Research article

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Polymorph-induced photosensitivity change in titanylphthalocyanine revealed by the charge transfer integral

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Abstract: The crystal form of semiconductor materials is keenly correlated with the photosensitivity of optoelectronic devices. Thus, understanding the crystal form-dependent photosensitivity mechanism is critical. In this work, the microemulsion phase transfer method was adopted to prepare α - and β -titanylphthalocyanine (TiOPc NPs) with an average diameter of 35 nm. The photosensitivity ($E_{1/2}$) of α -TiOPc NPs was 2.73 times better than that of β -TiOPc NPs, which was characterized by photoconductors under the same measurement conditions. DFT was performed to explain the relationship between crystal form and photosensitivity by systematically calculating the charge transfer integrals for all possible dimers in the two different crystal forms. The hole and electron reorganization energies of TiOPc were respectively calculated to be 53.5 and 271.5 meV, revealing TiOPc to be a typical *p*-type semiconductor. The calculated total hole transfer mobility (μ_h) ratio (2.83) of α - to β -TiOPc was almost identical to the experimental $E_{1/2}$ ratio (2.73) and the calculated photogeneration quantum efficiency (η_{e-h}) ratio (2.23). In addition, the optimum hole transfer routes in the crystal of α - and β -TiOPc were all along with the [1 0 0] crystal

orientation, which was determined by the calculated μ_h . A high charge transfer mobility leads to a high photosensitive TiOPc crystal. Consequently, these results indicate that the selected theoretical calculation method is reasonable for indirectly explaining the relationship between crystal form and photosensitivity. The TiOPc molecular solid-state arrangements, namely, the crystal forms of TiOPc, have a strong influence on the charge transport behavior, which in turn, affects its photosensitivity.

Keywords: titanylphthalocyanine; photosensitivity; crystal form; charge transfer integral.

1 Introduction

Owing to the high potential of novel organic photodetectors, such as organic photoconductors (OPCs) [1, 2], organic photodiodes (OPDs) [3–5] and organic phototransistors (OPTs) [6–8], which are based on organic semiconductor materials, there is a need to better understand the inherent photosensitivity mechanisms in these materials. For the polycrystalline semiconductor materials, molecular packing arrangements can significantly affect their photosensitivity, which not only has a vital impact on the hole/electron reorganization energy and hole/electron coupling capacity (absolute transfer integral) [9–11], but also result in different charge transport networks [12–18]. Highly photosensitive detectors require efficient charge photogeneration and charge transfer mobility to separate the photogenerated electron-hole pairs into long-lived dissociated charges with a high quantum yield. Nevertheless, the experimental and theoretical evidence presented so far have steadily revealed that the efficiency of dissociation of the charge-transfer state into free charge carriers plays a crucial role in determining the charge photogeneration quantum yield [1, 2, 19–21]. The charge-transfer properties for nano-crystalline materials, especially following photoexcitation, are mainly affected by four issues: electric field, interfacial energetics, nanomorphology and crystal

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form [22]. Stimulated by the significance of the promising applications, more studies have been devoted to developing proper organic photoconductive materials and applying them in optimized architectures with the appropriate crystal form in order to satisfy the different requirements of photoelectronic characteristics. As most of the organic semiconductors exist as polymorphs, identifying the relationship between crystal form and photosensitivity property has technological and scientific value in understanding and optimizing the performance of organic photoelectric devices.

Among small-weight semiconductors, titanophthalocyanine (TiOPc) has been widely used in diverse photodetectors because of its significant electronic and optical properties associated with high thermal and chemical stability [23–28]. The TiOPc molecule has a large conjugate system, in which Ti=O is perpendicular to the center of the approximately planar macrocyclic. Various weak intermolecular π -electron and van der Waals interactions between adjacent TiOPc molecules bring about diverse crystal forms with different ordered and crystalline arrays [29]. The α -phase (triclinic) and β -phase (monoclinic) of TiOPc are the two important crystal forms used as photoactive materials in organic photodetectors [30–32]. By controlling the preparation conditions, different crystal forms of TiOPc can be obtained. For pleomorphism nanomaterials, the rate-determining step for charge generation is considered as the photoinduced charge transfer between the two nearest-neighbor molecules [33–35]. Thus, the charge transfer mobility of pleomorphism semiconductors depend on the structure of molecular packing [36] which, in turn, reflects the relative superiority or inferiority of photosensitivity. However, to the best of our knowledge, combining experimental data and theoretical calculation to understand the relationship between crystal form and photosensitivity has not yet been carried out despite the important role of molecular packing in the semiconductor crystal materials in the photosensitivity of organic photodetectors.

In the current work, on the basis of our research interests in OPCs and organic photodetectors [37, 38], we investigated the relationship between crystal forms and photosensitivity. The microemulsion phase transfer method was adopted to prepare α - and β -TiOPc NPs with an average diameter of ≈ 35 nm, respectively. The multilayered OPCs fabricated with α - and β -TiOPc NPs as photoactive materials were used to characterize the photosensitivity ($E_{1/2}$). According to the results of the photoinduced discharge curves (PIDs), the photogeneration quantum efficiencies ($\eta_{\text{e-h}}$) were calculated to further compare the photosensitivities of α - and β -TiOPc NPs. The

density functional theory (DFT) was employed to calculate the hole and electron reorganization energies ($\lambda_{\pm}$) for TiOPc at the B3LYP/(6-31G*, Lanl2dz) level. The DFT/PW91PW91/(6-31G*, Lanl2dz) level was used to systematically calculate the hole and electron transfer integrals ($\tau_{\pm}$) in all possible pathways composed of two neighboring molecules for α - and β -TiOPc. In combination with the experimental results, the calculated $\tau_{\pm}$ and the corresponding charge transfer mobilities ($\mu_{\pm}$) for α - and β -TiOPc were used to theoretically explain the relationship between the crystal forms and photosensitivity. Therefore, the present effort toward theoretically understanding the crystal form-dependent photosensitivity mechanism on the basis of experimental results and DFT calculations can be beneficial in the future development of highly photosensitive organic semiconductors with definite crystal forms for various optoelectronic applications.

2 Materials and methods

2.1 Materials

The synthesis of crude TiOPc was based on the previous literature report [39]. Other materials were all commercially available and used without further purification. Polycarbonate (PC, $M_w=45,000$) and polyvinyl butyral (PVB, $M_w=90,000$ – $120,000$) were purchased from Sigma-Aldrich (Saint Louis, Missouri, USA) and Aladdin Industrial Corporation (Beijing, China), respectively. The *m*-TPD (N,N'-diphenyl-N,N'-di(3-tolyl)-4-benzidine) was purchased from Aladdin Industrial Corporation (Beijing, China). The cyclohexanone (CYC), methyl ethyl ketone (MEK), 1,2-dichloroethane and other reagents were all supplied by Jiangtian Chemical Technology Co., Ltd (Tianjin, China). The deionized water was purified through an Ultra-pure Water System (Beijing Epoch Company).

2.2 Preparation

The microemulsion phase transfer method was adopted according to our previous work [37]. The processes can be described as follows: TiOPc/ H_2SO_4 solution (273 K, 20 ml, $w:v=1:30$) was added dropwise into the $\text{H}_2\text{O}/o\text{-PhCl}_2$ microemulsion (288 K and 338 K, 500 ml, $v/v=1/1$) at the stirring speed of 500 rpm, respectively. The microemulsion was demulsified with methanol to separate the colorless water phase and the blue *o*-PhCl₂ phase after 30 min. The blue *o*-PhCl₂ phase was diluted

with 500 ml of methanol, and was stored for 24 h at 273 K to precipitate the TiOPc NPs. The TiOPc NP precipitation was washed with methanol, followed with water until the conductivity of washing water $<5 \mu\text{S}/\text{cm}$, and then dried by freeze dehydration to generate specific crystal forms of the TiOPc NPs.

2.3 Fabrication

About 0.2 g of TiOPc (α - and β -phase) NPs and 0.2 g of PVB were added into the MEK/CYC solution (21 ml, $v/v=6:1$), and then ball-milled for 2 h to generate a stable coating dispersion. The dispersion was coated onto the aluminum plate (10 cm $\times$ 10 cm) with an undercoat layer (UCL, Polyamide, 0.5 μm) to form a charge generation layer (CGL). The thickness of the CGL was about 1 μm after drying at 333 K for 30 min. The charge transport layer (CTL, about 22 μm) was fabricated with PC blending *m*-TPD ($w:w=1:1$) by coating on the CGL, then drying at 353 K for 60 min.

2.4 Characterization

A Rigaku MinFlex600 diffractometer (Rigaku Corporation, Japan) was used to measure the X-ray diffraction (XRD) patterns of the TiOPc samples. The scanning electron microscope (SEM) photographs of the TiOPc NPs were collected by utilizing S-4800 with an accelerating voltage of 3 kV (Hitachi Ltd., Japan). The thicknesses of the functional layers were measured using a surface roughness tester (DEKTAK-6M, Veeco, USA). The DFT calculations were carried out with Gaussian 09.

The photosensitivity properties of the OPCs fabricated with α - and β -TiOPc NPs were investigated by photoinduced discharging measurement on the advanced photoconducting printer test system (PDT-2000LTM, Quality Engineering Associates, Inc., USA). The typical measurement process can be described as follows: After the OPC was loaded on the operator, a corona voltage of -4.4 to -4.8 kV was required to adjust the initial surface potential (V_0) of the OPC to be -700 ± 2 V. Then, an electrostatic voltmeter and LED erase light source (780 nm, exposure radius: 0.9 mm) simultaneously scanned with the speed of 50 mm/s for 26 times. The exposure intensity increased from 0–5 $\mu\text{J}/\text{cm}^2$ with the increase of scanning times. Therefore, the surface potential of OPC decreased with the increase of the exposure intensity. The PIDC can be obtained with the x -axis of exposure intensity and the y -axis of the surface potential $E_{1/2}$ of OPC was defined as the exposure intensity for surface potential to a half-decay.

The residual potential (V_r) is defined as the potential after ending the exposure process.

2.5 Computational details

The hole/electron reorganization energies are defined as the vertical ionization (cationic/anionic) of a neutral molecule, followed by geometric relaxation, and then vertical neutralization of a charged molecule followed by geometric relaxation. Nielsen's four-point method was adopted to calculate the $\lambda_{\pm}$ at the DFT level using the B3LYP functional and a 6-31G* (Lanl2dz) basis set [40–42]. The crystal geometries of α - and β -TiOPc were obtained from Hiller et al.'s previous single crystal data [43]: α -TiOPc crystallizes triclinic in the space group $P\bar{1}$ with the lattice constants $a=1216.6(4)$ pm, $b=1258.4(5)$ pm, $c=864.1(3)$ pm, $\alpha=96.28(3)^\circ$, $\beta=95.03(4)^\circ$, $\gamma=67.86(4)^\circ$ and $Z=2$. The β -TiOPc forms a monoclinic structure in the space group $P2_1/c$ and a unit cell of dimensions $a=1341.1(6)$ pm, $b=1323.0(3)$ pm, $c=1381.0(4)$ pm, $\beta=103.72(3)^\circ$ and $Z=4$.

We adopted the incoherent hopping model, which has been proven to be a dominant mechanism for organic semiconductors at high temperature by Brédas et al. [10]. In the incoherent hopping model, the hole/electron transfer could be described as a self-exchange electron-transfer reaction between a neutral molecule and a neighboring radical cation/radical anion. The calculation methods of both $\tau_{\pm}$ and $\mu_{\pm}$ for α - and β -TiOPc were based on the relevant literatures [31, 36]. The $\mu_{\pm}$ values for all possible molecular dimers extracted from the unit cell of α - and β -TiOPc were systematically calculated by DFT at the PW91PW91/(6-31G*, Lanl2dz) level using the fragment orbital approach in combination with a basis set orthogonalization procedure [44].

3 Results and discussion

Figure 1 illustrates the preparation process of the α - and β -TiOPc NPs by the microemulsion phase transfer method in the $\text{H}_2\text{O}/o\text{-PhCl}_2$ microemulsion, which could be described as follows: a–b) Purification of crude TiOPc, b–c) Transformation of the amorphous TiOPc to the specific crystal form of TiOPc, c–d) demulsification, d–e) Filtration, and e–f) Vacuum freeze-drying. Compared with the traditional two-step preparation method [39], namely, the purification-transformation process, the microemulsion phase transfer method successfully constructed a stable $\text{H}_2\text{O}/o\text{-PhCl}_2$ microemulsion to combine purification and transformation into a one-pot process.

Figure 1: The schematic of the microemulsion phase transfer method for preparing the α - and β -TiOPc NPs, the inset is the 3D model of a TiOPc molecule.

(A) $\text{H}_2\text{O}/o\text{-PhCl}_2$ microemulsion, (B) TiOPc/ H_2SO_4 solution dropwise into the $\text{H}_2\text{O}/o\text{-PhCl}_2$ microemulsion, (C) TiOPc NPs transfer into $o\text{-PhCl}_2$ phase, (D) Microemulsion stratification, (E) Frozen filter cake, (F) Obtaining TiOPc NPs.

Figure 2(A, B) shows that the XRD patterns of the TiOPc NPs obtained at 288 K and 338 K exhibit a typical α -type crystal form (2θ : 7.5° , 25.3° , 28.6°), and β -type crystal form (2θ : 9.2° , 10.4° , 26.2°), respectively [45, 46]. As shown

in Figure 2(C, D), the diameters of the α - and β -TiOPc NPs prepared with the present method are all less than 50 nm. Upon randomly selecting 100 particles in Figure 2(C, D) for statistical analysis, the average diameters of α - and β -TiOPc are 34.4 ± 7.3 and 35.0 ± 7.6 nm, respectively. Therefore, different types of TiOPc NPs can be simply prepared with the microemulsion phase transfer method by controlling the microemulsion temperature. The approximate particle size between α - and β -TiOPc represents the similar specific surface area, which is propitious in reducing the interference factors and in studying the relationship between crystal form and photosensitivity in the later work.

The TiOPc has polymorphs characteristics and is prone to crystal transformation under the action of mechanical forces. Owing to the preparation of CGL dispersion, which requires both ball milling and ultrasonic treatment for α - and β -TiOPc, the stable crystal forms of α - and β -TiOPc are important prerequisites for studying the relationship between crystal form and photosensitivity. As shown in Figure 3, neither the α -TiOPc NPs nor the β -TiOPc NPs have presented obvious changes after ball milling or ultrasonic treatment for 1–4 h. This observation indicates that the α - and β -TiOPc NPs prepared by the one-pot microemulsion phase transfer method have excellent crystal stability.

OPCs are used to investigate the photosensitivity properties of the α - or β -TiOPc NPs. Figure 4 exhibits the configuration and photoinduced discharging process of negatively charged OPCs. The process can be described as follows: (1) After loading the OPC into the operating black

Figure 2: The crystal form and particle size of TiOPc NPs.

(A, B) The XRD patterns of the TiOPc NPs obtained from $\text{H}_2\text{O}/o\text{-PhCl}_2$ microemulsion at 288 and 338 K, respectively. (C, D) The SEM photographs of the TiOPc NPs obtained at 288 and 338 K, respectively.

Figure 3: Characterization of crystal form stability.

The XRD patterns of the α - and β -TiOPc NPs before and after ultrasonic treatment (A, C) and ball milling (B, D) for 1–4 h, respectively.

Figure 4: The configuration and the photoinduced discharging process of a negatively charged dual-layered OPC.

box, a corona voltage of -4.4 to -4.8 kV was required to adjust the initial surface potential (V_0) of the OPC to be -700 ± 2 V; (2) illumination of a negatively charged OPC results in the formation of electron-hole pairs ($e-h$) in the CGL; (3) the photogenerated holes are injected to the CTL wherein the injected holes migrate across the CTL under the electric field and become neutralized [1]. All OPCs were measured on a QEA PDT-2000 LTM photoconducting printer drum test system to get PIDCs (Photoinduced Discharge Curves). For a more accurate comparison of photosensitivity, all OPCs are measured with a corona voltage of -4.4 to -4.8 kV to adjust V_0 to be 700 ± 2 V. The wavelength of the monochromatic light is 780 nm.

Figure 5 shows the PIDCs of the OPCs with the α - and β -TiOPc NPs. From the curves, the values of V_0 , $E_{1/2}$ and V_t can be obtained. The related characteristic parameters are listed in Table 1. The $E_{1/2}$ of the OPC containing the α -TiOPc

Figure 5: The PIDCs of the OPCs containing the α -TiOPc NPs (black) and β -TiOPc NPs (red) as charge generation materials (CGMs).

Table 1: The photosensitivity properties of the OPCs fabricated with the α - and β -TiOPc NPs.

CGM	Charge (kV)	V_0 (V)	$E_{1/2}$ ($\mu\text{J}/\text{cm}^2$)	V_r (V)
α -TiOPc	-4.7	700.9	0.18	27.0
β -TiOPc	-4.5	701.2	0.49	11.2

NPs as photoactive material is $0.18 \mu\text{J}/\text{cm}^2$, which is about 2.72 times more sensitive than the OPC with the β -TiOPc NPs ($E_{1/2} = 0.49 \mu\text{J}/\text{cm}^2$). The surface voltage variation of the OPC with the α -TiOPc NPs under the same exposure intensity is obviously higher than that of the OPC based on β -TiOPc NPs, which not only indirectly proves that the α -TiOPc NPs can generate more e - h pairs than the β -TiOPc NPs, but also shows better photosensitivity than the β -TiOPc NPs under the same condition.

The photogeneration quantum efficiency can also be used to compare the photosensitivity properties of α - and β -TiOPc NPs given that the two OPCs in this work have the same composition, except for the photoactive materials. The physical configuration of OPCs could be deemed as the parallel plate capacitors. After exposure, the number of photogenerated carriers (N_{e-h}) is related to the surface voltage variation of OPCs, which can be calculated by the following equation:

$$N_{e-h} = \frac{\epsilon_r \times \epsilon_0 \times S \times \Delta V}{d \times e}, \quad (1)$$

where ϵ_r is the relative permittivity (3.0 measured by AC impedance spectroscopy measurement), ϵ_0 is the vacuum permittivity, S is the exposure area, ΔV is the variation of surface voltage and d is the functional layer thickness.

The number of incident photons (N_p) can be described as

$$N_p = \frac{P_{\text{inc}} \times \lambda \times S}{c \times h}, \quad (2)$$

where P_{inc} is the exposure intensity, λ is the incident wavelength, c the velocity of light and h the Planck constant.

Therefore, the photogeneration quantum efficiency (η_{e-h}) can be calculated as follows:

$$\eta_{e-h} = \frac{N_{e-h}}{N_p} = \frac{\epsilon_r \times \epsilon_0 \times \Delta V \times c \times h}{P_{\text{inc}} \times d \times \lambda \times e}. \quad (3)$$

Figure 6 shows that η_{e-h} of the OPC based on the α -TiOPc NPs is obviously larger than that of the OPC containing the β -TiOPc NPs under the same exposure intensity. The η_{e-h} is negatively correlated with the exposure intensity. The reason for this phenomenon is that the incident photon number is much larger than the number of

Figure 6: The photogeneration quantum efficiency as a function of exposure intensity.

photogenerated e - h pairs as the incident exposure intensity increases. The η_{e-h} of the OPC with the α -TiOPc NPs under the lowest exposure intensity is 2.23 times higher than that of the OPC containing the β -TiOPc NPs, which indicates that the crystal form of TiOPc has an important influence on photosensitivity.

3.1 Charge transfer integral and corresponding charge transfer mobility in the α - and β -TiOPc crystals

In addition, as the photosensitivity property is closely correlated with the charge transfer mobility resulting from the interaction of neighboring molecules in organic crystal materials [19, 47], quantum chemical calculations are used to gain further insights into the hole/electron transfer mobilities of the α - and β -TiOPc. The incoherent hopping model, the dominant mechanism in organic semiconductors, is adopted to describe the hole/electron transfer mobilities [48]. As we know, TiOPc crystals belong to the π -conjugated system, in which the charge transfer mobility must be controlled by the strong coupling existing between the electronic and geometric structures [49, 50]. The $\lambda_{\pm}$ and $\tau_{\pm}$ are two key parameters in determining the self-exchange hole/electron transfer rates and, ultimately, the hole/electron mobility. Small reorganization energy and large transfer integral are propitious to obtaining large charge transfer mobility. The charge reorganization energies are calculated at the DFT/B3LYP/(6-31G*, Lanl2dz) level, in which the hybrid density functional B3LYP and the Lanl2dz basis set have been proven reliable for calculating large molecules with heavy metals [51–53]. The calculated λ_{+} and λ_{-} of the

TiOPc molecule are 53.5 and 271.5 meV, respectively. The ratio of λ_- to λ_+ is 5.07, which indicates that the hole transfer mobility of the TiOPc is significantly larger than the electron transfer mobility. The λ_+ of the TiOPc is obviously smaller than that of pentacene (82 meV) and copper phthalocyanine (170 meV), suggesting that the TiOPc is an excellent *p*-type semiconductor material [54].

The charge transfer integral representing the magnitude of the intermolecular electronic coupling can be achieved by directly calculating the dimer Fock matrix with the unperturbed monomer's molecular orbitals at the DFT/PW91PW91/6-31G* (Lanl2dz) level. The Fock matrix is evaluated as $F^0 = SC\epsilon C^{-1}$, where S is the overlap matrix for the dimer, and the Kohn-Sham orbital C and eigenvalue ϵ are obtained by diagonalizing the zeroth-order Fock matrix without any self-consistent field iteration. The direct dimer Hamiltonian evaluation method is used to evaluate the hole/electron transfer integral, [55] which can be written as

$$t = \langle \phi_{\text{HOMO/LUMO}}^{0,\text{site1}} | F^0 | \phi_{\text{HOMO/LUMO}}^{0,\text{site2}} \rangle, \quad (4)$$

where $\phi_{\text{HOMO/LUMO}}^{0,\text{site1}}$ and $\phi_{\text{HOMO/LUMO}}^{0,\text{site2}}$ represent the HOMO or LUMO of the isolated molecules 1 and 2, respectively, among the neighbor molecules.

Figure 7: The unit cell pictures of the α - and β -TiOPc NPs [43].

The charge transfer mobilities of the π -conjugated semiconductors depend critically on the charge transfer integrals, which are highly sensitive to the relative orientations of neighboring molecules and crystal packing [56, 57]. Figure 7 shows the unit cells of the α - and β -TiOPc, respectively.

The τ_+ and τ_- for the molecular pairs are extracted from the corresponding crystal structures with the radius of 20 Å between the center molecule and the surrounding molecules. Figure 8 shows all the charge transfer routes between one randomly selected center molecule and all its possible neighbors on the basis of the crystal structure, 15 routes for α -TiOPc and 15 routes for β -TiOPc. As the sign of charge transfer integral caused by the orbital phase has no effect on the evaluation of charge transfer mobility, the numerical values of charge transfer integral are only shown as absolute values. Additionally, some transfer routes with charge transfer integrals < 2 meV are neglected here as they make little contribution to charge transfer mobility.

The calculated charge transfer integrals, together with the corresponding molecular pairs, transfer distances and transfer mobility for the α -TiOPc and β -TiOPc are tabulated in Tables 2 and 3, respectively. As can be seen in Tables 2 and 3, the molecular pairs in the crystals of the α - and β -TiOPc can be divided into three types according to the arrangements of molecules: type I for the same direction pairs, type II for the convex pairs and type III for the concave pairs. Type I belongs to the edge-to-edge stacking mode, and both Types II and III belong to the face-to-face stacking mode. Among the three types of molecular pairs, the τ_+ and τ_- of type I are obviously smaller than those of types II and III due to the smaller π -orbital overlaps and the larger distances between the neighboring molecules. This phenomenon indicates that the face-to-face stacking

Figure 8: The charge transfer routes in the crystal structures of the α -TiOPc and β -TiOPc. The red ball represents the oxygen atom of the TiOPc molecule facing outward, and the gray ball represents the oxygen atom facing inward.

Table 2: The main molecular pairs and the corresponding calculated charge transfer integrals and charge transfer mobilities in the α -TiOPc crystals.

Route	Type	Ti-Ti distance (Å)	Transfer integral (meV)		Transfer mobility (cm ² V ⁻¹ s ⁻¹)	
			Hole	Electron	Hole	Electron
1st	I	12.584	3.603	2.307	3.712E-05	1.038E-06
2nd	II	12.584	3.603	2.305	3.712E-05	1.034E-06
3rd	II	7.680	40.495	55.038	2.555E-01	1.450E-01
4th	II	6.993	133.799	33.510	2.573E+01	1.683E-02
5th	III	12.724	10.072	7.746	2.107E-03	1.226E-04
6th	III	6.409	47.989	38.917	1.981E-01	1.425E-02
Total					26.190	0.177

pairs are the most favorable charge transfer route for both hole and electron.

According to the calculated τ_+ and τ_- , the charge transfer mobility μ_+ and μ_- for hole and electron can be evaluated from the Einstein relation [36, 58] expressed as

$$\mu = \frac{e}{k_B T} D, \quad (5)$$

where k_B is the Boltzmann constant, T is the temperature, and D is the diffusion coefficient.

The results are listed in Tables 2 and 3. As expected, the trends in the changes of μ_+ and μ_- of different TiOPc pairs along with different stacking mode are consistent with the corresponding τ_+ and τ_- due to the same λ of the TiOPc molecule for either the hole or electron. As the μ is in direct proportion to the τ^2 for a given λ and transfer distance, the magnitude of μ is much greater than that of the corresponding τ . Thus, it can be inferred that the electronic coupling is a crucial factor affecting charge transfer mobility.

Tables 2 and 3 also show that τ_+ and μ_+ are remarkably larger than τ_- and μ_- , which also proves that both the α - and β -TiOPc are excellent *p*-type semiconductor materials, and that the hole transport behavior plays a dominant role in the photosensitivity of the α - and β -TiOPc. The calculated total hole transfer mobility of α -TiOPc is 26.19 cm²V⁻¹s⁻¹, which is 2.83 times larger than that of β -TiOPc (9.255 cm²V⁻¹s⁻¹). It is worth noting

this calculated result is very close to the experimental result (the $E_{1/2}$ ratio of α -TiOPc to β -TiOPc is 2.72), and is even similar to the calculated photogeneration quantum efficiency ratio (2.23) of α -TiOPc to β -TiOPc. Therefore, these results indicate that the selected theoretical calculation method is reasonable for indirectly explaining the relationship between crystal form and photosensitivity.

Moreover, Figure 8 and Tables 2 and 3 also show the anisotropy of charge transport in single crystals. The combination of different coupling molecules can form different charge transport routes, which can expand the charge transport to the whole multidimensional space. Based on the calculated charge transfer mobilities in Tables 2 and 3, Figure 9 shows the optimum hole transfer routes in the crystals of the α - and β -TiOPc, respectively. The optimum hole transport route of the α -TiOPc is composed of the molecule pair 4th for 25.73 cm²V⁻¹s⁻¹ and 6th for 0.1981 cm²V⁻¹s⁻¹, indicating that the best crystal growing direction is [1 0 0] crystal orientation. For the β -TiOPc, the optimum hole transport route is based on the molecule pair 7th for 8.384 cm²V⁻¹s⁻¹ and 8th for 0.511 cm²V⁻¹s⁻¹, along with the [1 0 0] crystal orientation. Therefore, this result provides a theoretical basis for the preparation of highly photosensitive semiconductor materials with a specific crystal orientation. All in all, the TiOPc molecular solid-state arrangements, namely, crystal forms of TiOPc, have a strong influence on the charge transport behavior, which in turn, affects its photosensitivity.

Table 3: The main molecular pairs and corresponding calculated charge transfer integrals and charge transfer mobilities in the β -TiOPc crystals.

Route	Type	Ti-Ti distance (Å)	Transfer integral (meV)		Transfer mobility (cm ² V ⁻¹ s ⁻¹)	
			Hole	Electron	Hole	Electron
1st	I	13.230	4.727	2.608	2.484E-04	6.461E-06
2nd	I	13.230	4.728	2.607	2.486E-04	6.451E-06
3rd	II	9.534	28.639	22.928	1.738E-01	2.004E-02
4th	II	9.534	28.67	22.942	1.745E-01	2.009E-02
5th	II	9.591	5.942	11.305	3.259E-04	1.199E-03
6th	III	9.591	5.930	11.283	3.233E-04	1.189E-03
7th	III	7.200	86.852	8.141	8.384	1.817E-04
8th	III	9.730	37.128	13.887	5.113E-01	2.809E-03
9th	III	14.700	8.296	9.172	2.909E-03	1.220E-03
Total					9.255	0.0468

Figure 9: The optimum hole transfer routes in the α -TiOPc and β -TiOPc crystals.

4 Conclusions

In this work, the relationship between the crystal forms of TiOPc and their photosensitivities was investigated according to the experimental and theoretical calculation results. Both the α - and β -TiOPc NPs with almost the same diameter of ≈ 35 nm were prepared with the microemulsion phase transfer method. The α - and β -TiOPc NPs as photoactive materials were used to fabricate the multilayered OPCs to characterize the photosensitivities. The test results showed

that the $E_{1/2}$ of OPCs based on α -TiOPc was 2.73 times better than that of OPCs with β -TiOPc. According to the PIDCs, the calculated η_{eh} of the OPC with α -TiOPc NPs is 2.23 times higher than that of the OPC with β -TiOPc NPs. The λ_+ and λ_- for TiOPc were respectively calculated to be 53.5 meV and 271.5 meV at the DFT/B3LYP/(6-31G*, Lanl2dz) level. These reveal that the TiOPc molecule is a typical p -type semiconductor. The DFT/PW91PW91/(6-31G*, Lanl2dz) level was used to systematically calculate the τ_+ and τ_- in all possible pathways composed of two neighboring molecules for 17

dimers from the α -TiOPc and 19 dimers from the β -TiOPc. The calculated corresponding total hole transfer mobility of the α -TiOPc was $26.19 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, about 2.83 times larger than that of β -TiOPc ($9.255 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). The calculated total μ_+ ratios of α - to β -TiOPc were almost in agreement with the experimental $E_{1/2}$ ratio (2.73) and $\eta_{\text{e-h}}$ ratio (2.23). In addition, the optimum hole transfer routes in the α - and β -TiOPc crystals were respectively founded based on the calculated μ , both of which are along with the [1 0 0] crystal orientation. Consequently, these results indicated that the selected theoretical calculation method was reasonable for indirectly explaining the relationship between crystal form and photosensitivity. The TiOPc molecular solid-state arrangements, namely, crystal forms of TiOPc, have a strong influence on the charge transport behavior, which in turn, affect its photosensitivity. We hope these studies on TiOPc can provide a fertile theoretical ground with the synthesis novel high-photosensitivity materials for organic photodetectors.

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