Supporting Information for

Effects of End-On Oriented Polymer Chains at the Donor/Acceptor Interface in Organic Solar Cells

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Section S1. Surface segregation behavior of P3DDFT and P3BT-F₁₇ in P3HT films

The surface segregation behavior of P3DDFT and P3BT-F₁₇ in P3HT films was investigated by X-ray photoelectron spectroscopy (XPS) (Figure S1). P3DDFT/P3HT films were prepared from the mixed solution of P3DDFT and P3HT with a fixed total polymer concentration of 7.6 mg mL⁻¹ and various component ratios to obtain similar film thicknesses. Figure S1a shows the surface F/C atomic ratios determined by the peak intensities of F 1s and the non-fluorinated C 1s in XPS as a function of the P3DDFT concentration in solution. A surface-segregated monolayer (SSM) of P3DDFT with a high surface coverage was formed on top of the P3HT film with an F/C atomic ratio (0.37) similar to that in previous reports at the optimized concentrations of P3DDFT (0.6 mg mL⁻¹) and P3HT (7 mg mL⁻¹).¹⁻³ P3BT-F₁₇/P3HT films were prepared by spin-coating from mixed solutions of P3HT with a fixed concentration (5 mg mL⁻¹) and P3BT-F₁₇ with various concentrations (0–5 mg mL⁻¹). Figure S1b shows the F/C atomic ratios as a function of the P3BT- F_{17} concentration in the solution. A SSM of P3BT- F_{17} with a high surface coverage was formed on top of the P3HT film with an F/C atomic ratio (0.27) similar to that in previous reports at the optimized concentrations of P3BT- F_{17} (2.6 mg mL⁻¹) and P3HT (5 mg mL⁻¹).³⁻⁴ These results indicate that the coverages of P3DDFT and P3BT- F_{17} on the surface of the

P3HT films were over 95% according to an idealized bilayer model analysis.⁵ Therefore, P3HT (7.6 mg mL⁻¹), P3DDFT (0.6 mg mL⁻¹)/P3HT (7 mg mL⁻¹), and P3BT-F₁₇ (2.6 mg mL⁻¹)/P3HT (5 mg mL⁻¹) films were used for the subsequent experiments.



Figure S1. Surface F/C atomic ratios of (a) P3DDFT/P3HT and (b) P3BT- F_{17} /P3HT films measured by XPS plotted against the concentrations of the semifluoroalkyl polymers in the solutions. The concentrations used for subsequent experiments are indicated by the green arrows.



Figure S2. X-ray reflectivity of P3HT (orange), P3DDFT/P3HT (blue) and P3BT-

 F_{17} /P3HT (red) films on a Si substrate. The calculated thicknesses are 66, 63, and 65 nm,

respectively. Fitting curves are shown as black dotted lines.



Figure S3. Atomic force microscopy height images of (a) P3HT (arithmetic mean roughness (R_a) = 1.44 nm), (b) P3DDFT/P3HT (R_a = 1.83 nm), and (c) P3BT-F₁₇/P3HT (R_a = 1.39 nm).



Figure S4. (a) Molecular orbitals (MOs) and (b) density-of-state (DOS) spectrum calculated for the regioregular decamer of 3-methylthiophene. The first four to five MOs from the HOMO contribute to the broad first peak and the next 11 MOs to the 2nd peak in the DOS spectrum. The structure is optimized at the B3LYP/6-31G(d) level (Gaussian16). The DOS spectrum is simulated with the full-width-half-maximum of 0.54 eV for each MO.

Section S2. Evaluation of the EAs of the polymer films by LEIPS

Figures S5a–c show the LEIPS spectra of P3HT, P3DDFT/P3HT, and P3BT- F_{17} /P3HT films measured at three photoemission energies. To determine the EAs of the polymer films accurately, the onsets of the LEIPS spectra were plotted as electron kinetic energy as a function of photon energy (Figure S5d). The EAs of the films were extracted from the intercept with the *x*-axis, where the electron kinetic energy is zero, of the linear regression with a slope of unity. The EAs are shown in Figure S5d and summarized in the main text.



Figure S5. LEIPS profiles measured at different photon energies for (a) P3HT, (b) P3DDFT/P3HT, and (c) P3BT- F_{17} /P3HT films. The arrows indicate the onsets of the spectra. (d) Onset of the electron kinetic energy plotted against the photon energy. The solid lines are the linear regressions with a slope of unity and the intercepts with the *x*-axis give the EAs of the films.

Section S3. Detailed discussion of orientation-dependent electronic structures

The differences in the electronic structures between P3DDFT/P3HT and P3BT- F_{17} /P3HT in Figure 3 can be divided into three main factors, the effects of which are discussed below.

1) Electronic induction effects of semifluoroalkyl chains

The introduction of the semifluoroalkyl chains pull the electrons from the π -conjugated main chains, which may deepen the HOMO and LUMO of the polymers. For P3DDFT, we previously used cyclic voltammetry to estimate this effect as +0.17 eV, which can be regarded as a molecular property.⁶ In the UPS spectra of P3DDFT/P3HT films, however, P3DDFT forms a monolayer with a thickness of about 0.8 nm, which is thinner than the detection depth of UPS (3–6 nm). Because the HOMO energy of P3DDFT is deeper than that of P3HT, the HOMO peak of P3DDFT overlaps with the broad HOMO-derived feature of P3HT underneath and the Fermi-edge onset is determined by the HOMO-edge of P3HT. Therefore, we conclude that the electronic induction effects of the side chain on the IE estimation can be omitted from the discussion on the electronic structure of P3DDFT/P3HT film. For P3BT-F₁₇, we performed DFT calculations on the 10mer of 3-alkylthiophene with and without the semifluoroalkyl chain at one end. The results show that the induction effect is small; the difference in HOMO energy with and without the terminal semifluoroalkyl chain is only +0.05 eV. This small effect is reasonable because only one semifluoroalkyl chain is attached to the oligomer end, and this effect would be even smaller for the P3BT- F_{17} polymer. Based on these results, we neglected the induction effect and assumed that the HOMO and LUMO energies of P3DDFT and P3BT- F_{17} isolated molecules are the same as those of P3HT.

2) Surface dipole effects of semifluoroalkyl chains

We assumed that the shifts in the vacuum levels (Δ) in P3DDFT/P3HT and P3BT-F₁₇/P3HT from P3HT are solely ascribed to the change in the surface dipole layer. In principle, both the density and the orientation of the fluoroalkyl chains can affect Δ . To verify this hypothesis, we performed UPS on P3DDFT/P3HT and P3BT-F₁₇/P3HT films with various concentrations of the semifluoroalkyl polymers in solution (Figures S6a and b). Δ was plotted against the semifluoroalkyl polymer concentration (Figures S6c and d). P3DDFT/P3HT and P3BT-F₁₇/P3HT showed a linear increase in Δ up to 0.6 and 2.6 mg mL⁻¹, respectively, and saturation of Δ above those concentrations, which is the same behavior as the surface F/C atomic ratios (Figure S1). This indicates that only the surface coverage of the semifluoroalkyl chains affects Δ and the surface dipole effect can be discussed separately from the other factors.

3) Electrostatic effects of molecular orientations

The rigid shift of IE and EA observed for the P3BT- F_{17} /P3HT film can be explained by the change in the polarization energy induced by the end-on orientation, as discussed in the main text. To support this result further, we plotted the binding energy onset relative to $E_{\rm F}$ (i.e., HOMO edge) against the semifluoroalkyl polymer concentration for P3DDFT/P3HT and P3BT-F₁₇/P3HT films (Figures S6e and f). P3DDFT/P3HT showed almost no dependence of the binding energy onset on the concentration, reflecting no change in the molecular orientation from the P3HT film. This produced the same dependence of the IE on the concentration as that of Δ (Figure S6g). In striking contrast, P3BT-F₁₇/P3HT showed an abrupt shift of the binding energy onset at a concentration of 1.0 mg mL⁻¹ and gradual saturation above that (Figure S6f). We performed XRD on the same films to investigate the change of the film structures. P3BT-F₁₇/P3HT showed a drastic change in the crystalline structure at a concentration of 1.0 mg mL⁻¹ (Figure S7). The lamellar peak intensity of P3HT at 5.6° in the out-of-plane direction decreased to about the half of that in the pristine P3HT film (Figure S7b). This result suggests that even a small amount of P3BT- F_{17} on the surface (about 1/3 of the maximum coverage) can dramatically change the orientation of the surrounding P3HT molecules from the edge-on to end-on orientations. This could explain the abrupt shift of the binding energy at a low concentration, given that the change of the

polymer orientation affects the polarization energy. At higher P3BT-F₁₇ concentrations, the diffraction peak intensties of P3HT in the out-of-plane direction changed more gradually (Figure S7b) and the peak for crystalline P3BT-F₁₇ at the surface appeared at 6.6° in the inplane direction (Figure S7a). The simultaneous change in the surface diople moment and polarization energy resulted in the complicated dependence of the IE of P3BT-F₁₇/P3HT films on the P3BT-F₁₇ concentration (Figure S6h).

We also calculated electrostatic potentials generated by the quadrupole moments of the oligothiophene using a model (see Section S4 for details).⁷ The potentials for the end-on and face-on orientations showed upward and downward rigid energy shifts, respectively, relative to that for the edge-on orientation. This result qualitatively agrees with our observations for P3BT-F₁₇/P3HT in the present study and previous studies of face-on oriented P3HT films.⁸⁻⁹ Furthermore, the model confirmed that the quadrupole moments generated no surface dipole layer, indicating that the orientations of the polymer backbone affected only the energy levels and not the vacuum levels.



Figure S6. UPS spectra in Fermi-edge and cut-off regions (insets) of (a) P3DDFT/P3HT films and (b) P3BT-F₁₇/P3HT films with various semifluoroalkyl polymer

concentrations in the spin-coating solution. Vacuum level shift (Δ), the binding energy onset relative to $E_{\rm F}$ and IEs of the (c, e, and g) P3DDFT/P3HT and (d, f, and h) P3BT-F₁₇/P3HT films plotted as a function of the semifluoroalkyl polymer concentration in solution.



Figure S7. (a) In-plane and (b) out-of-plane XRD patterns of P3BT- F_{17} /P3HT films with the P3HT concentration fixed at 5 mg mL⁻¹ and P3BT- F_{17} concentration of 0 to 5 mg mL⁻¹

1.

Section S4. Electrostatic energy calculation from charge-quadrupole interaction

To discuss the orientation-dependent energy level, we calculated the electrostatic potential formed by permanent quadrupoles of bithiophene units in a disk cluster with thickness *t* and diameter *d* (Figure S8). The cartesian coordinate was defined as in the figure with the origin at the center of the disk cluster. The potential energy *U* was calculated by $U = e/(4\pi\varepsilon_0 r^5)\sum r \mathbf{qr}$, where *e* and ε_0 are the elementary charge and the permittivity of vacuum, respectively, and the sum runs over molecular positions *r* with respect to the charge. Quadrupole tensor *Q* of bithiophene was calculated by DFT at the B3LYP/6-311+G(d,p) level to be $Q_{xx} = 8.22$, $Q_{yy} = 1.43$, $Q_{zz} = -9.64$, $Q_{xy} = Q_{yx} = -1.61$, and $Q_{xz} = Q_{zx} = Q_{yz} = Q_{zy} = 0.00$ Debye Å.

Figure S9 shows the potential maps for the clusters with t = 10 nm and d = 50 nm. The calculated potentials inside the cluster were almost uniform and depended on the molecular orientation. The potentials were -1.22, -1.06, and -0.81 eV for the end-on, edge-on, and face-on orientations, respectively. These values agree qualitatively with the results in this study and in previous reports.⁸⁻⁹

Figure S10 shows the electrostatic potentials along the *y*-axes for the cluster with d = 50 nm and various *t*. As the thickness of the cluster increased to the aspect ratio t/d = 1, the potentials

at the center of the cluster (y = 0) approached the common value of -1.03 eV. This trend is similar to the previous report.⁷ However, the potentials at the surface region were deeper than, similar to, or shallower than the common value for the end-on, edge-on, and face-on orientations, respectively, for all thicknesses. Therefore, the potential of the surface region depended on the orientation of the polymer backbone regardless of the film thickness. No dipole layers arising from the discontinuity of the permanent quadrupoles were formed at the surface, indicating that interfacial molecular dipole moment and quadrupole moment of the polythiophenes independently affected the energy level alignments.



Figure S8. Structural model for the electrostatic potential calculation. The unit cell contains two thiophenes with permanent dipoles that cancel each other. The film is simplified to a disc cluster with thickness t and diameter d.



Figure S9. Potential maps calculated for oligothiophene clusters with t = 10 nm and d = 50 nm and (a) end-on, (b) edge-on, and (c) the face-on orientations.



Figure S10. Cross-sectional potential energy along the *y*-axis for clusters with (a) end-on,(b) edge-on, and (c) face-on orientations. *t* is changed from 4 to 50 nm, whereas *d* is fixed at 50 nm.



Figure S11. UPS spectra of PCBM (orange), PCBM//P3DDFT/P3HT (blue), and PCBM//P3BT- F_{17} /P3HT (red) films in cut-off and Fermi-edge regions. The films were prepared on ITO substrates and irradiated with He(I) with a photon energy of 21.2 eV.

Section S5. Numerical electrostatic simulation of energy level alignment in PHJs

Numerical electrostatic simulations for the bilayer films were performed based on the model proposed by Oehzelt et al.¹⁰ HOMO and LUMO are assumed to be a gaussian function with σ of 0.23 eV (determined by fitting UPS spectra) and spin degeneracy of 2. The centers of the gaussians (E_{HOMO} and E_{LUMO}) are chosen to reproduce the experimental IE and EA by assuming the relationships IE = $|E_{HOMO}+2\sigma|$ and EA = $|E_{LUMO}-2\sigma|$. The thicknesses of the polymer layers are set to values similar to those of the samples for UPS measurements. The parameters used for the calculation are summarized in Table S1. The surface dipole layers of the semifluoroalkyl chains in P3DDFT and P3BT-F₁₇ are simulated with a molecular dipole layer of fixed charge pairs with a thickness of 1 nm and a dielectric constant ε_r of 3.0. The size and the density of the molecular dipole are set to 1.75 Debye and $3.3 \times 10^{18} \text{ m}^{-2}$, respectively, based on DFT calculation and material density.¹ The work function of ITO is set to 4.54 eV, measured by UPS. The discretization size of the matrix is 1 nm. The electrostatic potential and the charge densities are obtained by solving the Poisson equation in PHJ structures numerically according to a standard iteration procedure. The results are summarized and shown in Figure S12 and Table S2.

	$E_{\rm F}({\rm eV})$	$E_{\rm HOMO}~({\rm eV})$	$E_{\rm LUMO}({\rm eV})$	<i>E</i> r	N (m ⁻³)	Surface dipole
PCBM	-4.45	-6.41	-3.30	3.9	1.11 × 10 ²⁷	No
РЗНТ	-3.45	-5.16	-1.78	3.0	4.76×10^{27}	No
P3DDFT	-3.45	-5.16	-1.78	3.0	4.76×10^{27}	Yes
P3BT-	-3.45	-4.66	-1.28	3.0	4.76×10^{27}	Yes
F ₁₇						

 Table S1. Materials parameters used for the numerical calculations.



Figure S12. Schematic of the bilayer structures (top), calculated energy diagrams (middle), and charge density distributions (bottom) for (a) ITO/PCBM//P3DDFT/P3HT and (b) ITO/PCBM//P3BT-F₁₇/P3HT.

Table S2. Summary of the observed and calculated electronic structures at the surfaces of

 the PHJ films.

	$\Delta^{a} (\mathrm{eV})$		IE (eV)		$IE - E_F (eV)$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
PCBM//P3DDFT/P3HT	0.85	0.73	4.79	4.70 ^b	1.10	0.89
PCBM//P3BT-F ₁₇ /P3HT	0.85	0.88	4.78	4.70 ^b	1.09	1.04

^{*a*} Vacuum level shift from ITO/PCBM sample. ^{*b*} Input parameter for the calculation.



Figure S13. Temperature dependence of V_{OC} for the PHJ devices PCBM//P3DDFT/P3HT (blue) and PCBM//P3BT-F₁₇/P3HT (red) under white LED light irradiation. The lines show the best linear fittings for the data. E_{CT} was obtained from the extrapolation of V_{OC} to 0 K.

Section S6. DFT calculations of the CT state and charge binding energy based on model interfaces

To isolate the orientation effects of the polymer chains on the CT state energy, model interfaces for the calculations were constructed with an 18mer of thiophene and a C₆₀ (Figure S14). The structure of each molecule was optimized by DFT calculation at the B3LYP/6-31G(d) level before placing them in the same space. The distances between the oligothiophene and the C₆₀ were set to 4 and 12 Å. Time-dependent DFT single-point calculations were performed on the models at the CAM-B3LYP/6-31G+(d,p) and ω B97XD/6-31+G(d,p) levels. Using long-range correlation (LC) functionals is necessary to calculate the CT excited state accurately.¹¹⁻¹² The lowest energy states with the CT nature from the oligomer to C₆₀ were used to estimate E_{CT} (Figure S14). DFT single-point calculations were performed on the same models with neutral, negatively, and positively charged structures and their energy differences were used to calculate the energy of the free charges at the interface (E_{DA}). The binding energy (E_b) was calculated from $E_{DA} - E_{CT}$.

The calculated E_{CT} , E_{DA} , and E_{b} values are summarized in Table S3. Because all the calculations were performed in a vacuum and the effect of the dielectric medium was neglected, the calculated values of both E_{CT} and E_{DA} were much higher than the experimental values.¹³ Therefore, the results can only be compared qualitatively for different distances and orientations between the donor and the acceptor. The results with the two LC functionals qualitatively showed the same dependence of the energies on the distance and orientations. E_{CT} increased with distance, regardless of the molecular orientation. E_{DA} was less sensitive to the distance because the energy of the charged species was not affected substantially by

the intermolecular interactions. Consequently, E_b decreased as the distance increased, as expected from the point-charge approximation. At the same molecular distance, the end-on orientation gave a higher E_{CT} than the edge-on orientation, with no change in E_{DA} , resulting in the lower E_b , regardless of the distance. These results support the intuitive picture that the intramolecular hole delocalization on the polymer chains in the direction vertical to the interfacial plane of CTS reduces the Coulombic interactions between the charge pairs (Figure S14). The results with ω B97XD consistently gave smaller E_b values than those with CAM-B3LYP, which may be attributed to the difference in the LC functions.

Functional	Model	$E_{\rm CT} ({\rm eV})$	$E_{\mathrm{DA}}\left(\mathrm{eV}\right)$	$E_{\rm b}({\rm eV})$
	Edge-on (4 Å)	2.44	3.67	1.23
	End-on (4 Å)	2.80	3.71	0.91
CAM-B3L I P	Edge-on (12 Å)	2.79	3.76	0.97
	End-on (12 Å)	2.99	3.76	0.77
	Edge-on (4 Å)	3.03	3.86	0.83
DO7VD	End-on (4 Å)	3.53	3.90	0.37
ωβ9/ΔD	Edge-on (12 Å)	3.59	3.96	0.37
	End-on (12 Å)	3.88	3.97	0.08

Table S3. E_{CT} , E_{DA} , and E_b calculated by time-dependent DFT.



Figure S14. Molecular model structures for the interface of the polythiophenes and PCBM with (a) edge-on and (b) end-on orientations and their calculated charge density differences for the CT state, cation, and anion from the ground state. The closest atomic distance between the oligomer and C_{60} is set to 4 Å. The blue and red surfaces represent the isovalue surface (0.0004) of negative and positive charges, respectively.



Figure S15. Temperature dependence of J_{SC} for two PHJ devices of PCBM//P3DDFT/P3HT (blue) and PCBM//P3BT-F₁₇/P3HT (red) under the white LED light irradiation. The lines and the formulae show the best linear fitting for the data. The activation energy E_a was obtained from the slope of the line.



Figure S16. Light intensity dependence of J_{SC} at room and low temperatures for two PHJ devices of PCBM//P3DDFT/P3HT and PCBM//P3BT-F₁₇/P3HT under the white LED light irradiation.

Section S7. Estimation of the PL quenching efficiency

Steady-state photoluminescence (PL) quenching measurements were performed on two donor films of P3DDFT/P3HT and P3BT-F₁₇/P3HT to evaluate exciton diffusion and charge transfer processes. A cross-linkable fullerene derivative (C-PCBSD) was selected as the exciton quencher to avoid the diffusion of fullerene into the polymer layers. A chlorobenzene solution containing PCBSD precursor was spin-coated on a quartz substrate to form an 18nm-thick thin film. The as-cast film was annealed at 160 °C for 1 h in a glove box to form C-PCBSD by thermal cross-linking (Figure S17a). C-PCBSD//polymer PHJs were obtained by contact film transfer and the PL intensties of the PHJs were measured from the C-PCBSD side, which was close to the D/A interface. Figures S17b-d show the PL spectra of pristine films of P3DDFT/P3HT and P3BT-F₁₇/P3HT and PHJs of C-PCBSD//P3DDFT/P3HT and C-PCBSD//P3BT-F₁₇/P3HT at different excitation wavelengths (450, 520, and 555 nm) taken on a spectrofluorometer (Nanolog, HORIBA). In the spectra, the PL intensities of the peak tops of the pristine films were normalized to 1 and the intensities of PHJs were normalized by the values for their corresponding pristine films. The quenching efficiencies and the statistical analyses are summarized in Figure S17e. The PL quenching efficiencies of C-PCBSD//P3DDFT/P3HT and C-PCBSD//P3BT-F₁₇/P3HT were 68.6% (69.9% and 70.3%) and 74.6% (76.0% and 74.9%) with an excitation wavelength of 450 nm (520 and 555 nm), respectively. C-PCBSD//P3BT-F₁₇/P3HT showed a higher PL quenching efficiency than C-PCBSD//P3DDFT/P3HT despite the excitation wavelength. Both the exciton diffusion and charge transfer can affect the observed PL quenching efficiency. This result suggests that C-PCBSD//P3BT-F₁₇/P3HT may have better exciton diffusion and/or charge transfer caused by the end-on orientation. Recent reports suggest that the polymer chains oriented end-on towards the D/A interface could promote exciton diffusion because an efficient Förster energy transfer pathway through intrachain dipole-dipole coupling is available.¹⁴⁻¹⁶ However, we cannot determine which factor makes the larger contribution to the PL quenching efficiency.



Figure S17. (a) Chemical structures of PCBSD and C-PCBSD. PL spectra of pristine films (solid line) and PHJs (dashed line) with excitation wavelengths of (b) 450, (c) 520, and (d) 555 nm. The peak tops of pristine films were normalized to 1 and the intensities of the PHJs were normalized by the values for their corresponding pristine films. (e) Statistical data for the PL quenching efficiency of the two PHJs at three excitation wavelengths.

Section S8. Estimation of the charge separation probability under short-circuit conditions

To investigate the charge separation and charge collection processes affected by the end-on and the edge-on orientations, the dependence of the photocurrent (J_{ph}) on the effective voltage (V_{eff}) was measured for the PCBM//P3DDFT/P3HT and PCBM//P3BT-F₁₇/P3HT PHJ devices (Figure S18a). J_{ph} is defined as $J_{light} - J_{dark}$, where J_{light} and J_{dark} are current densities under AM1.5 illumination and in the dark, respectively. $V_{eff} = V_0 - V$, where V_0 is the voltage at $J_{\rm ph} = 0$ and V is the applied voltage. At high $V_{\rm eff}$ with a large electric field in the drift region, we obtained the maximum current density (J_{sat}) assuming that all the photogenerated bound pairs at CTS could dissociate into free charges, transport to the electrode, and contribute to the photocurrent.¹⁷ Therefore, by normalizing the results in Figure S18a with respect to J_{sat} of each device, we could compare the charge separation probability of two PHJ devices under short-circuit conditions (Figure S18b).¹⁸ The values were 81.8% and 89.8% for the PCBM//P3DDFT/P3HT and PCBM//P3BT-F17/P3HT devices, respectively. The higher value for the PCBM//P3BT-F₁₇/P3HT device suggests that a PHJ device with end-on-oriented polymer chains at D/A interface has better charge separation and charge collection efficiency than that with edge-on-oriented polymer chains.



Figure S18. (a) Photocurrent density (J_{ph}) and (b) normalized photocurrent density (J_{ph}/J_{sat}) plotted against effective voltage (V_{eff}) in the PCBM//P3DDFT/P3HT (blue) and PCBM//P3BT-F₁₇/P3HT (red) PHJs. The charge separation probabilities for PCBM//P3DDFT/P3HT and PCBM//P3BT-F₁₇/P3HT under short-circuit conditions are indicated by blue and red dashed lines, respectively.

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