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Structure–optical, thermal properties studies on thiophene containing benzothiazole groups

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Abstract

(2-Benzothiazolidene)-3-thiophene, 3-(2-benzothiazolyl) thiophene and (6-ethoxy-2-benzothiazolidene)-3-thiophene were synthesized. Influences of structure on optical and thermal properties of the above compounds were studied in detail. The experimental studies were supported by predictions based on molecular orbital calculations. The studies reveal that in a single compound, photoluminescence covering the whole visible range can be obtained by suitably substituting thiophene ring with benzothiazolyl group. The intensity of absorption of poly3-benzothiazolyl thiophene (PBTT) is high when compared to other systems and emission is in the blue region.

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Keywords: Conjugated polymer; UV–visible spectroscopy; Band gap; Photoluminescence; Molecular orbital calculations; Thermal stability

1. Introduction

In recent days, molecular electronic materials viz, conductive polymers with novel opto-electronic properties have gained importance in the area of advanced material research [1]. These conjugated polymers are being explored for applications like opto-electronics, polymeric field effect transistors, etc. Polymeric light emitting diodes that can emit light virtually on any part of the visible spectrum and polymeric diode lasers are expected to replace conventional inorganic devices [2,3]. Among the polymers studied as emissive layers, more attention has been given to poly alkyl thiophenes, because of their higher environmental stability, easy processability and solubility in most of the organic solvents upon functionalisation in the 3-position of the thiophene ring [4]. The physical properties and color tuning of emission can be tailored using structural modification to suit the end applications. The formation of supramolecular architectures of polymeric materials can be achieved both by controlling the microstructure of the macromolecules and their 3D packing [5,6]. The steric effect produced by the substituent, influences the structure and properties of the substituted thiophene polymer. Substitution of bulky groups at the 3-position of the thiophene

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ring decreases the overlap between the orbitals of consecutive rings and hence shortens the effective conjugation length.

High efficiencies and reliability are the principal requirements of polymeric light emitting materials for commercial applications [7]. Development of multi layer technology in organic light emitting diodes has been proved to have device efficiency comparable to that of inorganic semiconductors [8]. Functionalisation of electron transporting hole-blocking (ETHB) groups in to 3-position of thiophene ring will be expected to exhibit high device efficiency. Oxadiazoles, phenyl quinoxalines, etc. are proven to be good candidates for ETHB functioning [9].

It is aimed to achieve electro luminescence through the whole visible spectrum with a single compound formed in to single emissive layer with high luminescence efficiency. So et al. [10] demonstrated that some compounds containing the benzoxazole and benzothiazole rings (in the main chain) exhibit interesting photo physical and fluorescent properties. It has also been an interesting strategy to synthesise ETHB incorporated materials because of great possibilities in the variation of direction and magnitude of their mesomorphism and potential electro-optical properties [11].

In the present study, synthesis, photoluminescence and thermal characteristics of 2-benzothiazolidene-3-thiophene (AZBT) (containing the benzothiazolyl group in the side chain) are investigated (Fig. 1). In general the bulky substituent will cause more strain to the backbone and hence blue shifting in optical properties is expected. In order to understand the influence of strain on the optical and thermal properties, thiophene bearing benzothiazole group linked through CH=N linkage was studied and the results were compared with poly thiophene containing benzothiazolyl groups directly attached to the thiophene ring (BTT). In order to understand the influence of substituent on the side chain benzothiazolyl ring, the properties of ethoxy substituted 2-benzothiazolidene-3-thiophene (AZEBT) were compared.

The intrinsic electronic and optical properties of a material are governed by the band gap of conjugated polymers in connection with their chemical structures. In recent days researchers are showing interest on oligomers, which are assumed to allow a more precise structure–activity relationship and also to allow extrapolation of these relationships towards those, expected for polymers [12]. Computing highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energies with different substituents may be helpful in predicting the substituent effect on polymer band gap. Hence the effects of substitution on the optical properties were predicted using molecular orbital calculations in the present investigation.

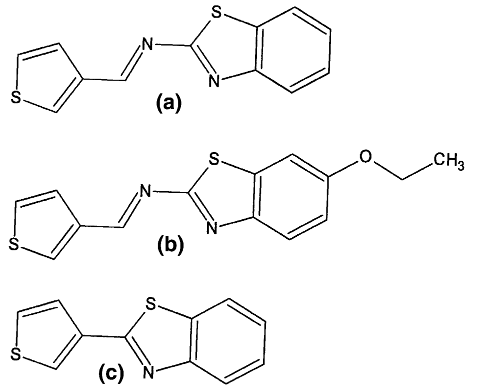

Fig. 1. Chemical structure of different monomers used in this study. (a) AZBT, (b) AZEBT and (c) BTT.

2. Experimental

2.1. (2-Benzothiazolidene)-3-thiophene(AZBT)

1.5 g of 2-amino benzothiazole (0.01 mol) was reacted with 1.12 g of thiophene-3-carboxaldehyde (0.01 mol) in 30 ml of dry ethanol containing catalytic amount of acetic acid in a 250 ml R.B. flask fitted with a condenser. The mixture was refluxed for an hour and the resulting solid obtained on cooling was filtered. The compound was purified by recrystallisation with ethanol.

IR (cm^{-1}): 3096, 3062, 2949, 2847, 1602, 1538, 1446, 1412, 1309, 1261, 1218, 1162, 1101, 1016, 936, 884, 840, 789, 749, 691,623, 577, 473 and 430. ^1H NMR (DMSO, ppm): 9.14 (s, 1H), {[7.84 (d), 7.76 (s), 7.61 (d), 7.39 (m), 7.18 (t)], 7H}.

^{13}C NMR (DMSO, ppm): 164.60, 161.07, 152.11, 141.08, 130.61, 128.48, 126.67, 125.52, 122.87, 121.29, 120.95 and 118.52.

2.2. *(6-Ethoxy-2-benzothiazolidene)-3-thiophene (AZEBT)*

(6-Ethoxy-2-benzothiazolidene)-3-thiophene was synthesized by condensing 1.94 g of 2-amino-6-ethoxy benzothiazole (0.01 mole) with 1.12 g of thiophene-3-carboxaldehyde in ethanolic medium by adopting the similar procedure mentioned earlier. The compound was purified by recrystallisation.

IR (cm^{-1}): 3083, 2973, 2923, 2857, 1604, 1519, 1449, 1390, 1333, 1261, 1221, 1121, 1051, 943, 905, 869, 821, 795, 710, 681, 645, 586 and 526. ^{1}H NMR (CDC1$_3$, ppm): 8.91 (s, 1H), {[7.96 (s), 7.82 (d), 7.72 (d)], 3H}, {[7.36 (t), 7.21 (d), 7.03 (dd)], 3H}, 4.03 (q, 2H), 1.42 (t, 3H). ^{13}C NMR (CDCl$_3$, ppm): 169.14, 158.32, 156.83, 145.80, 139.42, 135.51, 133.77, 126.97, 126.10, 123.45, 115.84, 104.91, 63.89 and 14.65.

2.3. *3-(2-Benzothiazolyl) thiophene (BTT)*

3-Bromo thiophene (0.01 mol) and magnesium turnings (0.01 mol) were introduced together with dry diethyl ether in a three-necked flask fitted with a condenser, a dropping funnel and nitrogen inlet. The entrainer, 1, 2-dibromo ethane (0.01 mol) in anhydrous diethyl ether is then added at ice-cold temperature for a period of 8 h. After the reaction has begun, the solution was brought to ambient temperature. The resulting Grignard compound was transferred to a second dropping funnel fitted to a second three-necked flask containing 2-chloro benzothiazole (0.01 mol) and 1,3-bis (diphenyl phosphino propane) nickel (II) chloride (Nidppp) in anhydrous diethyl ether. After cooling with an ice bath, the Grignard compound was added in drops and the resulting adduct was allowed to warm up to ambient temperature. The contents were stirred for 1 h before being refluxed for 24 h. The mixture obtained was poured onto very dilute aqueous hydrochloric acid. The organic layer was washed with water, dried and concentrated. The crude product was purified on a silica gel column using petroleum ether (boiling range 60–80 °C) as eluent.

IR (cm^{-1}): 3087, 3057, 1588, 1539, 1477, 1432, 1398, 1373, 1312, 1240, 1184, 1123, 1074, 993, 943, 893, 870, 838, 786, 765, 730, 689, 653, 588 and 436. ^{1}H NMR (CDCl$_3$, ppm): 8.02(t,2H), 7.85(d,1H), 7.69(d,1H) and 7.39(m,3H). ^{13}C NMR (CDCl$_3$, ppm): 162.6, 153.8, 135.9, 134.6, 126.8, 126.5, 126.2, 126.0, 125.0, 123.0 and 121.5.

3. Chemical polymerization

Polymers of AZBT, AZEBT and BTT were synthesized by chemical oxidative polymerization using ferric chloride following a procedure similar to that of Sugimoto et al. [13]. In a three-necked flask, 0.012 M ferric chloride was dissolved in chloroform under nitrogen to which a solution of 0.003 M of monomer in chloroform was added in drops. The mixture was stirred for 24 h at room temperature under inert atmosphere and the solution was precipitated using methanol and subsequently washed with methanol and acetone through Soxhlet extractions. The obtained neutral polymer was dried in vacuum at 50 °C.

The NMR spectra of the monomers and polymers were studied in chloroform solution using Bruker 300 spectrometer using TMS standard. The infrared spectra of the compounds were studied using Nicolet Impact 400 FTIR spectrometer using KBr pellet. The absorption spectra of the compounds (chloroform solution) were studied using Shimadtzu-UV-160A, while the emission spectra of the chloroform solution of the monomer and polymers were studied using Hitachi-650-40 spectrofluorimeter. Thermal degradation of the polymers was studied using Seiko SSC 5200 containing TGA module.

4. Theoretical methodology for molecular orbital calculations

DFT (B3LYP/3-21G*), AM1 and ZINDO calculation have been performed using the G 98 w suite of packages [14]. The starting geometries have been generated using model-building tools available in the Cerius^2 package from Molecular Simulation Inc (San Diego, CA). The initial geometries have been optimized using AM1 Hamiltonian. All calculations have been made for AM1 optimized geometries. Excitation energies (HOMO-LUMO gap) calculated using B3LYP/3-21G*, AM1 methods and extrapolated to infinite chain length [15].

5. Results and discussion

Side chains have a profound effect on the properties like optical properties and band gap in polymers. The absorption and emission spectrum of monomer and polymers of AZBT, AZEBT and BTT are presented in Figs. 2–4. All the monomers and polymers are showing characteristic absorptions (Table 1) at 264, 270 and 279 nm, which may be due to the contribution of aromatic π-electrons transitions. Monomer of BTT showing absorption at 300 nm region [that] is red shifted in the case of AZBT and much more red shifted in the case of AZEBT. On comparing the polymers with monomers, similar trend of red shifting from BTT to AZEBT along with the overall red shift of ~20 nm was obtained which can be attributed to the extension of conjugation from the monomer to polymer. The observed red shift in the case of AZEBT compared to that of AZBT could be attributed to the electronic effect of the ethoxy group, which is present in the side chain, viz benzothiazole unit. The hypsochromic shift of the absorption spectrum of BTT compared to that of AZBT suggests that the chromophore may be in a non-planar conformation due to steric hindrance introduced by the substituent benzothiazole unit, which is connected directly to the 3-position of the thiophene ring. The linkage of this five-membered

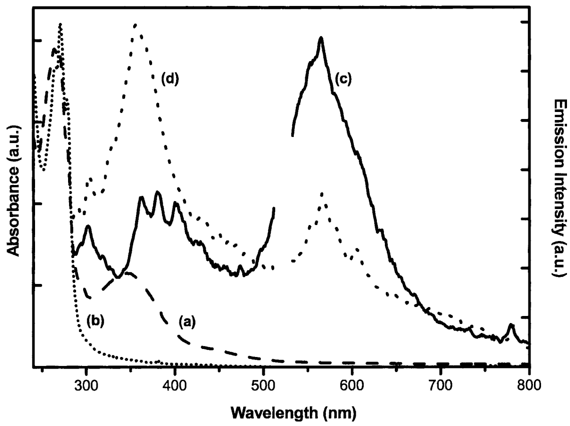

Fig. 2. Absorption and emission spectrum of monomer and polymer of AZBT (a) absorption spectrum of monomer, (b) absorption spectrum of polymer, (c) emission spectrum of monomer and (d) emission spectrum of polymer.

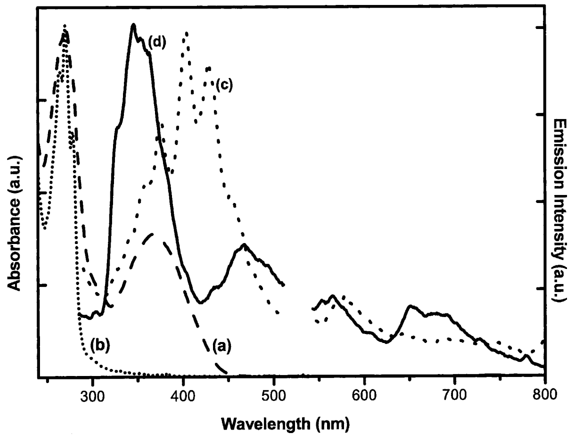

Fig. 3. Absorption and emission spectrum of monomer and polymer of AZEBT (a) absorption spectrum of monomer, (b) absorption spectrum of polymer, (c) emission spectrum of monomer and (d) emission spectrum of polymer.

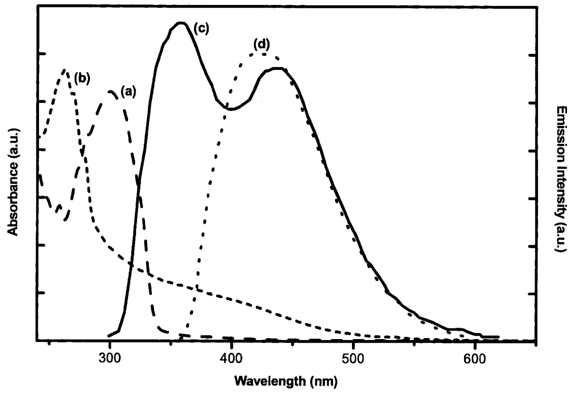

Fig. 4. Absorption and emission spectrum of monomer and polymer of BTT (a) absorption spectrum of monomer, (b) absorption spectrum of polymer, (c) emission spectrum of monomer and (d) emission spectrum of polymer.

Table 1
Absorption values of different monomers and polymers (in chloroform)

Compound	λ absorption (nm)	$E^{a,b}$
AZBT	264	2500
	270	2460
	279	1720
	293	690
	346	740
Poly AZBT	265	175
	270	200
	278	155
	326	7
	380	3
AZEBT	263	1590
	271	1725
	279	1470
	312	400
	369	705
Poly AZEBT	264	135
	270	155
	279	107
	329	3
	382	2
BTT	248	303
	258	287
	272	354
	280	435
	300	528
PBTT	257	213
	263	223
	270	202
	279	152
	320	60

[a] E = absorbance of a 1% solution of the substance in a 1.0 cm cell.

[b] Relationship between E and molar extinction coefficient $10\varepsilon = E \times \text{mol.wt}$ [22].

ring directly connected to the thiophene (BTT) may create more strain, when it is connected through CH=N link (as in AZBT). The theoretically generated oligomer models also support the effect of strain produced by the side chain.

The AM1 optimized geometrical structures of the monomer, dimmer and trimmer of BTT, AZBT and AZEBT were critically analyzed and the obtained geometries of the trimmers are presented in Fig. 5. In the case of monomer of BTT, both the side chain and thiophene main chain rings are lying in the same plane, whereas in the case of trimmer the substituent benzothiazole unit is 56° deviated from the thiophene unit. This suggests that in the case of macromer, the substituent unit will be tilted to reduce the strain which in turn reduce the mean conjugation length and hence the blue shifting. In the case of AZBT and AZEBT, there is a bending observed after the CH=N link. The presence of CH=N link not only reduces the strain and also extends conjugation. Even in the case of monomer, bending is observed and in the trimmer it is observed that all the thiophene units are not much deviated from the plane of the main chain. The reduction in strain maintains the effective conjugation length and over all red shift, compared to that of BTT. Roncali et al. [16] reported that the steric effect of the branched alkyl chain on the polymerization is neutralized when two methylene groups separate the branched chain from the thiophene ring. In our studies, the steric effect is suppressed by the presence of CH=N instead of two methylene groups in the case PAZBT

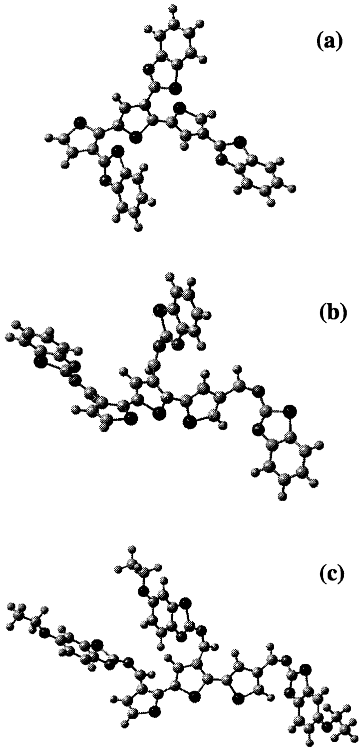

Fig. 5. AM1 optimized geometrical structures of trimers (a) BTT, (b) AZBT and (c) AZEBT.

and PAZEBT in contrast to PBTT. The deviation in values of theoretically obtained excitation energies of the compounds with the values obtained from experiments is due to the fact, that the values obtained from the absorption spectrum was obtained experimentally using chloroform solution of the compounds. While in the case of theoretically obtained results, vacuum conditions were assumed. More over the excitation energy (band gap) values were predicted for ordered HT–HT coupled polymers, while in the experimentally obtained polymers, apart from ordered structures, disordered structures were also obtained due to very high steric hindrance produced by the side chains.

The photoluminescence of these monomers and polymers reveal that these materials may have the ability to emit the light throughout the visible region of electromagnetic spectrum. AZBT monomer is showing bunch of peaks from 337 to 469 nm with the bandwidth of 130 nm, covering blue and ultraviolet regions. An additional cluster of peaks falls in the green and red region with the bandwidth of 245 nm from 478 to 723 nm. In general, the photoemissions of 3-alkyl substituted thiophenes fall in the green region [1]. In the case of AZBT and AZEBT monomers and polymers, the emission peaks obtained around 320 nm can be attributed to the azomethine linkage attached to the thiophene ring. In the case of Poly AZBT an emission centered at 356 nm with the spectral bandwidth of 110 nm. Comparing monomers and polymers, blue shifting of the peaks obtained in the ultra violet region can be explained by the overall strain caused by the bulky benzothiazole substituent. But extension of conjugational effects of side chain through main chain shows its fingerprints in the red region.

Monomer AZEBT exhibits cluster of emissions in ultraviolet and blue regions along with the emission at 580 nm. In the case of polymer the ultraviolet region is shifted more towards lower wavelengths. Additional distinct peaks at 468 and 565 nm also observed with emission in the red region from 624 to 771 nm in this AZEBT polymer. The red region peak can be attributed to the extension conjugation through CH=N link.

The BTT monomer shows emission in the range of 300–575 nm with two maxima at 358 and 437 nm, whereas the polymer shows emission from 350 to 590 nm with maximum at 425 nm. Compared to AZBT, PBTT is showing emission prominently in blue region with wide bandwidth. In the polymer, there is a blue shift observed with respect to monomer, which suggests the overall non-planar effect induced by the bulky substituent benzothiazole.

Over all the photoemission these compounds falls in the broad area of the electromagnetic spectrum. The emission in ultraviolet/blue region attributed sterical contribution of the bulky side chain benzothiazole. The effect of azomethine link that can contribute to the sterical dilution could explain the peaks at red region due to extended conjugation. In contrast Poly AZBT and Poly AZEBT, the absence of red region peaks in PBTT may prove the influence of CH=N link. In the case of ethoxy substituted system an additional peak at 565 nm is also observed which may be explained on the basis of electronic effect.

Our objective is to illustrate the usefulness of quantum-chemical methods in the field of conjugated oligomers and polymers with a focus on optical properties. The major motivation of oligomeric research is to establish relations between chain length and physical properties using molecular orbital calculations. The calculated excitation energies for these oligomers of AZBT, AZEBT and BTT at different levels of theory are plotted against inverse number of monomer units [15] and it is extrapolated to infinite number of units to get the value of the polymer as shown in Fig. 6. The predicted values of monomer using AM1 and DFT (B3LYP/3-21G*) are compared with the absorption edges [17] calculated from UV–visible spectra of corresponding monomers and polymers as shown in Table 2. In the case of monomers, the theoretically predicted excitation energies are nearer to low wavelength absorption edges while in the case of polymers, the predicted values are closer to the high wavelength absorption edges. Even though the predicted values are a little higher than the experimental values, the observed trend follows the experimental trend as explained earlier and supports our discussions on the effect of substitution

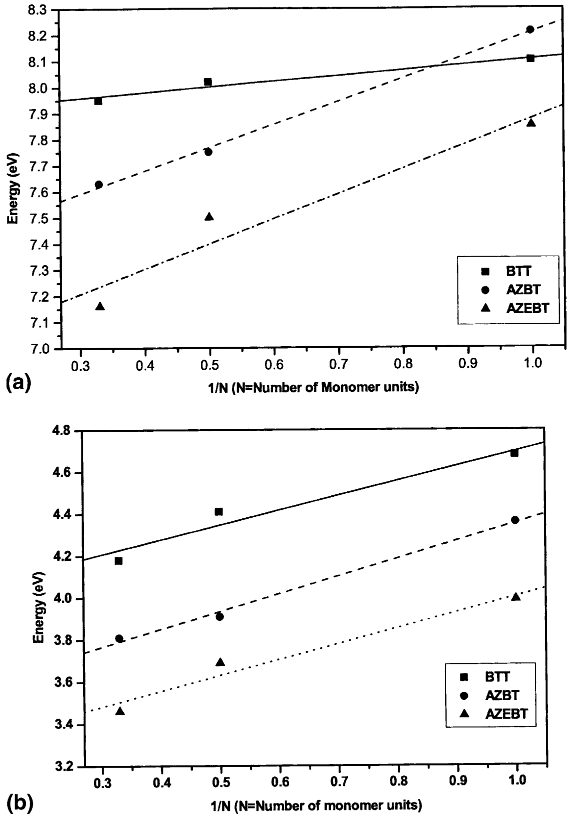

Fig. 6. Band gaps extrapolated from plots of $E_{\rm exc}$ versus the inverse number of monomer units for different thiophenes (a) AM1 and (b) B3LYP/3-21G*.

on the properties. The monomer of BTT exhibits a higher value of band gap than the AZBT and AZEBT, which may be due to the strain influenced by the 5-membered ring of benzothiazole directly attached to the 3-position of the thiophene ring, while in the case of AZBT and AZEBT, the linkage is through azomethine bridge. The values obtained from B3LYP 3-21G* are closer to the experimental value while the AM1 method give overestimated values. In the case of polymer also, the observed trend is same as above. In general the computed values from theoretical methods resemble [to] the gaseous phase while the obtained experimental value is in solution phase, which may add some non-planarity to the system [15]. In addition to environmental effects electron correlation would also influence the excitation energies calculated from molecular orbital calculations.

The calculated values from ZINDO for the AM1 optimized parameters are compared with the peak maximums of the UV–visible absorption spectra. In the case of ZINDO the molecular orbital calculations gave three band gaps, which correspond to different transitions. The values are extrapolated to infinite chain length and compared with experimentally obtained values. Comparison of the extrapolated excitation energies of PBTT to that of PAZBT shows the hypsochromic shift, which is the observed experimental trend as well.

6. Thermal studies

Thermal stability of emissive polymers is important since in organic LEDs, much of energy has been spent in non-radiative process and the heat produced instantaneously raises the temperature [18,19]. The thermal stability of PBTT, PAZEBT and PAEBT were studied using TGA and the obtained thermo grams are presented in Fig. 7. Comparisons of thermograms (Fig. 7) suggest that PBTT shows a major degradation between 623 and 873 K whereas a major loss of 24% is observed in the case of PAZBT between 593 and 773 K. In the case of PAZEBT degradation starts at 473 K with an abrupt loss of 3% up to 493 K and the major loss continues up to 773 K. The percentage degradation obtained from thermo grams of PBTT, PAZBT and PAZEBT are presented in Table 3. The results obtained from thermal degradation shows that at 473 K, 12% was lost in the case PBTT and PAZEBT, while 13% was degraded PAZBT. At 673 K, a similar degradation trend is observed.

The activation energy for different stages of degradation was calculated for the different polymers using the Doyle equation [20]

$$\begin{aligned}&\ln(1-C)\\&\quad=-2.315A/B+0.4567\ (A/B)\ (E/R)\ (1/T)\end{aligned}$$

where C is the concentration of the polymer that remain after degradation at temperature T, R the universal gas constant and A and B are constants. Energy of activation was calculated from the slope obtained from the plot of $\ln(1-C)$ against

Table 2
Calculated excitation energies (eV) of the different thiophene systems at the various computational levels

System		AM1 (eV)	B3LYP/3-21G* (eV)	ZINDO (eV)
BTT	M	8.10	4.68	3.95, 4.27, 4.37
	M(exptl)	4.43, 4.35, 3.69, 3.63, 2.82		5.00, 4.81, 4.56, 4.43, 4.13
	D	8.02	4.41	3.92, 4.00, 4.29
	T	7.95	4.18	3.74, 4.01, 4.02
	P	7.90	4.00	3.71, 3.84, 3.96
	P(expt)	4.33, 4.30, 4.20		4.83, 4.72, 4.59, 4.44, 3.87
AZBT	M	8.21	4.36	3.73, 4.18, 4.31
	M(exptl)	4.30, 4.26, 3.87, 2.97		4.70, 4.59, 4.44, 4.23, 3.58
	D	7.75	3.91	3.43, 3.86, 3.89
	T	7.63	3.81	3.29, 3.75, 3.93
	P	7.33	3.51	3.09, 3.54, 3.66
	P(expt)	4.51, 4.33, 4.30, 3.68, 3.23		4.68, 4.59, 4.46, 3.80, 3.26
AZEBT	M	7.85	3.99	3.62, 4.08, 4.19
	M(exptl)	4.10, 2.81		4.71, 4.58, 4.44, 3.97, 3.36
	D	7.50	3.69	3.36, 3.70, 3.78
	T	7.16	3.46	–
	P	6.92	3.26	–
	P(expt)	4.47, 4.37, 4.33, 3.69, 3.21		4.70, 4.59, 4.44, 3.77, 3.25

M—Monomer, D—Dimer, T—Trimer and P—Polymer.

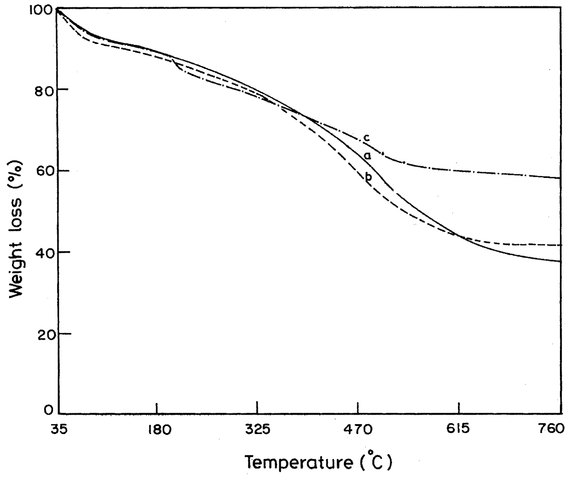

Fig. 7. Thermograms of different poly thiophenes (a) PBTT, (b) PAZBT and (c) PAZEBT.

Table 3
Effect of structure on the level of degradation at different temperatures (%)

Temperature (K)	PBTT	PAZBT	PAZEBT
473	12.45	13.18	12.40
573	18.60	18.60	20.93
673	27.91	30.23	27.91
773	41.86	45.74	35.66

(1000/T). The calculated energy of activation for different degradation stages is presented in Table 4. In the case of PAZEBT, the first stage of degradation requires more energy of activation than PAZBT and PBTT. In the third stage of degradation, the activation energy is almost same for PAZBT and PAZEBT in contrast to PBTT, which requires higher energy.

Table 4
Energy of activation for different thermal degradation ranges (in KJ mol^{-1})

PBTT		PAZBT		PAZEBT	
Temperature (K)	E_a	Temperature (K)	E_a	Temperature (K)	E_a
352–503	12.09	345–440	10.80	466–489	17.10
503–698	16.33	440–634	14.13	489–687	14.94
698–938	26.04	634–903	24.23	687–811	23.79

Thermal studies of the above polymers show that, PAZEBT has better thermal stability than other systems. This may be explained on the basis of bond energy values [21]. Presence of CH=N and C–O bridges in the case of PAZEBT makes it more stable than PBTT since the bond energy values are high for these linkages compared to that of C–S and C–C linkages.

7. Conclusions

The above studies suggest that with a single compound, it is possible to achieve that photoluminescence covering the whole visible range, by suitably substituting thiophene ring with benzothiazolyl group. Emission spectra results obtained for different benzothiazolyl thiophene compounds suggest that due to higher steric hindrance produced by the benzothiazolyl rings, when directly attached to the thiophene ring, the emission was in the blue region. The thermal stability was also influenced by the structure and it is higher in the case of PAZEBT, due to the presence of azomethine linkage and the ethoxy group.

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