Design of Acceptors with Suitable Frontier Molecular Orbitals to Match Donors via Substitutions on Perylene Diimide for Organic Solar Cells

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Abstract: A series of perylene diimide (PDI) derivatives have been investigated at the CAM-B3LYP/6-31G(d) and the TD-B3LYP/6-31+G(d,p) levels to design solar cell acceptors with high performance in areas such as suitable frontier molecular orbital (FMO) energies to match oligo(thienylenevinylene) derivatives and improved charge transfer properties. The calculated results reveal that the substituents slightly affect the distribution patterns of FMOs for PDI-BI. The electron withdrawing group substituents decrease the FMO energies of PDI-BI, and the electron donating group substituents slightly affect the FMO energies of PDI-BI. The di-electron withdrawing group substituents can tune the FMOs of PDI-BI to be more suitable for the oligo(thienylenevinylene) derivatives. The electron withdrawing group substituents result in red shifts of absorption spectra and electron donating group substituents result in blue shifts for PDI-BI. The –CN substituent can improve the electron transport properties of PDI-BI. The –CH3 group in different positions slightly affects the electron transport properties of PDI-BI.

Keywords: perylene diimide derivatives; frontier molecular orbitals; optical properties; charge transport property; organic solar cells

1. Introduction

Organic solar cells (OSCs) with high power conversion efficiencies (PCEs) exceeding 10% have been fabricated [1]. Among them, organic small molecules as solar cell materials based on π-conjugate polymers are attractive because of their rapid energy payback time [2], low cost, flexibility, light weight, solution-based processing, and the capability to fabricate flexible large-area devices [3]. The PCEs of the OSCs have exceeded 11% when the conventional fullerene as the acceptors [4,5]. However, the fullerene and its derivative acceptors have several limitations, such as costly production, fixed band alignment, and limited optical absorption, which significantly prevent the development of new donor materials. Thus, developing and investigating novel acceptors has become a focus around the world. Up to now, many small molecule acceptors have been reported, such as 9,9′-bifluorenylidene [6,7], dicyan substituted quinacridone [8], diketopyrrolopyrrole derivatives [9,10], vinazene [11,12], fluoranthene-fused imide [13,14], naphthalene diimides [15,16], electron-deficient pentacenes [17], and perylene diimides (PDIs) [18–21]. Among the small molecule acceptors, PDI and its derivatives have attracted much attention in the past decade due to their superior optical
and electric properties—for example, excellent chemical, photochemical, and thermal stabilities [22], high absorption (450 and 650 nm) [23], promising electron mobility [24–26], and excellent electron affinity [27]. Yao et al. obtained solar cells with 4.34% efficiency on the basis of PDI [21]. Nguyen et al. prepared the PDI bulk heterojunction solar cell [1]. Shin et al. obtained OSCs with a power conversion efficiency of 0.18% under AM 1.5 using PDI derivatives as acceptors [28]. Tang et al. [29,30] and Won Suk Shin et al. prepared some PDI derivatives, and molecule PDI-BI had suitable properties as a solar cell acceptor [28]. In this manuscript, in order to improve the performance of PDI-BI, we have designed various PDI-BI derivatives (Table 1), which have different functional groups, to find the most promising acceptors with suitable frontier molecular orbital energies (FMOs) to match the OSC donor oligothienylenevinylene derivatives (X1 and X2, Figure 1) with favourable properties designated by Yong et al. [32]. Generally, the higher the lowest unoccupied molecular orbital (LUMO) of the acceptor, the larger the open circuit voltage ($V_{oc}$), because the difference in energy between the highest occupied molecular orbital (HOMO) energy of the donor and LUMO of the acceptor is in direct proportion to the $V_{oc}$. In addition, to ensure separation of charge, the differences between the LUMO energies of the donor and the acceptor should be greater than 0.30 eV [33]. Considering the fact that the substituent groups affect the molecular properties significantly, we designed two kinds of molecules (PDI-BI-1-26) to study the push (–CH$_3$) and pull (–CN and –NO$_2$) substituent groups effects. The density function theory (DFT) [34] has been used for evaluating a variety of ground state properties of these molecules, such as FMO, including HOMO and LUMO energies, and the HOMO–LUMO gaps ($E_g$). The optical properties (absorption spectra) of the designed molecules have been predicted by the time dependent DFT [35–37] approach (TD-DFT). The reorganization energy ($\lambda$) was also calculated. Additionally, we discussed the correlation between structures and properties of these molecules.

Table 1. Chemical structure of PDI-BI derivatives (Rn are –H except for mentioned in the Table).

| Molecules | R-Groups | Molecules | R-Groups |
|-----------|----------|-----------|----------|
| PDI-BI-1  | R$_1$ = –CN | PDI-BI-14 | R$_3$ = –CN R$_6$ = –CN |
| PDI-BI-2  | R$_2$ = –CN | PDI-BI-15 | R$_3$ = –CN R$_6$ = –NO$_2$ |
| PDI-BI-3  | R$_3$ = –CN | PDI-BI-16 | R$_4$ = –CN R$_5$ = –NO$_2$ |
| PDI-BI-4  | R$_4$ = –CN | PDI-BI-17 | R$_4$ = –NO$_2$ R$_5$ = –NO$_2$ |
| PDI-BI-5  | R$_5$ = –CN | PDI-BI-18 | R$_3$ = –NO$_2$ R$_6$ = –NO$_2$ |
| PDI-BI-6  | R$_6$ = –CN | PDI-BI-19 | R$_1$ = –CH$_3$ |
| PDI-BI-7  | R$_7$ = –CN | PDI-BI-20 | R$_2$ = –CH$_3$ |
| PDI-BI-8  | R$_8$ = –CN | PDI-BI-21 | R$_3$ = –CH$_3$ |
| PDI-BI-9  | R$_1$ = –NO$_2$ | PDI-BI-22 | R$_4$ = –CH$_3$ |
| PDI-BI-10 | R$_2$ = –NO$_2$ | PDI-BI-23 | R$_5$ = –CH$_3$ |
| PDI-BI-11 | R$_3$ = –NO$_2$ | PDI-BI-24 | R$_6$ = –CH$_3$ |
| PDI-BI-12 | R$_4$ = –NO$_2$ | PDI-BI-25 | R$_7$ = –CH$_3$ |
| PDI-BI-13 | R$_4$ = –CN R$_5$ = –CN | PDI-BI-26 | R$_8$ = –CH$_3$ |
2. Results and Discussion

2.1. Frontier Molecular Orbitals

The electronic and optical properties of molecules are related to the values of FMOs and \( E_g \). Thus, in order to gain insight into the influence of the optical and electronic properties, the distribution patterns of the FMOs for the designed molecules are studied, and the electronic density contours of the designed molecules in ground states are shown in Figure 2. The evaluations of HOMO and LUMO energies (\( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \)) for designed molecules are plotted in Figure 3 and listed in Table 2.
Figure 2. Cont.
Figure 2. Cont.
Figure 2. The distribution patterns of FMO for PDI-BI and its derivatives at the CAM-B3LYP/6-31G(d) level.

Table 2. The predicted $E_{\text{HOMO}}$, $E_{\text{LOMO}}$, $E_g$, $\lambda_{\text{abs-max}}$, $\lambda_{\text{abs-min}}$, and $R$ values of PDI-BI and its derivatives at the TD-B3LYP/6-31+G(d,p)//CAM-B3LYP/6-31G(d) Level.

|          | $E_{\text{HOMO}}$ | $E_{\text{LOMO}}$ | $E_g$  | $\lambda_{\text{abs-max}}$ | $\lambda_{\text{abs-min}}$ | $R$  |
|----------|-------------------|-------------------|--------|-----------------------------|-----------------------------|------|
| PDI-BI   | -6.88             | -2.44             | 4.44   | 570.40                      | 269.50                      | 300.90 |
| PDI-BI-1 | -7.14             | -2.74             | 4.40   | 581.24                      | 282.68                      | 298.56 |
| PDI-BI-2 | -7.14             | -2.75             | 4.39   | 580.46                      | 281.54                      | 298.92 |
| PDI-BI-3 | -7.16             | -2.75             | 4.41   | 572.27                      | 281.43                      | 290.84 |
| PDI-BI-4 | -7.15             | -2.72             | 4.43   | 569.68                      | 278.77                      | 290.91 |
| PDI-BI-5 | -7.13             | -2.74             | 4.39   | 588.55                      | 278.84                      | 309.91 |
| PDI-BI-6 | -7.12             | -2.76             | 4.36   | 595.24                      | 280.40                      | 314.84 |
| PDI-BI-7 | -7.14             | -2.76             | 4.38   | 590.79                      | 281.67                      | 309.12 |
| PDI-BI-8 | -7.14             | -2.75             | 4.39   | 592.00                      | 280.06                      | 311.94 |
| PDI-BI-9 | -7.17             | -2.74             | 4.43   | 574.08                      | 297.82                      | 276.26 |
| PDI-BI-10| -7.12             | -2.71             | 4.41   | 584.98                      | 300.92                      | 284.06 |
| PDI-BI-11| -7.19             | -2.70             | 4.49   | 557.27                      | 298.59                      | 258.68 |
| PDI-BI-12| -7.18             | -2.72             | 4.46   | 564.87                      | 298.98                      | 265.89 |
| PDI-BI-13| -7.40             | -3.00             | 4.40   | 584.00                      | 289.49                      | 294.51 |
| PDI-BI-14| -7.39             | -3.05             | 4.34   | 596.19                      | 291.72                      | 304.47 |
| PDI-BI-15| -7.40             | -3.00             | 4.40   | 585.19                      | 305.80                      | 279.39 |
| PDI-BI-16| -7.43             | -3.01             | 4.42   | 581.03                      | 307.99                      | 273.04 |
| PDI-BI-17| -7.45             | -3.02             | 4.43   | 582.91                      | 311.98                      | 270.93 |
| PDI-BI-18| -7.43             | -2.95             | 4.48   | 567.95                      | 343.18                      | 224.77 |
| PDI-BI-19| -6.86             | -2.39             | 4.47   | 564.68                      | 270.26                      | 294.42 |
| PDI-BI-20| -6.83             | -2.37             | 4.46   | 559.84                      | 271.85                      | 287.99 |
| PDI-BI-21| -6.84             | -2.37             | 4.47   | 557.89                      | 271.51                      | 286.38 |
| PDI-BI-22| -6.85             | -2.39             | 4.46   | 564.76                      | 269.00                      | 295.76 |
| PDI-BI-23| -6.85             | -2.39             | 4.46   | 567.34                      | 270.18                      | 297.16 |
| PDI-BI-24| -6.82             | -2.37             | 4.45   | 564.37                      | 272.33                      | 292.04 |
| PDI-BI-25| -6.82             | -2.37             | 4.45   | 562.73                      | 272.19                      | 290.54 |
| PDI-BI-26| -6.84             | -2.39             | 4.45   | 571.83                      | 270.17                      | 301.66 |
The di-CN, di-NO groups in different substituent positions can decrease the $E_{HOMO}$, $E_{LOMO}$, and $E_g$ values of PDI-BI, except that $–NO_2$ in 3 or 4-position increases the $E_g$ value of PDI-BI (PDI-BI-11 and PDI-BI-12), and the deviations of $E_{HOMO}$, $E_{LOMO}$, and $E_g$ values for molecules PDI-BI-1-12 are similar, respectively. For molecules PDI-BI-1-8, the decrease of the $E_{HOMO}$ value is the largest when the –CN group is in the 3-position of PDI-BI. The decrease of the $E_{LOMO}$ value is the largest when the –NO_2 group is in the 6 or 7-position of PDI-BI. The $E_g$ value is the smallest when the –CN group is in the 6-position of PDI-BI. For molecules PDI-BI-9-12, the decrease of the $E_{HOMO}$ value is the largest when the –NO_2 group is in the 3-position of PDI-BI. The decrease of the $E_{LOMO}$ value is the largest when the –NO_2 group is in the 1-position of PDI-BI. The $E_g$ value is the smallest when the –NO_2 group is in the 2-position of PDI-BI. The di-CN, di-NO_2, or –CN and –NO_2 groups in different substituent positions can decrease the $E_{HOMO}$, $E_{LOMO}$, and $E_g$ values of PDI-BI, except that the $–NO_2$ in 3 and 6-positions increase the $E_g$ values of PDI-BI (PDI-BI-18), and the decreased amounts of $E_{HOMO}$, $E_{LOMO}$, and $E_g$ values for molecules PDI-BI-13-18 are similar, respectively. The $E_{HOMO}$ value decrease is the largest when the –NO_2 groups are in the 4 and 5-positions of PDI-BI. The decrease of the $E_{LOMO}$ value is the largest when the –CN groups are in the 3 and 6-positions of the molecule PDI-BI. The $E_g$ value is the largest when the –NO_2 groups are in the 3 and 6-positions the molecule PDI-BI. For molecules PDI-BI-19-26, the –CH_3 group in different substituent position affects the $E_{HOMO}$, $E_{LOMO}$, and $E_g$ of PDI-BI slightly. These results reveal that the electron withdrawing substituents can decrease the $E_{HOMO}$, $E_{LOMO}$, and $E_g$ values of PDI-BI. The electron donating substituents affect $E_{HOMO}$, $E_{LOMO}$, and $E_g$ values of PDI-BI slightly.

The $E_{HOMO}$ and $E_{LOMO}$ values of FMO for molecules X1, X2, PDI-BI-1, PDI-BI-13, and PDI-BI-19 are plotted in Figure 4. The molecules PDI-BI-1, PDI-BI-13, and PDI-BI-19 are the representatives of the different kinds of substituent molecules, respectively. As shown in Figure 4, one can see that the LUMO energies of PDI-BI-13 are lower (0.32 and 0.30 eV) than those of X1 and X2, which indicates that PDI-BI-13 is suitable for the FMOs of X1 and X2, respectively. That is to say, molecules PDI-BI-14, PDI-BI-15, PDI-BI-16, and PDI-BI-17 are also suitable for the FMOs of X1 and X2, respectively. This reveals that the di-CN, di-NO_2, or –CN and –NO_2 groups substituents can decrease the FMOs of PDI-BI. Thus, proper substitutions can tune the FMOs of PDI-BI to be more suitable to X1 and X2. Moreover, we calculated the triplet energies of X1, X2, and PDI-BI-13. The calculated results show that the triplet energies are higher than the corresponding singlet energies for X1, X2, and PDI-BI-13.
respectively. This indicates that there may be no triplet loss when \(X_1, X_2,\) and \(\text{PDI-BI-13}\) are used as the candidates for OSCs devices [38–40].

**Figure 4.** Evaluation of the computed HOMO and LUMO energies for \(\text{PDI-BI}, \text{PDI-BI-1}, \text{PDI-BI-13},\) and \(\text{PDI-BI-19}\) as well as the HOMO and LUMO energies for \(X_1\) and \(X_2\) at the CAM-B3LYP6-31G(d)//PBE0/6-31G(d) level. The black line represents singlets, and the red line represents triplets.

### 2.2. Absorption Spectra

The longest and the shortest wavelengths of the absorption spectra (\(\lambda_{\text{max}}\) and \(\lambda_{\text{min}}\)) and adsorption region (\(R\)) of the designed molecules are listed in Table 2. The simulated adsorption spectra, plotted using GaussSum 1.0 [41], are shown in Figure 5. The first 20 excited states were considered.

**Figure 5.** Cont.
Figure 5. The calculated absorption spectra of PDI-BI and its derivatives (value of full width at half maximum is 3000 cm⁻¹).
As shown in Table 2 and Figure 5, the –CN group in different positions could increase the $\lambda_{\text{abs-max}}$ and $\lambda_{\text{abs-min}}$ values of PDI-BI, respectively, except the –CN group in 4-position could decrease the $\lambda_{\text{abs-max}}$ value of PDI-BI slightly. The –CN group in the 5, 6, 7, or 8-position can increase the $R$ values of PDI-BI, and the $R$ value increase is larger than the other positions when the –CN group in the 6-position. For –NO$_2$ substituent molecules, the $\lambda_{\text{abs-max}}$ values are, in increasing order, PDI-BI-11 < PDI-BI-12 < PDI-BI < PDI-BI-9 < PDI-BI-10, the $\lambda_{\text{abs-min}}$ values are, in decreasing order, PDI-BI-10 > PDI-BI-11 ≈ PDI-BI-12 > PDI-BI-9 > PDI-BI, and the $R$ values are in the order PDI-BI-11 < PDI-BI-12 < PDI-BI-9 < PDI-BI-10 < PDI-BI. This shows that the –NO$_2$ group in 2-position could produce a larger increase of $\lambda_{\text{abs-max}}$ and $\lambda_{\text{abs-min}}$ values than the other positions for PDI-BI, and the –NO$_2$ group in 3-position could produce a larger decrease of the $R$ value than the other positions for PDI-BI. For di-substituent molecules, the substituent groups could increase the $\lambda_{\text{abs-max}}$ and $\lambda_{\text{abs-min}}$ values of PDI-BI, respectively, except the di-NO$_2$ groups in 3 and 6-position decrease the $\lambda_{\text{abs-max}}$ value of PDI-BI, obviously. The di-substituents could decrease the $R$ values of PDI-BI, respectively, except the di-CN groups in 3 and 6-position increase the $R$ value of PDI-BI significantly. The –CH$_3$ groups in different positions affect the $\lambda_{\text{abs-max}}, \lambda_{\text{abs-min}},$ and $R$ values of PDI-BI slightly. These results reveal that the mono-pull group can increase the $\lambda_{\text{abs-max}}, \lambda_{\text{abs-min}},$ and $R$ values of PDI-BI, and the push group affects the $\lambda_{\text{abs-max}}, \lambda_{\text{abs-min}},$ and $R$ values of PDI-BI slightly. Among these molecules, PDI-BI-14 has the largest $\lambda_{\text{abs-max}}$ value and PDI-BI-6 has the largest $R$ value, which indicates that it could be a good candidate for the solar cell acceptor.

2.3. Reorganization Energy

The charge transport property of material is important to design the acceptor for a solar cell device, and the reorganization energy plays a role in charge transport and charge separation. It is well-known that the lower the $\lambda$ values, the better the charge transport property. Thus, we calculated the $\lambda_e$ and $\lambda_h$ values of PDI-BI and its derivatives. The calculated results are listed in Table 3.

|          | $\lambda_e$ | $\lambda_h$ |
|----------|-------------|-------------|
| PDI-BI   | 0.298       | 0.210       |
| PDI-BI-1 | 0.278       | 0.222       |
| PDI-BI-2 | 0.277       | 0.215       |
| PDI-BI-3 | 0.278       | 0.221       |
| PDI-BI-4 | 0.272       | 0.222       |
| PDI-BI-5 | 0.282       | 0.226       |
| PDI-BI-6 | 0.285       | 0.224       |
| PDI-BI-7 | 0.286       | 0.230       |
| PDI-BI-8 | 0.278       | 0.232       |
| PDI-BI-9 | 0.296       | 0.225       |
| PDI-BI-10| 0.360       | 0.236       |
| PDI-BI-11| 0.290       | 0.222       |
| PDI-BI-12| 0.320       | 0.234       |
| PDI-BI-13| 0.265       | 0.240       |
| PDI-BI-14| 0.266       | 0.240       |
| PDI-BI-15| 0.343       | 0.249       |
| PDI-BI-16| 0.279       | 0.245       |
| PDI-BI-17| 0.312       | 0.264       |
| PDI-BI-18| 0.476       | 0.250       |
| PDI-BI-19| 0.297       | 0.201       |
| PDI-BI-20| 0.296       | 0.201       |
| PDI-BI-21| 0.296       | 0.195       |
| PDI-BI-22| 0.298       | 0.200       |
| PDI-BI-23| 0.299       | 0.205       |
| PDI-BI-24| 0.298       | 0.206       |
| PDI-BI-25| 0.298       | 0.200       |
| PDI-BI-26| 0.300       | 0.213       |
As shown in Table 3, the –CN group in different positions can decrease the $\lambda_e$ values and increase the $\lambda_h$ values of PDI-BI. This implies that the –CN substituent can improve the electron transport property of PDI-BI. The –CN substituent in the 4-position (PDI-BI-4) owns the largest electron transfer rate. For the –NO$_2$ substituent molecules, the substituent groups can increase the $\lambda_e$ and $\lambda_h$ values of PDI-BI, except the –NO$_2$ group in 1 or 3 position, which can decrease the $\lambda_e$ values of PDI-BI slightly. For the di-substituent molecules, the substituent groups can increase the $\lambda_e$ and $\lambda_h$ values of PDI-BI, except the di-CN groups (PDI-BI-13 and PDI-BI-14) and –CN in 4-position and –NO$_2$ in 5-position (PDI-BI-16) substituents, which can decrease the $\lambda_e$ values of PDI-BI. This indicates that the electron transfer rates of PDI-BI-13, PDI-BI-14, and PDI-BI-16 are higher than that of PDI-BI. For –CH$_3$ substituent molecules, the –CH$_3$ group in different positions affects the $\lambda_e$ values of PDI-BI slightly and decreases the $\lambda_h$ values of PDI-BI, except the –CH$_3$ group in 8-position, which can increase the the $\lambda_h$ values of PDI-BI. This shows that the –CH$_3$ substituent can improve the hole transport property of PDI-BI. The $\lambda_e$ values of PDI-BI-4, PDI-BI-13, and PDI-BI-14 are smaller than that of the typical electron transport material tris(8-hydroxyquinolinato) aluminium(III) (Alq3) ($\lambda_e = 0.276$ eV) [42], indicating that their electron transfer rates are higher than that of Alq3. The $\lambda_h$ values of molecules PDI-BI-1-26 are smaller than that of N,N' -diphenyl-N,N' -bis(3-methylphenyl)-(1,10-biphenyl)-4,4'-diamine (TPD) ($\lambda_h = 0.290$ eV), which is a typical hole transport material [43]. This implies that their hole transfer rates are higher than that of TPD. Among these molecules, PDI-BI-13 has the best electron transport property, and PDI-BI-21 has the best hole transport property.

3. Materials and Methods

**Computational Methods**

All the calculations were performed with the Gaussian 09 software [44]. Our previous work [31] suggested that the DFT method CAM-B3LYP with the 6-31G(d,p) basis set was reliable for optimization of PDI and its derivatives, and the TD-B3LYP/6-31+G(d,p) method was reasonable for optical property simulation. Hence, the CAM-B3LYP/6-31G(d,p) method was employed to optimize all the geometry including neutral, cation, and anion PDI-BI-1-26 molecules. The absorption spectra of PDI-BI-1-26 molecules were predicted by the B3LYP/6-31+G(d,p) method. The PBE1PBE/6-31G(d) method was used to optimize the geometry of molecules X1 and X2 [32], and the HOMO and LUMO energies of molecules X1 and X2 were calculated at the CAM-B3LYP/6-31G(d,p) level on the basis of the single point energy. The B3LYP/6-31G(d,p) functional was successful in calculating the charge transport parameters [45]. Thus, we calculated the single point energy at the B3LYP/6-31G(d,p) level. The necessary parameters, such as single point energies of neutral, cation, and anion molecules in the ground state (S0), were recomputed for calculating the electronic properties of the molecules. The reorganization energy (λ) was predicted on the basis of the single point energy at the B3LYP/6-31G(d,p) level optimised neutral, cationic, and anionic geometries. Herein, the environmental relaxation and changes were ignored, and the reorganization energy of the isolated active organic \( \pi \) conjugated systems was the internal reorganization energy. As a result, Equations (1) and (2) can be used for calculating the values of electron reorganization energy (\( \lambda_e \)) and hole reorganisation energy (\( \lambda_h \)) [46]:

\[
\lambda_e = [E_0^+ - E_0] + [E^0 - E_0]
\]

\[
\lambda_h = [E_0^- - E_0] + [E^0 - E_0]
\]

$E_0^+$ and $E_0^-$ are the cation and anion single point energies obtained by the optimized structure of the neutral molecule. $E_0^+$ and $E_0^-$ are the cation and anion single point energies calculated on the basis of the optimized structures of cation and anion molecules. $E_0^0$ and $E_0^-$ are the neutral single point energies obtained via the optimized structures of cation and anion molecules. $E_0$ is the neutral single point energy calculated by the optimized structure of the neutral molecule at S0.
4. Conclusions

In the present work, we report a theoretical investigation predicting the substitution effects on optical and electronic properties for PDI-BI. The calculated results show that the substituents slightly affect the distribution patterns of FMOs for PDI-BI. The –CN and –NO$_2$ groups in different substituent positions can decrease the $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, and $E_g$ of PDI-BI. The –CH$_3$ group in different substituent positions affects the $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, and $E_g$ of PDI-BI slightly. The –CN group in different positions can decrease the $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, and $E_g$ of PDI-BI, respectively, and the –CN group in the 5, 6, 7, or 8-position can increase the $R$ values of PDI-BI. The –NO$_2$ group in 2-position could produce a larger increase in $\lambda_{\text{abs-max}}$ and $\lambda_{\text{abs-min}}$ values, and the –NO$_2$ group in 3-position could produce a larger decrease of the $R$ value of PDI-BI. The –CH$_3$ groups in different positions slightly affect the $\lambda_{\text{abs-max}}$, $\lambda_{\text{abs-min}}$, and $R$ values of PDI-BI. Among these molecules, PDI-BI-14 has the largest $\lambda_{\text{abs-max}}$ value and PDI-BI-6 has the largest $R$ value. The –CN group in different positions can decrease the $\lambda_e$ values and increase the $\lambda_h$ values of PDI-BI. In the –NO$_2$ substituent molecules, the substituent groups can increase the $\lambda_e$ and $\lambda_h$ values of PDI-BI. The –CH$_3$ group in different positions slightly affects the $\lambda_e$ values, and decreases the $\lambda_h$ values of PDI-BI. PDI-BI-13 and PDI-BI-21 have the best electron and hole transport properties, respectively. On the basis of these results, we suggest that PDI-BI-13, PDI-BI-14, PDI-BI-15, PDI-BI-16, and PDI-BI-17 are suitable acceptors for X1 and X2. This study should be helpful in further theoretical investigations on such systems and also in the experimental study of solar cell acceptor materials.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

| Abbreviation | Definition |
|--------------|------------|
| PDI | Perylene diimide |
| OSCs | Organic solar cells |
| PCEs | Power conversion efficiencies |
| FMOs | Frontier molecular orbital energies |
| HOMO | Highest occupied molecular orbital |
| LUMO | Lowest unoccupied molecular orbital |
| DFT | Density function theory |

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