

Molecular Understanding of How Interfacial Structure Impacts on Open-Circuit Voltage of Highly Crystalline Polymer Solar Cells

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Abstract:

Herein, we study the origin of difference in open-circuit voltage (V_{OC}) for polymer:fullerene solar cells employing highly crystalline conjugated polymers (PTzBT) based on the same thiophene–thiazolothiazole backbone with different side chains. By analyzing temperature dependence of V_{OC} and cyclic voltammogram, we find that the difference in V_{OC} originates in different cascaded energy structures for highest occupied molecular orbital (HOMO) levels in interfacial mixed phase. Furthermore, we find that this is due to the stabilization of HOMO caused by different branching of side chains on the basis of density functional theory calculation. Finally, we discuss the molecular design strategy based on side-chain engineering for ideal interfacial cascaded energy structures leading to higher V_{OC} and photocurrent simultaneously.

Introduction

Organic photovoltaics (OPVs) have attracted considerable attention as next generation energy sources because of their low cost, lightness in weight, and flexibility. Over the last three decades, a power conversion efficiency (PCE) of OPVs has increased significantly and recently exceeded 18%.^{1–5} Nonetheless, further improvement in PCE is demanded for practical application. One challenging issue is to improve the open-circuit voltage (V_{OC}) further.^{6,7} In OPV devices, V_{OC} is reported to be linearly dependent on the energy level offset, E_{DA} defined as the energy difference between electron donor highest occupied molecular orbital (HOMO) level (E_H) and electron acceptor lowest unoccupied molecular orbital (LUMO) level (E_L).^{8–11} Consequently, most studies have focused on developments of new materials with deeper E_H or shallower E_L to improve V_{OC} , which is the simplest design strategy for obtaining high V_{OC} . More properly, V_{OC} is dependent on the energy of charge transfer (CT) state, E_{CT} , formed at a donor/acceptor interface in blends. Recent studies have shown that interfacial molecular orientation has impact on E_{CT} and hence V_{OC} .^{12–14} In addition, minimization of the voltage loss is also important for improving V_{OC} . It has been reported that voltage losses due to radiative and nonradiative charge recombination are dependent on crystallinity of the materials.^{15,16} Very recently, it has also been reported that hybridization between highly emissive local excitation (LE) and CT states is the key to suppressing nonradiative recombination loss.^{17–19} As such, V_{OC} is dependent on various factors mentioned above and therefore it is difficult to predict V_{OC} on the basis of the simple design strategy using E_{DA} . Thus, it is highly required to understand the origin of V_{OC} even more.

On the other hand, there have been some interesting exceptions to the simple design rule mentioned above. Osaka *et al.* have reported highly efficient photovoltaic performances for polymer solar cells based on crystalline polymers with a thiophene–thiazolothiazole (TzBT) unit

in the main chain.²⁰ They synthesized a series of eleven polymers with different length and branching of side chains. A remarkable trend in V_{OC} was observed depending on the branching of side chains. Polymers with all-branched side chains gave V_{OC} of 0.88–0.90 V, whereas polymers with linear and branched side chains gave V_{OC} of 0.81–0.82 V even though they have the same backbone structure of TzBT and thus the same E_H of about -5.2 eV (evaluated by photoelectron yield spectroscopy (PYS)). Here, we focus on two representative polymers among them: PTzBT-BOHD with all-branched side chains (2-butyloctyl/BO and 2-hexyldecyl/HD) (Figure 1a) gave larger V_{OC} by 80 meV than PTzBT-12OD with linear and branched side chains (dodecyl/12 and 2-octyldodecyl/OD) (Figure 1b) while both polymers provided similar short-circuit current density (J_{SC}) and fill factor (FF) and thereby the all-branched one showed a higher efficiency. There would be two possible mechanisms for the difference in V_{OC} . One is that there would be a difference in E_{CT} between the two solar cells in spite of the same E_H in each neat film evaluated by the PYS measurement. The PYS is a technique sensitive not to the bulk but to the surface of a sample because the photoelectron attenuation length is a few nanometers as reported previously.²¹ The other is that there would be difference in the voltage loss due to charge recombination: radiative and/or nonradiative charge recombination loss would be different.^{6,19}

Herein, we study the origin of the difference in V_{OC} of polymer solar cells based on blends of highly crystalline polymers with different side chains (PTzBT-BOHD and PTzBT-12OD) and a fullerene derivative (PCBM) in order to discuss how branching of side chains impacts on V_{OC} of polymer solar cells. We measured the temperature dependence of V_{OC} and cyclic voltammetry of the devices while monitoring the absorption spectra simultaneously. As a result, we found that the interfacial effective bandgap (E_g^{eff}) between the two solar cells is different because of the difference in the HOMO levels of PTzBT polymers in disordered phases. More importantly, we

further study why the HOMO level is dependent on the branching position of the side chain in terms of the structure–property relationship. On the basis of quantum chemical calculation, we revealed that branching at the β position is essential for obtaining deep HOMO level while keeping high polymer crystallinity, thereby leading to large J_{SC} and V_{OC} simultaneously. As such, we propose a molecular design strategy based on side-chain engineering for developing highly efficient crystalline polymer solar cells with large J_{SC} as well as high V_{OC} .

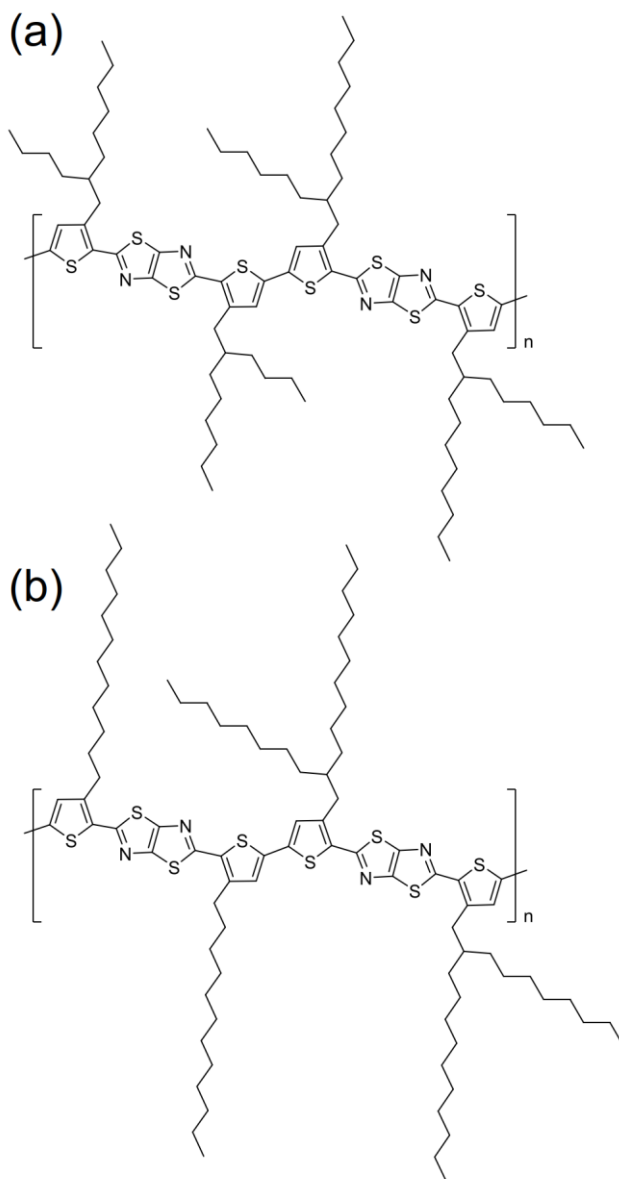


Figure 1. Chemical structures of (a) PTzBT-BOHD with all-branched side chains and (b) PTzBT-12OD with linear and branched side chains (BO = 2-butyl-octyl group, HD = 2-hexyl-dodecyl group, 12 = dodecyl group, OD = 2-octyl-dodecyl group).

2. Results and Discussion

2.1. Photovoltaic Performance

Figure 2 shows the current density–voltage (J – V) curves of PTzBT-BOHD/PCBM and PTzBT-12OD/PCBM solar cells with a conventional structure of ITO/PEDOT:PSS/polymer:PCBM/Ca/Al. As shown in the figure, J_{SC} was as large as $\sim 10 \text{ mA cm}^{-2}$ for both solar cells. This is consistent with almost the same absorption spectra of these two PTzBT polymers. The FF was also as high as 0.76 for both solar cells. This is because both PTzBT polymers are highly crystalline materials and hence exhibit high hole mobilities as reported previously.²⁰ On the other hand, there was a clear difference in V_{OC} between the two solar cells: it was 0.89 V for PTzBT-BOHD/PCBM and 0.81 V for PTzBT-12OD/PCBM solar cells. In addition, a similar difference in V_{OC} was also found for solar cells with an inverted structure (Figure S1). These V_{OC} s were well reproducible and thus statistically significant difference. This is not consistent with the same E_H of these two PTzBT neat films evaluated by PYS measurements (Figure S2). The photovoltaic parameters are summarized in Table 1, which are in good agreement with the results reported previously. As a result, PCE was also higher in PTzBT-BOHD/PCBM than in PTzBT-12OD/PCBM solar cells because of the larger V_{OC} . This finding suggests that even though similar polymers with the same backbone are employed, a higher V_{OC} can be obtained by careful selection of side chains. We will discuss how the difference in V_{OC} would be ascribed to the difference in E_{CT} state or to the difference in voltage losses due to radiative and/or nonradiative recombination.

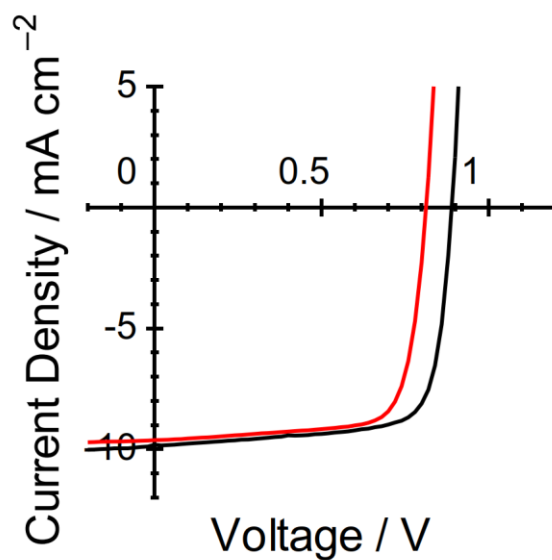


Figure 2. J - V curves of PTzBT-BOHD/PCBM (black line) and PTzBT-12OD/PCBM (red line) solar cells.

Table 1. Photovoltaic parameters of PTzBT/PCBM solar cells. The data in brackets are the average values and standard deviation acquired from at least ten independent devices.

Polymer	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	PCE [%]
PTzBT-BOHD	9.8	0.89	0.76	6.6
	(9.5 ± 0.2)	(0.88 ± 0.01)	(0.72 ± 0.02)	(6.1 ± 0.3)
PTzBT-12OD	9.6	0.81	0.76	5.9
	(9.2 ± 0.8)	(0.81 ± 0.004)	(0.71 ± 0.03)	(5.3 ± 0.6)

2.2. Energy of Interfacial Charge Transfer State

We first focus on the energy of the CT state formed at the donor/acceptor interface E_{CT} . As reported previously,^{22–26} the E_{CT} can be evaluated on the basis of the Marcus theory. For the CT state, the external quantum efficiency (EQE) and electroluminescence (EL) spectra are given by

$$EQE(E)E = \frac{f_A}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(E_{CT} + \lambda - E)^2}{4\lambda k_B T}\right) \quad (1)$$

$$\frac{EL(E)}{E} = \frac{f_E}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(E_{CT} - \lambda - E)^2}{4\lambda k_B T}\right) \quad (2)$$

where E is the photon energy, k_B is the Boltzmann's constant, T is the absolute temperature, λ is the reorganization energy, and f_A (f_E) is the coupling constant associated with the absorption (emission). Figure 3 shows the reduced EQE ($EQE(E)E$) and EL ($EL(E)/E$) spectra of the PTzBT/PCBM solar cells. The E_{CT} was evaluated to be 1.44 eV ($\lambda = 0.17$ eV) for PTzBT-BOHD/PCBM and 1.36 eV ($\lambda = 0.17$ eV) for PTzBT-12OD/PCBM solar cells from an intersection of two fitting curves based on Eqs 1 and 2 (Table 2). Thus, the difference in E_{CT} is 80 meV, which is in good agreement with the difference in V_{OC} (80 mV) as mentioned above.

We further measured the temperature dependence of V_{OC} to address the origin of the difference in V_{OC} . As reported previously,^{27–31} V_{OC} is expressed as

$$qV_{OC} = E_g^{\text{eff}} - k_B T \ln\left(\frac{N_0^2}{np}\right) \quad (3)$$

where q is the elementary charge, E_g^{eff} is the interfacial effective bandgap, N_0 is the effective density of electronic states, and n and p are the density of electrons and holes, respectively. Here, the first term E_g^{eff} is also a measure of E_{CT} , and the second term represents the charge recombination loss.²⁷ Thus, we can distinguish the origin of the difference in V_{OC} : if it is due to the difference in E_{CT} , the first term should be different while if it is due to the difference in charge

recombination losses, the second term should be different. The first term E_g^{eff} can be obtained as an intercept of the linear extrapolation of qV_{OC} at 0 K. Figure 4 shows the temperature dependence of qV_{OC} for each blend cell. In both systems, the V_{OC} increased linearly as the temperature decreased. Note that it was confirmed that the change in V_{OC} was negligibly small before and after the temperature-dependent measurement (Figure S6). As summarized in Table 2, E_g^{eff} was evaluated to be 1.27 eV for PTzBT-BOHD/PCBM and 1.18 eV for PTzBT-12OD/PCBM solar cells. The difference in E_g^{eff} is 90 meV, which is again close to the difference in V_{OC} (80 mV). We also measured the temperature dependence of EL spectra and evaluated the temperature dependence of E_{CT} . As reported previously, V_{OC} can be correlated to several parameters of CT states, and the linear extrapolation of V_{OC} at 0 K coincides that of E_{CT} .^{9,27,32} As shown in Figure 4, both linear extrapolations converge to the same energy for both blend systems, supporting the reliability of evaluation of E_{CT} . On the other hand, the temperature-dependent second terms in Eq 3 are similar, indicating that the charge recombination loss is similar for the blend systems. Note that light intensity dependent J - V measurement and transient photovoltage/photocurrent (TPV/TPC) measurement also indicated that the recombination loss is similar (Supporting Information). We thus conclude that the origin of the difference in V_{OC} is ascribed to the difference in E_{CT} between the two PTzBT/PCBM solar cells.

However, the result is seemingly inconsistent with the same E_{H} of the PTzBT neat films evaluated by PYS measurements. This is probably because PYS measurement would be sensitive to the electronic properties at the film surface where conjugated polymers are likely to be highly crystalline because of a larger free volume.³³ It is worth mentioning that V_{OC} should be dependent on the charge recombination at a donor/acceptor interface in the blend film. Recent studies have shown that there are three phases in blend films: pure phases of donor and acceptor materials and

an interfacial mixed phase of them.^{34–37} In this case, there would be a crystalline phase of PTzBT, aggregated phase of PCBM, and interfacial mixed phase of PTzBT and PCBM where PTzBT would be disordered. We will therefore discuss the E_H of disordered PTzBT polymers in the mixed phase as well as the E_H of ordered PTzBT polymers in the crystalline phase in the next section.

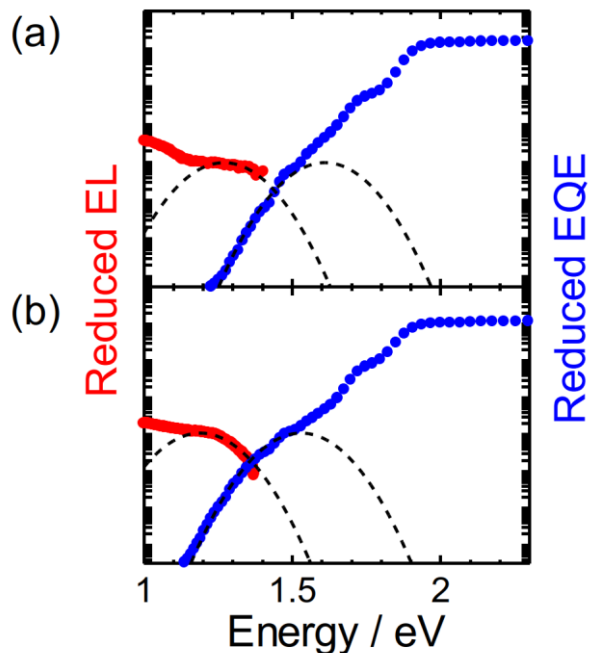


Figure 3. Reduced EQE (blue circles) and EL (red circles) spectra for (a) PTzBT-BOHD/PCBM and (b) PTzBT-12OD/PCBM solar cells. EL spectra are scaled to the height of the respective CT absorption band. The broken lines represent the fitting curves with Equations 1 and 2. The E_{CT} was evaluated from an intersection of the two fitting curves.

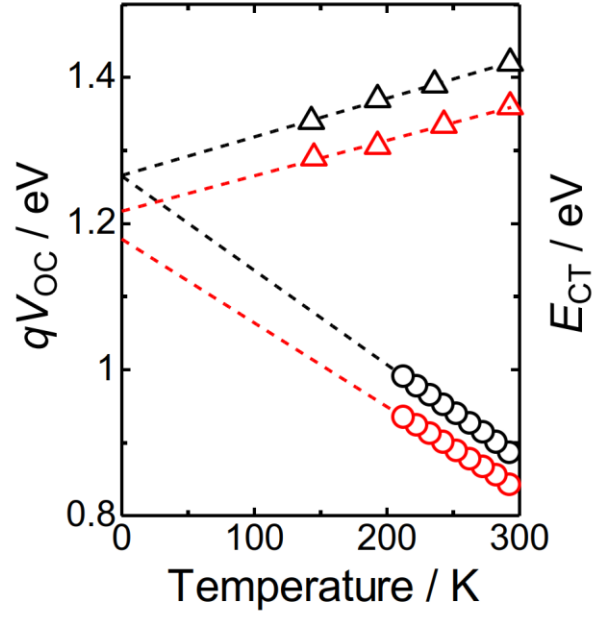


Figure 4. Temperature dependence of qV_{OC} (circles) and E_{CT} (triangles) of PTzBT-BOHD/PCBM (black line) and PTzBT-12OD/PCBM (redline) solar cells. The broken lines represent linear extrapolation of the plots.

Table 2. Energy of charge transfer state (E_{CT}) and interfacial effective bandgap (E_g^{eff}) of the solar cells.

Blend system	E_{CT} / eV	E_g^{eff} / eV	V_{OC} / V
PTzBT-BOHD/PCBM	1.44	1.27	0.89
PTzBT-12OD/PCBM	1.36	1.18	0.81

2.3. Energy Levels in Crystalline and Interfacial Mixed Phase

It was a challenging issue to evaluate the HOMO energies of mixed and crystalline domains in crystalline polymer films separately. Recently, McGhee *et al.* have reported that these energies can be evaluated by cyclic voltammetry separately and importantly can be assigned to each domain by in-situ absorption measurements.^{36,37} In accordance with this report, we thus evaluate the HOMO energies of mixed and crystalline domains in PTzBT/PCBM blend films. Figure 5a shows the cyclic voltammograms of the blend films. The lower axis is redox potential based on the Ag/Ag⁺ reference electrode. The upper axis is the energy level from the vacuum based on ferrocenium/ferrocene redox couple (Figure S9).³⁸ As shown in the figure, two peaks were observed on the forward scan. For the PTzBT-BOHD/PCBM blend film, the first peak was observed at around 0.48 V and the second peak was observed at around 0.75 V. For the PTzBT-12OD blend film, the first peak was observed at around 0.48 V and the second peak was observed at around 0.7 V.

To assign these peaks, we measured *in situ* absorption spectra of the films during the CV measurements. Figures S10a and S10b show the absorption spectra of the blend films at each applied voltage. For both blend films, the absorption in the visible region decreased with spectral broadening while a new broad absorption increased in the near-IR region. The new absorption is most likely ascribed to polymer polarons generated by the electrochemical oxidation of the film. Figures 5b and 5c show the normalized absorption change in the near-IR region for the first and second oxidation peaks shown in Figure 5a. During the first oxidation (0 – 0.6 V for PTzBT-BOHD/PCBM and 0 – 0.5 V for PTzBT-12OD/PCBM), two absorption peaks were found at around 700 and 1000 nm, which is consistent with the absorption spectrum of donor polarons measured by transient absorption spectroscopy for PTzBT-BOHD/PCBM.³⁹ This spectrum is also

similar to that of polymer polarons formed at an ordered phase as reported for blend films of crystalline regioregular poly(3-hexylthiophene) (RR-P3HT) and PCBM.⁴⁰ During the second oxidation (0.6 – 0.7 V for PTzBT-BOHD/PCBM and 0.5 – 0.65 V for PTzBT-12OD/PCBM), on the other hand, another absorption peak was found at around 800 nm. This spectrum is similar to that of polymer polarons formed at disordered phases as reported for blend films of amorphous regiorandom poly(3-hexylthiophene) (RRa-P3HT) and PCBM.⁴¹ This agreement is rational because PTzBT consists of thiophene units in the backbone structure as is the case for P3HT. Note that the peaks are not due to the generation of bipolarons because it is reported that bipolarons have broad absorption around 1600 nm for P3HT films.^{42–44} We therefore conclude that the first oxidation peak is ascribed to polymer polarons in the crystalline phase and the second oxidation peak is ascribed to polymer polarons in the interfacial amorphous phase.

The first oxidation peak was observed at around –5.2 eV for both blend films. This is in good agreement with the E_H evaluated by the PYS measurement, which is sensitive to the film surface and therefore mainly detects signals from a highly crystalline film surface. This agreement suggests that both polymers exhibit almost the same crystalline structures. Indeed, as shown in Figures S14 and Table S4, two-dimensional grazing incidence X-ray diffraction (2D-GIXD) measurements have shown that both blend films exhibit similar diffraction patterns and π -stacking distances.^{20,45} The lamellar distances were almost the same for each neat and blend films, suggesting that the intercalation of PCBM is negligible. In addition, no notable difference was found in absorption spectra and in AFM and TEM images of the blend films (Figures S15 and S16), suggesting that mixed and crystalline domains are similar for both blends. This is again consistent with both polymers exhibit almost the same crystalline structures with the same E_H .

A remarkable difference was observed for the second oxidation peak. However, the voltammogram peaks are so broad that it would be difficult to estimate the oxidation energy quantitatively. Instead, we thus use the onset voltage of the oxidation signals to discuss the difference in energy or voltage. The onset voltage was well reproducible and independent of voltage scan rate (Figure S11). As shown in Figure 5a, the onset for the second oxidation was found to be ~ 0.51 V for PTzBT-BOHD/PCBM and ~ 0.58 V for PTzBT-12OD/PCBM. The results indicate that whereas the E_{HS} for PTzBT-BOHD and -12OD are similar in the crystalline phase, the E_{HS} for the two polymers are different in the interfacial mixed phase as summarized in Figure 5d. Interestingly, the voltammogram of each polymer neat film showed almost the same oxidation peaks as blend films (Figure S12). In other words, the E_{H} in the crystalline phase is almost the same but the E_{H} in the amorphous phase is different between PTzBT-BOHD and PTzBT-12OD neat films. This suggests that the difference in E_{H} in interfacial mixed phase is not due to the difference in miscibility of polymer with fullerene. Instead, the difference in E_{H} reflects amorphous form of the polymer, which is inherent to each molecular structure. The difference in the E_{H} is evaluated to be ~ 70 meV from the second oxidations. On the other hand, no difference in the E_{L} of PCBM was found for both blend films (Figure S13). Thus, the difference between E_{H} of polymer and E_{L} of PCBM is calculated to be ~ 70 meV, which is close to the difference in E_{CT} and also V_{OC} of the solar cells. We therefore conclude that the difference in the V_{OC} is due to the difference in the E_{H} in the interfacial mixed phase. The origin of the different E_{H} will be discussed in the next section.

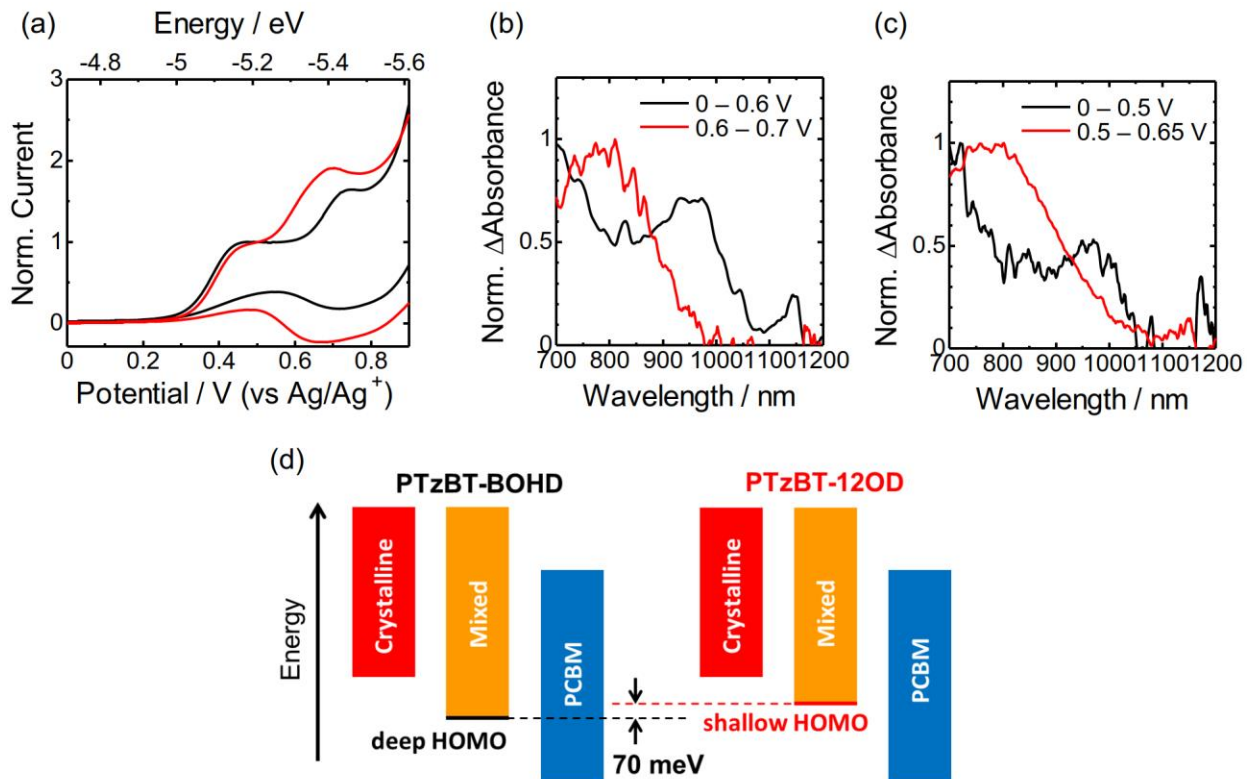


Figure 5. (a) Cyclic voltammograms of the PTzBT-BOHD/PCBM (black line) and PTzBT-12OD/PCBM (red line) blend films normalized at the first peaks on the forward scan. Normalized absorbance change in the near-IR region during (b) the first oxidation peak (0 – 0.6 V, black line) and the second oxidation peak (0.6 – 0.7 V, red line) for PTzBT-BOHD/PCBM and (c) the first oxidation peak (0 – 0.5 V, black line) and the second oxidation peak (0.5 – 0.65 V, red line) for PTzBT-12OD/PCBM blend films. (d) Schematic diagram of interfacial cascaded energy structure.

2.4. Origin of the Difference in the HOMO energy

To examine the origin of the difference in the E_H in interfacial mixed phase in terms of local molecular structures, we conducted DFT calculation (CAM-B3LYP/6-31G(d,p)) for monomer model compounds of the corresponding polymers. We optimized the molecular structures of each monomer unit to evaluate the E_H of them. First, we focus on the optimized molecular structures of the monomer model without side chains. As shown in Figure S17, the optimized molecular structure is completely planar: each conjugation unit in the main chain is aligned in the same plane. This structure gives an E_H of -6.497 eV. Such a planar structure is likely to be π - π stacked and hence would be ascribed to a molecular structure in crystalline domains. This value is different from the E_H of -5.2 eV experimentally obtained because it is calculated not for condensed solid state but for an isolated molecule under vacuum condition. We therefore will compare the relative values here. Next, we focus on the optimized molecular structures of the monomer models with side chains and discuss only the difference in energy among each model. As shown in Figure 6a, the monomer model for PTzBT-BOHD is more twisted than that for PTzBT-12OD because of larger steric hindrance of all-branched BOHD side chains than that of linear and branched 12OD side chains. As a result, the E_H calculated is -6.357 eV for PTzBT-BOHD, which is deeper than -6.285 eV for PTzBT-12OD. These twisted structures would be ascribed to polymer chains in disordered mixed phases. Indeed, the difference in E_H calculated is 72 meV, which is in good agreement with our observations of the difference in E_H obtained by the CV measurement and also the difference in V_{OC} of the solar cells.

We further calculated E_H for other different model structures to discuss how E_H is affected by the effect of π -conjugation plane in the main chain or by the electronic effect of side chains. First, we focus on the effect of the π -conjugation plane in the main chain. To eliminate the electronic

effect of side chains, the optimized structures of the model compounds for both the polymers as shown above were fixed and then all the side chains were replaced with the hydrogen atom. Subsequently, a single point energy calculation was conducted for the modified model compounds where the backbone structure is unchanged. The resulting E_H decreased from -6.357 to -6.529 eV for PTzBT-BOHD and from -6.285 to -6.504 eV for PTzBT-12OD. As a result, the difference in E_H is as small as 25 meV, which is only the one third of the total difference in E_H (72 meV). In other words, the difference in E_H is ascribed partially to the effect of π -conjugation plane in main chain but rather mainly to the electronic effect of side chains.

We next focus on the electronic effect of side chains to discuss how two different side chains of BOHD and 12OD contribute to the difference in E_H . As shown in Figures 6c and 6d, the dihedral angle between the main chain and the branched side chain is $\sim 70^\circ$ for PTzBT-BOHD and the dihedral angle between the main chain and the linear side chain is $\sim 0^\circ$ for PTzBT-12OD. The larger dihedral angle probably originates in the larger steric hindrance caused by the branched side chain of PTzBT-BOHD. Such a difference would have an impact on the $\text{CH}\cdots\text{S}$ interaction between an antibonding σ^* orbital of C-H in the side chain and a nonbonding n orbital of the sulfur atom in the thiazolothiazole ring.^{46,47} As reported previously,⁴⁸⁻⁵¹ the $\text{CH}\cdots\text{S}$ interaction is a kind of hydrogen bond, which could have impact on molecular properties such as conformation of molecules and structure of molecular assembly. To compare the σ^*-n interaction, we performed natural bond orbital (NBO) analysis.⁵² Figures 6e and 6f show NBOs of a nonbonding n orbital of the sulfur atom and an antibonding σ^* orbital of a C-H bond in the position indicated by broken lines in panels (a) and (b). For PTzBT-BOHD with a large dihedral angle, one of CH bonds is directed toward the sulfur atom. On the other hand, for PTzBT-12OD with a negligibly small dihedral angle, no CH bonds are directed toward the sulfur atom. As a result, the second order

perturbation energies (E_2) for the orbital overlap between CH group and sulfur atom is as large as 2.76 kcal mol⁻¹ for PTzBT-BOHD but as small as 0.5 kcal mol⁻¹ for PTzBT-12OD. In other words, the larger interaction would stabilize the HOMO of the molecule, which is consistent with deeper E_H for PTzBT-BOHD.

We further examine how the branching position of side chains affects E_H on the basis of DFT calculation of modified monomer models. Here, we focus on three different PTzBT-12OD derivatives where the branching position of the branched group is systematically altered. More specifically, as shown in Figures 7a–c, the octyl branch is attached to the α -, β -, and γ -position of dodecyl chain referred to as PTzBT-12OD- α , PTzBT-12OD- β (same as PTzBT-12OD), and PTzBT-12OD- γ , respectively. We conducted the same calculation on these models and separated the effect of π -conjugation plane in the main chain and the electronic effect of side chains as described before. As shown in the figures, PTzBT-12OD- γ exhibited a negligibly small dihedral angle and hence most planar conjugated plane in the main chain, and also negligibly small second-order perturbation energy. We therefore consider the E_H of PTzBT-12OD- γ as a standard and discuss the difference from it. The E_H obtained is summarized in Figure 8. The broken line represents the E_H of PTzBT-12OD- γ . The red and blue bars represent the stabilization energy due to the main chain and the side chain, respectively, from the standard. The effect of the main chain makes E_H deeper with the branching point getting closer to the main chain. This is because branching near the main chain causes large steric hindrance and thus largely twisted main chain, as shown in Figures S18a–S18c. The effect of the side chain is the largest for PTzBT-12OD- β and the smallest for PTzBT-12OD- γ , which are consistent with the CH $\cdots$ S interaction evaluated by the NBO analysis as shown in Figures 7d–f: The E_2 is 1.17 kcal mol⁻¹ for PTzBT-12OD- α , 2.47 kcal mol⁻¹ for PTzBT-12OD- β , and less than 0.5 kcal mol⁻¹ for PTzBT-12OD- γ . As a result, the overall

E_H is the deepest for PTzBT-12OD- α , which is deeper by only 8 meV than that of PTzBT-12OD- β , and the shallowest for PTzBT-12OD- γ . We should note that such twisted backbones in PTzBT-12OD- α would give large V_{OC} but would disturb the intermolecular packing of polymer chains and hence would cause lower crystallinity. We therefore conclude that branching at the β position is suitable for realizing both deep E_H and high crystallinity.

Finally, we note that the cascaded energy structure shown in Figure 5d would be ideal for efficient crystalline polymer solar cells with higher J_{SC} , FF and V_{OC} . In such an energy structure, hole carriers are energetically more stable in the polymer crystalline phase than in the mixed phase and hence will be spatially separated from the interface, which could suppress charge recombination with electron carriers. Recently, McGehee *et al.* have shown by simulations that the presence of mixed phase and local high mobility of charge carriers plays a crucial role for 90% field-independent internal quantum efficiency,⁵³ high FF,⁵⁴ and suppressed charge recombination.²⁴ They also pointed out that V_{OC} remains the same in the presence or absence of cascaded energy structures with the same E_{CT} because it is dependent on E_{CT} at the interface. These findings suggest that a cascaded energy structure consisting of the mixed phase with deep E_{CT} and the polymer pure phase with high crystallinity is ideal for highly efficient OPVs. In PTzBT-BOHD/PCBM and PTzBT-12OD/PCBM blend systems, the energy cascade is formed at the interface in both blends and crystallinity of polymers are similarly high, resulting in similarly high J_{SC} s and FFs. On the other hand, E_{CT} was larger in PTzBT-BOHD/PCBM with deeper E_H in the mixed phase, leading to higher V_{OC} . We therefore conclude that the cascaded energy structure in PTzBT-BOHD/PCBM blends is ideal for obtaining higher V_{OC} while keeping high J_{SC} and FF as well, which can be designed by side-chain engineering of branching position. Previous studies have reported that higher V_{OC} was obtained by employing polymers with branched side chains.^{55–}

⁶⁰ In some cases, however, significant change in polymer ordering structure or decrease in other device parameters such as J_{SC} or FF have been observed. The reason why such structural changes have not been observed for PTzBT polymers would be that the polymer has highly planar backbone and therefore large intermolecular interaction. Therefore, it would be important to design high planarity of backbone and moderately branched side chain. This is an effective and simple strategy for improving all photovoltaic parameters at the same time in highly crystalline polymer solar cells.

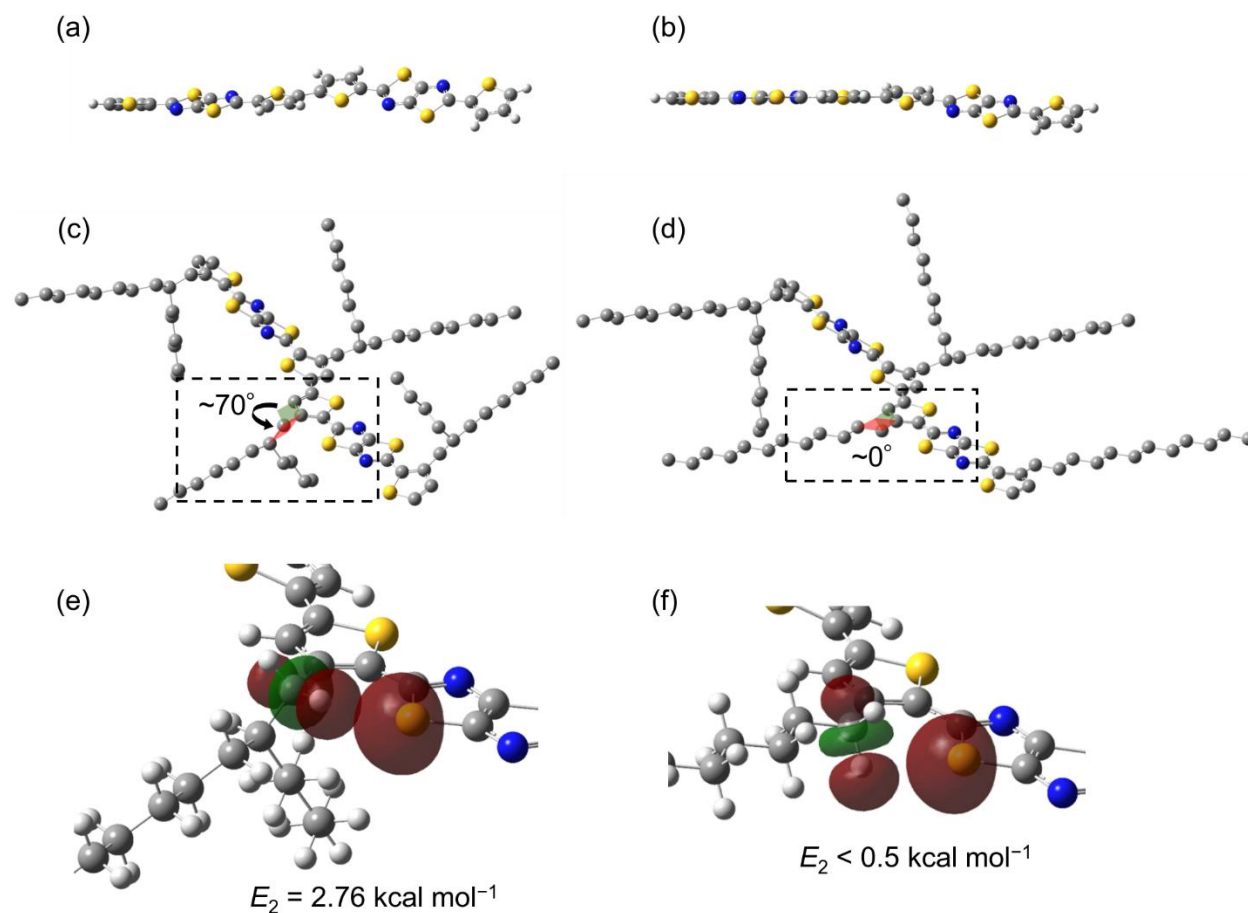


Figure 6. Side view of main chain geometry of monomer unit for (a) PTzBT-BOHD and (b) PTzBT-12OD. PTzBT-BOHD and PTzBT-12OD were optimized with respective side chains and then the side chains were replaced with a hydrogen atom. Optimized geometry of monomer unit of (c) PTzBT-BOHD and (d) PTzBT-12OD. The hydrogen atoms are omitted. (e), (f) Natural bond orbitals involved in the CH...S interaction: a nonbonding n orbital of the sulfur atom and antibonding σ^* orbital of the C-H bond in the position is indicated by broken lines in panel (c) and (d), respectively. The second order perturbation energies (E_2) for the orbital overlap are also shown.

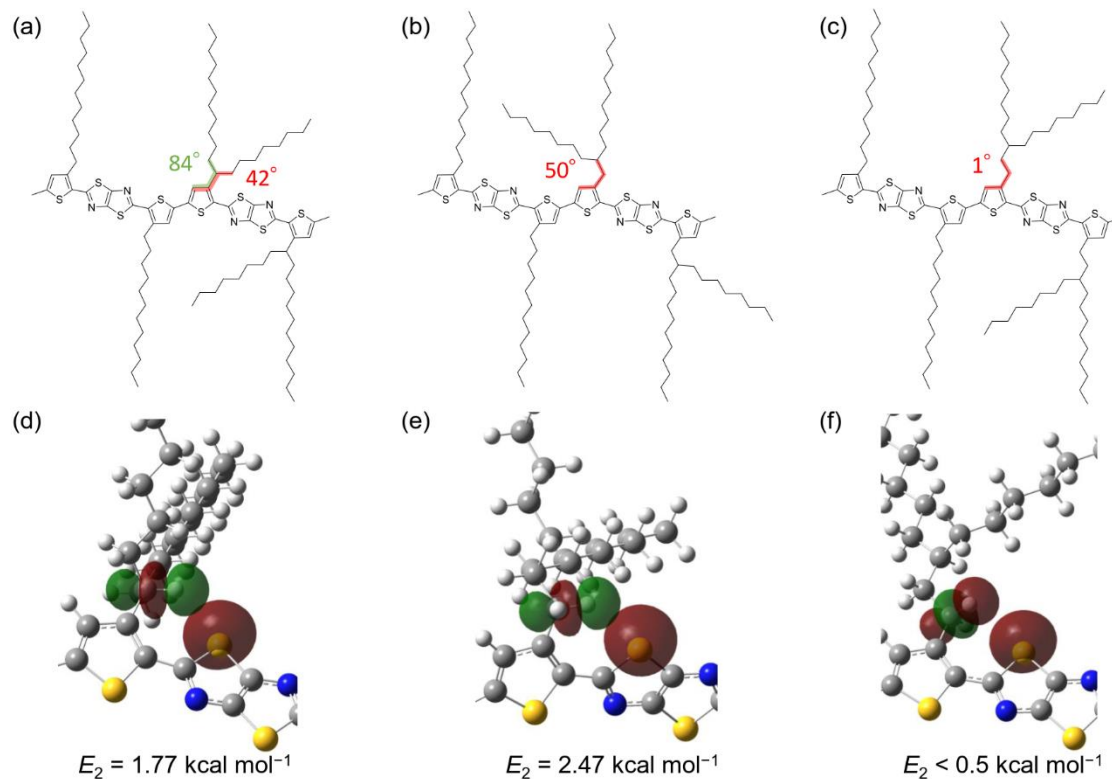


Figure 7. Chemical structures of (a) PTzBT-12OD- α , (b) PTzBT-12OD- β , and (c) PTzBT-12OD- γ . The dihedral angle of the side chains determined by DFT calculation is also shown. Natural bond orbitals involved in the CH $\cdots$ S interaction and E_2 for the orbital overlap of the monomer unit of (d) PTzBT-12OD- α , (e) PTzBT-12OD- β , and (f) PTzBT-12OD- γ .

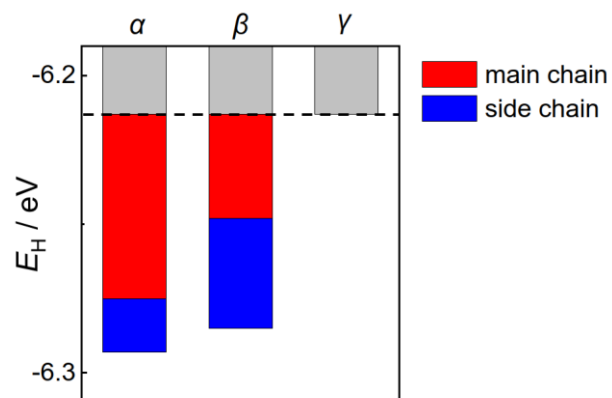


Figure 8. E_H of the optimized structure of the modified monomer models. The E_H of PTzBT-12OD- γ is shown as a broken line, and the difference from that was divided into the effect of π -conjugation plane in the main chain (red bar) and the electronic effect of side chains (blue bar).

3. Conclusion

In this study, we discussed the origin of the 80-mV difference in V_{OC} of the solar cells employing PTzBT-BOHD and PTzBT-12OD, which have different side chains. The interfacial effective bandgap was evaluated from the temperature dependence of V_{OC} . It was found that the origin of the difference in V_{OC} is caused by the difference in E_{CT} in blend films. Then, the HOMO levels were evaluated for crystalline and interfacial mixed phase separately by the CV measurement of the blend films. As a result, it was found that the HOMO levels in the crystalline phase are identical whereas the HOMO levels in the interfacial mixed phase differ by 70 meV, which is close to the difference in V_{OC} . In order to address the origin of the different HOMO energy, we further studied local molecular structures of the polymers by DFT calculation. The calculation indicated that one third of the difference in HOMO levels is caused by twisting of the main chain induced by steric hindrance of side chains. On the other hand, two thirds of the difference is caused by the electronic effect of the side chains due to the difference in dihedral angle between the main chain and side chain. We thus ascribed the larger V_{OC} in PTzBT-BOHD based cells to the deeper HOMO levels in the interfacial mixed phase caused by the different branching position of side chains in PTzBT-BOHD. Of particular importance is to realize not only a deeper HOMO level in disordered polymer domains but also shallower HOMO level in highly crystalline polymer domains simultaneously. This cascaded energy structure is beneficial for highly efficient polymer solar cells with high V_{OC} as well as high J_{SC} and FF. We therefore propose that such an ideal cascaded energy structure can be designed by the side-chain engineering of conjugated polymers.

4. Experimental Section

Materials. PTzBT-BOHD/12OD were synthesized according to the reported procedure.²⁰ PCBM was purchased from Frontier Carbon.

Device fabrication. Indium–tin–oxide (ITO) substrates were cleaned by ultrasonication in toluene, acetone, and ethanol each for 15 min, dried with a nitrogen gas flow, and cleaned with a UV–ozone cleaner. A transparent conductive layer of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS; H. C. Starck, PH500) was spin-coated on the ITO substrate, which was annealed at 140 °C for 10 min in air. Subsequently, a photoactive layer was spin-coated from a chlorobenzene solution containing 2.5 g L⁻¹ of the polymer and PCBM with the 1:2 ratio at 600 rpm for 20 s. Finally, a metal electrode of Ca(10 nm)/Al(70 nm) was thermally deposited on top of the active layer under vacuum at $\sim 10^{-4}$ Pa.

Measurements. The E_H of the polymers was measured with a photoelectron yield spectrometer (Riken Keiki, AC-3). The current density–voltage (J – V) characteristics were measured with a source meter (Keithley, 2611B) in the dark and under AM1.5G simulated solar illumination at 100 mW cm⁻². The light intensity was calibrated using a standard cell for amorphous Si solar cells (Bunkokeiki, BS-520). Temperature dependence of the J – V characteristics was measured with a DC voltage and current source/monitor (Advantest, R6243) in a vacuum prober system (ALS Technology, VPS3-50) under the illumination from a 100 W Xe lamp (Asahi Spectra, LAX-C100) equipped with a uniform illumination lens unit (Asahi Spectra, RLQL80-0.5). Cyclic voltammetry (CV) measurements were performed using a potentiostat/galvanostat (Princeton Applied Research, model 273A) in an Ar-bubbled acetonitrile solution containing 0.1 M of tetrabutylammonium tetrafluoroborate as a supporting electrolyte with an Ag/AgCl wire as a reference electrode and a Pt mesh as a counter electrode. In situ absorption spectra were measured using a

spectrophotometer (Hitachi, U-4100). To minimize the effect of absorption change during the measurement, the wavelength scan rate was set to 1200–1500 nm min⁻¹ while the voltage scan rate of CV measurements was set to 1 mV s⁻¹ during the measurements. DFT calculations were conducted using Gaussian 09 software.⁶¹ Calculations were carried out at the CAM-B3LYP level of theory with the basis set 6-31G(d,p). Natural bond orbital (NBO) analysis were performed using NBO 3.1 program as implemented in Gaussian 09.⁶²

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

J – V characteristics of solar cells with an inverted structure, photoelectron yield spectra, electroluminescence spectra, temperature dependence of J – V curves, light intensity dependent J – V measurements, transient photovoltage (TPV) and transient photocurrent (TPC) measurement, CV measurement, two-dimensional grazing incidence wide-angle X-ray diffraction patterns, DFT calculation for a trimer of the polymers.

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Notes

The authors declare no competing financial interest.

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