\left(-\frac{\lambda}{4k_B T}\right) \qquad (2)$$

where λ, V, and T respectively being the reorganization energy, the transfer integral and the temperature of the system while h and k_B are the Planck and Boltzmann constants. Usually, larger transfer integral will leads to larger transfer rate.

In this work, both of the two models were used to describe the transport properties of the studied crystals. Electronic band structure calculation was performed by a density functional theory (DFT) method implemented in the Vienna Ab-initio Simulation Package (VASP) [43, 44] with Perdew-Burke-Emzerhof (PBE) for the exchange correlation functionals and a plane-wave basis set with an energy cut-off of

400 eV [45, 46]. For crystal structure **a**, **b**, and **c** space groups were $P2_1/c$, $P2_1/c$, and $P\text{-}1$, respectively. Also K-grids were 6 × 2 × 2, 6 × 8 × 2, and 6 × 4 × 2 for these crystal structures, respectively. The Monkhorst–Pack scheme was used to sample the K-grids in the Brillouin zone.

The hole or electronic coupling (charge transfer integral) was calculated with the PW91 functional Slater-type triple-ζ plus polarization (TZP) basis set for all atoms through the Amsterdam Density Functional (ADF) package [47-49].

Meanwhile, Γ point wave functions calculations were performed through Dmol3 within the Material Studio [50, 51] package with the generalized gradient approximation (GGA) in Perdew–Burke–Ernzerhof (PBE) form and all-electron double numerical basis set with polarized function (DNP basis set) [52].

3 Results and discussion

3.1 Geometric Structure

The structures of studied molecules **1**, **2**, and **3** were shown in Fig. 1. Molecules **1**, **2**, and **3** are decafluoro, pentafluoro, and nonfluoro substituted dibenzalacetone, respectively.

The crystal structures **a**, **b**, and **c** together with the main intermolecular interactions in these crystals are shown in Fig. 2. The packing motifs of crystals **a**, **b**, and **c** were herringbone packing without π-π overlap, slipped π–stacking, and lamellar motif, respectively. All of these molecules show planar molecular structures in the studied crystals. Here we only introduce the intermolecular interactions that proofed to have contribution to charge transport in these crystals since it is the charge transport abilities of these materials that we concern. Crystals **a** and **b** only contain one kind of molecule, which are molecule **1** for crystal **a** and molecule **2** for crystal **b**, respectively. Crystal **a** is the only crystal of the three that do not contain π-π_F interaction, since there is not any overlaps between molecular layers. There are just hydrogen bonding interactions, which are C-H···O and C-H···F interactions, stretching parallel to the molecular layer, in this crystal with distances being 2.6 and 2.5 Å, respectively. In crystal **b**, the π-π_F interaction is in the direction of the *a*-axis with the perpendicular distances between the interacting ring planes around 3.5 Å. While C-H···O and C-H···F interactions in this crystal stretch parallel to the *ab* plan. Distances between the interacting atoms are from 2.5 to 2.7 Å for C-H···O and from 2.5 to 2.6 Å for C-H···F. Crystal **c** is the 1:1 mixture of the decafluorinated derivative **1** and the nonfluorinated parent **3**. The π-π_F interaction in this crystal is in the same direction as it in crystal **b**, which is along the *a*-axis, with the perpendicular distances between the interacting ring planes around 3.4 Å. ~~However,~~While the C-H···F interactions in this crystal~~, not like the others,~~ stretch along two different directions. One of the directions is along the *b*-axis together with C-H···O interactions. The distance of these interactions are 2.5 Å for C-H···F and 2.4 Å for C-H···O, respectively. While the other direction with only C-H···F interaction is along *c*-axis. The distance of interaction is from 2.6 Å.

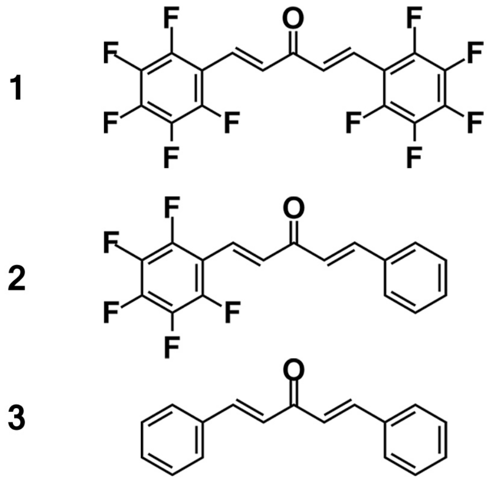


Fig. 1. The molecular structures of **1**, **2**, and **3**.

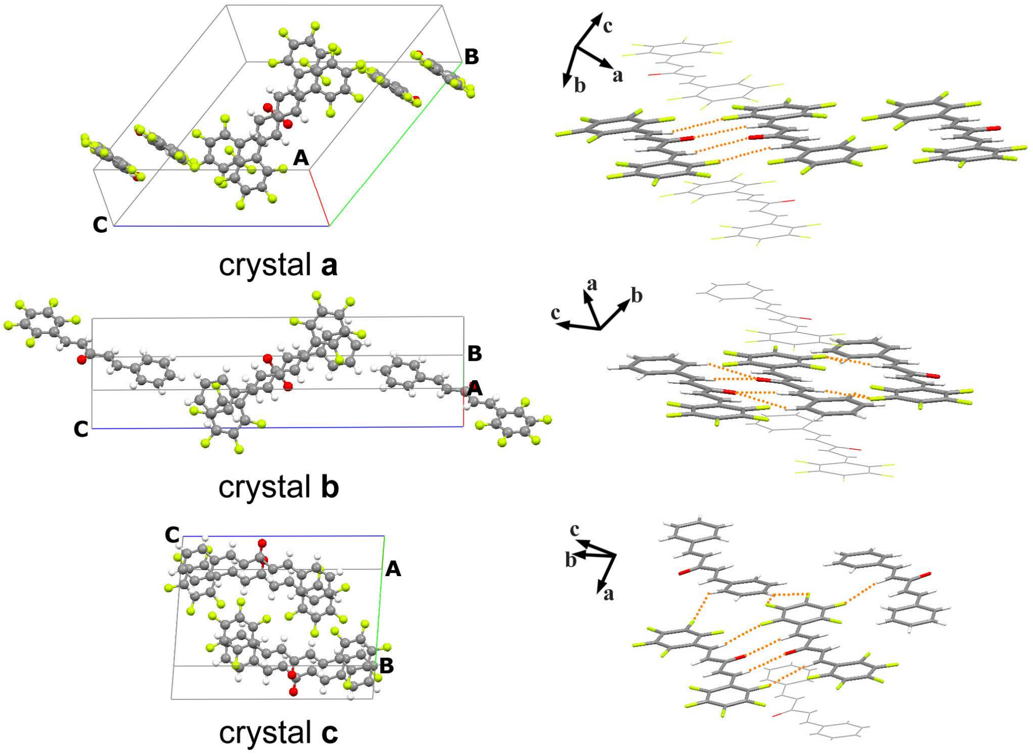


Fig. 2. The crystal structures and the main intermolecular interactions of **a**, **b**, and **c**.

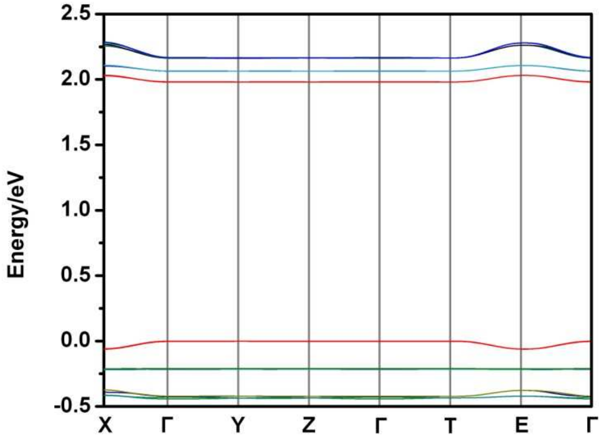
The intermolecular hydrogen bonding interactions are connected by dash orange lines.

3.2 Band structure.

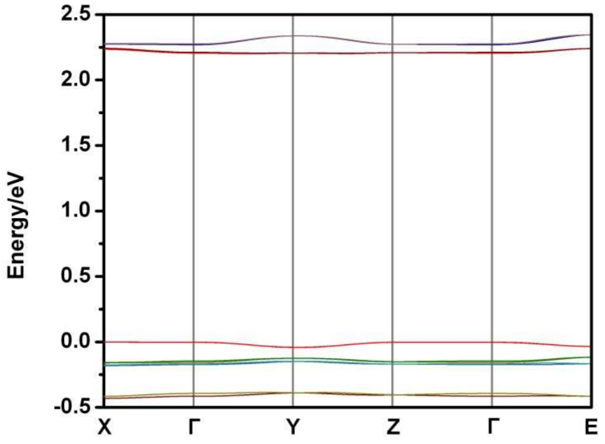
The appearances of bands, dispersive or flat, are both reflections of the anisotropy in the charge transports of the crystal. Generally, the stronger dispersion of band is, the larger carrier mobility it will be. With the help of first principle calculations, we have calculated the band structures along high symmetry directions of these crystals, and the results were shown in Fig. 3. Crystal **a** is direct bandgap semiconductors with band gap of 1.98 eV, since its maxima of valence band (VB) and conductive band (CB) is at Γ point. And crystal **b** and **c** are indirect bandgap semiconductors with band gaps of 2.20 and 1.84 eV and their maximun of valence band respectively at X and Γ point while minimun of conduction band both at Y point.

The calculated larger bandwidths in VB and CB along with their corresponding directions in the first Brillouin zone were listed in Table 1. Through comparing bandwidths of VB and CB, it is clearly for us to find that crystals **a** and **c** are respectively ambipolar and electron transport materials. While the band dispersion in crystal **b** show anisotropy between two directions, which are almost vertical with each other, and result in electron and ambipolar charge tranport respectively in the two directions. Crystal **a** do not has π-π_F interation and contains only C-H···O and C-H···F hydrogen bonding interactions, which have contribution to charge transport. By analysis the crystal structure of this crystal, we have already known that both of the two hydrogen bonding interactions are stretching parallel to the molecular layer, corresponding to direction Γ→E in the first Brillouin zone. The bandwidth of VB and

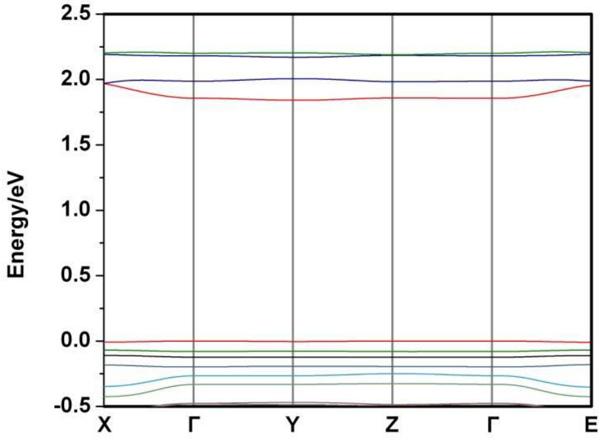
CB of this direction are respectively being 0.060 and 0.051 eV, which suggest similar but not identical charge transport abilities for both hole and electron.



crystal **a**



crystal **b**



crystal **c**

Fig. 3. The band structures of **a**, **b**, and **c**. High symmetry *k*-points in the first Brillouin zone are Γ = (0, 0, 0), X = (0.5, 0, 0), Y = (0, 0.5, 0), Z = (0, 0, 0.5), T = (0, 0.5, 0.5), E = (0.5, 0.5, 0.5).

Table 1. The largest bandwidths in VB and CB of **a**, **b**, and **c** along high symmetry directions in eV.

	Directions	Interactions	VB	CB
a	ΓE	C-H···F and C-H···O	0.060	0.051
	ΓT	-	-	0.001
b	ΓX	$\pi - \pi_F$	0.003	0.029
	ΓE	C-H···F and C-H···O	0.032	0.035
c	ΓZ	C-H···F	0.003	0.018
	ΓY	C-H···F and C-H···O	0.003	0.015
	ΓX	$\pi - \pi_F$	0.008	0.111

Crystal **b** has $\pi - \pi_F$ interaction in high symmetry direction Γ→X in the first Brillouin zone, corresponding to *a*-axis in the real space. This kind of interaction is mainly responsible for electron transport, since the bandwidth (0.029 eV) in the CB is much larger than that (0.003 eV) in the VB, which is in contrast to $\pi - \pi$ interaction forms between ordinary phenyl rings that have been reported as mainly responsible for hole transport [53-56]. The hydrogen bonding interactions C-H···O and C-H···F in this crystal coexist in the same direction parallel to the molecular layer, corresponding to direction Γ→E, and end up with identical bandwidths of VB and CB, which are 0.032 and 0.035 eV, respectively, suggesting equal charge tranport abilities in both hole and electron.

As to crystal **c**, the $\pi\text{-}\pi_F$ interaction also stretches along *a*-axis in the real space, same as crystal **b**, and corresponds to high symmetry direction Γ→X in the first Brillouin zone. With bandwidths (0.111 eV) in the CB significantly larger than that (0.008 eV) in VB, $\pi\text{-}\pi_F$ interaction in crystal **c** also turns out to be mainly responsible for electron transport. The hydrogen bonding interactions C-H···O and C-H···F in this crystal also coexist in the same direction, which is along *b*-axis in real space, corresponding to high symmetry direction Γ→Y in the first Brillouin zone. However, bandwidths in this crystal do not show much dispersions, unlike what was found in crystals **a** and **b**.

In general, what we can find from the electronic band structure calculations is that $\pi\text{-}\pi_F$ interaction is mainly responsible for electron transport, which is greatly different from the typical $\pi\text{-}\pi$ interaction. Our finding might enable an opportunity for the performance of n-type carrier transport, which is far behind of the p-type carrier transport [9]. And further calculation should be performed before we can finally determine which part of the role that C-H···O and C-H···F interactions play in charge transport.

3.3 Transfer integral.

Besides band model, we also calculated the transfer integrals of these systems by using hopping model. The transfer integrals are believed to be an important parameter when assessing charge transport properties of organic semiconductor material. It is the separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which requires large π-overlap area between neighboring molecules [57]. Since it is calculated only between neighboring molecules, we are expecting a seperation of each kind of intermolecular interactions, which should allow us to determine how exactily each kind of interaction affect charge transport. And in general, we are expecting larger transfer integral in order to achieve a better charge mobility.

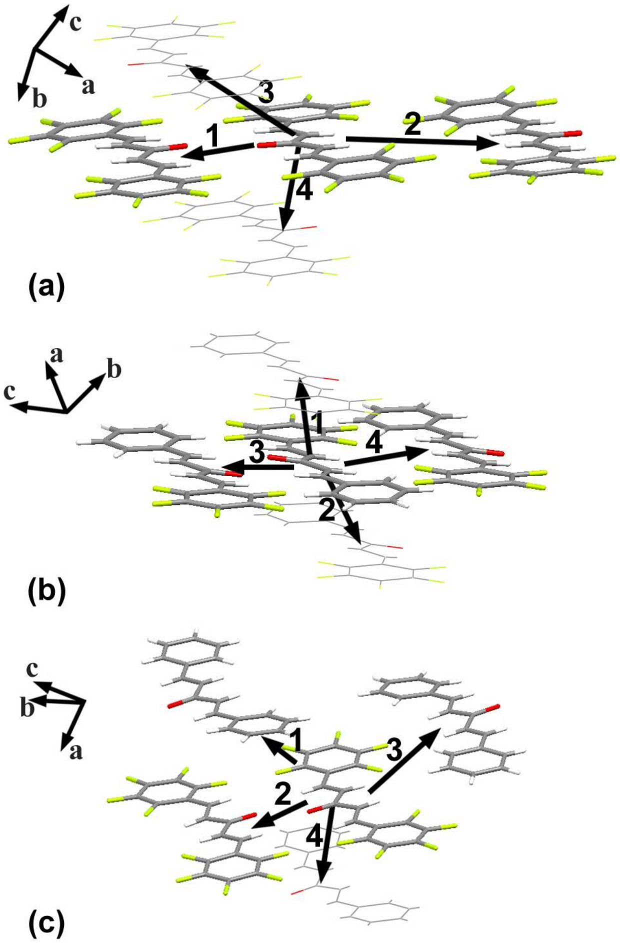


Fig. 4. The pathways of charge transfer integral corresponding to intermolecular interactions in crystals **a**, **b**, and **c**.

Table 2. Hole (t_h) and electron (t_e) transfer integrals of **a**, **b**, and **c** in the pathways along high symmetry directions.

	Directions	Interactions	Pathways	t_h(meV)	t_e(meV)
a	ΓE	C-H···F and C-H···O	1	83.88	37.69
		C-H···F	2	0.30	1.09
	ΓT	-	3	3.22	25.51
			4	23.14	28.90
b	ΓX	$\pi - \pi_F$	1	22.68	31.40
			2	2.15	11.00
	ΓE	C-H···F and C-H···O	3	57.65	19.56
		C-H···F	4	0.48	0.23
c	ΓZ	C-H···F	1	0.10	0.07
	ΓY	C-H···F and C-H···O	2	100.02	39.93
		C-H···F	3	10.78	45.13
	ΓX	$\pi - \pi_F$	4	0.45	45.35

The hole and electron transfer integrals were calculated with the PW91 functional Slater-type TZP basis set for all atoms through the ADF package. The pathways corresponding to intermolecular interactions are shown in Fig. 4. The calculated results together with the directions in the first Brillouin zone of each selected pathways are listed in Table 2.

By comparing bandwidths and transfer integrals in each direction, it is easy to tell that the results generally fit with each other and have provided us evidence to identify the responsibilities that each kind of intermolecular interaction is taking during charge transport. Pathways 2 and 4 in crystal **b** together with pathway 4 in crytal **c** are all contain π-π_F interaction. As we are looking at the transfer integrals in each of these pathways, it is clearly for us to see that the electron transfer integrals tend to be larger than hole's. So the π-π_F interaction turns out to be mainly responsible for electron transport, which is corresponding to previous discussion.

While the hydrogen bonding interactions C-H···O and C-H···F in these crystals are not in such simple situation as the π-π_F interaction, which is apart from other kind of interactions, since they are stretching in the same direction in the first Brillouin zone and acting between same pair of molecules in most circumstances. However, it is still able for us to find two pathways, though not in the same crytal, which contains C-H···O or C-H···F, respectively. Pathway 1 in crystal **b** contains only C-H···O interaction and its hole transfer integral (57.65 meV) is apparently larger than its electron transfer integral (19.56 meV). Yet pathway 1 in crystal **c**, which contains only C-H···F interaction, has a rather small hole transfer integral (10.78 meV) than its electron transfer integral (45.13 meV). It turns out that C-H···O interaction is mainly responsible for hole transport while C-H···F interaction is mainly responsible for electron transport. The other pathways such as pathway 2 in crystal **a** and pathway 3 in crystal **c** also support this conclusion since they have great transfer integrals for both hole and electron transport as C-H···O and C-H···F interactions coexist. Moreover, the larger hole transport integrals in the pathways also give the reason to larger bandwidthes in VB than CB of Γ→E direction in crystal **a**, which indicate stronger C-H···O interaction than C-H···F interaction in this direction.

3.4 Γ point wave functions.

In general, there is a close relationship between the charge transport and distribution of frontier molecular orbitals. The wave functions of the band-edge state at the Γ point are equivalent to the frontier molecular orbitals, namely, the HOMO for the hole and LUMO for the electron. Here, the calculated Γ point wave functions are shown in Fig. 5. As the figure shows, it is obvious that the three crystals have almost identical electric cloud distributions in either their HOMO or LUMO dispite the different packing motifs. The distributions of HOMO in these crystals are all shaped like butterfly and localized around the C = O bond, well attach to neighbouring molecules, which confirmed the previous conclusion that the C-H···O interaction is mainly responsible for hole transport. The LUMO of crystal **b** and **c** all show good distributions on their phenyl and pentafluorophenyl rings, which also confirmed the previous conclusion that the $\pi - \pi_F$ interaction turns out to be mainly responsible for electron transport.

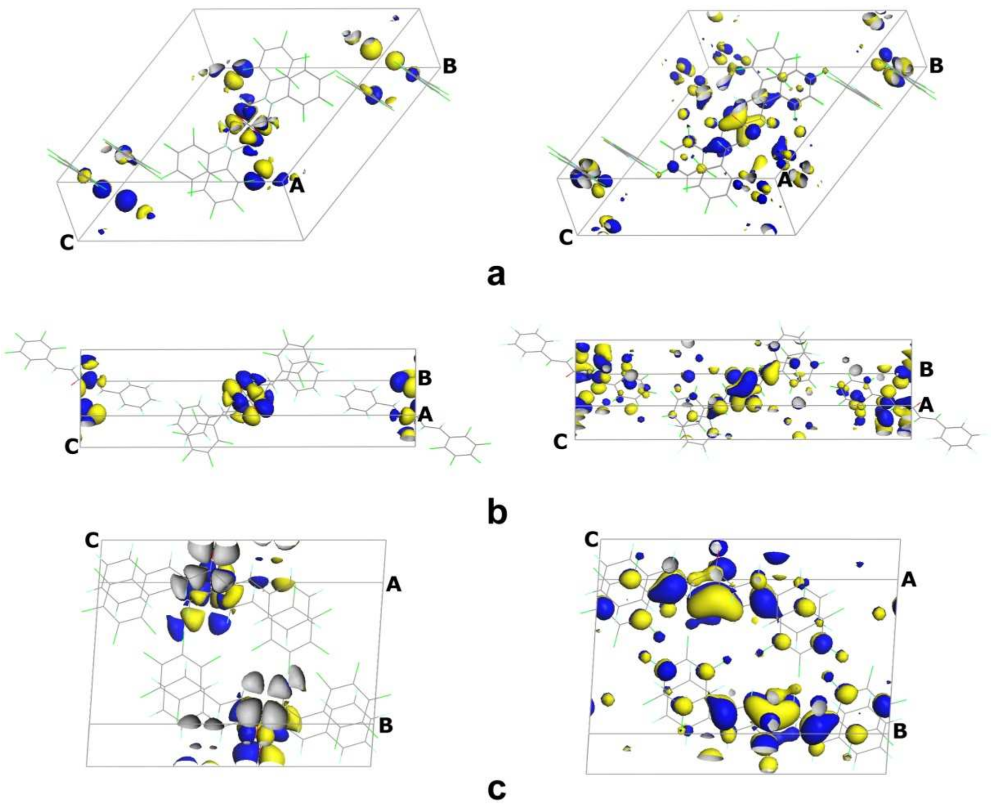


Fig. 5. Γ point wave functions of **a**, **b**, and **c**. HOMO (left), LUMO (right).

4. Conclusions

Through analyzing the molecular structures and the calculated results of these crystals, it is easy to tell that crystals **a** and **c** are ambipolar and electron transport materials, respectively. While the band dispersion in crystal **b** show anisotropy between two directions and result in electron and ambipolar charge transport respectively in the two directions. In contrast to π-π interaction formed between ordinary phenyl rings for hole transport, the π-π_F interaction turns out to be mainly responsible for electron transport in these crystals, which provide an good opportunity to realize n-type charge carrier. Hydrogen-bonding interactions C-H···F and C-H···O also affect charge transport in different ways. Specifically, C-H···F interactions is mainly responsible for electron transport while the C-H···O interaction for hole transport. These results might be favorable for further understanding the charge transport property of this kind of compounds and give some hints for material design.

5. Acknowledgements

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