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Graphical Abstract

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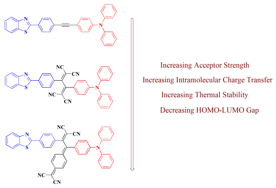

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Prabhat Gautam, Ramesh Maragani, Rajneesh Misra*

Department of Chemistry, Indian Institute of Technology Indore, MP 452017, India.[1]

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ABSTRACT

A series of push–pull benzothiazoles were designed and synthesized by the Pd-catalyzed Sonogashira cross-coupling and [2+2] cycloaddition–retroelectrocyclization reactions. The photonic and electrochemical properties of these systems exhibit strong donor–acceptor interaction. The BTs **5**–**8** show strong intramolecular charge-transfer in the near-infrared (NIR) region. The absorption studies indicate systematic lowering of optical HOMO–LUMO gap with increase in acceptor strength. The computational studies reveal that incorporation of strong acceptors TCNE and TCNQ results in substantial stabilization of LUMO level compared to HOMO level, leading to low HOMO–LUMO gap and bathochromic shift of the absorption spectrum. The TCBD and DCNQ linked BTs **5**–**8** exhibit multi-step redox waves and improved thermal stability.

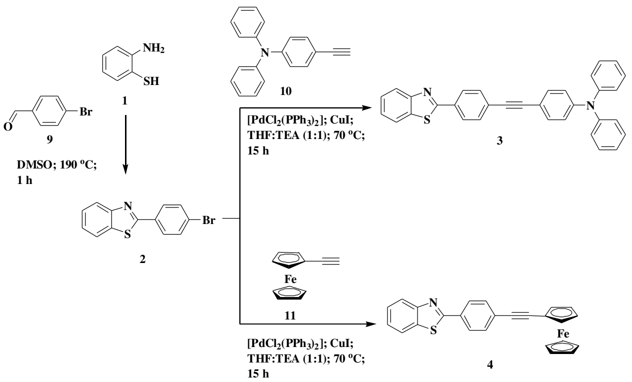
In recent years research on π-conjugated donor–acceptor (D–A) molecular systems with low HOMO–LUMO gap and strong intramolecular charge-transfer (ICT) has gained momentum due to their application in nonlinear optics (NLO) and organic photovoltaics (OPVs).[1,2,3] The photonic properties of the donor–acceptor system can be tuned either by varying the π-linker between donor and acceptor or by increasing the donor/acceptor strength.[4] Thiazoles are strong acceptor and their derivatives benzothiazole, benzothiadiazole and thiazolothiazole have been attached with a variety of donors.[5,6,7] A variety of donor-substituted benzothiazoles (BTs) have been reported in literature which exhibit ICT. To the best of our knowledge there are few reports on tuning of the HOMO–LUMO gap and increasing the ICT of D–A BTs.[7,8]

The cyano-based acceptors tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) undergo [2+2] cycloaddition–retroelectrocyclization reaction with electron rich alkynes and exhibits ICT.[9,10] Our group is engaged in the design and synthesis of efficient D–A systems for optoelectronic applications.[11]

We have explored triphenylamine and ferrocene as strong electron donors and have attached with various acceptors.[12,13] We were interested to study the ICT and HOMO–LUMO gap of triphenylamine and ferrocene substituted BTs and their TCNE and TCNQ derivatives. In this contribution we wish to report donor–acceptor BTs of the type D–π–A and D–A_1–A_2, where triphenylamine and ferrocene are donors and BT, TCNE and TCNQ are acceptors (Chart 1). We have explored the effect of acceptor by varying its strength on the HOMO–LUMO gap, ICT and thermal stability in BT-based molecular system.

The synthesis of D–A benzothiazoles (BTs) **3**–**8** are shown in Scheme **1** and **2.** The bromo-BT **2** was synthesized by the condensation reaction of 2-aminothiophenol (**1**) with 4-bromobenzaldehyde (**9**) in dimethyl sulfoxide (DMSO) at 190 °C for 1 h (Scheme 1).[14]

The donor-substituted BTs **3** and **4** were designed to explore the D–A interaction of BT with triphenylamine and ferrocene via acetylene linkage and to facilitate the click type [2+2] cycloaddition–retroelectrocyclization reaction with TCNE and TCNQ. The Pd-catalyzed Sonogashira cross-coupling reaction of BT **2** with 4-ethynyl-*N*,*N*-diphenylaniline (**10**) and ethynylferrocene (**11**) resulted donor-substituted acetylene bridged BTs **3** and **4** in 70 % and 85 % yields respectively (Scheme 1).[15]



Scheme 1. Synthesis of BT chromophores **3** and **4**

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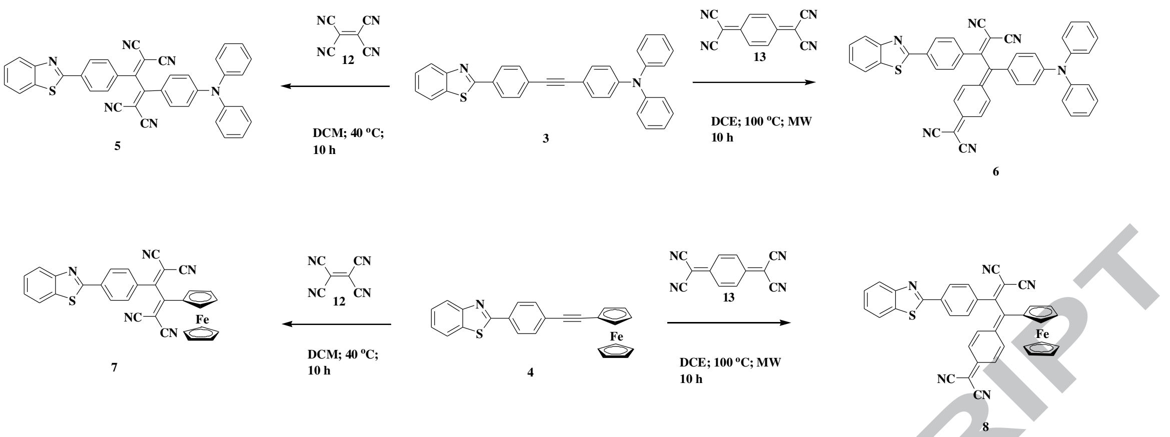
* Corresponding author. Tel.: +91 7312438710; fax: +91 7312361482; e-mail: rajneeshmisra@iiti.ac.in



Scheme 2. Synthesis of BTs **5–8**

The BTs **5**–**8** were designed to study the effect of the additional cyano-based acceptors (TCNE and TCNQ) on the ICT, HOMO–LUMO gap and thermal stability. The BTs **5**–**8** were synthesized by the [2+2] cycloaddition–retroelectrocyclization reaction of the acetylene linked BTs **3/4** with TCNE **12** and TCNQ **13**.

The [2+2] cycloaddition–retroelectrocyclization reaction of BTs **3** and **4** with one equivalent of TCNE **12** in dichloromethane (DCM) resulted BTs **5** and **7** in 75 % and 80 % yield respectively (Scheme **2**).[16] The reaction of TCNQ with BTs **3** and **4** were sluggish in nature. To overcome this barrier the reactions were carried out under the microwave irradiation. The reaction of BTs **3** and **4** with one equivalent of TCNQ in 1,2-dichloroethane (DCE) at 100 ºC under the microwave irradiation for 10 h resulted BTs **6** and **8** in 60 % and 68 % yields respectively. BTs **3**–**8** were purified by silica-gel column chromatography and well characterized by ^{1}H, ^{13}C NMR, and HRMS techniques.

Thermal stability of the organic chromophores is one of the essential criteria for practical applications. In order to study the thermal stability of BTs **3**–**8** thermogravimetric analysis (TGA) were carried out at a heating rate of 10 °C min^{-1}, under nitrogen atmosphere (Figure S23; see ESI) and the decomposition temperatures (T_d) for 5 % weight loss are listed in Table S1 .

The acetylene linked BTs **3** and **4** exhibit T_d values at 155 ºC and 201 ºC, whereas tetracyanobutadiene (TCBD) and dicyanoquinodimethane (DCNQ) linked BTs **5**–**8** exhibits improved T_d values in the range of 271–472 ºC. The trend in thermal stability follows the order **7** > **5** > **8** > **6** > **4** > **3**, which indicates following: (a) The Ferrocenyl substituted BTs **4**, **7** and **8** exhibit better thermal stability compared to their respective triphenylamine analogue BTs **3**, **5** and **6**. (b) Incorporation of TCBD and DCNQ units improves the thermal stability of BTs **5**–**8**.

The electronic absorption spectra of the BTs **3**–**8** were recorded in dichloromethane at room temperature and the data are shown in Table 1. The BTs **3**–**8** exhibit strong absorption between 300–450 nm, corresponding to $\pi \rightarrow \pi^*$ transition.[7,17] The incorporation of the TCBD and DCNQ acceptor unit in BTs result in strong intramolecular charge-transfer (ICT) indicating strong donor–acceptor interaction in BTs **5**–**8** (Figure 1).[12d,17,18] The ICT band in BTs **5**–**8** exhibits red-shift, on increasing the solvent polarity indicating CT character (see ESI, Figure S19).[16] The presence of strong CT transition result in intense color solution of BTs **5**–**8** in dichloromethane (Figure 2).

The optical energy gaps in donor–acceptor BTs were derived from the onset wavelength of UV/Vis absorption spectra in dichloromethane.[19] The optical HOMO–LUMO gap values in BTs follow the order **3** > **4** > **5** > **7** > **6** > **8**, which indicate that the incorporation of TCBD and DCNQ groups lowers the HOMO–LUMO gap. These results show that acceptor strength is these BTs are inversely proportional to the HOMO–LUMO gap.

The emission property of BT **3** was studied in dichloromethane (see ESI; Figure S20) and the corresponding data is given in Table 1. The triphenylamine-substituted BT **3** emits at 522 nm. The ferrocenyl-substituted BT **4** and TCBD and DCNQ linked BTs **5**–**8** are non-emissive in nature.

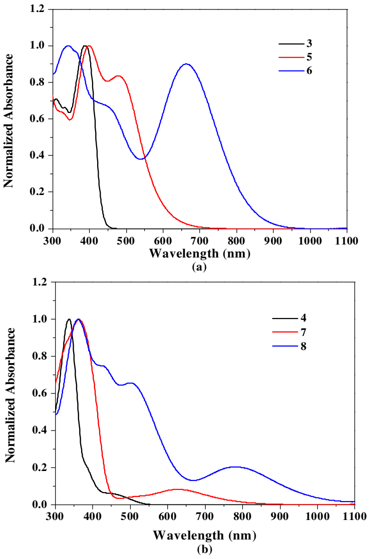


Figure 1. Normalized electronic absorption spectra of (a) BTs **3**, **5** and **6**, and (b) BTs **4**, **7** and **8** in dichloromethane.

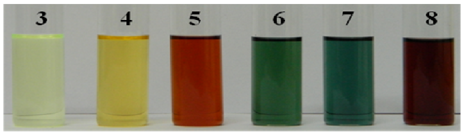


Figure 2. Benzothiazoles **3**-**8** at 1 × 10^{-4} M concentration in dichloromethane.

Table 1. Photophysical data of benzothiazoles **3**–**8**.

BT	**Photophysical data**[a]			
	λ_{abs} **(nm)**	ε **(M^{-1} cm^{-1})**	λ_{em} **(nm)**	**Optical Gap (eV)**[b]
3	388	38043	522	2.75
4	337	41932	–	2.53
5	400	33815	–	1.95
	480	28212		
6	342	23132	–	1.45
	450	sh		
	663	20483		
7	363	42297	–	1.75
	627	3589		
8	360	37909	–	1.35
	426	sh		
	502	24863		
	780	7786		

[a] Absorbance measured in dichloromethane at 1×10^{-5} M concentration; sh = shoulder; λ_{abs}: absorption wavelength; λ_{em}: emission wavelength measured in dichloromethane; ε: extinction coefficient. [b]determined from onset wavelength of the UV/Vis absorption.

The electrochemical properties of the BTs **3**–**8** were studied by the cyclic voltammetric (CV) and differential pulse voltammetric (DPV) analysis in dry dichloromethane (DCM) solution at room temperature (with 0.1 M TBAPF$_6$, all potentials vs Fc/Fc$^+$). The electrochemical data are listed in Table S1, and the cyclic and differential pulse voltammograms are shown in Figure 3, S21 and S22.

BTs **3**, **5** and **6** exhibits irreversible oxidation wave corresponding to the oxidation of triphenylamine unit in the region between 0.52 V to 0.65 V.[20] On the other hand BTs **4**, **7** and **8** exhibit reversible oxidation wave corresponding to the oxidation of ferrocene to ferrocenium ion in the region between 0.10 V to 0.45 V.[12b] The TCBD and DCNQ linked BTs **5**–**8** exhibit higher oxidation potential compared to BTs **3** and **4** reflecting strong electronic communication.

BTs **5**, **6** and **7** exhibit two reversible reduction waves corresponding to the successive one-electron reductions of the dicyanovinyl (DCV) groups of the TCBD and DCNQ units. BT **8** undergoes simultaneous electrochemical reduction of the dicyanovinyl (DCV) groups of DCNQ unit and exhibits one reduction wave.[12d] The comparison of first reduction potential of BT **5**–**8** reflects that the DCNQ linked BTs **6** and **8** were easier to reduce compared to TCBD linked BTs **5** and **7**, reflecting strong electron accepting nature of the DCNQ unit.[18]

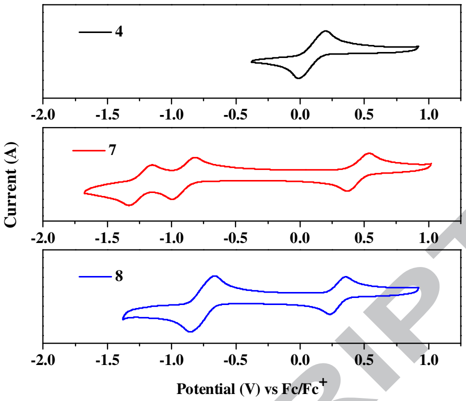


Figure 3. Cyclic voltammograms of the BTs **4, 7** and **8**.

In order to explore the electronic structure of the D–A benzothiazoles **3**–**8**, density functional theory (DFT) calculations were performed at the B3LYP/6-31G** level and the Lanl2DZ level for Fe. The contours of HOMO and LUMO are shown in Figure S24. The HOMO orbitals in BTs **3**–**8** are mainly located on electron donating triphenylamine and ferrocene unit whereas the LUMO orbitals are delocalized over BT, TCBD and DCNQ acceptor units.

The computational HOMO–LUMO gap follows the order **4 > 3 > 7 > 5 > 8 > 6**. The trend indicates that BTs **6** and **8** with DCNQ linkage exhibit lowest HOMO–LUMO gap followed by TCBD linked BTs **5** and **7**, and acetylene linked BTs **3** and **4**. The analysis of HOMO and LUMO energy levels reveal that incorporation of strong acceptor TCNE and TCNQ in BTs **5**–**8** results in greater stabilization of the LUMO level compared to the HOMO level leading to low HOMO–LUMO gap and large bathochromic shift of the electronic absorption (Figure S25).

A series of D–A benzothiazoles (BTs) **3**–**8** were synthesized by the Pd-catalyzed Sonogashira cross-coupling reaction and [2+2] cycloaddition–retroelectrocyclization to study the effect of the acceptor strength on the HOMO–LUMO gap and intramolecular charge-transfer (ICT). The single photon absorption properties of BTs reveal that the incorporation of TCNE and TCNQ groups result in strong ICT bands and low HOMO–LUMO gap. The computational studies indicate that the strong acceptors stabilize the LUMO energy level to greater extent compared to the HOMO level. The incorporation of cyano-based groups (TCNE and TCNQ) in D–A BTs improves the thermal stability. The results ushers the design of D–A BT-based molecular systems with strong ICT, low HOMO–LUMO gap and better thermal stability. The BTs **3**–**8** are potential candidates for optoelectronic applications. The study towards their organic photovoltaic applications is ongoing in our laboratory.

Acknowledgments

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Supplementary Material

Supplementary data (detailed experimental procedures, synthesis, and characterization of all compounds associated with this article can be found, in the online version.

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