Comparative opto-electronic properties of perylene diimides derivatives with cyclization and high polarizability cores

Wenhuan Zhu1, Xiaodong Liu2, * and Hongyu Ni3

1Department of Micro/Nano Electronics, School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, Shanghai, China
2Shanghai Institute of Aerospace Science, industry and electrical appliances Co., Ltd., Shanghai, China
3State Grid Shaoxing Power Supply Company, Shaoxing, China

*Corresponding author: liuxiaodong528@sjtu.edu.cn

Abstract. Recently, perylene diimides (PDIs) show great application potentials in the field of organic opto-electronics, which can be widely used in OLEDs, OPVs, OFETs, etc. In order to obtain more efficient PDIs derivatives, there are two typical methods including cyclization and high polarizability cores. However, numerous valuable molecules cannot be experimental synthesized easily, which are available for theoretical prediction via simulation and calculation. Therefore, we design four model molecules of PDIs derivatives, whose opto-electronic properties are calculated by the DFT method afterwards. By comparing simulation results, we can further extend the comprehension of structure-property relationships of PDIs, which is beneficial to the high-efficiency PDIs derivatives design.

Keywords: perylene diimides, opto-electronic, cyclization, high polarizability core, DFT calculation.

1. Introduction

Solar energy is currently one of the largest neutral and the fastest growing renewable energy sources. Among the various photovoltaics technologies, organic photovoltaics (OPVs) have attracted wide research interests due to their remarkable characteristics, such as low manufacturing cost, simple coating or printing large area fabrication process, environmentally friendly nature and so on [1]. In organic semiconductors, perylene diimides (PDIs) are considered as one of the most promising candidates for electron absorption in the construction of high-performance non-fullerene acceptors (NFAs), owing to their easy functionalization, high electron mobility and high absorption coefficient [2]. However, PDI-based NFAs generally exhibit large coplanar configurations, leading to excessive aggregation and thus large domains in the active layer causing a drop in the donor/acceptor interface and a limitation of exciton dissociation. Normally, in order to alleviate the problem, researchers adopted the “multiple-wing propeller” molecular design strategy, which can break the coplanar structure [3-5]. The introduction of large twisting angles between the PDI units brings a series of molecules with fascinating properties. For instance, two of the three PDI units in Ta-PDI show more twisted geometry (19°) compared with pristine-PDI, therefore, Ta-PDI exhibits higher electron mobility and a considerably
higher power conversion efficiency [6]. In the molecule design strategy, it is of great significance to select suitable bonding pattern and appropriate core in the PDI derivatives. Ring fusion is an effective way to enhance the coplanarity of molecules, which results in enhanced molecular orientation and facilitates charge carrier transport. Besides, high polarizability groups as the PDIs derivatives core mainly have three typically features: easy synthesis and modification, strong absorption curves and easily tunable energy levels [7-10].

As we know, some valuable molecules cannot be easily synthesized via chemistry reactions. However, it is worth understanding the structure-property relationships of these molecules due to their great research value, which can be investigated by computation and simulation. In this work we applied the multiple-wing propeller design strategy to obtain four model molecules of PDI derivatives and calculated their various parameters by DFT method subsequently. By this effective way, we could figure out the role of cyclization and high polarizability groups in the opto-electronic properties of these molecules, which can provide an important reference point for the high-efficiency NFAs molecule design.

2. Results and Discussions

PDI monomers are prone to strongly aggregate in a domain size, allowing efficient exciton dissociation. Therefore, the introduction of PDI functionalization at different positions to distort the molecule is crucial to reduce aggregation. Depending on the functionalization position, PDI-based NFAs can be classified into α and bay functionalized derivatives (figure 1). The bay position is the most common grafting position as its synthesis is feasible and it is effective in reducing intermolecular aggregation.

![Figure 1. Two typical functionalized positions of PDIs.](image)

Another effective way to introduce molecular torsion is choosing different numbers of PDIs to conform to the central core degree of functionality. Therefore, the selection of central core is very important to improve the opto-electronic properties of organic semiconductors. One important method is selecting high polarizability groups as the core, for example the heteroaromatic rings with N, S, Se atoms. The introduction of heteroatoms would gain more twisted structures and higher lowest unoccupied molecular orbital (LUMO) levels. Based on the fundamental understanding of the two typical modification methods, we design four molecules, giving a sufficient consideration for the parallel comparison. The formula and molecular orbital information have been shown in figure 2 and table 1, and the collection, calculation, processing methods of the corresponding data refer to [11-13].

As shown in figure 2, the central core of PDI-1 and PDI-2 is indaceno[3, 2-b] thiophene with four thiophene side-chain branchings and the PDI-3 and PDI-4 are 9, 9’-bifluorenylidene derivatives. The thiophene in the PDI-1 and PDI-2 possesses much higher polarizability leading to a lower dipole moment, as shown in table 1, with the Debye value of 0.64, 0.62, respectively.
Figure 2. The molecular structural formula, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) level of (a) PDI-1, (b) PDI-2, (c) PDI-3 and (d) PDI-4.

Table 1. The calculated results of PDI-1, PDI-2, PDI-3 and PDI-4.

| Compounds | HOMO (eV) | LUMO (eV) | Band gap (eV) | Dipole (Debye) |
|-----------|-----------|-----------|---------------|----------------|
| PDI-1     | -5.46     | -3.78     | 1.68          | 0.64           |
| PDI-2     | -5.63     | -3.59     | 2.04          | 0.62           |
| PDI-3     | -4.52     | -3.04     | 1.48          | 3.44           |
| PDI-4     | -4.79     | -3.09     | 1.70          | 2.75           |

The HOMO in the ground state configuration contains two electrons with opposite spins in neutral organic molecules. The absorption of an incident photon promotes the entry of one electron in the HOMO into LUMO, leaving a hole to form an electron-hole pair. In an ideal photovoltaic system, the electron-hole pairs can be easily separated to form long-lived, high-quantum-yield free charge carriers. When carriers are collected by the electrodes, a large photocurrent can be generated. However, this efficient generation of free carriers requires electron-hole pairs to overcome their mutual Coulomb attraction, $V$, given by

$$ V = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r} $$
Where $e$ is the electron charge, $\varepsilon_0$ is the dielectric constant of the vacuum, $\varepsilon_r$ is the dielectric constant of the surrounding medium, and $r$ is the distance between the electron-hole pairs. In solar cells based on inorganic semiconductors, such as silicon p-n junctions, the electron-hole pairs can easily overcome their Coulombic attraction to generate free charges due to the high dielectric constant ($\varepsilon_r \approx 12$ in silicon) and the highly delocalized nature of the photoexcited state (corresponding to large $r$ in equation (1)) [14-16]. Due to strong Coulomb interactions between electrons and holes, as well as strong electron-lattice and electron-electron interactions, photoexcitation of organic conjugate materials produces a tightly bound electron-hole pair, namely, an exciton. Due to the conservation of spin, these primary photoexcitations have singlet (zero spin) properties. In order to promote efficient charge generation, it is necessary to separate these singlet excitons by overcoming their binding energies [17].

In figure 2, the difference between PDI-1 and PDI-2 is the formation of the fused ring, where cyclization obviously changed the configuration of PDI derivatives. The PDI-2 has more coplanar structure and higher band gap than PDI-1. Similarly, after cyclization to PDI-3, the PDI-4 possesses lower dipole moment, higher band gap and more coplanar structure. By comparison, different central cores as thiophene derivatives with higher polarizability have lower dipole moment and higher bandgap. We applied the LUMO level to denote electron affinity, following the standard usage for discussing organic electronics. Much higher twisted molecular structure of the PDI-3 and PDI-4 leads to higher LUMO level that is beneficial to match with common donor materials. This structure effect makes both HOMO and LUMO levels slightly shift upward, thus increasing the open-circuit voltage of the same donor polymer while improving the nanoscale morphology. However, by the introduction of high polarizability groups in PDI-1 and PDI-2, as shown in figure 2, the delocalization of orbital energy levels between HOMO and LUMO seems stronger than PDI-3 and PDI-4 with a hydrocarbon aromatic central core. This sort of distribution is more favourable to effective exciton dissociation.

3. Conclusions
In this work, we design four organic semiconductor molecules with considering several factors, including central core, formation of fused ring. Compared with these structure-property relationships, we have investigated the influence of cyclization and high polarizability central core on the opto-electronic properties for these molecules. Based on the DFT calculation, we obtained certain crucial information, such as HOMO-LUMO level, band gap, dipole moment. In summary, we mainly have three conclusions: (1) the introduction of high polarizability conjugated central core will significantly improve the delocalization of $\pi$ electron; (2) the central core with space geometrical structure could make PDIs derivatives have more co-planar structure; (3) the formation of fused ring will cause more coplanar configuration, which could reduce molecular polarity and enhance molecular order that is avail to charge carrier transport. Our findings can assist the design of high-performance organic optoelectronic molecules.

Acknowledgments
This work was financially supported by the Startup Fund for Youngman Research at SJTU (SFYR at SJTU) (No. 19X100040004). Our computations were partially supported by the center for HPC, Shanghai Jiao Tong University.

References
[1] G. Zhang, J. Zhao, P.C.Y. Chow, K. Jiang, J. Zhang, Z. Zhu, J. Zhang, F. Huang, H. Yan, Nonfullerene acceptor molecules for bulk heterojunction organic solar cells, Chem. Rev. 118 (2018) 3447 - 3507.
[2] C. Li, H. Fu, T. Xia, Y. Sun, Asymmetric nonfullerene small molecule acceptors for organic solar cells, Adv. Energy Mater. 9 (2019) 1900999.
[3] H. Lin, S. Chen, H. Hu, L. Zhang, T. Ma, J. Y. L. Lai, Z. Li, A. Qin, X. Huang, B. Tang, H. Yan, Reduced intramolecular twisting improves the performance of 3D molecular acceptors in non-fullerene organic solar cells, Adv. Mater. 28 (2016) 8546 - 8551.
[4] Y. Liu, C. Mu, K. Jiang, J. Zhao, Y. Li, L. Zhang, Z. Li, J. Y. L. Lai, H. Hu, T. Ma, R. Hu, D. Yu, X. Huang, B. Z. Tang, H. Yan, A Tetraphenylethylene core-based 3D structure small molecular acceptor enabling efficient non-fullerene organic solar cells, Adv. Mater. 27 (2015) 1015 - 1020.

[5] S. Li, W. Liu, C.-Z. Li, F. Liu, Y. Zhang, M. Shi, H. Chen, T. P. Russell, A simple perylene diimide derivative with a highly twisted geometry as an electron acceptor for efficient organic solar cells, J. Mater. Chem. A 4 (2017) 10659 - 10665.

[6] Y. Duan, X. Xu, H. Yan, W. Wu, Z. Li, Q. Peng, Pronounced effects of a triazine core on photovoltaic performance–efficient organic solar cells enabled by a PDI trimer-based small molecular acceptor, Adv. Mater., 29 (2017) 1605115.

[7] Z. Luo, T. Liu, Z. Chen, Y. Xiao, G. Zhang, L. Huo, C. Zhong, X. Lu, H. Yan, Y. Sun, C. Yang, Isomerization of perylene diimide based acceptors enabling high-performance nonfullerene organic solar cells with excellent fill factor, Adv. Sci. 6 (2019) 1802065.

[8] J. Yang, F. Chen, J. Hu, Y. Geng, Q. Zeng, A. Tang, X. Wang, E. Zhou, Planar benzofuran inside-fused perylenediimide dimers for high VOC fullerene-free organic solar cells, ACS Appl. Mater. Inter. 11 (2019) 4203 - 4210.

[9] P. E. Keivanidis, G. Itskos, Z. Kan, E. Aluicio-Sarduy, H. Goudarzi, V. Kamm, F. Laquai, W. Zhang, C. Brabec, G. Floudas, I. McCulloch, Afterglow effects as a tool to screen emissive nongeminate charge recombination processes in organic photovoltaic composites, ACS Appl. Mater. Inter. 12 (2020) 2695 - 2707.

[10] R. Singh, M. Kim, J.-J. Lee, T. Ye, P.E. Keivanidis, K. Cho, Excimer formation effects and trap-assisted charge recombination loss channels in organic solar cells of perylene diimide dimer acceptors, J. Mater. Chem. C. 8 (2020) 1686 - 1696.

[11] F. Nepse, The ORCA program system, Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2 (2012) 73 - 78.

[12] T. Lu, F. Chen, Multiwfn: A multifunctional wavefunction analyzer, J. Comput. Chem. 33 (2012), 580 - 592.

[13] W. Humphrey, A. Dalke, K. Schulten, VMD: Visual Molecular Dynamics. J. Molec. Graphics 14 (1996) 33 - 38.

[14] T. M. Clarke, J. R. Durrant, Charge photogeneration in organic solar cells, Chem. Rev. 110 (2010) 6736 - 6767.

[15] B. A. Gregg, Excitonic solar cells. J. Phys. Chem. B 107 (2003) 4688 - 4698.

[16] C. Deibel, V. Dyakonov, Polymer-fullerene bulk heterojunction solar cells. Rep. Prog. Phys. 73 (2010) 096401.

[17] J. L. Bredas, Molecular understanding of organic solar cells: the challenges. AIP Conf. Proc. 1519 (2013) 55 - 58.