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REGULAR ARTICLE

Electron Transfer Pathways in the Z-schematic Donor-donor-acceptor Organic Solar Cells

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Abstract: In the tandem organic solar cell, two or more subcells are generally connected in series to generate a high open circuit voltage by using an interlayer for charge carrier recombination. In this communication, a donor-donor-acceptor organic solar cell model without the interlayer is suggested for generation of high open circuit voltage. The mechanism of this model, similar to the Z-scheme, requires that both of two donors absorb sunlight step-by-step to perform a high energy charge transfer state. Although there are many competitive electron transfer (ET) processes taking place between two donors after photo excitations, the possibility of this mechanism is theoretically demonstrated by using electronic structure calculations and Marcus ET theory from a model solar cell where the substituent of DFHCO4TCO and P3DOT are taken as donors, and $PC_{61}BM$ as an acceptor. It is found that the obtained open circuit voltage is twice as large as that in the organic solar cell with single donor.

AMS subject classifications: 65D18, 68U05

Key words: donor-donor-acceptor organic solar cells, electron transfer, Z-scheme, open circuit voltage, driving force, substituent

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1 Introduction

Organic photovoltaic devices are becoming one of potential candidates in the solar cells for their low-cost, flexibility, ease of processing and low toxicity [1-3]. An organic solar cell typically consists of p-type (donor) and n-type (acceptor) semiconductors, interfaced in a bulk heterojunction (BHJ) configuration, and its open-circuit voltage (V_{oc}) is one of significant factors to determine the power conversion efficiency[4, 5]. The experiments have demonstrated that V_{oc} displays a linear relationship with the energy gap between the ionization potential of donor and electronic affinity of acceptor [6-8]. This energy gap essentially corresponds to the energy difference between the highest occupied molecular orbital (HOMO) of donor and the lowest unoccupied molecular orbital (LUMO) of acceptor [9]. Accordingly, the weak donor- strong-acceptor strategy has been proposed to design the polymer donor in the solar cell with a large V_{oc}, where the strong-acceptor part of the polymer is used to reduce the band gap and the weak-donor part keeps the HOMO energy at a low level [10, 11]. To further improve the conversion efficiency, organic tandem solar cells have been designed to achieve higher overall solar absorption [12-16]. In this kind of solar cells, two subcells are stacked via an interlayer for the charge recombination. Meanwhile, with the series connection of two subcells, the open circuit voltage of an ideal tandem solar cell should equal to the sum of those of the subcells. Based on the rule to produce the tandem solar cell with a high V_{oc}, where the electron and hole recombine at the interlayer, one may get an inspiration that when the HOMO and LUMO energy levels in two donors match well, the excited electron in the LUMO of the left donor and the hole in the HOMO of the right one may also recombine in the D-D-A solar cell. With this scheme, the V_{oc} might be doubly enlarged compared to that of the D-A solar cell. Indeed, the similar mechanism, known as Z-scheme, has been confirmed by the experiments of artificial photosynthesis, photocatalytic reactions and etc[17-21], where the systems are pumped step-by-step to the high excited states. In this paper, we theoretically illustrate the possibility of the Z-schematic D-D-A solar cell through electronic structure calculations and Marcus ET theory[22, 23].

2 Model

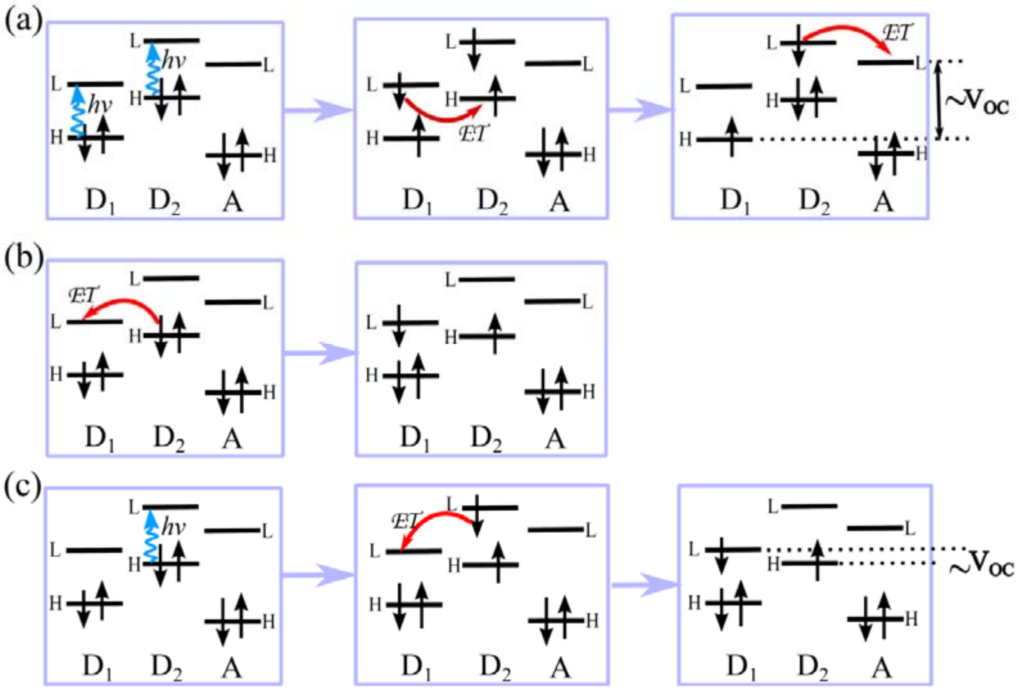

Figure 1: Energy levels of D_1, D_2 and A. (a) represents the favorable pathway, (b) and (c) represent other possible pathways which should be suppressed.

Figure 1 displays the molecular orbital (MO) energy level scheme for the D-D-A solar cell where the double donors absorb the sunlight. According to the Z-scheme mechanism, the energy level of LUMO for one donor (D_1) should be much lower than that of the other one (D_2) but close to the HOMO of D_2. In this case, it involves many ET pathways. Three dominant pathways are illustrated in **Figure 1**, denoted as (a), (b) and (c). In the pathway (a), both D_1 and D_2 absorb the sunlight with different wavelengths initially, and the excited complex is denoted as D^*_1-D_2^*-A, where the asterisk represents the excited state. Subsequently, the excited electron in the LUMO of D_1 transfers to HOMO of D_2, as a result, the charge separated state D^+_1 -D^-_2-A is formed. Finally, the promoted electron in the LUMO of D_2 migrates to the LUMO of A, and corresponding state becomes D^+_1-D_2-A^-. Along this ET pathway, the V_{oc} doubly increases compared to that in the solar cell with one donor and an acceptor. This mechanism is similar to that of the Z-schematic inorganic semiconductor solar cells, where an electrolyte is commonly employed [24]. The second typical pathway, labeled by (b), is that the electron in the HOMO of D_2 may directly transfer to LUMO of D_1 without absorbing sunlight, leading to the D^-_1-D^+_2-A state. In this charge-separated state, both ionic donors can still absorb the sunlight. However, the ET rates in the corresponding pathways should be slower than those in the neutral donors due to the stronger Coulomb interactions. As one donor dominantly absorbs the sunlight, it is divided into two cases. When only D_1 absorbs the light, ET process terminates because the unoccupied MO levels of D_2 are much higher than the occupied MO levels of D_1, at the same time, the electron cannot move to A. because it is far away from D_1. Therefore, the generated exciton in D_1 annihilates by fluorescence. When only D_2 absorbs the light, the excited electron in LUMO of D_2 may transfer to LUMO of D_1, illustrated by the pathway (c), or to LUMO of A, and both ET processes compete with each other. Actually, two donors act as a donor-acceptor system in the case of pathway (c). It should be mentioned that the excited electron at the first step of the pathway (a) may also transfer from LUMO of the D_2 to LUMO of the D_1 leading to the D^{-*}_1-D^{+}_2-A state. However, this process badly impacts on the Z-schematic ET efficiency. In order to get rid of this negative effect, one should well suppress such ET process.

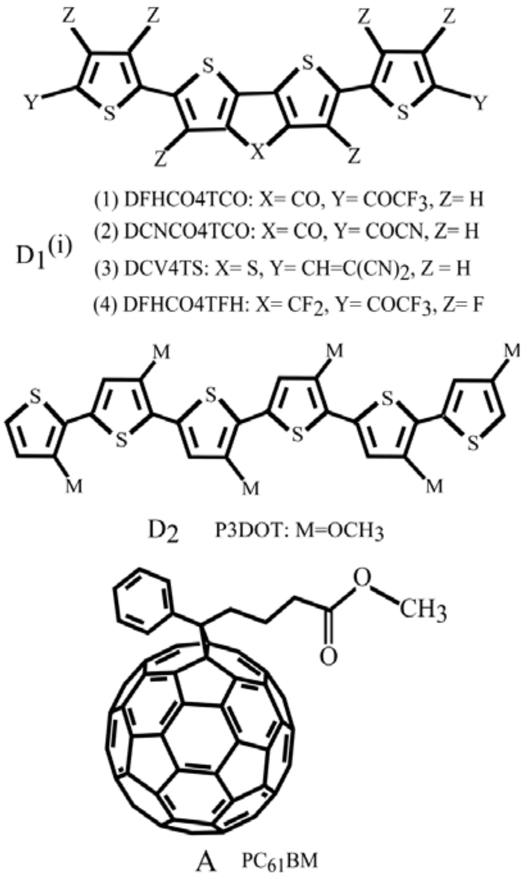

Figure 2: The molecular structures of $D^{(i)}_1$ (i=1~4), D_2 and A.

To design Z-schematic D-D-A solar cells, it is essential to carefully select the candidates for the donors and acceptor whose MO energy levels match well for the favorable charge transfer. We note that the BHJ organic solar cell consisting of the regioregular poly(3-hexylthiophene) (P3HT) as donor and [6,6]-phenyl-C61-butyric acid methyl ester (PC$_{61}$BM) as acceptor has been investigated in both experiments and theories[25-28]. Further investigation indicates that the alkoxy side chain bonding to poly(thiophene) results in the optical band gap narrow. In the present work, therefore, we choose regioregular poly(3-decyloxythiophene-2,5-diyl) (P3DOT) and PC$_{61}$BM as D_2 and A, respectively. Since it is required that the MO energies of D_1 are lower than those of D_2, and recently, Yoon et al. [29, 30] reported that 2,7-[bis-(5-perfluorohexylcarbonylthien-2-yl)]-4H-cyclopenta[2,1-b:3,4-b′]-di-thiophen-4-one (DFHCO4TCO) is a high mobility organic semiconductor and the corresponding energies of HOMO and LUMO were -6.39 eV and -4.19 eV, respectively, we finally chose the DFHCO4TCO as the D_1, whose MOs may match well with those of P3DOT. In the concrete calculations, we adopt simplified compounds of D_1 and D_2, as schematically represented in **Figure 2**. The D_2, namely P3DOT, is chosen as the six-thiophene-ring model which can well describe the ET and charge-recombination processes in P3HT/PC$_{61}$BM solar cell[28]. Furthermore, the -OCH$_3$ group takes the place of the -OC$_{10}$H$_{21}$ group because the side chain, which usually causes the rise of solubility, has few effect on the electronic structure and optical properties of the polymer[31, 32]. As an analogy, -C$_6$F$_{13}$ segment is replaced by the -CF$_3$ group in DFHCO4TCO, denoted as $D^{(1)}_1$ in **Figure 2**. With the simplified models, two donor and one acceptor molecules are put together in a stacking structure and the separated distance is set as 3.5 angstrom. Moreover, it is found that the substituents of X, Y and Z in **Figure 2**, which stand for the different functional groups, are able to adjust the HOMO and LUMO levels and further to optimize the ET pathways.

In fact, the energy gap is not the sole factor to determine the ET pathway. Therefore, the reliable method is the calculation of the ET rate to select the possible candidates of the high-performance solar cells. Here, we use the well-known Marcus formula to estimate the ET rate, and it can be evaluated by[22, 23]

$$k_{et} = \frac{1}{\hbar} V_{DA}{}^{2} \sqrt{\frac{\pi}{\lambda k_B T}} \exp[-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}]. \tag{1}$$

Here, k_B and T are the Boltzmann constant and the temperature, respectively. ΔG is the driving force, which closely relates to the energy gap and can be estimated from Rehm-Weller equation[33]. V_{DA} represents the electronic coupling, which can be calculated by the direct coupling method with the constructed diabatic states[34-36]. λstands for the total reorganization energy, it can be evaluated with four-point method[37-41]. All of them are calculated from electronic structure methods. Although the Marcus formula is limited to the weak electronic coupling[42], it should be qualitatively suitable for the present purpose. In the electronic structure calculations, all geometry optimizations and reorganization energies calculations were performed at the B3LYP level with the 6-31G** basis set adopting the Gaussian 09 program[43], and the atomic orbitals were expanded to the 6-311++G** basis set in the energy calculations of states (It should be addressed that the MO energies in the above discussion are only corresponding to a schematic picture, and in the Marcus formula, the driving force is the energy difference of states). The electronic coupling calculation for each complex was based on Hartree-Fock (HF) method with 6-31G basis set on NWChem package[44].

3 Results and discussion

Table 1 lists the calculation results of ET parameters for three types of possible ET processes between D_1 and D_2, as well as between D_2 and A. With sulfenyl or difluoromethyl instead of carbonyl in D_1, the λ between D_1 and D_2 evidently trends to descent in favor of the ET processes. However, in consideration of the substituent effects on the driving force, it is found that ΔG is more sensitive to substituent alteration, More importantly, the substituents greatly influence on the ΔG difference between types (a) and (b). As shown from Table 1, the ΔG difference in the complex $D^{(4)}_1$-D_2 is about 0.23 eV, but it changes to 0.82 eV in $D^{(3)}_1$ -D_2. It means that ΔG may play a key role in the control of ET pathways by means of the substituent modifications. It is also noted that the largest ΔG of type (c) for each complex is ascribed to the remarkable energy difference of LUMOs in D_1 and D_2. For the electronic couplings, it seems that the substituents have weak impact on them for all three types of ET pathways. In addition, the electronic couplings of type (a) and (b) appreciably differ from those of type (c), as a consequence of the overlaps of the different wavefunctions. For the types (a) and (b), the wavefunctions are tightly related to the LUMO of D_1 and HOMO of D_2, however, the HOMO is replaced by LUMO of D_2 for type (c).

From **Table 1**, we also find the obtained ET rates for type (a) are 10^{10}~10^{14} s^{-1}, which are much larger than that for D_2 to A (10^6 s^{-1}). In principle, such large ET rates between D_1 and D_2 can fulfill the goal of the proposed strategy. Furthermore, the ET for type (b) and (c) should be considered to suppress. Since the electronic coupling and reorganization energy are almost independent on the substituents of the present complexes, the ET rate should be dominantly determined by the exponential term of $(\Delta G + \lambda)^2/\lambda$, and as the result, the ET rate reaches maximum when ΔG equals $-\lambda$. Accordingly, the ET rate can be manipulated by ΔG easily, which relates to the MO energies. The further investigation manifests the LUMO energy of D_1 should be higher than the HOMO energy of D_2 with a reasonable value. For the present complexes, since the reorganization energy and the Coulomb interaction are around 0.2 eV and -0.3eV, respectively, it is expected that the energy of LUMO for D_1 should be about 0.5 eV higher than that of HOMO for D_2 according to our theoretical prediction. Otherwise, a too high LUMO energy of D_1 may induce it to be close to that of D_2, as a result, the rate for the type (c) can reach up to ~10^9 s^{-1} in the complex $D^{(1)}_1$ -D_2. On the contrary, a too small energy gap between LUMO of D_1 and HOMO of D_2 may cause a small $|\Delta G+\lambda|$ of type (b). For instance, the ET rate reaches up to ~10^7 s^{-1} in the $D^{(4)}_1$ -D_2 . Although the ET rates of types (b) and (c) are much lower than those of type (a) for all present complexes, those rates are still quite high compared to those from D_2 to A. These fast ET processes may destroy the generation of high open-circuit voltage.

Table 1: The electron transfer parameters and the corresponding rates.

complex	Type	λ (eV)	ΔG (eV)	V_{DA} (meV)	k_{et} (s^{-1})
$D_1^{(1)}$-D_2	(a)	0.28	-0.10	22.75	5.35×10^{12}
	(b)	0.36	0.60	21.88	2.37×10^{2}
	(c)	0.25	-0.86	359.6	2.43×10^{9}
$D_1^{(2)}$-D_2	(a)	0.27	0.12	17.72	4.36×10^{10}
	(b)	0.33	0.40	18.56	1.66×10^{6}
	(c)	0.21	-1.06	357.8	1.67×10^{1}
$D_1^{(3)}$-D_2	(a)	0.10	-0.17	64.62	1.38×10^{14}
	(b)	0.29	0.65	63.66	2.01×10^{1}
	(c)	0.17	-0.81	220.4	1.50×10^{5}
$D_1^{(4)}$-D_2	(a)	0.17	0.16	50.30	2.10×10^{11}
	(b)	0.35	0.39	51.40	2.01×10^{7}
	(c)	0.24	-1.07	357.3	3.84×10^{3}
D_2-A		0.21	-0.74	7.32	4.72×10^{6}

From above discussions, we find that the kinetic pathways are much different in the present four systems owing to the substituent effects. In $D^{(1)}_1$ -D_2-A, after both donors absorb the sun light, the excited electron in the LUMO of $D^{(1)}_1$ can easily shift to the HOMO of D_2 due to the large ET rate in the pathway (a). Subsequently, the other promoted electron in the LUMO of D_2 migrates to the LUMO of $D^{(1)}_1$ rather than to the LUMO of A because the ET rate in pathway (c) is bigger than that from D_2 to A. In this way, D_2 turns back to neutral ground state one and the excited $D^{(1)}_1$ may release the energy by fluorescence emission. Thus, it is not appropriate for a solar cell. For $D^{(2)}_1$ -D_2-A or $D^{(4)}_1$ -D_2-A, the excited electron can also transfer from LUMO of D_1 to the HOMO of D_2 along pathway (a), but the large ET rate in the pathway (b) induces the electron to iteratively transfer between LUMO of D_1 and the HOMO of D_2. Regardless of the influence of fluorescence, each of systems should generate a large V_{oc} because the electron and hole are separated on the HOMO of D_1 and LUMO of D_2, respectively. However, the experiment shows that the fluorescence lifetime is about 250 ps for P3HT[45], and this reciprocal value has the same order as the ET rates in the pathway (a). Therefore, in these two systems, some photoinduced excitons may annihilate by fluorescence leading to the low energy conversion. However, in $D^{(3)}_1$ -D_2-A, the ET rate for the pathway (a) is quite fast as compared to fluorescence emission, and meanwhile, the rate of ET from D_2 to A is also larger than that from D_2 to $D^{(3)}_1$. Therefore, this system should be a good candidate as a solar cell with a large open circuit voltage. Assuming the V_{oc} is dominantly determined by the energy difference of HOMO of $D^{(3)}_1$ and LUMO of D_2, we expect that the V_{oc} can reach up to 2.56 eV, which is about twice as large as those in the organic solar cells with a single polymer donor[11]. The working mechanisms of the solar cell $D^{(3)}_1$ -D_2-A is shown in **Figure 3**.

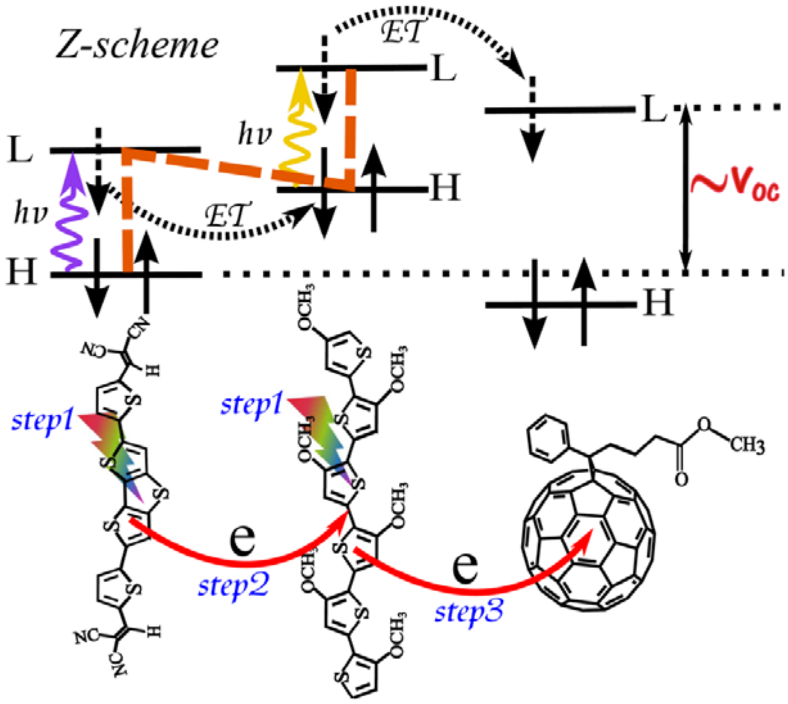

Figure 3: The working mechanisms of the Z-schematic organic solar cell $D^{(3)}_1$ -D_2-A.

4 Concluding remarks

In this communication, we have proposed a new strategy to design the organic solar cell with a high open-circuit voltage by using two donors. The strategy is similar to the Z-schematic mechanism in which both of donors are required to absorb sunlight step-by-step to generate the charge transfer with a high excitation energy. The possibility of this strategy has been demonstrated by DCV4TS/P3DOT/$PC_{61}BM$ three-layer sandwich organic solar cell. It is found that its open-circuit voltage may reach up to 2.56 eV, nearly twice higher than those in the conventional solar cells. Theoretical investigation shows that there are many complicated ET processes competing with each other in the Z-schematic D-D-A organic solar cells, and some intermolecular ET processes are harmful to the efficiency of the solar cell. Besides those ET processes, one has to consider other unfavorable processes, such as radiation annihilation of excitons, intersystem crossing, as well as ET from the LUMO of D_2 to the LUMO+1 of A or D_1. In addition, it may be also a challenge to experimentally construct the molecular arrangement to the requested three-layers D_1-D_2-A configuration due to the difficulty of technologies. However, the present model may open a possible way to design the organic solar cell with a high open circuit voltage.

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