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Quantum chemical studies on polythiophenes containing heterocyclic substituents: Effect of structure on the band gap

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Color tuning by the tailoring of substituents at the 3-position of thiophene is very encouraging, and comparative experimental and theoretical studies proved to be powerful in the search for a suitable design for the above. Since the novel polythiophene-based materials substituted with five-membered/six-membered ring containing sulphur and nitrogen at different positions are proven to be potential candidates for electron-transporting hole blocking functions, the structure-property relationship of these systems have been focused in the present study. Molecular-orbital calculations are applied to obtain the optimized geometries and band gaps of the thiophene oligomers. An oligomeric approach has been implemented for calculating the band gaps, and the theoretically obtained band gaps for the different model compounds are compared. Density-functional theory B3LYP/6-31G* predicted band-gap values are compared with the experimental band gaps obtained from optical-absorption edge. The predicted values show little deviations from experimental band gaps, but the trend in band gap is found to be the same in experimental and theoretical results in most of the cases. Hence, this study illustrates the usefulness of quantum-mechanical calculations in understanding the effects of various structural parameters on optical band gap. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2072947]

I. INTRODUCTION

Organic light-emitting diodes (OLED) are emerging as a potential application of organic semiconductors. Two classes of organic materials are used in OLEDs: conjugated polymers such as polyparaphenylenevinylene, polythiophene, etc., and low-molecular-weight molecules.[1,2] Polythiophene has advantages of environmental stability and ease of synthesis. Tailoring of the side chain of polythiophene appeared very encouraging, and comparative experimental and theoretical studies proved to be powerful in the search for suitable compounds.[3,4] One of the major achievements of these studies is the fundamental understanding of the structure-property relationship that might form the basis for the design of novel materials with tailored properties. The band gap of simple conjugated organic polymers can be tuned by modifying the nature of the repeat unit and changing the substituents. The intrinsic band gap of conjugated polymers is generally ascribed to five contributions viz. bond-length alternation, aromaticity, conjugation length, substituents effects, and intermolecular interactions related to the conjugated polymer backbone.[5] As the color of the emitted light depends on the band gap of the π-π^* transition, which is a function of the polymer's structure, modifications of the above will affect the band gap, and consequently, the emitted color and intensity. Understanding the mutual influences of these factors will play a key role in modern molecular engineering. Hence the influence of one or more components that has to be mastered to control the band gap/color of emission and intensity has been taken for study.

A fundamental challenge in organic electronic materials development is the establishment of reliable, instructive, and computationally efficient theoretical methodologies for predicting the optical properties of new substances.[6] The most common approximation for predicting the band gaps of a conjugated polymer relies on extrapolating the band gaps of the full polymer from scaling of the band gaps of a series of oligomeric molecules having increasing lengths. This approximation is particularly accurate, when compared to explicit calculations on the polymer itself, since this applied methodology not only incur small errors overall, but is also well matched to both large and small π-systems.[7] On the other hand, oligomers serve as well-defined molecular species for a reliable correlation of structure and properties.[8] Moreover, many optical and electrical features of conjugated polymers may closely correspond to those of oligomers containing only a few repeat units. When monitoring the physical properties as a function of chain length, extrapolation towards the behavior of a defect-free polymer becomes possible.[9]

Apart from the ease of synthesis, chemically tunable color of emission over the entire visible range, the high emission efficiency is also an important parameter in designing electroluminescent materials. In order to achieve high efficiency, a multilayer technology is being adopted, where materials containing π-electron-deficient heterocyclic moieties have been utilized as electron-transporting hole blocking (ETHB) layer.[10] But these additional layers may

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cause inhomogeneity in the device due to phase separation/crystallization, which in turn will affect the efficiency. This necessitates the designing of ETHB-incorporated single-layer devices. The potential candidates for ETHB function are the nitrogen-oxygen-containing π-electron-deficient heterocyclic moieties such as oxadiazoles, triazoles, triazines, pyridines, pyrimidines, quinolines, quinoxalines, extended benzoderivatives, etc.[11–14]

Hence in the present study structure-property relationship has been focused to explore the novel polythiophene-based materials substituted with five-membered/six-membered ring containing sulphur and nitrogen at different positions. Semiempirical and density-functional molecular-orbital calculations are applied to obtain the optimized geometries and energy band gaps of the thiophene oligomers. The obtained theoretical results are correlated to the experimentally determined band-gap values.

II. THEORETICAL METHODOLOGY

The CERIUS (Ref. 2) package from Accelrys has been used for generating the initial geometries; GAUSSIAN 98 program[15] has been used for semiempirical AM1 and density-functional calculations (B3LYP/6-31G*). The geometries of the oligomers are optimized using semiempirical AM1 Hamiltonian. Then density-functional theory (DFT) (B3LYP/6-31G*) single-point calculations have been made for geometries optimized from AM1 calculation. For comparison, the parent thiophene oligomers (T) have also been optimized.

These molecular-orbital calculations are performed to estimate the band gaps (Eg); it is calculated by taking the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Band gap is extrapolated to infinite chain length by using an oligomeric approach in order to get the polymer value.[8] The geometry characterizations have been extended to measure the torsion angles between adjacent thiophene rings and other substituents in the side chain.

III. RESULTS AND DISCUSSION

Recently, it has been reported that time-dependant density-functional theory gives a satisfactory reproduction of the excitation energies.[16] In addition, the DFT method has successfully been used to study band gaps in conjugated polymers, where the HOMO-LUMO difference provides a good estimate of the excitation energy. Recently Levy and Nagy[17] developed a DFT version of Koopmans' theorem, showing that the energy gap can be estimated from the eigenvalues of Kohn-Sham equations.

Since oligomers may serve as model compounds for the respective polymers, the investigation of well-defined model oligomers has therefore become useful to gain insight in the structural and electronic peculiarities of the corresponding polymers. Hence, in the present study, theoretical calculations on monomer, dimer, trimer, and tetramer were performed, which provide more insights on how the property varies with the increase of chain length. The band gap is now well correlated to the conjugated chain length, and hence, real structure-property relationships become more viable.

In the present study, semiempirical Austin model 1 (AM1) is used for the geometry optimization. Molecular-orbital calculations were performed using density-functional theory with Becke-type three-parameter functional and the 6-31G* basis sets to estimate HOMO, LUMO energies and its derived parameter such as band gap. Since the study involves molecules, consisting of a large number of atoms, the analysis is restricted only to the single-point calculations using the density-functional method. The band gap for the polymer is obtained from oligomer calculations, by plotting the respective results against inverse chain length $(1/N)$, and extrapolated to infinite value. The tailor-made structures of thiophene-based polymers are grouped based on their structural similarity in understanding the effect of structure on band gap. Based on the type of substituents, nature and position of ring, and the level of steric hindrance, the model compounds have been classified into four groups, which are presented in Figs. 1(a)–1(d)

A. Structure-band gap relationships in Group I

Unsubstituted thiophene oligomers are effectively planer and there is no region regularity; therefore any deviation in the structure results in the increase of the band gap. While analyzing the band gap obtained from B3LYP/6-31G* for the monomers of Group I (Table I), monomer 4 shows a high value (4.50 eV) and monomer 8 takes the low values of 3.65 eV. This may be attributed to the high extent of conjugation and lower band-gap value in the case of monomer 8. Compared to the benzothiazole side chain, benzothiadiazole has more number of π-bonds, which leads to the redshift. Adding to the above view, resonance stabilization of the quinonoid structure may also be the contributing factor for the low band-gap value.

It can be found from Fig. 1(a) that compounds 4, 5, 6, and 7 have benzothiazole as side chain and in compounds 5, 6, and 7, the hetero aromatic ring is connected to thiophene through a –CH=N linkage. At the monomer level, an additional π-conjugation may reflect redshift compared to that of compound 4. But the observed redshift in compounds 6 and 7 compared to that of compound 5 is due to the substituent group attached to the benzothiazole group viz. NO_2 in compound 7 and $–OC_2H_5$ in compound 6. In compound 3, the presence of –COOH reduces the band gap compared to compound 2 monomer. Even though both monomers of compounds 4 and 5 have the same benzothiazole unit, in compound 5 it is linked to the thiophene ring through –CH=N linkage. Hence the large band-gap value in compound 4, when compared to compound 5, is due to the presence of the CH=N link.

Even though the monomers of compounds 9 and 8 are basically bearing the thiadiazole group, the extended benzo derivative (compound 8) (benzothiadiazole) is showing redshifting in band gap than compound 9, which is due to the variation in linkage. Both compounds 6 and 7 show redshift,

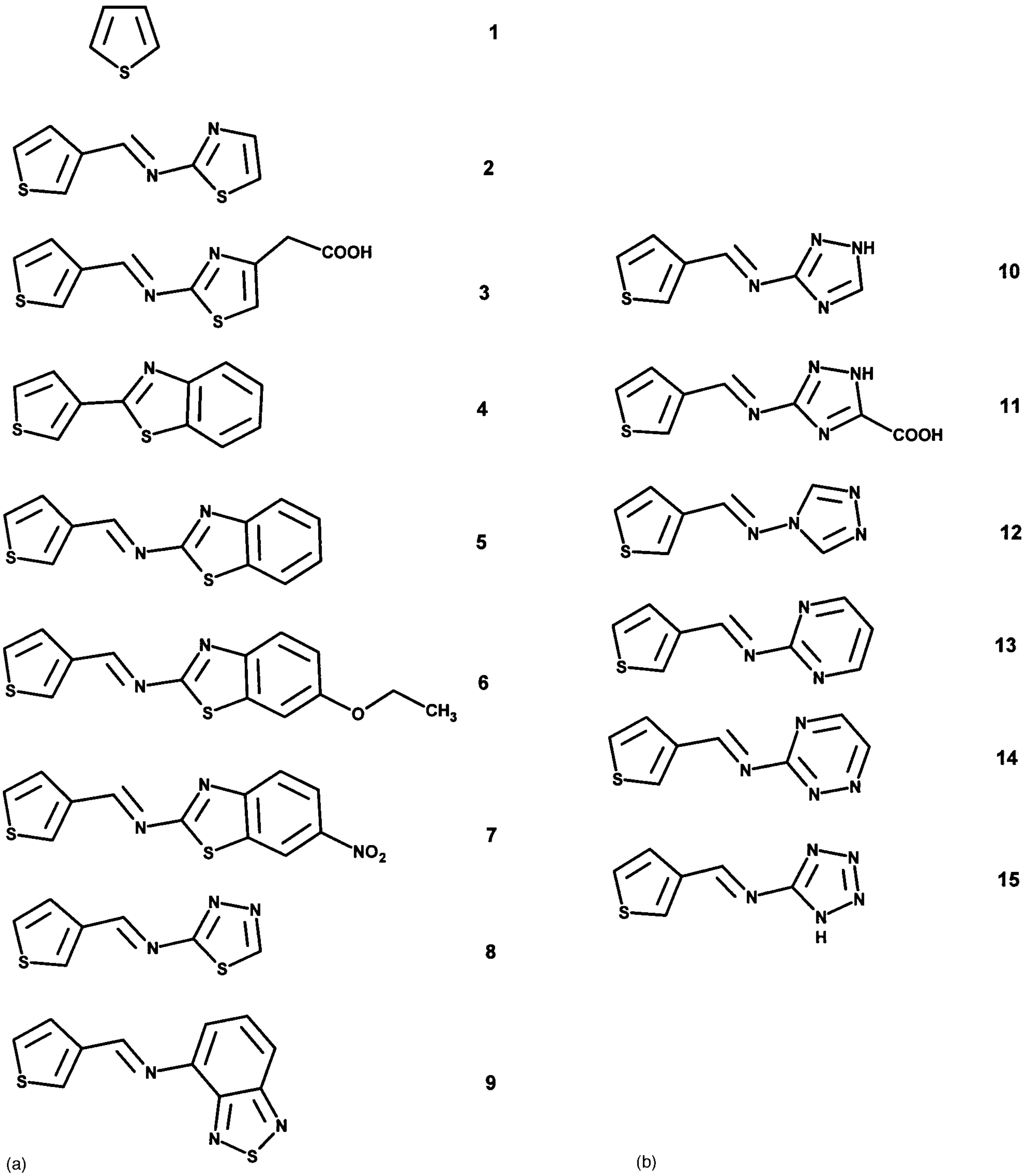

FIG. 1. Different chemical structures of (a) Group I, (b) Group II, (c) Group III, and (d) Group IV.

respectively, from the band gap of monomers 5. This indicates the influence of $-OC_2H_5$ and $-NO_2$ groups on the band gap. Similarly, due to the influence of $-CH_2COOH$ group, the band gap of compound 3 is redshifted when compared to compound 2 monomer.

In absorption spectra, major blueshifts of the absorption peaks occur if large differences in the torsional angle between different rings are induced by the substituents. As long as the coplanarity is not distorted, quite similar absorption spectra are observed when compared to unsubstituted oligothiophenes.[18,19] Alkyl substitution influences the absorption spectra in thin films by their influence on the coplanarity of the molecules. Similarly, directly linked electron-donating or -accepting groups have a much higher influence compared to simple alkyl substituents. The location of the absorption maxima is significantly shifted as well, depending on the hydrocarbon substituents, and ranges from ~420 to 505 nm (yellow to red). These observations mean that the variations in the hydrocarbon side groups significantly influence the electronic structure of the polythiophenes. This can be seen typically in comparison of poly(3-isobutyl thiophene) with poly(3-butyl thiophene). In

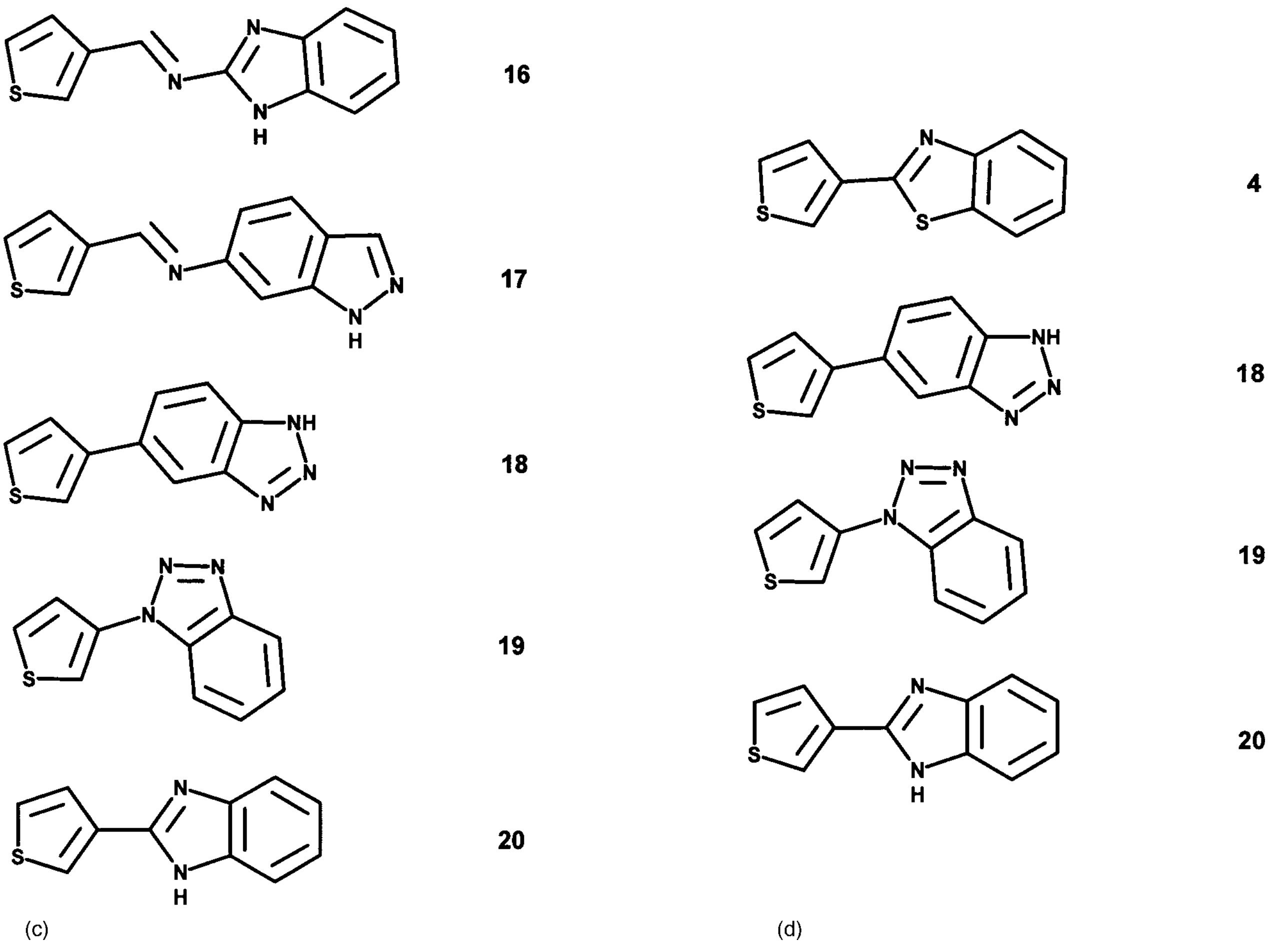

FIG. 1. (*Continued*).

polyconjugated systems, the electro-optical properties of the material, besides the nature of the monomers, are mainly influenced by the kind of packing.

The arrangement of the monomer units in substituted polythiophenes, especially with bulky substituents, can modify their conformational features, which in turn, govern the degree of π-π conjugation between adjacent rings.[20,21] Compounds 4 and 8 dimer structures show the highest and lowest band gap similar to the band gaps of monomer. Since steric interactions play a vital role in dimers, the order is found to be slightly different with other structures, when compared to monomers. Hence it is important to consider the torsion between the thiophene units.

The schematic representation of different torsional angles is presented in Fig. 2. The calculated torsional angle for compounds grouped in category 1 is summarized in Table II. It is evident from the torsion angles (α) that, in the case of the dimer of compound 4, the two-thiophene units are twisted to the extent of 90°. Though the dimer of 8 shows a deviation of 57° (α), there is a twist observed near the –CH=N linkage plane (γ), which may reduce strain in the molecule; moreover, the extent of π-conjugation is high in compound 8. The dimer of compound 9, exhibits a torsional angle of 93° (α) and the side chain is perfectly planar, and hence, the effective conjugation length increases in each unit, which may be responsible for the redshift. In dimers of compounds 5, 6, and 7, bending is observed in the vicinity of the –CH=N link (γ– 150° away from –CH=N linkage plane), which makes the reduction in conjugation length. The redshift of compounds 6 and 7 compared to that of 5 may be attributed to the effect of the side chain of substituents (viz. –OC_2H_5 and –NO_2 in compounds 6 and 7, respectively). In comparing the band gap in the dimers of compounds 4 and 5, compounds 5 shows a lower value of the band gap. This higher magnitude in compound 4 may be attributed to the direct linkage of benzothiazole groups, which forces the thiophene rings to keep a distance. The presence of benzothiadiazole group in compound 8 reduces the band gap when compared to thiadiazole in compound 9. The band gap of the molecular structures of Group I shows the minor contributions of ethoxy or nitro group to the dimers of compounds 6 and 7 compared to that of compound 5. The presence of –CH_2COOH does not significantly influence the properties of the thiazole group of dimer 3.

In trimers of Group I, the trend is found to be similar to dimers except in 9. The observed deviations can be understood with the help of torsional angle values. In the dimer, the interring torsional angle between the first and second thiophene ring and the second and third thiophene ring is calculated to be a maximum of ~90° (α), which disturbs the effective conjugation length, and hence, the observed blueshift in the calculated values.

In the case of tetramers, compound 6 is shown to have the lowest band gap of about 3.07 eV unlike in the earlier

TABLE I. Calculated B3LYP/6-31G* band gap of various structures.

	Group I	Eg (eV)		Group II	Eg (eV)		Group III	Eg (eV)		Group IV	Eg (eV)
1	M	6.391	10	M	4.377	20	M	4.473	4	M	4.498
				M (expt.)	4.42						
	D	4.399		D	3.983		D	4.142		D	4.337
	T	3.617		T	3.780		T	3.985		T	4.20
	TT	3.214		TT	3.680		TT	3.871		TT	4.133
	P	2.225		P	3.48		P	3.717		P	4.055
				P (expt.)	3.63						
2	M	3.919	11	M	4.316	16	M	3.649	20	M	4.473
	M (expt.)	4.02		M (expt.)	4.19		M (expt.)	3.08			
	D	3.679		D	3.996		D	3.491		D	4.142
	T	3.561		T	3.776		T	3.385		T	3.985
	TT	3.408		TT	3.508		TT	3.335		TT	3.871
	P	3.319		P	3.398		P	3.253		P	3.717
	P (expt.)	4.06		P (expt.)	4.22		P (expt.)	3.51			
3	M	3.856	12	M	4.394	17	M	4.040	18	M	4.769
	M (expt.)	4.02					M (expt.)	3.61		M (expt.)	4.60
	D	3.620		D	4.108		D	3.825		D	4.731
	T	3.545		T	3.991		T	3.566		T	4.660
	TT	3.230		TT	3.879		TT	3.555		TT	4.665
	P	3.206		P	3.754		P	3.401		P	4.630
	P (expt.)	3.98					P (expt.)	3.72		P (expt.)	4.29
4	M	4.498	15	M	4.703	18	M	4.769	19	M	4.814
	M (expt.)	4.35		M (expt.)	4.06		M (expt.)	4.60		M (expt.)	4.30
	D	4.337		D	3.935		D	4.731		D	4.758
	T	4.210		T	3.306		T	4.660		T	4.684
	TT	4.133		TT	3.645		TT	4.665		TT	4.579
	P	4.055		P	3.031		P	4.630		P	4.572
	P (expt.)	4.20		P (expt.)	3.75		P (expt.)	4.29		P (expt.)	4.15
5	M	4.251	13	M	5.363	19	M	4.814			
	M (expt.)	4.26					M (expt.)	4.30			
	D	3.814		D	5.024		D	4.758			
	T	3.711		T	4.856		T	4.684			
	TT	3.438		TT	4.543		TT	4.579			
	P	3.297		P	4.45		P	4.572			
	P (expt.)	3.23					P (expt.)	4.15			
6	M	3.885	14	M	4.234						
	M (expt.)	4.10		M (expt.)	3.43						
	D	3.588		D	4.070						
	T	3.353		T	3.604						
	TT	3.068		TT	3.595						
	P	2.972		P	3.424						
	P (expt.)	3.21		P (expt.)	3.38						
7	M	4.133									
	D	3.612									
	T	3.438									
	TT	3.137									
	P	2.950									
8	M	3.647									
	M (expt.)	3.80									
	D	3.282									
	T	3.248									
	TT	3.082									
	P	2.955									
	P (expt.)	3.11									
9	M	3.982									
	M (expt.)	4.25									
	D	3.567									
	T	3.667									
	TT	3.608									
	P	3.447									
	P (expt.)	3.21									

cases where compound 8 is found to have the lowest band gap in the monomer, dimer, and trimer forms. The analysis of optimized geometry may often support the lowest value of compound 6. In contrast to the monomer, dimer, and trimer, the tetramer of compound 6 does not have twisting in the vicinity of the CH=N linkage (γ) (Fig. 3). Since the side chain shows greater planarity, the effective conjugation length increases. However, other tetramers of Group I are found to follow the same trend as observed in dimers and trimers.

The calculated band gap for the polymer of compound 4 has a high value of 4.06 eV, whereas both compounds 7 and

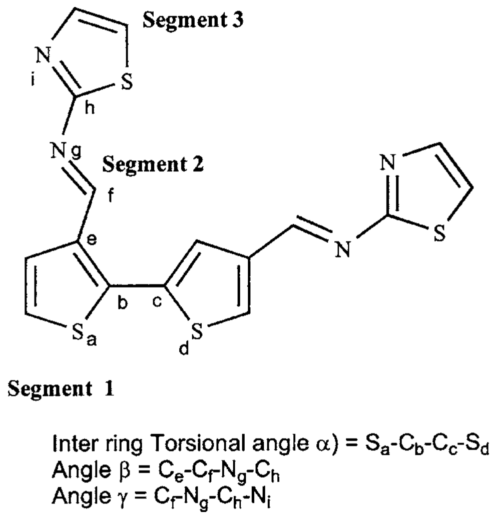

FIG. 2. Representative figure showing different segments and angles used in this study.

8 polymers are found to have the lowest value of 2.95 eV. Polymers of Group I follow different trends in band-gap values as shown in Table I. The magnitude of the band gap increases from monomer to polymer when the chain length increases. Compared to other structures of Group I, the polymer of compound 4 continued to show a high band gap. It has been reported that the dihedral angle and thus the π-orbital overlap between adjacent thiophene rings along the polymer backbone determine the effective conjugation length along the polymer chain. In the polymer of compound 4, the substituent benzothiazole may impose a more steric hindrance to the main chain and lead to the large dihedral angle between the rings and short conjugation along the polymer backbone, which resulted in a higher blueshifted band gap. Roncali *et al.*[22] have reported that the steric effect of the branched alkyl chain on the polymerization behavior is reduced when the thiophene ring is separated from the branched side chain with more than two carbon atoms. Even though both have benzothiazole side chains, the presence of the –CH═N link may decrease the strain in compound 5 polymer, and hence, lower the band gap for both.

B. Structure-band gap relationships in Group II

Nitrogen-based heterocycles are proven to be promising candidates for the charge-transporting layer in OLEDs. In Group II, nitrogen-rich heterocyclic systems are chosen as side chains and the influence of their structure on the band gap and the calculated properties of the compounds are presented in Table I. Monomer 13 shows the maximum band gap of 5.36 eV and monomer 14 exhibits the lowest band gap of about 4.23 eV. In order to understand further, the torsion angles of different segments of the compounds are presented in Table III. The optimized geometry of monomer 13 shows a torsion of about 53° (β) between segments 1 and 2 and about 94° (γ) is observed between segments 2 and 3. This may reduce the π-conjugation, resulting in high band gap for the respective cases. The extent of torsion, β and γ, is low when compared to monomers 13 and 15. The comparison of monomers 10 and 11 show that segment 3 of monomer 10 is twisted due to the presence of the COOH group, unlike in monomer 11, which has more planarity. Overall results show that monomer 14 has the lowest band gap.

TABLE II. Calculated interthiophene ring torsional angles for the AM1 optimized geometry (Group I).

		Interring torsional angles		
Compound		Thiophene ring 1 & 2	Thiophene ring 2 & 3	Thiophene ring 3 & 4
1	D	179.98		
	T	180	−179.98	
	TT	−180	180	−180
2	D	60.26		
	T	61.16	60.58	
	TT	−49.03	−45.19	91.83
3	D	61.55		
	T	95.92	46.48	
	TT	49.18	−137.08	136.50
4	D	−90.36		
	T	−84.61	−91.70	
	TT	−86.93	63.57	63.60
5	D	31.11		
	T	32.36	64.80	
	TT	−98.76	49.97	−93.37
6	D	31.69		
	T	30.67	30.08	
	TT	45.99	−60.79	−95.06
7	D	26.51		
	T	−60.17	27.74	
	TT	33.63	31.11	27.95
8	D	57.24		
	T	44.12	57.86	
	TT	50.11	−42.35	57.00
9	D	−93.20		
	T	−90.73	−93.61	
	TT	−92.36	92.90	−94.94

The influence of the position of linkage can be better understood by comparing the band gap in compounds 10 and 12. The value of compound 12 is slightly on the higher side than compound 10 due to the influence of the attachment of ring nitrogen to the azomethine nitrogen. Although compounds 13 and 14 contain six-membered rings (segment 3), the increase in the number of nitrogen atoms and its position in the ring decrease the magnitude of the band gap. The results (Table I) reveal that due to ring size, the band gap decreases. Compound 10 contains five-membered rings, while compound 14 has six-membered rings, but contain the same number of nitrogen. The variation in properties in these compounds can be attributed to the ring size.

The dimers of Group II, compounds 13 and 15, respectively, show the highest and lowest band-gap values. The high deviation in band gap from thiophene in the case of compound 13 may be due to the torsional angle variation

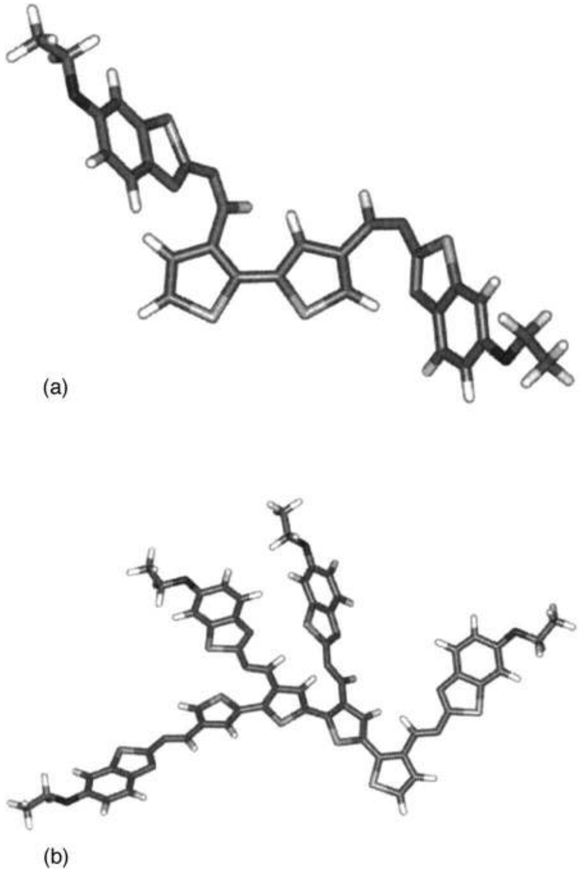

FIG. 3. Optimized geometries of compound 6 (a) dimer and (b) tetrameter.

TABLE III. Calculated interring torsional angles for the AM1 optimized geometry (Group II).

Compound		Interring torsional angles		
		Thiophene ring 1 & 2	Thiophene ring 2 & 3	Thiophene ring 3 & 4
10	D	−99.85		
	T	−97.11	−103.03	
	TT	−58.31	−103.57	103.35
11	D	−57.48		
	T	−57.86	−57.29	
	TT	49.31	−106.46	102.76
12	D	89.12		
	T	89.34	89.11	
	TT	89.72	90.10	89.07
15	D	−34.40		
	T	32.76	−30.77	
	TT	71.15	35.67	93.72
13	D	−105.07		
	T	−104.34	−106.76	
	TT	−112.23	−113.76	−116.44
14	D	−111.88		
	T	−130.86	−133.25	
	TT	−119.98	132.48	−119.88

(Table III). The interring torsion angle α is found to be about 105° for compound 13. In addition, the angle between segments 1 and 2 (β) and segments 2 and 3 (γ) is also found to be 55° and 91°, respectively, for compound 13. This resulted in the reduction of conjugation length; hence these are highly blueshifted. The interring torsion angle (α) of compound 15 is found to be quite low (34°), which makes the dimer of compound 15 to exhibit the lowest band gap.

Analysis of the results obtained for Group II trimer shows that compounds 13 and 15 exhibit high and low values like in dimers. The interring torsion angle (α) of compound 14 is calculated to be higher than that of compound 15. Hence blueshift is observed in compound 13 compared to that of compound 15. Comparison of the band gap in compounds 10 and 12 shows that the latter has a higher deviation value than the former. This may be attributed to the attachment of segment 2 to segment 3 through nitrogen. Compound 15 shows a lower value compared to that of compound 10, which may be due to the number of nitrogen atoms present in segment 3 (compound 15).

The calculated band gap of compound 13 tetramer from unsubstituted thiophene tetramer shows the highest value, which can be understood from optimized geometry visualization of compound 13 tetramer (Fig. 4). The observed bending ($\gamma=95°$) between segments 2 and 3 can be the reason for the blueshift. The side chains are planar (segments 2 and 3) in compound 12, but the interring torsion angle (α) is found to be maximum, which contributes for higher blueshift. The high values of band gap in compound 15 tetramer in contrast to its trimer can be due to the increased interring torsion angles. Increase in planarity and reduced interring torsion angle may be the reason for the lowest value in compound 11. Comparison of the band gap in the tetramers of compounds 10 and 12 shows the effect of the position of linkage viz. linkage through nitrogen, exhibiting higher deviation in compound 12 than compound 10. The decrease in band gap in compound 15 compared to compound 10 may be due to the presence of tetrazole ring (in compound 15) in contrast to triazole in compound 10.

In the case of polymers, the extrapolated band-gap results show that compounds 12 and 15 have the highest and lowest band gaps. The trend of band gap is almost similar to the trend in dimer and trimer. Comparison of the band gap in polymers of Group II shows that, as in earlier cases, the position of linkage may vary the band gap. An increase in the number of nitrogen atoms reduces the band gap, which can be understood by comparing the band gap of compounds 13 and 14, and 10 and 15. The ring size as well as the terminal substituent may also have little influence on the band gap. Analysis of the band gap shows that the band-gap deviation (from unsubstituted thiophene) increases with an increase in chain length.

C. Structure-band gap relationships in Group III

Substituted polythiophenes containing an electron-transporting group such as benzotriazole and chlorobenzotriazole have been studied by Ahn *et al.*[11] In these studies benzotriazole was attached to the thiophene through ethyl groups, which may reduce the strain of the molecule. Group

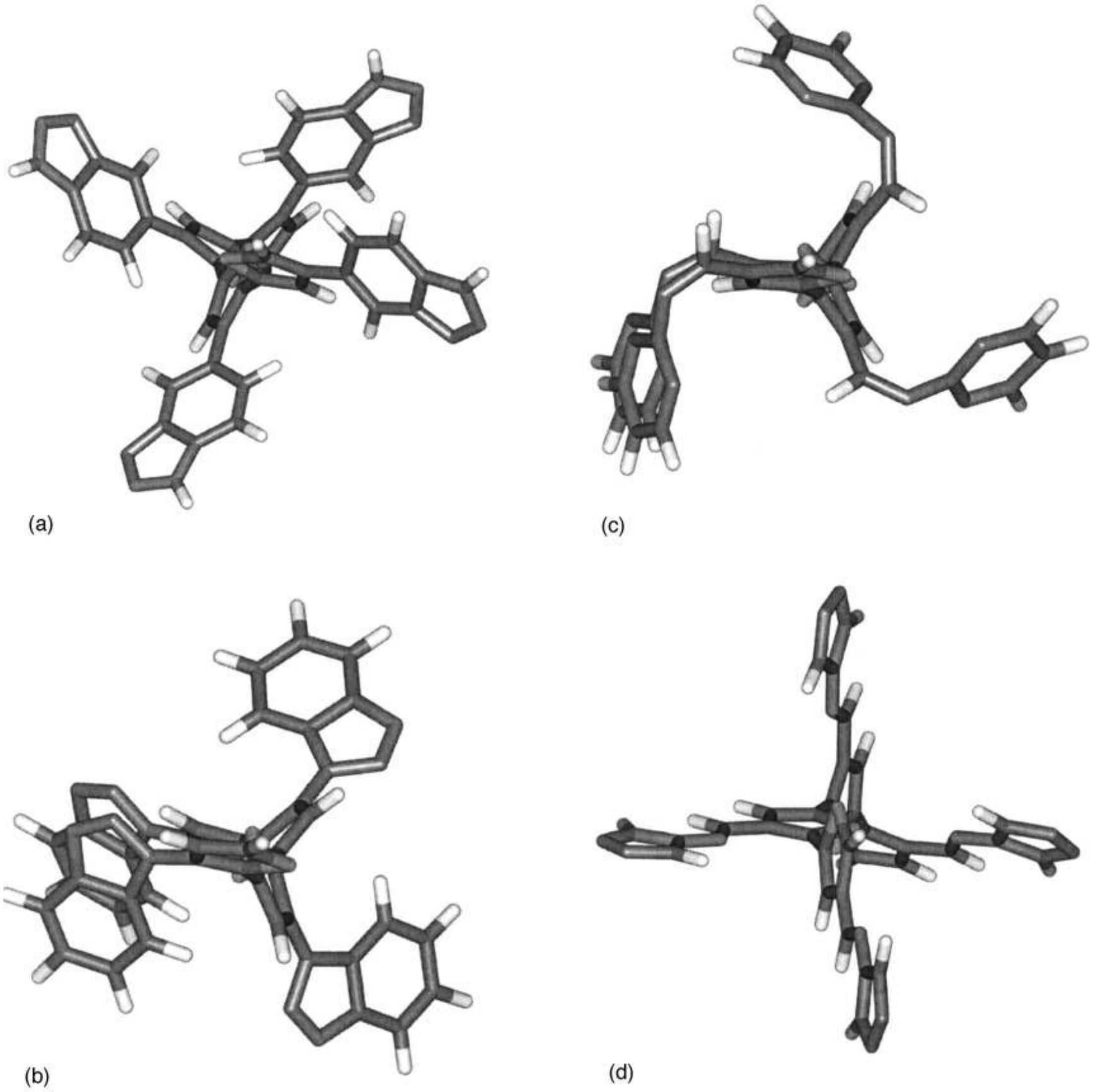

FIG. 4. Optimized geometries of tetramers of compounds (a) 18, (b) 19, (c) 13, and (d) 12 (side view).

III mainly considers the benzo derivatives (fused rings) of nitrogen-based hetereocycle substituted thiophenes to systematically understand the influence of steric and other effects of the structures on optical properties. The theoretically obtained results for Group III compounds are presented in Table I. In Group III monomers, compound 19 shows a high band gap of 4.93 eV, while compound 16 takes the lowest value of 3.86 eV. The observed higher values of band gap in compounds 19 and 18 can be due to the direct linkage of benzotriazole group to thiophene ring. Compound 20 has the thiophene structure containing a benzimidazole group directly attached to the ring. Compounds 16 and 17 have a azomethine linkage, which can additionally contribute to the extension of conjugation in the molecule leading to redshift. There is a deviation of about 38° in segment 3 (γ) of compound 17 unlike in compound 16 (Fig. 5), which has a planar structure. The order of band gap of Group IV structures is also supported by the interring torsional angles between the rings as is shown in Table IV.

In the case of tetramers, compound 18 shows a higher band gap than compound 19 due to the interring torsion (α $-94°$) in compound 18, which is higher than that of compound 19 accounting for more blueshift in compound 18 than in compound 19. The polymer of Group IV structures follows the trend of tetramer structures. The magnitude of deviation increases from monomer to polymer, which is similar to the observations made in other group structures.

D. Structure-band gap relationship in Group IV

In order to understand the steric influence on properties such as band gap and other properties, thiophene-containing bulky heterocyclic rings have been studied using molecular-orbital calculations. These are expected to create molecular overcrowding and their calculated band-gap values are presented in Table I. In monomers, compound 19 shows a high band gap of 4.81 eV and compound 20 shows a lower value of 4.47 eV. Compound 18 shows a redshifted value than compound 19 due to the position of linkage. The effective conjugation length may be increased in the case of compound 19, where the thiophene unit is directly attached to a highly conjugated phenyl ring. The attachment through a

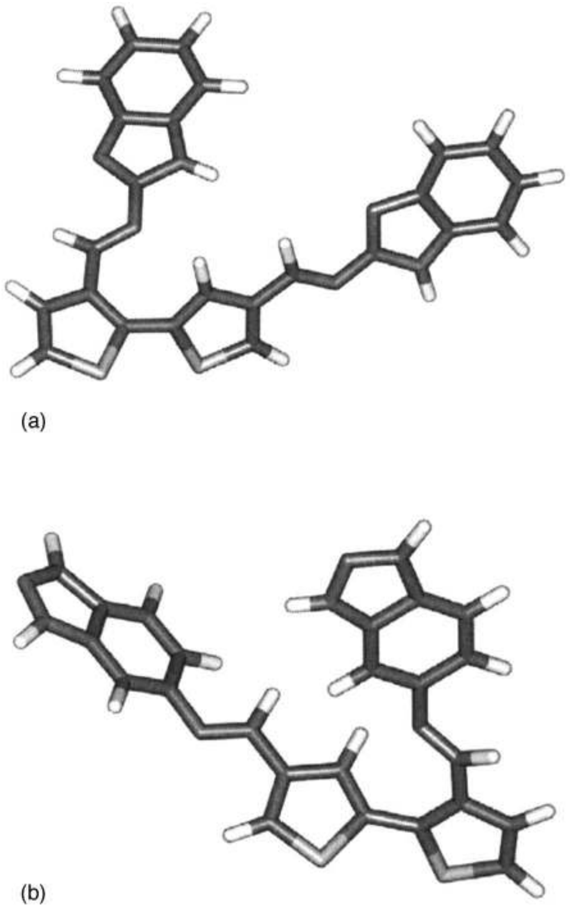

FIG. 5. Optimized geometries of dimers of compounds (a) 16 and (b) 17.

benzothiazole or benzimidazole ring, compounds 4 and 20 realizes less strain than compounds 18 and 19. This may be supported with torsional angle (β) (Table V) between thiophene (segment 1) and the side chain (segment 2). β is found to be 0° in the case of compounds 4 and 19, i.e., molecule is planar, which led to the increase of conjugation and hence redshift.

In dimers, even though α values of compounds 18 and 19 are comparable, β values are found to be high in compound 18 (β and β' values of compound 18 are 41° and 31° and for compound 4 are 6° and 28°). Overall, the torsion angle β is observed to follow the order of deviation in band gap. The trend is found to be the same in the case of trimer, which may also be supported with torsional angle values.

In the case of tetramers, compound 18 shows a higher value than compound 19. The interring torsion angle (α) (Table V) shows that compound 18 has a higher value of torsion compared to others in the group. The order of torsion (α) is observed to follow the order of band gap. It shows the dependence of steric influence on band gap. The extrapolated band gap of Group IV polymers reflects the same trend for tetramers.

E. Comparison of band gap and effect of structure

TABLE IV. Calculated interring torsional angles for the AM1 optimized geometry (Group III).

Compound		Interring torsional angles Thiophene ring 1 & 2	Thiophene ring 2 & 3	Thiophene ring 3 & 4
20	D	−78.90		
	T	78.60	78.25	
	TT	78.28	77.60	77.68
16	D	61.19		
	T	61.70	60.98	
	TT	61.78	61.50	60.77
17	D	58.83		
	T	−50.25	59.15	
	TT	96.82	−53.65	59.13
18	D	93.49		
	T	−96.07	95.26	
	TT	94.22	93.88	93.82
19	D	110.81		
	T	111.11	109.69	
	TT	−111.74	−110.68	−109.79

The band gap predicted from B3LYP/6-31G* calculations of all polymers belonging to Groups I–IV are compared. The compounds in order of decreasing band-gap values are presented below:

18,19,13,4,12,20	10,9,14,17,11,2,5	16,3,15,6,8,7
4.63−3.72 eV	3.48−3.30 eV	3.25−2.95 eV

Thiophene containing directly linked benzotriazole substituent (compounds 18 and 19) show extremely high band gap. Further, compound 4 (which is also has a direct linkage between thiophene and benzothiazole) is also showing high band gap, but relatively lower than that of compound 19. The above results clearly indicate that the direct linkage produces high strain to the molecule, which is reflected in the blueshift

TABLE V. Calculated interring torsional angles for the AM1 optimized geometry (Group IV).

Compound		Interring torsional angles Thiophene ring 1 & 2	Thiophene ring 2 & 3	Thiophene ring 3 & 4
4	D	−90.36		
	T	−84.61	−91.70	
	TT	−86.93	63.57	63.60
20	D	−78.90		
	T	78.60	78.25	
	TT	78.28	77.60	77.68
18	D	93.49		
	T	−96.07	95.26	
	TT	94.22	93.88	93.82
19	D	110.81		
	T	111.11	109.69	
	TT	−111.74	−110.68	−109.79

of band-gap values. The other systems such as compounds 13, 12, and 20 also are considered in the category of high band-gap materials. In general, the steric influence profoundly dominates in deciding the band gap of these molecules rather than electronic effects.

On the other hand, compound 7 shows the lowest band gap within the compounds taken for study. The polymers such as in compounds 8, 6, 15, 3, and 16 all fall in this lower-band-gap category. Electronic effect dominates in all these cases. The compounds bearing terminal electron-withdrawing/releasing substituents in side chain fall in this region. Hence, it is observed to be the electronic effect which is pronounced.

Compounds 11, 2, 5, and 16 all fall in the middle region. Here the observed band gap is considered to be due to the compromised effect of both electronic and steric contributions. In the case of compound 11, even though it has a similar structure to compound 10 (which falls in the high-band-gap region), the presence of COOH groups keeps it in the middle region.

Overall, the high-band-gap materials all have a high torsion angle and their spatial distribution observed from its optimized geometry are also different from the geometries of the medium- and low-band-gap materials. The optimized geometries of these strained molecules are found to be distributed uniformly in space. The representative geometry of this kind is shown in Fig. 4, which is obtained for the tetramers of various structures. The side view of the geometrical structures shows that all thiophene units of tetramers fall in an axis and the side chains are evenly placed in an organized manner. This kind of three-dimensional (3D) packing may affect the formation of supramolecular architectures, which in turn modify the band gap. In the case of tetramers of low- and mid-band-gap materials, such a kind of organized geometry is not observed.

F. Comparison of experimental and theoretical band gaps

The band gap of the molecules are generally determined from the optical absorption threshold.[23] The comparable absorption edge determined from UV-visible spectra in methanol solution is correlated with theoretically obtained band gap (B3LYP/6-31G*). The overlapping absorption edge value is taken for comparison (Table I). In Group I, monomers 4 and 8 show high and low band gaps both in solution and in thin film. In general, the decreasing order of band gap obtained from experimental data follows the same trend of B3LYP/6-31G* calculated values. The monomer of compound 9 has good overlap of band gap with theory, while polymer 9 shows more deviation from the experimentally determined value in solution. Unlike other compounds of Group I, the dihedral angles for this compound (9) do not show characteristic change. Experimental band-gap data of monomers of Group I show more overlap with its corresponding theoretical value than their corresponding polymers. The absorption edge is also determined for thin films (prepared from $CHCl_3$ solution) and compared with theoretically obtained band gap (B3LYP/6-31G*). The variation between the band gap calculated from solution and thin film data also match well, unlike their corresponding polymers.

The polymers of compounds containing thiazole (2) and thiadiazole (9) at the terminal point of the side chain show more deviation from experiment. The deviation between the experimental and calculated band-gap values is observed to be high in the case of compounds, which has terminal functional groups in the side chain (which again influences the solvato chromism/aggregate formation) as in the case of compounds 3 and 6. This is much pronounced in compound 3, where the presence of terminal carboxylic acid may play a role in the deviation. On the other hand, polymers containing fused phenyl rings in the side chain such as compounds 4 and 5 show very high overlap in values of theory and experiment.

In Group II, the monomer of compound 15 shows deviation from the theoretical order in both solution and thin film similar to compound 9. Of all the compounds in Group II, compound 14 shows a good overlap of experimental data with theory. It is interesting to note that except in compound 14, other experimentally synthesized compounds, a proton in the terminal heteroaromatic ring of the side chain is present, and it is basic. This proton may route for aggregation and polarity enhancement. It may also influence solvato chromism, which ultimately aids for deviation from theory. This view is again supported on the basis of deviations seen in polymers of compound 11 too, which contain a polar carboxylic acid group.

The experimental trend determined from the solution absorption edge of experimentally synthesized Group III compounds follows the theoretical trend except the change in the position of compounds 18 and 19 and only a marginal change is observed in theoretical data. Compound 16 shows the lowest band gap as predicted by theoretical calculations. A deviation in the trend is observed in thin-film data. It is observed that in monomers, the obtained band gaps from solution data are always lower than that of the theoretical data. Similar to Group II compounds, Group III compounds also have a labile basic proton, which may be the reason for deviation.

The experimental band gap obtained for the synthesized compounds of Group IV are compared and their overlap with the theoretical data is presented in Table I. The data obtained for monomer and polymer of compound 18 show more band gaps than others. The experimental and theoretical trends do not match well in Group IV. This may be due to molecular overcrowding, which may change the packing pattern. The variation in three-dimensional packing will change the band-gap values, while theory does not take these factors for band-gap calculations.

Although the band gaps show little deviation from the experimental band gaps, the trend in band gap is found to be the same in experimental and theoretical results in most of the cases. The possible reasons for the deviation in results may be that (i) the gas phase is considered in the theoretical calculation and (ii) only HT-HT coupling is considered in the theoretical calculations.[24] But in real case, the polymer may have regio-random configurations. (iii) Intermolecular interactions are not considered in the calculations.

IV. CONCLUSIONS

Molecular-orbital calculations prove to be extremely useful when dealing with π-conjugated oligomers and polymers. In the present study semiempirical and density-functional molecular-orbital calculations are performed on polythiophene containing five-membered/six-membered ring bearing sulphur and nitrogen at different positions. The optimized geometries are obtained using AM1 calculations and single-point calculations are performed at the DFT B3LYP/6-31G* level to predict the band gap. The results reveal that thiophene containing directly linked benzotriazole substituent shows extremely high band gap. Direct linkage produce high strain to the molecule, which is reflected in the blueshift of band-gap values. The compounds bearing terminal electron-withdrawing/releasing substituents in side chain fall in the low-band-gap region. Overall, the high-band-gap materials all have high torsion angle and their spatial distribution observed from its optimized geometry are also different from the geometries of the medium- and low-band-gap materials. Comparison of predicted band gaps with experimentally observed data shows that although the predicted values have little deviations from experimental band gaps, the trend in band gap is found to be the same in experimental and theoretical results in most of the cases. Hence the results from the study clearly reveal that the theoretical study provided simple trends for the connection between the band gap and the amplitude of torsion angles/the substitution patterns, which will be really useful in designing novel structures for optoelectronics.

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