

Unraveling the Role of π - Conjugation in Thiophene Oligomers for Optoelectronic Properties by DFT/TDDFT Approach

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ABSTRACT

Thiophene oligomer has been investigated using DFT/TDDFT calculations with an aim to check its suitability for optoelectronic applications and also to analyse the influence of π -bridge. Our results revealed that thiophene oligomers have excellent π -conjugation throughout. FMO analysis give an estimate of band gap of thiophene oligomer and further revealed HOMO are localized on π - bridge, donor group and LUMO are localized on π - bridge and acceptor group. A TDDFT calculation has been performed to understand the absorption properties of them in gas phase and solvent phase. PCM calculations convey that absorption maxima show positive solvatochromism. Among the designed candidates, the one with more π - bridge show higher wavelength of absorption maxima and would be a choice for better optoelectronic materials. NBO analysis provides support for complete delocalization in these systems. It is interesting to note that oligomer with more π -bridge display an enhanced optoelectronic properties than with less π - bridge.

Key words: Thiophene oligomer, π - bridge, TDDFT, PCM, NBO.

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INTRODUCTION

The last few decades has been endorsed by growing importance taken by two classes of materials, namely organic polymers and inorganic semiconductors. Materials capable of demonstrate the properties of organic polymers and semiconductors have gained interest both for academic and industrial research in different pasture of chemistry, solid state physics and electrochemistry. Among them, conducting polymers are intensively studied as they present potential technological applications such as, antistatic coating and extended to sophisticated organic electronic components or selective modified electrodes and sensors¹. Conducting polymers have been prepared by electro polymerization method in 1979. Poly pyrrole² have been prepared first and later on extended to thiophene^{3,4}, furan, indole⁴, carbazole, azulene, pyrene⁵, benzene⁶ and fluorine⁷.

In spite of other poly heterocycles, thiophene oligomers have gained momentum due to its simple structure, extended π -conjugation, planarity, rigidity in the ring and flexibility in tuning the electronic properties. Taking into account all these aspect, evaluation of thiophene oligomers for optoelectronic applications have been made using density functional theory (DFT) and time dependent density functional theory (TDDFT) methods. The assessment of thiophene oligomers is twofold, one is to analyse the electronic properties of oligomers and then to ascertain the role played by π -bridge in the thiophene oligomer.

In the present study, a typical design of opto electronic material of the type D – π – A i.e. a donor group linked to an acceptor group through the π - bridge has been made. This strategy helps to tune the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), thereby band gap and extends the absorption spectra of the oligomer. In this work, dimethyl amine (donor) linked to NO₂ (acceptor) via thiophene ring (π – bridge) was chosen based on our earlier study⁸ as it perform well in tuning the HOMO and LUMO energy level. By retaining the same donor and acceptor group, the π -bridge alone was extended by introduction of additional thiophene rings and appraises how π -bridge extension has swayed the optoelectronic properties of thiophene oligomers (monomer (1), dimer (2), trimer (3), tetramer (4), pentamer (5) was analyzed. The performance of designed thiophene oligomer was studied through the HOMO and LUMO energy levels, band gap, absorption spectra and the NLO property. So the main objective of this work is to throw light on electronic properties and also to assess the influence of extended π – bridge on the electronic application of thiophene oligomers (1, 2, 3, 4 &5).

COMPUTATIONAL METHODS

The ground state geometries of the oligomers were optimized by B3LYP^{9,10} functional using 6-311++g (d, p) level of theory. The frequency calculations at the same level of theory show that, designed oligomers are at minimum energy without imaginary frequency. To instill the solvent effect, the self consistent reaction field (SCRF) calculations was done using Tomasi's polarizable continuum model¹¹ (PCM). In this method, solute molecules reside in a cavity representing a solvent medium defined by its dielectric constant, radius, density and molecular volume. In the present study, a dielectric constant of 8.93 is used to specify the dichloromethane medium (DCM). Based on ground state optimized geometry, the absorption spectra of oligomer was calculated using DFT functional within the frame work of time dependent DFT (TDDFT) method using M062X¹² functional at 6-31g (d) level of theory. It was found that, the difference between experimental (406 nm) and calculated absorption wavelength of synthesized monomer (1) by

M062X method is less and found to be 12 nm (394 nm) and therefore same functional is utilized for TDDFT calculations throughout.

A detailed NBO^{13,14} analyses was performed to understand the hyper conjugation interaction, which chiefly contributes for stabilization of thiophene oligomers. The second order perturbation analyses among the filled and empty orbital, expose the secret of donation and acceptance by delocalization of electron population in the orbitals of thiophene oligomers. All calculations have been performed using Gaussian 03 and 09 suites of program¹⁵

RESULTS AND DISCUSSION

Ground State Geometries:

The role of structural parameters such as bond length (BL), bond angle (BA) and dihedral angle (DA) appreciably contributes in the determination of molecular properties. Hence an exhaustive structural analysis has been made to have an insight on molecular geometry of thiophene oligomers. The optimized structure of oligomers (1, 2, 3, 4 & 5) is shown in **figure (1)**. The selected bond parameters of oligomers are displayed in **table (1)**. It is clear from the table (1) that, the ground state geometries of **1** showed C=C BL as 1.398 Å, indicating the closeness of C=C BL towards C-C BL. The C=C BL in **1** has been elongated to become a C-C BL. For instance, the C₃=C₉ BL is 1.39 Å. This shows that all C-C BL are well placed between C=C BL, thereby complete delocalization of electron in **1** is evident. The same trend of delocalization was found in other oligomer (2, 3, 4 & 5). It is clear that, C-C BL in **2** is 1.43 Å, 1.40 Å has tend to become C=C BL. The C-S BL in **1**, is 1.74 Å and remains the same for 2, 3, indicating the reliability of DFT method in evaluating structural parameters.

The C-C-C angle varies from 124-130° in all the oligomers. The torsional angle of **1**, range from -176 and -0.16° indicates planar configuration. Similarly **2** and **3** shows planarity in their geometry, which is a very essential criterion for the flow of electron from donor and acceptor via the π-bridge. The analyzed bond parameters specify the existence of planarity and delocalization of π-bond throughout the oligomer.

Table 1: Selected bond parameters in the ground state of thiophene oligomers calculated at B3LYP/6-311++g(d, p) level of theory.

Oligomers	C-C (Å °)	C=C (Å °)	C-S (Å °)	C-C-C (°)	Torsional angle
Monomer	1.43/1.42/1.40/	1.39/1.39	1.74	126/130	-176/-0.16
Dimer	1.39/1.42/1.43	1.40/1.39	1.75	129/125/132/128	179/-174
Trimer	1.40/1.38/1.43	1.39/1.39	1.74	129/129/125/124	-179/180
Tetramer	1.40/1.43/1.41	1.38/1.38	1.75	129/129/128/129	-179/-178
Pentamer	1.43/1.43/1.44	1.39/1.38/	1.74	129/129/129/126	170/-170

Frontier Molecular Orbital Analysis:

An in-depth understanding about the FMO of organic molecules is essential while studying the optoelectronic properties of molecules. The HOMO and LUMO energies and the gap between them in thiophene oligomers calculated at B3LYP/6-311++g (d, p) level of theory are illustrated in **figure (2)**. An efficient optoelectronic material should have small HOMO-LUMO gap (band gap). Here, the discussion is focused on examining the reduction in band gap upon increasing the π-bridge. Accordingly, monomer with one π-bridge acquire HOMO and LUMO values as -5.14 eV and -2.27 eV respectively and own 2.69 eV as band gap. Now by increasing the π-bridge, with substitution of another two thiophene rings, the

band gap was found to be 1.85 eV for **3** i.e, 0.84 eV reduction in band gap from that of **1** was noticed. Further, oligomer **5** was designed by extending π -bridge of **3**, with the induction of another two thiophene rings. The inclusion of two thiophene rings in **3** decreased the band gap by 0.38 eV. The band gap of designed oligomer range between 1.47-2.69 eV, indicating the effect of π -bridge on the energy levels and band gap of the oligomers. The FMO encompass the orbital range from HOMO-1 to LUMO+1 of thiophene oligomers calculated at B3LYP/6-311++g (d, p) level of theory and are presented in **figure (3)**. It can be observed from the figure (3), that HOMO and LUMO of thiophene monomer was delocalized over the entire molecule.

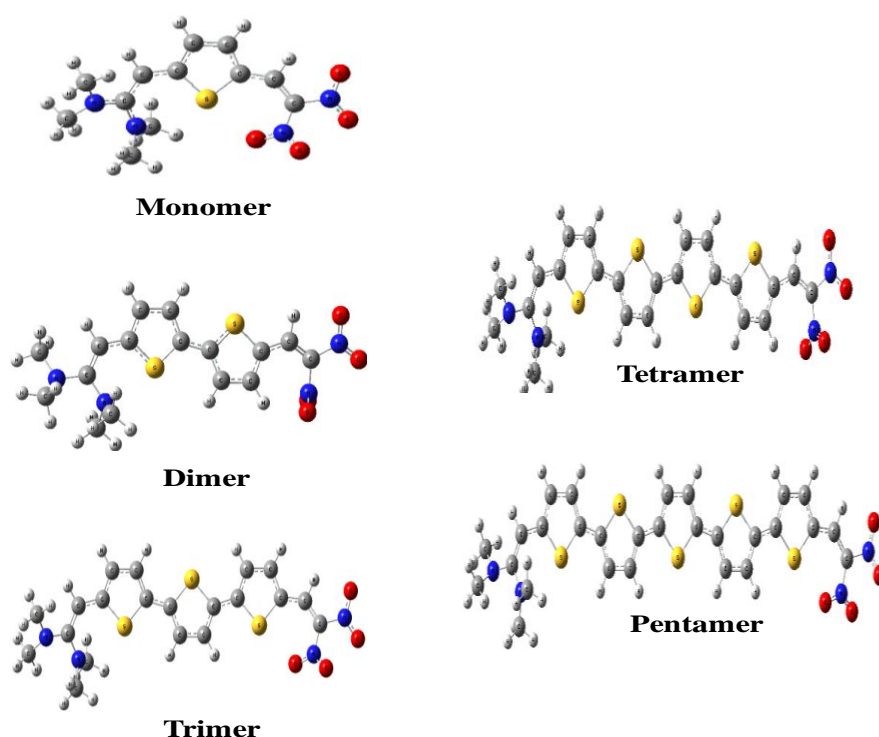


Figure 1: Optimized ground state geometries of thiophene oligomers calculated at B3LYP/6-311++g (d, p) level of theory.

Meanwhile LUMO of pentamer was delocalized over the whole molecule but with strong delocalization on two of the thiophene rings and acceptor groups. The HOMO of pentamer is strongly delocalized over the two thiophene rings. In tetramer and pentamer, the HOMO and LUMO delocalization of electron is different from mono, dimer and trimer, where in **5** HOMO is delocalized on donor groups and partial delocalization over three thiophene rings is noticed. Meanwhile, LUMO are delocalized on the acceptor groups and on three thiophene rings. This distinct feature of the oligomer **5** is attributed due to the presence of five thiophene rings. For high electron injection and improved efficiency, a molecule's LUMO should be delocalized on the acceptor group¹⁶. Accordingly, **1** cannot be used for optoelectronic applications, whereas **4** and **5** can be considered for making optoelectronic materials.

In order to quantify the % contribution of various fragments in oligomer towards HOMO and LUMO stabilization, calculations was made using QM forge program¹⁷. To achieve this task, the whole molecule has been fragmented into three

segments namely, π - bridge, donor and acceptor groups. The results of fragmentations analysis are shown in **figure (4)**. As the discussion spotlight on the π -bridge, the % contribution made by π -bridge alone is exploited. It is interesting to note that pentamer, the lowest band gap candidate gets 72% contribution from π -bridge to HOMO and has 68% in LUMO. Meanwhile, both HOMO and LUMO of monomer, (wider band gap) is stabilized by π -bridge only upto 49 - 47%. In trimer, 67% towards π - bridge to HOMO and 65% towards LUMO. Thus, it is evident that, π -bridge helps to contribute significantly towards stabilizing HOMO and LUMO. So the hint in tuning HOMO of thiophene oligomers stretches out only on π -bridge and not in other fragments of molecules.

Electronic Absorption Spectra (gas phase)

The absorption spectra of the thiophene oligomers calculated for ten low lying excited states, along with their, oscillator strength(f), excitation energy and assigned configurations at M062X/6-31g (d) level of theory in gas phase are summarized in **table (2)**. It is important to note, that all thiophene oligomers show S_0 - S_1 electronic transitions.

It can be observed that, absorption maxima of oligomers in gas phase are significantly red shifted with respect to monomer. As expected monomer, absorbs at lower wavelength of 450 nm with high excitation energy (2.75 eV). This arises due to 97% contributions from HOMO \rightarrow LUMO. When the π - bridge of monomer is increased by addition of another two thiophene rings, the absorption spectra of the trimer are red shifted. The above fact has been confirmed in pentamer which possess an intense band at 574 nm and this is associated with configuration assignments from HOMO \rightarrow LUMO (60%) through $n \rightarrow \pi^*$ transition.

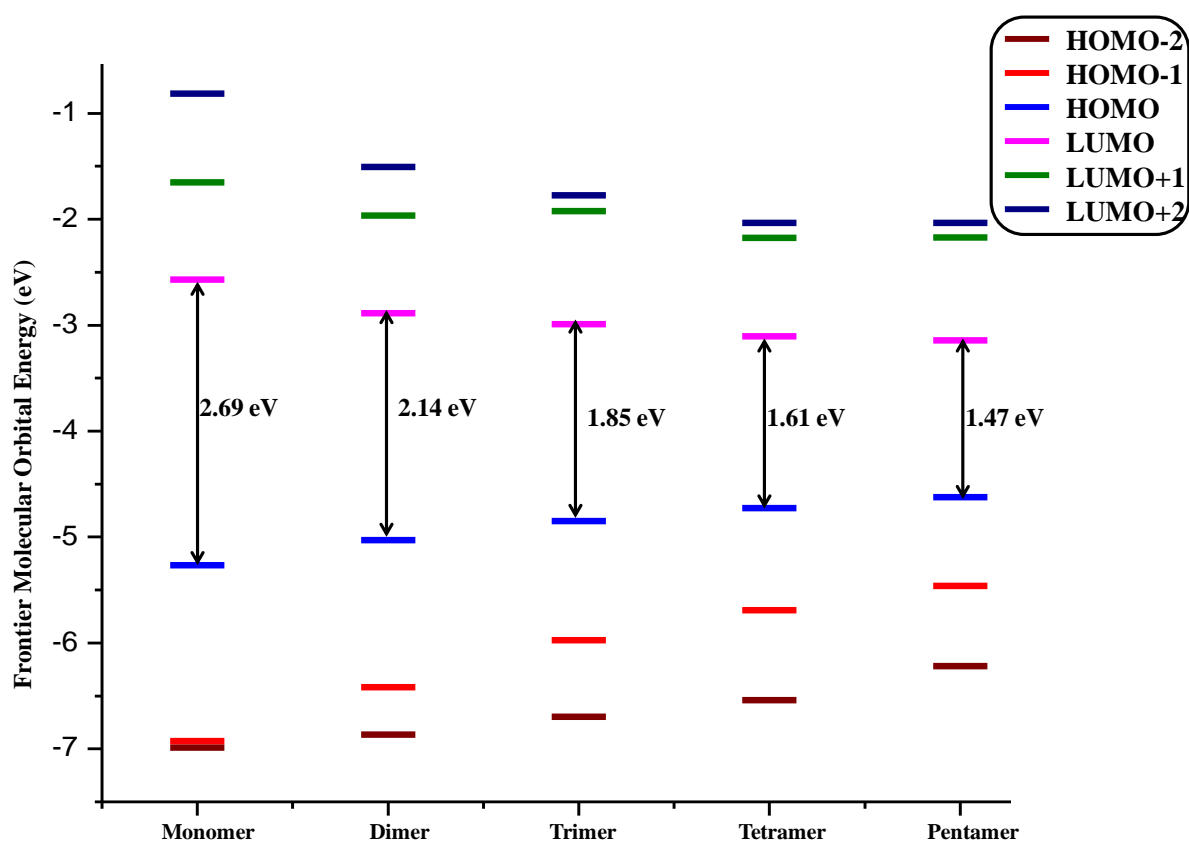


Figure 2: Frontier Orbital energy level diagram of thiophene oligomers calculated at B3LYP/6-311++g (d, p) level of theory.

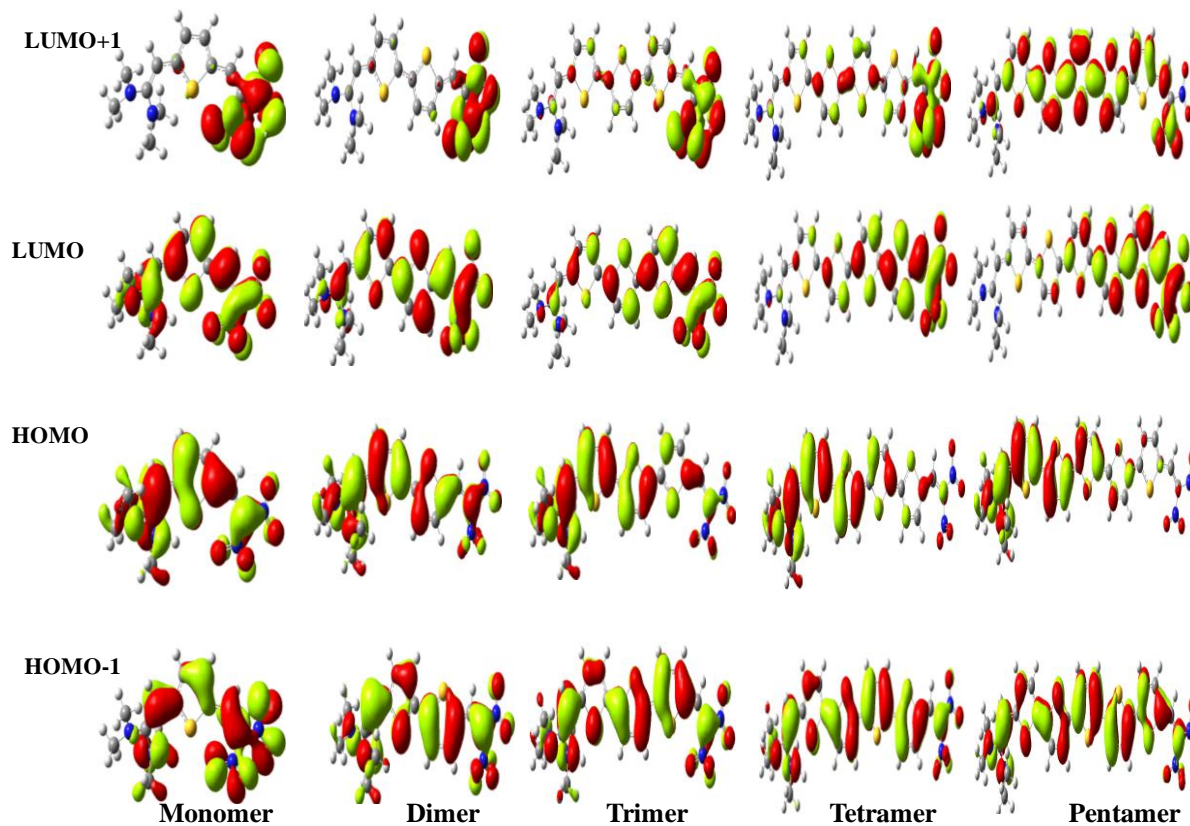


Figure 3: Frontier Molecular Orbitals comprising HOMO-2 to LUMO+2 of thiophene oligomers calculated at B3LYP/6-311++g (d, p).

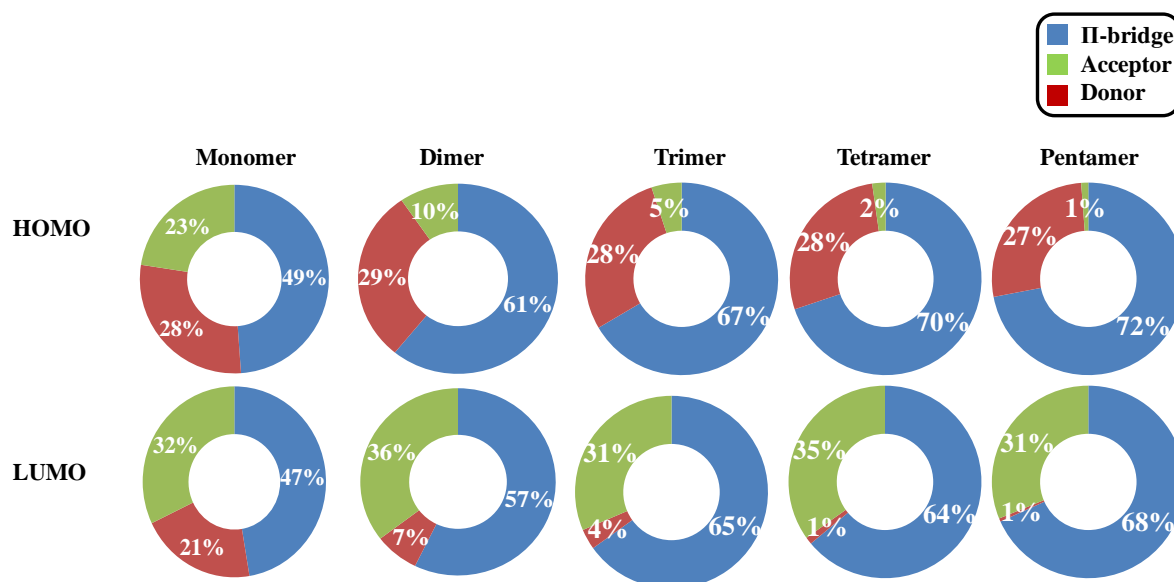


Figure 4: Molecular Orbital Composition (%) of oligomers calculated at B3LYP/6-311++g (d, p) level of theory.

This high wavelength of absorption is tagged with low excitation energy (2.16 eV). When compared with monomer, the extension of π -bridge, via increasing the number of thiophene rings red shifts the absorption maxima by 124 nm. The above results clearly show that the extension of π -bridge through the inclusion of thiophene rings provides an effective conjugation and red shifts the absorption spectra momentarily from 27.12% to 35.82%.

The absorption spectrum of pentamer is observed at 574 nm and is mainly contributed by HOMO \rightarrow LUMO (60%). This transition arises due to $n \rightarrow \pi^*$ with associated oscillator strength of 1.86. Again a positive shift is observed in pentamer with respect to its counterparts. This drives the conclusion that observed shift in absorption maxima can be directly correlated with the number of π -bridge in the oligomers.

4. Electronic Absorption Spectra upon Solvation.

In order to investigate the influence of solvent on the absorption maxima of the oligomers screened here, PCM M062X/6-31g (d) calculations have been performed on the optimized geometry in DCM medium and the results are in **table (2)**. It can be observed that, absorption maxima of thiophene oligomers are significantly red shifted with respect to gas phase. As expected monomer, absorbs at lower wavelength of 498 nm with high excitation energy (2.75 eV). When the π -bridge of monomer is increased by addition of another two thiophene rings, the absorption spectra of the oligomer are red shifted. The above fact has been confirmed in pentamer which possess an intense band at 625 nm. This higher wavelength of absorption is tagged with lowest excitation energy (2.00 eV). When compared with monomer, the extension of π -bridge, via increasing the number of thiophene rings red shifts the absorption maxima by 127 nm. The above results clearly show that the extension of π -bridge through the inclusion of thiophene rings provides an effective conjugation and red shifts the absorption spectra momentarily from 27.92% to 36.25%.

The absorption spectrum of pentamer is observed at 625 nm. This transition arises due to $n \rightarrow \pi^*$ with associated oscillator strength of 2.05. Again a positive shift is observed in 3 with respect to oligomer 1 by 127 nm and in terms of % it is increased from 27.92% to 35.82%. Overall, these oligomers show positive solvate chromism.

Table 2: Absorption Maxima (λ_{\max} in nm), electronic transition energies (ΔE in eV), and oscillator strength (f) of thiophene oligomers calculated using TDDFT method at M062X/6-31 g (d) level of theory.

Oligomers	λ_{\max} (gas*/DCM)		f	Transition assignments
	nm	eV		
Monomer	450*	2.75*	0.81*	H \rightarrow L (97%)
	498	2.48	0.97	H \rightarrow L (96%)
Dimer	517	2.39	1.21	H \rightarrow L (92%) H \rightarrow L+1 (8%)
	603	2.05	1.38	H \rightarrow L (89%) H \rightarrow L+1 (10%)
Trimer	557*	2.22*	1.43*	H \rightarrow L (88%) H \rightarrow L+1 (5%)
	610	1.94	1.57	H \rightarrow L (87%) H \rightarrow L+1(6%) H-1 \rightarrow L (6%)

Tetramer	565*	2.19	1.65	H→L (75%) H→L+1 (2%)
	619	2.02	1.78	H→L (72%) H→L+1 (5%) H-1→(8%)
Pentamer	574*	2.16*	1.86*	H→L (60%) H-1→L (22%) H→L+1(5%)
	625	2.00	2.05	H→L (59%) H-1→L (24%) H→L+1(+8%)

Dipole Moment:

The dipole moment is an important property which discloses the secret about electronic charge distribution in the molecule. Extensive awareness about dipole moment of organic molecule is essential while designing the materials for optoelectronic applications. The calculated dipole moment of the studied oligomer in gas phase at B3LYP/6-311++g (d, p) level of theory are displayed in **table (3)**. It is recognized from the table, dipole moment increases significantly upon the addition of π -bridge. In the midst of other oligomers, thiophene monomer owns the low dipole moment, due to lack of extensive conjugation. This has been verified, by considering trimer, in which the number of thiophene ring was increased from one to three. Trimer bears 18.02 debye in gas phase. When compared with monomer, dipole moment in gas phase for trimer was increased from 14.48 to 18.02 Debye.

Yet again, with the addition of two more thiophene rings, dipole moment value acquires a hike in gas phase. A maximum dipole moment in gas phase is hold by pentamer, apparently the one with more π -bridge. This is a marked piece of evidence that the π -bridge played in boosting the dipole moment value.

Table 3: Dipole moment (μ) in gas and Hyperpolarizability (β^0) of each oligomer calculated by B3LYP/6-311++g (d, p) level of theory.

Oligomers	Dipole moment (Debye) Gas phase	Hyperpolarizability (esu)
Monomer	14.48	56
Dimer	17.40	346
Trimer	18.02	915
Tetramer	19.28	2221
Pentamer	19.38	3279

NLO properties:

The NLO activity of thiophene oligomers have been calculated at B3LYP/6-311++g (d, p) level of theory and the results are shown in **table (3)**. The NLO activity is characterized by the third rank tensor (β_0) described by a 3X3X3 matrix and can be reduced to 10 components from 27 components according to Kleinmann symmetry^{18, 19, 20}. From the table (3) it can be seen that the first hyper polarizability (β_0) of the studied oligomers increases with an increase in π -bridge. For instance, (β_0) of thiophene monomer is 56 esu. This is the lowest β_0 value than the other oligomer due to the absence of extended π -bridge. In order to validate this, consider trimer, in which there are two additional thiophene rings which displayed 915 esu as β_0 . Now comparing β_0 of monomer and trimer, a hike in % from 1.86 to 17.73 was observed, nearly a 15 time increase just by inclusion of thiophene rings. Again evaluating β_0 for pentamer which own an additional two thiophene ring, demonstrate 3279 esu. When compared the β_0 value of pentamer with other oligomers, it

presents a 80.41% hike from 17.73%, a 5 times large magnitude value from 2 was noticed. Among the other oligomers, pentamer with more π – bridge owns a highest β_0 . This again holds up the key in enhancing the NLO activity of thiophene oligomer through the inclusion of π – bridge.

Natural Bond Orbital (NBO) Analysis:

NBO analysis disclose the secrets about the stability, bonding, donor – acceptor interaction relationship which are all essential contributing factors to reveal the electronic structure property of the thiophene oligomers under investigation. Particularly, the second order perturbation analysis award a detailed note on electron density, individual orbital energy, energy gap, energetic stabilisation due to hyper conjugative interaction of thiophene oligomers. The delocalization of electron can be achieved by promotion of electron density from Lewis donor orbital to a non- Lewis acceptor orbitals. Mathematically it is expressed as

$$\Delta E_{(i,j)}^{(2)} = - \frac{q_i |F_{(i,j)}|^2}{\epsilon_j - \epsilon_i}$$

Where $\Delta E_{(i,j)}^{(2)}$ is the stabilization energy of respective interaction, q_i represents occupancy of donor orbital, $F_{(i,j)}$ denotes Fock, Kohn – sham matrix which explains donor-acceptor mixing called delocalization. ϵ_i , ϵ_j denotes donor, acceptor orbital energies. The stabilization energy is associated with energy gap $\epsilon_j - \epsilon_i$ and $F_{(i,j)}$ matrix. **Table (4)** lists the stabilization energy, donor, acceptor and their interactions.

The highest stabilization energy is favoured by dimer, due to the interaction from LP (3) O₄₂ donor to π^* (N₃₉-O₄₃) acceptor by 154.51 KCal/mol. The next largest stabilization energy was possessed by tetramer with 152.73 KCal/mol of stabilization energy through LP (3) O₄₉, π^* (N₄₅-O₄₇) where lone pair of LP (3) O₄₉ take part as Lewis donor and π^* (N₄₅-O₄₇) participate as non-Lewis acceptor. The donor acceptor interaction for pentamer includes LP (3) O₆₁ \rightarrow π^* (N₅₉-O₆₀). The stabilization energy for this interaction is 147.66 K Cal/mol. This interaction originates from the lone pair of O₆₁ and an empty non lewis orbital of π^* (N₅₉-O₆₀). The overall observations from NBO analysis on thiophene oligomers markedly highlight the factors that are largely take part for the stabilization of the molecular system.

Table 4: Second order perturbation analysis of Fock matrix by NBO analysis for thiophene oligomers calculated at B3LYP/6-311++g (d, p) level of theory.

Oligomer	Donor (i)	Acceptor (j)	E(2) K.Cal/mol
Monomer	LP(3) O ₃₅	π^* (N ₇ -O ₃₇)	146.68
Dimer	LP(3) O ₄₂	π^* (N ₃₉ -O ₄₃)	154.51
Trimer	LP(3) O ₁₉	π^* (N ₂₀ -O ₅₀)	146.82
Tetramer	LP(3) O ₄₉	π^* (N ₄₅ -O ₄₇)	152.73
Pentamer	LP(3) O ₆₁	π^* (N ₅₉ -O ₆₀)	147.66

CONCLUSIONS

In this paper, a detailed investigation on the thiophene oligomer has been executed by DFT and TDDFT methods. The studied thiophene oligomer majorly differs in the number of (thiophene rings) π -bridge, resulting in different π -conjugated oligomer with wide-ranging electronic structures and optoelectronic properties. The oligomer 1 offers the planar geometry, have the highest band gap, pretty low

HOMO and highest LUMO and the calculated shortest absorption maxima, tied with low dipole moment and poor NLO activity. The oligomer 3 also bears planar geometry, but with low band gap, low HOMO, high LUMO, the long absorption maxima with better dipole moment and NLO activity. A gradual increase in optoelectronic properties was observed when increased the number of π -bridge in oligomer 3. It is notable that, the oligomer 5 with planar geometries, showcased the lowest band gap, low HOMO, high LUMO, the longest calculated absorption maxima, resulted in high dipole moment and enhanced NLO activity. The foremost difference is the number of π -bridge that turns out distinct in their electronic and optical properties. In summary, the calculations predict, addition of 5π -bridge in thiophene oligomers, can alter the optoelectronic properties to a greater extent, there by sets a trend for optoelectronic applications.

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