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SYNTHESIS AND PROPERTIES OF NOVEL ARYLAMINE DERIVATIVES OF BENZOTHIENO[3,2-b][1]BENZOTHIOPHENE

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Abstract

Thienothiophenes are essential components for the development of effective organic semiconductors. This study is devoted to the synthesis of novel arylamine derivatives of benzothieno[3,2-b][1]benzothiophene (BTBT) and investigation of their optical and thermal properties. For this purpose, the Buchwaldt–Hartwig reaction was used to couple 2,7-dibromo-BTBT with various arylamines. The fluorescence quantum yield of the resulting molecules decreased from 60 to 16%, as the complexity of the amine moiety increased. The materials synthesized exhibit relatively high glass transition temperatures and thermal stability, which suggests potential applications in organic electronics.

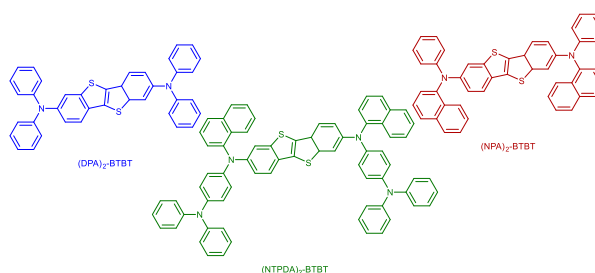
Key words: benzothieno[3,2-b][1]benzothiophene, arylamine, synthesis, fluorescence, thermal properties.

Introduction

Organic layers, in particular, hole transport layers play a crucial role in the operation of organic light-emitting diodes (OLED) devices [1]. Recently, Shi *et al.* [2] described a new hole transporting material (HTM) based on benzo[4,5]thieno[3,2-b]benzofuran with diphenylamine substituents. This material demonstrated excellent charge carrier mobility, good thermal stability, and a high triplet energy, which are better than those of the commercial HTM derived from the benzidine derivative *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenyl-[1,1'-biphenyl]-4,4'-diamine (NPD). Since many derivatives of BTBT have very high charge carrier mobility [3] and thermal stability [4] and can be processed into thin films, and since BTBT is a very popular building block for organic electronic devices, it was proposed to synthesize and investigate some novel derivatives of BTBT with aromatic amine substituents and investigate their properties.

Albeit BTBT derivatives are rarely used in OLEDs, diarylamine derivatives of Ph₂BTBT [5] and diphenylfluorene derivatives of BTBT [6] have shown characteristics comparable to and even superior than those of NPD in terms of performance, heat resistance, and service life in OLED displays. 2,7-Dioctyl benzothieno[1,3,2-b]-benzothiophene (C8-BTBT) has been used as a p-type charge transfer material in OLEDs and has shown outstanding electrical characteristics, with ON/OFF ratios exceeding 10⁶ and mobilities in the range of ~0.5–2.3 cm²·V⁻¹·s⁻¹ [7].

The structures containing both BTBT and arylamines have not been adequately described in the literature and remain unexplored, while several individual molecules of these

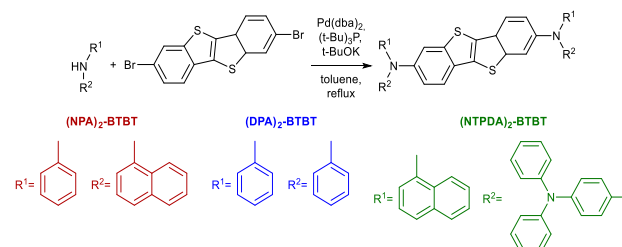


structures can be found in the patent literature. The goal of this work was to synthesize and investigate such structures.

Results and discussion

Syntheses

A synthetic route to the target compounds (DPA)₂-BTBT, (NPA)₂-BTBT and (NTPDA)₂-BTBT was based on the Buchwald–Hartwig reaction between 2,7-dibromo-BTBT and the corresponding secondary amines in the presence of a palladium catalyst (Scheme 1, Table 1). 2,7-Dibromo-BTBT was synthesized according to the published procedure [8]. The results presented in Table 1 demonstrate that, as the amine structure becomes more complex, the reaction yields decrease due to steric hinderances. This is mainly due to the formation of the larger molecular weight by-products.



Scheme 1. Synthesis of (DPA)₂-BTBT, (NPA)₂-BTBT and (NTPDA)₂-BTBT.

The crude products were purified using standard methods (recrystallization or column/flash chromatography), which afforded the target compounds with over 99% purity according

to the results of gel permeation chromatographic analysis. This is very important for measuring the electrical properties and manufacturing organic electronic devices. The resulting compounds are soluble in THF, toluene, and DCM.

Table 1. Conditions for the synthesis and yields of the target molecules

BTBT derivative	Reaction time, h	Purification method	Isolated yield, %
(DPA) ₂ -BTBT	15	recrystallization	92
(NPA) ₂ -BTBT	7	column	63
(NTPDA) ₂ -BTBT	3	chromatography	54

Investigation of the optical properties

The absorption and fluorescence spectra of the resulting molecules are shown in Fig. 1. Table 2 presents their main optical characteristics obtained for dilute solutions in THF: molar extinction coefficients and fluorescence quantum yields. An increase in the size of the donor moiety (amine) in the DPA, NPA, NTPDA series only slightly affects the position of the long-wavelength absorption maximum and significantly increases the molar extinction coefficient. This is due to both an increase in the π -system as a whole and an increase in the number of electrons of heteroatoms (nitrogen) involved in the π -conjugation. The spectral width of the absorption bands increases with an increasing size of the donor moiety (amine) in the DPA, NPA, NTPDA series: 3000 cm^{-1} , 4400 cm^{-1} , 5000 cm^{-1} . This is caused by an increase in the conformational diversity and natural oscillation frequencies due to a greater number of branches and corresponding rotational capabilities in the donor moieties. The position of the maximum of the fluorescence spectrum shifts towards higher wavelengths with an increasing size of the donor moiety.

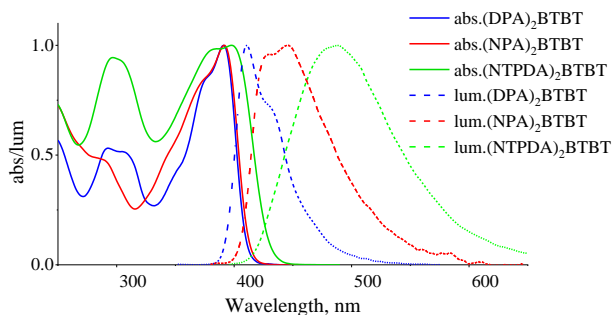


Figure 1. Absorption and luminescence spectra of (DPA)₂-BTBT, (NPA)₂-BTBT, and (NTPDA)₂-BTBT.

Table 2. Optical properties of the compounds obtained in diluted THF solutions

BTBT derivative	λ_{abs}^{max} , nm	λ_{fluor}^{max} , nm	ε^{max} , $\text{M}^{-1}\cdot\text{cm}^{-1}$	Q, %
(DPA) ₂ -BTBT	391	411/430 ^{sh}	29700	60
(NPA) ₂ -BTBT	392	420 ^{sh} /446	68500	29
(NTPDA) ₂ -BTBT	398	488	67900	16

At the same time, the magnitude of the Stokes shift in the DPA, NPA, NTPDA series increases: 1200 cm^{-1} , 1700 cm^{-1} , 4500 cm^{-1} . An increase in the Stokes shift is explained by the large energy losses due to rotational vibrations of the rings, which are parts of the DPA, NPA, NTPDA moieties. The spectral width of the fluorescence bands increases in the same

way as the long-wavelength absorption bands: 2400 cm^{-1} , 3900 cm^{-1} , 4200 cm^{-1} . There is a fairly good mirror symmetry of the absorption and fluorescence spectra. Consequently, the sets of conformations and natural oscillation frequencies of the ground and excited states are approximately the same.

The quantum yield of fluorescence in the DPA, NPA, NTPDA series is consistently decreasing (Table 2). This is due to changes in the relative positions of singlet and triplet $\pi\pi^*$ and $n\pi^*$ junctions, which is determined by the geometry of the molecule and the number of heteroatoms included in the conjugation chain.

Investigation of the thermal properties and phase behavior

As is shown in Table 3, the materials under investigation exhibited good thermal stability and melting points (T_m) that fall within the operating and manufacturing range of OLED devices.

Table 3. Thermal properties of the resulting materials

BTBT derivative	T_d , °C	T_m , °C	T_g , °C
(DPA) ₂ -BTBT	442	316	–
(NPA) ₂ -BTBT	506	273	136
(NTPDA) ₂ -BTBT	526	318	163
NPD [2]	490	–	104

The higher glass transition temperature (T_g) indicates the better morphological stability of the BTBT-based compounds compared to commercially available HTM-NPD [2]. Therefore, the novel materials are expected to have good charge transport properties owing to their composition and excellent thermal stability. The thermal properties of these materials are comparable to or better than those of commercially available NPD, which opens up opportunities for further research.

Conclusions

The new BTBT derivatives were synthesized and their optical and thermal properties were investigated. The results indicate that (DPA)₂-BTBT, (NPA)₂-BTBT, and (NTPDA)₂-BTBT may be of interest as light-emitting components of OLEDs and/or as auxiliary transport components of the same devices owing to their high glass transition temperatures and appropriate spectral characteristics. To assess the potential for their application, the main focus will remain on estimating the electrical properties and the lifetime of devices. Furthermore, our molecular design strategy and the expansion of the library of BTBT-based materials demonstrated in this work will contribute to the commercialization of OLED devices. We believe that BTBT derivatives may also perform well in solution-processed TADF OLED, OPV, PLED, and QLED systems, providing outstanding solubility and stability.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the synthetic procedures and NMR, GPC, DSC, TGA, and optical data for the compounds obtained. For ESI, see DOI: 10.32931/ioXXXXXx.

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