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From molecules to materials: electronic and crystal engineering of bis-silylethynylated acenes for high carrier mobility

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ABSTRACT

Now considerable attention should be placed for the search of high-performance air-stable organic semiconductor materials (OSCMs) to fulfill the meet of applications. Crystal structure prediction (CSP) is a powerful tool to predict the CT properties of OSCMs. In this paper, using a new combined QM and MM method, the packing motifs of the experimental and the other possible polymorphisms of TIPS-PEN and TIPS-TBT were successful predicted. Here, we successfully predicted their charge transport properties with nothing more than the molecular geometry as the starting point and provide a rational method in designing of OSCMs.

Key words: organic semiconductor materials; crystal structure prediction; charge transport; DFT-D

INTRODUCTION

Organic Field-Effect Transistors (OFETs) have attracted widespread interest since the first report in 1986.[1] Compared to inorganic semiconductor devices, their unique advantages such as light weight, low-cost, flexibility and easy fabrication of large-areas make them highly promising for electronic paper, sensors, radio frequency identification tags, and organic active matrix displays. These potential applications of OFETs are closely related with the CT (charge transport) properties of organic semiconductors materials (OSCMs). In recent years, a lot of OSCMs have been designed and studied, such as linear,[2]star-shaped,[3] X-shaped,[4] butterfly-shapedmolecules.[5] Among these materials, linear molecules, such as thienoacenes or acenes with a planar π-conjugated structure, tend to have high charge carrier mobilities.[6] Some key correlations between organic semiconductors and their performance had been set up. One of the most important factors is the packing mode of OSCMs. For example, thienoacenes with high performance always have closing and ordering arrangement, which made it effective that intrastack electronic coupling via strong π-π intermolecular interactions, and interstack electronic coupling via lateral S•••S and CH•••π interactions in the solid state.[7] Introduction of long alkyl groups or other groups to organic molecules are expected an effective approach to change the packing motifs, from herringbone to lamellar, if the length of the substituents was approximately half the length of the acene core.[8] Nowadays series of pentacene and thienoacenes derivatives with alkyl or aryl substituents were synthesized and presented excellent charge transport properties. For example, the mobilities of **TIPS-PEN** and **TIPS-TBT** (shown in Fig. 1) were reported to be 1.8 $cm^2V^{-1}s^{-1}$ and1.0 $cm^2V^{-1}s^{-1}$ because of their 2-D bricklayer structure.[9]

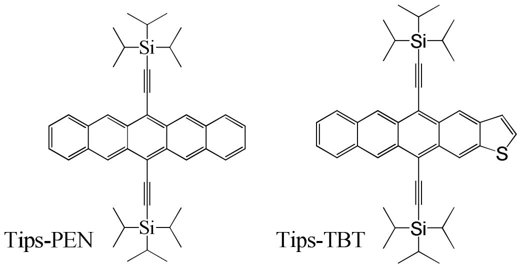


Fig. 1 Molecules studied in this paper

It is worth noting that the ability to predict crystal structures of OSCMs in advance would not only be critical forthe predictionof transport properties, but also make it much more feasible for the examination of the transport properties without the time, expense, and hazard of synthesizing them in the laboratory.

Up to now, CT properties could be roughly predicted through theoretical simulations by the analysis of single molecular properties, such as, energy levels, IP (ionization potential)/EA (electron affinity) and reorganization energy. A relatively accurate prediction of the CT properties would be available only for those materialswhich have certain crystal structures. For most studies, the approximate treatment is inevitable because of the unknown crystal structures of OSCMs.[10]' It is no doubt that crystal structure prediction (CSP) is apparently much more accurate and reliable approach than the simple approximation. Nowadays there are three main methods forCSP: molecular mechanics (MM)force-field，quantum mechanics(QM) and QM/MM methods. While each of these methods has demonstrated some degree of success, there remain many limitations in handling the different types of inter-interactions including hydrogen–bonding, electrostatics, and Van der Waals dispersion interactions and so on. Traditional classical MM calculations have advantages of low computational cost and universality, but reveal nothing about electron distributions in molecules. High-level quantum chemical methods, such as DFT-D[11] and periodic MP2, are much more reliable, but too computationally demanding for crystal-structure prediction. In this paper, a combined of the QM and MM approach were used to predict the most possible packing motifs of the studied molecules (Fig.1). During this approach, a faster but less accurate force field method were explored the plausible packing modes and QM are implemented in the molecule optimization and the final analysis of the trial crystal structures.

THEORETICAL METHODOLOGY

To describe the charge-transport properties of the systems, the incoherent hopping model was employed, in which charge can transfer only between neighboring molecules. Each hopping step has been considered as a non-adiabatic electron-transfer reaction involving the self-exchange charge from a charged molecule to an adjacent neutral one. A widely used method to estimate the charge transfer rate is Marcus equation [12]:

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

Here h and k_B are the Planck and Boltzmann constants. T is the temperature, V is the charge transfer integral between the initial and final states, and λ is the reorganization energy. For a fixed temperature, the large transfer rate can be attributed to the maximal transfer integral and the minimal reorganization energy.

The reorganization energy λ includes two parts: the inner reorganization energy and the external polarization.[13] When the contributions[14]due to the polarization of the medium and to molecular vibrations are neglected, the inner reorganization energy (see Fig.2), is usually evaluated based on adiabatic potential energy surfaces (AP):

$$\lambda^{(1)} = E^{(1)}(M) - E^{(0)}(M) \;, \; \lambda^{(2)} = E^{(1)}(M^{\bullet +}) - E^{(0)}(M^{\bullet +})$$

where,$E^{(0)}$(M) and $E^{(0)}(M^{\bullet +})$ denote the ground-state energies of the neutral state and of the charged state, respectively; $E^{(1)}$(M) is the energy of the neutral molecule in the optimized geometry of the ion state, and $E^{(1)}(M^{\bullet +})$ is the energy of the charged state at the optimized geometry of the neutral molecule.

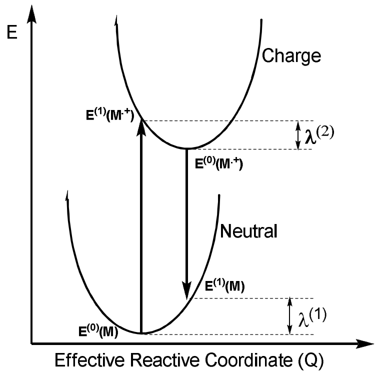


Fig. 2. Sketch of the adiabatic potential energy surfaces for neutral state and charged state, and the internal reorganization energy $\lambda^{(1)}$ and $\lambda^{(2)}$

The transfer integral V characterizes the strength of the electronic coupling between two adjacent molecules, which can be written as:[15]

$$V_{mn} = \frac{\tilde{V}_{mn} - \frac{1}{2}(\tilde{e}_m + \tilde{e}_n)S_{mn}}{1 - S_{mn}^2}$$

Here, $\tilde{e}_m = \langle \tilde{\Phi}_m | H | \tilde{\Phi}_m \rangle$, $\tilde{V}_{mn} = \langle \tilde{\Phi}_m | H | \tilde{\Phi}_n \rangle$, where $\tilde{\Phi}_m$ and $\tilde{\Phi}_n$ are the frontier molecular orbital of the isolated molecule m and n in the dimer representation. Namely, for hole transport, the highest occupied molecular orbital (HOMO) should be plugged in. H and S are the dimer Hamiltonian and the overlap matrices, respectively.

Within the thermally activated hopping model, the diffusion coefficient can be evaluated from[16]:

$$D = \frac{1}{2n} \sum_i d_i^2 k_i P_i$$

where d is the intermolecular center-to-center distance, n is the spatial dimension, k_i is the charge transfer rate due to charge transfer to the i_{th} neighbor, and P_i is the relative probability for charge transfer to a particular i_{th} neighbor, i.e.

$$P_i = \frac{k_i}{\sum_i k_i}$$

Summing over all possible hops leads to the diffusion coefficient in the equation above. The drift mobility of hopping, μ, is then evaluated from the Einstein relation[17]

$$\mu = \frac{e}{\kappa_B T} D$$

where e is the electron charge.

COMPUTATIONAL DETAILS

The molecular geometries were fully optimized with tight convergence criteria at the B3LYP/6-31+G(d) level using the Gaussian 09 program package. With the same level of the theory, the reorganization energies were evaluated using adiabatic potential-energy surfaces method[18] for isolated molecules. Transfer integrals were performed with the site-energy corrected method at the DFT-pw91pw91/6-31g* level,[19] and the drift mobility was calculated on the basis of the Marcus theory.

CSP was performed using the polymorph predictor (PP) module in Cerius2. The calculations were carried out using the PBE functional and the Dreiding force field[20], which is considered to be more appropriate force fields for molecular crystal prediction recently[21], and space groups were restricted to the most popular five space groups, P21/c, P-1, $P2_12_12_1$, $P2_1$, and C_{2c} according to the statistics result of the Cambridge Structural Data base. Then the most likely candidates were optimized with analytical gradients for the unit cell and internal parameters using a modified version of CRYSTAL09 and the B3LYP+D* method[22]with the 3-21G(d) basis set[23] has been implemented. In this method the S_6scaling factor was set to 1.00 and a scaling factors of 1.05 and 1.30 was applied to the atomic van der Waals radii of heavy atoms and hydrogen[24]. The level of accuracy in evaluating the

Coulomb and exchange series is controlled by five thresholds, for which values of 10^{-6}, 10^{-6}, 10^{-6}, 10^{-6}, 10^{-12} were used for the Coulomb and the exchange series. The shrinking factor (2 4) of the reciprocal space net for each system was set to define a mesh of k-points in the irreducible Brillouin zone for which the total energies are fully converged. The threshold for the maximum force, the RMS force, the maximum atomic displacement, the RMS atomic displacement on all atoms, and the energy change have been set to 0.00045, 0.00030, 0.00180, 0.00120 and 10^{-7}a.u. respectively.

RESULTS AND DISCUSSION

SINGLE-MOLECULE "TRANSPORT" LEVELS

It's well known that the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) levels are useful for investigation of the properties of OSCMs. These frontier molecular orbitals are closely related to the abilities of hole or electron injection from the electrode to the organic semiconductors. The reorganization energies, description of local electron-vibration coupling in the charge transfer process, here are calculated by adiabatic potential surfaces (AP). The ionization potentials (IPs), reorganization energies, as well as energies of the HOMOs and LUMOs obtained withB3LYP/6-31+G(d) for the studied molecules are listed in Table 1. The calculated values are similar. The DFT calculations show that the HOMOs and LUMOsof **TIPS-TBT** and **TIPS-PEN** are of π nature and spread over the whole core (shown in Fig. 3). **TIPS-TBT**has relatively lower HOMO level and high IP than those of**TIPS-PEN**. Above all, **TIPS-TBT** might havesimilar CT properties like the**TIPS-PEN** based on their energy levels.

Table 1 λ /IP/HOMO_LUMODFT/B3LYP/ 6-31+G(d)

Molecular	HOMO/eV	LUMO/eV	V_IP/eV	AP_IP/eV	λ(meV)
Tips-PEN	-4.89	-3.00	5.88	5.94	134.1
Tips-TBT	-4.96	-2.86	5.96	6.03	130.9

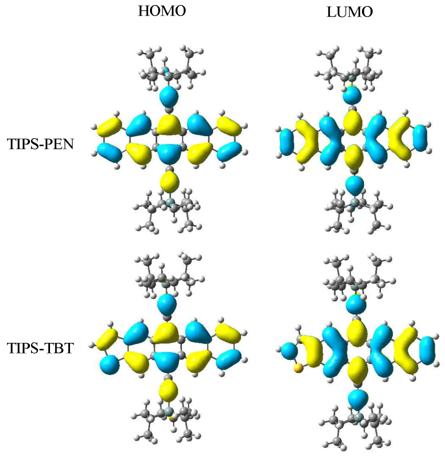


Fig. 3 The highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) orbitals for TIPS-PEN and TIPS-TBT

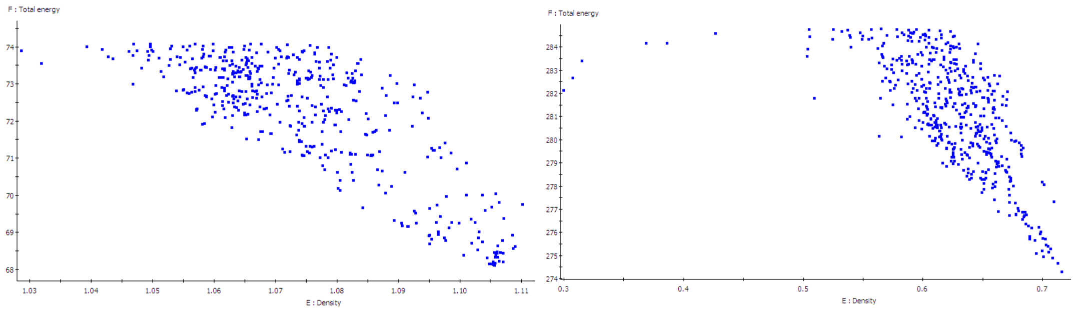


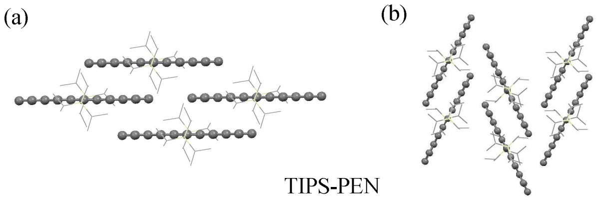
Fig. 4 density-energy plots for (a) TIPS-PEN and (b) TIPS-TBT

CRYSTAL STRUCTURE PREDICTION

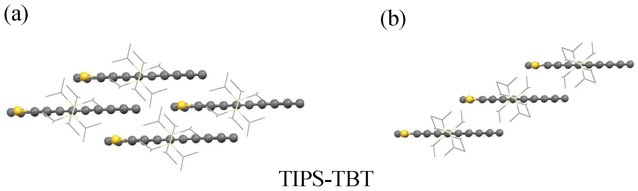
The crystal structure plays significant roles in the determination of thetransport properties of OSCMs. Our approach for CSP would obviously assist the designof new OSCMs. We take **TIPS-PEN**, whose stable structure has been found to be2D bricklayer constructions, as an example to examine our method.

First of all, quantum chemical optimization of molecule **TIPS-PEN** was performed using theB3LYP/6-31+G*, and Gaussian electrostatic potential (ESP) charges were obtained. The initial search was made in the PP module in Cerius^{2}by employing the PBE functional and the Dreiding force field under the most popular five space groups. After the initial searching, thousands of crystal structures were generated for the molecule **TIPS-PEN**. To make a further analysis, density-energy plots (Fig. 4) were made for the first 500 structures with low lattice energy. It could be found that structures with low energies generally have relatively high densities. The energy difference is small among these predicted structures. It is hard to extract the most stable crystal structures without the risk of missing any possible ones based on the lattice energies calculated by the MM force-field. But it is quite expensive to make a precisely QM calculation of the vast amount of conformers. A primary screen is necessary. The intermolecular arrangement is much more important for determination the CT properties of OSCMs than the size and shape of their unit cells. In contrast to the 230 space groups, there are only four different kinds of intermolecular packing motifs: (1) herringbone packing without π-π overlap between adjacent molecules; (2) slipped π-stacking (herringbone packing with π-π overlap between adjacent molecules); (3) one-dimension (1-D) lamellar packing, and (4) two-dimension (2-D) bricklayer π-stacking.

The relatively stable hundreds of structures with low lattice energies and high densities were observed. It could be found that for **TIPS-PEN** no matter what the space groups and the lattice energies are, most of the predict crystal structures presented 2-D bricklayerconfigurations coupled with some herringbone packing motifs (Fig. 5). In fact, crystal polymorphism in OSCMs is a prevalent phenomenon[25] and provide an opportunity to study the structure-property relationships. Molecule TTF exhibits two crystalline forms in the solid state.For the α phase of TTF, the highest mobility reached 1.2 cm^{2}V^{-1}s^{-1}, while the β phase only showed the maximum mobility about 0.23 cm^{2}V^{-1}s^{-1}.[26]In the case of **TIPS-PEN**, two packing motifs (2-D bricklayer and herringbone) with low energy obtained from preliminary predictions were selected for the further accurate optimization using a modified B3LYP+D* method considering the long-range dispersion contributions. The unit cell and the molecule were alternately optimized to converge. The predicted structure of **TIPS-PEN(a)** closely resembles the reported experimental crystal structure with overlap similarity up to 97%(Fig.6), which indicates that our method could give an excellent prediction of packing modes for this type cross-shaped molecule. The crystal structures of**TIPS-TBT** were also predicted using the same procedure. Two crystal structures, 1-D lamellar packing and 2-D bricklayer packing, were obtained for **TIPS-TBT** shown in Fig. 5.



TIPS-PEN



TIPS-TBT

Fig. 5The main packing modes for studied systems

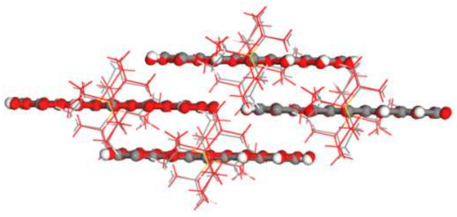


Fig. 6 Overlay of experimental form (red) and predicted (TIPS-PEN(a) colored by element) crystal structure for TIPS-PEN

Table 2 Transfer integrals

	TIPS-PEN		TIPS-TBT (a)		TIPS-TBT (b)	
	d/ Å	V_h/meV	d/ Å	V_h/meV	d/ Å	V_h/meV
P1	10.16	17	9.96	11	8.78	31.33
P2	7.28	32	7.28	35		

Table 3 The calculated hole Mobilitiesμcal(cm^2/Vs) and experimental values μexp (cm^2/Vs) for TIPS-PEN and TIPS-TBT.

Compounds	Hole Mobility cm^2/Vs	
	μ_{exp}	μ_{cal}
TIPS-PEN	0.4(vacuum-deposited) 1.8(drop –casting)[27] 1.42(self-assembled)[28]	1.35
TIPS –TBT(a)	1.25(vacuum-deposited)[9]	1.29
TIPS–TBT(b)	0.8(average)	1.26

TRANSFER INTEGRALS AND MOBILITIES

In organic transport materials, the charge transfer occurs through weak intermolecular interactions that are mostly confined to the nearest neighboring molecules. The charge transport properties are, therefore, closely related to their packing manners. Based on the crystal structures obtained from CCDC and the predicted ones, the charge transport properties of **TIPS-PEN** and **TIPS-TBT** were investigated through Marcus electron transfer theory coupled with site-energy corrected simulation of the hole transfer integrals(V_h). The data are listed in Table 2 and 3. It could be seen from Table 2, that **TIPS-PEN^{exp}** and **TIPS-TBT(a)** with 2-D bricklayer constructions have similar transfer channels. In both systems, transporting path P2 along theπ-π stacking direction is the best transfer pathway with Vh of 32 and 35meV respectively. But for **TIPS-TBT(b)**,there is only one main charge hopping path way with Vh of 31.3 meV. Combining the Marcus formula with Einstein-Smolu-chowski relation, we evaluated the hole mobilities of **TIPS-PEN** and **TIPS-TBT**. The results listed in Table 3 show that the calculated mobilities correspond relatively well to the experimental values.

CONCLUSION

Using a combined QM and MM method, we predicted the crystal packing of two cross shaped molecules with nothing more than the molecular geometry as the starting point. In our study, we successful predicted the crystal polymorphisms of **TIPS-PEN** and **TIPS-TBT**. Based on the predicted packing motifs, the CT properties were studied and correspond relatively well to the experimental values. Ultimately, this theory-guided material design strategy would be helpful both in CSP and the truly rational design of high performance CT materials.

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REFERENCES

[1] H Klauk. Chem. Rev., **2010**, 39(7), 2643-2666.
[2] K Niimi; S Shinamura; I Osaka; E Miyazaki.K Takimiya. *Journal of the American Chemical Society,* **2011**, 133(22), 8732-8739.
[3] KH Kim; Z Chi; MJ Cho; J-I Jin; MY Cho; SJ Kim; J-s Joo.DH Choi. *Chemistry of Materials,* **2007**, 19(20), 4925-4932.
[4] X Sun; Y Zhou; W Wu; Y Liu; W Tian; G Yu; W Qiu; S Chen.D Zhu. *The Journal of Physical Chemistry* B, **2006**, 110(15), 7702-7707.
[5] W Zhang; X Sun; P Xia; J Huang; G Yu; MS Wong; Y Liu.D Zhu. *Organic Letters,* **2012**, 14(17), 4382-4385.
[6] AY Amin; A Khassanov; K Reuter; T Meyer-Friedrichsen.M Halik. *Journal of the American Chemical Society,* **2012**, 134(40), 16548-16550.
[7] Y Qiao; Z Wei; C Risko; H Li; J-L Bredas; W Xu.D Zhu. *Journal of Materials Chemistry,* **2012**, 22(4), 1313-1325.
[8] C Wang; H Dong; W Hu; Y Liu.D Zhu. *Chemical Reviews,* **2012**, 112(4), 2208-2267.
[9] ML Tang; AD Reichardt; T Siegrist; SCB Mannsfeld.Z Bao. *Chemistry of Materials,* **2008**, 20(14), 4669-4676.
[10] S Sanyal; AK Manna.SK Pati. *J. Phys. Chem. C,* **2013,** 117(2), 825-836.
[11] S Grimme; J Antony; S Ehrlich.H Krieg. *J. Chem. Phys.,* **2010**, 132(15), 154104.
[12] A Gavezzotti. *Top. Curr. Chem.,* **2012**, 315(1-32.
[13] MA Neumann; FJJ Leusen.J Kendrick. Angew. *Chem., Int. Ed.,* **2008**, 47(13), 2427-2430.

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[14] S Curtarolo; D Morgan; K Persson; J Rodgers.G Ceder. *Phys. Rev. Let*t., **2003**, 91(13), 135503.
[15] Edward F. Valeev, Veaceslav Coropceanu, Demetrio A. da Silva Filho, Seyhan Salman,†and Jean-Luc Bredas. J.Am.Chem.Soc., **2006,** 128(30), 9882–9886.
[16] CC Fischer; KJ Tibbetts; D Morgan.G Ceder. *Nat Mate*r, **2006**, 5(8), 641-646.
[17] AROaCW Glass. J. Chem. Phys., **2006**, 124(244704.
[18] RS Rathore; Y Alekhya; AK Kondapi.K Sathiyanarayanan. *CrystEngComm*, **2011**, 13(16), 5234-5238.
[19] X-D Tang; Y Liao; H Geng.Z-G Shuai. *Journal of Materials Chemistry*, **2012**, 22(35), 18181-18191.
[20] E Manas, in, American Chemical Society, **2007**, pp. MARM-215.
[21] B Zhang; Y-H Kan; Y Geng; Y-A Duan; H-B Li; J Hua.Z-M Su. *Org. Electron*., **2013**, 14(5), 1359-1369.
[22] B Civalleri; CM Zicovich-Wilson; *L Valenzano.P Ugliengo. CrystEngComm*, **2008**, 10(4), 405-410.
[23] MU Schmidt.U Englert. *Journal of the Chemical Society, Dalton Transactions*, **1996**, 0(10), 2077-2082.
[24] J Kendrick; GA Stephenson; MA Neumann.FJJ Leusen. *Crystal Growth & Design*, **2013**, 13(2), 581-589.
[25] GP Stahly. *Crystal Growth & Design*, **2007**, 7(6), 1007-1026.
[26] M Mas-Torrent; P Hadley; ST Bromley; N Crivillers; J Veciana.C Rovira. *Appl. Phys. Lett.*, **2005**, 86(1), 012110.
[27] SK Park; TN Jackson; JE Anthony.DA Mourey. *Applied Physics Letters*, **2007**, 91(6), 063514-063513.
[28] DH Kim; DY Lee; HS Lee; WH Lee; YH Kim; JI Han.K Cho. *Advanced Materials*, **2007**, 19(5), 678-682.