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DESIGNING OF THE CONDUCTING POLYMERS USING COMPUTATIONAL CALCULATIONS

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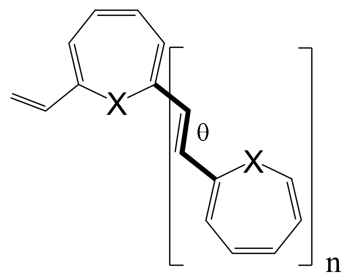
Abstract
The band gap of vinylene-linked seven membered organic heterocyclic conducting polymers **1** to **4**, are calculated by implementing DFT with B3LYP/6-31G(d,p) method. The effect of chemical modification by introducing heteroatom on the electronic structure of polymers is discussion. The fact that introducing a heteroatom increases conjugation, chemical stability and affects the band gap of the aromatic ring is also discussed. It is concluded that vinylene-linked, azepine based polymer **2** has the lowest band-gap among all the investigated systems and hence has a better conducting properties. Our results highlight the use of computation for designing materials with enhanced photovoltaic applications.
Keywords: Vinylene-linked, Heterocyclic polymers, Photovoltaic, Azepine

Introduction
The conducting polymers having conjugated heterocyclic ring systems are the unique *class* of *organic materials* and are highly studied due to their delocalization of electrons, highly conjugated π-bonding systems, electronic properties, and chemical stability. In view of all this, much current research is now being directed towards developing organic photovoltaic material as these are less expensive and easy to synthesize.[1] Consequently, this has resulted in significant technological advances in developing photovoltaic materials[2,3] including organic field-effect transistors[4] and organic light-emitting diodes.[5,6] The relative ease in chemical functionalization of these materials by using electron donor/acceptor groups made it possible to design small band-gap polymers, neglecting the necessity for further additional electrostatic doping of the system. However, the technological material's development with desired properties has been a time consuming, challenging, and an expensive task. Hence, the rapid advancements in the electronic-structure methods development by computation have revolutionized the process of materials design and development.[7-10]

Herein, we implemented computational calculations DFT with B3LYP/6-31G(d,p) basis sets for designing the polymers with low band gaps by introducing heteroatom in vinylene-linked seven membered conjugated ring systems (**Fig. 1**) with the aim of designing polymers with enhanced electronic transport properties.



X = CH_2 , NH, O, S

Fig. 1 Structure of Conducting Polymer used for investigation

Computational Method

The conducting polymers investigated are shown in **Fig. 1**. These particular polymers were chosen for this study as they belong to first- and second-row of heterocycles which are synthetically accessible too. To save the computational cost and time we used dimers for computational calculations. All the calculations were performed using Spartan quantum chemistry program package.[11] All the structures were fully optimized with density functional theory (DFT) by using B3LYP method[12] with 6-31G(d,p) basis set. This method has been utilized successfully for band-gap calculations of conjugated heterocyclic polymers.[13] All calculations were based on ideal gas-phase conditions. Exactly zero imaginary vibrations characterize stationary points.

Results and Discussion

The structures of all the vinylene-linked, seven membered polymers **1** to **4** are investigated using DFT. The inter ring dihedral angle 'ɵ' (shown in Fig. 1) are given in Table 1. It is found that the carbon atoms of the heterocyclic ring are coplanar with its vinylene-linking unit, which indicates high conjugation due to the valence π-orbitals of carbon-carbon double bonds. However, inter ring dihedral angle does not show the significant changes.

The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO), are given in Table 1. The band-gap refers to the energy difference (in electron volts) between the HOMO and LUMO of these polymers. The calculated band-gap in decreasing order are 2.98 eV > 2.86 eV > 2.78 eV >2.50 eV for polymers CH_2, S, O, and NH, respectively.

Table 1: The dihedral angle, HOMO, LUMO and Band-Gap, calculated by B3LYP/6-31G(d,p) are given.

Polymer	Functional Group X	Dihedral Angle 'ɵ' (°C)	HOMO (eV)	LUMO (eV)	Band-Gap (eV)
1	CH_2	179.83	-4.95	-1.97	2.98

2	NH	179.76	-4.47	-1.97	2.50
3	O	-179.67	-4.96	-2.18	2.78
4	S	179.68	-5.16	-2.30	2.86

Following calculations on all vinylene-linked heterocyclic conjugated polymers, we conclude that introduction of heteroatom in the polymer backbone decreases its band-gap. HOMO, LUMO energy map of all the calculated structures and their band gaps are presented in Fig. 2. It is found that vinylene-linked heterocyclic conjugated polymer **2** has the lowest band-gap among all the investigated polymers. However, the band gaps are affected by the oligomer size i.e. the increase of oligomer size decreases band gap.[14] Smaller band gaps in conducting polymers typically lead to higher current and higher performing efficiencies. Hence, it is concluded that N containing polymer **2** has the highest conductivity and thus would have better performing efficiencies among all the investigated structures. Finally, we concluded that the vinylene-linked, azepine based polymer is an interesting building block to carry out further material synthesis. This study provides a basis for constructing organic heterocyclic conducting polymers-based future electronic devices.

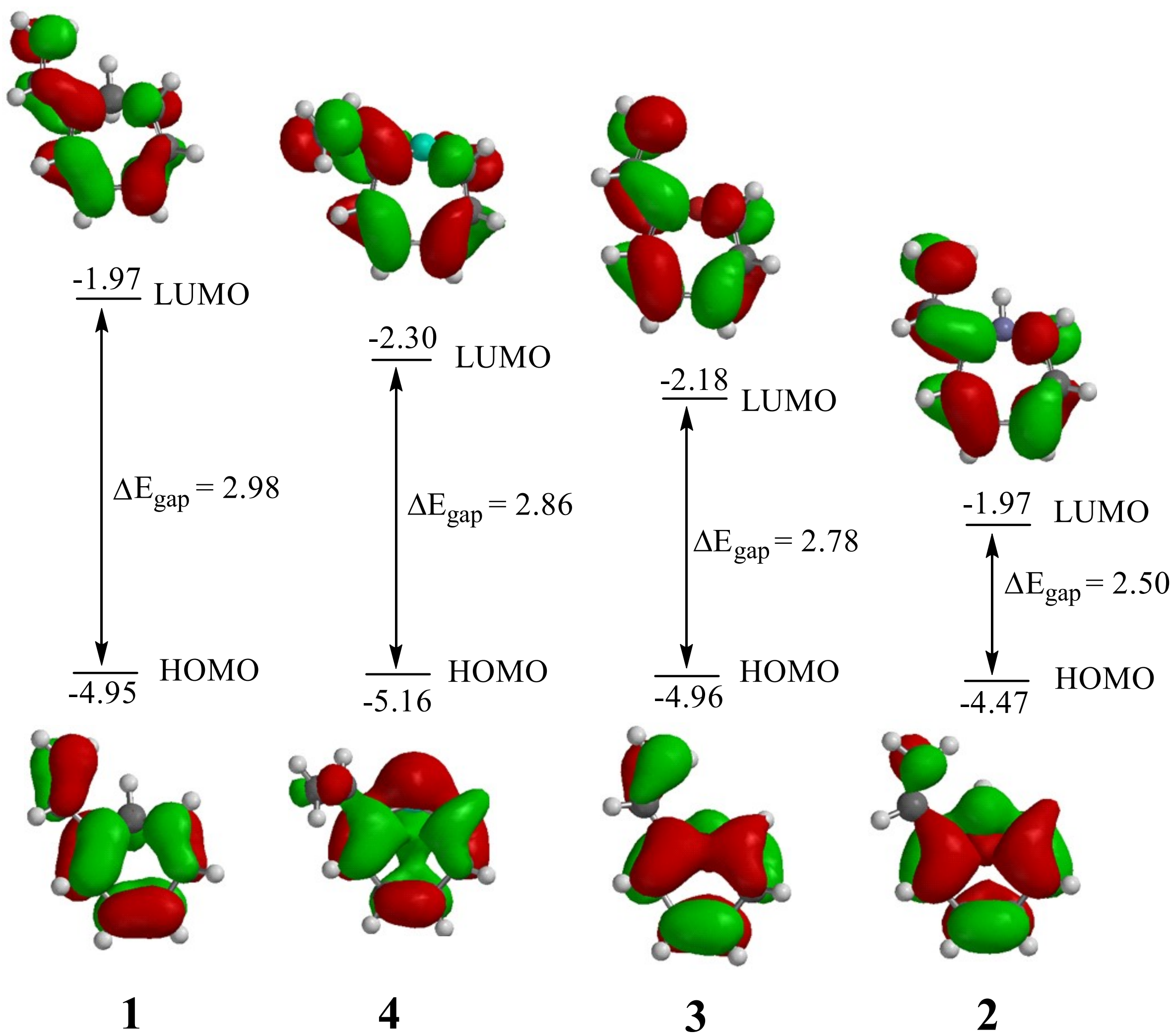


Fig. 2: Band gap of compound **1, 2, 3** and **4**

Conclusion

It is found that the introduction of the heteroatom like oxygen, nitrogen, and sulphur decreases the band gap in conjugated polymers and hence increases conducting properties. Based on computational results, vinylene-linked, azepine based polymer **2** has the lowest band-gap values among all, and hence concluded as a better conducting polymer. It is believed that this study is very useful for understanding the band gap and structural properties of the systems, which would provide a platform for the design of future electronic devices.

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