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Deciphering the Role of Fluorination: Morphological Manipulation Prompts Charge Separation and Reduces Carrier Recombination in All-Small-Molecule Photovoltaics

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Abstract

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Fluorination has proven effective in increasing the absorption, downshifting the energy levels, and enhancing the crystallinity of high-performance fused-ring electron acceptors (FREAs). However, an in-depth understanding of the effects of fluorination is still lacking, as research efforts have mainly focused on increasing the power conversion efficiency (PCE). Additionally, fluorination on FREAs has rarely been reported in all-small-molecule organic solar cells (ASM-OSCs). Herein, fluorination on FREAs is systematically studied in ASM-OSCs by employing the popular FREA IDIC and its fluorinated analog paired with DRCN5T, an oligothiophene donor seldom investigated in ASM-OSCs to date. We conduct (photo)physical studies on both systems and identify that, along with the aforementioned ones, fluorination exerts several additional effects, including: first, it optimizes the morphology, thereby accelerates charge separation and reduces geminate recombination charge pairs; second, it suppresses energetic disorder; and third, it prolongs the carrier lifetime and thus aids charge extraction. Consequently, the short-circuit current density and fill factor are significantly enhanced, and in turn, the PCE yields a 36% improvement, climbing to 9.25% and rivaling that of the current state-of-the-art oligothiophene-donor/nonfullerene ASM-OSCs. Our insights decipher the working mechanism of ASM-OSCs that employ fluorinated FREAs, paving the way towards high-performance ASM-OSCs.

1. Introduction

Solution-processed bulk-heterojunction (BHJ) organic solar cells (OSCs) have arisen as a promising contender for next-generation photovoltaic technology by virtue of their low carbon footprint, short energy payback time, and easy fabrication into flexible, light-weight, and semitransparent devices.^[1-6] All-small-molecule (ASM) OSCs, in particular, have attracted considerable academic and industrial interest, due to their advantageous properties, such as a well-defined chemical structure, easy purification, and scalability with excellent batch-to-batch reproducibility.^[7] Traditional ASM OSCs consist of a small-molecule electron donor (typically based on donor moieties using benzodithiophene (BDT), thiophene, dithienosilole (DTS), and indacenodithiophene (IDT), etc.)^[8-9] and fullerene derivatives as electron acceptors (e.g., PC₆₁BM and PC₇₁BM), which have resulted in an over 11% power conversion efficiency (PCE) due to the concerted efforts in rational molecular design and device engineering.^[10] However, fullerene acceptors suffer from several drawbacks, such as their weak absorption in the visible and near-infrared (NIR) range, limited tunability of energy levels, and poor thermal stability. In addition, the difficulty of simultaneously controlling the crystallinity and phase segregation of the active layer limit the further advancement of ASM OSCs.^[11] The recent gamechanger in OSCs is nonfullerene acceptors, which feature stronger absorption, tunable energy levels, and easy modification of their chemical structure and crystallinity.^[12-13]

Fused-ring electron acceptors (FREAs), consisting of electron-donating fused-ring cores and two strong electron-withdrawing terminal groups (TGs) linked by planar π -conjugated bridges, have become the most promising fullerene substitutes in ASM OSCs to date.^[14-16] More specifically, IDIC, introduced by Zhan's group, has been used in the majority of high-performance ASM OSCs.^[17] Lu's group reported a pair of small-molecule donors with BDT as the central electron-donating building block and esterified rhodamine as the TG, namely, BDT-RO and BDT-RN, which demonstrated encouraging PCEs of 9.01% and 8.36% when paired with IDIC, enabled by the high mobilities and optimized phase-separated D-A networks in the blend films.^[18] Zhang's group reported a BDT core small molecule with a dual-acceptor unit, SBDT-BDD, which yielded a 9.2% efficiency enabled by its complementary absorption and energy levels matching those of IDIC.^[19] Li's group designed H22, a small-molecule donor featuring an alkyl silyl-thienyl substituted BDT central unit and a cyanoacetic acid ester TG, which exhibited improved charge carrier mobilities compared to its counterpart with rhodanine groups as well as enhanced 3D charge transport pathways when paired with IDIC, leading to a high PCE of 10.29%.^[11] **Table 1** summarizes the figures of merit of highly efficient FREA-based ASM OSCs. Recent progress has clearly

demonstrated the success of IDIC as a fullerene substitute in ASM OSCs is mainly attributed to its complementary absorption to the donor molecule, crystallinity and phase-segregation upon posttreatment.^[20-22] Despite its outstanding properties, derivatives of IDIC have heretofore rarely been investigated in ASM OSCs.

A proven design strategy to improve the performance of FREAs is fluorination, which leads to redshifted absorption, downshifted energy levels, and enhanced crystallinity.^[23-28] Several promising reports have shown that fluorinated FREAs can significantly enhance the performance of polymer solar cells (PSCs) compared with nonfluorinated counterparts.^[29-30] **Table S1** summarizes the photovoltaic parameters of representative PSCs, which are indicative of the effectiveness of fluorination in advancing PSCs' performance. For instance, PCE improvements can clearly be seen in the cases of IDT-T (6.28%) vs. IDTT2F (8.75%),^[25] INPIC (4.31%) vs. INPIC-4F (13.13%),^[26] IDT2Se (9.36%) vs. IDT2Se-4F (11.19%),^[31] ITVIC (7.34%) vs. ITVffIC (10.54%)^[32] and ITIC (11.05%) vs. IT4F (13.10%).^[30] In addition, fluorination on small molecule donor also dramatically improves the fullerene-based ASM OSCs. For example, DI3T (0.83%) vs. DI3T (7.80%),^[28] BTID-0F (8.30%) vs. BTID-2F (11.30%).^[10] However, such a facile yet effective strategy has rarely been applied in FREA-based ASM OSCs, and the effect of fluorination of FREAs on high-performance ASM OSCs is still unclear and requires further investigation.

Herein, we selected IDIC-4F, the fluorinated analog of IDIC, bearing difluorinated dicyanomethylene indanone termini and an indacenodithiophene core and combined it with the high-performance oligothiophene-based small-molecule donor DRCN5T in ASM OSCs. We chose DRCN5T mainly based on two considerations. First, DRCN5T exhibits absorption spectra and energy levels complementary to IDIC and IDIC-4F. Second, more importantly, DRCN5T has a simpler structure, can be more easily synthesized than the widely investigated BDT-based small-molecule donors (summarized in **Table 1**) and thus is an ideal candidate for NF ASM-OSCs.^[33-34] We found that fluorination not only led to redshifted absorption, downshifted energy levels, and enhanced crystallinity but also, in DRCN5T:IDIC-4F devices, to reduced geminate recombination, fast charge separation (50 vs. 3 ps), suppressed energetic disorder (91 vs. 75 meV), a prolonged carrier lifetime (1.36 vs. 1.92 μ s), and inhibited non-geminate recombination, thereby facilitating charge extraction (0.34 vs. 0.28 μ s). Note, we extracted the geminate recombination rate, the apparent nongeminate recombination order, the nongeminate decay rate, and the effective bimolecular recombination coefficient, which contributed to the quantification of the photophysics process influenced by fluorination on the FREA. These advances noticeably increased the PCE by improving the short-circuit current density (J_{sc}) from 12.35 to 16.07 mA cm^{-2} , and enhancing the fill factor (FF) from 60.4% to 70.9%. To the best of our knowledge, the PCE of 9.25% we achieved

here is among the best values of oligothiophene-donor-based NF ASM OSCs,^[23, 35-36] which indicates the effectiveness of acceptor fluorination in ASM OSCs. Our results provide insights into the complex effects of FREA fluorination in high-performance ASM OSCs.

Table 1. Photovoltaic parameters of FREA-based ASM OSCs.

Donor	Acceptor	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF [%]	Avg. PCE [%]	Max. PCE [%]	Ref
2F-C4C6		0.90	12.05	57.20	6.13	6.21	[37]
2F-C6C8		0.90	13.98	65.20	8.05	8.23	[37]
DRTB-T		0.98	14.22	65	8.82	9.06	[38]
H11		0.98	15.21	65.46	9.56	9.73	[20]
H12		0.96	10.51	54.89	5.39	5.51	[20]
H21		0.90	13.00	65.58	7.34	7.62	[11]
H22		0.94	15.38	71.15	9.96	10.29	[11]
DR3TBDTT		0.87	15.2	64	8.4	8.7	[21]
NDTSR	IDIC	0.92	14.13	61.95	7.90	8.05	[39]
SBDT-BDD		0.97	15.15	62.5	8.9	9.2	[19]
W-CN		0.90	11.58	50.45	5.18	5.26	[40]
SM1		0.91	15.18	73.55	9.85	10.11	[22]
SM2		0.77	10.77	64.40	5.21	5.32	[22]
SM-BT-2OR		0.94	13.57	56.5	6.86	7.20	[41]
BDTF-CA		0.99	12.09	51.14	5.88	6.12	[42]
BDT-RO		0.88	15.37	66.56	8.85	9.01	[18]
BDT-RN		0.87	14.85	64.88	8.03	8.36	[18]

Figure 1 Molecular structures of (a) IDIC and IDIC-4F, and (b) DRCN5T. (c) Normalized UV-vis absorbance spectra of DRCN5T, IDIC, and IDIC-4F thin films. (d) Energy level diagram of DRCN5T, IDIC, and IDIC-4F. (e) Device architecture.

2. Results and discussion

Figure 1a and **1b** depicts the molecular structures of IDIC, IDIC-4F and the oligothiophene donor (DRCN5T). The two FREAs, IDIC and IDIC-4F, differ in the fluorine substitution on the INCN termini. **Figure 1c** shows the normalized UV-vis absorbance spectra of DRCN5T, IDIC, and IDIC-4F pristine films. The IDIC-4F film displays an absorption maximum at 722 nm, redshifted by 15 nm relative to that of IDIC, indicating that fluorination of FREA can broaden the absorption. The blueshifts of the absorption peak from the solid state to an extremely dilute CF solution are 46 and 39 nm for IDI-4F and IDIC, respectively (**Figure S1**), implying the existence of strong intermolecular interactions in both solid films. IDIC and IDIC-4F exhibit absorption onsets of 780 and 800 nm, respectively, which account for the respective optical bandgaps of 1.59 and 1.55 eV. In addition, the IDIC-4F pristine film exhibits a slightly higher maximum absorption coefficient of $8.46 \times 10^{-4} \text{ cm}^{-1}$ than the nonfluorinated counterpart ($8.10 \times 10^{-4} \text{ cm}^{-1}$), which potentially harvests more photons. **Figure 1d** displays the energy level diagram of DRCN5T, IDIC, and IDIC-4F. Owing to the strong electron-withdrawing ability of fluorine atoms, IDIC-4F possesses the lowest unoccupied molecular orbital (LUMO) level of -3.93 eV and the highest occupied molecular orbital (HOMO) level of -5.76 eV, slightly deeper than those of IDIC (-3.91 eV/ -5.69 eV) and both FREAs when associated with DRCN5T (-3.41 eV/ -5.22 eV) in terms of energy levels.^[17, 33, 43] The

low-lying energy level of IDIC-4F helps form a larger driving force for charge separation, which is also clear from the transient absorption (TA) spectroscopy measurements.

As shown in **Figure 1e**, we chose the conventional device architecture of ITO/PEDOT:PSS/active layer/phenyl(2-naphthyl) diphenylphosphine oxide (DPO)/Ag to fabricate bulk-heterojunction (BHJ) ASM OSCs. The BHJ devices were optimized by tuning the donor:acceptor (D:A) ratio and varying the posttreatment techniques.^[44-45] **Table 2** summarizes the figures of merit of the optimized OSCs under simulated AM1.5G irradiation (100 mW cm^{-2}). **Figure 2a** depicts the current density–voltage (J – V) characteristics of the optimized OSCs, and **Figure 2c** presents the PCEs histograms obtained from 20 devices for both IDIC- and IDIC-4F-based ASM OSCs.

Table 2. Photovoltaic performance of optimized OSCs based on DRCN5T: IDIC and DRCN5T:IDIC-4F under simulated AM1.5G illumination (100 mW cm^{-2}).

Donor: Acceptor	V_{OC}^a [V]	J_{SC} [mA cm^{-2}]	Calc. J_{SC}^b [mA cm^{-2}]	FF [%]	PCE [%]
DRCN5T:IDIC	0.91 (0.90 ± 0.01)	12.35 (12.04 ± 0.36)	11.79	60.4 (60.02 ± 0.8)	6.80 (6.64 ± 0.11)
DRCN5T:IDIC-4F	0.81 (0.81 ± 0.01)	16.07 (16.03 ± 0.26)	15.47	70.9 (68.9 ± 1.6)	9.25 (8.98 ± 0.16)

^a Values are for the champion PCE device, with the average values obtained from 20 devices listed in parentheses. ^b The J_{SC} values from the integration of the EQE spectra are within a 5% error of those from the J-V curves.

The IDIC BHJ device shows a moderate PCE of 6.80% with a V_{OC} of 0.91 V, a J_{SC} of 12.35 mA cm^{-2} , and an FF of 60.4%. By introducing fluorine atoms into the FREA, the FF is dramatically enhanced from 60.4% to 70.9%, and the J_{SC} is evidently boosted from 12.35 to 16.07 mA cm^{-2} , which jointly cover the Voc drop from 0.91 to 0.81 eV and lead to the excellent PCE of 9.25% for the corresponding IDIC-4F-based ASM OSCs. The PCE of 9.25% represents an $\sim 36\%$ enhancement compared with the PCE of the IDIC BHJ control device and is among the best-performing values for oligothiophene-based NF ASM OSCs to our knowledge.

Figure 2 (a) J-V characteristics, (b) EQE spectra, (c) PCE Histograms, and (d) photocurrent density (J_{ph}) as a function of the effective voltage (V_{eff}) of the optimized OSCs.

Figure 2b shows the external quantum efficiency (EQE) spectra of the optimized devices based on DRCN5T:IDIC and DRCN5T:IDIC-4F. The IDIC-4F-based BHJ device shows slightly broader spectrum than the IDIC-based BHJ control device, which is in accordance with the redshifted absorption feature of IDIC-4F. Additionally, the IDIC-4F BHJ device exhibits a stronger photoresponse than that of the control device in the range of 400–850 nm, which contributes to the enormously increased J_{SC} ; the EQE maximum of the former device is 67.70%, significantly higher than 51.04%. This notable difference cannot be solely explained by the slightly increased absorption of the fluorinated FREA (IDIC-4F). Other reasons for the enhanced EQE possibly originate from one or more of the following processes: acceleration of charge carrier extraction, reduction of geminate recombination during generation of charge carriers, and suppression of nongeminate recombination during transport and collection of charge carriers (the details will be discussed in the following sections). The J_{SC} values of the IDIC and IDIC-4F BHJ devices integrated from the EQE spectra are 11.79 and 15.47 mA cm⁻², respectively, consistent with the J_{SC} values measured from the solar simulator (within a 5% error, **Table 2**).

In addition to the largely increased J_{SC} , another significantly improved parameter is the FF, which is responsible for roughly one-third of the overall performance enhancement. Generally, the FF mainly depends on efficient charge extraction as well as balanced hole and electron mobilities under a bias voltage. Recently, studies also have demonstrated that the FF is largely correlated with the competition between charge recombination and extraction, both of which have a nonlinear incremental relationship with the charge carrier mobility.^[46-47] The fluorination strategy in this work effectively enhances the FF and boosts the J_{SC} ; and thus, closely checking both parameters by examining the extraction, transport, collection and recombination behavior of photogenerated charge carriers is important.

First, the photocurrent density (J_{ph}) as a function of the effective voltage (V_{eff}) was plotted to investigate the charge generation and extraction properties (**Figure 2d**). $J_{ph} = J_L - J_D$, in which J_L is the current density under illumination and J_D is that in the dark. $V_{eff} = V_0 - V_A$, where V_0 is the voltage when J_{ph} is equal to 0 and V_A is the applied bias voltage. At a high V_{eff} of 2.5 V, all the photogenerated excitons are assumed to be dissociated into free charge carriers and collected by electrodes. The IDIC-4F-based device displays a saturation current density (J_{sat}) of 16.33 mA cm⁻², noticeably higher than that of the IDIC-based device (14.50 mA cm⁻²), which agrees with the better light absorption capability of the fluorinated blend. The exciton dissociation efficiency ($\eta_{diss} = J_{SC}/J_{sat}$) and charge collection efficiency ($\eta_{coll} = J_{max\ power}/J_{sat}$) were calculated under the short-circuit

and maximum power output conditions, respectively. The IDIC-4F-based BHJ device exhibits a η_{diss} of 98.5% and a η_{coll} of 84.4%, higher than those of the IDIC-based BHJ (η_{diss} of 85.2% and η_{coll} of 63.4%) device, indicating that the fluorination strategy improves the efficiency of exciton dissociation and charge collection.

Figure 3 Picosecond-nanosecond TA spectra (a,b) after excitation at 700 nm and integrated kinetics in the 1.25-1.35 eV probe region for different fluences (c, d) of DRCN5T:IDIC and DRCN5T:IDIC-4F. We note that the region around 1.5-1.6 eV is affected by scattered laser light (800 nm) used to generate the supercontinuum probe. Nanosecond-microsecond (ns- μ s) TA kinetics after excitation at 532 nm in the 1.25-1.35 eV probe region (e and f) of DRCN5T:IDIC and DRCN5T:IDIC-4F, respectively for a wide range of fluences. The solid lines are the two-pool model global fits to the experimental data.

TA pump-probe spectroscopy was used to monitor the charge generation and recombination following photoexcitation of the BHJ blend films. Experimental details of the TA measurements

can be found in the Supporting Information (SI) and in our previous works.^[48-49] **Figure 3a,c** presents the picosecond-nanosecond (ps-ns) TA spectra and kinetics of a DRCN5T:IDIC blend film excited at 750 nm, that is, under acceptor excitation. The early-time spectra show an excited state absorption (ESA) band centered at 1.4 eV that quickly disappears, followed by the emergence of a new band at 1.3 eV in approximately ~ 5 ps. The former was assigned to singlet exciton-induced absorption of IDIC excitons and the latter to charge-induced absorption of charge carriers generated by exciton quenching at the interface. The kinetics integrated in the 1.25-1.35 eV probe region, assigned to charge carriers (**Figure 3c**), show an increasing signal in the first 100 ps, indicating diffusion-limited charge generation, possibly due to the presence of larger acceptor domains in this blend. **Figure 3b,d** shows the respective ps-ns TA spectra and kinetics of a DRCN5T:IDIC-4F blend film under similar excitation conditions as for the DRCN5T:IDIC blend films. The TA signatures of the fluorinated FREA are comparable (**Figure 3b**) to those of the nonfluorinated compound (**Figure 3a**) however, the kinetics are significantly different. In fact, in IDIC BHJ blends, ~ 50 ps is required to complete the charge generation (**Figure 3c**), while charge generation is concluded in approximately ~ 3 ps in IDIC-4F BHJ blends (**Figure 3d**). This result suggests an improved morphology, specifically, more intimate mixing of the donor and acceptor and a larger interfacial area with smaller domain sizes, when the fluorinated FREA is used, which is in line with the improved exciton dissociation efficiency of 98% for IDIC-4F BHJ blends compared to 85% for IDIC-based blends (**Figure 2d**). The more intimate mixing in DRCN5T:IDIC-4F blend films could potentially lead to faster nongeminate charge recombination competing with charge extraction in devices however, this was not observed, as discussed below. After charge generation is concluded, both blends exhibit fluence-dependent charge carrier decay, indicating the presence of free (separated) charge carriers undergoing nongeminate recombination.

In addition to the ps-ns charge generation and recombination, we further probed the charge recombination dynamics in the nanosecond-microsecond (ns- μ s) time range (**Figure 3e-f**) following excitation at 532 nm, that is, under donor excitation. The ns- μ s TA spectra are shown in **Figure S2**. Both blends appear to exhibit a combination of fluence-independent and fluence-dependent charge carrier decay (**Figure 3e and f**), but to different extents. In fact, a qualitative comparison of the carrier dynamics measured at different fluences suggests a larger fraction of geminate recombination in IDIC BHJ blends, whereas recombination appears to be mostly non-geminate in IDIC-4F BHJ blends. Hence, we parametrized the charge carrier decay dynamics using a two-pool recombination model, introduced earlier by Howard et al., and thereafter applied to several other fullerene and nonfullerene OSC blends.^[48, 50-51] **Figure 3e** shows the fits of the experimentally-measured charge carrier decay dynamics to the model. The fit was performed globally, that is,

across all fluences measured, using a shared set of parameters. We assumed $2 \times 10^{-16} \text{ cm}^2$ for the charge carrier absorption cross-section, as obtained in a recent work on similar material systems.^[48] The fit parameters are displayed in Table 3. The fit indicates that free charges account for $\sim 91\%$ of the recombination in IDIC-4F BHJ blends, whereas for IDIC BHJ blends, this fraction accounts for only $\sim 77\%$ of the recombination. Clearly, the IDIC blends exhibit more geminate recombination (23%). The effective bimolecular recombination coefficient (β) was calculated from the nongeminate recombination coefficient γ and apparent recombination order ($\lambda+1$), both obtained from the two-pool fit to the data. For further details of the two-pool model, we refer to our previous works.^[48, 50] We obtained a β of $0.7 \times 10^{-12} \text{ cm}^3/\text{s}$ for IDIC-4F BHJ blends and a β of $2.6 \times 10^{-11} \text{ cm}^3/\text{s}$ for IDIC BHJ blends assuming a carrier concentration of $1 \times 10^{16} \text{ cm}^{-3}$, corresponding to the steady-state carrier concentration under 1-sun illumination conditions.^[48] The slower non-geminate recombination in IDIC-4F BHJ blends implies that more charge carriers can be extracted in devices. Here, we hypothesize that the slower non-geminate recombination in IDIC-4F BHJ blends is possibly a consequence of altered donor-acceptor interaction at the interface and changes of the energetic landscape responsible for charge separation and recombination. Importantly, the fluorination of the acceptor reduces geminate recombination and facilitates charge separation in donor:FREA blends, leading to the improved photovoltaic performance (**Table 2**), similar to the effect of backbone fluorination of donor polymers in polymer:fullerene blends reported recently.^[52]

Table 3. Fit parameters obtained from the global fit to the ns- μs charge carrier recombination dynamics in optimized IDIC and IDIC-4F blends.

Parameter	IDIC	IDIC-4F
$f(\%)^a$	~ 77	~ 91
$(1-f)(\%)$	~ 23	~ 9
$k_{\text{CT-GS}}(\text{s}^{-1})^b$	7×10^8	1×10^8
$\lambda+1^c$	2.20 ± 0.003	2.11 ± 0.007
$\gamma ([\text{cm}^3]^\lambda \text{s}^{-1})^d$	$1.70 \pm 0.1 \times 10^{-30}$	$1.2 \pm 0.1 \times 10^{-30}$
$\beta (\text{cm}^3/\text{s})^e$	2.6×10^{-11}	0.7×10^{-12}

^a f is the fraction of free charge carriers. ^b $k_{\text{CT-GS}}$ is the geminate recombination rate.

^c $\lambda+1$ is the apparent nongeminate recombination order. ^d γ is the nongeminate decay constant, and ^e β is the effective bimolecular recombination coefficient for IDIC and IDIC-4F-based BHJ blends calculated for a carrier density of $1 \times 10^{16} \text{ cm}^{-3}$, equivalent to the carrier density under one-sun illumination.

Figure 4 (a) J_{SC} versus P_{light} and (b) V_{OC} versus P_{light} of the optimized devices. (c) TPV and (d) TPC of the optimized devices. (e) $J \times d$ as a function of the electric field, and (f) zero-field electron mobility $\mu_{0,e}$ versus $(1000/T)^2$.

To examine the fate of the free charge carriers in the devices, J-V curves under various incident light intensities and the transient photovoltage/photocurrent (TPV/TPC) were measured. Previous works have demonstrated that the bimolecular recombination losses can be estimated by employing the power-law relation of $J \propto I^\alpha$ to fit J_{SC} as a function of the incident light intensity.^[53-55] In brief, a value of α equal to unity reflects the extreme case where all the free carriers are swept out and collected at the electrodes before recombination. From **Figure 4a**, we obtained α values of 0.989 and 0.997 for IDIC and IDIC-4F BHJ devices, respectively, which are indicative of negligible bimolecular recombination losses for both systems. The low bimolecular recombination losses directed us to analyze another loss mechanism: trap-assisted Shockley-Read-Hall (SRH) recombination. To analyze the trap-assisted SRH loss, we measured V_{OC} as a function of the incident light intensity and plotted the results as shown in **Figure 4b**. The data were fitted according

to the expression $V_{OC} \propto nkT/q \ln(I)$, where k , T , and q are the Boltzmann constant, the temperature in Kelvin, and elementary charge, respectively. The parameter n (generally in the range of 1 to 2) reflects the presence of carrier traps across the active layer or at the interfaces of the electrodes. Any deviation from 1 (trap-free condition) indicates the existence of trap-assisted recombination. The fitted data shown in **Figure 4b** led to derived n values of 1.49 and 1.10 for IDIC and IDIC-4F BHJ devices, suggesting that the former device suffers from more severe trap-assisted recombination than the latter device. These results reveal that fluorination of FREAs can simultaneously suppress bimolecular recombination and reduce trap-assisted recombination, which accounts for the remarkable improvement of the DRCN5T:IDIC-4F device.

Further insights into the charge recombination dynamics and extraction across BHJ active layers in complete devices were obtained through TPV and TPC measurements. The carrier lifetimes (τ) under open-circuit conditions (**Figure 4c**) were extracted from the TPV decay dynamics using monoexponential fits under a 1 sun bias.^[21, 56-57] The IDIC-4F BHJ device exhibits a τ value of 1.92 μ s, obviously longer than that of the IDIC counterpart (1.36 μ s), in agreement with the lower extent of recombination analyzed above. In addition to the carrier lifetime, the charge extraction properties are also important. TPC measurements were performed to study the competition between carrier sweep-out and recombination during operation. The photocurrent decay time under short-circuit conditions is 0.28 μ s for the IDIC-4F BHJ device, smaller than that for the IDIC BHJ device (0.34 μ s), illustrating that fluorination of FREA can effectively facilitate charge carrier extraction, which is in line with the aforementioned higher charge collection efficiency of 84.4% in the IDIC-4F-based BHJ device (**Figure 2d**).

The carrier mobilities were derived from the dark current density-voltage curves by fitting the J-V curves with the space-charge-limited current (SCLC) model^[58-60] (**Figure 4e**). Electron-only devices were fabricated with the structure of ITO/Al/active layer/LiF/Al. The pristine film of the fluorinated FREA (IDIC-4F) exhibits a zero-field electron mobility ($\mu_{0,e}$) of $4.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, higher than that of IDIC ($1.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). By blending with DRCN5T, the IDIC-based film shows an order of magnitude smaller $\mu_{0,e}$ of $5.2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, whereas the DRCN5T:IDIC-4F film retains a $\mu_{0,e}$ value of $1.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which illustrates that fluorination can boost the electron mobilities of not only the FREA pristine film but also the DRCN5T:FREA blend film, finally leading to the impressive improvement in the overall device performance. In addition, the zero-field hole mobilities were obtained on hole-only devices of the structure ITO/PEDOT:PSS/active layer/MoO₃/Ag; $6.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for IDIC-based BHJ thin films and $4.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for IDIC-4F-based BHJ thin films (Table S6). The more balanced charge carrier

mobilities of the IDIC-4F BHJ ($\mu_h/\mu_e = 4.2$, **Table S6**) compared to the IDIC BHJ ($\mu_h/\mu_e = 12.1$, **Table S6**) is considered the reason that leads to the substantial enhancement of the device FF from 60.4% to 70.9%.

The electron energy disorder, σ_e , was also evaluated by temperature-dependent electron transport measurements using the Gauss disorder model (GDM):

$$\mu_0 = \mu_\infty \exp \left[- \left(\frac{2\sigma}{3kT} \right)^2 \right] \exp (\beta \sqrt{F})$$

where k is the Boltzmann constant, T is the temperature, μ_0 is the zero-field mobility, β is the Poole-Frenkel slope, F is the applied electric field, and μ_∞ is the y-intercept from the plot of μ_0 versus $(1000/T)^2$.^[61-62] **Figure 4f** depicts the $\mu_{0,e}$ of the films as a function of the ambient temperature and the linear fit to the experimental data, the slope of which can be used to derive σ_e . IDIC and its fluorinated derivative IDIC-4F exhibit σ_e values of 81 and 76 meV, respectively. However, when donor materials were loaded into the film, σ_e significantly increased to 91 meV in the DRCN5T:IDIC-based film, indicating the generation of a large number of energetic defects therein. In contrast, the σ_e of the DRCN5T:IDIC-4F film was maintained at a low value of 75 meV, which was even slightly lower than that of the IDIC-4F pristine film. We inferred from these results that fluorination suppresses electron energetic disorder in the active layer, thereby improving the J_{SC} and FFs in the corresponding devices, confirming the reduced trap-assisted recombination in the fluorinated devices.

Figure 5 2D GIWAXS patterns of films based on (a) IDIC, (b) IDIC-4F, (c) DRCN5T:IDIC and (d) DRCN5T:IDIC-4F. (e) Corresponding GIWAXS intensity profiles along the in-plane (purple lines) and out-of-plane (red lines) directions.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) was adopted to investigate the molecular packing and orientation in the thin films (**Figure 5**), and the corresponding GIWAXS parameters are summarized in **Table S5**. As **Figure S4** shows, the oligothiophene donor DRCN5T displays a preferential edge-on orientation, whereas both FREAs show a preferential face-on orientation, in line with previously reported work.^[17, 33] The IDIC pristine film presents a sharp (100) lamellar peak at $q_{xy} \approx 0.40 \text{ \AA}^{-1}$ with a crystal coherence length (CCL) of 7.07 nm. In contrast, the fluorinated IDIC-4F film displays a much stronger (100) lamellar peak at $q_{xy} \approx 0.39 \text{ \AA}^{-1}$ with a CCL of 13.79 nm and an extra (100) lamellar peak at $q_z \approx 0.70 \text{ \AA}^{-1}$ with a CCL of 6.35 nm, indicating that fluorination can increase the FREA crystallinity and modify the molecular packing and orientation.

For the optimized blend films, both BHJ blend films demonstrate preferential edge-on orientation, resembling the DRCN5T pristine film (**Figure 5c and d, Table S5**). The IDIC-based BHJ film exhibits (100), (200) and (300) lamellar peaks at $q_z \approx 0.35, 0.70$ and $1.05 \text{ \AA}^{-1}$ and a π - π peak at $q_{xy} \approx 1.76 \text{ \AA}^{-1}$ (CCL=3.21 nm). In comparison, its fluorinated counterpart IDIC-4F-based BHJ film also shows a (400) lamellar peak in the out-of-plane direction, in addition to the (100), (200) and (300) lamellar peaks and the π - π peak at $q_{xy} \approx 1.76 \text{ \AA}^{-1}$ (CCL=4.25 nm). The higher index of the (n00) out-of-plane lamellar peaks and the larger CCL of the stronger in-plane π - π peak in the IDIC-4F-based BHJ film soundly evidence that the fluorination strategy endows the resulting blend film with stronger crystallinity and thus higher electron mobility. Moreover, the more crystalline nature of the IDIC-4F BHJ blend enables ultrafast charge separation inside it. In addition, the more ordered out-of-plane lamellar packing in the IDIC-4F-based BHJ film facilitates charge transport in the vertical direction, which is consistent with its higher charge collection efficiency (**Table 2**).

Figure 6 AFM height images (a, d), phase images (b, e), and TEM images (c, f). (a, b, c) DRCN5T:IDIC and (d, e, f) DRCN5T:IDIC-4F blends.

Donor/acceptor phase separation in the active layer was studied by both atomic force microscopy (AFM) and transmission electron microscopy (TEM) (**Figure 5a-f**). As the AFM height images show (**Figure S3**), the IDIC and IDIC-4F pristine films have root mean square roughness (R_q) values of 0.611 and 0.729 nm, implying that fluorination increases FREA aggregation, which is in conformity with the stronger crystallinity of the IDIC-4F film ascertained by GIWAXS characterization. Likewise, the IDIC-4F-based BHJ film displays a R_q of 1.88 nm, which is obviously larger than that of the IDIC-based counterpart (1.43 nm). As the AFM phase images indicate, relative to the IDIC-based BHJ film, the IDIC-4F-based blend film presents a uniform yet more obvious nanofibrillar network (**Figure 5b and d**), which is advantageous for both interface contact and charge transport.^[8-9, 63-73] (**Table 3**). As shown in the TEM images, the IDIC-4F BHJ film displays clear phase separation with a scale of ~ 25 nm and a clear donor/acceptor interpenetrating network, which facilitates exciton dissociation and charge transport. In contrast, the IDIC-based blend shows larger phase separation with a scale of ~ 35 nm. These morphology data are in accord with the information from TA (**Figure 3**).

As the GIWAXS, AFM and TEM results together show, fluorination enhances the crystallinity, improves the molecular packing, adjusts the phase separation scale to a more reasonable range, and helps shape the donor/acceptor interpenetrating network, contributing to the stronger photon harvesting and better charge separation, transport, and collection in the IDIC-4F BHJ device.

3. Conclusion

In summary, we present a systematic study of the impact of acceptor fluorination by employing IDIC and IDIC-4F in ASM OSCs paired with the oligothiophene donor DRCN5T. In particular, we investigated the mechanism behind the performance enhancement caused by fluorination of the FREA and found morphological changes leading to faster exciton dissociation, reduced geminate recombination of the generated charge pairs, reduced energetic disorder, a prolonged carrier lifetime (1.36 vs. 1.92 μ s), and thereby an improved charge separation efficiency (85.2% vs. 98.5%) as well as facilitated charge extraction (0.34 vs. 0.28 μ s). It is noteworthy that we extracted the key parameters of the geminate, non-geminate and bimolecular recombination to unveil the photophysics process influenced by fluorination on the FREA. Consequently, the fluorination strategy remarkably improved the PCE from 6.80% to 9.25%, which places the system reported here among the top-performing oligothiophene-donor-based NF ASM OSCs. Our findings

demonstrate the effectiveness of FREA fluorination for high-performance ASM OSCs and reveal the mechanism behind the performance increase caused by fluorination.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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We pioneered in the systematic working principle study of fluorination on fused-ring electron acceptors (FREAs) paired with an oligothiophene donor, including the quantification of the key parameters to unveil the involving photophysics process, and enables top-performing oligothiophene-based all-small-molecule photovoltaic.

Keywords: fluorination, charge separation, carrier lifetime, energetic disorder, organic solar cells

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Deciphering the Role of Fluorination: Morphological Manipulation Prompts Charge Separation and Reduces Carrier Recombination in All-Small-Molecule Photovoltaics