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## The substituent effects of naphthalene diimide as acceptor for organic solar cells: A theoretical study

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## ABSTRACT

The substituent effects of naphthalene diimide (**NDI**) have been investigated by employing the CAM-B3LYP/6-31G(d) and TD-B3LYP/6-31+G(d,p) methods in order to design proper acceptor of solar cell with excellent performances, for example, the suitable frontier molecular orbital (FMO) energies to match those of oligo(thienylenevinylene) derivatives. The simulated results show that the different substituents significantly affect the distribution patterns of FMOs for **NDI**. The pull substituents could decrease the FMO energies and energy gap of **NDI**. Introducing the proper substituents to molecule **NDI** could make their FMOs being suitable for oligo(thienylenevinylene) derivatives. The different substituents significantly affect the absorption spectra of **NDI**. The electron withdrawing group and/or electron donating group substituents can improve the electron transfer properties of **NDI**.

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## 1. Introduction

Since the organic solar cells (OSCs) appeared, owing to its lightweight, mechanical flexibility, potential of low cost fabrication, and rapid energy payback time [1], it received worldwide attention in both academia and industry [2]. Now the OSCs mainly utilize fullerene and its derivatives, such as [6,6]-phenyl-C<sub>61</sub>(or C<sub>71</sub>)-butyric acid methyl ester (PC<sub>61</sub>BM or PC<sub>71</sub>BM), as the electron acceptor materials. Fullerene and its derivatives are good electron acceptors and electron transporting materials. Nevertheless, it is difficult to modify the backbone of fullerene and its derivatives chemically. Thus, the absorption region and the frontier molecular orbit (FMO) energy levels cannot be readily tuned [3]. Recently, more and more researchers pay attention to the organic small molecules on the basis of the  $\pi$ -conjugate system as the acceptor materials of the OSCs, because of their various molecular structures, easily tunable absorption region and FMO energy levels, low cost, and light weight [4]. Among these organic acceptors, naphthalene diimide (**NDI**) based on the conjugated polymer has

been recognized as the most effective acceptor material [5–7]. Zhou et al. investigated the active layer photovoltaic performance, charge transport, and blend morphology of the all-polymer OSCs construct of p-type **PTPD3T** and n-type **N2200** (**NDI** derivative) [8]. Their work not only could highlight the importance of molecular weight tuning for both polymer components, but also could provide a promising strategy and relevant synthetic methodologies to utilize the conjugated polymers with desired molecular weight for optimizing future efficiencies of all-polymer solar cells. Zhou et al. fabricated the OSCs on the basis of the copolymer of **NDI** and bithiophene as the near-infrared absorber and electron acceptor, and **PTB7** was as the electron donor [9]. The external quantum efficiency spectra of the OSCs displayed photoresponse up to 900 nm with the efficiency of 25% at 800 nm. Earmme et al. provided an investigation of three **NDI** copolymers as electron acceptors in OSCs. They found that the highest power conversion efficiency (PCE) of OSCs on the basis of the **NDI** copolymer as acceptor and the thiazolothiazole copolymer as donor is 3.3% [10]. Its short circuit current density and external quantum efficiency are 7.78 mA/cm<sup>2</sup> and 47%. Lee et al. produced a highly efficient OSC device with the PCE of 5.96% by taking a series of naphthalene diimide-based polymer as the acceptors [11]. Hwang et al. achieved an OSC device with the PCE of 7.7% utilizing the naphthalene diimide–selenophene copolymer as acceptor and

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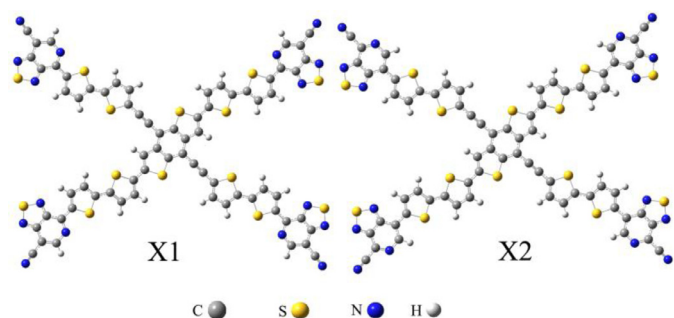
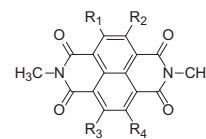


Fig. 1. The structures of donors **X1** and **X2**.

benzodithiophene–thieno[3,4-*b*]thiophene copolymer as donor [12]. Gao et al. prepared OSCs with a high PCE of 8.27% and a high fill factor of 70.24% using **N2200** as acceptor and **J51** as donor [13]. Hwang et al. designed a series of **NDI**/perylene diimide (PDI)–selenophene random copolymers, and investigated them as acceptors in OSCs [14]. They obtained the fine performances with the highest PCE of 6.3% and external quantum efficiency of 91%. Sakai et al. reviewed researches of the core-substituted naphthalene diimides [15] and investigated the electron- and hole-transporting pathways of naphthalene diimide derivatives [16]. Yushchenko et al. gave the comparison of charge-transfer dynamics of naphthalene diimide triads in solution [17]. Monti et al. investigated a series of donor–antenna–acceptor molecular rectifiers designed as modules for artificial photosynthesis devices with the naphthalene diimides as the antenna and secondary electron acceptor [18]. They also proposed a photoanode in which a TiO<sub>2</sub> substrate is functionalized with the naphthalene diimide dye [19].

In the present work, we investigated a series of **NDI** derivatives with different substituent groups as OSCs acceptors. The purpose of introducing substituent groups is to improve the performances of **NDI**, such as the proper FMO energy levels matching those of the donors oligo(thienylenevinylene) derivatives (**X1** and **X2**, Fig. 1) with excellent performances investigated by Yong and Zhang before [20], broad absorption region, and high charge transfer rate. Molecules **X1** and **X2** are the donor molecules in the study of Yong and Zhang with excellent properties, such as superior absorption properties. The difference between them is that the position of atom N in the substituent group connected with the thiophene is different. It is well known that, increasing the lowest unoccupied molecular orbital (LUMO) energy of the acceptor could increase the open circuit voltage ( $V_{oc}$ ), because the  $V_{oc}$  value increases along with the difference between the highest occupied molecular orbital (HOMO) energy of the donor and LUMO energy of the acceptor increasing. Additionally, the LUMO energy of the donor should be higher than that of acceptor larger than 0.30 eV. The substituent groups could affect the molecular properties significantly, thus three kinds of molecules (**NDI1–22**, Scheme 1) were designed to study the push ( $-OCH_3$  and  $-C_6H_6$ ), pull ( $-CN$  and  $-NO_2$ ), and push–pull ( $-CN$  and  $-OCH_3$  as well as  $-C_6H_6$  and  $-NO_2$ ) substituent groups effects. We investigated the ground state properties of these molecules by using the density functional theory (DFT) [21], for example HOMO energy, LUMO energy, and HOMO–LUMO gap ( $E_g$ ). The absorption spectra of the designed molecules were evaluated by the time dependent DFT [22–24] approach (TD-DFT). We also simulated the charge transfer properties (reorganization energy,  $\lambda$ ). Moreover, the correlation between structures and properties of the designed molecules were discussed.



- NDI1:**  $R_1 = -CN$   
**NDI2:**  $R_1 = R_2 = -CN$   
**NDI3:**  $R_1 = R_3 = -CN$   
**NDI4:**  $R_1 = R_4 = -CN$   
**NDI5:**  $R_1 = -OCH_3$   
**NDI6:**  $R_1 = R_2 = -OCH_3$   
**NDI7:**  $R_1 = R_3 = -OCH_3$   
**NDI8:**  $R_1 = R_4 = -OCH_3$   
**NDI9:**  $R_1 = -CN, R_2 = -OCH_3$   
**NDI10:**  $R_1 = -CN, R_3 = -OCH_3$   
**NDI11:**  $R_1 = -CN, R_4 = -OCH_3$   
**NDI12:**  $R_1 = -C_6H_6$   
**NDI13:**  $R_1 = R_2 = -C_6H_6$   
**NDI14:**  $R_1 = R_3 = -C_6H_6$   
**NDI15:**  $R_1 = R_4 = -C_6H_6$   
**NDI16:**  $R_1 = -NO_2$   
**NDI17:**  $R_1 = R_2 = -NO_2$   
**NDI18:**  $R_1 = R_3 = -NO_2$   
**NDI19:**  $R_1 = R_4 = -NO_2$   
**NDI20:**  $R_1 = -C_6H_6, R_2 = -NO_2$   
**NDI21:**  $R_1 = -C_6H_6, R_3 = -NO_2$   
**NDI22:**  $R_1 = -C_6H_6, R_4 = -NO_2$

Scheme 1. Chemical structures of **NDI** derivatives.

Table 1

The predicted  $E_{HOMO}$ ,  $E_{LUMO}$ , and  $E_g$  values of **NDI** and its derivatives at the CAM-B3LYP/6-31G(d) level.

	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	$E_g$ (eV)
<b>NDI</b>	-8.34	-2.28	6.07
<b>NDI1</b>	-8.74	-2.74	6.00
<b>NDI2</b>	-9.05	-3.09	5.96
<b>NDI3</b>	-9.12	-3.16	5.96
<b>NDI4</b>	-9.10	-3.18	5.92
<b>NDI5</b>	-7.90	-2.12	5.77
<b>NDI6</b>	-8.19	-2.11	6.09
<b>NDI7</b>	-7.71	-1.98	5.73
<b>NDI8</b>	-7.45	-1.99	5.46
<b>NDI9</b>	-8.60	-2.65	5.95
<b>NDI10</b>	-8.28	-2.57	5.71
<b>NDI11</b>	-8.24	-2.56	5.68
<b>NDI12</b>	-7.98	-2.22	5.76
<b>NDI13</b>	-7.70	-2.14	5.56
<b>NDI14</b>	-7.96	-2.15	5.81
<b>NDI15</b>	-7.83	-2.17	5.66
<b>NDI16</b>	-8.78	-2.70	6.08
<b>NDI17</b>	-9.13	-3.07	6.06
<b>NDI18</b>	-9.21	-3.11	6.10
<b>NDI19</b>	-9.18	-3.11	6.07
<b>NDI20</b>	-8.25	-2.57	5.68
<b>NDI21</b>	-8.31	-2.62	5.70
<b>NDI22</b>	-8.22	-2.63	5.60

## 2. Computational details

Recently, DFT method attracts extensive attention in OSCs field worldwide because of its application in explanation and predicting the properties of OSCs [25,26]. The DFT method CAM-B3LYP/6-31G(d,p) was proved to be reasonable for optimization of perylene diimide (PDI) and its derivatives, and the TD-B3LYP/6-31+G(d,p) method reliable for optical property simulation by our previous works [27,28]. Moreover, the chemical structure of **NDI** (Scheme S1) and the calculated results (Table S1) are listed in the supporting information. It could be seen that the CAM-B3LYP method was reliable in comparison with the crystal data [29]. Consequently, we employed the CAM-B3LYP/6-31G(d,p) method to optimize all the geometry parameters including neutral, cation, and anion of molecules **NDI1–22** with no symmetry. The B3LYP/6-31+G(d,p) method was used to predict the absorption spectra of molecules **NDI1–22**. There is no imaginary frequency in the calculations. The PBE1PBE/6-31G(d) method was used to optimize the geometry of molecules **X1** and **X2** [20], and the HOMO and LUMO energies of molecules **X1** and **X2** were calculated at the CAM-B3LYP/6-

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