Research Article

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Color tunable benzothiadiazole-based small molecules for lightening applications

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Abstract: 2,1,3-Benzothiadiazole (BTD) is a key motif for the chemistry of photoluminescence molecules and its application in lightening technology as well as cell imagining. Evaluating the characteristics and reaction mechanisms of the BTD derivatives in molecular is critical for molecular designing. Research has been turned to BTD-extended derivatives owing to their possible usage in organic photovoltaics, organic light-emitting diodes, liquid crystal devices, dye-sensitized solar cells, and many other applications. Herein, three small molecules with a BTD core, 4,7-dim-tolybenzo[c][1,2,5]thiadiazole (NK1), 4,7-bis(3,4,5-trifluorophenyl)benzo[c][1,2,5]thiadiazole (NK2), and 4,7-bis(5-(m-toly1thiophen-2-yl)benzo[c][1,2,5]thiadiazole (NK3), were designed and synthesized and their molecular structures were elucidated. Additionally, their photophysical and electrochemical behaviors as well as the aggregation-induced enhanced emission properties were examined to investigate their possible usage in cell imaging and organic electronic applications. The HOMO energy level of molecules has been found as −5.96, −5.58, and −5.60 eV, respectively. In the emission spectra, it was seen that molecules showed green, blue, and red emission, respectively.

Keywords: benzothiadiazole, small organic molecule, molecular characterization, single crystal

1 Introduction

π-Conjugated organic structures have an important place in industrial and academic studies for organic electronic applications like organic light-emitting diodes (OLEDs), thin film organic field-effect transistors, as well as the fluorescence probes, organic solid lasers, and due to their
electrochemical and optical characteristics [1,2,3]. Especially in the organic electronic field, molecules containing quinoxaline [4], benzimidazole [5], and 2,1,3-benzothiadiazole (BTD) building blocks have been used as a π-conjugated organic structure [6]. BTD is one of the most crucial classes of conjugated structures due to the relatively higher reduction potentials and electron affinity (EA) required for the usage. In fact, the π-extended conjugated structures' HOMO/LUMO levels are defined by their electrochemical reduction/oxidation potentials, or their EA and ionization potentials that are strongly related to the energy of the beginning of the absorption peak in the solid phase spectrum [7].

BTD, as an electron-withdrawing acceptor group, has received considerable attention for photovoltaic systems as well as fluorescent sensors, and photocatalytic studies [8]. BTD can be functionalized with various donor groups after the bromination reaction (Figure 1). Thanks to this feature, it has been possible to develop bright molecules with many different purposes.

In 2021, Nie et al. classified small molecules with a BTD core into four groups according to the number of having BTD core and compared their efficiency [9]. The efficiency of the molecules using the BTD motif in organic photovoltaics was compared depending on the functional groups they have. In another study conducted in 2022, the efficacy of functional groups attached to the BTD group in photocatalysis was assessed [10].

Special phenomena termed aggregation-induced emission (AIE) and aggregation-induced enhanced emission (AIEE) occur in molecules that show increased emission intensity at higher concentrations than in dilute solutions.
AIEE active organic compounds can be used as luminescent analytical/biochemical probes, cell imaging, phototherapy, liquid crystals, and organic electronics due to their high emissivity. AIEE active BTD derivatives are limited in the literature. The initial strategy used for the development of AIE-active molecules with a BTD core was to attach the tetraphenylethylene to the BTD core (Figure 2) [14]. In recent years, Pazini et al. have presented a series of BTD-derived molecules, studying the presence of AIEE properties in acetone/water mixture. They presented eight new organic molecules (given in Figure 2) with BTD core and they showed AIEgenic feature in the high polarity mixture. AIEgenic molecules that contain BTD motifs published to date are presented in Figure 2.

One of the biggest problems in developing emissive molecules for OLEDs is the aggregation-inducing quenching effect. This effect is that molecules that show high emissivity in the solution phase do not show emissivity or low emissivity by clustering at the coating stage in device production. In this sense, the obtaining of new organic molecules that can exhibit intense light emission in the solid phase has significance.

It is known that molecules with BTD cores have many applications. Based on this, three molecules that have BTD cores were designed in the study. The trifluoro phenyl group has been attached due to fluorine atom’s strong electron-drawing characteristics which effectively reduce their frontier orbital levels. The methyl phenyl group has been used as an electron-donating group in the NK2 molecule. 2-(m-Tolyl)thiophene group increased conjugation thus it enabled to obtained lower band gap. It was examined how these groups affected the photophysical and electrochemical properties of the molecule, and it was also investigated whether they were AIEgenic in the mixture of acetone/water for possible applications.

2 Results and discussion

2.1 Molecular characterization

The pathways of the synthesis of NK1, NK2, and NK3 molecules are presented in Scheme 1. Synthesis details of NK series molecules and related intermediates are presented in the Supporting Information (SI). The most widely utilized precursor for synthesizing the π-conjugated photoluminescence molecules with a BTD core is Br-BT. Br-TBT was obtained by the bromination of TBT with NBS in THF. TBT was prepared by Stille C–C coupling reaction between Br-BT and (2-thienyl)tributylstannane with a palladium catalyst in a moderate yield. NK1 and NK2 were designed in the study.

![Figure 1: Structure of BTD (X: functional group).](image1)

![Figure 2: AIEgenic molecules containing BTD motif presented to date.](image2)
synthesized by Suzuki C–C coupling reaction between Br-BT and 3-tolylboronic acid or 3,4,5-trifluorophenylboronic acid in the presence of the Pd(PPh₃)₄ catalyst which is the same procedure in the literature [16]. NK3 was synthesized by Suzuki C–C coupling reaction between Br-TBT and 3-tolylboronic acid. The molecular structures of NK1, NK2, and NK3 were illuminated by ¹H NMR and ¹³C NMR. NMR and the mass spectral data of the final products and intermediates have been presented in SI.

As can be seen from the HNMR spectrum of NK1, aromatic protons appear between 7.0 and 7.9 ppm (Figure S4). NK1 has two methyl groups and these six protons appear at 2.52 ppm as a singlet. All integrations are compatible with the calculated proton numbers. NK2 has six aromatic protons. Four protons have the same environment, and other two protons have the same environment, so it is usual to observe just two peaks. The integration of one of them is equal to two and another’s integration is equal to four as expected. For the NK3 molecule, there are two methyl groups, and these six protons appear at 2.45 ppm as a singlet. In the aromatic region, the integration is compatible with the calculated proton numbers. NK3 has 14 aromatic protons. The total integration is equal to 14 as expected. All ¹³C NMR results are compatible with the obtained structures.

2.2 Confocal Raman microscopy

The Raman spectra of NK1, NK2, and NK3 are presented in Figure 3. The core structures of the molecules were the same for all new molecules which were designed to aim polarity differences and to shift the light absorption bands of molecular structures. Raman bands of compounds seem similar; however, the bonds’ shifts could be observed clearly in their spectra. The main S–N bonds of BTD were observed at 1,000 cm⁻¹. This bond intensity changed with the substituent group’s electron-repelling behavior and affected electron density distribution on the core BTD structure. NK1’s side groups have increased polarity on the S–N bonds and elevated band count rates than NK2 and NK3. Crystalline properties of NK1, NK2, and NK3 might be carried out from the S–N deformation band that was the same as the Br-TBT crystal form. BTD core
groups packing into the NK1 crystallinity were higher than NK2 and NK3 crystallinity because of the bandwidth increment. The vibrational polarization bands of aromatic \(\equiv\)C–H bond were seen at around 3,000 cm\(^{-1}\), but it could not be seen because of low count rates and low polarities than to the other molecular bonds due to spectrums focused on between 1,750 and 100 cm\(^{-1}\) [17]. The attaching of a substituent to a molecule inversely affects the intensities of these bands. The increase of substituents in the aromatic ring decreases the intensity of C–H bonds. Whereas the bands of \(-\)C–C– aromatic bonds were seen at 1,556, 1,552, and 1,543 cm\(^{-1}\), the asymmetric vibration bands of \(-\)C=\(\equiv\)N– were noticed at 1,355, 1,371, and 1,368 cm\(^{-1}\) for NK1, NK2, and NK3, respectively [18] which is related to benzoazole moiety [19,20]. The C–S bonds appear in the range 570–720 cm\(^{-1}\) in the Raman spectrum [21]. C–S bonds in NK3 molecule were seen at 621 cm\(^{-1}\). The deformation of Ph-F bands was observed at 995 cm\(^{-1}\) for the NK1 molecule.

2.3 Photophysical and electrochemical characteristics

The absorption characteristics of the compounds were measured in \(10^{-5}\) M CHCl\(_3\) solution and given in Figure 4. In the spectra of the compounds, the \(\pi/\pi^*\) transition bands correspond to higher energy regions seen at 272, 270, and 339 nm for NK1, NK2, and NK3, respectively. The lower energy absorption band that was seen at 383, 381, and 485 nm may correspond to intramolecular charge transfer (ICT). The red-shifted (~30 nm) maxima of NK3 compared to NK1 and NK2 are related to increased conjugation thanks to the two thiophene rings. The determination of the characteristic features of these types of molecules, such as energy gap and optical and electrochemical band gap, is important for photovoltaic applications. The most common approach for the identification of optical band gap (\(E_{\text{opt}}^g\)) is to define the wavelength corresponding to the onset value of the maximum absorption peak. The absorption onset of molecules appears at 432, 449, and 568 nm, respectively. According to this approach, the \(E_{\text{opt}}^g\) of NK1, NK2, and NK3 were determined to be 2.87, 2.76, and 2.18 eV, respectively.

The fluorescence spectra of the molecules were done in different solvents for the investigation of the solvacro-mism effect and given in Figure 5. The emission maxima of the molecules were seen at 492, 480, and 614 nm in CHCl\(_3\), respectively.

The emission maxima of the NK1, NK2, and NK3 are red-shifted (~9 nm) as polarity increases. It is possible to indicate that a molecule has solvachromism by increasing the HOMO/LUMO energy gap (\(\lambda_{\text{max}}\)) due to increasing solvent polarity. To put it differently, the excited state could be stabilized by the polar solvents than the ground state, resulting in the transition energies (redshift) decrease in such solvents. In general, increasing the solvent polarity

![Figure 4: Absorption spectra of NK1, NK2, and NK3 molecules in CHCl\(_3\).](image)

![Figure 5: The fluorescence spectra of NK1 (a), NK2 (b), and NK3 (c) molecules in solvents of different polarity.](image)
leads to an increase in both the emission band and the Stoke shift, indicating a rise in the dipole moment on excitation [22]. The photophysical features of the molecules are summarized in the Table 1. The fluorescence lifetimes of the molecules found 15.00, 12.10, and 12.00 ns in CHCl₃ from the time-resolved fluorescence decays (presented in SI). A molecule’s or material’s photoluminescence quantum yield (PLQY) is defined as the number of photons emitted as a proportion of the number of photons absorbed. It is a crucial measurement of luminescent materials. The PLQYs of the NK1, NK2, and NK3 molecules in the solution phase were measured as 96.38, 83.96, and 66.62%, respectively (Figures S16–S18). For NK1, the existence of methyl substituent could hinder the π–π interactions due to a more distorted spatial arrangement and decrease the non-radiative transition. This situation might lead to obtaining the highest PLQY (ΦPL ≈ 96%) value in the NK series molecules. Film phase PLQY has also been measured and found as 68.6, 36.5, and 32.3%, respectively (Figures S19–S21). It can be said that the reason the PLQY of the films is lower than the solution ones is the aggregation that occurs in the film phase. Aggregation caused quenching, resulting in a decrease in quantum yields.

Electrochemical characteristics of the molecules were done by cyclic voltammetry (CV) in acetonitrile and resulting voltammograms are given in Figure 6. The oxidation potential (Eox) onset of the molecules was observed at 1.56 eV for NK1. For NK2 and NK3, two oxidation peaks were observed and corresponding to the onset values of these peaks evaluated as 1.18 and 1.49 for NK2 and 1.20 and 1.46 eV for NK3 molecule. Fluorine substitution on any compound is known to decrease the band gap by synergistic HOMO and LUMO stabilization [23]. As expected, it is seen that the band gap decreases with fluorine substitution with the addition of fluorine atoms. The HOMO energy levels of the molecules were determined from the onset values of the reduction potentials (Ered) by using the equation HOMO = −(Eox + 4.4) eV [24]. HOMO values were calculated and found as −5.96, −5.58, and −5.60 eV, respectively.

The reduction potential onset of the NK3 exhibited at −0.97 V, corresponding to a LUMO energy level of −3.43 eV.

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<th>Table 1: Photophysical features of NK1, NK2, and NK3 molecules</th>
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<td>NK1</td>
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<td>NK2</td>
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<td>NK3</td>
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*PLQY (%) measurements were performed in CHCl₃ with an absorption value of 0.1 A.

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<th>Table 2: Electrochemical properties of NK1, NK2, and NK3 molecules</th>
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Cyclic voltammograms measured in degassed ACN with 0.1 M [n-Bu₄N] PF₆ as the supporting electrolyte with the scan rate = 150 mV s⁻¹.

*Values were determined from the optical band gap.

Figure 6: Cyclic voltammogram of NK1 (a), NK2 (b), and NK3 (c) molecules.
for NK3. The electrochemical band gap of NK3 was found as 2.17 eV and this value is compatible with its optical band gap value (2.18 eV). The onset $E_{\text{ox}}$ and $E_{\text{red}}$ were determined from the voltammograms of the molecules and given in Table 2. LUMO energy level of NK1 and NK2 has been determined by using the optical band gap. For the optical band gap calculation, the following equation was used.

$$E_{\text{gap}}^{\text{opt}} = \frac{1.241}{\lambda(\text{nm})^2}.$$ 

2.4 Aggregation induced enhanced emission characteristics

To evaluate the AIEE characteristics, the emission characteristics of NK series molecules were examined in the mixture of acetone/water with a rising water volume ratio ($f_w$). With an increasing water ratio, a decrease in emission intensities was recorded due to the alteration in solvent polarity affecting the ICT mechanism in the excited state for all molecules. However, a significant increase in fluorescence emission intensities for NK2 and NK3 was observed at the critical point of the water content at which the aggregation occurred, supporting the AIEE mechanism. In Figure 7, steady-state fluorescence spectra of NK1, NK2, and NK3 and the relationship between the acetone/water mixture emission and only acetone emission ($I/I_0$) are presented.

A redshift was observed in the NK1 compound with increasing water content, which contributes to the maintenance of the supramolecular structure’s rigidity and is attributed to the bulk packing effects also seen in the previously described AIE/AIEE molecules [25]. For NK1, emission intensity was not changed up to 40% water content. To understand the effect of fluorine atoms on AIEE properties, the emission profile of NK2 was investigated in water/acetone mixtures. For NK2, fluorescence enhancement was observed when the water content increased from 0 to 10%. For molecules that do not have AIEE properties, the fluorescence emission intensity decreases as the water content increases. In contrast, no significant change in emission intensity was observed in the NK2 molecule up to 60% water content.

For the NK3, the maximum emission intensity was observed at 20% water content. The intensity gradually decreased with the increasing water content. After 60% water content, no emission was observed.

![Figure 7: Steady-state fluorescence emission spectra of NK1 (a), NK2 (b), and NK3 (c) in the mixture of acetone/water with different $f_w$ and the relation between acetone/water mixture emission and pure acetone emission ($I/I_0$) (d).](image-url)
2.5 Thermal properties

Thermal properties of the molecules thermogravimetric analysis were examined to understand their thermal stability. The TGA thermogram of the molecules is given in Figure 8(a). According to the TGA thermogram, molecules showed a single and clear degradation step and chemical degradation starts above 200°C for all molecules. NK2 degradation temperature ($T_d$) was higher than NK1. This result could be explained by the higher internal and external interactions. This might be attributed to halogen atoms, which lead to an increase in the thermal stability, melting temperature ($T_m$), and $T_d$ values of the molecule with external and internal molecular bonds, respectively [26,27]. NK3 had the highest thermal stability among the series with a 405°C of degradation temperature. Additional thiophene rings might lead to more stability for molecules and increased molecular weight. The weight losses of molecules were found as 95, 97, and 83% at 600°C, respectively.

The differential thermal analysis (DTA) gives more information on the compounds, shown in Figure 8(b). Two main peaks were observed in the DTA thermogram. According to Figure 8(b), the first peaks showed the melting temperature ($T_m$) of the compounds. $T_m$ values of samples were found as 65, 238, and 226°C for NK1, NK2, and NK3, respectively. With the increased molecular weight, $T_m$ values increased. The existence of the fluorine atoms might increase the polarity of the molecule, and this increased the $T_m$ value, too. The second peak showed the degradation temperature ($T_d$) of samples. $T_d$ values of samples were found as 293, 295, and 475°C, respectively. The presence of the thiophene rings increased the $T_d$ value.

Figure 8: % weight change thermogram (a) and temperature difference thermogram (b) of NK1, NK2, and NK3.
Table 3: Some important bond lengths and angles

<table>
<thead>
<tr>
<th>Bond angles</th>
<th>Bond lengths</th>
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<tr>
<td>S5 C20 Br1 120.4(4)</td>
<td>S4 N6 1.606(6)</td>
</tr>
<tr>
<td>C17 C20 Br1 127.6(6)</td>
<td>S5 C16 1.736(6)</td>
</tr>
<tr>
<td>C17 C20 S5 112.0(6)</td>
<td>S3 C9 1.712(7)</td>
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<tr>
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<td>S5 C16 1.736(6)</td>
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<td></td>
<td>S4 N6 1.606(6)</td>
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<tr>
<td></td>
<td>S5 C20 1.719(7)</td>
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<tr>
<td></td>
<td>S3 C12 1.725(7)</td>
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<tr>
<td></td>
<td>N6 C15 1.337(7)</td>
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<td></td>
<td>N7 C11 1.343(8)</td>
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2.6 Crystallographic properties

The single crystals of Br-TBT were chosen for an X-ray crystallographic investigation. The optimized structure of the Br-TBT molecule is seen in Figure 9 and crystallographic features are given in Table S1. A proper single crystal of the Br-TBT was obtained by slow diffusion of THF. It was understood that the single crystal had a monoclinic crystal structure with dimensions of $a = 20.831(2)$ Å, $b = 3.8875(3)$ Å, $c = 20.1835(18)$ Å, and $Z = 1$.

The lengths of the S–N bonds within the benzothiadiazole group have been found as 1.606(6) and 1.618(6) Å which is between the S–N single bond length (1.73 Å) and S–S double bond length (1.53 Å). The C–N bond lengths are 1.337(7) and 1.343(8) Å which is like the value for the N-heterocyclic molecules [28]. Some important bond angles and lengths of the molecule have been selected and presented in Table 3.

In the crystal structure of the Br-TBT molecule, two thiophene rings are syn to each other. It can be attributed to strong S–N intramolecular interaction. In the thiophene groups, carbon atoms (C20 and C9) that are linked to the bromine atom have slightly distorted tetrahedral geometry because of the steric hindrance of sulfur atoms. The molecule is almost planar and rigid molecular conformation which results in high interchain charge transport. The mode of the 3D supramolecular packing framework of Br-TBT is known J-aggregation mode which can enhance the charge transfer throughout the molecules. J-aggregates generally produce a red shift in the absorption spectrum compared to solution [29]. The packing arrangement of the compound did have any π–π interactions owing to being nearly planar with torsional angles between C12–C8–C11–N7 = -2.2(10)° and C16 C10 C15 N6 = 1.5(10)°.

3 Conclusion

In this study, three small organic molecules with a benzothiadiazole core have been designed and characterized. The photophysical characteristics of the molecules have been investigated in different solvents to understand their behaviors for solvachromism. AIEE properties have been also examined for possible imaging applications and it has been understood that they were AIEgenic molecules. The introduction of fluorine atoms instead of the methyl group caused the band gap of the molecule to decrease and the AIEE property to increase. They showed high PLQY in solution (between 66 and 96%) and moderate in film phase (between 68 and 32%) which is needed for the high device performance in OLEDs. The decrease in PLQY can be explained by the aggregation in the film phase, resulting in quenching luminescence. The molecular structure of the Br-TBT has also been illuminated with a single-crystal X-ray study in this work first time. The crystal structure of the Br-TBT molecule showed an almost planar and rigid structure. The 3D packing of the structure showed a J-aggregation mode that increase the charge transfer between molecules. The study is quite comprehensive in terms of providing ideas for those working on molecule design not just for organic photovoltaic applications but also for cell imaging thanks to their AIEE properties and high PLQY values.

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Ethics approval: The conducted research is not related to either human or animal use.

Data availability statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.
References


