Synthesis and photophysical properties of fluorine substituted end group for benzo[1,2-b:4,5-b'] diselenophene-based small molecule acceptor

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Abstract: A-D-A types non-fullerene small molecule acceptors (NF-SMAs) have achieved excellent progress in recent years, while the development of series of new materials. Herein, a new NF-SMA, named **BDSe-4F**, based on linear benzo[1,2-b:4,5-b'] diselenophene with the difluorinated 5,6-difluoro-3-(dicyanomethylene) indanone (**IC-2F**) was synthesized and investigated. Due to the introduction of **IC-2F**, the intramolecular charge transfer is enhanced. Furtherly, the **BDSe-4F** exhibits a wider absorption from 600-800 nm in solution. From solution to film, the absorption spectrum shows an obvious red-shifted in the range of 800-900 nm and the maximum absorption peak red-shifted at 31 nm, suggesting that much stronger intermolecular interactions caused by non-covalent bond of F...S, F...Se, and S...O. The **BDSe-4F** possesses good spectral absorption range and excellent molecular stacking, which beneficial to achieve high J_{SC} and electron mobility. These results illustrate that the synergistic strategy of using benzo[1,2-b:4,5-b'] diselenophene core unit and **IC-2F** end group is a promising strategy to enhance performance in organic solar cells.

1 Introduction

Solution-processed bulk-heterojunction (BHJ) organic solar cell (OSCs) have advantages of flexible, low-cost and large-area printing via roll-to-roll process.[1-4] The power conversion efficiencies (PCE) of OSCs could improve along with synthesis of new materials and innovation of fabrication techniques.[5-7] On the other hand, as the important component of the active layer, nonfullerene small molecule acceptors (NF-SMAs) play an important role in order to blend with SMAs scientifically and achieve optimal morphology. At present, the PCE have exceeded 17% for single junction cells, [8-11] indicating that OSCs have potential commercial application value.

Over the last few years, lots of molecular engineering strategies have been exploited in the synthesis of A-D-A type NF-SMAs to improve the performance of organic solar cells.[12-15] Generally, the design strategies of A-D-A type NF-SMAs depend on the following two parts: the central donor core (D) and electron-withdrawing end groups (A). Thus, NF-SMAs could be easily regulated absorption spectrum, energy levels and film morphology by changing D or A unit.[16-17] Benzothiophene (BDT) and its derivatives possessed good plane nature and electron-rich feature has been widely used as D unit to structure rich electronic core.[18] In addition, introducing halogen atoms into the NF-SMAs is an effective strategy to regulate the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO)

energy levels simultaneously, such as introducing strong electronegativity units on donor core or using strong electron-withdrawing end groups.[19] 5,6-difluoro-3-(dicyanomethylene)indanone (IC-2F), 5,6-dichloro-3-(dicyanomethylene)indanone (IC-2CI) and 5,6-bibromo-3-(dicyanomethylene)indanone (IC-2Br) both can enhance intermolecular π - π interactions and improve intermolecular charge transfer owing to the push-pull electronic effect of donor core and end groups.

Herein, we designed and synthesized a new NF-SMA linear BDSe-4F based on benzo[1,2-b:4,5-b'] diselenophene as donor core with the difluorinated 5,6difluoro-3-(dicyanomethylene) indanone (IC-2F)electron-withdrawing units. The BDSe-4F exhibits a narrow optical band gap of 1.45 eV. Due to strong electron-rich core of benzo[1,2-b:4,5-b'] diselenophene, intramolecular charge transfer is enhanced, which beneficial to improve J_{SC} . Simultaneously, the weak intermolecular interaction of F...S, F...Se, and S...O can ameliorate the molecular stacking and morphology to achieve better electron mobility.

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2 Synthesis



Scheme 1. Synthetic route of BDSe-4F

The synthetic route of **BDSe-4F** was depicted in Scheme 1. The target compound **BDSe-4F** was obtained by the Knoevenagel condensation reaction between compound **BDSe-CHO** and compound **IC-2F** in 88% yield. In a 100 mL two-neck round-bottom flask, **BDSe-CHO** (0.10 g, 0.08 mmol), **IC-2F** (0.11 g, 0.48 mmol) was added. The reaction mixture was evacuated and backfilled with N₂ three times, and then freshly degassed chloroform (50 mL) and pyridine (0.5 mL) were added into the reaction mixture. The reaction mixture was stirred at room temperature for 6 h. Then the solution was poured into

methanol and the precipitate was filtered off and washed with methanol. The crude product was purified by silica gel column chromatography, eluting with petroleum ether/dichloromethane (1:1) to give the product as purple solid (0.12 g, 88%). The pure target compound **BDSe-4F** was characterized by ¹H NMR. As shown in **Figure 1**, ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.84 (s, 2H, =CH), 8.51-8.55 (m, 2H, Ph-H), 8.03 (s, 2H, Th-H), 7.64-7.68 (m, 4H, Ph-H), 7.09-7.16 (m, 16H, Ph-H), 2.54-2.58 (t, *J* = 7.6 Hz, 8H, CH2), 1.55-1.60 (m, 10H, CH2), 1.28-1.32 (m, 22H, CH2), 0.85-0.88 (m, 12H, CH3)



Fig. 1.¹H NMR spectra of BDSe-4F.



Fig. 2. Normalized absorption spectra of BDSe-4F in chloroform solution and films.

Table 1. Photophysical pr	roperties of BDSe-4F	in solution and thin films.
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Compound	$\lambda_{max}abs.(sol)$ [nm]	$\lambda_{max}abs.(film)$ [nm]	λ _{onset} (film) [nm]	$E_{g(opt)}$ [eV]
BDSe-4F	725	756	855	1.45

3 Results and discussion

The normalized absorption spectra of **BDSe-4F** in dilute chloroform solution and thin film were measured and the relevant parameters are described in Table 1.

As shown in Figure 2, the compound BDSe-4F shows considerable absorption range from 600 nm to 800 nm in dilute chloroform solutions. The maximum absorption peaks of BDSe-4F is exhibited at 725 nm in dilute chloroform solutions. In solid-state films, the maximum absorption peaks of BDSe-4F is exhibited at 756 nm. While for the thin films, the absorption extended broader with an obvious red-shift in the range of 800-900 nm, which attributed to the good intermolecular π - π stacking in the solid state. In addition, it is important to match with polymer donor on absorption spectrum, which are guideline for choosing donors to pair with NF-SMAs. The compound BDSe-4F better complementary with that of PM6 with the broad cover of the absorption region of 400-800 nm, which is beneficial to capture more photons thus will help increase J_{SC} in PSCs.

The onset absorption of the compound **BDSe-4F** shows at 855 nm. Furthermore, the optical bandgap of **BDSe-4F** was calculated from their absorption edge of the thin film to be 1.45 eV. The compound **BDSe-4F** exhibits a narrower optical bandgap induced by the two fluorine atoms on IC terminal.

4 Conclusion

In summary, an A-D-A structure NF-SMA was synthesized and investigated, combined benzo[1,2-b:4,5b']diselenophene and the difluorinated 5,6-difluoro-3-(dicyanomethylene) indanone (IC-2F). The BDSe-4F shows broad absorption in the range of 600-800 nm in neat film and exhibits optical band gap of 855 nm. This acceptor is typical narrow band gap NF-SMA. These results indicate that the BDSe-4F can match well with medium band gap polymer donors. In addition, Due to the existence of the F atom from end groups, the BDSe-4F have weak non-covalent interaction due to F...S, F...Se, and F...S, which beneficial to improve intermolecular π - π stacking and enhance electron mobility. This work demonstrated that the synergistic strategy of end group IC-2F and rich electronic core is a reliable strategy to construct efficient NF-SMAs.

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