Tetrahedron 74 (2018) 4308–4314

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of B←N embedded indacenodithiophene chromophores and effects of bromine atoms on photophysical properties and energy levels

Yongchun Li [a], Huifeng Meng [a], Dong Yan [b], Yuqing Li [a], Bo Pang [a], Kai Zhang [a], Genggeng Luo [a], Jianhua Huang [a, *], Chuanlang Zhan [b, **]

[a] *College of Materials Science and Engineering, Huaqiao University, Xiamen, 361021, PR China*

[b] *Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, PR China*

ARTICLE INFO

Article history:
Received 19 May 2018
Received in revised form
12 June 2018
Accepted 15 June 2018
Available online 26 June 2018

Keywords:
B←N coordination
Indacenodithiophene
Structural modification
Photophysical properties
Energy levels

ABSTRACT

Developing novel fused π-conjugated chromophores has been an energetic research realm and knowing how to adjust their photophysical properties and energy levels through structure tailoring is of pivotal importance. Herein, based on the ladder-type π-conjugated indacenodithiophene (IDT) moiety, four B←N embedded IDT structures, namely, **BNIDT**, **BNIDT-2Br**, **BNIDT-4Br**, and **BNIDT-6Br** are synthesized and fully characterized. The influences of B←N unit embedded in the IDT backbone and Br atoms anchoring at the periphery on the photophysical properties and energy levels are discussed systematically. From IDT to **BNIDT**, a new intra-molecular charge transfer (ICT) transition band appears at lower energy (400–600 nm) in the absorption spectra with reduced optical bandgaps (E_g) from 3.25 eV to 2.11 eV and the fluorescence emission peaks red-shift from 390 nm to 565 nm along with remarkably extended fluorescence lifetimes from 1.2 ns to 12.4 ns due to the introduction of electron-deficient B←N into the backbone. Further anchoring Br atoms at the periphery of the backbone gives rise to depressed optical bandgaps, decreased fluorescence quantum yields (Φ), and shortened fluorescence lifetimes (τ) from **BNIDT** ($E_g = 2.11$ eV, $\Phi = 0.46$, $\tau = 12.4$ ns), **BNIDT-2Br** ($E_g = 2.08$ eV, $\Phi = 0.18$, $\tau = 4.9$ ns), **BNIDT-4Br** ($E_g = 1.67$ eV, non-emission) to **BNIDT-6Br** ($E_g = 1.61$ eV, non-emission). The HOMO and LUMO levels estimated from ultraviolet photoelectron spectroscopy (UPS) and optical bandgaps also experience synergetic lowering from IDT to **BNIDT-6Br**. This work indicates that backbone modification with electron-deficient B←N unit and side groups tailoring with halogen atoms are powerful to manipulate the optical properties and energy levels of fused π-conjugated chromophores.

1. Introduction

Ladder-type π-conjugated molecules have attracted intense interest and been frequently used in organic optoelectronic materials and devices [1–4], e.g., organic light emitting diodes (OLED), organic thin film transistors (OTFT), and organic photovoltaics (OPV), due to their coplanar and rigid structures, favorable packing properties, enhanced degree of π-conjugation, strong photoluminescence, and considerable charge carrier mobility. Among the massive ladder-type π-conjugated structures, indacenodithiophene (IDT) is a typical heteroarene-fused coplanar chromophore that features phenylene and thiophene fused skeleton. Since its original synthesis in 2006 [5], IDT unit has been widely used to construct organic semiconductor materials for OTFT [6–8] and OPV [9–19] applications. In these applications, IDT unit was adopted as the electron-donor building block due to its electron-rich features. To expand its applications, for instance, as an electron-drawing block, further structural modifications of IDT unit to tailor the energy levels, e.g., highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) and optical properties, e.g., optical absorption and fluorescence emission spectra are desirable.

It has been well established that Lewis acid-base interaction

---

* Corresponding author.
** Corresponding author.

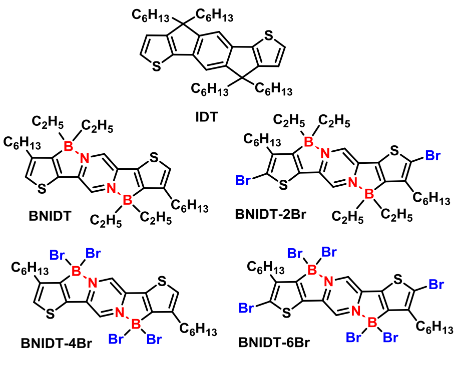
E-mail addresses: huangjianhua@hqu.edu.cn (J. Huang), clzhan@iccas.ac.cn (C. Zhan).

https://doi.org/10.1016/j.tet.2018.06.035

between boron (B) and nitrogen (N) can alter the energy levels and optical properties of conjugated structures. The B, equipped with a vacant p-orbital and N, possessing a lone pair of electron is prone to form the coordinating bond B←N upon electron sharing. This B←N unit is highly polarization, with N showing cationic feature (positive charge) and B exhibiting anionic character (negative charge). Bandgaps and energy levels were demonstrated to be effectively depressed by adding boride, e.g., BF_3, BCl_3, and $B(C_6F_5)_3$ to conjugated systems containing aromatic nitrogens due to the formation of B←N adducts, which elevates the static potential of the π-system, and thus boosts the electron-deficient nature of the π-system [20–22]. Similarly, when embedding B←N unit to the π-conjugated molecules, one can obtain electron-deficient units with low-lying energy levels and bathochromic absorption/fluorescence properties [23–34]. Recently, several conjugated molecules and polymers containing B←N have been developed and successfully used for non-fullerene acceptor materials in OPV owing to their low-lying LUMO, strong light harvesting ability, and high electron mobility [35–38]. Accordingly, the B←N unit is a desirable candidate that can be considered when designing novel structures with low-lying energy levels and bathochromic absorption/fluorescence properties.

On the other hand, the side group functionalization can be also helpful in fine-tuning the optoelectronic properties. Particularly, the halogenation of the conjugated backbone, namely, substituting the skeleton with F, Cl, or Br etc. has been widely used in the past decades as a route to tailor the molecular properties [39]. For example, F and Cl have been employed to conjugated materials to adjust the optoelectronic properties and solid state assembly of organic semiconductors [40–47]. However, Br-functionalized molecules were seldom revealed [48,49]. It's well known that Br atom also has several attractive properties. For instance, Br atom has strong electron-deficient nature and heavy atom weight in contrast to the carbon atom, which may be powerful to manipulate the optoelectronic properties, e.g., energy levels, optical absorption, and fluorescence emission when introduced into the π-conjugated molecules [39]. Moreover, from the synthesis strategies, introducing Br atoms into conjugated molecules can be feasibly achieved via N-bromosuccinimide (NBS) or bromine (Br_2). Additionally, the Br substituted carbons can also provide reaction sites, e.g., metallic coupling reaction sites for further structural tailoring or construction of conjugated copolymers. As such, Br is a valuable atom to be utilized for structural tailoring of π-conjugated molecules.

In this work, B←N unit was introduced to the IDT, obtaining B←N embedded IDT chromophores (**BNIDT**). Although similar backbones have been revealed [34], as shown in Scheme S1a, the known structures are not stable enough for chromatographic purification due to hydrolysis and no reaction sites were reserved for further construction of more complex semiconductors. Our representative design prevents these disadvantages, as shown in Scheme S1b. Furthermore, the desirable properties of Br atom drive us to use Br as substituent to finely tune the optoelectronic properties of **BNIDT**. Consequently, a series of Br-functionalized and B←N doped IDT units, i.e., **BNIDT**, **BNIDT-2Br**, **BNIDT-4Br**, and **BNIDT-6Br** are revealed in this work (Scheme 1). For comparison, the IDT unit was also included in the tests. We performed various photophysical, photoelectronic, electrochemical, and X-ray crystallography tests as well as theoretical simulations on these molecules. The systematical studies revealed a good structure-property relationships upon anchoring Br atoms on the B←N embedded IDT units.

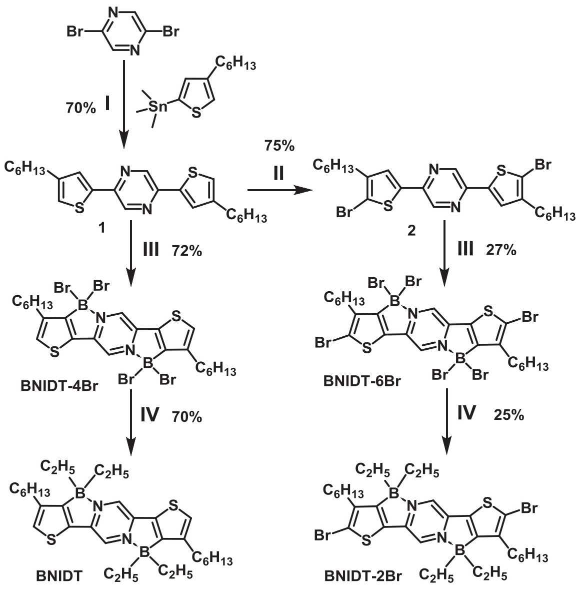


Scheme 1. Molecular structures of IDT, **BNIDT**, **BNIDT-2Br**, **BNIDT-4Br**, and **BNIDT-6Br**.

2. Results and discussion

2.1. Materials synthesis and single crystal structures

Scheme 2 shows the synthesis routes toward the four B←N doped IDT units. Starting from 2,5-dibromopyrazine, a Stille coupling reaction led to the intermediate of **1**. Compound **1** was subjected to electrophilic cyclization by BBr_3 in the presence of triethylamine (NEt_3), whose mechanism has been clarified by Murakami et al. [28], affording the four-Br substituted B←N doped IDT, **BNIDT-4Br**. Then **BNIDT-4Br** was treated by organometallic reagent, $AlEt_3$, to replace the four Br atoms by ethyl groups, obtaining **BNIDT**. In another path, the compound **1** was brominated using NBS at the α site of thiophene, producing compound **2**. Then, **BNIDT-6Br**, and **BNIDT-2Br** were synthesized with the same procedures to **BNIDT-4Br** and **BNIDT**, respectively. All the four B←N doped IDT units were confirmed by ^{1}H, ^{13}C, ^{11}B NMR, mass spectra (MALDI-TOF), and elemental analysis. For the ^{11}B NMR spectra, **BNIDT-4Br** ($\delta = -3.94$ ppm) and **BNIDT-6Br** ($\delta = -3.87$ ppm) show upfield ^{11}B resonance signals in comparison to those of **BNIDT** ($\delta = 6.18$ ppm) and **BNIDT-2Br** ($\delta = 6.50$ ppm), due to the electron-drawing property of Br atom located on the boron center (Fig. S1). On the other hand, the electron-drawing substituent of Br on the B atom renders its strong Lewis acid property. Thus, **BNIDT-4Br** and **BNIDT-6Br** were purified by re-crystallization without chromatographic treats because they are subjected to hydrolysis. When the



Scheme 2. Synthesis routes toward the four B←N embedded IDT units. Reagents and conditions: (I) $Pd(PPh_3)_4$, CuI, CsF, DMF, 120 °C, 12 h; (II) NBS, $CHCl_3$, RT, 12 h; (III) BBr_3, NEt_3, CH_2Cl_2, 0 °C, 24 h; (IV) CH_2Cl_2, 0 °C, $AlEt_3$, 30 min.