



# Theoretical study on naphthobis(chalcogenadiazole) conjugated polymer systems and C61 derivative as organic photovoltaic semiconductors

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**Theoretical study on naphthobischalcogenadiazole conjugated polymer systems and C61 derivative as organic photovoltaic semiconductors**

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3 **Abstract**  
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6 We investigated the charge-transfer reactions of solar cells including a quaterthiophene  
7 copolymer with naphtho-bis-thiadiazole (PNTz4T) and naphtho-bis-oxadiazole  
8 (PNOz4T) using constrained density functional theory (CDFT). According to our  
9 calculations, the high electron-transfer rate results in a highly efficient solar cell, and the  
10 stable charge-transfer state results in low energy loss. Our computations imply that the  
11 following three factors are crucial to improve the performance of semiconducting  
12 polymers: (i) large structural changes following charge-transfer, (ii) narrow band gap, and  
13 (iii) spatially delocalized lowest unoccupied molecular orbital (LUMO) of the ground  
14 state.  
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39 **Keywords**  
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41 density functional theory; semiconducting polymers; charge transfer; solar cells  
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## 1. Introduction

Polymer-based bulk-heterojunction solar cells (PSCs) [1] are a type of organic photovoltaic cells (OPVs). Although dye-sensitized solar cells [2] suffer from sealing defects because they utilize liquid electrolytes, PSCs are expected to function effectively as durable solid photoelectric conversion devices. The implementation of polymer films in PSCs as the charge transport material makes them superior to inorganic solar cells in terms of weight and cost. However, two key issues must be addressed before PSCs can be used in practice. The first is their low power conversion efficiency (PCE) relative to inorganic solar cells, and the second is their large energy loss ( $E_{\text{loss}}$ ) [3] (0.7–0.8 eV) as solar energy is converted into electric power.

Although PSCs have several problems generating free electron–hole pairs from sunlight, one method to improve their low PCE and large  $E_{\text{loss}}$  is to effectively combine their constituent materials. PSCs consist of two types of organic semiconductors with many  $\pi$  electrons; that is, hole transport and electron transport materials with electron-donating and electron-accepting properties, respectively. Current PSCs are composed of polycyclic aromatic hydrocarbons or  $\pi$ -electron conjugated (semiconducting) polymers as the hole transport materials and fullerene derivatives as the electron transport materials. Charge recombination [4], which negatively affects charge-transfer, is assumed to be the

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3 main cause for the low PCE of PSCs. For materials with low bulk electrical conductivity,  
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6 charge recombination is attributed to unstable electron–hole pairs. Therefore, it is helpful  
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9 to analyse several combinations of hole transport and electron transport materials to  
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12 better understand their electronic structure.  
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16 To increase the PCE of PSCs, semiconducting polymers [5-7] have been developed in  
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18 the framework of two essential aspects; one is to control the thin film structure, such as its  
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20 crystallinity and orientation, so as to enhance the efficiency of charge transport, whereas  
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22 the other aspect is to control the polymers' electronic structure, such as the absorption  
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24 wavelength and the energy levels of the frontier orbitals, which are important for exciton  
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26 formation. Regarding the electronic structure, a semiconducting polymer with a narrow  
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28 band gap and deep highest occupied molecular orbital (HOMO) level is preferable to  
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30 widen the absorption region and increase the open circuit voltage. Osaka *et al.* reported an  
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32 effective copolymer based on quaterthiophene and naphtho-bis-thiadiazole (PNTz4T) [8],  
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34 with the PCE of PNTz4T with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM)  
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36 (PNTz4T/PCBM) reaching more than 10%. In addition, they also reported a  
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38 quaterthiophene and naphtho-bis-oxadiazole copolymer (PNOz4T) [9]. Both PNTz4T  
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40 and PNOz4T have a high crystallinity, narrow band gap, and deep HOMO level.  
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42 Although the PCE of the PSC with PNOz4T was relatively low (9%), PNOz4T has  
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3 received considerable attention, particularly because of its small  $E_{\text{loss}}$  (0.53–0.55 eV).  
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6 Although clarifying the difference between PNTz4T/ and PNOz4T/PCBM will be helpful  
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9 to develop more efficient materials, experiments are often not suitable to observe details  
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12 of the charge-transfer process.  
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16 To this end, quantum chemical analyses are a powerful tool to obtain detailed  
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19 understanding of charge-transfer processes. However, conventional density functional  
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22 theory (DFT) struggles to describe the charge-transfer states where positive and negative  
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25 charges are localized in the hole transporting and electron transporting materials. This  
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28 shortcoming of several exchange–correlation DFT functionals results from  
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31 self-interaction error (SIE) [10], which includes unphysical electron interactions in the  
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34 energy evaluation.  
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38 Constrained density functional theory (CDFT) of Deberich *et al.* [11,12] is an effective  
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41 tool for solving charge-localized systems. CDFT can minimize the energy of the system  
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44 under the constraint that the charges and spins remain localized in particular regions of  
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47 the system by adding a Lagrange multiplier to the conventional Kohn-Sham DFT  
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50 equations. Wu *et al.* developed CDFT further by reporting a way to efficiently explore the  
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53 diabatic potential energy curves in Marcus' electron-transfer theory [13], as well as a way  
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56 to accurately predict the driving force and reorganization energy [14]. Indeed, using Wu's  
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3 approach, a lot of electron-transfer reactions were explained [15-17] by computing the  
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6 electron-transfer rate constant within the Condon approximation [18]. Because of this  
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9 success, we adopted CDFT to estimate the charge-transfer reactions in PSCs.  
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12 This study aims to understand the qualitative differences between PNTz4T and PNOz4T  
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14 by comparing the electron-transfer rates ( $k_{ET}$ ) and the stability of the charge-transfer state  
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16 between PNTz4T/PCBM and PNOz4T/PCBM. Moreover, we also investigated the  
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19 conformational dependence of these molecular species on  $k_{ET}$ .  
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## 28 29 **2. Method**

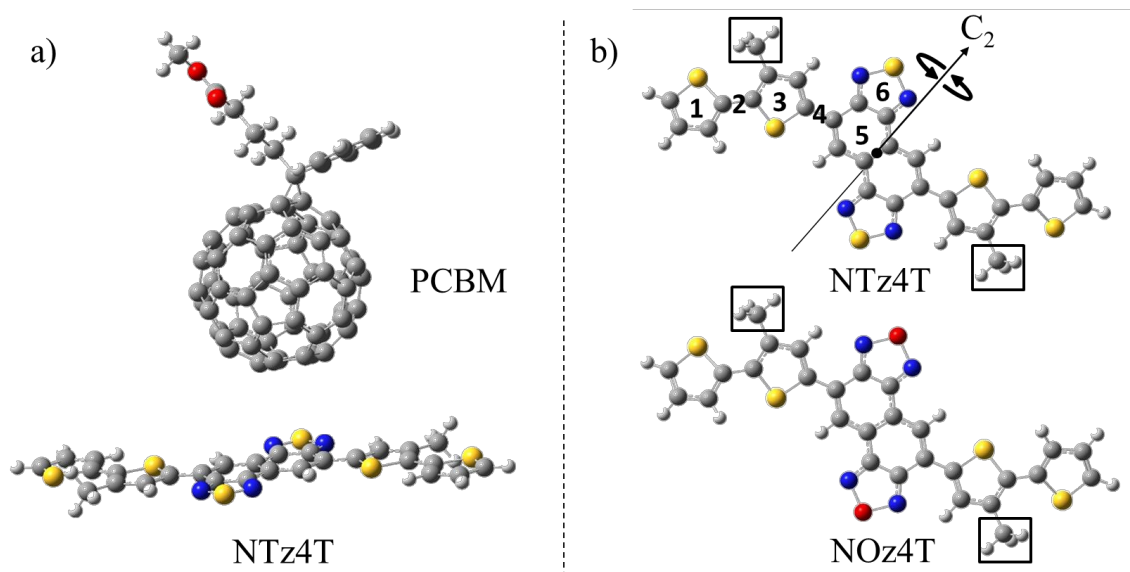
### 30 31 **2.1. Modelling**

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35 In this study, we used a donor/acceptor complex extracted from the interface between  
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37 bulk PCBM and PNTz4T/PNOz4T. PNTz4T or PNOz4T was adopted as the electron  
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39 donor, and PCBM [19] was chosen as the electron acceptor, as in the experiments of  
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42 Osaka *et al.* [9]. The PCBM model systems with PNTz4T or PNOz4T were prepared as  
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48 follows. First, PNTz4T and PNOz4T were orientated face-on to PCBM at the interfaces,  
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51 and the polar substituents of PCBM were directed toward the bulk region due to  
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54 electrostatic repulsion. Hence, we created the donor–accepter complex models as shown  
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58 in Figure 1a. The initial structures were prepared to ensure that the nearest distance  
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3 between the donor and acceptor atoms was approximately 4.0 Å. (see the SI for the  
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6 detailed initial structures.) For computational convenience, PNTz4T and PNOz4T were  
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9 modelled as monomers by replacing the alkyl chains with methyl groups, which are  
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12 hereafter termed NTz4T and NOz4T, respectively. We found that these small model  
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15 systems are sufficiently representative of the actual systems to reproduce the three  
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18 relevant electronic states of the system (i.e. before light irradiation, after exciton  
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21 formation, and after charge-transfer).  
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26 Additionally, we prepared six models for each NTz4T/PCBM and NOz4T/PCBM  
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28 complex (Figure 2) by rotation around the C<sub>2</sub> axis (Figure 1b) to examine their  
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31 conformational dependence on  $k_{ET}$ . These models are hereafter referred to as **s1-s6**. As  
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34 shown in Figure 1b, PCBM was placed above the thiophene rings or the carbon-carbon  
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37 bonds of NTz4T or NOz4T.  
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**Figure 1.** (a) Model of the NTz4T complex with PCBM (NTz4T/PCBM). Blue, red, yellow, white, and grey spheres indicate nitrogen, oxygen, sulfur, hydrogen, and carbon atoms, respectively. (b) Structures of NTz4T and NOz4T. PCBM is placed above the NTz4T or NOz4T moieties and labelled from **1** to **6**, as depicted as **s1-s6** in Figure 2. Face-on conformations were ensured by enforcing  $C_{2h}$  symmetry of NTz4T/NOz4T.

## 2.2. Geometry Optimization and Single-Point Energy Calculations

All calculations in this study were performed using the B3LYP [20] hybrid density functional and the 6-31G(d) basis set. The total energy of these models was determined through the following three steps: (i) all-atom geometry optimization of the ground state, (ii) geometry optimization of each molecule, and (iii) single-point energy calculations.

All models were optimized using GAUSSIAN 09 [21]. Only the donor was extracted from

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3 the optimized structures of **s1-s6**, and geometry optimizations of the singlet ground and  
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6 excited states and the radical cation state were performed. Time-dependent DFT  
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9 (TD-DFT) [22] as implemented in GAUSSIAN 09 was used to calculate the singlet excited  
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12 state. For PCBM, geometry optimizations of the singlet ground and radical anion states  
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15 were also performed. These optimized molecules were then combined while maintaining  
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18 their ground-state interatomic distances. Finally, single point-energy calculations were  
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21 performed using our own CDFT program [15-17]. After the charge-transfer was  
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24 calculated for each system, the constraint was set to ensure charges of +1 and -1 for the  
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27 donor and acceptor, respectively.  
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### 36 **2.3. Electron Transfer Rate and Stabilization Energy**

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38 The electron-transfer rate constants,  $k_{ET}$ , were calculated using Equation (1) [23]:  
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$$44 \quad k_{ET} = \frac{4\pi^2}{h} \frac{|H_{ab}|^2}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T}\right) \quad (1)$$

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51 where  $h$ ,  $k_B$ , and  $T$  are Planck's constant, Boltzmann's constant, and absolute temperature,  
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54 respectively. The driving force ( $\Delta G^0$ ), reorganization energy ( $\lambda$ ), and electron coupling  
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57 constant ( $H_{ab}$ ) were calculated from the energy and orbitals obtained by single-point  
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3 energy calculations at the CDFT level of theory.  $k_{ET}$  was determined with  $T = 300$  K and  
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6  $H_{ab}$  was calculated based on the theory proposed by Wu *et al.* [18]. Because CDFT  
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9 struggles to describe singlet excited states,  $H_{ab}$  was approximated by assuming that the  
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12 triplet excited state is equal to the singlet excited state.  
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16 Hereafter, we use the standard notation  $E(a|b)$  to represent the energy in the “ $a$ ” state  
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18 with the equilibrium structure in the “ $b$ ” state. For example, each energy of the system  
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20 before light irradiation, after exciton formation, and after charge-transfer is expressed as  
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22  $E(DA|DA)$ ,  $E(D^*A|D^*A)$ , and  $E(D^{+\bullet}A^{-\bullet}|D^{+\bullet}A^{-\bullet})$ , respectively. Here, D and A indicate the  
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24 donor and acceptor, respectively.  $\Delta G^0$  was obtained approximately from the difference  
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26 between the internal energies of the systems as follows:  
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$$\Delta G^0 \cong E(D^{+\bullet}A^{-\bullet}|D^{+\bullet}A^{-\bullet}) - E(D^*A|D^*A) \quad (2)$$

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44 Because we assumed that the electron-transfer occurs in a gas phase, outer sphere  
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46 reorganization energy due to the solvent relaxation is not taken into account. In this  
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48 case, the total reorganization energy  $\lambda$  is equal to its inner sphere energy  $\lambda_i$  as:  
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$$\lambda = \lambda_i = E(D^{+\bullet}A^{-\bullet}|D^*A) - E(D^{+\bullet}A^{-\bullet}|D^{+\bullet}A^{-\bullet}) \quad (3)$$

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3 A stabilization energy  $E_{st}$  was introduced to assess the stability of the charge-transfer  
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6 state ( $D^{+\bullet}$  and  $A^{-\bullet}$ ); larger values of  $E_{st}$  indicate higher stability of this state.  
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$$E_{st} = E(D^{+\bullet}|D^{+\bullet}) + E(A^{-\bullet}|A^{-\bullet}) - E(D^{+\bullet}A^{-\bullet}|D^{+\bullet}A^{-\bullet}) \quad (4)$$

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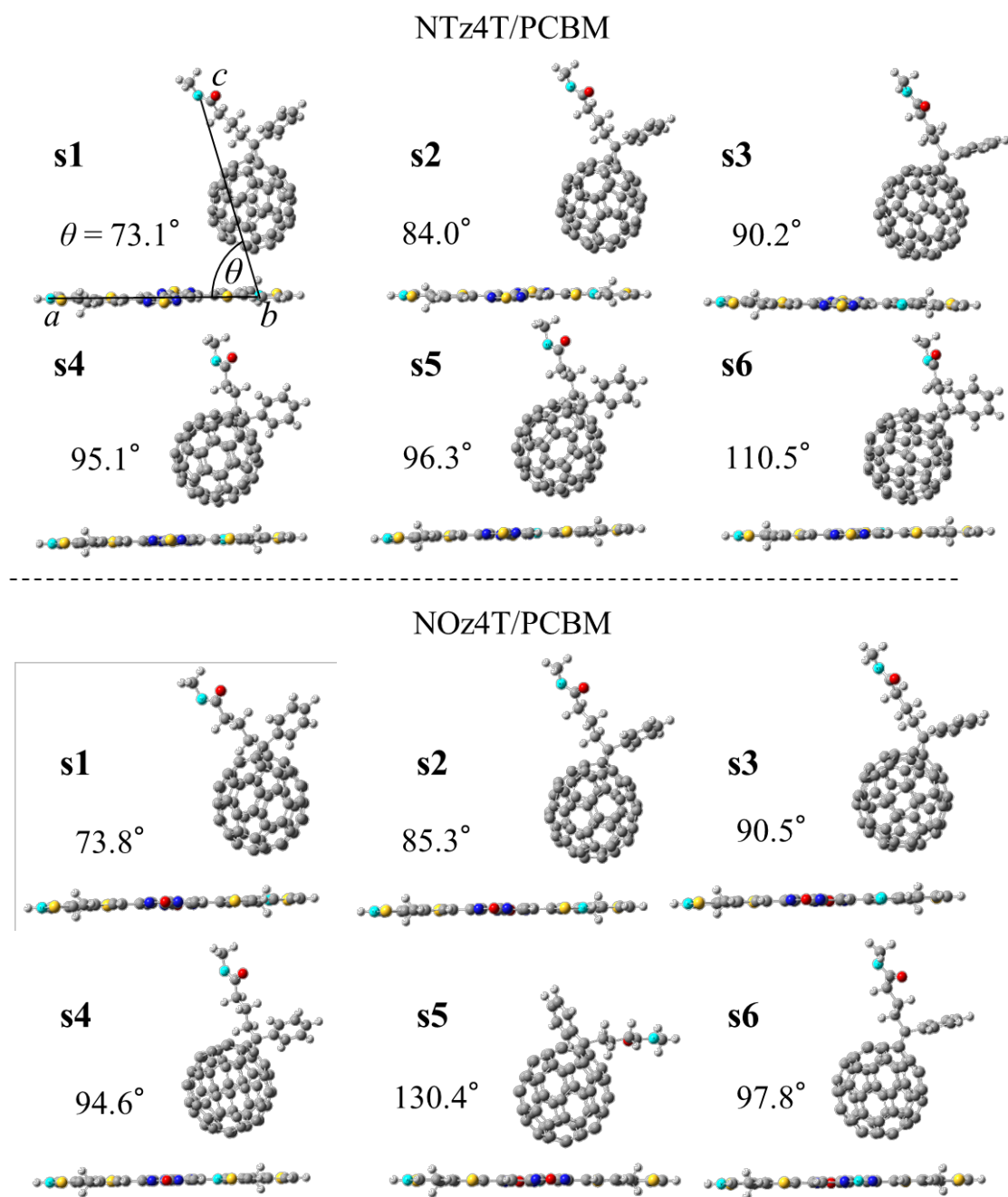
### 23 **3. Results and Discussion**

#### 24 25 **3.1 Structural Changes**

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28 Figure 2 shows the optimized structures of **s1-s6**. Relative to their initial structures, no  
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30 significant changes of **s1-s4** were evident. However, the optimized structures of **s5** and **s6**  
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33 show slightly longer distances from NTz4T and NOz4T compared with their initial  
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39 structures.

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42 Although NTz4T and NOz4T have slightly bent ground-state structures, they are almost  
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45 planar in the lowest-energy singlet excited state. The geometric difference between the  
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3 We also calculated  $\lambda_{\text{NTz4T}}$ ,  $\lambda_{\text{NOz4T}}$ , and  $\lambda_{\text{PCBM}}$  to evaluate the contribution of the  
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6 reorganization energy to the stability of the entire system. The respective average values  
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9 of all conformations (**s1-s6**) are  $\overline{\lambda_{\text{NTz4T}}} = 8.38$  kJ/mol,  $\overline{\lambda_{\text{NOz4T}}} = 9.06$  kJ/mol, and  
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12  $\overline{\lambda_{\text{PCBM}}} = 12.71$  kJ/mol. Clearly, PCBM contributes the most to the total reorganization  
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15 energy, and NOz4T has a slightly larger contribution than NTz4T.  
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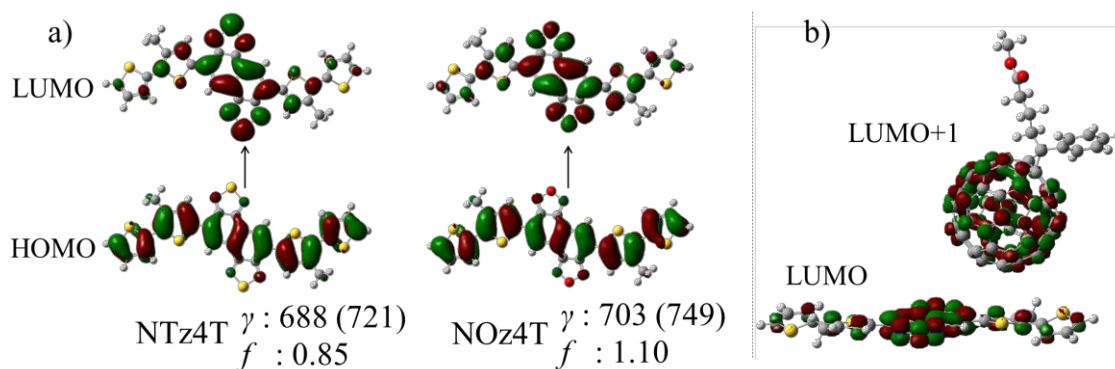


**Figure 2.** Fully optimized structures of **s1-s6**. The nearest intermolecular distance between the donor and acceptor atoms is almost identical to that of the initial structure. The angles ( $\theta$ ) between the cyan-coloured *a*, *b*, and *c* atoms are shown. *a*: terminal carbon atom of the NTz4T or NOz4T ring. *b*: nearest atom to PCBM. *c*: ether bonding

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3 oxygen atom of PCBM.  $\alpha$  of NOz4T/PCBM has an especially large angle because the  
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6 orientation of the functional groups of PCBM is reversed.  
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### 10 11 12 **3.2 Absorption Wavelengths and Molecular Orbitals**

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16 We compared the absorption wavelengths ( $\lambda$ ) of NTz4T and NOz4T at the TD-DFT level  
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19 of theory with the experimental values [9] to examine whether the singlet excited state  
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22 corresponds to the actual system. According to our calculations, the first  
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25 transition-allowed excited state could be attributed to a single electron excitation from the  
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28 HOMO to the lowest unoccupied molecular orbital (LUMO) of NTz4T and NOz4T  
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31 (Figure 3). Although the computed absorption wavelength was slightly shorter than the  
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34 experimental value (<50 nm), because of the short-conjugated monomer model [24], the  
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37 tendency is consistent with experimental results; that is, NTz4T has a shorter absorption  
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40 wavelength and weaker oscillator strength than NOz4T [9]. It is expected that excitation  
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43 of NOz4T occurs more efficiently than that of NTz4T because the oscillator strength of  
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46 the HOMO–LUMO excitation of NOz4T is larger than that of NTz4T (Figure 3).  
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**Figure 3.** (a) HOMO/LUMO of NTz4T and NOz4T (isovalue of 0.020). The values of  $\gamma$  are given in nm, and the experimental values are shown in parentheses. The values of the absorption oscillator strength ( $f$ ) are also given. (b) LUMO and LUMO+1 of NOz4T/PCBM (isovalue of 0.020), which are almost degenerate (<5 kJ/mol).

### 3.3 Calculated $k_{ET}$ and $E_{st}$

Table 1 shows the  $k_{ET}$  and  $E_{st}$  of the systems and the three Marcus parameters. The overlap integrals between the donor and acceptor are shown in parentheses as a supplement to  $H_{ab}$ . For clarity, the qualitative differences of these were considered. Although efficient charge-transfer is expected in both models on the basis of  $k_{ET}$ , the NTz4T/PCBM model has a relatively larger  $k_{ET}$  than that of NOz4T/PCBM. These results reflect the high efficiency of PSCs using PNTz4T. Since the right-hand side of Eq. (1) contains  $(\Delta G^0 + \lambda)^2$  in the exponential term, the  $k_{ET}$  difference between the models is mainly due to the difference between  $\Delta G^0$  and  $\lambda$ . The average  $\Delta G^0$  values in **s1-s6** in the



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3 NTz4T/PCBM and NOz4T/PCBM models are -70.71 and -85.21 kJ/mol, respectively. As  
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6 for the average  $\lambda$  in **s1-s6**, we obtain 16.72 kJ/mol for NTz4T/PCBM and 19.76 kJ/mol for  
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9 NOz4T/PCBM. From these results, this reaction occurs in the inverted region of Marcus  
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12 theory for both models, and the large  $k_{ET}$  of NTz4T/PCBM is attributed to its small  $(\Delta G^0$   
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Moreover, the  $k_{ET}$  values of **s4-s6** in NTz4T/PCBM tend to be much larger than those in  
**s1-s3**, indicating that  $k_{ET}$  is conformation dependent. The primary difference between  
**s4-s6** and **s1-s3** is attributed to the difference in  $H_{ab}$ ;  $H_{ab}$  for **s4-s6** are ~100 times larger  
than those of **s1-s3**. Therefore, we can speculate that conformation contributes to  $H_{ab}$ ,  
which increases when the donor and acceptor couple strongly. The strength of the  
coupling between the donor and acceptor is reflected in the value of the overlap integral,  
which is increased when the MOs of the donor and acceptor are closer. Indeed, as shown  
in Figure 3, the LUMOs in the ground state of NTz4T and NOz4T are localized in the  
naphtho-bis-thiadiazole (NTz) and naphtho-bis-oxadiazole (NOz) moieties, and PCBM  
in **s4-s6** is in the proximity of these orbitals. Therefore, the overlap integral becomes large  
(Table 1), and strong coupling occurs between the donor and acceptor.

Although the same tendency is found in **s4-s6** of NOz4T/PCBM, the reorganization  
energy has an important contribution to the large  $k_{ET}$  in **s5** and **s6**. In addition, the

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3 calculated coupling constant for **s5** is very small. Structurally, PCBM is out of the ring  
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6 plane from the first step of the geometry optimization (Figure 4). The structural  
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9 specificity of **s5** can also be ascertained from its relatively large angle involving PCBM  
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12 and its counterpart (Figure 2). Although it differs from the assumed conformation, we can  
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15 gauge the magnitude of the contribution of  $\lambda$  by comparing **s5** with **s1-s3**.  
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19 The average value of  $E_{st}$  for the NTz4T/PCBM system (136.94 kJ/mol) is smaller than  
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21 that of NOz4T/PCBM (143.28 kJ/mol). This result suggests that the large  $E_{st}$  could be a  
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23 factor for lowering  $E_{loss}$ .  $E_{loss}$  is defined as  $E_g - eV_{OC}$ , where  $E_g$  is the bandgap,  $e$  is the  
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25 elementary charge, and  $V_{OC}$  is the open-circuit voltage.  $E_{st}$  is a value derived using the  
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27 total energy of the system, whereas  $E_{loss}$  is a value derived using the bandgap; comparing  
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29 these two values directly is therefore questionable. Nevertheless, the values of  $E_g$  as  
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31 derived from  $\gamma$  are 1.80 eV for PNTz4T and 1.76 eV for PNOz4T, which do not differ  
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33 considerably from the experimental values [9]. Although there is no research that reports  
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35 the correlation between  $E_{st}$  and  $E_g$ , or  $E_{st}$  and  $E_{loss}$ , these properties could have a negative  
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37 correlation with each other. We intend to confirm the correlation between  $E_{st}$  and  $E_g$ , and  
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39 subsequently  $E_{st}$  and  $E_{loss}$ , in future studies by increasing the number of calculation  
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41 targets.  
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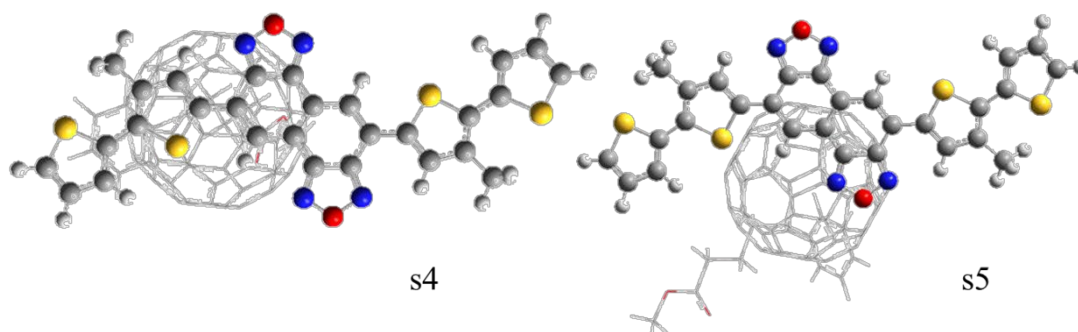
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58 Consistent with our expectations, **s4** and **s5** of NTz4T/PCBM have larger  $E_{st}$  values than  
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those of NOz4T/PCBM, because NTz4T has a large overlap integral with PCBM in these conformations. The same tendency is also observed in **s4** of NOz4T/PCBM.

**Table 1.** Calculated values of  $\Delta G^0$ ,  $\lambda$ ,  $|H_{ab}|$ ,  $k_{ET}$ , and  $E_{st}$ , with the overlap integral between NTz4T/NOz4T and PCBM in parentheses.

|                           | <b>s1</b>             | <b>s2</b>          | <b>s3</b>             | <b>s4</b>             | <b>s5</b>             | <b>s6</b>          |
|---------------------------|-----------------------|--------------------|-----------------------|-----------------------|-----------------------|--------------------|
| NTz4T/PCBM                |                       |                    |                       |                       |                       |                    |
| $\Delta G^0$ <sup>a</sup> | -79.44                | -78.35             | -77.39                | -55.95                | -60.23                | -72.87             |
| $\lambda$ <sup>a</sup>    | 15.52                 | 15.43              | 16.11                 | 18.77                 | 15.52                 | 18.95              |
| $ H_{ab} $ <sup>a</sup>   | 0.49                  | 0.14               | 0.43                  | 17.76                 | 16.24                 | 10.70              |
|                           | (0.006)               | (0.002)            | (0.006)               | (0.167)               | (0.149)               | (0.095)            |
| $k_{ET}$ <sup>b</sup>     | $6.65 \times 10^0$    | $1.08 \times 10^0$ | $1.03 \times 10^2$    | $1.42 \times 10^{12}$ | $2.53 \times 10^{11}$ | $1.73 \times 10^8$ |
| $E_{st}$ <sup>a</sup>     | 133.23                | 135.26             | 136.05                | 155.85                | 154.09                | 143.23             |
| NOz4T/PCBM                |                       |                    |                       |                       |                       |                    |
| $\Delta G^0$ <sup>a</sup> | -86.23                | -88.84             | -86.27                | -80.66                | -86.39                | -82.89             |
| $\lambda$ <sup>a</sup>    | 16.09                 | 19.59              | 16.30                 | 15.69                 | 25.05                 | 25.85              |
| $ H_{ab} $ <sup>a</sup>   | 0.42                  | 0.09               | 0.15                  | 12.36                 | 0.56                  | 9.13               |
|                           | (0.012)               | (0.001)            | (0.008)               | (0.095)               | (0.007)               | (0.077)            |
| $k_{ET}$ <sup>b</sup>     | $6.67 \times 10^{-2}$ | $1.18 \times 10^0$ | $1.56 \times 10^{-2}$ | $2.34 \times 10^3$    | $5.74 \times 10^5$    | $1.95 \times 10^9$ |
| $E_{st}$ <sup>a</sup>     | 142.41                | 139.41             | 142.39                | 149.50                | 141.11                | 144.87             |

<sup>a</sup> kJ/mol. <sup>b</sup> s<sup>-1</sup>.



**Figure 4.** Structures of **s4** and **s5** (NOz4T/PCBM) viewed from the side of NOz4T.

NOz4T and PCBM are depicted by ball-and-stick and wireframe styles, respectively.

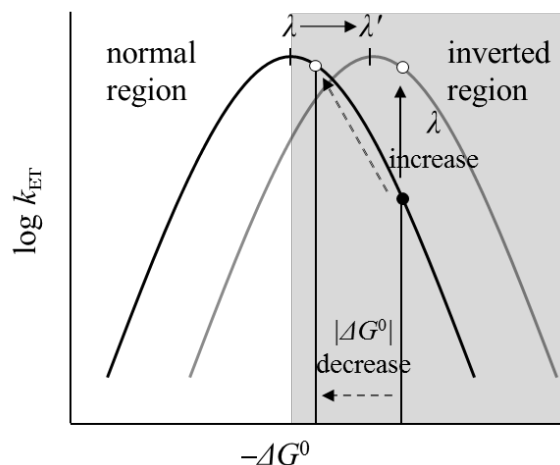
### 3.4 Discussion

Osaka *et al.* [9] have estimated that the driving force for the electron-transfer reaction at the PNOz4T/PCBM interface is  $\sim 12$  kJ/mol on the basis of the energy gap between the LUMO of the donor and acceptor ( $\Delta E_L$ ). Its corresponding PCE is  $\sim 9\%$ , which implies that this reaction is efficient. However, the driving force of 12 kJ/mol is smaller than the empirically known threshold value [25] of 0.30 eV ( $\sim 30$  kJ/mol) for efficient electron-transfer, indicating that the PNOz4T/PCBM interface is an exception to the rule suggested in Ref. 25. In this study, the driving force at the PNOz4T/PCBM interface was estimated by using the total energy of the system, and a sufficient driving force was attained even in the PSC using PNOz4T.

The results show that a semiconducting polymer with a high PCE has a large  $k_{ET}$  and that

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3 a small energy loss has a large  $E_{st}$ . Therefore, a semiconducting polymer with an  
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6 improved PCE and small  $E_{loss}$  has both a large  $k_{ET}$  and  $E_{st}$ .  
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9  $\lambda$  and  $\Delta G^0$  contribute greatly in determining the magnitude of  $k_{ET}$ . Since the sum of  $\lambda$  and  
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11  $\Delta G^0$  is negative, the reactions assumed in this study occur in the Marcus inverted region.  
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13 Here,  $k_{ET}$  increases with an increase of  $\lambda$  or a decrease of  $|\Delta G^0|$  (Figure 5). Because the  
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15 correlation between  $\Delta G^0$  and  $\lambda$  is relatively weak, we conclude that these parameters are  
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17 mutually independent. In contrast,  $\Delta G^0$  and  $E_{st}$  are correlated through the energy of the  
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19 charge-transfer state  $E(D^{+\bullet}A^{\bullet-} | D^{+\bullet}A^{\bullet-})$ . Therefore, semiconducting polymers should be  
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21 designed by focusing on lowering the energy of the lowest-energy singlet excited state  
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23  $E(D^*A | D^*A)$  to decrease the absolute value of  $\Delta G^0$  without affecting  $E_{st}$ ; that is,  
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25 semiconducting polymers with a narrow bandgap are preferable. However, polymers that  
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27 experience large structural changes before and after charge-transfer should be considered  
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29 to increase  $\lambda$ .  
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**Figure 5.** Conceptual diagram of the Marcus curve. Solid and dotted arrows represent the direction of the  $\lambda$  increase and  $|\Delta G^0|$  decrease, respectively. The filled and open dots indicate plots of the actual and ideal systems, respectively.

To improve  $E_{st}$ , increasing the contribution of charge delocalization (i.e. expanding the  $\pi$ -conjugated system) seems to be effective. Because  $E_{st}$  also tends to increase as  $H_{ab}$  increases, it is also conceivable to design a semiconducting polymer with a spatially delocalized LUMO in the ground state.

#### 4. Conclusion

This study investigated the electron-transfer rate constant ( $k_{ET}$ ) by Marcus theory and the stabilization energy of the charge-transfer state ( $E_{st}$ ) for each conformation of the NTz4T/PCBM and NOz4T/PCBM models at the CDFT level. A high PCE is predicted

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3 for NTz4T/PCBM with a large  $k_{\text{ET}}$ , and NOz4T/PCBM with a large  $E_{\text{st}}$  has a small  $E_{\text{loss}}$ .  
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6 In the **s4-s6** conformations where PCBM exists above the NTz and NOz moieties, the  
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8 LUMO in the ground state of the donor has a large overlap integral with the acceptor,  
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10 resulting in a large  $k_{\text{ET}}$ . Therefore, we found that NOz and NTz, as introduced into a  
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12 semiconducting polymer by Osaka *et al.*, greatly contribute to enhancing the efficiency of  
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14 electron-transfer.  
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22 It was also found that the PSC based on PNOz4T possesses a satisfactory driving force  
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24 for electron-transfer, as estimated from the total energy of the system. Overall, our  
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26 computational results support the high efficiency of PSCs based on PNOz4T, and the  
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28 scheme introduced by Wu *et al.* is applicable for estimating electron-transfer reactions in  
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30 PSCs. We expect that their scheme is effective to the electron-transfer reactions of other  
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32 PSC systems as well.  
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41 In order to develop semiconducting polymers with effectual PCE and small  $E_{\text{loss}}$ , it is  
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43 necessary to increase the magnitudes of both  $k_{\text{ET}}$  and  $E_{\text{st}}$ . The requirements to improve the  
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45 performance of semiconducting polymers include: (i) large structural changes through  
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47 charge-transfer to enhance  $\lambda$ , (ii) narrow band gap to lower the driving force, and (iii)  
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49 spatially delocalized LUMO of the ground state to increase electronic coupling.  
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