



Synthesis and properties of benzothiadiazole-pyridine system: The modulation of optical feature



Xiao Han^a, Weixiang Gong^b, Yue Tong^a, Donghui Wei^a, Yanyan Wang^a, Jie Ding^{a,**},
Hongwei Hou^{a,*}, Yinglin Song^{b,***}

^a College of Chemistry and Molecular Engineering, Zhengzhou University, Henan, 450001, China

^b School of Physical Science and Technology, Soochow University, Suzhou, 215006, China

ARTICLE INFO

Article history:

Received 27 August 2016

Received in revised form

8 October 2016

Accepted 8 October 2016

Available online 11 October 2016

Keywords:

Benzothiadiazole

Buchwald-Hartwig amination

Optical property

Nonlinear optics (NLO)

ABSTRACT

In this work, two new benzothiadiazole (BTD)-based compounds **1** and **2** were elaborately designed and synthesized, to explore the modulation on the interesting optical properties. Briefly, bipyridine-substituted compound **1** was synthesized via a modified Buchwald-Hartwig amination reaction with relatively high yield, and then derivative **2** was prepared by a following dehydrogenation reaction. The result in steady-state spectroscopic analysis and DFT/TDDFT calculation suggest the readily polarized nature of **1**. In contrast, the readily polarized nature was declined in π -conjugated molecule **2**, indicating the blue-shifted absorption and emission. Interestingly, negative cubic nonlinear refraction behavior in **1** is greater than that in π -conjugated system **2**. Furthermore, in case **1** or **2**, the photophysical property was considerably influenced by the external transition metal ion ($M = Ag^+$, Cu^{2+} or Fe^{3+}). Especially, because of the existence of external Fe^{3+} in case **1**, initially negative nonlinear refraction signal became a positive one. Such exciting result is quietly useful for the design and synthesis of new functional BTD-based dye material.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Benefited by architectural flexibility and photophysical feature, organic dye materials are highly active in the optoelectronics area [1–4], including organic photovoltaics (OPVs) [5], organic light-emitting diodes (OLEDs) [6], and organic field effect transistors (OFETs) [7] and nonlinear optics (NLO) [8,9]. Since the last decade, one π -conjugated building block, 2,1,3-benzothiadiazole (BTD), have been mainly focused on polymer optoelectronics technique [10–16]. Indeed, BTD species normally possess several desirable natures for the application in molecular optoelectronics [17,18]. Actually, BTD-based molecule is normally efficient chromophore with favorably optical versatility. Secondly, because this heterocyclic unit has a strong electron-withdrawing capacity, such derivatives are possible candidates for electron carriers. Meanwhile, BTD compound is expected to use as a unit of electron acceptor in

molecular optoelectronic device because of relatively high reduction potential and electron affinity (EA).

Up to now, elaborately designed molecular BTD derivatives also are appropriately used for many optoelectronic applications [19–28]. For example, some BTD compounds were considered as the potential red-light material, which was originated from the electrogenerated chemiluminescence (ECL) [29,30] or strong phosphorescence at room temperature [31]. A series of Au(I) and Pt(II) acetylide complexes contained electron-withdrawing BTD unit were explored for the two-photon absorption (2PA) application [32]. Currently, only few traditional donor-acceptor (D-A) BTD-based molecules have been studied for the cubic NLO properties [33,34], which may be favorable for optical parametric oscillation, frequency up-conversion, and intensity-dependent refractive index modulation. In particular, current research suggested that molecules with negative $Re(\gamma)$ capability was critical for the applications on all-optical switch (AOS) and data transmission [35,36].

Commonly, these electron-poor BTD moieties have been incorporated into the materials via the Suzuki or Stille coupling reactions, in which their organometallic derivatives are as the precursors. Actually, organometallic coupling partners sometimes give the poor coupling efficiencies [37–39], while in many cases, it

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: jieding@zzu.edu.cn (J. Ding), housongw@zzu.edu.cn (H. Hou), yisong@suda.edu.cn (Y. Song).

is challenging for the synthesis of tin and boron electron-poor derivatives. Hence, the development of alternative coupling methodologies may be considerably useful, such as C–H bond activation [40] and Sonogashira reaction [33,34,41]. In 2002, T. Hirao and the co-workers reported that some BTD derivatives were obtained by the Buchwald–Hartwig amination reactions [42,43]. When the weak electron-withdrawing pyridine group is linked on the BTD unit by the secondary amine group, it is expected that this new molecule will show the readily polarized nature, displaying the red-shifted absorption and emission, even the cubic NLO property. On the other hand, such optical performance will be modulated after an easily dehydrogenated reaction, which may result in the weakened anisotropic polarizability and relatively rigid structure. Except these, new coordinating site can be rationally modified on the BTD unit that is also actively coordinated. It will enhance the interaction between the external metal ion and BTD-based organic molecule, which probably results in the visible changes of optical capability. Inspired by these, bipyridine-substituted compound **1** (Scheme 1) was successfully synthesized via the modified amination route with relatively high yield in relatively short reaction time. Interestingly, the readily polarized nature of **1** was demonstrated by the steady-state spectroscopy and DFT/TDDFT calculation. The relatively rigid derivative **2** was subsequently prepared by the simple dehydrogenation, which showed the decline of readily polarized nature. In cubic NLO property investigations, negative cubic nonlinear refraction behavior of **1** is superior than that of **2**. Furthermore, in case **1** or **2**, the photophysical property was considerably influenced by the external transition metal ion ($M = \text{Ag}^+$, Cu^{2+} or Fe^{3+}). Because of the existence of external Fe^{3+} in case **1**, initially negative nonlinear refraction signal became the positive one.

2. Experimental section

2.1. Materials

All chemicals and solvents were purchased from commercial sources and used without further purification, unless otherwise indicated.

2.2. Measurements

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AVANCE III 400 spectrometer. Mass spectra (MS) were recorded on a Bruker Esquire 3000 plus ion trap mass spectrometer (Bruker-Franzen Analytik GmbH, Bremen, Germany). Elemental analyses were carried out on a FLASH EA 1112 analyzer. All spectroscopic experiments were performed in solution. UV/Vis absorption spectra were obtained from Hewlett Packard 8453 UV/Vis Spectrophotometer. The measurements of steady-state emission spectra were conducted on a Hitachi F-4600 fluorescence spectrophotometer at room temperature. The absolute quantum yield and lifetime of emission in sample was detected with a photoluminescence quantum yield measurement system (Edinburgh Instruments Ltd FLS980 Fluorescence Spectrometer, the fluorescence lifetime measurement range is 100 ps–50 μs .) at room

temperature. CV was conducted on a CHI660E electrochemical analyzer. In this work, a platinum mesh was used as the working electrode, a platinum mesh as the auxiliary electrode, and SCE as reference electrode. Electrochemical experiments were performed under nitrogen atmosphere in deoxygenated MeCN/DCM (V/V = 9:1) with 0.1 M Bu_4NClO_4 as supporting electrolyte at a scan rate of 200 mV s^{-1} . The top-hat Z-scan experiments and time-resolved pump-probe experiments were performed on TNLO-TR transient nonlinear refractometer (Suzhou micronano laser photon technology Co., Ltd.) with a Q-switched Nd:YAG 532 nm laser (GKPPL-1064-1-10, Beijing GK Laser technology Co., Ltd.) as the light source, where the sample solution was in 2 mm quartz cell. For the solution sample, the solvent was selected as DCM or DCM/DMF (V/V = 1: 1), and the concentration was of 5×10^{-4} M.

2.3. Syntheses

2.3.1. Compound 1

4,7-Dibromo-2,1,3-benzothiadiazole (294 mg, 1.0 mmol), 2-aminopyridine (207 mg, 2.2 mmol), 2-(dicyclohexylphosphino)-2',4',6'-triisopropylbiphenyl (Xphos, 38.2 mg, 0.08 mmol), $\text{Pd}_2(\text{dba})_3$ (36.6 mg, 0.04 mmol), and t-BuONa (269 mg, 2.8 mmol) were mixed in 10 mL anhydrous toluene, and subsequently stirred at 100 °C in 10 h under the nitrogen atmosphere. After the reaction mixture was filtered and evaporated, the raw product was purified by column chromatography on silica gel (EA/PE, 1:5). The pure target was red brown, with a yield of 75%. ^1H NMR (δ , CDCl_3 , 400 MHz): 8.31 (d, $J = 8$ Hz, 4H), 7.58–7.54 (m, 4H), 6.92 (d, $J = 8$ Hz, 2H), 6.81–6.79 (m, 2H). ^{13}C NMR (δ , CDCl_3 , 400 MHz): 154.90, 148.88, 148.06, 137.50, 126.10, 115.40, 114.12, 110.47. EI-MS $[\text{M}+\text{H}]^+$: 321.28. Elemental analysis calcd. (%) for $\text{C}_{16}\text{H}_{12}\text{N}_6\text{S}$: C 59.98, H 3.78, N 26.23, S 10.01; found: C 59.49, H 3.74, N 25.81, S 10.77.

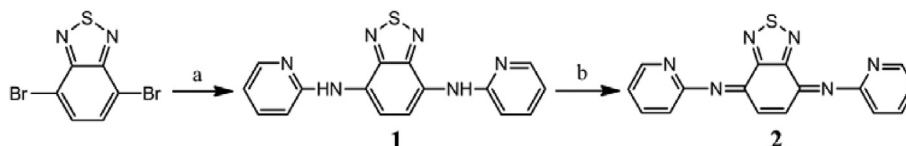
2.3.2. Compound 2

After the compound **1** (320 mg, 1.0 mmol) dissolved in THF, Ag_2O (278 mg, 1.2 mmol) was added and stirred at room temperature for 12 h. The reaction mixture was filtered and evaporated to obtain the raw product, which was further purified by column chromatography on silica gel (EA/DCM, 1:5). The pure target was orange, with a yield of 40%. ^1H NMR (δ , CDCl_3 , 400 MHz): 9.21 (s, 1H), 8.54 (d, $J = 4$ Hz, 1H), 8.42 (d, $J = 4$ Hz, 1H), 8.22 (s, 1H), 7.86 (d, $J = 8$ Hz, 1H), 7.67–7.63 (t, $J = 8$ Hz, 1H), 7.43–7.39 (t, $J = 8$ Hz, 1H), 7.03–7.00 (m, 1H), 6.96–6.89 (m, 2H). ^{13}C NMR (δ , CDCl_3 , 400 MHz): 154.80, 147.03, 137.86, 126.94, 124.51, 118.72, 115.73, 111.94. EI-MS $[\text{M}+\text{H}]^+$: 319.32. Elemental analysis calcd. (%) for $\text{C}_{16}\text{H}_{10}\text{N}_6\text{S}$: C 60.36, H 3.17, N 26.40, S 10.07; found: C 60.32, H 3.28, N 26.67, S 9.85.

3. Results and discussion

3.1. X-ray crystal structures

As shown in Scheme 1, the double amination was directly accomplished without using any organometallic precursor. In optimal condition at present, compound **1** was obtained with a relatively high yield of 75% in only 10 h. Interestingly, for compound



Scheme 1. Synthesis of compounds **1** and **2**. Reagents and conditions: (a) Pd_2dba_3 , Xphos, t-BuONa, 2-aminopyridine, toluene, reflux, 10 h; (b) 1.2 eq. Ag_2O , r.t. 12 h, THF.

Download English Version:

<https://daneshyari.com/en/article/4766308>

Download Persian Version:

<https://daneshyari.com/article/4766308>

[Daneshyari.com](https://daneshyari.com)