

# DFT studies of perylenetetracarboxylic dianhydride and perylene diimide derivatives

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## ABSTRACT

Perylenetetracarboxylic dianhydride (PTCDA) and perylene diimide (PDI) have been widely used as photosensitizers in many applications. Photophysical properties are key factors for efficient application of these materials. Furthermore, many functionalization of these materials come from the motivation of tuning their solubility, which may affect the photophysical properties of the resulting materials. As such, it is imperative to study the electronic and photophysical properties of PTCDA and PDI derivatives. In this work, we report DFT studies of 36 molecules consisting 18 PTCDA molecules and 18 PDI derivatives with the same set of functionalization at the bay positions. DFT results show that the impact of functionalization is similar in HOMO and LUMO energies to both PTCDA and PDI derivatives. Analysis of electronic results indicates extension of electron delocalization along the bay positions 1 and 7 is important in altering absorption wavelengths or HOMO-LUMO gaps.

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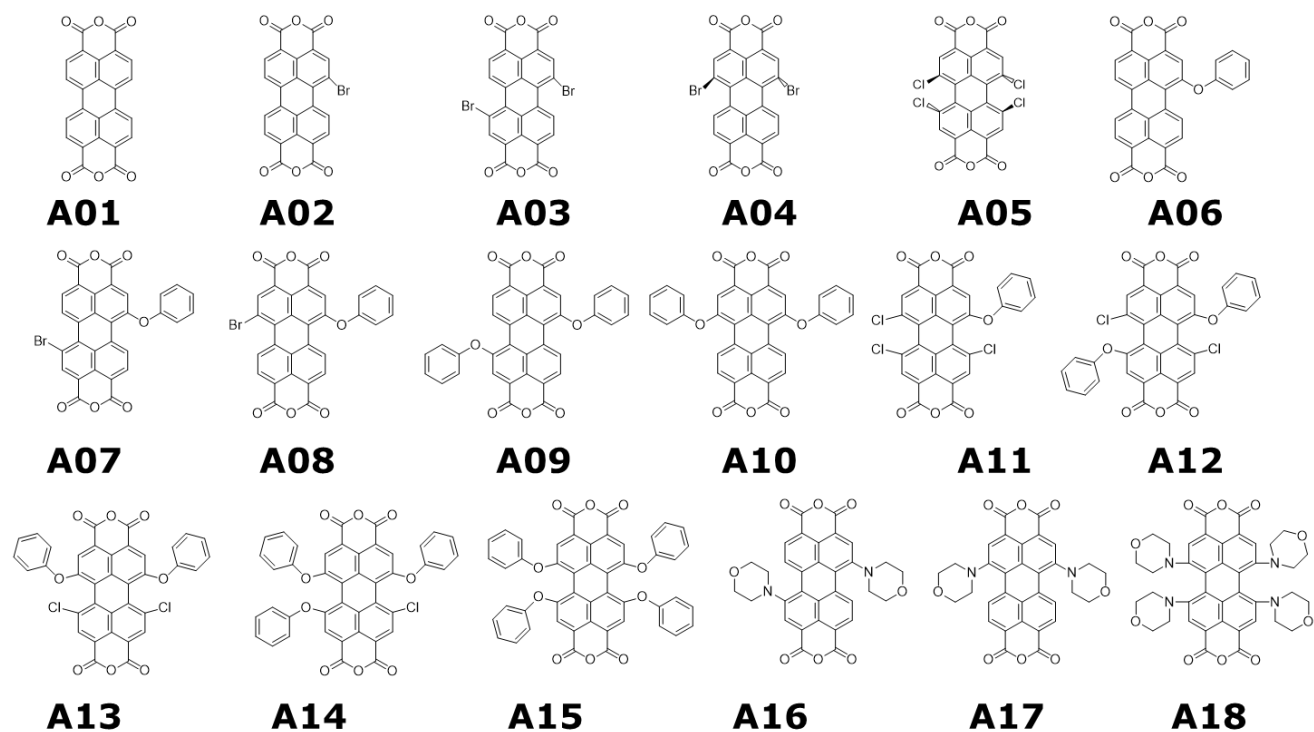
## 1. Introduction

Perylene derivatives have been widely used in many applications, such as in nonlinear optical microcavities,<sup>1</sup> organic electronics,<sup>2</sup> and in luminescence,<sup>3,4</sup> which may have potential to play important roles in luminescence sensors.<sup>5-11</sup> Perylene derivatives were also studied as electron acceptors<sup>12-15</sup> in the solar cell applications,<sup>16-31</sup> in batteries,<sup>32,33</sup> and in supercapacitors.<sup>34</sup> For instance, used as electron transporting materials, tetrahydroxy-perylene bismide was found to be effective in non-fullerene organic solar cells.<sup>15</sup> Recently, using Perylene derivatives as electron transport materials, performance can achieve 10% in scalable organic photovoltaics.<sup>31</sup> In the search for panchromatic materials for solar cell applications, perylene derivatives were covalently linked to porphyrin to form a dyad to meet the requirement.<sup>35-37</sup> They have also been found in applications in the construction of memory device,<sup>38</sup> as the photodynamic therapy agent,<sup>39,40</sup> in imaging,<sup>41</sup> and as building blocks of the D-A type molecules<sup>42-47</sup> to generate polarization like inorganic materials.<sup>48</sup> One of the most recent active area of research related to perylene derivatives is in singlet fission<sup>49-52</sup> due to their unique properties related to the triplet states.<sup>53-62</sup> Not surprisingly, many studies were carried out on the photophysical properties<sup>63-85</sup> and stabilities<sup>86-88</sup> of these molecules.

Different functionalization of perylene derivatives allows to fine tune excitons of the materials.<sup>89,90</sup> Relatively facile functionalization and matured synthesis of perylene derivatives<sup>2</sup> makes the design of such materials appealing without heavily involving studies of (reaction) dynamics<sup>91,92</sup> and/or catalysis.<sup>93-101</sup> Many applications of perylene derivatives involve formation of aggregates.<sup>102-133</sup> In an excellent review, Wurthner, et al,<sup>133</sup> has summarized the progress of various aggregates that were formed through  $\pi$ -stacking, hydrogen-bonding, metallosupramolecular or ionic interactions. Successful assembly of the perylene derivatives are

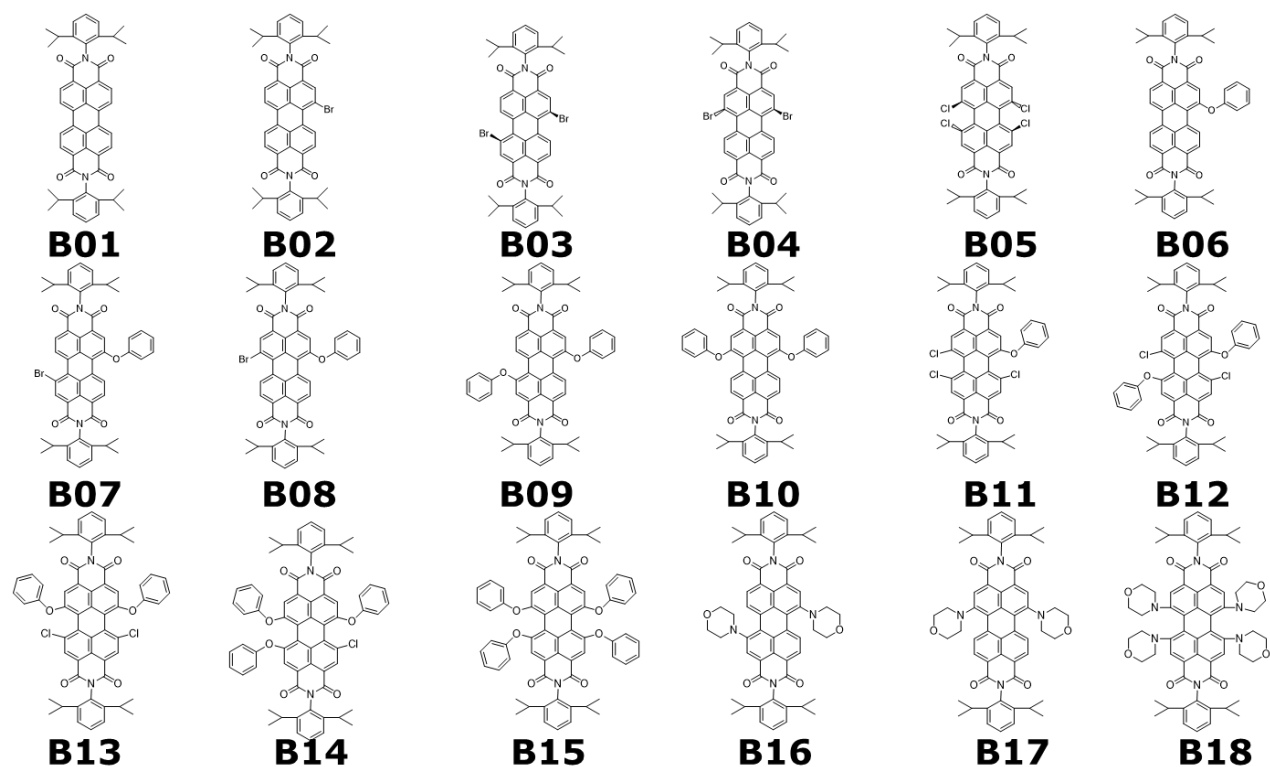
challenging due to the solubility issue.<sup>134</sup> Therefore, functionalization to tune the solubility of perylene derivatives becomes a very popular strategy. For instance, addition of propylthioether side groups was found to make the molecule more soluble.<sup>134</sup> However, such functionalization can also affect the electronic and optical properties of the materials. Furthermore, functionalization of perylene at single molecule level can also increase the performance in the applications based on single dye molecules.

Therefore, it is important to systematically study the electronic and optical properties of perylene derivatives to have a better understanding of the correlation between functionalization and the electronic properties. In particular, the effect of bay positions on the energy levels of frontier orbitals is crucial for the device performance and is worthy exploring. Towards this goal, we studied perylenetetracarboxylic dianhydride (PTCDA) and its seventeen derivatives as shown in Fig.1 using DFT calculations. We used four functional groups: Cl, Br, phenoxy, and morpholino (oligomer), in the current study and placed them as various bay positions. The first two, Cl and Br, are two electron withdrawing groups and the latter two are electron donating groups. Previous functionalization studies have shown that different groups have different impact on electron delocalization of the final molecules with respect to the parent molecule.<sup>89</sup>



**Figure 1.** Perylenetetracarboxylic dianhydride (PTCDA) and seventeen PTCDA derivatives.

We also studied eighteen derivatives of perylene diimide (PDI), which are shown in Fig. 2. PDI derivatives are often also denoted as PBI. Similar to PTCDA molecules, we used the same four types of functional groups and in the similar positions and the number of functional groups. This allows us to make direction comparisons on whether the same functionalization has similar effect in the change of electronic properties, namely the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). DFT calculations on these 36 molecules were performed to investigate the effect of functionalization on the electronic and optical properties and comparisons were made based on the DFT results to understand the impact of the position of functionalization and property of functional group, such as electronic withdrawing or donating ability on the electronic and optical properties.



**Figure 2.** Eighteen derivatives of perylene diimide (PDI)

## 2. Computational details

DFT calculations were performed for a total of 36 molecules, which consist of 18 PTCDA derivatives shown in Fig. 1 and 18 PDI derivatives depicted in Fig. 2 with a combination of different number and types of functional groups. The four functional groups investigated in this work are Cl, Br, phenoxy, and morpholino (oligomer). The same type of functional groups were used for both molecules to explore the effect of functional groups on the electronic properties, especially on the HOMO and LUMO energies. All calculations were performed using the three-parameter functional of Becke and correlation functional of Lee, Yang and Parr (B3LYP).<sup>135,136</sup> with the 6-31G+(d,p) basis set. Fully geometry optimizations were carried out without any symmetry constraints. To confirm the obtained structures are indeed stable, frequency calculations

at the same level of theory were performed and the results confirmed that no imaginary frequency existed. All geometry optimizations were obtained with the default criteria, namely the SCF, gradient, and energy convergence of  $10^{-8}$ ,  $10^{-4}$ , and  $10^{-5}$  a.u., respectively.

The absorption spectra were obtained for seven PDI derivatives using TDDFT calculations with the same functional and basis set as the DFT calculations. All the calculations were performed using the Gaussian 09 package.<sup>137</sup> The same methodology has been used in our previous studies of organic small molecules.<sup>36,138-140</sup>

### 3. Results

Thirty six PTCDA and PDI derivatives were studied in this work using DFT calculations. Synthesis of the polycyclic aromatic hydrocarbons was often carried out without too much challenges.<sup>2,141,142</sup> In this work, we functionalized the PTCDA and PDI parent molecules, **A01** and **B01**, with various substitutions at the 1, 6, 7, and 12 positions. DFT results are discussed in sections A and B below.

#### A) Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and its derivatives

The energies of HOMO, LUMO, and HOMO-LUMO gap of PTCDA and seventeen derivatives are summarized in Table 1. When one Br is functionalized at the bay position (**A02**), the HOMO and LUMO energies are lowered as shown in Table 1 but the HOMO-LUMO energy gap remains the same. When the second Br is introduced at position 6 (**A03**), the HOMO, LUMO energies were further decreased while the HOMO-LUMO gap remains the same. Interestingly, no changes in the HOMO, LUMO, HOMO-LUMO gap were observed when the second Br is introduced to the position 7 (**A04**). When 4 Cl are introduced to the bay positions to form **A05**, the

HOMO energy lowers slightly more than that of LUMO, resulting slight increase in HOMO-LUMO gap.

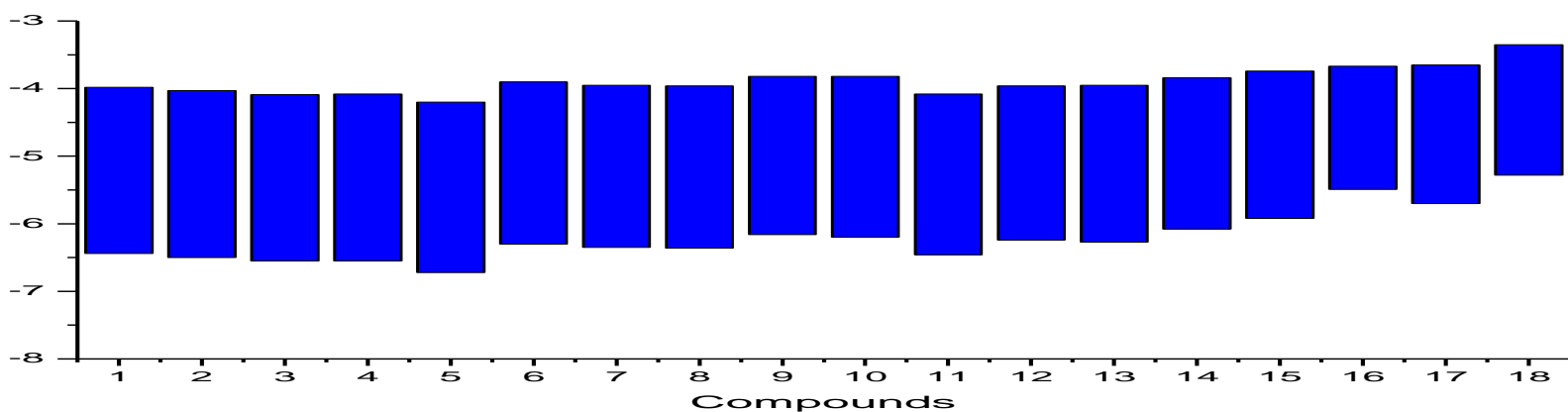
**Table 1.** The HOMO, LUMO, and HOMO-LUMO energies of eighteen PTCDAs

	HOMO (eV)	LUMO (eV)	HOMO-LUMO Gap (eV)		HOMO (eV)	LUMO (eV)	HOMO-LUMO Gap(eV)
<b>A01</b>	-6.44	-3.98	2.46	<b>A10</b>	-6.20	-3.82	2.38
<b>A02</b>	-6.50	-4.03	2.47	<b>A11</b>	-6.46	-4.08	2.38
<b>A03</b>	-6.55	-4.09	2.46	<b>A12</b>	-6.24	-3.96	2.28
<b>A04</b>	-6.55	-4.08	2.47	<b>A13</b>	-6.27	-3.95	2.32
<b>A05</b>	-6.72	-4.20	2.52	<b>A14</b>	-6.08	-3.84	2.24
<b>A06</b>	-6.30	-3.90	2.40	<b>A15</b>	-5.92	-3.74	2.18
<b>A07</b>	-6.35	-3.95	2.40	<b>A16</b>	-5.49	-3.67	1.82
<b>A08</b>	-6.36	-3.96	2.40	<b>A17</b>	-5.70	-3.65	2.05
<b>A09</b>	-6.16	-3.82	2.34	<b>A18</b>	-5.28	-3.35	1.93

When a phenoxy is added to the bay position (**A06**), the energies of HOMO and LUMO increases with HOMO increasing slightly more, which results in the reduction of HOMO-LUMO gap. Introduction of Br to position 6 to **A06**, the HOMO and LUMO energies are lowered slightly (**A07**) and the HOMO-LUMO gap remains the same. However, when Br is introduced to position 8 to form **A08**, the HOMO and LUMO energies further increase with respect to **A06** and the HOMO-LUMO gap remains nearly the same. On the other hand, when the second functional group is phenoxy to form **A09** or **A10**, the HOMO and LUMO energy levels are further increased. Similar to the Br cases, the second phenoxy is introduced at position 6 (**A09**), the HOMO, LUMO energies were further decreased while the HOMO-LUMO gap remains the same. Interestingly, no changes in the HOMO, LUMO, HOMO-LUMO gap were observed when it is introduced to the position 7

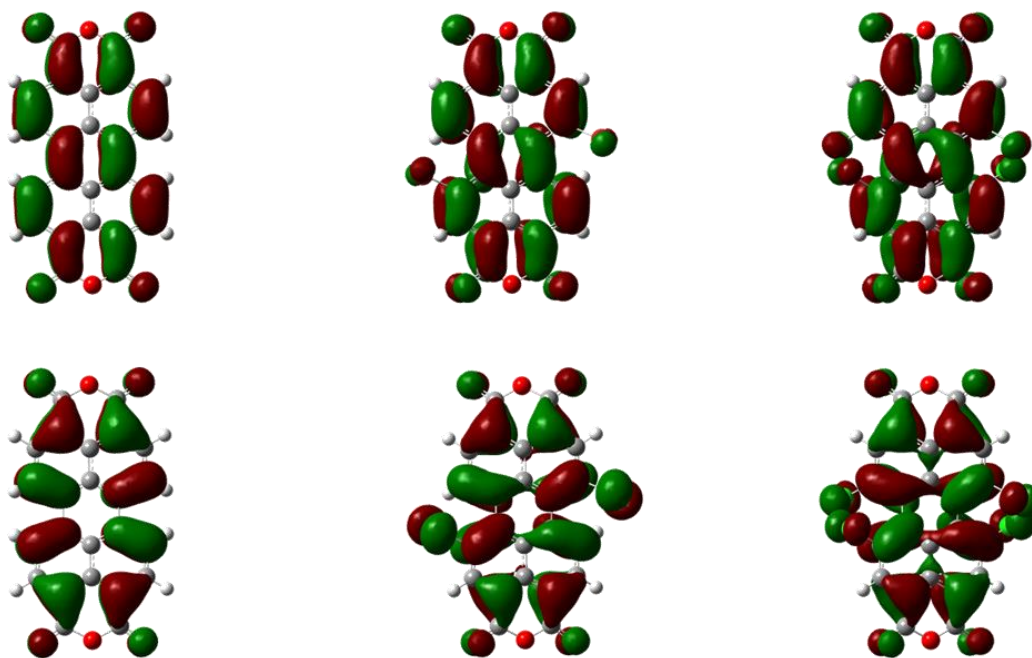
(A10). Various combination of phenoxy and Cl to form A11-A15, HOMO-LUMO gap are generally decreased. The most drastic HOMO-LUMO gap reduction comes from the functionalization using morpholino oligomers (A16-A18). Different from Br and phenoxy cases, when the second functional group is introduced, the position where it is introduced matters. Introduction in position 7 (A16) has a higher HOMO energy level and smaller HOMO-LUMO gap than A17 where the second functional group is introduced at position 6.

A comprehensive comparison of the electronic properties of the 18 molecules can be seen in Fig. 3. It is interesting to note the effect of functionalization at different bay positions, i.e. 1,6 vs 1, 7. There are five pairs designed for comparison: A03 and A04, A07 and A08, A09 and A10, A12 and A13, and A16 and A17. There are no apparent differences in the first three pairs when the substitutions taking place at 1,6 or 1,7. However, substitutions at 1,7 positions reduce the HOMO-LUMO gap more than the substitutions at 1,6 positions. To explain the decreasing in HOMO and LUMO level from A01 to A03 and further to A05, we plotted the HOMO and LUMO contours in Fig.4. The delocalization of electrons due to the introduction of the functional groups caused lowering the energies of these frontier orbitals.



**Figure 3.** HOMO and LUMO energies of eighteen PTCDA molecules





**Figure 4.** HOMO and LUMO contours of three PTCDA molecules: **A01** (left), **A03** (middle), and **A05** (right).

## **B) Perylene-3,4,9,10-tetracarboxylic diimide (PDI) derivatives**

The DFT results of the HOMO, LUMO, and HOMO-LUMO gap of 18 PDIs are summarized in Table 2. The HOMO and LUMO energy levels of **B01** is increased by about 0.3 eV compared to **A01**, though HOMO-LUMO gap remains nearly unchanged. The trend observed after functionalization is very similar to those of PTCDAs. When one Br is functionalized at the bay position (**B02**), the HOMO and LUMO energies are lowered as shown in Table 2 but the HOMO-LUMO energy gap remains the same. When the second Br is introduced at position 6 (**B03**), the HOMO, LUMO energies were further decreased while the HOMO-LUMO gap remains the same. Interestingly, no changes in the HOMO, LUMO, HOMO-LUMO gap were observed when the second Br is introduced to the position 7 (**B04**).

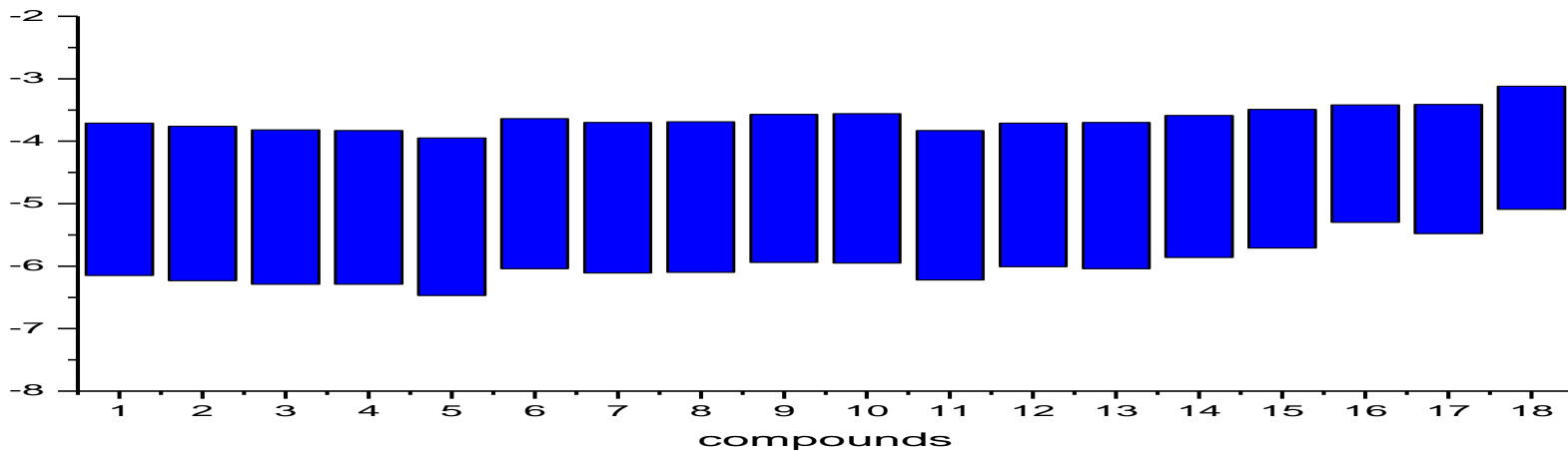
**Table 2.** The HOMO, LUMO, and HOMO-LUMO energies of eighteen PDIs

	HOMO (eV)	LUMO (eV)	HOMO-LUMO Gap (eV)		HOMO (eV)	LUMO (eV)	HOMO-LUMO Gap (eV)
<b>B01</b>	-6.15	-3.71	2.44	<b>B10</b>	-5.95	-3.56	2.39
<b>B02</b>	-6.23	-3.76	2.47	<b>B11</b>	-6.22	-3.83	2.39
<b>B03</b>	-6.29	-3.82	2.47	<b>B12</b>	-6.01	-3.71	2.30
<b>B04</b>	-6.29	-3.83	2.46	<b>B13</b>	-6.04	-3.70	2.34
<b>B05</b>	-6.47	-3.95	2.52	<b>B14</b>	-5.86	-3.59	2.27
<b>B06</b>	-6.04	-3.64	2.40	<b>B15</b>	-5.71	-3.49	2.22
<b>B07</b>	-6.11	-3.70	2.41	<b>B16</b>	-5.30	-3.42	1.88
<b>B08</b>	-6.10	-3.69	2.41	<b>B17</b>	-5.48	-3.41	2.07
<b>B09</b>	-5.94	-3.57	2.37	<b>B18</b>	-5.09	-3.12	1.97

Similar to the PTCDA cases, when 4 Cl are introduced to the bay positions to form **B05**, the HOMO energy lowers slightly more than that of LUMO, resulting slight increase in HOMO-LUMO gap. When a phenoxy is added to the bay position (**B06**), the energies of HOMO and LUMO increases with HOMO increasing slightly more, which results in the reduction of HOMO-LUMO gap. Introduction of Br to position 6 to **B06**, the HOMO and LUMO energies are lowered slightly (**B07**) and the HOMO-LUMO gap remains the same. However, when Br is introduced to position 8 to form **B08**, the HOMO and LUMO energies further increase with respect to **B06** and the HOMO-LUMO gap remains nearly the same. On the other hand, when the second functional group is phenoxy to form **B09** or **B10**, the HOMO and LUMO energy levels are further increased.

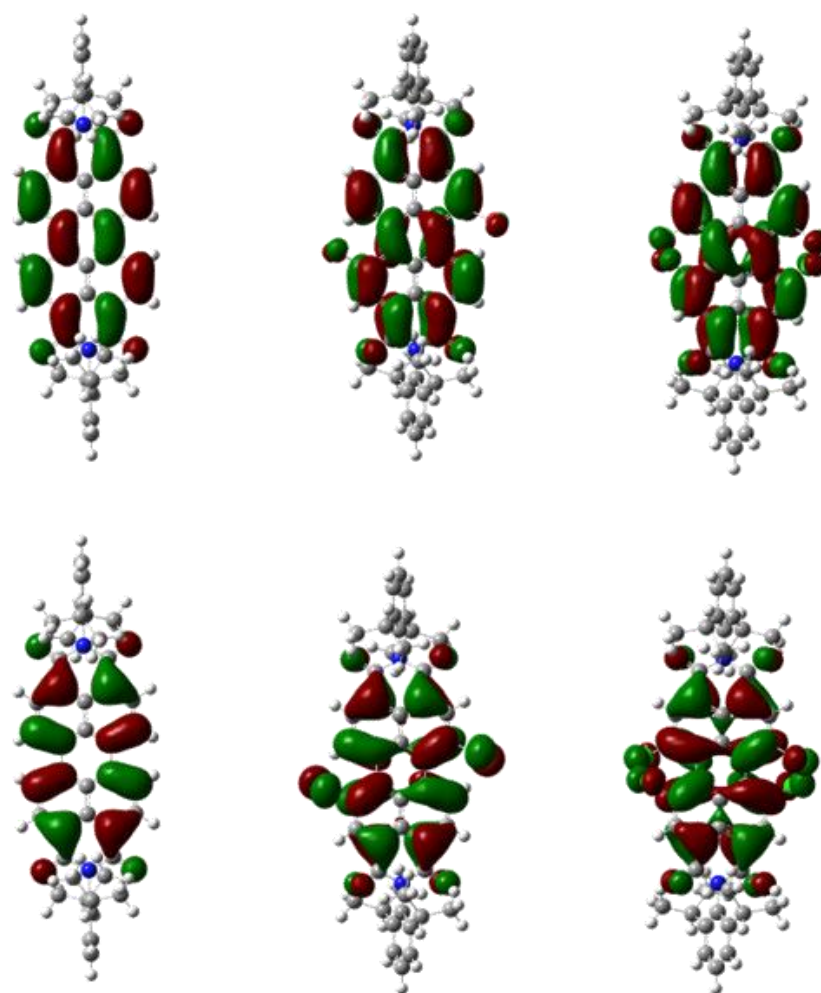
Finally, when various combination of phenoxy and Cl to form **B11-B15**, the HOMO-LUMO gap are decreased just as the PTCDA molecules. The most drastic HOMO-LUMO gap reduction

comes from the functionalization using morpholino oligomers (**B16-B18**). A comprehensive comparison of the electronic properties of the 18 molecules can be seen in Fig. 5. It is shown clearly that B16 has the smallest HOMO-LUMO gap. Just like the PTCDA series, the effect of functionalization at different bay positions, i.e. 1,6 vs 1, 7, on the electronic properties is functional group dependent. Among the five pairs: **B03** and **B04**, **B07** and **B08**, **B09** and **B10**, **B12** and **B13**, and **B16** and **B17**, there are no apparent differences in the first three pairs when the substitutions taking place at 1,6 or 1,7. However, substitutions at 1, 7 positions (**B16**) reduce the HOMO-LUMO gap more than the substitutions at 1, 6 positions (**B17**).

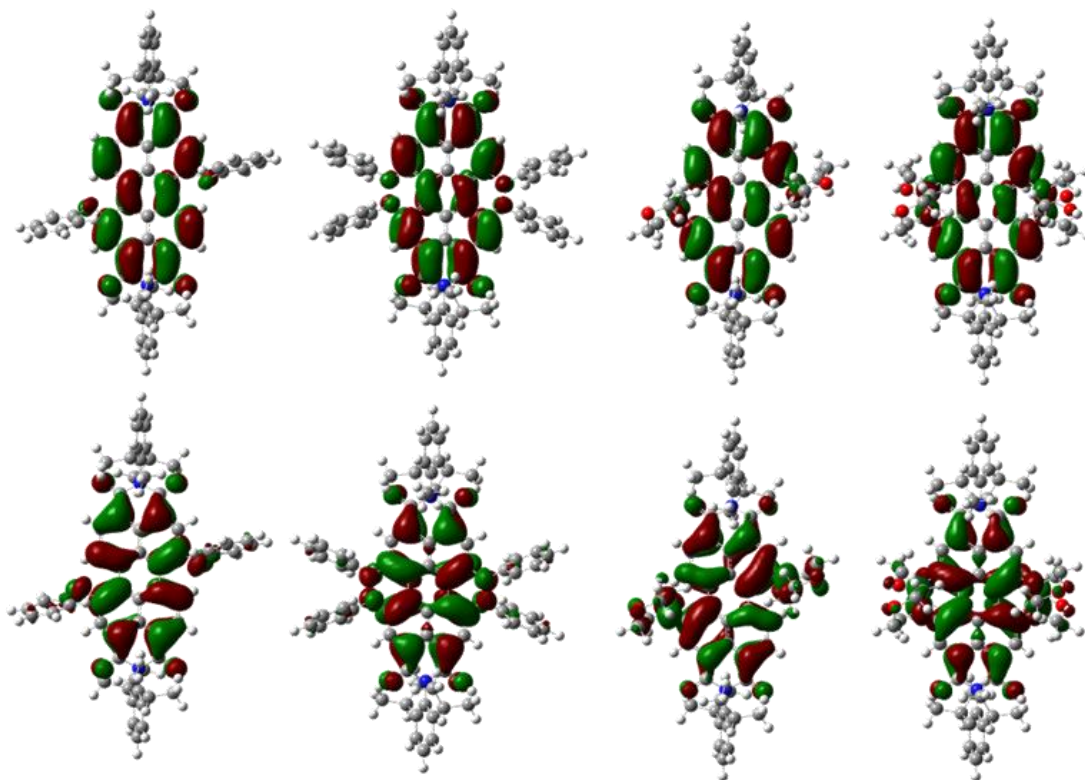


**Figure 5.** HOMO and LUMO energies of eighteen PDI derivatives.

To explain the decreasing in HOMO and LUMO level from **B01** to **B03** and further to **B05**, we plotted the HOMO and LUMO contours of these molecules in Fig. 6. The delocalization of electrons due to the introduction of the functional groups is the cause to lowering the energies of these frontier orbitals. The HOMO, LUMO contour plots of **B09**, **B15**, **B16**, and **B18** are shown in Fig. 7. In the case of the electron donating group functionalization, the visible delocalization of electrons leads to the increase of the HOMO energy levels.



**Figure 6.** HOMO and LUMO contours of three PDI molecules: **B01**(left), **B03**(middle), and **B05**(right).

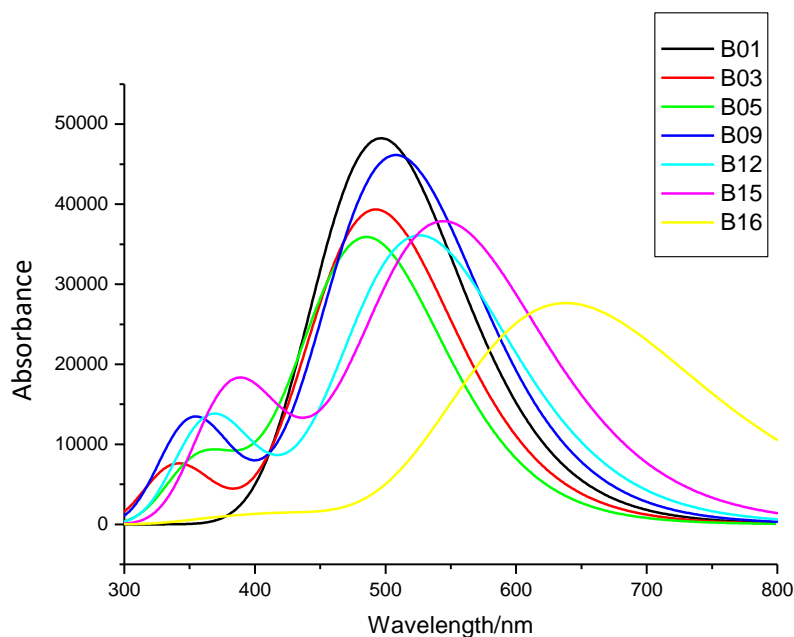


**Figure 7.** HOMO and LUMO contours of four PDI molecules (from left to right): **B09**, **B15**, **B16**, and **B18**.

To understand the optical properties of the PDI derivatives, we performed TDDFT calculations on seven molecules, **B01**, **B03**, **B05**, **B09**, **B12**, **B15**, and **B16**. The choice of these PDIs among 36 molecules being studied here is mainly due to their facile synthesis, which makes future comparisons with the experimental results very feasible. The calculated UV-Vis spectra are depicted in Fig. 8. As we anticipated, the absorption wavelength increases with the decrease of the HOMO-LUMO gap. When electron withdrawing groups are functionalized to **B01** at the bay positions to form **B3** and **B05**, blue shifts are observed. On the other hand, when electron donating groups are at the bay positions, **B9**, **B12**, **B15**, and **B16**, red shifts are shown with respect to the parent molecule **B01**. It is interesting to note that when the number of functionalization increases,

such as from 2 in **B12** to 4 in **B15**, the amount of red shifts increases. The longest red shift among the seven molecules is **B16** with more than 100 nm (Fig. 8).

Furthermore, a shorter wavelength absorption ( $\sim 350$  nm), which seems to be a splitting from the longer wavelength absorption, appears in five out of six molecules after functionalization of **B01**. The most red-shifted **B16** does not show the splitting in the UV-Vis spectrum as shown in Fig. 8. The absorption intensity is decreased after functionalization with the most significant reduction in **B16**. While comparisons between DFT results and experiments may show differences in absolute absorption wavelength, we expect the relative shifts or at least the directions of the shifts after functionalization predicted by DFT calculations will be accurate. Future experimental work and comparisons with the DFT results are ongoing.



**Figure 8.** UV-Vis spectra of seven PDI molecules.

#### 4. Conclusions

Understanding and tuning electronic and optical properties of PTCDA and PDI molecules are important to many electro-optical applications. As such, DFT calculations were performed to study the electronic and optical properties of 36 PTCDA and PDI derivatives. Among the 36 molecules, there are 18 PTCDA molecules and 18 PDI derivatives. The same set of functional groups at the bay positions was used for both types of molecules. In general, HOMO and LUMO energies of PTCDAs are about 0.3 eV lower than those of PDIs with the same functionality. Furthermore, DFT results show that functionalization has very similar effect on the HOMO and LUMO energies to both PTCDA and PDI derivatives. Analysis of electronic results demonstrates that extension of electron delocalization along the 1 and 7 bay positions is responsible to shifting absorption wavelength or HOMO-LUMO gap with respect to the parent PTCDA (**A01**) and PDI (**B01**) molecules. Molecule **B16** has the longest absorption wavelength among the seven molecules studied here with more than 100 nm red-shifted compared to the parent molecule **B01**.

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