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Graphical Abstract

An A₁-(D-A)₂-D-A₁ type oligomer DRCN4FBT is designed and synthesized by simply inserting a D-A unit in an A₁-D-A-D-A₁ type small molecule DRCN2FBT. Its absorption and energy level, mobility, morphology are well supervised by inserting D-A unit. As a result, both PCE and J_{sc} are increased by about 20% for the DRCN4FBT/PC₇₁BM based devices. It indicates that simply increasing D-A unitis an efficient strategy to improve photovoltaic properties.



An efficient strategy to supervise absorption, mobility, morphology of photovoltaic molecule by inserting a D-A unit

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Abstract:

The absorption, mobility and morphology of molecules in the active layer have a crucial influence on photovoltaic properties of organic solar cells. In this work, we design an A₁-(D-A)₂-D-A₁ type oligomer DRCN4FBT on the basis of an A₁-D-A-D-A₁ type small molecule DRCN2FBT by inserting D-A unit. It is found that oligomer DRCN4FBT exhibits wider absorption spectrum and higher carrier mobility and better morphology than small molecule DRCN2FBT in active layer using fullerene PC71BM as acceptor. The absorption and energy level, mobility, morphology of DRCN4FBT in active layer are well supervised by inserting D-A unit in DRCN2FBT. As a result, its power conversion efficiency and short current density are increased by about 20% for the DRCN4FBT/PC71BM based organic solar cells in comparison with the DRCN2FBT/PC₇₁BM based devices. It indicates that simply increasing D-A unit in small molecules to construct oligomer is an efficient strategy to improve photovoltaic properties.

KEYWORDS: Oligomer; Benzodithiophene; Benzodithiophene-4,8-dione; Fullerene; Organic solar cells.

1. Introduction

Organic solar cells (OSCs), compared with thin-film inorganic solar cells, have attracted more and more attention due to their advantages, such as easy solution processability, light weight, good mechanical flexibility and low cost.¹⁻⁶ In the past few years, due to the rapid development of non-fullerene receptors, power conversion efficiencies (PCEs) for polymer based organic solar cells (P-OSCs) have exceeded 14% in single-junction structure,^{7.8} and 17.3% in double-junction structure.⁹ And PCEs of single-junction small molecules based organic solar cells (SM-OSCs) are about 11% in a binary-component structure¹⁰⁻¹³ and 13% in a three-component structure.¹⁴ It is still a challenge to obtain high-performance organic photovoltaic materials and their organic solar cells.

As is known to all, the PCE value is determined by three key parameters, i.e. open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), and filling factor (*FF*). These factors are closely related to the absorption spectra, energy levels and morphology of the photovoltaic materials in active layer.¹⁵ In general, low HOMO energy level for donor material is available to obtain high V_{oc} . And wide absorption spectrum and high extinction coefficient for the donor and acceptor materials are available to achieve high J_{sc} .^{16,17}

However, to obtain a high *FF* level, good phase separation and interpenetrating net work are simultaneously required between the donor and acceptor in the active layer, which is a huge challenge for SM-OSCs, because the crystallinity of small molecules is too strong.¹⁸ In order to solve this problem and obtain high-performance bulk heterojunction (BHJ) OSCs using fullerene as acceptor, the common strategy is to construct oligomers with bigger conjugated frame work by introducing some electronic donor(D)–acceptor(A) elements into the main chain.¹⁹⁻²⁵ For example, Bazan *et al* introduced a combined unit of dithieno(3,2-b;2',3'-d)-silole (DTS) and benzothiadiazole (BT) in main chain to obtain a type of oligomers, which exhibited a PCE of 6.5% in these oligomer-based organic solar cells (OM-OSCs).¹⁹ Wei *et al* reported another oligomers with an impressive PCE up to 9.25% in their OSCs.²² The crystallinity and dispersion in active layer is regulated by designing oligomer instead of small molecules to some extent. However, the structure-property relationship has not still uncovered for these oligomers completely.

In this work, we constructed an A_1 -(D-A)₂-D-A₁ type oligomer of DRCN4FBT and its parent A₁-D-A-D-A₁ type small molecule of DRCN2FBT to study the influence of oligomer structure on optoelectronic properties, in which bisfluorobenzothiadiazole (2FBT), thiophene and cyanorhodanine groups were used as basic elements. Their molecular structures are shows in Figure 1. Inserting D-A configuration is considered to strengthen the intra-molecular charge transfer (ICT) effect and improve the molar extinction coefficient and film formation. Introducing of electron-deficient cyanorhodanine terminal is suggested to reduce the HOMO energy level, which is beneficial to increase the open-circuit voltage.²⁶ Our results demonstrate that, with an inserting D-A framework, the oligomer DRCN4FBT exhibits more intense absorption with a red-shifted absorption spectrum, higher carrier mobility, better film formation in comparison with the small molecule DRCN2FBT. Benefited from these qualities, DRCN4FBT exhibit better photovoltaic properties with a higher power conversion efficiency (PCE) of 5.43%, which is increased by about 20% in comparison with the DRCN2FBT in these fullerene-based OSCs. This work provides an efficient strategy to supervise molecular absorption, carrier mobility, active layer morphology, further improve the photovoltaic performance by designing oligomer instead of its parent small molecule.



Scheme 1. Synthetic routs of DRCN2FBT and DRCN4FBT.

2. Experimental Section

2.1. Materials and Synthesis

All reagents were purchased. Tetrahydrofuran and toluene were distilled over sodium before used. The other reagents were directly used without further purification. The synthetic routes of DRCN2FBT and DRCN4FBT are depicted in Scheme 1. Their

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molecular structures are characterized by ¹H, ¹³C NMR, high resolution mass spectrometry (HRMS) and elemental analysis (EA), which are depicted in Electronic Supporting Information (ESI). Good solubility in hot common solvents (such as chloroform and chlorobenzene) is exhibited for both molecules.

Synthesis of compound 1^[27]

A solution of 4,7-dibromo-5,6-difluoro-2,1,3-benzothiadiazole (1.63 g, 4.94 mmol), tributyl(4-(2-ethyl-hexyl)thiophen-2-yl)stannane (6.0 g, 12.40 mmol), and Pd₂(dba)₃ (226.2 mg, 0.62 mmol), tri(o-tolyl)phosphine (300.7 mg, 2.48 mmol) and toluene (50 mL) was degassed in a 100 mL two-neck round-bottom flask and stirred at refluxing temperature for 4 h under the N₂ atmosphere. After being cooled to room temperature, the mixture was poured into water (150 mL) and extracted with CH₂Cl₂ (30 mL×3). The organic phases were combined and dried over anhydrous MgSO₄. The solvents were then removed off under reduced pressure and there was purified by silica gel chromatography using PE as eluent to give yellow solid with a yield of 86% (2.38 g). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 2H), 7.19 (s, 2H), 2.66 (d, *J* = 6.9 Hz, 4H), 1.65-1.60 (m, 2H), 1.40-1.25 (m, 16H), 0.94-0.90 (m, 12H).

Synthesis of compound 2^[27]

To a solution of compound **1** (2.3 g, 4.10 mmol) in 50 mL THF, was added *N*-bromosuccinimide (1.68 g, 9.43 mmol) in portions over a course of 30 min without light. The mixture was stirred for another 12 h at room temperature and 100 mL water was added in it to quench the reaction. The mixture was extracted with CH_2Cl_2 and the resulting organic phase was washed with brine and dried over anhydrous MgSO₄. The solvent was removed off under reduced pressure and the residue was purified by silica gel chromato-graphy using PE as an eluent to give orange red solid with a yield of 82% (2.42 g). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 2H), 2.62 (d, *J* = 7.2 Hz, 4H), 1.80-1.66 (m, 2H), 1.45-1.23 (m, 16H), 0.99-0.85 (m, 12H).

Synthesis of compound 3

A solution of compound 2 (1.0 g, 1.39 mmol), (5-(1,3-dioxolan-2-yl) tributylstannane (1.86 g, 4.17 mmol) and Pd₂(dba)₃ (63.6 mg, 0.21 mmol), tri(o-tolyl)phosphine (84.6 mg, 0.84 mmol) and toluene (50 mL) was degased with N_2 flew in a 100 mL two-neck round-bottom flask, and was stirred at refluxing temperature for 4 h under the N₂ atmosphere. After being cooled to room temperature, 30 mL THF solution with 10% dilute hydrochloric acid was added. The mixture was stirred overnight at room temperature and poured into water (150 mL), then extracted with CH_2Cl_2 (30 mL×3). The organic phases were collected and dried over anhydrous MgSO₄. The solvents were then removed off under reduced pressure and the residue was purified by silica gel chromatography using PE-DCM(1:1, v/v) as an eluent to give amaranth solid with a yield of 70%(760 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.93 (s, 2H), 8.14 (s, 2H), 7.76 (d, J = 4.0 Hz, 2H), 7.39 (d, J = 4.0 Hz, 2H), 2.87 (d, J = 7.3 Hz, 4H), 1.91-1.68 (m, 2H), 1.42-1.25 (m, 16H), 0.92-0.87 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 182.68, 148.63, 145.60, 142.99, 141.47, 136.75, 135.00, 133.90, 131.24, 127.02, 40.12, 37.13, 33.88, 32.77, 32.50, 31.96, 29.91, 29.28, 29.22, 28.65, 27.12, 25.79, 22.91, 14.17, 10.80. Elemental analysis for [C₄₀H₄₂F₂N₂O₂S₅], calculated: C 61.51%, H 5.42%, N 3.59%; found: C 61.39%, H 5.67%, N 3.72%.

Synthesis of compound 4

A solution of compound 2 (1.0 g, 1.39 mmol), (5-(1,3-dioxolan-2-yl) tributylstannane

(0.62 g, 1.39 mmol) and Pd(PPh₃)₄ (80.3 mg, 0.07 mmol) and toluene (20 mL) was degased with N₂ flew in a 100 mL two-neck round-bottom flask, and was stirred at refluxing temperature for 4 h under the N₂ atmosphere. After being cooled to room temperature, 30 mL THF solution with 10% dilute hydrochloric acid was added. The mixture was then stirred overnight at room temperature and poured into water (150 mL), then extracted with CH₂Cl₂ (30 mL×3). The organic phases were combined and dried over anhydrous MgSO₄. The solvents were then removed off under reduced pressure and the residue was purified by silica gel chromatography using with PE-DCM(1:1, v/v) as an eluent to give red solid with a yield of 42% (438 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.95 (s, 1H), 8.12 (s, 1H), 7.96 (s, 1H), 7.78 (d, J = 4.0 Hz, 1H), 7.40 (d, J = 4.0 Hz, 1H), 2.88 (d, J = 7.3 Hz, 2H), 2.62 (d, J = 7.2 Hz, 2H), 1.77 (d, J = 25.4 Hz, 2H), 1.36 (s, 16H), 0.93 (d, J = 4.4 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 182.63, 148.43, 145.63, 142.93, 141.84, 141.40, 136.69, 134.79, 133.67, 132.47, 131.19, 126.94, 115.35, 111.24, 40.05, 33.81, 32.49, 28.72, 25.75, 23.09, 14.16, 10.83. Elemental analysis for [C₃₅H₃₉BrF₂N₂OS₄], calculated: C 56.06%, H 5.24%, N 3.74%; found: C 56.01%, H 5.30%, N 3.93%.

Synthesis of compound 5

A solution of compounds 4 (438 mg, 0.58 mmol), 2,5-bis(trimethylstannyl)thiophene (119 mg, 0.29 mmol), and $Pd_2(dba)_3$ (13.3 mg, 0.67 mmol), tri(o-tolyl)phosphine (17.7 mg, 2.66 mmol) in toluene (20 mL) was degased with N₂ flew in a 100 mL two-neck round-bottom flask and was stirred at refluxing temperature for 12 h under the N₂ atmosphere. After being cooled to room temperature, the mixture was poured into water

(150 mL) and extracted with CH₂Cl₂ (30 mL×3). The organic phases were combined and then dried over anhydrous MgSO₄. The solvents were then removed off under reduced pressure and the residue was purified by silica gel chromatography using PE-DCM(1:3, v/v) as an eluent to give purple solid with a yield of 67% (276 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.87 (s, 2H), 8.05 (d, J = 8.5 Hz, 4H), 7.69 (s, 2H), 7.33 (s, 2H), 7.19 (s, 2H), 2.80 (t, J = 9.3 Hz, 8H), 1.78 (s, 4H), 1.34 (s, 32H), 0.88 (s, 24H). ¹³C NMR (101 MHz, CDCl₃) δ 182.38, 148.31, 145.57, 142.51, 141.08, 138.29, 136.55, 135.83, 135.56, 134.60, 134.30, 134.27, 133.43, 131.30, 128.80, 126.41, 126.03, 111.31, 109.85, 39.84, 33.95, 32.52, 29.08, 28.63, 26.93, 25.76, 23.20, 22.64, 19.46, 14.24, 11.46, 10.81. Elemental analysis for [C₇₄H₈₀F₄N₄O₂S₉], calculated: C 62.50%, H 5.67%, N 3.94%; found: C 62.32%, H 5.61%, N 4.05%.

Synthesis of compound DRCN2FBT

Compound 3 (250 mg, 0.32 mmol), 2-(3-ethyl-4-oxo-thiazolidine-2-methylene) propane (620 mg, 3.2 mmol), triethylamine (0.25 mL) and chloroform (30 mL)were added in 50 mL two-neck bottles in turn. The mixture was reacted at 60 °C for 12 h under nitrogen protection. After cooled to room temperature, the reaction liquid was poured into anhydrous methanol (200 mL) to form precipitation. The precipitation was filtered and purified by silica gel chromatography using dichloromethane as an eluent to obtain DRCN2FBT as purple black solid with a yield of 52% (190 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.16 (s, 2H), 8.09 (s, 2H), 7.50 (d, *J* = 4.1 Hz, 2H), 7.42 (d, *J* = 4.1 Hz, 2H), 4.39-4.29 (m, 4H), 2.92-2.83 (m, 4H), 1.81-1.74 (m, 2H), 1.48-1.19 (m, 16H), 1.15-0.79 (m, 18H). HRMS (m/z) for C₅₆H₅₂F₂N₈O₂S₇, calculated: [M]⁺ 1130.2226, found: [M]⁺

1130.2376. Elemental analysis for [C₅₆H₅₂F₂N₈O₂S₇], calculated: C 59.44%, H 4.63%, N 9.90%; found: C 59.26%, H 4.51%, N 10.02%.

Synthesis of compound DRCN4FBT

Compounds **5** (270 mg, 0.19 mmol), 2-(3-ethyl-4-oxo-thiazolidine-2-methylene) propane (367 mg, 1.9 mmol), triethylamine (0.2 ml) and chloroform (30 mL) were added in 50 mL two-neck bottles in turn. The mixture was reacted at 60 °C for 12 hunder nitrogen protection. After cooled to room temperature, the reaction liquid was poured into anhydrous methanol (200 mL) to form precipitation. The precipitation was filtered and purified by silica gel chromatography using dichloromethane as an eluent to obtain DRCN4FBT as purple black solid with a yield of 48%(206 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.58-7.60 (m, 6H), 7.00 (s, 2H), 6.88 (s, 2H), 6.43 (s, 2H), 4.05 (s, 4H), 2.47 (s, 8H), 1.56 (s, 4H), 1.32 (m,32H), 0.96 (m, 30H). HRMS (m/z) of C₉₀H₉₀F₄N₁₀O₂S₁₁ calculated [M]⁺ 1772.4520, found: [M]⁺ 1772.4022. Elemental analysis for [C₉₀H₉₀F₄N₁₀O₂S₁₁], calculated: C 60.99%, H 5.12%, N 7.90%; found: C 60.74%, H 5.07%, N 8.12%.

3. Results and Discussion

3.1. Thermal Properties and Crystallinity

The thermo-gravimetry (TGA) curves of DRCN2FBT and DRCN4FBT are shown in Figure S1. Under a nitrogen atmosphere, both molecules exhibit good thermal stability with high decomposition temperature over 390 °C at 5% weight loss. Their differential scanning calorimetry (DSC) curves are further depicted in Figure S2. It is observed that both molecules have obvious melting temperature ($T_{\rm m}$) upon heating and crystallization

peak (T_c) upon cooling. Furthermore, DRCN2FBT has higher T_c and T_m values, indicating that oligomer has a subdued crystallinity in comparison with small molecule.²⁸

3.2. Optoelectronic Properties

The UV-vis absorption spectra of DRCN2FBT and DRCN4FBT in 10^{-5} mol L⁻¹dilute chloroform solution and their thin films are depicted in Figure 2. The detailed optical data are listed in Table 1. In dilute chloroform solution, DRCN4FBT delivers a red-shifted absorption profile with a π - π * absorption peak in 300-400 nm and an ICT absorption peak in 400-650 nm in comparison with DRCN2FBT. Moreover, the maximum extinction coefficient is increased from $9.1 \times 10^4 \,\text{M}^{-1} \text{cm}^{-1}$ of DRCN2FBT to $1.23 \times 10^5 \,\text{M}^{-1} \text{cm}^{-1}$ of DRCN4FBT. It indicates that DRCN4FBT has more intense absorp -tion than DRCN2FBT. Oligomer is more benefited to increase absorption than small molecule. In addition, from the solution to the thin film, the absorption spectra of both molecules exhibit significant bathochromic profile due to their closer intermolecular stacking in the thin films.²⁹ The maximum absorption peak locates at 585 nm for the DRCN2FBT film and 623 nm for the DRCN4FBT film. Thus, their optical band gaps (E_s^{opt}) are 1.70 eV and 1.61 eV, respectively, estimated from the onset of the film absorption. It indicates that absorption can be improved by introducing a D-A building into small molecule.



Figure 2. (a) UV-vis absorption spectra in chloroform solution and (b) UV-vis absorption spectrain chloroform solution and in their neat films by normalized treatment for DRCN2FBT and DRCN4FBT.

3.3. Electrochemical Properties

Figure S3 displays the electrochemical cyclic voltammetry (CV) curves for DRCN2-FBT and DRCN4FBT. The onset oxidation and reduction potentials (E_{ox}/E_{red}) are 1.10 V/-0.89 V and 0.98 V/-0.82 V vs Ag/Ag⁺ for DRCN2FBT and DRCN4FBT, respectively. The calculated electrochemical data are listed in Table 1. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels (E_{HOMO} / E_{LUMO}) are estimated to be -5.46 eV/ -3.47 eV for DRCN2FBT and -5.28 eV /-3.54 eV for DRCN4FBT based on empirical equation.²⁷ Here, oligomer DRCN4FBT deliversan increasing HOMO energy level compared to small molecule DRCN2FBT. And both molecules show appropriate HOMO and LUMO energy levels to the PC₇₁BM acceptor, which have enough force to promote exciton dissociation in the PC₇₁BM-based OSCs.



Figure 3. (a) The device structure and (b) Energy levels of DRCN2FBT, DRCN4FBT and PC₇₁BM.

Table 1. Optical and electrical properties of DRCN2FBT and DRCN4FBT.

Donor	λ_{max} (nm)		$\lambda_{onset.film}$	$E_{\rm g}^{\rm opt}$	$E_{\rm HOMO}$	E_{LUMO}
	Solution	Film	(nm)	$(eV)^{a}$	$(eV)^{b}$	$(eV)^{b}$
DRCN2FBT	548	585,653	720	1.72	-5.46	-3.47
DRCN4FBT	550	623	777	1.60	-5.28	-3.54

^aCalculated from the absorption band edge of the films, $E_g^{opt}=1240/\lambda_{onset}$ ^bCalculated from empirical equation: $E_{HOMO} = -(E_{ox} + 4.8)$ eV, $E_{LUMO} = (E_{red} + 4.8)$ eV(The formal potential of Fc/Fc⁺ is 0.44 V vs. Ag/AgCl measured in this work)

3.4. Theoretical Calculations

Figure 4 shows the optimized conformations (front and side view) and their calculated LUMO and HOMO surfaces of DRCN2FBT and DRCN4FBT using the hybrid density functional theory (DFT) at the B3LYP/6-31G* level using Gaussian 09W, in which all alkyl side chains in thiophene or rhodanine units are replaced with shorter methyl in order to simplify their calculation. It is seen that both molecules have good planarities from the front and side view of the molecular skeleton. Their torsion angle between elements is less than 10 degrees. The small torsion angle is beneficial to the π - π stacking between molecules and can improve the hopping charge transfer ability. However, due to

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longer molecular skeleton, oligomer DRCN4FBT exhibits more widely distributed electron clouds for HOMO and LUMO and more electron cloud overlap between HOMO and LUMO than small molecule DRCN2FBT. Here, this tunable planar structure and extended electron clouds distribution are available to further result in higher extinction coefficient and promote charge transmission.²²



Figure 4. Optimized geometries of the front and side views, HOMO and LUMO orbitals calculated for DRCN2FBT and DRCN4FBT using Gaussian at the B3LYP/6-31G* level.

3.5. XRD Analysis

The ordered structures of DRCN2FBT and DRCN4FBT in the solid state were investigated by powder X-ray diffraction (XRD) measurement. Figure 5 shows the XRD patterns of the DRCN2FBT and DRCN4FBT powders. It is clear that, in the small-angle region, an intense diffraction peak from (100) at $2\theta = 5.45^{\circ}$ (d-spacing of 16.2 Å), but only a weak diffraction peak at $2\theta = 5.65^{\circ}$ (d-spacing of 15.23 Å) is exhibited for the DRCN4FBT powder. At the same time, in the wide-angle region, an intense diffraction

peak from (010) at $2\theta = 25.07$ ° (d-spacing of 3.55 Å) for the DRCN2FBT solid and a weak diffraction peak at $2\theta = 25.13$ ° (d-spacing of 3.54 Å) for the DRCN4FBT solid are observed. In comparison with their different diffraction peaks and their intensity in XRD patterns of both molecules, DRCN2FBT has more ordered lamellar structures and higher crystallinity than DRCN4FBT.^{21,22} This is coincident with more planar structure of DRCN2FBT.



Figure 5. XRD patterns of DRCN2FBT and DRCN4FBT pristine solid powders.

3.6. Photovoltaic Properties

Figure 3 shows the bulk heterojunction architecture and energy levels of the devices. The donor/acceptor ratios of 1:0.8, 1:1 and 1:1.2, as well as concentrations of 1,8-diiod -octane (DIO) from 0.2 wt% to 0.6 wt% were selected to optimize device performances. The measured photovoltaic parameters of these solar cells are summarized in Table S1, S2, S3 and S4. The current density–voltage (J–V) curves are shown in Figure S4, S5, S6 and S7 under an illumination of AM1.5G simulated solar light at 100 mW/cm². It is found that the donor/acceptor ratio and the additives amount have a significant effect on the photovoltaic properties. The optimum donor-acceptor ratio and the additive dosage

are 1:1 and 0.4%, respectively for these cells.

Under the optimal conditions, the corresponding current density-voltage (*J-V*) curves of the devices are shown in Figure 6, and their photovoltaic parameters are summarized in Table 2. It is observed that the optimal DRCN4FBT:PC₇₁BM based solar cell exhibit better photovoltaic properties than the optimal DRCN2FBT:PC₇₁BM based solar cell. The maximum PCE value is 5.43% for the DRCN4FBT:PC₇₁BM based solar cell with a circuit current density (J_{sc}) of 13.43 mA cm⁻², a V_{oc} of 0.72 V, and a fill factor (*FF*) of 56.24%. Obviously, the DRCN4FBT:PC₇₁BM cell exhibits increasing PCE, J_{sc} , and *FF* values except for V_{oc} in comparison with the DRCN2FBT:PC₇₁BM cell. Furthermore, The PCE and J_{sc} values are increased by 20% for the device using oligomer DRCN4FBT instead of small molecule DRCN2FBT as an electron-donating material. These results indicates that using oligomer instead of small molecule, simply with inserting a D-A building, is efficient approach to improve photovoltaic properties for these fullerene based OSCs.

Figure 6(b) shows the external quantum efficiency (*EQE*) spectra of the optimal DRCN2FBT:PC₇₁BM and DRCN4FBT:PC₇₁BM based solar devices. A broader spectral response region from 300 nm to 800 nm, but with a reduced maximum *EQE* of 65%, is observed in the DRCN4FBT:PC₇₁BM blend film rather than the DRCN2FBT:PC₇₁BM blend film. It is suggested that, as a whole, DRCN4FBT:PC₇₁BM based cell should have better photon response. Thus, this cell delivers a higher J_{sc} than the DRCN2FBT:PC₇₁BM based cell.



Figure 6. (a) J-V curves of the DRCN2FBT:PC₇₁BM and DRCN4FBT:PC₇₁BM based solar cells at an optimal processing condition under a simulated AM 1.5 G irradiation (100 mW cm⁻²) and (b) *EQE* curves of the optimized devices based on DRCN2FBT:PC₇₁BM and DRCN4FBT:PC₇₁BM.

Table 2. Photovoltaic parameters of the solar cells based on DRCN2FBT:PC71BM and

Donor	DIO	$V_{ m oc}$	$J_{ m sc}$	EE(0/)	$PCE_{max}(\%)$	R _s	\mathbf{R}_{sh}
		(V)	(mAcm^{-2})	FF (%)	PCE _{ave} (%)	$(\Omega.cm^2)$	$(\Omega.cm^2)$
DRCN2FBT	NO	0.75	8.48	39.7	2.52(2.31)	24.2	172.4
	0.4%	0.75	11.93	53.0	4.53(4.26)	18.4	195.1
DRCN4FBT	NO	0.72	10.15	42.8	3.13(2.82)	21.8	185.3
	0.4%	0.72	13.43	56.2	5.43(5.16)	14.4	260.5

DRCN4FBT:PC₇₁BM at an optimal processing condition.

The best PCE values, and the average PCE values are provided in parentheses from 15 devices.

3.7. Film Morphology and Charge Mobility

Figure 7 shows the height and phase images of the DRCN2FBT:PC₇₁BM and DRCN2-FBT:PC₇₁BM blend films recorded by the atomic force microscopy (AFM) using the trapping mode. It is found that the root-mean-square (RMS) roughnesses are 3.96 and 2.76 nm for the DRCN2FBT:PC₇₁BM blend films before and after adding the DIO additive, respectively. However, the RMS roughnesses are much decreased to 3.04 and

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2.26 nm for the DRCN4FBT: PC₇₁BM blend films at the corresponding condition, respectively. It is distinct that the DIO additive has a great impact on the morphology of the active layer. From the reduced RMS value, it indicates that adding DIO additive can reduce the aggregation of the DRCN2FBT:PC71BM and DRCN4FBT:PC71BM blend film,^[31] and is beneficial to form appropriate phase separation size of the active layer, thereby improve the charge mobility.^[32] Compared to the phase images in Figure 7, DRCN4FBT:PC71BM blend film has a more uniform morphology of the active layer. It is further found that the DRCN4FBT:PC71BM blend film has more uniform morphology than the DRCN2FBT:PC71BM blend film. After a treatment of the DIO additive, a well-organized morphology with nano-fibrils is observed in the DRCN4FBT:PC71BM blend film. Therefore, introducing oligomer of DRCN4FBT and adding the DIOtreatment areavailable to improve the active layer morphology. It is considered that, with inserting D-A unit, the crystallinity should be reduced and the self-aggregation ability should be weakened for the oligomer, which are available for DRCN4FBT to form appropriate phase separation with the receptor $PC_{71}BM$ in the their blend films and make its device exhibit much increase for J_{sc} and FF values.³¹⁻⁴⁰

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Figure 7. AFM height images (a, b, c, d) and phase images (e, f, g, h) of the active blends. (a. e) DRCN2FBT:PC₇₁BM without DIO; (b. f) DRCN2FBT:PC₇₁BM with DIO; (c, g) DRCN4FBT:PC₇₁BM without DIO; (d, h) DRCN4FBT:PC₇₁BM with DIO.

In addition, by the equation: $E_{\text{loss}} = E_{\text{g}} - qV_{\text{oc}}$, where E_{loss} is the minimum energy loss, E_{g} is the optical gap of donor, it is found that the E_{loss} of DRCN2FBT is 0.97 eV, which is higher than 0.09 eV for that of DRCN4FBT. The high E_{loss} is related to the poor phase separation of the active layer and should result in excessive non-radiation energy loss.⁴¹⁻⁴⁵ Therefore, moderately inserting the D-A unit in the molecular main chain can effectively adjust the morphology of the blend film and decrease the E_{loss} of devices.

Photoluminescence (PL) spectra of the DRCN2FBT and DRCN4FBT neat films, as well as their blend films with $PC_{71}BM$ were measured to investigate charge transfer in the photoactive layers. As shown in Figure S8, the DRCN2FBT and DRCN4FBT neat films show emission maxima at 585 nm and 623 nm, respectively. However, the PL emissions of DRCN2FBT and DRCN4FBT are quickly quenched by $PC_{71}BM$ with a quenching efficiency of 30.8% and 71.8%, respectively. It implies that the DRCN4FBT/PC₇₁BM blend. This further explains the reason of higher J_{sc} and FF for the DRCN4FBT:PC₇₁BM based cells. To investigate the charge transport performance of both active layer under optimal conditions, the hole $(\mu_{\rm h})$ and electron mobility $(\mu_{\rm e})$ of blend films were measured by space-charge-limited current (SCLC) method with the Mott–Gurney equation.⁴¹ Thus, the hole-only device with a structure of Glass/ITO/ PEDOT:PSS/active layer/ MoO₃/Au and the electron-only device with a structure of Glass/Al/active layer/Al were made. Figure 8 shows the $J^{1/2}$ -V characteristics of these devices. The detail results are summarized in Table 3. The higher hole mobility of 1.11×10^{-4} cm⁻²V⁻¹s⁻¹ and electron mobility of 7.32×10^{-5} cm⁻²V⁻¹s⁻¹ are achieved for the DRCN4FBT:PC₇₁BM based devices. In contrast, the hole and electron mobility of the DRCN2FBT:PC71BM based devices are only 6.38×10^{-5} and 3.73×10^{-5} cm⁻²V⁻¹s⁻¹, respectively. By comparison, it is found that the ratio of hole/electron mobility for the DRCN4FBT:PC71BM based devices is 1.52, which is more balance than that value of 1.72 for the DRCN2FBT:PC₇₁BM based devices. It is well known that the balance between the hole and electron mobility in the active layer plays an important role in the improvement of FF and PCE^{46,47}. Therefore, higher and more balanced hole and electron mobility is the reason why the DRCN4FBT:PC₇₁BM based devices have higher J_{sc} and FF.



Figure 8. (a) $J^{1/2}$ -V characteristics of the hole-only devices based on DRCN2FBT: PC₇₁BM and DRCN4FBT:PC₇₁BM; (b) $J^{1/2}$ -V characteristics of the electron-only devices based on DRCN2FBT:PC₇₁BM and DRCN4FBT:PC₇₁BM.

 Table 3. Hole and electron mobilities of the devices based on DRCN2FBT:PC71BM and

 DRCN4FBT:PC71BM blend films under optimal conditions.

Active layer	$(\text{cm}^2 \text{V}^{-1} \text{s}^{-1})$	$(\text{cm}^2 \text{V}^{-1} \text{s}^{-1})$	$\mu_{\rm h}/\mu_{\rm e}$	
DRCN2FBT:PC71BM	6.38×10 ⁻⁵	3.73×10 ⁻⁵	1.71	
DRCN4FBT:PC71BM	1.11×10^{-4}	7.32×10 ⁻⁵	1.52	

4. Conclusions

In summary, an A1-D-A-D-A-D-A1 type oligomer DRCN4FBT and its parent A1-D-A-D-A1 type small molecule DRCN2FBT were obtained. By a simple inserting D-A unit, oligomer DRCN4FBT exhibits a stronger and wider absorption spectrum, higher and more balanced carrier mobility in comparison with its parent small molecule DRCN2FBT. What's more, the slightly reduced crystallinity of DRCN4FBT improves the blending property and makes its PC₇₁BM based active layer form a better nano phase separation structure. As a result, the DRCN4FBT:PC₇₁BM based solar cells present a significantly improved photovoltaic properties with a higher PCE of 5.43%.

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Supporting Information

The characterization and measurement, ¹H, ¹³C NMR spectra and HRMS data, TGA, DSC, CV and PL measurement, fabrication and characterization of the solar cells and the detail *J-V* curves of the solar cells at different processing conditions.

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Research Highlights

>An A₁-(D-A)₂-D-A₁ type oligomer DRCN4FBT and its prototypical small molecule DRCN2FBT are synthesized.

>The strategy to supervise molecular absorption, mobility, crystallinity is provided.

>Their optical, electrochemical, morphological and photovoltaic properties are studied.

>DRCN4FBT shows better photovoltaic properties than DRCN2FBT in the PC₇₁BM based solar cells.