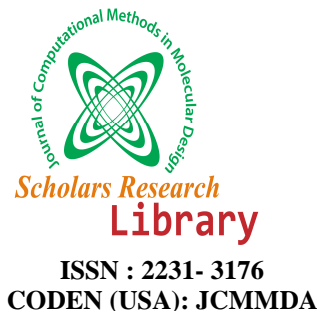




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DFT/B3LYP study of bridging effect on structural and electronic properties of a short π -conjugated systems based on thiophene and phenylene

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ABSTRACT

We report in this article a DFT study of the bridging effect on structural and electronic properties of a several π -conjugated systems of thiophene and phenylene based on Cylopenta-ThienylenePhenylene (CPTP) co-oligomers in which both 3 and 2' positions (fig. 1a) were bridged with different fragment such as: CH_2 , SiH_2 , $\text{C}(\text{CN})_2$, S , $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{CH}_2$ and $\text{C}=\text{C}(\text{CN})_2$. The important reduction of the gap energy observed for the whole series of the bridged compounds studied here is explained on the basis of an orbital interaction analysis. The calculations methods were performed by using Gaussian09 program at density functional theory DFT/B3LYP level. The compounds bridged by $\text{C}=\text{S}$ and $\text{C}=\text{C}(\text{CN})_2$ have small LUMO–HOMO gaps; leading to suggest them as the promising candidates for the optoelectronic device applications.

INTRODUCTION

Conjugated co-oligomers based on thiophene and phenylene possess extensive π -electron delocalization along the molecular backbone, which makes them interesting for various optoelectronic applications [1-4].

Due to this applicative interest and to the fact that these shirt systems can be used as model compounds for the parent polymer, they have been extensively studied[5-7]. Also, Due to their controllable and precisely defined structure, physical properties can be followed and correlated with the side chains and conjugation length. With the implementation of these molecular structures by functionalization at the terminal and side positions permit their application as molecular materials in organic field-effect transistors[8-6], light-emitting devices[17, 18, 19,23], photovoltaic cells [24-37], or even as molecular wires for information storage or transfer [38, 39].

Polymers and oligomers with low band gap are expected to show not only good intrinsic conductivity but also nonlinear optical properties [40, 41]. For their successful design, it is necessary to have a complete understanding of the relationship between the chemical structure of polymers and its electronic properties[42, 43]. Various routes are presently followed for designing novel conducting polymers, one is provided by donor–acceptor polymers, based on the approach suggested for the first time by Havinga et al. [44]. The study of conjugated oligomers is very attractive due to the fact that finite size systems can be obtained with high purity and a well-defined chemical structure. This opens the way for the investigation of electronic properties as a function of chain length and extent of the parent π -electron system.

The results found for unsubstituted thienylene phenylene co-dimer, display two most stable conformation ($\theta = 27^\circ$ and $\theta = 152^\circ$)[45]. The gap energy calculated decreases as function of the increase of the chain length from the co-dimer to the co-octamer[5]. The gap energy value of thienylene phenylene co-octamer (4TP; 2.97 eV) is nearly close to those of poly(thienylene phenylene) in the case of poly(OCH_3TP)[45]. Thus, this oligomer with 8 units (4TP) is the useful model to understand electronic properties of the parent polymers[5, 45, 46].

To reduce the energy gap in these co-oligomers, it is interesting to weaken the torsion angles between thiophene and phenylene rings from 27° to 0° by bridging them by various groups. In this article, we present a detailed DFT (B3LYP/6-31(d)) study of several co-oligomers based on thiophene and phenylene in which inter-ring torsional angles have been blocked by chemical bridging. Fig. 1 shows the types of adjacent ring bridging studied here; this rigid bridge contains CH_2 , SiH_2 , S , $\text{C}(\text{CN})_2$, $\text{C}=\text{CH}_2$, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{C}(\text{CN})_2$ groups. We focus on the electronic properties and geometric structure of these compounds. We will, first investigate the effect of bridging on thienylene-phenylene (TP); then we will discuss the influence of the bridging on the structural and electronic properties of these bridged co-oligomers and corresponding polymers. The chemical structure of the co-polymers and the optimized structures of the bridged co-dimers are shown in fig. 1.

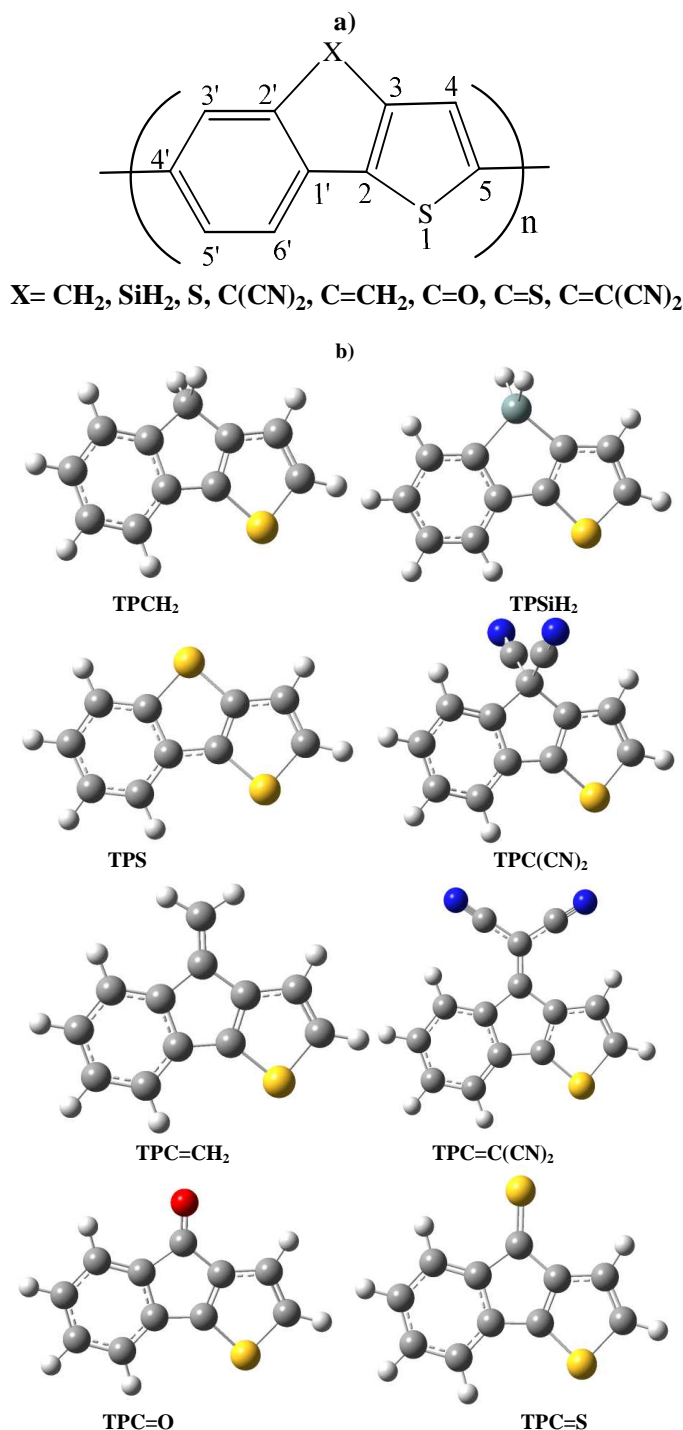


Fig. 1. (a) Chemical structures of compounds under investigation. (b) The theoretical geometric structures of the co-dimers optimized by B3LYP/6-31G(d).

The general abbreviation of our bridged compounds is TPX co-dimer, 2TPX (co-tetramer) and 4TPX (co-octamer) where X:CH₂, SiH₂, S, C(CN)₂, C=CH₂, C=O, C=S, and C=C(CN)₂ where n, the number of bridged thienylenephenylene, varies between 1 and 4.

2. Calculations methodology

The calculations on the geometries of both co-oligomers chains have been performed under density functional theory (DFT) at the B3LYP level of theory and the 6-31G(d) basis set [47]. The notation B3 indicates a three-parameter of Becke[48] and LYP indicates the Lee–Yang–Parr functional [49]. Calculations were carried out using the Gaussian 09 program package [50].

All structures are fully optimized by B3LYP/6-31G(d) without any constraint.

RESULTS AND DISCUSSION

3.1. Geometric structure results

The geometries of the bridged thienylenephenylene-co-oligomers TPX (X: C=CH₂, C=O, C=S, C=C(CN)₂) and (X: CH₂, SiH₂, S, C(CN)₂) are presented in Fig. 1b.

We present in Table 1 the optimized structural parameters of bridged and unbridged thienylenephenylenes as calculate using B3LYP/6-31G(d) method. We observed that the optimized bridged structures of co-dimers are plan (Fig. 1b).

Table 1: Optimized structural parameters (bond length (in Å), angle (in degree)) of the bridged co-dimers TPX obtained at B3LYP/6-31G(d).

Parameter	X = C=O	X = C=S	X = C=CH ₂	X = C(CN) ₂	X = S	X = CH ₂	X = C(CN) ₂	X = SiH ₂	TP
C ₁ -C ₂	1.41577	1.41577	1.42305	1.42525	1.42121	1.41829	1.41232	1.42261	1.40874
C ₂ -C ₃	1.38153	1.38153	1.38867	1.39035	1.39589	1.38761	1.38390	1.39296	1.39203
C ₃ -C ₄	1.40653	1.40653	1.40146	1.40530	1.39270	1.40177	1.40183	1.40109	1.39644
C ₄ -C ₅	1.39384	1.39384	1.39734	1.39232	1.40442	1.39776	1.39726	1.39545	1.39612
C ₅ -C ₆	1.40715	1.40715	1.40002	1.40470	1.38936	1.39774	1.39865	1.39718	1.39272
C ₆ -C ₁	1.38648	1.38648	1.39212	1.38573	1.40463	1.39542	1.39389	1.39722	1.40755
C ₂ -X	1.51164	1.51164	1.48967	1.48902	1.77280	1.52294	1.55136	1.88812	-----
C ₃ -X	1.49261	1.49261	1.47332	1.46336	1.75836	1.51071	1.53191	1.87023	-----
C ₁ -C ₂	1.47123	1.47123	1.45737	1.45883	1.43691	1.45542	1.45582	1.46887	1.46621
C ₂ -C ₄	1.38063	1.38063	1.38352	1.38720	1.38423	1.37850	1.37481	1.38607	1.37667
C ₃ -C ₄	1.42121	1.42121	1.42437	1.42929	1.42499	1.42202	1.41876	1.42712	1.42527
C ₄ -C ₅	1.36977	1.36977	1.36948	1.36742	1.36759	1.37148	1.37078	1.36913	1.36772
C ₅ -S ₁	1.75384	1.75384	1.75183	1.75334	1.74831	1.74886	1.74867	1.74269	1.73456
S ₁ -C ₂	1.72174	1.72174	1.72873	1.71699	1.74264	1.73350	1.72802	1.74113	1.75424
C ₁ -C ₂ -X	109.32295	109.32292	109.19664	108.35396	112.65174	110.30931	109.99872	108.38673	-----
C ₂ -C ₃ -X	108.29056	108.29058	108.65903	108.07824	112.10767	109.61896	109.52672	106.73669	-----
C ₂ -X-C ₃	104.55923	104.55921	104.98622	106.14160	90.40598	102.22410	101.42182	92.31098	-----

For both systems, we observe major difference in the optimized bond lengths and angles when we change compounds bridging.

The C-S bond lengths do not show a significant change for all compounds, we note that the C₅-S₁ show the particularity of having smaller values than C₂-S₁ by 0.032 Å (Table 1). The values of C₁X-C₄ angle decrease when we pass from the sp² (X: C=CH₂, C=O, C=S, C=C(CN)₂) bridged groups to sp³ bridged groups (X: CH₂, SiH₂, S, C(CN)₂).

3.2. Electronic properties of thienylenephenylene co-dimers bridged by X= C=CH₂, C=O, C=S, C=C(CN)₂, CH₂, SiH₂, S, C(CN)₂.

In order to care out the bridging effect on the electronic properties of the molecules under study, calculations were performed by B3LYP/6-31(d) method. Table 2 shows calculated values of E_{HOMO}, E_{LUMO}, and energy gaps (E_g) for bridged and unbridged thienylenephenylene co-dimers.

Comparing the values obtained after bridging, we find the known result that bridging by the substituted sp² carbon atom reduces the gap energies in all cases. We notice that the value of energy gap decrease when we pass from the TPX (X: CH₂, SiH₂, S, C(CN)₂) to TPX (X: C=CH₂, C=O, C=C(CN)₂, C=S). The gap energy values of the latter compounds are nearly similar to that of planar thienylenephenylene, therefore the bridges with substituted sp² causes the flatness thiophene and phenylene adjacent rings.

Table 2: E_{HOMO} , E_{LUMO} and E_g energy values of the studied co-dimers.

Compound	$E_{\text{HOMO}}(\text{eV})$	$E_{\text{LUMO}}(\text{eV})$	$E_g(\text{eV})$
TP	-5,74	-0,96	4,78
TPCH ₂	-5,48	-0,86	4,62
TPSiH ₂	-5,71	-1,29	4,42
TPS	-5,75	-1,04	4,71
TPC(CN) ₂	-6,37	-1,79	4,58
TPC=CH ₂	-5,54	-1,57	3,97
TPC=O	-5,99	-2,33	3,66
TPC=C(CN) ₂	-6,31	-3,29	3,02
TPC=S	-6,00	-3,02	2,98

The orbital patterns of the highest occupied molecular orbital HOMO and the lowest unoccupied molecular orbital LUMO calculation, for both TPC=S and TPC=C(CN)₂, are shown in Fig.2(a). It is interesting to note that the contribution of the electron accepting groups X: C=S and C=C(CN)₂ to the HOMO is negligibly small while it makes a significant contribution to the LUMO. In the light of these results, one can rationalize the small band gap values obtained in these two compounds by visualizing their formation (Fig. 2a and 2b) via the interaction of unbridgedthienylenebenzene skeleton with an electron accepting group X terminated by H atoms (X: H₂C=S, H₂C=C(CN)₂).

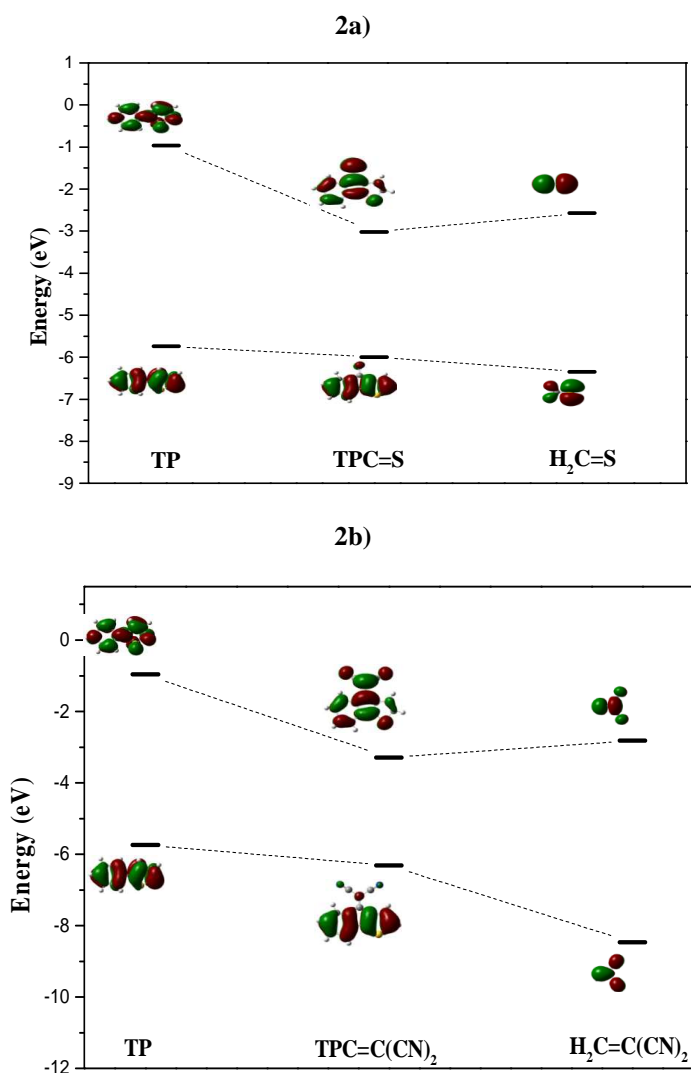


Fig. 2. (a) Contour plots of the frontier orbitals of TP, TPC=S, and H₂C=S (contour value 0.02 (e/bor³)^{1/2}). (b) Contour plots of the frontier orbitals of TP, TPC=C(CN)₂, and H₂C=C(CN)₂ (contour value 0.02(e/bor³)^{1/2}).

The band gap of TPC=S and TPC=C(CN)₂ are determined by strength of bonding interaction between the LUMO of the thienylenebenzene skeleton and LUMO of the electron accepting group X. The smaller band gap of

TPC=Sas compared to that of TPC=C(CN)₂ is due the lower-lying value of LUMO (2.575 eV) of H₂C=S compared with that of H₂C=C(CN)₂ (2.820 eV).

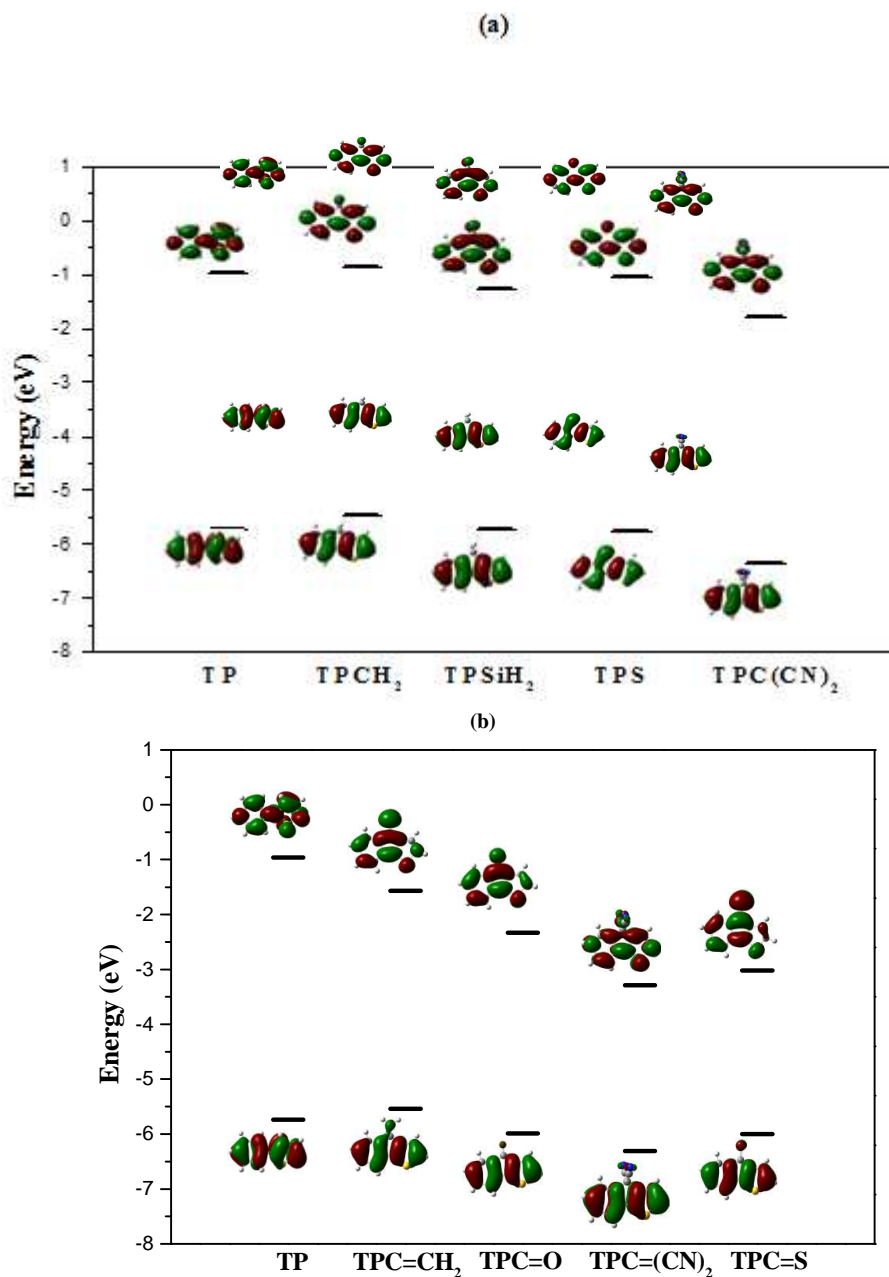


Fig. 3. (a) Contour plots of the HOMO and LUMO of TP, TPCH₂, TPSiH₂, TPS, TPC(CN)₂, (contour value 0.02 (e/bor³)^{1/2}). (b) Contour plots of the HOMO and LUMO of TP, TPC=CH₂, TPC=O, TPC=S, and TPC=C(CN)₂ (contour value 0.02 (e/bor³)^{1/2}).

The orbital HOMO and LUMO of the bridged compounds are shown in Fig. 3a and 3b. The formation of these co-dimers are realized by interaction of the unbridgedthienylene-phenylene orbital with the sp³ hybrid group (X: CH₄, SiH₄, H₂S, and H₂C(CN)₂) and the sp² hybrid group (X: H₂C=CH₂, H₂C=O, H₂C=S, H₂C=C(CN)₂). For the sp³ groups, we note that SiH₄ group presents a lower LUMO. The LUMO of hybrid sp² C=S group is much lower in energy. This energy decreases when passing from C=CH₂, C=O, C=C(CN)₂ and C=S. The decrease of energy is due to the combined effects of small energy lowering of π* molecular orbital of the group X and the slight increase of the X weight in the LUMO of species[51]. The orbital of the HOMO for both species are found to be nearly similar.

3.4. Electronic structures of bridged co-octamers

The gap energy value of thienylene-phenyleneoctamer is close to that of the corresponding copolymers [5]. This value has permitted to take the co-octamer as a model since it reflects properties of the copolymers parent. Therefore in this part, we examine the highest occupied orbitals HOMO and the lowest virtual orbitals LUMO for these oligomers because the relative ordering of the occupied and virtual orbitals provide a reasonable qualitative

indication of the excitation properties [52] and of the ability of electron transitions or hole transport. We have plotted the contour plots of the HOMO and LUMO orbitals of 4TPX (X: CH₂, SiH₂, S, C(CN)₂) and 4TPX (X: C=O, C=S, C=CH₂, C=C(CN)₂) in their completely optimized conformation B3LYP/6-31G(d) in Fig. 4.

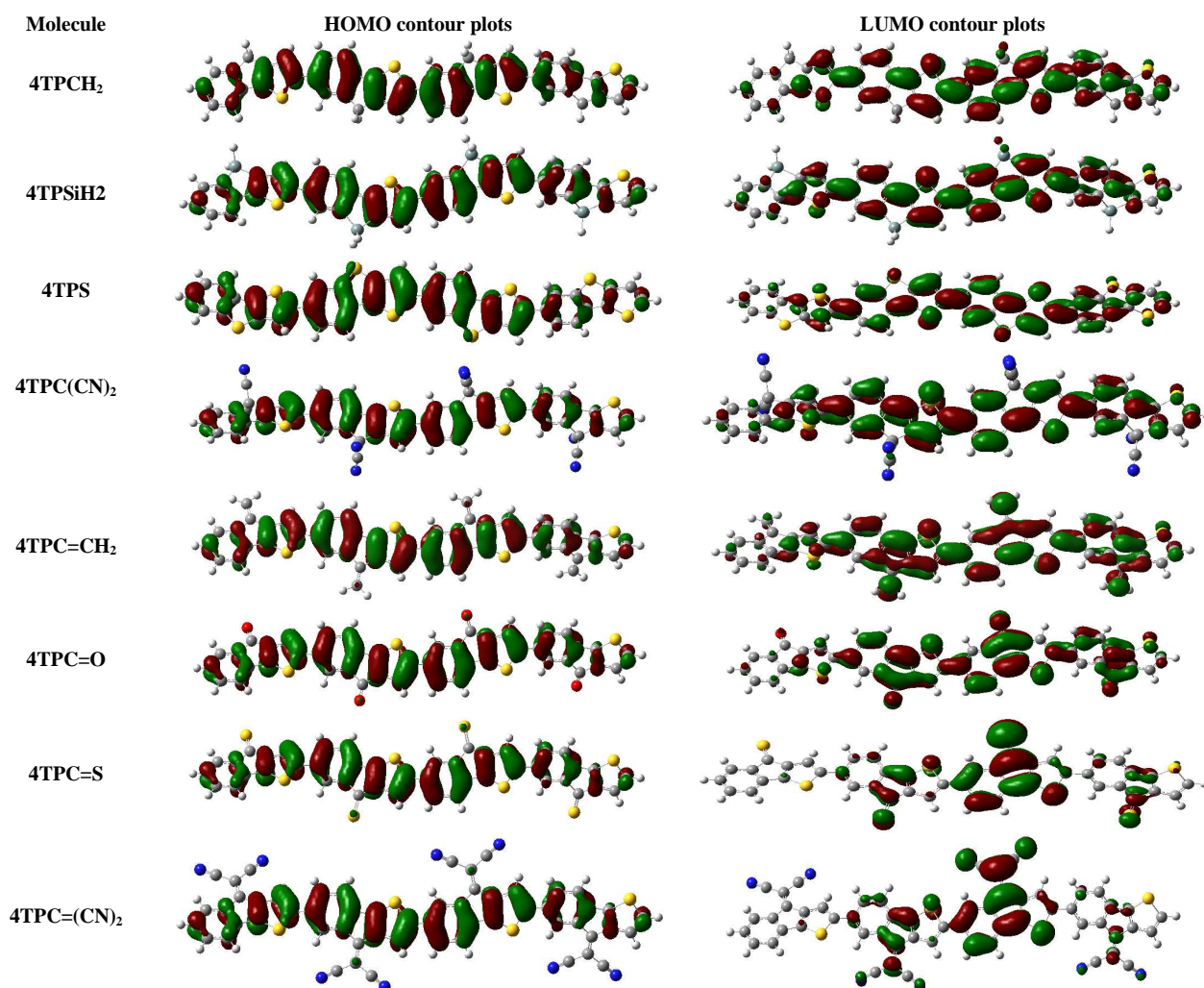


Fig. 4. The HOMO and LUMO orbitals of 4TPX (X: C=CH₂, C=O, C=S, C=C(CN)₂, CH₂, SiH₂, S, C(CN)₂) obtained by B3LYP/6-31G(d).

Analysis of fig. 4 reveals that for both HOMO and LUMO orbitals, the same appearance is observed for all compounds except those of the co-oligomers 4TPX (X: C=O, C=S, C=C(CN)₂) bridged by sp² carbon atoms. They have a delocalized character over all the backbone, and do not differ in respect with unbridged co-octamers. Those bridged by C=S, C=O and 4TPC=C(CN)₂ are delocalized at the innermost ring with a clear participation of C=S, C=O and C(CN)₂ in LUMO orbital.

Table 3: Calculated values of E_{HOMO}, E_{LUMO}, and E_g of the bridged thienylenephenyleneoctamers 4TPX (eV).

Dimmer	E _{HOMO}	E _{LUMO}	E _g
4TP	- 4.94	- 1.97	2.97
4TPCH ₂	- 4.79	- 1.93	2.86
4TPSiH ₂	- 5.03	- 2.08	2.95
4TPS	- 5.15	- 2.02	3.13
4TPC(CN) ₂	- 5.90	- 2.87	3.03
4TPC=CH ₂	- 4.85	- 2.06	2.79
4TPC=O	- 5.40	- 2.80	2.60
4TPC=C(CN) ₂	- 5.76	- 3.63	2.13
4TPC=S	- 5.41	- 3.290	2.12

In Table 3, we present the bridging co-oligomers leading to reduction of the band gap. This is possibly due to the stabilization of the LUMO in the bridged co-oligomers caused by the planarization of the co-octamers skeletons.

Besides we notice that the gaps energy of C=S and C=C(CN)₂ bridged derivatives are weaker than the other compounds. The possible reason of this decrease is certainly the electronic character of the C=S and C=C(CN)₂ groups. The values of the band gap are 2.12 and 2.13 eV for 4TPC=S and 4TPC=C(CN)₂, respectively. These values are nearly in accordance with that measured experimentally for poly(thienylene-phenylene) bridged with CHC₆H₅ (2.58 eV, 480nm) [53]; which are lower than the unbridged thienylene-phenylene-co-octamer 4TP (2.97 eV) [5].

CONCLUSION

The geometric parameters of thienylene-phenylene co-oligomers bridged by (X: CH₂, SiH₂, S, C(CN)₂) and (X: C=CH₂, C=O, C=S, and C=C(CN)₂) were obtained by B3LYP/6-31G(d) calculations. The most stable conformations are quasiplanar. The gap energy calculated with the same method decreases when we pass from compounds with (X: CH₂, SiH₂, S, C(CN)₂) to those with (X: C=CH₂, C=O, C=S, and C=C(CN)₂). The insertion of a bridging group between thiophene and phenylene rings leads to a reduction of the HOMO–LUMO energy gaps. This is mainly due to the stabilization of the LUMO level of several compounds. Concerning the C=C(CN)₂ and C=S groups, the lowering of the energy gap observed is likely to insure the better electronic properties for the corresponding polymers. These results indicated that the bridged (TPC=S)_n and (TPC=C(CN)₂)_n copolymers are promising materials for optoelectronic application.

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REFERENCES

- [1] P. Damman, M. Dosière, M. Brunel, J. C. Wittmann, *J. Am. Chem. Soc.*, **1997**, 119, 4633.
- [2] S. Hotta, M. Goto, R. Azumi, M. Inoue, M. Ichikawa and Y. Taniguchi, *Chem. Mater.*, **2004**, 16, (2), 237.
- [3] S. Hotta; L. H. Kimura, S. A. Tamaki, *J. Heterocycl. Chem.*, **2000**, 37, 281.
- [4] S. Hotta, T. Katagiri, *J. Heterocycl. Chem.*, **2000**, 40, 845.
- [5] H. Zgou, M. Hamidi, M. Bouachrine, *Journal of Molecular Structure: Theochem.*, **2007**, 814, 25–32.
- [6] S. M. Bouzzine, S. Bouzakraoui, M. Bouachrine, M. Hamidi, *Journal of Molecular Structure: THEOCHEM.*, **2005**, 726, 271–276.
- [7] M. Amine, M. Hamidi, S. M. Bouzzine, A. Amine, M. Bouachrine, *Adv. Mat. Lett.*, **2012**, 3(1), 15–20.
- [8] L. L. Chua, J. Zausen, J. F. Chang, E. C. W. Ou, P. K. H. Ho, H. Sirringhaus, R. H. Friend, *Nature*, **2005**, 434, 194–199.
- [9] M. X. Chen, X. Crispin, E. Perzon, M. R. Andersson, T. Pullerits, M. Andersson, O. Inganäs, M. Berggren, *Appl Phys Lett*, **2005**, 87, 252105–252107.
- [10] W. Y. Lee, K. F. Cheng, T. F. Wang, C. C. Chueh, W. C. Chen, C. S. Tuan, J. L. Lin, *Macromol. Chem. Phys.*, **2007**, 208, 1919–1927.
- [11] Cheng K. F., Liu C. L., Chen W. C., *J. Polym. Sci. Part A: Polym. Chem.*, **2007**, 45, 5872–5883.
- [12] C. L. Liu, J. H. Tsai, W. Y. Lee, W. C. Chen, S. A. Jenekhe, *Macromolecules.*, **2008**, 41, 6952–6959.
- [13] R. D. Champion, K. F. Cheng, C. L. Pai, W. C. Chen, S. A. Jenekhe, *Macromol Rapid Commun.*, **2005**, 26, 1835–1840.
- [14] A. Babel, Y. Zhu, K. F. Cheng, W. C. Chen, S. A. Jenekhe, *Adv Funct Mater*, **2007**, 17, 2542–2549.
- [15] Y. Zhu, R. D. Champion, S. A. Jenekhe, *Macromolecules.*, **2006**, 39, 8712–8719.
- [16] E. J. Zhou, Z. Tan, Y. Yang, L. J. Huo, Y. P. Zou, C. H. Yang, Y. F. Li, *Macromolecules*, **2007**, 40, 1831–1837.
- [17] C. Ego, D. Marsitzky, S. Becker, J. Y. Zhang, A. C. Grimsdale, K. Mullen, J. D. MacKenzie, C. Silva, R. H. Friend, *J. Am. Chem. Soc.*, **2003**, 125, 437–443.
- [18] J. Liu, X. Guo, L. J. Bu, Z. Y. Xie, Y. X. Cheng, Y. H. Geng, L. X. Wang, X. B. Jing, F. S. Wang, *Adv Funct Mater*, **2007**, 17, 1917–1925.
- [19] W. C. Wu, C. L. Liu, W. C. Chen, *Polymer*, **2006**, 47, 527–538.
- [20] R. Q. Yang, R. Y. Tian, J. G. Yan, Y. Zhang, J. Yang, Q. Hou, W. Yang, C. Zhang, Y. Cao, *Macromolecules.*, **2005**, 38, 244–253.
- [21] Y. Lin, Z. K. Chen, T. L. Ye, Y. F. Dai, D. G. Ma, Z. Ma, Q. D. Liu, Y. Chen, *J Polym Sci Part A: Polym Chem*, **2010**, 48, 292–301.
- [22] W. H. Tang, L. Ke, L. W. Tan, T. T. Lin, T. Kietzke, Z. K. Chen, *Macromolecules*, **2007**, 40, 6164–6171.
- [23] W. H. Tang, T. T. Lin, L. Ke, Z. K. Chen, *J Polym Sci Part A: Polym Chem.*, **2008**, 46, 7725–7738.
- [24] G. Dennler, M. C. Scharber, T. Ameri, P. Denk, K. Forberich, C. Waldauf, C. Brabec, *J. Adv. Mater.*, **2008**, 20, 579–583.
- [25] Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray, L. Yu, *J. Am. Chem. Soc.*, **2009**, 131, 7792–7799.

- [26] K. M. Coakley, M. D. McGehee, *Chem. Mater.*, **2004**, 16, 4533–4542.
- [27] C. P. Chen, S. H. Chan, T. C. Chao, C. Ting, B. T. Ko, *J. Am. Chem. Soc.*, **2008**, 130, 12828–12833.
- [28] S. H. Chan, C. P. Chen, T. C. Chao, C. Ting, C. S. Lin, B. T. Ko, *Macromolecules*, **2008**, 41, 5519–5526.
- [29] C. Y. Yu, C. P. Chen, S. H. Chan, G. W. Hwang, C. Ting, *Chem. Mater.*, **2009**, 21, 3262–3269.
- [30] J. P. Lu, F. S. Liang, N. Drolet, J. F. Ding, Y. Tao, R. Movileanu, *Chem. Commun.*, **2008**, 42, 5315–5317.
- [31] J. H. Tsai, C. C. Chueh, M. H. Lai, C. F. Wang, W. C. Chen, B. T. Ko, C. Ting, *Macromolecules*, **2009**, 42, 1897–1905.
- [32] M. H. Lai, C. C. Chueh, W. C. Chen, J. L. Wu, F. C. Chen, *J. Polym. Sci. Part A: Polym. Chem.*, **2009**, 47, 973–985.
- [33] G. Li, V. Shrotriya, J. S. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nat Mater*, **2005**, 4, 864–868.
- [34] Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C. S. Ha, M. Ree, *Nat. Mater.*, **2006**, 5, 197–203.
- [35] J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, G. C. Bazan, *Nat Mater.*, **2007**, 6, 497–500.
- [36] W. Y. Wong, X. Z. Wang, Z. He, A. B. Djuricic, C. T. Yip, K. Y. Cheung, H. Wang, C. S. K. Mak, W. K. Chan, *Nat. Mater.*, **2007**, 6, 521–527.
- [37] K. Hara, M. Kurashige, Y. Dan-Oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, *New J. Chem.*, **2003**, 27, 783.
- [38] C. M. Carcel, J. K. Laha, R. S. Loewe, P. Thamyongkit, K.-H. Schweikart, V. Misra, D. F. Bocian, J. S. Lindsey, *J. Org. Chem.*, **2004**, 69, 6739–6750.
- [39] A. A. Yasserli, D. Syomin, R. S. Loewe, J. S. Lindsey, F. Zaera, D. F. Bocian, *J. Am. Chem. Soc.*, **2004**, 126, 15603–15612.
- [40] B. Chandrakantha, Arun M. Isloor, Kishore Sridharan, Reji Philip, Prakash Shetty, Mahesh Padaki, *Arabian Journal of Chemistry*, **2013**, 6, 97–102.
- [41] A. J. Heeger, J. Orenstein, D. Ulrich (Eds.), *Nonlinear Optical Properties of Polymers*, vol. 109, *Materials Research Society, Pittsburgh*, **1988**.
- [42] Sadiq M-H. Ismael, Kawkab A. Hussain, Hasanain A S. A Majeed, *Der Pharmacia Lettre*, **2012**, 4, (6), 1826–1831.
- [43] I. A. Adejoro, O. E. Oyeneyin, O. O. Adeboye, J. A. Obaleye, *J. Comput. Methods Mol. Des.*, **2012**, 2 (4):142–148.
- [44] E. E. Havinga, T. Hoeve, H. Wynberg, *Synth. Met.*, **1993**, 55, 299.
- [45] H. Zgou, M. Hamidi, M. Bouachrine, K. Hasnaoui, *Phys. Chem. News*, **2006**, 32, 81–87.
- [46] H. Zgou, M. Hamidi, J.-P. Lère-Porte, F. Serein-Spirau, R. A. Silva, M. Bouachrine, *J. Mater. Environ. Sci.*, **2010**, 1, (S1), 293–302.
- [47] V. A. Rassolov, M. A. Ratner, J. A. Pople, P. C. Redfern, L. A. Curtiss, *J. Comp. Chem.*, **2001**, 22, 976.
- [48] A. D. Becke, *J. Chem. Phys.*, **1993**, 98, 5648.
- [49] C. Lee et al., *Phys. Rev. B*, **1988**, 37, 785.
- [50] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.
- [51] H. A. Aouchiche, S. Djennane, A. Boucekkine, *Synth. Met.*, **2004**, 140, 127.
- [52] M. A. De Oliveira, H. A. Duarte, J. M. Pernant, W. B. De Almeida, *J. Phys. Chem.*, **2000**, A104, 8256.
- [53] W. B. Torsten, B. S. Nehls, F. Galbrecht, K. Schottler, C. J. Kudla, M. Volk, J. Pina, J. S. Seixas de Melo, H. D. Burrows, H. Scherf, *Journal of Polymer Science: Part A: Polymer Chemistry*, **2008**, 46, 7342–7353.