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Review

Naphthodithiophene-based donor materials for solution processed organic solar cells

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ABSTRACT

As an emerging donor building block, naphthodithiophene (NDT) is causing more concerns in the field of organic semiconductors. With the rigid and coplanar molecule structure, NDT will exhibit more application space relying on its own advantage for facilitating the charge carrier transport. In this review article, we have summarized the development progress on the NDT-based donor materials for solution processed organic solar cells. Discussions and comments on those representative NDT type materials about structure and property are also presented.

1. Introduction

Naphthodithiophene (NDT) is composed of one naphthalene ring and two thiophene rings. With the different combination, it could afford many kinds of geometric isomers [1]. As an emerging donor building block, it has previously been suggested that NDT seems to be a very promising candidate unit for the design and construction of novel organic semiconductors, but the lack of practical methods for the effective synthesis of NDTs severely limits their further investigation [2]. Until 2010, Takimiya and co-workers successfully established a practical synthetic route of NDT [2] and reported NDT-based organic semiconductors with extremely high field-effect mobilities [3]. Since then many other organic semiconductors based on NDT unit were synthesized for high performance organic field-effect transistors (OFETs) [4]. Even so, when compared with the widespread usage of benzodithiophene (BDT, one benzene ring and two thiophene rings) in both OFETs and organic solar cells (OSCs) [5], it can be found that the deep study of NDT about the application in photovoltaic still needs to be strengthened. Marks and co-workers reported the first application of NDT-based donor material for OSCs in 2011 [6], which had raised the curtain on the research of NDT in the organic solar cells. Later, a few more research groups began to focus on this respect, which had promoted the development of NDT-based photovoltaic materials. In this short review, we will summarize the relevant conclusions and advances focusing on the most common linear and zigzag NDT (Fig. 1) based small molecules and polymers reported by several excellent research groups.

2. NDT-based small molecules for organic solar cells

lNDT is the first type of NDT unit to be used for the design and construction of organic photovoltaic donor materials. In order to improve the solubility of the small molecule and ensure the film uniformity, 2-ethylhexyloxy groups were introduced into the lNDT core at the 5,10 positions by Marks and co-workers in 2011 [6]. Furthermore, to broaden the absorption spectrum and lower the optical bandgap, thiophene-capped diketopyrrolopyrrole (DPP) units were attached to the each side of lNDT. When donor material **1** (Fig. 2) was combined with the electron acceptor [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$), the power conversion efficiency (PCE) of 4.06% (Table 1) was achieved—a record for a $PC_{61}BM$-based small-molecule OSCs at that time. Later, Lee and co-workers first introduced zNDT as the central building block into the small molecule system and reported a zNDT-based donor material **2** (Fig. 2) using triphenylamine capped benzothiadiazole (BT) as arms [7]. Unlike lNDT type materials, there are no side chains attached on the central zNDT unit, so the solubility was

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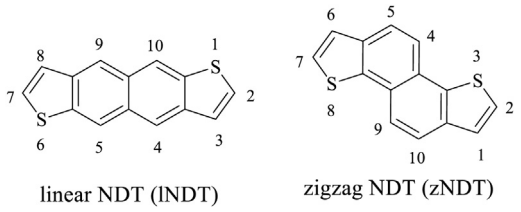

Fig. 1. Chemical structures of linear NDT (lNDT) and zigzag NDT (zNDT).

ensured only by the long alkyl side chains of adjacent thiophene π bridge. Since the optical bandgap of small molecule **2** was very large and the charge carrier transport ability was very poor, the optimized PCE of the corresponding device was only 2.2% (Table 1). After that, they replaced the acceptor unit from BT to bithiazole, the PCE of the derived small molecule **3** (Fig. 2) actually fell to 1.62% (Table 1), mainly due to the increased HOMO energy level and optical bandgap leading to a much lower V_{oc} and J_{sc} [8]. In order to further improve the photovoltaic performance of the zNDT-based small molecules, Marks and co-workers first introduced the alkoxy groups to the zNDT unit at 4,9-positions. Compared with the linear molecule **1**, molecule **4** (Fig. 2) exhibited enhanced J_{sc}, FF and a slightly higher PCE of 4.7% (Table 1) mainly due to the greater hole mobility [9]. Recently, Wei and co-workers reported two novel A–D–A type small molecules **5** and **6** (Fig. 2), based on the zNDT unit containing alkylthienyl or alkylphenyl as side chains, respectively [10]. Compared with its counterpart using BDT as the donor unit (PCE = 5.26%) [11], small molecule **5** exhibited a slightly smaller PCE (4.71%), which was mainly due to the blue-shifted absorption spectrum. When changing the conjugated side chains from alkylthienyl to alkylphenyl, both charge transport property and film formation capability were improved, leading to the higher fill factor (FF, 0.71 *vs.* 0.69), higher current density (J_{sc}, 10.77 *vs.* 7.4 mA/cm^2), and higher PCE (7.2% *vs.* 4.71%) even with much thicker active layers (Table 1). In particular, the optimal PCE for small molecule **6** was achieved with an active layer thickness beyond 300 nm, which is the best result reported for NDT-based small molecule solar cells up to date.

3. NDT-based polymers for organic solar cells

Research about NDT-based photovoltaic polymers also started with lNDT. In 2012, Peng and co-workers reported a donor–acceptor (D–A) copolymer **7** (Fig. 3) utilizing the lNDT as the donor block and electron-deficient DPP as the acceptor unit. Donor material **7** exhibited a much better photovoltaic performance with a PCE of 5.37% (Table 2) in the conventional device structure when compared with its counterpart which used BDT as the donor block (PCE = 2.91%), which benefited from the higher V_{oc} and FF of the NDT-based polymer [12]. And when utilizing the inverted device structure, both the J_{sc} and FF had been much increased, and consequently an impressively high PCE of 6.92% (Table 1) was

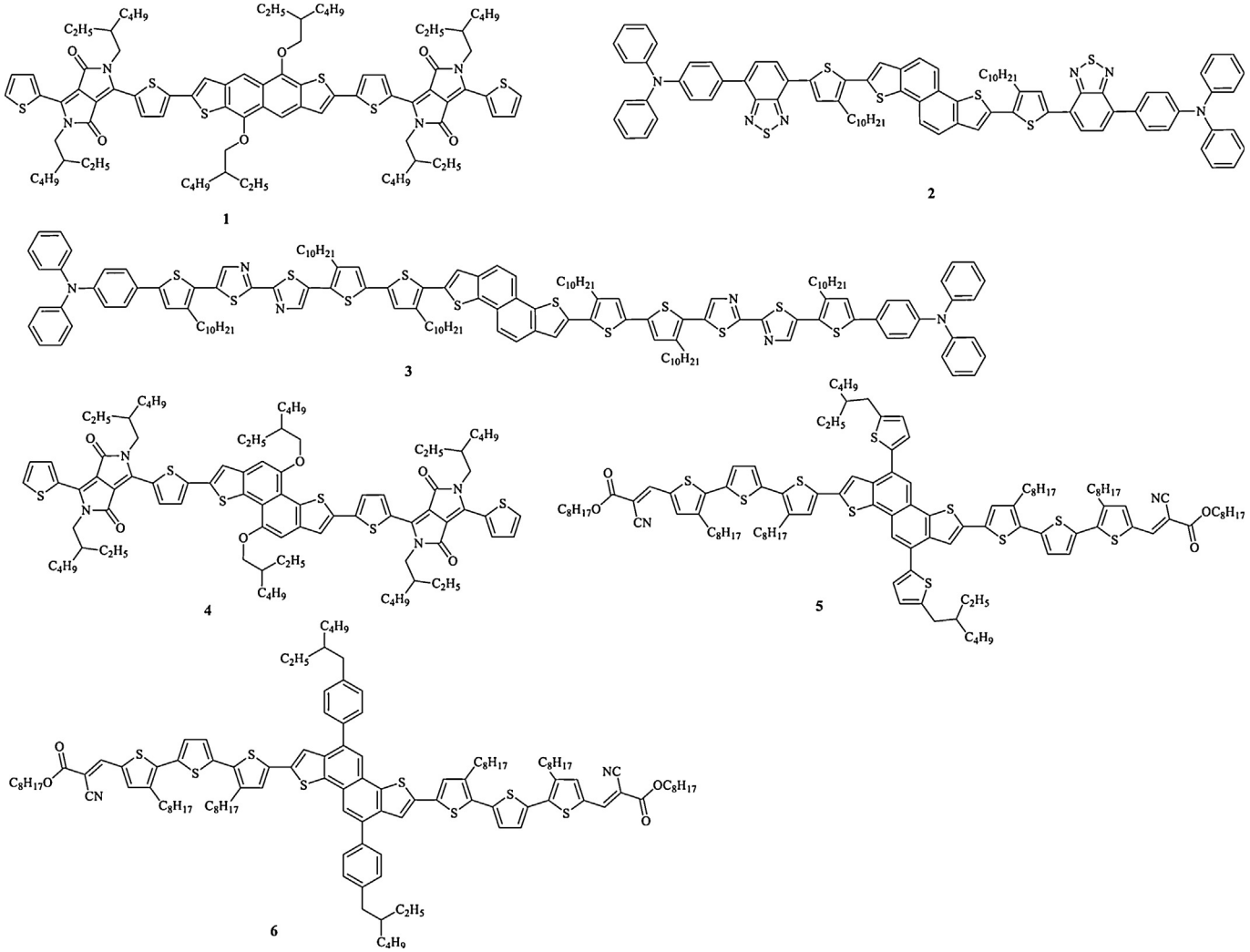

Fig. 2. Chemical structures of NDT-based small molecules **1–6**.

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