Design, Synthesis and Photophysical Properties of Chlorinated Small Molecule Non-fullerene Acceptor Based on Benzotriazole for Organic Solar Cells

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Abstract: A novel narrow band-gap chlorinated non-fullerene pentacyclic small molecule acceptor based on benzotriazole with extended absorption edge to the near-infrared (NIR) region, named BZIC-4Cl, was designed and synthesized. Through introducing multi-fused benzotriazole and IC-2Cl, BZIC-4Cl could maintain a lower optical bandgap of 1.38 eV with broad and efficient absorption band from 500 to 950 nm due to increased π−π interactions by the covalently locking thiophene and benzotriazole units. There is a stronger intermolecular charge transfer (ICT) effects between the BZTP core and IC-2Cl end-group. The purity and chemical structure of the acceptor, namely BZIC-4Cl, were tested by 1H NMR. Even though BZIC-4Cl showed slightly poor solubility in certain organic solvents, BZIC-4Cl showed broad and strong absorption with a narrow band-gap which can be matched with polymer donor for efficient organic solar cells.

1. Introduction

In the last decade, Organic solar cells (OSCs) have attracted significant attention because of their low cost, light weight, high flexibility and easy solution-processing [1]. Meantime, the bulk heterojunction (BHJ) organic solar cells (OSCs) based on small molecular non-fullerene acceptors have achieved much amazing progress with the power conversion efficiencies (PCEs) over 18% for single junction cells [2], and 17% for tandem solar cells [3], which are higher than those of devices based on fullerene and its derivatives. Even though the PCEs of OSCs have made great breakthroughs recently [4], it is still rather necessary for us to optimize and improve the performance of the OSCs towards the industrial mass production.

However, we still have a long way to go for further improving the PCEs of the OSCs based on low band-gap small molecular NFAs through designing and synthesizing novel small molecular NFAs. To further extended the absorption spectra of small molecular NFAs to the near-infrared (NIR) region, many proper manipulation methods of the intramolecular charge transfer (ICT) effects were taken by introducing F or Cl atom (electron-deficient unit) [5] or CH3 (electron-rich unit) onto the end-group unit [6]. In the past few years, many novel near-infrared (NIR) region A-DA’D-A structure small molecular NFAs (such as Y1, Y1-4F, Y5 and Y6) [7] with absorption onset at about 900 nm, have been sequentially reported as excellent NFAs by Zou’s group and Yang’s group.

In this work, non-halogen small molecular non-fullerene acceptor BZIC [8] was structurally modified by using stronger electron-deficient chlorinated substituents to enhance the ICT effects and then to
extend the absorption spectra. Hence, a novel low-band-gap A-DA'D-A structure small molecule non-fullerene acceptor, namely BZIC-4Cl, was designed and synthesized. Figure 1 displays the chemical structures of two small molecule non-fullerene acceptors based on benzotriazole. After the strong electron-deficient chlorine atom (Cl) were introduced to its end-capping unit, the intramolecular charge transfer (ICT) effects are strengthened and thus lower energy levels and then wide absorption spectrum can be obtained owing to large dipole moment of C-Cl [9]. Furthermore, the introduction of electron-deficient chlorine atom (Cl) can shape more significant intermolecular stacking to further broaden the absorption spectrum of small molecule non-fullerene acceptors [10]. On the basis of the onset absorption [11], the $E_{g}^{opt}$ of BZIC-4Cl was estimated to 1.38 eV. These results imply that introduction of chlorine atom in the small molecule non-fullerene acceptors end-capping unit is a feasible strategy to extend the spectrum absorption, and thus obtain outstanding PCEs for efficient OSCs.

Figure 1. Chemical structures of BZIC and BZIC-4Cl

2. Synthesis

BZIC-4Cl was synthesized through Knoevenagel reaction between BZP-CHO and IC-2Cl with a yield of 74%. The core compound BZP-CHO (60 mg, 0.086 mmol) and the electron-accepting unit IC-2Cl (114 mg, 0.436 mmol) were added to the chloroform (8 mL) under the protection of nitrogen. Then, 0.5 mL of pyridine was added slowly. The reaction was stirred for 5 hours at room temperature. The mixture was purified by silica gel column chromatography using dichloromethane/petroleum ether (2/1, v/v) as the eluent. 75 mg of black-blue solid was obtained as the product (75 mg, 74%).

The chemical structure of acceptor molecule BZIC-4Cl was tested by $^1$H NMR. As shown in Figure 3, $^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 9.01 (s, 2H, CH$_2$), 8.78 (s, 2H, Ph-H), 8.07 (s, 2H, Ph-H), 7.97
(s, 2H, Th-H), 4.71-4.74 (d, $J = 7.6$ Hz, 2H, $CH_2$), 4.53-4.55 (d, $J = 7.6$ Hz, 2H, $CH_2$), 2.36-2.43 (m, 1H, $CH$), 1.94-1.97 (m, 2H, $CH$), 1.27-1.47 (m, 11H, $CH_2$), 0.94-1.02 (m, 13H, $CH_2$), 0.88-0.92 (t, 6H, $CH_3$), 0.68-0.71 (t, 6H, $CH_3$), 0.60-0.64 (t, 6H, $CH_3$).

Figure 3. $^1$H NMR spectra of BZIC-4Cl

3. Results and discussion

BZIC-4Cl showed slightly poor solubility than that of BZIC in certain common organic solvents such as CH$_2$Cl$_2$, CHCl$_3$ and THF. Figure 4 and Table 1 show the UV-visible absorption spectrum and the optical data of BZIC-4Cl in solid film state.

Figure 4. The UV-visible absorption spectrum of BZIC-4Cl in solid film state.

BZIC-4Cl shows a broad and strong absorption area from 500 to 1000 nm in solid film state owing to its large conjugated rigid framework structure. In solid film state, the maximum absorption peak is
located at 822.5 nm and then by theoretically computing, the optical band gap is 1.38 eV. The apparent absorption peaks are observed in the range of 500-750 nm owing to the intermolecular π-π* transition effects. The broad and strong absorption peaks are observed in the range of 750-950 nm owing to the intramolecular charge transfer (ICT) effects. Moreover, the A-DA'D-A type acceptor molecules with the push-pull electronic effects turn to extend absorption to the near-infrared (NIR) region. In the solid film state, BZIC-4Cl showed notably red-shifted absorption than that in the diluted chloroform solution, which reveals the good planarity of the acceptor molecule, stronger intermolecular interaction, better crystallinity and proper π-π stacking. The distance of the molecular π-π stacking becomes shorter and the molecular arrangement becomes highly ordered.

Table 1. The optical data of BZIC-4Cl.

| Compound | $\lambda_{\text{max}}^\text{film}$ [nm] | $E_g^\text{opt}$ [eV] |
|----------|-------------------------------------|---------------------|
| BZIC-4Cl | 822.5                               | 1.38                |

4. Conclusion

To sum up, a novel narrow band-gap chlorinated non-fullerene pentacyclic small molecule acceptor based on benzotriazole with extended absorption and strong intermolecular charge transfer (ICT) effects between the chlorinated IC-2Cl end-group and the fused BZTP donor core, BZIC-4Cl, was designed and synthesized. The purity and chemical structure of the acceptor BZIC-4Cl were tested by $^1$H NMR. BZIC-4Cl showed slightly poor solubility than that of BZIC in certain common organic solvents. But BZIC-4Cl showed wider and stronger absorption with a low bandgap of 1.38 eV. Moreover, in the solid film state, BZIC-4Cl showed notably red-shifted absorption than that in the diluted chloroform solution. Our research confirmed that chlorination strategy and the introduction of benzotriazole is an effective way to design novel non-fullerene small molecule acceptor for efficient organic solar cells.

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