

Benzotriazole containing conjugated polymers for multipurpose organic electronic applications

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Benzotriazole (BTz) containing polymers have recently emerged in organic electronic applications and they are increasingly attracting a great deal of attention. These polymers are reviewed from a general perspective in terms of their potential use in three main fields, electrochromics (ECs), organic solar cells (OSCs) and organic light emitting diodes (OLEDs). In order to have a better insight into the properties of these polymers, they were compared with similar polymers. Good solubility, optical and electronic properties and synthetic availability make them multipurpose materials. They combine many desired properties in polymers and their use in different device applications is examined in detail.

Introduction

Conjugated polymers (CPs) have been a fundamental subject over the past couple of decades and they have been used as active materials in numerous industrial applications.¹ Many different types and derivatives of conducting polymers have been successfully prepared and their potential as advanced materials has been investigated since synthetic availability for small structural modifications on the polymer backbone allows tuning of the band gap and hence their optical and electronic properties.² In order to obtain polymers with desired properties recent research interest has mainly focused on donor–acceptor (DA)

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Abidin Balan received his BSc in chemistry from Bilkent University in 2007. He then joined the group of Professor Levent Toppare to pursue an MSc in chemistry. In his MSc studies, he focused on the synthesis of the Donor–Acceptor type polymers, mainly benzotriazole derivatives. He worked in the group of Prof. N. S. Sariciftci as a short term visitor during his MSc. He has published many papers on electrochromic and photovoltaic properties of conjugated polymers. Recently, he has started

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type materials where alternating electron rich and electron deficient groups are present on the backbone.³

The DA type CPs generally exhibit lower band gaps and wider bandwidths than either of the corresponding parent homopolymers. This statement is true for the polymers which satisfy necessary intramolecular interactions. The basic idea here is the contributions of donor and acceptor heterocyclics to HOMO and LUMO energy levels of the polymer.⁴ Mainly, the polymer concerned is expected to have an ionization potential (IP) close to the donor and an electron affinity (EA) close to the acceptor units.⁵ Salzner *et al.* theoretically proved that the D–A match is the keystone towards lower band gap polymers.⁶ It has been shown that in DA type polymers band gap can be decreased only if there is a high enough interaction between D and A moieties which is a consequence of low difference in HOMO–LUMO energy levels of these different groups. However, DA theory is applied not only to obtain low band gap polymers, but also to produce polymers with optical, mechanical and electronic properties which otherwise cannot be achieved by their corresponding homopolymers.

Benzotriazole (BTz) is a nitrogen containing heterocyclic benzazole derivative which exhibits high electron transporting ability due to the electron withdrawing imine ($-\text{C}=\text{N}-$) on its backbone. Katritzky *et al.* reported the extensive use of BTz as a precursor in several types of reactions.^{7–9} However, conjugated polymers containing BTz units in the main chain were investigated in the comprehensive reports of Yamamoto *et al.* They elaborated on n-type π -conjugated polymers; poly(benzotriazole) (p(BTz)) (**1**), poly(benzimidazole) (p(BIm)) (**2**), poly(benzothiadiazole) (p(BTd)) (**3**) and poly(benzoselenadiazole) (p(BSe)) (**4**) where all are potential acceptor units (Scheme 1).^{10–15} It has been showed that their electrochemical and optical characteristics are slightly different since they possess different atoms in the 2-positions (N, C, S, Se) in their isoelectronic structures. Among them **4** was shown to be the best electron accepting unit which can be explained by the large polarizability and the electrochemical amphotericity of selenium



Scheme 1

atoms.^{11,16} All these aromatic heterocycles have electronic characters affected by the polarizability differences between the atoms at 2-positions. Although a different substituent on the 2-position affects the electron density of the entire system in **1** and **2** and can change the order; present examples suggest that the electron accepting ability of these benzazoles increases from **1** to **4**. Thus, **1**, a moderate electron acceptor polymer can be classified as the worst electron accepting homopolymer among its homologues **2–4**. However the properties achieved from the current examples of copolymers of BTz make BTz bearing CPs interesting for optoelectronic applications. Additionally, BTz polymers are synthetically easy to achieve and due to their possible functionalization site they are easily modified, thus combining a huge synthetic diversity with great optoelectronic properties. BTz containing polymers with different DA combinations and numerous different repeating units utilized in three major fields of organic electronics, ECDs, OPVs and OLEDs, are examined in detail.

Electrochromics (ECs)

During the search for soluble, fast switching, high optical contrast and stable CPs for electrochromic devices, neutral state blue, red or green polymers with redox achievable transmissive states were aimed for. However, obtaining all these properties in a unique polymer was only possible with benzotriazole containing CPs which is the subject of this section.

To the best of our knowledge, the first CPs containing BTz in the main chain (**5**, **9** and **11**) were synthesized by Tanimoto and Yamamoto in 2004.¹³ Hexyl substitution in **5** was not enough to have good solubility in common organic solvents. On the other hand all other polymers in the series **5–13** (Scheme 2) with longer pendant alkyl chains showed excellent solubility. Charge transfer between carbazole (CBz) pendant groups and BTz chain was proven for polymers **5–8**. **5a** revealed a maximum absorption in the visible region at a shorter wavelength than its longer alkyl chain substituted analogue **5b**. This is probably due to having different molecular weights in the soluble part of the polymers. However, longer wavelength absorption in **5a** compared to **1** showed possible contribution of a charge transfer between CBz and BTz backbone.¹² Additionally, photoluminescence (PL) experiments showed that the intensity of CBz emission is weaker in **5a** than **5b**. This suggests that photoenergy transfer from CBz pendant group to BTz main chain is more effective in shorter spacer case. Electrochemical polymerization of CBz units as in **6** and **8** yielded insoluble CPs which hindered further characterization.¹² Hoger *et al.* reported the synthesis of orange-red polymers **12** and **13** as the building blocks for low bandgap



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Scheme 2

poly(arylene-ethynylene)s with 2.35 and 2.32 eV band gaps respectively.¹⁷ Red shifted visible absorption (40–50 nm) compared to the alkyl substituted **11**¹³ can be attributed to the increase in π -stacking due to phenyl pendant group. Those polymers were not characterized in detail in terms of their optoelectronic properties however; they would be great candidates for OSCs and/or OLEDs.

The first electro-polymerizable BTz containing heterocycle in the main chain was synthesized by our group in 2008.¹⁸ BTz was coupled with ethylenedioxythiophene (EDOT) which is a well known electron donor, to give a linearly polymerizable, symmetric monomer structure like other benzazole derivatives (**14–18**) (Table 1). The polymer, **19** showed that the presence of BTz unit in the polymer backbone exceptionally enhanced the electrochromic properties of the parent polymer, PEDOT, in terms of optical contrast, switching time and coloration efficiency (Table 2). Additionally this polymer revealed an ambipolar character due to electron deficient BTz contribution with high stability (6% decrease in total charge after 4000 cycles), whereas PEDOT is not n-type dopable at all.¹⁹ Monomer of compound **19**, 4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-dodecyl-2H-benzo [1,2,3] triazole (BEBT), was used as the comonomer against benzoquinoxaline and pyrrole bearing ones and it has been shown that copolymerization with BEBT increases the optical and kinetic properties of the resulting polymer even more efficiently than simple copolymerization with Bi-EDOT.^{20,21}

Benzazole-EDOT bearing DA type ECPs, **14** and **15**, revealed a green color in their neutral states accompanied by highly transmissive oxidized states.^{22,23} They showed two π - π^* transitions which was claimed as essential to obtain green colored polymers.^{24–27} These are generally attributed to two transitions: (1) between the valence band and antibonding orbital, and (2) between the valence band and the narrow conduction band.²⁸ Lower band gap and red shifted absorption in **15** (compared to **14**) suggest that the D–A match is superior in **15**. However, in terms of electrochromism, **14** showed better properties such as switching time and high optical contrast in the NIR region, besides being the first green to transmissive electrochromic polymer in the literature.²² Compared to others (**14–18**) **19** showed a high energy absorption with a negligibly weak intensity which indicates that the polymer have a dominant donor character rather than DA as was the case for BIm bearing polymers.²⁹ BIm and EDOT containing polymers **16–18** are great examples of the fact that the substituent is affecting the entire electronic and optical properties in such polymers, *i.e.* fine color tuning can be achieved with different substituent groups.

Enhancing the electrochromic properties of PEDOT in **19** opened a new gate for electrochromic polymers (Fig. 1). Addition of benzotriazole might also yield soluble conjugated polymers due to the alkyl substitution on N1 position of BTz unit (designated as R in Fig. 1). In this manner, thiophene was also coupled to BTz in order to improve its electrochromic properties. Although solution processable red to highly transmissive

Table 1 Chemical structures of EDOT bearing benzazoles, their colors in neutral and various oxidized states and electrochromic properties

Polymer	Colors	$E_{m,a}$ (V)	$E_{p,a}$ $E_{p,c}$ (V)	λ_{max} (nm)	E_g^a (eV)	$\% \Delta T^b$	ST^c (s)
		0.95	-0.06 -0.26	428 755	1.19	23.0%–755 nm 72.0%–1500 nm	0.4
		0.85	-0.09 -1.24	343 448 796	1.13	27.3%–448 nm 10.9%–796 nm	2.1
		0.82	0.56 0.38	580	1.75	44.5%–580 nm 75.3%–1800 nm	0.4
		0.80	0.51 0.33	560	1.69	44.5%–560 nm 71.4%–1800 nm	0.4
		0.96	1.06 0.40	513	1.77	10.0%–513 nm 36.0%–1370 nm	2.5

^a Optical band gaps calculated from the onset of the π - π^* transition in the visible region of the neutral polymer. ^b Percent transmittance difference between neutral and fully oxidized states of the polymer film. ^c Switching time of the polymers in the visible region between neutral and fully oxidized states. **14** Adapted with permission from ref. 22, Copyright 2007 The Royal Society of Chemistry; **15** Adapted with permission from ref. 23, Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany; **16**, **17**, **18** Adapted with permission from ref. 29, Copyright 2010 Elsevier B. V.

Table 2 Comparison of **19** and PEDOT in terms of their electrochromic properties

Polymer	Optical Contrast ($\% \Delta T$)	Switching Time (s)	Coloration Efficiency (cm^2/C)	n-Doping
19	53	1.1	211	✓
PEDOT	44	2.2	183	✗

polymers have been synthesized recently,³⁰ poly(3,4-ethylenedioxythiophene) (PEDOP) was the only example for red to transmissive switching ECP, although it lacks solution processability.³¹ Thus, upon addition of BTz units to the PTh chain a red to transmissive switching solution processable ECP could have been realized. However, this attempt in polymer **20** showed unexpected properties such as switching between all primary colors of RGB,^{32,33} solution processability and photoluminescence.³⁴ It is noteworthy that this was the first example to show all these properties in a single polymer. After this outstanding invention, curiosity to see the effect of other donor groups on color and kinetic properties of BTz bearing polymers was arisen, leading to the production of polymers **21**–**26**. Selenophene, for instance, has a lower oxidation potential and higher electron donating character than those of thiophene.³⁵ Low oxidation potential increases the quality of electrochemically produced polymer film by minimizing overoxidation. Selenophene coupled polymer **22** was shown to have red-purple neutral and highly transmissive oxidized states.³⁶ Even though thiophene

and selenophene seem very similar in their natures, **22** did not show multicolored oxidation states due to its low energy polaronic states (≥ 800 nm). Visible absorption of polymer chain was diminished upon oxidation and transition state colors between neutral and oxidized forms could not be observed.

Diaz *et al.* reported electrochemical properties of polypyrrole which is an electron rich and easy to polymerize heterocycle both chemically and electrochemically.^{37,38,39} Thin polypyrrole film is yellow/green in the neutral and blue/violet in the doped state and it has 2.7 eV E_g .⁴⁰ The most important drawback with the pyrrole containing CPs is their insolubility. However, pyrrole derivative **23** was shown to be both p and n type dopable and soluble⁴¹ which are unusual properties for a pyrrole containing polymer.⁴ Although, DA type benzoquinoline polymers bearing a pyrrole unit showed green to transmissive electrochromic switching,^{42,43} thin film of **23** switched between blue and highly transmissive states in a low working potential range (between 0.2 V and 0.4 V).

Thienothiophene (TTh) is an electron rich aromatic heterocycle with extended conjugation compared to its single ring counterpart, thiophene.⁴⁴ Despite this fact, the DAD type monomer of **24** has the highest oxidation potential among all BTz containing monomers.⁴⁵ This can be attributed to the high resonance stabilization energy of the fused Th rings in TTh. It resulted in a low lying HOMO causing the extraction of electron difficult from the system.⁴⁶ As its thiophene containing homologue **20**, **24** also showed multicolored electrochromic properties. Stepwise oxidation of **24** allowed the observation of several different colored oxidation states. Moreover, it surprisingly

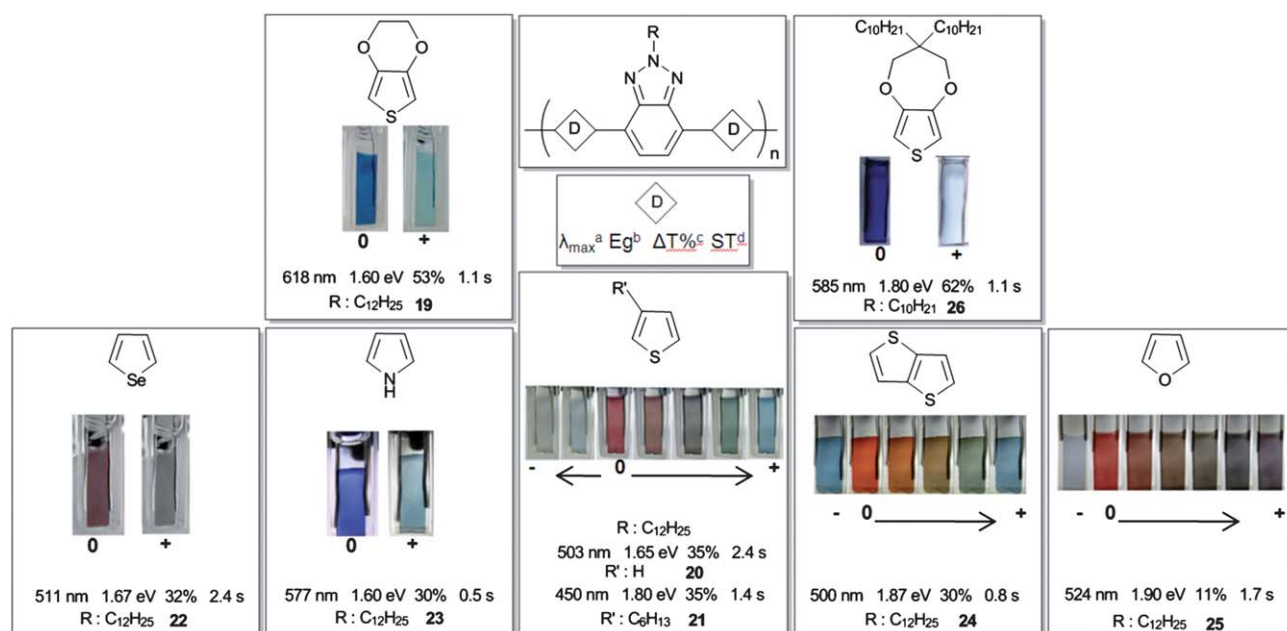


Fig. 1 Chemical structures of representative BTz containing conjugated polymers, their colors in neutral, various oxidized and reduced states and electrochromic properties of the polymer films. ^a Absorption maximum of the neutral state polymer films in visible region. ^b Optical band gap. ^c Percent transmittance in the visible region. ^d Switching time in the visible region. **19** Adapted with permission from ref. 18, Copyright 2008 American Chemical Society; **20** Adapted with permission from ref. 34, Copyright 2009 The Royal Society of Chemistry; **21** Adapted with permission from ref. 146, Copyright 2010 American Chemical Society; **22** Adapted with permission from ref. 36, Copyright 2009 Elsevier B. V.; **23** Adapted with permission from ref. 41, Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany; **24, 25** Adapted with permission from ref. 45, Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

revealed the same color for p-doped and n-doped states which is not likely to be seen due to the energy difference between positively and negatively charged polymer chains.⁴⁷

Usually, polymers for organic electronic applications are not biodegradable, and even worse, extensive use of them results in hazardous waste production.⁴⁸ On the other hand, furan bearing conjugated polymers deserve a close scrutiny in terms of biodegradable polymer applications.⁴⁹ Additionally, among aforementioned heterocyclics, only furan can be obtained from entirely renewable resources.⁵⁰ BTz and furan with all their good reputations were coupled in **25**.⁴⁵ In case of furan, electrochemical polymerization has always been difficult due to its high tendency to be overoxidized.⁵¹ Electrochemically produced polymer has low conductivity since overoxidation usually breaks the conjugation along the polymer backbone. However, reversible cycles for **25** in CV showed an increase in current density for polymer redox coupling during electrochemical polymerization. This indicates that the electroactive surface area on the electrode is increasing; hence a conducting polymer film is coated on the surface. This is related to the low potential requirement for monomer to initiate the electrochemical polymerization (1.15 V). Thin films of **25** also revealed multicolored electrochromism as its thiophene bearing analogue **20**, with six different colored oxidation states. To the best of our knowledge, this was the maximum number of achievable different colors resulting from the oxidation of a single polymer. Additionally a highly transmissive n-doped state allows this polymer to be exploited in non-emissive electrochromic applications.

Although, **19** was introduced as the polymer which enhanced the electrochromic properties of EDOT, insolubility was the

main drawback. Alkyl substitution on BTz unit was not sufficient to provide solubility to the electrochemically produced polymer. Later on, it has been shown that chemically produced polymer was soluble in common organic solvents with blue shifted absorption for neutral state. That might be due to shorter polymer chains compared to the electrochemically produced ones.⁵² On the other hand, Önal and Cihaner *et al.* reported the DA type polymer **26**; 3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b]-[1,4]dioxepine coupled with BTz in the main chain which switches between deep blue and highly transmissive states.⁵³ Additional alkyl chains on the donor group compared to **19** provided good solubility as well as further improvement in electrochromic properties which were also better than its BTz containing blue to transmissive switching counterpart.⁵⁴

Polymers **27–30** in Fig. 2 illustrate the effects of substitution on optical and electrochemical properties for BTz bearing CPs. Benzyl substituted **27**,⁵⁵ analogous to the alkyl substituted **19**, showed lower optical contrast. It should be noted here that long alkyl chains on the polymer backbone increase the optical contrast for the polymer which can be attributed to the separation between polymer chains.⁵⁶ Increased separation facilitates the injection/ejection of the counter ion and provides higher optical contrast.⁵⁷ In the case of **28** which has an isomeric structure to **27**, benzyl group was substituted from N1-position of BTz instead of N2. This change in position of substitution decreased the effective conjugation length in **28** compared to **27**, and entire properties of the polymer changed accordingly. Neutral state absorbance was blue shifted from 625 nm to 477 nm, thus colors of the polymer films in their neutral states were completely different. Polaronic state absorbance was also



Fig. 2 Chemical structures of D-A type BTz polymers and their colors in neutral, oxidized and reduced states. **27, 28** Adapted with permission from ref. 55, Copyright 2010 Elsevier B. V.; **29, 30** Adapted with permission from ref. 58, Copyright 2010 Elsevier B. V.

blue shifted to higher energy region which resulted in a colored oxidized state rather than transmissive. The difference between N2-substituted **29** and N1-substituted **30** was even more dramatic when thiophene was the donor group.⁵⁸ Neither of the N1-substituted polymers showed tendency for n-type doping in the working potential range due to the change in the effective conjugation length of acceptor unit which hindered the negative charge carrier formation on polymer backbone.

Towards solution processable multicolored electrochromic CPs, **31–34** with different benzotriazole bridged thiophene chains were investigated (Scheme 3). All three polymers, **31, 32** and **33**, differing only in the length of alkyl chain, were red in their neutral states and blue in their oxidized states.⁵⁹ However their spectral responses upon stepwise oxidation were different. Alkyl chains on the polymer backbone affected the doping rate due to aforementioned reasons and with increasing the length of the alkyl pendant group a greater number of different colors became detectable. The slowest switching time for **33** is also a possible reason for the observation of several different colored states. The most important properties for these polymers are their potential candidacy to be used as multicolor to transmissive switching ECPs since reduction of the neutral chains resulted in the depletion of optical absorbance in the visible region. Reported results showed that **33** has 27% optical contrast between red and transparent states and 12% optical contrast between blue and transparent states. It switches between these states within 1.7 and 2.3 s respectively. Additional substitution of the phenyl and thiophene units (compare to **20**) increased the doping rates in **34**



Scheme 3

and **35**, which in turn, led to the detection of fewer colors.⁶⁰ The fraction of benzotriazole moieties per repeating unit on the **34** and **35** decreased compared to **20** and this allowed more accessible volume in the polymer films where dopant ions can easily be incorporated. Faster switching due to facilitated ion accumulation impeded the occurrence of two distinct transitions and observation of green colored state. On the other hand, they can be classified as fast switching ECPs accompanied with the multicolored to transmissive switching properties.

Poly-9,9-dialkylfluorenes (PFOs) and their copolymers with different groups are considered as some of the most promising materials to be used in organic electronics.^{61–64} Especially BTd-PFO copolymers were exploited in highly efficient OPVs, OLEDs and OFETs.^{65–68} Copolymerization of BTz derivatives with fluorene as in **10**, **36** and **37**, yielded soluble multicolored polymers with moderate band gaps compared to their parent polymers or BTd containing counterparts.⁶⁹ Addition of trifluoroacetic acid (TFA) to the solutions of **36** and **37** in toluene also resulted in the observation of different colors. Since polymers regain their neutral state colors after the addition of triethylamine, these polymers can be used as solution processable pH responsive chromophores.

BTz bearing CPs were mostly multicolored polymers as explained so far. Multicolored polymers with a redox accessible transmissive state could be great tools for the realization of low cost and flexible devices in EC display technology.⁷⁰ However, for possible smart windows applications of ECPs, black colored conjugated polymers integrated with a transmissive state should also be designed.⁷¹ They would provide easier processing through printing, spraying and coating methods and lower the cost compared to their inorganic counterparts.⁷² In addition, efficient light harvesting which is one of the most important parameters in organic solar cells could be achieved with these materials.⁷³ It has been shown that black colored polymers with a transmissive oxidized state can be achieved by donor acceptor type BTd containing copolymers with extended neutral state absorption over the entire visible region.^{74,75} Recently BTz bearing random copolymers were also employed as black to transmissive switching ECPs. Electrochemical polymerization in the presence of two different monomers resulted in black colored soluble polymer **38** (Scheme 4) which was deposited as a thin film on ITO.⁷⁶

The main idea here is the combination of different oligomers absorbing in different regions of the spectrum to obtain full visible absorption. Benzoquinoxaline or BSe containing polymers were shown to be green in their neutral states.^{23,77} It has been well established that neutral state green conjugated polymers reveal two distinct λ_{\max} maxima at around 400 and 700 nm.²² On the other hand, BTz and thiophene bearing polymers, for example, are red in their neutral states with λ_{\max} at ca. 500 nm. Thus, combination of benzoquinoxaline or BSe and BTz with Th as in **39–41** should allow different segments on the same polymer chain (Scheme 4) ending up with the absorption of all the visible light.⁷⁸

Due to dominant absorbance at 600 nm, **39** was blue; whereas a strong and blue shifted absorption resulted in purple color in the neutral state for **41**. However, since almost all visible light was absorbed by **40** it revealed black colored neutral state where the oxidation of polymer resulted in a highly transmissive oxidized state.



Scheme 4

Organic solar cells (OSCs)

Polymer bulk heterojunction (BHJ) solar cells based on DA type conjugated homopolymers and composites as donor materials are aroused interest and offer pledge for the realization and improvement of a low cost, printable and flexible clean energy source.^{79–83} Over the past decade, classical polymer donor molecules, such as dialkoxy-substituted poly(*para*-phenylene)s (PPVs) and poly(3-hexylthiophene) (P3HT) have been investigated in detail regarding their photovoltaic applications.^{84,85} Therefore, in some sense, poly[2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV), (poly[2-methoxy-5-(3,7-dimethyl-octyloxy)]-1,4-phenylenevinylene) (MDMO-PPV) and poly(3-hexylthiophene) (P3HT) (Scheme 5) can be classified as milestones and have been addressed in previous reviews.^{73,86–88} New avenues for the development of novel conjugated polymers as donor materials with improved efficiencies are required to be used in OPVs. In this part of the review, we summarize the most recent developments in conjugated polymers as active layers used either with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) or [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) (Scheme 5) to construct highly efficient OPV devices. Several reviews on photovoltaic devices have summarized the device physics and use of conjugated polymers in organic solar cells (OSCs).^{89–91} Thus, we focused on the progress of the novel polymer donors starting from fluorenes, cabazoles and benzodithiophenes including benzotriazole (BTz) that have paved the pathway toward high efficiency photovoltaic devices which might be the promising candidates for the future applications of large area solar panels.

Polyfluorenes (PFOs) have been used in BHJ solar cells; however, these devices were mainly absorbing at short



Scheme 5

wavelengths due to their large band gaps, although a few exceptions exist.^{92–95} The first breakthrough in fluorene based polymer solar cells was pointed out by Andersson *et al.* in 2003.⁹⁶ They synthesized poly[2,7-(9-2'-ethylhexyl)-9-hexylfluorene]-*alt*-5,5-(e',7'-di-2-thienyl-2,1,3-benzothiadiazole) (**42**) (Scheme 6). This polymer has an extended absorption in the visible region to 650 nm and 2.5% efficiencies were achieved using an ITO/PEDOT:PSS/Polymer:PC₆₁BM/LiF/Al device architecture. After their report, many groups highlighted the significance of low band gap fluorene copolymers with benzothiadiazole and benzoselenadiazole (**44–46**) (Scheme 6).^{97–101} In 2005, alkyl-substituted fluorene with 4,7-diselenophen-2-yl-2,1,3-benzoselenadiazole was shown by Yang *et al.* and the polymer showed only 1% efficiency with 0.85 V V_{oc} and 2.53 mAcm⁻² J_{sc} using 1 : 3 polymer: PC₆₁BM ratio.¹⁰² When the co-monomer was changed into 4,7-di-2-thienyl-2,1,3-benzoselenadiazole (**43a**) (Scheme 6) the absorption was shifted to near-infrared region and 0.91% PCE was recorded.¹⁰³ The so-called “APFO-Green” series comprising PFO and various donor–acceptor segments

have provided fresh air for OPVs by virtue of their high solubilities and low band gaps.^{104–107} With different alkyl chains or using strong electron acceptor units such as BTd,⁶⁷ BSe⁹⁷ and thienopyrazine,¹⁰⁸ several fluorene based copolymers have been synthesized and characterized in terms of their photovoltaic performances.^{68,109,110} Very recently, BTz was also involved in the PFO-based copolymers as given by Zhang *et al.*¹¹¹ **47** (Scheme 6) was synthesized *via* Suzuki coupling and HOMO–LUMO energy levels and optical band gap values were calculated from CV measurements as –5.67, –3.43 and 2.24 eV, respectively. Fabricated devices with PC₆₁BM and alcohol-soluble poly[(9,9-dioctyl-2,7-fluorene)-*alt*-(9,9-bis(3,2-(*N,N*-dimethylamino)propyl)-2,7-fluorene)] (PFN) as the cathode modification layer yielded a maximum of 1.3% PCE using 1 : 2 ratio. Its BTd bearing counterpart (APFO-3) **43b** (Scheme 6) showed 2.7% PCE using dichlorobenzene as the solvent and PC₇₁BM as the acceptor unit.¹¹² Nevertheless, since low band gap PFOs have relatively low hole mobility, design of new materials was an urgent need for high efficiency solar cells.^{113–115} Poly(*N*-vinyl carbazole) (PVCz) was utilized due to its well-known excellent photoconductivity.¹¹⁶ In 2006, Müllen *et al.* have reported 0.6%¹¹⁷ and 0.8% efficient solar cells with PVCz derivatives as the start of these studies. However, with the growing demand for technology, important progress has been made in understanding the device structures and improvements in device efficiencies. Leclerc and his group reported a processable, high molecular weight and highly conjugated PVCz derivative to be used in efficient BHJ solar cells in 2007.¹¹⁸ **50** was synthesized *via* Suzuki coupling and its electrochromic and photovoltaic properties were reported. HOMO–LUMO energy levels were determined as –5.5 eV–3.6 eV for the polymer which were reasonable electronic energy levels for OSCs (E_{HOMO} level between –5.2 and –5.8 eV; and E_{LUMO} level between –3.7 and –4.0 eV).¹¹⁹ 3.6% efficient solar cells were fabricated using **50**:PC₆₁BM in 4 : 1 ratio with 0.89 V open circuit voltage (V_{oc}), 6.52 mA cm⁻² short circuit current (J_{sc}) and 63% fill factor (FF). Moreover, this study was improved using titanium oxide (TiOx) as the optical spacer by Park and colleagues in 2009.¹²⁰ 6.1% power conversion efficiency was obtained having 10.6 mA cm⁻² J_{sc} with BHJ composites comprising **50**:PC₇₁BM. Almost 100% internal quantum efficiencies were reported in the paper, implying that all photo-generated charge carriers were collected at the electrodes. The results were also confirmed by National Renewable Energy Laboratory (NREL). These studies were further investigated by



R_1 : 2-ethylhexyl, R_2 : C ₆ H ₁₃ X : S	42
R_1, R_2 : C ₈ H ₁₇ X : Se	43a
R_1, R_2 : C ₈ H ₁₇ X : S	43b
R_1, R_2 : 2-ethylhexyl X : S	44
R_1, R_2 : 3,7-dimethyloctyl X : S	45
R_1, R_2 : 2-ethylhexyl X : Se	46
R_1, R_2 : C ₈ H ₁₇ X : N-C ₁₂ H ₂₅	47

Scheme 6



Scheme 7

replacing the BTd group with BTz on the polymer backbone. Very recently, **55** was synthesized from 4,7-dibromothiényloctyl-1,2,3-benzotriazole and a poly(2,7-carbazole) derivative *via* Suzuki cross-coupling polymerization.¹²¹ HOMO–LUMO energies and the optical band gap values were calculated as -5.70 , -3.82 and 2.16 eV respectively. BTz group on the polymer chain lowered the HOMO–LUMO energy levels probably due to its strong electron accepting ability.¹²² The fabricated devices showed that 1 : 2; **55**:PC₆₁BM ratio has the highest performance and 77 nm thick solar cells yielded the best efficiency of 2.1%, 0.9 V V_{oc} , 5.57 mA cm⁻² J_{sc} and 42% FF.

To have an insight into the chemical structure and ideal donor polymer for the BHJ solar cells, many acceptor units were inserted into the CBz containing polymer backbones. Numerous donor molecules bearing PVCz as the comonomer were designed with either benzazoles or pyridine derivatives (**48–53**) (Scheme 7).¹²³ HOMO–LUMO energy levels were determined more precisely for the polymers **48–53** due to the dual electrochemical properties of the polymers. It has been seen that altering the electron deficient part of the polymer chain did not change the polymer oxidation potential significantly. On the other hand, LUMO levels responded differently. The LUMO energy levels were strongly affected by the electron withdrawing center on the polymer chain and stronger electron-deficient units resulted in low lying LUMO levels. For comparison purposes a BTz and CBz derivative **55** (Scheme 7) was also synthesized *via* Suzuki coupling by Zhang *et al.*¹¹¹ The polymer was used as the donor material together with PC₆₁BM. Devices comprising either PFN as cathode modification layer showed obvious improvements of PV performance.^{124,125} Its BSe homologue **54** (Scheme 7) was also synthesized recently by Zhao *et al.*¹²⁶ Incorporation of BSe unit into the polymer backbone resulted in a lower optical band gap (1.73 eV) compared to its BT (1.88 eV) and BTz (2.18 eV) analogues and **50** (1.85 eV).^{111,127,128} Next to **50**, **55** exhibited the highest power conversion efficiencies among the other CBz derivatives. The low efficiencies of **51** and **53** were probably due

to low molecular weight and mobilities.¹²⁹ The slightly lower V_{oc} value for **54** is due to the higher HOMO energy level of the polymer since it has been suggested that V_{oc} can be correlated with the difference between LUMO level of the acceptor and HOMO energy level of the donor units. Better PCE values were obtained when PC₆₁BM was replaced by PC₇₁BM which has stronger absorption in the visible region (Table 3).¹³⁰

In order to modulate the band gap and energy levels, different copolymers of BTd and BSe were designed and synthesized. For instance, copolymers with fluorene, CBz, dithienylsilole, dithienylpyrrole and benzodithiophene (BDT) were used with strong electron acceptor benzazoles such as BTd and BSe.^{96,126,131,132} Among others, BDT comprising copolymers have become of great interest since 2008. Hou *et al.* synthesized and characterized a series of 4,8-bis-dodecyloxy-BDT copolymers **56–60** (Scheme 8) to investigate the effects of copolymerized functional groups on band gap.¹³³ Changing the acceptor unit, band gap lowering abilities of the electron deficient units were determined as thieno[3,4-*b*]pyrazine (TPZ) \gg BSe > 2,3-diphenylquinoxaline (DPQ) > BTd. The power conversion efficiencies of the devices were only up to 0.9% with BTdas the acceptor. In 2009, Liang and co-workers synthesized a COOR₃ (R₃: C₁₂H₂₅) substituted thienothiophene and BDT derivative **61** (Scheme 8) (PCE %: 5.30),¹³⁴ and the copolymer exhibited 5.6% efficiency with a corrected J_{sc} of 15.6 mA cm⁻² by NREL. Hou and his group, in 2009, synthesized two other BDT derivatives **62** and **63** (Scheme 8) with alkyl and alkoxy chains on the thiophene units to examine the side chain effect.¹³⁵ After annealing both **62** (1.95% PCE) and **63** (1.28% PCE) revealed higher photovoltaic performances with PC₇₁BM. Szarko and co-workers also focused on BDT with various side chains and obtained 7.4% PCE with 2-ethylhexyl and 2-ethylhexyloxy branched alkyl chains (**67**) (Scheme 8) using both PC₆₁BM and PC₇₁BM.¹³⁶ Liang *et al.* also reported a BDT derivative **67** showing 7.4% power conversion efficiency with 14.50 mA cm⁻² J_{sc} using chlorobenzene and 1,8-diiodobenzene (DIB).¹³⁷ By changing the fluorinated electron

Table 3 Photovoltaic performances of fluorene and CBz incorporated conjugated polymers (42 to 55)

Number	Device architecture	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
42	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM/LiF/Al	1.04	4.66	46	2.2
43a	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 3)/Ba/Al	0.85	2.53	32.7	0.91
43b	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM (1 : 3)/LiF/Al	0.94	6.2	0.46	2.7
44	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM (1 : 3)/Ca/Al	0.95	8.4	44	3.50
45	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM (1 : 3)/Ca/Al	0.97	9.1	51	4.50
46	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM (1 : 3)/Ca/Al	0.52	5.0	34.3	0.89
47	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 2)/PFN/Al	1.0	2.64	51.5	1.30
48	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 4)/Al	0.95	3.0	56	1.80
49	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 4)/Al	0.90	2.6	44	1.10
50	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 4)/Al	0.86	6.8	56	3.60
50	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM/TiOx/Al	0.88	10.6	66	6.10
51	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 4)/Al	0.71	2.9	32	0.70
52	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 4)/Al	0.96	3.7	60	2.40
53	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 4)/Al	0.85	1.4	60	0.80
54	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 4)/Al	0.80	4.15	44	1.46
54	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM (1 : 4)/Al	0.75	7.23	45	2.58
55	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 2)/Al	0.90	5.57	42	2.1
55	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 2)/Al	0.80	3.91	48.4	1.51
55	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 2)/PFN/Al	0.90	4.68	65.3	2.75



Scheme 8



Scheme 9

acceptor unit to an alkyl chain a poly[4,8-bis-substituted-benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-4-substituted-thieno[3,4-b]thiophene-2,6-diyl] derivative **68** (Scheme 8) was synthesized. It revealed a very high PCE % of 7.73 which certified by NREL as 6.77%.¹³⁸ Alternating BDT and N-alkylated dioxypyrrolothiophene copolymers (**69** and **70** (Scheme 8)) were also used for OPVs and 3.42% and 4.79% PCE were achieved with 2% diiodooctane (DIO) and PC₇₁BM

as the acceptor.¹³⁹ Recently, Leclerc's group raised the efficiency of the BDT and thieno[3,4-c]pyrrole-4,6-dione (**71**) copolymer (Scheme 8) to 5.5% using PC₇₁BM.¹⁴⁰ Frechet and co-workers improved the efficiency to 6.8% with 1 : 1.5 polymer : PC₆₁BM ratio using a chlorobenzene/DIO (99/1, v/v) solution.¹⁴¹ Alternating bisthiophene-phthalimide (PhBT) and BDT copolymers **64** and **65** (Scheme 8) were also synthesized *via* Stille coupling by Zhang *et al.* recently; however, only 1.08% and 1.54% maximum efficiencies were recorded which were not as high for the previous BDT derivatives.¹⁴² Lately, combination of BDT with BTz was also utilized and their photovoltaic properties were investigated in detail.¹⁴³ The polymer **72** (was obtained *via* Stille coupling and additional Th units added to **72** yielded the low band gap polymer **73**(Scheme 8) . Since the polymers were only p-type dopable, LUMO energies were estimated from the optical band gap and HOMO values. Photovoltaic devices were fabricated using PC₆₁BM and PC₇₁BM with a device architecture of ITO/(40 nm) PEDOT:PSS/active layer/(20 nm) Ca/(60 nm) Al. The optimal results for BDT and BTz based copolymer/PC₆₁BM devices were 0.61 V V_{oc} , 3.1 mA cm⁻² J_{sc} , 37% FF and 0.7% PCE. For **73**/PC₆₁BM devices best results were obtained with a 1 : 3 ratio (V_{oc} : 0.61 V, J_{sc} : 4.4 mA cm⁻², FF: 55%, PCE: 1.5%). When the acceptor unit was replaced by PC₇₁BM the power conversion efficiencies were raised up to 1.4% and 1.7% for **72** and **73**, respectively due to the higher absorption coefficient of PC₇₁BM.¹³⁰ Later the BDT unit in **73** was replaced with alkoxybenzene (**74** (Scheme 9)) and the optical band gap was lowered as well as the HOMO–LUMO energy levels.¹¹¹ It was surprising that although the HOMO level was lowered *ca.* 0.14 eV, V_{oc} for **74**:PC₆₁BM devices decreased to 0.55 V compared to **73** (0.61 V) and could not even be improved with PFN/Al cathode modification bilayer. Maximum 1.39% power conversion efficiencies were reported for **74**:PC₆₁BM devices with 4.5 mA cm⁻² J_{sc} (Table 4).

Table 4 Photovoltaic performances of **56** to **74**

Number	Device architecture	V_{oc} (V)	J_{sc} (mAcm ⁻²)	FF (%)	PCE (%)
56	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 1)/Ca/Al	0.60	1.54	26	0.23
57	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 2)/Al	0.56	1.16	38	0.25
58	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 2)/Al	0.68	2.97	44	0.90
59	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 2)/Al	0.55	1.05	32	0.18
60	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 2)/Al	0.22	1.41	35	0.11
61	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 1)/Ca/Al	0.58	12.5	65.4	4.76
61	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM (1 : 1)/Ca/Al	0.56	15.0	63.3	5.30
62	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 3)/Ca/Al (Annealed)	0.84	6.25	36.9	1.95
63	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 3)/Ca/Al (Annealed)	0.40	5.27	60.6	1.28
64	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 1)/LiF/Al	0.90	2.40	50	1.08
65	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM (1 : 1)/LiF/Al	0.93	2.96	56	1.54
66	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM (1 : 1.2)/Ca/Al	0.56	15.0	63.3	5.60
67	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM (1 : 1.5)/Ca/Al	0.74	14.5	68.9	7.40
68	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM (1 : 1.5)/Ca/Al + 3% DIO	0.76	15.2	66.9	7.73
69	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 2)/LiF/Al + 2% DIO	0.93	6.58	56	3.42
70	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 2)/LiF/Al + 2% DIO	0.91	10.34	51	4.79
71	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM (1 : 2)/LiF/Al	0.85	9.81	66	5.50
71	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 1.5)/Ca/Al + 2% DIO	0.85	11.5	68	6.80
72	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 3)/Ca/Al	0.61	3.10	37	0.70
72	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM (1 : 3)/Ca/Al	0.61	4.80	47	1.40
73	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 3)/Ca/Al	0.61	4.40	55	1.50
73	ITO/PEDOT:PSS/Polymer:PC ₇₁ BM (1 : 4)/Ca/Al	0.61	4.50	62	1.70
74	ITO/PEDOT:PSS/Polymer:PC ₆₁ BM (1 : 2)/PFN/Al	0.55	4.50	56.1	1.39



Fig. 3 (a) Polymer structures of **RF-B**, **RF-G**, and **RF-R** polymers. (b) The energy diagram of ITO, PEDOT:PSS, poly[(9,9-dioctylfluorene)-*co*-(4-butylphenyldiphenylamine)] (**TFB**), Poly(9,9-dioctylfluorene) (**F8**), **RF-B**, **RF-G**, **RF-R**, and Ca. Adapted with permission from ref. 156, Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.

In order to increase the power conversion efficiencies electron donor groups were widely used with BTd, benzoquinoxaline¹⁴⁴ and thieno(3,4-*b*)pyrazine cores.¹⁴⁵ Nevertheless, photovoltaic and photophysical investigations of BTz homopolymers were not carried out yet. Recently, BTz and a 3HT derivative **21** was polymerized by our group using FeCl₃ as the oxidizing agent and characterized in terms of its photovoltaic properties.¹⁴⁶ The polymer was unique since BTz was used as the acceptor moiety in OSCs for the first time. The polymer **21** was fluorescent and both p and n-type dopable. HOMO–LUMO levels and electrochemical band gap values were calculated from the EVS and CV measurements as -5.45 eV and -2.95 eV and 2.55 eV, respectively. Using different PC₆₁BM loadings, several solar cells were produced with **21** and preliminary results showed that 2.35 mA cm⁻² short circuit density and V_{oc} values up to 0.85 V could be achieved. Once it has been realized that BTz incorporated donor–acceptor type polymers can be used for photovoltaic applications, a chemically synthesized BTz derivative homopolymer **19** was also used as the donor material in BHJ solar cells with PC₆₁BM. **19** showed that **19**:PC₆₁BM blends can yield a maximum V_{oc} of 250 mV and J_{sc} of 1.5 mA cm⁻² under AM 1.5 conditions. The low open circuit potential of the blends may be attributed to the high HOMO energy level of **19** compared to other donor materials which lie between -5.2 and -5.8 eV.⁵²



Fig. 4 Operating pixels of the patterned EL device described in a) Adapted with permission from ref. 155, Copyright 2010 American Chemical Society; b) Adapted with permission from ref. 156, Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.

Ultimately, a BTz and Th bearing chemically polymerized homopolymer **20** was also utilized in organic photovoltaics as the donor material with PC₆₁BM. The preliminary results showed that the devices with different feed ratios can have 0.65 V V_{oc} , 4.02 mA cm⁻² J_{sc} and 0.8% PCE using dichlorobenzene.¹⁴⁷ Due to its dual properties, the polymer was also used as an n-type material but no significant results were obtained.

Organic light emitting diodes (OLEDs)

After the breakthrough discovery of electroluminescence (EL) in conjugated polymers reported in 1990,¹⁴⁸ a considerable effort has been devoted to develop conjugated materials as the active layers in OLEDs for use in display fabrication.¹⁴⁹ Polymer LEDs which can be deposited on large areas show high efficiency and fine color variation whereas these are not attainable with inorganic materials.¹⁵⁰ Nevertheless, suitable processing methods can provide a wide range of patterning options for OLEDs.¹⁵¹

The earliest example for BTz containing fluorescent conjugated polymer is **75a** which contains BTz as the electron-accepting pendant group.¹⁵² Its showed orange-red electroluminescence (EL) ($\lambda_{max} = 580$ nm) with an efficiency much higher than that of octyl substituted Ths.¹⁵³ Cl substitution on BTz unit as in **75b** resulted in a lower EL efficiency than that of **42a**.

Although Yamamoto *et al.* reported the synthesis and photoluminescence properties of PFO and BTz copolymers, electroluminescence properties of **75a** and **75b** (Scheme 9) were investigated by Cao *et al.*¹⁵⁴ Three different polymers were prepared with different fractions of BTz units in the polymer backbone by random copolymerization. Increasing BTz content resulted in a slight decrease in the optical band gap and HOMO/LUMO levels of copolymers. It was shown that 1.62% external quantum efficiency and 2.69 of cd A⁻¹ luminance efficiency with high color stability could be obtained when **75b** was used.

Ober *et al.* synthesized PFO and BTz copolymer **76** and its semiperfluoroalkyl substituted derivatives **77** (Scheme 9) and **RF-B** (Fig. 3).^{155,156} These fluorinated polymers in film form remained unaffected when exposed to organic solvents and spin coated from hydrofluoroether solution on to a prepatterned ITO substrate to show polymers are patternable under conventional photolithographic conditions. This patterned device allowed pixel array operation and gave light emission in 100 μm scale. (Fig. 4) After this report, the same group also achieved the photolithographic patterning of multilayer solution processed devices.¹⁵⁶ The authors claimed that using fluorinated alkyl

chains they overcome the organic solvent damage on light emitting polymers which are solution processed and photolithographically patterned.

Outlook

A number of BTz containing CPs are described in the literature and briefly highlighted in this review. Polymers with BTz in main chain are great candidates for use in organic electronic devices. Especially in terms of electrochromic applications, these polymers were proven to have the most important desired properties such as multicolored electrochromism, transmissive state and photoluminescence with a single polymer. However, for the display technology switching times of these polymers should be shortened which might allow fast response of polymers to external stimuli change. For OPVs and OLEDs BTz bearing polymers are still hiding their mystery because of the lack of scientific invention. Device performance is directly affected by the construction conditions, thus optimization studies can provide higher efficiencies in such devices which have not been completely studied yet. A number of different derivatives to vary the electron accepting ability of the BTz unit can be synthesized and their potentials in organic electronics can be investigated due to the promising optoelectronic properties of BTz. From the application point of view, new materials should be designed and tested for these devices in order to connect high efficiency to state of the art devices. Although only optoelectronic properties of BTz bearing CPs are being reported, biochemical applications of these polymers can be a topic of investigation. With all these results and curiosity about BTz bearing polymers, they will attract more attention in the near future.

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