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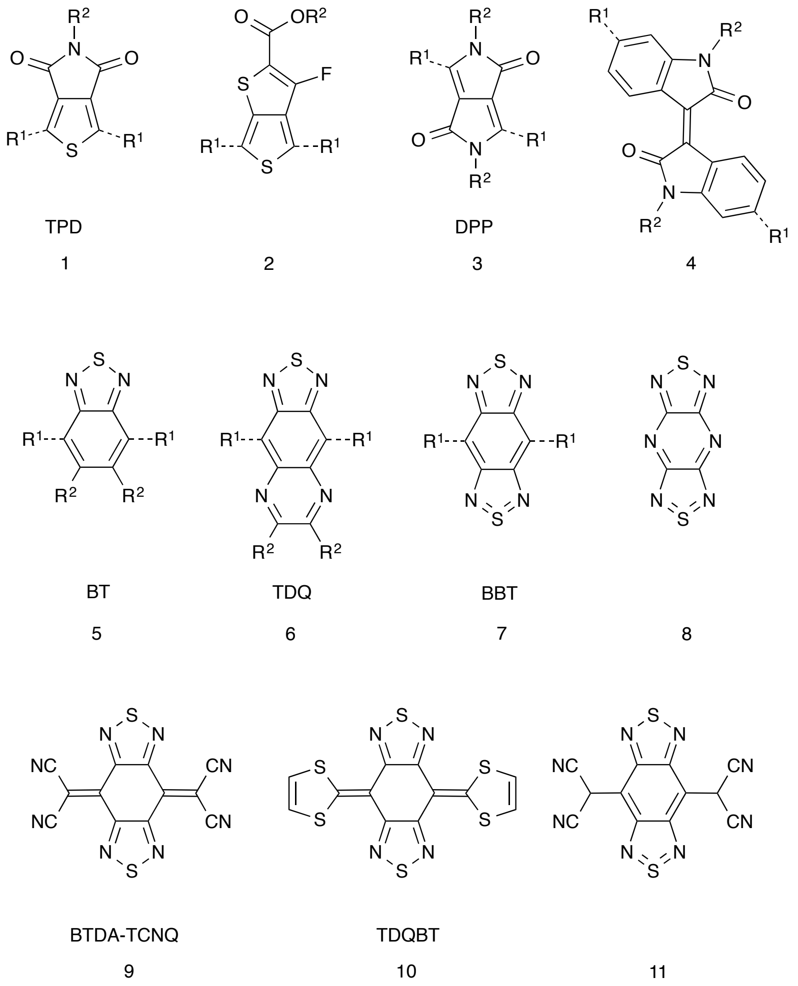
Introduction.

The ability to precisely tune properties such as conductivity, charge-carrier mobility, light absorption, and light emission in π-conjugated materials often impacts the performance of devices such as organic photovoltaics (OPVs), dye-sensitized solar cells (DSSCs), organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and electrochromics devices (ECDs). As a consequence, organic chemists must carefully control, and often achieve a balance between, various redox, optical, and electronic properties in both polymers and small molecules. Fundamental to tuning a material's electronic properties are the energies of both the highest occupied molecular orbital (E_{HOMO}) related to the ionization energy (IE) of the molecule and the lowest unoccupied molecular orbital (E_{LUMO}) related to the electron affinity (EA) of the molecule or polymer, as well as the difference (E_g) between these energies. Indeed, although other material properties, such as morphology and microstructure play a critical role,[1-3] IE and EA generally must be appropriately aligned relative to the work-functions, IEs, or EAs of known electrode materials, interfacial materials, and/or other adjacent organic layers to enable efficient charge-carrier injection or extraction, or photoinduced charge separation in devices.[4, 5]

One approach to tuning the properties of π-conjugated small molecules or polymers[6] is the covalent coupling of at least one electron donor (D) to at least one electron acceptor (A), either directly or through a π-conjugated bridge (π). Several different structural motifs have been extensively studied during the past two decades, leading to advances in: (i) second-order nonlinear optical (NLO) chromophores (D-π-A);[7] (ii) two-photon absorbing (TPA) chromophores (D-A-D, D-π-A, and A-D-A);[8, 9] (iii) electrochromics ($\text{-D}_n\text{-A-}$);[10-13] (iv) chromophores for dye-sensitized solar cells (DSSCs, D-π-A and D_2A);[14-17] (v) polymers $(\text{-D-A-})_n$ and small molecules (D-A) for OLEDs;[18] (vi) small-molecule donors (D-A)[19] and acceptors[20] and polymers $(\text{-D-A-})_n$ for OPVs;[21-26] (vii) polymers $(\text{-D-A-})_n$ for OFETs,[27, 28] and (viii) polymers $(\text{-D-A-})_n$ for electrochromism.[29, 30]

Early D-A polymers that demonstrated the utility of the approach in modifying optical absorption energies typically used discrete electron accepting groups such as cyano, nitro, or sulfonyl groups as substituents on an aryl subunit or a vinylene in the polymer backbone.[31, 32] More recently, heterocycles with high EAs have gained favor as stronger and more synthetically variable acceptors. Although a variety of heterocyclic acceptors have been studied and are covered in extensive reviews,[22, 23] some of the more often-used acceptors, shown in **Figure 1**, include thieno[3,4-*c*]pyrrole-4,6-dione (TPD, **1**),[33, 34] esters of 3-fluorothieno[3,4-*b*]thiophene-2-carboxylic acid[35] (**2**), diketopyrrolo[3,4-*c*]pyrrole[36] (DPP, **3**), isoindigo (**4**),[37-39] and 2,1,3-benzothiadiazole (BT, **5**).[40] **Figure 1** also shows the heterocyclic numbering scheme for BT, which will be used extensively in this review. In particular, BT and its 5-monofluoro- (MFBT) and 5,6-difluoro- (DFBT) derivatives have been used in a variety of materials including both polymers[41-43] and small molecules[44, 45] in OPVs, in OFETs,[46, 47] as electron-deficient π-bridges in DSSC chromophores,[48, 49] TPA chromophores,[50-52] electrochromics,[53, 54] and as emitters in small-molecule and polymer OLEDs that include white light emitters,[55] emitters with colors spanning the visible spectrum,[56-60] and near-infrared emitters.[61] The 5,6-dinitro BT derivative also has exhibited strong electron withdrawing ability.[62]

Generally, BT is an effective electron acceptor; the presence of the imine functionalities with relatively low energy π*-orbitals gives BT a relatively high EA itself. The molecule can be described as a quasi-quinoidal structure (*i.e.*, with localized, relatively short π-bonds in the benzo ring) rather than a 10π-electron heteroaromatic system; this can increase electronic coupling between substituents in the 4- and 7-positions relative to that found across 1,4-substituted aromatic moieties in both small molecules and polymers. Although BT has proven to be useful, there is still a desire to develop stronger electron acceptors, for example, to decrease the optical gap (E_g^{opt}) in D-A polymers in order to increase light absorption in the near infrared (NIR) and, therefore, to utilize the solar spectrum more efficiently in OPVs,[63] to provide electron-accepting materials in OPVs that might replace the currently used fullerene derivatives,[64] or to provide air-stable electron-transport materials for n-channel OFETs.[65] One way to increase the electron-accepting strength of BT is to heteroannulate at the 5- and 6-positions to give acceptors such as [1,2,5]thiadiazolo[3,4-*g*]quinoxaline (TDQ, **6**) and benzo[1,2-*c*:4,5-*c*']bis[1,2,5]thiadiazole (benzobisthiadiazole, BBT, **7**). BBT is structurally similar to the known strong acceptor **8**[66] as well as the core heterocyclic framework of both bis([1,2,5]thiadiazolo)tetracyanoquinodimethane (BTDA-TCNQ, **9**) (**Figure 1**), which is an electron acceptor that forms conductive charge-transfer crystals with organic donors,[67-69] and bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole) (TDQBT, **10**) (**Figure 1**), which forms single-component crystals that have high Hall charge-carrier mobility (3 cm^2 V^{-1} s^{-1}).[70-75] In fact, the first known isolated derivative of BBT was 4,8-bis(dicyanomethyl) derivative **11**, which was obtained from two-electron reduction of BTDA-TCNQ and protonation of the stable, isolable disodium salt.[76] Indeed, in recent years the number of research articles on heteroannulated BT-containing materials has increased significantly, allowing an initial critical assessment of their properties and performance, which is the subject of this current review. Herein, we highlight key aspects of the electronic structure of heteroannulated BT derivatives that give rise to controllable optical and electronic properties and describe how materials containing these acceptors have been employed in organic electronic and photonic applications.



R^1 = typical bonding site to donors in materials; R^2 = typical site of other substitution

Figure 1. Heterocyclic acceptors used in organic electronics. Dashed lines indicate bonds to donor groups in materials.

Electronic Structure of BBT and derivatives.

The stability of **11** and the structural similarity of BBT to the known strong acceptor **8**, as well as the intriguing valence-bond representation in which there is a formally tetravalent sulfur atom in an aromatic 14 π-electron ring system, inspired Yamashita and co-workers to develop a synthetically useful route to BBT and TDQ derivatives that provided a variety of compounds **12-20** (**Figure 2**) from 1994 to 1997.[77-80] More recently, an alternative synthesis of key intermediates **12** and **17** was reported.[81] The acceptor strength of BBT and TDQ compared to the parent BT was initially assessed using optical absorption and electrochemistry of **15-17**. Both TDQ derivative **16** (λ_{max} = 524 nm) and BBT derivative **17** (λ_{max} = 702 nm) showed marked red shifts compared to BT **15** (λ_{max} = 445 nm). Assuming that these electronic transitions represent excitation from a HOMO delocalized over the thiophene rings and the six-membered ring to a LUMO located on the fused-ring heterocycles, these shifts suggest that TDQ and BBT are strong intramolecular π-acceptors; however, it should be pointed out that substituents can sterically interact with the BBT ring, causing a torsion that may decrease intramolecular charge transfer. This is likely the case for both the methyl group on the pyrrole in **18**, which causes a *blue* shift of 8 nm compared to the weaker thiophene donor in **17**, and the proximal methoxy group in **19**, which causes a reduced red shift of only 6 nm even though the dimethoxy substituted benzene ring in **19** should be a significantly stronger donor than the phenyl group of **13**. The strength of BBT in particular as a intramolecular π−acceptor is manifested by the near-infrared absorption (λ_{max} = 732 nm) of the relatively short chromophore **20**. Additionally, electropolymerized **17** and **18**—the first reported D-A polymers incorporating BBT—showed E_g^{opt} (taken as the low energy onset of the optical absorption) of 0.5 eV and 0.6 eV, respectively, which was amongst the lowest E_g^{opt} reported for any polymer at the time.[79] Reduction potentials (E_{red}) of TDQ derivative **16** (-0.72 V *vs*. SCE) and BBT derivative **17** (-0.53 V *vs*. SCE) are less cathodic than that of BT derivative **15** (-1.22 V *vs*. SCE), consistent with the trend in acceptor strength deduced from optical data; however, the oxidation potentials (E_{ox}) were also less anodic than that of their BT counterpart (+0.98, +0.95, and +1.23 V *vs*. SCE, respectively), indicating that although the EA may indeed be increased, the IE may also be *lowered* in TDQ and BBT compounds relative to their BT analogues. While this might be good for lowering E_g^{opt}, it may have deleterious effects for materials in certain applications such as OPV as the lower IE can lead to a decrease in the open-circuit voltage (see below).[82] Nevertheless, these initial results by Yamashita and coworkers on both small molecules and polymers show the potential of TDQ and BBT as good electron acceptors that might be used for a variety of organic electronic applications where tunable and facile redox properties and/or low-energy optical absorptions are desirable.

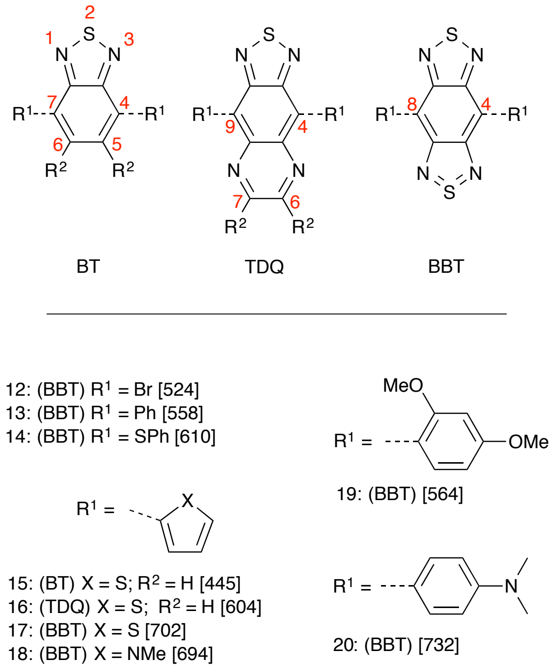


Figure 2. BBT derivatives prepared by Yamashita and coworkers and related compounds. Number in brackets is λ_{max} (nm) in $CHCl_3$. Red numbers indicate heterocyclic numbering scheme for that specific parent.

In addition to the interest in the effects of BBT on material properties, the bonding in BBT is intriguing itself in terms of the “tetravalent sulfur” (-N=S=N-) present in the formal representation shown in **Figure 1**, which to maintain a formal charge of zero, must expand its octet to a 10 valence-electron configuration. Other compounds with formally tetravalent sulfur have been reported as a means to probe classical structure and bonding theories including thieno[3,4-*c*]thiophene derivatives **21** and **22**[83] (**Figure 3**) and thiaphenalene **24** that were reported by Cava and coworkers,[84] with **24** independently reported by Schlessinger and Ponticello.[85] Although originally shown as having a tetravalent sulfur, these compounds each have the ylidic resonance structure **27** and the 1,3-dipolar resonance structure **28**. Indeed, **21**, **22**, and **24** each were reportedly unstable and their transient existence as intermediates was only inferred *via* formation of stable adducts with *N*-phenylmaleimide (**29**, **Figure 3**), which may occur as a result of a 1,3-dipolar addition of the resonance form **28**. The following year, isolable versions were reported by Ponticello and Schlessigner (**25**)[86] *via* sterically deactivating the reactive tetravalent sulfur with adjacent, out-of-plane phenyl rings, and were followed by reports of **23**[87] and **26**[88] in back-to-back publications. An X-ray structure of **23**[89] showed that, compared to thiophene, the length of the S-C bonds shortened by 0.008 Å, nearly within experimental error, that the average C=C bond lengths adjacent to S increased by 0.037 Å, and that the fused bond increased by 0.029 Å. These bond length increases are consistent with somewhat less intrathiophene localization in favor of a 10 π-electron annulene-like delocalization. Likewise, relevant bond lengths for [1,2,5]thiadiazole **30**, which were determined from gas-phase electron-diffraction[83] measurements (and independently from microwave spectroscopy[82]) and from the X-ray crystal structure of 4,7-diphenyl BT **31**,[90] can be compared to those determined for 4,8-diphenyl BBT **13** (**Figure 3**, Table 1) using X-ray crystallography.[80] The diphenyl derivatives were chosen for comparison since the Ph groups are twisted out of plane by 35-43° (BT **31**, the range of four independent angles for two independent molecules in the crystal) and 44° (BBT **13**), thereby reducing conjugation between the substituents and the heteroaromatic rings that might affect the bonding within the heteroaromatic cores. As seen in Table 1, on going from thiadiazole to BT **31**, there is a lengthening of both the imine bonds ("B") and the C-C bond ("C"; 7a-3a in BT; 8a-3a in BBT, (the lettering scheme for the bond is given in **Figure 3**)), indicating a shift in BT away from intrathiadiazole delocalization and toward peripheral annulene-type delocalization; however, note that the benzannulated bonds "D" and "F" are longer than "E" by 0.062 Å and 0.052 Å, respectively (the lettering scheme for the bond is given in **Figure 3**). On going from BT to BBT, the decrease in the S-N "A" bond lengths (0.028 Å) is much more pronounced than that seen going from thiadiazole to BT (0.003 Å), the F bond (equivalent to 8a-3a in BBT (**Figure 3**)) lengthens (0.028 Å). Furthermore, in BBT the D bond shortens (0.031 Å), and the E bond lengthens (0.031 Å) such that the bond alternation between D and E is lost and the bonds are equivalent by symmetry at 1.406 Å, similar to the aromatic bonds in benzene. Taken together, such bond distortions on going from BT to BBT are consistent with an increase both in multiple-bond character on the S, which could be expected if there is tetravalent sulfur bonding in BBT, and in annulene-type 14 π-electron delocalization (**32**) compared to the Kekulé representation (**13**). To our knowledge, there have been no detailed characterization studies carried out on BBT *specifically* to test the degree of aromatic delocalization; however, more detailed insight into the bonding in BBT has been explored through computational studies, the results of which are generally useful to rationalize and predict property changes on incorporation of BBT units into small molecules and polymers, as discussed below.

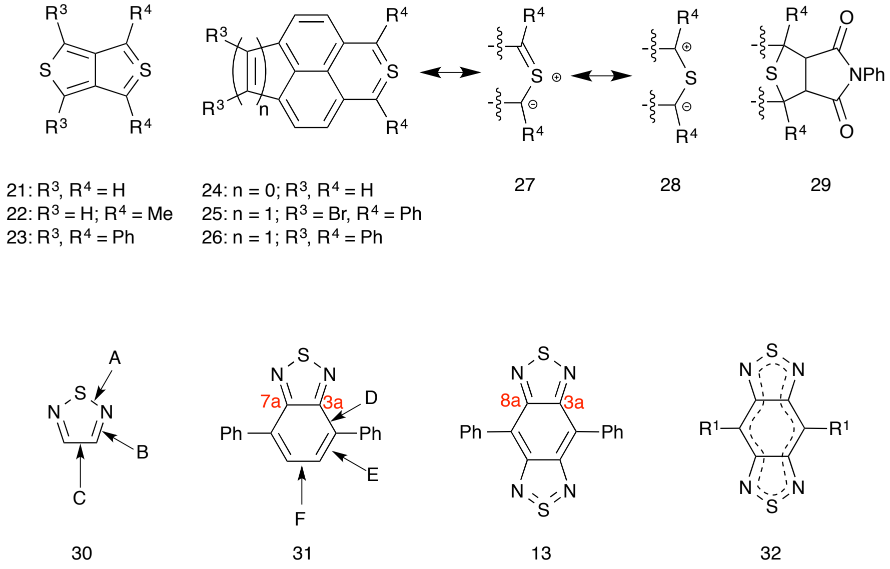


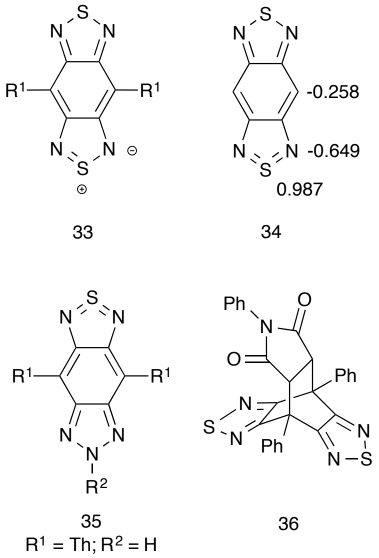
Figure 3. Non-classical bonding in sulfur heterocycles and bonding considerations in thiadiazole, BT, and BBT.

Table 1. Bond-Length Changes in BBT and Parent Molecules

Compound	A	B	C	D	E	F
30 (Thiadiazole)	1.632[a]	1.329[a]	1.413[a]	-	-	-
31 DiPh(BT)[b]	1.629[d] (−0.003)[e]	1.355[d] (+0.026)[e]	1.452 (+0.039)[e]	1.437[d]	1.375[d]	1.427[d]
13 DiPh(BBT)[c]	1.601[d] (−0.028)[e]	1.378[d] (+0.023)[e]	1.455[d] (+0.003)[e]	1.406[d] (−0.031)[e]	1.406[d] (+0.031)[e]	1.455 (+0.028)[e]

[a] Values from gas-phase electron diffraction. [b] Two complete molecules in the asymmetric unit, each with approximate non-crystallographic C_s symmetry. [c] Half a molecule in the asymmetric unit; the molecule has crystallographic inversion symmetry and approximate C_{2h} symmetry. [d] Averages of multiple chemically equivalent but crystallographically independent bond lengths. [e] Values in parentheses are the difference between the bond length in the compound and the bond length in the compound immediately above.

A long-standing question relevant to the proposed tetravalent sulfur bonding is whether the bonding can be better represented as an ylidic structure with and 8-electron sulfur such as in **33** (**Figure 4**) rather than as a 10-electron sulfur, as in **34**. Strassner and Fabian[91] examined a number of structures for various degrees of tetravalent sulfur bonding including acyclic sulfur diimides, thiadiazole, BT, and BBT using density functional theory (DFT, at the B3LYP/6-31G* level). The main finding was that, generally, for compounds that have tetravalent sulfur in Kekulé representations (such as BBT), there was a higher degree of positive charge on the S atoms and a higher degree of negative charge on the N atoms compared to thiadiazole and BT, which is consistent with an increased contribution from the ylidic valence-bond structures such as **33**. This is consistent with *d*-orbitals on S typically having little direct bonding with *p*-orbitals on N and is also in agreement with a more recent charge density study on acyclic S-N multiple bond containing compounds.[92] Another component of the Strassner and Fabian work was the identification of a relatively small singlet-triplet (S_0/T_1) energy gap of 20.1 kcal/mol, which, according to the definition proposed by Wirz,[93] put BBTs on the borderline of having some degree of diradicaloid character. Similarly, DFT calculations by Bhanuprakash and coworkers[94, 95] have also shown that BBT and like-molecules, depending on the nature of the chemical modification and the density functional employed (*i.e.*, the amount of [non-local] Hartree-Fock exchange included in hybrid functionals), can have diradicaloid character. These results for BBT were largely confirmed by Shen and coworkers,[96] who additionally showed that the Wiberg bond indices of the bonds A, B, and D (**Figure 3**) in BBT indicated a "considerable" degree of conjugation around the BBT periphery; this was associated with an aromatic ring current according to their calculations. The natural charges from Shen *et al.* are also shown in **Figure 4** (**34**), and they are consistent with Strassner and Fabian's[91] calculated ylidic structure. Indeed, this strongly positive sulfur has recently been identified by Reynolds and coworkers as the source of the tendency of BBT and the BT-heteroannulated derivative benzo(triazole-dithiazole) **35** to lower the (B3PW91/6-31**)-calculated LUMO energy of materials relative to BT.[97] It should be noted that Yamashita and coworkers reported formation of the Diels-Alder-like adduct **36** in 89% yield by refluxing BBT derivative **13** with *N*-phenylmaleimide in xylene; however, the existence of **36** should not be used to infer a formal 4+2 cycloaddition from a Kekulé-type form such as **32** since symmetry allowed cycloadditions may still follow a stepwise "diradical" cyclization mechanism,[98] which may be reasonable to expect from diradicaloid structures.



33 34

35
R^1 = Th; R^2 = H

36

Figure 4. Structural considerations in BBT and BBT cyclization adduct **36**

Although the nature of bonding in BBT is interesting from a theoretical standpoint, a more practical question is to what extent material properties are affected upon extension of BT to afford TDQ, BBT, and other possible BT heteroannulation derivatives. DFT studies on small molecules[97, 99-102] and oligomers[103-110] (to represent polymers) have been carried out to explore the electronic, redox, and optical properties of these moieties in a number of donor-acceptor architectures. These investigations show that a subtle interplay between steric and electronic effects (*e.g.*, relative co-planarity of the subunits) on the electronic coupling between the electron donor and acceptor moieties affects the key energy levels of the materials; however, these studies also indicate that replacement of BT with TDQ and, in particular, BBT tends to lead to lower E_{LUMO} and similar or slightly higher E_{HOMO}. These tendencies can be explained using a simple perturbational illustration as shown in **Figure 5**, which is similar to the analysis used in a wholly computational approach taken by Pandey *et al*. on a range of acceptors.[111] In **Figure 5**, the local B3LYP/6-31G* calculated E_{HOMO} and E_{LUMO} of a "donor" (bithiophene, **37**), represented by dashed lines across the graph, along with the E_{HOMO} and E_{LUMO} values of BT, TDQ, and BBT are shown. In D-A-D molecules, mixing of the much lower energy LUMOs of TDQ and BBT with the average donor LUMO would be expected to significantly decrease E_{LUMO} of the D-A systems compared to their BT analogue (ΔE_{LUMO}); on the other hand, the slightly higher local E_{HOMO} of both TDQ and BBT could be expected to *raise* E_{HOMO} of the D-A system somewhat relative to BT (ΔE_{HOMO}), and such trends are consistent with the calculated E_{HOMO} and E_{LUMO} values for the D-A-D molecules. This would result in a significant narrowing of the fundamental gap (green arrows) across the series BT → TDQ → BBT, and thus, assuming that the lowest lying transition is well-described as a HOMO-LUMO transition, lead to a red shift in the absorption band. Another potential consequence of the relatively low E_{LUMO} for TDQ and BBT is that one might expect the LUMO of a D-A-D system would have higher coefficients in the acceptor portion of the molecule for A = TDQ and BBT than for A = BT. On the other hand, there should be relatively little change in the acceptor contributions to the HOMOs of D-A derivatives, since the E_{LUMO} trend (ΔE_{LUMO}) going from BT to BBT is significantly larger than the E_{HOMO} trend (ΔE_{HOMO}). This may mean that, for a given donor, there would be less overlap between the HOMO and LUMO in the TDQ and BBT systems compared to their BT analogues, which can in turn decrease the oscillator strength of the optical transitions, such as was computed and discussed in the work by Köse for a range of acceptors;[100] however, as is often the case, these effects will be subject to the modulations of the D-A electronic couplings, and may not be manifested if steric interactions force the D-A moieties significantly out of coplanarity in TDQ- or BBT-containing materials.

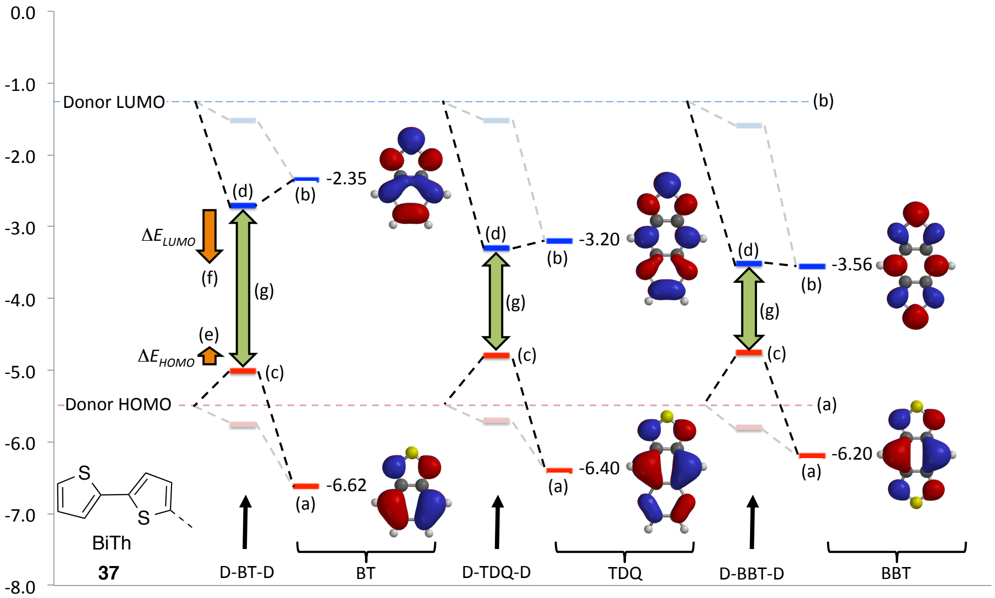
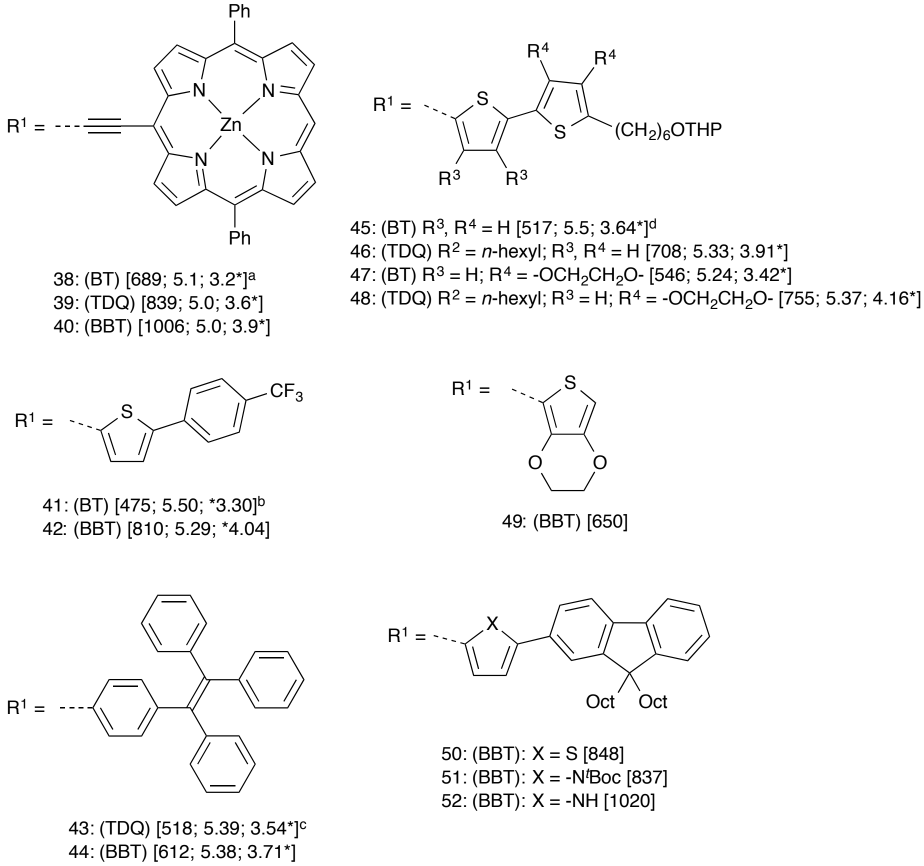


Figure 5. Perturbational analysis of bonding D-A-D systems with BT, TQD, and BBT acceptors and BiTh donors. (a) E_{HOMO} levels of acceptors; (b) E_{LUMO} levels for the acceptors; (c) E_{HOMO} levels of the D-A-D compound; (d) E_{LUMO} levels for the D-A-D compounds; (e) E_{HOMO} trend across the series; (f) E_{LUMO} trend across the series; (g) HOMO-LUMO gaps. Calculations performed at the B3LYP/6-31G*

To examine the extent to which the above-mentioned trends are supported by experiment, examples of small molecules with a D-A-D general structure are compared in **Figure 6**. Care should be taken in comparing data between the six groups of compounds in **Figure 6** since different measurements conditions and assumptions were used by the various authors (see figure notes). The porphyrin derivatives **38-40** reported by Therien and coworkers,[102] the thiophene donor molecules **41** and **42** reported by Yamashita and coworkers[112, 113] and **43** and **44** reported by Wang and coworkers[114] all largely show the general trends discussed above in that EA is substantially increased while IE either decreases or is approximately the same. Other D-A-D derivatives of TDQ such as **45** and **46** reported by Reynolds and coworkers[115-118] also follow these trends; however, other compounds such **47** and **48** that are substituted with bulkier 3,4-ethylenedioxythiophene (EDOT),[119] display *higher* IE than the BT counterpart (ΔIE = +0.13 eV from BT → TDQ). This is presumably due to a greater distortion from planarity in the case of the TDQ-EDOT system than its BT-EDOT analogue, which was seen in the EDOT derivative **49**, where a torsion between the plane of the BBT and the EDOT thiophenes (53° in the X-ray crystal structure)[115] results in a blue shift (λ_{max} 650 nm) compared to the weaker donor thiophene **17** (**Figure 1**, λ_{max} = 702 nm in CH_2Cl_2[78]).

The importance of coplanarity is also demonstrated in the series of D-A-D compounds **50-52**,[113, 114, 120-123] where there is a small *blue* shift on going from thiophene donor **50** to the more electron-donating pyrrole donor in **51**, but the expected large red shift when the *t*-Boc group is removed (**52**), allowing for planarization. Thus, it is clear from the available small-molecule data and computations that, in the absence of large donor-acceptor torsions in TDQ and BBT derivatives, substituting BT with TDQ and BBT results in a red-shift of λ_{max} arising mostly from a relatively large decrease in E_{LUMO} (increase in EA) and, in many cases, a relatively small increase in E_{HOMO} (decrease in IE); however, the effect on IE is subtle and may differ depending on the donors and the specifics of bonding.



38: (BT) [689; 5.1; 3.2*][a]
39: (TDQ) [839; 5.0; 3.6*]
40: (BBT) [1006; 5.0; 3.9*]

45: (BT) R^3, R^4 = H [517; 5.5; 3.64*][d]
46: (TDQ) R^2 = *n*-hexyl; R^3, R^4 = H [708; 5.33; 3.91*]
47: (BT) R^3 = H; R^4 = $-OCH_2CH_2O-$ [546; 5.24; 3.42*]
48: (TDQ) R^2 = *n*-hexyl; R^3 = H; R^4 = $-OCH_2CH_2O-$ [755; 5.37; 4.16*]

41: (BT) [475; 5.50; *3.30][b]
42: (BBT) [810; 5.29; *4.04]

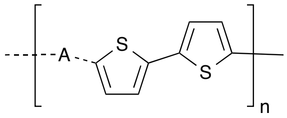
49: (BBT) [650]

43: (TDQ) [518; 5.39; 3.54*][c]
44: (BBT) [612; 5.38; 3.71*]

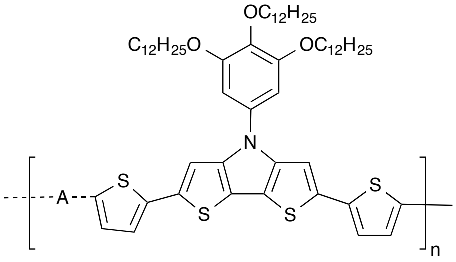
50: (BBT): X = S [848]
51: (BBT): X = -N^{t}Boc [837]
52: (BBT): X = -NH [1020]

Figure 6. Small molecule D-A-D compounds for A = BT, TDQ, or BBT. For all compounds: (BT, TDQ, or BBT) refer to the parent compounds and R^1; R^2 refer to parent substituents in **Figure 2**. Data are [λ_{max} (nm); IE (eV); EA* (eV)]. IE and EA given are: [a]Reported $E_{1/2ox}$ or $E_{1/2red}$ + 4.8 eV. [b]eEox onset or eE_{red} onset +4.8 eV. [c]$eE_{1/2ox}$ or $eE_{1/2red}$ + 4.34 eV. [d]$eE_{1/2ox}$ or $eE_{1/2red}$ + 5.1 eV.

Although many polymers containing BT, TDQ, and BBT have been prepared, relatively few studies have directly compared polymers containing each of the three acceptors. Again, comparisons among studies are difficult due to differences in conditions and methods for measuring properties such as λ_{max}, E_g from the optical absorption onset (E_g^{Opt}), IE, and EA. Because of these difficulties, we restrict discussion of acceptor trends in polymers to a few studies that have incorporated each of BT, TDQ, and BBT units into comparable polymers, and other TDQ and BBT containing polymers will be discussed below in the sections on device properties. Early on, Yamashita and coworkers electropolymerized monomers **15**, **16**, and **17** (**Figure 2**) using an ITO electrode to give corresponding polymers **53-55** (**Figure 7**), respectively.[78, 79] Polymers **53-55** were intractable solids with E_g^{Opt} of 1.2 eV, 0.7 eV, and 0.5 eV, respectively, in the solid state, and with EA increased markedly by TDQ and BBT, both of which are roughly in line with what is seen in BT, TDQ, and BBT small molecules and this trend is consistent with calculations on oligomeric systems. Although the 0.5 eV E_g^{opt} was among the narrowest optical gaps reported at the time, the extremely poor solubility of **53-55** limited more complete characterization. More recently, Marder, Reynolds, and coworkers reported soluble polymers **56-58** (**Figure 7**) with the strong DTP donor, which were prepared *via* Stille cross coupling reactions.[109, 110] The solubility of these polymers allowed more thorough characterization, and the data in **Figure 7** show both increasing λ_{max} and decreasing E_g^{Opt} across the series BT → TDQ → BBT while the electrochemically estimated IE decreases between BT polymer **56** and BBT polymer **58** (4.9 eV to 4.7 eV). The EA increase was more pronounced across the series BT → TDQ → BBT (3.2 eV → 3.5 eV → 4.0 eV). Again, the properties of polymers in **Figure 7** were generally consistent with those discussed above for small molecules and for computations. The implications of these property trends for materials and device performance in OPVs, NIR OLEDs, and OFETs are discussed below.



53: (BT) [(1.2); 4.22; 3.02*][a]
54: (TDQ) R^2 = H [(0.7); [4.32; 3.62*]
55: (BBT) [(0.5); 4.22; 3.72*]



56: (BT) [674; (1.41); 4.9; 3.2*][b]
57: (TDQ) R^2 = Ph [931; (0.87); 4.9; 3.7*]
58: (BBT) [1154; (0.56); 4.7; 4.0*]

Figure 7. Polymers comparing A = BT, TDQ, and BBT. For all compounds: (BT, TDQ, or BBT) refer to the parent compounds and R^1; R^2 refer to parent substituents in **Figure 2**. Data are [λ_{max} (nm); (E_g^{Opt} (eV)); IE (eV); EA* (eV)]. [a]EA = reported eE_{pc} + 4.4, IE = EA + E_g^{opt}. [b]IE = eE_{ox}^{onset} + 4.4; EA = eE_{red}^{onset} + 4.4

OPVs

Blends of conjugated donor-acceptor hole-transporting polymers with electron-transporting fullerenes are widely studied as active layers in organic bulk-heterojunction (BHJ) photovoltaic cells. Numerous optical, electronic, and morphological criteria are required by a candidate polymer-fullerene system and have been discussed elsewhere.[26, 124-126] For the present discussion it is important to note that increasing the power conversion efficiency (PCE) depends on maximizing both the short-circuit current density, J_{SC}, and the open-circuit voltage, V_{OC}. Three factors that influence these quantities will be considered here. Firstly, large J_{SC} requires efficient dissociation of the polymer excited states to form well-separated holes and electrons in polymer and fullerene, respectively. It should be noted that such a hole-electron pair is often referred to as a "charge-separated" state, whereas an electrostatically bound geminate ion pair is referred to as a "charge-transfer" state.[127] To be thermodynamically feasible ($\Delta G_{\mathrm{CS}} < 0$), charge separation from the polymer excited state (P*) requires that the EA of the fullerene, EA(F), exceeds the excited-state IE of the polymer, IE(P*) = IE(P) – $E_{\mathrm{g}}^{\mathrm{opt}}$, where $E_{\mathrm{g}}^{\mathrm{opt}}$ is the energy of the relaxed excited state relative to the ground state (generally estimated from the low-energy onset of the absorption spectrum in a film). Secondly, minimizing $E_{\mathrm{g}}^{\mathrm{opt}}$ can potentially increase J_{SC} by allowing more photons (over a wider range of the solar spectrum) to be absorbed assuming absorbance is not substantially lost from other parts of the absorption spectrum. Thirdly, V_{OC} is limited by IE(P)–EA(F). Thus, there is a tradeoff between these quantities; increasing IE(P) to increase V_{OC} will, for a given $E_{\mathrm{g}}^{\mathrm{opt}}$, lead to a reduced driving force for charge separation. Indeed, to optimize the tradeoff between V_{OC} and J_{SC} in a single-layer BHJ cell, it has been proposed that $E_{\mathrm{g}}^{\mathrm{opt}}$ for the polymer should be ca. 1.3-1.5 eV (ca. 830-950 nm).[128]

The low-lying LUMOs of the TDQ and BBT acceptors lead to lower energy optical absorption in donor-acceptor polymers incorporating these moieties than in analogous BT systems (see Table 2). Examples examined in OPVs as blends with fullerenes include (**Figure 8**): oligothiophene donor polymers **59**, **60**,[129, 130] and **61**;[131] the rigid thiophene-phenylene-thiophene (TPT) donor polymers **62** and **63**;[132] the dithiophene-pyrrole donor polymer **64**;[133] the thiophene-fluorene-thiophene donor polymers **65**[134] and **66**;[135] and the DTP donor polymers **56-58**[110](**Figure 7**). In Table 2, the polymers are grouped by publications in shaded rows. As well as optical and OPV data, the table also lists IE and EA values, along with driving forces for formation of a well-separated polymer / fullerene ion pair from the polymer excited state ($-\Delta G_{\mathrm{CS}}$). These values are estimates and comparison between studies is complicated by the use of different assumptions and approximations; however, we have attempted to standardize the methods used for estimation for all compounds; moreover, the trends, if not the absolute numbers, within a given study can provide useful insight.

Although the low-energy absorptions possible in donor-acceptor polymers incorporating BBT and TDQ acceptors are attractive from the point of view of extending solar harvesting into the near-IR, in many cases, especially those where these acceptors are coupled with electron-donating quaterthiophene (**60**), dithiophene-pyrrole (**64**), or dithiophene DTP donors (**57,58**), these absorptions extend to longer wavelength than the optimal 830-950 nm referenced above. In several studies, this results in BBT and TDQ derivatives performing much more poorly than the corresponding BT derivative (**60** vs. **59**; **63** vs. **62**, **57** and **58** vs. **56**). Multiple factors may contribute to this; for example, a significantly lower absorptivity is found for **60** vs. **59**, and open-circuit voltages are often smaller for the BBT and TDQ derivatives (this effect being much more significant than the effect attributable to the slightly lower estimated IEs relative to BT analogues). However, an important role is presumably played by the lower, in some cases negative, driving forces estimated for charge-separation from the excited states of the BBT and TDQ materials. Indeed, for some compounds (e.g., **58**) the electrochemically estimated EAs exceed that of [60]PCBM. Reasonably efficient devices with large open-circuit voltages are obtained for the TDQ derivative, **66**; however, in this particular case the assumptions used to estimate the IE (and, therefore, $-\Delta G_{\mathrm{CS}}$) and EA were not described, meaning these values are difficult to reliably compare to those for other materials.

The remainder of the table summarizes the properties of materials with less straightforward alternating donor-acceptor structures: copolymers containing both TDQ- and BT-containing monomers (**67**-**69**),[136] polymers containing platinum in the main chain (**70**, **71**),[137] and a small-molecules with electron-withdrawing substituents on the periphery (**72**).[138] Other more recent polymers incorporating dithienosilole[139] and benzodithiophene[140] donors showed similar results. Although some of these materials lead to moderate efficiencies, charge separation is again estimated to be of marginal thermodynamic feasibility.

Overall, the relatively low fundamental HOMO-LUMO gaps of the TDQ and, especially, BBT building blocks create a challenge in achieving both efficient charge separation and a moderate open-circuit voltage in simple single-layer BHJ devices. The best prospects are for materials with less electron-donating co-monomers or substituents in the case of small molecules. However, it is worth noting that, given the very low-energy absorptions seen for some of these materials, TDQ and BBT materials may be useful in tandem cells,[141-143] in which a low-voltage cell that harvests longer wavelength light is sandwiched with, and connected in series to, a higher voltage cell that harvests shorter wavelengths. TDQ and BBT materials with near-IR absorptions could potentially be used in the low-voltage portion either as hole-transport materials, perhaps in conjunction with higher EA electron-transport materials than [60]- or [70]PCBM to ensure efficient charge separation, or, given that electron-transport has been observed in some BBT derivatives (see below), as a light-harvesting electron-transporting component in conjunction with a more electron-donating hole-transporting polymer. Indeed, Wong and coworkers recently reported a dual acceptor polymer **73** containing both BBT and benzotriazole that was used as a PCBM replacement in conjunction with P3HT as a donor, albeit with low reported efficiencies so far (PCE = 0.4%).[144] Moreover, some of these materials, in conjunction with appropriate partner materials, may be useful in near-IR photodetectors,[145] where a measureable efficient photocurrent generation is required, but a photovoltage is not.

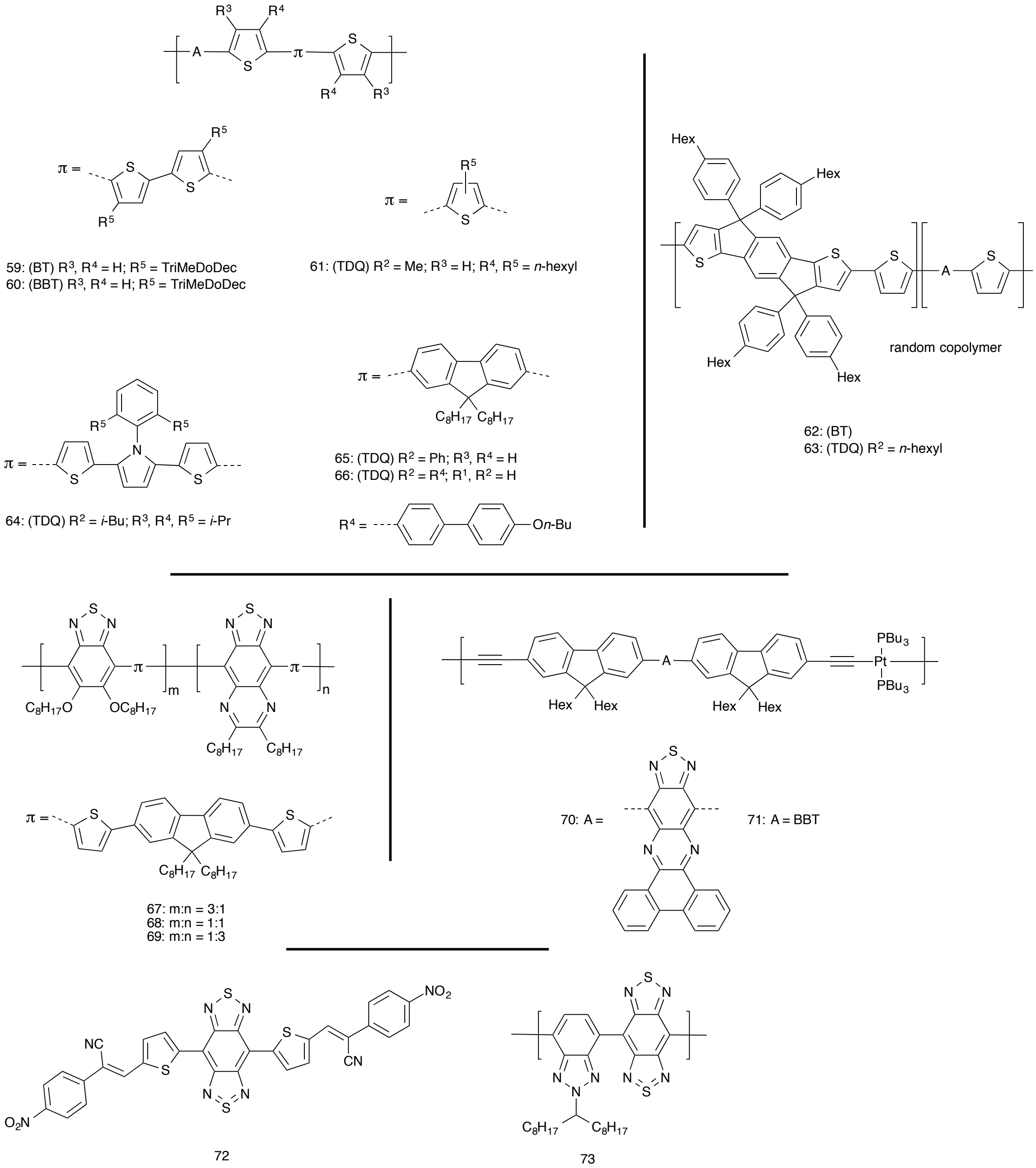


Figure 8. Polymers containing A = BT, TDQ, and BBT used to fabricate BHJ OPVs. For all compounds: (BT, TDQ, or BBT) refer to the parent compounds and R^1; R^2 refer to parent substituents in **Figure 2**.

Table 2. Materials Properties and OPV Performance Data for BHJ OPVs containing BT, TDQ, or BBT-based materials in conjunction with [60]PCBM or [70]PCBM. Shaded rows group entries by same or closely related publications. Top part of the Table represents conventional D-A polymers while the bottom part represents other materials.

X	A	λ_{max} / *nm*	$E_g^{opt\,a}$ / eV	IE / eV	EA / eV	$-\Delta G_{CS}{}^{b}$ / eV	J_{sc} / mA cm^{-2}	V_{oc} / V	PCE / %
59	BT	597	1.7	4.7^c	–	0.8	2.87^i	0.60	0.55
60	BBT	902	0.7	4.3^c	–	0.1	0.00719^i	0.04	-
62	BT	514	1.7	5.3^d	3.5^e	0.2	10.1^j	0.8	4.3
63	TDQ	~875	1.0	5.2^d	3.7^e	–0.4	3.6^j	0.54	0.84
56	BT	674	1.4	4.9^d	3.2^e	0.3	3.9^i	0.510	1.3
57	TDQ	931	0.9	4.9^d	3.7^e	–0.2	1.7^i	0.268	0.22
58	BBT	1154	0.6	4.7^d	4.0^e	–0.3	0.20^i	0.109	0.001
65	TDQ	815	1.2	5.1^d	3.9^e	–0.1^f	3.4	0.58	0.70
66	TDQ	788	1.3	5.2^g	3.9^g	–0.1^g	7.35^j	0.82	2.36
61	TDQ	703	1.4	5.0^d	3.8^e	0.2	1.58^i	0.58	0.48
64	TDQ	756	1.1	4.8^d	3.7^e	0.1	3.41^j	0.39	0.43
67	TDQ	820	1.5	5.5^d	3.6^e	–0.2	5.75^i	0.77	2.44
68	TDQ	833	1.4	5.4^d	3.6^e	–0.1	3.50^i	0.72	1.32
69	TDQ	872	1.4	5.3^d	3.5^e	–0.1	4.25^i	0.65	1.42
70	TDQ	776	1.7	>5.2^h	3.5^h	<0.3^h	~3.04^j	~0.72	-
71	BBT	810	1.5	>5.2^h	3.6^h	<0.2^h	4.95^j	0.66	1.02
72	BBT	636	1.6	5.3^d	3.5^e	0.2	3.50^i	0.72	1.05^k

[a] From onset of absorption. [b] Driving force for charge separation from X to [60]PCBM estimated by $\Delta G = \mathrm{IE}_X - E_g{}^{opt}{}_X - \mathrm{EA}_{PCBM}$, using an $\mathrm{EA}_{[60]PCBM}$ value of 3.8 eV from IPES.[146] A similar value of 3.7 eV is also obtained for both [60]- and [70]PCBM using electrochemical data[147] and assuming $\mathrm{EA} = eE_{1/2(PCBM)} + 4.8$ eV (potential vs. $\mathrm{FeCp_2}^{+/0}$). [c] From UPS. [d] Estimated from electrochemical onset oxidation potentials using the assumption that $\mathrm{IE} = eE_{ox} + 4.8$ eV where the potential is quoted vs. $\mathrm{FeCp_2}^{+/0}$ (equivalent to offsets of 4.4 eV for SCE or AgCl/Ag reference or 4.7 eV for $\mathrm{Ag^+/Ag}$ reference). [e] Estimated from electrochemical onset reduction potential using $\mathrm{EA} = eE_{red} + 4.8$ eV (potential vs. $\mathrm{FeCp_2}^{+/0}$) or an

equivalent relation. [f]Driving force given applies to PCBM; a somewhat larger driving force is expected for the fullerene employed in the OPV work, the EA of which was estimated to be 4.2 eV. [g]Estimated from electrochemical data, but assumptions used not specified. [h]Reduction potentials vs. AgCl/Ag used to estimate EAs using an offset of 4.4 eV, rather than the 4.72 eV in the original publication, for consistency with other data here. No oxidation potentials given; lower limit for IEs estimated from values of EA and E_g^{opt}. [i]Values refer to devices with [60]PCBM; [j]Values refer to devices with [70]PCBM; [k]higher V_{oc}, J_{sc}, and PCE (up to 2.02%) were obtained with a related acceptor that presumably exhibits a similar EA, but contributes increased light absorption.

NIR OLEDs and Related Materials

Near-infrared emitting organic light-emitting diodes (NIR-OLEDs) have applications in telecommunications, defense, and biomedicine. The long wavelength absorption of the TDQ and BBT derivatives make them potentially good candidates for NIR-OLEDs. Fortunately, there are many small molecule and polymer hosts that have been developed for OLEDs that may be used to match the energy levels in the TDQ and BBT derivatives, which is advantageous compared to state-of-the-art BHJ solar cell applications where, as discussed above, the various energy levels of the TDQ and BBT donor polymers often must be aligned to those of C_{60} or C_{70} derivatives. However, one drawback is that NIR luminescence of organic molecules is limited by the energy gap law of radiationless transitions,[148] meaning that quantum yields of luminescence for NIR emitters will likely be low. Nevertheless, some TDQ and BBT derivatives and polymers have been used in NIR-OLEDs: selected materials are shown in **Figure 9**, and materials and device properties are summarized in Table 3. Included in these tabulations are TDQ copolymers **74** and **75** studied by Cao[149] and Sun and coworkers,[150] a series of triarylamine donor D-A-D compounds reported by Wang and coworkers including examples **76-78**,[120, 122] a series of tetraphenylethene D-A-D-type compounds also reported by Wang and coworkers[114] including examples **43** and **44**, and the EDOT D-A-D compounds **80** and **49** (**Figure 6**) reported by Xue, Reynolds, and coworkers.[116, 117] Most of these materials electroluminesce in the NIR, but solution photoluminescent quantum yields (ϕ_f) are mostly under 15%. Consequently, the external quantum efficiency (EQE) of optimized devices are mostly under 1%, although Xue, Reynolds, and coworkers were able to increase the EQEs of **80** and **49** to 3.1% and 1.5%, respectively, by using sensitized fluorescence with organometallic dopants.[117] Although these materials do not approach the EQEs of the most efficient small-molecule and polymer OLEDs due to fundamental limitations in the luminescent yields at these long wavelengths, the variety of host materials available to match the high EA and relatively low IE of TDQ and especially BBT materials may allow sufficient optimization for certain applications. In addition to NIR OLEDs, another potential application was reported by Wang and coworkers; the NIR photoluminescence of D-A-D chromophore **79** was found to be sensitive to cyanide concentrations, which was proposed to attack one of the partially positively charged sulfur atoms of BBT as shown in **34** (**Figure 4**), suggesting its use as a potential sensing agent.[121] In related work, Wang and coworkers demonstrated NIR chemiluminescence from D-A-D chromophores structurally similar to **76-79**.[123] Finally, BBT was used as a core to give NIR-absorbing and emitting hexagonal columnar liquid crystals (**82**) that, among other properties, showed the expected red-shift in $\lambda_{\max}$ from the BT compound **81**.[151] This demonstrated the ability of BBT to provide materials that are NIR fluorescent with reasonable quantum yields, which may be useful in applications outside of organic electronics such as NIR biosensing; however, the EQEs presented in Table 3 are still about 10 times less than those reported for Pt-porphyrin OLEDs.[152, 153]

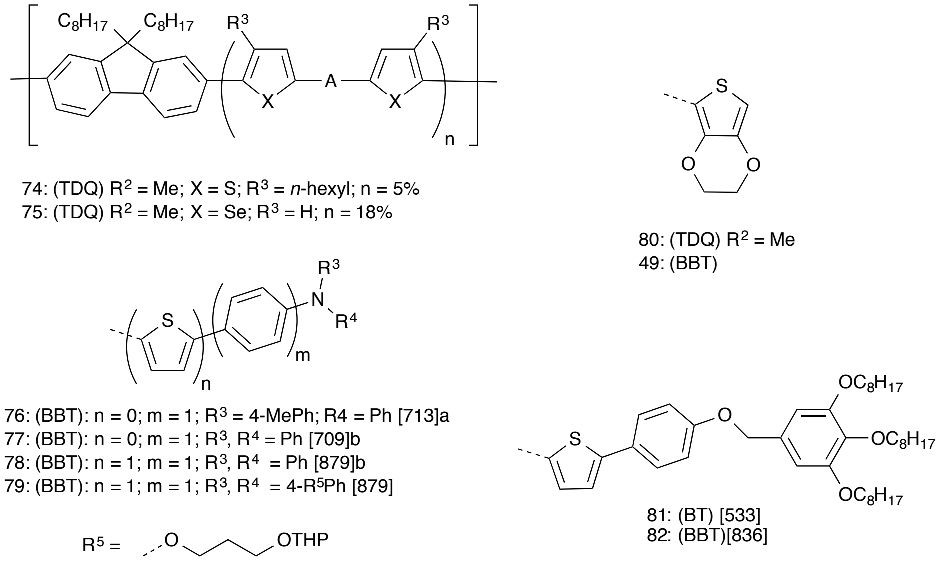


Figure 9. A = BT, TDQ, or BBT polymers **74-75** and D-A-D compounds **76-82** studied for NIR electroluminescence and fluorescence. Data are [λ_{max} (nm)]. ^{a}In toluene. ^{b}In CH_2Cl_2. For all compounds: (BT, TDQ, or BBT) refer to the parent compounds and R^1; R^2 refer to parent substituents in **Figure 2**.

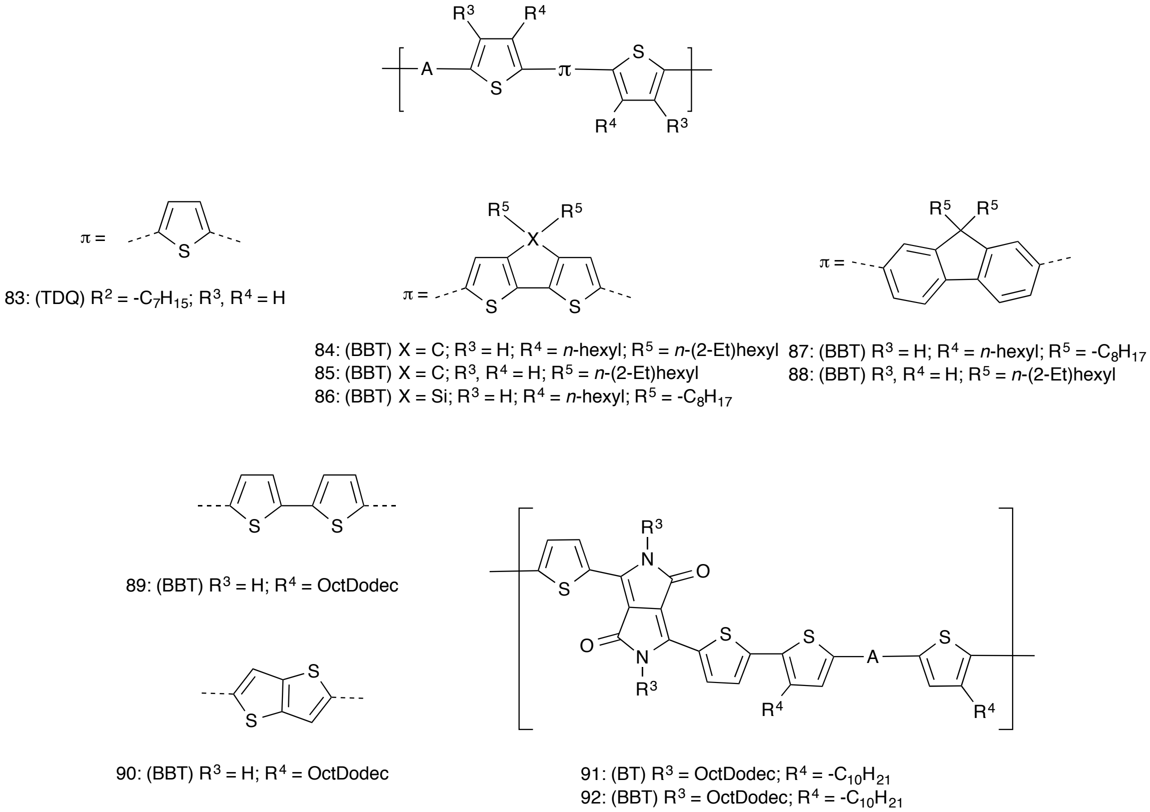
Table 3. Material Properties of NIR-emitting TDQ and BBT derivatives and properties of OLEDs using these materials as emitters. Shaded rows group entries by same or closely related publications.

X	A	IE / *eV*	EA / *eV*	ϕ_f / %	λ_{El} / nm	*EQE / %*
74	TDQ	5.7[a]	4.2[b]	-	849	0.013
75	TDQ	5.7[a]	4.3[b]	-	859	-
76	BBT	5.2[a]	3.8[d]	5.8	1080	0.73
77	BBT	5.2[a]	3.9[d]	7.4	1050	0.05
78	BBT	5.0[a]	4.0[c]	4.9	-	
43	TDQ	5.4[a]	3.5[c]	10.1	706	0.89
44	BBT	5.4[a]	3.7[c]	13.0	802	0.43
80	TDQ	5.6[d]	3.7[d]	21	692	1.6
49	BBT	5.6[d]	4.1[d]	7.6	815	0.51

[a] Estimated from electrochemical oxidation potential using IE = eE_{ox} + 4.8 eV where the potential is quoted vs. $\text{FeCp}_2^{+/0}$ (equivalent to offsets of 4.3-4.4 eV for SCE or AgCl/Ag references). [b] Estimated from EA = eE_{red} + 4.8 eV (potential vs. $\text{FeCp}_2^{+/0}$) or equivalent expression. [d] Estimated from electrochemical data and optical absorption data, but assumptions used are not specified.

OFETs

The sizable increase of EA typically seen when replacing BT with TDQ and BBT raises the possibility of TDQ and BBT materials exhibiting oxygen-stable electron-transporting properties.[154] Several BBT containing materials, mostly D-A polymers (**Figure 10**), have been studied in OFETs and properties of selected materials are summarized in Table 4. Of the small molecules studied by Yamashita and coworkers, the fluorinated derivative **42** (**Figure 6**) shows an air-stable electron mobility[112, 155] (μ_e, Table 4) of 0.40 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, optimized to 0.77 $\text{cm}^2\text{V}^{-1}\text{s}^{-}1$ by modifying deposition conditions, which was 10-fold higher than that of the corresponding BT derivative **41**.[156] Additionally, Th-BBT-Th **17** (**Figure 2**) showed ambipolar transport behavior under similar conditions. The D-A polymers **56-58**[109, 110] (**Figure 7**) and the TDQ polymer **83** (**Figure 10**) showed mostly hole transport, but BBT polymer **58** showed ambipolar charge transport. More recently, ambipolar behavior was also observed in a series of BBT-containing polymers **84**, **86**, and **87** reported by the groups of Heeger and Wudl,[157] and in the structurally similar **85** reported by the groups of Lee and Prasad.[158] However, in contrast the fluorene-bridged polymer **87**, no μ_e was reported for structurally similar polymer **88**,[158] which may be yet another example of how changes in structure and/or processing conditions can lead to differing properties. Another example of this is found in work by the Heeger and Wudl groups with the quarterthiophene-bridged polymer **89**, which shows quite high μ_h relative to other BBT-containing polymers yet very low μ_e[159]; in contrast, substitution of two of the thiophene units in **89** with the thienylthiophene unit in polymer **90** results in optimized ambipolar behavior.[160] Once more, an example of the ability of BBT to both increase EA and lower IE, and to provide ambipolar charge transport, is demonstrated with the mixed acceptor diketopyrrolopyrrole (DPP)-BT/BBT polymers **91** and **92**, where substitution of BT in **91** with BBT to give **92** results in an increase in μ_h and gives rise to measurable μ_e.[161] Generally, this tendency of BBT to raise EA significantly while either maintaining or lowering IE is probably closely related to the ability of BBT polymers to exhibit relatively high μ_e while also exhibiting relatively high μ_h, although inter- and intrachain electronic coupling must also play a role, perhaps with some contribution from the larger π-surface of BBT compared to BT leading to better A-A interchain overlap in BBT polymers.



83: (TDQ) $R^2 = -C_7H_{15}$; R^3, R^4 = H

84: (BBT) X = C; R^3 = H; R^4 = *n*-hexyl; R^5 = *n*-(2-Et)hexyl
85: (BBT) X = C; R^3, R^4 = H; R^5 = *n*-(2-Et)hexyl
86: (BBT) X = Si; R^3 = H; R^4 = *n*-hexyl; $R^5 = -C_8H_{17}$

87: (BBT) R^3 = H; R^4 = *n*-hexyl; $R^5 = -C_8H_{17}$
88: (BBT) R^3, R^4 = H; R^5 = *n*-(2-Et)hexyl

89: (BBT) R^3 = H; R^4 = OctDodec

90: (BBT) R^3 = H; R^4 = OctDodec

91: (BT) R^3 = OctDodec; $R^4 = -C_{10}H_{21}$
92: (BBT) R^3 = OctDodec; $R^4 = -C_{10}H_{21}$

Figure 10. Polymers with A = BT, TDQ, or BBT studied in OFETs. For all compounds: (BT, TDQ, or BBT) refer to the parent compounds and R^1; R^2 refer to parent substituents in **Figure 2**.

Table 4. Properties and OFET Data for BBT D-A Polymers. Shaded rows group entries by same or closely related publications.

X	A	IE (eV)	EA (eV)	μ_h (cm^{2}V^{-1}s^{-1})	μ_e (cm^{2}V^{-1}s^{-1})
41	BT	5.50[a]	3.30[b]	-	0.04
42	BBT	5.29[a]	4.04[b]	-	0.40
17	BBT	5.32[a]	3.96[b]	3.4E-07	1.6E-4
56	BT	4.9[a]	3.2[b]	1.2E-04	-
57	TDQ	4.9[a]	3.7[b]	2.2E-03	-
58	BBT	4.7[a]	4.0[b]	1.6E-03	7.9E-04
83	TDQ	4.84[a]	3.63[b]	3.8E-03	-
84	BBT	4.8[c]	4.0[c]	1.1E-01	7.4E-02
86	BBT	4.8[c]	4.1[c]	1.9E-03	1.1E-02
87	BBT	5.1[c]	3.9[c]	5.6E-03	7.0E-04
85	BBT	5.33[d]	4.32[d]	7.1E-04	3.3E-03
88	BBT	5.12[d]	3.92[d]	3.1E-04	-
89	BBT	4.6[e]	3.8[b]	2.5	low
90	BBT	4.36[f]	3.8[b]	1.0	0.7
91	BT	4.75[f]	3.4[b]	0.17	-
92	BBT	4.55[f]	3.9[b]	0.89	0.99

[a] Estimated from electrochemical onset oxidation potentials using the assumption that IE = eE_{ox} + 4.8 eV where the potential is quoted vs. $\mathrm{FeCp_2}^{+/0}$ (equivalent to offsets of 4.4 eV for SCE or AgCl/Ag reference or 4.7 where the reference is $\mathrm{Ag^+/Ag}$). [b] Estimated from electrochemical onset reduction potential using EA = eE_{red} + 4.8 eV (potential vs. $\mathrm{FeCp_2}^{+/0}$) or an equivalent relation. [c] Method for determining IE and EA not specified. [d] Estimated from onset of eE_{ox} or eE_{red}, but assumptions used not specified. [e] From UPS. [f] Estimated from EA - E_{g}^{opt} (determined from the absorption onset).

Conclusion

The many small-molecule and polymer examples given above show that TDQ and BBT can be considered strong acceptors compared to BT, lowering E_g and increasing EA. However, they can also generally be considered as stronger *donors* in that they often lead to lower IE than in BT analogues, although this effect is subtle and subject to bonding specifics in a system. This has materials property implications, particularly for use as donors in OPVs relying on PCBM for charge separation and electron transport, where high EA of the donor polymer (assuming it closely approximates the excited state oxidation potential) may lead to much lower J_{sc} compared to BT, while at the same time lower IE may lead to lower V_{oc} compared to BT polymers near the "ideal" EA and IE values.[26, 126] However, for NIR OLEDs, the strong tendency for heteroannulation to decrease E_g^{opt} from BT → TDQ → BBT is less of a limitation since many OLED host materials have been developed with varying IE and EA, although the Energy Gap Law tends to limit overall performance for NIR emitters. For OFET, the tendency for BBT in particular to lower the IE and raise the EA imparts BBT-based materials with a strong potential for ambipolar charge transport, and the strong lowering of EA by BBT makes it an intriguing option in the development of air-stable electron-transport materials. Thus, much caution should be exercised when developing OPV materials using heteroannulated BT acceptors; but certain applications in NIR OLEDs, ambipolar OFETs, and air-stable electron transport materials may prove feasible with careful materials and device design.

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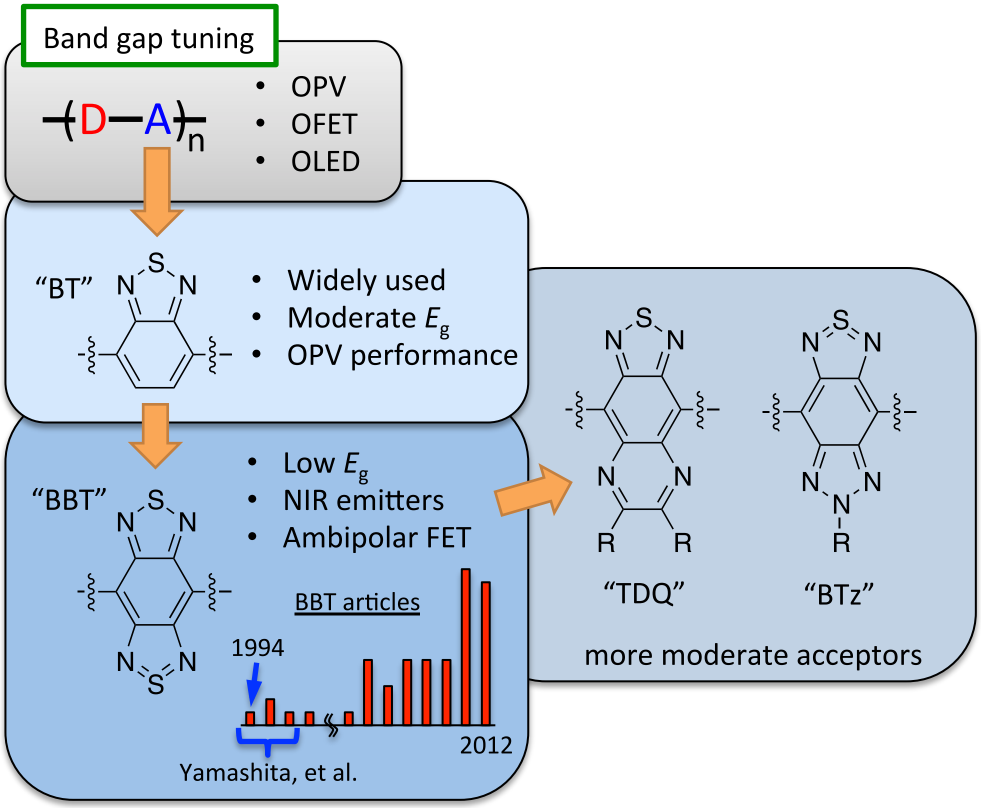
Band gap tuning
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